Supporting Information

One pot synthesis of highly functionalized pyrimido[1, 2-b]indazoles via 6-endo-dig cyclization

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Experimental section:
All commercially available reagents were used without any further purification and the reactions were monitored by TLC. $^1$H and $^{13}$C NMR were obtained using a Bruker Avance 400 Mz spectrometer in CDCl$_3$ solvent with TMS as an internal standard. Chemical shift values (δ) were expressed in parts per million (ppm). Abbreviations are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Melting points were measured on Elchem Microprocessor based DT apparatus using an open capillary tubes and are corrected with benzoic acid. Mass spectra were obtained by high resolution mass spectrometer. UV-vis spectrum was obtained on UV-2550, Shimadzu Corporation, Kyoto, Japan. The fluorescence spectra were obtained on Hitachi F-7000 FL spectrophotometer.

**General procedure for the synthesis of 2,4-diphenylpyrimido [1,2-b] indazole 4 (a-q) via metal mediated condition:**

A mixture of 1H-indazol-3-amine (1mmol), aldehydes (1mmol) and acetylenes (1mmol) in 5 mL of toluene. Then added CuSO$_4$. 5H$_2$O (21 mol %) followed by para –toluene sulphonic acid (10 mol %) in the presence of nitrogen atmosphere. The mixture was refluxed at 121 °C for 8 h 30 min. The progress of the reaction was monitored by TLC. After the completion of the reaction, evaporated the solvent and the crude was purified by column chromatography afford the product as a solid.

**Experimental design & Mathematical model:**

An experimental design for the series of parameters used for the synthesis of 2,4-diphenylpyrimido [1,2-b] indazole by two reaction methods such as metal mediated and metal free conditions. The model was built by Response Surface Methodology (RSM) with the Design – Expert Version 9.0.5.1 (State-Ease, Inc., Minneapolis, USA). Levels of selection for each variable based on the results of the preliminary studies. The three components for each reaction method, such as the catalyst loading (A1), reaction temperature (B1) and response time (C1) were utilized for metal mediated reaction.. The actual isolated yields $Y_1$ was chosen to be the target or response parameter as dependent variables. The $X_1$ was denoted as predicted isolated yields. Seventeen sets of experiments were performed for each both reaction methods according to Box-Behnken experimental design (BBD). The variables were tested at the three levels by associating negative sign (-1) for lower level, Zero (0) indicating the core value and plus signs (+1) for higher stages (Table 1). The quadratic polynomial equation recommended by RSM was used to predict the optimal value and examine the interaction between the response of experimental design (actual
yield) and the variables (process parameters). The general form of quadratic polynomial was as follows

\[ Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \]

Where \( \beta_0 \) is constant coefficient of the models. The regression coefficients (\( \beta_1, \beta_2 \) and \( \beta_3 \)), (\( \beta_{11}, \beta_{22} \) and \( \beta_{33} \)) and (\( \beta_{12}, \beta_{13} \) and \( \beta_{23} \)) respectively represent linear, quadratic and interaction effects of the model estimated by multiple regression analysis.

**Figure S1:** The solvatochromism spectra of the compound 4a.
**Figure S2.** UV/Vis absorbance spectra of the pyrimido[1,2-b]indazoles 4(a-t) in ethyl acetate.

**Figure S3:** Fluorescence emission spectra of the pyrimido[1,2-b]indazoles 4(a-t) in ethyl acetate.
Spectral characterization of the compound 4(a-t):

2,4-diphenylpyrimido[1,2-b]indazole (4a)

Yellow solid; Isolated yield - 90 %; mp: 154-156 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43 (d, $J = 7.2$ Hz, 1H), 8.30-8.27 (m, 2H), 8.23-8.20 (m, 2H), 7.86 (d, $J = 8.8$ Hz, 1H), 7.75 (s, 1H), 7.67-7.50 (m, 7H), 7.33-7.29 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$108.6,113.9, 116.6, 120.7, 121.2, 127.2, 128.8, 129.0, 129.5, 129.8, 130.1, 131.1, 131.8, 137.3, 145.0, 145.3, 151.6, 152.6; HRMS: m/z calcd. for C$_{22}$H$_{15}$N$_3$ 321.1266 found 321.1256.

4-(4-bromophenyl)-2-phenylpyrimido[1,2-b]indazole (4b)

Yellow solid; Isolated yield - 89 %; mp: 170-172 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.39 (d, $J = 8.4$ Hz, 1H), 8.20-8.12 (m, 4H), 7.86-7.84 (m, 1H), 7.69-7.59 (m, 7H), 7.32-7.29 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 108.1, 113.9, 116.6, 120.9, 121.1, 124.7, 128.6, 128.9, 129.4, 130.0, 131.1, 131.6, 132.2, 136.2, 144.9, 145.3, 151.1, 151.6; HRMS: m/z calcd. for C$_{22}$H$_{14}$BrN$_3$ 399.0371 found 399.0370.

4-(4-methoxyphenyl)-2-phenylpyrimido[1,2-b]indazole (4c)

Yellow solid; Isolated yield - 85 %; mp: 170-172 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31 (d, $J = 8.4$ Hz, 1H), 8.15-8.10 (m, 3H), 7.74 (d, $J = 8.8$ Hz, 1H), 7.57-7.49 (m, 5H), 7.21-7.17 (m, 1H), 6.97 (d, $J = 7.6$ Hz, 2H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 55.4, 108.1, 113.7, 114.4, 116.5, 120.4, 121.2, 128.6, 128.8, 129.5, 129.7, 129.8, 130.9, 131.9, 145.0, 145.2, 151.5, 152.4, 161.4; HRMS: m/z calcd. for C$_{23}$H$_{15}$N$_3$O 351.1372 found 351.1371.

2-phenyl-4-(thiophen-2-yl)pyrimido[1,2-b]indazole (4d)

Brown solid; Isolated yield - 81 %; mp: 202-204 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.41 (d, $J = 8.0$ Hz, 1H), 8.23-8.20 (m, 2H), 7.86-7.82 (m, 2H), 7.69-7.56 (m, 6H), 7.33-7.29 (m, 1H), 7.22-7.21 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 107.5, 113.6, 116.5, 120.6, 121.3, 126.8, 128.4, 128.8, 129.5, 129.9, 131.0, 131.6, 143.2, 144.6, 145.2, 148.0, 151.6; HRMS: m/z calcd. for C$_{20}$H$_{13}$N$_3$S 327.0830 found 327.0829.
4-(4-chlorophenyl)-2-phenylpyrimido[1,2-b]indazole (4e)

Yellow solid; Isolated yield - 89 %; mp: 202-204 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.0 (d, \(J = 8.4\) Hz, 1H), 8.23-8.19 (m, 4H), 7.85 (d, \(J = 8.4\) Hz, 1H), 7.65 (s, 1H), 7.65-7.59 (m, 4H), 7.53-7.51 (m, 2H), 7.31-7.29 (m, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 108.2, 113.2, 116.6, 120.9, 121.1, 128.4, 128.9, 129.2, 129.4, 129.9, 131.1, 131.7, 135.7, 136.3, 144.9, 145.4, 151.1, 151.6; HRMS: m/z calcd. for C\(_{22}\)H\(_{14}\)N\(_3\)Cl 355.0876 found 355.0875.

4-(2,4-dimethoxyphenyl)-2-phenylpyrimido[1,2-b]indazole (4f)

Yellow solid; Isolated yield - 87 %; mp: 160-162 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.32 (d, \(J = 8.0\) Hz, 1H), 8.15-8.14 (m, 2H), 7.92 (s, 1H), 7.76 (d, \(J = 8.4\) Hz, 1H), 7.55-7.50 (m, 4H), 7.21-7.18 (m, 2H), 6.66 (d, \(J = 8.4\) Hz, 1H), 6.54 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 55.5, 55.8, 99.0, 105.7, 113.0, 113.7, 116.4, 120.0, 120.1, 121.2, 128.7, 129.5, 129.6, 130.6, 132.2, 132.4, 143.8, 144.9, 151.2, 152.0, 158.8, 162.5; HRMS: m/z calcd. for C\(_{24}\)H\(_{19}\)N\(_3\)O\(_2\) 381.1477 found 381.1477.

4-(furan-2-yl)-2-phenylpyrimido[1,2-b]indazole (4g)

Brown solid; Isolated yield - 79 %; mp: 206-208 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.38 (d, \(J = 8.0\) Hz, 1H), 8.20-8.17 (m, 2H), 7.83-7.79 (m, 2H), 7.65-7.47 (m, 5H), 7.18-7.15 (m, 2H), 7.77 (d, \(J = 7.6\) Hz, 2H), 3.01 (s, 6H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 107.5, 113.6, 116.5, 120.6, 121.3, 126.8, 128.4, 128.9, 131.0, 131.6, 143.2, 144.6, 145.2, 148.0, 151.6; HRMS: m/z calcd. for C\(_{20}\)H\(_{13}\)N\(_3\)O 311.1059 found 311.1058.

N,N-dimethyl-4-(2-phenylpyrimido[1,2-b]indazol-4-yl)aniline (4h)

Brown solid; Isolated yield - 84 %; mp: 147-149 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (d, \(J = 8.4\) Hz, 1H), 8.13-8.11 (m, 3H), 8.12 (d, \(J = 8.8\) Hz, 1H), 7.57-7.47 (m, 5H), 7.18-7.15 (m, 2H), 7.77 (d, \(J = 7.6\) Hz, 2H), 3.01 (s, 6H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 40.2, 107.8, 112.1, 113.6, 116.3, 119.9, 121.3, 124.7, 128.3, 128.7, 129.4, 129.5, 130.7, 132.2, 151.5; HRMS: m/z calcd. for C\(_{24}\)H\(_{20}\)N\(_4\) 364.1688 found 364.1688.
4-(2-phenylpyrimido[1,2-b]indazol-4-yl)benzonitrile (4i)

Yellow solid; Isolated yield - 78 %; mp: 252-254 °C; 1H NMR (400 MHz, CDCl$_3$) δ 8.39 (d, J = 8.4 Hz, 1H), 8.20-8.12 (m, 4H), 7.86-7.84 (m, 1H), 7.69-7.59 (m, 7H), 7.32-7.29 (m, 1H); 13C NMR (100 MHz, CDCl$_3$) δ 108.1, 113.9, 116.6, 120.9, 121.1, 124.7, 128.6, 128.9, 129.4, 130.0, 131.1, 131.6, 132.2, 136.2, 144.9, 145.3, 151.1, 151.6; HRMS: m/z calcd. for C$_{23}$H$_{14}$N$_4$ 346.1218 found 346.1217.

4-(4-nitrophenyl)-2-phenylpyrimido[1,2-b]indazole (4j)

Yellow solid; Isolated yield - 75 %; mp: 272-274 °C; 1H NMR (400 MHz, CDCl$_3$) δ 8.48-8.40 (m, 5H), 8.24-8.22 (m, 2H), 7.90 (d, J = 8.8 Hz, 1H), 7.79 (s, 1H), 7.69-7.65 (m, 4H), 7.40-7.36 (m, 1H); 13C NMR (100 MHz, CDCl$_3$) δ 108.4, 114.2, 116.9, 121., 121.5, 124.2, 127.8, 128.9, 129.5, 130.3, 131.3, 143.1, 144.9, 145.5, 148.6, 149.1, 151.8; HRMS: m/z calcd. for C$_{22}$H$_{14}$N$_4$O$_2$ 366.1117 found 366.1115.

4-(2-phenylpyrimido[1,2-b]indazol-4-yl)phenol (4k)

Brown solid; Isolated yield - 80 %; mp: 306-308 °C; 1H NMR (400 MHz, CDCl$_3$) δ 9.76 (s, 1H), 8.36-8.33 (m, 3H), 8.15 (s, 1H), 7.89-7.71 (m, 3H), 7.70-7.63 (m, 4H), 7.42-7.32 (m, 2H), 6.99-6.96 (m, 1H); 13C NMR (100 MHz, CDCl$_3$) δ 108.9, 113.0, 113.7, 116.2, 117.5, 118.2, 120.6, 120.7, 128.4, 129.8, 129.9, 130.0, 130.9, 131.2, 137.9, 144.0, 144.7, 150.6, 152.1, 157.9; HRMS: m/z calcd. for C$_{22}$H$_{13}$N$_3$O 337.1215 found 337.1214.

4-(4-isopropylphenyl)-2-phenylpyrimido[1,2-b]indazole (4l)

Yellow solid; Isolated yield - 87 %; mp: 156-158 °C; 1H NMR (400 MHz, CDCl$_3$) δ 8.42 (d, J = 8.4 Hz, 1H), 8.22-8.19 (m, 4H), 7.84 (d, J = 8.8 Hz, 1H), 7.72 (s, 1H), 7.66-7.59 (m, 4H), 7.43-7.41 (m, 2H), 7.31-7.28 (m, 1H), 3.05-2.98 (m 1H), 1.32 (d, J = 7.2 Hz, 6H); 13C NMR (100 MHz, CDCl$_3$) δ 23.8, 34.1, 108.5, 113.8, 116.5, 120.5, 121.2, 127.2, 128.8, 129.5, 129.8, 130.9, 131.9, 135.0, 131.9, 135.0, 145.0, 151.3, 151.5, 152.8; HRMS: m/z calcd. for C$_{25}$H$_{21}$N$_3$ 363.1735 found 363.1734.
2-phenyl-4-(p-tolyl)pyrimido[1,2-b]indazole (4m)  
[Chemical structure image]  
Yellow solid; Isolated yield - 90 %; mp: 202-204 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.43-8.40 (m, 1H), 8.22-8.17 (m, 4H), 7.84 (d, J = 8.8 Hz, 1H), 7.72 (s, 1H), 7.64-7.58 (m, 4H), 7.36 (d, J = 8.0 Hz, 2H), 7.31-7.28 (m, 1H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 21.4, 108.4, 113.8, 116.5, 120.5, 121.2, 127.1, 128.8, 129.5, 129.8, 130.9, 131.9, 134.6, 140.4, 145.0, 145.2, 151.6, 152.7; HRMS: m/z calcd. for C₂₃H₁₇N₃ 335.1422 found 335.1420.

4-(naphthalen-1-yl)-2-phenylpyrimido[1,2-b]indazole (4n)  
[Chemical structure image]  
Brown solid; Isolated yield - 81 %; mp: 180-182 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.44-8.37 (m, 2H), 8.27-8.25 (m, 2H), 8.01-7.85 (m, 4H), 7.66-7.53 (m, 8H), 7.32 (t, J = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 113.1, 113.8, 116.6, 120.8, 121.2, 125.3, 126.2, 127.1, 128.2, 128.6, 128.8, 129.5, 129.9, 130.0, 130.9, 131.1, 131.5, 134.1, 136.4, 144.9, 151.6, 154.7; HRMS: m/z calcd. for C₂₆H₁₇N₃ 371.1422 found 371.1420.

4-(2-nitrophenyl)-2-phenylpyrimido[1,2-b]indazole (4o)  
[Chemical structure image]  
Brown solid; Isolated yield - 77 %; mp: 200-202 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, J = 7.6 Hz, 1H), 8.22-8.19 (m, 2H), 8.04-8.01 (m, 1H), 7.89-7.85 (m, 2H), 7.76-7.75 (m, 1H), 7.66-7.61 (m, 5H), 7.41 (s, 1H), 7.33-7.32 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 110.6, 113.9, 116.7, 121.1, 121.3, 124.8, 128.9, 129.5, 130.1, 131.0, 131.2, 131.3, 131.5, 132.8, 133.6, 144.6, 145.3, 149.0, 150.4, 151.6; HRMS: m/z calcd. for C₂₂H₁₄N₄O₂ 366.1117 found 366.1115.

4-(2-chlorophenyl)-2-phenylpyrimido[1,2-b]indazole (4p)  
[Chemical structure image]  
Yellow solid; Isolated yield - 70 %; mp: 198-200 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, J = 8.4 Hz, 1H), 8.26-8.24 (m, 2H), 7.91-7.88 (m, 2H), 7.76 (s, 1H), 7.66-7.43 (m, 7H), 7.34-7.32 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 112.8, 113.9, 116.6, 120.9, 121.0, 127.4, 128.8, 129.5, 129.8, 130.4, 130.5, 131.1, 131.5, 131.8, 132.4, 137.5, 144.2, 144.9, 151.4, 152.2; HRMS: m/z calcd. for C₂₂H₁₄N₃Cl 355.0876 found 355.0875.
(4-phenylpyrimido[1,2-b]indazol-2-yl)methanol (4q)

Brown solid; Isolated yield - 76 %; mp: 206-208 °C; 1H NMR (400 MHz, CDCl₃) δ 8.41 (d, J = 8.4 Hz, 1H), 8.24 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.8 Hz, 1H), 7.73 (s, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.58-7.49 (m, 3H), 7.32 (t, J = 8.0 Hz, 1H), 5.33 (s, 2H), 4.28 (bs, 1H); 13C NMR (100 MHz, CDCl₃) δ 61.1, 106.0, 113.8, 116.0, 120.9, 121.3, 127.3, 129.1, 130.2, 130.3, 137.1, 144.9, 151.5, 153.2; HRMS: m/z calcd. for C₁₇H₁₃N₃O 275.1059 found 275.1059.

2-(4-bromophenyl)-4-phenylpyrimido[1,2-b]indazole (4s)

Yellow solid; Isolated yield - 76 %; mp: 168-170 °C; 1H NMR (400 MHz, CDCl₃) δ 8.43 (d, J = 8.0 Hz, 1H), 8.29-8.27 (m, 2H), 8.23-8.31 (m, 2H), 7.86 (d, J = 8.4 Hz, 1H), 7.74 (s, 1H), 7.65-7.51 (m, 6H), 7.31 (t, J = 7.6 Hz, 1H); 13C NMR (100 MHz, CDCl₃) δ 108.6, 113.9, 116.6, 120.7, 121.2, 127.2, 128.5, 129.0, 129.5, 129.8, 130.1, 131.0, 131.8, 137.3, 145.0, 145.3, 151.6, 152.6; HRMS: m/z calcd. for C₂₂H₁₄BrN₃ 399.0371 found 399.0370.

4-(4-phenylpyrimido[1,2-b]indazol-2-yl)benzonitrile (4t)

Yellow solid; Isolated yield - 76 %; mp: 232-234 °C; 1H NMR (400 MHz, CDCl₃) δ 8.46 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 8.0 Hz, 2H), 8.30 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.8 Hz, 1H), 7.79 (s, 1H), 7.67-7.56 (m, 7H); 13C NMR (100 MHz, CDCl₃) δ 108.8, 114.0, 114.5, 116.5, 118.1, 121.2, 127.1, 129.1, 130.2, 130.3, 130.4, 132.5, 136.0, 136.9, 142.9, 145.0, 151.6, 152.5; HRMS: m/z calcd. for C₂₃H₁₄N₄ 346.1218 found 346.1218.

5,7-diphenyl-[1,2,4]triazolo[1,5-a]pyrimidine (4u)

Off-White solid; Isolated yield - 65 %; mp: 160-161 °C; 1H NMR (400 MHz, CDCl₃) δ 8.54 (s, 1H), 8.27 (s, 2H), 8.14 (d, J = 5.2 Hz, 2H), 7.67-7.56 (m, 7H); 13C NMR (100 MHz, CDCl₃) δ 106.6, 127.8, 128.3, 128.5, 129.0, 129.1, 129.3, 130.2, 131.3, 131.8, 133.1, 136.4, 148.1, 156.3, 161.7; HRMS: m/z calcd. for C₁₇H₁₂N₄ 272.1062 found 272.1060.
5,7-diphenylpyrazolo[1,5-a]pyrimidine (4v)

Brown solid; Isolated yield - 60 %; mp: 84-85 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.17-8.06 (m, 5H), 7.58-7.46 (m, 6H), 7.35 (s, 1H), 6.80 (s, 1H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 97.2, 105.2, 127.3, 128.3, 128.5, 128.7, 128.9, 129.7, 130.3, 130.9, 131.5, 137.5, 145.2, 146.8, 149.9, 156.2; HRMS: m/z calcd. for C\(_{18}\)H\(_{13}\)N\(_3\) 271.1109 found 272.1109.

2,4-diphenylbenzo[4,5]imidazo[1,2-a]pyrimidine (4w)

Off-White solid; Isolated yield - 35 %; mp: 276-277 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.25-8.23 (m, 2H), 7.90 (d, \(J = 8.0\) Hz, 1H), 7.64-7.60 (m, 4H), 7.59-7.46 (m, 4H), 7.38-7.37 (m, 2H), 7.20-7.19 (m, 1H), 6.96-6.60 (m, 1H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 104.2, 113.4, 119.2, 120.1, 124.9, 126.8, 127.3, 127.9, 128.4, 130.0, 130.2, 131.5, 135.6, 144.5, 148.3, 160.1; HRMS: m/z calcd. for C\(_{22}\)H\(_{15}\)N\(_3\) 321.1266 found 321.1265.

Copies of \(^1\)H NMR, \(^1^3\)C NMR and HRMS of 4(a-t):

\(^1\)H NMR spectrum of compound (4a):
Expanded $^1$H NMR spectrum of compound (4a):

$^{13}$C NMR spectrum of compound (4a):
DEPT – 135 spectrum of compound (4a):

HRMS spectrum of compound (4a):
$^1$H NMR spectrum of compound (4b):

Expanded $^1$H NMR spectrum of compound (4b):
$^{13}$C NMR spectrum of compound (4b):

HRMS spectrum of compound (4b):
$^1$H NMR spectrum of compound (4c):

Expanded $^1$H NMR spectrum of compound (4c):
$^{13}$C NMR spectrum of compound (4c):

HRMS spectrum of compound (4c):
$^1$H NMR spectrum of compound (4d):

Expanded $^1$H NMR spectrum of compound (4d):
$^{13}$C NMR spectrum of compound (4d):

HRMS spectrum of compound (4d):
$^1$H NMR spectrum of compound (4e):

Expanded $^1$H NMR spectrum of compound (4e):
$^{13}$C NMR spectrum of compound (4e):

HRMS spectrum of compound (4e):
\(^1\)H NMR spectrum of compound (4f):

Expanded \(^1\)H NMR spectrum of compound (4f):
$^{13}$C NMR spectrum of compound (4f):

HRMS spectrum of compound (4f):
$^1$H NMR spectrum of compound (4g):

Expanded $^1$H NMR spectrum of compound (4g):
$^{13}$C NMR spectrum of compound (4g):

HRMS spectrum of compound (4g):
$^1$H NMR spectrum of compound (4h):

Expanded $^1$H NMR spectrum of compound (4h):
$^{13}$C NMR spectrum of compound (4h):

HRMS spectrum of compound (4h):
$^1$H NMR spectrum of compound (4i):
Expanded $^1$H NMR spectrum of compound (4i):

$^{13}$C NMR spectrum of compound (4i):
HRMS spectrum of compound (4i):

\[ \text{\textsuperscript{1}H NMR spectrum of compound (4j):} \]
Expanded $^1$H NMR spectrum of compound (4j):

$^{13}$C NMR spectrum of compound (4j):
HRMS spectrum of compound (4j):

\[ \text{HRMS spectrum of compound (4j)} \]

\[ \text{HRMS spectrum of compound (4k)} \]

\[ \text{HRMS spectrum of compound (4k)} \]
Expanded $^1$H NMR spectrum of compound (4k):

$^{13}$C NMR spectrum of compound (4k):
HRMS spectrum of compound (4k):

\[ \text{OH} \]

4k

\[ \begin{array}{c}
160.0100 \\
168.1600 \\
203.2007 \\
213.2003 \\
219.1912 \\
226.1624 \\
252.1574 \\
308.2724 \\
320.3004
\end{array} \]

\( \text{m/z} \)

1H NMR spectrum of compound (4l):
$^{13}$C NMR spectrum of compound (4l):

HRMS spectrum of compound (4l):
$^1$H NMR spectrum of compound (4m):

Expanded $^1$H NMR spectrum of compound (4m):
$^{13}$C NMR spectrum of compound (4m):

HRMS spectrum of compound (4m):
$^1$H NMR spectrum of compound (4n):

Expanded $^1$H NMR spectrum of compound (4n):
$^{13}$C NMR spectrum of compound (4n):

HRMS spectrum of compound (4n):
\(^1\)H NMR spectrum of compound (4o):

Expanded \(^1\)H NMR spectrum of compound (4o):
$^{13}$C NMR spectrum of compound (4o):

HRMS spectrum of compound (4o):
$^1$H NMR spectrum of compound (4p):

Expanded $^1$H NMR spectrum of compound (4p):
\(^{13}\)C NMR spectrum of compound (4p):

HRMS spectrum of compound (4p):
\(^1\)H NMR spectrum of compound (4q):

Expanded \(^1\)H NMR spectrum of compound (4q):
$^{13}$C NMR spectrum of compound (4q):

HRMS spectrum of compound (4q):
$^1$H NMR spectrum of compound (4s):

Expanded $^1$H NMR spectrum of compound (4s):
$^{13}$C NMR spectrum of compound (4s):

HRMS spectrum of compound (4s):
$^1$H NMR spectrum of compound (4t):

Expanded $^1$H NMR spectrum of compound (4t):
$^{13}$C NMR spectrum of compound (4t):

HRMS spectrum of compound (4t):
$^1$H NMR spectrum of compound (4u):

Expanded $^1$H NMR spectrum of compound (4u):
$^{13}$C NMR spectrum of compound (4u):

HRMS spectrum of compound (4u):
$^1$H NMR spectrum of compound (4v):

Expanded $^1$H NMR spectrum of compound (4v):
$^{13}$C NMR spectrum of compound (4v):

HRMS spectrum of compound (4v):
$^1$H NMR spectrum of compound (4w):

$^{13}$C NMR spectrum of compound (4w):
HRMS spectrum of compound (4w):