Supporting Information for

Silver-Catalyzed Decarboxylative Radical Azidation of Aliphatic Carboxylic Acids in Aqueous Solution

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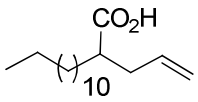
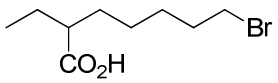
1. Characterizations of New Substrates

The following substrates were commercially available and recrystallized prior to use: 1-adamantanecarboxylic acid (**A-2**), 2-methyl-4-oxo-4-phenylbutanoic acid (**A-18**), 4-chlorophenoxyaceticacid (**A-24**), 2,3-dihydro-benzo[*b*][1,4] dioxine-2-carboxylic acid (**A-25**), tetradecanoic acid (**A-27**), stearic acid (**A-28**), 2,2-dimethylpentanedioic acid (**A-30**). The rest substrates were readily prepared by conventional methods.

Characterizations of New Substrates:

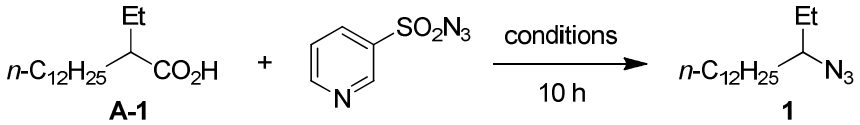


2-Allyltetradecanoic acid (A-15). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82-5.72 (m, 1H), 5.10-5.02 (m, 2H), 2.48-2.23 (m, 3H), 1.66-1.46 (m, 2H), 1.26 (br s, 20H), 0.88 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 135.2, 116.9, 45.2, 36.1, 31.9, 31.5, 29.6, 29.5, 29.4, 29.3, 27.2, 22.7, 14.1; IR (neat): ν (cm^{-1}) 3080, 2925, 2854, 1708, 1643, 1465, 1417, 1285, 1249, 916; EIMS (m/z): (rel intensity) 268 (M^+, 6), 129 (8), 113 (68), 100 (100), 83 (26), 69 (47), 57 (35), 55 (48), 43 (45), 41 (51); HRMS calcd for $C_{17}H_{32}O_2$ [M]: 268.2402; found: 268.2400.



7-Bromo-2-ethylheptanoic acid (A-17). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.3 (br, 1H), 3.34 (t, J = 6.8 Hz, 2H), 2.28-2.21 (m, 1H), 1.84-1.77 (m, 2H), 1.64-1.28 (m, 8H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.8, 46.9, 33.6, 32.5, 31.4, 28.0, 26.4, 25.1, 11.7; IR (neat): ν (cm^{-1}) 2937, 1705, 1462, 1416, 1228, 943, 783, 646; EIMS (m/z): (rel intensity) 157 (5), 139 (6), 113 (33), 100 (33), 88 (100), 73 (47), 69 (31), 55 (29), 41 (28); HRMS calcd for $C_9H_{17}O_2$ [M-Br]: 157.1229; found: 157.1225.

2. Table S1. Optimization of Reaction Parameters

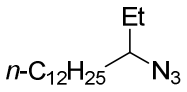


Entry	$AgNO_3$ (equiv)	$K_2S_2O_8$ (equiv)	3-$PySO_2N_3$ (equiv)	Solvent (v:v)	Temp (^oC)	Yield (%)
1	0.2	2	2	CH_2Cl_2/H_2O (1:1)	50	18
2	0.2	2	2	H_2O	50	35
3	0.2	2	2	acetone/H_2O (1:1)	50	45
4	0.2	2	2	CH_3CN/H_2O (1:1)	50	76
5	0.2	2	2	CH_3CN/H_2O (1:1)	40	28
6	0.2	1.5	2	CH_3CN/H_2O (1:1)	50	66
7	**0.2**	**2**	**3**	**CH_3CN/H_2O (1:1)**	**50**	**98**
8	0	2	3	CH_3CN/H_2O (1:1)	50	0
9	0.2	0	3	CH_3CN/H_2O (1:1)	50	0

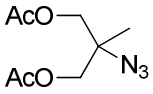
3. Typical Procedure for Silver-Catalyzed Decarboxylative Azidation

2-Ethyltetradecanoic acid (**A-1**, 51.2 mg, 0.20 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), $K_2S_2O_8$ (108 mg, 0.40 mmol) and 3-$PySO_2N_3$ (110 mg, 0.60 mmol) were placed in a Schlenk tube. Acetonitrile (1 mL) and water (1 mL) were then added under nitrogen atmosphere. The reaction solution was stirred at 50 °C for 10 h. The resulting mixture was cooled down to RT and extracted with CH_2Cl_2 (5 mL × 4). The combined organic phase was dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane as the eluent to give the pure product 3-azidopentadecane (**1**) as colorless oil. Yield: 49.6 mg (98%). R_f = 0.55 (hexane).

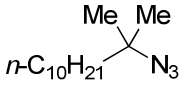
4. Characterizations of New Products



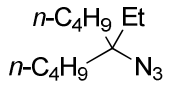
3-Azidopentadecane (1). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.21-3.14 (m, 1H), 1.60-1.47 (m, 4H), 1.26 (brs, 20H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 64.6, 33.9, 31.9, 29.6, 29.5, 29.4, 29.3, 27.4, 26.1, 22.7, 14.1, 10.5; IR (neat): ν (cm^{-1}) 2925, 2854, 2096, 1464, 1273, 1253; EIMS: *m/z* (rel intensity) 224 (5), 196 (100), 168 (5), 140 (7), 126 (11), 112 (15), 98 (60), 84 (29), 71 (62), 58 (34); HRMS calcd for $C_{13}H_{26}N$ ($M–C_2H_5N_2$): 196.2065; found: 196.2064.



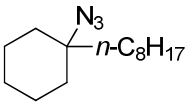
2-Azido-2-methylpropane-1,3-diyl diacetate (3). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.11-4.05 (AB, *J* = 16 Hz, 4H), 2.08 (s, 6H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 66.6, 61.1, 20.6, 18.5; IR (neat): ν (cm^{-1}) 2958, 2108, 1751, 1466, 1380, 1234, 1049, 604; ESI-MS (m/z): 238 $[M+Na]^+$; HRMS calcd for $C_8H_{13}N_3NaO_4$ [M+Na]: 238.0798; found: 238.0803.



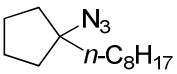
2-Azido-2-methyldodecane (4). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43-1.39 (m, 2H), 1.20 (brs, 16H), 1.17 (s, 6H), 0.81 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.7, 41.4, 31.9, 29.9, 29.6, 29.5, 29.3, 25.9, 24.2, 22.7, 14.1; IR (neat): ν (cm^{-1}) 2928, 2855, 2095, 1467, 1388, 1369, 1260, 1143, 1096, 1019, 804, 722; EIMS (m/z): (rel intensity) 182 (10), 126 (3), 113 (3), 98 (13), 85 (17), 71 (31), 56 (100), 43 (20); HRMS calcd for $C_{12}H_{24}N$ [$M-CH_3N_2$]: 182.1919; found, 182.1912.



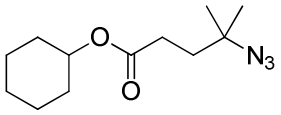
5-Azido-5-ethylnonane (5). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.57-1.46 (m, 6H), 1.35-1.25 (m, 8H), 0.94-0.87 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 66.9, 35.6, 29.0, 25.6, 23.1, 14.0, 7.9; IR (neat): ν (cm^{-1}) 2959, 2932, 2861, 2093, 1464, 1256; EIMS (m/z): (rel intensity) 155 (14), 140 (5), 112 (7), 99 (7), 84 (100), 71 (17), 57 (51), 41 (25); HRMS calcd for $C_9H_{18}N$ [M-$C_2H_5N_2$]: 140.1439; found: 140.1436.



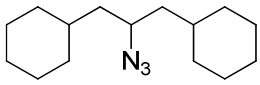
1-Azido-1-octylcyclohexane (6). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68-1.65 (m, 2H), 1.56-1.50 (m, 7H), 1.39-1.29 (m, 15H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 64.2, 40.2, 34.6, 31.8, 30.0, 29.5, 29.2, 25.5, 23.2, 22.6, 22.1, 14.0; IR (neat): ν (cm^{-1}) 2933, 2855, 2100, 1449, 1259, 1148, 902; EIMS (m/z): (rel intensity) 208 (1), 195 (11), 180 (4), 166 (21), 138 (10), 124 (19), 111 (37), 96 (100), 83 (26), 69 (32), 55 (32), 41 (24); HRMS calcd for $C_{14}H_{26}N$ [M-HN_2]: 208.2065; found: 208.2067.



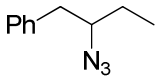
1-Azido-1-octylcyclopentane (7). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82-1.59 (m, 8H), 1.55-1.50 (m, 2H), 1.44-1.36 (m, 2H), 1.29 (brs, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 73.7, 39.0, 36.8, 31.8, 30.0, 29.5, 29.2, 25.1, 23.7, 22.6, 14.0; IR (neat): ν (cm^{-1}) 2928, 2855, 2097, 1465, 1257; EIMS (m/z): (rel intensity) 194 (3), 181 (6), 166 (13), 152 (15), 124 (19), 110 (47), 97 (100), 82 (33), 55 (29), 41 (27); HRMS calcd for $C_{13}H_{24}N$ [M-HN_2]: 194.1909; found: 194.1907.



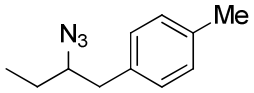
Cyclohexyl 4-azido-4-methylpentanoate (8). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.78-4.72 (m, 1H), 2.36 (t, *J* = 8.0 Hz, 2H), 1.88-1.79 (m, 4H), 1.76-1.63 (m, 2H), 1.58-1.49 (m, 2H), 1.46-1.32 (m, 4H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 72.8, 60.8, 36.2, 31.6, 29.8, 25.8, 25.3, 23.7; IR (neat): ν (cm^{-1}) 2938, 2860, 2099, 1732, 1451, 1371, 1260, 1185, 1124, 1038, 1016; ESI-MS (m/z): 262 $[M+Na]^+$; HRMS calcd for $C_{12}H_{21}N_3NaO_2$ [M+Na]: 262.1526; found: 262.1527.



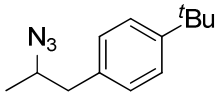
(2-Azidopropane-1,3-diyl)dicyclohexane (9). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.42-3.35 (m, 1H), 1.78-1.64 (m, 10H), 1.47-1.39 (m, 4H), 1.31-1.10 (m, 8H), 0.97-0.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 57.5, 42.4, 34.5, 33.8, 32.8, 26.5, 26.3, 26.1; IR (neat): ν (cm^{-1}) 2924, 2852, 2100, 1448, 1342, 1260, 965; EIMS (m/z): (rel intensity) 220 (2), 178 (10), 152 (12), 124 (100), 109 (7), 97 (23), 81 (28), 67 (22), 55 (98), 41 (34); HRMS calcd for $C_{15}H_{26}N$ [M-HN_2]: 220.2065; found: 220.2061.



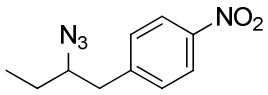
(2-Azidobutyl)benzene (10). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, *J* = 7.6 Hz, 2H), 7.18-7.13 (m, 3H), 3.40-3.33 (m, 1H), 2.73 (d, *J* = 7.2 Hz, 2H), 1.60-1.40 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 129.3, 128.5, 126.7, 65.7, 40.6, 27.1, 10.5; IR (neat): ν (cm^{-1}) 2965, 2927, 2877, 2855, 2097, 1496, 1455, 1344, 1259, 743, 699; EIMS (m/z): (rel intensity) 146 (1), 118 (4), 91 (100), 77 (2), 65 (9), 51 (2), 39 (3); HRMS calcd for $C_{10}H_{12}N$ [M-HN_2]: 146.0970; found: 146.0971.



1-(2-Azidobutyl)-4-methylbenzene (11). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.08 (m, 4H), 3.44-3.38 (m, 1H), 2.76 (d, *J* = 6.8 Hz, 2H), 2.32 (s, 3H), 1.64-1.48 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 134.8, 129.2, 129.1, 65.8, 40.1, 27.0, 21.1, 10.6; IR (neat): ν (cm^{-1}) 2925, 2854, 2096, 1516, 1461, 1378, 1341, 1254, 803; EIMS (m/z): (rel intensity) 189 (M^+, 2), 132 (4), 105 (100), 91 (9), 77 (8), 63 (2); HRMS calcd for $C_{11}H_{15}N_3$ [M]: 189.1266; found: 189.1270.

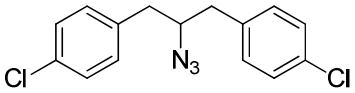


1-(2-Azidopropyl)-4-(*tert*-butyl)benzene (12). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.70-3.62 (m, 1H), 2.80 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.67 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.31 (s, 9H), 1.25 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 134.7, 129.0, 125.4, 59.0, 42.0, 34.4, 31.4, 19.1; IR (neat): ν (cm^{-1}) 3025, 2965, 2869, 2104, 1517, 1458, 1364, 1269, 1249, 1124, 1109, 1021, 837; EIMS (m/z): (rel intensity) 217 (M^+, 3), 175 (2), 147 (100), 132 (22), 117 (17), 105 (12), 91 (11), 65 (4); HRMS calcd for $C_{13}H_{19}N_3$ [M]: 217.1579; found: 217.1577.

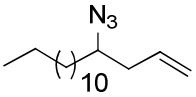


1-(2-Azidobutyl)-4-nitrobenzene (13). Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 3.53-3.47 (m, 1H), 2.95 (dd, *J* = 14.0, 4.8 Hz, 1H), 2.85 (dd, *J* = 14.0, 8.4 Hz, 1H), 1.71-1.55 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 145.7, 130.2, 123.8, 65.1, 40.3, 27.4, 10.5; IR (neat): ν (cm^{-1}) 2969, 2933, 2100, 1606, 1519, 1347, 1270, 1110, 855, 745, 699; EIMS (m/z): (rel intensity) 192 (2), 179 (4), 137 (100), 120 (23), 107 (44), 90 (71), 78 (52), 56 (40); HRMS calcd for $C_{10}H_{12}N_2O_2$ [M-N_2]: 192.0899; found:

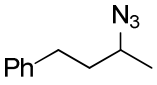
192.0896.



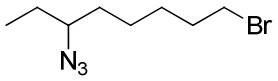
4,4'-(2-Azidopropane-1,3-diyl)bis(chlorobenzene) (14). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.0 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 4H), 3.75-3.69 (m, 1H), 2.86-2.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9, 132.8, 130.6, 128.8, 65.0, 39.9; IR (neat): ν (cm^{-1}) 2922, 2111, 1492, 1409, 1341, 1273, 1247, 1092, 1016, 831, 806; EIMS (m/z): (rel intensity) 305 (M^+, 4), 139 (8), 125 (100), 91 (28), 84 (98), 49 (30); HRMS calcd for $C_{15}H_{13}N_3Cl_2$ [M]: 305.0487; found: 305.0488.



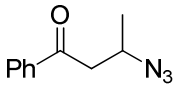
4-Azidohexadec-1-ene (15). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87-5.76 (m, 1H), 5.17-5.11 (m, 2H), 3.35-3.29 (m, 1H), 2.30 (t, *J* = 6.8 Hz, 2H), 1.55-1.35 (m, 2H), 1.26 (brs, 20H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0, 118.0, 62.3, 38.8, 33.9, 31.9, 29.6, 29.5, 29.4, 29.3, 26.0, 22.7, 14.1; IR (neat): ν (cm^{-1}) 2926, 2854, 2101, 1465, 1377, 1340, 1256, 918; EIMS (m/z): (rel intensity) 236 (1), 196 (13), 138 (4), 110 (11), 96 (26), 84 (50), 71 (57), 57 (100), 43 (84); HRMS calcd for $C_{16}H_{30}N$ [M-HN_2]: 236.2378; found: 236.2381.



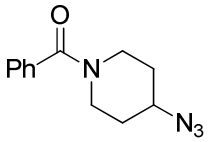
(3-Azidobutyl)benzene (16). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.21-7.18 (m, 3H), 3.47-3.39 (m, 1H), 2.79-2.62 (m, 2H), 1.87-1.71 (m, 2H), 1.29 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 128.5, 128.4, 126.0, 57.2, 37.9, 32.3, 19.5; IR (neat): ν (cm^{-1}) 2924, 2852, 2098, 1458, 1259, 1098; EIMS (m/z): (rel intensity) 146 (77), 105 (43), 132 (15), 117 (13), 104 (100), 91 (99), 77 (27), 65 (19); HRMS calcd for $C_{10}H_{12}N$ [M-HN_2]: 146.0970; found: 146.0974.



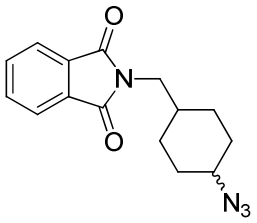
6-Azido-1-bromooctane (17). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.41 (t, *J* = 6.8 Hz, 2H), 3.21-3.15 (m, 1H), 1.90-1.84 (m, 2H), 1.60-1.37 (m, 8H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 64.4, 33.8, 33.7, 32.6, 27.9, 27.4, 25.3, 10.5; IR (neat): ν (cm^{-1}) 2967, 2938, 2096, 1462, 1406, 1342, 1253; EIMS (m/z): (rel intensity) 206/204 (1/1), 178 (28)/176 (28), 107 (13)/109 (12), 98 (32), 84 (30), 69 (100), 56 (53), 41 (69); HRMS calcd for $C_8H_{15}NBr$ [M-HN_2]: 204.0388; found: 204.0382.



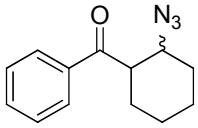
3-Azido-1-phenylbutan-1-one (18). Lightyellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 4.18-4.10 (m, 1H), 3.18 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.94 (dd, *J* = 17.2, 5.8 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 136.6, 133.5, 128.7, 128.1, 53.8, 44.7, 19.8; IR (neat): ν (cm^{-1}) 3060, 2975, 2931, 2101, 1686, 1648, 1598, 1449, 1422, 1367, 1219, 919, 757, 689; ESI-MS (m/z): 212 $[M+Na]^+$; HRMS calcd for $C_{10}H_{11}N_3NaO$ [M+Na]: 212.0794; found: 212.0788.



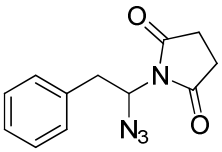
(4-Azidopiperidin-1-yl)(phenyl)methanone (20). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.28 (m, 5H), 4.08 (br, 1H), 3.65-3.61 (m, 2H), 3.26 (br, 2H), 1.84 (br, 2H), 1.56 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 135.7, 129.8, 128.5, 126.8, 57.2, 45.1, 39.5, 31.0, 30.4; IR (neat): ν (cm^{-1}) 3480, 2929, 2864, 2097, 1632, 1446, 1363, 1248, 1021, 789, 732, 710; ESI-MS (m/z): 253 $[M+Na]^+$; HRMS calcd for $C_{12}H_{14}N_4NaO$ [M+Na]: 253.1060; found: 253.1056.



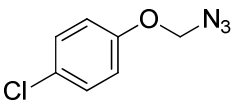
2-((4-Azidocyclohexyl)methyl)isoindoline-1,3-dione (21). This compound was isolated as the mixture of two stereoisomers in about 74:26 ratio determined by ^{1}H NMR (400 MHz). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of two stereoisomers): δ 7.83-7.80 (m, 2H), 7.71-7.69 (m, 2H), 3.78 (br s, 0.7H), 3.56-3.52 (m, 2H), 3.25-3.18 (m, 0.3H), 2.00-1,78 (m, 4H), 1.55-1.09 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 134.0/133.9, 132.0/131.9, 123.3/123.2, 59.9/57.5, 43.2/43.1, 36.0/35.6, 30.9/28.9, 28.7/25.0; IR (neat): ν (cm^{-1}) 2926, 2360, 2342, 2091, 1768, 1709, 1466, 1434, 1397, 1362, 1052, 724; ESI-MS (m/z): 307 $[M+Na]^+$; HRMS calcd for $C_{15}H_{16}N_4NaO_2$ [M+Na]: 307.1166; found: 307.1179.



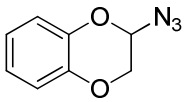
(2-Azidocyclohexyl)(phenyl)methanone (22). This compound was isolated as the mixture of two stereoisomers in about 74:26 ratio determined by ^{1}H NMR (400 MHz). Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of two stereoisomers): δ 7.96/7.85 (2d, J = 7.6 Hz, 2H), 7.57-7.43 (m, 3H), 4.10 (br s, 0.3H), 3.85 (td, J = 10.8 4.4 Hz, 0.7H), 3.41/3.30 (2td, J = 10.8 Hz, 3.2 Hz, 1H), 2.19-2.09 (m, 1H), 1.96-1.70 (m, 3H), 1.63-1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6/200.9, 136.3, 133.3/132.9, 128.7, 128.3/128.1, 61.2/59.5, 50.2/47.6, 31.0/29.6, 29.9/24.1, 24.8/23.3, 24.4/20.8; IR (neat): ν (cm^{-1}) 2937, 2860, 2100, 1681, 1597, 1448, 1316, 1255, 1216, 1200, 1179, 700; ESI-MS (m/z): 252 $[M+Na]^+$; HRMS calcd for $C_{13}H_{15}N_3NaO$ [M+Na]: 252.11073; found: 252.11078.



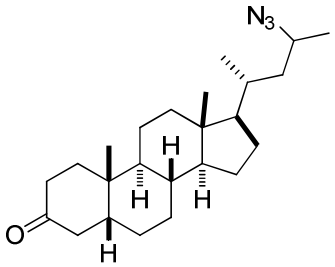
1-(1-Azido-2-phenylethyl)pyrrolidine-2,5-dione (23). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.19 (d, *J* = 7.2 Hz, 2H), 5.55 (t, *J* = 7.6 Hz, 1H), 3.52-3.41 (m, 2H), 2.68-2.53 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 134.9, 129.0, 128.8, 127.4, 67.1, 36.4, 27.8; IR (neat): ν (cm^{-1}) 3030, 2940, 2108, 1780, 1713, 1391, 1362, 1241, 1166; ESI-MS (m/z): 267 $[M+Na]^+$; HRMS calcd for $C_{12}H_{12}N_4NaO_2$ [M+Na]: 267.0852; found: 267.0840.



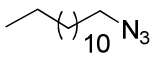
1-(Azidomethoxy)-4-chlorobenzene (24). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.18 (m, 2H), 6.88-6.85 (m, 2H), 5.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 128.6, 126.8, 116.3, 78.9; IR (neat): ν (cm^{-1}) 2963, 2924, 2108, 1596, 1584, 1490, 1261, 1204, 1171, 1094, 1026, 896, 825; EIMS (m/z): (rel intensity) 183 (M^+, 9), 141 (14), 128 (100), 111 (13), 99 (23), 73 (10), 65 (15); HRMS calcd for $C_7H_6N_3OCl$ [M]: 183.0199; found: 183.0203.



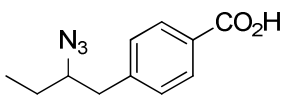
2-Azido-2,3-dihydrobenzo[b][1,4]dioxine (25). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99-6.91 (m, 4H), 5,59 (t, *J* = 2.8 Hz, 1H), 4.15-4.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 140.6, 122.7, 122.3, 117.7, 117.3, 82.7, 65.2; IR (neat): ν (cm^{-1}) 2962, 2930, 2118, 1597, 1495, 1263, 1113, 1093, 906, 833, 749; EIMS (m/z): (rel intensity) 177 (M^+, 46), 135 (14), 121 (100), 109 (15), 93 (9), 81 (13), 63 (18), 52 (12); HRMS calcd for $C_8H_7N_3O_2$ [M]: 177.0538; found: 177.0537.



(5R,8R,9S,10S,13R,14S,17R)-17-((2R)-4-Azidopentan-2-yl)-10,13-dimethyltetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3(2*H*)-one (26). This compound was isolated as the mixture of two diastereoisomers in ~1:1 ratio. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of two stereoisomers): δ 3.53-3.41 (m, 1H), 2.66 (t, *J* = 14.4 Hz, 1H), 2.30 (td, *J* = 14.8, 5.2 Hz, 1H), 2.13 (d, *J* = 14.4 Hz, 1H), 2.03-1.98 (m, 3H), 1.89-1.77 (m, 3H), 1.59-0.83 (m, 26H), 0.68 (d, *J* = 8.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.3, 56.7, 56.6, 56.4, 56.0, 55.2, 44.3, 42.8, 42.3, 42.2, 40.7, 40.1, 40.0, 37.2, 37.0, 35.5, 34.8, 33.7, 33.1, 28.5, 28.3, 26.6, 25.7, 24.1, 22.6, 21.1, 20.5, 19.0, 18.7, 18.4, 12.0, 11.9; IR (neat): ν (cm^{-1}) 2936, 2865, 2100, 1715, 1446, 1378, 1256; EIMS (m/z): (rel intensity) 357 (2), 342 (10), 288 (1), 231 (3), 176 (5), 124 (100), 111 (16), 98 (18), 84 (21), 57 (15); HRMS calcd for $C_{24}H_{39}NO$ [M-N_2]: 357.3032; found: 357.3029.

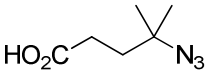


1-Azidotridecane (27). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (t, *J* = 6.8 Hz, 2H), 1.63-1.56 (m, 2H), 1.26 (br s, 20H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.5, 31.9, 29.6, 29.5, 29.3, 29.1, 28.8, 26.7, 22.7, 14.1; IR (neat): ν (cm^{-1}) 2925, 2854, 2096, 1466, 1256; EIMS (m/z): (rel intensity) 196 (6), 168 (4), 154 (7), 140 (6), 126 (7), 112 (12), 98 (19), 84 (39), 70 (100), 56 (35), 43 (46); HRMS calcd for $C_{13}H_{26}N$ [M-HN_2]: 196.2065; found: 196.2061.

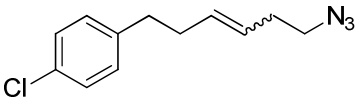


4-(2-Azidobutyl)benzoic acid (29). White solid, mp: 100-102 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (br, 1H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H),

3.53-3.46 (m, 1H), 2.93-2.83 (m, 2H), 1.70-1.52 (m, 2H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 144.4, 130.5, 129.4, 127.8, 65.2, 40.6, 27.2, 10.5; IR (KBr): ν (cm^{-1}) 2926, 2102, 1675, 1610, 1427, 1321, 1293, 1184, 945, 755; ESI-MS (m/z): 218 [M^+-H]; HRMS calcd. for $C_{11}H_{12}N_3O_2$ [M-H]: 218.0935; found: 218.0933.

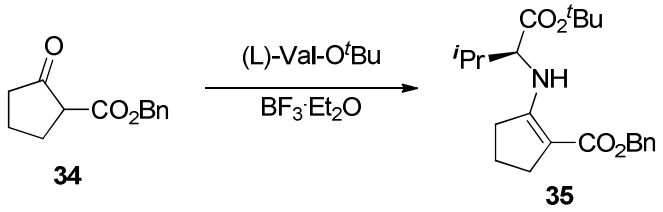


4-Azido-4-methylpentanoic acid (30). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (t, J = 8.0 Hz, 2H), 1.84 (t, J = 8.0 Hz, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9, 60.6, 35.9, 29.1, 25.8; IR (neat): ν (cm^{-1}) 2976, 2933, 2100, 1712, 1418, 1372, 1297, 1259, 1209, 1131; EIMS (m/z): (rel intensity) 115 (40), 97 (62), 84 (7), 73 (45), 69 (91), 56 (100), 41 (40); HRMS calcd for $C_6H_{11}O_2$ [M-N_3]: 115.0759; found: 115.0761.



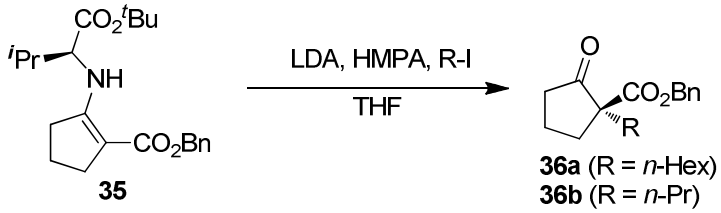
1-(6-Azidohex-3-en-1-yl)-4-chlorobenzene (33). This compound was isolated as the mixture of two stereoisomers in about 82:18 ratio determined by ^{1}H NMR (400 MHz). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of two stereoisomers): δ 7.23 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.59-5.49 (m, 1H), 5.43-5.34 (m, 1H), 3.24 /3.15 (2t, J = 6.8 Hz, 2H), 2.64 (t, J = 7.6 Hz, 2H), 2.38-2.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 132.4, 131.5, 129.9, 129.8, 128.4, 128.3, 126.7, 125.9, 51.0, 50.9, 35.0, 34.2, 32.1, 29.1, 27.0; IR (neat): ν (cm^{-1}) 2927, 2857, 2096, 1492, 1452, 1262, 1092, 1015, 969, 817; EIMS (m/z): (rel intensity) 206 (6), 152 (4), 127 (34), 125 (100), 89 (9), 82 (12); HRMS calcd. for $C_{12}H_{13}NCl$ [M-HN_2]: 206.0737; found: 206.0739.

5. Synthesis of (-)-Indolizidine 209D and 167B



34 **35**

To the solution of benzyl 2-oxocyclopentanecarboxylate (3.92 g, 18 mmol) and L-valine *tert*-butyl ester (4.70 g, 27 mmol) in benzene (150 mL) was added $BF_3{\cdot}Et_2O$ (0.50 mL), and the reaction mixture was heated to reflux using Dean-Stark apparatus for 12 h. The resulting mixture was cooled down to rt and washed successively with aqueous $NaHCO_3$ (100 mL), water (100 mL), saturated NaCl solution (100 mL). The aqueous phase was extracted with ether (100 mL × 4). The combined organic phase was dried over anhydrous $NaSO_4$. Evaporation of the solvent gave the crude product, which was purified by column chromatography on silica gel with hexane/EtOAc (10 : 1, v:v) to give compound **35** (6.52 g, 97%) as a colorless oil. $[\alpha]_D^{25}$ = +77.9 (c 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (br, 1H), 7.38-7.26 (m, 5H), 5.18 (AB, *J* = 12.8 Hz, 2H), 3.64 (dd, *J* = 10.0, 5.6 Hz, 1H), 2.58 (t, *J* = 6.8 Hz, 2H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.15-2.06 (m, 1H), 1.86-1.78 (m, 2H), 1.45 (s, 9H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 167.8, 163.7, 137.4, 128.3, 127.6, 127.5, 94.3, 81.6, 64.3, 63.8, 32.3, 31.7, 29.2, 28.0, 20.9, 19.2, 17.7; IR (neat): ν (cm^{-1}) 2965, 1735, 1663, 1604, 1456, 1369, 1261, 1154, 1131; ESI-MS (m/z): 374 [M^++H]; HRMS calcd for $C_{22}H_{31}NO_4Na$ [M+Na]: 396.2145; found: 396.2131.

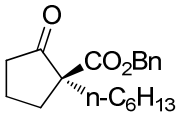


35

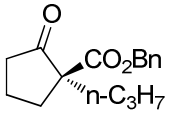
36a (R = *n*-Hex)
36b (R = *n*-Pr)

n-BuLi (1 mL, 2.5 M in hexane, 2.5 mmol) was added to the solution of $^i Pr_2NH$ (0.36

mL, 2.5 mmol) in toluene (3 mL) at -78 °C, and the mixture was stirred at 0 °C for 0.5 h. A solution of compound **35** (0.75 g, 2 mmol) in toluene (2 mL) was then added at -78 °C and the resulting solution was stirred at -78 °C for 1 h. HMPA (0.44 mL, 2.5 mmol) was added and the reaction mixture was stirred at -78 °C for 1 h. Alkyl iodide (2.5 mmol) was added and the reaction mixture was stirred at -25 °C for 3 h. The reaction mixture was then warmed up to rt and stirred overnight. The reaction was quenched with 1N HCl (5 mL) and the resulting mixture was stirred at room temperature for 1 h and then extracted with Et_2O (10 mL × 4). . The organic phase was dried over anhydrous Na_2SO_4, concentrated to leave the crude product, which was purified by column chromatography on silica gel with hexane/EtOAc (20:1, v:v) as the eluent to give compound **36**.

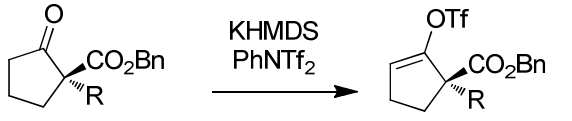


Compound 36a (0.470 g, 78%), Colorless oil; $[\alpha]_D^{24}$ = +15.0 (c 0.40, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 5H), 5.13 (AB, *J* = 12.4 Hz, 2H), 2.56-2.48 (m, 1H), 2.41-2.34 (m, 1H), 2.29-2.20 (m, 1H), 1.99-1.81 (m, 4H), 1.60-1.52 (m, 1H), 1.23 (br s, 8H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9, 170.9, 135.7, 128.5, 128.2, 127.9, 66.9, 60.7, 38.0, 33.9, 32.6, 31.5, 29.5, 24.7, 22.5, 19.6, 14.0; IR (neat): ν (cm^{-1}) 2955, 2929, 2858, 1751, 1726, 1456, 1273, 1223, 1137, 697; ESI-MS (m/z): 325 [M^++Na]; HRMS calcd for $C_{19}N_{26}NaO_3$ [M+Na]: 325.1774; found: 325.1771. The chiral HPLC analysis indicated that the ee was 83%.



Compound 36b (0.398 g, 77%), Colorless oil; $[\alpha]_D^{24}$ = +9.3 (c 0.60, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 5H), 5.14 (s, 2H), 2.57-2.48 (m, 1H), 2.43-2.35 (m, 1H), 2.29-2.20 (m, 1H), 2.01-1.86 (m, 4H), 1.61-1.53 (m, 1H), 1.37-1.15 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.8, 170.9, 135.7, 128.5, 128.2, 127.8, 66.9, 60.7, 38.0, 36.0, 32.6, 19.6, 18.2, 14.3; IR

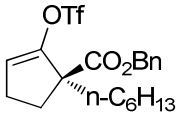
(neat): ν (cm^{-1}) 2962, 1751, 1725, 1456, 1274, 1220, 1143, 1101, 738, 698; ESI-MS (m/z): 283 [M^++Na]; HRMS calcd for $C_{16}N_{21}O_3$ [M+H]: 261.1485; found: 261.1485. The chiral HPLC analysis indicated that the ee was 88%.



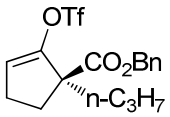
36a (R = *n*-Hex)
36b (R = *n*-Pr)

37a (R = *n*-Hex)
37b (R = *n*-Pr)

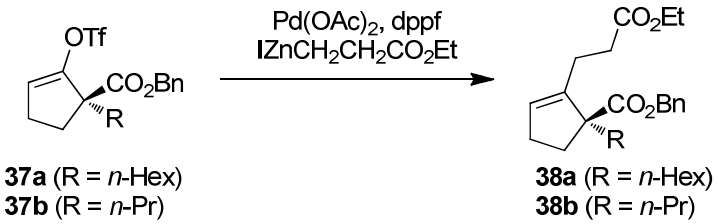
To a 100 mL flask containing KHMDS (6 mL, 1 M in THF, 6 mmol) in THF (20 mL) was added the solution of compound **36** (5 mmol) in THF (10 mL) at -78 ℃. The reaction mixture was stirred at -78 ℃ for 1 h. Then the solution of $PhNTf_2$ (1.8 g, 5 mmol) in THF (15 mL) was added dropwise over 10 min. The solution was maintained at -78 ℃ for 1 h, and then warmed up to room temperature. The reaction was quenched by the addition of aqueous NH_4Cl (20 mL) and extracted with Et_2O (20 mL × 4). The combined organic phase were dried over anhydrous Na_2SO_4 and concentrated. The crude material was chromatographed on silica gel with hexane/ether (20:1) as the eluent to afford compound **37**.



Compound 37a (1.97 g, 91%), Colorless oil; $[\alpha]_D^{26}$ = +24.2 (c 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.30 (m, 5H), 5.76 (s, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 2.60-2.43 (m, 2H), 2.37-2.30 (m, 1H), 1.98-1.89 (m, 2H), 1.65-1.59 (m, 1H), 1.28-1.17 (m, 8H), 0.86 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 148.4, 135.6, 128.5, 128.2, 128.1, 118.4 (q, J_{C-F} = 318.9 Hz), 117.8, 67.0, 57.7, 34.7, 31.6, 31.5, 29.4, 26.2, 24.2, 22.5, 14.0; IR (neat): ν (cm^{-1}) 2932, 2861, 1736, 1424, 1249, 1214, 1142, 840, 697, 608; ESI-MS (m/z): 457 [M^++Na]; HRMS calcd for $C_{20}H_{25}NaO_5F_3S$ [M+Na]: 457.1267; found: 457.1273.



Compound 37b (1.80 g, 92%), Colorless oil; $[\alpha]_D^{26}$ = +27.6 (c 0.44, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 5H), 5.76 (s, 1H), 5.19 (d, *J* = 12.4 Hz, 1H), 5.12 (d, *J* = 12.4 Hz, 1H), 2.55-2.42 (m, 2H), 2.38-2.30 (m, 1H), 1.97-1.89 (m, 2H), 1.66-1.58 (m, 1H), 1.32-1.20 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 148.4, 135.6, 128.5, 128.2, 128.1, 118.4 (q, J_{C-F} = 318.9 Hz), 117.8, 67.0, 57.7, 36.9, 31.6, 26.2, 17.6, 14.2; IR (neat): ν (cm^{-1}) 2963, 2878, 1736, 1655, 1423, 1215, 1141, 839, 697; ESI-MS (m/z): 415 [M^++Na]; HRMS calcd for $C_{17}H_{23}O_5NF_3S$ [M+NH_4]: 410.1244; found: 410.1239.

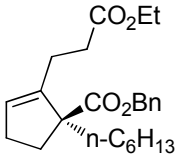


37a (R = *n*-Hex)
37b (R = *n*-Pr)

38a (R = *n*-Hex)
38b (R = *n*-Pr)

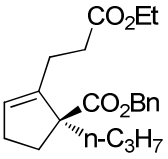
The zinc reagent $IZnCH_2CH_2CO_2Et$ was prepared by literature method.

To the solution of compound **37** (3.5 mmol), Pd $(OAc)_2$ (0.079g, 0.35 mmol), 1,1'-bis(diphenylphosphino)ferrocene (0.39 g, 0.70 mmol) in THF (18 mL) was added $IZnCH_2CH_2CO_2Et$ (14 mmol in 15 mL THF). The resulting mixture was stirred at 50 °C for 18 h. The reaction was quenched with aqueous $NHCl_4$ (20 mL) and extracted with Et_2O (20 mL × 4). The combined organic phase was dried over anhydrous Na_2SO_4 and then concentrated to give the crude product, which was purified by chromatography on silica gel with hexane/EtOAc (20:1) as the eluent to afford compound **38**.

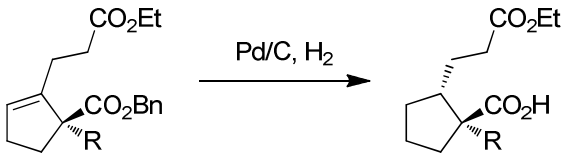


Compound 38a (0.98 g, 73%), Colorless oil; $[\alpha]_D^{27}$ = +55.6 (c 0.44, $CHCl_3$); ^1H

NMR (400 MHz, $CDCl_3$): δ 7.36-7.27 (m, 5H), 5.48 (s, 1H), 5.13 (d, *J* = 12.8 Hz, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.51-2.22 (m, 7H), 2.01-1.94 (m, 1H), 1.79-1.72 (m, 1H), 1.47-1.40 (m, 1H), 1.29-1.11(m, 11H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 173.2, 143.9, 136.3, 128.4, 128.0, 127.9, 126.8, 66.1, 61.4, 60.3, 35.7, 33.6, 32.7, 31.7, 30.7, 29.7, 24.7, 22.7, 22.6, 14.2, 14.0; IR (neat): ν (cm^{-1}) 2930, 2857, 1732, 1214, 1155, 697; ESI-MS (m/z): 409 [M^++Na]; HRMS calcd for $C_{24}H_{34}NaO_4$ [M+Na]: 409.2349; found: 409.2353.

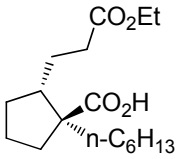


Compound 38b (0.88 g, 73%), Colorless oil; $[\alpha]_D^{27}$ = +66.0 (c 0.40, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.27 (m, 5H), 5.48 (s, 1H), 5.10 (AB, *J* = 12.4 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.50-2.21 (m, 7H), 2.00-1.92 (m, 1H), 1.81-1.74 (m, 1H), 1.48-1.40 (m, 1H), 1.29-1.15 (m, 5H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 173.2, 143.9, 136.3, 128.4, 128.0, 127.8, 126.8, 66.1, 61.4, 60.3, 37.9, 33.6, 32.7, 30.7, 22.7, 18.0, 14.6, 14.2; IR (neat): ν (cm^{-1}) 2956, 2872, 1732, 1456, 1217, 1155, 1106, 1030, 698; ESI-MS (m/z): 367 [M^++Na]; HRMS calcd for $C_{21}H_{29}O_4$ [M+H]: 345.2060; found: 345.2059.

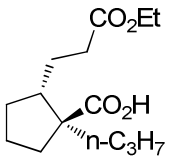


38a (R = *n*-Hex) **39a** (R = *n*-Hex)
38b (R = *n*-Pr) **39b** (R = *n*-Pr)

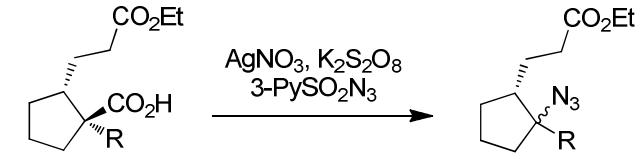
To the solution of compound **38** (3 mmol) in EtOH (30 ml) was added Pd/C (30% wt), and then the resulting mixture was hydrogenated for 24 h at 20°C. The reaction mixture was filtered and then filtrate was concentrated to give compound **39**.



Compound 39a (0.89 g, 99%), Colorless oil; $[\alpha]_D^{26}$ = +28.3 (c 0.42, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 4.12 (q, *J* = 6.8 Hz, 2H), 2.43-2.35 (m, 1H), 2.30-2.19 (m, 2H), 2.01-1.79 (m, 4H), 1.72-1.36 (m, 5H), 1.27-1.23 (m, 12H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 173.6, 60.3, 56.8, 50.3, 38.0, 33.9, 33.7, 31.7, 30.2, 29.9, 26.3, 25.8, 22.6, 22.2, 14.2, 14.0; IR (neat): ν (cm^{-1}) 2933, 2860, 1737, 1693, 1456, 1374, 1251, 1182, 1161; ESI-MS (m/z): 321 [M^++Na]; HRMS calcd for $C_{17}H_{30}NaO_4$ [M+Na]: 321.2036; found: 321.2025.



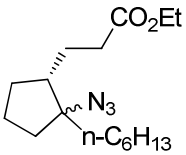
Compound 39b (0.76 g, 99%), Colorless oil; $[\alpha]_D^{27}$ = +29.0 (c 0.30, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 4.12 (q, *J* = 7.2 Hz, 2H), 2.42-2.35 (m, 1H), 2.30-2.19 (m, 2H), 2.04-1.80 (m, 4H), 1.72-1.18 (m, 11H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 173.6, 60.3, 56.8, 50.3, 40.3, 34.0, 33.7, 30.2, 26.2, 22.3, 19.1, 14.7, 14.2; IR (neat): ν (cm^{-1}) 2959, 2873, 1737, 1694, 1456, 1374, 1252, 1185, 1161, 1096, 1034; ESI-MS (m/z): 279 $[M+Na]^+$; HRMS (m/z): $[M+H]^+$ calcd. for $C_{14}H_{25}O_4$, 257.1747; found, 257.1746.



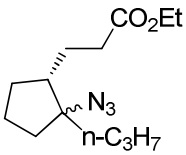
39a (R = *n*-Hex)
39b (R = *n*-Pr)

40a (R = *n*-Hex)
40b (R = *n*-Pr)

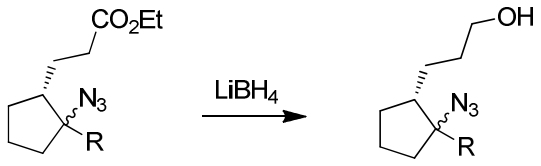
Compound **40** was prepared from the corresponding acid **39** according to the typical procedure for silver-catalyzed decarboxylative azidation of aliphatic carboxylic acids.



Compound 40a (0.056 g, 94%), Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15-4.09 (m, 2H), 2.40-2.18 (m, 2H), 1.97-1.23 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 173.5, 74.6, 74.2, 60.4, 60.3, 48.4, 47.2, 37.2, 35.0, 34.0, 33.2, 33.1, 33.0, 31.7, 29.7, 29.6, 28.6, 25.0, 24.8, 24.5, 24.1, 22.6, 20.8, 20.7, 14.2, 14.0; IR (neat): ν (cm^{-1}) 2960, 2872, 2099, 1737, 1261, 1180, 1097, 1023, 802; EIMS (m/z): (rel intensity) 266 (1), 253 (7), 210 (12), 180 (43), 138 (32), 110 (41), 97 (100), 55 (38), 41 (55); HRMS calcd for $C_{16}H_{28}NO_2$ [M-HN_2]: 266.2120; found: 266.2119.



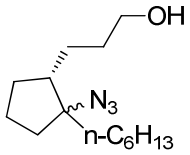
Compound 40b (0.049 g, 97%), Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17-4.10 (m, 2H), 2.41-2.19 (m, 2H), 1.99-1.31 (m, 13H), 1.28-1.23 (m, 3H), 0.97-0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 173.5, 74.6, 74.2, 60.4, 60.3, 48.3, 47.2, 39.5, 35.5, 35.0, 34.0, 33.2, 33.0, 29.6, 28.5, 25.0, 24.5, 20.9, 20.7, 18.2, 17.5, 14.5, 14.2; IR (neat): ν (cm^{-1}) 2962, 2100, 1737, 1261, 1096, 1021, 802; EIMS (m/z): (rel intensity) 224 (1), 211 (14), 180 (7), 165 (19), 138 (67), 124 (47), 96 (100), 81 (36), 67 (37), 55 (57), 41 (55); HRMS calcd for $C_{13}H_{22}NO_2$ [M-HN_2]: 224.1651; found: 224.1648.



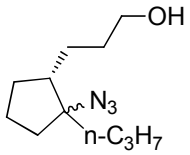
40a (R = *n*-Hex) **41a** (R = *n*-Hex)
40b (R = *n*-Pr) **41b** (R = *n*-Pr)

To the solution of compound **40** (0.30 mmol) in THF (0.50 mL) was added $LiBH_4$

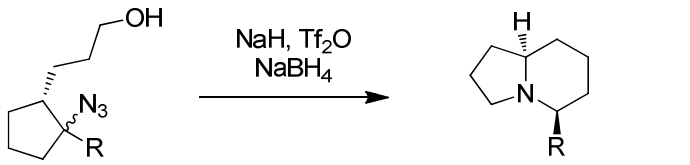
(0.30 mL, 2 M in THF, 0.60 mmol) at 0 °C, the resulting mixture was stirred at room temperature for 48 h. The reaction was quenched with aqueous NH_4Cl (0.5 mL), diluted with water (1 mL) and extracted with Et_2O (3 mL × 4). The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give the crude product, which was purified by chromatography on silica gel with hexane/EtOAc (5:1) as the eluent to give compound **41**.



Compound 41a (0.064 g, 84%), Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.69-3.60 (m, 2H), 2.00-1.84 (m, 2H), 1.82-1.24 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 74.8, 74.4, 63.1, 63.0, 49.3, 47.8, 37.3, 35.2, 34.1, 33.1, 31.7, 31.4, 30.0, 29.8, 29.7, 28.9, 26.0, 25.3, 24.9, 24.2, 22.6, 20.9, 20.8, 14.0; IR (neat): ν (cm^{-1}) 2933, 2861, 2097, 1457, 1263, 1057; EIMS (m/z): (rel intensity); 224 (2), 210 (5), 194 (10), 180 (41), 166 (17), 138 (26), 110 (70), 96 (100), 81 (35), 67 (47), 55 (42), 41 (51); HRMS calcd for $C_{14}H_{26}NO$ [M-HN_2]: 224.2014; found: 224.2012.



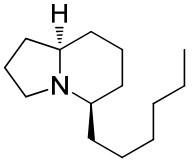
Compound 41b (0.054 g, 85%), Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66-3.61 (m, 2H), 1.99-1.84 (m, 2H), 1.80-1.21 (m, 14H), 0.96-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 74.8, 74.4, 63.1, 62.9, 49.3, 47.7, 39.6, 35.5, 35.2, 34.1, 31.7, 31.4, 30.0, 28.9, 26.0, 25.3, 20.9, 20.8, 18.3, 17.6, 14.5; IR (neat): ν (cm^{-1}) 3339, 2959, 2872, 2099, 1456, 1263, 1058; EIMS (m/z): (rel intensity); 182 (2), 168 (5), 152 (16), 138 (48), 124 (58), 110 (50), 96 (100), 81 (39), 67 (70), 55 (55), 41 (68); HRMS calcd for $C_{11}H_{20}NO$ [M-HN_2]: 182.1545; found: 182.1546.



41a (R = *n*-Hex)
41b (R = *n*-Pr)

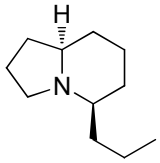
(-)-indolizidine 209D (65%)
(-)-indolizidine 167B (63%)

To the solution of NaH (0.024 g, 60% in oil, 0.6 mmol) in CH_2Cl_2 (1 mL) was added the solution compound **41** (0.30 mmol) in CH_2Cl_2 (3 mL) at -78 °C. The mixture was stirred at -78 °C for 1 h, then Tf_2O (102 mg, 0.36 mmol) was added. The resulting mixture was stirred at -78 °C for 8 h and then warmed up to rt and stirred overnight. $NaBH_4$ (0.080 g, 2.1 mmol) in 15% aqueous NaOH (0.5 mL) was added and the reaction mixture was stirred at rt for 3 h. The resulting mixture was extracted with CH_2Cl_2 (4 mL × 3) The combined organic phase was dried over anhydrous Na_2SO_4, concentrated in vacuo to give the crude product, which was purified by column chromatography on silica gel with pentane/Et_2O (10:1) as the eluent to afford (-)-Indolizidine 209D and 167B.



(-)-Indolizidine 209D

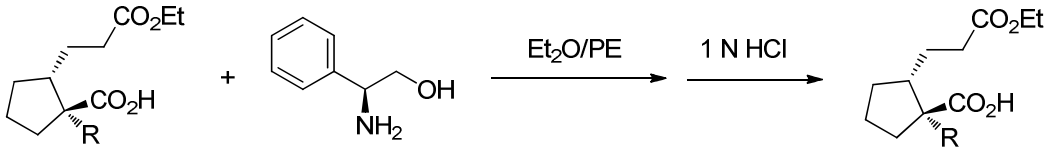
(-)-Indolizidine 209D (0.041 g, 65%), Colorless oil; $[\alpha]_D^{22}$ = -56.4 (c 0.45, $CHCl_3$). The chiral GC analysis indicated that the ee was 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (td, *J* = 8.8, 2.0 Hz, 1H), 1.97-1.60 (m, 9H), 1.44-1.10 (m, 14H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.0, 63.9, 51.5, 34.6, 31.8, 31.0, 30.8, 30.5, 29.7, 25.8, 24.7, 22.6, 20.4, 14.1. The ^{1}H and ^{13}C NMR spectra matched nicely with those reported in the literature.



(-)-Indolizidine 167B

(-)-Indolizidine 167B (0.032 g, 63%), Colorless oil; $[\alpha]_D^{24}$ = -50.7 (c 0.5, $CHCl_3$). The chiral GC analysis indicated that the ee was 86%. ^1H NMR (400 MHz, $CDCl_3$): δ 3.23 (t, *J* = 8.4 Hz, 1H), 1.97-1.59 (m, 9H), 1.44-1.10 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.0, 63.7, 51.5, 36.9, 31.0, 30.8, 30.5, 24.7, 20.4, 19.1, 14.5. The ^1H and ^{13}C NMR spectra matched nicely with those reported in the literature.

6. Optical Resolution of Compound 39



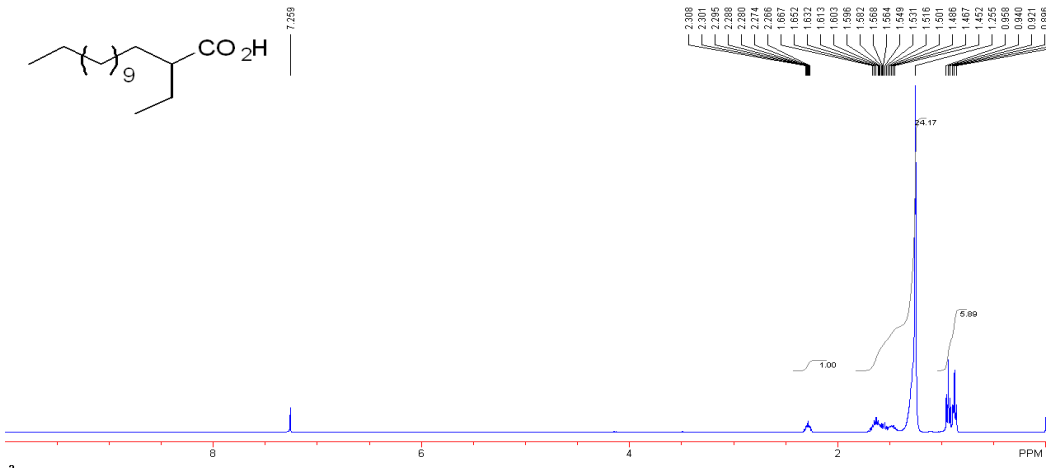
Compound **39** (0.50 mmol) and (S)-2-amino-2-phenylethanol (0.034 g, 0.25 mmol) were dissolved in Et_2O/Hexane (1:3, 12 mL). After an appropriate period of time, the precipitated salt was filtered and acidified with 1N HCl (1 mL) at 50°C. The resulting mixture was extracted with CH_2Cl_2 (3 mL × 4) and then the combined organic phase was dried over anhydrous Na_2SO_4. After the removal of solvent, optically pure **39** was obtained. (**39a**: $[\alpha]_D^{26}$ = +35.4 (c 0.34, $CHCl_3$), **39b**: $[\alpha]_D^{25}$ = +39.1 (c 0.40, $CHCl_3$)).

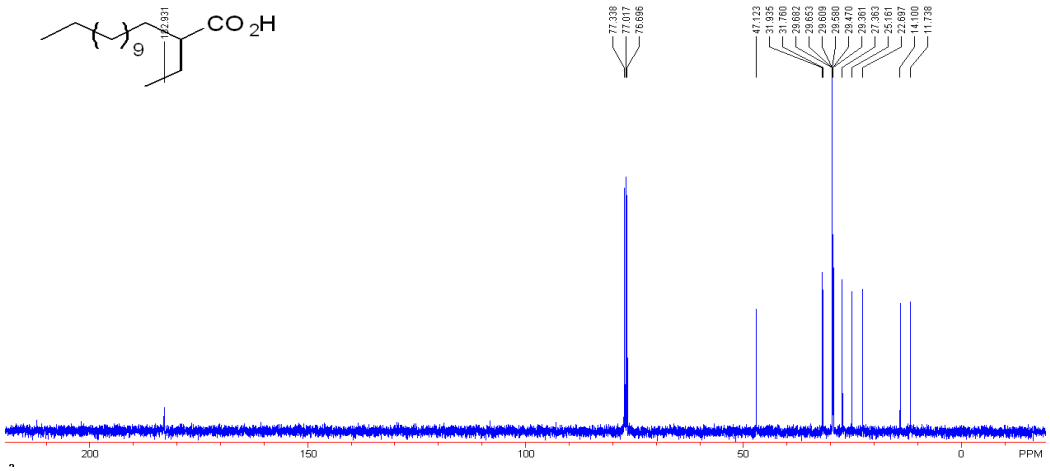
7. References of Known Compounds.

entry	references	compound
1	Wang, Z.; Zhu, L.; Yin, F.; Su, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 4258.	**A-1**, **A-4**, **A-6-10**, **A-14** **A-16**, **A-22**, **A-23, A-31**
2	Yin, F.; Wang, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 10401.	**A-3, A-21, A-26, A-29, A-33**
3	Liu, X.; Wang, Z.; Cheng, X.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 14330.	**A-5, A-11**
4	Yamada, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2005**, *70*, 5471.	**A-12**
5	Lellmann, E.; Schleich, C. *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 434.	**A-13**
6	Nyfeler, E.; Renaud, P. *Org. Lett.* **2008**, *10*, 985.	**A-19, 2, 19**
7	Cintas, P.; Martina, K.; Robaldo, B.; Garella, D.; Boffa, L.; Cravotto, G. *Collect. Czech. Chem. Commun.* **2007**, *72*, 1014.	**28**
8	Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2006**, *128*, 11693.	**31**
9	Yokota, M.; Fujita, D.; Ichikawa, J. *Org. Lett.* **2007**, *9*, 4639.	**32**
10	Christoffers, J.; Önal, N. *Eur. J. Org. Chem.* **2000**, 1633.	**34**
11	Yu, R. T.; Lee, E. E.; Malik, G.; Rovis, T. *Angew. Chem. Int. Ed.* **2009**, *48*, 2379.	**(-)-Indolizidine 209D**
12	Kapat, A.; Nyfeler, E.; Giuffredi, G. T.; Renaud, P. *J. Am. Chem. Soc.* **2009**, *131*, 17746.	**(-)-Indolizidine 167B**

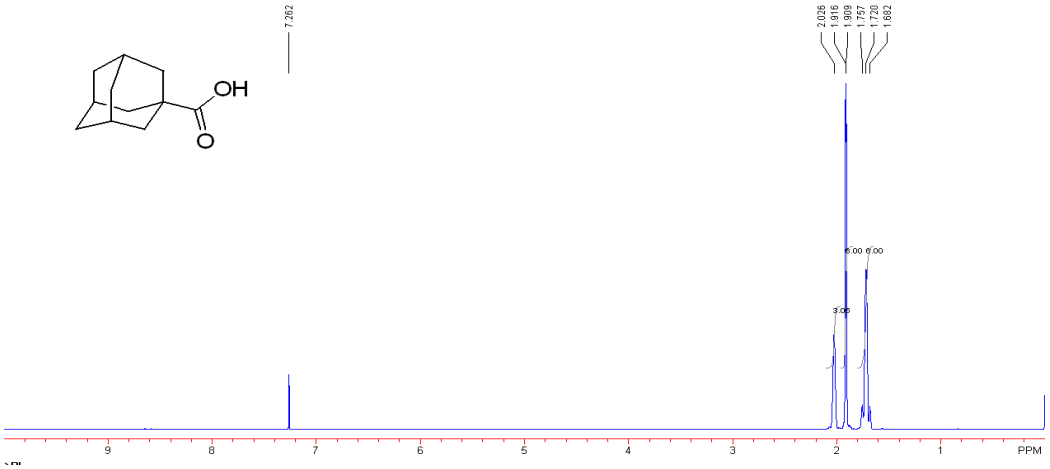
8. ^{1}H and ^{13}C Spectra of All Substrates

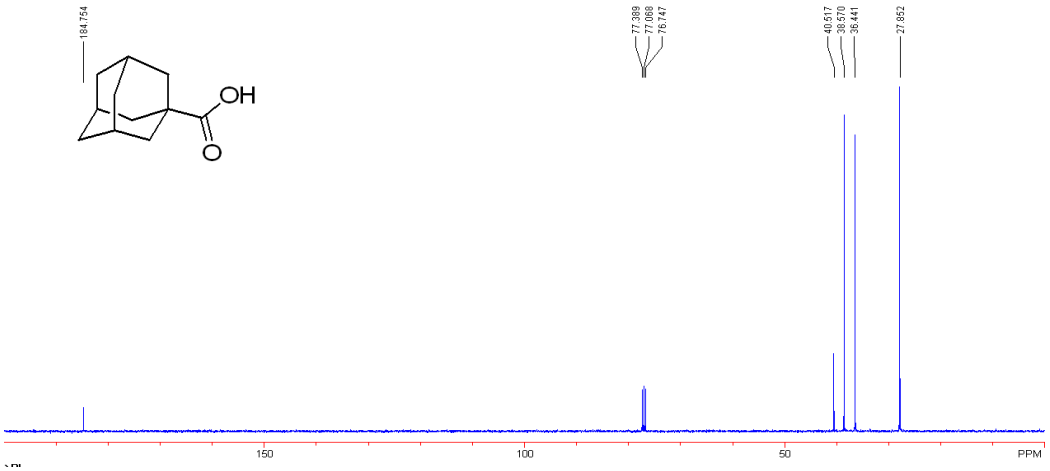
Compound **A-1**



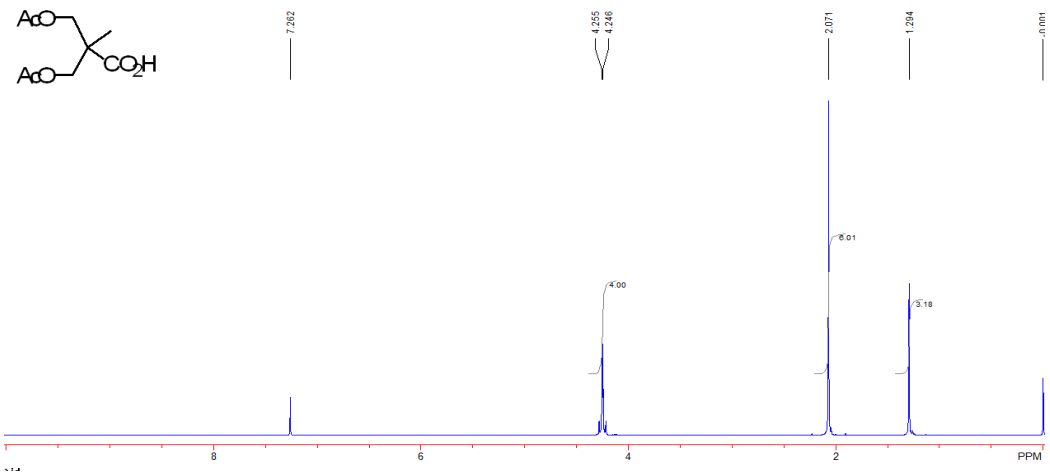


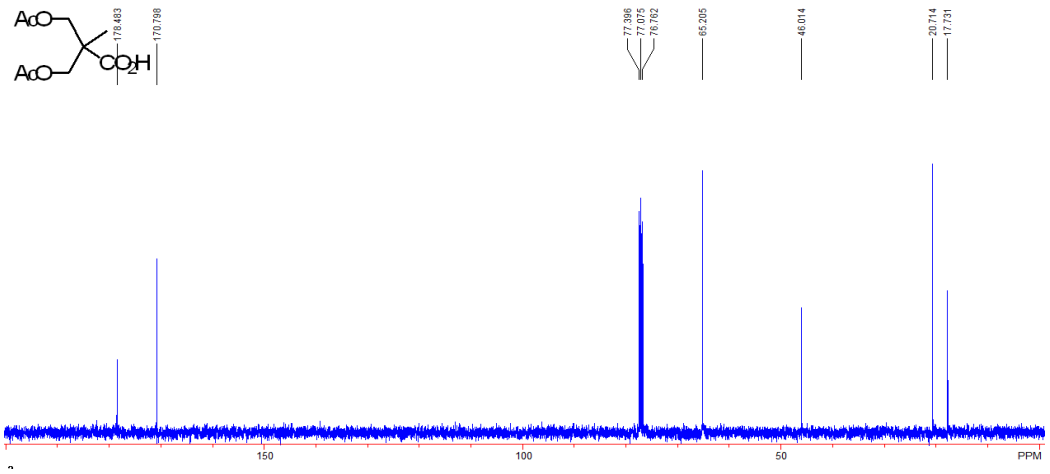
Compound **A-2**


7.282
2.026
1.916
1.909
1.757
1.720
1.682
6.00
6.00
3.06
OH
O
9
8
7
6
5
4
3
2
1
PPM

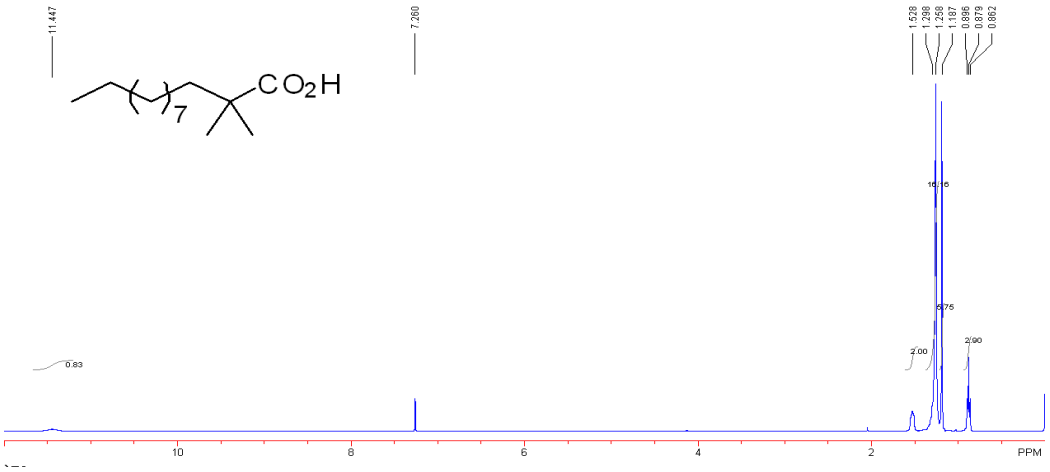

184.754
77.388
77.068
76.747
40.517
38.570
36.441
27.852
OH
O
150
100
50
PPM

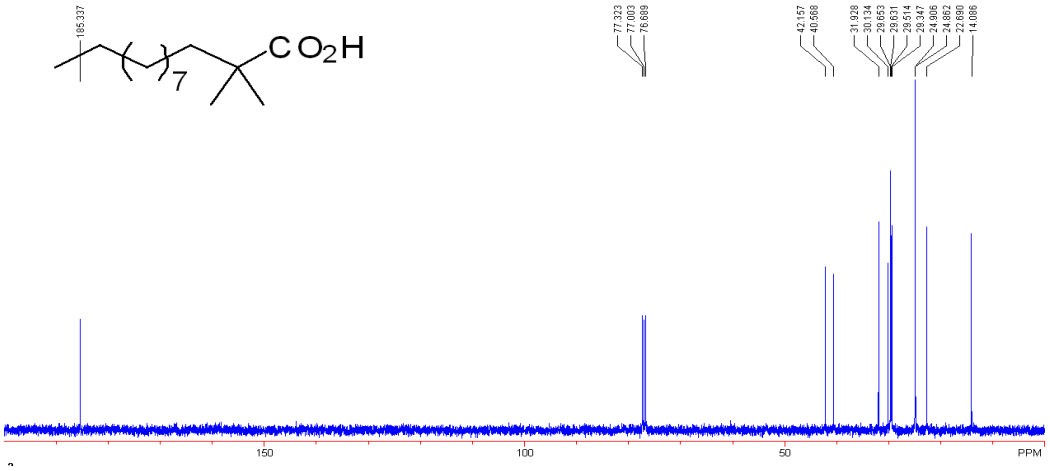
Compound **A-3**


AcO
AcO
CO2H
7.262
4.255
4.246
2.071
1.294
6.01
4.00
3.18
8
6
4
2
PPM

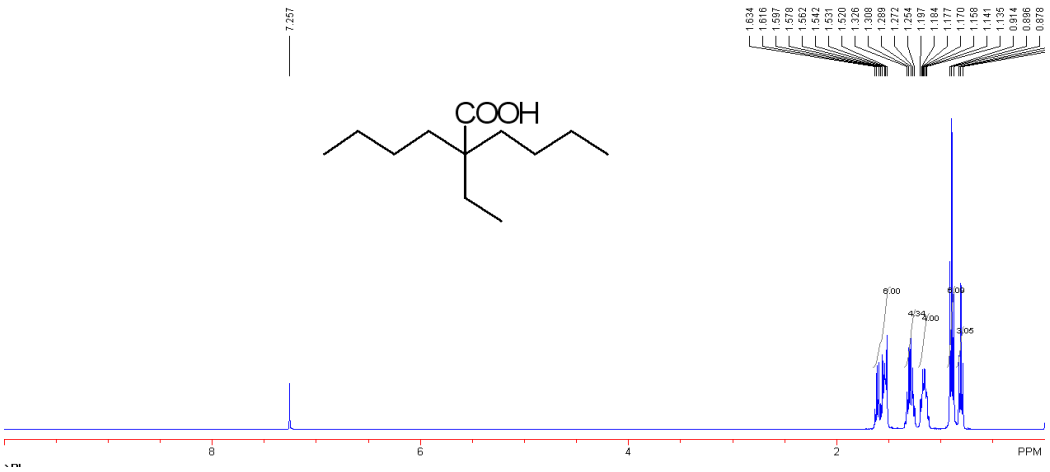

AcO
AcO
CO2H
170.483
170.798
77.396
77.075
76.762
65.205
46.014
20.714
17.731
150
100
50
PPM

Compound **A-4**


11.447
7.260
1.528
1.298
1.258
1.187
0.896
0.879
0.862
CO2H
7
16.16
6.75
2.00
2.90
0.83
10
8
6
4
2
PPM


185.337
77.323
77.003
76.689
42.157
40.568
31.928
30.134
29.653
29.631
29.514
29.347
24.906
24.862
22.690
14.086
CO2H
7
150
100
50
PPM

Compound **A-5**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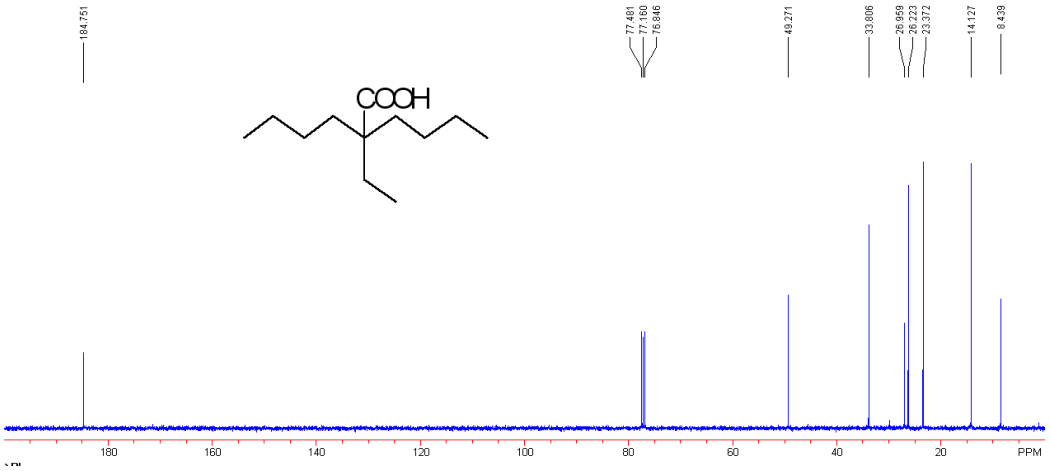
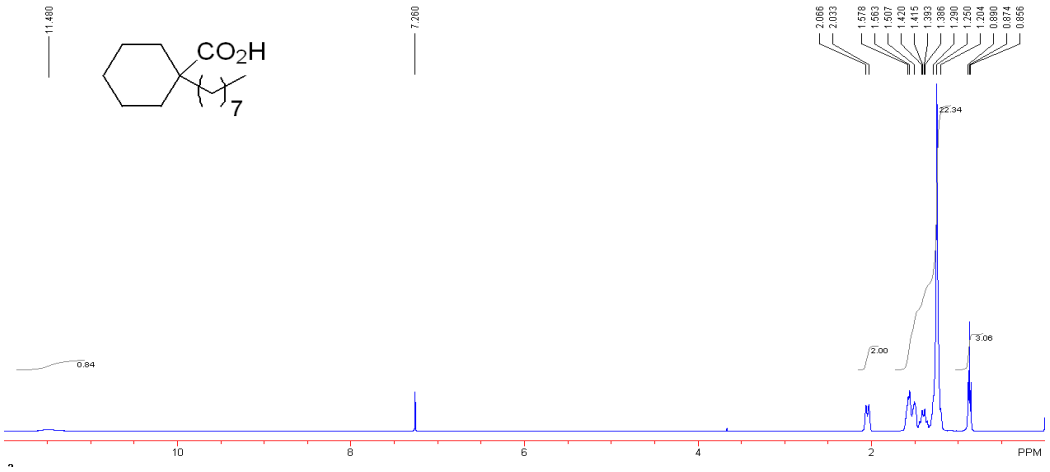
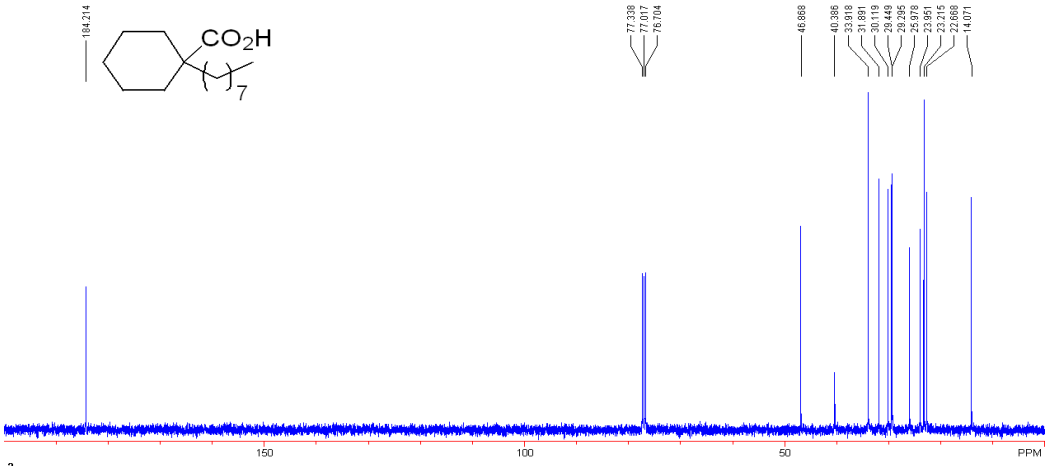
1.634
1.616
1.597
1.578
1.562
1.542
1.531
1.520
1.326
1.308
1.289
1.272
1.254
1.197
1.184
1.177
1.170
1.158
1.141
1.135
0.914
0.896
0.878
COOH
6.00
4.34
4.00
6.00
3.05
8
6
4
2
PPM


184.751
77.481
77.160
76.846
49.271
33.806
26.959
26.223
23.372
14.127
8.439
COOH
180
160
140
120
100
80
60
40
20
PPM

Compound **A-6**


11.480
7.260
2.066
2.033
1.578
1.563
1.507
1.420
1.415
1.393
1.386
1.290
1.250
1.204
0.890
0.874
0.856
22.34
3.06
2.00
0.84
CO2H
7
10
8
6
4
2
PPM


184.214
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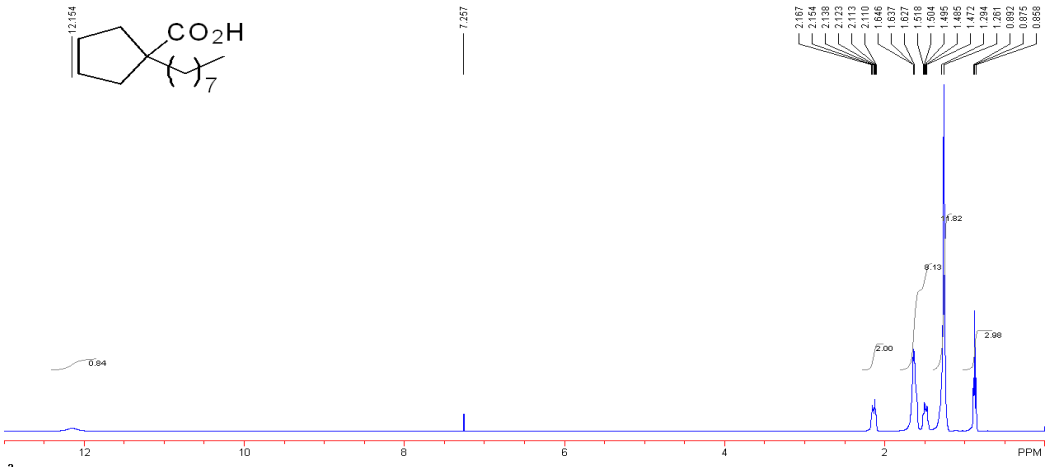
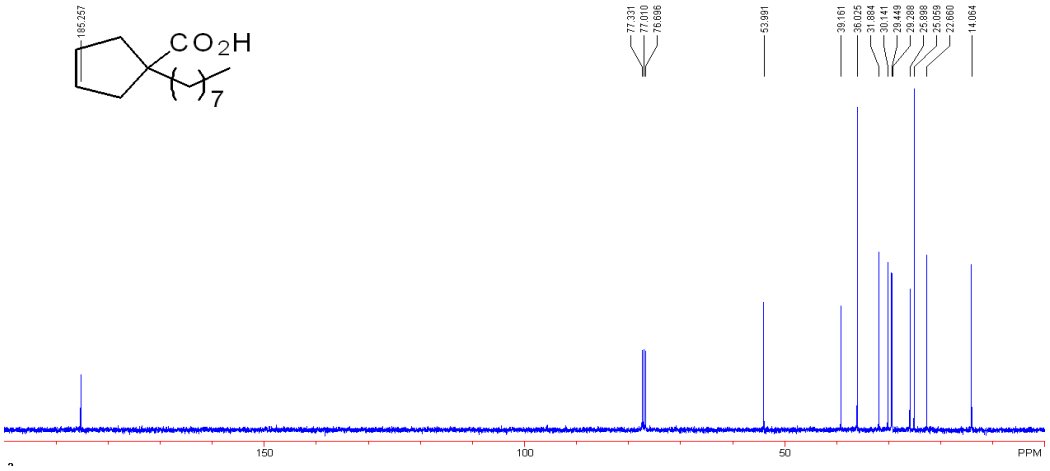
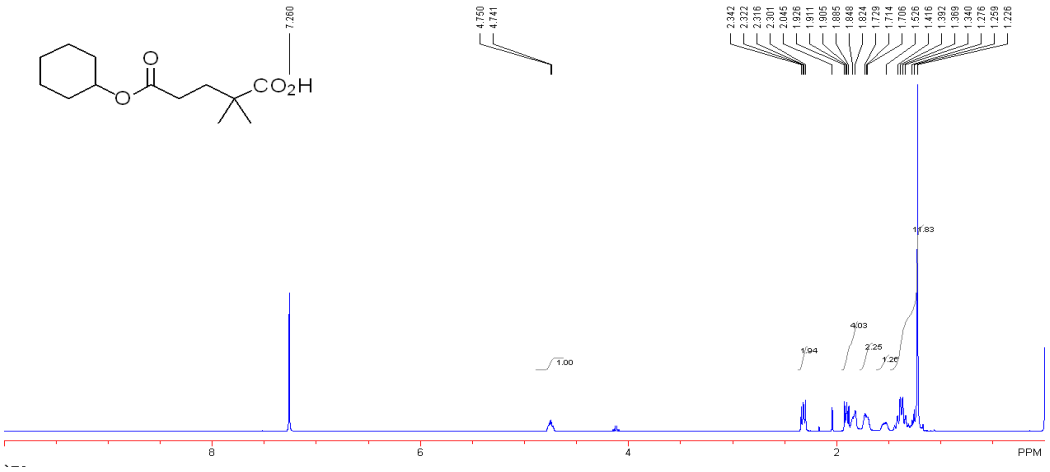
77.017
76.704
46.668
40.386
33.918
31.891
30.119
29.449
29.395
29.378
29.345
23.215
22.668
14.071
CO2H
7
150
100
50
PPM

Compound **A-7**


12.154
7.257
2.167
2.154
2.138
2.123
2.113
2.110
1.846
1.637
1.627
1.518
1.504
1.495
1.485
1.472
1.284
1.261
0.892
0.875
0.858
14.82
8.13
2.99
2.00
0.84
12
10
8
6
4
2
PPM


185.257
77.331
77.010
76.696
53.991
39.161
35.025
31.894
30.141
29.449
29.288
25.898
25.059
22.660
14.064
150
100
50
PPM

Compound **A-8**


7.260
4.750
4.741
2.342
2.322
2.316
2.301
2.045
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1.911
1.905
1.885
1.848
1.824
1.729
1.714
1.706
1.526
1.416
1.392
1.368
1.340
1.276
1.259
1.226
CO2H
O
O
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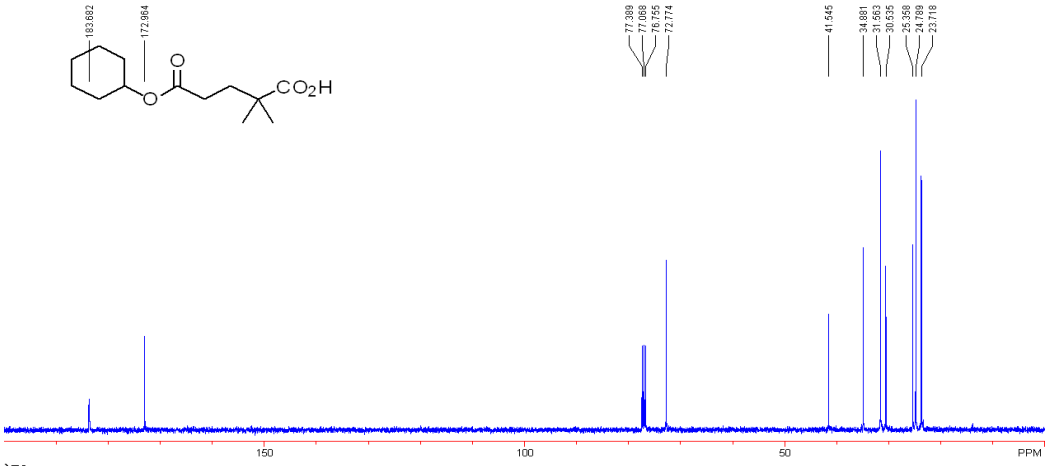
1.94
4.03
2.25
1.26
8
6
4
2
PPM


183.682
172.964
77.389
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72.774
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34.881
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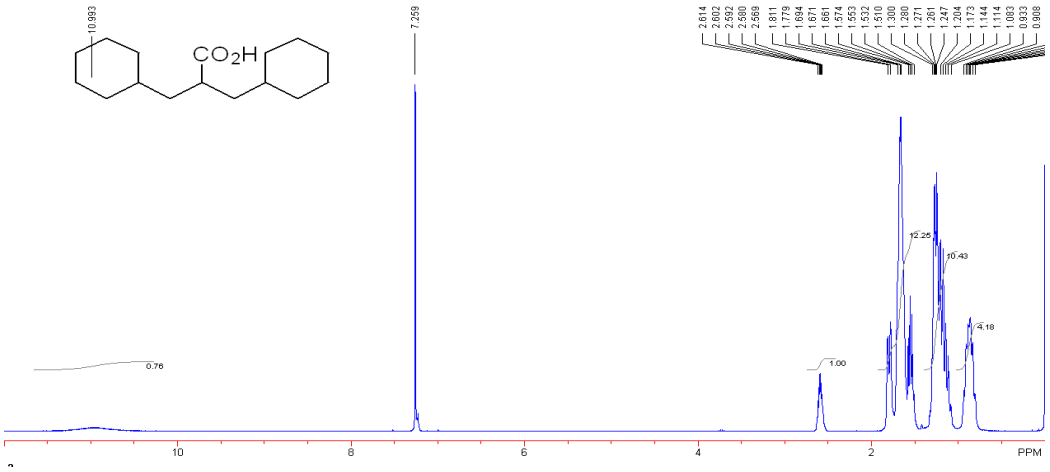
25.358
24.789
23.718
CO2H
O
O
150
100
50
PPM

Compound **A-9**


10.993
7.259
2.614
2.602
2.592
2.580
2.569
1.811
1.779
1.694
1.671
1.661
1.574
1.553
1.532
1.510
1.300
1.280
1.271
1.261
1.247
1.204
1.173
1.144
1.114
1.083
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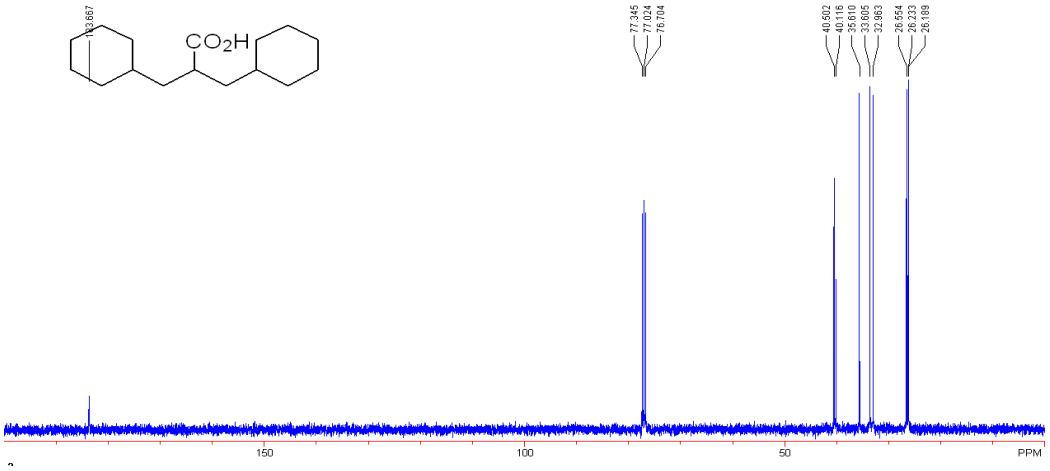
1.00
10
8
6
4
2
PPM


182.867
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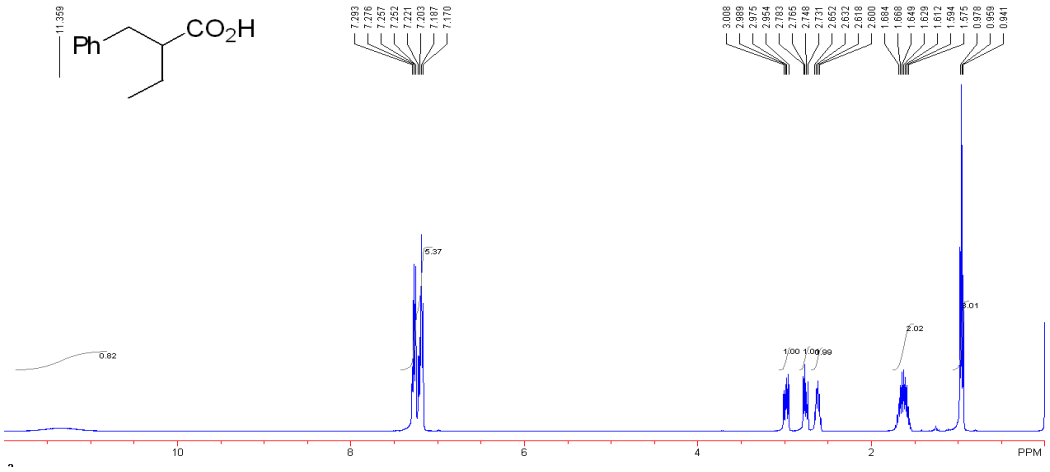
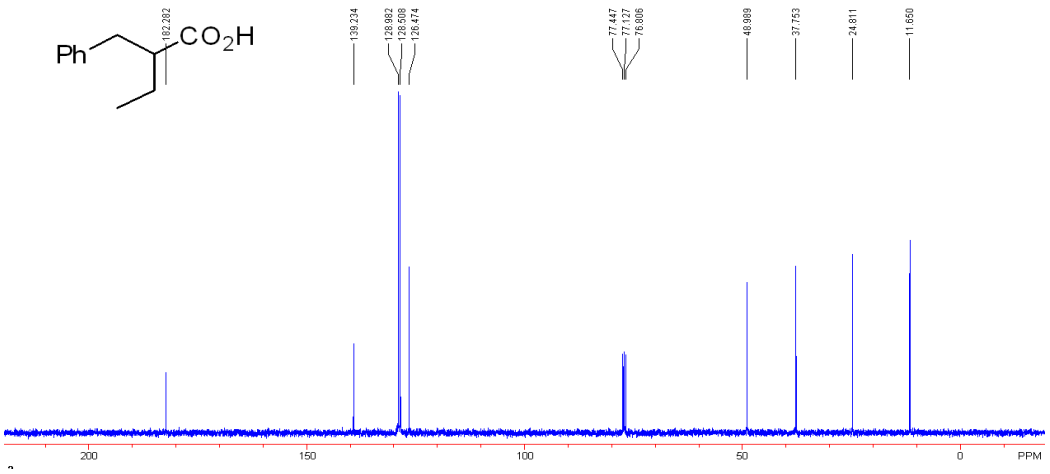
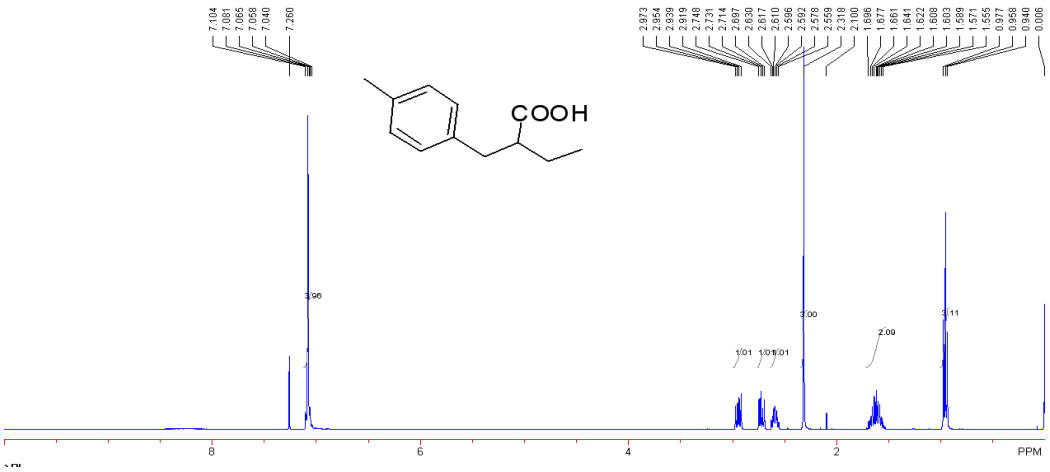
26.189
CO2H
150
100
50
PPM

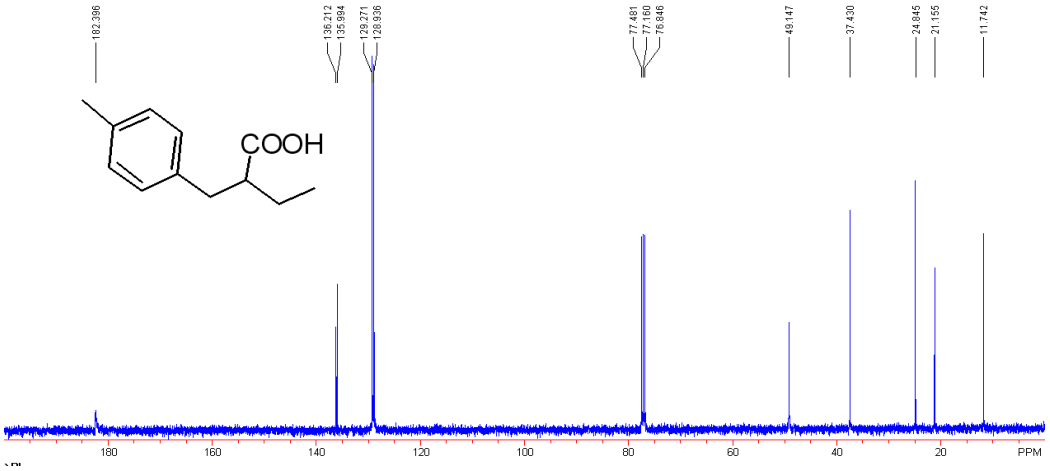
Compound **A-10**



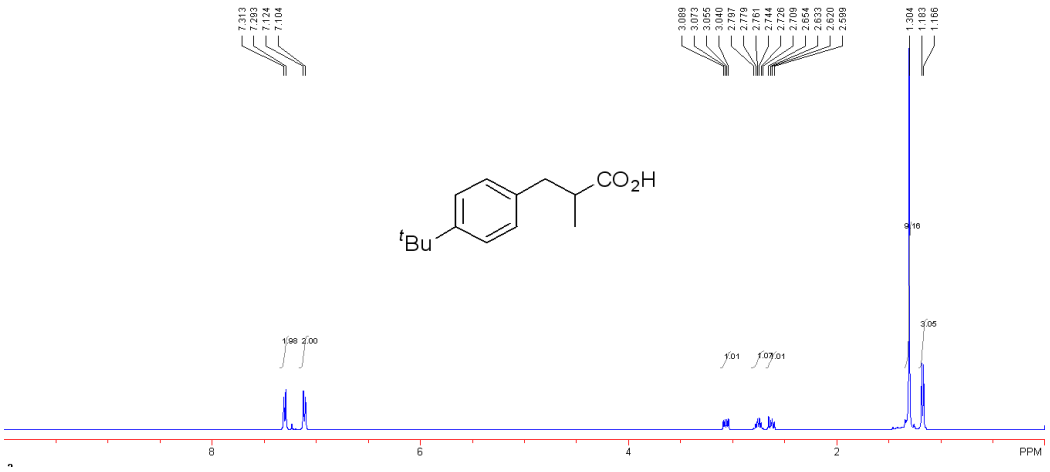


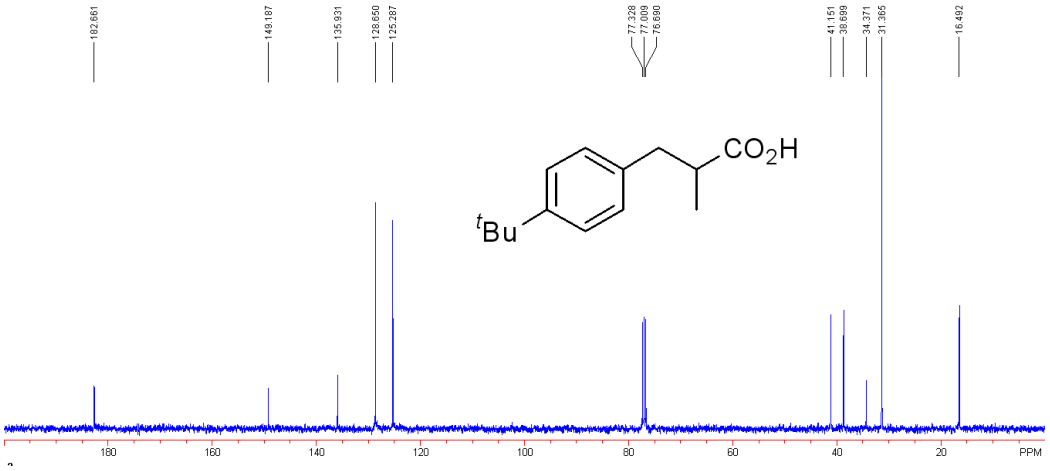
Compound **A-11**



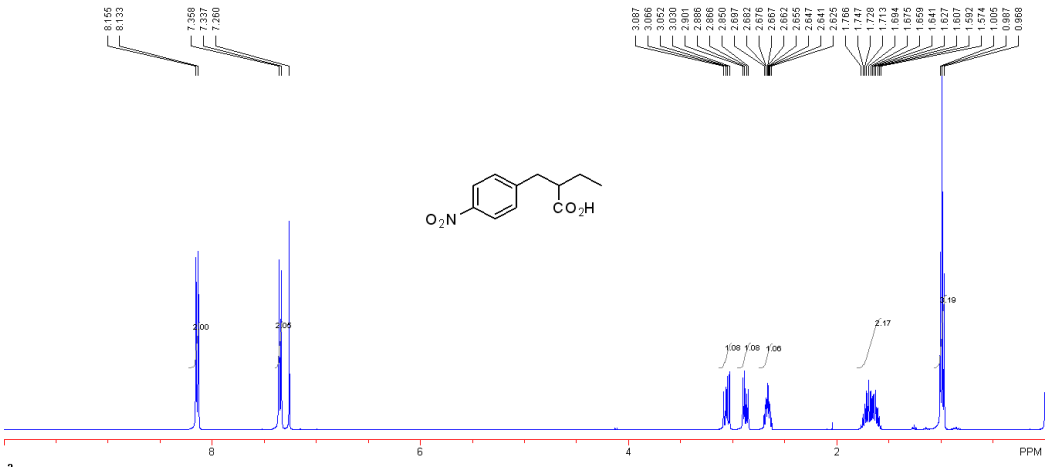


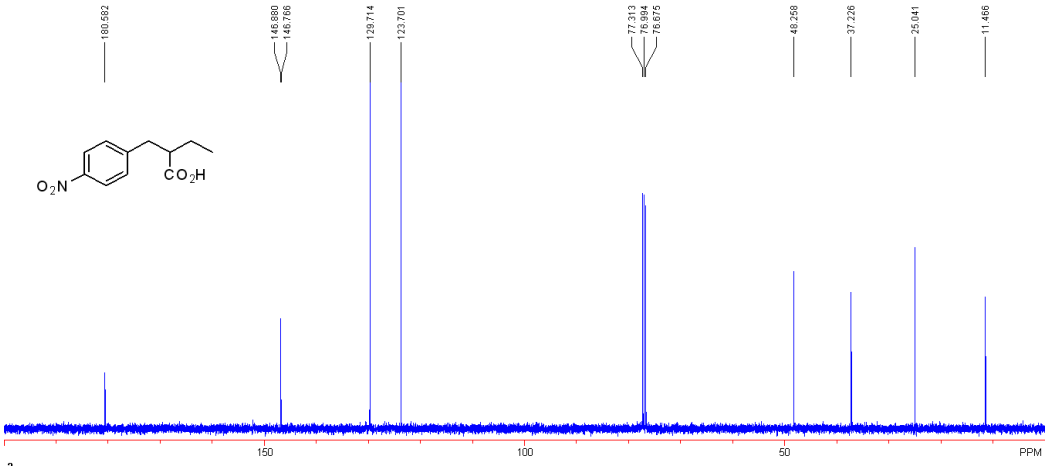
Compound **A-12**



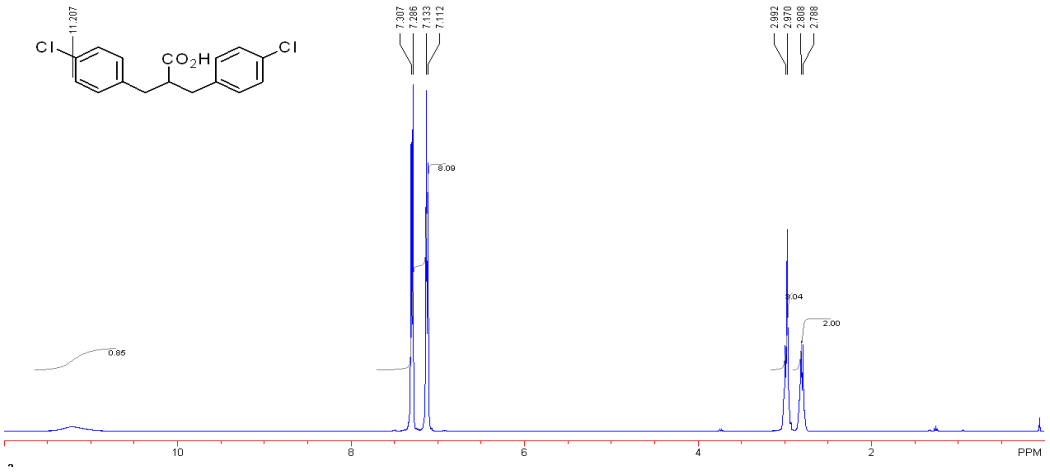


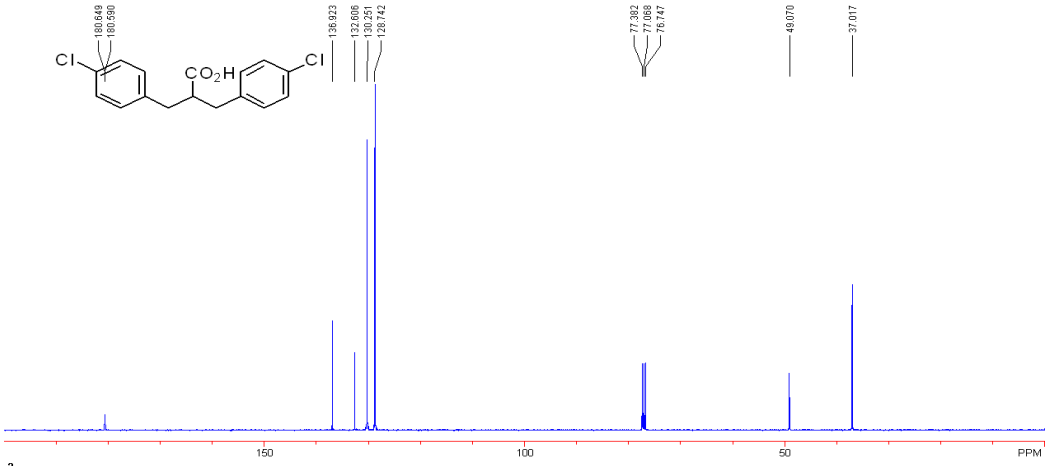
Compound **A-13**



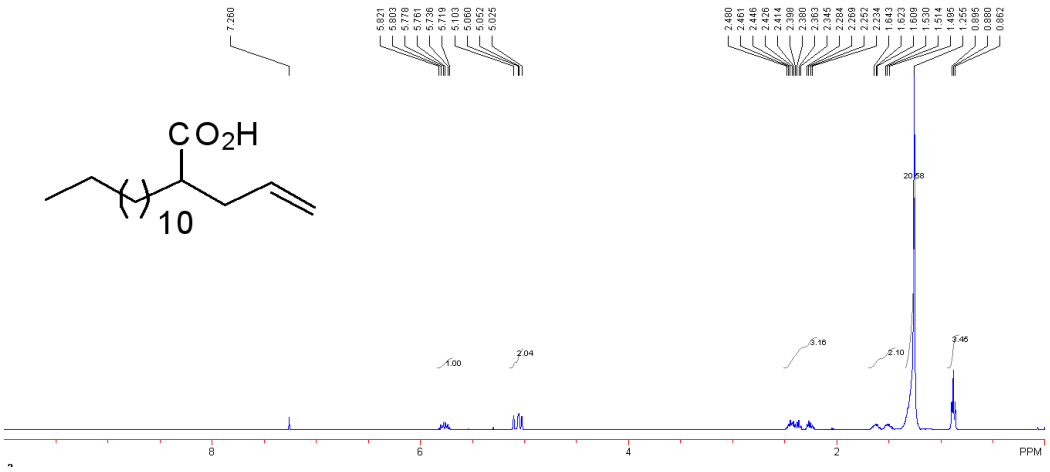


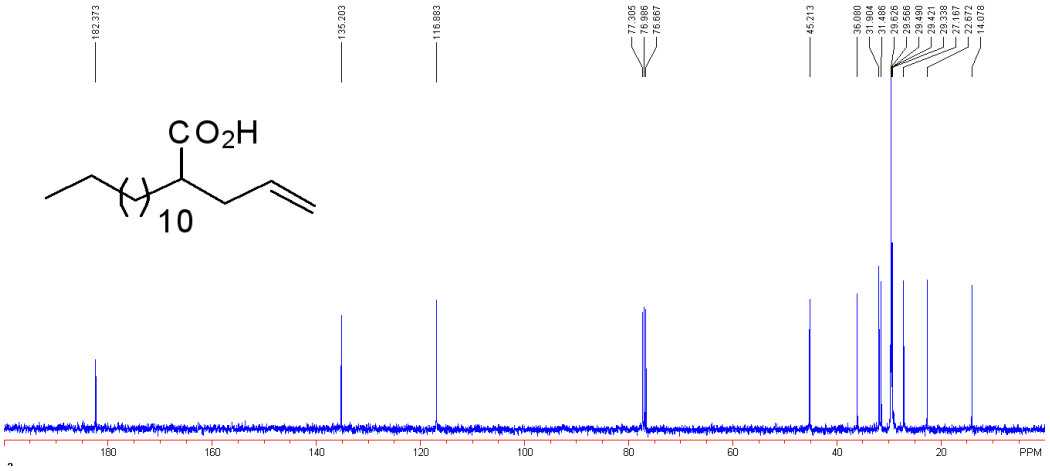
Compound **A-14**



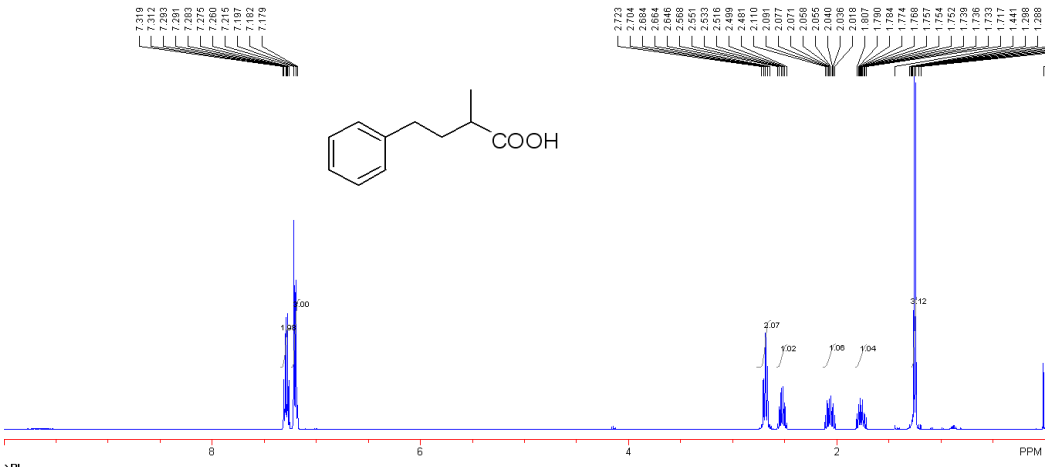


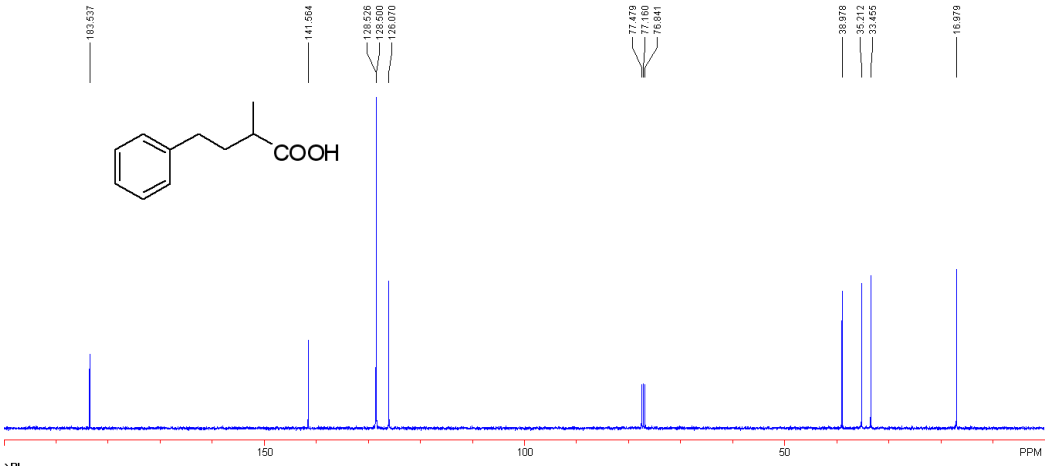
Compound **A-15**



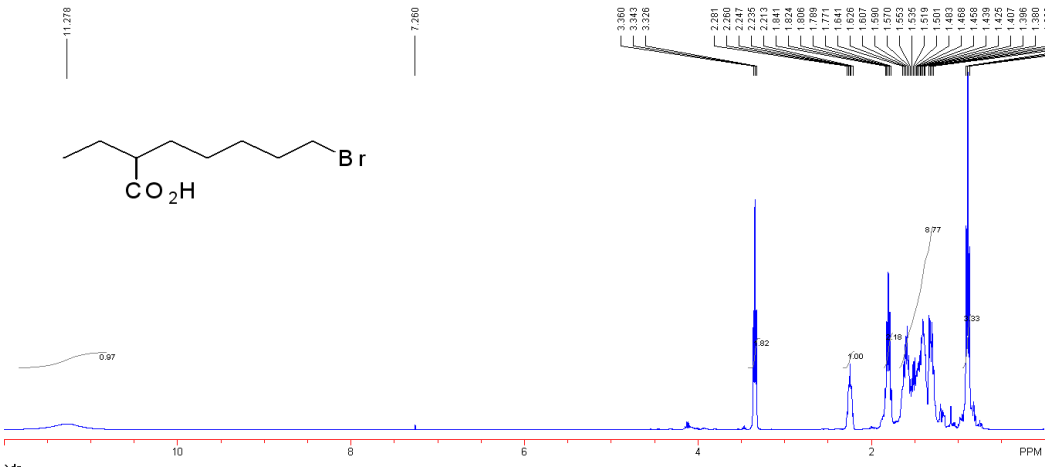


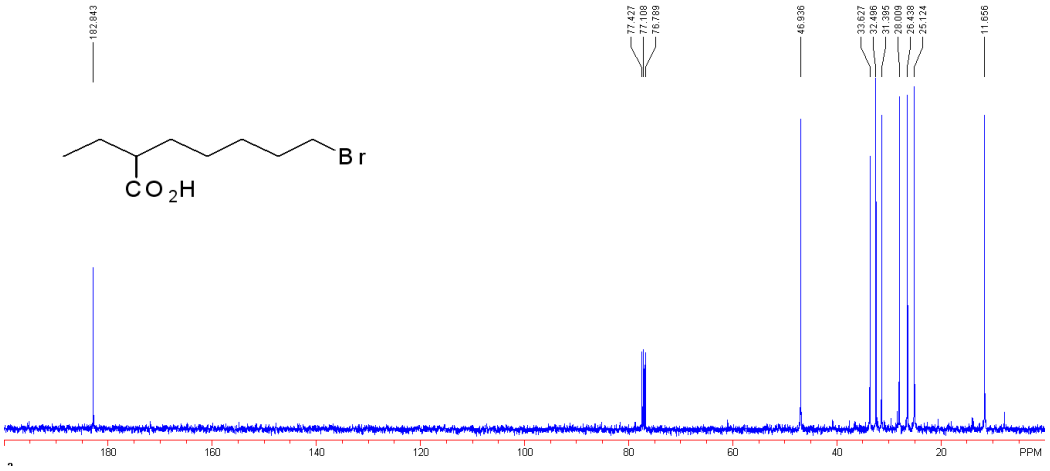
Compound **A-16**



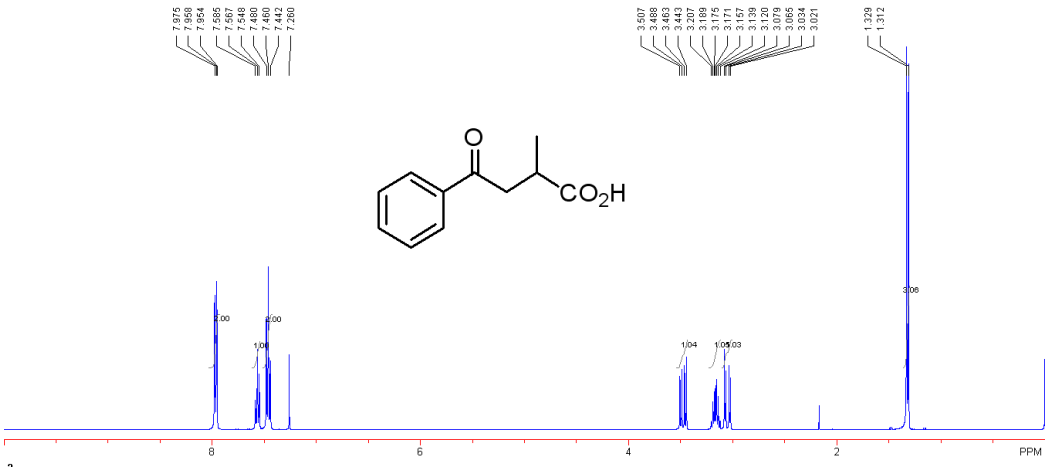


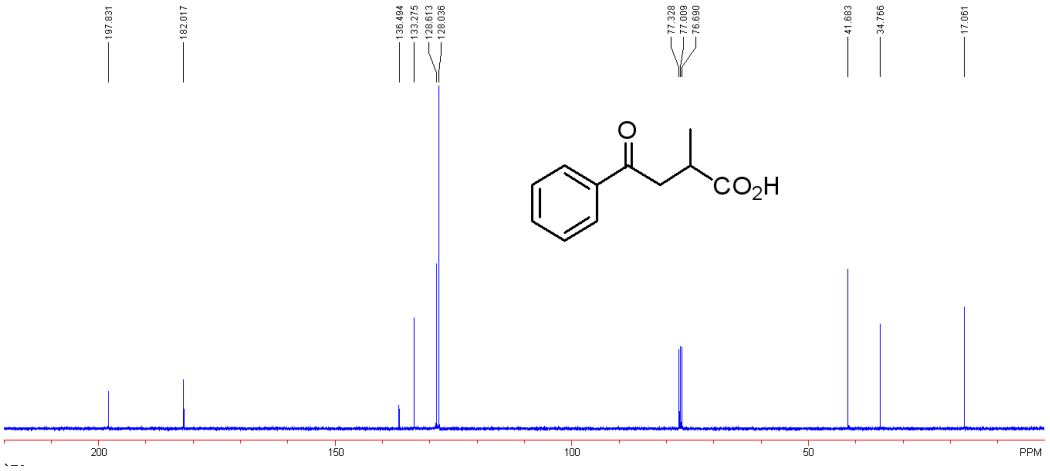
Compound **A-17**



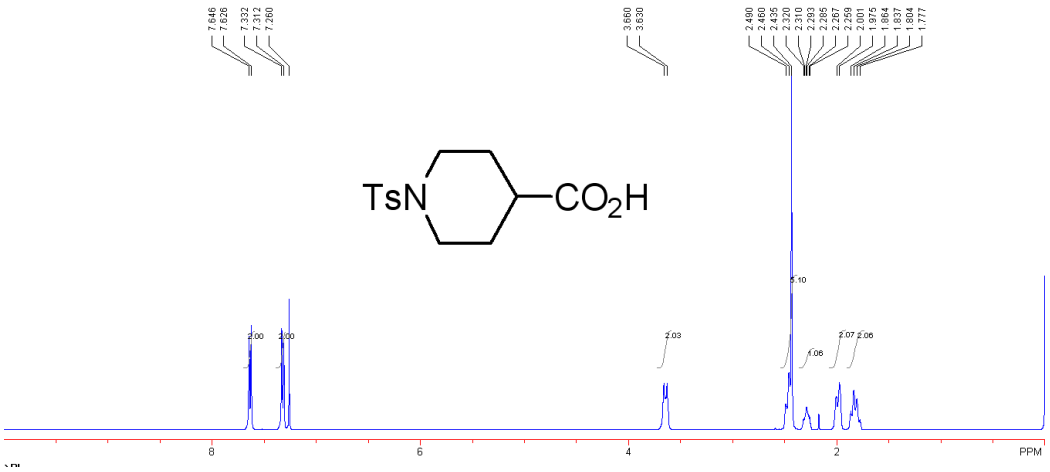


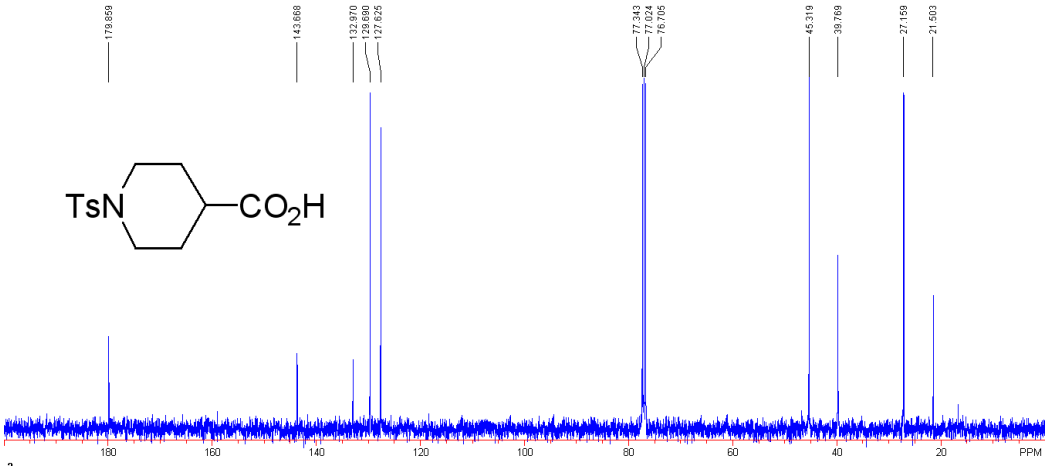
Compound **A-18**



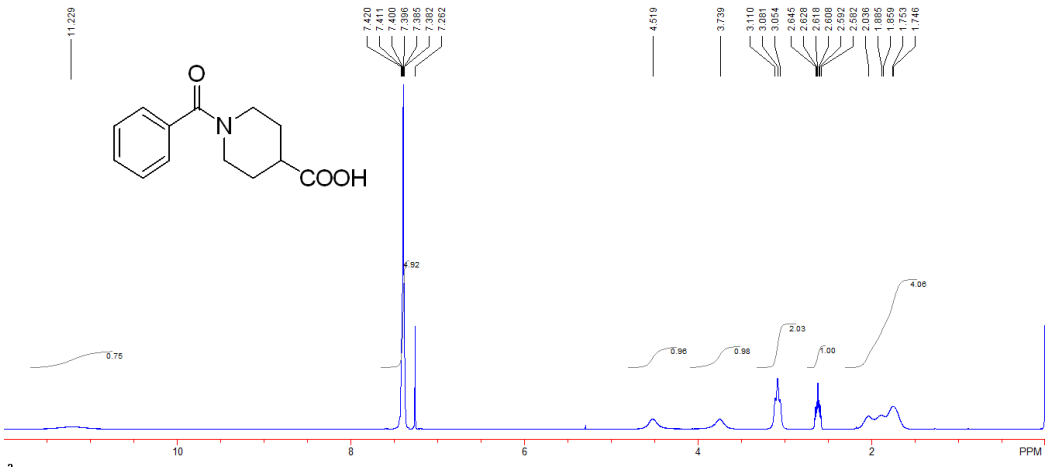


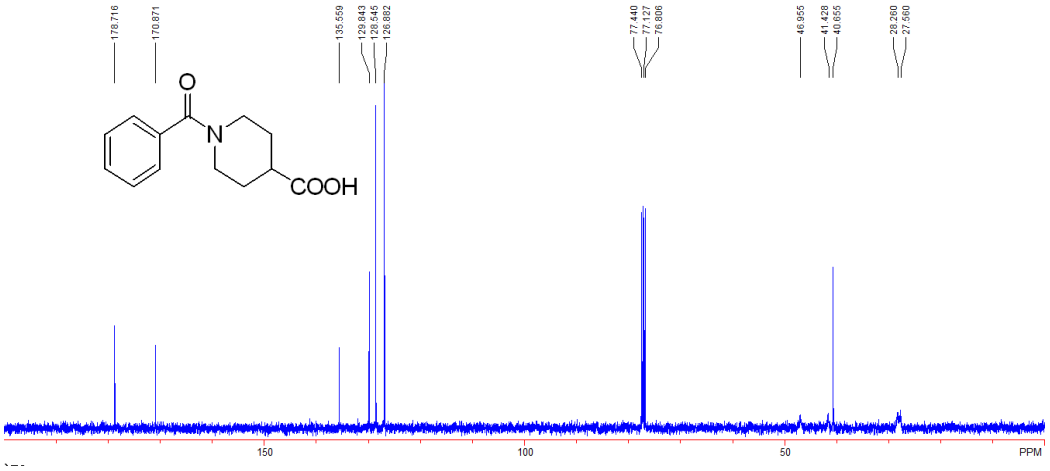
Compound **A-19**



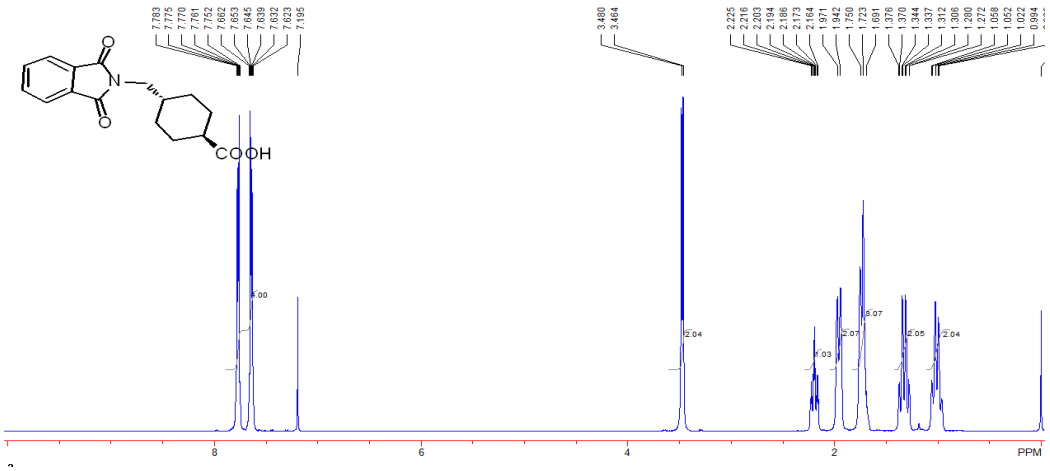


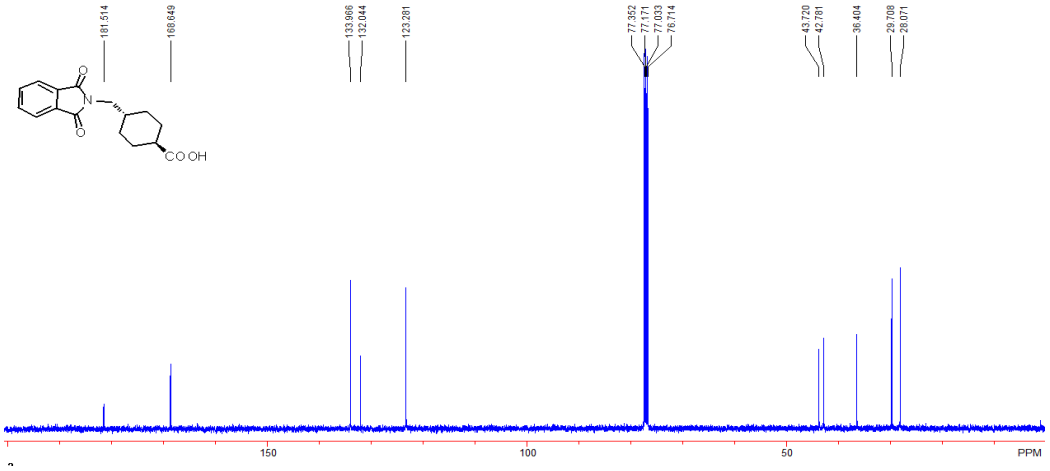
Compound **A-20**



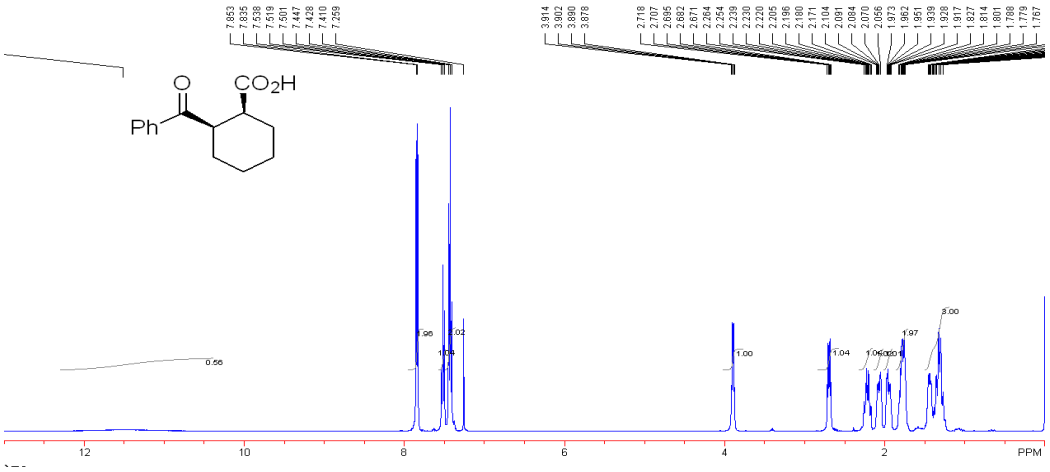


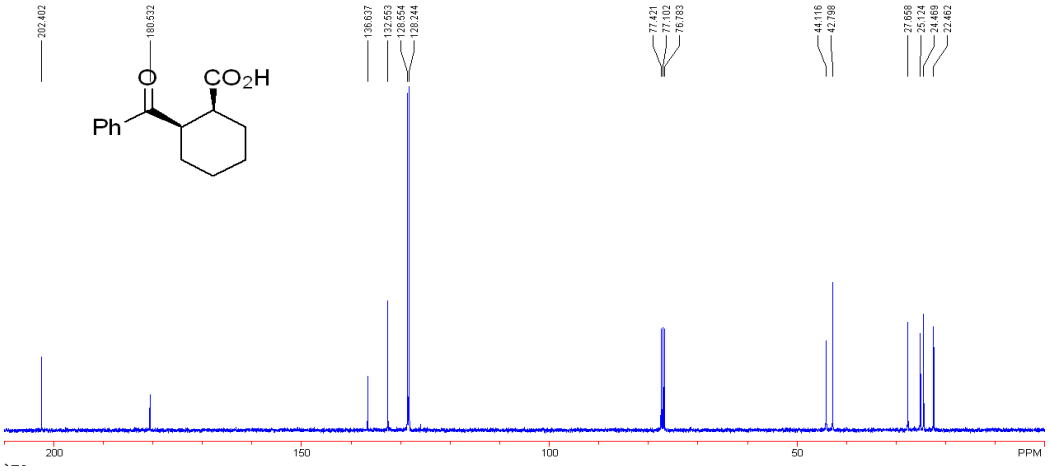
Compound **A-21**



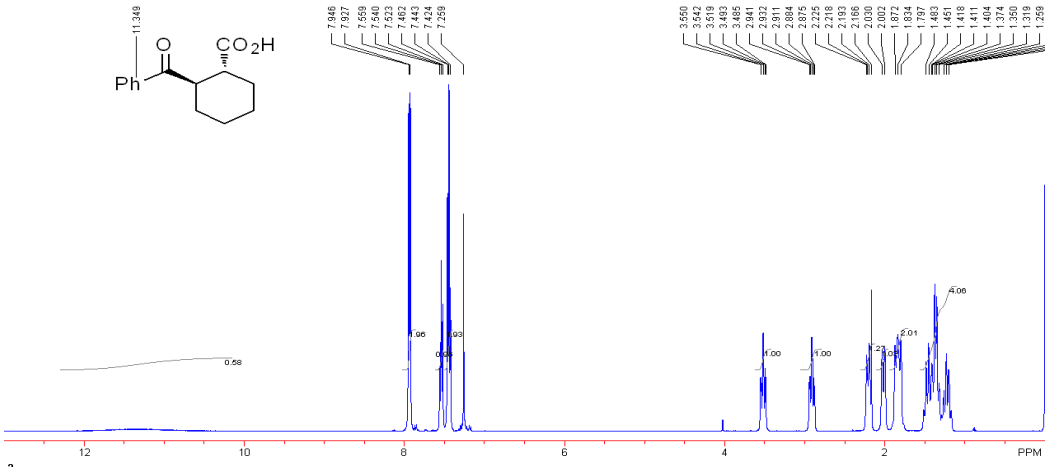


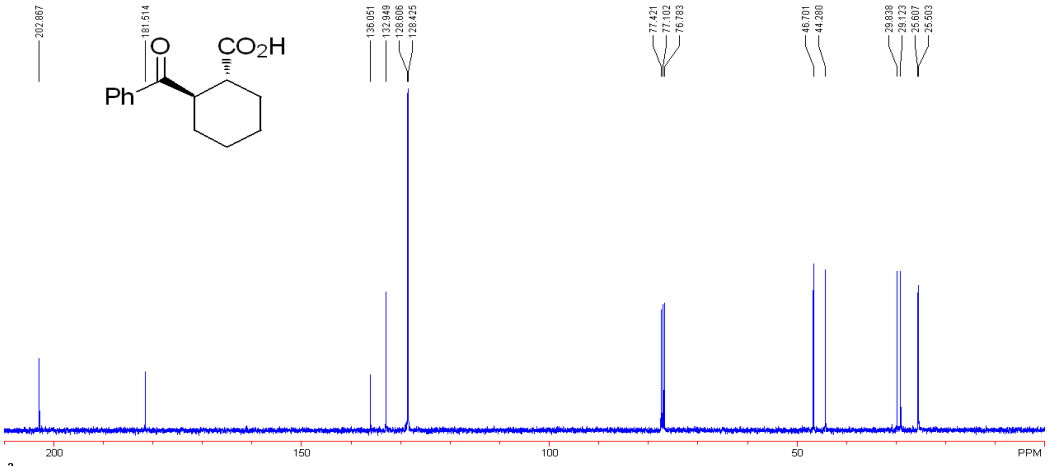
Compound **A-22-cis**



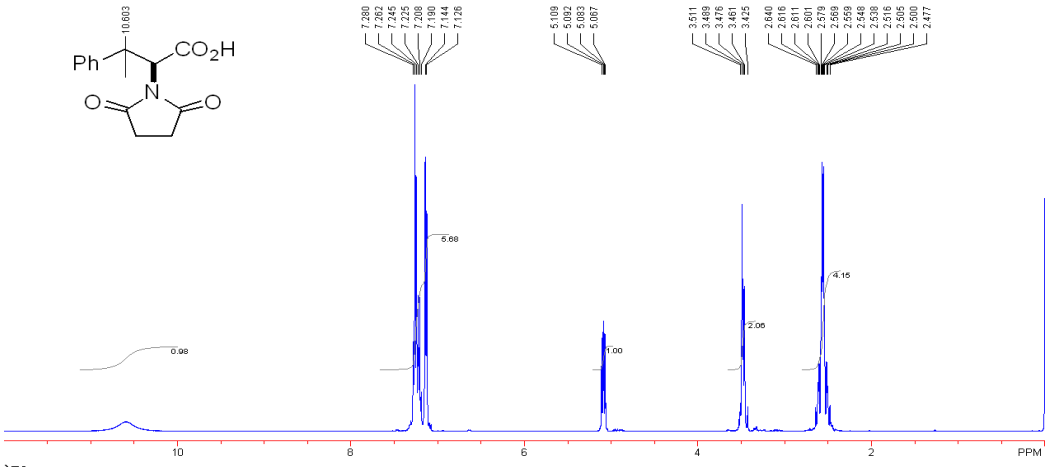


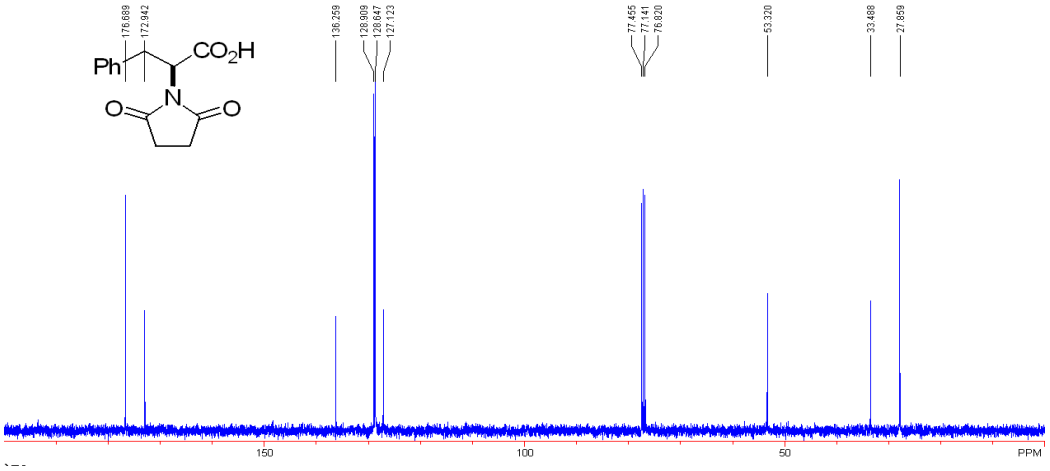
Compound **A-22-trans**



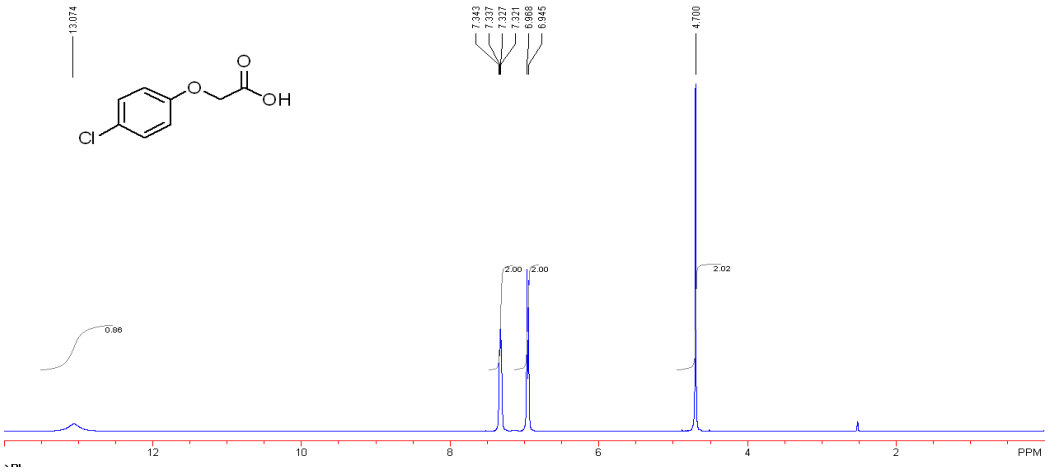


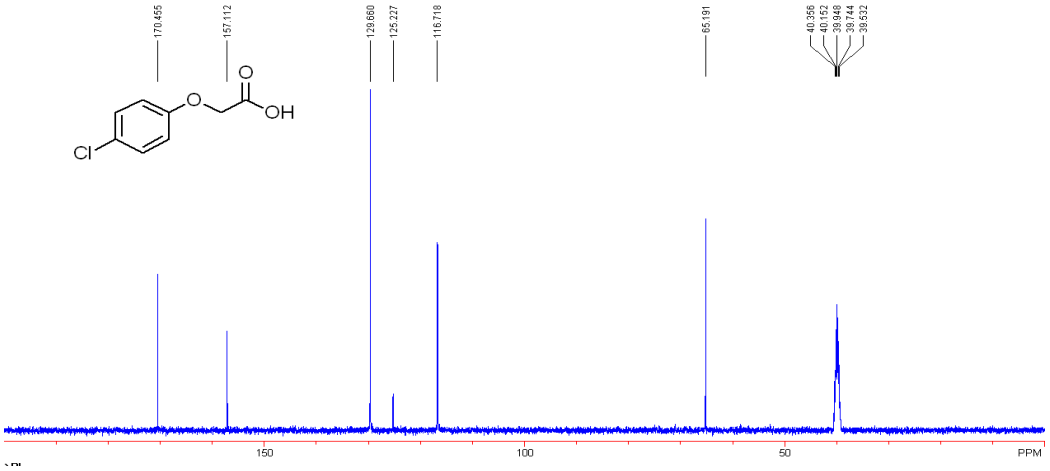
Compound **A-23**



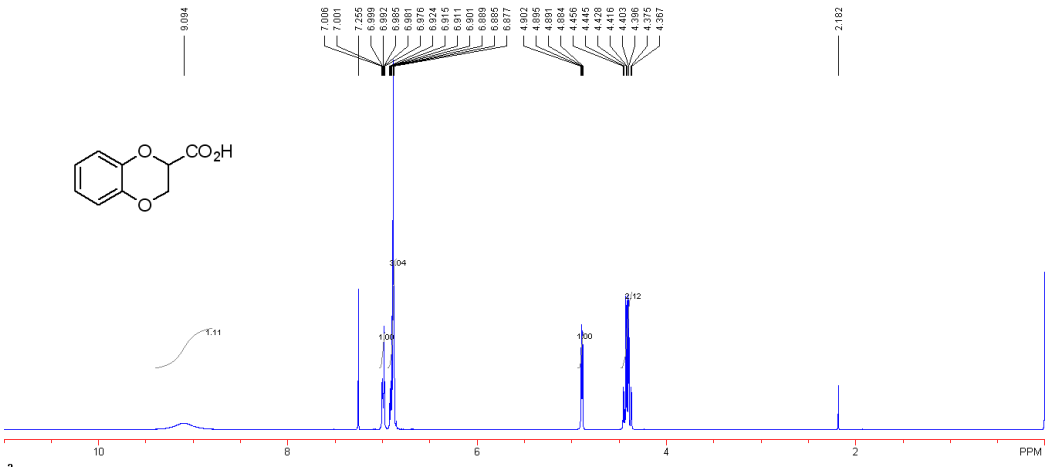


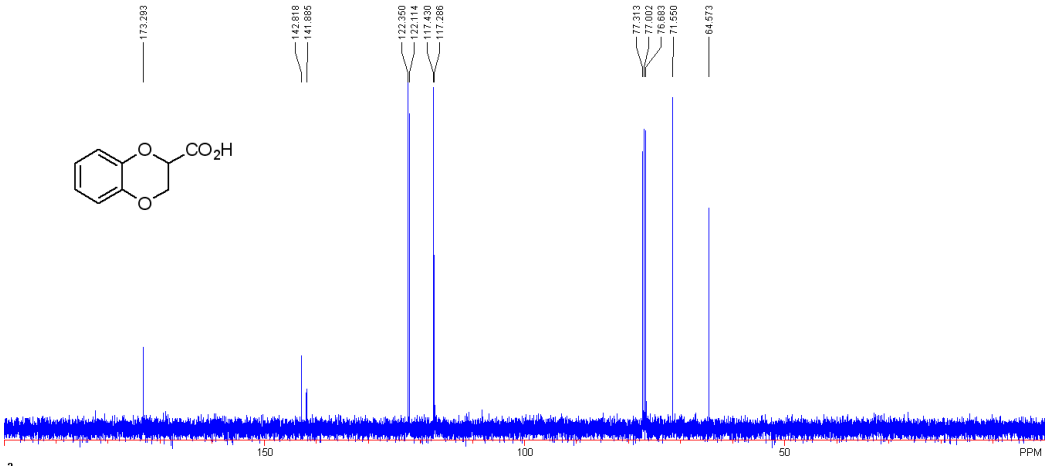
Compound **A-24**



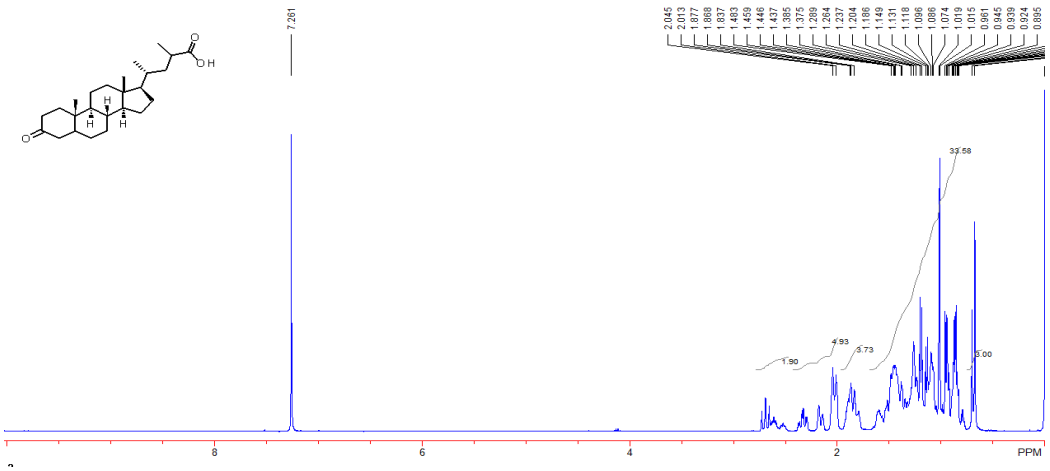


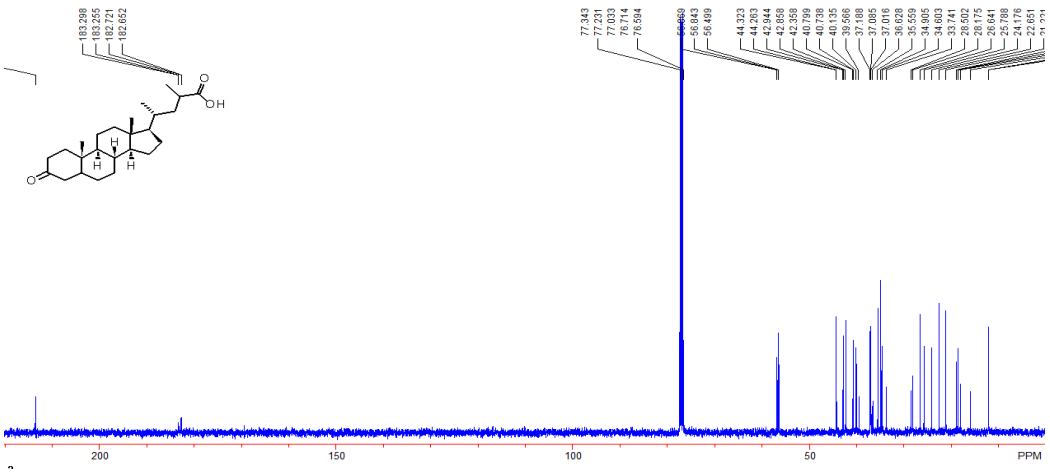
Compound **A-25**



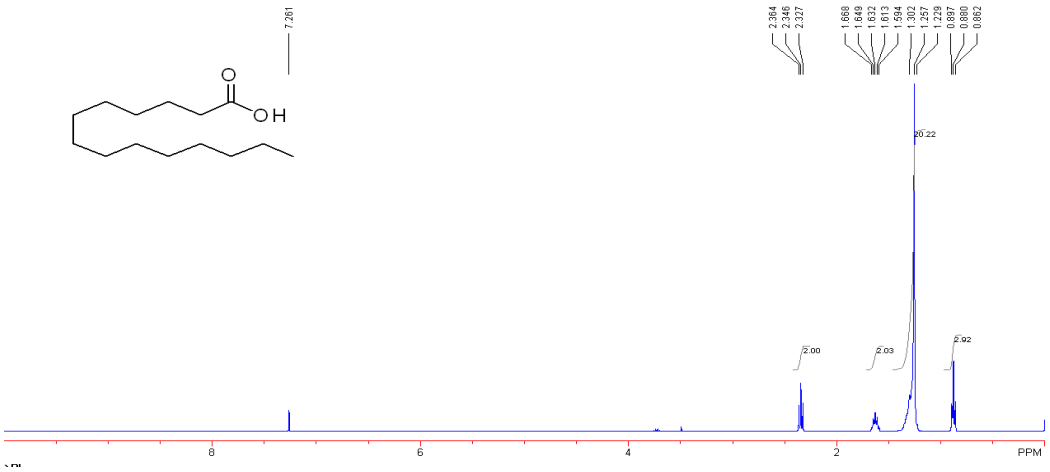


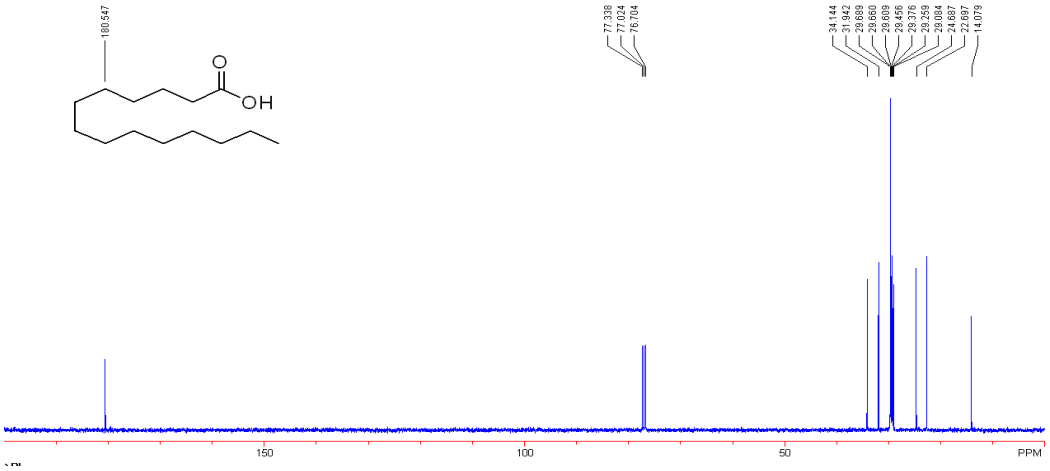
Compound **A-26**



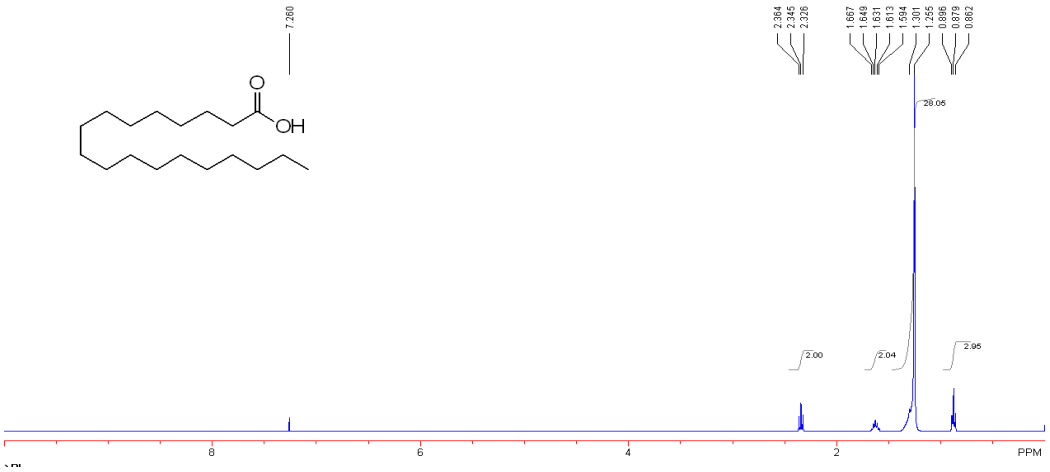


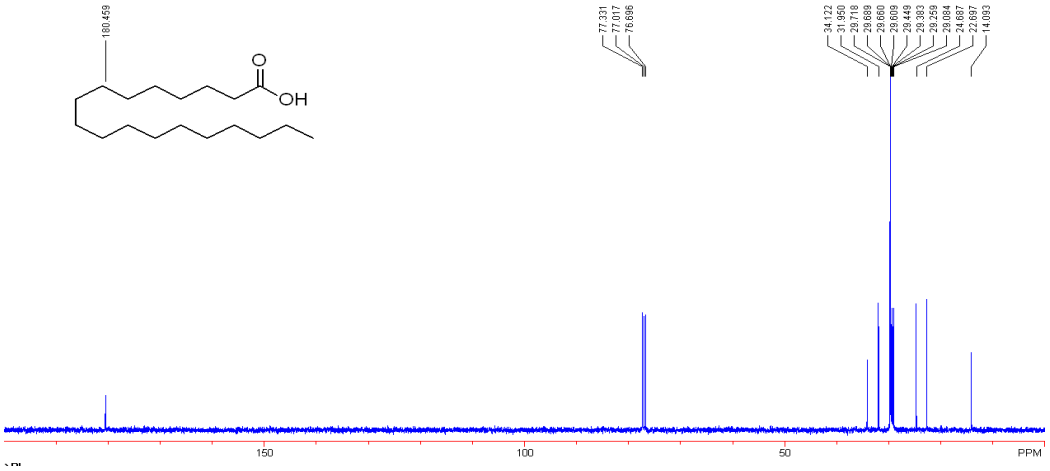
Compound **A-27**



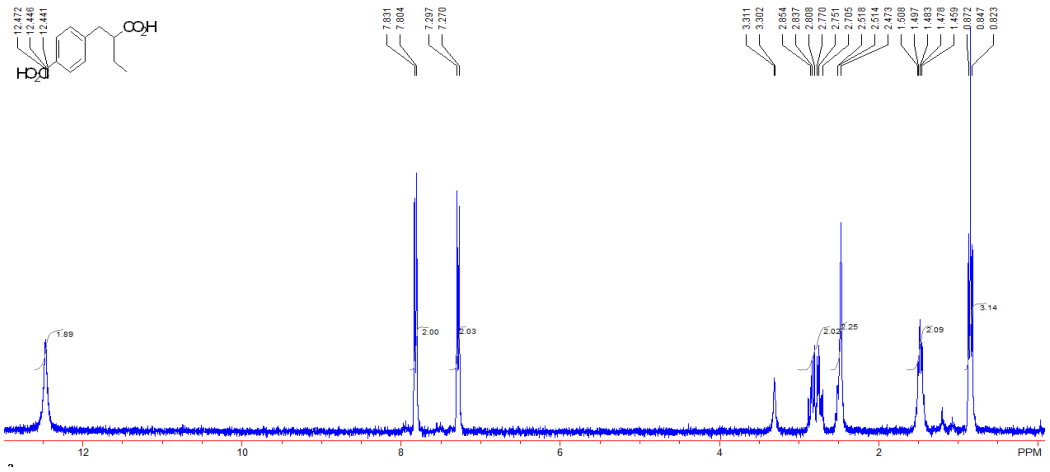


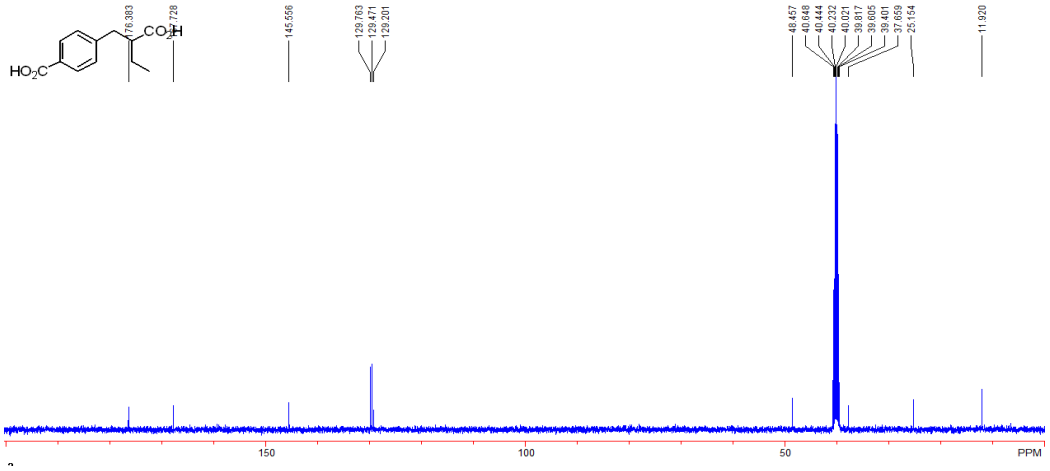
Compound **A-28**



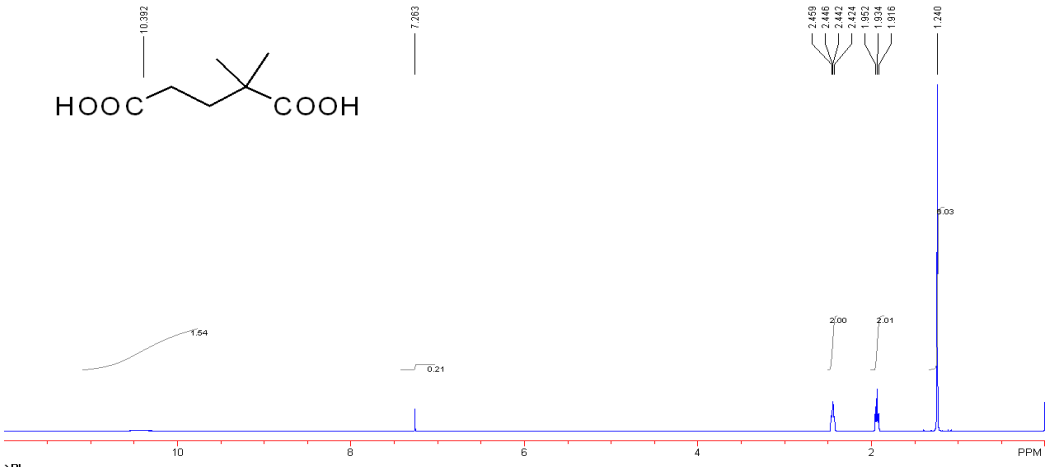


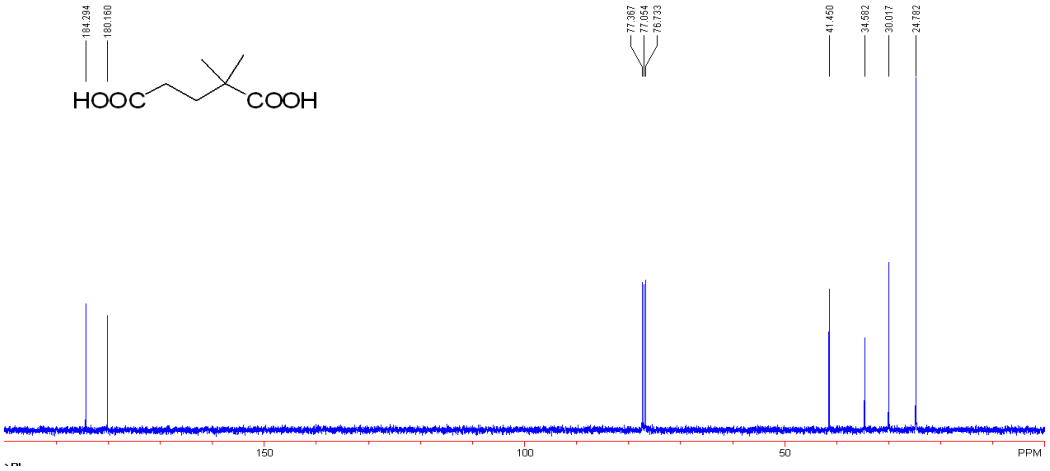
Compound **A-29**



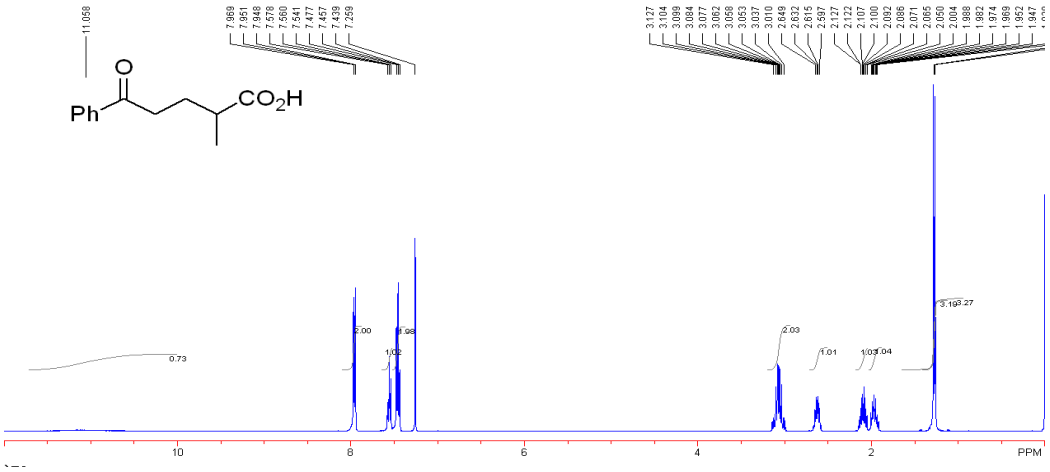


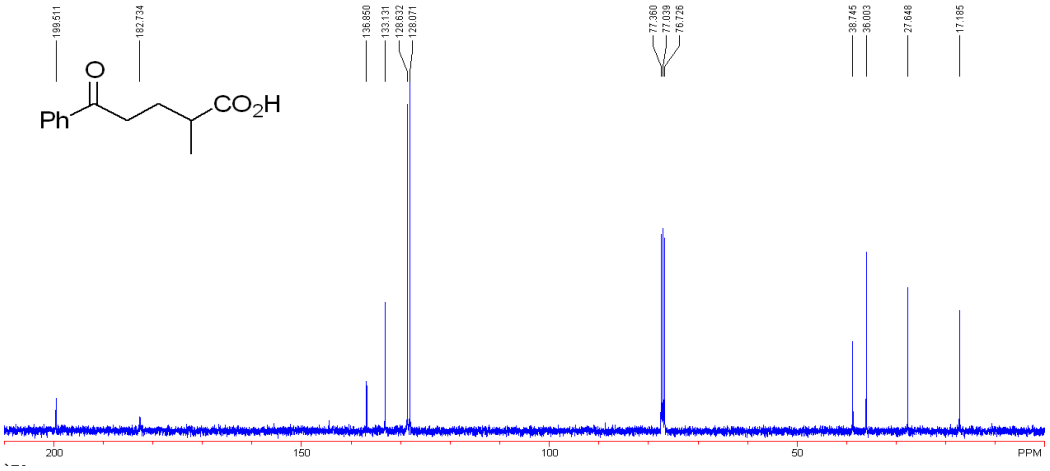
Compound **A-30**



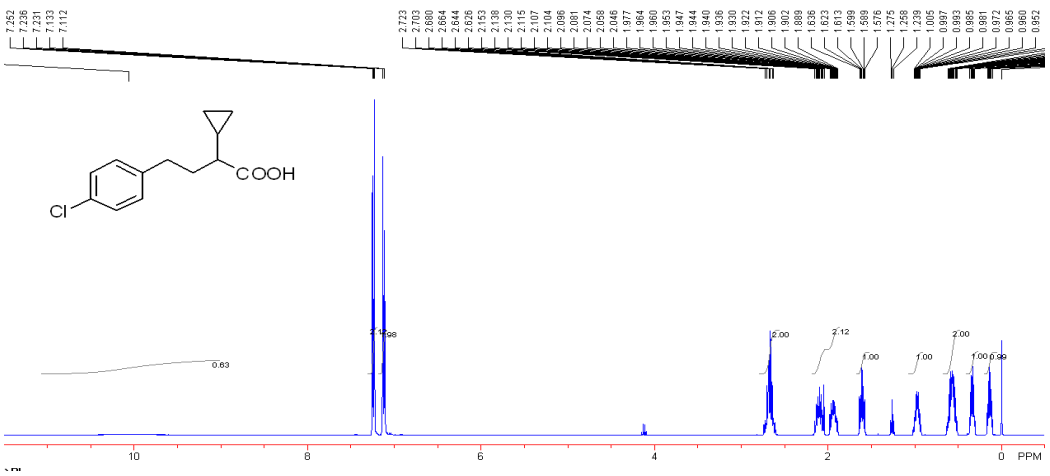


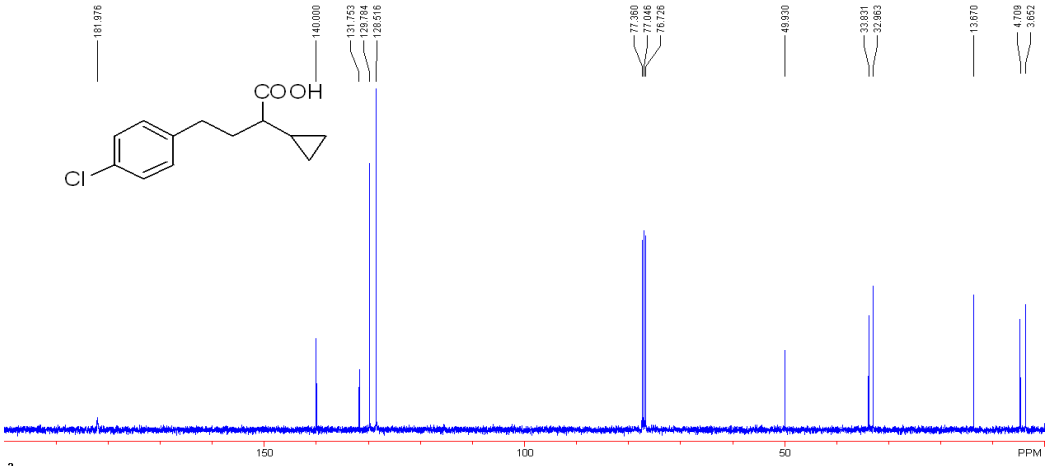
Compound **A-31**





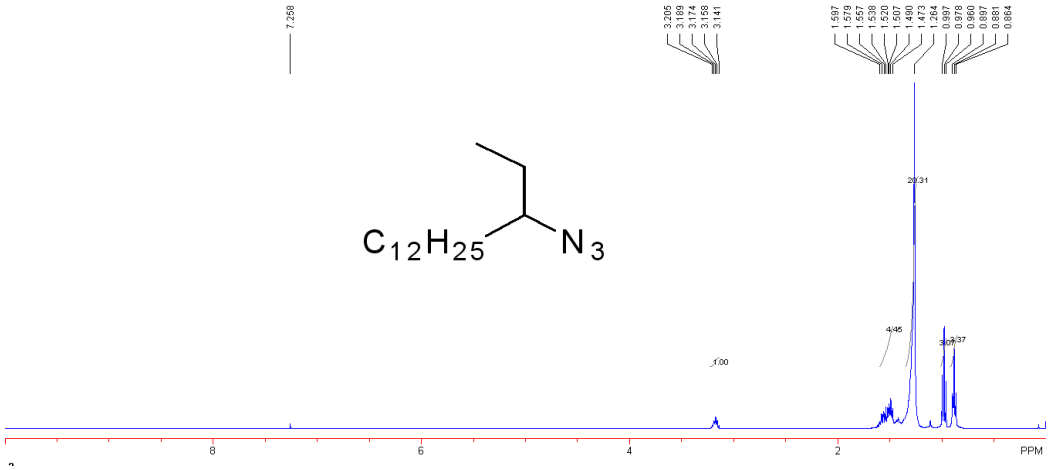
Compound **A-33**

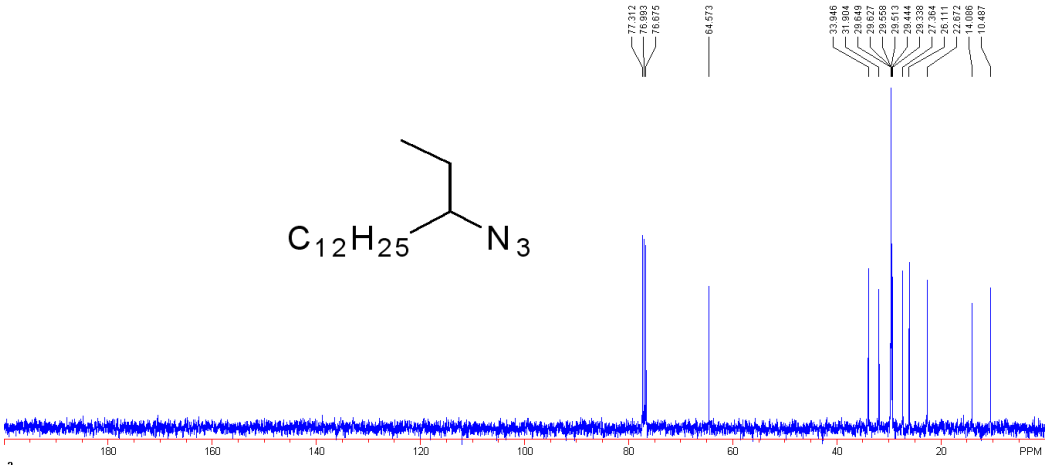




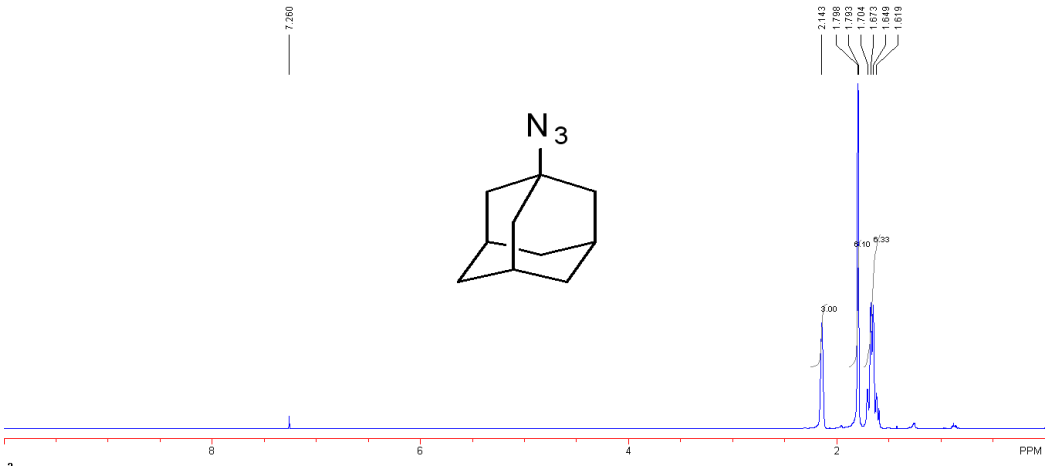
9. ^{1}H and ^{13}C Spectra of All Products

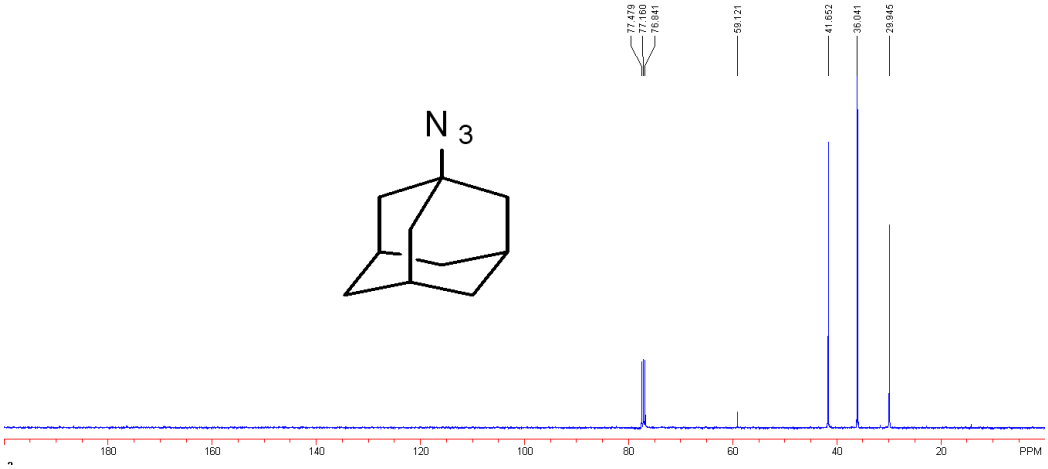
Compound **1**



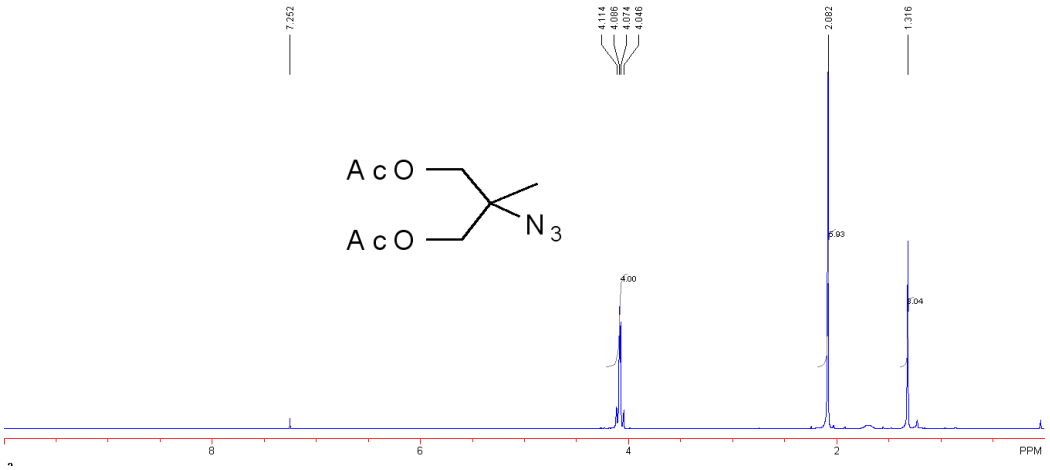


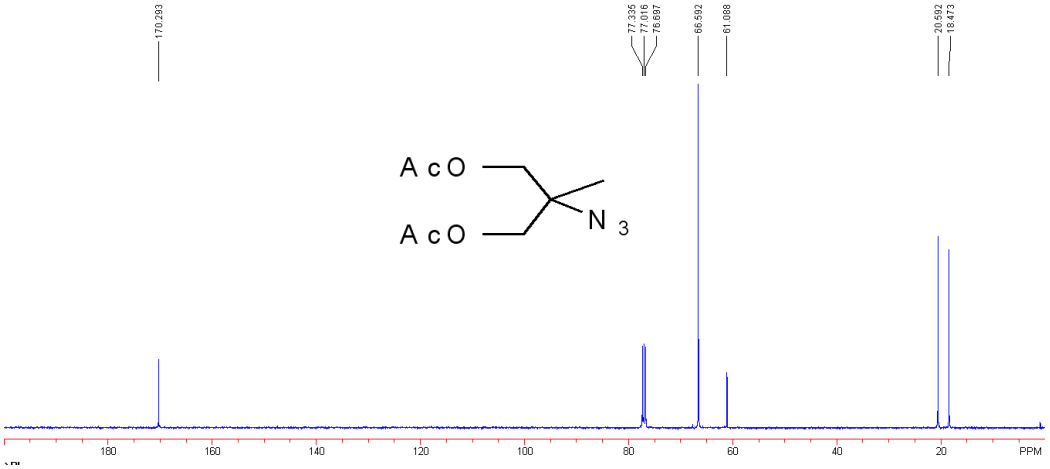
Compound **2**


7.260
2.143
1.798
1.793
1.704
1.673
1.649
1.619
N 3
6.10
5.33
3.00
8
6
4
2
PPM

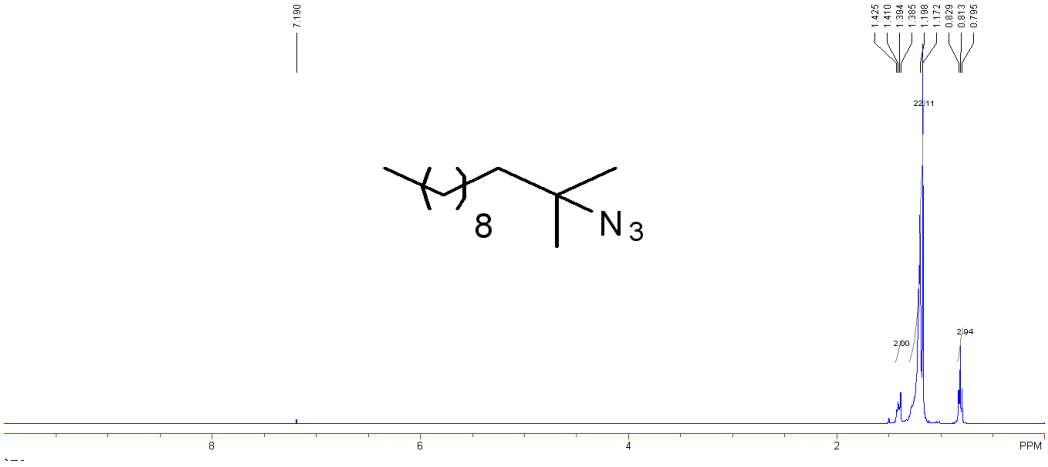

77.479
77.160
76.841
59.121
41.652
36.041
28.945
N 3
180
160
140
120
100
80
60
40
20
PPM

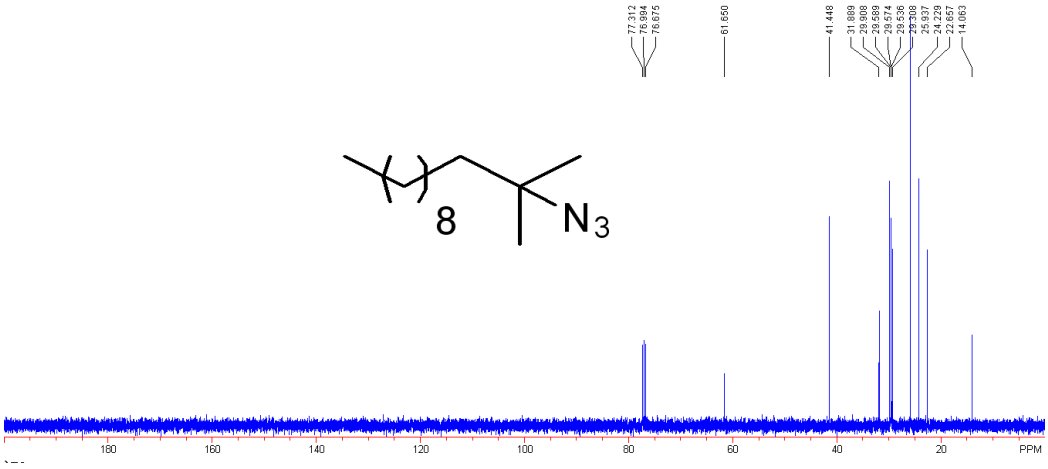
Compound **3**


7.252
4.114
4.086
4.074
4.046
2.082
1.316
AcO
AcO
N3
6.93
4.00
3.04
8
6
4
2
PPM

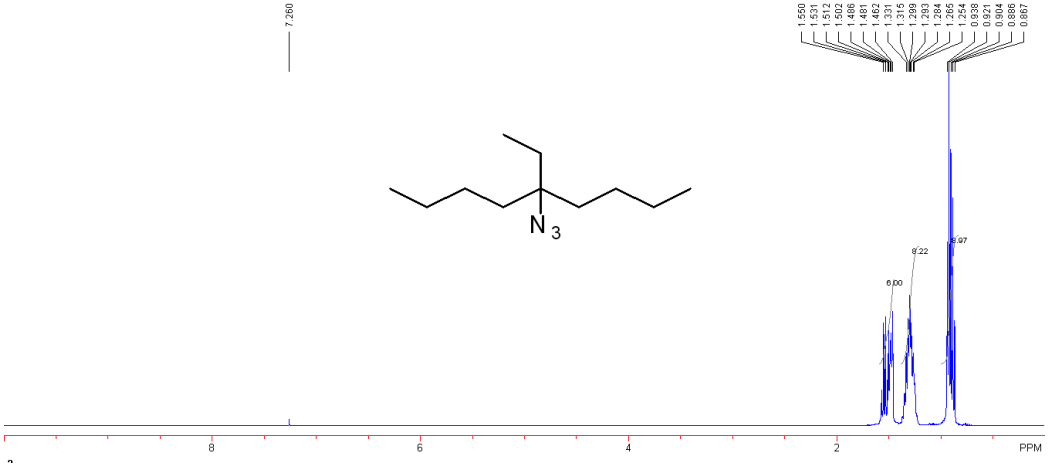

170.293
77.336
77.016
76.697
66.592
61.088
20.592
18.473
AcO
AcO
N3
180
160
140
120
100
80
60
40
20
PPM

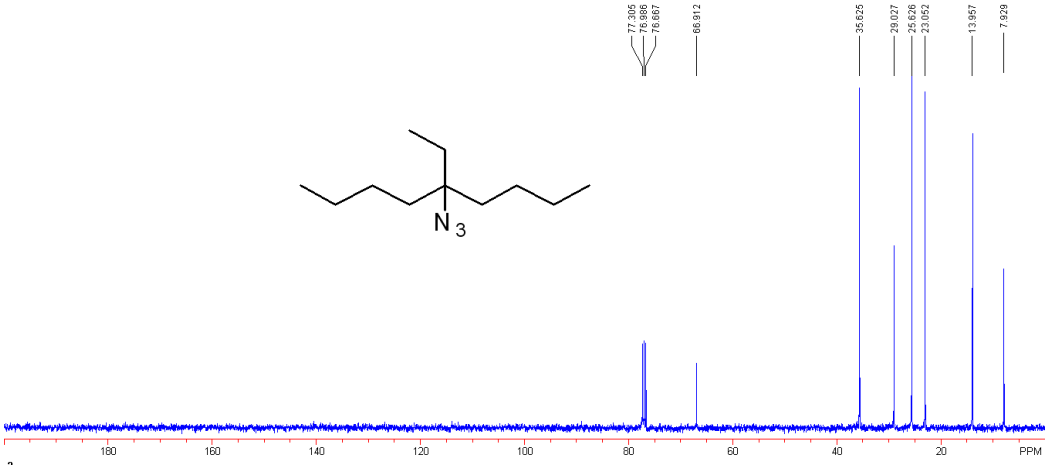
Compound **4**


7.190
1.425
1.410
1.394
1.384
1.198
1.172
0.829
0.813
0.795
22.11
2.00
2.04
8
N3
8
6
4
2
PPM

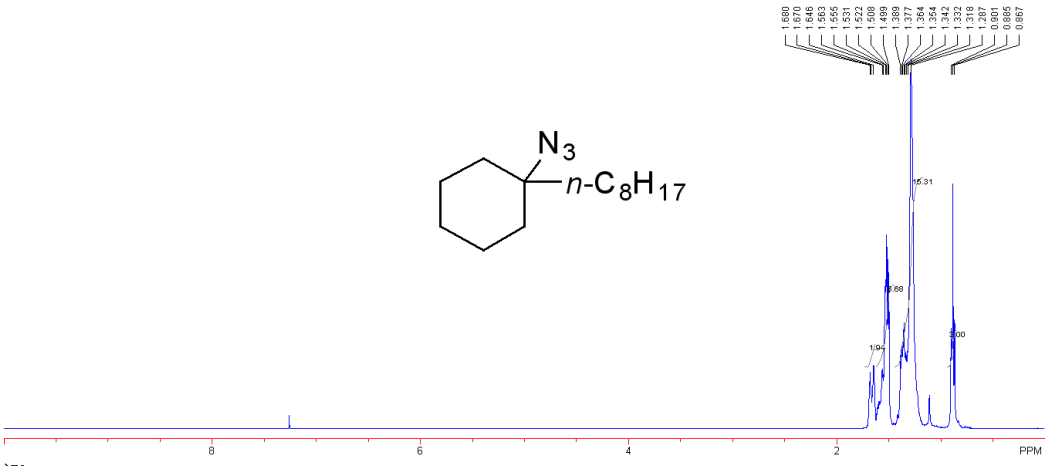

77.312
76.994
76.675
61.650
41.448
31.889
29.908
29.569
29.514
29.455
29.398
25.937
24.229
22.657
14.063
8
N3
180
160
140
120
100
80
60
40
20
PPM

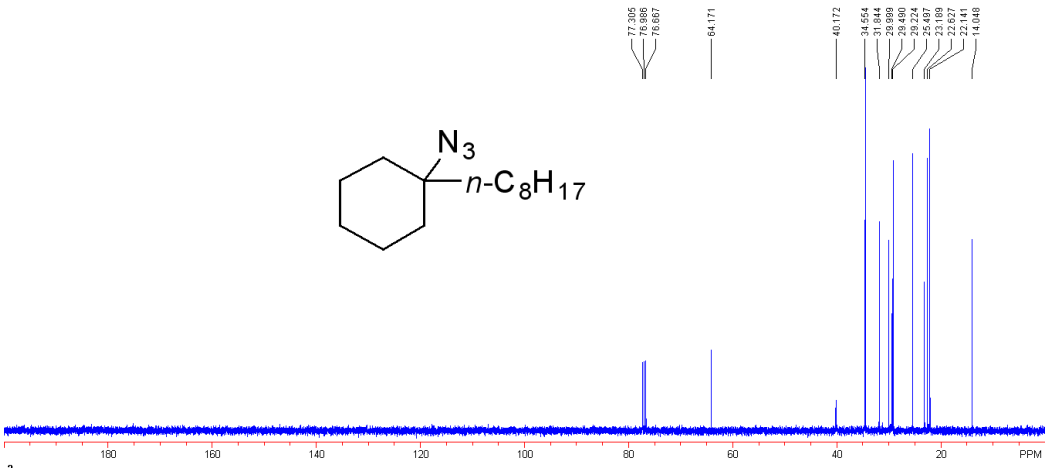
Compound **5**


7.260
1.560
1.531
1.512
1.502
1.486
1.481
1.462
1.331
1.315
1.305
1.293
1.284
1.265
1.254
0.938
0.921
0.904
0.886
0.867
6.00
9.22
8.97
N 3
8
6
4
2
PPM

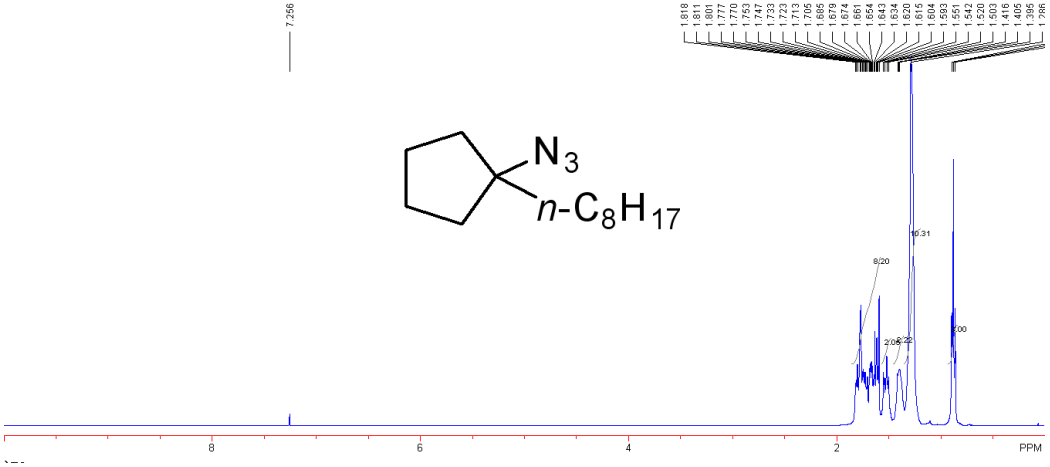

77.305
76.986
76.667
66.912
35.625
29.027
25.626
23.052
13.957
7.929
N 3
180
160
140
120
100
80
60
40
20
PPM

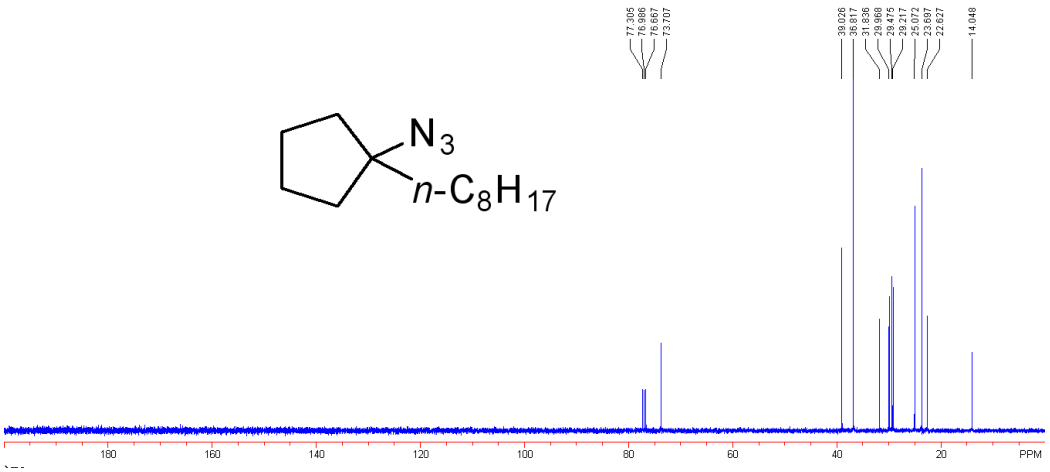
Compound **6**


1.690
1.670
1.646
1.563
1.555
1.531
1.522
1.498
1.498
1.389
1.377
1.364
1.354
1.342
1.332
1.318
1.287
0.901
0.885
0.867
15.31
8.88
1.94
8.00
N3
n-C8H17
8
6
4
2
PPM

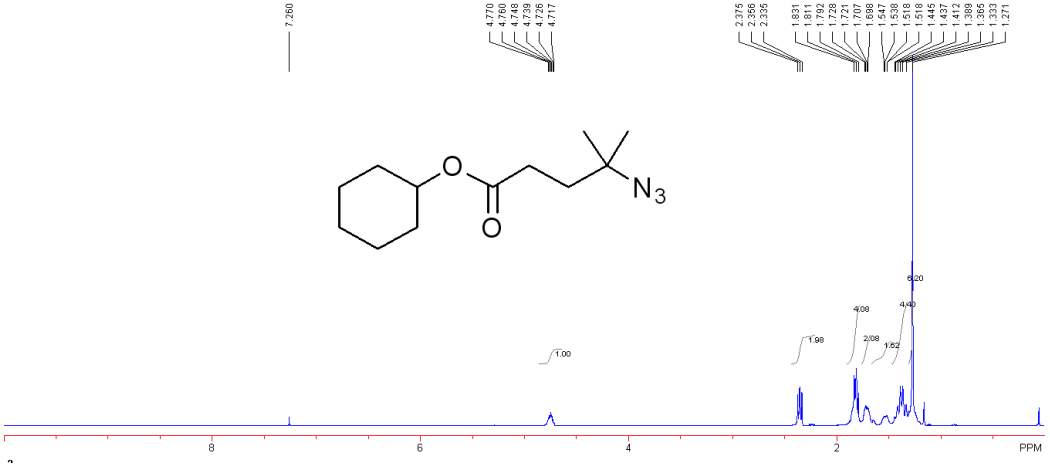

77.305
76.986
76.667
64.171
40.172
34.554
31.844
29.999
29.490
29.234
25.437
23.189
22.627
22.141
14.048
N3
n-C8H17
180
160
140
120
100
80
60
40
20
PPM

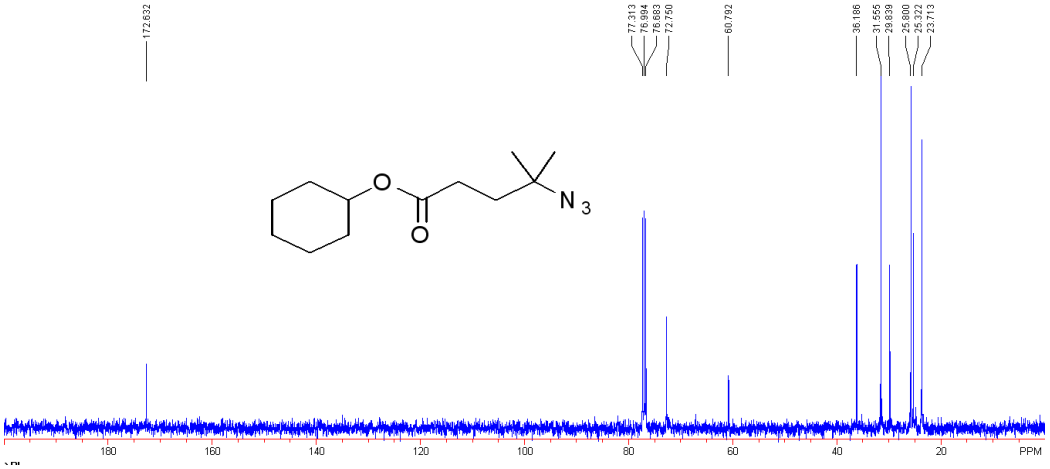
Compound **7**


7.256
1.818
1.811
1.801
1.777
1.770
1.753
1.747
1.733
1.723
1.713
1.705
1.685
1.679
1.674
1.656
1.654
1.643
1.634
1.620
1.615
1.604
1.593
1.561
1.543
1.520
1.503
1.416
1.405
1.395
1.266
N3
n-C8H17
10.31
8.20
2.04
2.22
2.00
8
6
4
2
PPM

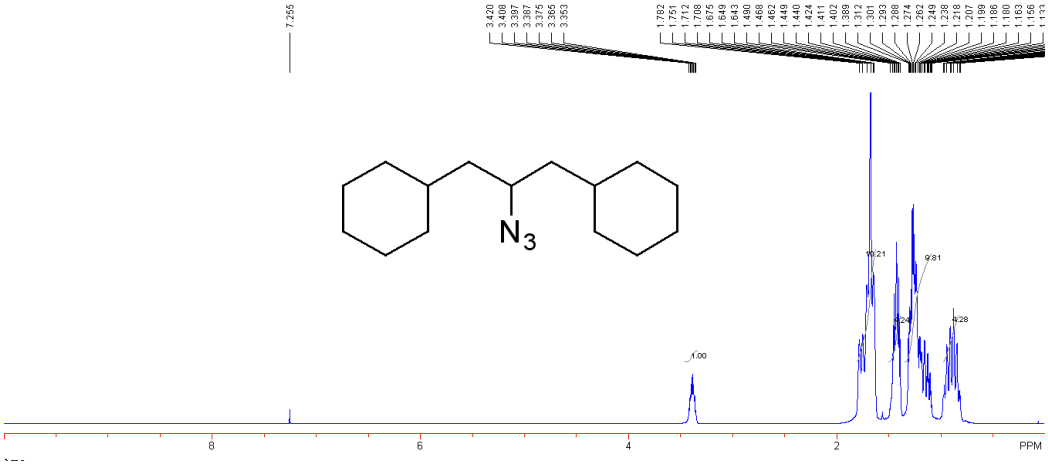

77.305
76.986
76.667
73.707
39.026
36.817
31.836
29.969
29.475
29.217
25.672
23.097
22.627
14.048
N3
n-C8H17
180
160
140
120
100
80
60
40
20
PPM

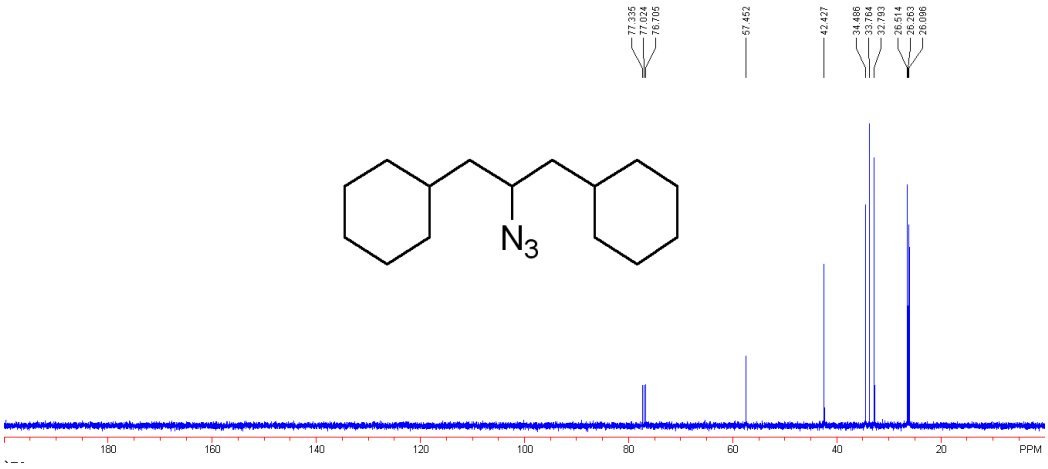
Compound **8**


7.260
4.770
4.760
4.748
4.739
4.726
4.717
2.375
2.356
2.335
1.831
1.811
1.792
1.728
1.721
1.707
1.698
1.547
1.538
1.518
1.518
1.445
1.437
1.412
1.388
1.365
1.333
1.271
O
O
N3
6.20
4.08
4.00
1.98
2.08
1.62
1.00
8
6
4
2
PPM

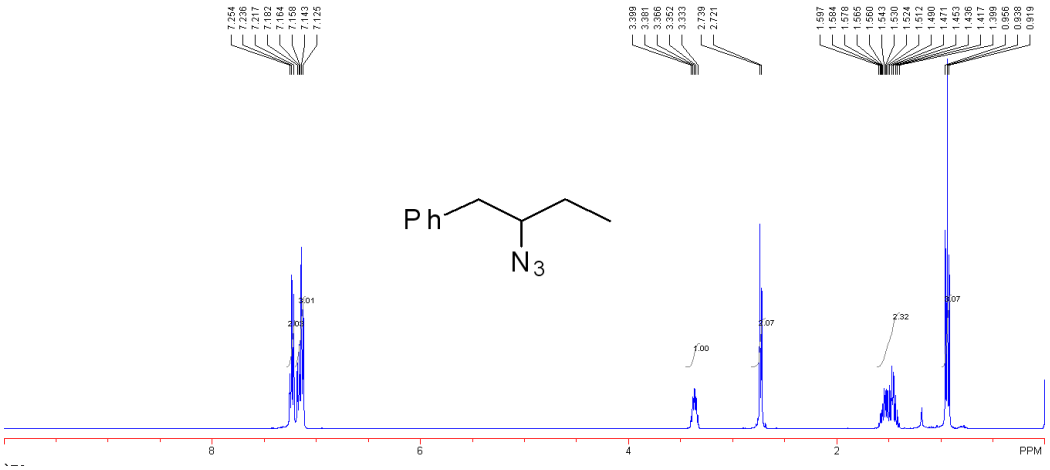

172.632
77.313
76.994
76.683
72.750
60.792
36.186
31.555
29.839
25.800
25.322
23.713
O
O
N 3
180
160
140
120
100
80
60
40
20
PPM

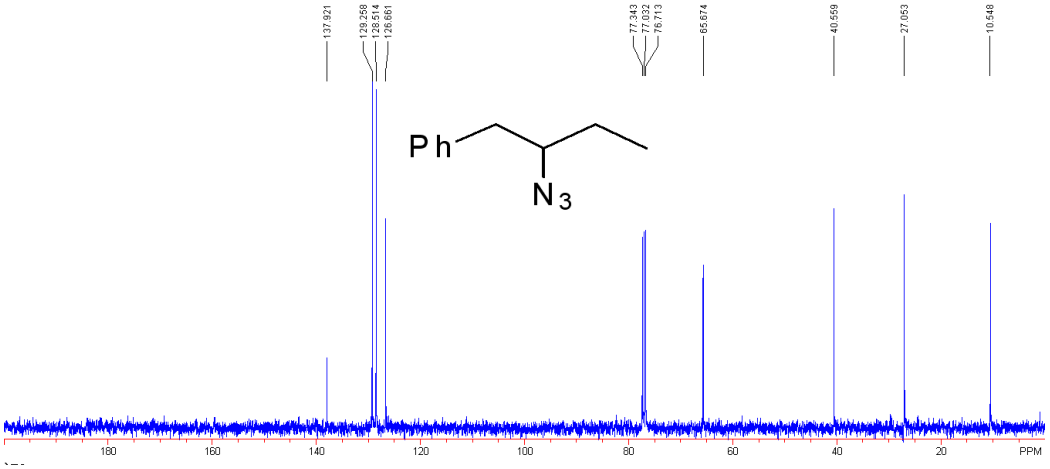
Compound **9**


7.255
3.420
3.408
3.397
3.387
3.375
3.365
3.353
1.782
1.751
1.712
1.708
1.675
1.649
1.643
1.490
1.466
1.462
1.449
1.440
1.424
1.411
1.402
1.389
1.312
1.301
1.293
1.288
1.274
1.262
1.249
1.238
1.218
1.207
1.199
1.186
1.180
1.163
1.156
N3
1.00
10.21
9.81
8.24
8.28
8
6
4
2
PPM

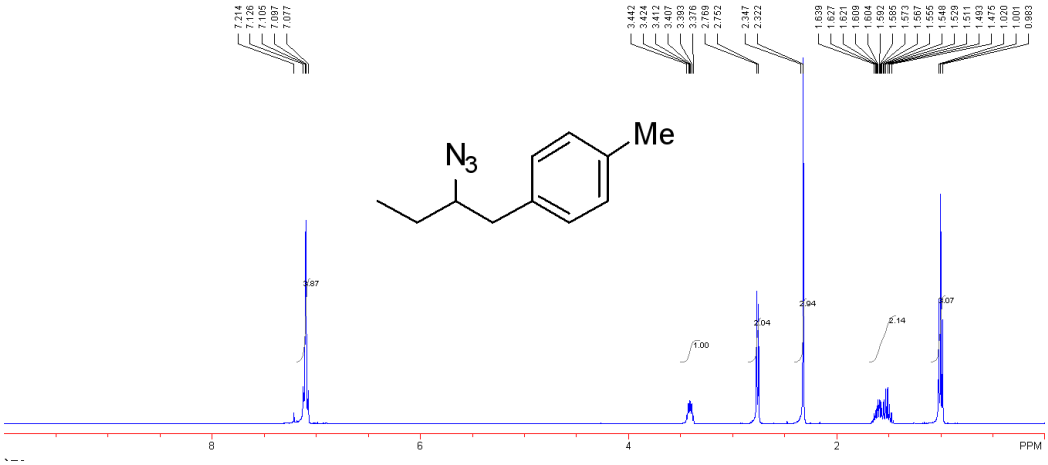

77.335
77.024
76.705
57.452
42.427
34.486
33.764
32.793
26.514
26.363
26.096
N3
180
160
140
120
100
80
60
40
20
PPM

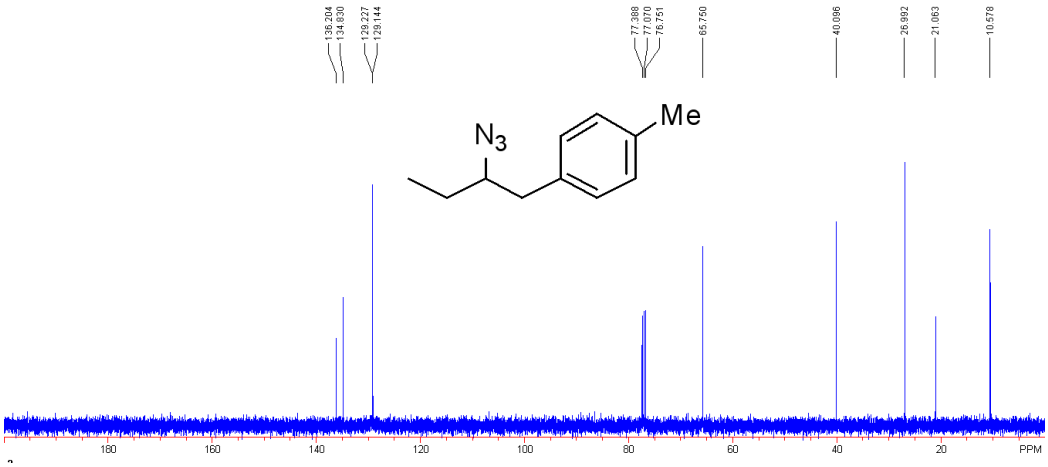
Compound **10**


7.254
7.236
7.217
7.182
7.164
7.158
7.143
7.125
3.399
3.381
3.366
3.352
3.333
2.739
2.721
1.597
1.584
1.578
1.565
1.560
1.543
1.530
1.524
1.512
1.490
1.471
1.453
1.436
1.417
1.399
0.956
0.938
0.919
Ph
N3
2.01
2.00
1.00
2.07
2.32
3.07
8
6
4
2
PPM

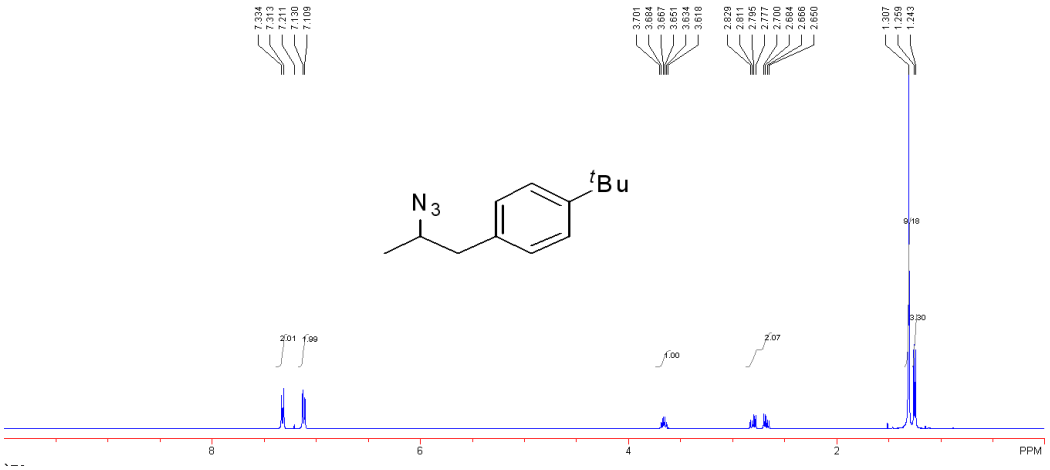

137.921
129.258
128.514
126.661
77.343
77.032
76.713
65.674
40.559
27.053
10.548
Ph
N3
180
160
140
120
100
80
60
40
20
PPM

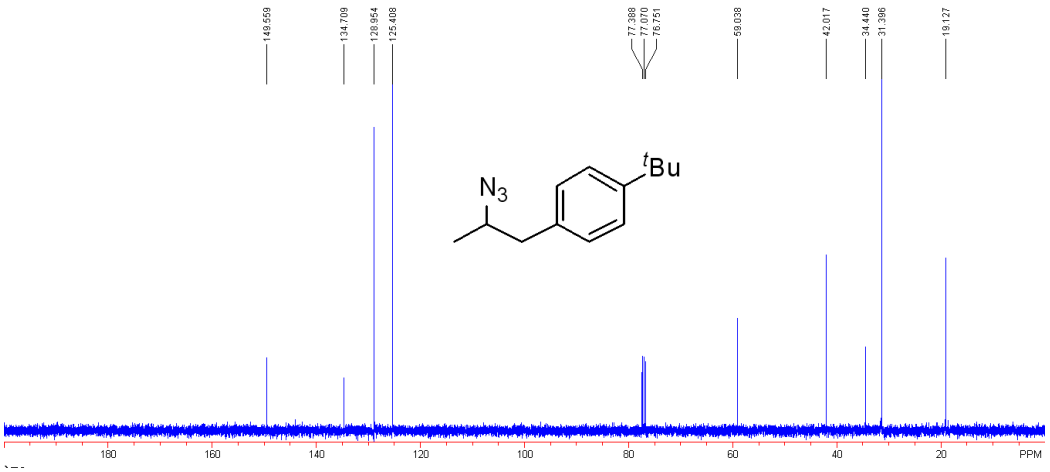
Compound **11**


7.214
7.126
7.105
7.097
7.077
3.442
3.424
3.412
3.407
3.393
3.376
2.769
2.752
2.347
2.322
1.639
1.627
1.621
1.609
1.604
1.592
1.585
1.573
1.567
1.555
1.548
1.526
1.511
1.493
1.475
1.020
1.001
0.983
N3
Me
3.87
1.00
2.04
2.94
2.14
3.07
8
6
4
2
PPM

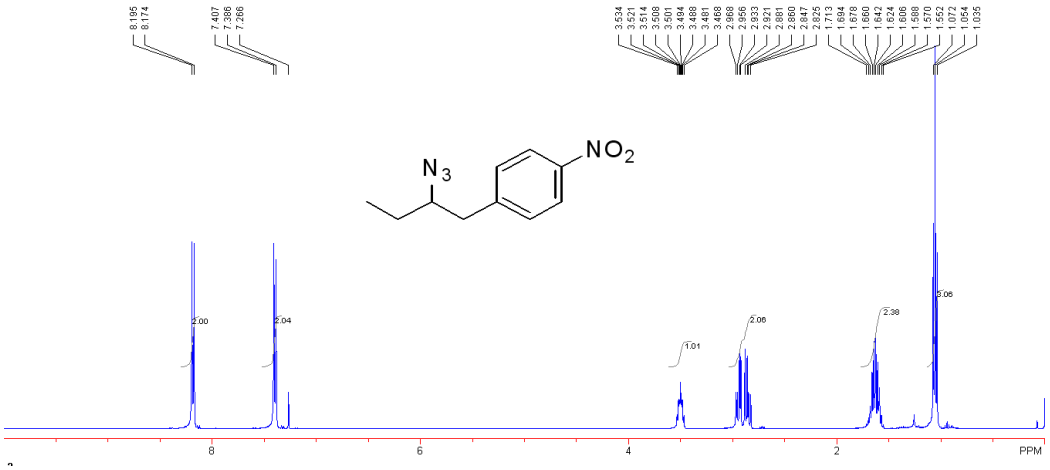

136.204
134.830
129.227
129.144
77.368
77.050
76.751
65.760
40.096
26.992
21.063
10.578
N3
Me
160
160
140
120
100
80
60
40
20
PPM

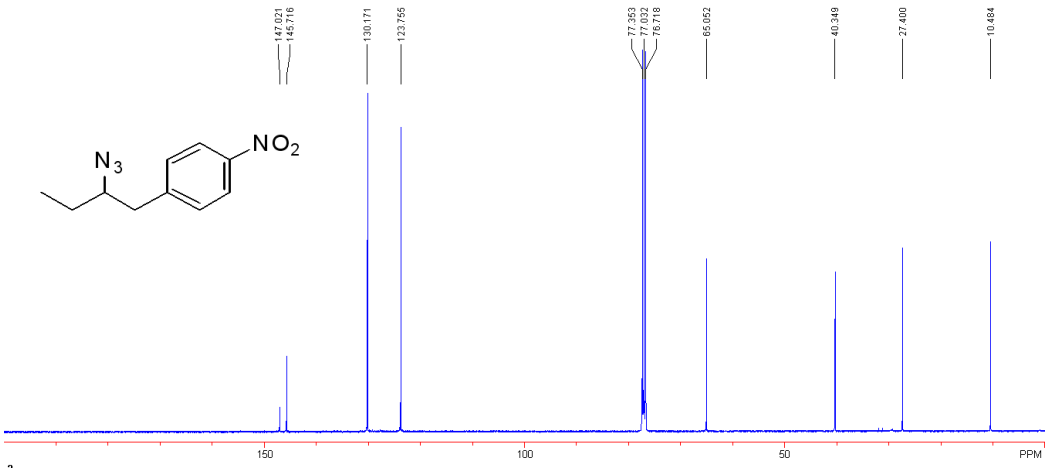
Compound 1**2**


7.334
7.313
7.211
7.130
7.109
3.701
3.684
3.667
3.651
3.634
3.618
2.829
2.811
2.795
2.777
2.700
2.684
2.666
2.650
1.307
1.259
1.243
^{t}Bu
N$_3$
9.18
9.30
2.01
1.99
1.00
2.07
8
6
4
2
PPM

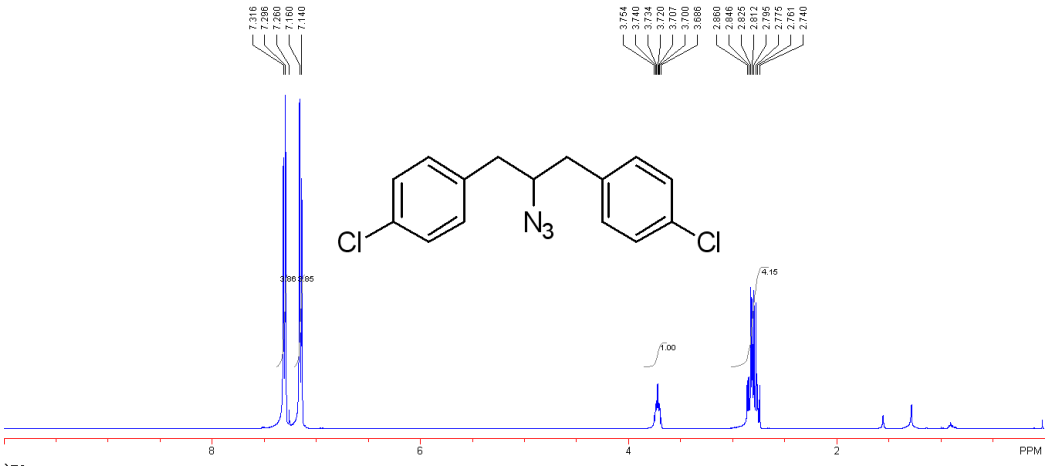

149.559
134.709
128.954
125.408
77.388
77.070
76.751
59.038
42.017
34.440
31.396
19.127
^{t}Bu
N$_3$
180
160
140
120
100
80
60
40
20
PPM

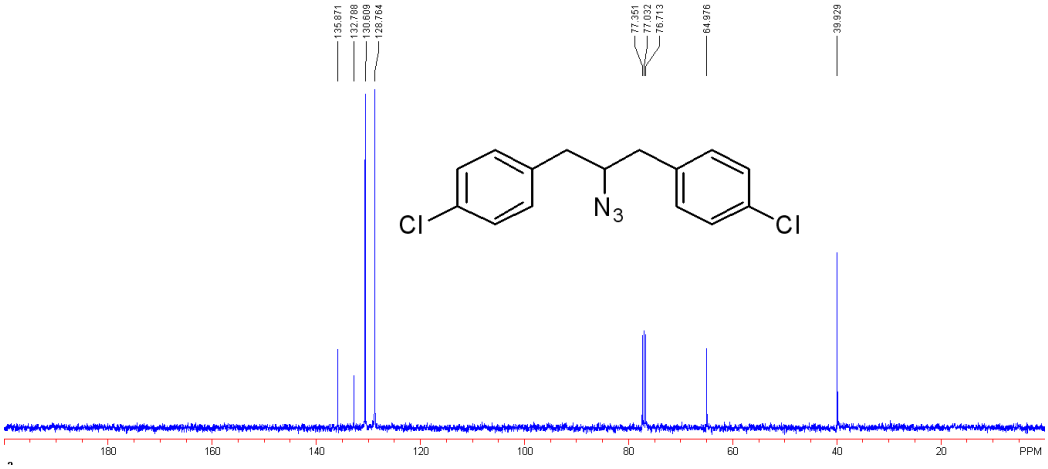
Compound **13**


8.195
8.174
7.407
7.385
7.266
3.534
3.521
3.514
3.508
3.501
3.494
3.488
3.481
3.468
2.968
2.956
2.933
2.921
2.881
2.860
2.847
2.713
1.694
1.678
1.660
1.642
1.624
1.606
1.588
1.570
1.552
1.072
1.054
1.035
N3
NO2
2.00
2.04
1.01
2.06
2.38
3.06
8
6
4
2
PPM

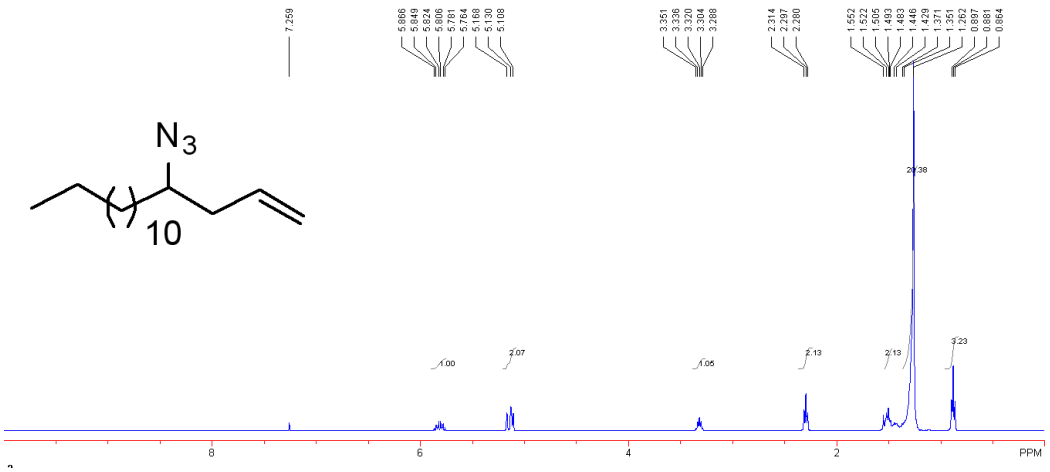

147.021
145.716
130.171
123.755
77.353
77.032
76.718
65.052
40.349
27.400
10.484
N3
NO2
150
100
50
PPM

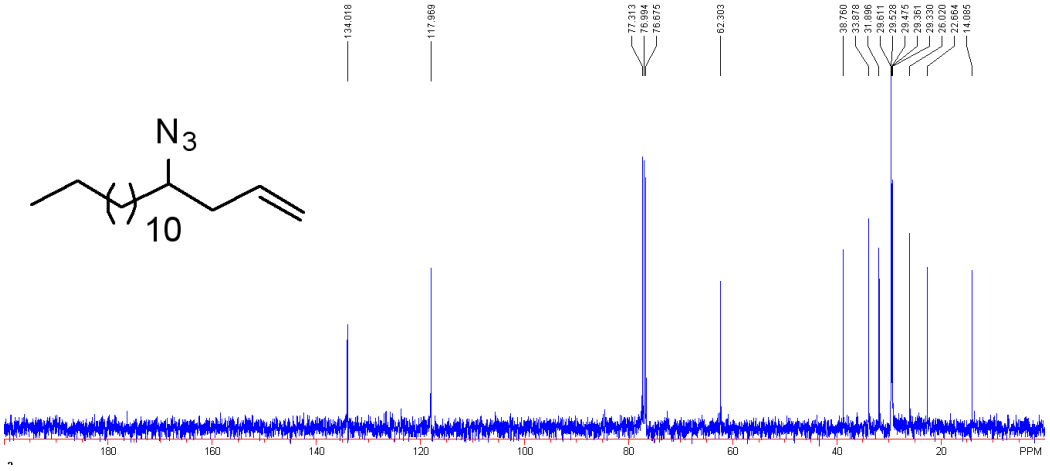
Compound **14**


7.316
7.296
7.260
7.160
7.140
3.754
3.740
3.724
3.720
3.707
3.700
3.686
2.860
2.846
2.825
2.812
2.795
2.775
2.761
2.740
Cl
N3
Cl
4.15
1.00
8
6
4
2
PPM

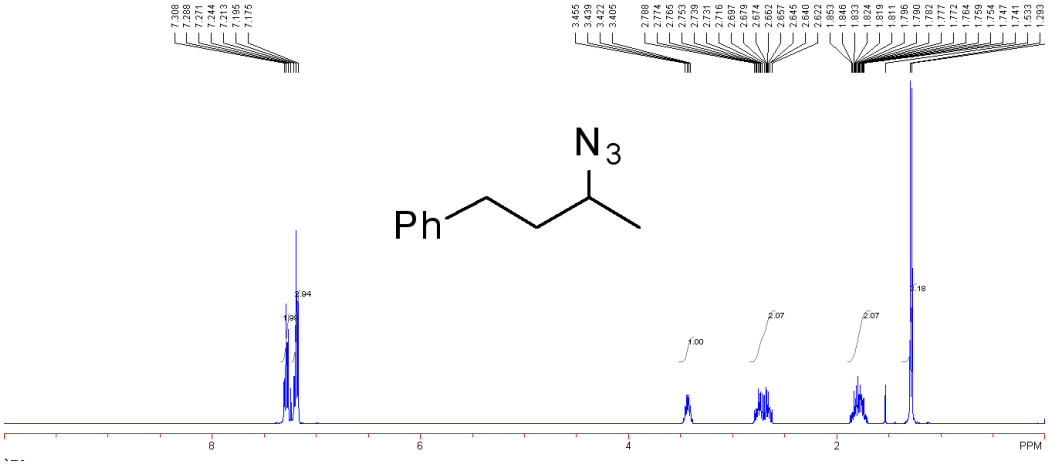

135.871
132.789
130.609
128.764
77.351
77.032
76.713
64.976
39.929
Cl
N3
Cl
180
160
140
120
100
80
60
40
20
PPM

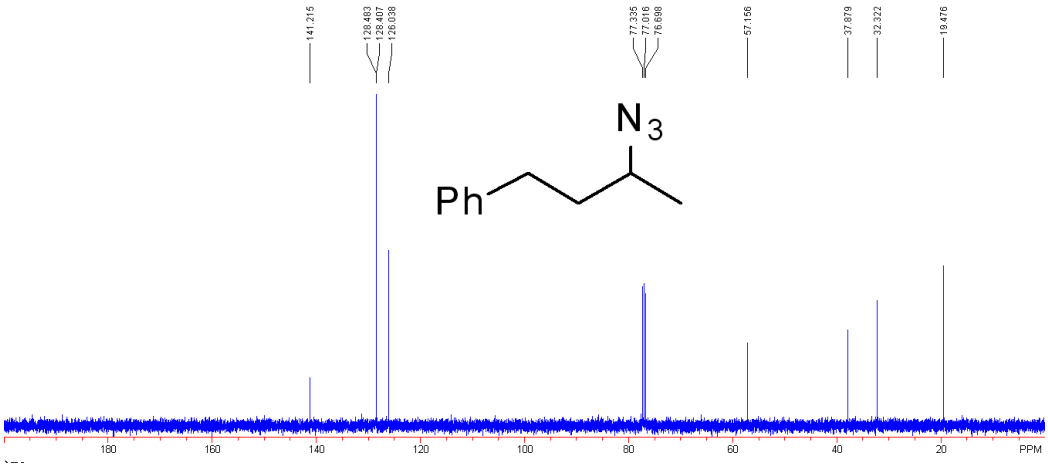
Compound **15**


7.259
5.866
5.849
5.824
5.806
5.791
5.764
5.168
5.130
5.108
3.351
3.336
3.320
3.304
3.288
2.314
2.297
2.280
1.552
1.522
1.505
1.493
1.463
1.446
1.429
1.371
1.351
1.262
0.897
0.881
0.864
N3
10
20.38
1.00
2.07
1.05
2.13
2.13
3.23
8
6
4
2
PPM

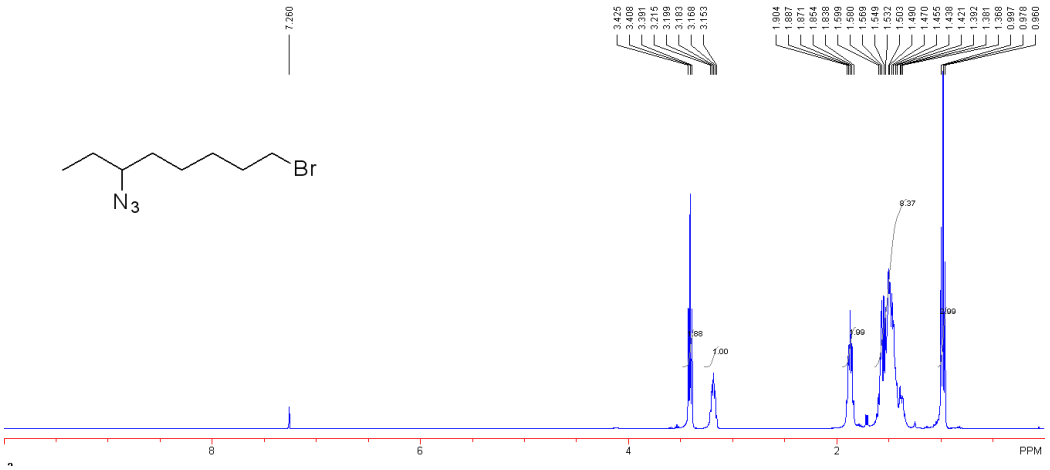

134.018
117.969
77.313
76.994
76.675
62.303
38.760
33.878
31.896
29.611
29.528
29.475
29.361
29.330
29.070
22.664
14.085
N3
10
180
160
140
120
100
80
60
40
20
PPM

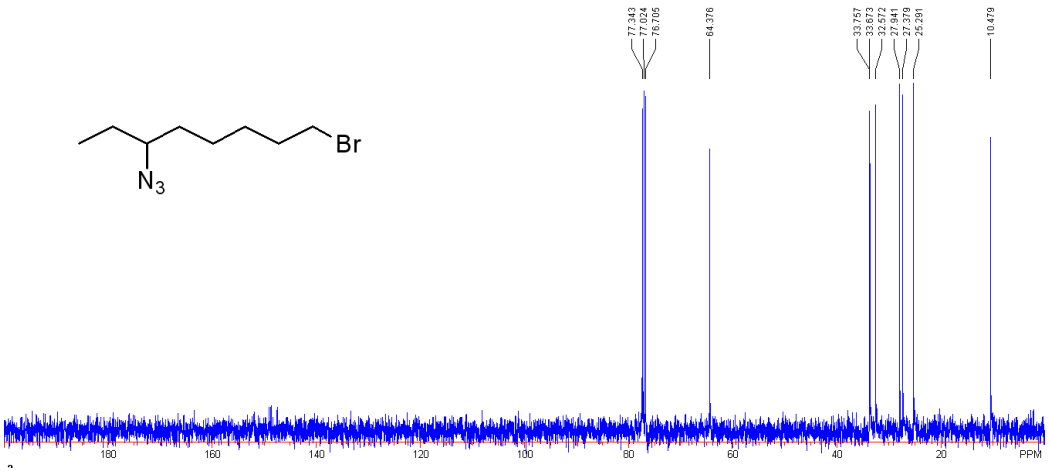
Compound **16**


7.308
7.298
7.271
7.244
7.213
7.195
7.175
3.455
3.439
3.422
3.405
2.788
2.774
2.765
2.753
2.739
2.731
2.716
2.697
2.679
2.674
2.662
2.657
2.645
2.640
2.622
1.853
1.846
1.833
1.824
1.819
1.811
1.796
1.780
1.762
1.777
1.772
1.764
1.759
1.754
1.747
1.741
1.533
1.293
N3
Ph
2.94
1.96
1.00
2.07
2.07
3.18
8
6
4
2
PPM

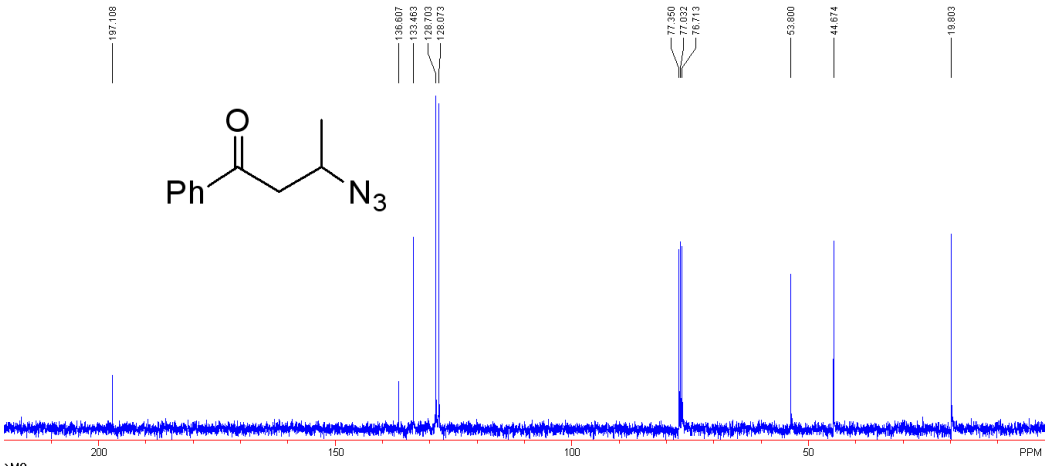

141.215
128.483
128.407
126.038
77.235
77.016
76.698
57.156
37.879
32.322
19.476
N3
Ph
180
160
140
120
100
80
60
40
20
PPM

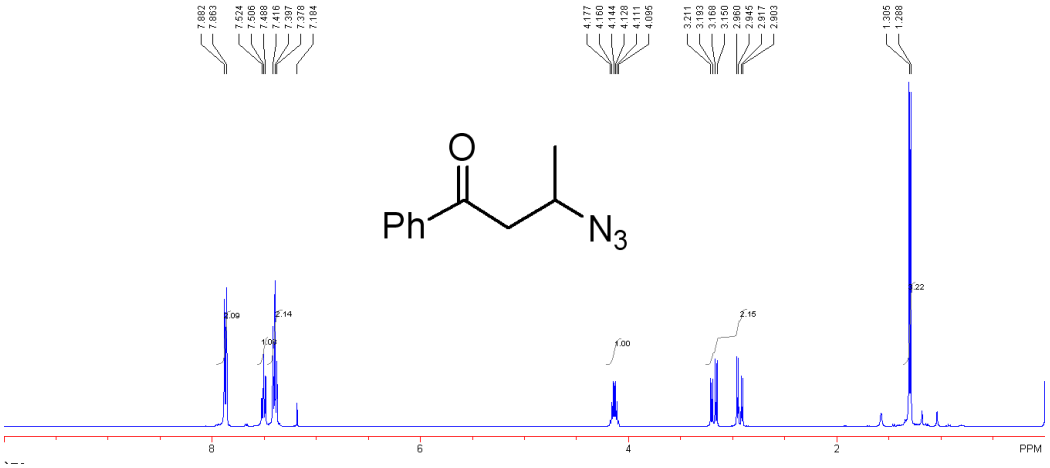
Compound **17**


7.260
3.425
3.408
3.391
3.215
3.199
3.183
3.168
3.153
1.904
1.887
1.871
1.854
1.838
1.599
1.580
1.569
1.549
1.532
1.503
1.490
1.470
1.455
1.438
1.421
1.392
1.361
1.338
0.997
0.978
0.960
Br
N3
6.37
1.88
1.00
1.99
3.09
8
6
4
2
PPM

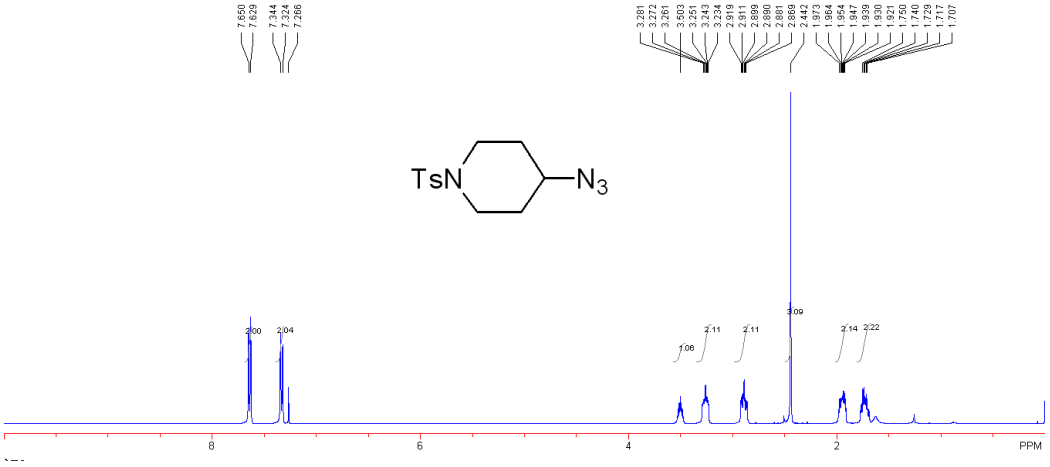

77.343
77.024
76.705
64.376
33.757
33.673
32.572
27.941
27.379
25.291
10.479
Br
N3
180
160
140
120
100
80
60
40
20
PPM

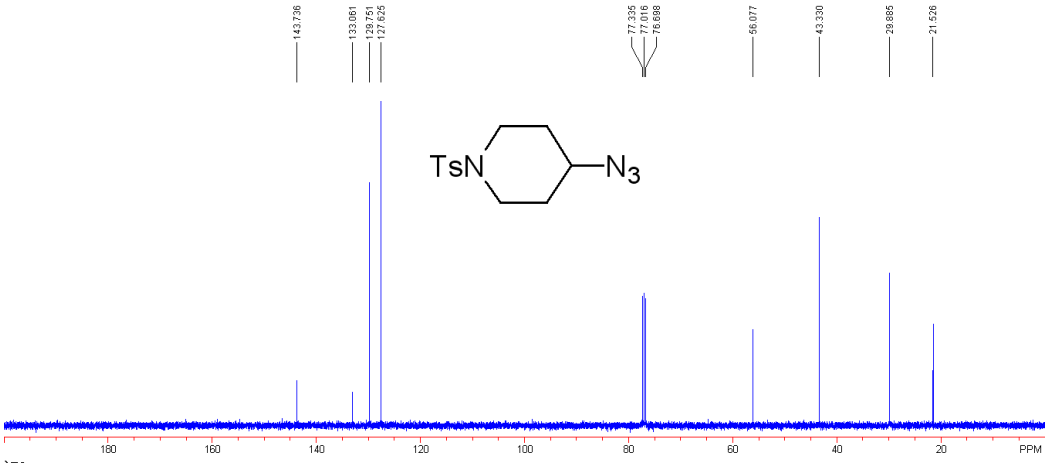
Compound **18**


197.108
136.607
133.463
128.703
128.073
77.350
77.032
76.713
53.800
44.674
19.803
O
Ph
N3
200
150
100
50
PPM

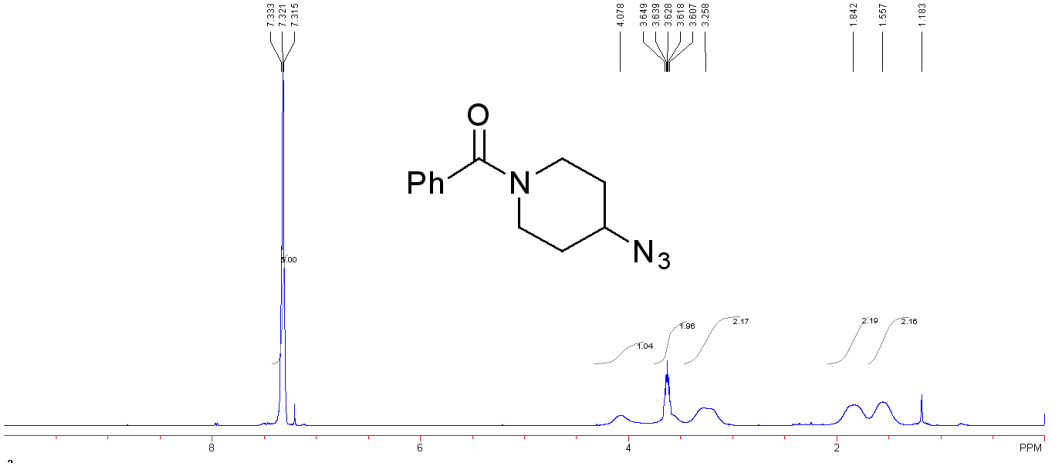

7.882
7.863
7.524
7.506
7.488
7.416
7.397
7.378
7.164
4.177
4.160
4.144
4.128
4.111
4.095
3.211
3.193
3.168
3.150
2.960
2.945
2.917
2.903
1.305
1.288
O
Ph
N3
2.09
2.14
1.09
1.00
2.15
9.22
8
6
4
2
PPM

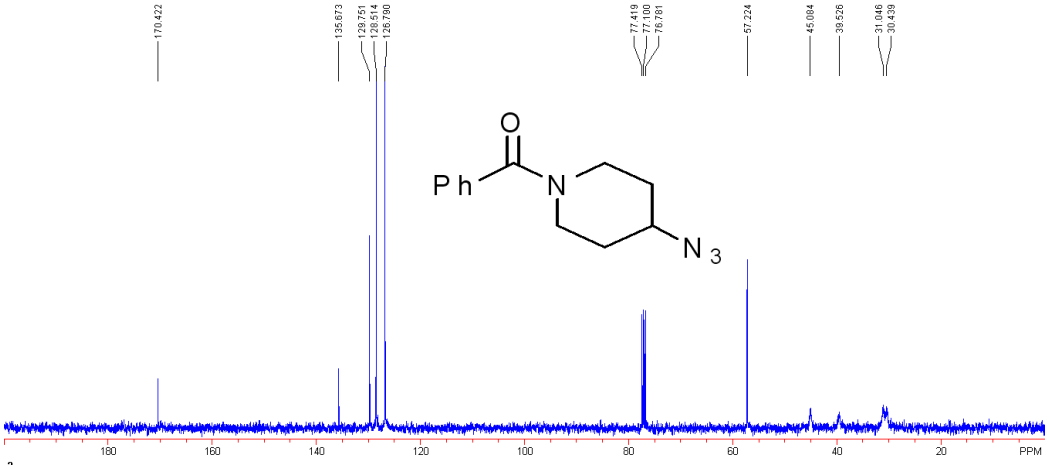
Compound **19**


7.650
7.629
7.344
7.324
7.266
3.281
3.272
3.261
3.503
3.251
3.243
3.234
2.919
2.911
2.899
2.890
2.881
2.869
2.442
1.973
1.964
1.954
1.947
1.939
1.930
1.921
1.750
1.740
1.729
1.717
1.707
TsN
N3
2.00
2.04
1.06
2.11
2.11
3.09
2.14
2.22
8
6
4
2
PPM

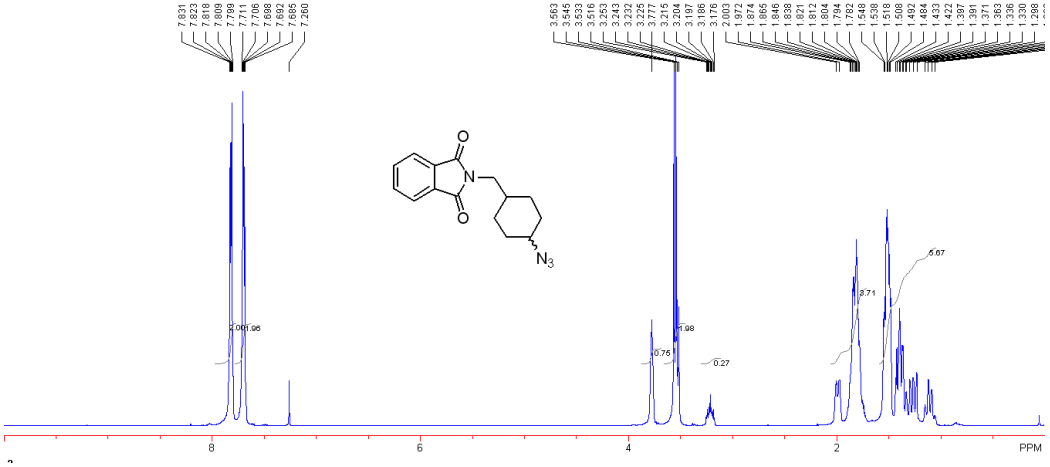

143.736
133.061
129.751
127.625
77.335
77.016
76.698
56.077
43.330
28.885
21.526
TsN
N3
160
160
140
120
100
80
60
40
20
PPM

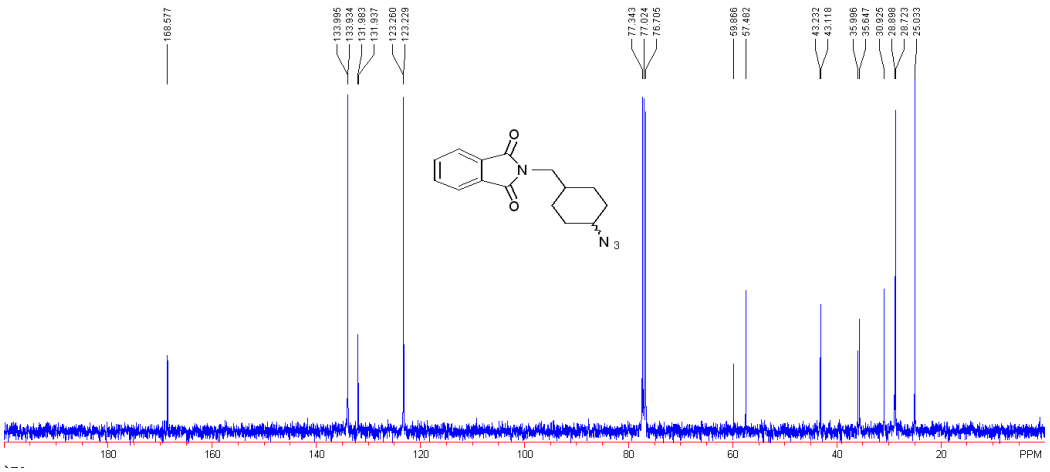
Compound **20**


7.333
7.321
7.315
4.078
3.649
3.639
3.628
3.618
3.607
3.258
1.842
1.557
1.183
O
Ph
N
N3
3.00
1.04
1.96
2.17
2.19
2.16
8
6
4
2
PPM

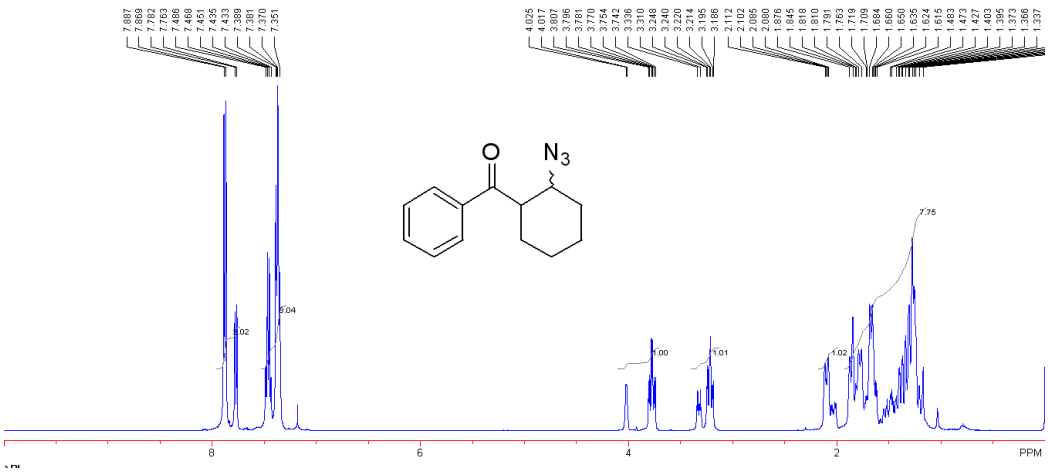

170.422
135.673
129.751
128.514
126.790
77.419
77.100
76.781
57.224
45.084
39.526
31.046
30.439
O
Ph
N
N3
180
160
140
120
100
80
60
40
20
PPM

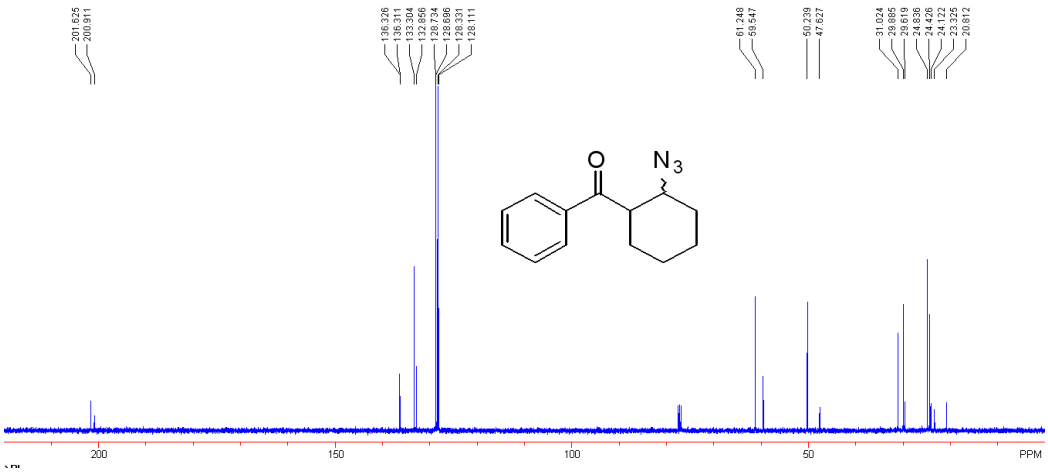
Compound **21**


7.831
7.823
7.818
7.809
7.799
7.711
7.705
7.698
7.692
7.685
7.260
3.563
3.545
3.533
3.516
3.253
3.243
3.232
3.225
3.215
3.204
3.191
3.186
3.176
2.003
1.972
1.874
1.865
1.846
1.838
1.821
1.812
1.804
1.794
1.782
1.548
1.538
1.518
1.508
1.492
1.484
1.433
1.422
1.397
1.391
1.371
1.363
1.338
1.330
1.298
2.00
1.98
0.75
0.27
3.71
5.67
8
6
4
2
PPM

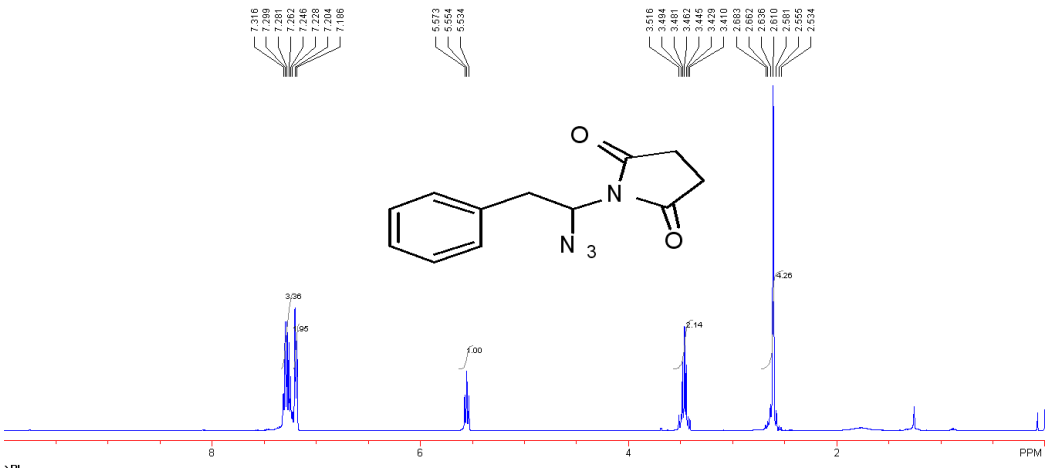

168.577
133.995
133.934
131.983
131.937
123.260
123.229
77.343
77.024
76.705
59.866
57.402
43.232
43.118
35.996
35.647
30.925
28.898
28.723
25.033
180
160
140
120
100
80
60
40
20
PPM

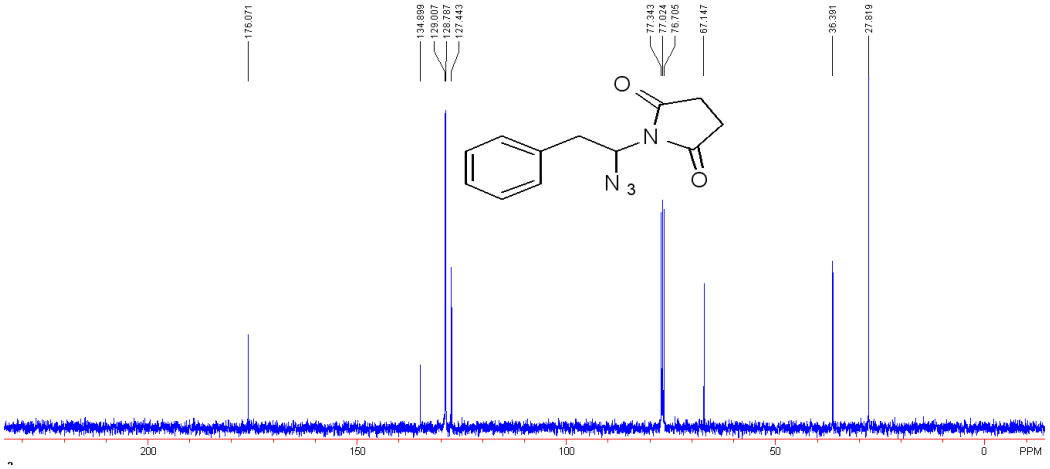
Compound **22**


7.887
7.869
7.782
7.763
7.486
7.468
7.451
7.435
7.433
7.389
7.381
7.370
7.351
4.025
4.017
3.807
3.796
3.781
3.770
3.754
3.742
3.336
3.310
3.248
3.240
3.220
3.214
3.195
3.186
2.112
2.102
2.085
2.080
1.876
1.845
1.818
1.810
1.791
1.763
1.719
1.709
1.684
1.660
1.650
1.635
1.624
1.615
1.483
1.473
1.427
1.403
1.395
1.373
1.366
1.337
O
N3
8.02
8.04
1.00
1.01
1.02
7.75
8
6
4
2
PPM

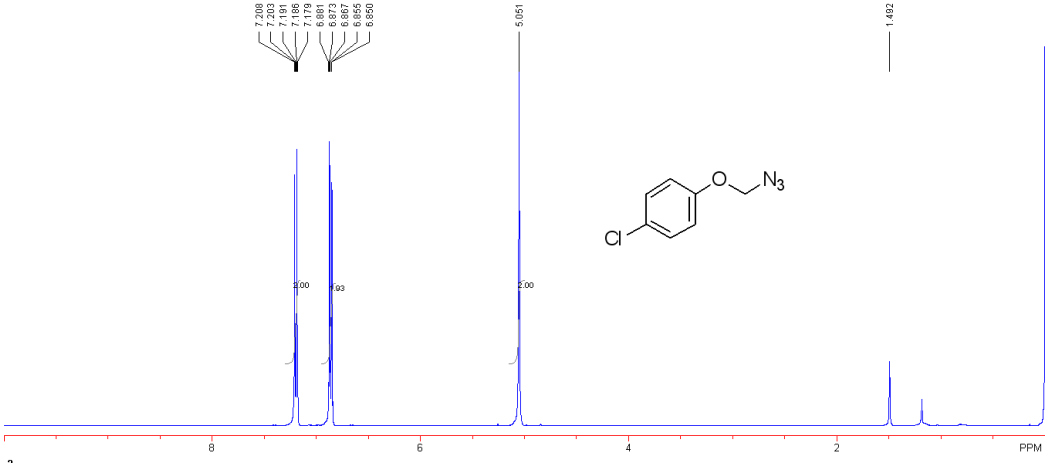

201.625
200.911
136.326
135.311
133.264
132.856
128.734
128.696
128.331
128.111
61.248
59.547
50.239
47.627
31.024
29.885
29.619
24.836
24.426
24.122
23.325
20.812
O
N3
200
150
100
50
PPM

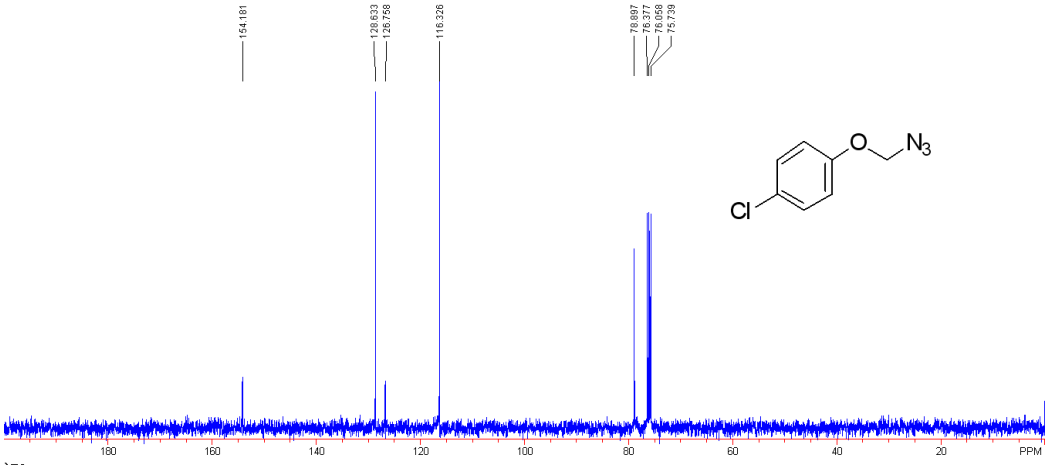
Compound **23**


7.316
7.299
7.281
7.262
7.246
7.228
7.204
7.166
5.573
5.554
5.534
3.516
3.494
3.481
3.462
3.445
3.429
3.410
2.683
2.662
2.636
2.610
2.581
2.555
2.534
O
N
N 3
O
3.36
2.95
1.00
2.14
4.26
8
6
4
2
PPM

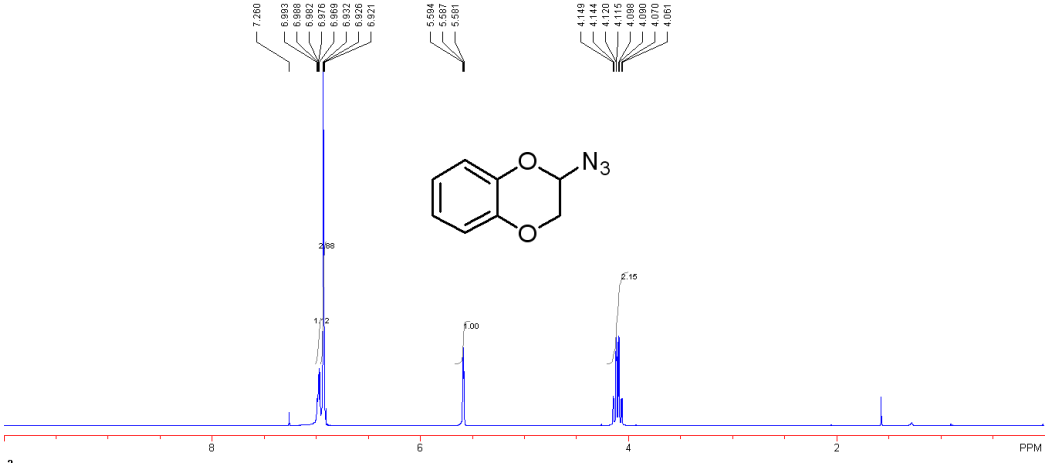

176.071
134.899
129.007
128.787
127.443
77.343
77.024
76.705
67.147
36.391
27.819
O
N
N 3
O
200
150
100
50
0
PPM

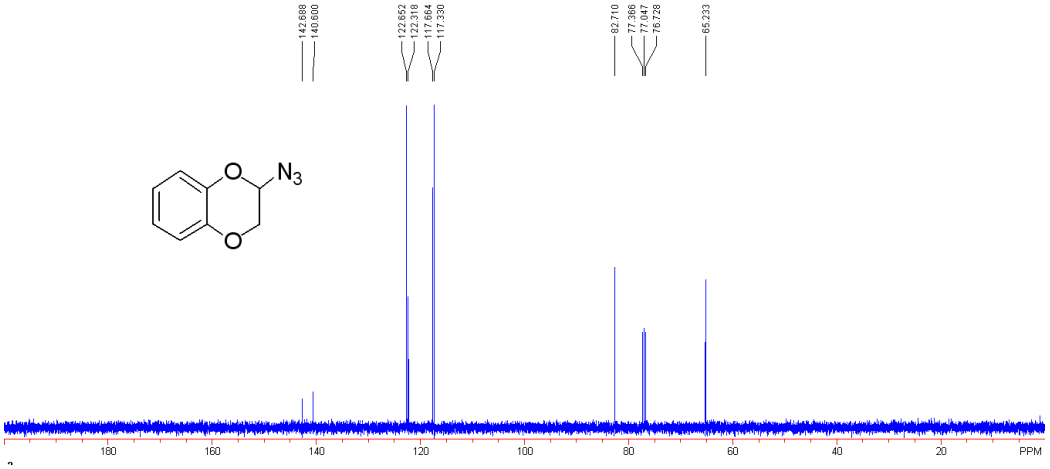
Compound **24**


7.208
7.203
7.191
7.186
7.179
6.881
6.873
6.867
6.855
6.850
5.051
1.492
3.00
2.93
2.00
Cl
O
N3
8
6
4
2
PPM

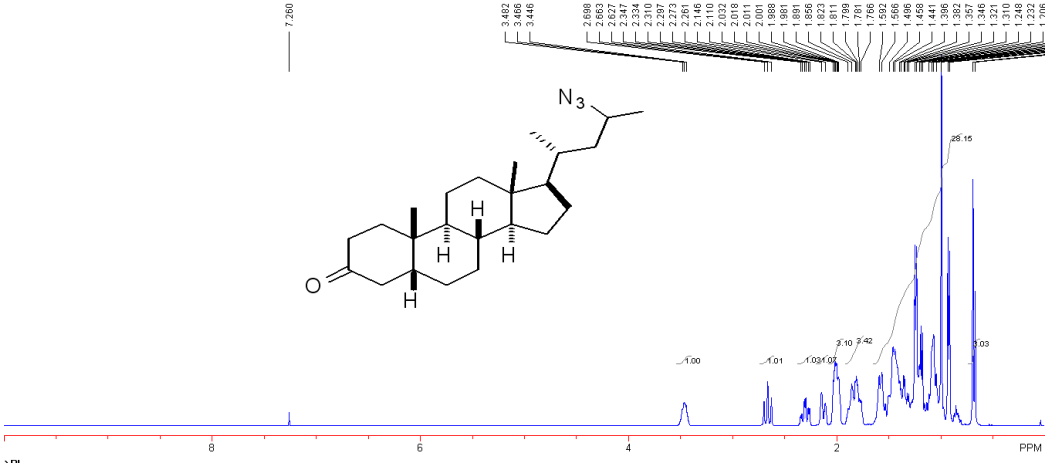

154.181
128.633
126.758
116.326
78.897
76.377
76.058
75.739
Cl
O
N3
180
160
140
120
100
80
60
40
20
PPM

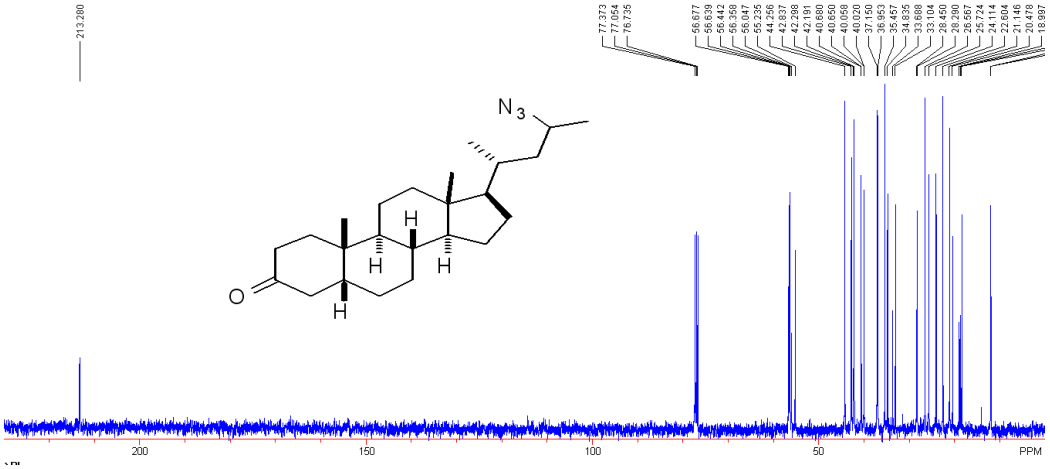
Compound **25**


7.260
6.993
6.988
6.982
6.976
6.969
6.932
6.926
6.921
5.594
5.587
5.581
4.149
4.144
4.130
4.115
4.098
4.090
4.070
4.061
N3
O
O
2.88
1.12
1.00
2.15
8
6
4
2
PPM

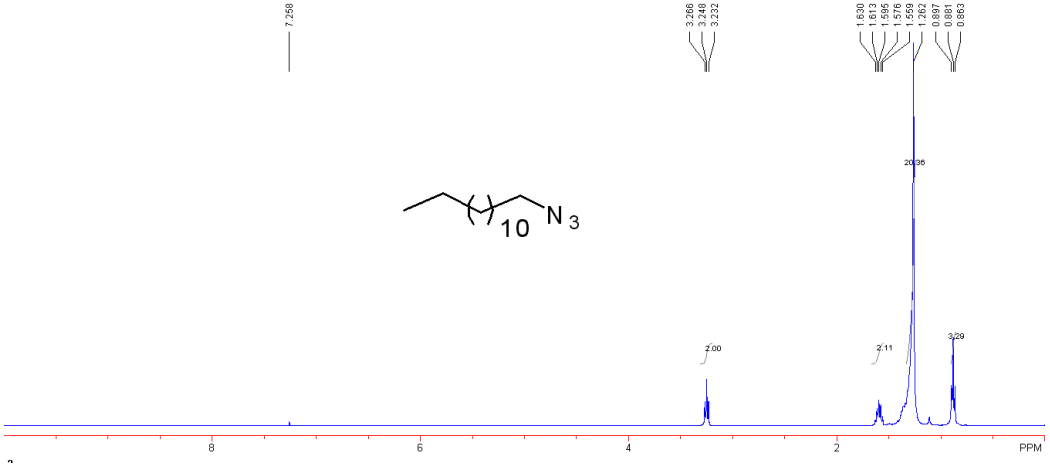

142.688
140.600
122.652
122.318
117.664
117.330
82.710
77.366
77.047
76.728
65.233
N3
O
O
180
160
140
120
100
80
60
40
20
PPM

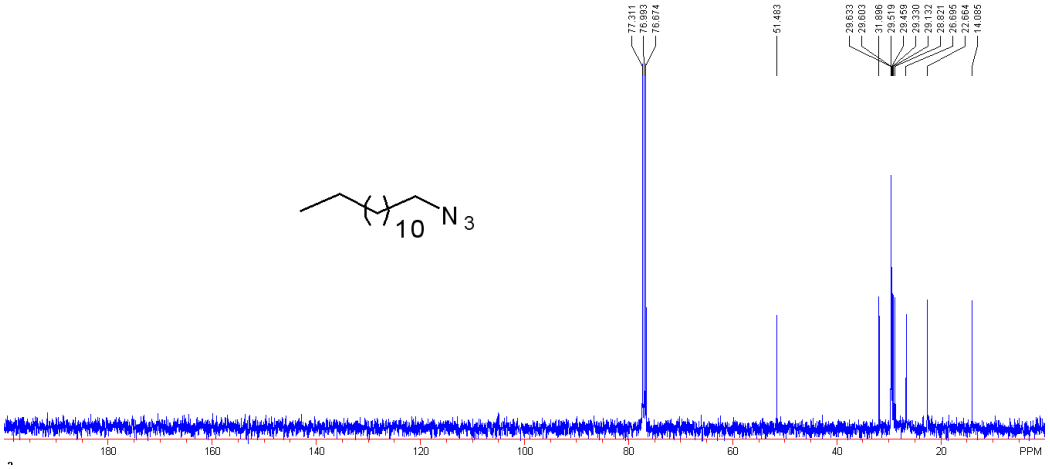
Compound **26**


7.260
N3
H
H
H
O
H
1.00
1.01
1.03
1.07
3.10
3.42
6.15
3.03
8
6
4
2
PPM

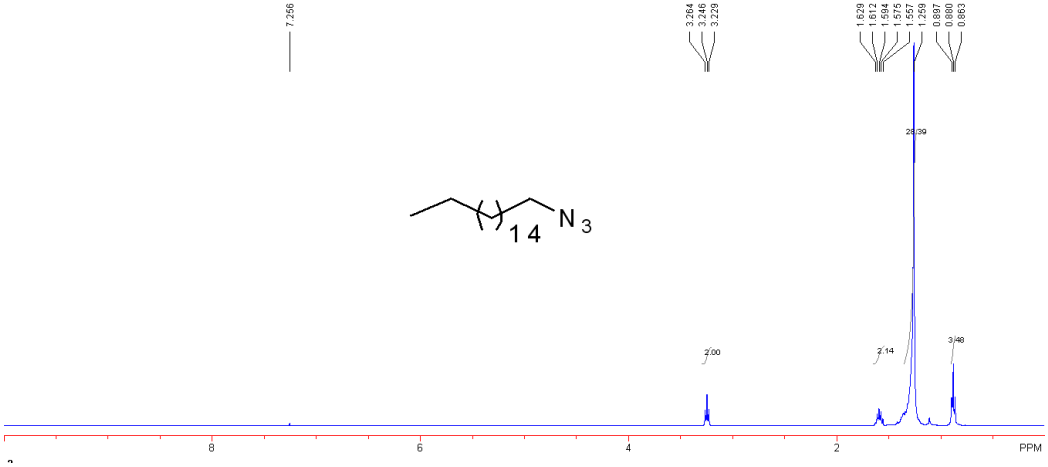

213.280
77.373
77.054
76.735
N3
H
H
H
O
H
200
150
100
50
PPM

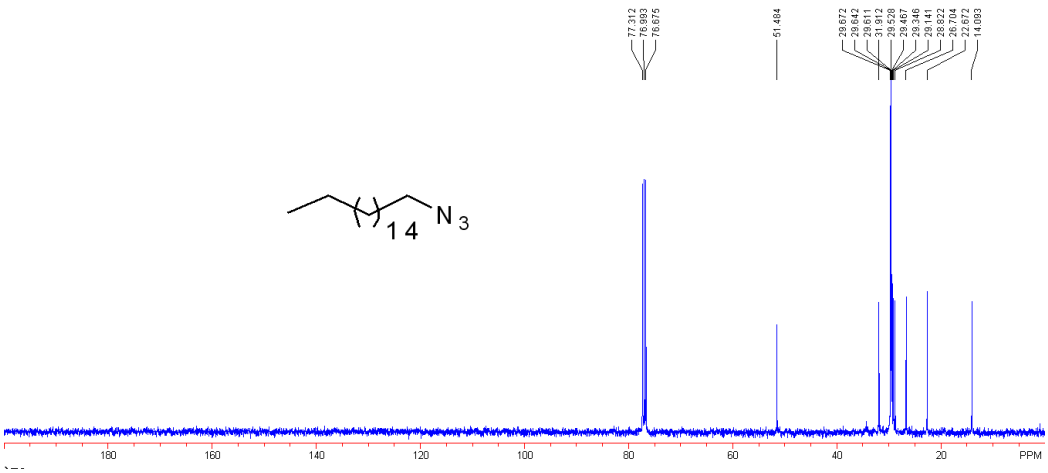
Compound **27**


7.258
3.266
3.249
3.232
1.630
1.613
1.595
1.576
1.559
1.262
0.897
0.881
0.863
20.36
2.00
2.11
3.29
10
N 3
8
6
4
2
PPM

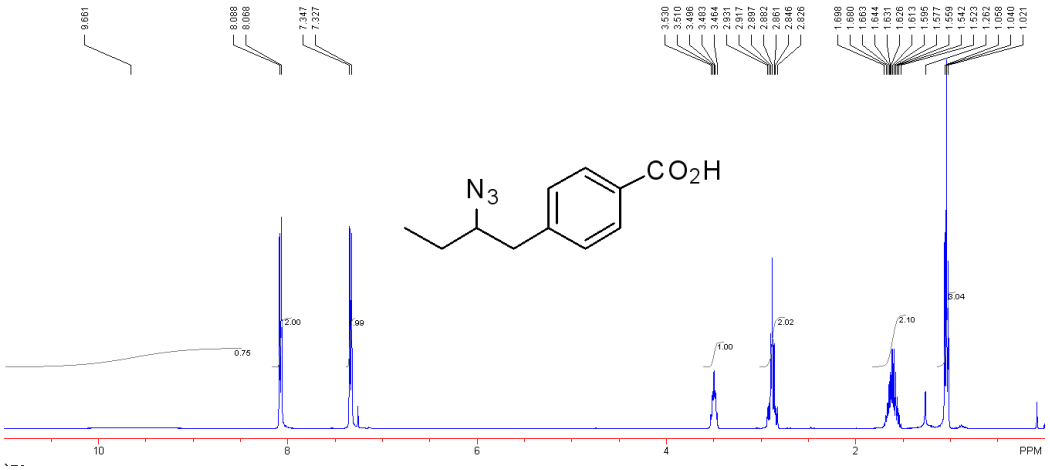

77.311
76.993
76.674
51.483
29.633
29.603
31.896
29.519
29.459
29.330
29.172
28.821
26.695
22.664
14.085
10
N 3
180
160
140
120
100
80
60
40
20
PPM

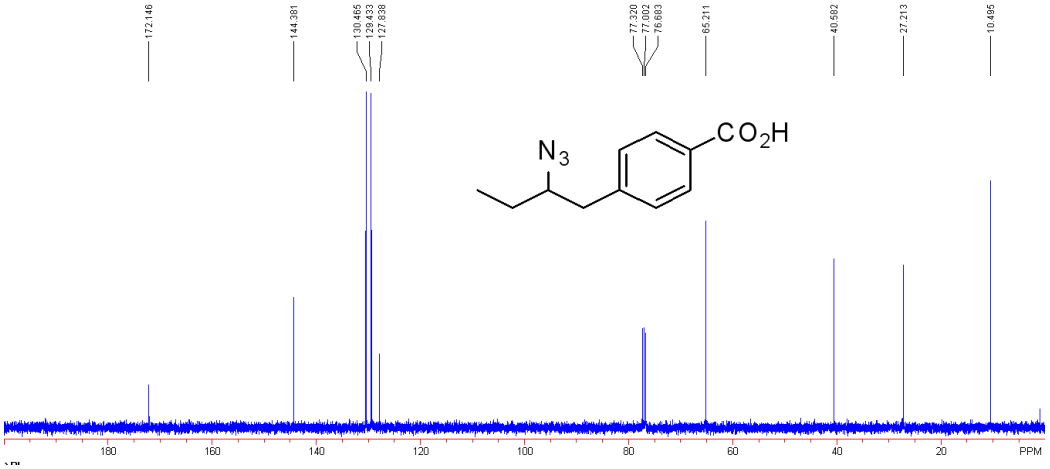
Compound **28**


7.256
3.264
3.246
3.229
1.629
1.612
1.594
1.575
1.557
1.259
0.897
0.880
0.863
28.39
2.00
2.14
3.48
14
N 3
8
6
4
2
PPM

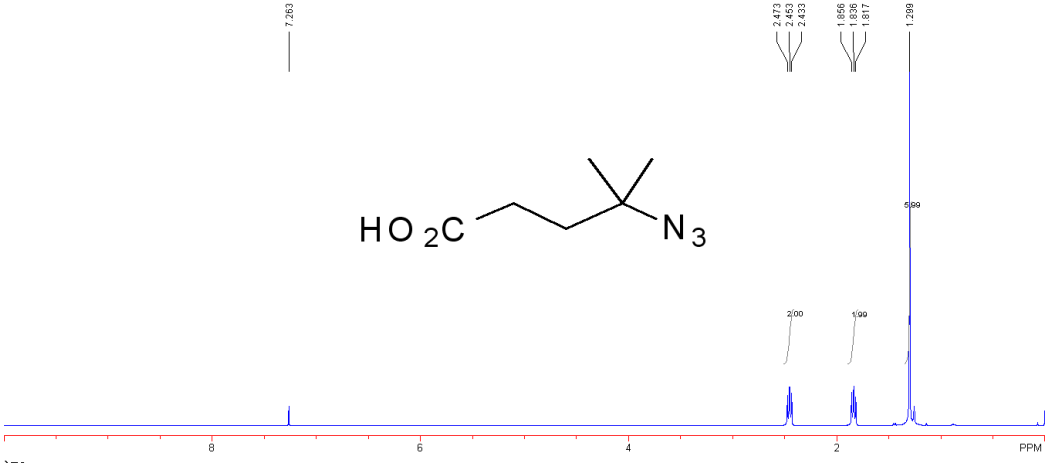

77.312
76.993
76.675
51.484
29.672
29.642
29.611
31.912
29.528
29.467
29.346
29.141
28.822
26.704
22.672
14.093
14
N 3
180
160
140
120
100
80
60
40
20
PPM

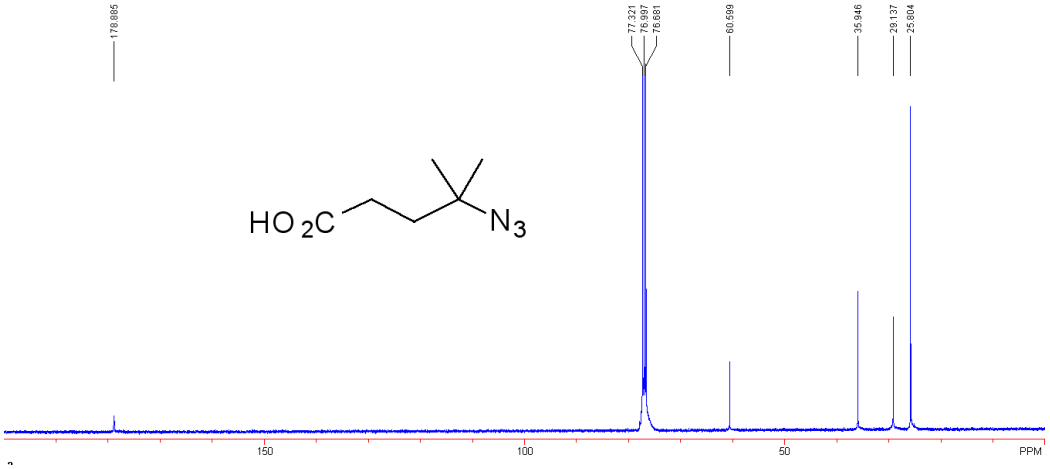
Compound **29**


9.661
8.088
8.068
7.347
7.327
3.530
3.510
3.496
3.483
3.464
2.931
2.917
2.897
2.882
2.861
2.846
2.828
1.698
1.680
1.663
1.644
1.631
1.626
1.613
1.595
1.577
1.559
1.542
1.523
1.262
1.058
1.040
1.021
N3
CO2H
0.75
2.00
.99
1.00
2.02
2.10
8.04
10
8
6
4
2
PPM

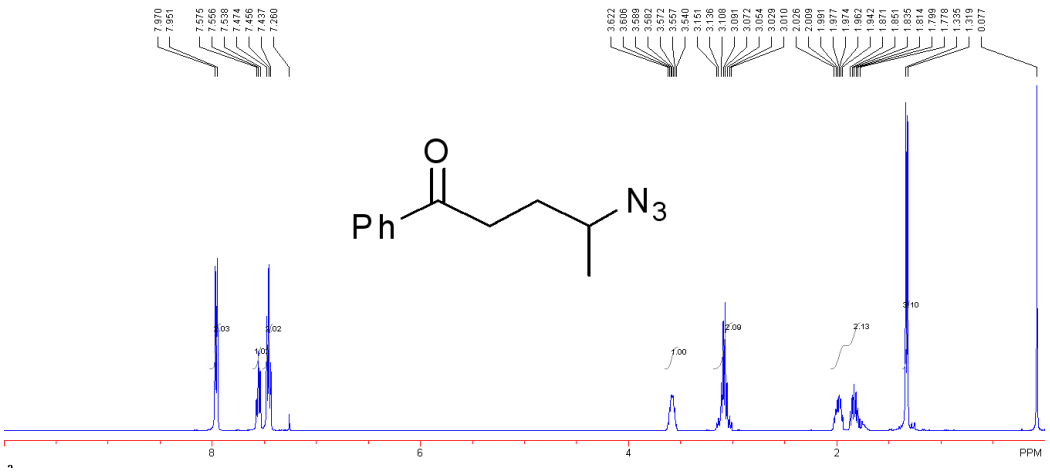

172.146
144.381
130.465
129.433
127.838
77.320
77.002
76.683
65.211
40.562
27.213
10.495
N3
CO2H
180
160
140
120
100
80
60
40
20
PPM

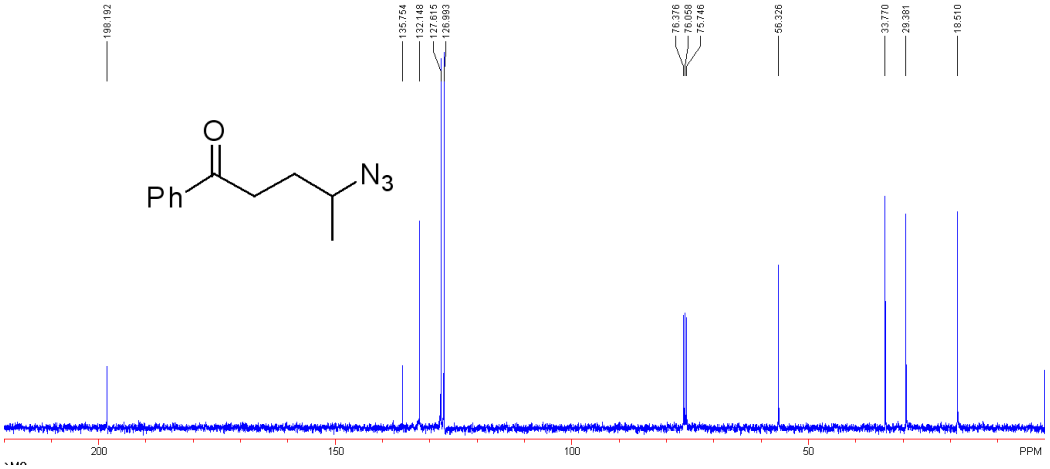
Compound **30**


7.263
2.473
2.453
2.433
1.856
1.836
1.817
1.299
5.99
2.00
1.99
HO 2C
N 3
8
6
4
2
PPM

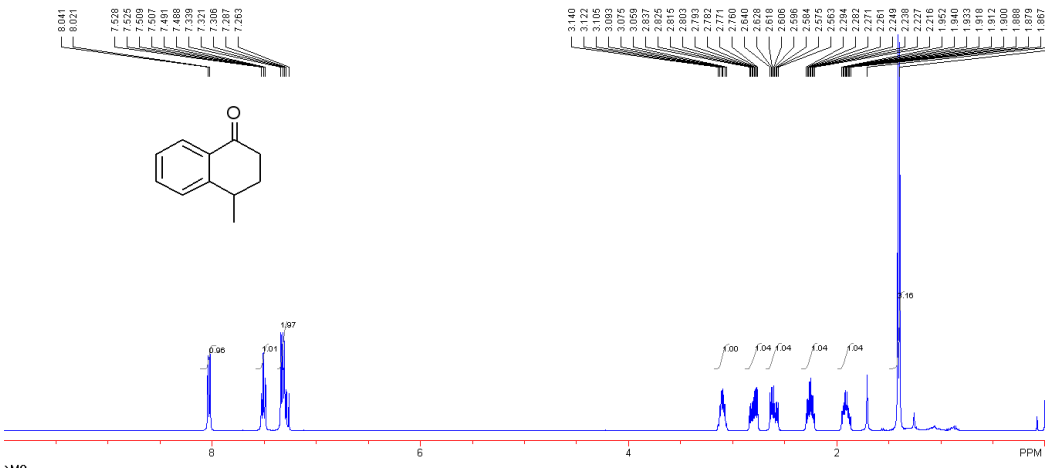

178.885
77.321
76.997
76.681
60.599
35.946
29.137
25.804
HO 2C
N 3
150
100
50
PPM

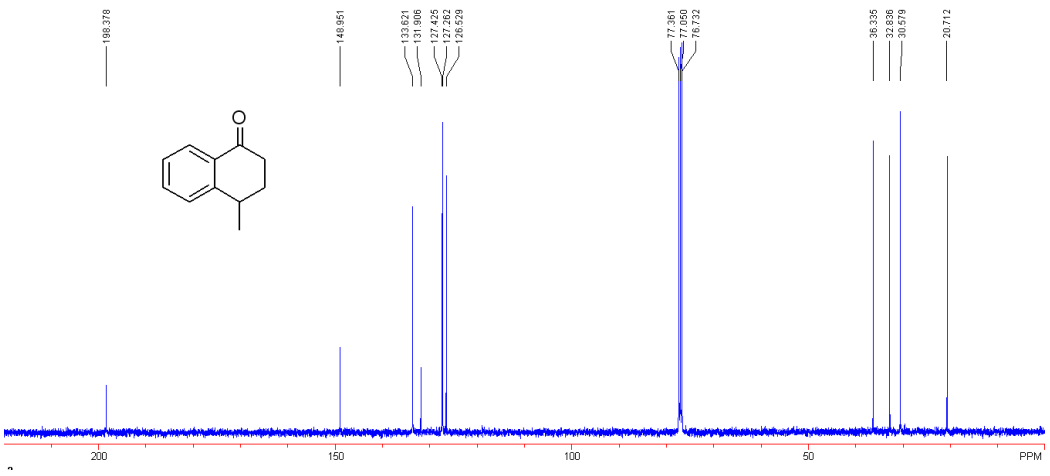
Compound **31**


7.970
7.951
7.575
7.556
7.538
7.474
7.456
7.437
7.260
3.622
3.606
3.589
3.572
3.557
3.540
3.151
3.136
3.108
3.091
3.072
3.054
3.029
3.010
2.026
2.009
1.991
1.977
1.974
1.962
1.942
1.871
1.851
1.835
1.814
1.799
1.778
1.395
1.374
0.077
O
Ph
N3
2.03
2.02
1.03
1.00
2.09
2.13
3.10
8
6
4
2
PPM

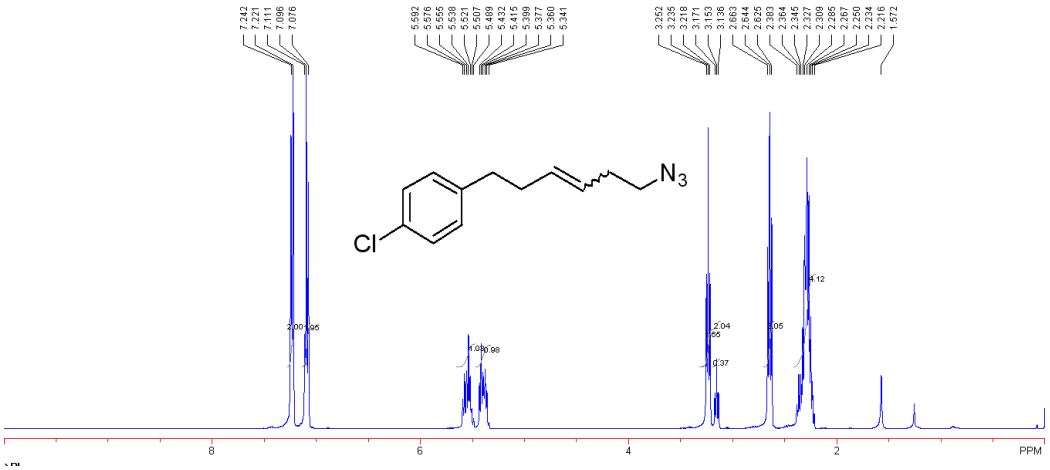

198.192
135.754
132.148
127.615
126.993
76.376
76.059
75.746
56.326
33.770
29.381
18.510
O
Ph
N3
200
150
100
50
PPM

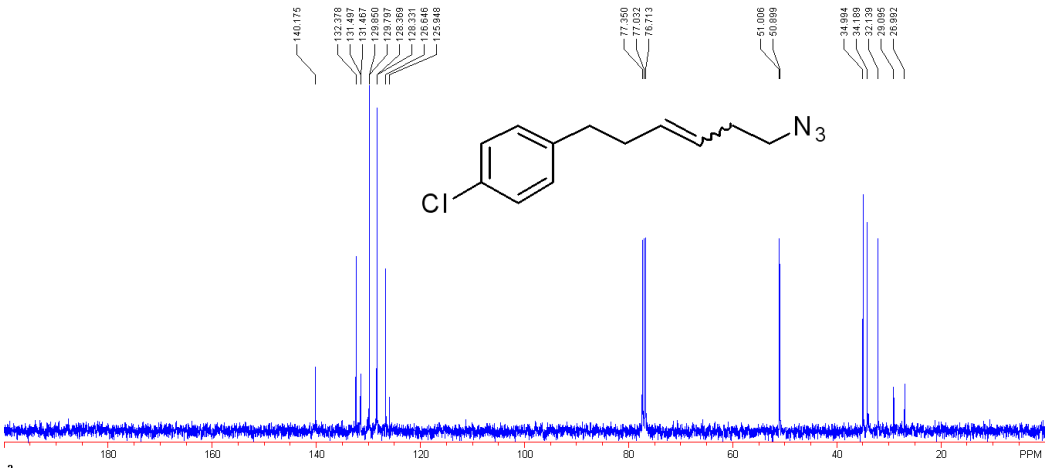
Compound **32**


8.041
8.021
7.528
7.525
7.509
7.507
7.491
7.488
7.339
7.321
7.306
7.287
7.263
3.140
3.122
3.105
3.093
3.075
3.059
2.837
2.825
2.815
2.803
2.793
2.782
2.771
2.760
2.640
2.628
2.618
2.606
2.596
2.584
2.575
2.563
2.554
2.282
2.271
2.261
2.249
2.238
2.227
2.216
1.952
1.940
1.933
1.918
1.912
1.900
1.888
1.879
1.867
0.96
1.01
1.97
1.00
1.04
1.04
1.04
1.04
3.16
8
6
4
2
PPM

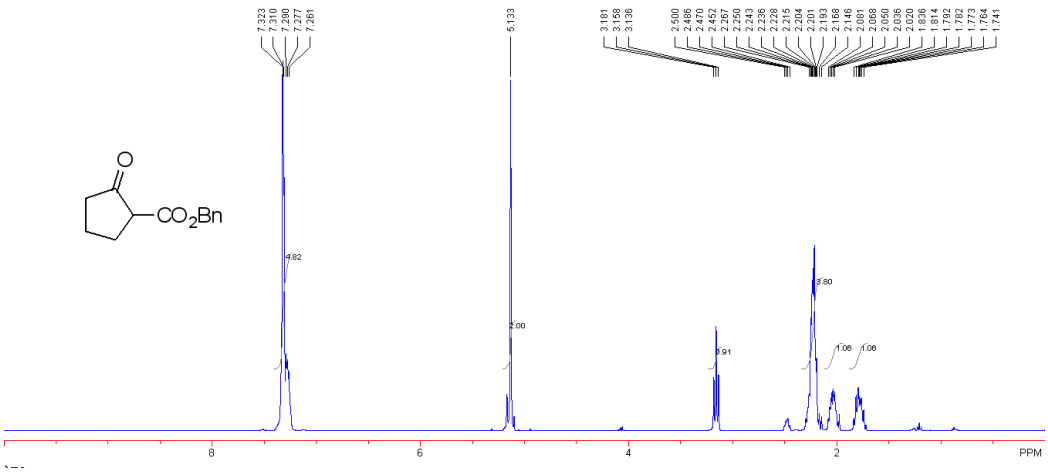

198.378
149.951
133.621
131.906
127.425
127.262
126.529
77.361
77.050
76.732
36.335
32.836
30.579
20.712
200
150
100
50
PPM

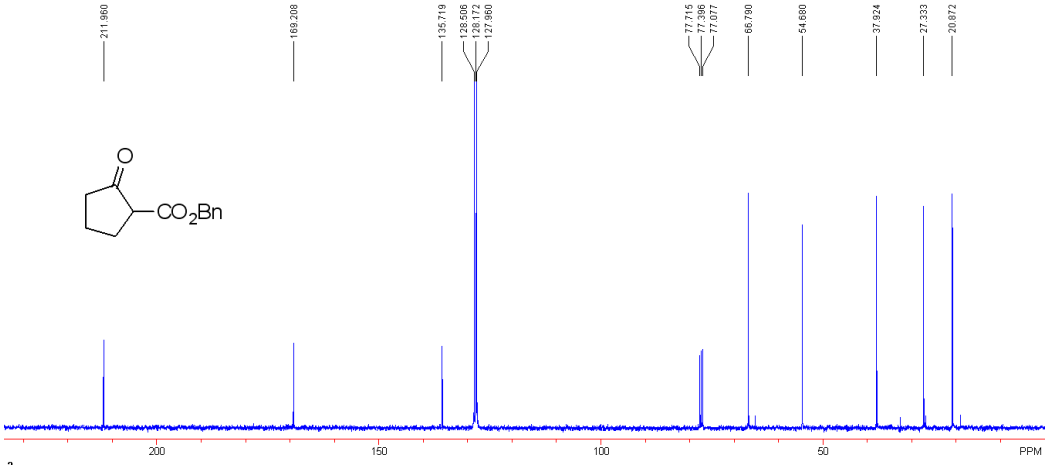
Compound **33**


7.242
7.231
7.111
7.096
7.076
5.592
5.576
5.555
5.538
5.521
5.507
5.489
5.432
5.415
5.399
5.377
5.360
5.341
3.252
3.235
3.218
3.171
3.153
3.136
2.803
2.644
2.625
2.383
2.364
2.345
2.327
2.309
2.285
2.267
2.250
2.234
2.216
1.572
N3
Cl
2.00
2.05
1.04
0.98
2.04
0.37
2.05
4.12
8
6
4
2
PPM

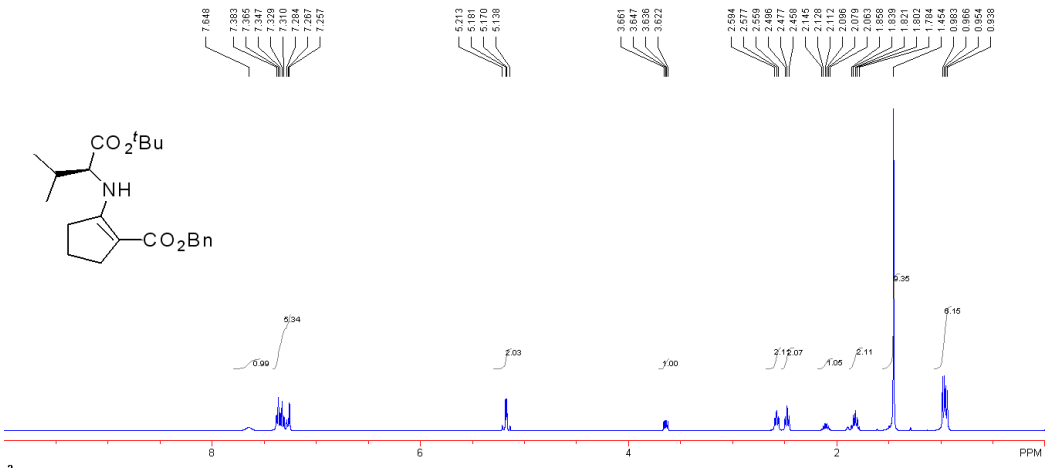

140.175
132.378
131.497
131.467
129.850
129.797
128.369
128.331
126.646
125.948
77.350
77.032
76.713
51.006
50.899
34.994
34.188
32.139
29.095
26.992
N3
Cl
180
160
140
120
100
80
60
40
20
PPM

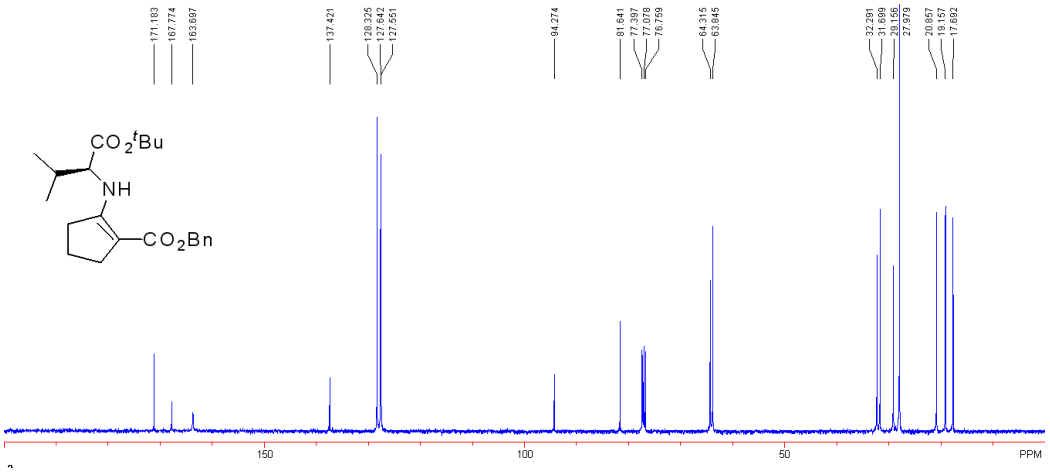
Compound **34**


7.323
7.310
7.290
7.277
7.261
5.133
3.181
3.158
3.136
2.500
2.486
2.470
2.452
2.267
2.250
2.243
2.236
2.228
2.215
2.204
2.201
2.193
2.168
2.146
2.081
2.068
2.050
2.036
2.020
1.836
1.814
1.792
1.782
1.773
1.764
1.741
4.82
2.00
0.91
3.80
1.06
1.06
O
CO2Bn
8
6
4
2
PPM

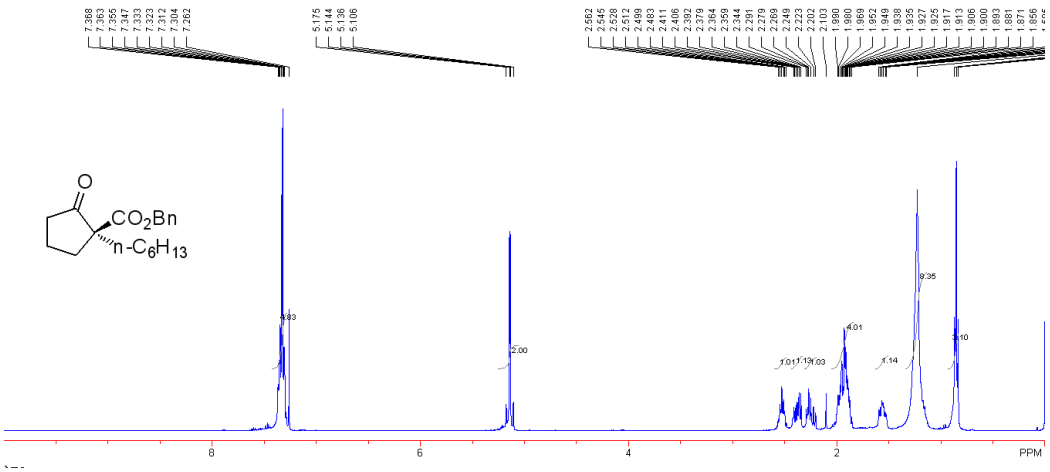

211.960
169.208
135.719
128.506
128.172
127.960
77.715
77.396
77.077
68.790
54.680
37.924
27.333
20.872
O
CO2Bn
200
150
100
50
PPM

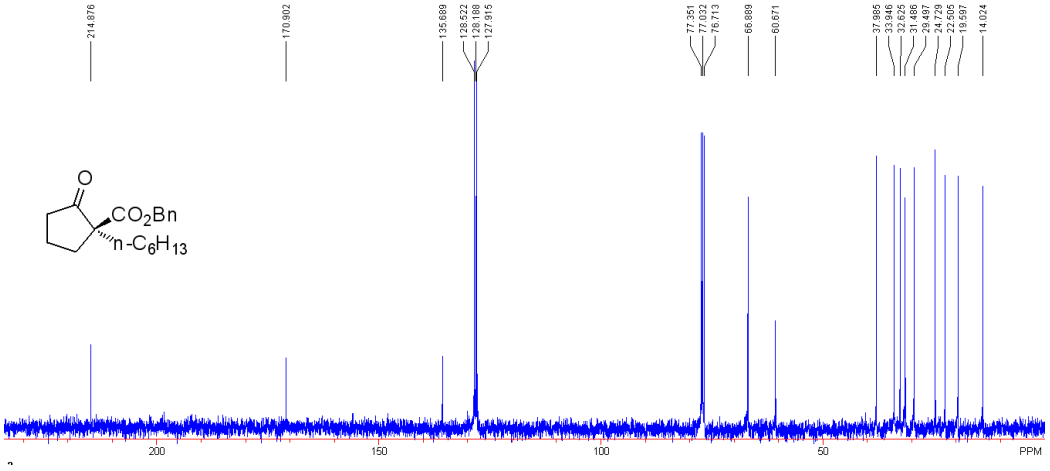
Compound **35**


7.648
7.383
7.365
7.347
7.329
7.310
7.284
7.267
7.257
5.213
5.181
5.170
5.138
3.661
3.647
3.636
3.622
2.594
2.577
2.559
2.496
2.477
2.458
2.145
2.128
2.112
2.096
2.079
2.063
1.858
1.839
1.821
1.802
1.784
1.464
0.983
0.966
0.954
0.938
CO2tBu
NH
CO2Bn
5.34
9.35
6.15
0.99
2.03
1.00
2.15
2.07
1.05
2.11
8
6
4
2
PPM

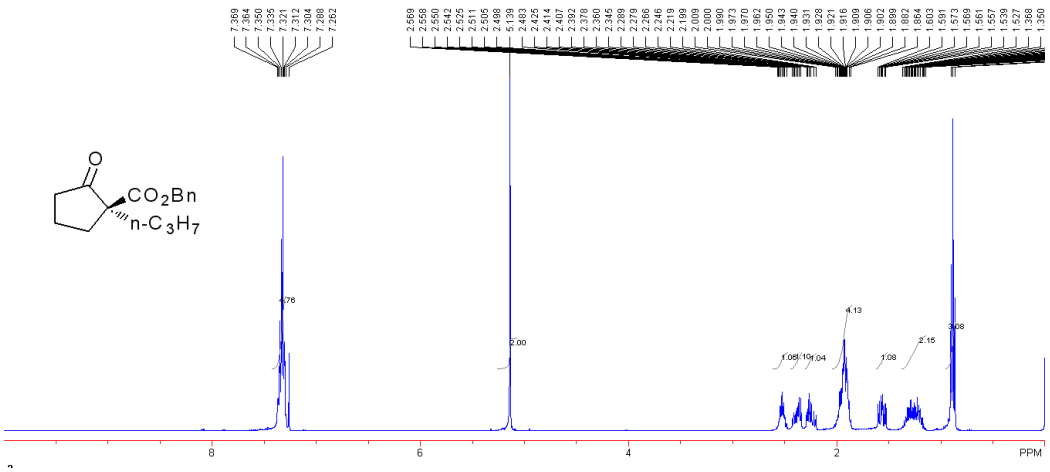

171.183
167.774
163.697
137.421
128.326
127.642
127.551
94.274
81.641
77.347
77.078
76.759
64.315
63.845
32.291
31.699
29.156
27.979
20.057
19.157
17.692
CO2tBu
NH
CO2Bn
150
100
50
PPM

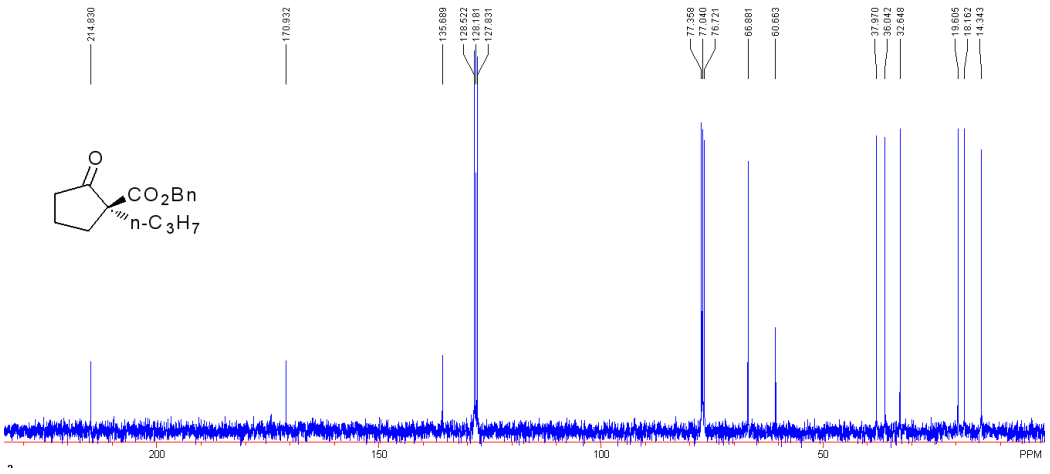
Compound **36a**



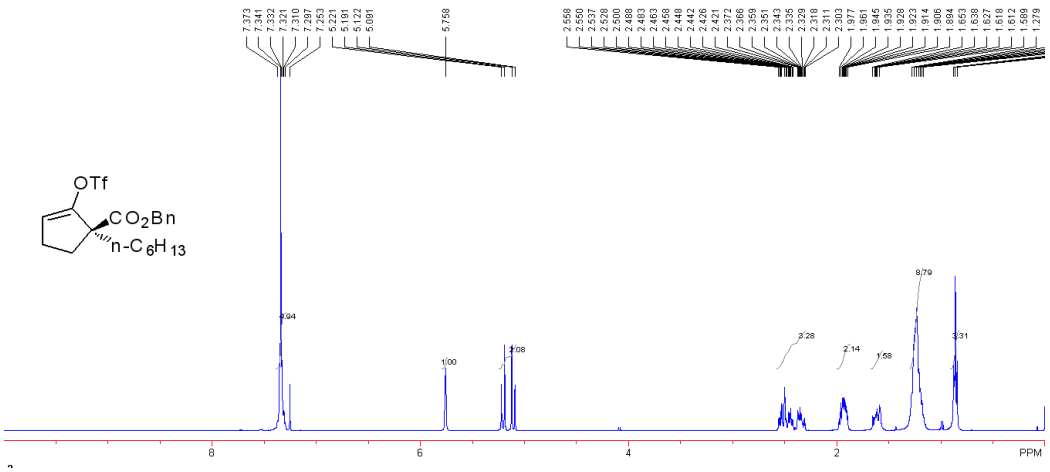


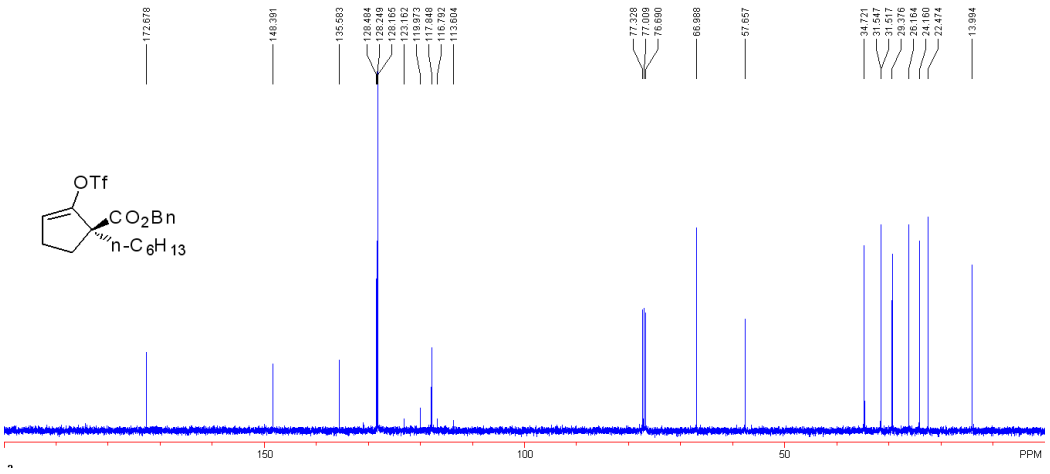
Compound **36b**



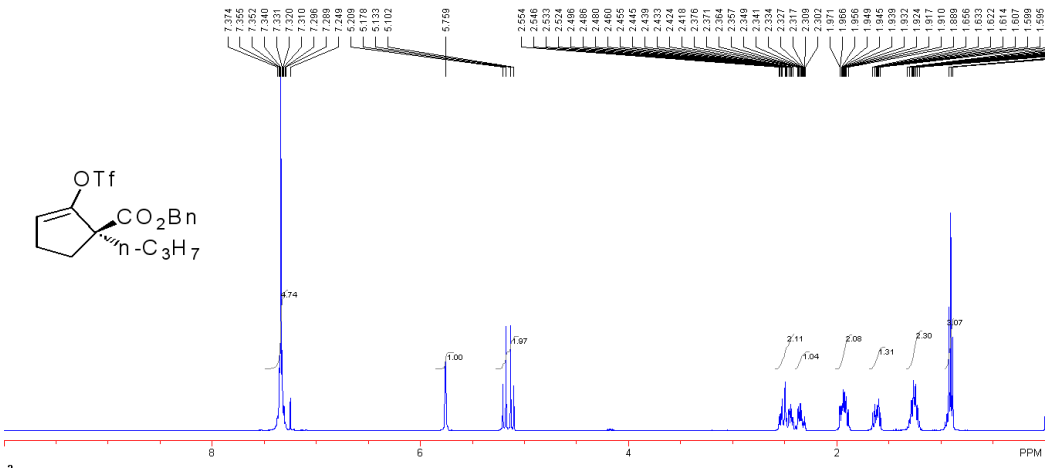


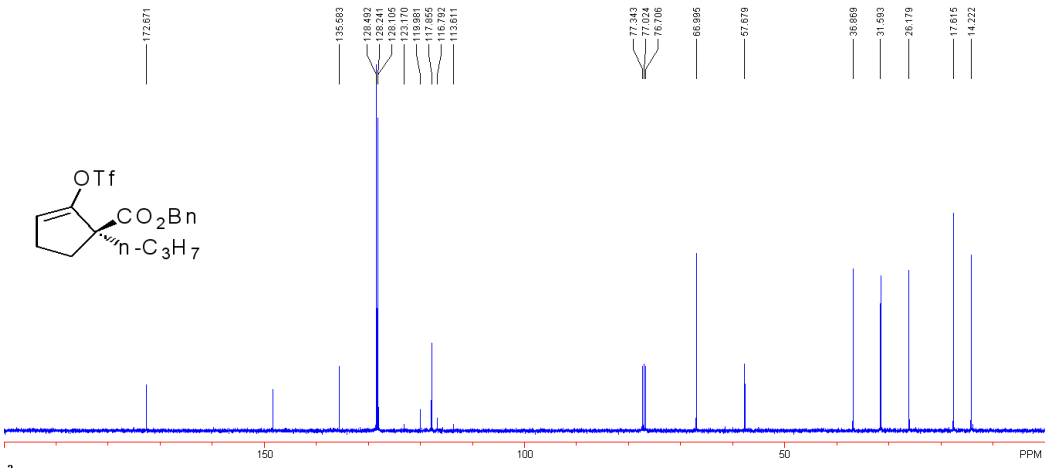
Compound **37a**



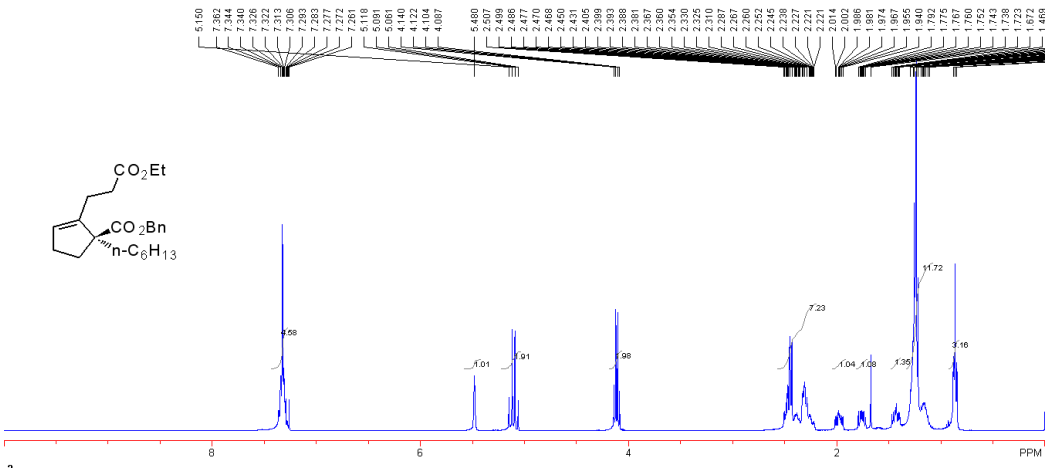


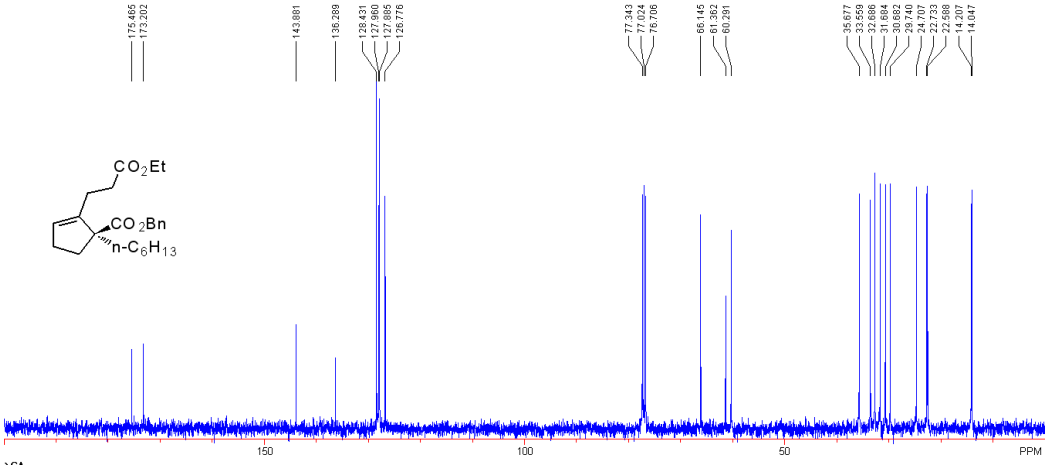
Compound **37b**



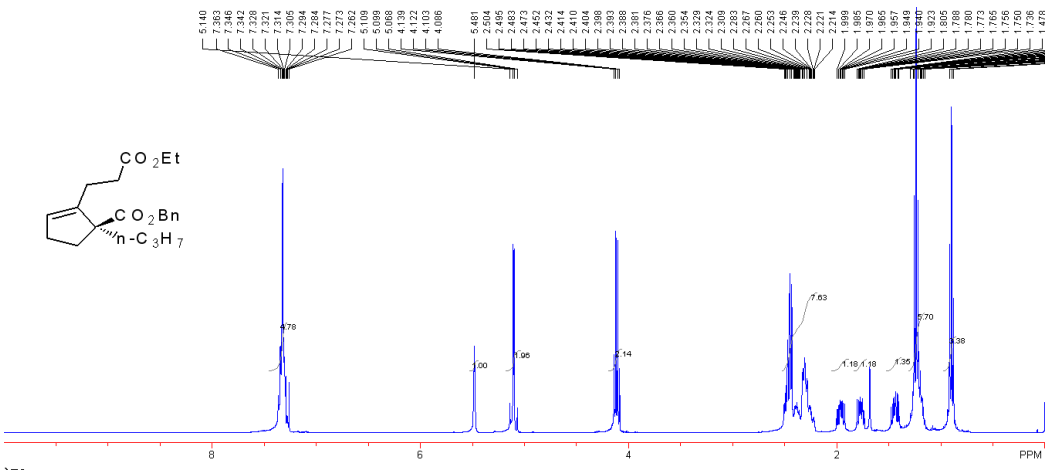


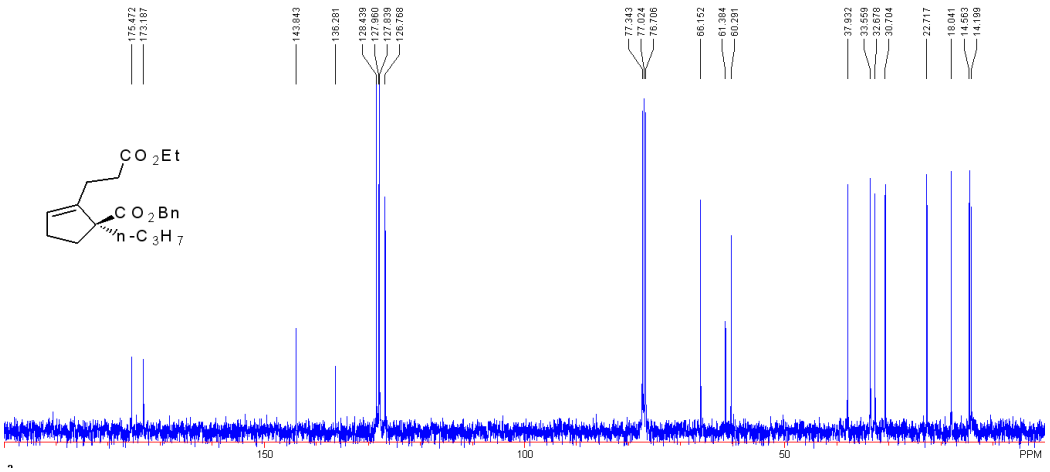
Compound **38a**



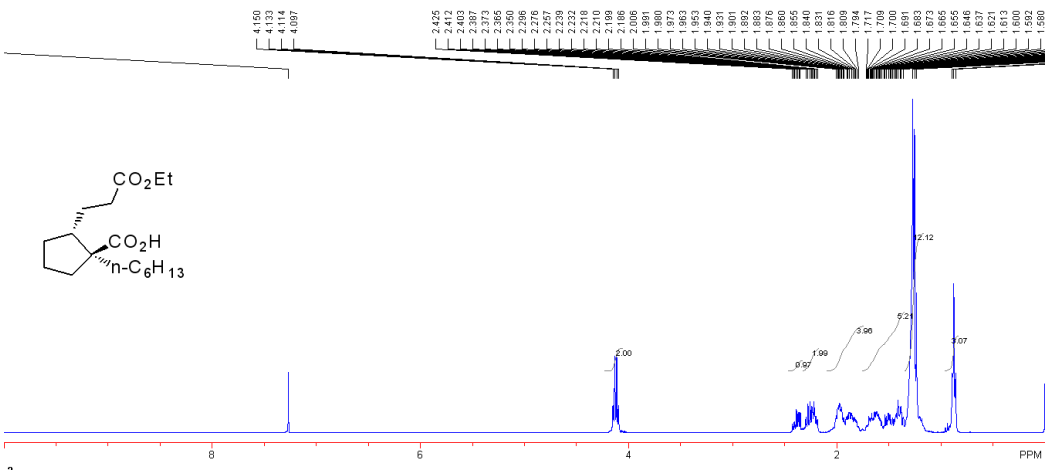


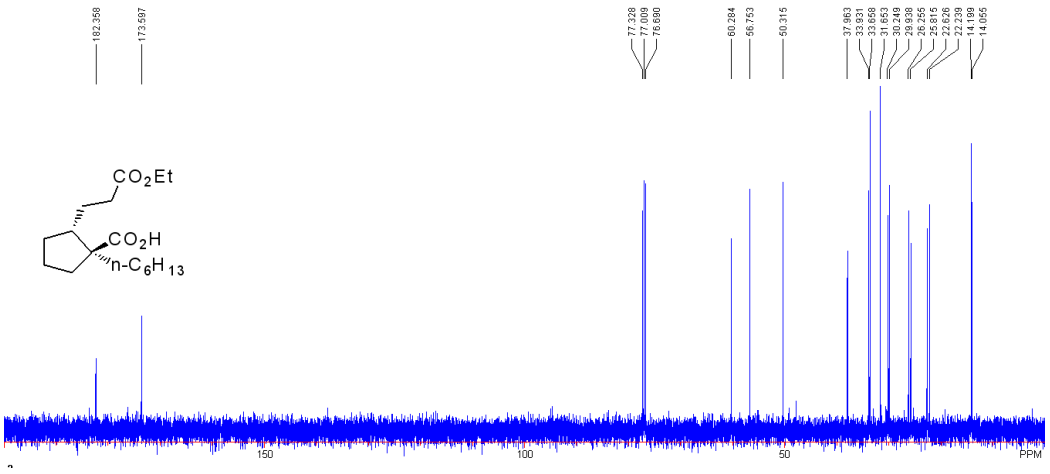
Compound **38b**



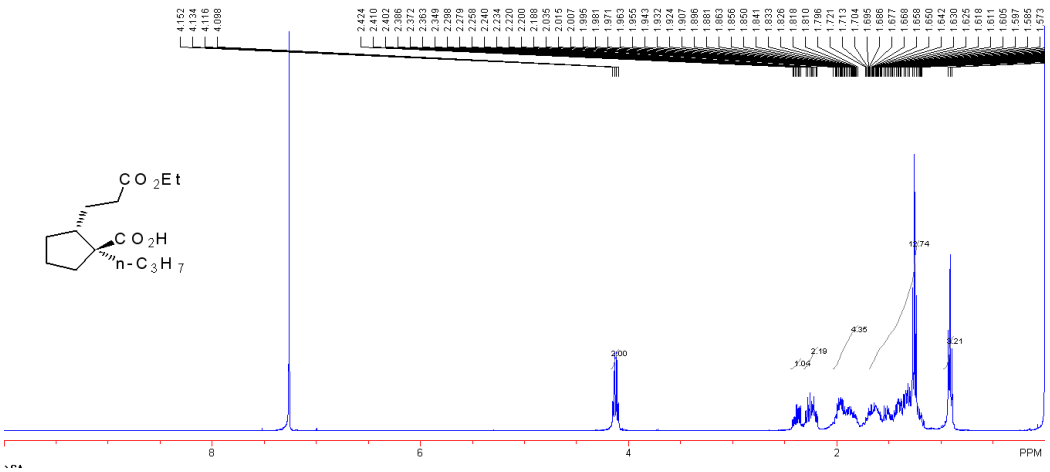


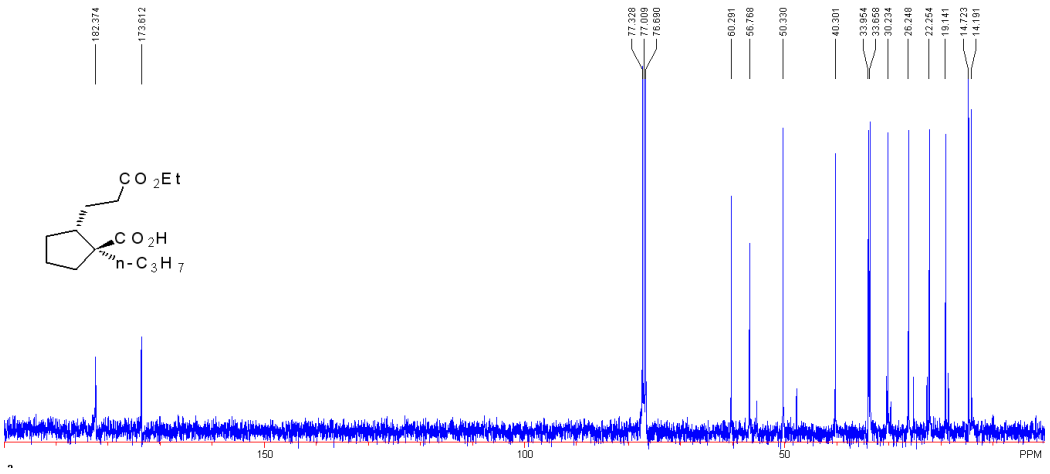
Compound **39a**





Compound **39b**





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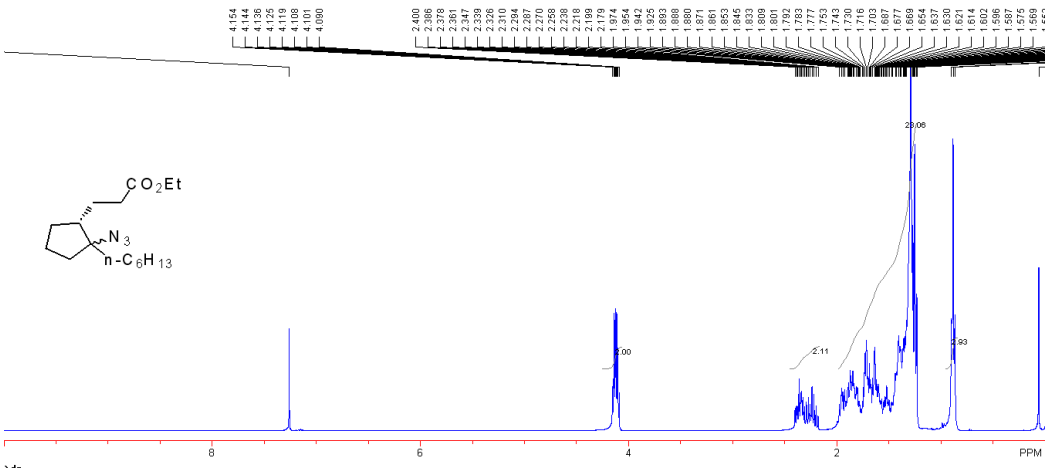
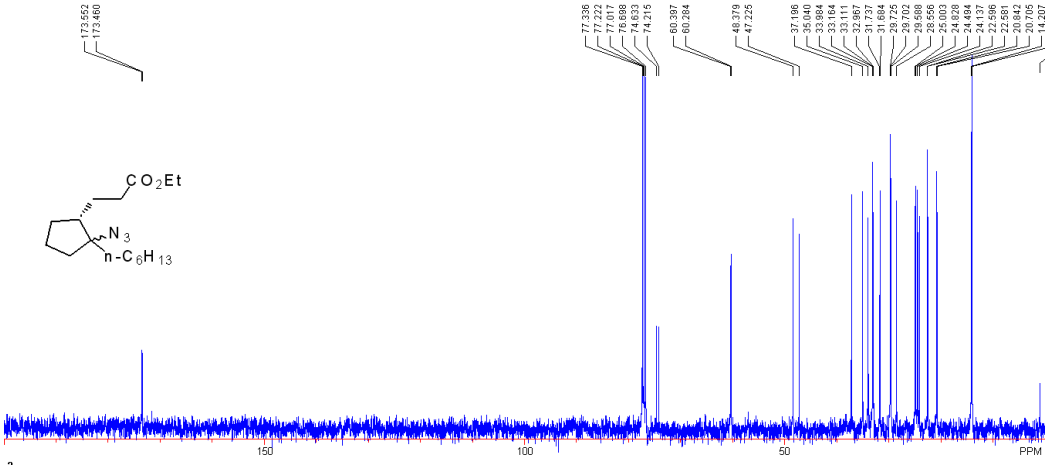
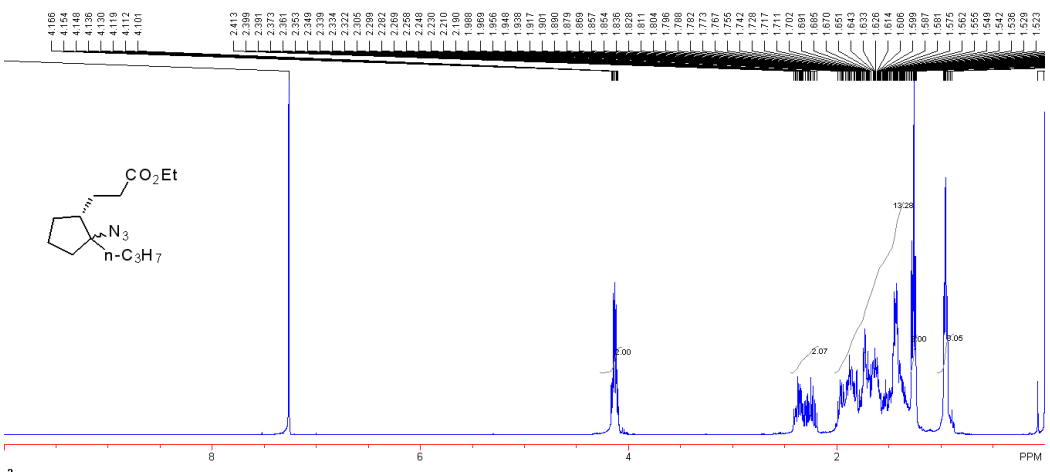
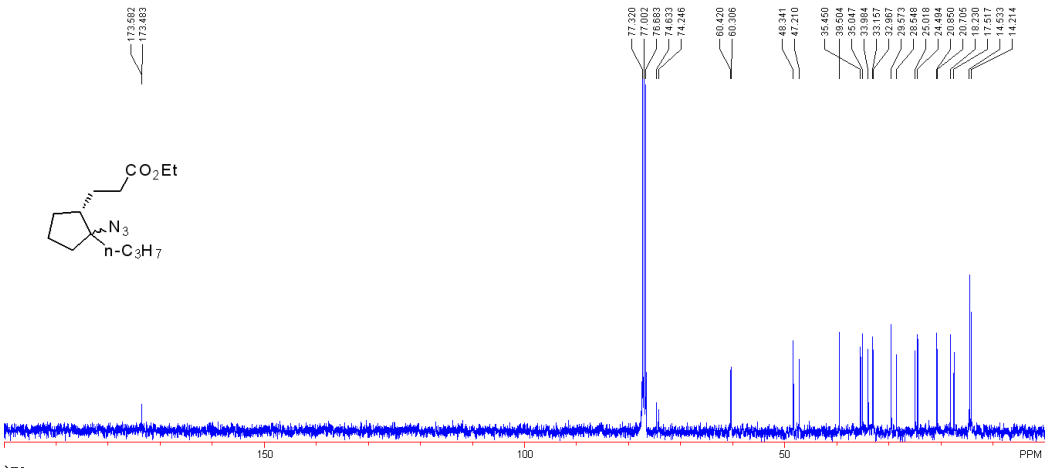


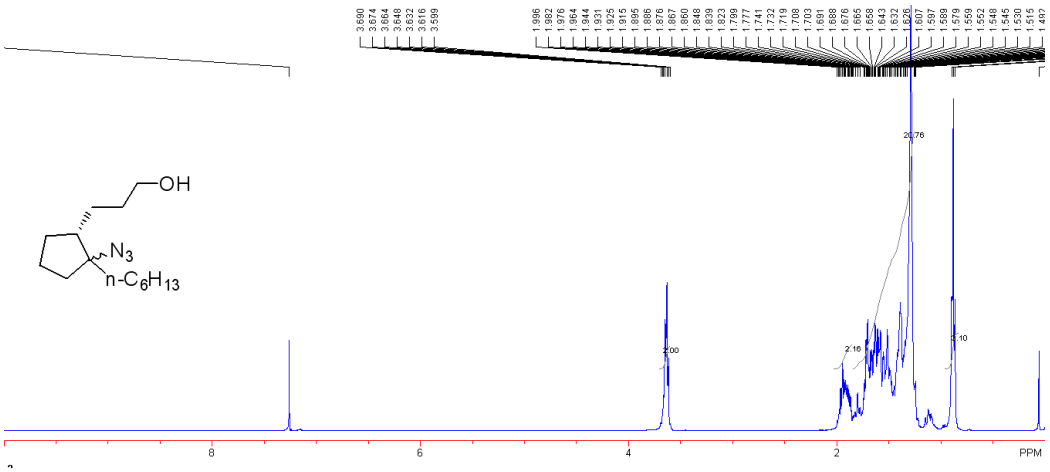


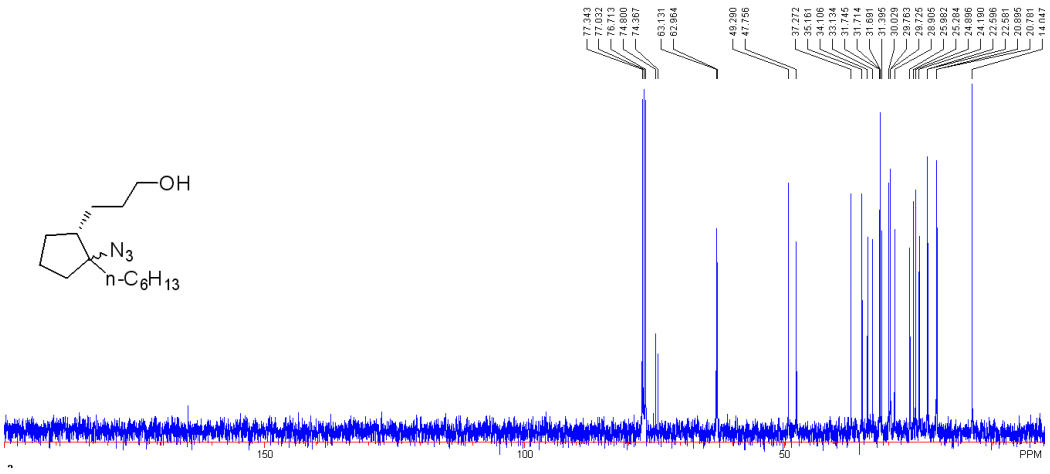
Compound **40b**



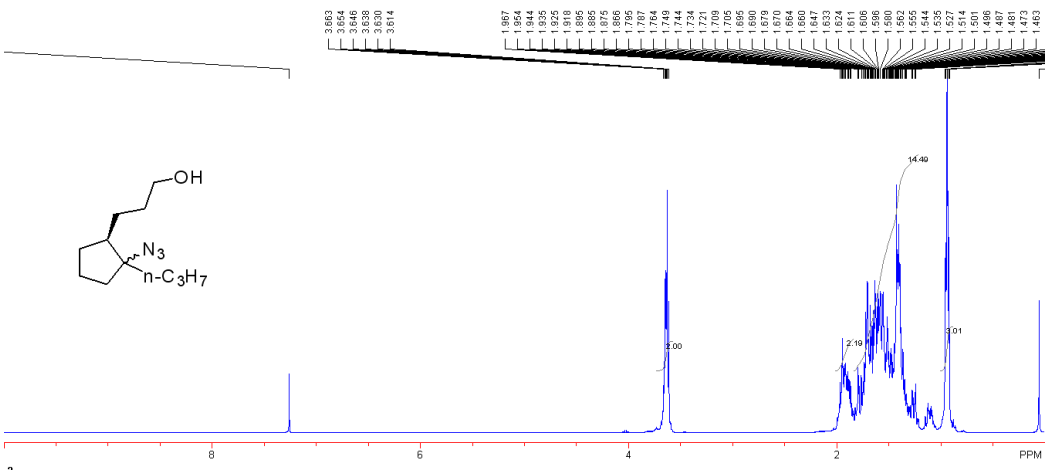


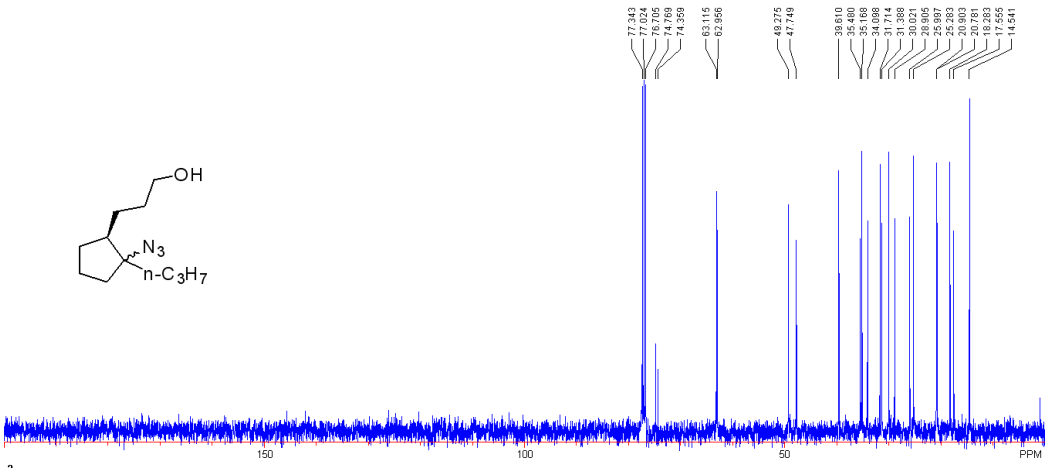
Compound **41a**



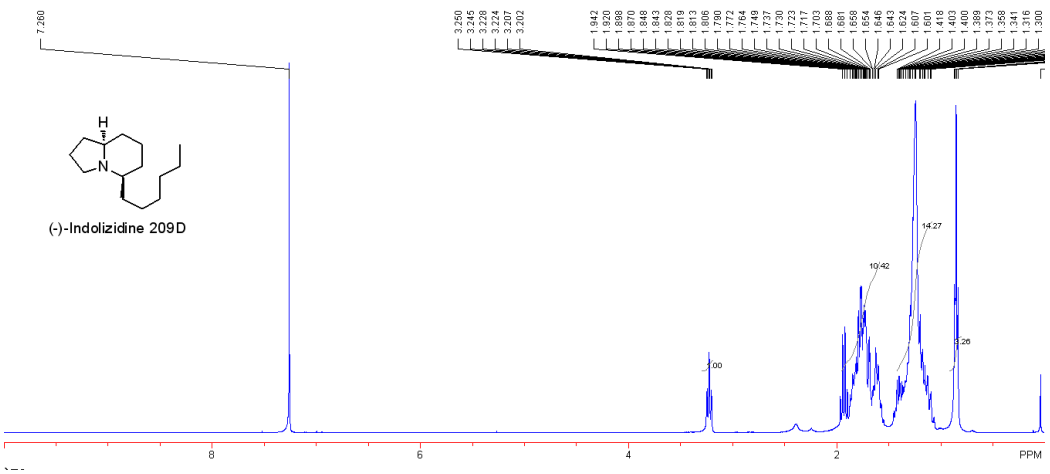


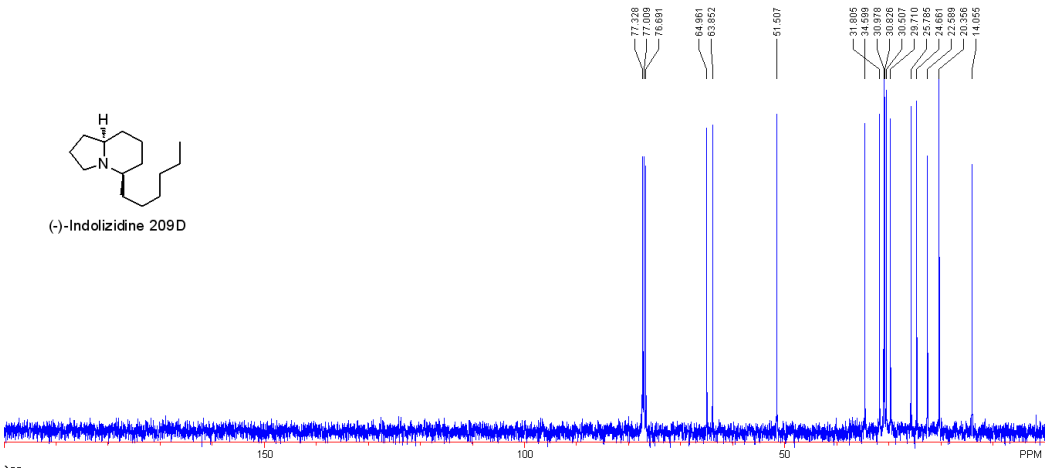
Compound **41b**





(-)-Indolizidine 209D





(-)-Indolizidine 167B