Microwave-promoted Synthesis of 4-Arylpyrimidines by Pd-Catalyzed Suzuki-Miyaura Coupling of 4-Pyrimidyl Tosylates in Water

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Experimental details

NMR spectra were recorded with a Bruker Avance 400-MHz equipment. IR spectra were measured with a Spectrum Two FT-IR (ATR) Perkin Elmer spectrometer. HRMS analyses were carried out with Varian Ionspec QFT-7 (ESI-FT ICRMS) and Agilent 6210 ESI-TOF instruments. Microwave-promoted reactions were carried out in an Anton Paar Monowave 300 microwave synthesis reactor. Ultrasound-promoted reactions were carried out in a Branson sonicator cup horn working at 19.7–20.0 kHz (75 W). Melting points were recorded with a Microthermal melting-point apparatus. All the reagents were purchased from AK Scientific and were used without further purification. Thin-layer chromatographic (TLC) analyses were performed on TLC plates purchased from Merck (silica gel 60, fluorescence indicator F254, 0.25 mm layer thickness). Products were purified by column chromatography on silica gel 60 (0.063–0.200 mm) acquired from Merck.

The starting 4-pyrimidyl tosylates employed in the present work were prepared according to literature.¹

Reference


¹H NMR of known compounds Suzuki-Miyaura products

6-Methyl-2,4-diphenylpyrimidine (3a)²
Colorless solid; yield: 140 mg (97%); mp 82–84 °C (lit.¹ mp 86–87 °C).

¹H NMR (CDCl₃, 400 MHz): δ = 8.59 (d, J = 7.5 Hz, 2H, Ph), 8.29 – 8.18 (m, 2H, Ph), 7.58 – 7.44 (m, 7H, Ph and H-5), 2.66 (s, 3H, CH₃).

Reference

Characterization of new substituted pyrimidines

General procedure for the Suzuki-Miyaura cross-coupling reactions

A 10-mL microwave vial was charged with the 4-pyrimidyl tosylate 1 (0.588 mmol), the aryl boronic acid 2 (0.705 mmol), tetrakis(triphenylphosphine)palladium (0.029 mmol), powdered potassium carbonate (0.588 mmol) and water (5 mL). The resulting reaction mixture was irradiated for 1 h at 100 °C. The reaction mixture was then extracted three times with dichloromethane (ca. 15 mL each). The combined organic phases were dried with anhydrous sodium sulfate and filtered. The filtrate was rotary evaporated and the obtained crude product was purified by column chromatography (silica gel, n-hexane:EtOAc).

Ethyl 4-(6-methyl-2-phenylpyrimidin-4-yl)benzoate (3c)

Colorless solid; yield: 131 mg (70%); mp 123–125 °C; Rf = 0.61 (n-Hexane/EtOAc, 5:1).

IR (ATR): 3072, 2982, 1714, 1570, 1531 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ = 8.61 – 8.55 (m, 2H, Ph), 8.28 (d, J = 8.4 Hz, 2H, ArH), 8.19 (d, J = 8.4 Hz, 2H, ArH), 7.56 – 7.48 (m, 4H, Ph + H5), 4.43 (q, J = 7.1 Hz, 2H, OCH₂), 2.68 (s, 3H, CH₃), 1.44 (t, J = 7.1 Hz, 3H, CH₂CH₃).

¹³C NMR (CDCl₃, 101 MHz): δ = 168.6, 166.6, 164.9, 163.0, 141.7, 138.3, 132.6, 131.1, 130.4, 128.9, 128.8, 127.5, 114.9, 61.7, 25.1, 14.8.


4-(4-Fluorophenyl)-6-methyl-2-phenylpyrimidine (3d)

Colorless solid; yield: 118 mg (76%); mp 95–97 °C; Rf = 0.35 (n-Hexane/EtOAc, 10:1).

IR (ATR): 3068, 2924, 1588, 1534 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ = 8.65 – 8.56 (m, 2H, ArH), 8.26 – 8.12 (m, 2H, ArH), 7.60 – 7.48 (m, 3H, ArH), 7.35 (s, 1H, H-5), 7.28 – 7.03(m, 2H, ArH), 2.62 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 101 MHz): δ = 167.9 (s), 164.5 (d, J = 250 MHz), 164.3 (s), 162.5 (s), 138.0 (s), 133.4 (d, J = 3 Hz), 130.6 (s), 129.2 (d, J = 9 Hz), 128.5 (s), 128.3 (s), 115.9 (d, J = 22 Hz), 113.6 (s), 24.6 (s).

¹⁹F NMR (CDCl₃, 376 MHz): δ = -110.06 (s, Ar-F).

4-(4-Methylsulfonylphenyl)-6-methyl-2-phenylpyrimidine (3e)

Colorless solid; yield: 99 mg (52%); mp 119–120 °C; Rf = 0.41 (n-Hexane/EtOAc, 5:1).

IR (ATR): 3068, 2924, 1592, 1550, 1375, 1194 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ = 8.25 – 8.16 (m, 2H, Ph), 8.00 (d, J = 8.2 Hz, 2H, ArH), 7.50 – 7.40 (m, 3H, Ph), 7.38 (d, J = 8.2 Hz, 2H, ArH), 6.82 (s, 1H, H-5), 2.58 (s, 3H, SCH₃), 2.46 (s, 3H, OCH₃).

¹³C NMR (CDCl₃, 101 MHz): δ = 168.0, 164.5, 163.4, 150.3, 148.8, 138.5, 131.9, 130.9, 128.9, 128.7, 122.1, 113.6, 108.9, 107.8, 102.0, 25.0.

HRMS (ESI-TOF): m/z [M + H⁺] calcd for C₁₈H₁₇N₂O₂S: 325.1006; found: 325.1101.

4-(4-Methoxyphenyl)-6-methyl-2-phenylpyrimidine (3f)

Colorless solid; yield: 138 mg (85%); mp 101–103 °C; Rf = 0.45 (n-Hexane/EtOAc, 5:1).

IR (ATR): 3068, 2960, 1572, 1531, 1254, 1173 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ = 8.64 – 8.54 (m, 2H, Ph), 8.20 (d, J = 8.9 Hz, 2H, ArH), 7.58 – 7.45 (m, 3H, Ph), 7.40 (s, 1H, H-5), 7.03 (d, J = 8.9 Hz, 2H, ArH), 3.89 (s, 3H, OCH₃), 2.63 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 101 MHz): δ = 167.8, 164.6, 163.6, 162.2, 138.7, 130.8, 130.1, 129.1, 128.8, 128.7, 114.6, 113.5, 55.8, 25.0.


6-Methyl-4-(4-phenoxyphenyl)-2-phenylpyrimidine (3g)

Colorless solid; yield: 163 mg (82%); mp 85–87 °C; Rf = 0.63 (n-Hexane/EtOAc, 5:1).

IR (ATR): 3072, 2972, 1575, 1537, 1251, 1168 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ = 8.64 – 8.55 (m, 2H, Ph), 8.21 (d, J = 8.7 Hz, 2H, ArH), 7.55 – 7.47 (m, 3H, Ph and ArH), 7.45 – 7.36 (m, 3H, Ph), 7.23 – 7.15 (m, 1H, Ph), 7.15 – 7.06 (4H, Ph), 2.65 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 101 MHz): δ = 168.1, 164.7, 163.4, 160.3, 156.8, 138.5, 132.3, 130.9, 130.4, 129.3, 128.9, 128.7, 124.4, 120.0, 118.9, 113.8, 25.0.

6-Methyl-4-(4-methylthiophenyl)-2-phenylpyrimidine (3h)

Colorless solid; yield: 132 mg (77%); mp 123–125 °C; R_f = 0.48 (n-Hexane/EtOAc, 5:1).

IR (ATR): 3066, 2918, 1573, 1525 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ = 8.65 – 8.53 (m, 2H, Ph), 8.15 (d, J = 8.4 Hz, 2H, ArH), 7.56 – 7.47 (m, 3H, Ph), 7.41 (s, 1H, H-5), 7.36 (d, J = 8.4 Hz, 2H, ArH), 2.63 (s, 1H, SCH₃), 2.55 (s, 1H, CH₃).

¹³C NMR (CDCl₃, 101 MHz): δ = 168.1, 164.7, 163.4, 142.7, 138.5, 134.0, 130.9, 128.9, 128.8, 127.9, 126.4, 113.8, 25.0, 15.6.

HRMS (ESI-TOF): m/z [M + H⁺] calcd for C₁₈H₁₇N₂S: 293.1107; found: 293.1109.

6-Methyl-4-(4-methylphenyl)-2-phenylpyrimidine (3i)

Colorless solid; yield: 130 mg (85%); mp 110–112 °C; R_f = 0.80 (n-Hexane/EtOAc, 5:1).

IR (ATR): 3068, 2922, 1572, 1531 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ = 8.63 – 8.54 (m, 2H, Ph), 8.12 (d, J = 8.1 Hz, 2H, ArH), 7.57 – 7.43 (m, 3H, Ph and H-5), 7.33 (d, J = 8.0 Hz, 2H, ArH), 2.64 (s, 3H, PyCH₃), 2.44 (s, 3H, ArCH₃).

¹³C NMR (CDCl₃, 101 MHz): δ = 168.0, 164.7, 164.1, 141.4, 138.6, 134.8, 130.8, 130.0, 128.8, 128.7, 127.5, 114.0, 25.0, 21.9.


6-Methyl-4-(3,4-methylenedioxyphenyl)-2-phenylpyrimidine (3j)

Colorless solid; yield: 152 mg (89%); mp 122–125 °C; R_f = 0.35 (n-Hexane/EtOAc, 5:1).

IR (ATR): 3072, 2891, 1571, 1531, 1241, 1038 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ = 8.63 – 8.48 (m, 2H, Ph), 7.77 (s, 1H, ArH), 7.73 (d, J = 8.1 Hz, 1H, ArH), 7.60 – 7.43 (m, 3H, Ph), 7.34 (s, 1H, H-5), 6.93 (d, J = 8.1 Hz, 1H, ArH), 6.04 (s, 2H, OCH₂O), 2.61 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 101 MHz): δ = 168.0, 164.5, 163.4, 150.3, 148.8, 138.5, 131.9, 130.9, 128.9, 128.7, 122.1, 113.6, 108.9, 107.8, 102.0, 25.0.

4-Methyl-2-phenyl-6-(thiophen-2-yl)pyrimidine (3k)

Colorless oil; yield: 125 mg (84%); $R_f = 0.60$ (n-Hexane/EtOAc, 5:1).

IR (ATR): 3010, 2960, 2920, 1570, 1530, 1400, 1370 cm$^{-1}$.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.60 - 8.48$ (m, 2H, Ph), 7.81 (dd, $J = 3.7, 1.2$ Hz, 1H, Th-H3), 7.56 - 7.47 (m, 4H, Ph and Th-H5), 7.31 (s, 1H, Py-H5), 7.17 (dd, $J = 5.0, 3.7$ Hz, 1H, Th-H4), 2.62 (s, 3H, CH$_3$).

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta =$ 162.7, 159.4, 153.8, 138.2, 132.8, 125.7, 124.7, 123.5, 123.4, 123.3, 122.0, 107.2, 19.6.

HRMS (ESI-TOF): $m/z$ [M + H$^+$] calcd for C$_{15}$H$_{13}$N$_2$S (M+H$^+$): 253.0794; found: 253.0795.

2,5-Bis(6-methyl-2-phenylpyrimidin-4-yl)thiophene (3l)

A 10-mL microwave vial was charged with the 4-pyrimidyl tosylate 1 (200 mg, 0.588 mmol), the 2,5-thiophenediybisboronic acid (61 mg, 0.355 mmol), tetrakis(triphenylphosphine)palladium (68 mg, 0.058 mmol), powdered potassium carbonate (163 mg, 1.176 mmol) and water (5 mL). The resulting reaction mixture was irradiated for 1 h at 100 °C. The reaction mixture was then extracted three times with dichloromethane ($ca$. 15 mL each). The combined organic phases were dried with anhydrous sodium sulfate and filtered. The filtrate was rotary evaporated and the obtained crude product was purified by column chromatography (silica gel, n-hexane:EtOAc, 20:1 $\rightarrow$ 2:1).

Colorless oil; yield: 166 mg (67%); $R_f = 0.57$ (n-Hexane/EtOAc, 5:1).

IR (ATR): 3030, 2960, 2925, 2870, 1610, 1570, 1530, 1400, 1380 cm$^{-1}$.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.57 - 8.50$ (m, 4H, Ph), 7.55 - 7.47 (m, 8H, Ph and Th), 7.32 (s, 2H, Py-H5), 2.62 (s, 6H, CH$_3$).

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta =$ 162.7, 159.4, 153.8, 138.3, 132.8, 125.6, 124.7, 123.4, 122.0, 107.2, 19.6.

HRMS (ESI-TOF): $m/z$ [M + H$^+$] calcd for C$_{18}$H$_{15}$N$_2$O$_2$ (M+H$^+$): 421.1482; found: 421.1487.

4-Methyl-2-phenyl-6-(pyridin-4-yl)pyrimidine (3m)

Colorless solid; yield: 101 mg (69%); mp 83–85 °C; $R_f = 0.27$ (n-Hexane/EtOAc, 5:1).

IR (ATR): 3320, 3080, 2970, 2780, 1735, 1675, 1590, 1435, 750 cm$^{-1}$.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.85 - 8.78$ (m, 2H, Py), 8.61 – 8.54 (m, 2H, Ph), 8.11 - 8.04 (m, 2H, Py), 7.56 - 7.49 (m, 4H, Ph and H-5), 2.70 (s, 3H, CH$_3$).

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta =$ 169.1, 165.1, 151.1, 138.0, 131.2, 129.0, 128.8, 127.7, 121.5, 114.8, 110.0, 25.1.

4,5-Dimethyl-2-phenyl-6-(p-tolyl)pyrimidine (3n)
Colorless solid; yield: 126 mg (75%); mp 81–82 °C; Rf = 0.68 (n-Hexane/EtOAc, 5:1).
IR (ATR): 3070, 2965, 2940, 2870, 1590, 1570, 1530, 1460, 1375 cm⁻¹.
¹H NMR (CDCl₃, 400 MHz): δ = 8.55 – 8.46 (m, 2H, Ph), 7.56 (d, J = 7.9 Hz, 2H, Ar), 7.51 – 7.41 (m, 3H, Ph), 7.31 (d, J = 7.9 Hz, 2H, Ar), 2.64, 2.45, 2.34 (4s, 3H each, 4×CH₃).
¹³C NMR (CDCl₃, 101 MHz): δ = 167.1, 165.2, 161.5, 139.2, 138.6, 136.6, 130.4, 129.7, 129.3, 128.7, 128.4, 124.3, 23.6, 21.8, 16.0.

2-Cyclopropyl-4-methyl-6-(p-tolyl)pyrimidine (3o)
Colorless oil; yield: 113 mg (86%); Rf = 0.43 (n-Hexane/EtOAc, 5:1).
IR (ATR): 3060, 2960, 2920, 2860, 1590, 1570, 1470, 1375, 820 cm⁻¹.
¹H NMR (CDCl₃, 400 MHz): δ = 7.96 (d, J = 8.2 Hz, 2H, Ar), 7.34 – 7.23 (m, 3H, Ar and H-5), 2.51, 2.41 (2s, 3H each, 2×CH₃), 2.32 – 2.23 (m, 1H, CH), 1.28 – 1.20, 1.09 – 1.01 (2m, 2H each, 2×CH₂).
¹³C NMR (CDCl₃, 101 MHz): δ = 172.0, 167.1, 163.9, 141.2, 134.8, 130.4, 115.8, 24.6, 21.8, 18.5, 10.8.

4-Isopropyl-2-phenyl-6-(p-tolyl)pyrimidine (3p)
Colorless solid; yield: 131 mg (77%); mp 55–57 °C; Rf = 0.71 (n-Hexane/EtOAc, 5:1).
IR (ATR): 2955, 2915, 2850, 1590, 1510, 1395, 910 cm⁻¹.
¹H NMR (CDCl₃, 400 MHz): δ = 8.67 – 8.58 (m, 2H, Ph), 8.13 (d, J = 8.0 Hz, 2H, Ar), 7.55 – 7.46 (m, 3H, Ph), 7.45 (s, 1H, H-5), 7.34 (d, J = 8.0 Hz, 2H, Ar), 3.13 (p, J = 6.9 Hz, 1H, CH), 2.45 (s, 3H, CH₃), 1.42 (d, J = 6.9 Hz, 6H, CH-CH₃).
¹³C NMR (CDCl₃, 101 MHz): δ = 176.5, 164.4, 164.3, 141.2, 138.9, 135.3, 130.7, 129.9, 128.8, 127.5, 111.6, 36.7, 22.3, 21.9.
2-Ethyl-4,5-dimethyl-6-(p-tolyl)pyrimidine  (3q)

Colorless oil; yield: 91 mg (68%); \( R_f = 0.29 \) (n-Hexane/EtOAc, 5:1).

IR (ATR): 2990, 2940, 2880, 1640, 1510, 1430, 1410 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.42 \) (d, \( J = 7.9 \) Hz, 2H, Ar), 7.26 (d, \( J = 7.9 \) Hz, 2H, Ar), 2.93 (q, \( J = 7.6 \) Hz, 2H, CH\(_2\)), 2.53, 2.40, 2.24 (3s, 3H each, 3×CH\(_3\)), 1.36 (t, \( J = 7.6 \) Hz, 3H, CH\(_2\)-CH\(_3\)).

\(^{13}\)C NMR (CDCl\(_3\), 101 MHz): \( \delta = 168.9, 166.7, 165.3, 139.1, 136.5, 129.3, 129.3, 123.3, 32.9, 23.3, 21.7, 15.7, 13.7.

HRMS (ESI-TOF): \( m/z \) [M + H\(^+\)] calcd for C\(_{15}\)H\(_{19}\)N\(_2\) (M + H\(^+\)): 227.3305; found: 227.3308.

2,4-Dimethyl-6-(p-tolyl)pyrimidine  (3r)

Colorless oil; yield: 86 mg (74%); \( R_f = 0.18 \) (n-Hexane/EtOAc, 5:1).

IR (ATR): 3040, 2960, 2920, 2870, 1605, 1530, 1400, 1375, 820 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.96 \) (d, \( J = 8.0 \) Hz, 2H, Ar), 7.35 (s, 1H, H-5), 7.29 (d, \( J = 8.0 \) Hz, 2H, Ar), 2.75, 2.54, 2.42 (3 s, 3H each, 3×CH\(_3\)).

\(^{13}\)C NMR (CDCl\(_3\), 101 MHz): \( \delta = 168.3, 167.5, 164.3, 141.3, 134.8, 130.0, 127.5, 113.4, 26.7, 24.7, 21.8.

HRMS (ESI-TOF): \( m/z \) [M + H\(^+\)] calcd for C\(_{13}\)H\(_{15}\)N\(_2\) (M + H\(^+\)): 199.1230; found: 199.1233.

4-Cyclopropyl-2-phenyl-6-(p-tolyl)pyrimidine  (3s)

Colorless solid; yield: 123 mg (73%); mp 77–80 °C; \( R_f = 0.62 \) (n-Hexane/EtOAc, 5:1).

IR (ATR): 3090, 3065, 3005, 1630, 1590, 1560, 1525, 1440, 930 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 8.61 – 8.55 \) (m, 2H), 8.13 (d, \( J = 8.0 \) Hz, 2H), 7.52 – 7.46 (m, 3H), 7.45 (s, 1H), 7.33 (d, \( J = 8.0 \) Hz, 2H), 2.45 (s, 3H), 2.15 – 2.03 (m, 1H), 1.38 – 1.33 (m, 2H), 1.15 – 1.08 (m, 2H).

\(^{13}\)C NMR (CDCl\(_3\), 101 MHz): \( \delta = 172.4, 164.3, 163.3, 141.1, 138.8, 135.1, 130.7, 129.9, 128.7, 127.5, 112.5, 17.7, 14.5, 11.2.

HRMS (ESI-TOF): \( m/z \) [M + H\(^+\)] calcd for C\(_{20}\)H\(_{19}\)N\(_2\) (M + H\(^+\)): 287.1543; found: 287.1547.
4-Butyl-5,6-dimethyl-2-phenylpyrimidine (3t)
Colorless solid; yield: 81 mg (57%); mp 80–83 °C; \( R_f = 0.40 \) (n-Hexane/EtOAc, 5:1).
IR (ATR): 2995, 2940, 2865, 1740, 1550, 1390, 1195, 745 cm\(^{-1}\).
\(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 8.44 – 8.38 \) (m, 2H, Ph), 7.51 – 7.40 (m, 3H, Ph), 2.81 (t, 2H, Py-CH\(_2\)), 2.54, 2.26 (2 s, 3H each, 2×Py-CH\(_3\)), 1.80 – 1.70 (m, 2H, CH\(_2\)), 1.46 (h, \( J = 7.4 \) Hz, 2H, CH\(_2\)), 0.98 (t, \( J = 7.4 \) Hz, 3H, CH\(_3\)).
\(^{13}\)C NMR (CDCl\(_3\), 101 MHz): \( \delta = 168.2, 165.3, 161.4, 138.9, 130.1, 128.8, 128.3, 124.7, 35.3, 31.4, 30.7, 23.1, 14.4, 14.0.\)
HRMS (ESI-TOF): \( m/z \) [M + H\(^+\)] calcd for C\(_{16}\)H\(_{21}\)N\(_2\) (M + H\(^+\)): 241.1700; found: 241.1705.

4-Hexyl-5,6-dimethyl-2-phenylpyrimidine (3u)
Colorless solid; yield: 67 mg (42%); mp 81–82 °C; \( R_f = 0.37 \) (n-Hexane/EtOAc, 5:1).
IR (ATR): 2930, 2855, 1740, 1550, 1400, 703 cm\(^{-1}\).
\(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 8.49 – 8.37 \) (m, 2H, Ph), 7.49 – 7.39 (m, 3H, Ph), 2.89 – 2.76 (m, 2H, Py-CH\(_2\)), 2.55, 2.26 (2 s, 3H each, 2×Py-CH\(_3\)), 1.84 – 1.71, 1.50 – 1.39 (2 m, 2H each, 2×CH\(_2\)), 1.38 – 1.31 (m, 4H, 2×CH\(_2\)), 0.94 – 0.87 (m, 3H, CH\(_3\)).
\(^{13}\)C NMR (CDCl\(_3\), 101 MHz): \( \delta = 168.3, 165.3, 161.4, 138.9, 130.1, 128.8, 128.3, 124.7, 35.6, 32.2, 29.7, 28.5, 23.3, 23.1, 14.5, 14.0.\)
$^1$H NMR and $^{13}$C NMR spectra of new Suzuki-Miyaura products

$^1$H NMR spectrum (CDCl$_3$) of compound 3b
$^{13}$C NMR spectrum (CDCl$_3$) of compound 3b

$^1$H NMR spectrum (CDCl$_3$) of compound 3c
$^{13}$C NMR spectrum (CDCl$_3$) of compound 3c

$^1$H NMR spectrum (CDCl$_3$) of compound 3d
$^{13}$C NMR spectrum (CDCl$_3$) of compound 3d

$^{19}$F NMR spectrum (CDCl$_3$) of compound 3d
$^1$H NMR spectrum (CDCl$_3$) of compound 3e

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3e
$^1$H NMR spectrum (CDCl$_3$) of compound 3f

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3f
$^1$H NMR spectrum (CDCl$_3$) of compound 3g

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3g
$^1$H NMR spectrum (CDCl$_3$) of compound $3h$

$^{13}$C NMR spectrum (CDCl$_3$) of compound $3h$
$^1$H NMR spectrum (CDCl$_3$) of compound 3i

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3i
$^1$H NMR spectrum (CDCl$_3$) of compound 3j

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3j
$^{1}H$ NMR spectrum (CDCl$_3$) of compound 3k

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3k
$^{1}H$ NMR spectrum (CDCl$_3$) of compound 31

$^{13}C$ NMR spectrum (CDCl$_3$) of compound 31
$^1$H NMR spectrum (CDCl$_3$) of compound 3m

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3m
$^1$H NMR spectrum (CDCl$_3$) of compound \textbf{3n}

$^{13}$C NMR spectrum (CDCl$_3$) of compound \textbf{3n}
$^1$H NMR spectrum (CDCl$_3$) of compound 3o

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3o
$^1$H NMR spectrum (CDCl$_3$) of compound 3p

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3p
$^{1}H$ NMR spectrum (CDCl$_3$) of compound $3q$

$^{13}C$ NMR spectrum (CDCl$_3$) of compound $3q$
\(^1\)H NMR spectrum (CDCl\(_3\)) of compound 3r

\(^{13}\)C NMR spectrum (CDCl\(_3\)) of compound 3r
$^{1}H$ NMR spectrum (CDCl$_3$) of compound 3s

$^{13}C$ NMR spectrum (CDCl$_3$) of compound 3s
$^{1}H$ NMR spectrum (CDCl$_3$) of compound 3t

$^{13}C$ NMR spectrum (CDCl$_3$) of compound 3t
$^1$H NMR spectrum (CDCl$_3$) of compound 3u

$^{13}$C NMR spectrum (CDCl$_3$) of compound 3u