Supporting Information

Regioselective Domino Synthesis of 2-Alkylflavans via Hidden Brønsted Acid Catalysis

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I. Condition optimization of mono-substituted allene

Table S1. Condition optimization of mono-substituted allene 1I.

<table>
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<tr>
<th>Entry</th>
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<th>Temp.</th>
<th>Time</th>
<th>Yield (3)(^a)</th>
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\(^a\) Determined by \(^1\)H NMR spectroscopy. \(^b\) Accompanied with 4Ii (15%) and 5Ii (6%).
II. Experimental procedures

General information:

Unless otherwise specified, all reactions were conducted under a slight positive pressure of dry nitrogen. All solvents were reagent grade and other commercially available reagents were used as received. Flash chromatography was carried out using silica gel (70-230 mesh ASTM).

Reactions were monitored by thin layer chromatography (TLC) using 0.25-mm E. Merck per-coated silica gel plates, and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into vanillin solution (9 g of vanillin and 1.5 mL of concentrated H$_2$SO$_4$ in 300 mL of MeOH), or KMnO$_4$ solution (3 g of KMnO$_4$, 20 g of K$_2$CO$_3$, and 5 mL of 5% NaOH solution on 300 mL of water).

NMR spectra were recorded in CDCl$_3$ using one of several spectrometers ($^1$H frequency, $^{13}$C frequency MHz): JEOL (300 MHz). Residual solvent signals were used for reference (CHCl$_3$ at $\delta$ 7.26 ppm for $^1$H, $\delta$ 77.0 for $^{13}$C NMR). Mass spectra were recorded using electron impact (EI) method.

General procedure for the synthesis of flavan derivatives:

Preparation of the hidden Brønsted acid catalyst was as follows: AgOTf (3 mol %) and t-BuCl (12 mol %) were stirred for 10 min at room temperature and any volatiles were removed under reduced pressure. The resulting concentrated mixture was diluted in DCE (0.5 M) and treated with allene 1 (1.5 mmol) and phenol 2 (1.0 mmol) at room temperature. The reaction mixture was monitored by TLC analysis, and quenched by addition of a saturated aqueous NH$_4$Cl solution (3 mL). The organic layer was separated, extracted with DCM (3 x 3 mL), dried over MgSO$_4$, and concentrated. Silica gel column chromatography provided flavan 3, and products were fully characterized by $^1$H and $^{13}$C NMR spectroscopy and HRMS analysis.

6-Methoxy-2-methyl-2-phenylchroman 3aa

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.37-7.15 (m, 5H), 6.90 (d, 1H, $J = 8.8$ Hz), 6.70 (dd, 1H, $J = 9.0, 3.1$ Hz), 6.48 (d, 1H, $J = 3.1$ Hz), 3.69 (s, 3H), 2.61 (dt, 1H, $J = 15.9, 4.3$ Hz),
2.47-2.31 (m, 2H), 2.10-1.99 (m, 1H), 1.61 (s, 3H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 153.1, 148.2, 145.7, 128.4, 126.7, 125.0, 122.1, 117.5, 113.8, 113.5, 78.0, 55.5 32.7, 30.1, 22.9 ppm; HRMS (EI): calcd for C\(_{17}\)H\(_{18}\)O\(_2\) (M\(^+\)) 254.1307, found 254.1304.

6-(Benzyloxy)-2-methyl-2-phenylchroman 3ab

According to the general procedure, a yellow solid was obtained after column chromatography on silica gel (hexane/EtOAc 80:1); mp. 122~123 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.42-7.17 (m, 10H), 6.90 (d, 1H, \(J = 8.8\) Hz), 6.78 (dd, 1H, \(J = 8.8, 2.9\) Hz), 6.58 (d, 1H, \(J = 2.9\) Hz), 4.95 (s, 2H), 2.62 (dt, 1H, \(J = 17.2, 5.3\) Hz), 2.49-2.33 (m, 2H), 2.16-2.01 (m, 1H), 1.62 (s, 3H) ppm.; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 152.6, 148.6, 145.9, 137.7, 128.7, 128.5, 128.0, 127.7, 126.9, 125.2, 122.4, 117.6, 115.2, 114.6, 78.2, 70.7, 32.9, 30.3, 23.0 ppm.; HRMS (EI): calcd for C\(_{23}\)H\(_{22}\)O\(_2\) (M\(^+\)) 330.1620, found 330.1621.

2,6-Dimethyl-2-phenylchroman 3ac

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.38-7.15 (m, 5H), 6.93 (d, 1H, \(J = 8.4\) Hz), 6.87 (d, 1H, \(J = 8.1\) Hz), 6.75 (s, 1H), 2.59 (dt, 1H, \(J = 16.7, 5.0\) Hz), 2.45-2.31 (m, 2H), 2.21 (s, 3H), 2.04 (ddd, 1H, \(J = 15.2, 9.9, 4.0\) Hz), 1.62 (s, 3H) ppm.; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 152.0, 145.9, 129.9, 129.5, 128.5, 128.2, 126.8, 125.1, 121.4, 116.8, 78.3, 33.0, 30.3, 22.6, 20.5 ppm.; HRMS (EI): calcd for C\(_{17}\)H\(_{18}\)O (M\(^+\)) 238.1358, found 254.1355.

6-(Tert-butyl)-2-methyl-2-phenylchroman 3ad

According to the general procedure, a yellow solid was obtained after column chromatography on silica gel (hexane/EtOAc 80:1); mp. 68~71 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.10-7.20 (m, 5H), 7.16 (dd, 1H, \(J = 8.4, 2.5\) Hz), 6.94 (d, 1H, \(J = 2.5\) Hz), 6.91 (d, 1H, \(J = 8.4\) Hz), 2.65 (dt, 1H, \(J = 15.9, 4.7\) Hz), 2.50-2.32 (m, 2H), 2.07 (ddd, 1H, \(J = 14.1, 8.8, 4.2\) Hz), 1.63 (s, 3H), 1.26 (s, 9H) ppm.; \(^{13}\)C NMR
(75 MHz, CDCl3) δ 152.0, 146.1, 142.7, 128.5, 126.8, 126.2, 125.2, 124.6, 120.8, 116.4, 78.3, 34.0, 33.2, 31.6, 30.1, 22.9 ppm.; HRMS (EI): calcd for C20H24O (M⁺) 280.1827, found 280.1828.

6-Chloro-2-methyl-2-phenylchroman 3ae

According to the general procedure and DCE(0.1M) was added, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 70:1). ¹H NMR (300 MHz, CDCl3) δ 7.39-7.16 (m, 5H), 7.08 (dd, 1H, J = 8.6, 2.4 Hz), 6.92 (d, 1H, J = 2.2 Hz), 6.90 (d, 1H, J = 8.8 Hz), 2.62 (dt, 1H, J = 17.0, 5.0 Hz), 2.47-2.34 (m, 2H), 2.05 (ddd, 1H, J = 15.2, 9.9, 4.0 Hz), 1.63 (s, 3H) ppm.; ¹³C NMR (75 MHz, CDCl3) δ 153.0, 145.3, 129.1, 128.6, 127.5, 127.1, 125.0, 124.8, 123.4, 118.4, 78.8, 32.5, 30.3, 22.6 ppm.; HRMS (EI): calcd for C16H15ClO (M⁺) 258.0811, found 258.0813.

3-methyl-3-phenyl-2,3-dihydro-1H-benzo[f]chromene 3af

According to the general procedure, a white solid was obtained after column chromatography on silica gel (hexane/EtOAc 80:1); mp. 94-97 °C. ¹H NMR (300 MHz, CDCl3) δ 7.76-7.65 (m, 3H), 7.44-7.38 (m, 5H), 3.04 (dt, 1H, J = 16.2, 4.3 Hz), 2.67-2.52 (m, 2H), 2.23 (ddd, 1H, J = 15.4, 9.7, 4.4 Hz), 1.70 (s, 3H) ppm.; ¹³C NMR (75 MHz, CDCl3) δ 151.5, 145.3, 132.9, 128.8, 128.4, 127.9, 126.8, 126.2, 124.9, 123.1, 122.0, 119.4, 113.5, 78.1, 32.5, 29.9, 19.2 ppm.; HRMS (EI): calcd for C20H18O (M⁺) 274.1358, found 274.1355.

7-Methoxy-2-methyl-2-phenylchroman 3ag

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1) in a 3:1 mixture of 3ag and its regioisomer (5-methoxy-2-methyl-2-phenylchroman). ¹H NMR (300 MHz, CDCl3) δ 7.38-7.21 (m, 5H), 6.84 (d, 1H, J = 8.0 Hz), 6.56 (d, 1H, J = 2.2 Hz), 6.41, (ddd, 1H, J = 8.4, 2.6 Hz), 3.80 (s, 3H), 2.62-2.55 (m, 1H), 2.41-2.30 (m, 2H),
2.10-2.00 (m, 1H), 1.64 (s, 3H) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.4, 155.0, 145.8, 130.0, 128.5, 126.8, 125.1, 113.9, 107.1, 101.7, 78.6, 55.4, 33.2, 30.1, 21.9 ppm.; HRMS (EI): calcd for C$_{17}$H$_{18}$O$_2$ (M$^+$) 254.1307, found 254.1311.

2,5,7,8-Tetramethyl-2-phenylchroman-6-ol 3ah

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.36-7.16 (m, 5H), 4.17 (s, 1H), 2.64-2.56 (m, 1H), 2.43-2.24 (m, 2H), 2.29 (s, 3H), 2.19 (s, 3H), 2.07 (ddd, 1H, $J = 12.5$, 6.6, 3.1 Hz), 2.00 (s, 3H), 1.59 (s, 3H) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 146.3, 145.8, 145.0, 128.5, 126.7, 125.0, 122.4, 121.2, 118.6, 117.7, 76.7, 32.8, 30.2, 21.1, 12.3, 12.0, 11.3 ppm.; HRMS (EI): calcd for C$_{19}$H$_{22}$O$_2$ (M$^+$) 282.1620, found 282.1622.

6-Methoxy-2-methyl-2-(p-tolyl)chroman 3ba

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.25 (d, 2H, $J = 8.0$ Hz), 7.09 (d, 2H, $J = 8.4$ Hz), 6.89 (d, 1H, $J = 9.0$ Hz), 6.70 (dd, 1H, $J = 8.6$, 2.7 Hz), 6.48(d, 1H, $J = 3.1$ Hz), 3.71 (s, 3H), 2.65-2.58 (m, 1H), 2.53-2.31 (m, 2H), 2.30 (s, 3H), 2.04 (ddd, 1H, $J = 14.6$, 9.1, 4.3 Hz), 1.67 (s, 3H) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.2, 148.4, 142.9, 136.4, 129.2, 125.1, 122.3, 117.6, 114.0, 113.7, 78.1, 55.7, 32.8, 30.4, 23.0, 21.0 ppm.; HRMS (EI): calcd for C$_{19}$H$_{20}$O$_2$ (M$^+$) 268.1463, found 268.1461.

6-Methoxy-2-(4-methoxyphenyl)-2-methylchroman 3ca

According to the general procedure, and DCE (0.1 M) was added, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.28 (d, 2H, $J = 8.1$ Hz), 6.89 (d, 1H, $J = 8.8$ Hz), 6.82 (d, 2H, $J = 8.8$ Hz), 6.71 (dd, 1H, $J = 8.1$, 2.9 Hz), 6.49, (d,
1H, J = 2.6 Hz), 3.77 (s, 3H), 3.72 (s, 3H), 2.70-2.53 (m, 1 H), 2.53-2.41 (m, 1 H), 2.41-2.29 (m, 1 H), 2.12-1.97 (m, 1 H), 1.60 (s, 3H) ppm.; ¹³C NMR (75 MHz, CDCl₃) δ 158.5, 153.3, 148.4, 138.0, 126.4, 122.3, 117.6, 114.0, 113.9, 113.7, 77.9, 55.7, 55.3, 32.9, 30.4, 23.0 ppm.; HRMS (EI): calcd for C₁₉H₂₀O₃ (M⁺) 284.1412, found 284.1407.

2-(4-Bromophenyl)-6-methoxy-2-methylchroman 3da

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.38 (m, 2H), 7.26-7.21 (m, 2H), 6.88 (d, 1H, J = 8.8 Hz), 6.71 (dd, 1H, J = 9.1, 2.9 Hz), 6.48 (d, 1H, J = 2.9 Hz), 3.72 (s, 3H), 2.64 (dt, 1H, J = 16.7, 4.6 Hz), 2.47-2.29 (m, 2H). 2.05 (ddd, 1H, J = 14.6, 9.3, 4.0 Hz), 1.59 (s, 3H) ppm.; ¹³C NMR (75 MHz, CDCl₃) δ 153.4, 148.0, 145.0, 131.7, 127.1, 122.1, 120.8, 117.7, 114.0, 113.8, 77.8, 55.7, 32.6, 30.3, 22.9 ppm.; HRMS (EI): calcd for C₁₇H₁₇BrO₂ (M⁺) 332.0412, found 332.0412.

6-Methoxy-2-methyl-2-(naphthalen-2-yl)chroman 3ea

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). ¹H NMR (300 MHz, CDCl₃) δ 7.81-7.75 (m, 4H), 7.50 (dd, J = 2.0, 8.6 Hz, 1H), 7.45-7.41 (m, 2H), 6.97 (d, 1H, J = 8.8 Hz), 6.74 (dd, 1H, J = 8.8, 2.9 Hz), 6.47 (d, 1H, J = 2.4 Hz), 3.70 (s, 3H), 2.66 (dt, 1H, J = 17.0, 5.2 Hz), 2.54-2.42 (m, 2H), 2.14 (ddd, 1H, J = 15.5, 10.0, 4.1 Hz), 1.70 (s, 3H) ppm.; ¹³C NMR (75 MHz, CDCl₃) δ 153.3, 148.4, 143.2, 133.4, 132.5, 128.3, 128.7, 126.2, 125.9, 124.1, 123.5, 122.3, 117.7, 114.0, 113.8, 18.3, 55.7, 32.8, 30.3, 23.1 ppm.; HRMS (EI): calcd for C₂₁H₂₆O₂ (M⁺) 304.1463, found 304.1460.

6-Methoxy-2-methyl-2-(thiophen-2-yl)chroman 3fa

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). ¹H NMR (300 MHz, CDCl₃) δ 7.22-7.14 (m, 1H), 6.91-6.83 (m, 3H), 6.70
(dd, 1H, $J = 9.0, 3.1$ Hz), 6.53 (d, 1H, $J = 3.3$ Hz), 3.73 (s, 3H), 3.73-2.66 (m, 1H), 2.37-2.29 (m, 1H), 2.18-2.08 (m, 1H), 1.71 (m, 1H) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 130.0, 127.3, 126.8, 124.1, 123.0, 121.8, 117.8, 114.0, 113.7, 77.3, 55.7, 34.1, 30.7, 23.0 ppm.; HRMS (EI): calcd for C$_{13}$H$_{18}$O$_2$S (M$^+$) 260.0871, found 260.0874.

2-ethyl-6-methoxy-2-phenylchroman 3ga

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.33-7.17 (m, 5H), 6.91 (d, 1H, $J = 8.8$ Hz), 6.71 (dd, 1H, $J = 8.8, 2.9$ Hz), 6.47, (d, 1H, $J = 2.9$ Hz), 3.71 (s, 3H), 2.60 (dt, 1H, $J = 16.5, 4.2$ Hz), 2.47-2.29 (m, 2H), 2.08 (dd, 1H, $J = 14.7, 9.2, 3.8$ Hz), 1.91 (dq, 2H, $J = 23.3, 7.1$ Hz) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.1, 148.3, 144.1, 128.3, 126.7, 125.9, 122.6, 117.6, 113.9, 113.6, 80.6, 55.7, 35.7, 30.9, 22.8, 7.7 ppm.; HRMS (EI): calcd for C$_{18}$H$_{20}$O$_2$ (M$^+$) 268.1463, found 268.1466.

2-isopropyl-6-methoxy-2-phenylchroman 3ha

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.29-7.14 (m, 5H), 6.89 (d, 1H, $J = 8.8$ Hz), 6.68 (dd, 1H, $J = 8.8, 2.9$ Hz), 6.41, (d, 1H, $J = 3.3$ Hz), 3.69 (s, 3H), 2.57-2.42 (m, 1H), 2.40-2.30 (m, 2H), 2.16-2.01 (m, 2H), 0.95 (d, 3H, $J = 7.0$ Hz), 0.87 (d, 3H, $J = 7.0$ Hz) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.1, 148.6, 142.8, 128.0, 126.8, 126.6, 122.8, 117.6, 113.9, 113.6, 28.6, 55.7, 38.7, 27.8, 22.9, 17.3, 16.9 ppm.; HRMS (EI): calcd for C$_{19}$H$_{22}$O$_2$ (M$^+$) 282.1620, found 282.1622.

6-Methoxy-2,2-dipentylchroman 3ia

According to the general procedure, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 80:1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.68-6.58 (m, 3H), 3.74 (s, 3H), 2.69 (t, 2H, $J = 7.0$ Hz), 1.78, (t, 2H, $J = 6.8$ Hz), 1.38-1.20 (m, 16H), 0.88, (t, 6H, $J = 7.0$ Hz) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 152.9, 134.7, 122.1, 117.9, 114.1, 113.4, 77.9, 55.8, 36.3, 32.4, 28.9, 23.0, 22.7, 22.3, 14.1 ppm.; HRMS (EI): calcd for C$_{20}$H$_{33}$O$_2$ (M$^+$H$^+$) 305.2481, found 305.2484.
1,3-Bis(6-methoxy-2-methylchroman-2-yl)benzene 3ja

According to the general procedure and p-methoxy phenol (0.10 g, 0.77 mmol, 2 eq) and 1,3-di(buta-2,3-dien-2-yl)benzene 1j (0.07 g, 0.38 mmol, 1 eq) was added, a yellow oil was obtained after column chromatography on silica gel (hexane/EtOAc 50:1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.34 (d, 1H, $J$ = 12.1 Hz), 7.20-7.19 (m, 3H), 6.88 (d, 1H, $J$ = 8.8 Hz), 6.83 (d, 1H, $J$ = 8.8 Hz), 6.72-6.66 (m, 2H), 6.45 (d, 1H, $J$ = 2.9 Hz), 6.41 (d, 1H, $J$ = 2.9 Hz), 3.71 (s, 6H), 2.63-1.96 (m, 8H), 1.60 (s, 3H), 1.53 (s, 3H) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.1, 148.2, 148.1, 145.7, 145.3, 128.5, 128.3, 123.5, 123.4, 122.4, 122.1, 121.9, 117.5, 113.8, 113.5, 113.4, 78.1, 55.6, 32.8, 32.5, 30.3, 30.0, 22.8, 22.6 ppm.; HRMS (EI): calcd for C$_{28}$H$_{30}$O$_4$ (M$^+$) 430.2144, found 430.2140.

6-Chloro-2-(4-chlorophenyl)chroman 3ke

According to the general procedure in DCE (0.1 M), a white solid was obtained after column chromatography on silica gel (hexane/EtOAc 80:1); mp. 94~97 ℃. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.39-7.31 (m, 4H), 7.07 (d, 2 H, $J$ = 9.0 Hz), 6.82 (d, 1H, $J$ = 9.2 Hz), 5.02 (dd, 1H, $J$ = 10.0, 2.5 Hz), 2.95 (ddd, 1H, $J$ = 16.8, 11.0, 6.0 Hz), 2.81-2.70 (m, 1H), 2.24-2.13 (m, 1H), 2.09-1.94 (m, 1H) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.1, 148.2, 148.1, 145.7, 145.3, 128.5, 128.3, 123.5, 123.4, 122.4, 122.1, 121.9, 117.5, 113.8, 113.5, 113.4, 78.1, 55.6, 32.8, 32.5, 30.3, 30.0, 22.8, 22.6 ppm.; HRMS (EI): calcd for C$_{16}$H$_{15}$ClO (M$^+$) 258.0811, found 258.0813.

($E$)-4-Methoxy-2-(3-phenylbut-2-enyl)phenol 4aa

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.41-7.29 (m, 4H), 7.26-7.22 (m, 1H), 6.82-6.78 (m, 1H), 6.74-6.71 (m, 1H), 6.68-6.65 (m, 1H), 5.93 (t, 1H, $J$ = 7.3 Hz), 3.75 (s, 3H), 3.53 (d, 2H, $J$ = 7.3 Hz), 2.16 (s, 3H) ppm.; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 147.9, 143.4, 137.0, 128.3, 128.0, 127.9, 127.0, 125.8, 125.3, 116.2, 115.8, 112.1, 55.7, 29.9, 15.9 ppm.
III. References

IV. Spectroscopic Data

$^1$H-NMR (300 MHz) spectrum of compound 3aa

$^{13}$C-NMR (75 MHz) spectrum of compound 3aa
$^{1}$H-NMR (300 MHz) spectrum of compound 3ab

$^{13}$C-NMR (75 MHz) spectrum of compound 3ab
$^1$H-NMR (300 MHz) spectrum of compound 3ac

$^{13}$C-NMR (75 MHz) spectrum of compound 3ac
S14

$^{1}H$-NMR (300 MHz) spectrum of compound 3ad

$^{13}C$-NMR (75 MHz) spectrum of compound 3ad
$^{1}H$-NMR (300 MHz) spectrum of compound 3ae

$^{13}C$-NMR (75 MHz) spectrum of compound 3ae
$^{1}H$-NMR (300 MHz) spectrum of compound 3af

$^{13}C$-NMR (75 MHz) spectrum of compound 3af
**1H-NMR (300 MHz) spectrum of compound 3ag and its regioisomer 3ag’ (3:1 mixture)**

**13C-NMR (75 MHz) spectrum of compound 3ag and its regioisomer 3ag’ (3:1 mixture)**
$\text{S18}$

$\text{3ah}$

$\text{1H-NMR (300 MHz) spectrum of compound 3ah}$

$\text{13C-NMR (75 MHz) spectrum of compound 3ah}$

S18
$^{1}$H-NMR (300 MHz) spectrum of compound 3ba

$^{13}$C-NMR (75 MHz) spectrum of compound 3ba
$^{1}H$-NMR (300 MHz) spectrum of compound 3ca

$^{13}C$-NMR (75 MHz) spectrum of compound 3ca
$^{1}H$-NMR (300 MHz) spectrum of compound 3da

$^{13}C$-NMR (75 MHz) spectrum of compound 3da
$^1$H-NMR (300 MHz) spectrum of compound 3ea

$^{13}$C-NMR (75 MHz) spectrum of compound 3ea
$1^H$-NMR (300 MHz) spectrum of compound 3fa

$1^3$C-NMR (75 MHz) spectrum of compound 3fa
$^{1}H$-NMR (300 MHz) spectrum of compound 3ga

$^{13}C$-NMR (75 MHz) spectrum of compound 3ga

S24
$^1$H-NMR (300 MHz) spectrum of compound 3ha

$^{13}$C-NMR (75 MHz) spectrum of compound 3ha
$^1$H-NMR (300 MHz) spectrum of compound 3ia

$^{13}$C-NMR (75 MHz) spectrum of compound 3ia
$^{1}$H-NMR (300 MHz) spectrum of compound 3ja

$^{13}$C-NMR (75 MHz) spectrum of compound 3ja
$^{1}H$-NMR (300 MHz) spectrum of compound 3ke

$^{13}C$-NMR (75 MHz) spectrum of compound 3ke
$^1$H-NMR (300 MHz) spectrum of compound 4aa and 2a (1:2 mixture)

$^{13}$C-NMR (75 MHz) spectrum of compound 4aa and 2a (1:2 mixture)