

Supporting Information

Direct Transformation of Arylpropynes to Acrylamides via a Three-Step Tandem Reaction

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1. General Methods

Unless stated otherwise, all reagents were purchased commercially without further purification. All reagents were weighed and handled in air at room temperature. All glassware was oven or flame dried immediately prior to use.

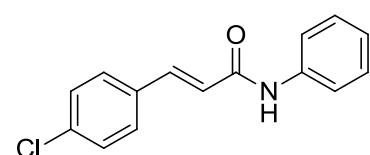
¹H NMR and ¹³C NMR were obtained at 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent. Chemical shifts are expressed in parts per million values (δ , ppm). ¹H NMR spectra were calibrated with DMSO-*d*₆ (δ = 2.50 ppm) and CDCl₃ (δ = 7.26 ppm). ¹³C-NMR spectra were obtained at 100 MHz and were calibrated with DMSO-*d*₆ (δ = 39.50 ppm) and CDCl₃ (δ = 77.00 ppm). Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet or unresolved, br= broad singlet, coupling constant(s) in Hz, integration). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. Purification was done by column chromatography on silica gel (200–300 mesh) with petroleum ether and ethyl acetate as the eluent to give the pure product.

2. Experimental Procedure

2.1 Synthesis of acrylamides from 1, 3-diarylpropynes:

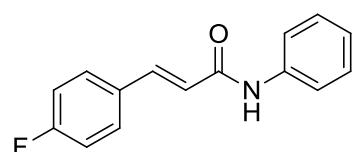
An oven-dried Schlenk tube was charged with **1** or **3** (1 mmol), NH₂-OH.HCl (0.035g, 0.5 mmol), DDQ (0.17 g, 0.75mmol), PPA (0.052g, 0.15mmol), HCOOH (1.5 mL) and CH₃CN (1.5 mL). The reaction mixture was stirred at 80°C for 12 h monitored by TLC. The mixture was allowed to cool to room temperature and was quenched with H₂O (10 mL). The mixture was extracted with DCM (3×10 mL), and the organic layer was washed with brine (10mL). The combined organic layers were dried with Na₂SO₄, concentrated under reduced pressure, and dried under high vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 15:1 to 8:1) to obtain the desired products **2** or **4**.

3. Characterization of the Compounds



(*E*)-3-(4-chlorophenyl)-*N*-phenylacrylamide (**2a**)¹

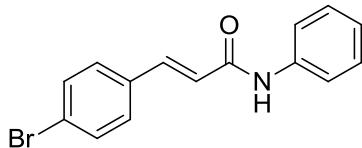
Eluent: petroleum ether/ethyl acetate (15:1). White solid (81% yield); **2a**: mp 176–178 °C (lit.^{2b} 180 °C). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.72 (d, *J* = 15.6 Hz, 1H), 7.65 (d, *J* = 6.8 Hz, 2H), 7.54(br, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.39–7.35 (m, 4H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.7, 141.1, 137.9, 135.9, 133.1, 129.2, 129.1, 127.6, 124.6, 121.4, 120.0. IR (KBr, cm⁻¹): ν = 3279, 1657, 1625, 1598, 1533, 1488, 1442, 1333, 1247, 1184, 1093, 1012, 974, 818, 745, 692, 617, 508. HRMS m/z (ESI) calcd. for C₁₅H₁₂ClNO (M+Na)⁺: 280.0505, found 280.0489.



(*E*)-3-(4-Fluorophenyl)-*N*-phenylacrylamide (**2b**)²

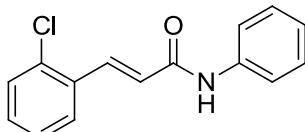
Eluent: petroleum ether/ethyl acetate (15:1). White solid (83% yield); **2b**: mp 164–165 °C. ¹H NMR

(400 MHz, CDCl₃, ppm): δ 7.74 (d, *J* = 15.6 Hz, 1H), 7.61-7.50 (m, 5H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 15.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.8, 163.7 (d, *J* = 249.7 Hz), 141.6, 136.5, 130.7 (d, *J* = 3.5 Hz), 129.8 (d, *J* = 8.4 Hz), 129.1, 121.2, 120.1, 116.1 (d, *J* = 21.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃, ppm): δ 109.72 (s, 1F). IR (KBr, cm⁻¹): ν = 3271, 1653, 1625, 1591, 1539, 1508, 1396, 1339, 1240, 1183, 1158, 10894, 1013, 970, 826, 738, 664, 528, 507. HRMS m/z (ESI) calcd. for C₁₅H₁₂FNO (M+Na)⁺: 264.0801, found 264.0785.



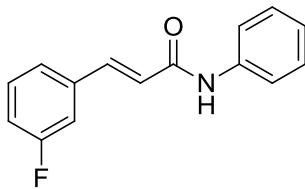
(E)-3-(4-Bromophenyl)-N-phenylacrylamide (2c)^{1a, 2}

Eluent: petroleum ether/ethyl acetate (15:1). White solid (77% yield); **2c**: mp 190-191 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 10.24(s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.60-7.55 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): δ 163.8, 139.6, 139.3, 134.5, 132.5, 130.1, 129.3, 123.9, 123.7, 123.4, 119.7. IR (KBr, cm⁻¹): ν = 3274, 3037, 1658, 1623, 1597, 1533, 1483, 1441, 1331, 1247, 1183, 1070, 1010, 973, 815, 742, 692, 574, 504. HRMS m/z (ESI) calcd. for C₁₅H₁₂BrNO (M+Na)⁺: 324.0000, found 324.0026.



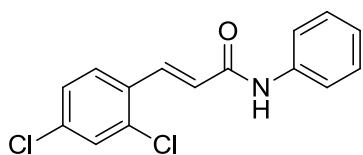
(E)-3-(2-chlorophenyl)-N-phenylacrylamide (2d)^{1a, 3}

Eluent: petroleum ether/ethyl acetate (15:1). White solid (72% yield); **2d**: mp 179-180 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.15(d, *J* = 15.6 Hz, 1H), 7.79(br, 1H), 7.67 (d, *J* = 6.8 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.32-7.23 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.5, 138.2, 137.9, 134.9, 133.0, 130.7, 130.2, 129.1, 127.7, 127.0, 124.6, 123.8, 120.0. IR (KBr, cm⁻¹): ν = 3245, 3037, 1658, 1624, 1596, 1548, 1496, 1443, 1348, 1270, 1245, 1124, 1036, 1003, 975, 861, 768, 748, 694, 684. HRMS m/z (ESI) calcd. for C₁₅H₁₂ClNO (M+Na)⁺: 280.0505, found 280.0493.



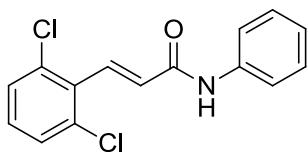
(E)-3-(3-(fluoromethyl) phenyl)-N-phenylacrylamide (2e)

Eluent: petroleum ether/ethyl acetate (15:1). White solid (78% yield); **2e**: mp 145-146 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.06 (br, 1H), 7.75-7.67 (m, 3H), 7.39-7.30 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.8, 163.0 (d, *J* = 245.1Hz), 141.1, 137.9, 136.9 (d, *J* = 7.6 Hz), 130.4 (d, *J* = 8.3 Hz), 129.1, 124.7, 124.1(d, *J* = 2.8 Hz), 122.3, 120.1, 116.8 (d, *J* = 21.3 Hz), 114.1(d, *J* = 21.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃, ppm): δ 112.58 (s, 1F). IR (KBr, cm⁻¹): ν = 3273, 3065, 1662, 1629, 1595, 1585, 1547, 1490, 1444, 1350, 1254, 1189, 1144, 979, 855, 785, 753, 692, 669, 553. HRMS m/z (ESI) calcd. for C₁₅H₁₂FNO (M+Na)⁺: 264.0801, found 264.0795.



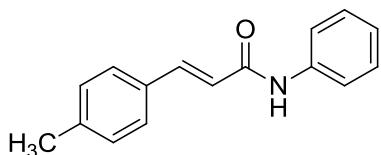
(E)-3-(2,4-dichlorophenyl)-N-phenylacrylamide (2f)

Eluent: petroleum ether/ethyl acetate (15:1). White solid (85% yield); **2f**: mp 176-177 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.06 (d, *J* = 15.6 Hz, 1H), 7.78 (br, 1H), 7.66 (d, *J* = 6.8 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.44 (s, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.3, 137.8, 137.1, 136.0, 135.5, 131.6, 130.0, 129.1, 128.3, 127.4, 124.7, 124.2, 120.0. IR (KBr, cm⁻¹): ν = 3277, 3132, 3061, 1656, 1626, 1599, 1543, 1498, 1466, 1442, 1341, 1258, 1186, 1100, 1002, 967, 863, 795, 752, 710, 688. HRMS m/z (ESI) calcd. for C₁₅H₁₁Cl₂NO (M+Na)⁺: 314.0115, found 314.0096.



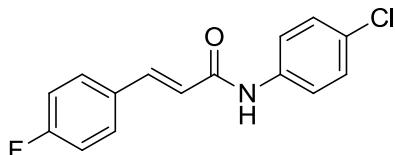
(E)-3-(2,4-dichlorophenyl)-N-phenylacrylamide (2g)

Eluent: petroleum ether/ethyl acetate (15:1). White solid (82% yield); **2g**: mp 177-179 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.89 (d, *J* = 15.6 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.48(br, 1H), 7.38 (t, *J* = 7.2 Hz, 4H), 7.29-7.15 (m, 2H), 6.76 (d, *J* = 16.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.1, 137.8, 135.9, 135.0, 132.3, 130.9, 129.6, 129.3, 129.1, 128.8, 124.6, 119.9. IR (KBr, cm⁻¹): ν = 3265, 1661, 1619, 1599, 1540, 1444, 1429, 1339, 1260, 1189, 1088, 1025, 975, 803, 777, 690, 617, 472. HRMS m/z (ESI) calcd. for C₁₅H₁₁Cl₂NO (M+Na)⁺: 314.0115, found 314.0114.



(E)-3-(p-Tolyl)-N-phenylacrylamide (2h) ^{1b, 2}

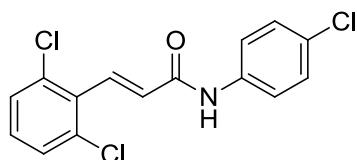
Eluent: petroleum ether/ethyl acetate (15:1). White solid (52% yield); **2h**: mp 166-168 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.76 (d, *J* = 15.6 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.41(br, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 2.40 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 164.2, 142.4, 140.4, 138.1, 131.9, 129.6, 128.0, 124.4, 119.9, 21.5. IR (KBr, cm⁻¹): ν = 3286, 3034, 2918, 1656, 1625, 1598, 1528, 1498, 1442, 1335, 1247, 1181, 1076, 1004, 975, 811, 718, 669, 589, 492. HRMS m/z (ESI) calcd. for C₁₆H₁₅NO (M+Na)⁺: 260.1051, found 260.1037.



(E)-3-(4-Fluorophenyl)-N-(4-chlorophenyl)acrylamide (2j)

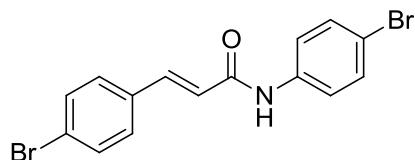
Eluent: petroleum ether/ethyl acetate (15:1). White solid (88% yield); **2j**: mp 169-170 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.73 (d, *J* = 15.2 Hz, 1H), 7.61-7.57 (m, 3H), 7.53-7.49 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.09 (t, *J* = 8.8 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.9, 163.8 (d, *J* = 249.7 Hz), 141.6, 136.5, 130.7, 129.8 (d, *J* = 8.4 Hz), 129.1, 121.2, 120.1, 116.1

(d, $J = 21.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3 , ppm): δ 109.68 (s, 1F). IR (KBr, cm^{-1}): $\nu = 3269, 3114, 3055, 2962, 1657, 1627, 1601, 1542, 1509, 1491, 1399, 1346, 1247, 1186, 1160, 1089, 1013, 983, 821, 800, 737, 529, 505, 425$. HRMS m/z (ESI) calcd. for $\text{C}_{15}\text{H}_{11}\text{FCINO}$ ($\text{M}+\text{Na}^+$): 298.0411, found 298.0408.



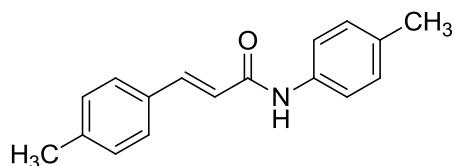
(E)-3-(2,4-dichlorophenyl)-N-(4-chlorophenyl)acrylamide (2k)

Eluent: petroleum ether/ethyl acetate (15:1). White solid (86% yield); **2k**: mp 186-189 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.88 (d, $J = 16.0$ Hz, 1H), 7.69(br, 1H), 7.62 (d, $J = 7.2$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.20 (t, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 15.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 163.2, 136.3, 135.1, 132.1, 129.7, 129.1, 129.0, 128.8, 128.3, 128.2, 121.2. IR (KBr, cm^{-1}): $\nu = 3287, 3049, 1661, 1635, 1595, 1537, 1491, 1429, 1396, 1339, 1261, 1186, 1087, 1012, 969, 818, 779, 706, 666, 501$. HRMS m/z (ESI) calcd. for $\text{C}_{15}\text{H}_{10}\text{Cl}_3\text{NO}$ ($\text{M}+\text{Na}^+$): 347.9726, found 347.9725.



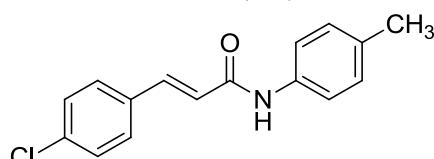
(E)- N, 3-Bis(4-bromophenyl)acrylamide (2l)²

Eluent: petroleum ether/ethyl acetate (15:1). White solid (83% yield); **2l**: mp 216-217 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, ppm): δ 10.38 (s, 1H), 7.67 (t, $J = 8.0$ Hz, 4H), 7.60-7.52 (m, 5H), 7.41 (d, $J = 8.4$ Hz, 1H), 6.83 (d, $J = 15.6$ Hz, 1H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, ppm): δ 163.9, 139.7, 139.0, 134.4, 132.5, 132.1, 130.2, 123.5, 123.3, 121.6, 115.5. IR (KBr, cm^{-1}): $\nu = 3286, 3044, 1667, 1624, 1590, 1537, 1488, 1390, 1334, 1256, 1180, 1090, 977, 819, 758, 705, 680, 501$. HRMS m/z (ESI) calcd. for $\text{C}_{15}\text{H}_{11}\text{Br}_2\text{NO}$ ($\text{M}+\text{Na}^+$): 403.9085, found 403.9093.



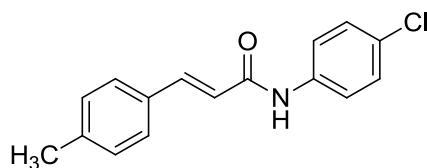
(E)- N, 3-Di- p-tolylacrylamide (2m)^{1c, 2, 4}

Eluent: petroleum ether/ethyl acetate (15:1). White solid (31% yield); **2m**: mp 173-175 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.75 (d, $J = 15.2$ Hz, 1H), 7.57-7.51 (m, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.51 (d, $J = 15.2$ Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100MHz, CDCl_3 , ppm): δ 164.1, 142.2, 140.2, 135.5, 134.0, 132.0, 129.6, 127.9, 120.0, 21.4, 20.9. IR (KBr, cm^{-1}): $\nu = 3237, 3030, 2915, 1657, 1619, 1523, 1405, 1337, 1244, 1172, 977, 815, 788, 622, 491$. HRMS m/z (ESI) calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}$ ($\text{M}+\text{Na}^+$): 274.1208, found 274.1199.



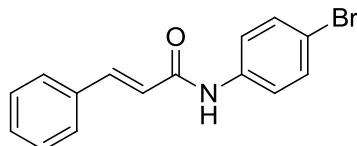
(E)-3-(4-chlorophenyl)-N-(p-tolyl)acrylamide (2n)

Eluent: petroleum ether/ethyl acetate (15:1). White solid (72% yield); **2n**: mp 174-176 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.71 (d, *J* = 15.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 (br, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 15.2 Hz, 1H), 2.35 (s, 1H). ¹³C NMR (100MHz, CDCl₃, ppm): δ 163.6, 140.8, 135.8, 135.3, 134.3, 133.2, 129.6, 129.1, 121.5, 120.1, 20.9. IR (KBr, cm⁻¹): ν = 3281, 3042, 2920, 1655, 1627, 1598, 1537, 1489, 1402, 1344, 1260, 1185, 1090, 1011, 973, 815, 708, 673, 540, 501. HRMS m/z (ESI) calcd. for C₁₆H₁₄ClNO (M+Na)⁺: 294.0662, found 294.0651.



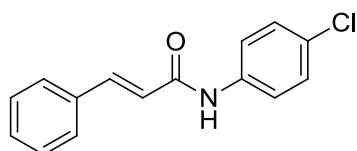
(E)-3-(p-Tolyl)-N-(4-chlorophenyl)acrylamide (2o)

Eluent: petroleum ether/ethyl acetate (15:1). White solid (61% yield); **2o**: mp 177-179 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.75 (d, *J* = 15.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.54 (br, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 15.6 Hz, 1H), 2.40 (s, 1H). ¹³C NMR (100MHz, CDCl₃, ppm): δ 164.2, 142.8, 140.6, 136.7, 131.7, 129.6, 129.1, 128.0, 121.2, 119.3, 21.5. IR (KBr, cm⁻¹): ν = 3281, 3044, 2919, 1654, 1629, 1595, 1537, 1491, 1398, 1343, 1250, 1185, 1093, 1012, 975, 814, 733, 659, 500. HRMS m/z (ESI) calcd. for C₁₆H₁₄ClNO (M+Na)⁺: 294.0662, found 294.0661.



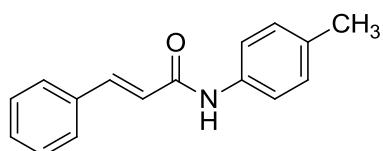
N-(4-Bromophenyl)cinnamamide (2p)⁵

Eluent: petroleum ether/ethyl acetate (15:1). White solid (75% yield); **2p**: mp 159-161 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.79 (d, *J* = 15.6 Hz, 1H), 7.57-7.54 (m, 4H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.43-7.41 (m, 3H), 7.34 (br, 1H), 6.55 (d, *J* = 15.2 Hz, 1H). ¹³C NMR (100MHz, CDCl₃, ppm): δ 164.1, 141.0, 138.0, 132.2, 130.1, 129.5, 129.3, 128.1, 121.5, 119.7. IR (KBr, cm⁻¹): ν = 3291, 1660, 1623, 1597, 1535, 1487, 1442, 1394, 1339, 1247, 1177, 1071, 1010, 973, 818, 763, 693, 627, 496. HRMS m/z(ESI) calcd. for C₁₅H₁₂BrNO (M+Na)⁺: 324.0000, found 323.9998.



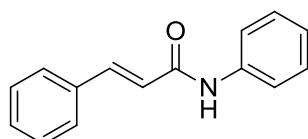
N-(4-chlorophenyl)cinnamamide (2q)^{1c, 6d}

Eluent: petroleum ether/ethyl acetate (15:1). White solid (77% yield); **2q**: mp 181-183 °C (lit.^{6d} 182-184 °C). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.78 (d, *J* = 15.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 3H), 7.54-7.52 (m, 2H), 7.41-7.40 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 3H), 6.58 (d, *J* = 15.2 Hz, 1H). ¹³C NMR (100MHz, CDCl₃, ppm): δ 164.0, 142.9, 136.6, 134.5, 130.2, 129.1, 128.9, 128.0, 121.2, 120.4. IR (KBr, cm⁻¹): ν = 3267, 1658, 1626, 1597, 1532, 1488, 1442, 1398, 1333, 1247, 1184, 1093, 1013, 973, 818, 745, 580, 504. HRMS m/z (ESI) calcd. for C₁₅H₁₂ClNO (M+Na)⁺: 280.0505, found 280.0501.



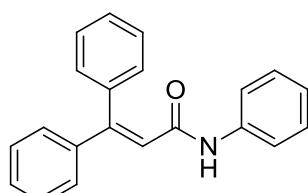
N-(*p*-Tolyl)cinnamamide (2r)^{2, 6a}

Eluent: petroleum ether/ethyl acetate (15:1). White solid (67% yield); **2r**: mp 157-159 °C (lit.^{6e} 159 °C). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.76 (d, *J* = 15.6 Hz, 1H), 7.63 (br, 1H), 7.55-7.51 (m, 4H), 7.39-7.37(m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 15.6 Hz, 1H), 2.34 (s, 1H). ¹³C NMR (100MHz, CDCl₃, ppm): δ 164.0, 142.1, 135.5, 134.7, 129.9, 129.6, 128.8, 127.9, 121.0, 120.1, 20.9. IR (KBr, cm⁻¹): ν = 3277, 3047, 2920, 1657, 1626, 1595, 1535, 1487, 1419, 1338, 1260, 1185, 1090, 1015, 978, 753, 733 673, 509. HRMS m/z (ESI) calcd. for C₁₆H₁₅NO (M+Na)⁺: 260.1051, found 260.1041.



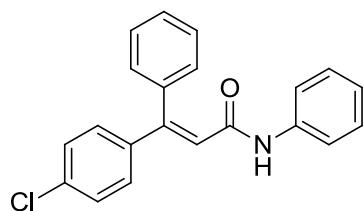
N-phenylcinnamamide (2s)^{1c, 2, 4c}

Eluent: petroleum ether/ethyl acetate (15:1). White solid (72% yield); **2s**: mp 170-172 °C (lit.^{4c} 168-172 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 7.78 (d, *J* = 15.6 Hz, 1H), 7.70-7.66 (m, 3H), 7.53-7.50 (m, 2H), 7.40-7.35 (m, 5H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 164.1, 142.4, 138.1, 134.6, 129.9, 129.1, 128.9, 128.0, 124.5, 120.9, 120.0. IR (KBr, cm⁻¹): ν = 3237, 3032, 1661, 1617, 1541, 1496, 1442, 1351, 1250, 1189, 977, 865, 760, 620, 485. HRMS m/z (ESI) calcd. for C₁₅H₁₄NO (M+Na)⁺: 246.0895, found 246.0893.



N, 3, 3-triphenylacrylamide (4a)⁷

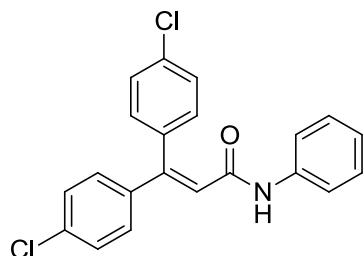
Eluent: petroleum ether/ethyl acetate (15:1). White solid (65% yield); **4a**: mp 130-132 °C (lit.⁷ 129-130 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 7.52-7.50 (m, 3H), 7.38-7.30 (m, 7H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.93 (br, 1H), 6.54 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 164.3, 150.4, 140.4, 138.1, 137.6, 129.5, 129.2, 129.1, 129.0, 128.8, 128.5, 128.0, 124.1, 123.1, 119.5. IR (KBr, cm⁻¹): ν = 3296, 3045, 1655, 1614, 1598, 1544, 1488, 1441, 1313, 1243, 1188, 1091, 1012, 884, 830, 758, 694, 490. HRMS m/z (ESI) calcd. for C₂₁H₁₇NO (M+Na)⁺: 322.1208, found 322.1213.



(E)or (Z)- 3-(4-chlorophenyl) -N, 3-diphenylacrylamide (4b)

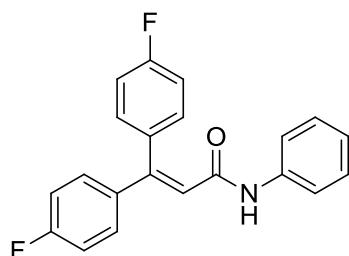
Eluent: petroleum ether/ethyl acetate (15:1). White solid (71% yield); **4b**: mp 189-191 °C. ¹H NMR

(400 MHz, CDCl₃, ppm): 7.43 (d, *J* = 8.0 Hz, 2H), 7.39-7.36(m, 3H), 7.31-7.28 (m, 8H), 7.11-7.07 (m, 1H), 7.06 (br, 1H), 6.48 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 164.0, 150.3, 140.4, 137.5, 136.7, 134.9, 130.9, 129.4, 129.0, 128.6, 128.1, 124.4, 122.7, 119.7. IR (KBr, cm⁻¹): ν = 3269, 3074, 1646, 1598, 1549, 1487, 1439, 1357, 1317, 1239, 1195, 1085, 1014, 862, 829, 760, 695, 548. HRMS m/z (ESI) calcd. for C₂₁H₁₆ClNO (M+Na)⁺: 356.0818, found 356.0821.



3, 3-Bis(4-chlorophenyl)-N-phenylacrylamide (4c)

Eluent: petroleum ether/ethyl acetate (15:1). White solid (75% yield); **4c**: mp 184-186 °C. ¹H NMR (400 MHz, CDCl₃, ppm): 7.42 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.29-7.26 (m, 6H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.12-7.09 (m, 2H), 6.45 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.7, 149.2, 138.9, 137.4, 136.3, 135.6, 135.2, 130.9, 129.4, 129.1, 129.0, 128.8, 124.5, 122.9, 119.7. IR (KBr, cm⁻¹): ν = 3297, 1655, 1616, 1599, 1544, 1488, 1441, 1313, 1243, 1188, 1091, 1013, 883, 830, 757, 694, 615, 489. HRMS m/z (ESI) calcd. for C₂₁H₁₅Cl₂NO (M+Na)⁺: 390.0428, found 390.0422.



3, 3-Bis(4-fluorophenyl)-N-phenylacrylamide (4d)

Eluent: petroleum ether/ethyl acetate (15:1). White solid (80% yield); **4d**: mp 169-170 °C. ¹H NMR (400 MHz, CDCl₃, ppm): 7.34-7.26 (m, 8H), 7.15 (t, *J* = 8.4 Hz, 2H), 7.08-7.04 (m, 4H), 6.43 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 164.0, 163.5 (d, *J* = 248.7 Hz), 163.0 (d, *J* = 248.1 Hz), 149.2, 137.5, 136.8, 134.0, 131.4 (d, *J* = 8.2 Hz), 130.0 (d, *J* = 8.4 Hz), 129.0, 124.4, 122.6, 119.7, 116.0 (d, *J* = 21.6 Hz), 115.6 (d, *J* = 21.6 Hz). ¹⁹F NMR (376 MHz, CDCl₃, ppm): δ 111.55 (s, 1F), 111.56 (s, 1F). IR (KBr, cm⁻¹): ν = 3266, 3072, 1645, 1600, 1550, 1506, 1441, 1316, 1238, 1197, 1159, 1101, 1004, 838, 826, 757, 697, 547. HRMS m/z (ESI) calcd. for C₂₁H₁₅F₂NO (M+Na)⁺: 358.1019, found 358.1005.

4. References

- (1) (a) S. Arunkumar, K. Ilango, R. S. Manikandan, N. Ramalakshmi, *E-Journal of Chemistry* **2009**, *6*, 123. (b) Y. Liu, Y. Zhang, *Organic Preparations and Procedures International*, 2001, *33*, 372. (c) C. Qin, W. Zhou, F. Chen, Y. Ou, N. Jiao, *Angew. Chem. Int. Ed.* 2011, **50**, 12595.
- (2) (a) J. Qiu, R. H. Zhang, *Org. Biomol. Chem.* 2013, **11**, 6008. (b) R. K. Mehra, K. C. Pandya, *Indian Academy of Sciences, Section A* 1939, **9A**, 508.
- (3) X. Huang, J. Pi, Z. Huang, *Heteroatom Chemistry* 1992, **3**, 535-7.
- (4) (a) M. A. Ali, P. Saha, T. Punniyamurthy, *Synthesis* 2010, **2010**, 908. (b) S. Kim, C. Lim, S. Lee, S. Lee, H. Cho, J. Y. Lee, D. S. Shim, H. D. Park, S. Kim, *ACS Combinatorial Science*, 2013, **15**, 208. (c) Weidner-Wells, M. A. Fraga-Spano, S. A. Turchi, *Journal of Organic Chemistry*, 1998, **63**, 6319.
- (5) (a) A. H. Blatt, R. P. Barnes, *Journal of the American Chemical Society*, 1934, **56**, 1148. (b) P. O. Bezugly, V. A. Georgiyants, L. O. Perekhoda, M. V. Rakhimova, N. A. Marusenko, A. V. Taran, *Farmatsevtichnii Zhurnal (Kiev)*, 2001, **6**, 45.
- (6) (a) S. Ueda, T. Okada, H. Nagasawa, *Chemical Communications*, 2010, **46**, 2462. (b) M. Zhang, X. Lu, H. J. Zhang, N. Li, Y. Xiao, H. Zhu, Y. Ye, *Medicinal Chemistry Research*, 2013, **22**, 986. (c) Z. H. Shi, N. G. Li, Q. P. Shi, H. Tang, Y. P. Tang, W. Li, L. Yin, J. P. Yang, J. A. Duan, *Bioorganic & Medicinal Chemistry Letters*, 2013, **23**, 1206. (d) X. Wang, L. He, Z. Li, W. Wang, J. Liu, *Synthetic Communications* 2009, **39**, 819. (e) T. Manimaran, T. K. Thiruvengadam, V. T. Ramakrishnan, *Synthesis* 1975, **11**, 739.
- (7) (a) K. Inamoto, T. Saito, K. Hiroya, T. Doi, *Journal of Organic Chemistry*, 2010, **75**, 3900. (b) D. S. Ryabukhin, A. V. Vasilyev, S. Y. Vyazmin, *Russian Chemical Bulletin*, 2012, **61**, 843.

5. NMR Charts

