ELECTRONIC SUPPLEMENTARY INFORMATION

Gold-Catalyzed Intermolecular Cyclocarboamination of Ynamides with 1,3,5-Triazinanes: En Route to Tetrahydropyrimidines

Zhongyi Zeng, Hongming Jin, Xinlong Song, Qian Wang, Matthias Rudolph, Frank Rominger, and A. Stephen K. Hashmi*

Organisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
Fax: (+49)-6221-54-4205
E-mail: hashmi@hashmi.de
Homepage: http://www.hashmi.de
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1. General remarks

Chemicals were purchased from commercial suppliers and used without further purification. Reagents 1 and 2 could be easily prepared according to the previous literatures.1,2 Dry solvents were dispensed from the solvent purification system MB SPS-800. Deuterated solvents were bought from Euriso-Top. NMR spectra were, if not mentioned otherwise, recorded at room temperature on the following spectrometers: Bruker Avance-III-300 and Bruker Avance-III-500. Chemical shifts were referenced to residual solvent protons and reported in ppm and coupling constants in Hz. The following abbreviations were used for 1H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). All 13C NMR spectra were measured with 1H-decoupling. The multiplicities mentioned in these spectra [s (singlet, quaternary carbon), d (doublet, CH-group), t (triplet, CH2-group), q (quartet, CH3-group)] were determined by DEPT135. HRMS were determined at the chemistry department of the University of Heidelberg under the direction of Dr. J. Gross. EI+ spectra were measured on a JOEL JMS-700 spectrometer. For ESI+ spectra a Bruker ApexQu FT-ICR-MS spectrometer was applied. IR spectra were recorded on a Bruker Vector 22, and the absorption maxima were given in wavelength in cm⁻¹ units. X-ray crystal structure analyses were measured at the chemistry department of the University of Heidelberg under the direction of Dr. F. Rominger on a Bruker Smart CCD or Bruker APEX-II CCD instrument using Mo-Kα-radiation. The structures were solved and refined by Dr. F. Rominger using the SHELXTL software package. Thin-layer chromatography (TLC) was performed on precoated polyester sheets (POLYGRAM SIL G/UV254), and components were visualized by observation under UV light. Melting points were uncorrected.
2. General procedure and characterization data

A round bottom flask equipped with a magnetic stirrer bar was charged with CyJohnPhosAuCl (5 mol%, 4.4 mg), AgNTf₂ (5 mol%, 2.9 mg), and 1,2-DCE (0.40 ml). The mixture was stirred for 5 minutes at room temperature. Ynamides 1 and 1,3,5-triazinanes 2 were added followed by 0.35 mL 1,2-DCE. The reaction mixture was then stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was concentrated and the residue was purified by chromatography on silica gel (eluent: PE/EA) to afford the desired product 3.

3aa: N-methyl-N-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide
Yield 90%, light yellow solid, m.p.: 59–60 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.57–7.55 (m, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.37–7.32 (m, 3H), 7.18–7.13 (m, 5H), 6.77 (t, J = 7.3 Hz, 1H), 6.68 (d, J = 8.6 Hz, 2H), 5.04 (s, 1H), 4.75 (s, 1H), 4.29 (s, 1H), 4.03 (s, 1H), 2.69 (s, 3H), 2.36 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 147.6 (s), 146.1 (s), 137.2 (s), 137.1 (s), 129.4 (d), 129.2 (d), 128.8 (d), 128.4 (d), 127.6 (d), 127.4 (d), 124.7 (d), 119.3 (d), 117.7 (s), 115.0 (d), 69.4 (t), 51.0 (t), 39.9 (q), 37.6 (q) ppm; IR (ATR): ν 3057, 3028, 2928, 2853, 1685, 1639, 1595, 1494, 1451, 1416, 1340, 1220, 1146, 1078, 1041, 1001, 960, 879, 768, 734, 698, 637, 619 cm⁻¹; HRMS (EI) calcd for [C₂₄H₂₅N₃O₂S]⁺ (M)⁺: 419.1647; found: 419.1662.

3ba: N,4-dimethyl-N-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)benzenesulfonamide
Yield 65%, light yellow solid, m.p.: 89–90 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, J = 7.5 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 8.2 Hz, 2H), 7.13 (t, J = 7.9 Hz, 2H), 7.07 (t, J = 7.7 Hz, 2H), 6.95 (t, J = 8.8 Hz, 3H), 6.75–6.72 (m, 3H), 6.62 (d, J = 8.3 Hz, 2H), 4.80 (s, 2H), 4.14 (s, 2H), 2.77 (s, 3H), 2.32 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 147.6 (s), 145.9 (s), 142.5 (s), 137.9 (s), 137.3 (s), 137.2 (s), 129.2 (d), 128.9 (d), 128.7 (d), 128.5 (d), 128.4 (d), 127.5 (d), 126.7 (d), 123.7 (d), 123.5 (d), 119.0 (d), 118.2 (s), 114.7 (d), 69.2 (t), 51.0 (t), 38.6 (q), 21.4 (q) ppm; IR (ATR):  ν 3416, 3058, 3029, 2960, 2926, 2872, 2852, 1638, 1600, 1494, 1448, 1341, 1287, 1215, 1154, 1088, 1078, 1029, 995, 961, 931, 863, 813, 761, 696, 668, 646, 607 cm⁻¹; HRMS (EI) calcd for [C₃₀H₂₉N₃O₃S]⁺ (M)⁺: 495.1975; found: 495.1978.

3ca: 3-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)oxazolidin-2-one
Yield 70%, light yellow solid, m.p.: 82–83 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.42–7.37 (m, 4H), 7.33–7.28 (m, 3H), 7.19–7.11 (m, 5H), 6.79 (t, J = 7.3 Hz, 1H), 6.73 (d, J = 8.1 Hz, 2H), 4.90 (s, 2H), 4.20 (s, 2H), 4.01 (t, J = 8.0 Hz, 2H), 3.50 (t, J = 8.0 Hz, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 154.9 (s), 147.7 (s), 145.4 (s), 137.6 (s), 132.0 (s), 129.4 (d), 129.2 (d), 128.7 (d), 127.7 (d), 127.3 (d), 124.8 (d), 123.8 (d), 119.6 (d), 116.3 (s), 115.4 (d), 69.5 (t), 61.9 (t), 50.8 (t), 45.2 (t) ppm; IR (ATR):  ν 3059, 3030, 2981, 2850,
1754, 1681, 1596, 1493, 1447, 1401, 1389, 1324, 1206, 1120, 1070, 1034, 992, 973, 933, 910, 804, 749, 696, 650 cm⁻¹; HRMS (ESI) calcd for [C₂₃H₂₅N₂O₂Na⁺]⁺ (M+Na⁺): 420.1682; found: 420.1686.

3da: 2-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide

Yield 94%, white solid, m.p.: 168–169 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.71 (s, 1H), 7.56 (d, J = 6.6 Hz, 2H), 7.42 (s, 2H), 7.32–7.12 (m, 10H), 6.98 (s, 1H), 6.80 (t, J = 6.7 Hz, 1H), 6.70 (d, J = 7.5 Hz, 2H), 4.98 (s, 2H), 4.26 (s, 2H), 4.20 (s, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 147.6 (s), 146.7 (s), 136.8 (s), 134.7 (s), 133.1 (s), 132.3 (d), 129.2 (d), 128.9 (d), 128.8 (d), 127.6 (d), 125.0 (d), 124.7 (d), 123.8 (d), 121.4 (d), 119.3 (d), 115.3 (s), 114.9 (d), 69.7 (t), 50.8 (t), 50.0 (t) ppm; IR (ATR): Ṽ 3062, 2865, 2783, 1650, 1597, 1505, 1490, 1456, 1372, 1304, 1294, 1277, 1267, 1204, 1169, 1131, 1104, 1066, 1056, 1036, 992, 971, 933, 900, 827, 794, 754, 734, 700, 661, 624, 609 cm⁻¹; HRMS (EI) calcd for [C₂₀H₁₅N₂O₅S⁺]⁺ (M⁺): 479.1662; found: 479.1668.

3ea: 1-(1-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-1H-indol-3-yl)ethanone

Yield 46%, white solid, m.p.: 96–97 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.19–8.17 (m, 1H), 7.56 (s, 1H), 7.53–7.50 (m, 1H), 7.24–7.21 (m, 2H), 7.17–7.08 (m, 7H), 7.04 (d, J = 7.4 Hz, 2H), 7.00–6.98 (m, 2H), 6.95 (t, J = 7.2 Hz, 1H), 6.86–6.80 (m, 3H), 5.10 (s, 2H), 4.40 (s, 2H), 2.28 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 193.4 (s), 147.5 (s), 154.0 (s), 136.5 (s), 134.7 (s), 129.4 (d), 129.2 (d), 128.6 (d), 127.2 (d), 1261 (s), 125.0 (d), 123.8 (d), 123.5 (d), 122.9 (d), 122.1 (d), 112.0 (d), 118.9 (s), 115.6 (d), 114.8 (s), 112.2 (d), 70.0 (t), 50.5 (t), 27.5 (q) ppm; IR (ATR): Ṽ 3056, 3028, 2922, 1738, 1649, 1597, 1530, 1492, 1454, 1376, 1347, 1310, 1271, 1201, 1154, 1069, 1028, 1016, 996, 973, 932, 909, 748, 695, 637, 615 cm⁻¹; HRMS (EI) calcd for [C₂₃H₂₂N₂O⁺]⁺ (M⁺): 469.2149; found: 469.2148.

3fa: N-(4-methoxybenzyl)-N-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide

Yield 81%, white solid, m.p.: 73–74 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.41–7.36 (m, 4H), 7.33–7.27 (m, 3H), 7.22 (t, J = 6.8 Hz, 1H), 7.16–7.12 (m, 4H), 7.08 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 8.5 Hz, 2H), 4.93 (d, J = 12.0 Hz, 1H), 4.68 (d, J = 12.1 Hz, 1H), 4.16 (d, J = 14.8 Hz, 2H), 4.06–3.96 (m, 2H), 3.81 (s, 3H), 2.04 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 159.5 (s), 147.7 (s), 145.8 (s), 137.9 (s), 135.1 (s), 131.4 (d), 129.42 (d), 129.35 (d), 129.2 (d), 128.3 (d), 127.6 (s), 127.4 (d), 125.9 (d), 125.7 (d), 119.7 (s), 119.1 (d), 114.8 (d), 113.7 (d), 69.8 (t), 55.3 (q), 51.9 (t), 51.8 (t), 41.8 (q) ppm; IR (ATR): Ṽ 3058, 3037, 2933, 2350, 2248, 1681, 1628, 1611, 1596, 1512, 1494, 1453, 1338, 1303, 1247, 1216, 1175, 1150, 1073, 1034, 962, 911, 834, 764, 730, 697, 647, 618 cm⁻¹; HRMS (EI) calcd for [C₃₂H₂₃N₂O₅S⁺]⁺ (M⁺): 525.2081; found: 525.2067.

3ga: N-(1,3-diphenyl-5-(p-tolyl)-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide
Yield 94%, white solid, m.p.: 69–70 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 7.9$ Hz, 2H), 7.35 (t, $J = 7.8$ Hz, 2H), 7.27–7.25 (m, 2H), 7.18–7.12 (m, 5H), 6.77 (t, $J = 7.2$ Hz, 1H), 6.68 (d, $J = 8.5$ Hz, 2H), 5.06 (s, 1H), 4.73 (s, 1H), 4.29 (s, 1H), 4.00 (s, 1H), 2.70 (s, 3H), 2.39 (s, 6H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 147.7 (s), 146.2 (s), 137.3 (s), 136.8 (s), 134.1 (s), 129.5 (d), 129.4 (d), 129.2 (d), 128.2 (d), 124.6 (d), 123.9 (d), 119.2 (d), 117.8 (s), 114.9 (d), 69.4 (t), 51.1 (t), 40.0 (q), 37.7 (q), 21.3 (q) ppm; IR (ATR): $\nu$ 3056, 3030, 2923, 2856, 2249, 1677, 1637, 1597, 1494, 1456, 1336, 1287, 1217, 1145, 1080, 1039, 996, 961, 931, 911, 867, 822, 798, 754, 731, 699, 648 cm$^{-1}$; HRMS (EI) calcd for [C$_{33}$H$_{25}$N$_5$O$_3$S]$^+$ (M$^+$): 433.1819; found: 433.1817.

3ha: N-(5-[(4-tert-butylphenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl]-N-methylmethanesulfonamide

Yield 85%, white solid, m.p.: 176–177 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.48 (q, $J = 7.8$ Hz, 4H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.18–7.12 (m, 5H), 6.77 (t, $J = 7.2$ Hz, 1H), 6.68 (d, $J = 8.0$ Hz, 2H), 5.04 (s, 1H), 4.74 (s, 1H), 4.29 (s, 1H), 4.01 (s, 1H), 2.70 (s, 3H), 2.37 (s, 3H), 1.36 (s, 9H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 150.5 (s), 147.7 (s), 146.2 (s), 136.8 (s), 134.1 (s), 129.4 (d), 129.2 (d), 128.0 (d), 125.6 (d), 124.6 (d), 123.9 (d), 119.2 (d), 117.7 (s), 117.5 (s), 114.9 (d), 69.4 (t), 51.0 (t), 40.0 (q), 37.7 (q), 34.7 (s), 31.4 (q); IR (ATR): $\nu$ 2951, 2866, 1623, 1599, 1505, 1491, 1455, 1395, 1335, 1273, 1209, 1145, 1084, 1060, 1030, 998, 965, 931, 852, 837, 796, 782, 751, 695, 644 cm$^{-1}$; HRMS (EI) calcd for [C$_{32}$H$_{25}$N$_5$O$_3$S]$^+$ (M$^+$): 475.2288; found: 475.2273.

3ia: N-(5-[[1,1'-biphenyl]-4-yl]-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

Yield 79%, white solid, m.p.: 159–160 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.70–7.62 (m, 6H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.38–7.34 (m, 3H), 7.18–7.13 (m, 5H), 6.77 (t, $J = 7.3$ Hz, 1H), 6.69 (d, $J = 8.0$ Hz, 2H), 5.07 (s, 1H), 4.74 (s, 1H), 4.35 (s, 1H), 4.04 (s, 1H), 2.74 (s, 3H), 2.40 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 147.6 (s), 146.1 (s), 140.5 (s), 140.1 (s), 137.3 (s), 136.1 (s), 129.4 (d), 129.2 (d), 128.9 (d), 128.7 (d), 127.4 (d), 127.3 (d), 127.0 (d), 124.7 (d), 123.9 (d), 119.3 (d), 117.1 (s), 115.0 (d), 69.4 (t), 50.9 (t), 40.0 (q), 37.8 (q) ppm; IR (ATR): $\nu$ 3060, 3029, 2954, 2924, 2852, 1633, 1598, 1502, 1488, 1454, 1339, 1279, 1212, 1147, 1082, 1032, 1006, 963, 932, 847, 766, 751, 730, 695, 643 cm$^{-1}$; HRMS (EI) calcd for [C$_{32}$H$_{25}$N$_5$O$_3$S]$^+$ (M$^+$): 495.1975; found: 495.1945.

3ja: N-(5-[(4-methoxyphenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl]-N-methylmethanesulfonamide

Yield 94%, white solid, m.p.: 145–146 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 8.6$ Hz, 2H), 7.35 (t, $J = 7.8$ Hz, 2H), 7.17–7.12 (m, 5H), 6.99 (d, $J = 8.7$ Hz, 2H), 6.76 (t, $J = 7.3$ Hz, 1H), 6.67 (d, $J = 8.2$ Hz, 2H), 5.06 (s, 1H), 4.70 (s, 1H), 4.28 (s, 1H), 3.97 (s, 1H), 3.85 (s, 3H), 2.70 (s, 3H), 2.41 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 159.0 (s), 147.6 (s), 146.3 (s), 136.7 (s), 129.5 (d), 129.4 (d), 129.3 (s), 129.2 (d), 124.6 (d), 123.8 (d), 119.2 (d), 117.5 (s), 114.9 (d), 114.1 (d), 69.4 (t), 55.3 (q), 51.1 (t), 40.1 (q), 37.7 (q) ppm; IR (ATR): $\nu$ 3030, 2933, 2838, 2254, 1738, 1641, 1598, 1504, 1494, 1460, 1336, 1278, 1246, 1217, 1205, 1179, 1145, 1081, 1032, 995, 961, 931, 911, 867, 835,
799, 755, 732, 702, 649, 615 cm⁻¹; HRMS (EI) calcd for [C₂₅H₂₇N₂O₃S]⁺ (M⁺): 449.1768; found: 419.1779.

3ka: N-methyl-N-(5-(4-phenoxypyphenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide

![Ph-N-N-Ph]

Yield 80%, light yellow solid, m.p.: 60–61 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.55–7.52 (m, 2H), 7.39–7.34 (m, 4H), 7.18–7.13 (m, 6H), 7.10–7.05 (m, 4H), 6.67 (t, J = 7.3 Hz, 1H), 6.68 (d, J = 7.9 Hz, 2H), 5.06 (s, 1H), 4.71 (s, 1H), 4.30 (s, 1H), 4.00 (s, 1H), 2.74 (s, 3H), 2.42 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 156.9 (s), 156.8 (s), 147.6 (s), 146.2 (s), 137.1 (s), 131.9 (s), 129.9 (d), 129.7 (d), 129.4 (d), 129.2 (d), 124.7 (d), 123.9 (d), 123.6 (d), 119.3 (d), 119.2 (d), 118.8 (d), 117.1 (s), 115.0 (d), 69.4 (t), 51.1 (t), 40.1 (q), 37.8 (q) ppm; IR (ATR): ʋ 3061, 3036, 2929, 2851, 2363, 2252, 1647, 1597, 1489, 1457, 1336, 1273, 1236, 1169, 1144, 1080, 1033, 995, 961, 932, 910, 868, 800, 750, 732, 694, 650 cm⁻¹; HRMS (EI) calcd for [C₃₀H₂₉N₂O₂S]⁺ (M⁺): 511.1924; found: 511.1920.

3la: N-(5-(4-fluorophenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

![Ph-N-N-F]

Yield 87%, light yellow solid, m.p.: 64–65 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.55–7.52 (m, 2H), 7.37–7.34 (m, 2H), 7.17–7.12 (m, 7H), 6.67 (t, J = 7.3 Hz, 1H), 6.66 (d, J = 7.9 Hz, 2H), 5.05 (s, 1H), 4.71 (s, 1H), 4.27 (s, 1H), 3.97 (s, 1H), 2.69 (s, 3H), 2.40 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 162.1 (s, d: J=13.4 Hz), 147.5 (s), 146.1 (s), 137.4 (s), 133.0 (s, d: J=13.4 Hz), 130.1 (d, d: J=13.4 Hz), 129.4 (d), 129.2 (d), 124.8 (d), 123.9 (d), 119.4 (d), 116.8 (s), 115.7 (d: J=13.4 Hz), 115.0 (d), 69.5 (t), 51.1 (t), 40.1 (q), 37.8 (q) ppm; ¹⁹F NMR (282 MHz, CDCl₃) δ -114.16 ppm; IR (ATR): ʋ 3063, 2929, 1681, 1638, 1595, 1494, 1336, 1222, 1157, 1146, 1099, 1080, 1040, 961, 912, 840, 799, 761, 729, 696, 648, 613 cm⁻¹; HRMS (EI) calcd for [C₃₀H₂₉N₂O₂S]⁺ (M⁺): 437.1568; found: 437.1557.

3ma: N-(5-(4-bromophenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

![Ph-N-N-Br]

Yield 91%, white solid, m.p.: 165–166 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 8.2 Hz, 2H), 5.05 (s, 1H), 4.70 (s, 1H), 4.29 (s, 1H), 3.98 (s, 1H), 2.70 (s, 3H), 2.39 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 147.5 (s), 146.0 (s), 137.6 (s), 136.1 (s), 131.9 (d), 130.0 (d), 129.5 (d), 129.3 (d), 124.9 (d), 124.0 (d), 121.5 (s), 119.5 (d), 116.4 (s), 115.0 (d), 69.4 (t), 50.8 (t), 39.9 (q), 37.8 (q) ppm; IR (ATR): ʋ 3067, 3035, 2862, 1641, 1599, 1490, 1461, 1424, 1385, 1362, 1329, 1295, 1283, 1199, 1142, 1080, 1041, 1008, 997, 963, 932, 893, 869, 833, 803, 789, 763, 733, 700, 658 cm⁻¹; HRMS (EI) calcd for [C₃₀H₂₉N₂O₂SBr]⁺ (M⁺): 497.0767; found: 497.0745.

3na: methyl 4-(6-(N-methylmethanesulfonamido)-1,3-diphenyl-1,2,3,4-tetrahydropyrimidin-5-yl)benzoate

Yield 86%, white s solid, m.p.: 81–82 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.18–7.12 (m, 5H), 6.78 (t, J = 7.3 Hz, 1H), 6.68
**3oa**: N-(1,3-diphenyl-5-(4-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

Yield 80%, light yellow solid, m.p.: 139–140 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.71–7.67 (m, 4H), 7.36 (t, \(J = 7.9\) Hz, 2H), 7.18–7.12 (m, 5H), 6.79 (t, \(J = 7.3\) Hz, 1H), 6.68 (d, \(J = 8.0\) Hz, 2H), 5.06 (s, 1H), 4.72 (s, 1H), 4.34 (s, 1H), 4.01 (s, 1H), 2.69 (s, 3H), 2.37 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 166.9 (s), 147.5 (s), 145.8 (s), 142.1 (s), 138.2 (s), 130.0 (d), 129.5 (d), 129.3 (d), 128.3 (d), 125.0 (d), 124.1 (d), 119.5 (d), 116.2 (s), 115.1 (d), 69.5 (t), 52.2 (q), 50.6 (t), 39.8 (q), 37.7 (q) ppm; IR (ATR): \(\tilde{\nu}\) 2951, 1717, 1685, 1637, 1597, 1494, 1456, 1337, 1278, 1182, 1146, 1039, 1020, 960, 933, 862, 828, 772, 697, 647 cm\(^{-1}\); HRMS (EI) calcd for [C\(_{26}\)H\(_{27}\)N\(_3\)O\(_4\)S]\(^+\) (M\(^+\)): 477.1717; found: 477.1701.

**3pa**: N-(5-(3-chlorophenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

Yield 82%, light yellow solid, m.p.: 78–79 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.52–7.48 (m, 2H), 7.39–7.29 (m, 4H), 7.18–7.12 (m, 5H), 6.78 (t, \(J = 7.3\) Hz, 1H), 6.67 (d, \(J = 7.9\) Hz, 2H), 5.03 (s, 1H), 4.71 (s, 1H), 4.27 (s, 1H), 4.00 (s, 1H), 2.71 (s, 3H), 2.37 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 147.5 (s), 145.9 (s), 139.1 (s), 137.9 (s), 134.4 (s), 130.1 (d), 129.5 (d), 129.2 (d), 128.1 (d), 127.6 (d), 126.9 (d), 124.9 (d), 124.1 (d), 119.5 (d), 116.1 (s), 115.1 (d), 69.4 (t), 50.7 (t), 39.8 (q), 37.9 (q) ppm; \(^{19}\)F NMR (470 MHz, CDCl\(_3\)) \(\delta\) -62.459, -62.464 ppm; IR (ATR): \(\tilde{\nu}\) 3063, 3030, 2929, 2854, 1639, 1594, 1562, 1493, 1455, 1411, 1337, 1277, 1213, 1148, 1114, 1066, 1033, 1016, 996, 935, 852, 850, 794, 769, 754, 694, 609 cm\(^{-1}\); HRMS (EI) calcd for [C\(_{24}\)H\(_{24}\)N\(_3\)O\(_2\)SCl]\(^+\) (M\(^+\)): 453.1272; found: 453.1265.

**3qa**: N-(5-(6-methoxynaphthalen-2-yl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

Yield 40%, white solid, m.p.: 188–189 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 1.1\) Hz, 1H), 7.80 (t, \(J = 9.3\) Hz, 2H), 7.71 (dd, \(J = 8.4\), 1.8 Hz, 1H), 7.37–7.34 (m, 2H), 7.19–7.12 (m, 7H), 6.77 (t, \(J = 7.3\) Hz, 1H), 6.70 (d, \(J = 7.9\) Hz, 2H), 5.10 (s, 1H), 4.75 (s, 1H), 4.44 (s, 1H), 4.06 (s, 1H), 3.94 (s, 3H), 2.67 (s, 3H), 2.39 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 157.9 (s), 147.7 (s), 146.2 (s), 137.3 (s), 133.8 (s), 132.3 (s), 129.6 (d), 129.4 (d), 129.2 (d), 128.9 (s), 127.2 (d), 127.1 (d), 126.6 (d), 124.6 (d), 123.8 (d), 119.3 (d), 119.2 (d), 117.5 (s), 114.9 (d), 105.7 (d), 69.3 (t), 55.4 (q), 51.0 (t), 40.0 (q), 37.8 (q) ppm; IR (ATR): \(\tilde{\nu}\) 2932, 2236, 1627, 1599, 1485, 1392.
N-methyl-N-(5-phenyl-1,3-di-p-tolyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide

3ab: Yield 86%, white solid, m.p.: 79–80 °C; 1H NMR (500 MHz, CDCl₃) δ 7.56 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 8.4 Hz, 2H), 4.91 (s, 1H), 4.66 (s, 1H), 4.23 (s, 1H), 3.99 (s, 1H), 2.76 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H), 2.22 (s, 3H) ppm; 13C NMR (125 MHz, CDCl₃) δ 145.5 (s), 143.7 (s), 137.4 (s), 137.2 (s), 134.4 (s), 129.9 (d), 129.7 (d), 128.72 (s), 128.70 (d), 128.5 (s), 127.4 (d), 124.1 (d), 117.4 (s), 115.3 (d), 70.2 (t), 51.3 (t), 40.0 (q), 37.6 (q), 20.9 (q), 20.4 (q) ppm; IR (ATR): v 3032, 3010, 2926, 2864, 2239, 1680, 1635, 1596, 1513, 1450, 1408, 1381, 1339, 1330, 1273, 1218, 1175, 1040, 961, 876, 819, 769, 729, 703, 645 cm⁻¹; HRMS (EI) calcd for [C₂₉H₂₉N₃O₂S]⁺ (M⁺): 499.1924; found: 499.1926.

3ac: N-(1,3-bis(4-isopropylphenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

Yield 73%, light yellow solid, m.p.: 140–141 °C; 1H NMR (500 MHz, CDCl₃) δ 7.58 (d, J = 7.8 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.35–7.32 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 7.7 Hz, 4H), 6.67 (d, J = 8.1 Hz, 2H), 4.98 (s, 1H), 4.68 (s, 1H), 4.29 (s, 1H), 2.90 (dt, J = 13.8, 6.9 Hz, 1H), 2.80 (dt, J = 13.8, 6.9 Hz, 1H), 2.70 (s, 3H), 2.40 (s, 3H), 1.25 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.9 Hz, 6H) ppm; 13C NMR (125 MHz, CDCl₃) δ 145.9 (s), 145.3 (s), 143.9 (s), 139.9 (s), 137.4 (s), 137.3 (s), 128.7 (d), 128.4 (d), 127.4 (d), 127.2 (d), 127.1 (d), 124.0 (d), 117.4 (s), 115.3 (d), 70.0 (t), 51.3 (t), 40.0 (q), 37.7 (q), 33.5 (q), 33.2 (q), 24.2 (q), 24.1 (q) ppm; IR (ATR): v 3402, 3053, 3022, 2833, 1738, 1627, 1598, 1509, 1472, 1440, 1386, 1361, 1291, 1264, 1220, 1176, 1145, 1125, 1030, 980, 956, 935, 832, 809, 746, 702, 653, 619 cm⁻¹; HRMS (EI) calcd for [C₃₀H₃₇N₃O₂S]⁺ (M⁺): 503.2601; found: 503.2590.

3ad: N-(1,3-di(1,1'-biphenyl)-4-yl)-N-methylmethanesulfonamide

Yield 70%, light yellow solid, m.p.: 150–151 °C; 1H NMR (500 MHz, CDCl₃) δ 7.61–7.57 (m, 6H), 7.49–7.32 (m, 13H), 7.22 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 5.12 (s, 1H), 4.80 (s, 1H), 4.35 (s, 1H), 4.10 (s, 1H), 2.72 (s, 3H), 2.42 (s, 3H) ppm; 13C NMR (125 MHz, CDCl₃) δ 146.9 (s), 145.3 (s), 140.8 (s), 140.1 (s), 137.4 (s), 137.1 (s), 137.0 (s), 132.1 (s), 128.9 (d), 128.8 (d), 128.7 (d), 128.4 (d), 128.0 (d), 127.9 (d), 127.6 (d), 127.3 (d), 126.8 (d), 126.5 (d), 124.0 (d), 117.9 (s), 115.1 (d), 69.1 (t), 51.0 (t), 40.1 (q), 37.7 (q) ppm; IR (reflection): v 3055, 3030, 2924, 2852, 1681, 1637, 1609, 1523, 1486, 1449, 1337, 1297, 1263, 1215, 1176, 1145, 1077, 1041, 1007, 960, 931, 911, 841, 762, 728, 697, 649 cm⁻¹; HRMS (ESI) calcd for [C₃₆H₃₇N₃O₂SNa]⁺ (M⁺+Na⁺): 594.2186; found: 594.2192.

3ae: N-(1,3-bis(4-methoxyphenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide
Yield 76%, light yellow solid, m.p.: 158–159 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.54–7.52 (m, 2H), 7.42 (t, \(J = 7.7\) Hz, 2H), 7.31 (t, \(J = 7.4\) Hz, 1H), 7.13–7.10 (m, 2H), 6.89–6.86 (m, 2H), 6.76–6.73 (m, 2H), 6.69–6.66 (m, 2H), 4.73 (s, 1H), 4.62 (s, 1H), 4.13 (s, 1H), 3.99 (s, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 2.68 (s, 3H), 2.33 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 157.0 (s), 153.6 (s), 142.0 (s), 139.4 (s), 137.6 (s), 137.2 (s), 128.7 (d), 128.6 (d), 127.4 (d), 126.0 (d), 117.6 (d), 117.1 (s), 114.6 (d), 114.4 (d), 71.9 (t), 55.6 (q), 55.4 (q), 52.1 (t), 39.7 (q), 37.4 (q) ppm; IR (ATR): \(\nu\) 1648, 1598, 1506, 1462, 1453, 1441, 1375, 1330, 1293, 1275, 1224, 2837, 2788, 1654, 1608, 1581, 1508, 1455, 1445, 1479, 1331, 1295, 1240, 1194, 1143, 1107, 1088, 1064, 1032, 963, 933, 876, 837, 828, 770, 747, 699 cm\(^{-1}\); HRMS (EI) calcd for [C\(_{26}H_{29}N_5O_4S]\(^+\) (M\(^+\)): 479.1873; found: 479.1874.

3af: N-(1,3-bis(4-phenoxophenyl)-5-phenyl-1,2,3,6-tetrahydropyrmenidin-4-y1)-N-methylmethanesulphonamide

Yield 90%, white solid, m.p.: 75–76 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.53 (d, \(J = 7.1\) Hz, 2H), 7.44 (t, \(J = 7.7\) Hz, 2H), 7.34–7.28 (m, 5H), 7.13–7.08 (m, 3H), 7.04–6.96 (m, 5H), 6.91–6.88 (m, 4H), 6.74–6.72 (m, 2H), 4.88 (s, 1H), 4.75 (s, 1H), 4.22 (s, 1H), 4.07 (s, 1H), 2.69 (s, 3H), 2.36 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 158.4 (s), 157.2 (s), 154.2 (s), 149.8 (s), 144.3 (s), 141.5 (s), 137.3 (s), 136.9 (s), 129.8 (d), 129.6 (d), 128.8 (d), 128.5 (d), 127.6 (d), 125.7 (d), 123.4 (d), 122.4 (d), 120.7 (d), 119.6 (d), 118.7 (d), 117.6 (d), 117.4 (s), 117.2 (d), 70.9 (t), 51.8 (t), 39.8 (q), 37.4 (q) ppm; IR (ATR): \(\nu\) 3059, 3039, 2988, 2958, 2914, 2837, 2788, 1654, 1608, 1581, 1504, 1487, 1338, 1291, 1234, 1198, 1144, 1105, 1076, 1023, 961, 931, 869, 841, 756, 692 cm\(^{-1}\); HRMS (ESI) calcd for [C\(_{32}H_{33}N_5O_4S]\(^+\) (M\(^+\)): 603.2186; found: 603.2183.

3ag: N-(1,3-bis(4-fluorophenyl)-5-phenyl-1,2,3,6-tetrahydropyrmenidin-4-y1)-N-methylmethanesulphonamide

Yield 83%, light yellow solid, m.p.: 154–155 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.50 (d, \(J = 7.1\) Hz, 2H), 7.43 (t, \(J = 7.5\) Hz, 2H), 7.33 (t, \(J = 7.2\) Hz, 1H), 7.18–7.14 (m, 2H), 7.03 (t, \(J = 8.5\) Hz, 2H), 6.87 (t, \(J = 8.6\) Hz, 2H), 6.67–6.62 (m, 2H), 4.74 (s, 2H), 4.09 (s, 2H), 2.69 (s, 13H), 2.26 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 160.1 (s, d: \(\delta_{CF} = 244.8\) Hz), 157.1 (s, d: \(\delta_{CF} = 239.0\) Hz), 144.2 (s, d: \(\delta_{CF} = 2.2\) Hz), 142.1 (s, d: \(\delta_{CF} = 2.8\) Hz), 137.37 (s), 136.72 (s), 128.78 (d), 128.65 (d), 127.64 (d), 126.21 (d, \(\delta_{CF} = 8.2\) Hz), 117.53 (s), 117.19 (d, \(\delta_{CF} = 7.6\) Hz), 116.11 (d, \(\delta_{CF} = 22.5\) Hz), 115.69 (d, \(\delta_{CF} = 22.3\) Hz), 71.25 (t), 51.88 (t), 39.58 (q), 37.12 (q); \(^{19}\)F NMR (282 MHz, CD\(_3\)Cl\(_2\)) \(\delta\) -122.45, -129.63 ppm; IR (ATR): \(\nu\) 3063, 3032, 3012, 2868, 2799, 1648, 1598, 1506, 1462, 1453, 1441, 1425, 1375, 1330, 1293, 1275, 1224, 1197, 1171, 1154, 1141, 1098, 1081, 1065, 1025, 997, 962, 934, 911, 883, 843, 822, 774, 762, 752, 733, 723, 701, 642, 608 cm\(^{-1}\); HRMS (ESI) calcd for [C\(_{24}H_{24}F_2N_4O_3S\]^+\) (M\(^+\)+Na\(^+\)): 478.1371; found: 478.1376.

3ah: N-(1,3-bis(4-chlorophenyl)-5-phenyl-1,2,3,6-tetrahydropyrmenidin-4-y1)-N-methylmethanesulphonamide

Yield 55%, yellow solid, m.p.: 170–171 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.50 (d, \(J = 7.1\) Hz, 12H), 7.44 (t, \(J = 7.7\) Hz, 2H), 7.35–7.30 (m, 3H), 7.11–7.09 (m, 4H), 6.58 (d, \(J = 8.9\) Hz, 2H), 4.81 (s,
2H), 4.10 (s, 2H), 2.67 (s, 3H), 2.30 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 146.1 (s), 144.5 (s), 137.0 (s), 136.5 (s), 130.4 (s), 129.6 (d), 129.1 (d), 128.8 (d), 128.5 (d), 127.8 (d), 125.4 (d), 124.4 (s), 118.0 (s), 116.3 (d), 69.5 (t), 51.2 (t), 39.8 (q), 37.2 (q); IR (ATR): $\tilde{\nu}$ 3092, 3061, 2932, 2851, 1685, 1635, 1595, 1492, 1451, 1391, 1377, 1358, 1337, 1293, 1273, 1245, 1222, 1205, 1147, 1094, 1077, 1056, 1016, 1001, 961, 927, 910, 854, 836, 816, 800, 780, 766, 756, 731, 701, 661, 632, 621 cm$^{-1}$; HRMS (EI) calcd for [C$_{24}$H$_{23}$N$_{3}$O$_{2}$SCl$_2$]$^+$ (M$^+$): 487.0883; found: 487.0877.

3ai: N-(1,3-bis(4-bromophenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

![Structure](image)

Yield 53%, light yellow solid, m.p.: 188–189 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.51–7.42 (m, 6H), 7.34 (t, $J$ = 7.3 Hz, 1H), 7.26–7.23 (m, 2H), 7.05–7.03 (m, 2H), 6.53 (d, $J$ = 9.0 Hz, 2H), 4.80 (s, 2H), 4.09 (s, 2H), 2.67 (s, 3H), 2.31 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 146.5 (s), 144.9 (s), 136.9 (s), 136.5 (s), 132.5 (d), 132.0 (d), 128.8 (d), 128.5 (d), 127.8 (d), 125.6 (d), 118.09 (s), 118.08 (s), 116.6 (d), 111.6 (s), 69.2 (t), 51.1 (t), 39.9 (q), 37.2 (q) ppm; IR (ATR): $\tilde{\nu}$ 3054, 3025, 2924, 2851, 1682, 1637, 1590, 1487, 1336, 1217, 1145, 1074, 1040, 1010, 961, 911, 872, 830, 768, 731, 701 cm$^{-1}$; HRMS (ESI) calcd for [C$_{24}$H$_{23}$N$_{3}$O$_{2}$S$^{79}$Br$^{35}$BrNa]$^+$ (M+Na$^+$): 599.9749; found: 599.9759.

3aj: N-methyl-N-(5-phenyl-1,3-di-m-tolyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide

![Structure](image)

Yield 86%, light yellow solid, m.p.: 149–150 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J$ = 7.9 Hz, 2H), 7.45 (t, $J$ = 7.7 Hz, 2H), 7.33 (t, $J$ = 7.4 Hz, 1H), 7.26–7.22 (m, 1H), 7.06 (t, $J$ = 7.7 Hz, 1H), 6.96–6.85 (m, 3H), 6.61 (d, $J$ = 7.4 Hz, 1H), 6.52–6.50 (m, 2H), 5.03 (s, 1H), 4.71 (s, 1H), 4.30 (s, 1H), 4.01 (s, 1H), 2.69 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H), 2.24 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 147.8 (s), 146.1 (s), 139.2 (s), 139.0 (s), 137.3 (s), 137.1 (s), 129.1 (d), 129.0 (d), 128.7 (d), 128.4 (d), 127.5 (d), 125.4 (d), 124.5 (d), 120.9 (d), 120.1 (d), 117.5 (s), 115.7 (d), 112.2 (d), 69.2 (t), 51.2 (t), 39.9 (q), 37.7 (q), 21.7 (q), 21.5 (q) ppm; IR (ATR): $\tilde{\nu}$ 3055, 3034, 3009, 2918, 1682, 1644, 1604, 1490, 1446, 1371, 1333, 1276, 1238, 1174, 1144, 1078, 1045, 1006, 962, 945, 894, 870, 858, 878, 787, 766, 742, 704, 688, 659, 610 cm$^{-1}$; HRMS (ESI) calcd for [C$_{24}$H$_{29}$N$_{3}$O$_{2}$S$^{79}$Na]$^+$ (M+Na$^+$): 470.1873; found: 470.1876.

3ak: N-(1,3-bis(2-fluorophenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

![Structure](image)

Yield 80%, white solid, m.p.: 160–161 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J$ = 7.5 Hz, 2H), 7.44 (t, $J$ = 7.7 Hz, 2H), 7.33 (t, $J$ = 7.4 Hz, 1H), 7.10–7.08 (m, 3H), 7.04–6.98 (m, 3H), 6.89–6.85 (m, 2H), 4.84 (s, 1H), 4.71 (s, 1H), 4.19 (s, 1H), 4.14 (s, 1H), 2.68 (s, 3H), 2.27 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 157.0 (s, d: $J_{CF}$ = 198.9 Hz), 155.1 (s, d: $J$ = 197.5 Hz), 137.4 (s), 136.3 (s, d: $J_{CF}$ = 8.9 Hz), 136.1 (s), 132.9 (s, d: $J_{CF}$ = 9.7 Hz), 128.8 (d), 127.6 (d), 127.2 (d), 126.4 (d, d: $J_{CF}$ = 7.8 Hz), 124.4 (d, d: $J_{CF}$ = 3.6 Hz), 124.0 (d, d: $J_{CF}$ = 3.8 Hz), 122.7 (d, d: $J_{CF}$ = 7.8 Hz), 119.6 (d), 119.6 (d), 117.3 (s), 116.2 (d, d: $J_{CF}$ = 20.0 Hz), 116.2 (d, d: $J_{CF}$ = 20.0 Hz), 72.5–67.8 (t, m), 52.5 (t), 39.5 (q), 37.0 (q) ppm; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -123.46, -124.26 ppm; IR (ATR): $\tilde{\nu}$ 3053, 2927, 2187, 1656, 1488, 1416, 1356, 1302, 1259, 1208, 1192, 1154, 1108, 1043,
1017, 980, 938, 883, 828, 793, 732, 714, 675, 612 cm⁻¹; HRMS (EI) calcd for [C₂₄H₂₂N₃O₂SF₂]⁺ (M)⁺: 455.1474; found: 455.1487.

3al: N-(1,3-bis(4-chloro-3-methylphenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

Yield 81%, light yellow solid, m.p.: 121–122 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.53–7.51 (m, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.36–7.29 (m, 2H), 7.09 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.94 (dd, J = 8.4, 2.5 Hz, 1H), 6.54 (d, J = 2.7 Hz, 1H), 6.45 (dd, J = 8.7, 2.8 Hz, 1H), 4.79 (s, 2H), 4.10 (s, 2H), 2.68 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.3 (s), 144.4 (s), 137.2 (s), 137.1 (s), 136.5 (s), 130.4 (s), 129.8 (d), 129.4 (d), 128.8 (d), 128.5 (d), 127.7 (d), 126.4 (d), 124.8 (s), 122.6 (d), 117.8 (s), 117.6 (d), 114.1 (d), 69.4 (t), 51.4 (t), 39.9 (q), 37.2 (q), 20.4 (q), 20.3 (q) ppm; IR (ATR): ν 2927, 2856, 1640, 1597, 1482, 1446, 1413, 1336, 1230, 1145, 1089, 1046, 962, 862, 817, 767, 700 cm⁻¹; HRMS (EI) calcd for [C₂₆H₂₇N₃O₂SCl]⁺ (M)⁺: 515.1196; found: 515.1198.

3. References

4. Copies of NMR spectra
5. X-Ray crystal structure analysis

The crystallographic data of compound 3da (CCDC 1525557) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
6. Mechanistic investigations

A round bottom flask equipped with a magnetic stirrer bar was charged with CyJohnPhosAuCl (10 mol%, 5.8 mg), AgNTf₂ (10 mol%, 3.9 mg), and 1,2-DCE (0.5 ml). The mixture was stirred for 5 minutes at room temperature. Ynamide 1a (0.1 mmol, 2 equiv.), 1,3,5-triazinanes 2a (0.09 mmol, 1.8 equiv.) and D₆-2a (0.09 mmol, 1.8 equiv.) were added followed by 0.5 mL 1,2-DCE. The reaction mixture was then stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was concentrated and the residue was purified by flash chromatography on silica gel (PE/EA = 5:1, v/v) to afford the crude product. Then such a crude product was subjected to HRMS analysis. The result showed that the formation of 3aa, D₄-3aa, D₂-3aa, and/or D₂-3aa’. See the copies of the HRMS spectra below.
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A round bottom flask equipped with a magnetic stirrer bar was charged with CyJohnPhosAuCl (10 mol%, 5.8 mg), AgNTf₂ (10 mol%, 3.9 mg), and 1,2-DCE (0.5 ml). The mixture was stirred for 5 minutes at room temperature. Ynamide 1a (0.1 mmol, 2 equiv.), 1,3,5-triazinanes 2a (0.09 mmol, 1.8 equiv.) and 2b (0.09 mmol, 1.8 equiv.) were added followed by 0.5 mL 1,2-DCE. The reaction mixture was then stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was concentrated and the residue was purified by flash chromatography on silica gel (PE/EA = 5:1, v/v) to afford the crude product. Then such a crude product was subjected to HRMS analysis. The result showed that the formation of 3aa, 3ab, 4 and/or 4’. See the copy of the HRMS spectrum below.
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