Control the Regioselectivity of Sulfonamidyl Radical Cyclization by Vinylic Halogen Substitution

Hongjian Lu, Qian Chen, and Chaozhong Li*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai
200032, P. R. China

clig@mail.sioc.ac.cn

Supporting Information

1. Characterizations of substrates **1**, **6**, **9**, **11-13**, **17**, **19**, **26**, **29** and **31**. S2
2. Characterizations of products **2**, **3**, **5**, **7**, **8**, **10**, **14-16**, **18**, **23**, **25**, **27**, **28**, **30** and **32**. S8
3. References for known compounds. S18
4. Computational results on the cyclization of radicals **A**. S19
5. ¹H and ¹³C NMR spectra of compounds without elemental analyses. S34

Characterization of substrates

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.72 (3H, s), 1.77-1.87 (2H, m), 2.09 (2H, t, $J = 7.2\text{ Hz}$), 2.47 (3H, s), 3.23 (2H, t, $J = 6.9\text{ Hz}$), 4.73 (2H, d, $J = 14.7\text{ Hz}$), 7.39 (2H, d, $J = 8.1\text{ Hz}$), 7.82 (2H, d, $J = 8.1\text{ Hz}$). ^{13}C NMR (CDCl_3) δ 21.6, 22.3, 25.1, 34.0, 56.2, 110.8, 129.5, 129.6, 130.2, 144.2, 145.3. EIMS: m/z (rel intensity) 287 (M^+ , 2), 252 (14), 238 (16), 198 (10), 184 (8), 155 (53), 132 (9), 91 (100). HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_2\text{S}(\text{M}^+-\text{Cl})$: 252.1058. Found: 252.1070.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.2\text{ Hz}$), 1.24-1.45 (4H, m), 1.79-1.87 (2H, m), 2.00 (2H, t, $J = 7.5\text{ Hz}$), 2.09 (2H, t, $J = 7.5\text{ Hz}$), 2.48 (3H, s), 3.23 (2H, t, $J = 6.9\text{ Hz}$), 4.73 (2H, d, $J = 8.4\text{ Hz}$), 7.39 (2H, d, $J = 8.1\text{ Hz}$), 7.82 (2H, d, $J = 8.1\text{ Hz}$). ^{13}C NMR (CDCl_3) δ 13.9, 21.7, 22.4, 25.3, 29.9, 32.3, 35.7, 56.3, 109.6, 129.5, 129.6, 130.1, 145.3, 148.4. EIMS: m/z (rel intensity) 329 (M^+ , 6), 294 (40), 280 (17), 184 (25), 155 (72), 140 (34), 91 (100), 77 (32). HRMS calcd for $\text{C}_{16}\text{H}_{24}\text{ClNO}_2\text{SNa}(\text{M}^++\text{Na})$: 352.1106. Found: 352.1109.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.90-1.99 (2H, m), 2.44-2.50 (5H, m), 3.25 (2H, t, $J = 6.3\text{ Hz}$), 5.22-5.24 (2H, m), 7.39 (2H, d, $J = 8.1\text{ Hz}$), 7.81 (2H, d, $J = 8.1\text{ Hz}$). ^{13}C NMR (CDCl_3) δ 21.7, 24.5, 35.5, 55.3, 113.6, 129.6, 129.7, 129.9, 141.0, 145.5. EIMS: m/z (rel intensity) 271 (M^+-HCl , 3), 206 (3), 184 (9), 155 (49), 139 (5), 118 (32), 91 (100), 65 (22). HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{NO}_2\text{S}(\text{M}^++1)$: 308.0282. Found: 308.0273.

White solid. Mp: 44-46 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.69-1.78 (2H, m), 2.42-2.47 (5H, m), 2.98 (2H, q, $J = 6.3$ Hz), 4.43 (1H, t, $J = 5.7$ Hz), 5.39 (1H, s), 5.55 (1H, s), 7.32 (2H, d, $J = 7.8$ Hz), 7.75 (2H, d, $J = 7.8$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 27.8, 38.2, 41.8, 117.7, 127.1, 129.8, 132.8, 136.9, 143.5. EIMS: m/z (rel intensity) 238 ($\text{M}^+ - \text{Br}$, 13), 199 (9), 183 (11), 155 (50), 139 (14), 98 (37), 91 (100), 83 (34). Anal. calcd for $\text{C}_{12}\text{H}_{16}\text{BrNO}_2\text{S}$: C, 45.29; H, 5.07; N, 4.40. Found: C, 45.42; H, 5.20; N, 4.22.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.68-1.78 (2H, m), 2.36 (2H, t, $J = 7.2$ Hz), 2.43 (3H, s), 2.96 (2H, q, $J = 6.6$ Hz), 4.51 (1H, t, $J = 6.3$ Hz), 5.13 (2H, d, $J = 9.3$ Hz), 7.32 (2H, d, $J = 8.4$ Hz), 7.75 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 27.1, 36.0, 41.9, 113.2, 127.1, 129.8, 136.8, 141.2, 143.5. EIMS: m/z (rel intensity) 274 ($\text{M}^+ + 1$, 0.4), 238 (4), 184 (8), 155 (49), 139 (6), 118 (50), 91 (100), 65 (31). Anal. calcd for $\text{C}_{12}\text{H}_{16}\text{ClNO}_2\text{S}$: C, 52.64; H, 5.89; N, 5.12. Found: C, 52.55; H, 5.98; N, 4.91.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.75-1.86 (2H, m), 2.42-2.54 (2H, m), 2.97 (3H, s), 3.12-3.25 (2H, m), 4.30 (1H, br), 5.76 (1H, s), 6.11 (1H, s). ^{13}C NMR (CDCl_3) δ 29.3, 40.3, 41.6, 42.0, 110.2, 126.8. EIMS: m/z (rel intensity) 290 ($\text{M}^+ + 1$, 0.4), 162 (6), 121 (3), 108 (58), 98 (18), 83 (100), 79 (12), 67 (19). Anal. calcd for $\text{C}_6\text{H}_{12}\text{INO}_2\text{S}$: C, 24.92; H, 4.18; N, 4.84. Found: C, 24.89; H, 4.24; N, 4.94.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.81-1.90 (2H, m), 2.53 (2H, t, $J = 7.2$ Hz), 2.98 (3H, s), 3.13-3.21 (2H, m), 4.34 (1H, br), 5.46 (1H, s), 5.65 (1H, s). ^{13}C NMR (CDCl_3) δ 28.2, 38.1, 40.2, 41.8, 117.9, 132.7. EIMS: m/z (rel intensity) 244 ($\text{M}^+(\text{}^{81}\text{Br})+1$, 1), 242 ($\text{M}^+(\text{}^{79}\text{Br})+1$, 1), 162 (13), 149 (4), 121 (7), 108 (64), 98 (28), 83 (100). Anal. calcd for $\text{C}_6\text{H}_{12}\text{BrNO}_2\text{S}$: C, 29.76; H, 5.00; N, 5.78. Found: C, 29.65; H, 5.09; N, 5.74.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.86 (2H, tt, $J = 6.6, 6.9$ Hz), 2.45 (2H, t, $J = 7.2$ Hz), 2.97 (3H, s), 3.17 (2H, q, $J = 6.9$ Hz), 4.40 (1H, br), 5.21 (2H, s). ^{13}C NMR (CDCl_3) δ 27.6, 36.0, 40.4, 42.0, 113.3, 141.3. EIMS: m/z (rel intensity) 198 (M^++1 , 1), 162 (3), 121 (10), 118 (25), 108 (100), 102 (6), 79 (18), 67 (15). Anal. calcd for $\text{C}_6\text{H}_{12}\text{ClNO}_2\text{S}$: C, 36.45; H, 6.12; N, 7.09. Found: C, 36.32; H, 6.22; N, 6.91.

White solid. Mp: 80-82 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 0.96 (6H, s), 2.30 (2H, s), 2.43 (3H, s), 2.76 (2H, d, $J = 7.2$ Hz), 4.84 (1H, br), 5.10 (1H, s), 5.25 (1H, s), 7.31 (2H, d, $J = 8.4$ Hz), 7.74 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 25.3, 34.7, 48.0, 52.6, 116.4, 127.0, 129.7, 137.1, 138.7, 143.4. EIMS: m/z (rel intensity) 301 (M^+ , 0.4), 184 (33), 155 (68), 146 (21), 139 (5), 91 (100), 77 (9), 65 (28). Anal. calcd for $\text{C}_{14}\text{H}_{20}\text{ClNO}_2\text{S}$: C, 55.71; H, 6.68; N, 4.64. Found: C, 55.72; H, 6.67; N, 4.64.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 0.89 (3H, d, $J = 6.6$ Hz), 1.93-2.18 (2H, m), 2.35-2.40 (1H, m), 2.42 (3H, s), 2.76-2.93 (2H, m), 5.02 (1H, br), 5.16 (1H, s), 5.30 (1H, s), 7.31 (2H, d, $J = 8.4$ Hz), 7.75 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 16.8, 21.4, 31.1, 43.6, 48.1, 114.1, 127.1, 129.7, 137.1, 140.5, 143.4. EIMS: m/z (rel intensity) 288 (M^++1 , 0.3), 252 (3), 184 (26), 155 (75), 132 (54),

112 (6), 91 (100), 65 (31). Anal. calcd for C₁₃H₁₈ClNO₂S: C, 54.25; H, 6.30; N, 4.87. Found: C, 54.37; H, 6.30; N, 4.53.

White solid. ¹H NMR (300 MHz, CDCl₃) δ 2.25-2.36 (4H, m), 2.43 (3H, s), 2.94-2.99 (2H, dd, *J* = 5.2, 6.6 Hz), 4.45 (2H, t, *J* = 6.6 Hz), 5.20 (4H, t, *J* = 12.6 Hz), 7.31 (2H, d, *J* = 8.4 Hz), 7.73 (2H, d, *J* = 8.4 Hz). ¹³C NMR (CDCl₃) δ 21.5, 33.8, 40.7, 44.6, 114.9, 127.1, 129.8, 136.8, 139.9, 143.6. EIMS: *m/z* (rel intensity) 348 (M⁺+1, 0.1), 312 (3), 192 (23), 184 (22), 155 (74), 116 (23), 91 (100), 65 (40). HRMS calcd for C₁₅H₁₉Cl₂NO₂SNa (M⁺+Na): 370.0408. Found: 370.0406.

Colorless oil. Z:E = 67:33. ¹H NMR (300 MHz, CDCl₃) δ 1.67-1.80 (2H, m), 2.11/2.25 (2H, 2q, *J* = 7.2 Hz), 2.41 (3H, s), 3.17 (2H, q, *J* = 6.3 Hz), 5.68-6.03 (2H, m), 7.33 (2H, d, *J* = 8.1 Hz), 7.75 (2H, d, *J* = 8.1 Hz). ¹³C NMR (CDCl₃) δ 21.8, 23.6/26.2, 25.9/27.2, 56.0/55.7, 119.5/118.4, 129.6, 129.7, 129.8, 130.0/132.0, 145.5. EIMS: *m/z* (rel intensity) 274 (M⁺-Cl, 0.3), 272 (0.8), 236 (3), 224 (18), 184 (4), 155 (33), 91 (100), 65 (25). HRMS calcd for C₁₂H₁₅Cl₂NO₂S (M⁺-Cl): 272.0510. Found: 272.0512.

Colorless oil. Z:E = 67:33. ¹H NMR (300 MHz, CDCl₃) δ 1.54-1.65 (2H, m), 2.07/2.21 (2H, 2q, *J* = 7.2 Hz), 2.44 (3H, s), 2.95 (2H, q, *J* = 6.6 Hz), 4.40-4.46 (1H, m), 5.64-6.05 (2H, m), 7.32 (2H, d, *J* = 8.1 Hz), 7.75 (2H, d, *J* = 8.1 Hz). ¹³C NMR (CDCl₃) δ 21.5, 24.0/27.7, 28.3/28.7, 42.5/42.2, 119.2/118.0, 127.1, 129.7, 130.1/132.2, 137.0, 143.4/143.5. EIMS: *m/z* (rel intensity) 274 (M⁺+1, 1), 238 (11), 210 (3), 184 (10), 155 (66), 118 (25), 91 (100), 65 (38). Anal. calcd for C₁₂H₁₆ClNO₂S: C, 52.64; H, 5.89; N, 5.12. Found: C, 52.53; H, 5.93; N, 5.08.

White solid. Z:E = 50:50. ^1H NMR (300 MHz, CDCl_3) δ 0.85 (3H, s), 0.91 (3H, s), 1.96 (1H, d, $J = 7.8$ Hz), 2.15 (1H, dd, $J = 1.5, 7.8$ Hz), 2.43 (3H, s), 2.68 (2H, dd, $J = 6.0, 6.9$ Hz), 4.37-4.63 (1H, m), 5.68-6.11 (2H, m), 7.31 (1H, d, $J = 8.1$ Hz), 7.32 (1H, d, $J = 8.1$ Hz), 7.73 (1H, d, $J = 8.1$ Hz), 7.74 (1H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.4, 24.7/24.8, 34.3/34.8, 36.5/40.3, 52.6/52.7, 119.2/120.1, 127.0, 127.4/129.4, 129.7, 137.0/137.1, 143.3/143.4. EIMS: m/z (rel intensity) 266 ($\text{M}^+ - \text{Cl}$, 6), 226 (2), 184 (35), 172(3), 155 (93), 126 (11), 91 (100), 65 (32). Anal. calcd for $\text{C}_{14}\text{H}_{20}\text{ClNO}_2\text{S}$: C, 55.71; H, 6.68; N, 4.64. Found: C, 55.83; H, 6.74; N, 4.61.

Colorless oil. Z:E = 75:25. ^1H NMR (300 MHz, CDCl_3) δ 1.54-1.66 (2H, m), 2.05/2.20 (2H, 2q, $J = 7.2$ Hz), 2.43 (3H, s), 2.96 (2H, q, $J = 6.9$ Hz), 4.49 (1H, br), 5.98-6.18 (2H, m), 7.31 (2H, d, $J = 8.1$ Hz), 7.75 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 26.7/28.4, 28.1/29.7, 42.5/42.2, 108.9/105.4, 127.1, 129.7, 133.3/136.4, 137.0, 143.5/143.4. EIMS: m/z (rel intensity) 238 ($\text{M}^+ - \text{Br}$, 9), 210 (4), 184 (12), 155 (56), 98 (36), 91 (100), 83 (26), 65 (31). Anal. calcd for $\text{C}_{12}\text{H}_{16}\text{BrNO}_2\text{S}$: C, 45.29; H, 5.07; N, 4.40. Found: C, 45.50; H, 5.29; N, 4.36.

Colorless oil. Z:E = 73:27. ^1H NMR (300 MHz, CDCl_3) δ 1.54-1.67 (2H, m), 2.01-2.19 (2H, m), 2.44 (3H, s), 2.91-3.02 (2H, m), 4.43 (1H, t, $J = 6.6$ Hz), 5.94-6.44 (2H, m), 7.31 (2H, d, $J = 8.1$ Hz), 7.75 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 27.9/28.2, 31.8/32.7, 42.5/42.2, 83.6/75.7, 127.1, 129.7, 137.0, 139.8, 143.4/144.8. EIMS: m/z (rel intensity) 366 ($\text{M}^+ + 1$, 0.8), 238 (6), 194 (6), 184 (16), 155 (42), 98 (47), 91 (100), 83 (47). Anal. calcd for $\text{C}_{12}\text{H}_{16}\text{INO}_2\text{S}$: C, 39.46; H, 4.42; N, 3.84. Found: C, 39.66; H, 4.69; N, 3.70.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.41-1.60 (4H, m), 2.37 (2H, t, $J = 6.6$ Hz), 2.43 (3H, s), 2.96 (2H, q, $J = 6.6$ Hz), 4.32 (1H, t, $J = 6.0$ Hz), 5.37 (1H, d, $J = 1.5$ Hz), 5.37 (1H, d, $J = 0.9$ Hz), 7.32 (2H, d, $J = 8.1$ Hz), 7.75 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 24.8, 28.3, 40.6, 42.8, 116.9, 127.1, 129.7, 133.8, 137.1, 143.4. EIMS: m/z (rel intensity) 252 ($\text{M}^+ - \text{Br}$, 11), 210 (5), 184 (14), 155 (57), 112 (18), 97 (29), 91 (100), 65 (29). Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{BrNO}_2\text{S}$: C, 46.99; H, 5.46; N, 4.22. Found: C, 47.38; H, 5.57; N, 3.84.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.45-1.59 (4H, m), 2.89 (2H, t, $J = 6.3$ Hz), 2.43 (3H, s), 2.92-3.00 (2H, m), 4.35 (1H, br), 5.10 (2H, d, $J = 14.4$ Hz), 7.32 (2H, d, $J = 8.4$ Hz), 7.75 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 24.0, 28.4, 38.4, 42.8, 112.4, 127.1, 129.7, 137.0, 142.1, 143.4. EIMS: m/z (rel intensity) 288 ($\text{M}^+ + 1$, 0.2), 252 (3), 210 (8), 184 (10), 155 (67), 132 (27), 91 (100), 65 (32). Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{ClNO}_2\text{S}$: C, 54.25; H, 6.30; N, 4.87. Found: C, 54.18; H, 6.18; N, 4.57.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.08 (6H, s), 1.25-1.42 (4H, m), 2.43 (3H, s), 2.92 (2H, q, $J = 6.0$ Hz), 4.60 (1H, t, $J = 6.0$ Hz), 5.07 (1H, t, $J = 1.5$ Hz), 5.15 (1H, s), 7.30 (2H, d, $J = 7.8$ Hz), 7.75 (2H, d, $J = 7.8$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 24.8, 26.7, 37.1, 41.4, 43.6, 111.5, 127.1, 129.7, 137.0, 143.4, 150.7. EIMS: m/z (rel intensity) 316 ($\text{M}^+ + 1$, 0.9), 280 (2), 210 (40), 184 (19), 160 (20), 155 (75), 91 (100), 65 (28). Anal. calcd for $\text{C}_{15}\text{H}_{22}\text{ClNO}_2\text{S}$: C, 57.04; H, 7.02; N, 4.43. Found: C, 57.05; H, 7.01; N, 4.30.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.23 (6H, s), 1.38-1.52 (4H, m), 2.43 (3H, s), 2.94 (2H, q, $J = 6.0$ Hz), 4.34 (1H, t, $J = 6.0$ Hz), 5.95-6.05 (2H, m), 7.31 (2H, d, $J = 8.4$ Hz), 7.75 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 25.1, 27.6, 36.8, 38.7, 43.8, 104.6, 127.1, 129.7, 137.1, 141.5, 143.3. ESIMS: m/z 360.0 [$\text{M}^+(\text{}^{79}\text{Br})+1$]. HRMS calcd for $\text{C}_{15}\text{H}_{22}\text{BrNO}_2\text{SNa}$ ($\text{M}^+(\text{}^{79}\text{Br})+\text{Na}$): 382.0451. Found: 382.0447.

Characterization of products

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.52 (3H, s), 1.63-1.91 (3H, m), 2.25-2.33 (1H, m), 2.43 (3H, s), 3.30-3.46 (2H, m), 3.85-3.89 (2H, m), 7.29 (2H, d, $J = 8.1$ Hz), 7.75 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 22.5, 23.8, 38.3, 49.8, 51.0, 67.9, 127.3, 129.5, 137.9, 143.1. EIMS: m/z (rel intensity) 287 (M^+ , 1), 238 (95), 198 (3.84), 155 (44), 149 (2), 132 (3), 91 (100), 65 (23). Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{ClNO}_2\text{S}$: C, 54.25; H, 6.30; N, 4.87. Found: C, 54.35; H, 6.42; N, 4.67.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 0.78 (3H, t, $J = 6.6$ Hz), 1.10-1.25 (4H, m), 1.61-1.96 (5H, m), 2.05-2.15 (1H, m), 2.34 (3H, s), 3.24-3.36 (2H, m), 3.68 (1H, d, $J = 10.8$ Hz), 3.98 (1H, d, $J = 10.8$ Hz), 7.20 (2H, d, $J = 8.1$ Hz), 7.68 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 13.9, 21.4, 22.9, 23.0, 26.7, 35.1, 37.3, 50.1, 51.6, 71.5, 127.2, 129.3, 138.1, 142.9. EIMS: m/z (rel intensity) 329 (M^+ , 0.2), 294 (2), 280 (78), 272 (28), 250 (3), 155 (67), 91 (100), 65 (27). Anal. calcd for $\text{C}_{16}\text{H}_{24}\text{ClNO}_2\text{S}$: C, 58.25; H, 7.33; N, 4.25. Found: C, 57.90; H, 7.52; N, 4.08.

White solid. Mp: 88-90 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.65 (3H, s), 1.62-1.97 (4H, m), 2.44 (3H, s), 2.94-3.06 (2H, m), 3.04 (1H, d, $J = 11.4$ Hz), 3.18 (1H, d, $J = 11.4$ Hz), 7.33 (2H, d, $J = 7.8$ Hz), 7.65 (2H, d, $J = 7.8$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 22.4, 38.2, 39.5, 45.8, 57.8, 65.7, 127.6, 129.7, 133.8, 143.6. EIMS: m/z (rel intensity) 287 (M^+ , 24), 252 (19), 236 (8), 198 (100), 155 (67), 132 (38), 103 (18), 91 (67). Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{ClNO}_2\text{S}$: C, 54.25; H, 6.30; N, 4.87. Found: C, 54.30; H, 6.45; N, 4.79.

White solid. Mp: 94-96 °C. ^1H NMR (300 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.2$ Hz), 1.25-1.61 (4H, m), 1.68-1.93 (6H, m), 2.43 (3H, s), 2.93-3.06 (2H, m), 3.13 (2H, s), 7.32 (2H, d, $J = 8.1$ Hz), 7.65 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 13.9, 21.5, 22.2, 22.7, 25.6, 37.7, 39.6, 46.0, 56.5, 69.8, 127.6, 129.7, 133.9, 143.6. EIMS: m/z (rel intensity) 329 (M^+ , 2), 294 (55), 250 (32), 198 (78), 184 (16), 174 (22), 155 (90), 91 (100). Anal. calcd for $\text{C}_{16}\text{H}_{24}\text{ClNO}_2\text{S}$: C, 58.25; H, 7.33; N, 4.25. Found: C, 58.24; H, 7.34; N, 4.07.

White solid. Mp: 92-94 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.88-1.95 (2H, m), 2.26 (2H, t, $J = 5.7$ Hz), 2.44 (3H, s), 3.08 (2H, t, $J = 5.4$ Hz), 3.53 (2H, s), 7.34 (2H, d, $J = 8.4$ Hz), 7.66 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 23.0, 43.8, 45.1, 59.9, 84.8, 127.5, 129.8, 134.1, 143.9. EIMS: m/z (rel intensity) 307 (M^+ , 14), 271 (5), 236 (2), 198 (61), 155 (63), 116 (17), 91 (100), 65 (40). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{Cl}_2\text{NO}_2\text{S}$: C, 46.76; H, 4.91; N, 4.54. Found: C, 47.04; H, 4.60; N, 4.17.

White solid. Mp: 60-62 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.63 (3H, s), 1.73-1.87 (3H, m), 2.20-2.25 (1H, m), 2.42 (3H, s), 3.33-3.45 (2H, m), 3.67 (1H, d, $J = 9.9$ Hz), 3.79 (1H, d, $J = 9.9$ Hz), 7.29 (2H, d, $J = 8.1$ Hz), 7.76 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 17.7, 21.5, 22.4, 24.6, 41.5, 49.9, 66.7, 127.4, 129.5, 137.9, 143.1. EIMS: m/z (rel intensity) 364 ($\text{M}^+ - \text{Me}$, 4), 252 (6), 238 (100), 155 (40), 139 (2), 96 (6), 91 (72), 65 (23). Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{INO}_2\text{S}$: C, 41.17; H, 4.78; N, 3.69. Found: C, 41.21; H, 4.79; N, 3.58.

Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.76-1.85 (2H, m), 2.43 (3H, s), 2.76 (2H, t, $J = 6.6$ Hz), 2.97 (2H, q, $J = 6.3$ Hz), 3.90 (2H, s), 4.48 (1H, t, $J = 6.0$ Hz), 7.31 (2H, d, $J = 8.1$ Hz), 7.72 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 23.6, 34.3, 36.3, 42.2, 127.0, 129.8, 136.7, 143.6, 201.7. ESIMS: m/z 336 ($\text{M}^+ + 1$), 334 ($\text{M}^+ + 1$). HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{BrNO}_3\text{SNa}$: ($\text{M}^+ + \text{Na}$) 355.9945. Found: 355.9927.

White solid. ^1H NMR (300 MHz, CDCl_3) δ 1.65-1.75 (2H, m), 2.33 (2H, t, $J = 5.7$ Hz), 2.45 (3H, s), 3.08 (2H, t, $J = 4.5$ Hz), 3.40 (2H, s), 7.34 (2H, d, $J = 8.1$ Hz), 7.66 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 1.61, 21.6, 26.1, 45.4, 50.9, 66.1, 127.5, 129.8, 133.8, 144.0. EIMS: m/z (rel intensity) 491 (M^+ , 0.3), 364 (41), 237 (100), 210 (4), 181 (3), 155 (10), 91 (69), 82 (43). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{I}_2\text{NO}_2\text{S}$: C, 29.35; H, 3.08; N, 2.85. Found: C, 29.55; H, 3.17; N, 2.74.

White solid. Mp: 120-122 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.70-1.93 (2H, m), 2.20-2.31 (1H, m), 2.44 (3H, s), 2.44-2.53 (1H, m), 2.99-3.17 (2H, m), 3.33 (1H, d, $J = 12.6$ Hz), 3.70 (1H, d, $J = 12.6$ Hz), 7.34 (2H, d, $J = 8.4$ Hz), 7.65 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 25.1, 33.5, 45.3, 49.0, 64.3, 127.5, 129.8, 134.1, 144.0. EIMS: m/z (rel intensity) 444($\text{M}^+(\text{}^{81}\text{Br})-1$, 0.3), 442 ($\text{M}^+(\text{}^{79}\text{Br})-1$, 0.2), 318 (64), 316 (67), 237 (6), 207 (4), 155 (73), 91 (100). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{BrINO}_2\text{S}$: C, 32.45; H, 3.40; N, 3.15. Found: C, 32.42; H, 3.47; N, 3.03.

White solid. Mp: 120-122 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.68-1.80 (1H, m), 1.89-2.00 (1H, m), 2.10-2.19 (1H, m), 2.45 (3H, s), 2.45-2.54 (1H, m), 3.08 (2H, t, $J = 5.7$ Hz), 3.31 (1H, d, $J = 12.3$ Hz), 3.69 (1H, d, $J = 12.3$ Hz), 7.34 (2H, d, $J = 8.1$ Hz), 7.66 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.6, 24.4, 45.3, 48.0, 48.1, 63.6, 127.5, 129.8, 134.1, 143.9. EIMS: m/z (rel intensity) 400 (M^++1 , 2), 364 (0.6), 304 (3), 272 (37), 237 (2), 155 (29), 91 (100), 65 (20). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{ClINO}_2\text{S}$: C, 36.06; H, 3.78; N, 3.50. Found: C, 36.27; H, 4.07; N, 3.41.

White solid. Mp: 132-134 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.70-1.78 (2H, m), 2.44 (2H, t, $J = 5.4$ Hz), 2.96 (3H, s), 3.33 (2H, t, $J = 5.4$ Hz), 3.64 (2H, s). ^{13}C NMR (CDCl_3) δ 2.6, 26.4, 38.4, 45.1, 51.1, 66.1. EIMS: m/z (rel intensity) 416 (M^++1 , 0.2), 288 (27), 181 (6), 161 (100), 151 (3), 127 (3), 82 (61), 55 (47). Anal. calcd for $\text{C}_6\text{H}_{11}\text{I}_2\text{NO}_2\text{S}$: C, 17.36; H, 2.67; N, 3.37. Found: C, 17.47; H, 2.82; N, 3.26.

White solid. Mp: 116-118 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.72-1.82 (1H, m), 1.87-2.00 (1H, m), 2.35-2.43 (1H, m), 2.57-2.66 (1H, m), 2.95 (3H, s), 3.30-3.40 (2H, m), 3.66 (1H, d, $J = 13.5$ Hz), 3.90 (1H, d, $J = 13.5$ Hz). ^{13}C NMR (CDCl_3) δ 25.4, 34.3, 38.5, 44.9, 49.1, 64.1. EIMS: m/z (rel intensity) 242 ($\text{M}^+(\text{}^{81}\text{Br})\text{-I}$, 100), 240 ($\text{M}^+(\text{}^{79}\text{Br})\text{-I}$, 82), 161 (60), 133 (16), 108 (12), 83 (68), 68 (8), 55 (86). Anal. calcd for $\text{C}_6\text{H}_{11}\text{BrINO}_2\text{S}$: C, 19.58; H, 3.01; N, 3.81. Found: C, 19.64; H, 3.27; N, 3.66.

White solid. Mp: 92-94 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.68-1.80 (1H, m), 1.92-2.10 (1H, m), 2.26-2.37 (1H, m), 2.53-2.66 (1H, m), 2.95 (3H, s), 3.22-3.34 (1H, m), 3.38-3.47 (1H, m), 3.67 (1H, d, $J = 13.5$ Hz), 3.91 (1H, d, $J = 13.5$ Hz). ^{13}C NMR (CDCl_3) δ 24.6, 38.7, 44.8, 48.1, 48.6, 63.4. EIMS: m/z (rel intensity) 324 (M^++1 , 1), 196 (63), 160 (6), 127 (15), 118 (83), 89 (75), 82 (86), 55 (100). Anal. calcd for $\text{C}_6\text{H}_{11}\text{ClINO}_2\text{S}$: C, 22.27; H, 3.43; N, 4.33. Found: C, 22.51; H, 3.53; N, 4.19.

White solid. Mp: 110-112 °C. ^1H NMR (300 MHz, CDCl_3) δ 0.95 (3H, s), 1.25 (3H, s), 2.36-2.64 (6H, m), 3.31 (1H, d, $J = 12.3$ Hz), 3.44 (1H, d, $J = 12.9$ Hz), 4.20 (1H, d, $J = 12.9$ Hz), 7.35 (2H, d, $J = 7.8$ Hz), 7.68 (2H, d, $J = 7.8$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 26.6, 29.0, 35.5, 45.2, 56.9, 60.0, 64.8, 127.4, 129.8, 134.6, 143.9. EIMS: m/z (rel intensity) 300 ($\text{M}^+\text{-I}$, 35), 252 (4), 167 (2), 155 (51), 144 (5), 108 (7), 91 (100), 65 (29). Anal. calcd for $\text{C}_{14}\text{H}_{19}\text{ClINO}_2\text{S}$: C, 39.31; H, 4.48; N, 3.27. Found: C, 39.38; H, 4.56; N, 3.12.

White solid. Mp: 134-136 °C. ^1H NMR (300 MHz, CDCl_3) δ 0.88/0.95 (3H, 2d, $J = 6.3$ Hz), 1.16-1.25/1.85-2.42 (3H, 2m), 2.17/3.17 (1H, 2d, $J = 12.6$ Hz), 2.46 (3H, s), 2.58/2.82 (1H, 2d, $J = 14.4$ Hz), 3.74-3.91 (1H, m), 4.19-4.25/4.41-4.47 (1H, 2m), 7.36 (2H, d, $J = 8.1$ Hz), 7.69 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 17.3/17.4, 21.6, 31.2/29.7, 46.2/48.7, 51.9/51.8, 56.0/56.4, 63.4/63.1, 127.5/127.4, 129.9/129.8, 134.4/134.1, 143.8/143.0. EIMS: m/z (rel intensity) 286 ($\text{M}^+ - \text{I}$, 50), 251 (0.7), 184 (1), 155 (59), 131 (4), 91 (100), 65 (21), 41 (20). Anal. calcd for $\text{C}_{13}\text{H}_{17}\text{ClINO}_2\text{S}$: C, 37.74; H, 4.14; N, 3.39. Found: C, 37.77; H, 4.31; N, 3.24.

White solid. ^1H NMR (300 MHz, CDCl_3) δ 1.25 (1H, dd, $J = 11.7, 13.5$ Hz), 1.99-2.40 (3H, m), 2.28/3.21 (1H, 2d, $J = 12.6$ Hz), 2.45 (3H, s), 2.55-2.66/3.17-3.26 (2H, 2m), 3.73-3.97 (1H, m), 4.18/4.43 (1H, 2d, $J = 16.5/12.9$ Hz), 5.15 (1H, s), 5.27 (1H, s), 7.33/7.34 (2H, 2d, $J = 8.1$ Hz), 7.67 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 32.4/34.0, 41.6/41.8, 45.2/47.6, 49.7/49.9, 53.2/53.7, 63.3/63.7, 114.9/115.0, 127.4/127.6, 129.8/129.9, 134.1/134.5, 138.4/138.5, 143.9/144.1. ESIMS: m/z 474.0 ($\text{M}^+ + 1$). HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{Cl}_2\text{INO}_2\text{S}$ ($\text{M}^+ + 1$): 473.9554. Found: 473.9553.

White solid. Mp: 80-82 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.41-1.52 (1H, m), 1.88-2.04 (2H, m), 2.19-2.28 (1H, m), 2.45 (3H, s), 3.27-3.36 (1H, m), 3.43-3.52 (1H, m), 4.01-4.06 (1H, m), 6.28 (1H, dd, $J = 0.9, 2.7$ Hz), 7.36 (2H, d, $J = 8.4$ Hz), 7.74 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 21.4, 24.3, 26.3, 50.1, 65.4, 75.5, 127.3, 129.8, 133.6, 144.0. EIMS: m/z (rel intensity) 307 (M^+ , 0.1), 272 (0.3), 224 (83), 155 (47), 139 (2), 91 (100), 65 (22), 41 (14). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{Cl}_2\text{NO}_2\text{S}$: C, 46.76; H, 4.91; N, 4.54. Found: C, 46.95; H, 4.91; N, 4.34.

White solid. Mp: 112-114 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.33-1.48 (1H, m), 1.91-2.08/2.21-2.31 (3H, 2m), 2.45 (3H, s), 3.12-3.16/4.17-4.25 (1H, 2m), 3.39-3.51 (2H, m), 6.28/6.32 (1H, 2d, J = 2.4/3.0 Hz), 7.35 (2H, d, J = 8.1 Hz), 7.71/7.74 (2H, 2d, J = 8.1 Hz). ^{13}C NMR (CDCl_3) δ 21.6, 24.2/24.6, 28.9/30.8, 35.7/40.6, 50.3/51.2, 65.8/67.5, 127.5/127.6, 129.9, 134.3, 144.0/144.2. EIMS: m/z (rel intensity) 399 (M^+ , 0.9), 376 (0.7), 272 (2), 224 (100), 205 (11), 155 (41), 125 (11), 91 (68). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{ClINO}_2\text{S}$: C, 36.06; H, 3.78; N, 3.50. Found: C, 36.27; H, 3.85; N, 3.42

White solid. ^1H NMR (300 MHz, CDCl_3) δ 0.47/0.54 (3H, 2s), 1.07/1.08 (3H, 2s), 1.80-2.14 (2H, m), 2.44 (3H, s), 3.13-3.42/4.32-4.39 (3H, 2m), 6.40/6.49 (1H, 2d, J = 3.0 Hz), 7.32/7.33 (2H, 2d, J = 8.1 Hz), 7.71-7.77 (2H, m). ^{13}C NMR (CDCl_3) δ 21.6, 25.3/25.4, 26.0/26.6, 35.0/37.7, 38.1/45.1, 42.7/42.8, 61.6/62.6, 65.5/67.0, 127.3/127.5, 129.8, 135.6/136.0, 143.8/144.0. ESIMS: m/z 428.0 (M^++1). HRMS calcd for $\text{C}_{14}\text{H}_{19}\text{ClINO}_2\text{SNa}$: (M^++Na) 449.9769. Found: 449.9762.

White solid. Mp: 116-118 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.30-1.47 (1H, m), 1.93-2.22 (3H, m), 2.45 (3H, s), 3.20-3.28/4.01-4.06 (1H, 2m), 3.43-3.53 (2H, m), 6.08-6.11 (1H, m), 7.35 (2H, d, J = 8.1 Hz), 7.72 (1H, d, J = 8.1 Hz), 7.73 (1H, d, J = 8.1 Hz). ^{13}C NMR (CDCl_3) δ 20.9/24.0, 21.6, 24.3/24.6, 30.3/31.6, 50.6/51.2, 65.9/67.2, 127.5/127.6, 129.9, 134.4, 144.1. ESIMS: m/z 445.8 ($\text{M}^+(\text{}^{81}\text{Br})+1$), 443.8 ($\text{M}^+(\text{}^{79}\text{Br})+1$). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{BrINO}_2\text{S}$: C, 32.45; H, 3.40; N, 3.15. Found: C, 32.63; H, 3.49; N, 3.07.

White solid. Mp: 130-132 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.33-1.45 (1H, m), 1.85-2.04 (2H, m), 2.17-2.30 (1H, m), 2.45 (3H, s), 3.24-3.30 (1H, m), 3.49-3.54 (2H, m), 5.71 (1H, d, $J = 2.7$ Hz), 7.35 (2H, d, $J = 8.1$ Hz), 7.72 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ -10.5, 21.6, 24.4, 32.9, 51.3, 66.8, 127.5, 129.9, 134.4, 144.1. ESIMS: m/z 491.8 ($\text{M}^+ + \text{H}$). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{I}_2\text{NO}_2\text{S}$: C, 29.35; H, 3.08; N, 2.85. Found: C, 29.62; H, 3.13; N, 2.68.

White solid. ^1H NMR (300 MHz, CDCl_3) δ 1.78-2.10 (3H, m), 2.18-2.29/2.47-2.59 (1H, 2m), 2.43/2.45 (3H, 2s), 3.17-3.25/3.66-3.74 (1H, 2m), 3.48-3.63 (1H, m), 4.13-4.22/4.29-4.36 (1H, 2m), 4.93/5.46 (1H, 2d, $J = 10.2/4.5$ Hz), 7.29/7.32 (1H, 2d, $J = 8.1$ Hz), 7.42/7.52 (1H, 2s), 7.75 (1H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.6, 22.9/23.5, 32.1/29.5, 45.7/48.2, 58.7/57.0, 64.7/62.7, 123.8/124.4, 129.8/129.6, 129.9/129.8, 134.1/133.8, 134.9/134.6, 143.3/143.4. EIMS: m/z (rel intensity) 271 (M^+ , 21), 236 (4), 172 (100), 157 (8), 138 (22), 115 (10), 103 (39), 77 (17). HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{ClNO}_2\text{S}$: ($\text{M}^+ + 1$) 272.0499. Found: 272.0507.

White solid. Mp: 124-126 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.04/1.20 (3H, 2s), 1.17/1.22 (3H, 2s), 1.51-1.59/2.27-2.35 (1H, 2m), 1.81-1.95 (1H, m), 2.43/2.46 (3H, 2s), 2.72/3.23 (1H, 2d, $J = 9.6$ Hz), 3.33/3.47 (1H, 2d, $J = 9.6$ Hz), 4.22-4.31/4.43-4.51 (1H, 2m), 4.96/5.55 (1H, 2d, $J = 10.5/5.4$ Hz), 7.26-7.33 (1H, m), 7.47-7.51 (1H, m), 7.72-7.77 (1H, m). ^{13}C NMR (CDCl_3) δ 21.7/21.6, 26.2/25.8,

26.9/27.2, 36.8/37.6, 43.0/46.5, 57.7/56.3, 61.0/59.6, 62.9/64.6, 123.8/124.6, 129.3/129.5, 129.6/129.8, 133.9/133.5, 135.0, 143.4/143.2. EIMS: m/z (rel intensity) 299 (M^+ , 22), 264 (4), 220 (4), 200 (100), 167 (9), 144 (18), 139 (22), 103 (32). Anal. calcd for $C_{14}H_{18}ClNO_2S$: C, 56.08; H, 6.05; N, 4.67. Found: C, 56.07; H, 5.98; N, 4.47.

White solid. Mp: 128-130 °C. 1H NMR (300 MHz, $CDCl_3$) δ 1.96-2.10 (3H, m), 2.42 (3H, s), 2.51-2.62 (1H, m), 3.47-3.56 (1H, m), 3.67-3.75 (1H, m), 4.29-4.40 (1H, m), 5.07 (1H, d, $J = 10.2$ Hz), 7.27 (1H, d, $J = 8.1$ Hz), 7.53 (1H, s), 7.74 (1H, d, $J = 8.1$ Hz). ^{13}C NMR ($CDCl_3$) δ 21.5, 22.7, 33.0, 46.0, 49.6, 65.0, 123.9, 129.9, 131.7, 134.4, 135.0, 143.2. EIMS: m/z (rel intensity) 317 ($M^+(^{81}Br)$, 10), 315 ($M^+(^{79}Br)$, 10), 236 (46), 172 (100), 157 (14), 144 (17), 115 (15), 103 (54). HRMS calcd for $C_{12}H_{15}BrNO_2S$: (M^++1) 315.9989. Found: 316.0001.

White solid. 1H NMR (300 MHz, $CDCl_3$) δ 1.64-2.05 (4H, m), 2.43 (3H, s), 3.27-3.33 (1H, m), 3.47-3.50 (1H, m), 4.31-4.35 (1H, m), 5.33 (1H, s), 5.57 (1H, s), 7.32 (2H, d, $J = 8.1$ Hz), 7.73 (2H, d, $J = 8.1$ Hz). ^{13}C NMR ($CDCl_3$) δ 21.5, 23.8, 31.1, 49.1, 64.3, 113.6, 127.5, 129.7, 135.2, 141.8, 143.6. EIMS: m/z (rel intensity) 285 (M^+ , 2), 224 (57), 155 (41), 130 (11), 102 (9), 91 (100), 65 (29), 41 (19). HRMS calcd for $C_{13}H_{17}ClNO_2S$: (M^++1) 286.0664. Found: 286.0663.

White solid. 1H NMR (300 MHz, $CDCl_3$) δ 1.43-1.52 (2H, m), 1.72-1.81 (2H, m), 2.44 (3H, s), 2.78 (2H, d, $J = 5.1$ Hz), 3.17 (2H, d, $J = 6.6$ Hz), 3.87 (2H, s), 7.32 (2H, d, $J = 8.1$ Hz), 7.70 (2H, d, $J = 8.1$

Hz). ^{13}C NMR (CDCl_3) δ 14.4, 21.6, 26.4, 27.0, 49.6, 57.1, 68.2, 127.5, 129.8, 135.4, 143.8. EIMS: m/z (rel intensity) 377 ($\text{M}^+ - \text{HI}$, 1), 333 (17), 319 (12), 302 (17), 256 (14), 202 (40), 103 (100), 77 (47). Anal. calcd for $\text{C}_{13}\text{H}_{17}\text{I}_2\text{NO}_2\text{S}$: C, 30.91; H, 3.39; N, 2.77. Found: C, 31.11; H, 3.48; N, 2.43.

White solid. ^1H NMR (300 MHz, CDCl_3) δ 1.50-1.58 (1H, m), 1.68-1.80 (3H, m), 2.44 (3H, s), 2.65-2.73 (1H, m), 2.82-2.86 (1H, m), 3.10-3.18 (1H, m), 3.21-3.29 (1H, m), 3.95 (1H, d, $J = 15.0$ Hz), 4.05 (1H, d, $J = 15.0$ Hz), 7.32 (2H, d, $J = 8.1$ Hz), 7.71 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 24.8, 27.3, 43.5, 49.8, 54.6, 66.9, 127.5, 129.8, 135.6, 143.7. ESIMS: m/z 457.9 ($\text{M}^+ + 1$). Anal. calcd for $\text{C}_{13}\text{H}_{17}\text{BrINO}_2\text{S}$: C, 34.08; H, 3.74; N, 3.06. Found: C, 34.21; H, 3.89; N, 2.83.

White solid. Mp: 104-106 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 1.45-1.52 (1H, m), 1.69-1.86 (3H, m), 2.44 (3H, s), 2.55-2.64 (1H, m), 2.75-2.84 (1H, m), 2.97-3.06 (1H, m), 3.35-3.42 (1H, m), 3.93 (1H, d, $J = 15.0$ Hz), 4.10 (1H, d, $J = 15.0$ Hz), 7.32 (2H, d, $J = 8.1$ Hz), 7.71 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.5, 23.6, 27.6, 49.7, 53.4, 57.0, 66.4, 127.4, 129.8, 135.7, 143.7. EIMS: m/z (rel intensity) 286 ($\text{M}^+ - \text{I}$, 42), 155 (51), 139 (5), 130 (11), 96 (16), 91 (100), 65 (25), 42 (26). Anal. calcd for $\text{C}_{13}\text{H}_{17}\text{ClINO}_2\text{S}$: C, 37.74; H, 4.14; N, 3.39. Found: C, 37.78; H, 3.93; N, 3.18.

White solid. ^1H NMR (300 MHz, CDCl_3) δ 1.23 (3H, s), 1.31 (3H, s), 1.53-1.80 (3H, m), 1.94-2.05 (1H, m), 2.43 (3H, s), 3.01-3.11 (1H, m), 3.35-3.45 (1H, m), 3.92 (1H, d, $J = 15.0$ Hz), 4.29 (1H, d, $J = 15.0$ Hz), 7.32 (2H, d, $J = 8.1$ Hz), 7.70 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 21.6, 21.8, 29.0, 29.8,

32.3, 46.9, 47.6, 62.0, 127.4, 129.7, 135.9, 143.6. ESIMS: m/z 442 ($M^+ + 1$). HRMS calcd for $C_{15}H_{22}ClINO_2S$ ($M^+ + 1$): 442.0100. Found: 442.0099.

White solid. 1H NMR (300 MHz, $CDCl_3$) δ 0.96/1.04 (3H, 2s), 1.13-1.26 (1H, m), 1.28/1.36 (3H, 2s), 1.42-1.53 (1H, m), 1.64-1.87 (1H, m), 2.04-2.22 (1H, m), 2.43 (3H, s), 3.46-3.71 (2H, m), 4.44/5.89 (1H, 2d, $J = 4.2$ Hz), 4.51/5.81 (1H, 2d, $J = 3.9$ Hz), 7.30 (2H, d, $J = 7.8$ Hz), 7.79/7.88 (2H, 2d, $J = 8.4$ Hz). ^{13}C NMR ($CDCl_3$) δ 9.2/9.6, 20.6/20.8, 21.8, 28.4, 29.2/29.3, 31.9, 35.2/35.6, 41.4/41.9, 67.4/67.8, 127.5/127.8, 129.4/129.6, 137.6/137.9, 143.3/143.4. EIMS: m/z (rel intensity) 359 ($M^+ (^{81}Br)\text{-HI}$, 0.7), 357 ($M^+ (^{79}Br)\text{-HI}$, 0.6), 266 (100), 200 (3), 155 (34), 110 (18), 91 (78), 65 (25). Anal. calcd for $C_{15}H_{21}BrINO_2S$: C, 37.05; H, 4.35; N, 2.88. Found: C, 37.17; H, 4.27; N, 2.54.

References for known compounds

Compound	Reference
4	Larock, R. C.; Yang, H.; Weinreb, S. M.; Herr, R. J. <i>J. Org. Chem.</i> 1994 , 59; 4172.
6a	Larock, R. C.; Tu, C.; Pace, P. <i>J. Org. Chem.</i> 1998 , 63 6859.
26a	Larock, R. C.; Tu, C.; Pace, P. <i>J. Org. Chem.</i> 1998 ; 63; 6859.
27a	Shaw, R. W.; Gallagher, T. <i>J. Chem. Soc. Perkin Trans. 1</i> , 1994 , 24, 3549.
27b	Jonasson, C.; Horvath, A.; Baeckvall, J. <i>J. Am. Chem. Soc.</i> 2000 , 122, 9600.

Computational (UB3LYP/6-31G*) Results on the Cyclization of Radicals A

A (R = H)

%chk=A (R = H)-radical

ub3lyp/6-31g* opt freq=noraman

calculate for A (R = H)-radical HF = -1070.160748

0 2

C

C 1 1.529347

C 2 1.540128 1 112.077367

C	3	1.504719	2	112.555643	1	178.041340
C	4	1.333216	3	125.179973	2	119.181726
N	1	1.453659	2	110.591063	3	-179.696219
S	6	1.703932	1	112.363048	2	-178.913833
O	7	1.471406	6	107.641064	1	-67.031648
O	7	1.471275	6	108.016380	1	64.781482
C	7	1.784831	6	101.610355	1	178.871483
C	10	1.395128	7	119.453987	6	90.139758
C	11	1.393181	10	118.938541	7	179.763193
C	12	1.402146	11	121.186913	10	-0.022710
C	13	1.402652	12	118.507770	11	-0.568559
C	14	1.392545	13	121.171437	12	0.567845
C	13	1.509917	12	120.841090	11	178.696207
H	1	1.103281	2	111.092206	3	-58.558133
H	1	1.102693	2	111.177129	3	58.687343
H	2	1.096307	1	109.247906	6	58.448650
H	2	1.097334	1	108.928058	6	-57.704046
H	3	1.098100	2	109.840242	1	-59.463701
H	3	1.101299	2	108.683872	1	56.728782
H	5	1.086702	4	121.818960	3	-179.673795
H	5	1.088430	4	121.678727	3	0.558440
H	4	1.091600	3	115.696806	2	-60.156887
H	11	1.084760	10	120.013898	7	0.780311
H	12	1.087124	11	119.336010	10	-179.589648
H	14	1.087187	13	119.492457	12	-178.974526
H	15	1.084742	14	121.061595	13	-178.931024
H	16	1.094603	13	111.535770	12	26.394425
H	16	1.094931	13	111.457496	12	147.426115
H	16	1.098086	13	110.898920	12	-93.182983

A (R = H)-TS (5-exo)

%chk= A (R = H)-TS (5-exo)

ub3lyp/6-31g* opt=(ts,noeigen,readfc,nofreeze) freq=noraman

calculate for A (R = H)-TS (5-exo) HF = -1070.147916

0 2

C

C 1 1.526559

C 2 1.535233 1 105.946158

S 1 2.634537 2 138.100474 3 34.434163

O 4 1.473743 1 89.336615 2 151.799275

O 4 1.473492 1 100.784068 2 -89.060638

C 3 1.515099 2 110.288980 1 -46.751871

C 7 1.387601 3 120.988820 2 137.572840

N 1 1.468013 2 104.842617 3 51.858390

C 4 1.792724 1 131.489501 2 37.046853

C 10 1.397696 4 119.806151 1 53.710142

C 11 1.391329 10 119.176973 4 177.164661

C 12 1.404465 11 121.204440 10 -0.797587

C 13 1.399991 12 118.396216 11 0.346188

C 10 1.393343 4 119.246613 1 -130.056246

C	13	1.510273	12	120.529126	11	-178.585367
H	1	1.097062	2	111.932647	3	169.234526
H	1	1.100017	2	110.633233	3	-70.450573
H	2	1.096745	1	109.388248	9	-66.931001
H	2	1.095404	1	111.651727	9	173.794334
H	3	1.097070	2	109.859064	1	73.629946
H	3	1.097807	2	110.986899	1	-168.069032
H	7	1.086686	3	115.898223	2	-70.558400
H	8	1.085533	7	121.085798	3	-20.725742
H	8	1.084942	7	121.351342	3	166.737809
H	11	1.084818	10	120.021075	4	-3.235173
H	12	1.087569	11	119.364955	10	179.528015
H	14	1.087306	13	119.488495	12	-179.916322
H	15	1.084799	10	119.493678	4	3.087936
H	16	1.095754	13	111.456730	12	-42.919375
H	16	1.097840	13	110.991095	12	76.352389
H	16	1.094396	13	111.529301	12	-163.841149

A (R = H)-TS (6-endo)

%chk= A (R = H)-TS (6-endo)

ub3lyp/6-31g* opt=(ts,noeigen,readfc,nofreeze) freq=noraman

calculate for A (R = H)-TS (6-endo) HF = -1070.145060

0 2

C

C	1	1.496264				
C	2	1.374053	1	120.024211		
N	3	2.147630	2	96.966989	1	64.235063
C	4	1.473833	3	101.549847	2	-58.335022
C	5	1.532479	4	111.282697	3	60.076344
S	4	1.694531	3	106.120518	2	-174.965232
O	7	1.475756	4	112.682845	3	40.552707
O	7	1.473804	4	106.412930	3	172.651177
C	7	1.791942	4	100.662422	3	-73.976634
C	10	1.393347	7	119.329207	4	118.342382
C	11	1.395970	10	119.164102	7	178.105468
C	12	1.399788	11	121.151490	10	-0.260946
C	13	1.404709	12	118.428205	11	0.048260
C	14	1.390922	13	121.200811	12	-0.232949
C	13	1.510235	12	121.071068	11	-178.916017
H	2	1.088658	1	118.103814	6	90.844336
H	1	1.098028	2	110.711052	3	48.720914
H	1	1.095506	2	111.905840	3	168.820196
H	6	1.096398	5	109.156309	4	55.154022
H	6	1.097252	5	108.618793	4	171.895625
H	5	1.101475	4	112.464610	3	-63.968779
H	5	1.098761	4	106.919178	3	179.258565
H	3	1.085712	2	120.548826	1	171.043393
H	3	1.086109	2	120.949541	1	-29.553462
H	11	1.084869	10	119.569005	7	-1.706390

H	12	1.087278	11	119.354365	10	179.914486
H	14	1.087524	13	119.428263	12	-179.984637
H	15	1.084833	14	120.826415	13	-179.598422
H	16	1.094370	13	111.531642	12	-16.833351
H	16	1.097850	13	111.018637	12	103.011047
H	16	1.095777	13	111.425146	12	-137.737051

A (R = Me)-radical

%chk=A (R = Me)-radical

ub3lyp/6-31g* opt freq=noraman

calculate for A (R = Me)-radical HF = -1109.479262

0 2

C

C 1 1.529513

C 2 1.541398 1 111.777992

C 3 1.515160 2 113.763439 1 -179.128620

C 4 1.336919 3 121.347967 2 112.080874

N 1 1.453713 2 110.566222 3 -179.045682

S 6 1.703759 1 112.399142 2 -179.293483

O 7 1.471444 6 107.716820 1 -66.183642

O 7 1.471245 6 107.969876 1 65.637182

C	7	1.784888	6	101.583979	1	179.794357
C	10	1.395282	7	119.342408	6	89.222674
C	11	1.392907	10	118.958527	7	179.840072
C	12	1.402237	11	121.178367	10	-0.060412
C	13	1.402553	12	118.504538	11	-0.572544
C	14	1.392787	13	121.183008	12	0.596225
C	13	1.509902	12	120.772937	11	178.661114
C	4	1.510151	3	116.865050	2	-68.301186
H	1	1.103126	2	111.065754	3	-57.886802
H	1	1.102805	2	111.215344	3	59.368534
H	2	1.096409	1	109.209547	6	59.409275
H	2	1.096160	1	108.598588	6	-56.712266
H	3	1.097419	2	109.062122	1	-56.786220
H	3	1.101281	2	108.608921	1	58.920334
H	5	1.087348	4	121.773647	3	-179.909670
H	5	1.087427	4	121.796964	3	0.193100
H	11	1.084760	10	120.004220	7	0.867532
H	12	1.087118	11	119.334613	10	-179.602187
H	14	1.087197	13	119.481891	12	-178.987076
H	15	1.084753	14	121.057592	13	-178.976284
H	16	1.094616	13	111.505539	12	26.939466
H	16	1.094942	13	111.504309	12	147.981770
H	16	1.098106	13	110.890076	12	-92.600263
H	17	1.098854	4	110.949406	3	-57.428255
H	17	1.097831	4	111.795934	3	61.322738
H	17	1.094047	4	111.480422	3	-177.954226

A (R = Me)-TS (5-exo)

%chk=A (R = Me)-TS (5-exo)

ub3lyp/6-31g* opt=(ts,noeigen,readfc,nofreeze) freq=noraman

calculate for A (R = Me)-TS (5-exo) HF = -1109.464588

0 2

C

C	1	1.525213				
C	2	1.535563	1	105.784193		
S	1	2.622129	2	138.981420	3	33.596069
O	4	1.473782	1	89.503567	2	150.299552
O	4	1.474053	1	100.195093	2	-90.696199
C	3	1.525056	2	110.792419	1	-47.010461
C	7	1.396626	3	118.012376	2	132.929859
N	1	1.469622	2	105.006339	3	50.534081
C	4	1.793337	1	132.437894	2	35.322573
C	10	1.398284	4	119.848264	1	55.626251
C	11	1.391341	10	119.203890	4	177.305550
C	12	1.404964	11	121.181556	10	-0.771325
C	13	1.399643	12	118.390655	11	-0.150217
C	10	1.393063	4	119.226758	1	-128.376490
C	13	1.510299	12	120.468203	11	179.558941
C	7	1.515757	3	116.258421	2	-77.801994
H	1	1.096981	2	112.070111	3	168.393694

H	1	1.100101	2	110.441306	3	-71.423391
H	2	1.096260	1	109.798838	9	-68.907619
H	2	1.095423	1	111.549274	9	171.951835
H	3	1.096265	2	109.345536	1	73.554115
H	3	1.097877	2	111.020837	1	-168.390856
H	8	1.084636	7	121.285016	3	-20.568611
H	8	1.085678	7	121.063765	3	167.130552
H	11	1.084893	10	119.992441	4	-2.739802
H	12	1.087618	11	119.369854	10	179.784631
H	14	1.087230	13	119.475819	12	-179.259467
H	15	1.084754	10	119.464247	4	2.715336
H	16	1.097688	13	111.166416	12	-69.906564
H	16	1.096125	13	111.338924	12	49.329717
H	16	1.094196	13	111.492016	12	169.989538
H	17	1.093006	7	111.200642	3	168.699725
H	17	1.098498	7	109.440286	3	-71.728066
H	17	1.092580	7	111.544478	3	48.038408

A (R = Me)-TS (6-endo)

%chk= A (R = Me)-TS (6-endo)

ub3lyp/6-31g* opt=(ts,noeigen,readfc,nofreeze) freq=noraman

calculate for A (R = Me)-TS (6-endo) HF = -1109.466815

0 2

C

C 1 1.504635

C 2 1.376817 1 117.518672

N 3 2.151597 2 96.888902 1 65.911383

C 4 1.473495 3 101.015119 2 -61.111721

C 5 1.532234 4 110.993278 3 60.429136

S 4 1.690611 3 106.369336 2 -177.710399

O 7 1.476192 4 112.724710 3 40.174382

O 7 1.474208 4 106.710195 3 172.415619

C 7 1.792736 4 100.687171 3 -74.317696

C 10 1.393367 7 119.427634 4 116.299615

C 11 1.395999 10 119.191254 7 178.005016

C 12 1.399910 11 121.135633 10 -0.280091

C 13 1.404532 12 118.425147 11 0.081587

C 14 1.391177 13 121.198328 12 -0.243272

C 13 1.510356 12 121.035993 11 -178.722017

C 2 1.499031 1 118.392213 6 93.553651

H 1 1.097664 2 110.621933 3 48.245175

H 1 1.096413 2 111.669132 3 167.970723

H 6 1.096735 5 109.049505 4 56.048990

H 6 1.097109 5 108.632419 4 172.542800

H 5 1.101719 4 112.435279 3 -63.302144

H 5 1.098672 4 107.264254 3 179.732611

H 3 1.086139 2 120.381918 1 172.700954

H 3 1.085260 2 121.117664 1 -27.781687

H 11 1.084905 10 119.520563 7 -1.687978

H 12 1.087336 11 119.367753 10 179.954606

H	14	1.087552	13	119.418049	12	-179.936835
H	15	1.084870	14	120.847360	13	-179.423107
H	16	1.094475	13	111.530275	12	-19.088930
H	16	1.097942	13	110.998430	12	100.680211
H	16	1.095640	13	111.457559	12	-140.035714
H	17	1.093838	2	112.101583	1	-173.830759
H	17	1.100324	2	110.935335	1	-53.035194
H	17	1.098934	2	110.834072	1	64.934087

A (R = Cl)-radical

%chk=A (R = Cl)-radical

ub3lyp/6-31g* opt freq=noraman

calculate for A (R = Cl)-radical HF = -1529.759272

0 2

C

C 1 1.529728

C 2 1.539800 1 111.489882

C 3 1.504098 2 113.866643 1 179.897041

C 4 1.330892 3 126.272591 2 113.017371

N 1 1.453294 2 110.305333 3 -179.466433

S 6 1.704438 1 112.315527 2 -177.136909

O	7	1.470958	6	108.119393	1	-63.604226
O	7	1.471515	6	107.377043	1	68.082451
C	7	1.784114	6	101.587163	1	-177.883652
C	10	1.395160	7	119.371371	6	91.010081
C	11	1.393112	10	118.929787	7	179.892417
C	12	1.402098	11	121.185801	10	-0.054875
C	13	1.402782	12	118.511584	11	-0.583635
C	14	1.392464	13	121.179497	12	0.604841
C	13	1.509798	12	120.808981	11	178.623516
Cl	4	1.774270	3	114.367983	2	-66.970802
H	1	1.103073	2	111.082235	3	-58.702719
H	1	1.102758	2	111.347666	3	58.761927
H	2	1.096049	1	109.330754	6	59.045552
H	2	1.094911	1	109.126460	6	-57.700732
H	3	1.097467	2	109.740154	1	-59.461490
H	3	1.098698	2	109.422465	1	57.564733
H	5	1.084030	4	122.519157	3	-179.858130
H	5	1.086347	4	119.693365	3	0.278484
H	11	1.084749	10	120.027807	7	0.854089
H	12	1.087069	11	119.328194	10	-179.641653
H	14	1.087176	13	119.487487	12	-178.978033
H	15	1.084734	14	121.056737	13	-178.981484
H	16	1.094566	13	111.524340	12	26.179415
H	16	1.094978	13	111.501194	12	147.227252
H	16	1.098073	13	110.868417	12	-93.381540

A (R = Cl)-TS (5-exo)

%chk= A (R = Cl)-TS (5-exo)

ub3lyp/6-31g* opt=(ts,noeigen,readfc,nofreeze) freq=noraman

calculate for A (R = Cl)-TS (5-exo) HF = -1529.739485

0 2

C

C	1	1.526978				
C	2	1.530979	1	105.255828		
S	1	2.628721	2	137.876333	3	29.089174
O	4	1.472428	1	88.940125	2	156.405997
O	4	1.473987	1	99.571486	2	-84.578469
C	3	1.517749	2	110.439870	1	-49.559284
C	7	1.388995	3	121.584845	2	140.011038
N	1	1.469710	2	105.153052	3	49.419485
C	4	1.789572	1	132.385706	2	41.180783
C	10	1.398116	4	119.857541	1	51.459126
C	11	1.390609	10	119.080213	4	176.817977
C	12	1.404796	11	121.224624	10	-0.697209
C	13	1.399749	12	118.435172	11	0.046390
C	10	1.393430	4	119.043378	1	-132.756560
C	13	1.510104	12	120.376047	11	-179.828955
Cl	7	1.783814	3	113.710251	2	-75.029119
H	1	1.096685	2	112.059321	3	166.826329

H	1	1.099754	2	110.410574	3	-72.802506
H	2	1.095149	1	110.186104	9	-69.358439
H	2	1.094866	1	111.556844	9	170.560151
H	3	1.097044	2	109.753965	1	68.785567
H	3	1.095320	2	112.160425	1	-171.533173
H	8	1.084267	7	119.323907	3	-26.866509
H	8	1.082844	7	121.600284	3	162.133224
H	11	1.084460	10	120.104212	4	-3.896362
H	12	1.087441	11	119.307598	10	179.461214
H	14	1.087126	13	119.502719	12	-179.652546
H	15	1.084748	10	119.619001	4	3.387026
H	16	1.096900	13	111.222209	12	-59.384370
H	16	1.096872	13	111.179456	12	59.765373
H	16	1.094126	13	111.548504	12	-179.852534

A (R = Cl)-TS (6-endo)

%chk=A (R = Cl)-TS (6-endo)

ub3lyp/6-31g* opt=(ts,noeigen,readfc,nofreeze) freq=noraman

calculate for A (R = Cl)-TS (6-endo) HF = -1529.745322

0 2

C

C	1	1.497661				
C	2	1.369642	1	121.051102		
N	3	2.163495	2	97.066080	1	62.613091
C	4	1.473427	3	101.862160	2	-56.952330
C	5	1.532797	4	111.373198	3	59.563257
S	4	1.696690	3	105.855333	2	-173.437922
O	7	1.475905	4	112.191323	3	40.660433
O	7	1.473096	4	106.400779	3	172.571077
C	7	1.790411	4	100.726509	3	-73.885328
C	10	1.393413	7	119.376119	4	117.360033
C	11	1.395941	10	119.125522	7	178.196453
C	12	1.399758	11	121.149649	10	-0.221229
C	13	1.404824	12	118.441950	11	0.018174
C	14	1.390634	13	121.211662	12	-0.201632
C	13	1.510100	12	121.082369	11	-179.048341
Cl	2	1.750032	1	116.576813	6	90.930560
H	1	1.097583	2	108.989585	3	49.632398
H	1	1.093490	2	111.639980	3	168.688671
H	6	1.095838	5	109.473305	4	55.093888
H	6	1.096780	5	108.590316	4	172.128422
H	5	1.101726	4	112.403867	3	-64.540742
H	5	1.098783	4	106.967119	3	178.814339
H	3	1.083955	2	121.048213	1	169.645993
H	3	1.085297	2	119.155513	1	-31.354008
H	11	1.084858	10	119.626099	7	-1.526833
H	12	1.087188	11	119.345038	10	179.952480
H	14	1.087424	13	119.434918	12	179.970759
H	15	1.084791	14	120.812287	13	-179.633305
H	16	1.094262	13	111.522987	12	-15.114020

H	16	1.097753	13	111.014349	12	104.792446
H	16	1.095828	13	111.390754	12	-135.974351

spec, CIOCI3,				USER: hp -- DATE: Thu Jul 14 01:16:02 2005	
F1: 75.475	F2: 1.000	SW1: 22676	OF1: 7548.2	PTSID: 32768	
EX: 29pg30	PW: 8.5 usec	PD: 2.0 sec	NA: 2048	LB: 0.0	WinNuts - J481C

spect. CDCl ₃ .		USER: hp -- DATE: Sat Aug 20 21:18:30 2005	
F1: 75.475	F2: 1.000	SW1: 22676	PTSLd: 32768
EX: zgpg30	PW: 8.5 usec	PD: 2.0 sec	WinNuts - J702C
		NA: 4096	LB: 0.0

6j203

F1: 300.055	F2: 75.456	SW1: 4803	PD: 1.0 sec	OE1: 1803.2	NA: 16	LB: 0.0	PTSLD: 16384
EX: s2pul		PW: 5.8 usec					

USER: -- DATE: Jul 21 2005

WinNuts - SJS92_21Jul2005

USER: sioc -- DATE: Thu May 18 10:21:19 2006

spec, CDC13,		USER: hp -- DATE: Mon Sep 19 18:49:04 2005	
F1: 75.475	F2: 1.000	SW1: 22676	PTSID: 32768
EX: 29pg30	PW: 8.5 usec	PD: 2.0 sec	WinNuts - K221C
		NA: 1024	
		LB: 0.0	