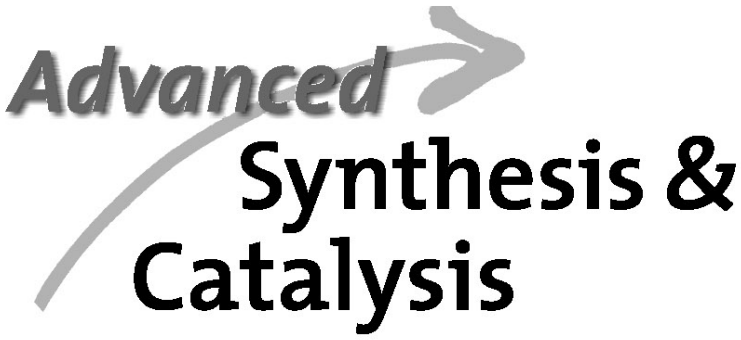

Supporting Information

Supporting Information

Stereoselective Synthesis of 3-Alkylideneoxindoles Using Tandem Indium mediated Carbometallation and Pd-catalyzed Cross-Coupling Reaction

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General

^{1}H NMR and ^{13}C NMR spectra were registered on JEOLJNM-LA500 using TMS as an internal standard. (s = singlet, d = doublet, dd = double doublet, ddd =doublet of double doublets, t = triplet, q = quartet, m = multiplet, br = broad). Nominal (LR-MS) and exact mass (HR-MS) spectra were recorded on a JEOL JMS-01SG-2 or JMS-HX/HX 110A mass spectrometer. For column chromatography, Kanto Silica gel 60 (spherical, 63-210 μm) was employed and preparative thin-layer chromatography (PTLC) was carried out using Silica gel 60F_{254} (Merck). Metallic indium was purchased from Kojundo Chemical Laboratory Co., Ltd. All reactions were carried out under a positive pressure of argon or nitrogen.

General procedures for the synthesis of 2-iodoalkynes (4)

(Scheme 3, path a) S. Kajigaeshi, T. Kakinami, H. Yamasaki, S. Fujisaki, T. Okamoto, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 600-602.

(Scheme 3, path b) M. Kunishima, C. Kawachi, J. Morita, K. Terao, F. Iwasaki, S. Tani, *Tetrahedron*. **1999**, *55*, 13159-13170.

(Scheme 3, path c) To a stirred solution of 2-iodoaniline (219 mg, 1.0 mmol) in THF (2 mL) was added a 1.56 M solution of *n*BuLi in hexane (0.76 mL, 1.2 mmol) at -78 ^{o}C and the mixture was stirred for 30 min. To the mixture was added ethyl hept-2-ynoate (184 mg, 1.2 mmol) at -78 ^{o}C, and stirred for 3 h. A saturated solution of NH_4Cl was added to the mixture and the whole was extracted with AcOEt. The organic phase was washed with successively with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was used for next reaction without further purification.

(Scheme 3, path d) R. N. Salvatole, S. I. Shin, V. L. Flandars. K. W. Jung, *Tetrahedron Lett*. **2001**, *42*, 1799-1801.

(Scheme 3, path e) To a stirred solution of iodoalkyne **4e** (271 mg, 1.0 mmol) in THF (2 mL) was added sodium hydride (26.4 mg, 1.1 mmol) at 0 ^{o}C and stirred for 10 min. To the mixture was added methyl iodide (156 mg, 1.1 mmol) and stirred for 5 h at room temperature. After being quenched with water, the mixture was extracted with AcOEt and dried over $MgSO_4$. The residue was purified by column chromatography [silica gel, hexane/AcOEt (5/1)] to give **4d** (278 mg, 90 %).

(Scheme 3, path f) To a stirred solution of iodoalkyne **4e** (271 mg, 1.0 mmol) in CH_2Cl_2 (2 mL) were added triethylamine (111.1 mg, 1.1 mmol) and methanesulfonyl chloride (427 mg, 1.1 mmol)

at 0 °C and stirred for 8 h. After being quenched with water, the mixture was extracted with AcOEt and dried over $MgSO_4$. The residue was purified by column chromatography [silica gel, hexane/AcOEt (5/1)] to give **4f** (279 mg, 80 %).

(Scheme 3, path g) To a stirred solution of 2-iodoaniline (219 mg, 1.0 mmol) in acetone (2 mL) were added 1-bromohept-2-yne (191 mg, 1.1 mmol) and K_2CO_3 (414 mg, 3.0 mmol) at room temperature and the mixture was srired for 1.5 h under reflux. After being quenched with water, the mixture was extracted with AcOEt and dried over $MgSO_4$. The residue was purified by column chromatography [silica gel, hexane/AcOEt (5/1)] to give **3b** (247 mg, 79 %).

(Scheme 3, path h) To a stirred solution of 2-iodoaniline (219 mg, 1.0 mmol) in acetone (2 mL) were added 1-bromobut-2-yne (146 mg, 1.1 mmol) and K_2CO_3 (414 mg, 3.0 mmol) at room temperature and the mixture was srired for 1.5 h under reflux. After being quenched with water, the mixture was extracted with AcOEt and dried over $MgSO_4$. The residue was purified by column chromatography [silica gel, hexane/AcOEt (5/1)] to give **3g** (214 mg, 79 %).

(Scheme 3, path i, j, k) D. E. Lizos, J. A. Murpy, *Org. Biomol, Chem.* **2003**, *1*, 117-122.

***N*-Benzyl-*N*-(2-iodophenyl)hept-2-ynamide (4a)**

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 4.9 Hz, 1H), 7.31–7.17 (m, 6H), 7.02 (t, *J* = 4.0 Hz, 1H), 6.75 (d, *J* = 4.9 Hz, 1H), 5.62 (d, *J* = 15.0 Hz, 1H), 4.04 (d, *J* = 15.0 Hz, 1H), 2.07–2.01 (m, 2H), 1.17–1.10 (m, 2H), 1.00–0.98 (m, 2H), 0.72–0.69 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 143.6, 139.7, 136.2, 131.5, 129.8, 129.5, 128.5, 127.7, 100.5, 94.5, 74.8, 29.3, 21.3, 18.2, 13.3; IR ($CHCl_3$) ν 3007, 1632 cm^{-1}; MS (FAB) m/z 418 (MH^+); HRMS (FAB) calcd for $C_{20}H_{21}INO$ (MH^+) 418.0669, found 418.0677.

***N*-Benzyl-*N*-(hept-2-ynyl)-2-iodobenzenamide (4b)**

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 6.7 Hz, 1H), 7.35–7.20 (m, 6H), 6.82–6.79 (m, 1H), 4.25 (s, 1H), 3.90 (d, *J* = 6.1 Hz, 1H), 3.68 (s, 2H), 2.20–2.14 (m, 2H), 1.49-1.32 (m, 4H), 0.92–0.85 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 139.6, 129.3, 128.9, 128.8, 128.6, 128.2, 127.1, 124.7, 123.8, 99.8, 85.9, 85.3, 75.1, 30.9, 21.7, 18.3, 13.5; IR ($CHCl_3$) ν 3029, 2857, 2238 cm^{-1}; MS (FAB) m/z 404 (MH^+); HRMS (FAB) calcd for $C_{20}H_{23}IN$ (MH^+) 404.0876, found 404.0880.

***N*-Benzyl-*N*-(2-iodophenyl)propiolamide (4c)**

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.4 Hz, 1H), 7.32–7.16 (m, 6H), 7.06 (t, *J* = 6.4 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 5.62 (d, *J* = 14.4 Hz, 1H), 4.04 (d, *J* = 14.4 Hz, 1H), 2.75 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 142.8, 139.9, 135.8, 131.4, 130.3, 129.5, 128.9, 128.7, 128.5, 127.9, 106.6, 100.2, 79.4, 76.1, 51.1; IR ($CHCl_3$) ν 3300, 1644 cm^{-1}; MS (FAB) m/z 362 (MH^+); HRMS (FAB) calcd for $C_{16}H_{13}INO$ (MH^+) 362.0043, found 362.0034.

***N*-(2-Iodophenyl)-*N*-propiolamide (4d)**

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.5 Hz, 1H), 7.43–7.42 (m, 1H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 3.23 (s, 3H), 2.75 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 144.9, 140.0, 130.3, 129.6, 128.4, 99.3, 79.0, 76.0, 35.3; IR ($CHCl_3$) ν 3010, 1632 cm^{-1}; MS (FAB) m/z 286 (MH^+); HRMS (FAB) calcd for $C_{10}H_9INO$ (MH^+) 285.9730, found 285.9728.

***N*-(2-Iodophenyl)propiolamide(4e)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 1H), 3.01 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 139.0, 137.4, 129.4, 126.9, 122.4, 89.5, 77.3, 74.7; IR ($CHCl_3$) ν 3010,1640 cm^{-1}; MS (FAB) m/z 272 (MH^+); HRMS (FAB) calcd for C_9H_7INO (MH^+) 271.9574, found 271.9576.

***N*-(2-Iodophenyl)-*N*-(methanesulfonyl)propiolamide (4f)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 3.16 (s, 3H), 2.39 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$)

δ 152.3, 140.9, 140.3, 131.2, 130.7, 129.3, 102.1, 78.1, 74.3, 40.5; IR ($CHCl_3$) ν 3010, 1680 cm^{-1}; Anal. Calcd for $C_{10}H_8INO_3S$: C, 34.40; H, 2.31; I, 36.35; N, 4.01; O, 13.75. Found: C, 34.43; H, 2.35; I, 36.40; N, 4.00; O, 13.73.

***N*- (2-Butynyl)-*N*-(iodophenyl)methanesulfonamide (4g)**

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 6.4 Hz, 1H), 7.58 (d, *J* = 6.4 Hz, 1H), 7.42 (t, *J* = 6.4 Hz, 1H), 7.11 (t, *J* = 6.4 Hz, 1H), 4.66 (d, *J* = 18.3 Hz, 1H), 4.02 (d, *J* = 18.3 Hz, 1H), 3.15 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 140.2, 131.1, 130.5, 129.1, 102.3, 82.2, 73.3, 41.2, 41.1, 3.5; IR ($CHCl_3$) ν 3029, 2857, 2236, 1347 cm^{-1}; MS (FAB) m/z 350 (MH^+); HRMS (FAB) calcd for $C_{11}H_{13}IO_2S(MH^+)$ 349.9713, found 349.9712.

2-Iodophenyl propiolate (4h)

colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 3.13 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 150.1, 139.7, 129.6, 128.4, 122.8, 89.7, 77.5, 74.0; IR ($CHCl_3$) ν 2984, 1731 cm^{-1}; MS (FAB) m/z 273 (MH^+); HRMS (FAB) calcd for $C_9H_6IO_2$ (MH^+) 272.9414, found 272.9418.

***N*-Benzyl-*N*-(2-iodo-4-methoxyphenyl)hept-2-ynamide (4i)**

white needles; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 3.0 Hz, 1H), 7.28–7.25 (m, 3H), 7.23–7.20 (m, 2H), 6.71–6.69 (m, 1H), 6.62 (d, *J* = 9.0 Hz , 1H), 5.59 (d, *J* = 14.0 Hz, 1H), 4.01 (d, *J* = 14.0 Hz, 1H), 3.77 (s, 3H), 2.10–2.06 (m, 2H), 1.20–1.16 (m, 2H), 1.06–1.03 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 136.5, 136.4, 136.3, 131.4, 129.5, 128.4, 127.6, 124.4, 114.4, 100.7, 94.1, 75.0, 55.5, 51.1, 29.4, 21.3, 18.3, 13.3; IR ($CHCl_3$) ν 3009, 2961, 2936, 2244, 1630, 1488, 1292 cm^{-1}; MS (CI) m/z 448 (MH^+); HRMS (CI) calcd for $C_{21}H_{23}INO_2$ (MH^+) 448.0773, found 448.0774. Anal. Calcd for $C_{21}H_{22}INO_2$: C, 56.39; H, 4.96; N, 3.13; O, 7.15. Found: C, 56.24; H, 4.96; N, 3.09; O, 7.39.

***N*-Benzyl-*N*-(2-iodo-4-methylphenyl)hept-2-ynamide (4j)**

white needles; ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.27–7.25 (m, 3H), 7.23–7.20 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 1H), 6.62 (d, *J* = 14.0 Hz, 1H), 5.58 (d, *J* = 9.0 Hz, 1H), 4.02 (d, *J* = 14.0 Hz, 1H), 2.30 (s, 3H), 2.09–2.04 (m, 2H), 1.16–1.14 (m, 2H), 1.03–0.95 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 141.0, 140.2, 140.1, 136.4, 130.9, 129.5, 128.7, 128.4, 127.7, 100.3, 94.1, 74.9, 51.0, 29.3, 21.3, 20.5, 18.3, 13.3; IR ($CHCl_3$) ν 2960, 2244, 1631, 1486, 1396, 1296, 1211 cm^{-1}; MS (CI) m/z 432 (MH^+); HRMS (CI) calcd for $C_{21}H_{23}INO$ (MH^+) 432.0824, found 432.0833; Anal. Calcd for $C_{21}H_{22}INO$: C, 58.48; H, 5.14; N, 3.25. Found: C, 58.41; H, 5.12; N, 3.27.

***N*-Benzyl-*N*-(4-chloro-2-iodophenyl)hept-2-ynamide (4k)**

white needles; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.31–7.26 (m, 3H), 7.24–7.16 (m, 3H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.60 (d, *J* = 10.0 Hz, 1H), 4.01 (d, *J* = 10.0 Hz, 1H), 2.13–2.05 (m, 2H), 1.23-1.16 (m, 2H), 1.06–1.01 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 142.4, 139.1, 136.3, 134.8, 131.9, 129.5, 128.9, 128.6, 127.9, 101.0, 94.7, 74.8, 50.8, 29.3, 21.4, 18.3, 13.3; IR ($CHCl_3$) ν 3009, 2916, 2935, 2244, 1635, 1468, 1393, 1294, 1099 cm^{-1}; Anal. Calcd for $C_{20}H_{19}ClINO$: C, 53.18; H, 4.24; Cl, 7.85; N, 3.10; O, 3.54. Found: C, 53.19; H, 4.21; Cl, 7.78; N, 3.07; O, 3.47.

***N*-Benzyl-*N*-(4-(trifluoromethyl)-2-iodophenyl)hept-2-ynamide (4l)**

white needles; ^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.46 (d, *J* = 6.0 Hz, 1H), 7.33–7.26 (m, 3H), 7.24–7.20 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.63 (d, *J* = 14.0 Hz, 1H), 4.06 (d, *J* = 14.0 Hz, 1H), 2.12–2.02 (m, 2H), 1.16–1.11 (m, 2H), 1.02–0.93 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 153.9, 147.0, 136.8, 135.8, 131.7, 129.5, 128.8, 128.7, 128.0, 125.7, 100.9, 95.0, 74.7, 50.3, 29.2, 21.3, 18.1, 13.1; IR ($CHCl_3$) ν 2935, 2243, 1640, 1388, 1320, 1175, 1138, 1079 cm^{-1}; Anal. Calcd for $C_{21}H_{19}F_3INO$: C, 51.97; H, 3.95; F, 11.74; I, 26.15; N, 3.13. Found: C, 51.99; H, 4.09; F, 11.72; I, 25.93; N, 2.89.

***N*-Benzyl-*N*-(4-cyano-2-iodophenyl)hept-2-ynamide (4m)**

white needles; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.90–7.26 (m, 3H), 7.19–7.17 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.62 (d, *J* = 14.0 Hz, 1H), 4.07 (d, *J* = 14.0 Hz, 1H), 2.09–2.06 (m, 2H), 1.19–1.16 (m, 2H), 1.05–1.01 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 147.9, 143.0, 135.5, 132.3, 132.0, 129.5, 128.7, 128.2, 116.3, 113.8, 101.2, 95.2, 74.6, 50.7, 29.2, 21.4, 18.2, 13.3; IR ($CHCl_3$) ν 2961, 2236, 1642, 1479, 1385, 1295, 1229 cm^{-1}; Anal. Calcd for $C_{21}H_{19}IN_2O$: C, 57.03; H, 4.33; N, 6.33; O, 3.62. Found: C, 56.96; H, 4.35; N, 6.24; O, 3.52.

***N*-Benzyl-*N*-(2-iodophenyl)pent-2-ynamide (4n)**

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.37–7.20 (m, 6H), 7.02 (t, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 5.61 (d, *J* = 14.4 Hz, 1H), 4.06 (d, *J* = 14.4 Hz, 1H), 2.01–1.98 (m, 2H), 0.79–0.75 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 143.6, 139.9, 136.3, 131.4, 129.8, 129.5, 128.9, 128.6, 127.7, 100.4, 95.3, 74.2, 55.4, 50.9, 12.7; IR ($CHCl_3$) ν 3004, 1633 cm^{-1}; MS (FAB) m/z 390 (MH^+); HRMS (FAB) calcd for $C_{18}H_{17}INO$ (MH^+) 390.4679, found 390.0361; Anal. Calcd for $C_{18}H_{16}INO$: C, 55.54; H, 4.14; N, 3.60; O, 4.11. Found: C, 55.47; H, 4.36; N, 3.59; O, 4.32.

***N*-Benzyl-4-(benzyloxy)-*N*-(2-iodophenyl)but-2-ynamide (4o)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.31–7.12 (m, 11H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.61 (d, *J* = 14.3 Hz, 1H), 4.14–4.01 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 143.0, 139.9, 136.9, 136.8, 136.4, 135.8, 131.4, 130.2, 129.5, 128.5, 128.3, 128.0, 100.4, 88.0, 80.0, 72.1, 70.8, 56.4, 51.0; IR ($CHCl_3$) ν 2935, 1699, 1639 cm^{-1}; MS (FAB) m/z 482 (MH^+); HRMS (FAB) calcd for $C_{24}H_{21}INO_2$ (MH^+) 482.0618, found 482.0601.

***N*-Benzyl-3-(4-(trifluoromethyl)phenyl)-*N*-(2-iodophenyl)propiolamide (4p)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.30–7.25 (m, 7H), 7.17–7.15 (m, 1H), 7.09 (t, *J* = 6.9 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 5.65 (d, *J* = 9.8 Hz, 1H), 4.18 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 143.2, 139.9, 135.9, 132.8, 131.4, 130.2, 129.5, 128.7, 128.6, 128.5, 127.9, 125.2, 123.9, 122.4, 100.5, 88.8, 84.0, 51.1; IR ($CHCl_3$) ν 2223, 1639 cm^{-1}; Anal. Calcd for $C_{23}H_{15}F_3INO$: C, 54.67; H, 2.99; N, 2.77; F, 11.27; I, 25.12. Found: C, 54.44; H, 3.21; N, 2.70; F, 11.30; I, 25.03.

***N*-Benzyl-*N*-(2-iodophenyl)-3-phenylpropiolamide (4q)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.32–7.19 (m, 9H), 7.09–7.05 (m, 3H), 6.85 (d, *J* = 7.9 Hz, 1H), 5.66 (d, *J* = 15.4 Hz, 1H), 4.14 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 143.5, 139.9, 136.2, 132.7, 132.5, 131.6, 130.0, 129.5, 128.8, 128.6, 128.3, 127.3, 120.2, 100.6, 91.0, 82.4, 51.0; IR ($CHCl_3$) ν 3008, 1633 cm^{-1}; Anal. Calcd for $C_{22}H_{16}INO$: C, 60.41; H, 3.66; N, 3.20; O, 3.66. Found: C, 60.70; H, 3.56; N, 3.43; O, 3.55.

***N*-Benzyl-*N*-(2-iodophenyl)but-2-ynamide (4r)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.37–7.18 (m, 6H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.61 (d, *J* = 14.3 Hz, 1H), 4.06 (d, *J* = 14.3 Hz, 1H), 1.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 143.3, 139.7, 136.1, 131.3, 130.3, 129.9, 128.6, 128.4, 128.0, 127.7, 100.3, 90.1, 73.9, 50.9; IR ($CHCl_3$) ν 3004, 1629 cm^{-1}; MS (FAB) m/z 376 (MH^+); HRMS (FAB) calcd for $C_{17}H_{15}INO$ (MH^+) 376.0200, found 376.0187.

***N*-Benzyl-*N*-(2-iodophenyl)-3-*p*-tolylpropiolamide (4s)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.31–7.20 (m, 6H), 7.07–6.93 (m, 5H), 6.83 (d, *J* = 7.7 Hz, 1H), 5.67 (d, *J* = 14.3 Hz, 1H), 4.13 (d, *J* = 14.3 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 140.6, 139.8, 136.3, 132.5, 131.7, 130.0, 129.6, 129.4, 129.1, 128.8, 128.5, 127.8, 117.1, 100.7, 91.6, 82.1, 50.9, 21.5; IR ($CHCl_3$) ν 2215, 1632 cm^{-1}; Anal. Calcd for $C_{23}H_{18}INO$: C, 61.21; H, 4.02; N, 3.10; O, 3.55. Found: C, 61.42; H, 4.08; N, 3.07; O, 3.36.

***N*-Benzyl-*N*-(2-iodophenyl)-3-(4-methoxyphenyl)propiolamide (4t)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.31–7.24 (m, 6H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.98 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.72 (d, *J* = 7.0 Hz, 2H), 5.68 (d, *J* = 14.4 Hz, 1H), 4.13 (d, *J* = 14.4 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 154.6, 143.5, 141.7, 139.7, 136.7, 134.5, 131.6, 130.6, 128.9, 128.0, 127.7, 113.9, 112.1, 111.9, 92.1, 81.8, 55.2, 52.0; IR ($CHCl_3$) ν 2215, 1632 cm^{-1}; MS (FAB) m/z 468 (MH^+); HRMS (FAB) calcd for $C_{23}H_{19}INO_2$ (MH^+) 468.0462, found 468.0466.

***N*-Benzyl-*N*-(2-iodophenyl)-3-(thiophen-3-yl)propiolamide (4u)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.32–7.21 (m, 7H), 7.15–7.13 (m, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 5.65 (d, *J* = 15.0 Hz, 1H), 4.13 (d, *J* = 15.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 143.4, 139.9, 136.1, 132.5, 131.6, 129.8, 129.5, 128.7, 128.1, 127.8, 126.1, 125.7, 119.4, 100.6, 86.4, 82.4, 50.9; IR ($CHCl_3$) ν 2215, 1632 cm^{-1}; Anal. Calcd for $C_{20}H_{14}INOS$: C, 54.19; H, 3.18; I, 28.63 N, 3.16; O, 3.61. Found: C, 54.37; H, 3.37; I, 28.36 N, 3.13; O, 3.37.

General procedure for indium mediated reductive radical cyclization

To a solution of iodoalkyne **4a** (41.8 mg, 0.10 mmol) in DMF were added indium (0) (22.8 mg, 0.20 mmol) and pyridinium bromide perbromide (31.9 mg, 0.10 mmol) and stirred for 12 h at room temperature under argon atmosphere. After being quenched with water, the mixture was extracted with AcOEt and dried over $MgSO_4$. The residude was purified by column chromatography [silica gel, hexane/AcOEt (5/1)] to give **6a** (23.3 mg, 80%).

(*E*)-1-Benzyl-3-pentylideneindolin-2-one (6a)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.27 (m, 5H), 7.14 (dd, *J* = 7.6, 7.4 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.7 (d, *J* = 7.6 Hz, 1H), 4.9 (s, 2H), 2.7 (q, *J* = 7.6 Hz, 2H), 1.65 (m, 2H), 1.47 (m, 2H), 0.9 7 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 142.8, 136.2, 128.7, 127.5, 127.3, 123.5, 122.5, 122.0, 109.0, 43.5, 30.6, 29.1, 22.5, 13.8; IR ($CHCl_3$) ν 2215, 1616 cm^{-1}; MS (FAB) m/z 292 (MH^+); HRMS (FAB) calcd for $C_{20}H_{22}NO$ (MH^+) 292.1701, found 292.1703.

1-Benzyl-3-methyleneindolin-2-one (6c)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–6.94 (m, 9H), 6.39–6.35 (m, 1H), 6.15–6.13 (m, 1H), 5.01 (br, 2H); IR ($CHCl_3$) ν 2215, 1630 cm^{-1}; MS (FAB) m/z 236 (MH^+); HRMS (FAB) calcd for $C_{16}H_{14}NO$ (MH^+) 236.1075, found 236.1065.

(*E*)-1-Benzyl-5-methoxy-3-pentylideneindolin-2-one (6i)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 4H), 7.26 (s, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.71–6.69 (m, 1H), 6.59 (d, *J* = 9.0 Hz, 1H), 4.93 (s, 2H), 3.77 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.66–1.61 (m, 2H), 1.47–1.44 (m, 2H), 0.97 (t, *J* = 14.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 155.5, 143.1, 136.6, 136.3, 128.7, 127.7, 127.5, 127.3, 123.5, 112.6, 111.4, 109.1, 55.9, 43.6, 30.6, 28.9, 22.5, 13.8; IR ($CHCl_3$) ν 3008, 2961, 2931, 1697, 1483, 1344, 1322, 1024 cm^{-1}; MS (FAB) m/z 322 (MH^+); HRMS (FAB) calcd for $C_{21}H_{24}NO_2$ (MH^+) 322.1807, found 322.1797.

(*E*)-1-Benzyl-5-methyl-3-pentylideneindolin-2-one (6j)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.30–7.24 (m, 5H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.94 (s, 2H), 2.70 (q, *J* = 13.0 Hz, 2H), 2.32 (s, 3H), 1.68–1.61 (m, 2H), 1.51–1.46 (m, 2H), 0.98 (t, *J* = 15.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 142.6, 140.5, 136.3, 131.4, 129.0, 128.7, 127.6, 127.4, 127.3, 124.3, 122.6, 108.8, 43.6, 30.7, 29.0, 22.5, 21.1, 13.8; IR ($CHCl_3$) ν 3008, 2960, 2929, 1698, 1486, 1346, 1189 cm^{-1}; MS (FAB) m/z 306 (MH^+); HRMS (FAB) calcd for $C_{21}H_{24}NO$ (MH^+) 306.1858, found 306.1860.

(*E*)-1-Benzyl-3-propylideneindolin-2-one (6n)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.31–7.16 (m, 5H), 7.17–7.08 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 4.95 (s, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 136.9, 128.8, 128.7, 127.5,

127.3, 127.0, 123.5, 122.4, 122.1, 109.0, 43.6, 22.7, 12.9; IR ($CHCl_3$) ν 3673, 3025, 1732, 1248 cm^{-1}; MS (FAB) m/z 264 (MH^+); HRMS (FAB) calcd for $C_{18}H_{18}NO$ (MH^+) 264.1388, found 264.1381.

(*E*)-1-Benzyl-3-(2-(benzyloxy)ethylidene)indolin-2-one (6o)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.23 (m, 12H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 4.94 (s, 2H), 4.68 (d, *J* = 5.5 Hz, 2H), 4.67 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 143.1, 137.9, 137.5, 135.9, 129.5, 128.8, 127.3, 124.4, 122.2, 121.6, 109.1, 72.9, 67.1, 43.6; IR ($CHCl_3$) ν 3010, 1706 cm^{-1}; Anal. Calcd for $C_{24}H_{21}NO$: C, 81.10; H, 5.96; N, 3.94. Found: C, 80.93; H, 6.11; N, 3.98.

(*E*)-3-(4-(Trifluoromethyl)benzylidene)-1-benzylindolin-2-one (6p)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.59–7.50 (m, 6H), 7.39–7.23 (m, 5H), 6.89–6.87 (m, 2H), 5.00 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 143.4, 137.6, 136.9, 135.1, 129.7, 129.6, 129.3, 128.9, 128.7, 127.6, 127.4, 122.9, 122.4, 121.8, 109.2, 43.5; IR ($CHCl_3$) ν 2225, 1638 cm^{-1}; MS (FAB) m/z 380 (MH^+); HRMS (FAB) calcd for $C_{23}H_{17}F_3NO$ (MH^+) 380.1262, found 380.1263.

(*Z*)-3-(4-(Trifluoromethyl)benzylidene)-1-benzylindolin-2-one (6p)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 2H), 7.58 (s, 1H), 7.52–7.39 (m, 3H), 7.39–7.25 (m, 5H), 7.10–6.90 (m, 3H), 5.00 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ; 168.7, 143.5, 137.7, 136.8, 135.1, 129.8, 129.7, 129.3, 128.9, 128.6, 127.6, 127.4, 122.9, 122.4, 121.8, 109.2, 43.6; IR ($CHCl_3$) ν 2230, 1640 cm^{-1}; MS (FAB) m/z 380 (MH^+); HRMS (FAB) calcd for $C_{23}H_{17}F_3NO$ (MH^+) 380.1262, found 380.1262.

(*E*)-1-Benzyl-3-benzylideneindolin-2-one (6q)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.72–7.60 (m, 3H), 7.52–7.39 (m, 3H), 7.39–7.23 (m, 5H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.00 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 143.4, 137.6, 136.1, 135.1, 129.7, 129.6, 129.3, 128.8, 128.7, 127.6, 127.4, 122.9, 121.8, 109.2, 43.8; IR ($CHCl_3$) ν 3690, 2361, 1692 cm^{-1}; MS (FAB) m/z 312 (MH^+); HRMS (FAB) calcd for $C_{22}H_{18}NO$ (MH^+) 312.1388, found 312.1394.

(*Z*)-1-Benzyl-3-benzylideneindolin-2-one (6q)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.7 Hz, 2H), 7.60 (s, 1H), 7.52–7.39 (m, 3H), 7.39–7.25 (m, 5H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.04 (t, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 4.99 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 143.5, 137.5, 136.3, 132.0, 130.1, 128.9, 128.7, 128.3, 127.5, 127.3, 125.9, 121.9, 119.1, 108.9, 43.6; IR ($CHCl_3$) ν 3615, 2361, 1606 cm^{-1}; MS (FAB) m/z 312 (MH^+); HRMS (FAB) calcd for $C_{22}H_{18}NO$ (MH^+) 312.1388, found 312.1396.

(*E*)-1-Benzyl-3-ethylideneindolin-2-one (6r)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 1H), 7.30–7.28 (m, 5H), 7.22 (q, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.01 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 4.95 (s, 2H), 2.31 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 142.7, 137.0, 136.2, 128.7, 128.6, 128.5, 127.5, 127.3, 123.5, 122.6, 122.1, 109.0, 43.5, 15.1; IR ($CHCl_3$) ν 3010, 1703 cm^{-1}; MS (EI) m/z 249 (M^+); HRMS (FAB) calcd for $C_{17}H_{15}NO$ (M^+) 249.1154, found 249.1155.

(*E*)-3-(4-Methylbenzylidene)-1-benzylindolin-2-one (6s)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.71 (d, *J* = 6.9 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.33–7.24 (m, 5H), 7.23–7.21 (m, 1H), 7.15–7.13 (m, 1H), 6.86 (m, 1H), 6.74 (d, *J* = 7.9 Hz, 2H), 5.00 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5 143.8, 137.5, 136.1, 135.1, 129.8, 129.6, 129.4, 128.8, 128.7, 127.6, 127.4, 122.9, 121.8, 110.0, 43.9, 21.6; IR ($CHCl_3$) ν 3690, 2360, 1692 cm^{-1}; MS (FAB) m/z 326 (MH^+); HRMS (FAB) calcd for $C_{23}H_{20}NO$ (MH^+) 326.1544, found 326.1535.

General procedure for tandem caboindation and palladium catalyzed cross-coupling reaction

To a solution of iodoalkyne **4c** (36.2 mg, 0.10 mmol) in DMF were added indium (0) (22.8 mg, 0.20 mmol) and pyridinium bromide perbromide (31.9 mg, 0.10 mmol) and stirred under at room temperature argon atmosphere. After 12 h, To a solution were successively added 4-iodotoluene (43.6 mg, 0.20 mmol), palladium(2) acetylacetonate (1.52 mg, $5.0x10^{-3}$ mmol) and lithium bromide (17.2 mg 0.20 mmol) and the mixture was stirred at 100 ^{o}C for 5 h. After being quenched with water, the mixture was extracted with AcOEt and dried over $MgSO_4$. The residude was purified by column chromatography [silica gel, hexane/AcOEt (5/1)] to give (*Z*)-**6s** (19.5 mg, 60%).

General procedure for copper mediated mild cross-coupling reaction

To a solution of iodoalkyne **4c** (36.2 mg, 0.10 mmol) in DMF were added indium (0) (22.8 mg, 0.20 mmol) and pyridinium bromide perbromide (31.9 mg, 0.10 mmol) and stirred at room temperature under argon atmosphere. After 12 h, to a solution were successively added 4-iodotoluene (43.6 mg, 0.20 mmol), bis(dibenzylideneacetone) palladium (0) (2.88 mg, $5.0x10^{-3}$ mmol), NHC ligand (4.74 mg, $1.5x10^{-2}$ mmol), copper bromide (I) (7.15 mg, 0.05 mmol) and lithium iodide (13.3 mg 0.10 mmol) and the mixture was stirred at 50 ^{o}C for 24 h. After being quenched with water, the mixture was extracted with AcOEt and dried over $MgSO_4$. The residude was purified by column chromatography [silica gel, hexane/AcOEt (5/1)] to give (*Z*)-**6s** (23.4 mg, 72%).

(*Z*)-3-(4-Methylbenzylidene)-1-benzylindolin-2-one(6s)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.3 Hz, 1H), 7.58 (s, 1H), 7.53–7.50 (m, 1H), 7.32–7.30 (m, 8H), 7.17–7.15 (m, 1H), 7.03 (t, *J* = 8.3 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.00 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ168.5 143.8, 137.5, 136.1, 135.1, 129.8, 129.6, 129.4, 128.8, 128.7, 127.6, 127.4, 122.9, 121.8, 110.0, 43.9, 21.8; IR ($CHCl_3$) ν 3690, 1692 cm^{-1}; MS (FAB) m/z 326 (MH^+); HRMS (FAB) calcd for $C_{23}H_{20}NO$ (MH^+) 326.1544, found 326.1537.

(*E*)-3-(4-Methoxybenzylidene)-1-benzylindolin-2-one (6t)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.8 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.29 (m, 5H), 7.14 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.88 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 5.00 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) d 169.0, 160.9, 143.1, 137.9, 136.2, 134.6, 131.5, 129.3, 128.8, 127.5, 127.3, 122.5, 121.7, 126.1, 114.1, 109.1, 55.4, 43.7; IR ($CHCl_3$) ν 1694 cm^{-1}; MS(EI^+) m/z 341 (M^+); HRMS (EI^+) calcd for $C_{23}H_{19}NO_2$ (M^+) 341.1416, found 341.1414.

(*Z*)-3-(4-Methoxybenzylidene)-1-benzylindolin-2-one (6t)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.9 Hz, 2H), 7.54 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.31–7.28 (m, 4H), 7.24–7.20 (m, 1H), 7.15–7.12 (m, 1H), 7.02–6.99 (m, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.72 (d, 7.9 Hz, 1H), 5.00 (s, 2H), 3.87 (s, 3H)

(*E*)-1-Benzyl-3-((thiophen-3-yl)methylene)indolin-2-one (6u)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.57–7.56 (m, 1H), 7.30–7.23 (m, 7H), 7.07–7.05 (m, 1H), 6.77 (t, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 4.98 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 142.0, 135.8, 134.7, 131.5, 129.7, 128.8, 128.6, 128.2, 127.6, 127.5, 127.3, 125.1, 123.8, 122.3, 119.4, 110.0, 43.8; IR ($CHCl_3$) ν3580, 1693 cm^{-1}; MS (FAB) m/z 318 (MH^+); HRMS (FAB) calcd for $C_{20}H_{16}NOS$ (MH^+) 318.0952, found 318.0954.

(*Z*)-1-Benzyl-3-((thiophen-3-yl)methylene)indolin-2-one(6u)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.3 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.57 (s, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.34–7.18 (m, 5H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 4.97 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 142.2, 135.9, 134.9, 131.8, 129.7, 128.8, 128.7, 128.6, 128.2, 127.6, 127.4, 125.1, 123.8, 122.2, 119.5, 109.0, 43.6; IR ($CHCl_3$) ν3690, 1692 cm^{-1}; MS (FAB) m/z 318 (MH^+); HRMS (FAB) calcd for $C_{20}H_{16}NOS$ (MH^+) 318.0952, found 318.0953.

***N*-Benzyl-*N*-(hept-2-ynyl)benzeneamine (7b)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 6.7 Hz, 2H), 7.27–7.17 (m, 5H), 6.70 (t, *J* = 11.6 Hz, 1H), 6.65 (d, *J* = 6.7 Hz, 2H), 4.33 (s, 2H), 3.89 (m, 2H), 2.18–2.16 (m, 2H), 1.47–1.36 (m, 4H), 0.92-0.83 (m, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 148.2, 129.3, 128.6, 127.5, 118.2, 117.5, 113.5, 112.8, 85.4, 75.2, 48.3, 34.3, 30.7, 22.6, 21.8, 14.1; IR ($CHCl_3$) ν 3690, 2200 cm^{-1}; MS (FAB) m/z 278 (MH^+); HRMS (FAB) calcd for $C_{20}H_{24}N$ (MH^+) 278.1908, found 278.1910.

***N*-Phenylpropiolamide (7e)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 7.6, 7.3 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 2.92 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 136.9, 129.2, 125.3, 120.0, 77.6, 73.9; IR ($CHCl_3$) ν 3690, 1692 cm^{-1}; MS (FAB) m/z 146 (MH^+); HRMS (FAB) calcd for C_9H_8NO (MH^+) 146.0606, found 146.0605.

***N*-(Methanesulfonyl)-*N*-phenylpropiolamide (7f)**

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.47 (m, 3H), 7.35 (d, *J* = 6.7 Hz, 2H), 3.48 (s, 3H), 3.05 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 134.5, 130.5, 130.2, 129.7, 83.5, 74.8, 41.9; IR ($CHCl_3$) ν 3690, 1692 cm^{-1}; Anal. Calcd for $C_{10}H_9NO_3S$: C, 53.80; H, 4.06; N, 6.27; O, 21.50. Found: C, 54.03; H, 4.18; N, 6.31; O, 21.40.

Phenylpropiolate (7h)

colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 6.4 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 3.06 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 149.8, 129.6, 126.6, 121.2, 77.2, 74.1; IR ($CHCl_3$) ν 3690, 1692 cm^{-1}; MS (FAB) m/z 147 (MH^+); HRMS (FAB) calcd for $C_9H_7O_2$ (MH^+) 147.0446, found 147.0436.

***N*-Benzyl-*N*-(4-chlorophenyl)hept-2-ynamide (7k)**

white needles; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.22 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.89 (s, 2H), 2.09 (t, *J* = 14.0 Hz, 2H), 1.23–1.19 (m, 2H), 1.06–1.00 (m, 2H), 0.75 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 140.1, 136.3, 133.6, 129.8, 128.9, 128.5, 128.3, 127.5, 94.9, 75.0, 51.8, 29.0, 21.2, 18.1, 13.1; IR ($CHCl_3$) ν 3009, 2227, 1672, 1492 cm^{-1}; MS (FAB) m/z 326 (MH^+); HRMS (FAB) calcd for $C_{20}H_{21}ClON$ (MH^+) 326.1312, found 326.1308; Anal. Calcd for $C_{20}H_{21}ClNO$: C, 73.72; H, 6.19; N, 4.30; O, 4.91. Found: C, 73.52; H, 6.31; N, 5.18; O, 4.27.

***N*-Benzyl-*N*-(4-(trifluoromethyl)phenyl)hept-2-ynamide (7l)**

white needles; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.26–7.19 (m, 7H), 4.96 (s, 2H), 2.09 (t, *J* = 6.7 Hz, 2H), 1.21–1.16 (m, 2H), 1.05–0.97 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 145.0, 136.3, 128.9, 128.5, 127.7, 126.0, 125.9, 124.8, 122.6, 95.3, 74.6, 51.9, 29.1, 21.2, 18.2, 13.0; IR ($CHCl_3$) ν 3009, 1236, 1635, 1389 cm^{-1}; MS (FAB) m/z 360 (MH^+); HRMS (FAB) calcd for $C_{21}H_{21}F_3NO$ (MH^+) 360.1575, found 360.1583.

***N*-Benzyl-*N*-(4-cyanophenyl)hept-2-ynamide (7m)**

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 7.6 Hz, 2H), 7.30–7.14 (m, 7H), 4.96 (s, 2H), 2.13–2.11 (m, 2H), 1.27–1.25 (m, 2H), 1.10–1.08 (m, 2H), 0.79–0.77 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8, 136.9, 134.5, 132.8, 129.3, 128.7, 128.5, 127.9, 118.1, 104.0, 95.7, 74.5, 51.8, 29.2, 21.5, 18.3, 13.3; IR ($CHCl_3$) ν 3011, 2231, 1636 cm^{-1}; MS (FAB) m/z 317 (MH^+); HRMS (FAB) calcd for $C_{21}H_{21}N_2O$ (MH^+) 317.1653, found 317.1649.

Synthesis of TMC-95A intermediate

To a stirred solution of 2-iodoaniline (1.00 g, 4.57 mmol) in CH_2Cl_2 (20 mL) were added triphosgene (452 mg, 1.52 mmol) and saturated aqueous solution of $NaHCO_3$ (20 mL) at 0 °C. After stirred at room temperature for 2 h, H_2O was added and aqueous layer was extracted with ether. The combined extracts were dried over $MgSO_4$, and then concentrated under reduced pressure. The crude isocyanate (1.10 g, 98%) was used for the next reaction without further purification. To a solution of **9**[23] (200 mg, 0.889 mmol) in THF (3.0 mL) was added a 1.58 M solution of *n*-butyllithium (0.56 mL, 0.889 mmol) in *n*-hexane. After the solution was stirred at -78 °C for 1 h, a solution of isocyanate prepared above (145 mg, 0.593 mmol) in THF (3.0 mL) was added to the

mixture. The reaction mixture was stirred at -78 °C for an additional hour, before warming to -40 °C. The mixture was then poured into a saturated aqueous solution of NH_4Cl and the mixture was extracted with diethyl ether. The combined organic extracts were dried and concentrated in vacuo and the crude product was purified by SiO_2 column chromatography (elution: 4:1 hexane/ethyl acetate) to give debenzylation compound of **10** (302 mg, 79%) as a colorless oil.

4-[(2-Iodophenylcarbamoyl)ethynyl]-2,2-dimethyloxazolidine-3-carboxylic acid *tert*-butyl ester

light yellow oil; $[\alpha]_D^{17}$ +283 (*c* = 0.30, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 1.46 (s, 12H), 1.61 (s, 3H), 4.05 (m, 2H), 4.67 (m, 1H), 6.81 (m, 1H), 7.28 (m, 1H), 7.70 (m, 2H), 8.11 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 24.0, 24.9, 25.8, 26.8, 28.2, 28.3, 48.2, 67.6, 67.7, 76.3, 80.8, 81.2, 85.4, 85.7, 89.4, 94.2, 94.7, 122.1, 122.3, 126.5, 129.2, 137.4, 137.5, 138.8, 150.0, 150.1, 150.9, 151.5; IR ($CHCl_3$) ν3372, 3017, 2360, 2234, 1696 cm^{-1}; MS (FAB) *m/z* 471 (MH^+, 7), 415 (65), 57 (100); HRMS (FAB) calcd for $C_{19}H_{24}IN_2O_4$ (MH^+) 471.0781, found 471.0784.

4-{[Benzyl-(2-iodophenyl)carbamoyl]ethynyl}-2,2-dimethyloxazolidine-3-carboxylic acid *tert*-butyl ester (10)

light yellow oil; $[\alpha]_D^{17}$+57.7 (*c* = 1.12, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 1.25–1.45 (m, 15H), 3.60 (m, 1H), 3.86 (m, 1H), 4.10 (m, 1H), 4.40 (m, 1H), 5.60 (m, 1H), 6.76 (m, 1H), 7.03 (m, 1H), 7.21 (m, 6H), 7.90 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 24.1, 25.8, 28.4, 48.3, 51.2, 68.0, 75.5, 80.8, 90.6, 95.5, 100.4, 128.0, 128.5, 128.6, 129.0, 129.7, 160.3, 161.1, 136.1, 140.3, 143.3, 153.8; IR ($CHCl_3$) ν3007, 2360, 1696, 1638 cm^{-1}; MS (FAB) *m/z* 561 (MH^+, 4), 505 (40), 91 (100); HRMS (FAB) calcd for $C_{26}H_{30}IN_2O_4$ (M^+) 561.1250, found 561.1243.

(*Z*)-4-(1-Benzyl-2-oxo-1,2-dihydroindol-3-ylidenemethyl)-2,2-dimethyloxazolidine-3-carboxylic acid *tert*-butyl ester (11)

colorless oil; $[\alpha]_D^{26}$+11.6 (*c* = 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 1.33 (s, 6H), 1.51 (s, 3H), 1.58 (s, 3H), 1.71 (s, 3H), 3.88 (m, 1H), 4.36–4.41 (m, 1H), 4.84–5.02 (m, 1H), 5.87–6.00 (m, 1H), 6.67–6.72 (m, 1H), 6.77–6.89 (m, 1H), 7.00–7.04 (m, 1H), 7.14–7.19 (m, 1H), 7.29 (m, 5H), 7.43 (d, *J* = 7.0 Hz, 1H); IR ($CHCl_3$) ν2931, 1707 cm^{-1}; MS (FAB) *m/z* 434 (M^+, 12), 322 (100); HRMS (FAB) calcd for $C_{26}H_{30}N_2O_4$ (M^+) 434.2205, found 434.2195.

(*E*)-4-(1-Benzyl-2-oxo-1,2-dihydroindol-3-ylidenemethyl)-2,2-dimethyloxazolidine-3-carboxylic acid *tert*-butyl ester (11)

colorless oil; $[\alpha]_D^{24}$+1.5 (*c* = 0.80, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 1.28 (s, 6H), 1.50 (s, 3H), 1.60 (s, 3H), 1.70 (s, 3H), 3.91 (dd, *J* = 9.0, 3.8 Hz, 1H), 4.33 (dd, *J* = 8.9, 6.7 Hz, 1H), 4.96 (m, 2H), 4.36–4.41 (m, 1H), 5.23–5.32 (m, 1H), 6.71 (m, 1H), 6.99–7.06 (m, 1H), 7.14–7.19 (m, 1H), 7.31 (m, 5H), 7.46 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 43.6, 67.1, 72.9, 109.1, 121.6, 122.2, 124.4, 127.3, 127.6, 127.8, 127.9, 128.0, 128.6, 128.8, 129.5, 136.0, 137.5, 137.9, 143.1, 167.4; IR ($CHCl_3$) ν2931, 1707 cm^{-1}; MS (FAB) *m/z* 434 (M^+, 8), 322 (100); HRMS (FAB) calcd for $C_{26}H_{30}N_2O_4$ (M^+) 434.2205, found 434.2197.

(*Z*)-1-Benzyl-3-(phenyl(*p*-tolyl)methylene)indolin-2-one (12a)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 1H), 7.37–7.19 (m, 13H), 7.05–7.03 (m, 1H), 6.67–6.65 (m, 2H), 6.54 (d, *J* = 7.0 Hz, 1H), 4.91 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 155.4, 142.4, 139.5, 136.4, 130.5, 130.4, 129.6, 129.5, 129.2, 128.9, 128.7, 128.7, 128.6, 128.5, 127.8, 127.5, 123.6, 123.5, 123.1, 121.4, 108.6, 43.4, 21.4; IR ($CHCl_3$) ν 3692, 2361, 1602 cm^{-1}; MS (FAB) m/z 402 (MH^+); HRMS (FAB) calcd for $C_{29}H_{24}ON$ (MH^+) 402.1857, found 402.1850.

(*E*)-1-Benzyl-3-(phenyl(*p*-tolyl)methylene)indolin-2-one (12a)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.34–7.20 (m, 10H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.67–6.61 (m, 2H), 6.37 (d, *J* = 8.0 Hz, 1H), 4.92 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 155.3, 142.3, 141.5, 139.6, 136.9, 136.5, 130.5, 129.6, 129.5, 129.2, 128.9, 128.6, 128.5, 128.4, 127.5, 123.6, 123.5, 127.5, 127.4, 123.6, 123.5,

123.0, 121.4, 108.6, 43.4, 21.5; IR ($CHCl_3$) ν 3692, 2361, 1602 cm^{-1}; MS (FAB) m/z 402 (MH^+); HRMS (FAB) calcd for $C_{29}H_{24}NO$ (MH^+) 402.1857, found 402.1850.

(*Z*)-1-Benzyl-3-[(4-trifluoromethyl)phenyl)(phenyl)methylene]indolin-2-one (12b)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.40–7.27 (m, 10H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.70–6.66 (m, 2H), 6.36 (d, *J* = 7.9 Hz, 1H), 4.91 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 142.8, 136.1, 130.3, 129.5, 129.3, 129.2, 129.1, 128.7, 127.6, 127.4, 124.9, 123.5, 121.7, 108.9, 43.5; IR ($CHCl_3$) ν 3690, 3213, 1602 cm^{-1}; MS (FAB) m/z 456 (MH^+); HRMS (FAB) calcd for $C_{29}H_{21}F_3NO$ (MH^+) 456.1575, found 456.1577.

(*E*)-1-Benzyl-3-[(4-trifluoromethyl)phenyl](phenyl)methylene]indolin-2-one(12b)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.49–7.44 (m, 5H), 7.33–7.27 (m, 7H), 7.08 (t, *J* = 6.4 Hz, 1H), 6.70–6.66 (m, 2H), 6.45 (d, *J* = 7.3 HZ, 1H), 4.90 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 143.8, 136.2, 130.5, 129.5, 129.3, 129.2, 129.1, 128.9, 127.7, 127.5, 124.9, 123.5, 121.7, 108.9, 43.6 ; IR ($CHCl_3$) ν 3013, 1698 cm^{-1}; MS (FAB) m/z 456 (MH^+); HRMS (FAB) calcd for $C_{29}H_{21}F_3NO$ (MH^+) 456.1575, found 456.1578.

(*Z*)-1-Benzyl-3-[(4-methoxyphenyl)(phenyl)methylene]indolin-2-one(12c)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.38-7.23 (m, 10H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 2H), 6.66 (d, *J* = 7.3 Hz, 1H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 7.3 Hz, 1H), 4.94 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 160.9, 155.3, 142.0, 141.6, 136.5, 132.7, 131.8, 129.8, 129.2, 128.9, 128.7, 128.1, 127.5, 127.4, 123.9, 122.9, 122.8, 121.3, 113.1, 108.5, 55.2, 43.4; IR ($CHCl_3$) ν 3165, 1602 cm^{-1}; MS (FAB) m/z 418 (MH^+); HRMS (FAB) calcd for $C_{29}H_{24}NO_2$ (MH^+) 418.1806, found 418.1799.

(*Z*)-1-Benzyl-3-[phenyl(thiophen-3-yl)methylene]indolin-2-one (12d)

light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.48–7.23 (m, 13H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.59 (t, *J* = 7.7 Hz, 1H), 6.13 (d, *J* = 8.0 Hz, 1H), 4.96 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 148.6, 142.1, 141.7, 140.4, 136.4, 130.5, 130.4, 129.4, 129.2, 129.0, 128.7, 128.3, 127.4, 123.8, 123.7, 123.3, 123.2, 121.4, 108.5, 43.5; IR ($CHCl_3$) ν 3565, 1602 cm^{-1}; MS (FAB) m/z 394 (MH^+); HRMS (FAB) calcd for $C_{26}H_{20}NOS$ (MH^+) 394.1265, found 394.1263.

General procedure for debenzylation with NHPI-$Co(OAc)_2$-$Mn(OAc)_2$ method

To a solution of (*Z*)-**12a** (45.5 mg, 0.10 mmol) in AcOH (1.0 mL) was added *N*-hydroxyphthalimide (16.3 mg, 0.10 mmol), cobalt(II) acetate (2.65 mg, $1.5x10^{-2}$ mmol) and manganese(II) acetate (1.73 mg, $1.0x10^{-2}$ mmol) and stireed for12 h at 100 ^oC. After being quenched with water, the mixture was extracted with AcOEt and dried over $MgSO_4$. The residude was purified by column chromatography [silica gel, hexane/AcOEt (5/1)] to give (*Z*)-**13a** (32.8 mg, 90%, *E*/*Z* = 4/96).

(*E*)-3-(Phenyl(*p*-tolyl)methylene)indolin-2-one (13a)

light red oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.34–7.20 (m, 6H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.05–7.02 (m, 1H), 6.65–6.61 (m, 2H), 6.37 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0 155.5, 141.8, 139.8, 136.9, 136.5, 130.4, 129.6, 129.5, 129.4, 128.9, 128.5, 128.4, 123.6, 123.4, 127.5, 127.4, 123.6, 123.5, 123.0, 121.4, 108.6, 21.5; IR ($CHCl_3$) ν 3792, 2371, 1602 cm^{-1}; MS (FAB) m/z 312 (MH^+); HRMS (FAB) calcd for $C_{22}H_{18}NO$ (MH^+) 312.3948, found 312.3952.

(*Z*)-3-(Phenyl(*p*-tolyl)methylene)indolin-2-one (13a)

light red oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.19 (m, 9H), 7.09–7.07 (m, 1H), 6.75 (d, *J* = 6.8 Hz, 1H), 6.67–6.65 (m, 2H), 6.54 (d, *J* = 7.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 155.3, 141.5, 139.6, 136.9, 136.5, 130.5, 129.6, 129.5, 129.2, 128.9, 128.6, 128.4, 123.6, 123.5, 127.5, 127.4, 123.6, 123.5, 123.0, 121.4, 108.6, 21.8; IR ($CHCl_3$) ν 3692, 2361, 1645 cm^{-1}; MS (FAB) m/z 312 (MH^+); HRMS (FAB) calcd for $C_{22}H_{18}NO$ (MH^+) 312.3948, found 312.3950.

(*Z*)-3-[(4-Trifluoromethyl)phenyl](phenyl)methylene]indolin-2-one (13b)

light red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.40–7.27 (m, 5H), 7.10–7.06 (m, 2H), 6.70 (br, 1H), 6.68 (t, J = 7.6 Hz, 1H), 6.33 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 142.8, 136.1, 130.3, 129.5, 129.3, 129.2, 129.1, 128.7, 127.6, 127.4, 124.9, 123.5, 121.7, 108.9; IR ($CHCl_3$) ν 3690, 1610 cm^{-1}; MS (FAB) m/z 366 (MH^+); HRMS (FAB) calcd for $C_{22}H_{15}F_3NO$ (MH^+) 366.1105, found 366.1106.

(*E*)-3-[(4-Trifluoromethyl)phenyl](phenyl)methylene]indolin-2-one (13b)

light red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.49–7.44 (m, 5H), 7.30–7.28 (m, 2H), 7.13 (t, *J* = 6.4 Hz, 2H), 6.70–6.66 (m, 1H), 6.77 (br, 1H), 6.45 (d, *J* = 7.3 HZ, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 142.8, 136.1, 130.3, 129.5, 129.3, 129.2, 129.1, 128.7, 127.6, 127.4, 124.9, 123.5, 121.7, 108.9; IR ($CHCl_3$) ν 3690, 1610 cm^{-1}; MS (FAB) m/z 366 (MH^+); HRMS (FAB) calcd for $C_{22}H_{15}F_3NO$ (MH^+) 366.1105, found 366.1107.

(*E*)-3-Pentylideneindolin-2-one (13c)

light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.31 (s, 1H), 7.14–7.10 (m, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.68–1.65 (m, 2H), 1.49–1.45 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 136.2, 128.7, 127.5, 127.3, 123.5, 122.5, 122.0, 109.0, 30.6, 29.1, 22.5, 13.8; IR ($CHCl_3$) ν 2215, 1680 cm^{-1}; MS (FAB) m/z 202 (MH^+); HRMS (FAB) calcd for $C_{13}H_{16}NO$ (MH^+) 202.1231, found 202.1235.