Supporting Information for

Silver-Catalyzed Decarboxylative Bromination of Aliphatic Carboxylic Acids

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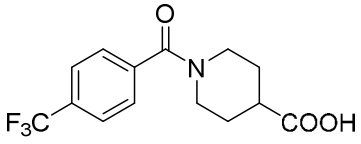
1. General Information.

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 F_{254} plates (250 μm). Nuclear magnetic resonance (NMR) spectra were recorded on a Agilent 400 or Bruker 400 instrument operating at 400, 100, and 376 MHz for ^{1}H, ^{13}C, ^{19}F, respectively. Chemical shifts were reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR, chloroform-d (δ 77.00) for ^{13}C 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-dimethylpentanedioic acid (**6**). The rest substrates were known compounds (except **1h**) and readily prepared by conventional methods.

Characterizations of New Substrates:



1h

(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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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; ^{19}F 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 $C_{14}H_{14}F_3NO_3$ [M]: 301.0926; found: 301.0929.

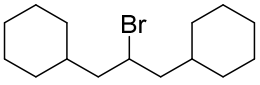
3. Typical Procedure for Decarboxylative Bromination.

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 CH_2Cl_2 (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%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02–3.96 (m, 1H), 1.90–1.78 (m, 4H), 1.52 (br, 1H), 1.41 (br, 1H), 1.26 (br, 18H), 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): ν (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), $Ag(Phen)_2OTf$ (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_2Cl_2 (3 × 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%).

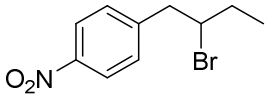
4. Characterizations of New Products.



3b

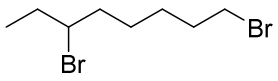
(2-Bromopropane-1,3-diyl)dicyclohexane. Yield: 52 mg (91%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.24-4.16 (m, 1H), 1.82-1.51 (m, 16H), 1.33-1.08 (m, 6H), 1.02-0.90 (m, 2H), 0.88-0.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.0, 47.4, 35.7, 33.6, 32.2, 26.6, 26.2, 26.0; IR (neat): ν (cm^{-1}) 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]:

207.2113; found: 207.2109.



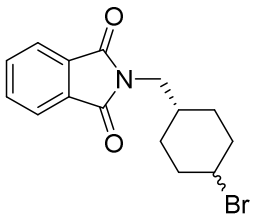
3c

1-(2-Bromobutyl)-4-nitrobenzene. Yield: 35 mg (68%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 147.0, 146.1, 130.1, 123.6, 57.8, 44.8, 31.8, 12.1; IR (neat): ν (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.



3e

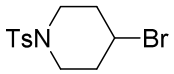
1,6-Dibromooctane. Yield: 50 mg (93%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02–3.94 (m, 1H), 3.42 (t, *J* = 6.8 Hz, 2H), 1.92–1.78 (m, 6H), 1.62-1.41 (m, 4H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.2, 38.5, 33.7, 32.6, 32.2, 27.6, 26.8, 12.1; IR (neat): ν (cm^{-1}) 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 $C_8H_{15}Br_2$ [M-H]: 268.9540; found: 268.9538.



3f

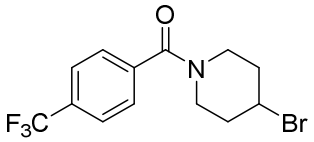
2-((4-Bromocyclohexyl)methyl)isoindoline-1,3-dione. This compound was isolated as the mixture of two stereoisomers in about 1:1 ratio determined by ^{1}H NMR (400 MHz). Yield: 49 mg (76%). White solid, mp: 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of two stereoisomers): δ 7.87-7.82 (m, 2H), 7.75-7.70 (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): ν (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

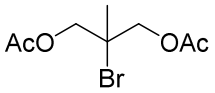
4-Bromo-1-tosylpiperidine. Yield: 44 mg (70%). White solid, mp: 132-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.27–4.21 (m, 1H), 3.24–3.16 (m, 2H), 3.14–3.05 (m, 2H), 2.44 (s, 3H), 2.23–2.14 (m, 2H), 2.09–2.01 (m, 2H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 133.4, 129.8, 127.6, 47.8, 43.8, 34.7, 21.5; IR (KBr): ν (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 $C_{12}H_{16}BrNO_2S$ [M]: 317.0085; found: 317.0083.



3h

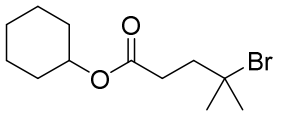
(4-Bromopiperidin-1-yl)(4-(trifluoromethyl)phenyl)methanone. Yield: 50 mg (75%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 4.48-4.42 (m, 1H), 3.95 (br, 1H), 3.80 (br, 1H), 3.62 (br, 1H), 3.32 (br, 1H), 2.22 (br, 1H), 2.07 (br, 2H), 1.94 (br, 1H); ^{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, CDCl3): δ -62.9 (s, 3F); IR (neat): ν (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 $C_{13}H_{12}BrF_3NO$ [M-H]: 334.0054; found: 334.0055.



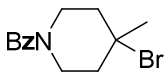
3j

2-Bromo-2-methylpropane-1,3-diyl diacetate. Yield: 45 mg (89%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.34 (d, *J* = 12.0 Hz, 2H), 4.26 (d, *J* = 12.0 Hz, 2H), 2.11 (s, 6H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 68.4, 60.0, 25.6, 20.7; IR (neat): ν (cm^{-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 $C_6H_{10}BrO_3$ [M-$COCH_3$]: 208.9813; found: 208.9815.



3k

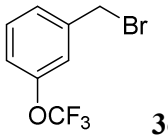
Cyclohexyl 4-bromo-4-methylpentanoate. Yield: 46 mg (83%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.80–4.74 (m, 1H), 2.59-2.53 (m, 2H), 2.14-2.09 (m, 2H), 1.87–1.83 (m, 2H), 1.76 (s, 6H), 1.74–1.69 (m, 2H), 1.58–1.52 (m, 1H), 1.47–1.20 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 72.8, 66.4, 41.9, 34.2, 32.1, 31.6, 25.4, 23.8; IR (neat): ν (cm^{-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 $C_{10}H_{22}BrO_2$ [M+H]: 277.0803; found: 277.0799.



3l

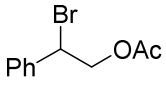
(4-Bromo-4-methylpiperidin-1-yl)(phenyl)methanone. Yield: 52 mg (92%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.38 (m, 5H), 4.63 (br, 1H), 3.67 (br, 1H), 3.47 (br, 1H), 3.25 (br, 1H), 2.13 (br, 1H), 1.98 (br, 1H), 1.89 (s, 3H), 1.71 (br, 1H), 1.55 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 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 $C_{13}H_{15}BrNO$ [M-H]: 280.0337; found: 280.0344.



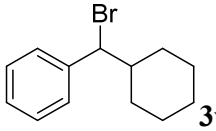
3o

1-(Bromomethyl)-3-(trifluoromethoxy)benzene. Yield: 44 mg (87%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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; ^{19}F 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 $C_8H_6BrF_3O$ [M]: 253.9554; found: 253.9552.



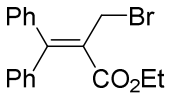
3u

2-Bromo-2-phenylethyl acetate. Yield: 44 mg (91%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{10}H_{11}BrO_2$ [M]: 241.9942; found: 241.9944.



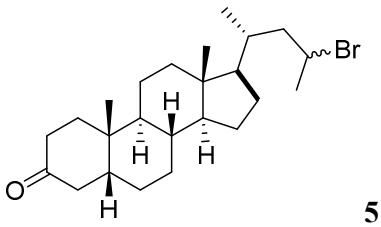
3v

(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.



3x

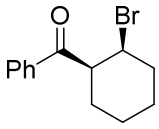
Ethyl 2-(bromomethyl)-3,3-diphenylacrylate. Yield: 36 mg (52%). White solid, mp: 95-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.34 (m, 5H), 7.31–7.26 (m, 3H), 7.12–7.08 (m, 2H), 4.32 (s, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 151.3, 141.6, 139.6, 129.1, 128.9, 128.86, 128.83, 128.5, 128.4, 128.0, 61.1, 32.5, 13.6; IR (KBr): ν (cm^{-1}) 2926, 1712, 1598, 1490, 1444, 1367, 1327, 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.



5

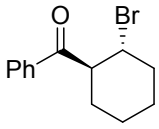
(5*R*,8*R*,9*S*,10*S*,13*R*,14*S*)-17-((2*R*)-4-Bromopentan-2-yl)-10,13-dimethylhexadecahydro-3*H*-cyclopenta[*a*]phenanthren-3-one. Yield: 72 mg (85%). This compound was isolated as the mixture of two stereoisomers in about 1:1 ratio determined by ^{1}H NMR (400 MHz). White solid, mp: 118-120 °C; ^{1}H 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,

2.4 Hz, 3H), 0.73 (s, 1.5H), 0.69 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.2, 213.1, 56.7, 56.50, 56.48, 56.39, 50.6, 49.1, 48.4, 47.6, 44.3, 42.9, 42.3, 40.75, 40.70, 40.12, 40.06, 37.2, 37.0, 35.5, 35.1, 34.9, 28.4, 28.1, 27.6, 26.6, 25.8, 25.7, 25.4, 24.1, 22.67, 22.65, 21.20, 21.18, 18.4, 18.1, 12.2, 12.1; IR (KBr): ν (cm^{-1}) 2937, 2865, 1714, 1445, 1378, 1265, 912, 733, 531; EIMS: *m/z* (rel intensity) 424 (11), 422 (M^+, 11), 354 (18), 352 (18), 231 (100), 176 (49), 161 (62), 107 (52), 95 (72), 81 (74), 79 (53), 67 (56), 55 (76), 41 (53); HRMS calcd for $C_{24}H_{39}BrO$ [M]: 422.2184; found: 422.2182.



cis-**9**

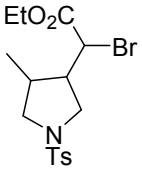
***cis*-(2-Bromocyclohexyl)(phenyl)methanone.** Yield: 20 mg (38%). White solid, mp: 86-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.83 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.73 (d, *J* = 3.2 Hz, 1H), 3.54 (dt, *J* = 10.8, 3.2 Hz, 1H), 2.27-2.23 (m, 1H), 2.07-1.98 (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, $CDCl_3$): δ 200.0, 136.3, 132.7, 128.8, 128.1, 54.3, 49.6, 35.0, 24.2, 22.8, 21.1; IR (KBr): ν (cm^{-1}) 2937, 2859, 1687, 1597, 1446, 1255, 965, 697, 659; EIMS: *m/z* (rel intensity) 187 (18), 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-**9**

***trans*-(2-Bromocyclohexyl)(phenyl)methanone.** Yield: 20 mg (38%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 201.0, 136.3, 133.3, 128.7, 128.4, 54.0, 51.4, 37.4, 31.9, 26.9, 24.8; IR (neat): ν (cm^{-1}) 2935, 2858, 1681, 1447, 1262, 1180, 959, 699, 662; EIMS: *m/z* (rel

intensity) 268 (1), 266 (M^+, 1), 187 (32), 105 (100), 82 (11), 77 (23), 67 (5), 51 (5); HRMS calcd for $C_{13}H_{15}BrO$ [M]: 266.0306; found: 266.0314.



11

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 $C_{16}H_{22}BrNO_4S$ [M]: 403.0453; found: 403.0455.

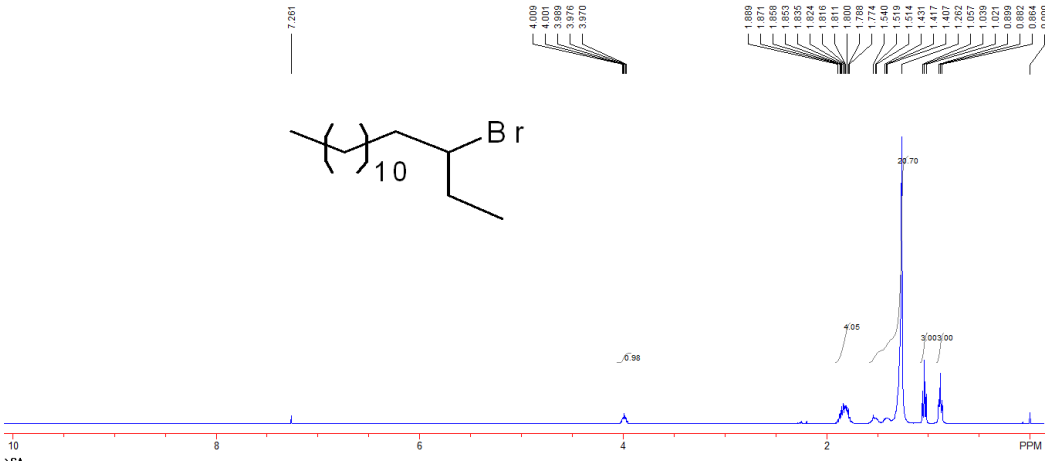
5. References for Known Compounds.

entry	references	compound
1	Wang, Z.; Zhu, L.; Yin, F.; Su, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 4258.	**1a**, **1b**, **1k**, **1s** **1u, 1w**, **1x**, **8, 10**
2	Yin, F.; Wang, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc*. **2012**,	**1f, 1j, 1l, 1y, 4**

	134, 10401.	
3	Liu, C.; Wang, X.; Li, Z.; Cui, L.; Li, C. *J. Am. Chem. Soc.* **2015**, *137*, 9820.	**1c, 1e, 1g**
4	De, P.; Van, L. *J. Org. Chem*. **1974**, *39*, 3360.	**3d**
5	Zhang, M.; Jia, T.; Sagamanova, I. K.; Pericas, M. A.; Walsh, P. J. *Org. Lett.* **2015**, *17*, 1164.	**3r, 3p, 3s**
6	Landge, K. P.; Jang, K. S.; Lee, S. Y.; Chi, D. Y. *J. Org. Chem.* **2012**, *77*, 5705.	**3m**
7	Frutos, O. D.; Rincon, J. A.; Mateos, C.; Kappe, C. O. *J. Org. Chem.* **2014**, *79*, 223.	**3n**
8	Champagne, P. A.; Pomarole, J.; Therien, M. E.; Benhassine, Y.; Beaulieu, S.; Legault, C. Y.; Paquin, J. F. *Org. Lett.* **2013**, *15*, 2210.	**3q**
9	Mizukami, Y.; Song, Z.; Takahashi, T. *Org. Lett.* **2015**, *17*, 5942.	**3i**
10	Soloshonok, V. A.; Tang, X.; Hruby, V. J.; Meervelt, L. V. *Org. Lett.* **2001**, 3, 341.	**3t**
11	Wang, G.; Jiang, J.; Bu, X.; Dai, J.; Xu, J.; Fu, Y.; Xu, H. *Org. Lett.* **2015**, 17, 3682.	**3y**
12	Li, C.; Han, K.; Li, J.; Zhang, H.; Ma, J.; Shu, X.; Chen, Z.; Weng, L.; Jia, X. *Org. Lett.* **2012**, *14*, 42.	**3z**
13	Adrio, L. A.; Quek, L. S; Taylor, J. G.; Kuok, H. K. *Tetrahedron* **2009**, *65*, 10334.	**7**

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

Compound **3a**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3.989
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1.853
1.835
1.824
1.816
1.811
1.800
1.788
1.774
1.546
1.519
1.514
1.431
1.417
1.407
1.262
1.057
1.039
1.021
0.899
0.882
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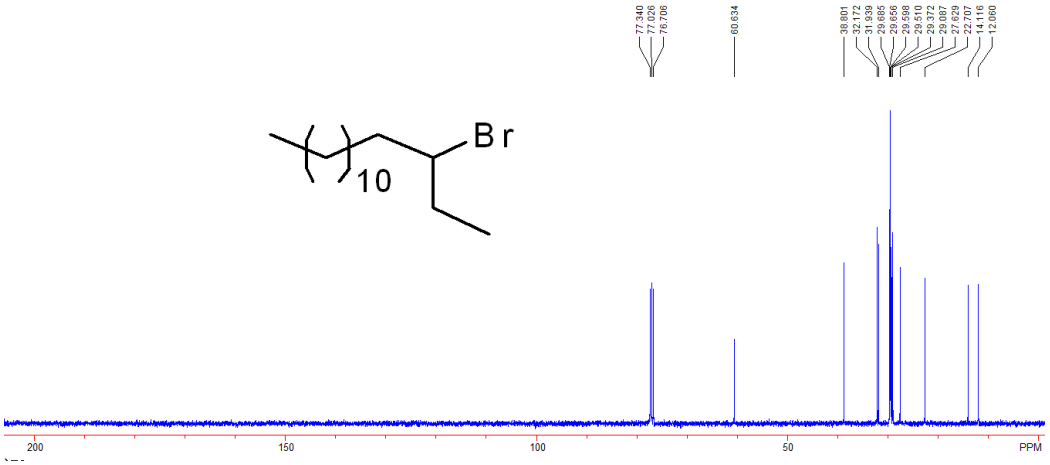
Br
10
29.70
4.05
3.00
0.98
10
8
6
4
2
PPM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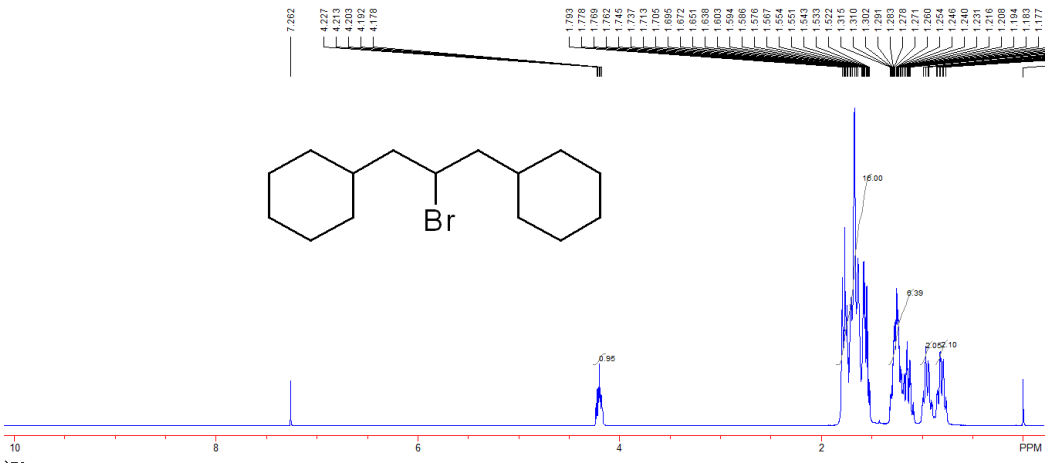
77.026
76.706
60.634
38.801
32.172
31.939
29.685
29.656
29.598
29.510
29.372
29.087
28.879
22.707
14.116
12.060
Br
10
200
150
100
50
PPM

Compound **3b**


7.262
4.227
4.213
4.203
4.192
4.178
1.793
1.778
1.769
1.752
1.745
1.737
1.713
1.705
1.695
1.672
1.651
1.638
1.609
1.594
1.586
1.576
1.567
1.554
1.551
1.543
1.533
1.522
1.315
1.310
1.302
1.291
1.283
1.278
1.271
1.260
1.254
1.246
1.240
1.231
1.216
1.208
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1.183
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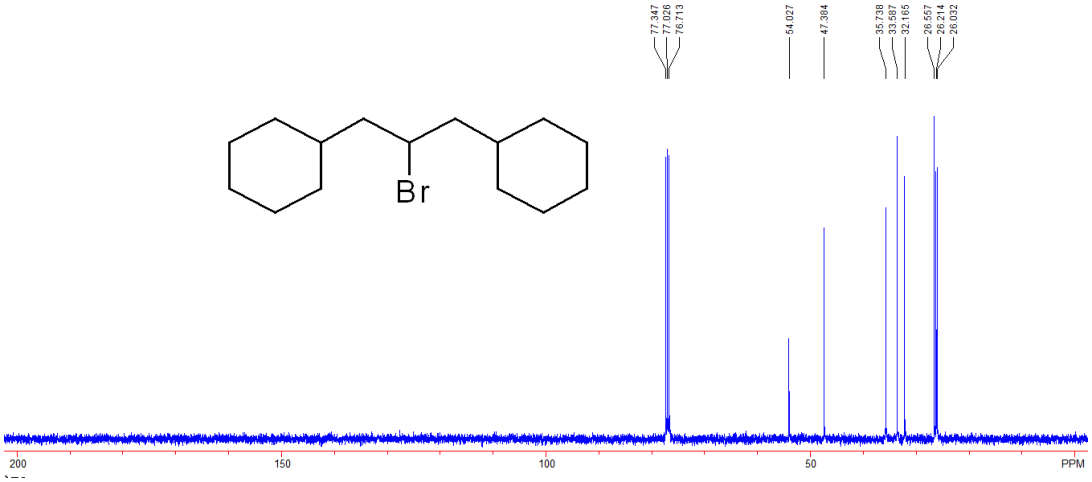
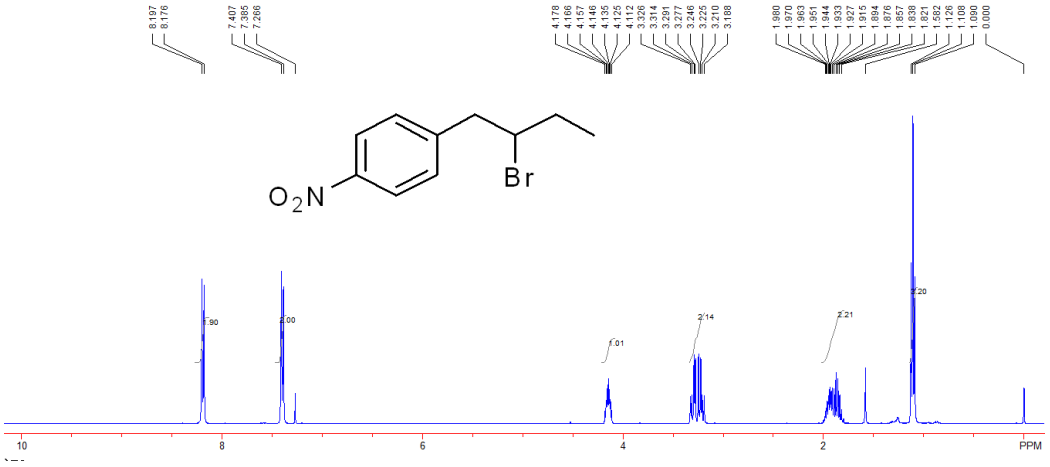
Br
16.00
9.39
2.05
2.10
0.96
10
8
6
4
2
PPM


77.347
77.026
76.713
54.027
47.384
35.738
33.587
32.165
26.557
26.214
26.032
Br
200
150
100
50
PPM

Compound **3c**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8.176
7.407
7.385
7.266
4.178
4.166
4.157
4.146
4.135
4.125
4.112
3.326
3.314
3.291
3.277
3.246
3.225
3.210
3.188
1.980
1.970
1.960
1.951
1.944
1.933
1.927
1.915
1.894
1.876
1.857
1.838
1.821
1.582
1.126
1.108
1.090
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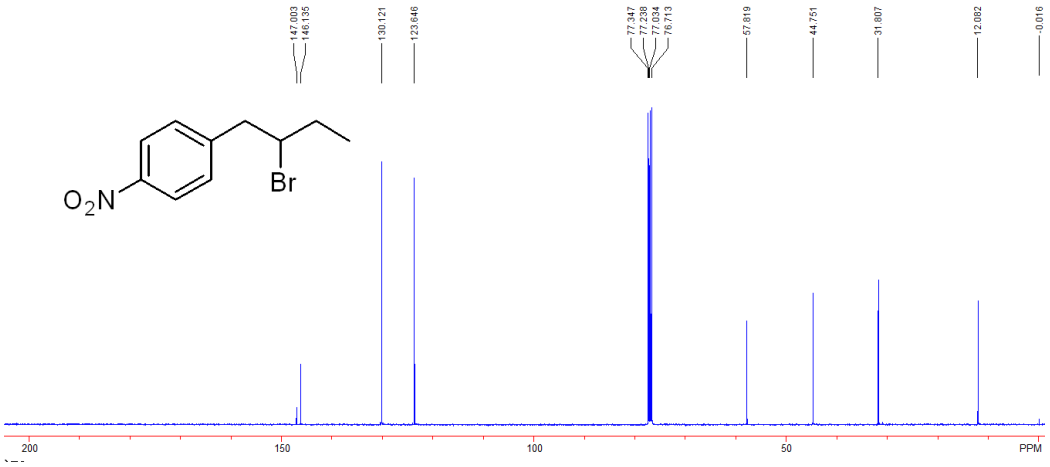
2.00
1.01
2.14
2.21
3.20
10
8
6
4
2
PPM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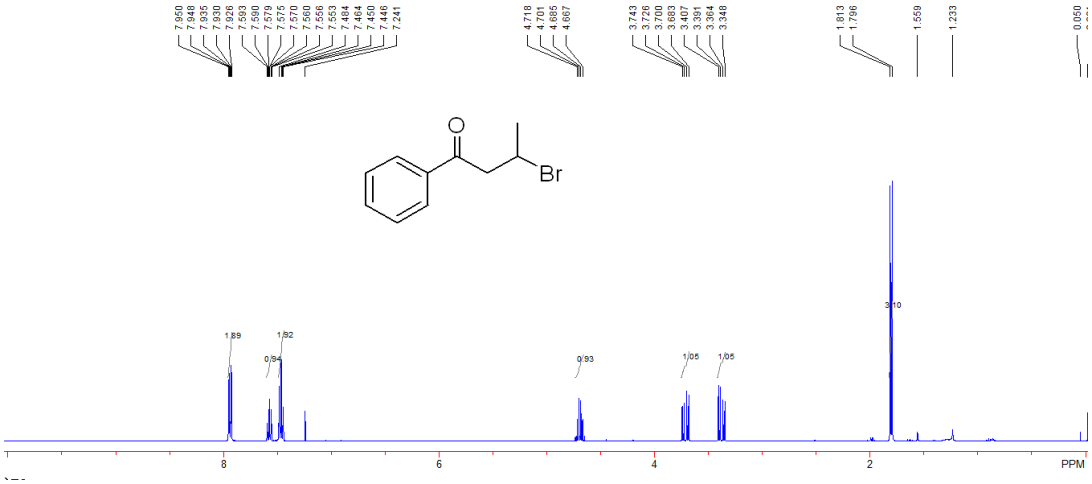
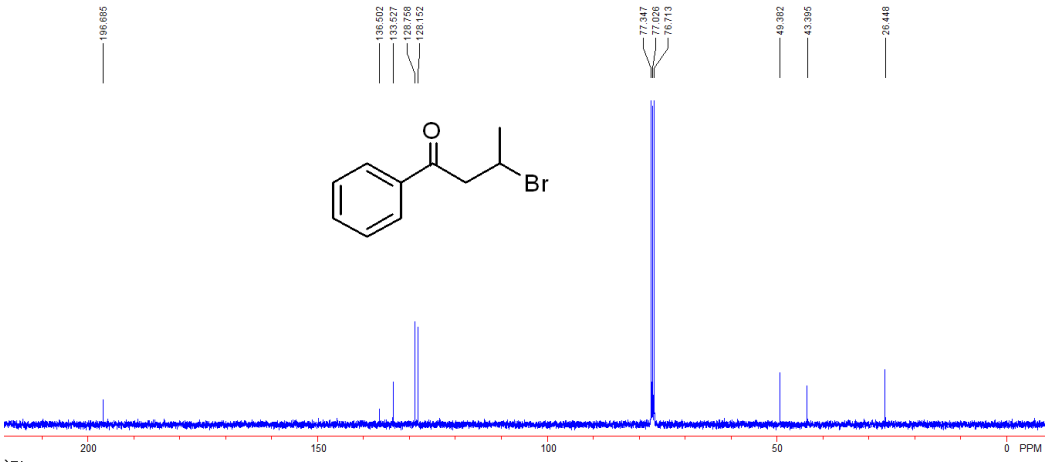
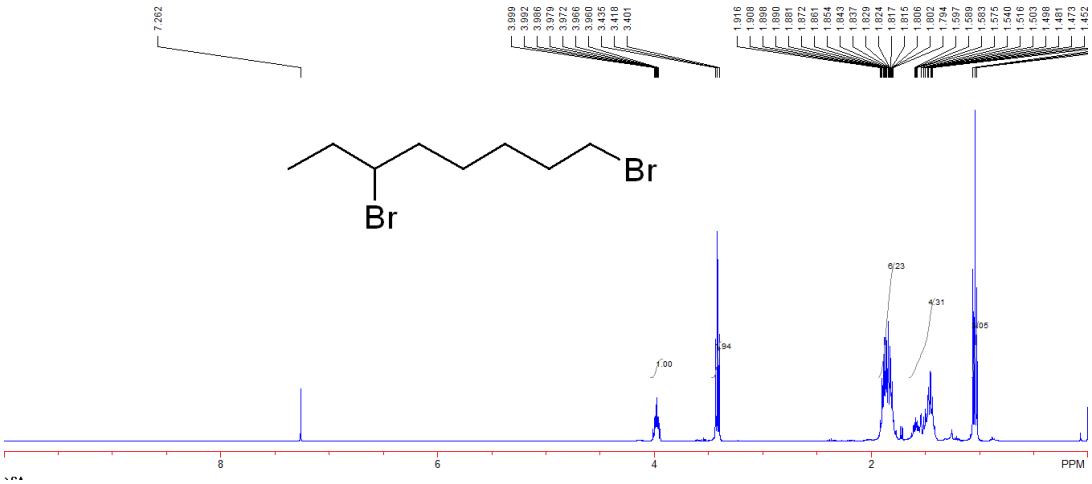
146.135
130.121
123.646
77.347
77.238
77.034
76.713
57.819
44.751
31.807
12.082
-0.016
O2N
Br
200
150
100
50
PPM

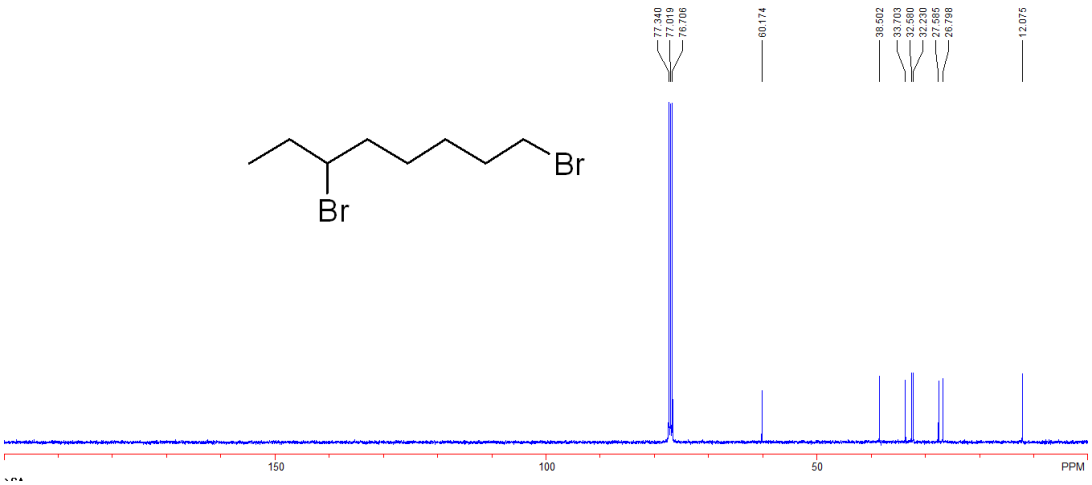
Compound **3d**



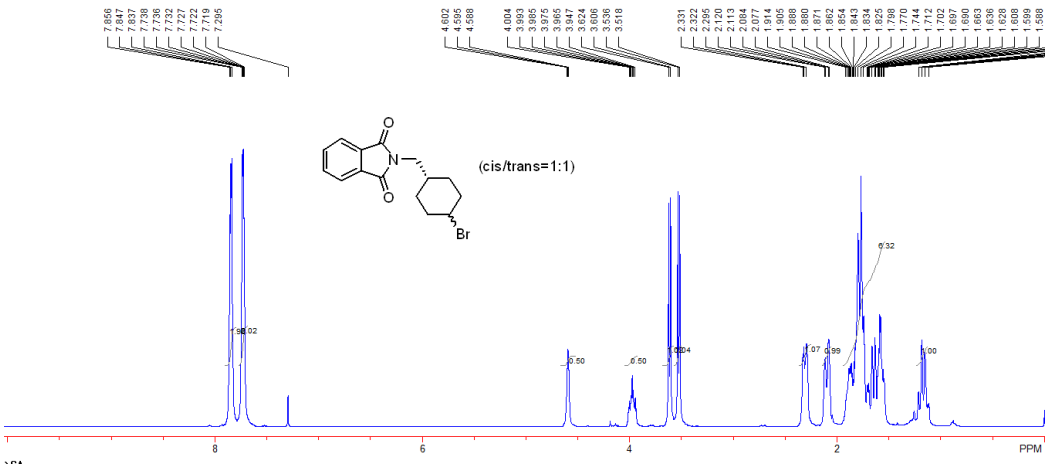


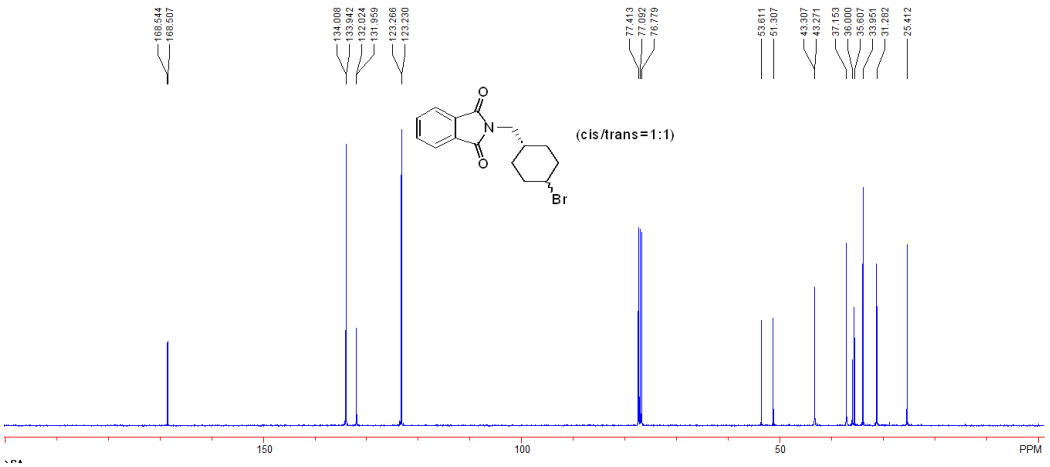
Compound 3**e**



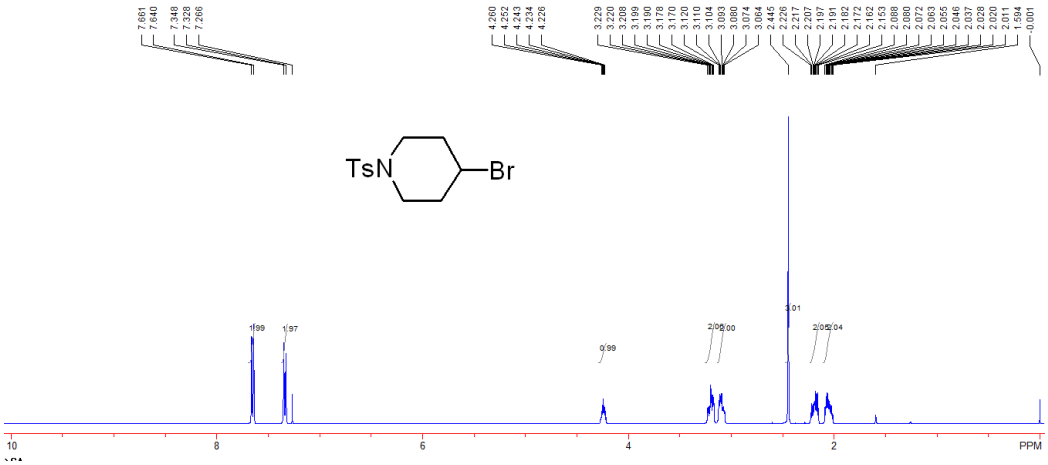


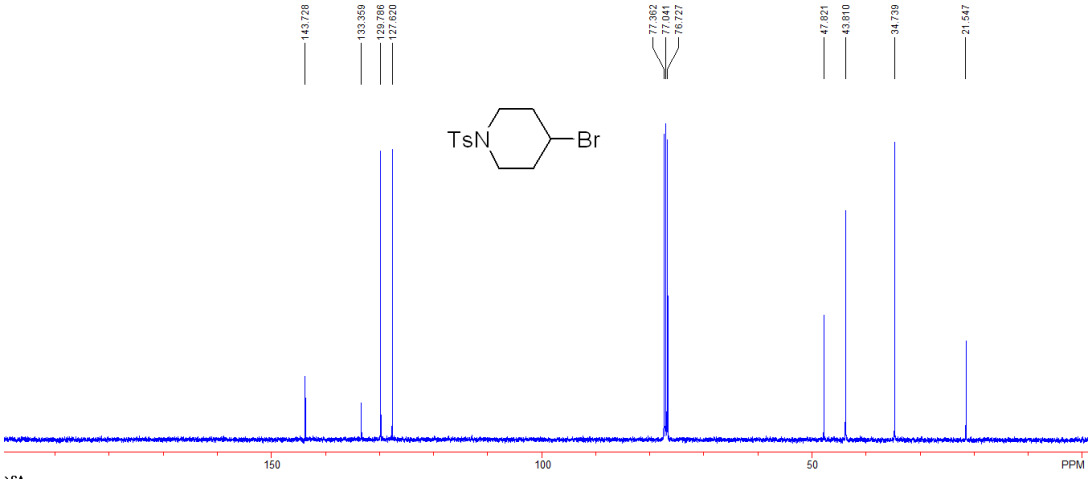
Compound **3f**



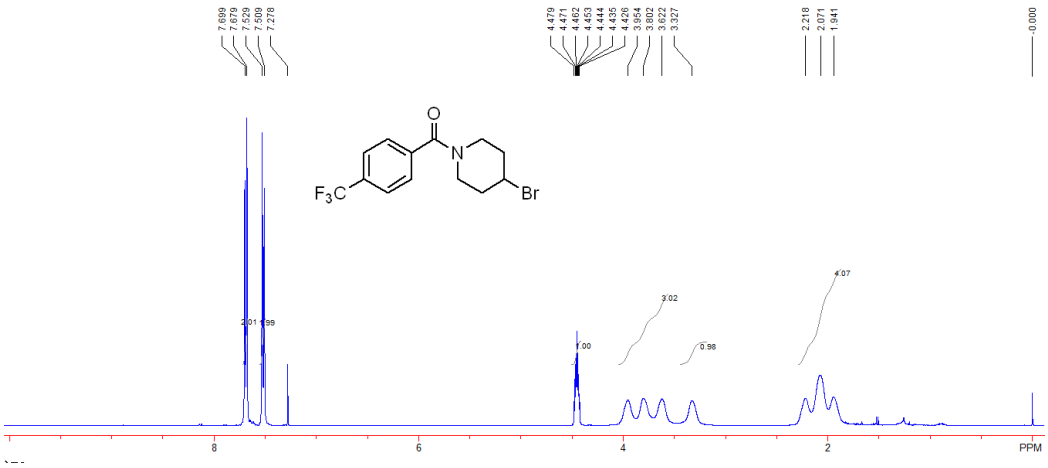


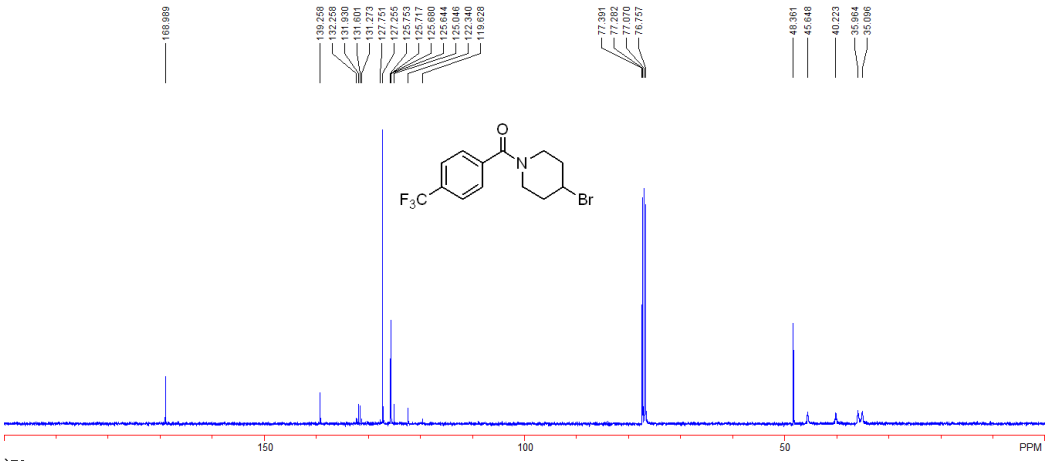
Compound **3g**





Compound **3h**

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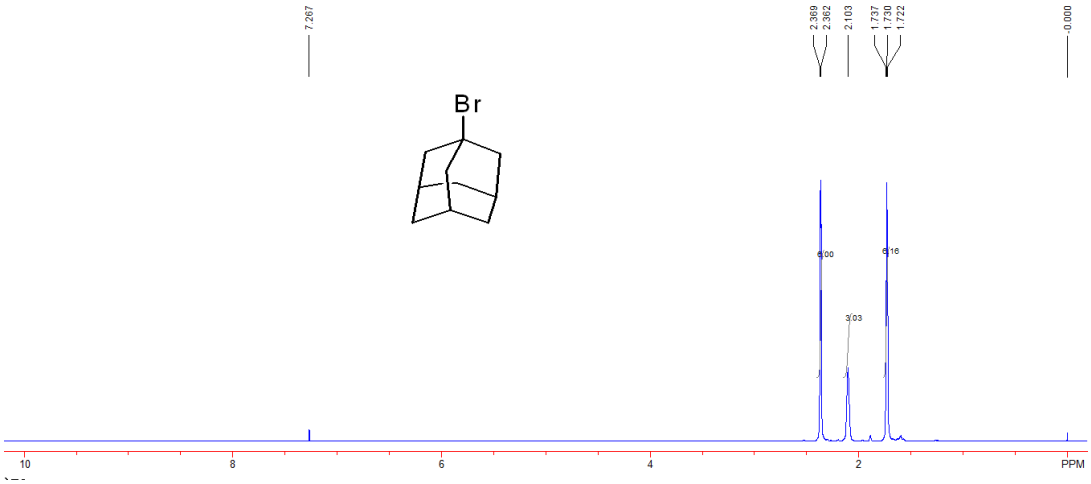
131.273
127.764
127.255
125.753
125.717
125.680
125.644
125.046
122.340
119.628
77.391
77.282
77.070
76.757
49.361
45.648
40.223
35.964
35.096
O
N
F3C
Br
150
100
50
PPM

Compound **3i**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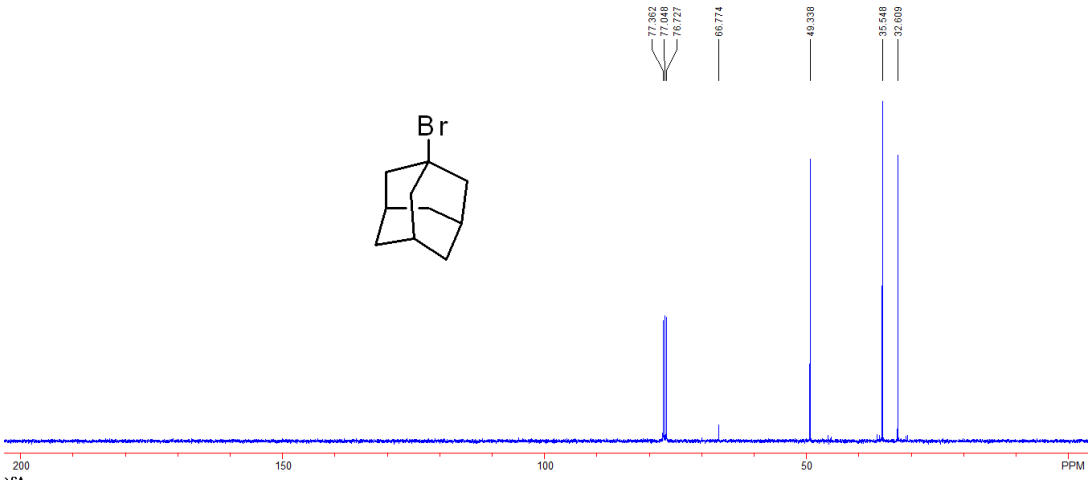
3.03
10
8
6
4
2
PPM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Br
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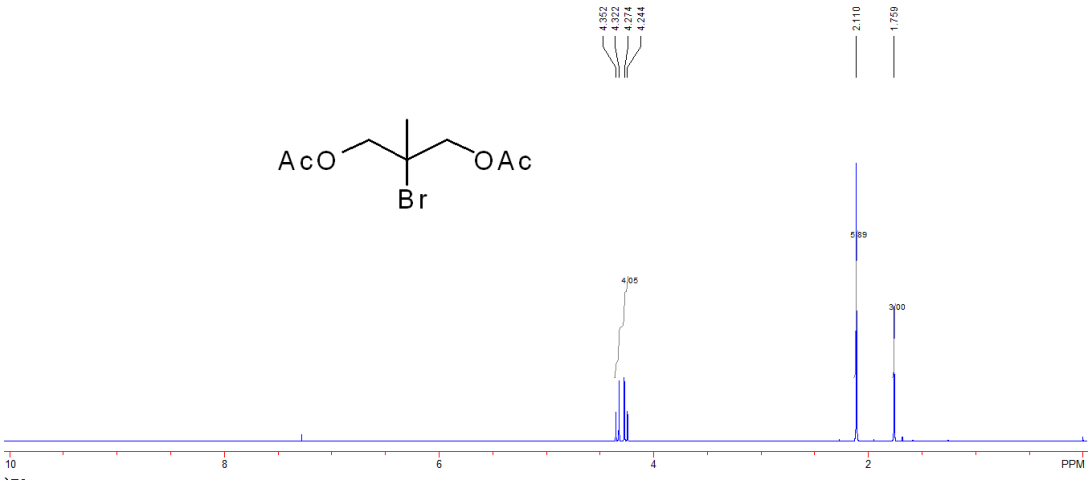
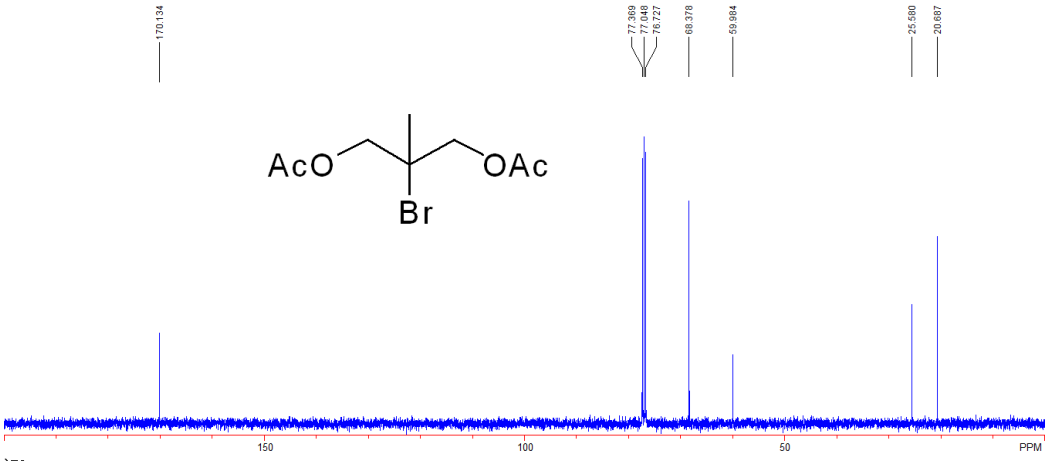
150
100
50
PPM

Compound **3j**





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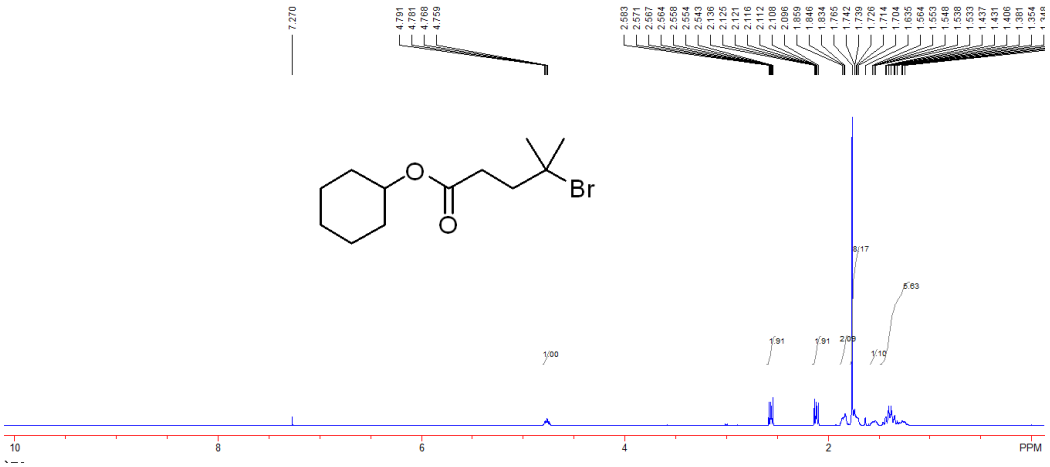
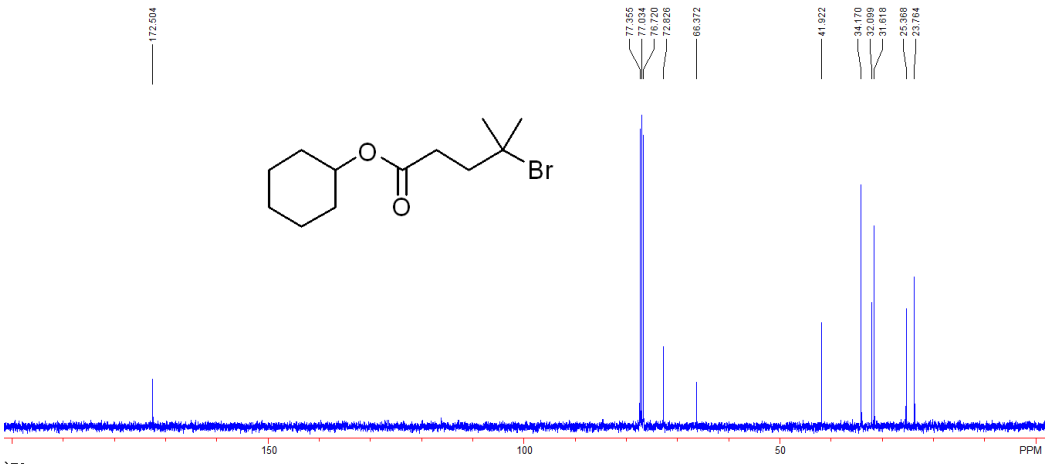
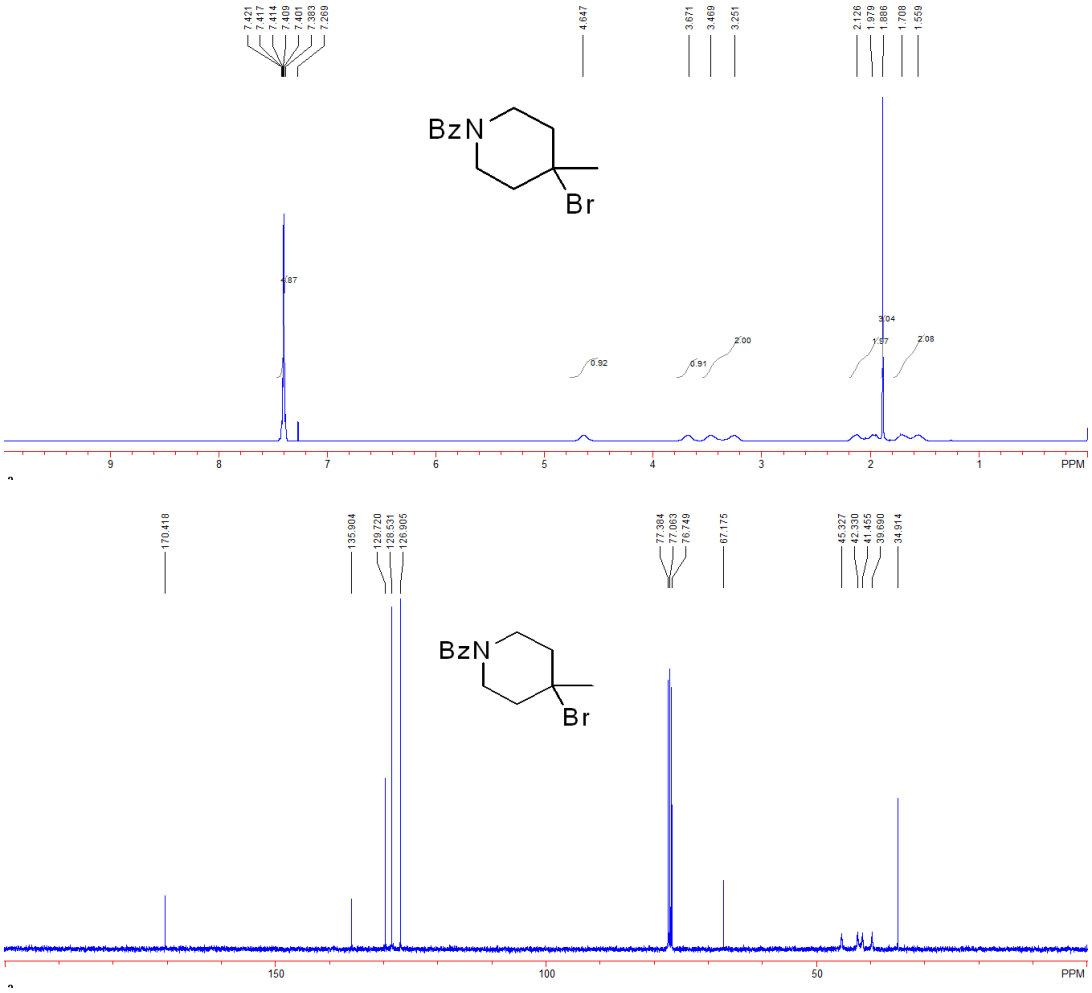
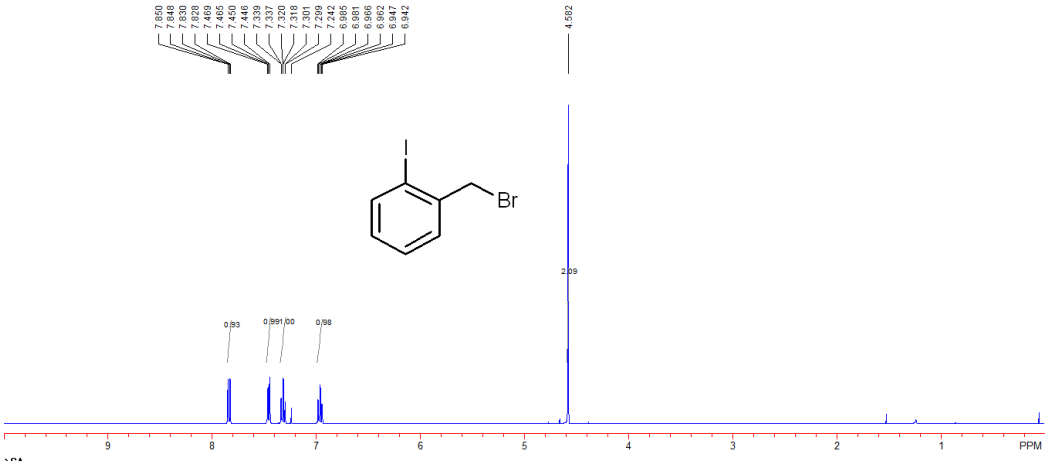


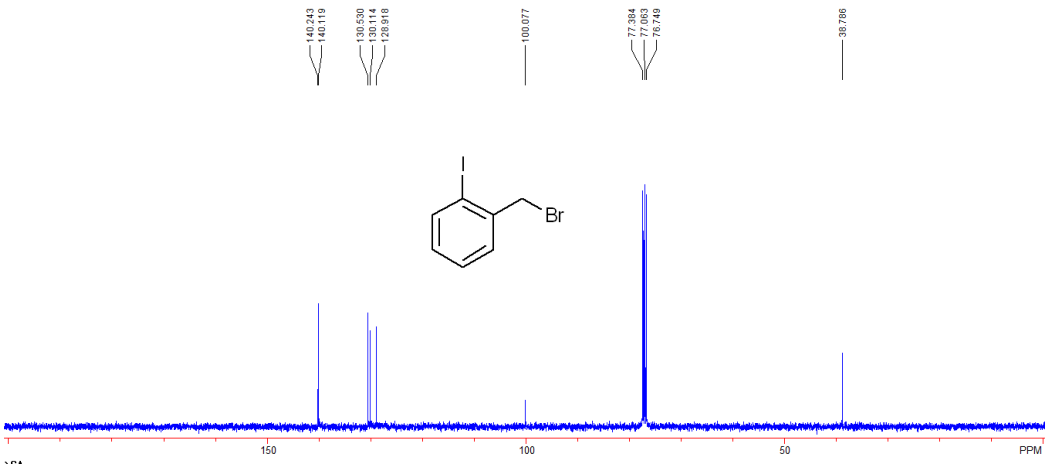


Compound **3l**

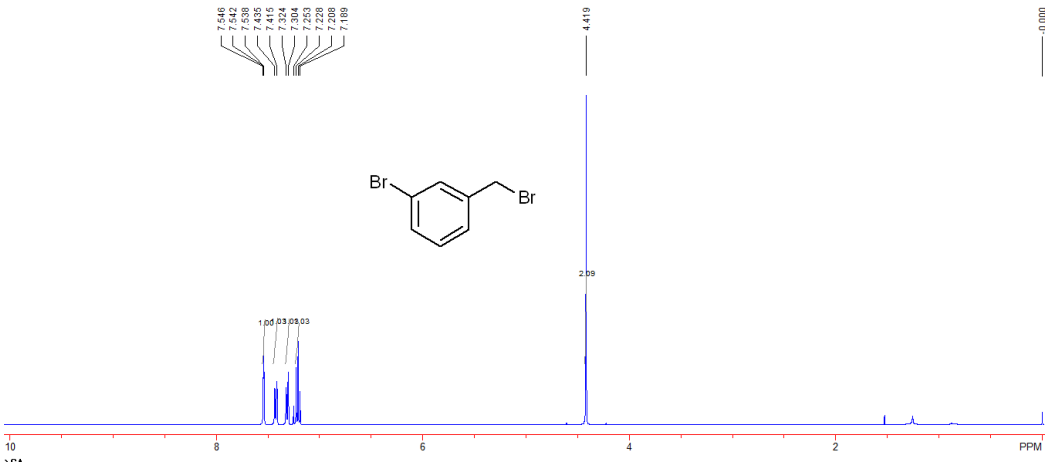


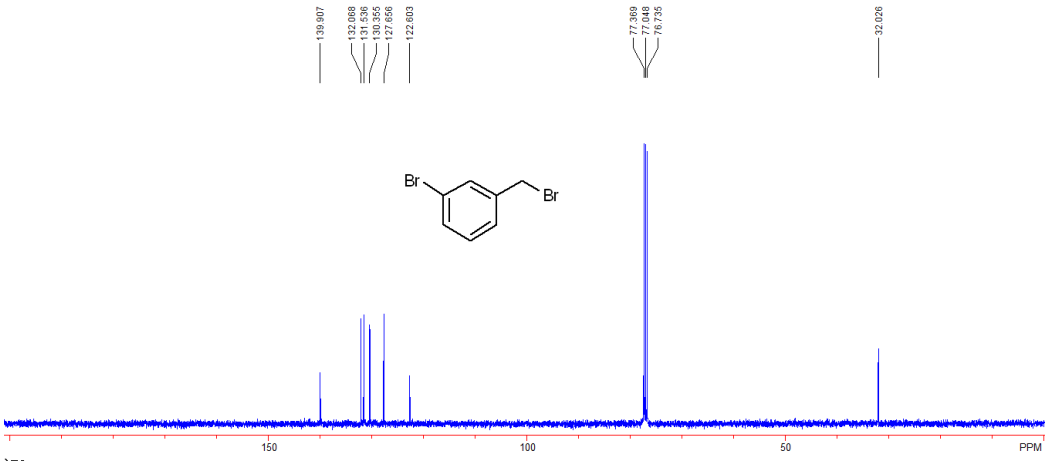
Compound **3m**


7.850
7.848
7.830
7.828
7.469
7.465
7.450
7.446
7.339
7.337
7.320
7.318
7.301
7.299
7.242
6.985
6.981
6.966
6.962
6.947
6.942
4.582
Br
2.09
0.93
0.991.00
0.98
9
8
7
6
5
4
3
2
1
PPM

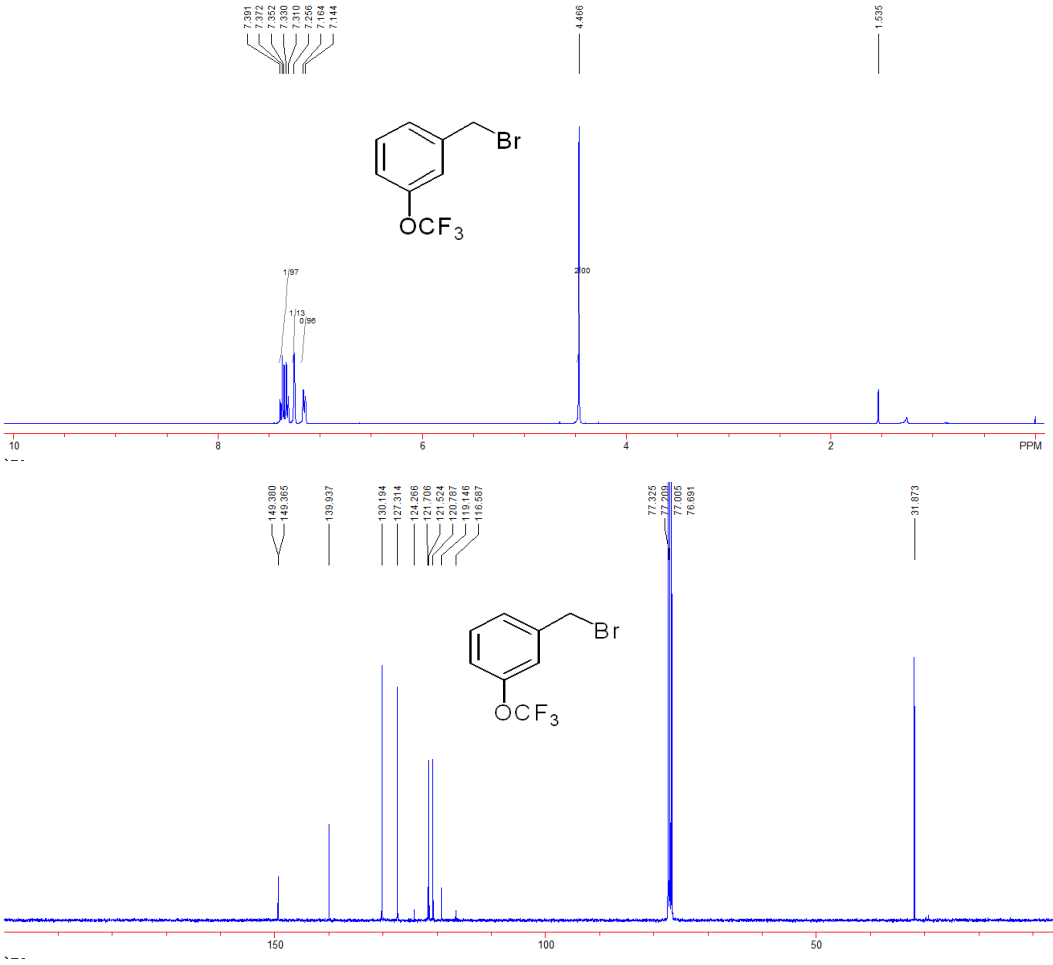

140.243
140.119
130.530
130.114
128.918
100.077
77.384
77.063
76.749
38.786
Br
150
100
50
PPM

Compound **3n**

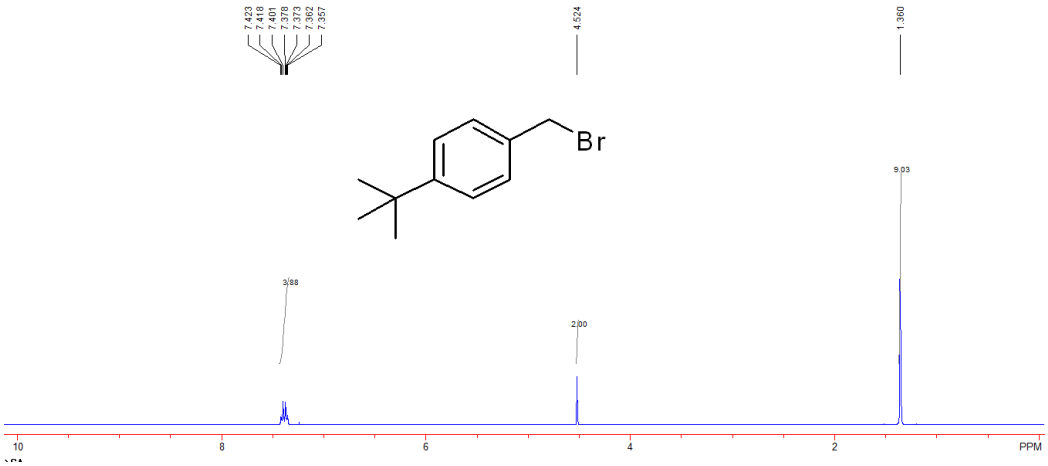

7.546
7.542
7.538
7.435
7.415
7.324
7.304
7.253
7.228
7.208
7.189
4.419
0.000
Br
Br
2.09
1.00
0.03
0.03
0.03
10
8
6
4
2
PPM

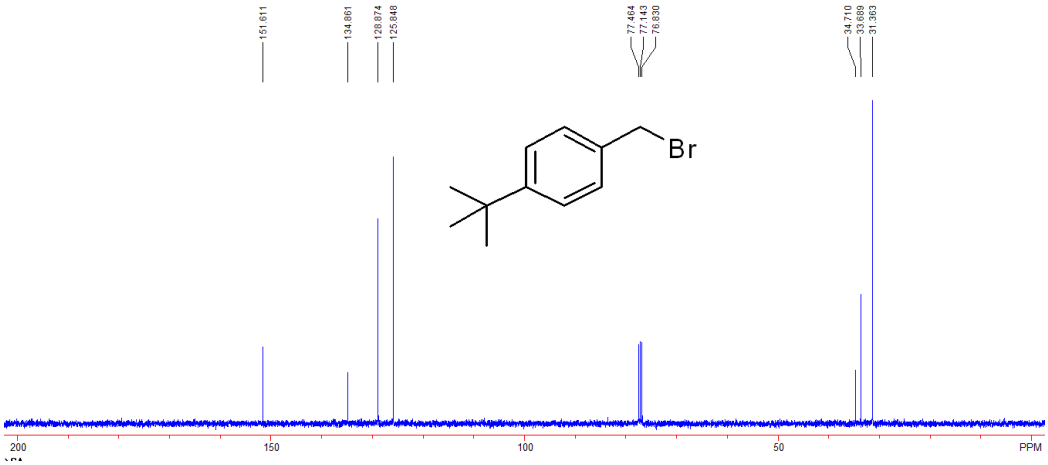

139.907
132.068
131.536
130.355
127.656
122.603
77.369
77.048
76.735
32.026
Br
Br
150
100
50
PPM

Compound **3o**

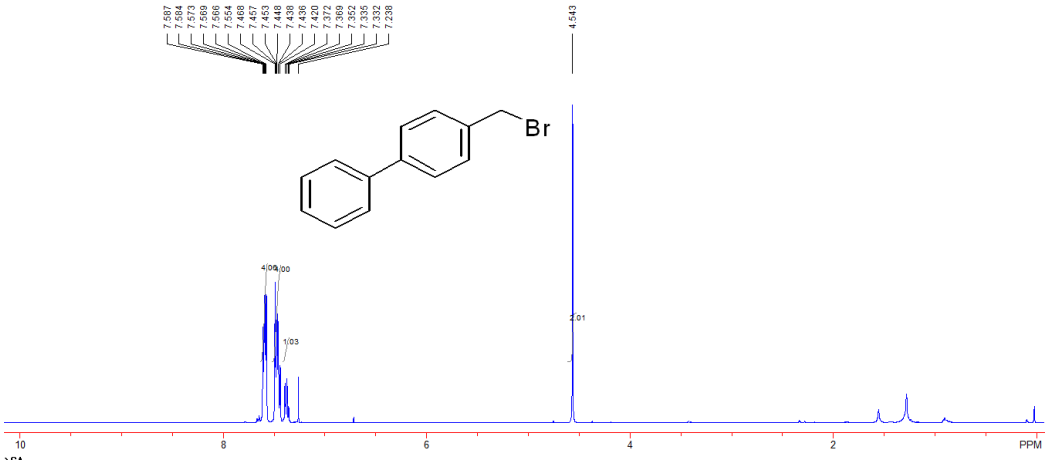

7.391
7.372
7.352
7.330
7.310
7.256
7.164
7.144
4.466
1.535
Br
OCF3
1.97
1.13
0.96
2.00
10
8
6
4
2
PPM
149.380
149.365
139.937
130.194
127.314
124.266
121.706
121.524
120.787
119.146
116.587
77.325
77.000
76.691
31.673
Br
OCF3
150
100
50
PPM

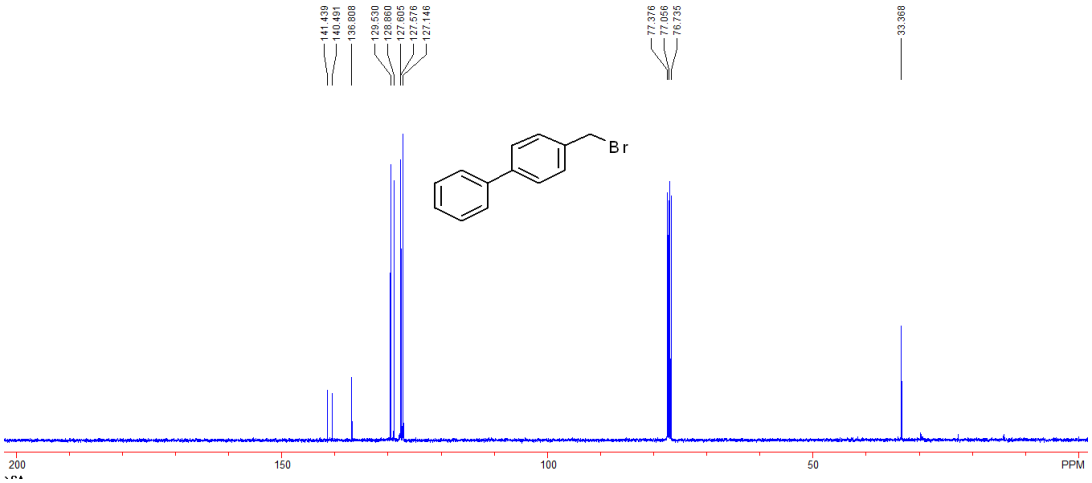
Compound **3p**



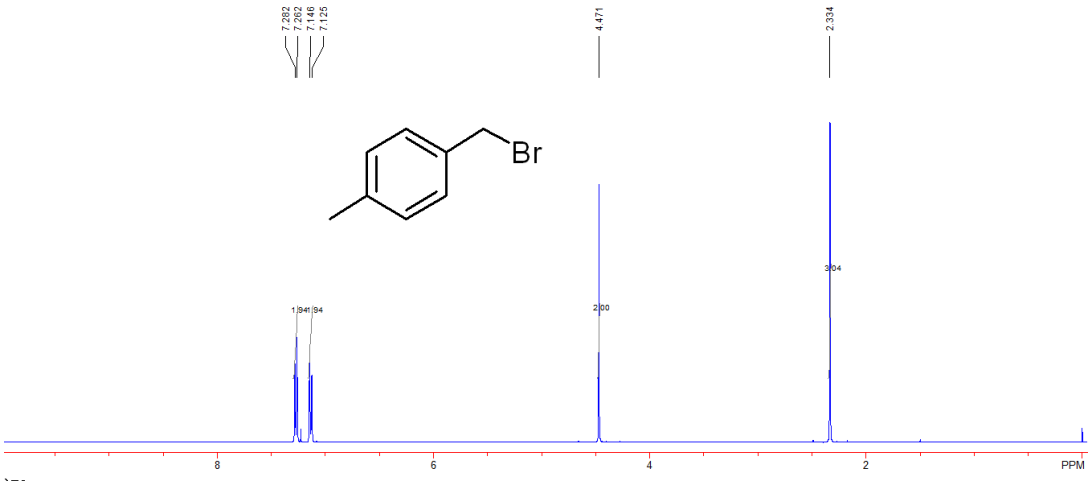


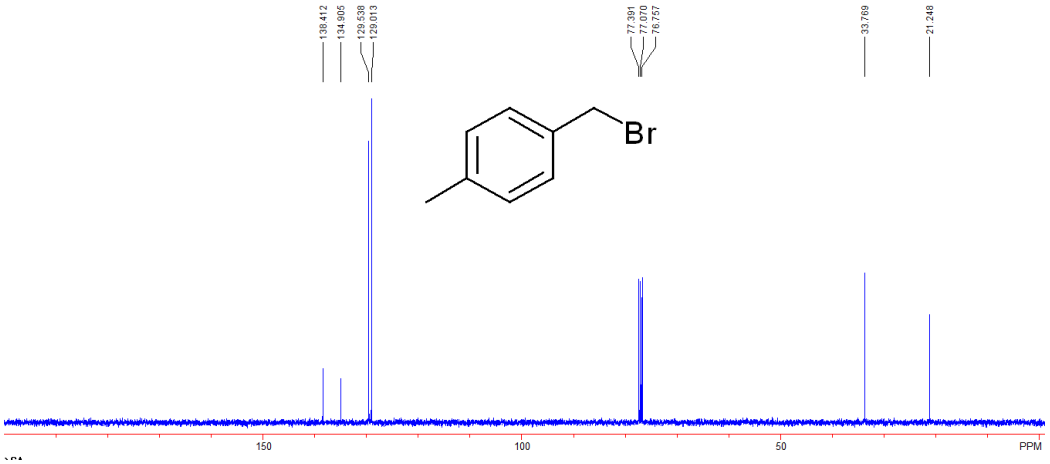
Compound **3q**



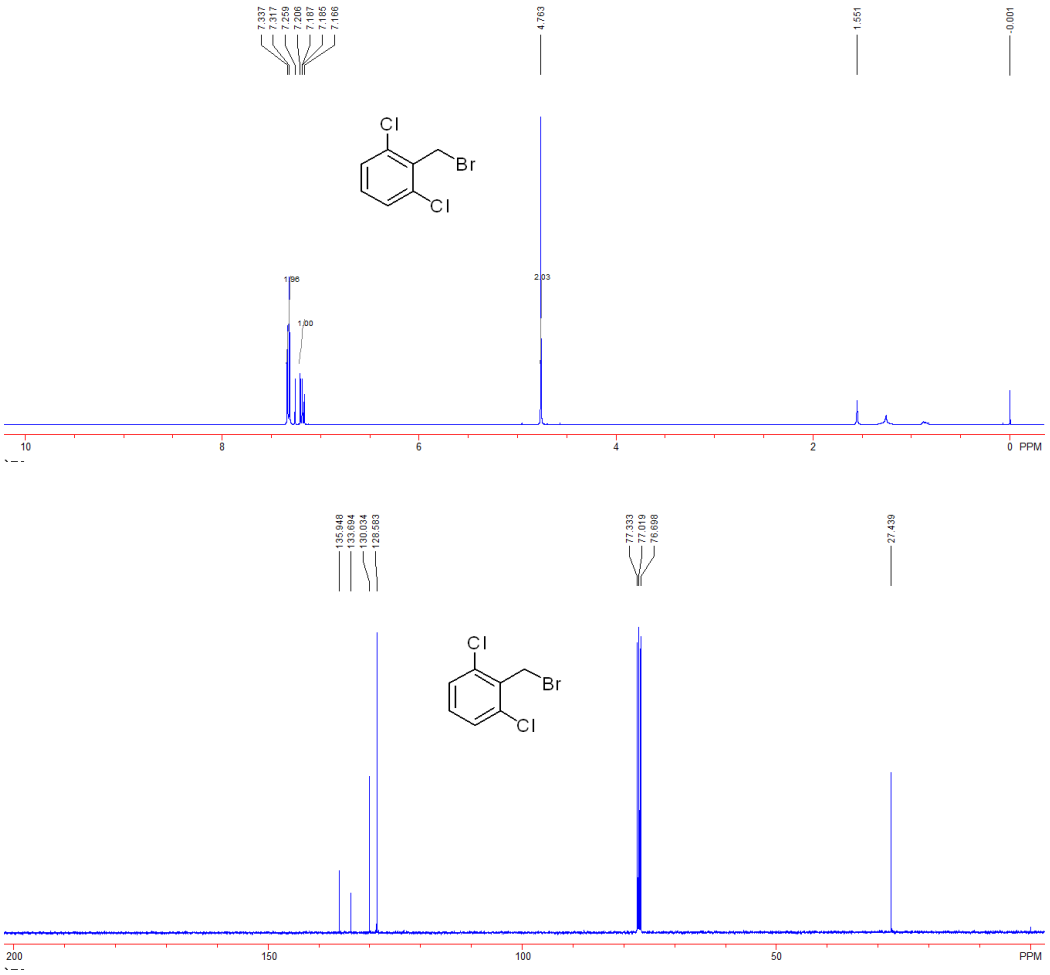

141.439
140.491
136.808
129.530
128.860
127.605
127.576
127.146
77.376
77.056
76.735
33.368
Br
200
150
100
50
PPM

Compound **3r**

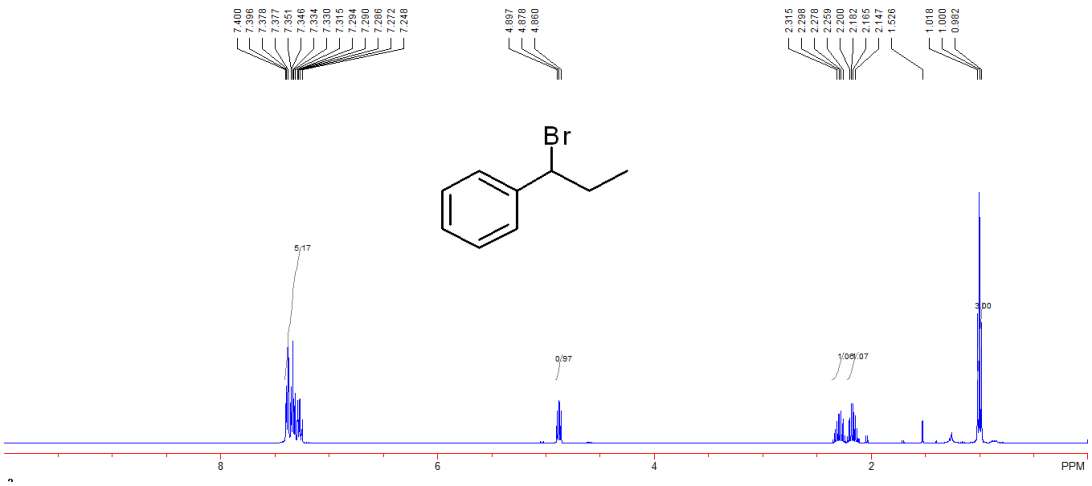

7.282
7.262
7.146
7.125
4.471
2.334
Br
1.94
1.94
2.00
3.04
8
6
4
2
PPM

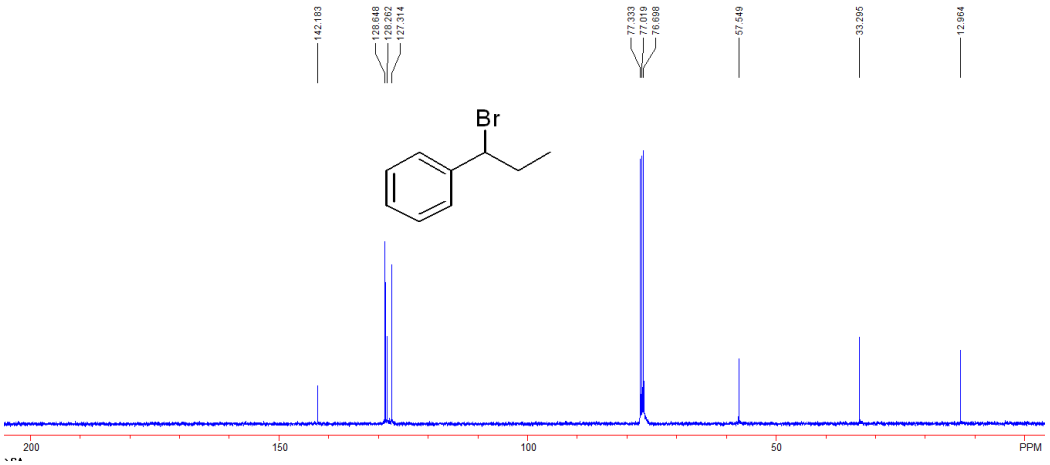

138.412
134.905
129.538
129.013
77.391
77.070
76.757
33.769
21.248
Br
150
100
50
PPM

Compound **3s**

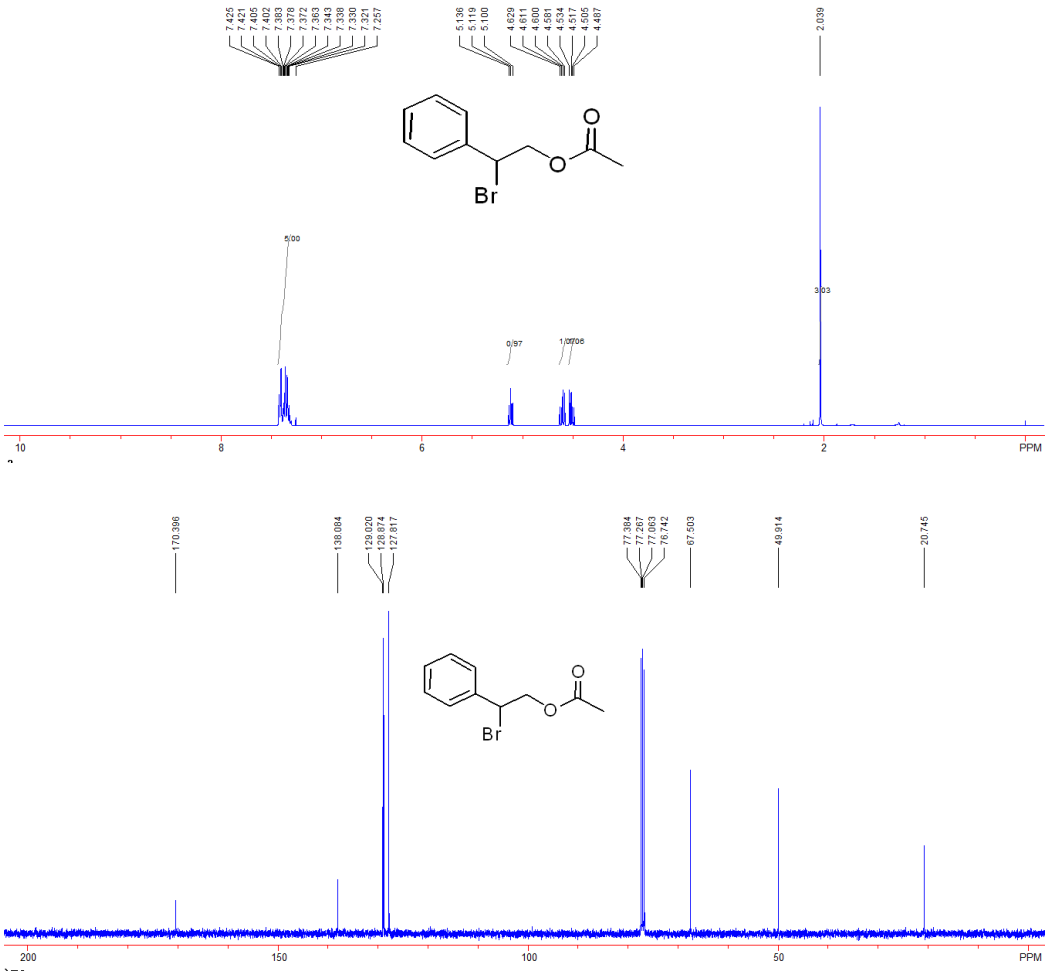


Compound **3t**

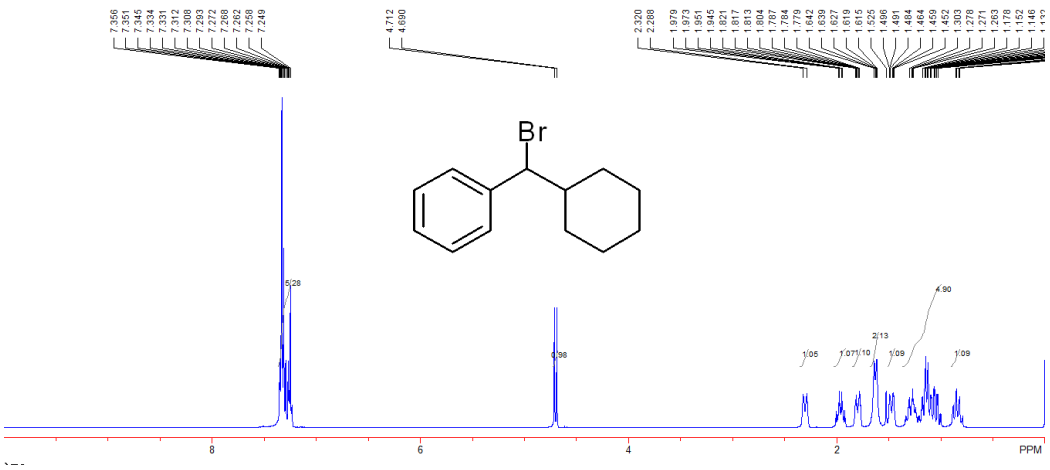


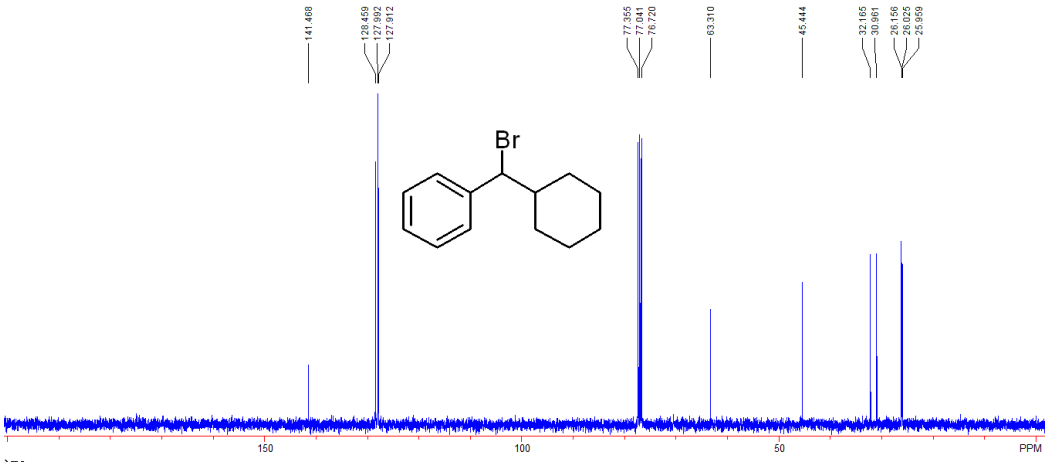


Compound **3u**

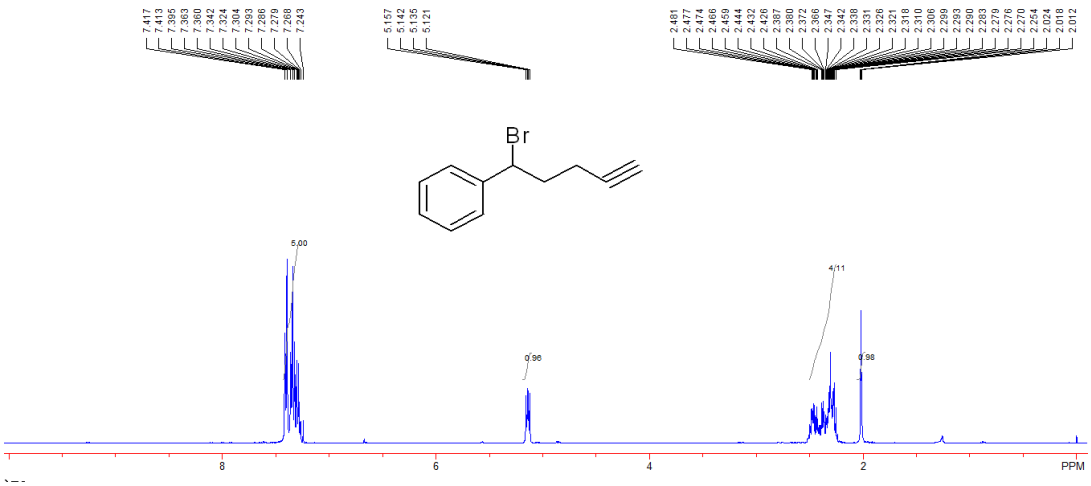


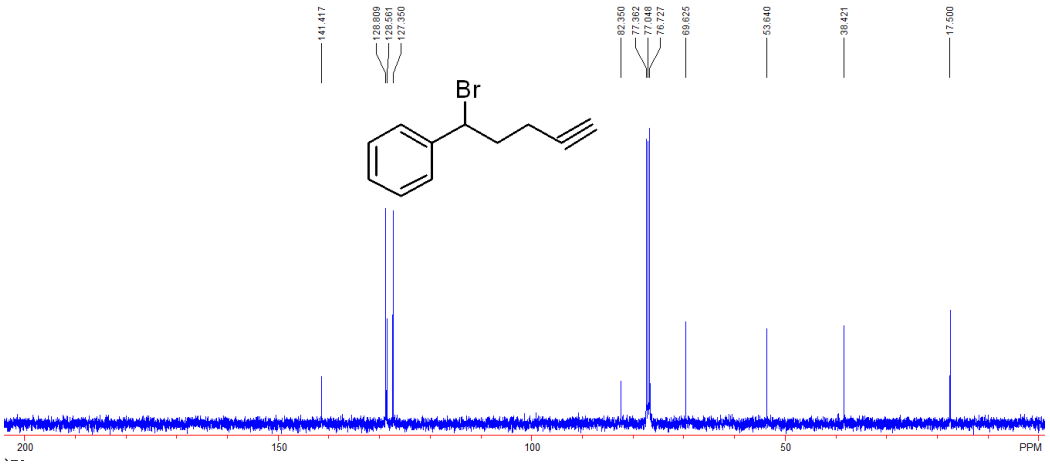
Compound **3v**


Br
5.28
0.98
1.05
1.07
1.10
2.13
1.09
4.90
1.09
8
6
4
2
PPM

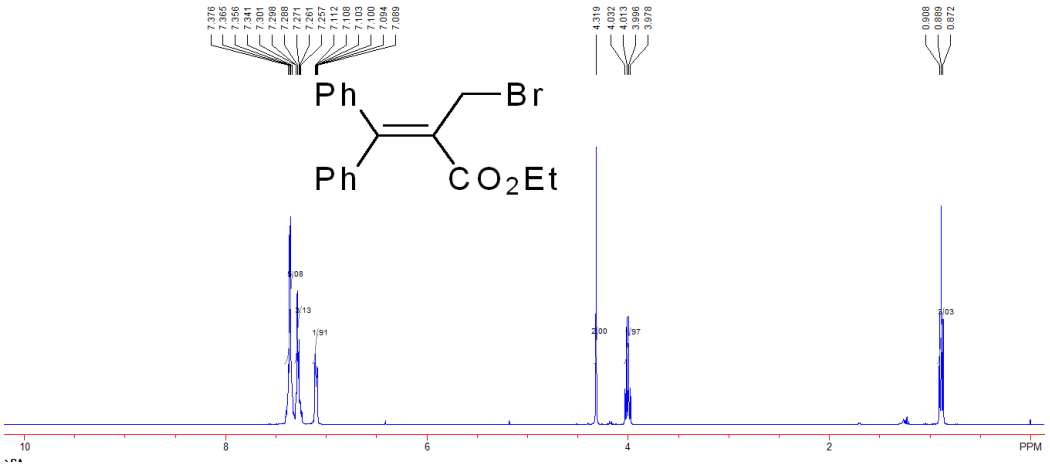

141.468
128.459
127.992
127.912
77.355
77.041
76.720
63.310
45.444
32.165
30.961
26.156
26.025
25.959
Br
150
100
50
PPM

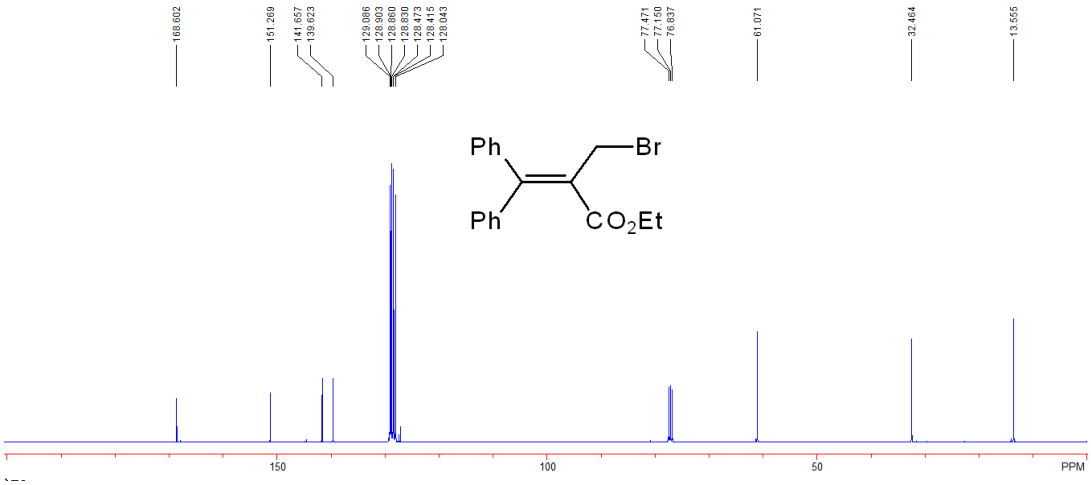
Compound **3w**


Br
5.00
0.96
4.11
0.98
8
6
4
2
PPM

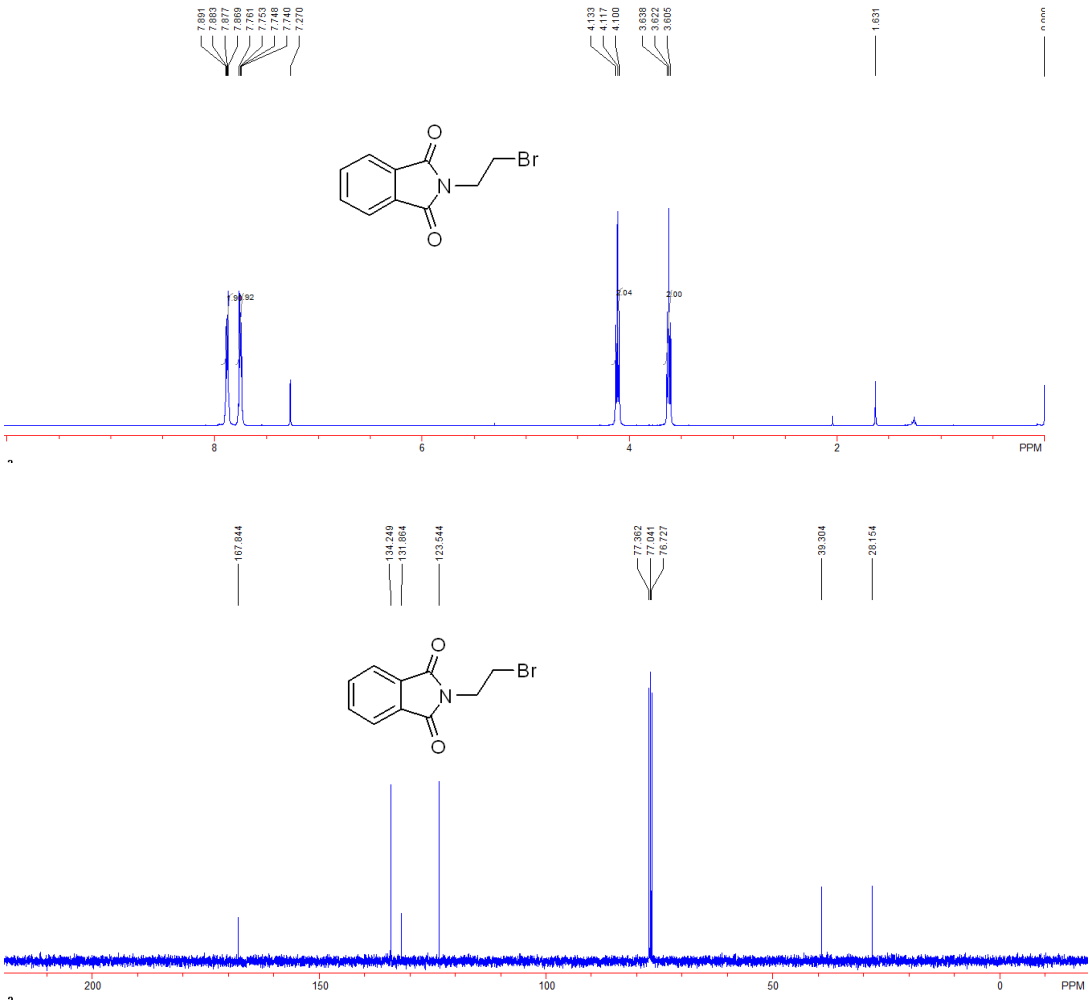


Compound **3x**

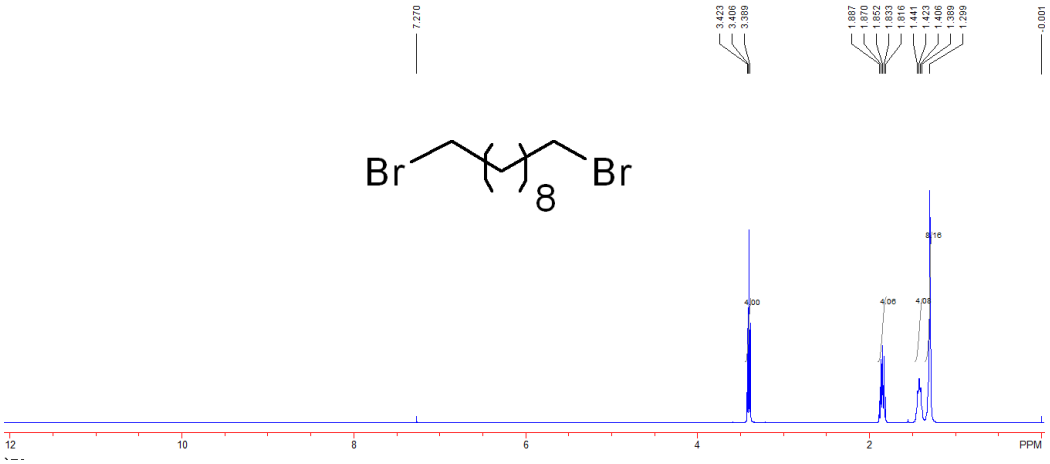


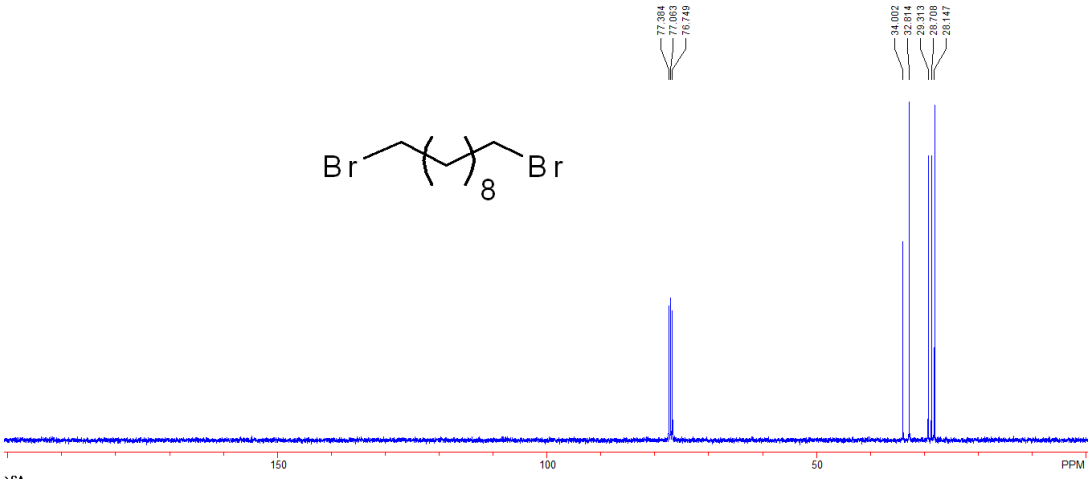


Compound **3y**

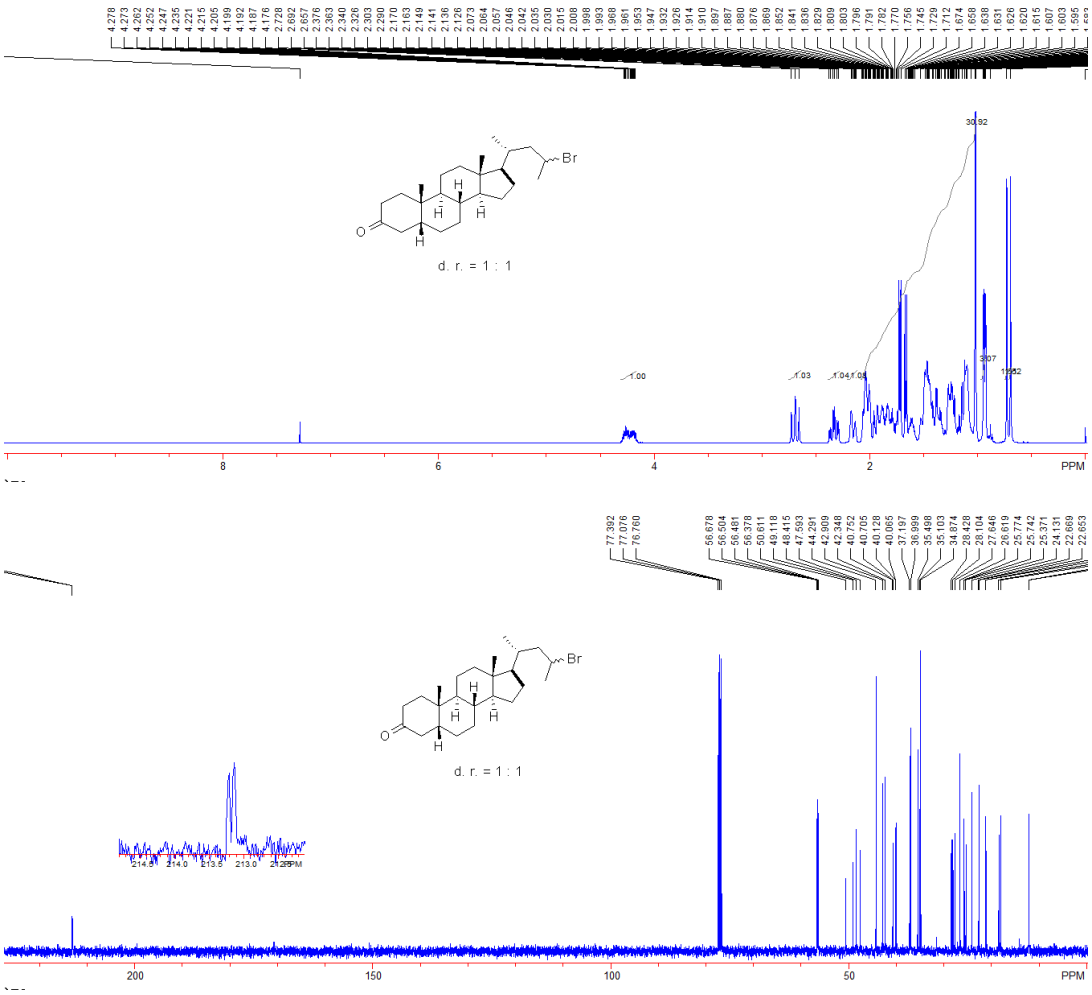

7.891
7.889
7.877
7.869
7.761
7.753
7.748
7.740
7.270
4.133
4.117
4.100
3.638
3.622
3.605
1.631
0.000
Br
O
N
O
1.92
7.04
2.00
8
6
4
2
PPM
167.844
134.249
131.864
123.544
77.362
77.041
76.727
39.304
28.154
Br
O
N
O
200
150
100
50
0
PPM

Compound **3z**

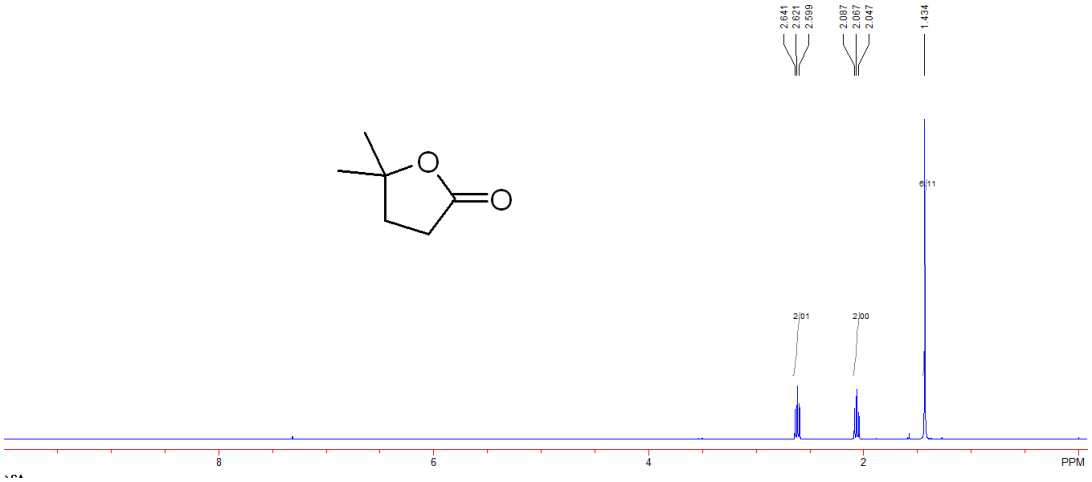

7.270
3.423
3.406
3.388
1.887
1.870
1.852
1.833
1.816
1.441
1.423
1.406
1.389
1.299
0.001
Br
8
Br
4.00
4.06
4.06
8.16
12
10
8
6
4
2
PPM

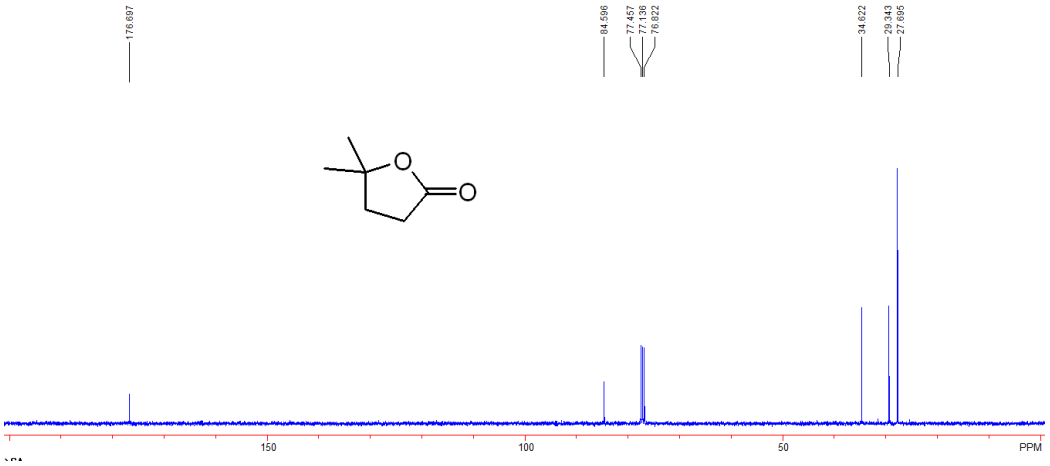


Compound **5**

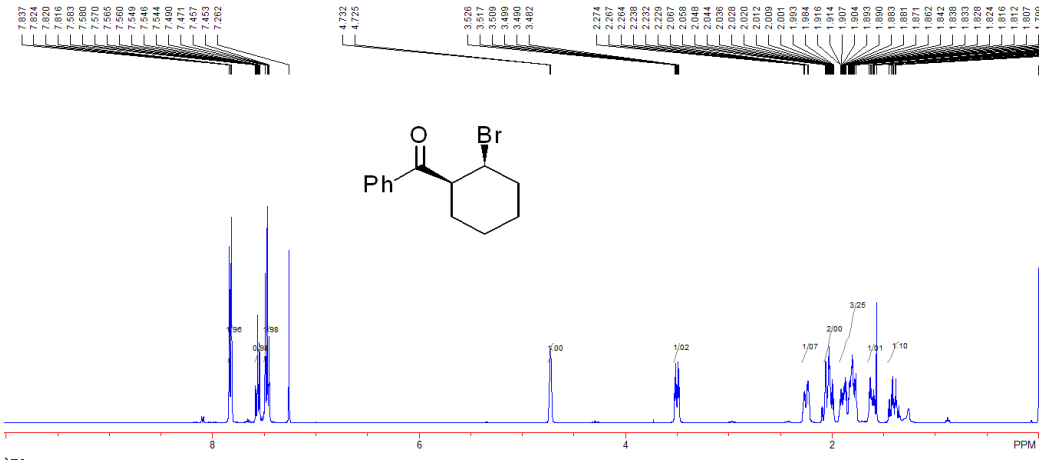


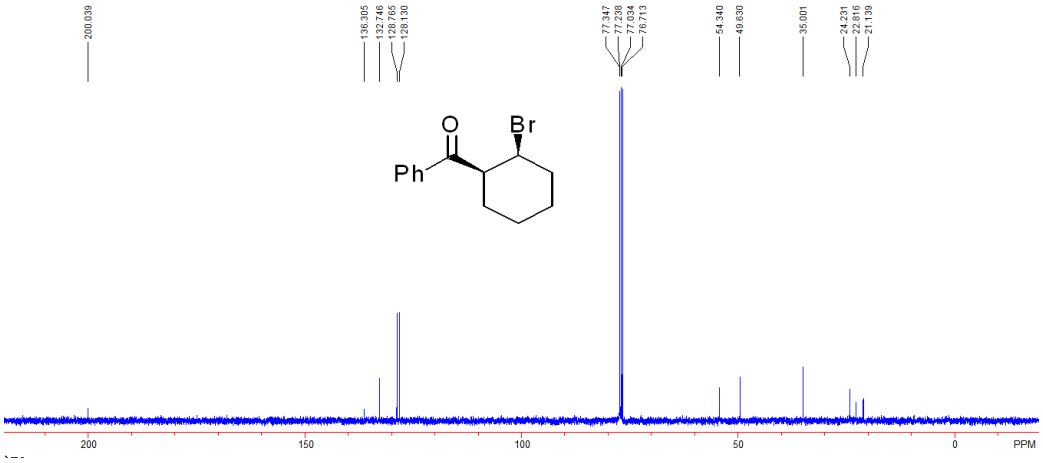
Compound **7**



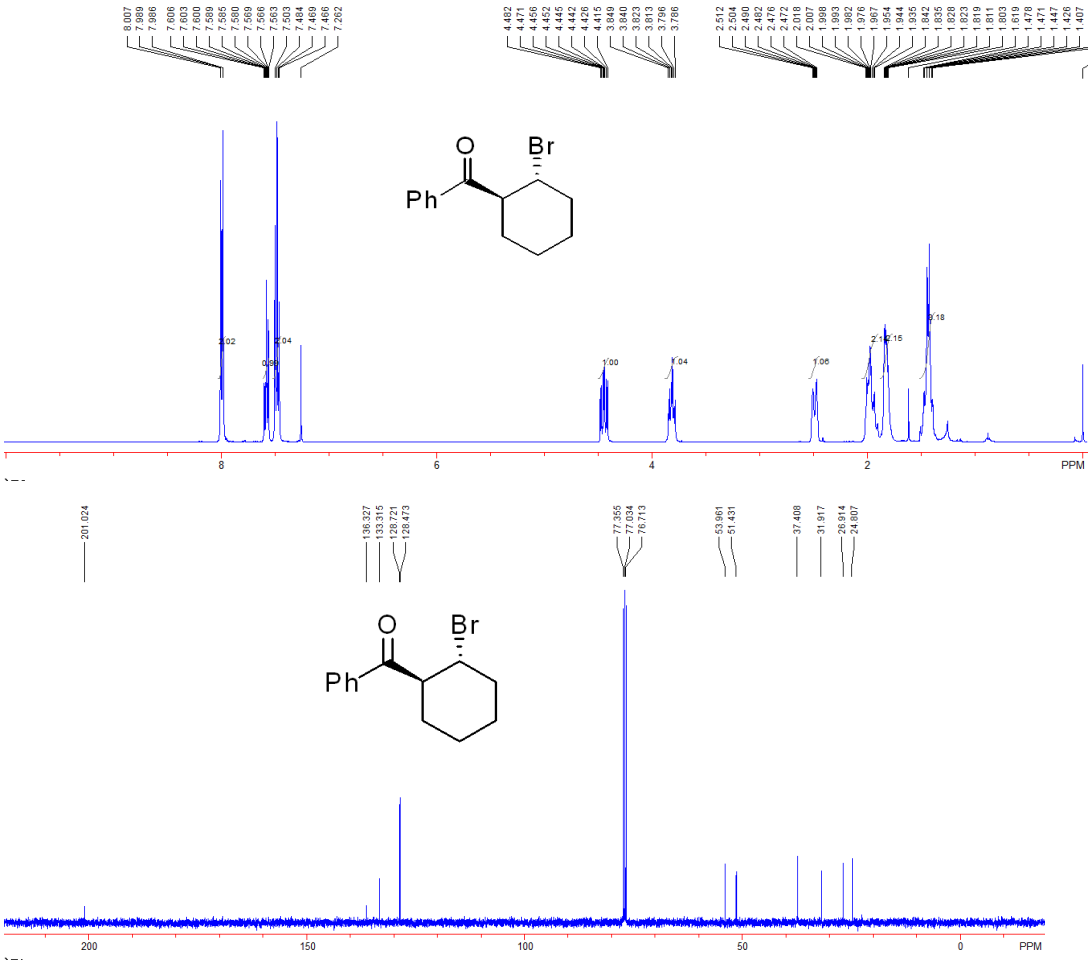


Compound *cis*-**9**

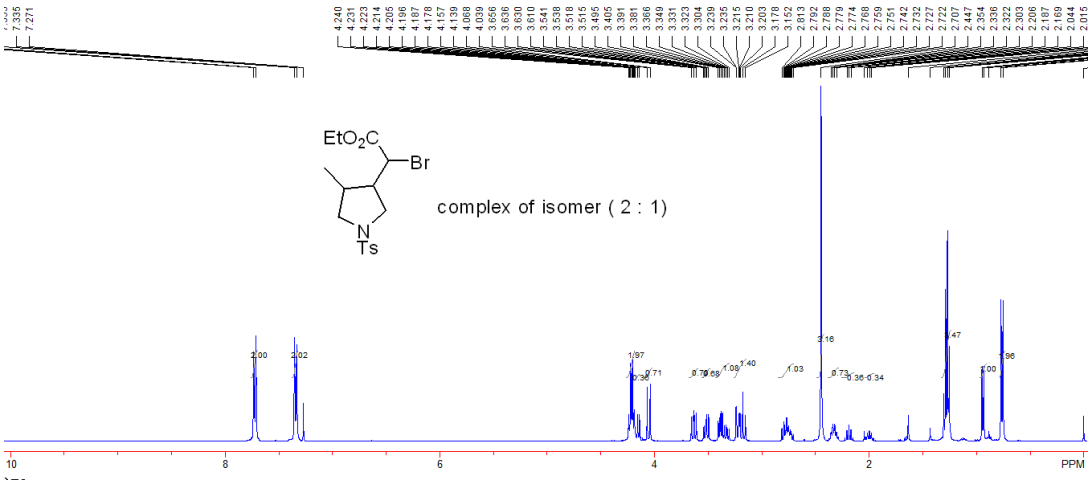


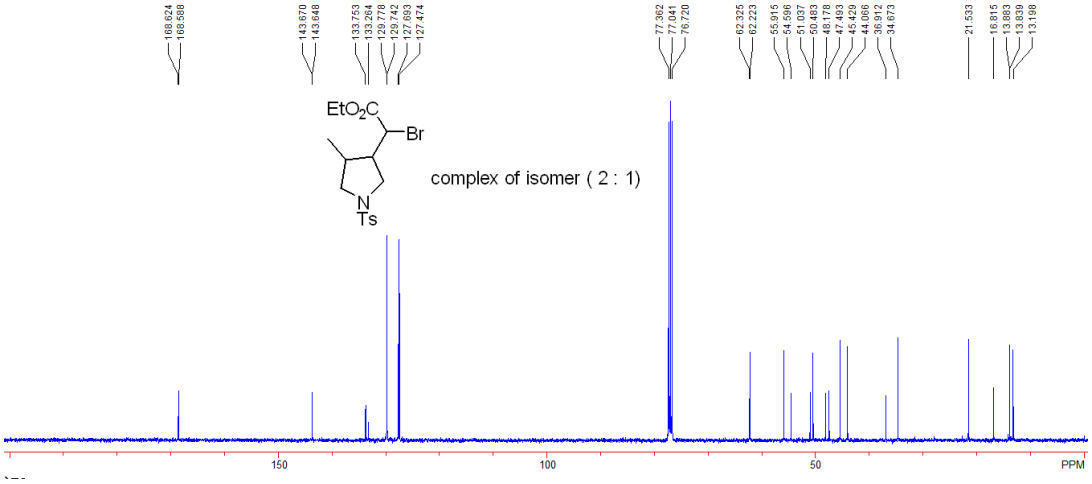


Compound *trans*-**9**



Compound **11**


EtO2C
Br
N
Ts
complex of isomer (2 : 1)
PPM


EtO2C
Br
N
Ts
complex of isomer (2 : 1)
PPM