Novel Functionalized Trisubstituted Allylboronates via Hosomi-Miyaura

Borylation of Functionalized Allyl Acetates.

P. Veeraraghavan Ramachandran*, Debarshi Pratihari, Debanjan Biswas, Amit Srivastava

and M. Venkat Ram Reddy

Herbert. C. Brown Center for Borane Research, 560 Oval Drive, Department of

Chemistry, Purdue University, West Lafayette, IN 47907-2084.

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8a.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.67 (s, 1H), 7.41-7.26 (m, 5H), 3.80 (s, 3H), 2.14 (s, 2H), 1.24 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 169.1, 137.6, 136.2, 130.2, 129.4, 128.3, 128.1, 83.5, 52.1, 24.7; ^{11}B NMR δ (ppm): 33; EI-MS: m/z 271 (M^+), 59 $[(\text{CO}_2\text{CH}_3)^+$, 100%]; CI-MS: m/z 303 ($\text{M}+\text{H}^+$), 271 $[(\text{M}+\text{H}-\text{HOCH}_3)^+$, 100%]; HRMS-CI: 303.1768 (calcd.), 303.1763 (actual).

8b.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.73 (s, 1H), 7.44-7.29 (m, 10H), 5.26 (s, 2H), 2.18 (s, 2H), 1.19 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 168.5, 137.9, 136.2, 130.2, 129.4, 128.5, 128.3, 128.1, 83.5, 66.7, 24.7; ^{11}B NMR δ (ppm): 33; EI-MS: m/z 278 ($\text{M}-\text{C}_7\text{H}_6^+$), 91 $[(\text{C}_7\text{H}_7)^+$, 100%]; CI-MS: m/z 379; HRMS-CI: 379.2081 (calcd.), 379.2071 (actual).

8c.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.64 (s, 1H), 7.42-7.30 (m, 5H), 4.26 (m, 2H), 2.49 (q, $J = 7.30$ Hz, 1H), 1.35 (t, $J = 7.12$ Hz, 3H), 1.26 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 168.3, 137.3, 136.3, 129.2, 128.4, 128.0, 83.3., 60.9, 24.9, 24.7,

15.6, 14.4; ^{11}B NMR δ (ppm): 33; EI-MS: m/z 330 (M^+), 315 [$(\text{M}-\text{CH}_3)^+$, 100%]; CI-MS: m/z 331 ($\text{M}+\text{H}^+$); HRMS-EI: 330.2002 (calcd.), 330.1997 (actual).

9a.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.82 (q, $J = 7.02$ Hz, 1H), 3.70 (s, 3H), 1.85 (s, 2H), 1.77 (d, $J = 7.05$ Hz, 2H), 1.23 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 168.5, 137.8, 135.7, 130.0, 83.3, 51.6, 24.6, 14.5; ^{11}B NMR δ (ppm): 32; EI-MS: m/z 240 (M^+), 54; CI-MS: m/z 241 ($\text{M}+\text{H}^+$); HRMS-EI: 240.1533 (calcd.), 240.1541 (actual).

9c.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.81 (q, $J = 7.11$ Hz, 1H), 4.17 (m, 2H), 2.15 (q, $J = 7.41$ Hz, 1H), 1.81 (d, $J = 7.14$ Hz, 3H), 1.27 (t, $J = 3.52$ Hz, 9H), 1.23 (s, 3H), 1.10 (d, $J = 7.26$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 167.8, 137.0, 135.8, 83.2, 60.4, 29.7, 24.9, 24.6, 15.1, 14.4, 14.3; ^{11}B NMR δ (ppm): 33; EI-MS: m/z 268 (M^+), 96; CI-MS: m/z 269 ($\text{M}+\text{H}^+$), 169; HRMS-EI: 268.1846 (calcd.), 268.1842 (actual).

9d.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.77 (q, $J = 6.93$ Hz, 1H), 4.71 (dt, $J = 10.59$ Hz, $J = 4.16$ Hz, 1H), 1.95 (m, 2H), 1.76 (d, $J = 6.99$ Hz, 3H), 1.41 (m, 2H), 1.22 (s, 12H), 1.01 (m, 3H), 0.87 (d, $J = 6.09$ Hz), 0.74 (d, $J = 6.84$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 167.7, 134.7, 130.8, 83.2, 74.1, 47.2, 41.0, 34.4, 31.4, 29.7, 26.2, 24.8, 23.4, 22.1,

20.9, 16.4, 14.5; ^{11}B NMR δ (ppm): 33; EI-MS: m/z 399 ($\text{M}-\text{CH}_3$) $^+$ 83; CI-MS: m/z 365 ($\text{M}+\text{H}$) $^+$, 209 [$(\text{M}+\text{H}-\text{Menthol})$] $^+$, 100%]; HRMS-CI: 365.2863 (calcd.), 365.2863 (actual).

10a.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.69 (s, 1H), 7.42-7.29 (m, 5H), 4.29 (dd, $J = 1.98$ Hz, $J = 2.04$ Hz), 3.81 (s, 3H), 2.32 (m, 1H), 2.19 (m, 2H), 2.05 (t, $J = 5.64$ Hz, 1H), 1.90 (m, 1H), 1.82 (m, 1H), 1.37 (s, 3H), 1.28 (s, 3H), 1.21 (d, $J = 10.71$ Hz), 0.84 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 169.1, 137.6, 136.2, 130.2, 129.4, 128.4, 128.1, 85.9, 78.0, 52.1, 51.3, 39.5, 38.2, 35.5, 28.6, 27.1, 26.3, 24.1; ^{11}B NMR δ (ppm): 32; EI-MS: m/z 354 (M) $^+$, 116; CI-MS: m/z 365 ($\text{M}+\text{H}$) $^+$, 203 [$(\text{C}_6\text{H}_5\text{CHC}(\text{CH}_2\text{BOH})\text{CO}_2\text{H})$] $^+$, 100%]; HRMS-EI: 354.2002 (calcd.), 354.2006 (actual).

10c.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.71 (s, 1H), 7.49-7.32 (m, 5H), 4.35 (m, 3H), 2.63 (m, 1H), 2.38 (m, 1H), 2.24 (m, 1H), 2.10 (q, $J = 5.9$ Hz, 1H), 1.94 (m, 2H), 1.48 (s, 1H), 1.37 (m, 13H), 0.89 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 167.3, 136.4, 135.2, 128.2, 127.3, 127.0, 84.7, 76.9, 59.8, 50.3, 38.5, 37.2, 34.6, 28.7, 27.6, 27.4, 26.1, 25.3, 23.0, 14.6, 13.3; ^{11}B NMR δ (ppm): 33; EI-MS: m/z 382 (M) $^+$; CI-MS: m/z 383 ($\text{M}+\text{H}$) $^+$, 231 [$(\text{M}+\text{H})-\text{C}_9\text{H}_{14}\text{O}_2$].

11a.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.81 (q, $J = 7.03$ Hz, 1H), 4.24 (s, $J = 8.58$ Hz, 1H), 3.69 (s, 3H), 2.25 (m, 1H), 2.14 (s, 2H), 2.02 (t, $J = 5.59$ Hz, 1H), 1.89 (s, 3H), 1.81 (m, 1H), 1.77 (d, $J = 6.99$ Hz, 3H), 1.35 (s, 3H), 1.26 (s, 3H), 1.19 (d, $J = 10.71$ Hz, 1H),

0,81 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 168.5, 135.7, 130.1, 85.7, 77.8, 51.6, 51.2, 39.5, 38.2, 35.5, 28.6, 27.1, 26.3, 24.0, 14.5; ^{11}B NMR δ (ppm): 32; EI-MS: m/z 292 (M) $^+$, 54; CI-MS: m/z 293 ($\text{M}+\text{H}$) $^+$, 141; HRMS-EI: 292.1846 (calcd.), 292.1840 (actual).

14.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.50 (s, 1H), 7.44-7.30 (m, 5H), 2.45 (s, 3H), 2.01 (s, 2H), 1.23 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 200.4, 140.3, 138.9, 136.2, 129.6, 129.3, 128.4, 83.2, 25.2, 24.8, 24.4; ^{11}B NMR δ (ppm): 33; EI-MS: m/z 286 (M) $^+$, 142; CI-MS: m/z 287 ($\text{M}+\text{H}$) $^+$; HRMS: 286.1740 (calcd.), 286.1737 (actual).

16.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.19 (q, $J = 6.91$ Hz, 1H), 1.95 (d, $J = 6.93$ Hz, 3H), 1.86 (s, 2H), 1.26 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 142.3, 141.8, 84.0, 29.7, 24.7, 17.3; ^{11}B NMR δ (ppm): 32; EI-MS: m/z 207 (M) $^+$, 192 ($\text{M}-\text{CH}_3$), 85 (C_6H_{13}) $^+$; CI-MS: m/z 208 ($\text{M}+\text{H}$) $^+$.

300 MHz ^1H NMR of compound **8a** in CDCl_3

75.5 MHz ^{13}C NMR of compound **8a** in CDCl_3

^{11}B NMR of compound **8a** in CDCl_3

300 MHz ^1H NMR of compound **8b** in CDCl_3

^{11}B NMR of compound **8b** in CDCl_3

300 MHz ^1H NMR of compound **8c** in CDCl_3

^{11}B NMR of compound **8c** in CDCl_3

300 MHz ^1H NMR of compound **9a** in CDCl_3

75.5 MHz ^{13}C NMR of compound **9a** in CDCl_3

^{11}B NMR of compound **9a** in CDCl_3

75.5 MHz ^{13}C NMR of compound **9c** in CDCl_3

^{11}B NMR of compound **9c** in CDCl_3

300 MHz ^1H NMR of compound **9d** in CDCl_3

75.5 MHz ^{13}C NMR of compound **9d** in CDCl_3

32.6583

^{11}B NMR of compound **9d** in CDCl_3

300 MHz ^1H NMR of compound **10a** in CDCl_3

75.5 MHz ^{13}C NMR of compound **10a** in CDCl_3

^{11}B NMR of compound **10a** in CDCl_3

300 MHz ^1H NMR of compound **10c** in CDCl_3

75.5 MHz ^{13}C NMR of compound **10c** in CDCl_3

^{11}B NMR of compound **10c** in CDCl_3

300 MHz ^1H NMR of compound **11a** in CDCl_3

75.5 MHz ^{13}C NMR of compound **11a** in CDCl_3

^{11}B NMR of compound **11a** in CDCl_3

300 MHz ^1H NMR of compound **14** in CDCl_3

75.5 MHz ¹³C NMR of compound 14 in CDCl₃

^{11}B NMR of compound **14** in CDCl_3

300 MHz ^1H NMR of compound **16** in CDCl_3

75.5 MHz ¹³C NMR of compound 16 in CDCl₃

^{11}B NMR of compound **16** in CDCl_3

300 MHz ^1H NMR of compound *cis*-17 in CDCl_3

75.5 MHz ^{13}C NMR of compound *cis*-17 in CDCl_3