Supporting Information for

Silver-Catalyzed Decarboxylative Bromination of Aliphatic Carboxylic Acids

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Table of Contents

1. General Information. ............................................. S2
2. Synthesis of Substrates. ........................................ S2 – S3
3. Typical Procedure for Decarboxylative Bromination. ... S3 – S4
4. Characterizations of New Products. ......................... S4 – S11
5. References for Known Compounds. ......................... S11 – S12
6. $^1$H and $^{13}$C NMR Spectra of All Products. .......... S12 – S33
1. General Information.

All reagents were obtained commercially unless otherwise noted. Dichloromethane, 1,2-dichloroethane, acetonitrile were distilled over calcium hydride prior to use. All reactions were performed using standard schlenk techniques under argon. Purification of products was accomplished using flash chromatography on silica gel 60 (40-63 µm). Thin layer chromatography was performed on silica gel 60 F254 plates (250 µm). Nuclear magnetic resonance (NMR) spectra were recorded on an Agilent 400 or Bruker 400 instrument operating at 400, 100, and 376 MHz for 1H, 13C, 19F, respectively. Chemical shifts were reported in δ ppm referenced to an internal SiMe₄ standard for 1H NMR, chloroform-d (δ 77.00) for 13C NMR. Multiplicities were reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI mode.

2. Synthesis of Substrates

The following substrates were commercially available and recrystallized prior to use: 2-methyl-4-oxo-4-phenylbutanoic acid (1d), 1-adamantanecarboxylic acid (1i), 2-(2-iodophenyl)acetic acid (1m), 2-(3-bromophenyl)acetic acid (1n), 2-(3-(trifluoromethoxy)phenyl)acetic acid (1o), 2-(4-(tert-butyl)phenyl)acetic acid (1p), 2-([1,1'-biphenyl]-4-yl)acetic acid (1q), 2-(p-tolyl)acetic acid (1r), 2-phenylbutanoic acid (1t), 2-cyclohexyl-2-phenylacetic acid (1v), 11-bromoundecanoic acid (1z), 2,2-dimethylpentanediolic acid (6). The rest substrates were known compounds (except 1h) and readily prepared by conventional methods.

Characterizations of New Substrates:
(1-(4-(Trifluoromethyl)benzoyl)piperidine-4-carboxylic acid). This compound was prepared by reaction of 4-trifluoromethylbenzoyl chloride with ethyl piperidine-4-carboxylate followed by hydrolysis under basic conditions. Yield: 1.37 g (91% over two steps). White solid, mp: 152–154 °C; 1H NMR (400 MHz, CDCl₃): δ 9.85 (br, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 4.51 (br, 1H), 3.65 (br, 1H), 3.11 (br, 2H), 2.67-2.50 (m, 1H), 2.07 (br, 1H), 1.87 (br, 1H), 1.81 (br, 1H), 1.69 (br, 1H); 13C NMR (100 MHz, CDCl₃): δ 179.0, 169.2, 139.2, 131.8 (q, J = 32.0 Hz), 127.2, 125.7 (q, J = 3.6 Hz), 123.7 (q, J = 271.0 Hz), 46.8, 41.5, 40.5, 28.2, 27.6; 19F NMR (376 MHz, CDCl₃): δ -62.9 (s, 3F); IR (KBr): ν (cm⁻¹) 2956, 1729, 1602, 1450, 1326, 1169, 1126, 1065, 849, 735; EIMS: m/z (rel intensity) 301 (M⁺, 47), 300 (84), 282 (9), 254 (10), 228 (6), 173 (100), 145 (48), 128 (23), 95 (5), 82 (6); HRMS calcd for C₁₄H₁₄F₃NO₃ [M]: 301.0926; found: 301.0929.

3. Typical Procedure for Decarboxylative Bromination.

3-Bromopentadecane (3a). Typical Procedure. To a 20 mL schlenk tube equipped with a stir bar were added 2-ethyltetradecanoic acid (1a, 51 mg, 0.2 mmol), Ag(Phen)₂OTf (3 mg, 0.005 mmol) and dibromoisocyanuric acid (2c, 46 mg, 0.16 mmol) under argon atmosphere. 1, 2-Dichloroethane (8 mL) was then added. The Schlenk tube was sealed and stirred at room temperature for 24 h. Thin layer chromatography (TLC) indicated that the starting material 1a was all consumed. The reaction mixture was filtered. The white precipitate was washed with CH₂Cl₂ (3 × 2 mL) and dried. Isocyanuric acid was thus obtained as a white solid. Yield: 18 mg (90% based on 2c). The combined organic phase was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 50:1) to afford the pure product 3-bromopentadecane (3a) as a colorless oil. Yield: 51 mg (88%). 1H NMR (400 MHz, CDCl₃): δ 4.02–3.96 (m, 1H), 1.90–1.78 (m, 4H), 1.52 (br, 1H), 1.41 (br, 1H), 1.26 (br, 1H), 1.04 (t, J = 7.2
Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 60.6, 38.8, 32.2, 31.9, 29.69, 29.66, 29.60, 29.5, 29.4, 29.1, 27.6, 22.7, 14.1, 12.1; IR (neat): v (cm$^{-1}$) 2924, 2853, 1462, 1379, 797, 721; EIMS: m/z (rel intensity) 211 (32), 155 (7), 141 (11), 127 (14), 113 (16), 99 (27), 85 (72), 71 (90), 57 (100), 43 (45), 41 (34); HRMS calcd for C$_{15}$H$_{31}$ [M-Br]: 211.2426; found: 211.2431.

**Typical Procedure at 1.0 mmol Scale.** To a 100 mL 3-necked flask were added 2-ethyltetradecanoic acid (1a, 256 mg, 1.0 mmol), Ag(Phen)$_2$OTf (11 mg, 0.025 mmol) and dibromoisocyanuric acid (2c, 230 mg, 0.80 mmol) under argon atmosphere. 1, 2-Dichloroethane (40 mL) was then added. The mixture was stirred at room temperature for 24 h. Thin layer chromatography (TLC) indicated that the starting material 1a was all consumed. The resulting mixture was filtered. The white precipitate was washed with CH$_2$Cl$_2$ (3 x 5 mL) and dried. Isocyanuric acid was thus obtained as a white solid. Yield: 94 mg (91% based on 2c). The combined organic phase was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 50:1) to afford the pure product 3-bromopentadecane (3a) as a colorless oil. Yield: 250 mg (86%).


![3b](image)

**(2-Bromopropane-1,3-diyl)dicyclohexane.** Yield: 52 mg (91%). Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 4.24-4.16 (m, 1H), 1.82-1.51 (m, 16H), 1.33-1.08 (m, 6H), 1.02-0.90 (m, 2H), 0.88-0.75 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 54.0, 47.4, 35.7, 33.6, 32.2, 26.6, 26.2, 26.0; IR (neat): v (cm$^{-1}$) 2922, 2851, 1447, 1276, 1233, 1168, 937, 890, 844; EIMS: m/z (rel intensity) 207 (82), 151 (10), 137 (14), 125 (42), 111 (97), 97 (97), 83 (100), 69 (44), 55 (76), 41 (27); HRMS calcd for C$_{15}$H$_{27}$ [M-Br]:
1-(2-Bromobutyl)-4-nitrobenzene. Yield: 35 mg (68%). Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.19 (d, $J$ = 8.4 Hz, 2H), 7.39 (d, $J$ = 8.4 Hz, 2H), 4.18-4.11 (m, 1H), 3.33-3.18 (m, 2H), 2.00-1.80 (m, 2H), 1.11 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.0, 146.1, 130.1, 123.6, 57.8, 44.8, 31.8, 12.1; IR (neat): v (cm$^{-1}$) 2969, 2935, 1605, 1519, 1346, 1109, 1019, 856, 745, 698; EIMS: m/z (rel intensity) 259 (10), 257 (M$^+$, 11), 178 (50), 136 (51), 117 (35), 106 (24), 90 (23), 89 (20), 78 (22); HRMS calcd for C$_{10}$H$_{12}$BrNO$_2$ [M]: 257.0051; found: 257.0050.

1,6-Dibromooctane. Yield: 50 mg (93%). Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.02–3.94 (m, 1H), 3.42 (t, $J$ = 6.8 Hz, 2H), 1.92–1.78 (m, 6H), 1.62-1.41 (m, 4H), 1.04 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 60.2, 38.5, 33.7, 32.6, 32.2, 27.6, 26.8, 12.1; IR (neat): v (cm$^{-1}$) 2964, 2936, 2858, 1460, 1433, 1239, 896, 797, 732, 650; EIMS: m/z (rel intensity) 273 (6), 271 (12), 269 (6), 191 (46), 149 (18), 135 (15), 111 (73), 109 (47), 69 (100), 57 (38), 55 (69), 41 (53); HRMS calcd for C$_8$H$_{13}$Br$_2$ [M-H]: 268.9540; found: 268.9538.

2-((4-Bromocyclohexyl)methyl)isoindoline-1,3-dione. This compound was isolated as the mixture of two stereoisomers in about 1:1 ratio determined by $^1$H NMR (400 MHz). Yield: 49 mg (76%). White solid, mp: 96-98 °C; $^1$H NMR (400 MHz, CDCl$_3$) (mixture of two stereoisomers): $\delta$ 7.87-7.82 (m, 2H), 7.75-7.70 (m, 2H), 4.60 (t, $J$ =...
2.8 Hz, 0.5H), 4.02–3.93 (m, 0.5H), 3.62 (d, J = 7.2 Hz, 1H), 3.53 (d, J = 7.2 Hz, 1H), 2.36–2.26 (m, 1H), 2.14–2.06 (m, 1H), 1.94–1.52 (m, 6H), 1.25–1.10 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 168.5, 134.0/133.9, 132.0/131.9, 123.3/123.2, 53.6/51.3, 43.3/43.2, 37.2/36.0, 35.6/34.0, 31.3/25.4; IR (KBr): v (cm\(^{-1}\)) 2937, 1771, 1705, 1433, 1397, 1363, 1192, 1049, 935, 720, 533; EIMS: \(m/z\) (rel intensity) 323 (17), 321 (M\(^+\), 18), 280 (3), 242 (5), 201 (4), 160 (100), 148 (47), 130 (16), 105 (36), 94 (12), 77 (25), 67 (8); HRMS calcd for C\(_{15}\)H\(_{16}\)BrNO\(_2\) [M]: 321.0364; found: 321.0368.

3g

4-Bromo-1-tosylpiperidine. Yield: 44 mg (70%). White solid, mp: 132-134 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.65 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.27–4.21 (m, 1H), 3.24–3.16 (m, 2H), 3.14–3.05 (m, 2H), 2.44 (s, 3H), 2.23–2.14 (m, 2H), 2.09–2.01 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 143.7, 133.4, 129.8, 127.6, 47.8, 43.8, 34.7, 21.5; IR (KBr): v (cm\(^{-1}\)) 2920, 1596, 1342, 1164, 1092, 928, 859, 812, 745, 713, 697, 651, 578, 551; EIMS: \(m/z\) (rel intensity) 319 (5), 317 (M\(^+\), 6), 238 (70), 184 (51), 155 (73), 91 (100), 82 (14), 65 (17), 42 (19); HRMS calcd for C\(_{12}\)H\(_{16}\)BrNO\(_2\)S [M]: 317.0085; found: 317.0083.

3h

(4-Bromopiperidin-1-yl)(4-(trifluoromethyl)phenyl)methanone. Yield: 50 mg (75%). Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.69 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 4.48-4.42 (m, 1H), 3.95 (br, 1H), 3.80 (br, 1H), 3.62 (br, 1H), 3.32 (br, 1H), 2.22 (br, 1H), 2.07 (br, 2H), 1.94 (br, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 169.0, 139.2, 131.8 (q, J = 32.0 Hz), 127.2, 125.7 (q, J = 3.6 Hz), 123.7 (q, J = 271.0 Hz), 48.4, 45.6, 40.2, 36.0, 35.1; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -62.9 (s, 3F); IR (neat): v (cm\(^{-1}\)) 2957, 2868, 1639, 1440, 1325, 1281, 1203, 1167, 1128, 1065, 999, 851; EIMS: \(m/z\) (rel intensity) 337 (18), 336 (41), 335 (17), 334 (42), 318 (4), 256
(17), 173 (100), 145 (34), 86 (30), 84 (46); HRMS calcd for C\textsubscript{13}H\textsubscript{12}BrF\textsubscript{3}NO [M-H]: 334.0054; found: 334.0055.

![3j](image)

**2-Bromo-2-methylpropane-1,3-diyl diacetate.** Yield: 45 mg (89%). Colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 4.34 (d, \(J = 12.0\) Hz, 2H), 4.26 (d, \(J = 12.0\) Hz, 2H), 2.11 (s, 6H), 1.76 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 170.1, 68.4, 60.0, 25.6, 20.7; IR (neat): \(\nu\) (cm\textsuperscript{-1}) 2934, 1749, 1461, 1378, 1235, 1055, 1034, 900, 645, 602; EIMS: \(m/z\) (rel intensity) 173 (26), 131 (22), 122 (27), 120 (27), 113 (52), 103 (33), 71 (16), 43 (100); HRMS calcd for C\textsubscript{6}H\textsubscript{10}BrO\textsubscript{3} [M-COCH\textsubscript{3}]: 208.9813; found: 208.9815.

![3k](image)

**Cyclohexyl 4-bromo-4-methylpentanoate.** Yield: 46 mg (83%). Colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 4.80–4.74 (m, 1H), 2.59-2.53 (m, 2H), 2.14-2.09 (m, 2H), 1.87–1.83 (m, 2H), 1.76 (s, 6H), 1.74–1.69 (m, 2H), 1.58–1.52 (m, 1H), 1.47–1.20 (m, 5H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 172.5, 72.8, 66.4, 41.9, 34.2, 32.1, 31.6, 25.4, 23.8; IR (neat): \(\nu\) (cm\textsuperscript{-1}) 2936, 2859, 1774, 1730, 1450, 1170, 1108, 1015; EIMS: \(m/z\) (rel intensity) 197 (5), 195 (5), 179 (7), 177 (7), 115 (100), 97 (37), 82 (14), 69 (32), 55 (17), 41 (12); HRMS calcd for C\textsubscript{10}H\textsubscript{22}BrO\textsubscript{2} [M+H]: 277.0803; found: 277.0799.

![3l](image)

**(4-Bromo-4-methylpiperidin-1-yl)(phenyl)methanone.** Yield: 52 mg (92%). Colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.43-7.38 (m, 5H), 4.63 (br, 1H), 3.67 (br, 1H), 3.47 (br, 1H), 3.25 (br, 1H), 2.13 (br, 1H), 1.98 (br, 1H), 1.89 (s, 3H), 1.71 (br, 1H), 1.55 (br, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 170.4, 135.9, 129.7, 128.5,
126.9, 67.2, 45.3, 42.3, 41.5, 39.7, 34.9; IR (neat): ν (cm⁻¹) 2945, 2928, 1633, 1430, 1286, 1250, 1125, 1099, 966, 708; EIMS: m/z (rel intensity) 282 (9), 280 (9), 202 (11), 201 (21), 200 (7), 106 (9), 105 (100), 77 (36), 51 (10), 41 (6); HRMS calcd for C₁₅H₁₅BrNO [M-H]: 280.0337; found: 280.0344.

![3o]

**1-(Bromomethyl)-3-(trifluoromethoxy)benzene.** Yield: 44 mg (87%). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.37 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.25 (s, 1H), 7.15 (d, J = 8.0 Hz, 1H), 4.47 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 149.4 (q, J = 1.5 Hz), 139.9, 130.2, 127.3, 121.5, 120.8, 120.4 (q, J = 256.0 Hz), 31.9; ¹⁹F NMR (376 MHz, CDCl₃): δ -57.8 (s, 3F); IR (neat): ν (cm⁻¹) 2926, 2855, 1612, 1591, 1488, 1448, 1253, 1216, 1165, 795, 691, 632; EIMS: m/z (rel intensity) 256 (10), 254 (M⁺, 10), 176 (11), 175 (100), 109 (31), 83 (14), 78 (9), 77 (5), 69 (4); HRMS calcd for C₈H₆BrF₃O [M]: 253.9554; found: 253.9552.

![3u]

**2-Bromo-2-phenylethyl acetate.** Yield: 44 mg (91%). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.43–7.29 (m, 5H), 5.12 (t, J = 7.2 Hz, 1H), 4.60 (dd, J = 11.6, 7.2 Hz, 1H), 4.51 (dd, J = 11.6, 7.2 Hz, 1H), 2.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 170.4, 138.1, 129.0, 128.9, 127.8, 67.5, 49.9, 20.7; IR (neat): ν (cm⁻¹) 3028, 3021, 2933, 1746, 1454, 1366, 1232, 1038, 763, 698; EIMS: m/z (rel intensity) 184 (30), 182 (29), 163 (100), 120 (25), 117 (35), 107 (57), 104 (40), 103 (52), 91 (23), 79 (28), 77 (27), 43 (82); HRMS calcd for C₁₀H₁₁BrO₂ [M]: 241.9942; found: 241.9944.
(Bromo(cyclohexyl)methyl)benzene. Yield: 46 mg (92%). Colorless oil; \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): δ 7.36–7.23 (m, 5H), 4.70 (d, \( J = 8.8 \) Hz, 1H), 2.33–2.28 (m, 1H), 2.01–1.91 (m, 1H), 1.83–1.77 (m, 1H), 1.65–1.61 (m, 2H), 1.50–1.45 (m, 1H), 1.34–0.98 (m, 4H), 0.90–0.78 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 141.5, 128.4, 128.0, 127.9, 63.3, 45.4, 32.2, 31.0, 26.2, 26.0, 25.9; IR (neat): ν (cm\(^{-1}\)) 2924, 2854, 1462, 1379, 1285, 1200, 797, 721; EIMS: \( m/z \) (rel intensity) 174 (11), 173 (73), 130 (15), 129 (14), 128 (13), 117 (13), 115 (32), 105 (15), 91 (100), 81 (11); HRMS calcd for C\(_{13}\)H\(_{17}\)Br [M]: 252.0514; found: 252.0518.

Ethyl 2-(bromomethyl)-3,3-diphenylacrylate. Yield: 36 mg (52%). White solid, mp: 95–97 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.40–7.34 (m, 5H), 7.31–7.26 (m, 3H), 7.12–7.08 (m, 2H), 4.32 (s, 2H), 4.01 (q, \( J = 7.2 \) Hz, 2H), 0.89 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 168.6, 151.3, 141.6, 139.6, 129.1, 128.9, 128.86, 128.83, 128.5, 128.0, 61.1, 32.5, 13.6; IR (KBr): ν (cm\(^{-1}\)) 2926, 1712, 1598, 1490, 1444, 1367, 1260, 1150, 1102, 1019, 766, 700; EIMS: \( m/z \) (rel intensity) 346 (1), 344 (M\(^+\), 1), 265 (100), 219 (44), 192 (57), 191 (94), 190 (24), 189 (38), 165 (27), 115 (32), 91 (11); HRMS calcd for C\(_{18}\)H\(_{17}\)BrO\(_2\) [M]: 344.0412; found: 344.0418.

(5R,8R,9S,10S,13R,14S)-17-((2R)-4-Bromopentan-2-yl)-10,13-dimethylhexadecahydro-3H-cyclopenta[a]phenanthren-3-one. Yield: 72 mg (85%). This compound was isolated as the mixture of two stereoisomers in about 1:1 ratio determined by \(^1\)H NMR (400 MHz). White solid, mp: 118–120 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) (mixture of two stereoisomers): δ 4.30–4.15 (m, 1H), 2.69 (t, \( J = 14.4 \) Hz, 1H), 2.33 (td, \( J = 14.4, 5.2 \) Hz, 1H), 2.19–2.12 (m, 1H), 2.08–1.06 (m, 29H), 0.93 (dd, \( J = 6.4, 1.9 \) Hz, 1H).
cis-(2-Bromocyclohexyl)(phenyl)methanone. Yield: 20 mg (38%). White solid, mp: 86-88 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.83 (d, \(J = 7.6\) Hz, 2H), 7.56 (t, \(J = 7.6\) Hz, 1H), 7.47 (t, \(J = 7.6\) Hz, 2H), 4.73 (d, \(J = 3.2\) Hz, 1H), 3.54 (dt, \(J = 10.8, 3.2\) Hz, 1H), 2.27–2.23 (m, 1H), 2.07–1.98 (m, 2H), 1.92–1.77 (m, 3H), 1.64–1.59 (m, 1H), 1.46–1.34 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 200.0, 136.3, 132.7, 128.8, 128.1, 54.3, 49.6, 35.0, 24.2, 22.8, 21.2; IR (KBr): \(\nu\) (cm\(^{-1}\)) 2935, 2858, 1681, 1447, 1262, 1180, 959, 699, 662; EIMS: \(m/z\) (rel intensity) 201 (100), 105 (100), 82 (11), 77 (28), 67 (6), 51 (7); HRMS calcd for C\(_{13}\)H\(_{15}\)BrO [M]: 266.0306; found: 266.0309.

trans-(2-Bromocyclohexyl)(phenyl)methanone. Yield: 20 mg (38%). Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.99 (d, \(J = 7.6\) Hz, 2H), 7.58 (t, \(J = 7.6\) Hz, 1H), 7.48 (t, \(J = 7.6\) Hz, 2H), 4.48–4.41 (m, 1H), 3.84–3.79 (m, 1H), 2.51–2.47 (m, 1H), 2.01–1.93 (m, 2H), 1.84–1.80 (m, 2H), 1.48–1.40 (m, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 201.0, 136.3, 133.3, 128.7, 128.4, 54.0, 51.4, 37.4, 31.9, 26.9, 24.8; IR (neat): \(\nu\) (cm\(^{-1}\)) 2935, 2858, 1681, 1447, 1262, 1180, 959, 699, 662; EIMS: \(m/z\) (rel
Ethyl 2-bromo-2-(4-methyl-1-tosylpyrrolidin-3-yl)acetate. This compound is the mixture of four stereoisomers. The two major isomers were purified by column chromatography on silica gel in about 2:1 ratio. While the other two isomers could not be obtained in pure forms. Data of the two major isomers (~2:1): Yield: 34 mg (42%). colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.72 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 4.25–4.17 (m, 2H), 4.15 (d, $J = 7.2$ Hz, 0.34H), 4.05 (d, $J = 11.6$, 0.66H), 3.63 (dd, $J = 10.4$, 8.0 Hz, 0.66H), 3.54-3.49 (m, 0.66H), 3.41-3.30 (m, 1H), 3.24–3.15 (m, 1.34H), 2.82-2.70 (m, 1H), 2.45 (s, 3H), 2.36-2.29 (m, 0.66H), 2.22-2.16 (m, 0.34H), 2.05-1.97 (m, 0.34H), 1.32-1.24 (m, 3H), 0.94 (d, $J = 7.2$ Hz, 1H), 0.76 (d, $J = 7.2$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 168.6, 143.7/143.6, 133.8/133.3, 129.8/129.7, 127.7/127.5, 62.3/62.2, 55.9/54.6, 51.0/50.5, 48.2/47.5, 45.4/44.1, 36.9/34.7, 21.5/16.8, 13.9/13.8, 13.2; IR (neat): ν (cm$^{-1}$) 2976, 2932, 1737, 1597, 1453, 1345, 1163, 1093, 1018, 815, 664, 592, 548; EIMS: $m/z$ (rel intensity) 324 (2), 278 (12), 250 (44), 248 (26), 168 (75), 155 (40), 122 (16), 91 (100), 82 (24), 65 (19), 42 (38); HRMS calcd for C$_{16}$H$_{22}$BrNO$_4$S [M]: 403.0455; found: 403.0455.

5. References for Known Compounds.

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<th>entry</th>
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<td>1</td>
<td>Wang, Z.; Zhu, L.; Yin, F.; Su, Z.; Li, Z.; Li, C. J. Am. Chem. Soc. 2012, 134, 4258.</td>
<td>1a, 1b, 1k, 1s</td>
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<td></td>
<td></td>
<td>1u, 1w, 1x, 8, 10</td>
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<td>2</td>
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<td>8, 10</td>
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<td>3</td>
<td>Liu, C.; Wang, X.; Li, Z.; Cui, L.; Li, C. <em>J. Am. Chem. Soc.</em> 2015, 137, 9820.</td>
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<td>4</td>
<td>De, P.; Van, L. <em>J. Org. Chem.</em> 1974, 39, 3360.</td>
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<td>5</td>
<td>Zhang, M.; Jia, T.; Sagamanova, I. K.; Pericas, M. A.; Walsh, P. J. <em>Org. Lett.</em> 2015, 17, 1164.</td>
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<td>3z</td>
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</table>

7. $^1$H and $^{13}$C Spectra of All Products

Compound 3a
Compound 3c
Compound 3d

Compound 3e
Compound 3f

Compound 3g
Compound 3h
Compound 3i
Compound 3j

Compound 3k
Compound 3l

Compound 3m
Compound 3n
Compound 3p

Compound 3q
Compound 3r
Compound 3s

Compound 3t
Compound 3u

Compound 3v
Compound 3w
Compound 3x

Compound 3y
Compound 3z
Compound 5

Compound 7
Compound *cis*-9
Compound *trans*-9

Compound 11
complex of isomer (2 : 1)