Inter- and intramolecular alkyne-carbonyl metathesis/1,6-addition/oxidative aromatization tandem reactions between 1,6-dienes and aldehydes

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General. ¹H NMR and ¹³C NMR spectra were recorded on 600 MHz spectrometer. Chemical Shifts are reported in δ (ppm) from tetramethylsilane as an internal standard. Data are reported as follows: chemical shifts, relative integration value, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz). Infrared spectra were obtained using an FT spectrometer. Mass spectroscopy experiments were performed on a double-focusing mass spectrometer by using EI as the ionization mode. Melting points were obtained on micro melting point apparatus without correction. All reactions were performed under an argon atmosphere. Column chromatography was performed with silica gel 60N (63−210 μm). Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254).

General procedure for the preparation of Alkynes 1 and 6
Alkynes 1a,¹¹ 1d,¹¹ and 1e ¹² are known compounds.
To a solution of aryl iodide (2.4 eq) in Et₃N (0.2 M) was added Pd(OAc)₂ (0.05 eq), PPh₃ (0.05 eq), CuI (0.05 eq) and 1,6-heptadiyne (10 mmol, 92 mg, 1.0 eq) and stirred at 40 °C under argon atmosphere. The reaction was monitored by TLC to establish completion. Saturated aqueous NH₄Cl solution was added to the reaction mixture and extracted with AcOEt (three times). The combined organic solution was washed with brine, dried over anhydrous MgSO₄, and concentrated at the reduced pressure. Column chromatography on silica gel using hexane/ethyl acetate (20:1) as an eluent afforded the corresponding coupling products 1 and 6.

1,7-bis(4-ethoxyphenyl)hepta-1,6-diyne (1b)

Yield: 2.722 g, 82%; yellow solid; mp 61–63 °C. ¹H-NMR (CDCl₃) δ: 7.32 (d, J = 8.9 Hz, 4H), 6.80 (d, J = 8.9 Hz, 4H), 4.01 (q, J = 7.0 Hz, 4H), 2.56 (t, J = 7.0 Hz, 4H), 1.88 (quin., J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 6H). ¹³C-NMR (CDCl₃) δ: 158.6, 133.0, 115.9, 114.5, 87.7, 81.1, 63.6, 28.3, 18.8, 14.9. IR (CHCl₃, cm⁻¹) 3036, 3007, 1607, 1508, 1454, 1285, 1248, 1173, 1026, 833. MS (EI): m/z = 332 (M⁺). HRMS (EI): m/z calcd for C₂₃H₂₄O₂: 332.1776; found: 332.1774.

1,7-bis(4-(benzyloxy)phenyl)hepta-1,6-diyne (1c)

Yield: 3.694 g, 81%; yellow solid; mp 112–115 °C. ¹H-NMR (CDCl₃) δ: 7.44–7.35 (m, 8H), 7.35–7.30 (m, 6H), 6.88 (d, J = 8.9 Hz, 4H), 5.05 (s, 4H), 2.56 (t, J = 7.0 Hz, 4H), 1.88 (quin., J = 7.0 Hz, 2H). ¹³C-NMR (CDCl₃) δ: 158.4, 136.8, 133.1, 128.7, 128.2, 127.6, 116.4, 114.9, 87.9, 81.0, 70.1, 28.3, 18.8. IR (CHCl₃, cm⁻¹) 3036, 3007, 1607, 1508, 1504, 1454, 1285, 1248, 1173, 1026, 833. MS (EI): m/z = 456 (M⁺). HRMS (EI): m/z calcd for C₃₅H₂₈O₂: 456.2089; found: 456.2088.

4,4’-(oxybis(prop-1-ynyl-3,1-diyil))bis((benzyloxy)benzene) (1f)
Yield: 3.801 g, 83%; yellow solid; mp 95–97 °C. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\): 7.48–7.29 (m, 14H), 6.91 (d, \(J = 8.2\) Hz, 4H), 5.06 (s, 4H), 4.51 (s, 4H). \(^{13}\)C-NMR (CDCl\(_3\)) \(\delta\): 159.1, 136.7, 133.5, 128.8, 128.2, 127.6, 115.0, 115.0, 86.8, 83.3, 70.1, 57.6. IR (CHCl\(_3\), cm\(^{-1}\)) 3026, 3022, 3018, 3011, 1606, 1507, 1074, 807, 786, 764, 757, 739, 732. MS (EI): \(m/z = 458\) (M\(^+\)). HRMS (EI): \(m/z\) calcd for C\(_{32}\)H\(_{26}\)O\(_3\): 458.1882; found: 458.1881.

**ethyl 5-(4-(benzyloxy)phenyl)-2-(3-(4-(benzyloxy)phenyl)prop-2-yn-1-yl)pent-4-ynoate (6)**

Yield: 4.435 g, 84%; yellow solid; mp 72–74 °C. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\): 7.46–7.36 (m, 8H), 7.36–7.29 (m, 6H), 6.88 (d, \(J = 8.8\) Hz, 4H), 5.05 (s, 4H), 4.22 (q, \(J = 7.4\) Hz, 2H), 2.95–2.79 (m, 5H), 1.28 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C-NMR (CDCl\(_3\)) \(\delta\): 173.3, 158.8, 137.0, 133.4, 129.0, 128.4, 127.8, 116.2, 115.1, 85.2, 82.6, 70.3, 61.3, 44.4, 21.6, 14.7. IR (CHCl\(_3\), cm\(^{-1}\)) 3036, 3007, 1728, 1607, 1508, 1244, 1194, 1173, 1018, 833. MS (EI): \(m/z = 528\) (M\(^+\)). HRMS (EI): \(m/z\) calcd for C\(_{36}\)H\(_{32}\)O\(_4\): 528.2298; found: 528.2298.

**Scale-up synthesis of 3aa**

To a solution of alkyne 1a (1.0 mmol) and aldehyde 2a (1.5 mmol) in DCE (3 mL) was added BF\(_3\)·Et\(_2\)O (0.1 mmol) and stirred at 40–50 °C for 20 h under argon atmosphere. After completion of the reaction as monitored by TLC, the solution was concentrated in vacuo. Column chromatography on silica gel using hexane/ethyl acetate (10:1) as an eluent afforded the corresponding 3aa (326.5 mg, 77%).

**General procedure for the synthesis of 3.**

To a solution of alkyne 1 (0.2 mmol) and aldehyde 2 (0.3 mmol) in DCE (1 mL) was added BF\(_3\)·Et\(_2\)O (0.02 mmol) and stirred at 40–50 °C under argon atmosphere. After completion of the reaction as monitored by TLC, the solution was concentrated in vacuo. Column chromatography on silica gel using hexane/ethyl acetate (10:1) as an eluent afforded the corresponding 3.

**\((E)-(4'-methoxy-6-(4-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-methoxyp henyl)methanone (3aa)**

Yield: 63.6 mg, 75%; colorless prisms; mp 116–118 °C. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\): 7.71 (d, \(J = 8.9\) Hz, 2H), 7.20–7.10 (m, 4H), 7.01 (d, \(J = 8.8\) Hz, 2H), 6.77 (d, \(J = 8.9\) Hz, 2H), 6.63 (d, \(J = 8.8\) Hz, 2H), 6.16 (s, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 2.88–2.82 (m, 2H), 2.57 (t, \(J = 6.0\) Hz, 2H), 2.33 (s, 3H), 1.98–1.87 (m, 2H). \(^{13}\)C-NMR (CDCl\(_3\)) \(\delta\): 199.3, 163.2, 158.6, 139.4, 138.6, 137.6, 136.5, 135.0, 131.9, 131.6, 130.8, 130.0, 129.8, 129.3, 128.9, 113.5, 113.2, 55.5, 55.2, 28.8, 27.4, 22.8, 21.3. IR (CHCl\(_3\), cm\(^{-1}\)) 3009, 1648, 1599, 1510, 1303, 1252, 1240, 1176, 1168, 1034. MS (EI): \(m/z = 424\).
(M+). HRMS (El): m/z calcd for C_{20}H_{28}O_{5}: 424.2038; found: 424.2043. Crystals for X-ray diffraction analysis were obtained by recrystallization from hexane-AcOEt. Crystal data for 3aa (CCDC 1953678): C_{20}H_{28}O_{5}, M = 424.54, monoclinic, space group P21/n, colorless block, a = 20.2410(5) Å, b = 6.08138(15) Å, c = 21.4473(6) Å, α = 90°, β = 117.947(8)°, γ = 90°, V = 2332.2(2) Å³, Z = 4, and Dc = 1.209 g cm⁻³. The reflection data of 21149 reflections with 4<θ<69° were collected on a Rigaku R-AXIS-RAPID diffractometer using monochromated CuKα radiation and ω-20 scan technique (-24≤h≤24, -7≤k≤7, -25≤l≤25). The structure was solved by SHELXT (sheldrick, 2014) and refined by SHELXL (sheldrick 2008). The final R value was 0.0571 for 4254 observed reflections (wR = 0.1193).

(4'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-methoxyphenyl)methanone (3b)

Yield: 32.2 mg, 50%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.71 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 6.62 (d, J = 8.7 Hz, 2H), 3.78 (s, 3H), 3.67 (s, 3H), 2.55–2.35 (m, 4H), 1.94–1.73 (m, 4H). ¹³C-NMR (CDCl₃) δ: 200.5, 163.2, 158.6, 138.0, 134.9, 134.6, 131.8, 129.7, 129.1, 113.5, 113.5, 55.5, 55.2, 30.9, 28.4, 23.1, 22.3. IR (CHCl₃): 3009, 1643, 1601, 1576, 1511, 1286, 1254, 1240, 1180, 1169, 1034. MS (El): m/z = 322 (M+).

HRMS (El): m/z calcd for C_{20}H_{28}O_{5}: 322.1569; found: 322.1571.

(E)-(4'-methoxy-6-(3-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-methoxyphenyl)methanone (3ab)

Yield: 54.3 mg, 64%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.71 (d, J = 8.8 Hz, 2H), 7.20 (t, J = 7.7 Hz, 1H), 7.06–6.99 (m, 5H), 6.77 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 6.17 (s, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 2.88–2.83 (m, 2H), 2.57 (t, J = 6.0 Hz, 2H), 2.32 (s, 3H), 1.96–1.90 (m, 2H). ¹³C-NMR (CDCl₃) δ: 199.2, 163.2, 158.6, 139.3, 138.8, 138.1, 137.8, 137.7, 131.8, 131.6, 130.7, 130.2, 129.7, 128.0, 127.4, 126.4, 113.5, 113.2, 55.5, 55.2, 28.8, 27.4, 22.8, 21.5. IR (CHCl₃, cm⁻¹): 3036, 3007, 1647, 1599, 1574, 1506, 1456, 1441, 1304, 1288, 1250, 1169, 1157, 1034, 843, 812. MS (El): m/z = 424 (M+). HRMS (El): m/z calcd for C_{22}H_{30}O_{6}: 424.2038; found: 424.2042.

(E)-(6-(4-fluorobenzylidene)-4'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-methoxyphenyl)methanone (3ac)

Yield: 64.2 mg, 75%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.71 (d, J = 8.6 Hz, 2H), 7.19–7.14 (m, 2H), 7.04–6.96 (m, 4H), 6.77 (dd, J = 8.8, 1.0 Hz, 2H), 6.66–6.62 (m, 2H), 6.14 (s, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 2.83–2.78 (m, 2H), 2.57 (t, J = 6.0 Hz, 2H), 2.00–1.88 (m, 2H). ¹³C-NMR (CDCl₃) δ: 199.1, 163.3, 161.5 (d, J = 245.6 Hz), 158.6, 139.0, 139.0, 138.2, 133.9 (d, J = 2.8 Hz), 131.8, 131.6, 130.9 (d, J = 8.3 Hz), 130.5,
129.6, 128.8, 115.0 (d, J = 21.5 Hz), 113.5, 113.2, 55.5, 55.1, 28.8, 27.2, 22.7. IR (CHCl₃, cm⁻¹) 3008, 1648, 1599, 1574, 1506, 1289, 1250, 1242, 1168, 1157, 1034, 833. MS (EI): m/z = 428 (M⁺).

HRMS (EI): m/z calc'd for C₂₇H₂₉NO₃: 428.1788; found: 428.1793.

(E)-4-((4'-methoxy-6-(4-methoxybenzoyl)-4,5-dihydro-[1,1'-biphenyl]-2(3H)-ylidene)methyl)benzonitrile (3ad)

Yield: 60.9 mg, 70%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.71 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 6.16 (s, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 2.84–2.79 (m, 2H), 2.59 (t, J = 6.0 Hz, 2H), 2.01–1.88 (m, 2H). ¹³C-NMR (CDCl₃) δ: 198.7, 163.5, 158.8, 142.7, 141.3, 140.9, 138.4, 131.9, 131.8, 131.7, 130.0, 129.9, 129.3, 128.0, 119.2, 113.6, 113.4, 109.8, 55.6, 55.2, 28.8, 27.4, 22.6. IR (CHCl₃, cm⁻¹) 3009, 2933, 2228, 1601, 1510, 1313, 1289, 1252, 1177, 1168, 1034, 842, 833. MS (EI): m/z = 435 (M⁺). HRMS (EI): m/z calc'd for C₂₉H₂₉NO₃: 435.1834; found: 435.1831.

(E)-4-((4'-ethoxy-6-(4-ethoxybenzoyl)-4,5-dihydro-[1,1'-biphenyl]-2(3H)-ylidene)methyl)benzonitrile (3bd)

Yield: 66.7 mg, 72%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.69 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 6.16 (s, 1H), 4.03 (q, J = 7.0 Hz, 2H), 3.91 (q, J = 7.0 Hz, 2H), 2.87–2.78 (m, 2H), 2.59 (t, J = 6.0 Hz, 2H), 2.01–1.89 (m, 2H), 1.41 (t, J = 7.0 Hz, 3H), 1.33 (t, J = 7.0 Hz, 3H). ¹³C-NMR (CDCl₃) δ: 198.7, 162.9, 158.2, 142.7, 141.3, 140.9, 138.4, 131.9, 131.7, 131.6, 129.9, 129.1, 128.0, 119.2, 114.0, 113.9, 109.8, 63.8, 63.3, 28.8, 27.4, 22.6, 14.9, 14.8. IR (CHCl₃, cm⁻¹) 3009,2933, 2228, 1601, 1510, 1313, 1289, 1252, 1177, 1168, 1034, 842, 833. MS (EI): m/z = 463 (M⁺). HRMS (EI): m/z calc'd for C₃₁H₂₉NO₃: 463.2147; found: 463.2149.

(E)-(4’-(benzyl oxy)-6-(4-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-(benzyl oxy)phenyl)methanone (3ca)

Yield: 85.2 mg, 74%; light yellow solid; mp 112–113 °C. ¹H-NMR (CDCl₃) δ: 7.69 (d, J = 8.7 Hz, 2H), 7.42–7.31 (m, 10H), 7.12 (s, 4H), 7.01 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 6.18 (s, 1H), 5.06 (s, 2H), 4.93 (s, 2H), 2.87–2.82 (m, 2H), 2.57 (t, J = 6.0 Hz, 2H), 2.33 (s, 3H), 1.96–1.88 (m, 2H). ¹³C-NMR (CDCl₃) δ: 199.3, 162.4, 157.9, 139.6, 138.6, 137.6, 137.1, 136.5, 136.3, 135.0, 131.9, 131.6, 131.1, 130.1, 129.3, 128.9, 128.8, 128.6, 128.3, 128.0, 127.6, 114.3, 114.1, 70.1, 69.9, 28.8, 27.4, 22.7, 21.3. IR (CHCl₃, cm⁻¹) 3036, 3007, 1645, 1597, 1574, 1506,

S5
(E)-(4'-(benzoxyl)-6-(3-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-(benzyl oxy)phenyl)methanone (3cb)

Yield: 86.4 mg, 75%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.69 (d, J = 8.9 Hz, 2H), 7.42–7.32 (m, 10H), 7.20 (t, J = 7.9 Hz, 1H), 7.06–6.98 (m, 5H), 6.84 (d, J = 8.9 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 6.18 (s, 1H), 5.05 (s, 2H), 4.92 (s, 2H), 2.89–2.82 (m, 2H), 2.57 (t, J = 6.0 Hz, 2H), 2.32 (s, 3H), 1.95–1.89 (m, 2H). ¹³C-NMR (CDCl₃) δ: 199.3, 162.4, 157.9, 139.5, 138.8, 138.1, 137.8, 137.7, 137.1, 136.3, 131.9, 131.6, 131.1, 130.3, 130.1, 130.0, 128.8, 128.6, 128.3, 128.0, 127.6, 127.5, 126.4, 114.3, 114.1, 70.2, 69.9, 28.8, 27.4, 22.8, 21.6. IR (CHCl₃, cm⁻¹) 3036, 3007, 1647, 1597, 1574, 1506, 1454, 1312, 1240, 1229, 1196, 1169, 1026. MS (EI): m/z = 576 (M⁺). HRMS (EI): m/z calcd for C₄₁H₃₈O₂: 576.2664; found: 576.2665.

(E)-(4'-(benzoxyl)-6-(2-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-(benzyl oxy)phenyl)methanone (3ce)

Yield: 92.2 mg, 80%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.72 (d, J = 8.8 Hz, 2H), 7.43–7.27 (m, 10H), 7.20–7.10 (m, 4H), 7.05 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 6.19 (s, 1H), 5.06 (s, 2H), 4.93 (s, 2H), 2.67–2.62 (m, 2H), 2.57 (t, J = 6.0 Hz, 2H), 2.09 (s, 3H), 1.95–1.87 (m, 2H). ¹³C-NMR (CDCl₃) δ: 199.3, 162.4, 157.9, 139.3, 138.4, 138.0, 137.2, 137.0, 136.8, 136.3, 131.7, 131.7, 131.1, 129.9, 129.9, 129.4, 129.1, 128.8, 128.6, 128.3, 128.0, 127.6, 127.0, 125.3, 114.3, 114.2, 70.2, 69.9, 29.0, 27.2, 22.8, 20.1. IR (CHCl₃, cm⁻¹) 3036, 3007, 1647, 1597, 1574, 1506, 1454, 1246, 1196, 1167. MS (EI): m/z = 576 (M⁺). HRMS (EI): m/z calcd for C₄₁H₃₈O₂: 576.2664; found: 576.2664.

(E)-(4'-(benzoxyl)-6-(4-methoxybenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-(benz yloxy)phenyl)methanone (3cf)

Yield: 100.6 mg, 85%; light yellow solid; mp 122–125 °C. ¹H-NMR (CDCl₃) δ: 7.69 (d, J = 8.7 Hz, 2H), 7.44–7.28 (m, 10H), 7.16 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 6.86–6.82 (m, 4H), 6.71 (d, J = 8.5 Hz, 2H), 6.15 (s, 1H), 5.06 (s, 2H), 4.93 (s, 2H), 3.80 (s, 3H), 2.87–2.80 (m, 2H), 2.57 (t, J = 5.9 Hz, 2H), 1.97–1.89 (m, 2H). ¹³C-NMR (CDCl₃) δ: 199.3, 162.3, 158.4, 157.9, 139.7, 138.3, 137.1, 136.8, 136.4, 131.9, 131.6, 131.2, 130.7, 130.5, 130.1, 129.8, 128.8, 128.7, 128.3, 128.0, 127.6, 114.3, 114.1, 113.6, 70.2, 69.9, 55.4, 28.8, 27.4, 22.8. IR (CHCl₃, cm⁻¹) 3038, 3007.
1647, 1597, 1574, 1510, 1454, 1302, 1254, 1167, 1026, 831, 812. MS (EI): m/z = 592 (M+). HRMS (EI): m/z calcd for C₄₆H₆₈O₇: 592.2614; found: 592.2616.

(E)-(4'-(benzoxyl)-6-(4-methoxy-3-nitrobenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-(benzoxyl)phenyl)methanone (3cg)

Yield: 95.6 mg, 75%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.73 (d, J = 1.8 Hz, 1H), 7.69 (d, J = 8.8 Hz, 2H), 7.42–7.29 (m, 11H), 7.03–6.97 (m, 3H), 6.85 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 6.09 (s, 1H), 5.07 (s, 2H), 4.94 (s, 2H), 3.95 (s, 3H), 2.84–2.78 (m, 2H), 2.58 (t, J = 6.0 Hz, 2H), 2.00–1.91 (m, 2H). ¹³C-NMR (CDCl₃) δ: 198.9, 162.5, 158.0, 151.5, 139.9, 139.4, 139.3, 138.7, 137.0, 136.3, 135.0, 131.8, 131.6, 130.6, 130.5, 129.7, 128.8, 128.7, 128.4, 128.1, 127.6, 127.0, 126.2, 114.4, 114.3, 113.3, 70.2, 70.0, 56.7, 28.7, 27.3, 22.6. IR (CHCl₃, cm⁻¹) 3036, 3007, 1647, 1597, 1574, 1530, 1506, 1454, 1352, 1248, 1196, 1167, 1022. MS (EI): m/z = 637 (M+). HRMS (EI): m/z calcd for C₄₆H₆₈NO₇: 637.2464; found: 637.2466.

(E)-(4'-methyl-6-(4-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone (3da)

Yield: 32.1 mg, 41%; light yellow solid; mp 165–167 °C. ¹H-NMR (CDCl₃) δ: 7.62 (d, J = 8.0 Hz, 2H), 7.14–7.06 (m, 6H), 6.97 (d, J = 7.8 Hz, 2H), 6.89 (d, J = 7.8 Hz, 2H), 6.16 (s, 1H), 2.89–2.81 (m, 2H), 2.56 (t, J = 6.0 Hz, 2H), 2.33 (s, 6H), 2.19 (s, 3H), 1.96–1.88 (m, 2H). ¹³C-NMR (CDCl₃) δ: 200.2, 143.4, 140.2, 138.6, 137.5, 136.7, 136.5, 135.4, 135.0, 134.3, 130.6, 130.3, 129.5, 129.3, 128.9, 128.9, 128.4, 28.8, 27.4, 22.7, 21.8, 21.3, 21.3. IR (CHCl₃, cm⁻¹) 3007, 1647, 1605, 1506, 1265, 1242, 1196, 1177, 818, 716. MS (EI): m/z = 392 (M+). HRMS (EI): m/z calcd for C₂₉H₂₃O: 392.2140; found: 392.2145.

(E)-(6-(4-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3ea)

Yield: 23.3 mg, 32%; colorless needles; mp 149–151 °C. ¹H-NMR (CDCl₃) δ: 7.65 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.14–7.01 (m, 8H), 6.15 (s, 1H), 2.91–2.84 (m, 2H), 2.62 (t, J = 6.0 Hz, 2H), 2.33 (s, 3H), 1.99–1.91 (m, 2H). ¹³C-NMR (CDCl₃) δ: 200.6, 141.0, 138.5, 138.4, 137.3, 137.2, 136.6, 134.8, 132.5, 130.8, 130.8, 129.3, 129.1, 128.9, 128.1, 127.7, 127.3, 28.7, 27.4, 22.7, 21.4. IR (CHCl₃, cm⁻¹) 3007, 1647, 1597, 1265, 1242, 1198, 752. MS (EI): m/z = 364 (M+). HRMS (EI): m/z calcd for C₂₇H₂₆O: 364.1827; found: 364.1830.

(Z)-(4-(benzoxyl)phenyl)(4-(4-(benzoxyl)phenyl)-5-(4-methylbenzylidene)-5,6-dihydro-2H-pyran-3-yl)methanone (3fa)
Yield: 89.0 mg, 77%; colorless needles; mp 125–127 °C. ¹H-NMR (CDCl₃) δ: 7.72 (d, J = 8.7 Hz, 2H), 7.42–7.29 (m, 10H), 7.21–7.14 (m, 3H), 7.10 (d, J = 8.5 Hz, 2H), 7.05–6.99 (m, 1H), 6.83 (d, J = 8.7 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 6.44 (s, 1H), 5.06 (s, 2H), 4.95 (s, 2H), 4.65 (s, 2H), 4.61 (s, 2H), 2.13 (s, 3H). ¹³C-NMR (CDCl₃) δ: 196.1, 162.6, 158.4, 137.7, 136.9, 136.9, 136.2, 133.3, 131.7, 131.5, 130.1, 129.9, 129.6, 129.0, 128.8, 128.7, 128.4, 128.1, 127.8, 127.6, 127.5, 125.6, 114.5, 114.4, 70.2, 70.0, 67.7, 66.1, 20.1. IR (CHCl₃, cm⁻¹) 3036, 3007, 1643, 1597, 1574, 1508, 1504, 1454, 1304, 1248, 1169. MS (EI): m/z = 578 (M⁺). HRMS (EI): m/z calcld for C₅₉H₃₈O₃: 578.2457; found: 578.2459.

*(E)-(4′-(benzylxylo)-6-(3-methylbutylidene)-3,4,5,6-tetrahydro-[1,1′-biphenyl]-2-yl)(4-(benzylxy)phenyl)methanone (3ch)*

Yield: 87.8 mg, 81%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.66 (d, J = 8.7 Hz, 2H), 7.41–7.32 (m, 10H), 6.93 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.6 Hz, 2H), 5.20 (t, J = 7.6 Hz, 1H), 5.05 (s, 2H), 4.92 (s, 2H), 2.57–2.52 (m, 2H), 2.50 (t, J = 6.1 Hz, 2H), 1.99 (t, J = 7.2 Hz, 2H), 1.95–1.87 (m, 2H), 1.60–1.52 (m, 1H), 0.84 (s, 3H), 0.83 (s, 3H). ¹³C-NMR (CDCl₃) δ: 199.6, 162.3, 157.7, 139.6, 137.1, 136.4, 136.3, 136.2, 131.7, 131.6, 131.4, 131.0, 130.2, 128.8, 128.6, 128.3, 128.0, 127.6, 114.2, 114.0, 70.1, 69.9, 37.4, 29.0, 28.8, 26.1, 22.6, 22.6. IR (CHCl₃, cm⁻¹) 3032, 3007, 2959, 2934, 1651, 1599, 1574, 1506, 1468, 1454, 1381, 1311, 1246, 1229, 1169, 1157, 1038, 1026, 1011, 841, 810, 777, 750. MS (EI): m/z = 542 (M⁺). HRMS (EI): m/z calcld for C₃₅H₃₈O₃: 542.2821; found: 542.2813.

*(E)-(4′-(benzylxylo)-6-(cyclohexylmethylene)-3,4,5,6-tetrahydro-[1,1′-biphenyl]-2-yl)(4-(benzylxy)phenyl)methanone (3ci)*

Yield: 88.6 mg, 78%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.65 (d, J = 8.7 Hz, 2H), 7.42–7.28 (m, 10H), 6.92 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 5.07–5.01 (m, 3H), 4.91 (s, 2H), 2.58–2.53 (m, 2H), 2.50 (t, J = 6.1 Hz, 2H), 2.37–2.27 (m, 1H), 1.95–1.87 (m, 2H), 1.70–1.54 (m, 5H), 1.27 (q, J = 12.7 Hz, 2H), 1.10 (q, J = 12.6 Hz, 1H), 0.95 (qd, J = 12.9, 3.2 Hz, 2H). ¹³C-NMR (CDCl₃) δ: 199.7, 162.2, 157.7, 139.8, 137.7, 137.1, 136.4, 136.3, 134.0, 131.8, 131.6, 131.4, 130.2, 128.8, 128.6, 128.3, 128.0, 127.6, 114.2, 113.9, 70.1, 69.9, 37.3, 32.9, 28.8, 26.1, 26.1, 26.1, 22.7. IR (CHCl₃, cm⁻¹) 3036, 3007, 2930, 1651, 1599, 1574, 1506, 1454, 1312, 1242, 1196, 1169, 1157, 1026. MS (EI): m/z = 568 (M⁺). HRMS (EI): m/z calcld for C₃₉H₄₃O₃: 568.2977; found: 568.2977.

*(E)-(4′-(benzylxylo)-6-(cyclopentylmethylene)-3,4,5,6-tetrahydro-[1,1′-biphenyl]-2-yl)(4-(benzylxy)phenyl)methanone (3cj)*
Yield: 88.6 mg, 80%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.65 (d, J = 8.8 Hz, 2H), 7.41–7.27 (m, 10H), 6.92 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.7 Hz, 2H), 5.13 (d, J = 9.1 Hz, 1H), 5.04 (s, 2H), 4.92 (s, 2H), 2.82–2.68 (m, 1H), 2.61–2.54 (m, 2H), 2.50 (t, J = 6.1 Hz, 2H), 1.97–1.87 (m, 2H), 1.82–1.70 (m, 2H), 1.64–1.47 (m, 4H), 1.17–1.06 (m, 2H).

¹³C-NMR (CDCl₃) δ: 199.6, 162.2, 157.7, 139.6, 137.3, 137.1, 136.4, 136.2, 134.5, 131.8, 131.6, 131.4, 130.3, 128.8, 128.6, 128.3, 128.0, 127.6, 114.2, 113.9, 70.1, 69.9, 39.3, 33.7, 28.8, 26.2, 25.5, 22.7. IR (CHCl₃, cm⁻¹) 3036, 3007, 2953, 1645, 1599, 1574, 1506, 1454, 1379, 1312, 1248, 1169, 1026, 841. MS (EI): m/z = 554 (M⁺). HRMS (EI): m/z calcd for C₃₉H₃₈O₃: 554.2821; found: 554.2820.

(E)-(4''-(benzyloxy)-6-(cyclopropylmethylene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-(benzoyloxy)phenyl)methanone (3ck)

Yield: 64.2 mg, 61%; light yellow oil. ¹H-NMR (CDCl₃) δ: 7.64 (d, J = 8.8 Hz, 2H), 7.45–7.27 (m, 10H), 6.90 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 5.04 (s, 2H), 4.90 (s, 2H), 4.55 (d, J = 9.8 Hz, 1H), 2.74–2.66 (m, 2H), 2.51 (t, J = 6.0 Hz, 2H), 2.01–1.93 (m, 2H), 1.66–1.56 (m, 1H), 0.79–0.74 (m, 2H), 0.28–0.24 (m, 2H). ¹³C-NMR (CDCl₃) δ: 199.6, 162.2, 157.7, 139.4, 137.1, 136.4, 135.9, 135.6, 134.4, 131.7, 131.6, 131.2, 130.4, 128.8, 128.6, 128.3, 128.0, 127.6, 114.2, 113.9, 70.1, 69.9, 28.8, 26.3, 22.6, 11.0, 7.9. IR (CHCl₃, cm⁻¹) 3036, 3007, 1651, 1597, 1574, 1506, 1454, 1379, 1312, 1248, 1169, 1026, 841. MS (EI): m/z = 526 (M⁺). HRMS (EI): m/z calcd for C₃₇H₃₄O₃: 526.2508; found: 526.2512.

General procedure for the synthesis of 4 and 5.

To a solution of alkyne (0.2 mmol) and aldehyde (0.3 mmol) in DCE (1 mL) was added BF₃·Et₂O (0.02 mmol) and stirred at 40–50 °C under argon atmosphere. After completion of the reaction as monitored by TLC, In(OTf)₃ (0.2 mmol) and PhI(OAc)₂ (0.44 mmol) were added to the reaction mixture. The solution was further stirred at room temperature under argon atmosphere. The progress of the reaction was monitored by TLC to establish its completion. Column chromatography on silica gel using hexane/ethyl acetate (10:1–8:1) as an eluent afforded the corresponding 4 and 5.

(7-methoxy-9-(p-tolyl)-9H-fluoren-4-yl)(4-methoxyphenyl)methanone (4aa)

Yield: 59.6 mg, 71%; colorless oil. ¹H-NMR (CDCl₃) δ: 7.95 (d, J = 8.9 Hz, 2H), 7.39 (d, J = 8.7 Hz, 1H), 7.36 (d, J = 7.3 Hz, 1H), 7.30–7.25 (m, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 7.9 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 6.80 (d, J = 2.4 Hz, 1H), 6.71 (dd, J = 8.7, 2.5 Hz, 1H), 4.99 (s, 1H), 3.88 (s, 3H), 3.72 (s, 3H), 2.33 (s, 3H). ¹³C-NMR (CDCl₃) δ: 197.1, 164.1, 159.8, 150.7, 149.0, 138.4, 138.3,
136.8, 133.4, 133.0, 132.4, 130.4, 129.6, 128.5, 127.2, 126.7, 125.4, 124.4, 114.0, 113.6, 110.5, 55.7, 55.5, 54.0, 21.3. IR (CHCl₃, cm⁻¹) 3009, 1653, 1599, 1510, 1289, 1262, 1168, 1154, 1154. MS (EI): m/z = 420 (M⁺). HRMS (EI): m/z calcd for C₂₀H₂₂O₃: 420.1725; found: 420.1732.

(7-methoxy-9-(m-tolyl)-9H-fluoren-4-yl)(4-methoxyphenyl)methanone (4ab)

![Structure of 4ab]

Yield: 52.1 mg, 62%; colorless oil. ¹H-NMR (CDCl₃) δ: 7.96 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 7.4 Hz, 1H), 7.25–7.17 (m, 2H), 7.07 (d, J = 7.4 Hz, 1H), 7.01–6.94 (m, 3H), 6.91 (s, 1H), 6.81 (s, 1H), 6.72 (d, J = 8.5 Hz, 1H), 4.98 (s, 1H), 3.88 (s, 3H), 3.73 (s, 3H), 2.30 (s, 3H). ¹³C-NMR (CDCl₃) δ: 197.1, 164.1, 159.8, 150.6, 148.9, 141.3, 138.6, 138.5, 133.4, 133.0, 132.4, 130.4, 129.2, 128.7, 128.0, 127.2, 126.8, 125.8, 125.4, 124.4, 114.0, 113.5, 110.6, 55.7, 55.6, 54.4, 21.6. IR (CHCl₃, cm⁻¹) 3009, 1653, 1597, 1465, 1420, 1307, 1289, 1262, 1198, 1169, 1154, 809, 796, 782, 774, 761. MS (EI): m/z = 420 (M⁺). HRMS (EI): m/z calcd for C₂₀H₂₂O₃: 420.1725; found: 420.1726.

(9-(4-fluorophenyl)-7-methoxy-9H-fluoren-4-yl)(4-methoxyphenyl)methanone (4ac)

![Structure of 4ac]

Yield: 61.1 mg, 72%; colorless oil. ¹H-NMR (CDCl₃) δ: 7.95 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.5 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.09 (dd, J = 8.0, 5.6 Hz, 2H), 6.99 (t, J = 8.5 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.77 (s, 1H), 6.72 (dd, J = 8.7, 2.3 Hz, 1H), 5.90 (s, 1H), 3.88 (s, 3H), 3.73 (s, 3H). ¹³C-NMR (CDCl₃) δ: 196.9, 164.2, 162.1 (d, J = 245.6 Hz), 159.9, 150.4, 148.6, 138.4, 137.1 (d, J = 2.8 Hz), 133.5, 133.0, 132.3, 130.3, 130.1 (d, J = 8.4 Hz), 127.4, 126.7, 125.5, 124.5, 115.8 (d, J = 20.6 Hz), 114.1, 113.6, 110.6, 55.7, 55.5, 53.6. IR (CHCl₃, cm⁻¹) 3008, 1653, 1597, 1574, 1508, 1490, 1465, 1420, 1306, 1289, 1260, 1242, 1168, 1154, 1034, 847, 839. MS (EI): m/z = 424 (M⁺). HRMS (EI): m/z calcd for C₂₉H₂₄O₃: 424.1475; found: 424.1480.

(7-ethoxy-9-(p-tolyl)-9H-fluoren-4-yl)(4-ethoxyphenyl)methanone (4ba)

![Structure of 4ba]

Yield: 61.8 mg, 69%; colorless oil. ¹H-NMR (CDCl₃) δ: 7.94 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.29–7.25 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.7 Hz, 2H), 7.01 (d, J = 7.7 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.79 (s, 1H), 6.70 (d, J = 8.6 Hz, 1H), 4.98 (s, 1H), 4.10 (q, J = 6.9 Hz, 2H), 3.93 (q, J = 6.6 Hz, 2H), 2.33 (s, 3H), 1.44 (t, J = 6.9 Hz, 3H), 1.33 (t, J = 6.9 Hz, 3H). ¹³C-NMR (CDCl₃) δ: 197.1, 163.5, 159.2, 150.7, 149.0, 138.5, 138.4, 136.7, 133.4, 133.0, 132.2, 130.2, 129.6, 128.5, 127.2, 126.7, 125.4, 124.4, 114.4, 113.9, 111.1, 64.0, 63.7, 54.0, 21.3, 14.9, 14.8. IR (CHCl₃, cm⁻¹) 3007, 1651, 1597, 1574, 1506, 1464, 1423, 1306, 1288, 1254, 1246, 1169, 1153, 1045. MS (EI): m/z = 448 (M⁺). HRMS (EI): m/z calcd for C₃₁H₂₈O₃: 448.2038; found: S10
(7-(benzyloxy)-9-(p-tolyl)-9H-fluoren-4-yl)(4-(benzyloxy)phenyl)methanone (4ca)

Yield: 76.6 mg, 67%; colorless oil. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\): 7.95 (d, \(J = 8.8\) Hz, 2H), 7.46–7.24 (m, 13H), 7.20 (t, \(J = 7.5\) Hz, 1H), 7.11 (d, \(J = 7.8\) Hz, 2H), 7.05–6.99 (m, 4H), 6.90 (s, 1H), 6.78 (dd, \(J = 8.6, 2.3\) Hz, 1H), 5.13 (s, 2H), 4.99 (s, 1H), 4.96 (s, 2H), 2.33 (s, 3H). \(^1^3\)C-NMR (CDCl\(_3\)) \(\delta\): 197.0, 163.3, 159.0, 150.8, 149.0, 138.5, 138.3, 136.9, 136.7, 136.2, 133.4, 133.0, 132.6, 130.6, 129.6, 128.9, 128.6, 128.5, 128.4, 128.1, 127.7, 127.6, 127.2, 126.8, 125.5, 124.4, 114.9, 114.3, 111.6, 70.3, 70.2, 54.0, 21.3. IR (CHCl\(_3\), cm\(^{-1}\)) 3034, 3009, 1651, 1597, 1574, 1506, 1454, 1422, 1306, 1288, 1258, 1223, 1198, 1167, 1153. MS (EI): \(m/z = 572\) (M\(^+\)). HRMS (EI): \(m/z\) calcld for C\(_{41}\)H\(_{32}\)O\(_3\): 572.2351; found: 572.2355.

(7-(benzyloxy)-9-(m-tolyl)-9H-fluoren-4-yl)(4-(benzyloxy)phenyl)methanone (4cb)

Yield: 81.2 mg, 71%; colorless oil. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\): 7.96 (d, \(J = 8.6\) Hz, 2H), 7.46–7.32 (m, 11H), 7.31–7.27 (m, 2H), 7.21 (dt, \(J = 11.2, 7.5\) Hz, 2H), 7.07 (d, \(J = 7.4\) Hz, 1H), 7.03 (d, \(J = 8.6\) Hz, 2H), 6.95 (d, \(J = 7.5\) Hz, 1H), 6.90 (s, 2H), 6.80 (d, \(J = 8.5\) Hz, 1H), 5.14 (s, 2H), 4.98 (s, 1H), 4.97 (s, 2H), 2.30 (s, 3H). \(^1^3\)C-NMR (CDCl\(_3\)) \(\delta\): 197.0, 163.3, 159.0, 150.6, 148.9, 141.2, 138.6, 138.5, 136.9, 136.2, 133.4, 133.0, 132.6, 130.6, 129.2, 128.9, 128.8, 128.7, 128.4, 128.1, 128.0, 127.7, 127.3, 126.8, 125.8, 125.5, 124.4, 114.9, 114.3, 111.7, 70.4, 70.2, 54.4, 21.6. IR (CHCl\(_3\), cm\(^{-1}\)) 3007, 1651, 1597, 1574, 1506, 1454, 1422, 1306, 1288, 1250, 1244, 1169, 1153, 1026. MS (EI): \(m/z = 572\) (M\(^+\)). HRMS (EI): \(m/z\) calcld for C\(_{41}\)H\(_{32}\)O\(_3\): 572.2351; found: 572.2354.

(7-(benzyloxy)-9-(4-fluorophenyl)-9H-fluoren-4-yl)(4-(benzyloxy)phenyl)methanone (4cc)

Yield: 78.3 mg, 68%; colorless oil. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\): 7.95 (d, \(J = 8.8\) Hz, 2H), 7.45–7.27 (m, 13H), 7.24–7.19 (m, 1H), 7.10–6.95 (m, 6H), 6.86 (s, 1H), 6.80 (dd, \(J = 8.6, 2.4\) Hz, 1H), 5.14 (s, 2H), 4.99 (s, 1H), 4.98 (s, 2H). \(^1^3\)C-NMR (CDCl\(_3\)) \(\delta\): 96.9, 163.3, 162.1 (d, \(J = 244.8\) Hz), 159.0, 150.4, 148.7, 138.4, 137.0 (d, \(J = 2.8\) Hz), 136.3, 136.2, 133.5, 133.0, 132.5, 130.5, 130.1 (d, \(J = 7.5\) Hz), 128.9, 128.7, 128.4, 128.1, 127.7, 127.6, 127.4, 126.7, 125.6, 124.5, 115.8 (d, \(J = 21.6\) Hz), 114.9, 114.4, 111.7, 70.4, 70.3, 53.5. IR (CHCl\(_3\), cm\(^{-1}\)) 3036, 3007, 1651, 1597, 1574, 1506, 1454, 1422, 1306, 1288, 1254, 1240, 1233, 1196, 1167, 1153, 1026. MS (EI): \(m/z = 576\) (M\(^+\)). HRMS (EI): \(m/z\) calcld for C\(_{41}\)H\(_{32}\)FO\(_2\): 576.2101; found: 576.2109.

cyclohexyl(4'-methoxy-6-(4-methoxybenzoyl)-[1,1'-biphenyl]-2-yl)methyl acetate (5ai)
Yield: 66.1 mg, 70%; colorless oil. $^1$H-NMR (CDCl$_3$) $\delta$: 7.58–7.50 (m, 3H), 7.42 (t, $J = 7.7$ Hz, 1H), 7.37 (dd, $J = 8.4$, 2.2 Hz, 1H), 7.30 (dd, $J = 7.6$, 1.0 Hz, 1H), 6.93 (dd, $J = 8.3$, 2.2 Hz, 1H), 6.78–6.69 (m, 4H), 5.59 (d, $J = 7.5$ Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 2.10 (s, 3H), 1.71–1.62 (m, 3H), 1.58–1.50 (m, 3H), 1.18–0.98 (m, 3H), 0.93–0.81 (m, 1H), 0.76–0.58 (m, 1H).

$^{13}$C-NMR (CDCl$_3$) $\delta$: 197.7, 170.5, 163.4, 158.7, 141.2, 139.3, 138.6, 132.3, 131.4, 130.7, 129.4, 127.8, 127.2, 126.4, 113.4, 113.1, 77.1, 55.5, 55.2, 43.9, 29.2, 28.5, 26.2, 26.0, 21.4. IR (CHCl$_3$, cm$^{-1}$) 3009, 2935, 1730, 1653, 1600, 1510, 1291, 1252, 1248, 1178, 1171, 1157, 1034. MS (EI): $m/z$ = 472 (M$^+$). HRMS (EI): $m/z$ calcd for C$_{36}$H$_{32}$O$_5$: 472.2250; found: 472.2256.

**cyclohexyl(4'-ethoxy-6-(4-ethoxybenzoyl)[1,1'-biphenyl]-2-yl)methyl acetate (5bi)**

Yield: 70.0 mg, 70%; colorless oil. $^1$H-NMR (CDCl$_3$) $\delta$: 7.54–7.48 (m, 3H), 7.42 (t, $J = 7.7$ Hz, 1H), 7.35 (d, $J = 8.5$ Hz, 1H), 7.30 (d, $J = 7.4$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 6.73–6.66 (m, 4H), 5.60 (d, $J = 7.4$ Hz, 1H), 4.02 (q, $J = 7.0$ Hz, 2H), 3.94 (q, $J = 7.0$ Hz, 2H), 2.10 (s, 3H), 1.71–1.61 (m, 2H), 1.56–1.46 (m, 3H), 1.40 (t, $J = 7.0$ Hz, 3H), 1.35 (t, $J = 7.0$ Hz, 3H), 1.18–0.94 (m, 4H), 0.92–0.82 (m, 1H), 0.72–0.61 (m, 1H). $^{13}$C-NMR (CDCl$_3$) $\delta$: 197.8, 170.5, 162.8, 158.1, 141.3, 139.3, 138.7, 132.3, 131.4, 130.5, 129.3, 127.7, 127.1, 126.4, 113.8, 113.7, 77.1, 63.8, 63.3, 43.9, 29.2, 28.5, 26.2, 26.0, 21.4, 14.9, 14.8. IR (CHCl$_3$, cm$^{-1}$) 3007, 2930, 1728, 1651, 1599, 1506, 1306, 1290, 1242, 1171, 1157, 1045. MS (EI): $m/z$ = 500 (M$^+$). HRMS (EI): $m/z$ calcd for C$_{35}$H$_{36}$O$_5$: 500.2563; found: 500.2566.

**(4'-benzylxoy)-6-(4-(benzyloxy)benzoyl)[1,1'-biphenyl]-2-yl(cyclohexyl)methyl acetate (5ci)**

Yield: 82.4 mg, 66%; colorless oil. $^1$H-NMR (CDCl$_3$) $\delta$: 7.52 (t, $J = 8.3$ Hz, 3H), 7.45–7.29 (m, 13H), 6.93 (dd, $J = 8.4$, 2.2 Hz, 1H), 6.83–6.75 (m, 4H), 5.59 (d, $J = 7.5$ Hz, 1H), 5.05 (s, 2H), 4.97 (s, 2H), 2.10 (s, 3H), 1.74–1.62 (m, 2H), 1.61–1.46 (m, 3H), 1.19–0.94 (m, 4H), 0.93–0.83 (m, 1H), 0.74–0.61 (m, 1H). $^{13}$C-NMR (CDCl$_3$) $\delta$: 197.7, 170.6, 162.5, 158.0, 141.2, 139.3, 138.6, 137.1, 136.3, 132.3, 131.4, 129.8, 128.8, 128.7, 128.4, 128.1, 127.8, 127.7, 127.6, 127.2, 126.4, 114.2, 114.2, 114.0, 77.1, 70.2, 69.9, 43.9, 29.2, 28.5, 26.2, 26.0, 21.4. IR (CHCl$_3$, cm$^{-1}$) 3036, 3007, 2932, 1728, 1651, 1599, 1506, 1454, 1290, 1242, 1196, 1171, 1157, 1026. MS (EI): $m/z$ = 624 (M$^+$). HRMS (EI): $m/z$ calcd for C$_{46}$H$_{39}$O$_5$: 624.2876; found: 624.2883.
1-((4′-(benzyloxy)-6-(4-(benzyloxy)benzoyl)-[1,1′-biphenyl]-2-yl)-3-methylbutyl acetate (5ch)

Yield: 76.5 mg, 64%; colorless oil. 1H-NMR (CDCl₃) δ: 7.59–7.52 (m, 3H), 7.44–7.28 (m, 13H), 6.94 (dd, J = 8.3, 1.7 Hz, 1H), 6.87–6.76 (m, 4H), 5.81 (dd, J = 10.0, 3.1 Hz, 1H), 5.07 (s, 2H), 4.98 (s, 2H), 2.09 (s, 3H), 1.68 (ddd, J = 14.3, 10.0, 4.3 Hz, 1H), 1.52–1.45 (m, 1H), 1.28–1.17 (m, 1H), 0.71 (d, J = 6.5 Hz, 3H), 0.48 (d, J = 6.4 Hz, 3H). 13C-NMR (CDCl₃) δ: 197.4, 170.5, 162.6, 158.1, 141.4, 141.0, 137.7, 137.1, 136.3, 132.4, 131.6, 131.1, 130.9, 129.6, 128.8, 128.7, 128.0, 127.6, 127.5, 126.5, 126.3, 114.6, 114.3, 71.8, 70.2, 69.9, 46.1, 24.9, 23.3, 21.4, 21.3. IR (CHCl₃, cm⁻¹) 3036, 3007, 2959, 2928, 2870, 1730, 1645, 1599, 1574, 1506, 1454, 1373, 1290, 1242, 1171, 1157. MS (EI): m/z = 598 (M⁺). HRMS (EI): m/z calcd for C₄₀H₃₈O₅: 598.2719; found: 598.2715.

(4′-(benzyloxy)-6-(4-(benzyloxy)benzoyl)-[1,1′-biphenyl]-2-yl)(cyclopen(tyl)methyl acetate (5cj)

Yield: 85.4 mg, 70%; light yellow oil. 1H-NMR (CDCl₃) δ: 7.58 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 8.7 Hz, 2H), 7.46–7.28 (m, 13H), 6.94 (dd, J = 8.3, 2.0 Hz, 1H), 6.83–6.74 (m, 4H), 5.69 (d, J = 8.1 Hz, 1H), 5.05 (s, 2H), 4.97 (s, 2H), 2.17–2.07 (m, 4H), 1.63 (tt, J = 12.3, 6.1 Hz, 1H), 1.52–1.38 (m, 2H), 1.37–1.18 (m, 4H), 0.96–0.86 (m, 1H). 13C-NMR (CDCl₃) δ: 197.7, 170.5, 162.5, 158.0, 141.2, 140.3, 138.2, 137.1, 136.3, 132.3, 131.5, 130.9, 129.8, 128.8, 128.7, 128.4, 128.0, 127.7, 127.6, 127.4, 126.5, 114.3, 114.2, 114.1, 76.2, 70.2, 69.9, 46.7, 29.0, 28.9, 25.0, 24.9, 21.5. IR (CHCl₃, cm⁻¹) 3036, 3007, 1730, 1655, 1599, 1574, 1506, 1454, 1373, 1290, 1242, 1171, 1155, 1026. MS (EI): m/z = 610 (M⁺). HRMS (EI): m/z calcd for C₄₁H₃₈O₅: 610.2719; found: 610.2721.

General procedure for the synthesis of 7 and 8.

To a solution of alkyne 6 (0.2 mmol) and aldehyde (0.48 mmol) in DCE (1 mL) was added BF₃·Et₂O (0.02 mmol) and stirred at 50 °C under argon atmosphere. After completion of the reaction as monitored by TLC, the solution was concentrated in vacuo. Column chromatography on silica gel using hexane/ethyl acetate (8:1) as an eluent afforded the corresponding 7 and 8.

(E)-ethyl 4-(4-(benzyloxy)benzoyl)-2-((E)-2-(4-(benzyloxy)benzoyl)-3-(p-tolyl)allyl)-5-(p-tolyl)pent-4-enoate (7)

Yield: 136.7 mg, 89%; colorless oil. 1H-NMR (CDCl₃) δ: 7.82–7.77 (m, 4H), 7.45–7.31 (m, 10H), 7.27 (d, J = 8.1 Hz, 4H), 7.17 (d, J = 8.1 Hz, 4H), 7.04 (s, 2H), 6.99 (d, J = 8.8 Hz, 4H), 5.11 (s, 4H), 3.78 (q, J = 7.0 Hz, 2H), 3.23–3.15 (m, 2H), 3.02–2.94 (m, 3H), 2.35 (s, 6H), 0.92 (t, J = 7.1 Hz, 3H). 13C-NMR (CDCl₃) δ: 197.6, 174.6, 162.1, 141.6, 138.7, 138.6, 136.4, 132.5, 132.4, 131.0, 129.4, 129.3, 128.8, 128.3, 127.6,
114.4, 70.2, 60.7, 44.2, 30.7, 21.5, 13.9. IR (CHCl$_3$, cm$^{-1}$) 3007, 1722, 1639, 1599, 1506, 1242, 1171. MS (EI): $m/z = 768$ (M$^+$$)$. HRMS (EI): $m/z$ calcd for C$_{52}$H$_{48}$O$_6$: 768.3451; found: 768.3454.

*(E)-ethyl 4-(4-(benzyloxy)benzoyl)-2-((E)-2-(4-(benzyloxy)benzoyl)-3-(4-fluorophenyl)allyl)-5-(4-fluorophenyl)pent-4-enoate (8)*

Yield: 141.2 mg, 91%; colorless oil. $^1$H-NMR (CDCl$_3$) $\delta$: 7.80 (d, $J = 8.8$ Hz, 4H), 7.45–7.32 (m, 14H), 7.08–6.98 (m, 10H), 5.12 (s, 4H), 3.80 (q, $J = 7.2$ Hz, 2H), 3.18–3.09 (m, 2H), 2.97–2.88 (m, 3H), 0.93 (t, $J = 7.2$ Hz, 3H). $^{13}$C-NMR (CDCl$_3$) $\delta$: 197.3, 174.6, 162.7 (d, $J = 248.9$ Hz), 162.3, 140.1, 139.1, 136.4, 132.3, 131.4 (d, $J = 4.2$ Hz), 131.1 (d, $J = 7.4$ Hz), 130.7, 128.8, 128.4, 127.6, 115.8 (d, $J = 21.6$ Hz), 114.5, 70.3, 60.8, 43.9, 30.6, 14.0. IR (CHCl$_3$, cm$^{-1}$) 3036, 3007, 1724, 1639, 1601, 1574, 1508, 1504, 1379, 1312, 1292, 1248, 1194, 1171, 1159. MS (EI): $m/z = 776$ (M$^+$$)$. HRMS (EI): $m/z$ calcd for C$_{36}$H$_{24}$F$_2$O$_6$: 776.2949; found: 776.2954.

References
Figure S1. Thermal ellipsoid plot of the crystallographic structure of 3aa (CCDC number: 1953678).
1,7-bis(4-ethoxyphenyl)hepta-1,6-diyne (1b)
1,7-bis(4-(benzyloxy)phenyl)hepta-1,6-diyne (1c)
1,7-di-p-tolylhepta-1,6-diyne (1d)

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1,7-diphenylhepta-1,6-diyne (1e)
4,4’-(oxybis(prop-1-yn-3,1-diyl))bis((benzyloxy)benzene) (1f)
ethyl 5-(4-(benzyloxy)phenyl)-2-(3-(4-(benzyloxy)phenyl)prop-2-yn-1-yl)pent-4-ynoate (6)
(4'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-methoxyphenyl)methanone (3b)

3a

OMe

3b

OMe
(E)-(4'-methoxy-6-(3-methylbenzylidene)-3,4,5,6-tetrahydro-1,1'-biphenyl]-2-yl)(4-methoxyphenyl)methanone (3ab)
(E)-(6-(4-fluorobenzylidene)-4'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-methoxyphenyl)methanone (3ac)
(E)-4-((4'-methoxy-6-(4-methoxybenzoyl)-4,5-dihydro-[1,1'-biphenyl]-2(3H)-ylidene)methyl)benzonitrile (3ad)
(E)-4-((4'-ethoxy-6-(4-ethoxybenzoyl)-4,5-dihydro-[1,1'-biphenyl]-2(3H)-ylidene)methyl)benzonitrile (3bd)
(E)-(4'-benzoyloxy)-6-(4-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yi(4-(benzoyloxy)phenyl)methanone (3ca)
(E)-4’-(benzyloxy)-6-(3-methylbenzyldiene)-3,4,5,6-tetrahydro-[1,1’-biphenyl]-2-yl)(4-(benzyloxy)phenyl)methanone (3cb)
(E)-(4'-(benzyloxy)-6-(2-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-(benzyloxy)phenyl)methanone (3ce)
$^{(E)}$-(4'-benzylxylo)-6-(4-methoxybenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl(4-(benzylxylo)phenyl)methanone (3cf)
(E)-(4"-(benzyloxy)-6-(4-methoxy-3-nitrobenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-(benzyloxy)phenyl)methanone (3cg)
(E)-(4'-methyl-6-(4-methylbenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone (3da)
(E)-(4'-benzyloxy)-6-(3-methylbutylenidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl(4-benzyloxyphenyl)methanone (3ch)
(E)-(4'-benzoxyl)-6-(cyclohexylene)-3,4,5,6-tetrahydro-[1,1’-biphenyl]-2-yl(4-(benzoxyl)phenyl)methanone (3ci)
(E)-(4'-benzoylxy)-6-(cyclopentylmethylene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl(4-(benzoylxy)phenyl)methanone (3cj)
(E)-4'-(benzyloxy)-6-(cyclopropylmethylene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl(4-(benzyloxy)phenyl)methanone (3ck)
(7-methoxy-9-(p-tolyl)-9H-fluoren-4-yl)(4-methoxyphenyl)methanone (4aa)
(7-methoxy-9-(m-tolyl)-9H-fluoren-4-yl)(4-methoxyphenyl)methanone (4ab)
(9-(4-fluorophenyl)-7-methoxy-9H-fluoren-4-yl)(4-methoxyphenyl)methanone (4ac)
(7-ethoxy-9-(p-tolyl)-9H-fluoren-4-yl)(4-ethoxyphenyl)methanone (4ba)
(7-(benzyloxy)-9-(p-tolyl)-9H-fluoren-4-yl)(4-(benzyloxy)phenyl)methanone (4ca)
(7-(benzyloxy)-9-(m-tolyl)-9H-fluoren-4-yl)(4-(benzyloxy)phenyl)methanone (4cb)
(7-(benzyloxy)-9-(4-fluorophenyl)-9H-fluoren-4-yl)(4-(benzyloxy)phenyl)methanone (4cc)
cyclohexyl(4'-methoxy-6-(4-methoxybenzoyl)-[1,1'-biphenyl]-2-yl)methyl acetate (5ai)
cyclohexyl(4'-ethoxy-6-(4-ethoxybenzoyl)-1,1'-biphenyl-2-yl)methyl acetate (5bi)
(4'-benzoyloxy)-6-(4-(benzoyloxy)benzoyl)-1,1'-biphenyl-2-yl(cyclohexyl)methyl acetate (Sci)
1-(4'-(benzyloxy)-6-(4-(benzyloxy)benzoyl)-[1,1'-biphenyl]-2-yl)-3-methylbutyl acetate (5ch)
(4'-benzyloxy)-6-(4-benzyloxybenzoyl)-[1,1'-biphenyl]-2-yl(cyclopentyl)methyl acetate (5cj)
(E)-ethyl 4-(4-(benzyloxy)benzoyl)-2-((E)-2-(4-(benzyloxy)benzoyl)-3-(p-tolyl)allyl)-5-(p-tolyl) penta-4-enoate (7)
(E)-ethyl 4-(4-(benzyloxy)benzoyl)-2-((E)-2-(4-(benzyloxy)benzoyl)-3-(4-fluorophenyl)allyl)-5-(4-fluorophenyl)pent-4-enoate (8)