Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting information

Introducing Deep Eutectic Solvents in Enolate Chemistry: Synthesis of 1-Arylpropan-2-ones under Aerobic Conditions

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1. General Methods and Materials

Deep Eutectic Solvents [choline chloride (ChCl)/D-Sorbitol (Sor) (1:1 mol/mol); ChCl/urea (1:2 mol/mol); ChCl/glycerol (Gly)/ (1:2 mol/mol); ChCl/lactic acid (LA) (1:2 mol/mol); D-fructose/urea (3:2 w/w), ChCl/isosorbide (1:2 mol/mol); menthol/LA (1:2 mol/mol); Gly/L-Pro (1:1 mol/mol)] were prepared by heating under stirring at 60–80 °C for 30–60 min the corresponding individual components until a clear solution was obtained. For ^{1}H NMR (500 or 600 MHz) and ^{13}C NMR (125 or 150 MHz), $CDCl_3$ was used as the solvent; chemical shifts are reported in parts per million (δ). FT-IR spectra were recorded on a Perkin-Elmer 681 spectrometer. GC analyses were performed on a HP 6890 model, Series II by using a HP1 column (methyl siloxane; 30 m × 0.32 mm × 0.25 µm film thickness). Analytical thin-layer chromatography (TLC) was carried out on pre-coated 0.25 mm thick plates of Kieselgel 60 F_{254}; visualization was accomplished by UV light (254 nm) or by spraying a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium (III) sulfate in 100 mL 17.6 % (w/v) aq. sulphuric acid and heating to 473 K until blue spots appeared. Chromatography was run by using silica gel 60 with a particle size distribution 40–63 µm and 230–400 ASTM. GC-MS analyses were performed on a HP 5995C model. EtOAc was used as the solvent in the work-up procedures. High-resolution mass spectrometry (HRMS) analyses were performed using a Bruker microTOF QII mass spectrometer equipped with an electrospray ion source (ESI). Full characterization data, including copies of ^{1}H and ^{13}C NMR spectra, have been reported for both the newly synthesized compounds and the known compounds. The following abbreviations have been used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

All reagents and solvents, unless otherwise specified, were purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA) and were used without any further purification, and handled under an air atmosphere and with vigorous magnetic stirring, whereupon they react quickly, also on a larger scale.

2. Experimental procedures and characterization details

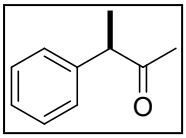
2.1 Synthesis of 1-alkyl-1-aryl-2-propanones 3a–m in ChCl/urea. General procedure.

A suspension of *t*-BuOK (2.25 mmol, 252 mg) and phenylacetone (0.75 mmol, 100 mg) in ChCl/urea (1:2 mol mol^{-1}) (2.0 g) was vigorously stirred at room temperature (RT) for 60 min. During this time, the color of the mixture changed from slightly yellow to orange. Then, the electrophile (1–10 mmol) was rapidly spread over the mixture, under air and with vigorous stirring at RT, and the mixture was left under stirring for 7–16 h (Schemes 1,2). After the reaction was complete (TLC analysis), NH_4Cl (sat. aq. solution) was added to the mixture, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The collected organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The crude was purified by flash chromatography (hexane/EtOAc 9:1) to provide the desired product (**3a**–**m**).

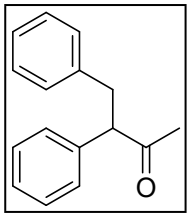
2.2 Synthesis of products 3n–r via Pd-catalyzed cross-coupling reactions between phenylacetone and (hetero)aryl halides in ChCl/urea. General procedure

A suspension of *t*-BuOK (1.56 mmol, 175 mg) and phenylacetone (0.52 mmol, 70 mg) in ChCl/urea (1:2 mol mol^{-1}) (2.0 g) was vigorously stirred in a 10 mL flask at RT for 60 min. Then, $Pd[P(t\text{-}Bu)_3]_2$ (5 mol%, 0.025 mmol, 13 mg) and aryl halide (0.55 mmol) were sequentially added to the orange mixture with vigorous stirring at room temperature (RT). The mixture was warmed to 70 °C with an oil bath and vigorously stirred for additional 2 h (Scheme 3). During this time, the color of the mixture changed from dark orange to brown. Then, the reaction mixture was cooled to RT and extracted with EtOAc (3 × 10 mL). The organic layer was filtered through a Celite pad, and the solvent was removed under reduced pressure. The crude was purified by flash chromatography (hexane/EtOAc 9:1) to provide the desired product (**3n–r**).

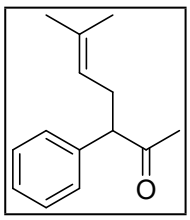
3. Spectroscopic data



3-Phenylbutan-2-one (3a)[1] (0.109 g, 98% yield from the reaction in ChCl/urea), yellow oil; ν_{max}/cm^{-1} 3062, 3028, 2977, 2932, 1714vs, 1600w, 1494s, 1453s, 1355s, 1165, 1069, 1030, 767, 737, 700s; δH (600 MHz; $CDCl_3$; TMS) 1.39 (d, ^3J(H,H)=6.8 Hz, 1H; CH_3), 2.04 (s, 3H), 3.75 (q, ^3J(H,H) = 6.8 Hz, 1 H CH), 7.21- 7.23 (m, 2 H), 7.25-7.29 (m, 1 H), 7.32-7.36 (m, 2 H); δC (150 MHz; $CDCl_3$; TMS) 17.1 28.3, 53.6, 127.1, 127.7, 128.8, 140.5, 208.8; *m/z* 148 (M^+, 9 %), 105 (100) $[C_6H_5O]^+$, 103 (13), 79 (14), 77 (17) $[C_6H_5]^+$,51 (5), 43 (13); HRMS (ESI) *m/z* calcd for $[C_{10}H_{12}O - H]^-$: 147.0815; found: 147.0811.



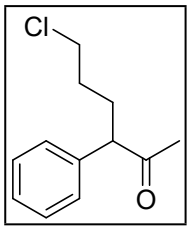
3,4-Diphenylbutan-2-one (3b)[2] (0.139 g, 83% yield), yellow oil; ν_{max}/cm^{-1} 3085, 3061, 3028, 3003, 2923, 2858, 1713, 1600, 1494, 1453, 1354, 1250, 1157, 1072, 1030, 775, 739, 698; δH (600 MHz; $CDCl_3$; TMS) 2.04 (s, 3 H), 2.93 (dd, ^2J(H,H) 13.9 Hz, ^3J(H,H) 7.4 Hz, 1H C*H*H), 3.45 (dd, ^2J(H,H) 13.9 Hz, ^3J(H,H) 7.4 Hz, 1H, C*H*H), 3.94 (t, ^3J(H,H)=7.7 Hz, 1 H), 7.15-7.17 (m, 1 H), 7.19-7.23 (m, 4 H), 7.26-7.28 (m, 1 H), 7.31-7.34 (m, 2 H); δC (150 MHz; $CDCl_3$; TMS) 29.4, 38.3, 61.5, 126.1, 127.3, 128.2, 128.3, 128.8, 128.9, 138.5, 139.7, 207.5; *m/z* 224 (M^+, 24 %), 182 (16), 181 (100) 179 (13), 178 (11), 166 (26), 165 (24), 152 (38), 115 (45), 103 (27), 91 (28), 77 (18), 65 (59), 51 (5), 43 (10); HRMS (ESI) *m/z* calcd for $[C_{16}H_{16}O - H]^-$: 223.1128; found: 223.1128.



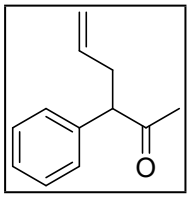
6-Methyl-3-phenylhept-5-en-2-one (3c)[3] (0.141 g, 93% yield), yellow oil; ν_{max}/cm^{-1} 3028, 2969, 2915, 1713, 1599, 1551, 1493, 1452, 1376, 1354, 1252, 1153, 1109, 828, 762, 700; δH (600 MHz; $CDCl_3$; TMS) 1.54 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.35-2.40 (m, 1 H), 2.72-2.76 (m, 1 H), 3.62-3.65 (m, 1 H), 4.98-5.01 (m, 1 H), 7.21-7.23 (m,

[1] P. Vitale, F. M. Perna, M. G. Perrone, A. Scilimati, *Tetrahedron Asymmetry*, 2011, **22**, 1985; P. Vitale, C. D'Introno, F. M. Perna, M. G. Perrone, A. Scilimati, *Tetrahedron Asymmetry*, 2013, **24**, 389;
[2] D. Méndez-Sánchez, J. Mangas-Sánchez, E. Busto, V. Gotor, V. Gotor-Fernández, *Adv. Synth. Catal.*, 2016, **358**, 122.
[3] T. Narender, S. Sarkar, K. Rajendar, S. Tiwari, *Org. Lett.* 2011, **13**, 6140.

2 H), 7.26-7.28 (m, 1 H), 7.32-7.36 (m, 2 H); δC (150 MHz; $CDCl_3$; TMS) 17.7, 25.7, 29.2, 30.7, 59.9, 121.3, 127.2, 128.2, 133.5, 138.8, 208.4; *m/z* 202 (M^+, 6 %), 159 (16), 135 (10), 134 (100), 131 (11), 129 (13), 128 (15), 117 (51), 115 (20), 111 (27), 105 (10), 91 (33), 77 (10), 69 (22) 43 (17), 41 (11); HRMS (ESI) *m/z* calcd for $[C_{12}H_4O + H]^+$: 203,1430; found: 203,1429.

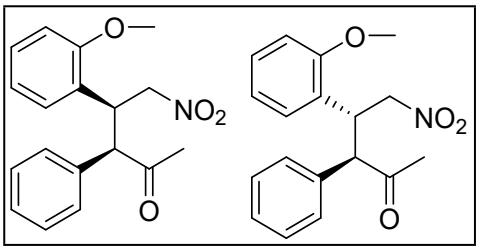


6-Chloro-3-phenylhexan-2-one (3d)[4] (0.137 g, 87%), yellow oil; ν_{max}/cm^{-1} 3061, 3028, 3001, 2956, 2869, 1711, 1634, 1600, 1493, 1453, 1355, 1266, 1165, 1072, 1028, 738, 701, 650; δH (600 MHz; $CDCl_3$; TMS) 2.07 (s, 3 H, CH_3), 2.24 (t, ^3J(H,H) 6 Hz ,1 H), 3.34 (t, ^3J(H,H) 6 Hz, 2 H), 3.65 (t, ^3J(H,H) 6 Hz, 2 H), 7.22-7.22 (m, 2 H), 7.27-7.30 (m, 1 H), 7.34-7.37(m, 2 H); δC (150 MHz; $CDCl_3$; TMS) 28.9, 29.0, 30.4, 35.4, 44.7, 59.0, 127.4, 128.2, 129.0, 138.4, 207.7; *m/z* 210 (M^+, 2%), 169 (16), 167 (48), 134 (8), 131 (28), 115 (10), 104 (12), 103 (11), 91 (100), 77 (9), 65 (4), 51 (4), 43 (19); HRMS (ESI) *m/z* calcd for $[C_{12}H_{15}OCl - H]^-$: 209.0739; found: 209.0735.

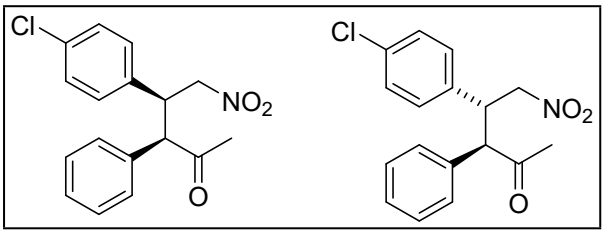


3-Phenylhex-5-en-2-one (3e)[4] (0.123 g, 94%), yellow oil; ν_{max}/cm^{-1} 3064, 2917, 1714, 1494, 1454, 1355, 1161, 916, 749, 700; δH (600 MHz; $CDCl_3$; TMS) 2.07 (s, 3 H, CH_3), 2.43-2.47 (m, 1 H), 2.79-2.84 (m, 1 H), 3.70-3.73 (m, 1 H, CH), 4.96-5.04 (m, 2 H), 5.65-5.72 (m, 1 H), 7.22-7.23 (m, 2 H), 7.27-7.29 (m, 1 H), 7.33-7.36 (m, 2 H); δC (150 MHz; $CDCl_3$; TMS) 29.0, 36.0, 59.3, 116.5, 127.2, 128.2, 128.6, 128.8, 135.6, 138.2, 207.6; *m/z* 174 (M^+, 1 %), 159 (2), 132 (11), 131 (100) 129 (19), 128 (10), 116 (17), 115 (15), 103 (9), 91 (43), 77 (11), 65 (4), 51 (4), 43 (13); HRMS (ESI) *m/z* calcd for $[C_{12}H_4O + H]^+$: 175.1117; found: 175.1108.

[4] A. W. D. Avison, A. L. Morrison, *J. Chem. Soc.*, 1950, 1474.

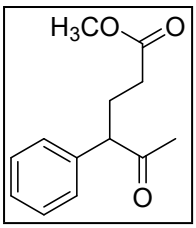


4-(2-Methoxyphenyl)-5-nitro-3-phenylpentan-2-one (3f) (dr: 31:69; separable mixture of diastereomers); *major diastereomer* (0.157 g, 67%), yellow oil; ν_{max}/cm^{-1} 3063, 3029, 3005, 2921, 2839, 1709, 1600, 1586, 1550, 1493, 1455, 1437, 1379, 1356, 1291, 1246, 1160, 1121, 1053, 1026, 809, 754, 701; δH (600 MHz; $CDCl_3$; TMS) 2.13 (s, 3 H, CH_3), 3.83 (s, 3 H, CH_3), 4.40-4.46 (m, 2 H), 04.71-4.74 (m, 1 H), 4.96-4.99 (m, 1 H), 6.66-6.71 (m, 2 H), 6.87-6.88 (m, 1 H),7.05-7.15 (m, 6H); δC (150 MHz; $CDCl_3$; TMS) 29.8, 42.6, 55.1, 59.2, 77.2, 110.6, 120.5, 124.8, 127.5, 128.6, 130.8, 136.0, 157.1, 207.0; *m/z* 313 (M^+, 8 %), 241 (10), 223 (45), 210 (29), 208 (11), 189 (8), 180 (10), 178 (13), 165 (22), 135 (12), 134 (100), 121(63), 119 (30), 115 (28), 105 (23), 91 (44), 77 (12), 65 (6), 43 (24); *minor diastereomer* (0.073 g, 31%), yellow oil; ν_{max}/cm^{-1} 3030, 3004, 2964, 2920, 2841, 1714, 1601, 1586, 1557, 1494, 1455, 1379, 1355, 1260, 1157, 1026, 800, 755, 702; δH (600 MHz; $CDCl_3$; TMS) 1.95 (s, 3 H, CH_3), 3.94 (s, 3 H, CH_3), 4.26-4.29 (m, 1 H), 4.43-4.47 (m, 1 H), 4.58-4.64 (m, 2 H), 6.88-6.93 (m, 2 H), 7.19-7.21 (m, 1 H), 7.23-7.27 (m, 1H),7.34-7.42 (m, 5H); δC (150 MHz; $CDCl_3$; TMS) 30.0, 42.8, 55.5, 59.3, 111.1, 111.2, 120.9, 121.0, 125.3, 128.4, 128.9, 129.0, 129.1, 129.2, 129.3, 129.5, 130.8, 130.9, 135.3, 157.2, 205.6; *m/z* 313 (M^+, 11 %), 266 (10), 241 (10) , 223 (27) , 210 (11) , 180 (12) , 165 (14), 135 (12), 134 (100), 121(18), 119 (21), 115 (22), 105 (16), 91 (31), 77 (9), 65 (4), 43 (16); HRMS (ESI) *m/z* calcd for $[C_{18}H_{20}NO_4 + H]^+$: 314.1387; found: 314.1302; *m/z* calcd for $[C_{18}H_{19}NO_4 + Na]^+$: 336.1206; found: 336.1201.

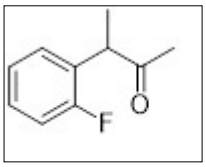


(4-Chlorophenyl)-5-nitro-3-phenylpentan-2-one (3g) (dr 33:67; separable mixture of diastereomers); *major diastereomer* (0.157 g, 66%), yellow oil; ν_{max}/cm^{-1} 3063, 3031, 2919, 1712, 1598, 1556, 1494, 1455, 1433, 1415, 1378, 1359, 1248, 1159, 1093, 1015, 831, 754, 670; δH (600 MHz; $CDCl_3$; TMS) 2.13 (s, 3 H, CH_3), 4.08 (d, $J_{1,3}$(H,H) 10.4Hz, 1 H), 4.11-4.17 (m, 2 H), 4.78-4.80 (m, 2 H), 6.93(d, $J_{1,3}$(H,H) 8 Hz, 2 H), 7.01 (d, $J_{1,3}$(H,H) 7 Hz, 2 H), 7.11 (d, $J_{1,3}$(H,H) 8 Hz, 2 H), 7.17-7.21 (m, 3 H); δC (150 MHz; $CDCl_3$; TMS) 31.6, 45.4, 61.2, 78.3, 128.0, 129.1, 129.5, 133.4, 134.9, 135.6, 206.4; *m/z* 317 (M^+, 1 %), 270 (2), 247 (12), 245 (34), 229 (34), 228 (22), 227 (100), 216 (17), 215 (11), 214 (52), 193 (29), 192 (39), 191 (24), 189 (12), 179 (31), 178 (46) , 165 (13), 151 (11), 149 (18) , 140 (14), 139 (12), 138 (41) , 137 (12), 134 (24), 133 (22), 127 (18), 125 (50), 116 (11), 115 (41), 107 (17), 105 (49), 103 (22), 102 (10), 91 (19), 89 (13), 77 (17), 43 (74); HRMS (ESI) *m/z* calcd for $[C_{17}H_{16}NO_3Cl + Na]^+$: 340.0711; found: 340.0697; *minor diastereomer* (0.076 g, 32%), yellow oil; ν_{max}/cm^{-1} 3086, 3032, 2917, 1712, 1597, 1541, 1492, 1454, 1431, 1416, 1381, 1361, 1259, 1202, 1184, 1160, 1091, 1014, 912, 842, 816, 752, 737, 718, 700, 673; δH (600 MHz; $CDCl_3$; TMS) 1.94 (s, 3 H, CH_3), 4.13-4.15 (m, 1 H), 4.26-4.32 (m, 2 H), 4.37-4.41 (m, 1 H), 7.25-7.28 (m, 2 H), 7.30-7.40 (m, 5 H), 7.42-7.45 (m, 2 H); δC (150 MHz; $CDCl_3$; TMS) 30.2, 45.0, 62.0, 78.5, 128.6, 128.8, 129.1, 129.4, 129.7, 133.8, 134.3, 136.6, 204.6; *m/z* 317 (M^+ 1 %), 272 (18), 271 (18), 270 (51), 255 (17), 245 (11), 229 (28), 228 (20), 227 (83), 216 (15), 214 (47), 193 (30), 192 (48), 191 (29), 189 (15), 179 (27), 178 (50), 176 (10), 165 (16), 151 (13), 149 (21), 140 (18), 139 (15), 138 (54), 137 (15), 134 (46), 133 (30), 127 (17), 125 (49), 116 (16), 115 (57), 107 (20), 105 (65), 103 (31), 102 (14), 101 (10), 91(26), 89 (17), 79 (10), 77 (25), 43 (100); HRMS (ESI) *m/z* calcd for $[C_{17}H_{16}NO_3Cl + Na]^+$: 340.0711; found: 340.0715.

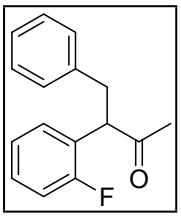
[5] Y. Tai, I. Noriaki, *Bulletin of the Chemical Society of Japan*, 1965, **38,** 1501.



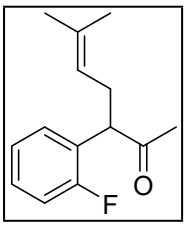
Methyl 5-oxo-4-phenylhexanoate (3h)[5] (0.150 g, 91%), yellow oil; ν_{max}/cm^{-1} 3062, 3029, 2953, 2921, 2849, 1713, 1600, 1493, 1453, 1357, 1259, 1204, 1168, 1068, 1028, 763, 701; δH (600 MHz; $CDCl_3$; TMS) 1.97-2.05 (m, 1 H), 2.06(s, 3 H, CH_3), 2.20-2.25 (m, 2 H), 2.30-2.37 (m, 1 H), 3.65 (s, 3 H), 3.73-3.71 (m, 1 H), 7.19-7.21 (m, 2 H), 7.27-7.30 (m, 1 H), 7.34-7.36 (m, 2 H); δC (150 MHz; $CDCl_3$; TMS) 26.8, 29.0, 31.4, 51.5, 58.3, 127.5, 128.3, 129.0, 138.0, 173.6, 207.6; *m/z* 220 (M^+, 19 %), 189 (20), 188 (21), 177 (28), 146 (11), 145 (19), 135 (11), 118 (12), 117 (100), 115 (22), 104 (20), 91 (18), 77 (7), 43 (16); HRMS (ESI) *m/z* calcd for $[C_{13}H_{15}O_3 - H]^-$: 219.1027; found: 219.1025.



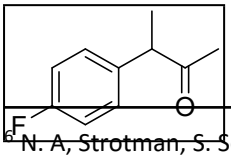
3-(2-Fluorophenyl)butan-2-one (3i)[2] (0.088 g, 71%), yellow oil; ν_{max}/cm^{-1} 3066, 2981, 2936, 1716, 1585, 1491, 1454, 1374, 1356, 1230, 1184, 1166, 1112, 1070, 950, 836, 787, 758; δH (600 MHz; $CDCl_3$; TMS) 1.40 (d, $J_{1,3}$(H,H) 6.8 Hz, 3 H, CH_3) 2.1 (s, 3 H), 4.07 (q, $J_{1,3}$(H,H) 7.0 Hz, 1 H, CH), 7.07-7.10 (m, 1 H), 7.13-7.15 (m, 1 H), 7.17-7.20 (m, 1 H), 7.25-7.27 (m, 1 H); δC (150 MHz; $CDCl_3$; TMS) 16.0, 28.4, 45.9, 115.8-115.5 (m), 124.7-124.5 (m), 127.7 (d, $J_{1,3}$(C,F) 15 Hz), 128.7-128.8 (m), 160.4 (d, $J_{1,1}$(C,F) 245 Hz), 208.0; δ_F (470 MHz; $CDCl_3$; $CFCl_3$) -(115.5-115.6 m); *m/z* 166 (M^+, 9 %), 124 (10), 123 (100), 122 (23), 103 (54), 101 (10), 96 (9), 77 (19), 43 (35); HRMS (ESI) *m/z* calcd for $[C_{10}H_{11}OF + H]^+$: 167.0867; found: 167.0863.



3-(2-Fluorophenyl)-4-phenylbutan-2-one (3j) (0.142 g, 78%) yellow oil; ν_{max}/cm^{-1} 3085, 3063, 3029, 2959 (CH), 2925 (CH), 2857 (CH), 1716vs, 1603, 1584, 1491vs, 1455S, 1355, 1230 (s), 1184, 1157, 1095w, 1077w, 1032w, 825, 757s, 699s; δ_H (600 MHz; $CDCl_3$; TMS) 2.05 (3 H, s, C*H*$_3$CO), 2.91 (1 H, dd, $J_{1,2}$ 13.8, 7.4, $J_{1,3}$ 7.4, C*H*HCH), 3.45 (1 H, dd, $J_{1,2}$ 13.8, 7.4, $J_{1,3}$ 7.4, C*H*HCH), 4.30 (1 H, t, $J_{1,3}$ 7.4, C*H*CH$_2$), 7.01-7.13 (4 H, m, Ar*H*F), 7.14-7.26 (5 H, m, Ar*H*); δ_C (150 MHz; $CDCl_3$; TMS) 29.6, 37.1, 53.2, 115.4-115.9 (m), 124.5-124.7 (m), 125.6 (d, $J_{1,2}$ 15.6), 126.1-126.4 (m), 128.2-128.4 (m), 128.8-129.1 (m), 129.2-129.4 (m), 139.3, 160.6 (d, $J_{1,2}$ 245.6), 206.8; δ_F (470 MHz; $CDCl_3$; $CFCl_3$) -(118.1-118.4) m; *m/z* 242 (M^+, 28%), 200 (16), 199 (100), 198 (13), 197 (11), 184 (12), 183 (14), 179 (22), 178 (21), 121 (15), 103 (14), 101 (12), 91 (30), 77 (11), 43 (22); HRMS (ESI) *m/z* calcd for $[C_{16}H_{15}FO+H]^+$: 243.1180; found: 243.1179.



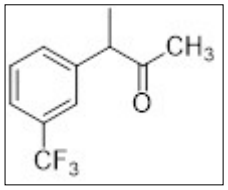
3-(2-Fluorophenyl)-6-methylhept-5-en-2-one (3k) (0.157 g, 95%), yellow oil; ν_{max}/cm^{-1} 2966 (CH), 2923 (CH), 2855 (CH), 1717vs, 1650w, 1586w, 1490s, 1455w, 1355, 1230 (s), 1184, 1153, 1093w, 1036w, 757s; δ_H (600 MHz; $CDCl_3$; TMS) 1.53 (3 H, s, Me), 1.63 (3 H, s, Me), 2.1 (3 H, s, COMe), 2.35-2.39 (1 H, m, C*H*H), 2.70-2.76 (1 H, m, C*H*H), 4.01 (1 H, t, $J_{1,3}$ 7.4, C*H*CH$_2$), 4.99-5.03 (1 H, m, C*H*CH$_2$),7.05-7.14 (2 H, m, Ar*H*), 7.17-7.20 (1 H, m, Ar*H*F), 7.23-7.26 (1 H, m, Ar*H*); δ_C (150 MHz; $CDCl_3$; TMS) 17.6, 25.6, 29.3, 29.6, 51.5, 115.3–115.7 (m), 120.9, 124.4-124.6 (m), 125.9 (d, $J_{1,2}$ 15.2), 128.7-128.8 (m), 160.6 (d, $J_{1,2}$ 245.3), 207.6; δ_F (470 MHz; $CDCl_3$; $CFCl_3$) -(118.0-118.1) m; *m/z* 220 (M^+, 8%), 177 (14), 152 (100), 149 (13), 147 (15), 146 (17), 135 (45), 133 (18), 122 (11), 115 (10), 111 (20), 109 (48), 69 (36), 43 (43); HRMS (ESI) *m/z* calcd for $[C_{14}H_{17}FO+H]^+$: 221.1336; found: 221.1335.



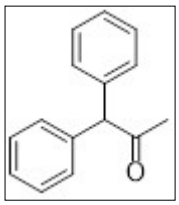
3-(4-Fluorophenyl)butan-2-one (3l)[6] (0.088 g, 71%), yellow oil; ν_{max}/cm^{-1} 2977 ~~(CH), 2917~~ (CH), 2849 (CH), 1716vs, 1601, 1508vs, 1355, 1224 (s), 1159, 837; δ_H

[6] N. A, Strotman, S. Sommer, G. C. Fu, *Angew. Chem. Int. Ed.,* 2007, **46**, 3556.

(600 MHz; $CDCl_3$; TMS) 1.38 (3 H, d, $J_{1,3}$ 6.9, CH_3CH), 2.06 (3 H, s, CH_3CO), 3.75 (1 H, q, $J_{1,3}$ 6.9, C*H*CH_3), 7.02-7.05 (2 H, m, C*H*CF), 7.18-7.20 (2 H, m, Ar*H*); δ_C (150 MHz; $CDCl_3$; TMS) 17.4, 28.3, 52.9 (d, $J_{1,5}$ 4.2), 65.9, 115.8 (d, $J_{1,2}$ 20.4), 129.3 (d, $J_{1,3}$ 6.5), 136.2, 162.0 (d, $J_{1,2}$ 245.6), 208.6; δ_F (470 MHz; $CDCl_3$; $CFCl_3$) -(115.5–115.6) m; *m/z* 166 (M^+, 12%), 124 (9), 123 (100), 122 (9), 103 (43), 77 (11), 43 (14); HRMS (ESI) *m/z* calcd for $[C_{10}H_{12}FO+H]^+$: 167.0867; found: 167.0869.



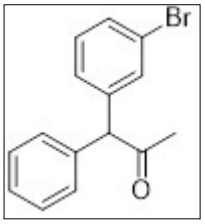
3-(3-(Trifluoromethyl)phenyl)butan-2-one (3m)[7] (0.081 g, 50%), yellow oil; ν_{max}/cm^{-1} 2981 (CH), 2936 (CH), 1714s, 1610w, 1492w, 1451w, 1330vs, 1167vs, 1126vs, 1074, 902, 857, 806, 703s; δ_H (600 MHz; $CDCl_3$; TMS) 1.42 (3 H, d, $J_{1,3}$ 7.0, CH_3CH), 2.08 (3 H, s, CH_3CO), 3.83 (1 H, q, $J_{1,3}$ 7.0, C*H*CH_3), 7.41 (1 H, d, $J_{1,3}$ 7.4, Ar*H*), 7.47 (1 H, t, $J_{1,3}$ 7.4, Ar*H*), 7.49 (1H, s, Ar*H*), 7.54 (1 H, d, $J_{1,3}$ 7.4, Ar*H*); δ_C (150 MHz; $CDCl_3$; TMS) 17.3, 28.4, 53.4, 124.0 (q, $J_{1,2}$ 272, *C*F_3), 124.1 (q, $J_{1,4}$ 4), 124.6 (q, $J_{1,4}$ 4), 129.4, 131.1, 131.3 (q, $J_{1,3}$ 32, *C*-CF_3), 141.5, 207.6; *m/z* 216 (M^+, 1%), 173 (13), 154 (20), 153 (14), 133 (22), 127 (11), 77 (6), 43 (100); HRMS (ESI) *m/z* calcd for $[C_{11}H_{11}F_3O-H]^-$: 215.0689; found: 215.0690.



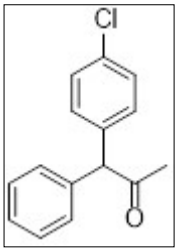
1,1-Diphenylpropan-2-one (3n)[8] (0.105 g, 96%), pale yellow oil; ν_{max}/cm^{-1} 3086 (CH), 3062 (CH), 3028, 2918 (CH), 2850w, 1714vs, 1660w, 1599w, 1495s, 1452w, 1355s, 1154s, 1081w, 1032w, 753s, 700s, 577w; δ_H (600 MHz; $CDCl_3$; TMS) 2.27 (3 H, s, COMe), 5.14 (1 H, s, ArC*H*), 7.25-7.30 (5 H, m, Ar*H*), 7.35-7.41 (5 H, m, Ar*H*); δ_C (150 MHz; $CDCl_3$; TMS) 30.0, 65.0, 122.5, 126.9, 127.2, 128.7, 129.0, 130.0, 131.5, 206.5; *m/z* 210 (M^+, 2%), 168 (15), 167 (100), 166 (16), 165 (48), 152 (22), 115 (5), 111 (20), 77 (1), 43 (4); HRMS (ESI) *m/z* calcd for $[C_{14}H_{17}FO+ H]^+$: 211.1117; found: 211.1116.

[7] M. Durandetti, S. Siblle, J. Nédélec, J. Périchon, *Synth. Commun*., 1994, **24**,145.

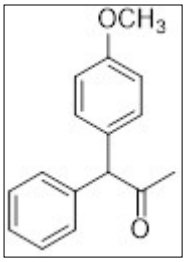
[8]CAS number-781-35-1; http://www.basechem.org/chemical/6939;



1-(3-Bromophenyl)-1-phenylpropan-2-one (3o) (0.135 g, 90%), yellow oil; ν_{max}/cm^{-1} 3061 (CH), 3027, 2923vs (CH), 2852s, 1718vs, 1663w, 1591w, 1558s, 1494w, 1452vs, 1403, 1354w, 1152s, 1075s, 869w, 770s, 709s, 670w; δ_H (600 MHz; $CDCl_3$; TMS) 2.25 (3 H, s, COMe), 5.07 (1 H, s, ArC*H*), 6.94-6.99 (1 H, m, Ar*H*), 7.14-7.41 (5 H, m, Ar*H*), 7.45-7.48 (1 H, m, Ar*H*), 7.61-7.65 (1 H, m, Ar*H*), 7.86-7.87 (1 H, m, Ar*H*); δ_C (150 MHz; $CDCl_3$; TMS) 29.7, 64.4, 123.1, 127.60, 128.9, 129.0, 130.1, 130.3, 130.8, 131.3, 136.1, 139.7, 205.6; *m/z* 290 (M^+, 3%), 288 (M^+, 3%), 248 (10), 247 (77), 246 (11), 245 (79), 167 (12), 166 (82), 165 (100), 164 (15), 163 (13), 139 (8), 43 (17); HRMS (ESI) *m/z* calcd for $[C_{15}H_{13}BrO - H]^-$: 287.0072 (100.0%), 289.0051 (97.3%); found: 287.0087 (91.0%), 289.0066 (100%).



1-(4-Chlorophenyl)-1-phenylpropan-2-one (3p)[9] (0.103, 81%), brown oil; ν_{max}/cm^{-1} 3029 (CH), 2917s (CH), 2849w, 1716vs, 1660w, 1599w, 1490s, 1453w, 1355w, 1154w, 1091s, 1015w, 754w, 698w; δ_H (600 MHz; $CDCl_3$; TMS) 2.23 (3 H, s, COMe), 5.07 (1 H, s, ArC*H*), 7.13-7.15 (2 H, m, Ar*H*), 7.19-7.21 (2 H, m, Ar*H*), 7.28-7.29 (3 H, m, Ar*H*), 7.32-7.35 (2 H, m, Ar*H*); δ_C (150 MHz; $CDCl_3$; TMS) 30.0**,** 64.2, 127.5, 128.7, 128.8, 128.9, 130.2, 133.1, 136.8, 137.7, 206.0; *m/z* 244 (M^+, 2%), 203 (33), 201 (100), 166 (53), 165 (91), 164 (13), 163 (11), 139 (6), 115 (4), 43 (9); HRMS (ESI) *m/z* calcd for $[C_{15}H_{13}ClO+ Na]^+$: 267.0547; found: 267.0538.

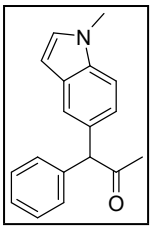


1-(4-Methoxyphenyl)-1-phenylpropan-2-one (3q)[10] (0.117 g, 94%), yellow oil; ν_{max}/cm^{-1} 3062 (CH), 3001, 2932 (CH), 2837w, 1714s, 1651w, 1589w, 1509w, 1487w, 1355w, 1286, 1246s, 1175s, 1151, 1031s, 821s, 700s; δ_H (600 MHz; $CDCl_3$; TMS) 2.26 (3 H, s, COMe), 3.81 (3 H, s, OMe), 5.09 (1 H, s, ArC*H*), 6.89-6.91 (2 H, m, Ar*H*), 7.17-7.18 (2 H, m, Ar*H*), 7.23-7.41 (5 H, m, Ar*H*); δ_C (150 MHz; $CDCl_3$; TMS) 29.9, 55.2, 64.3,

[9] Z. Zhang, L. Zhang, X. Zhang, J. Yang, Y. Yin, Y. Jiang, C. Zeng, G. Lu, Y. Yang, F. Mo, *Chem. Sci.*, 2020, **11**, 12021. E. J. Cragoe, Jr.; A. M. Pietruszkiewicz, C. M. Robb, *J. Org. Chem.* 1958, **23**, 971.

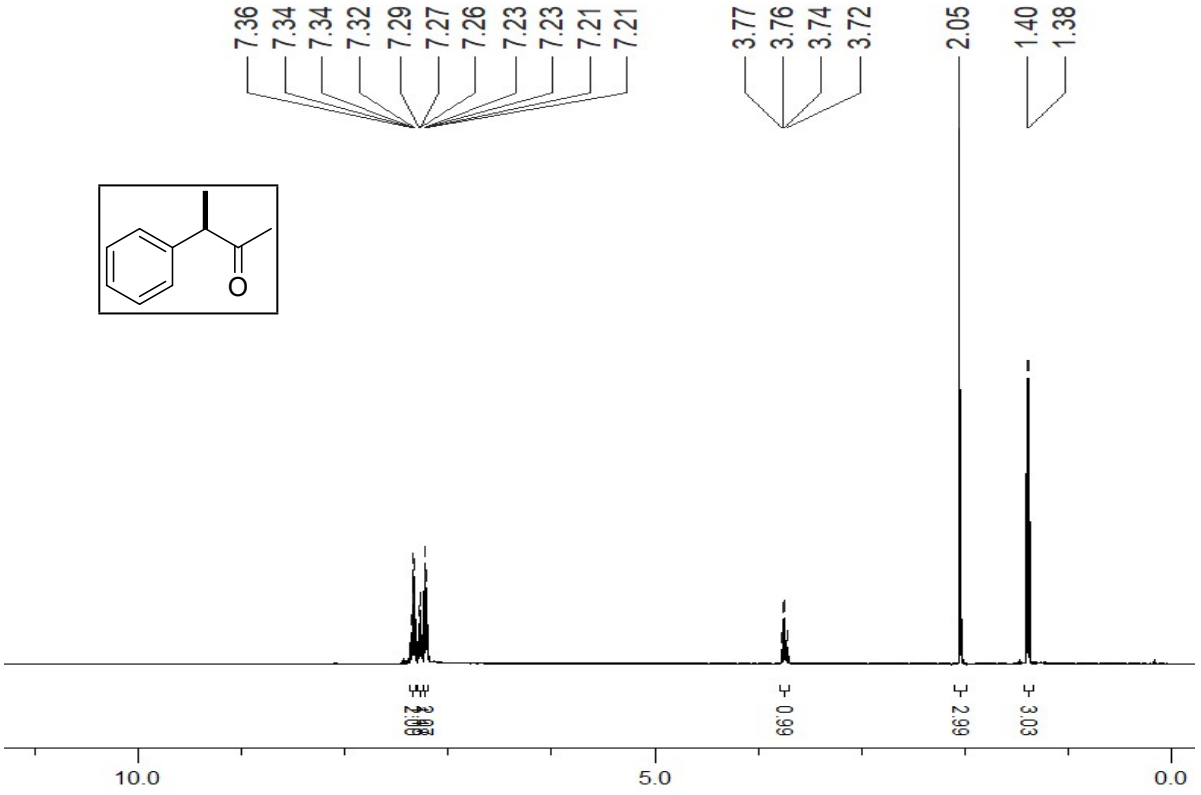
[10] A. R. Katritzky, D. Toader, L. Xie, *J. Org. Chem*., 1996, **61,** 7571.

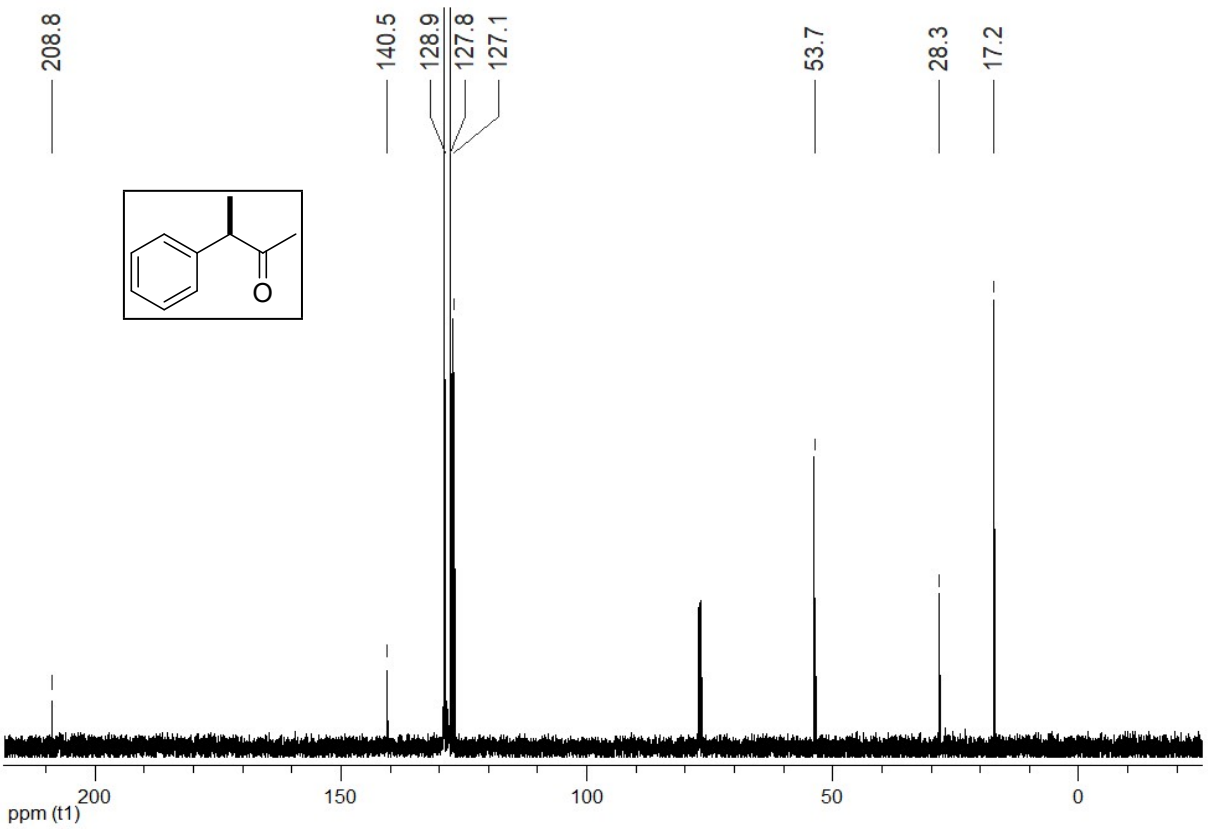
114.2, 127.1, 128.7, 128.9, 130.0, 130.4, 138.7, 158.8, 206.7; *m/z* 240 (M^+, 2%), 198 (16), 197 (100), 165 (19), 153 (29), 152 (17), 115 (3), 77 (3), 43 (7); HRMS (ESI) *m/z* calcd for $[C_{16}H_{16}O_2 + Na]^+$: 263.1043 (97.3%); found: 263.1033.

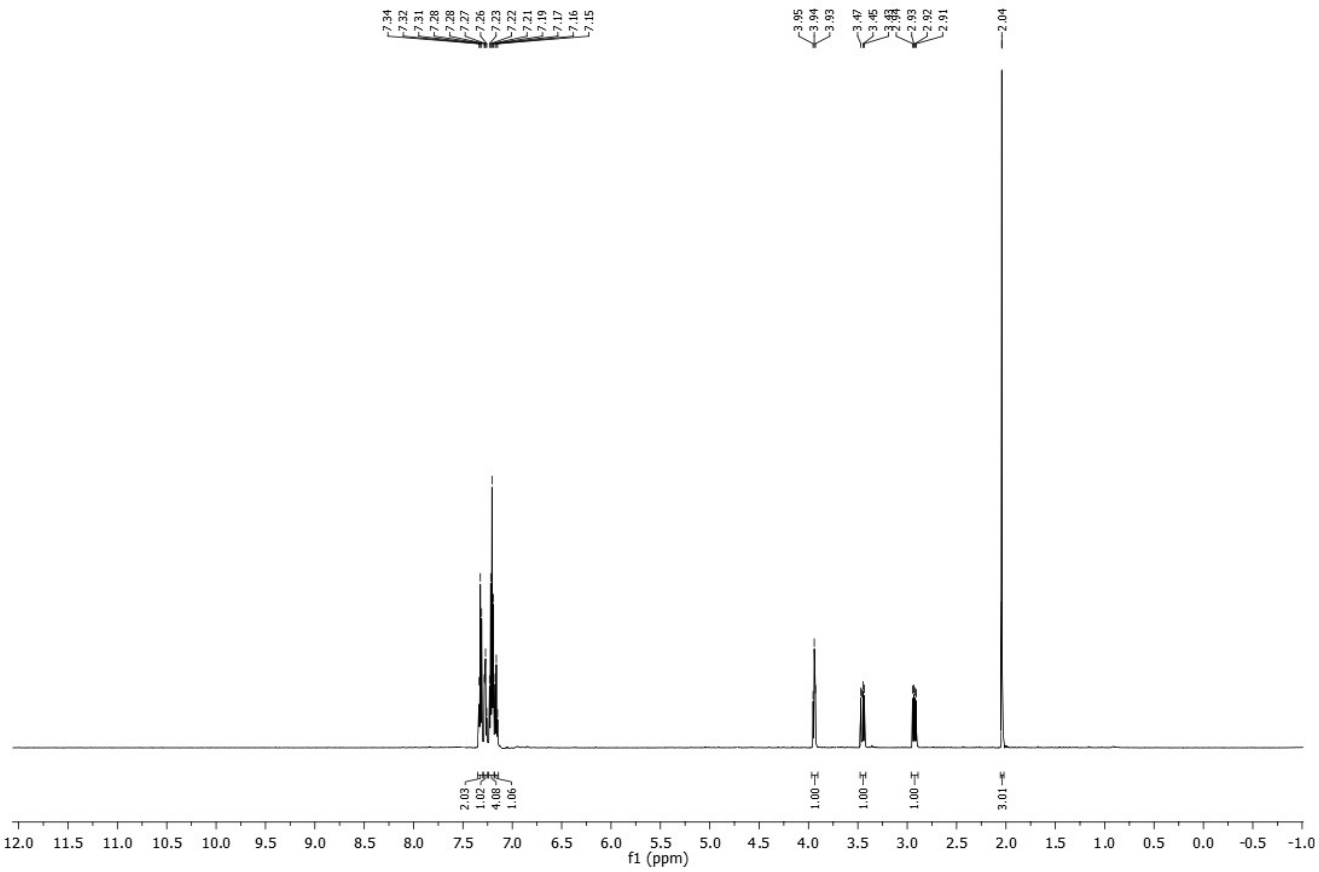


1-(1-Methyl-*1H*-indol-5-yl)-1-phenylpropan-2-one (3r) (0.077 g, 56%), pale yellow oil; ν_{max}/cm^{-1} 3026, 2920s (CH), 1715vs, 1601, 1513, 1494w, 1451, 1423, 1354w, 1247s, 1156s, 1080s, 910w, 794, 727w; δ_H (600 MHz; $CDCl_3$; TMS) 2.28 (3 H, s, COMe), 3.80 (3 H, s, NMe), 5.25 (1 H, s, ArC*H*), 6.47 (1 H, d, $J_{1,3}$ 3.0, ArC*H*NMe), 7.07 (1 H, d, $J_{1,3}$ 3.0, ArC*H*), 7.12 (1 H, dd, $J_{1,3}$ 8.5, $J_{1,5}$ 1.5, ArC*H*), 7.24-7.27 (3 H, m, ArC*H*), 7.30-7.34 (3 H, m, ArC*H*), 7.50-7.51 (1 H, m); δ_C (150 MHz; $CDCl_3$; TMS) 30.0, 32.8, 65.2, 101.1, 109.6, 121.3, 122.8, 126.9, 128.4, 128.8, 129.0, 129.1, 129.4, 136.0, 139.4, 207.3; *m/z* 263 (M^+, 9%), 221 (18), 220 (100), 205 (19), 204 (26), 178 (9), 176 (6), 165 (2), 151 (2), 109 (2), 102 (3), 77 (1), 43 (4); HRMS (ESI) *m/z* calcd for $[C_{18}H_{17}NO + Na]^-$: 286.1202; found: 286.1213.

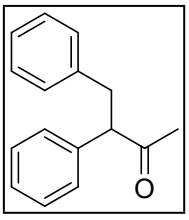
3-Phenylbutan-2-one (3a)

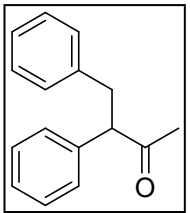


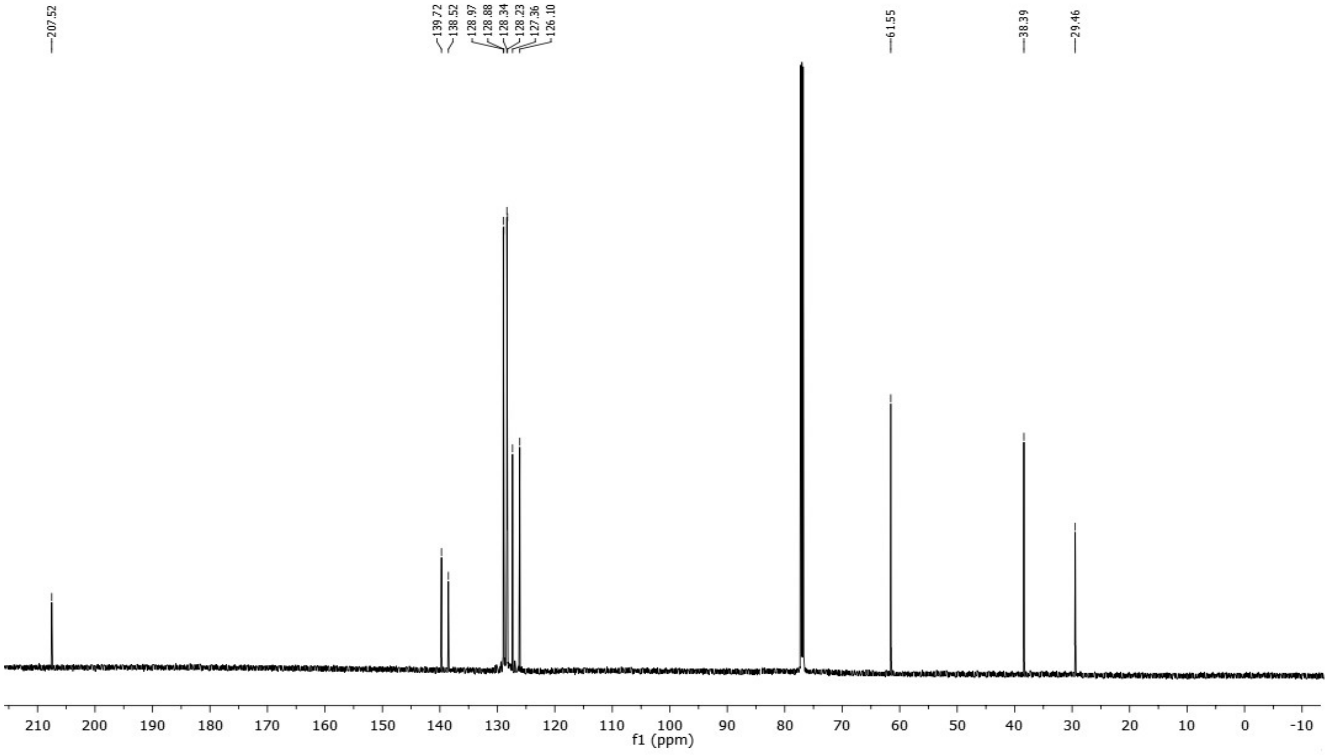


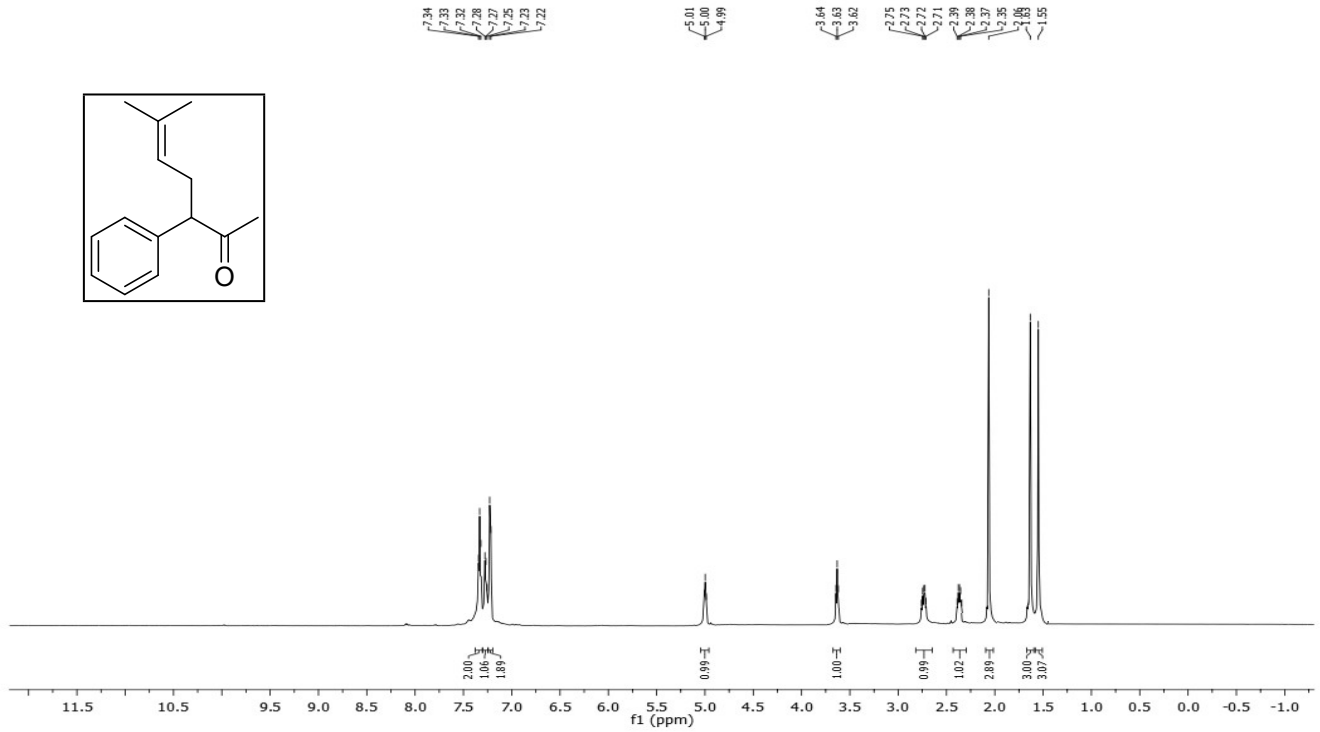


3,4-Diphenylbutan-2-one (3b)

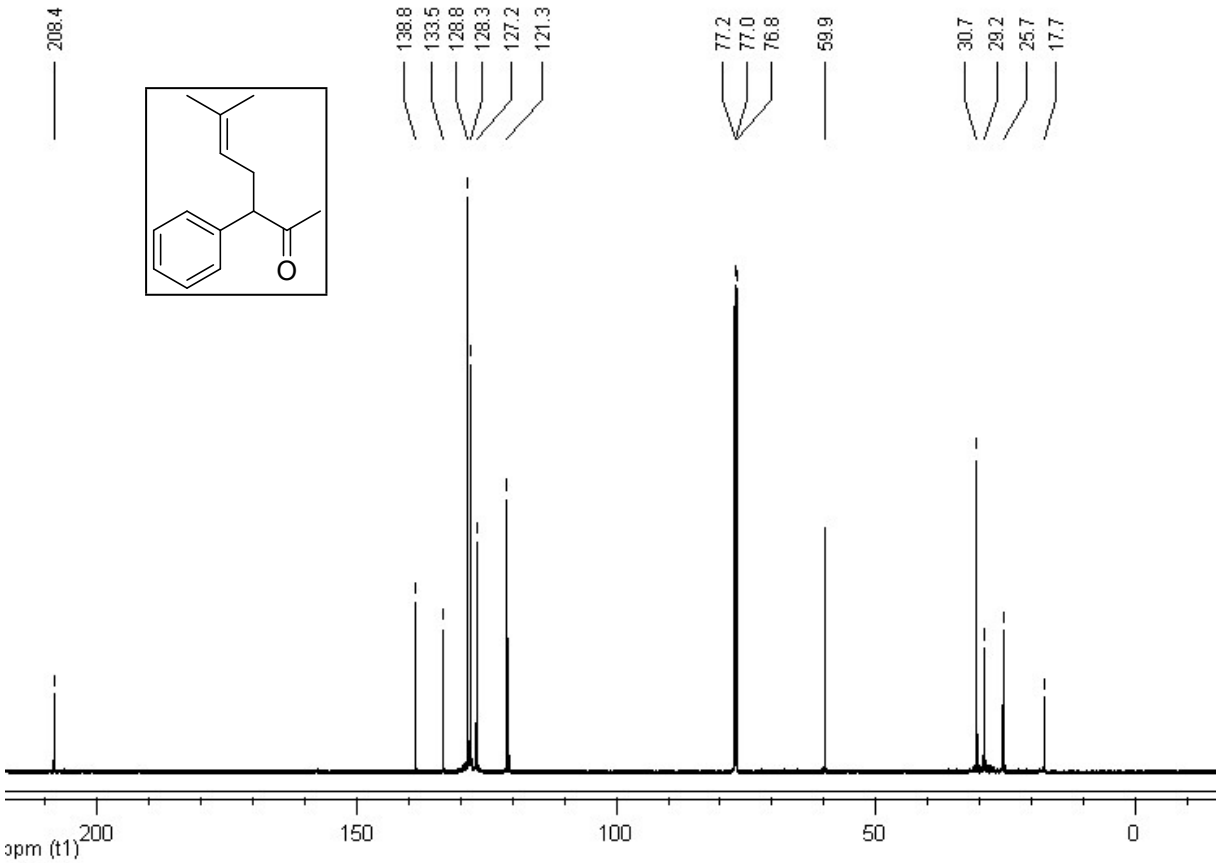


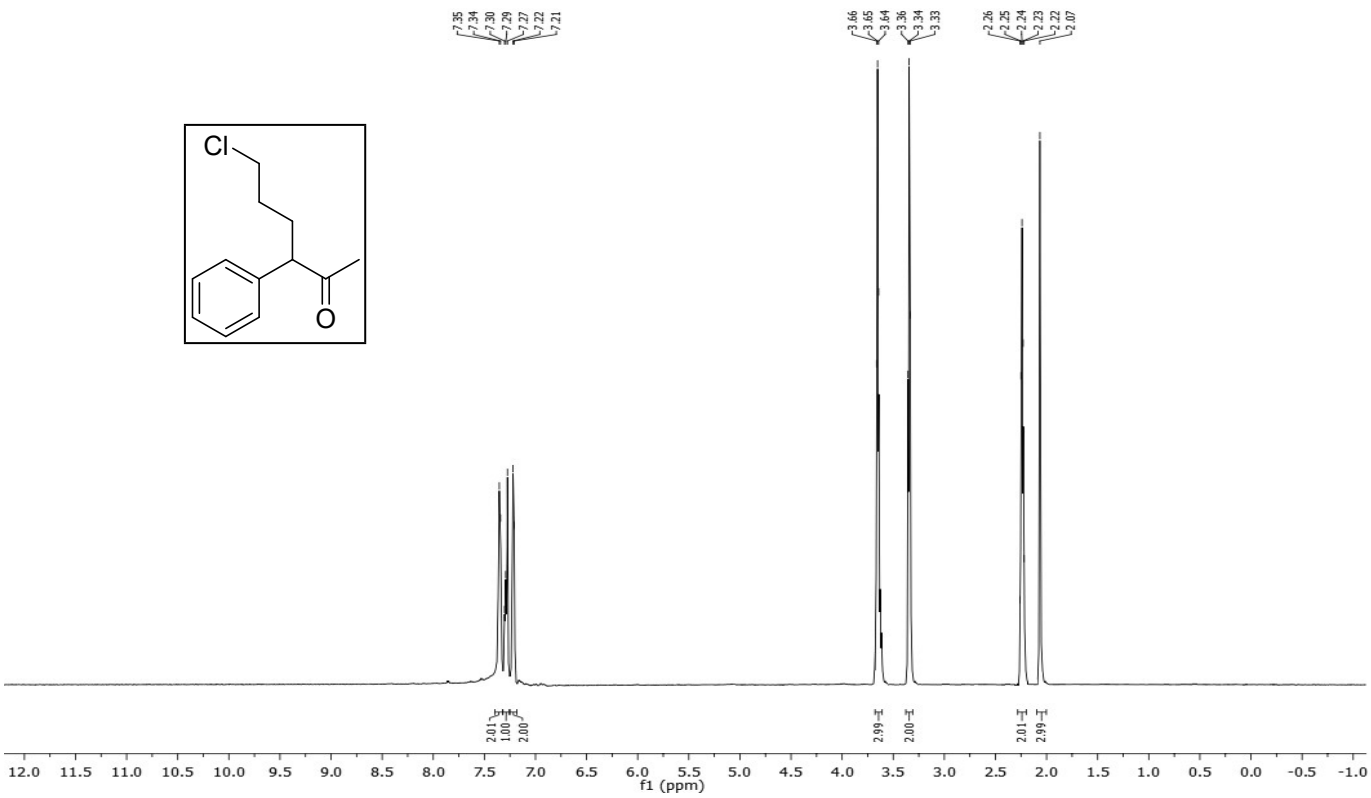



207.52
139.72
138.52
128.97
128.88
128.34
128.23
127.36
126.10
61.55
38.39
29.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

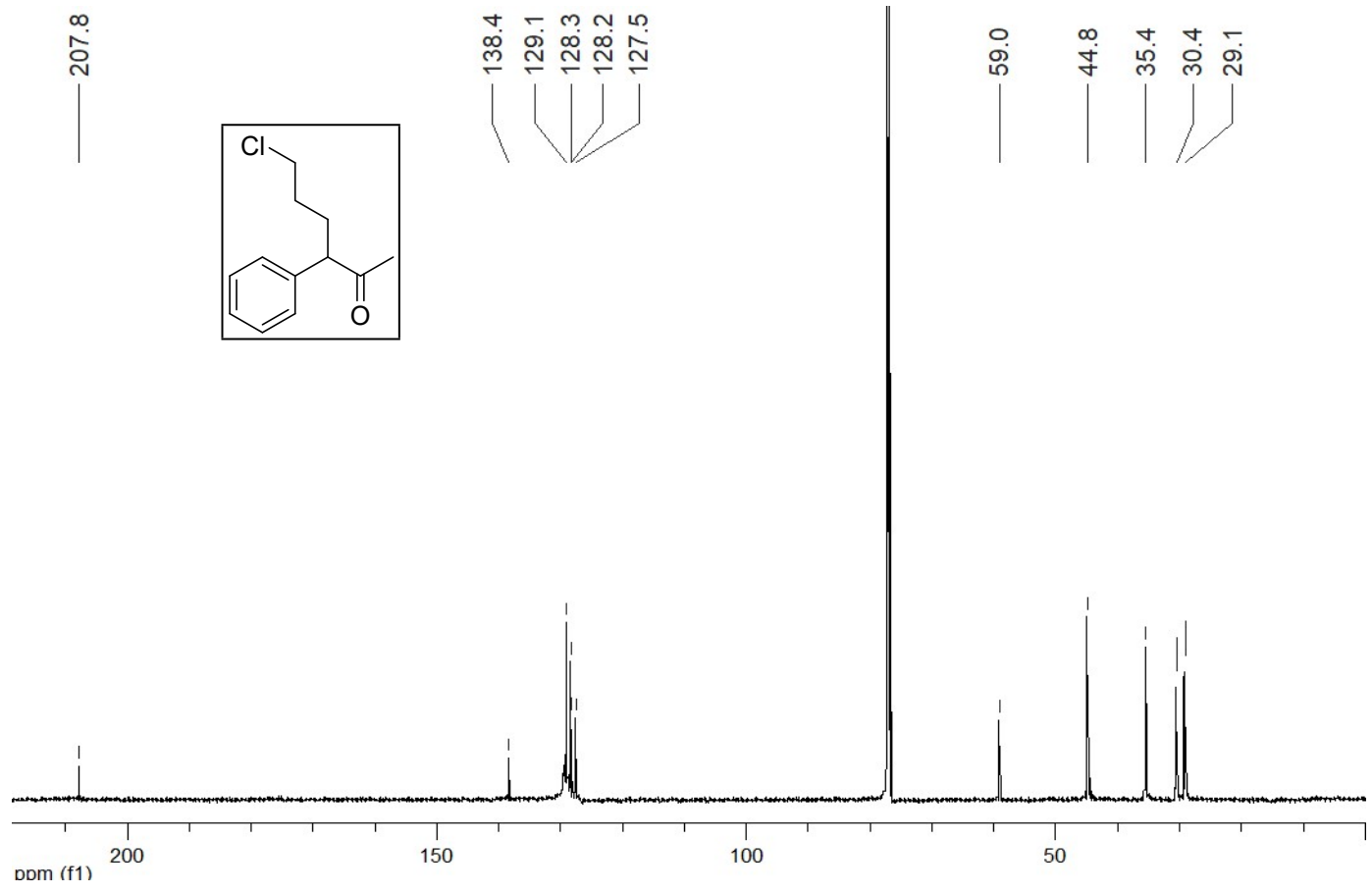


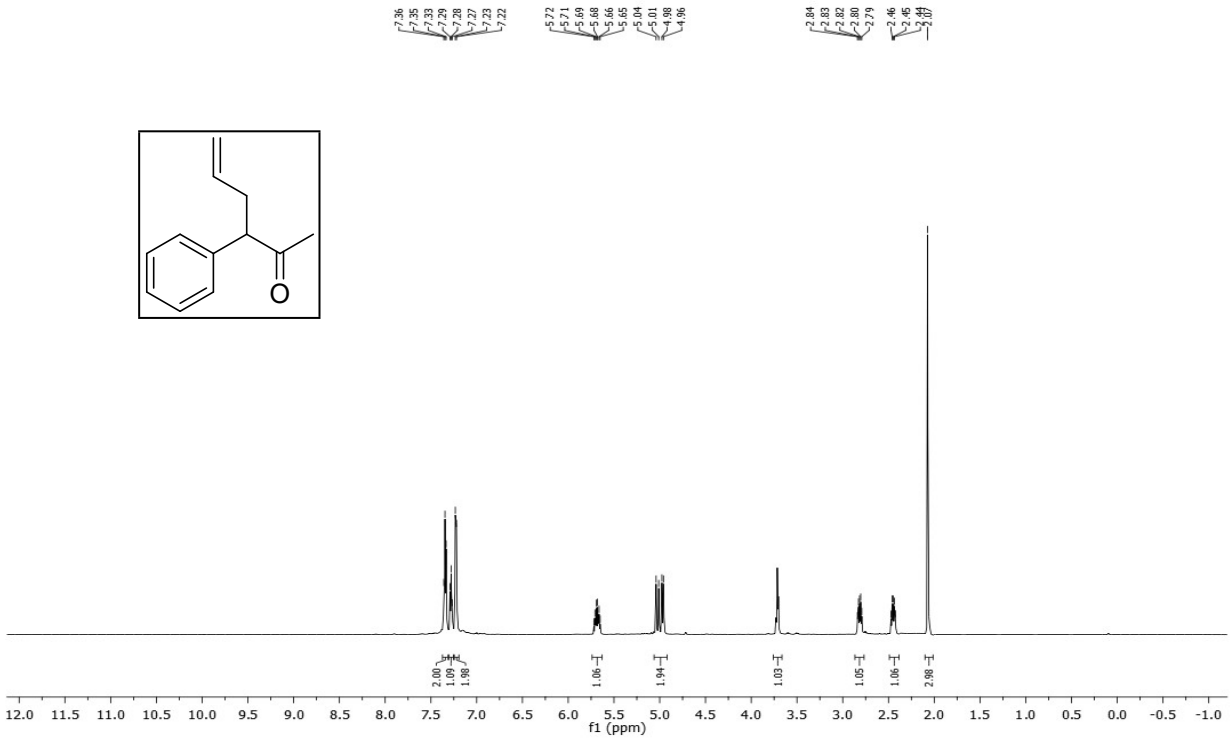
6-Methyl-3-phenylhept-5-en-2-one (3c)


208.4
138.8
133.5
128.8
128.3
127.2
121.3
77.2
77.0
76.8
59.9
30.7
29.2
25.7
17.7
O
200
150
100
50
0
ppm (t1)

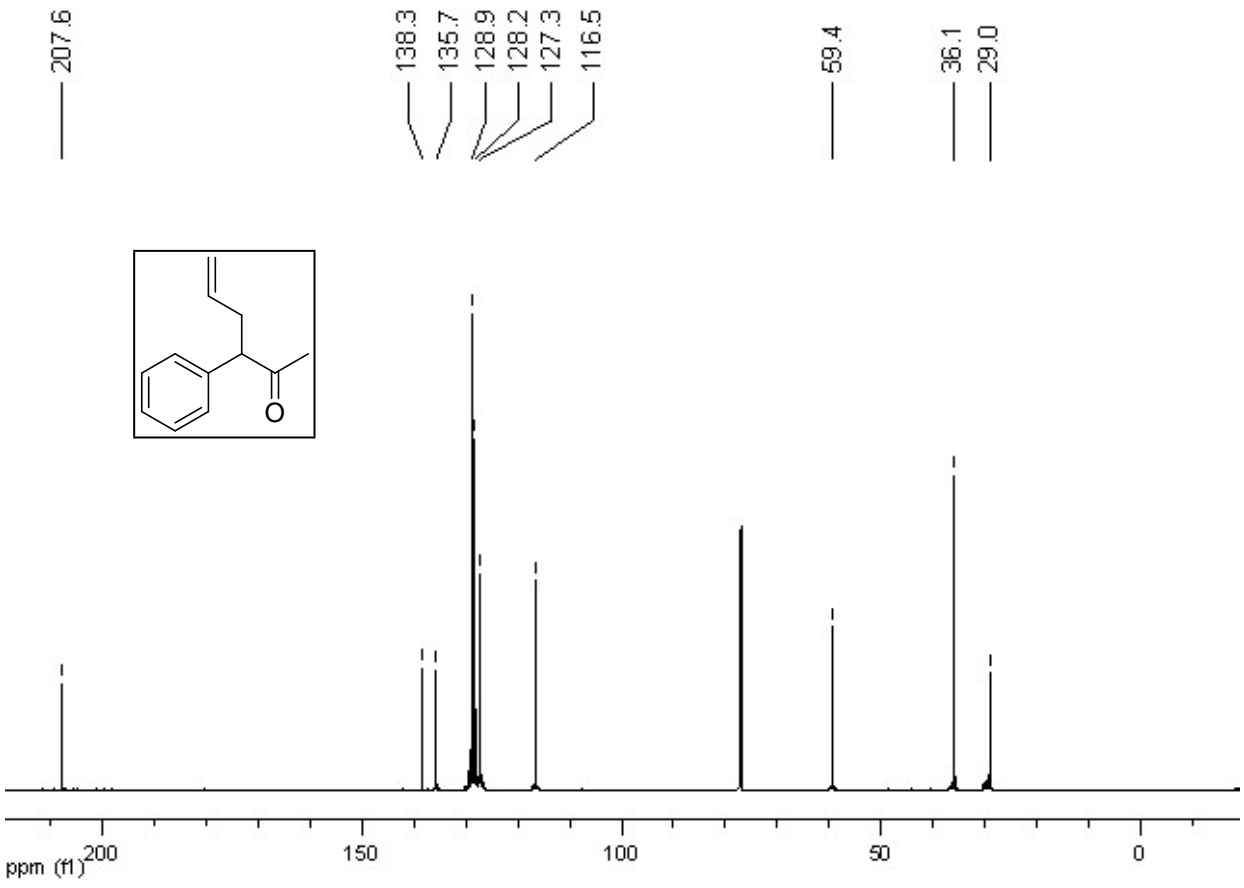


6-Chloro-3-phenylhexan-2-one (3d)

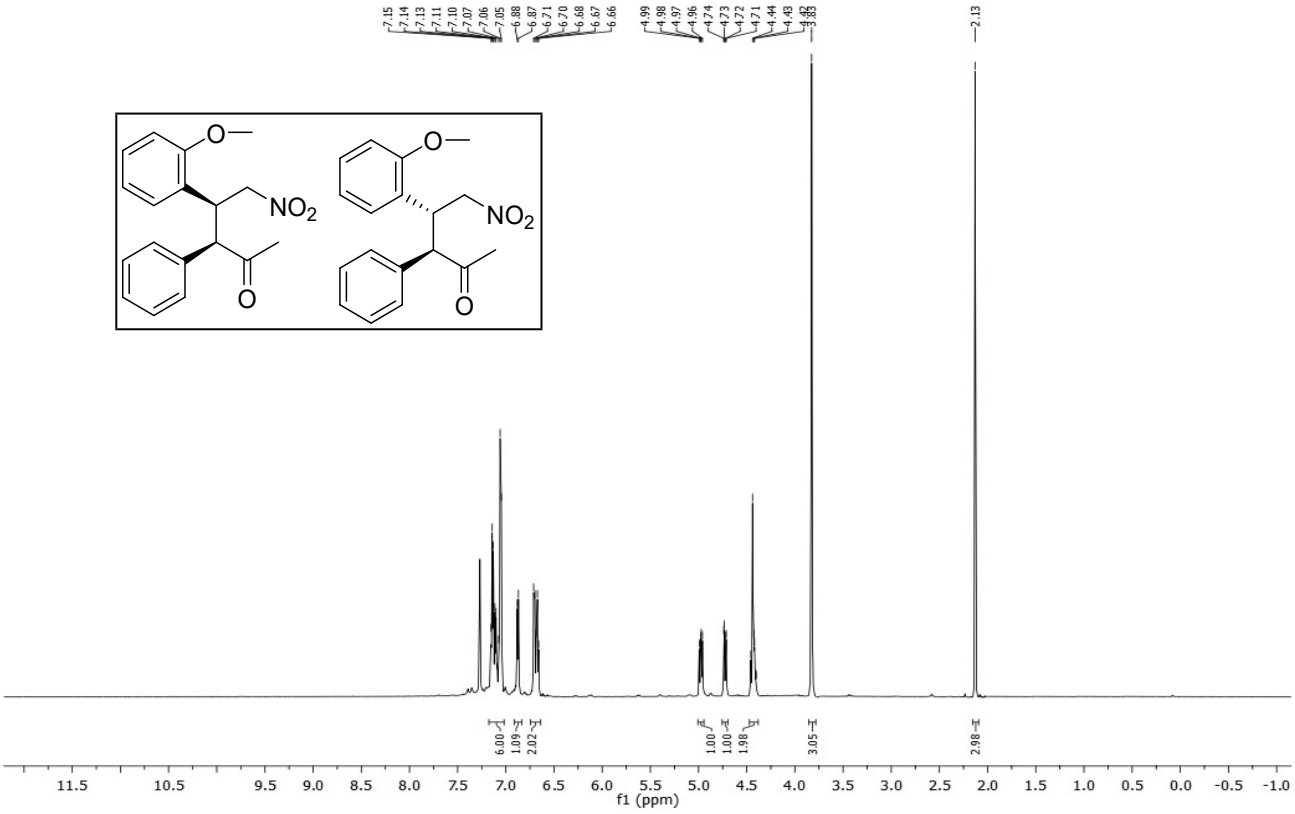




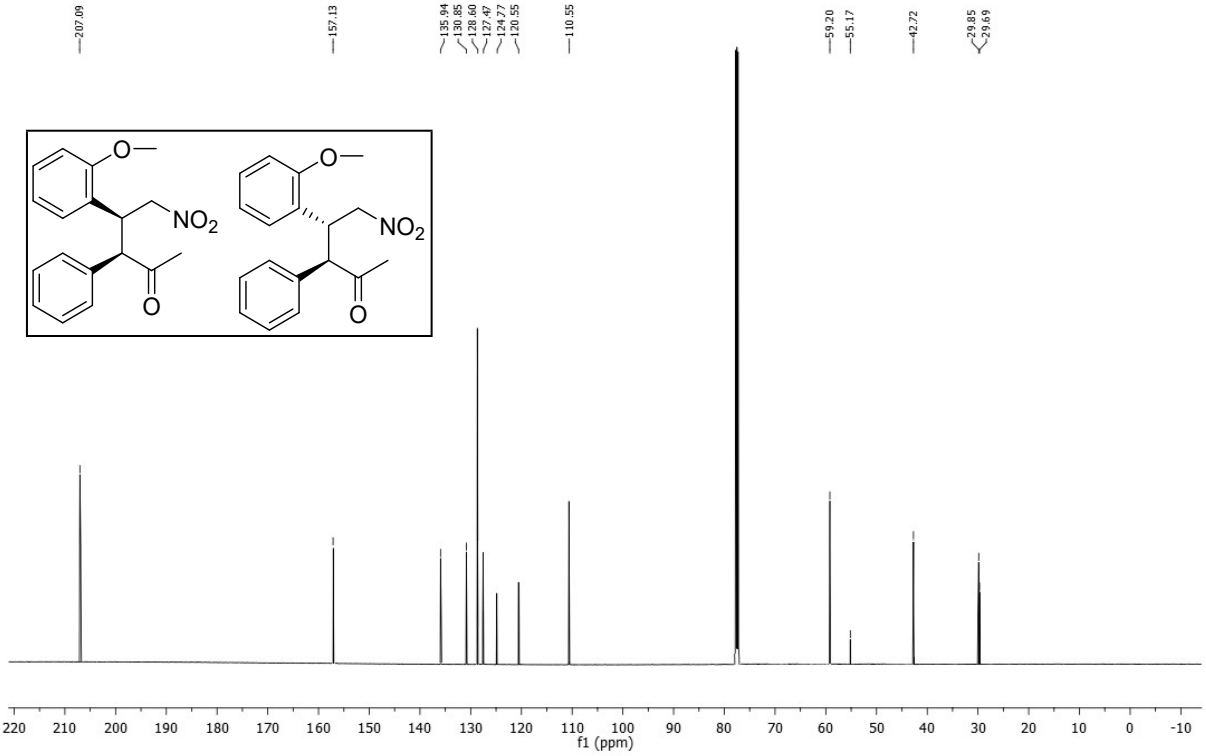
3-Phenylhex-5-en-2-one (3e)


207.6
138.3
135.7
128.9
128.2
127.3
116.5
59.4
36.1
29.0
O
ppm (f1)
200
150
100
50
0

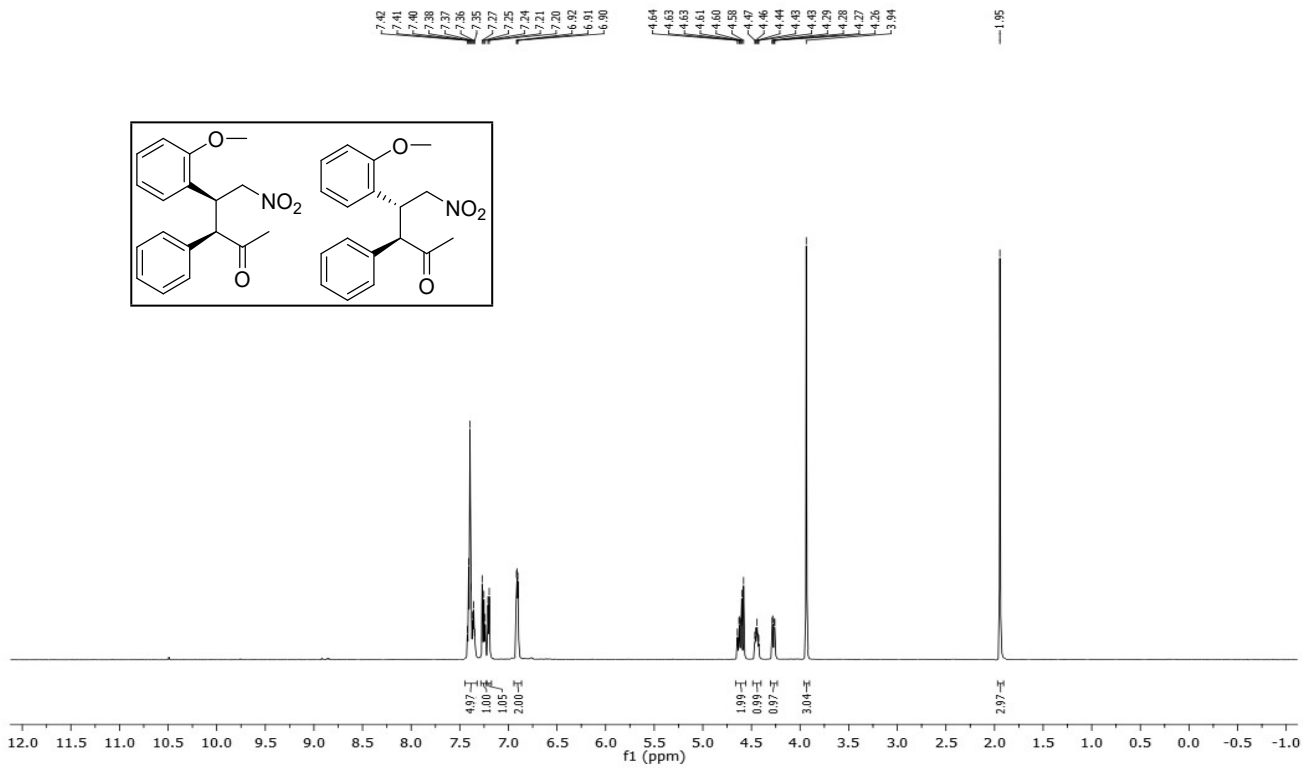
4-(2-Methoxyphenyl)-5-nitro-3-phenylpentan-2-one (3f)

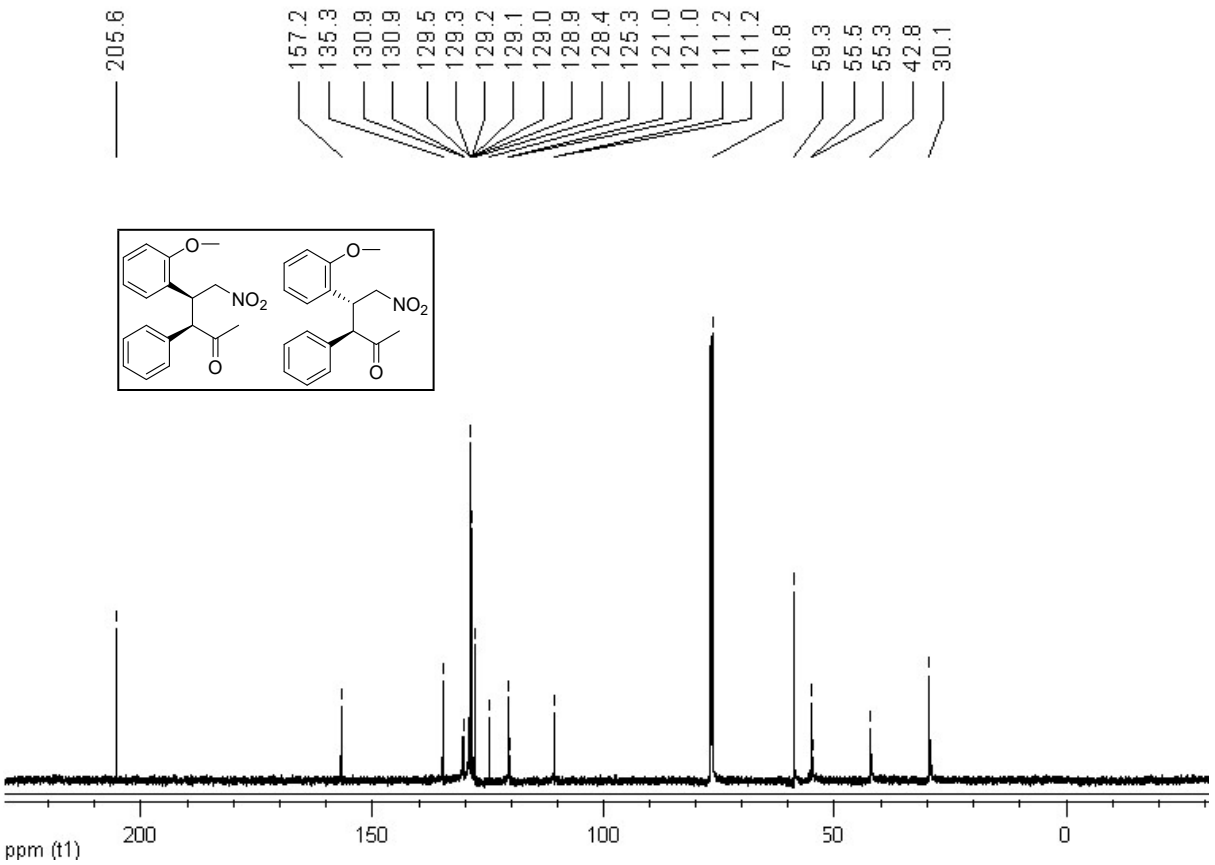


Major:



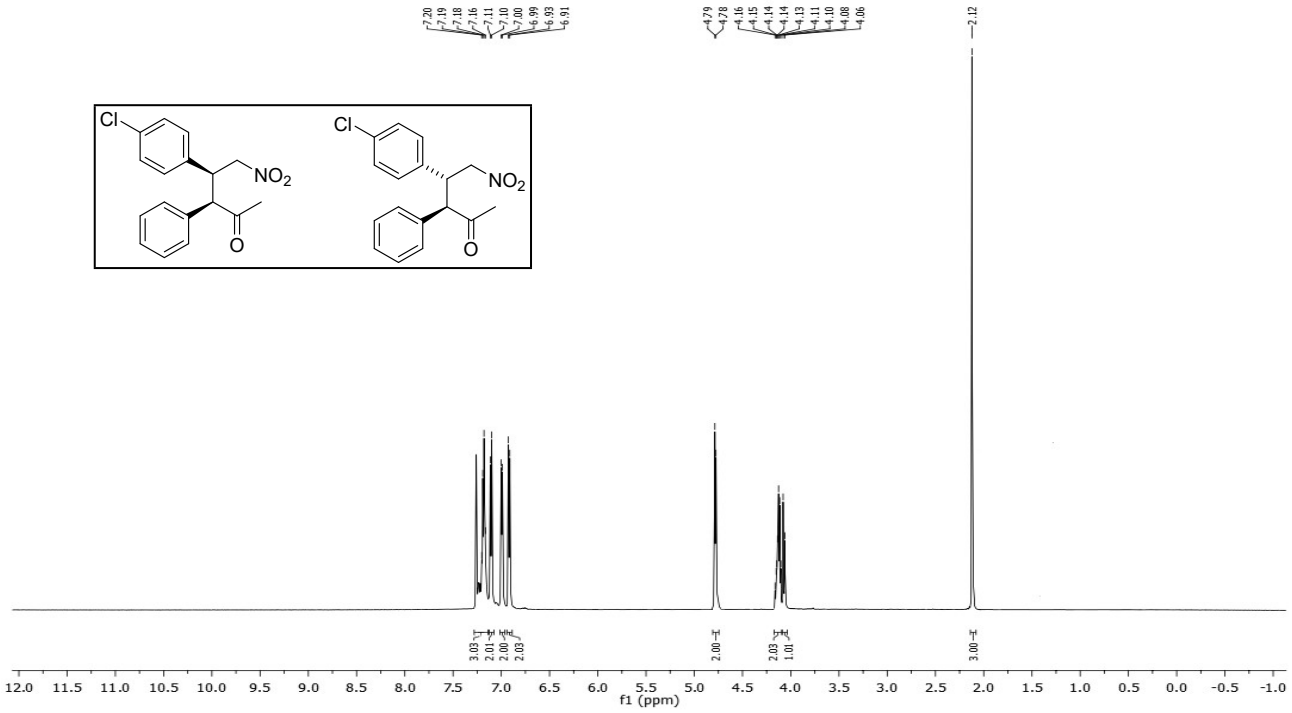
Minor:

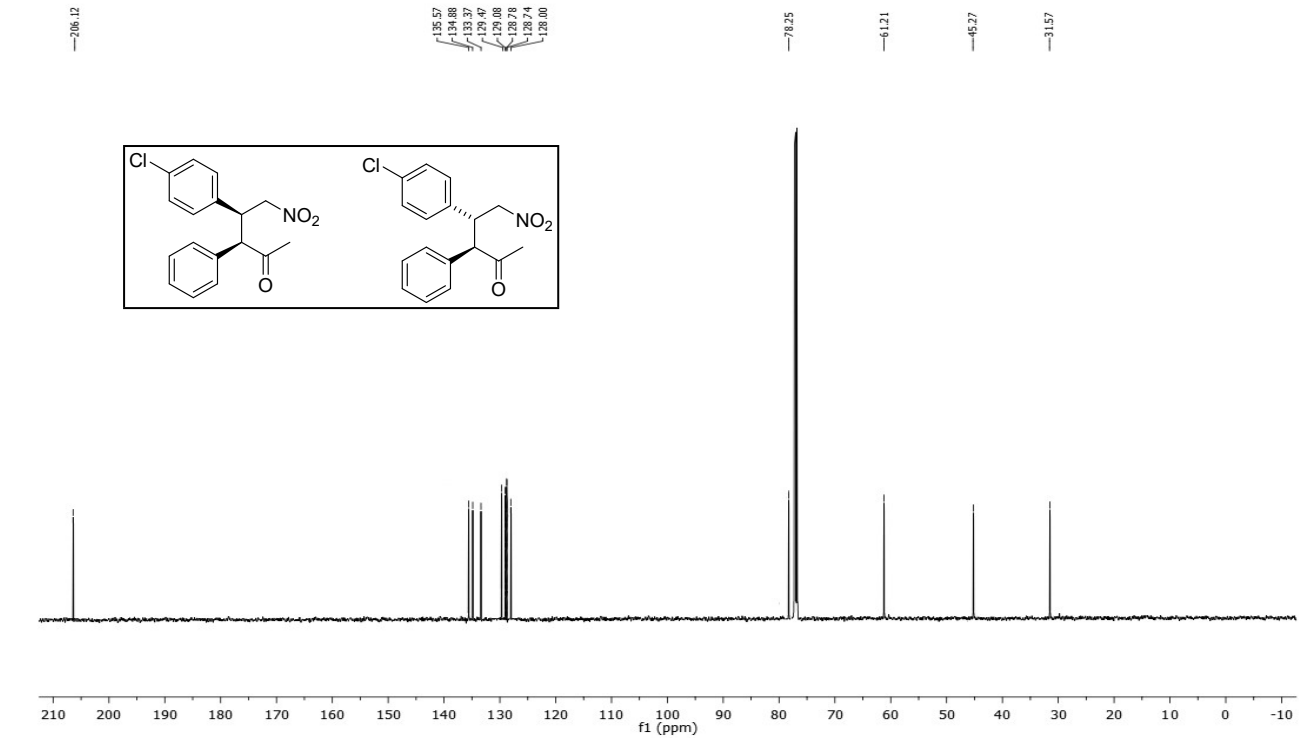

7.42
7.41
7.40
7.38
7.37
7.36
7.35
7.27
7.25
7.24
7.21
7.20
6.92
6.91
6.90
4.64
4.63
4.63
4.61
4.60
4.58
4.47
4.46
4.44
4.43
4.43
4.29
4.28
4.27
4.26
3.94
1.95
O
NO2
O
O
NO2
O
4.97
1.00
1.05
2.00
1.99
0.99
0.97
3.04
2.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


205.6
157.2
135.3
130.9
130.9
129.5
129.3
129.2
129.1
129.0
128.9
128.4
125.3
121.0
121.0
111.2
111.2
76.8
59.3
55.5
55.3
42.8
30.1
O
NO2
O
O
NO2
O
200
150
100
50
0
ppm (t1)

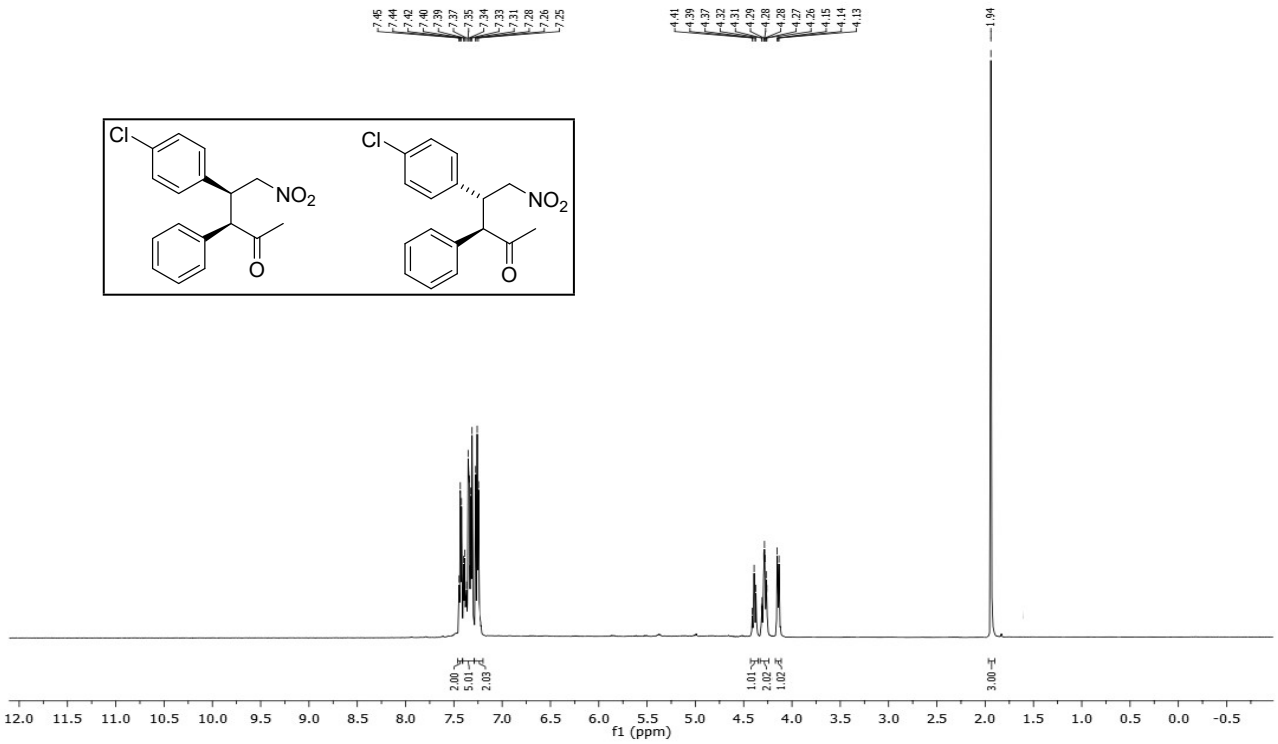
(4-Chlorophenyl)-5-nitro-3-phenylpentan-2-one (3g)

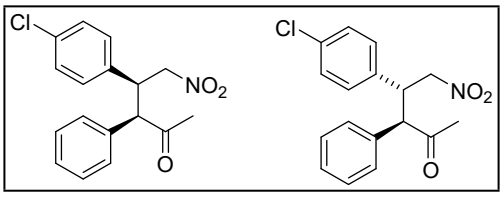
Major:

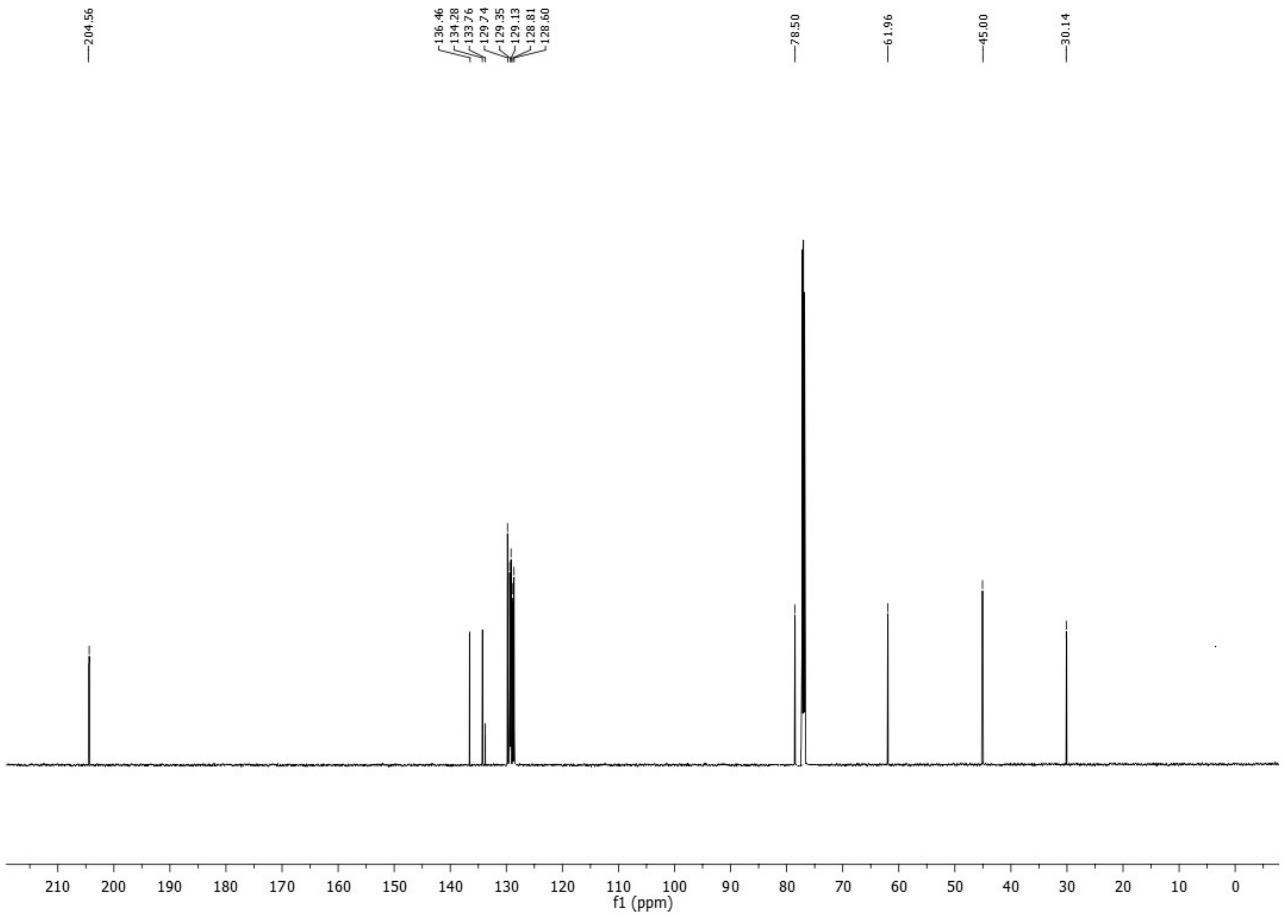




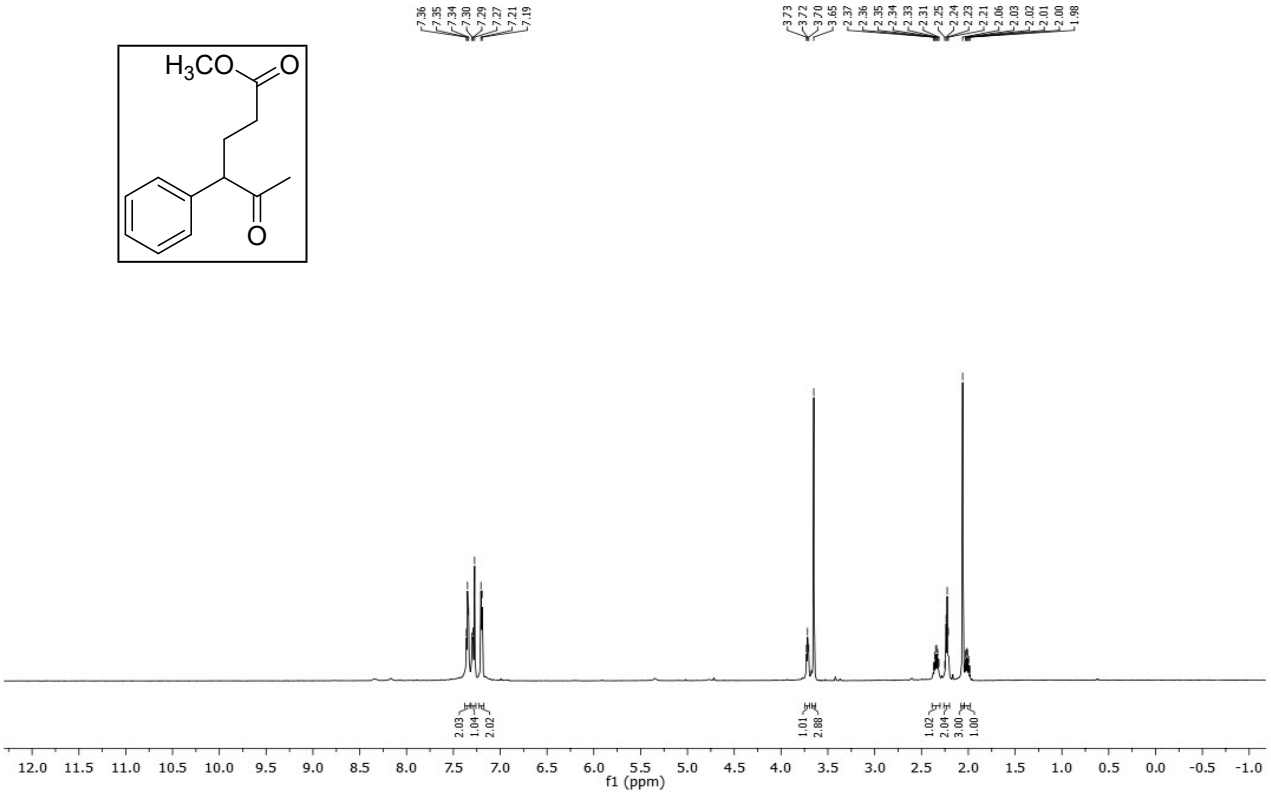
Minor:

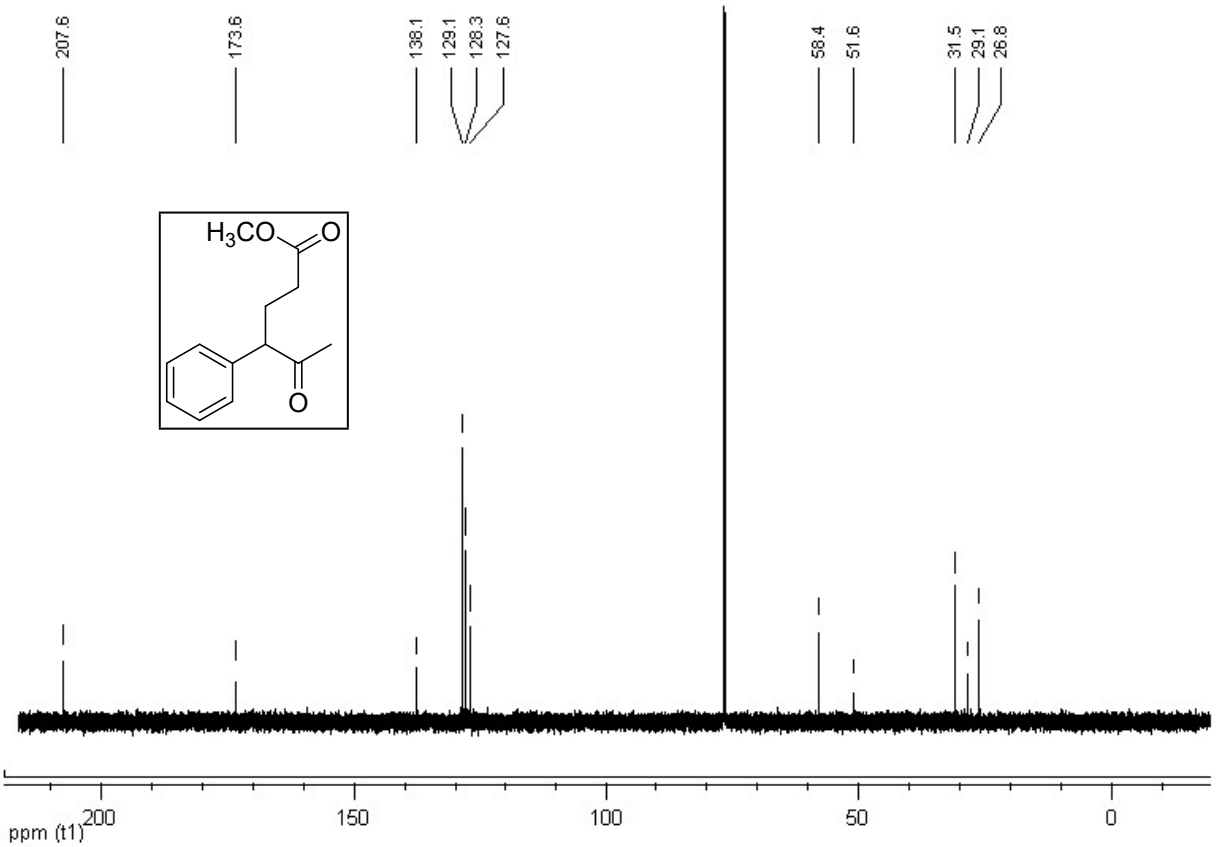

7.45
7.44
7.42
7.40
7.39
7.37
7.35
7.34
7.33
7.31
7.28
7.26
7.25
4.41
4.39
4.37
4.32
4.31
4.29
4.28
4.28
4.27
4.26
4.15
4.14
4.13
1.94
Cl
NO2
O
Cl
NO2
O
2.00
5.01
2.03
1.01
2.02
1.02
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

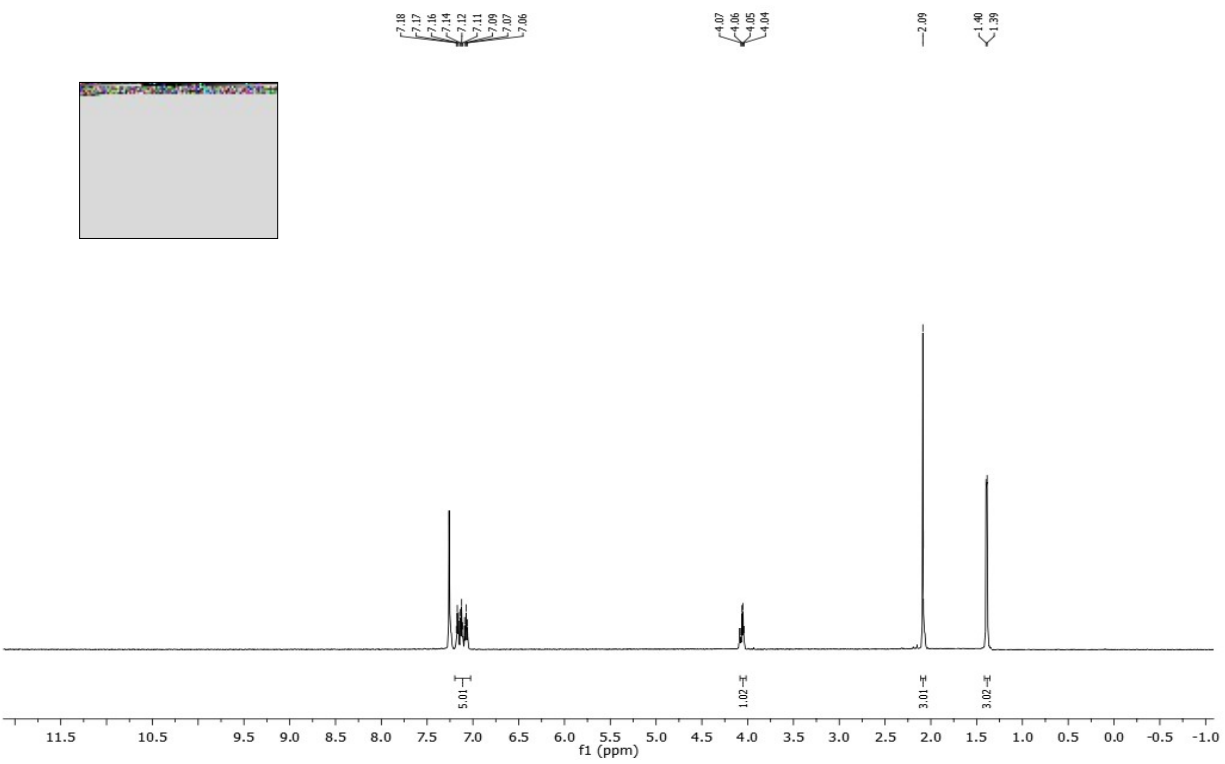

Cl
NO2
O
Cl
NO2
O


204.56
136.46
134.28
133.76
129.74
129.35
129.13
128.81
128.60
78.50
61.96
45.00
30.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

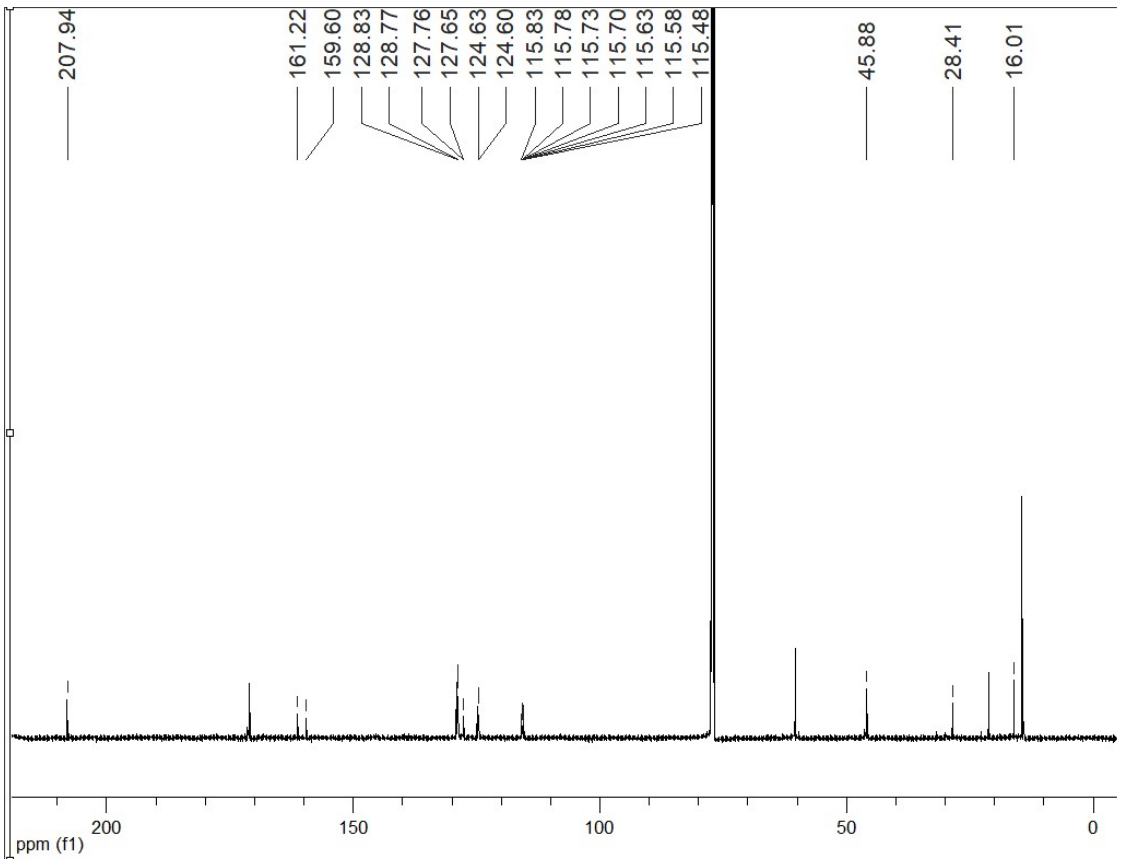
Methyl 5-oxo-4-phenylhexanoate (3h)

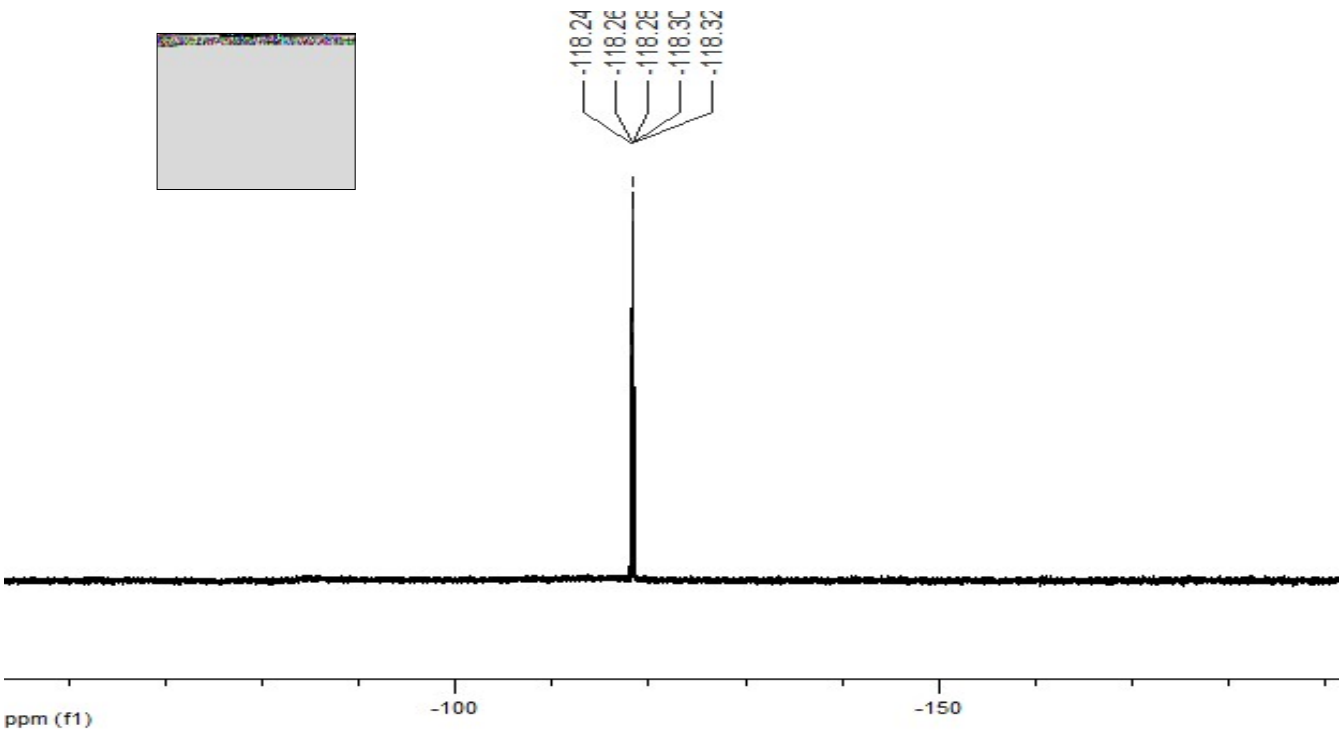




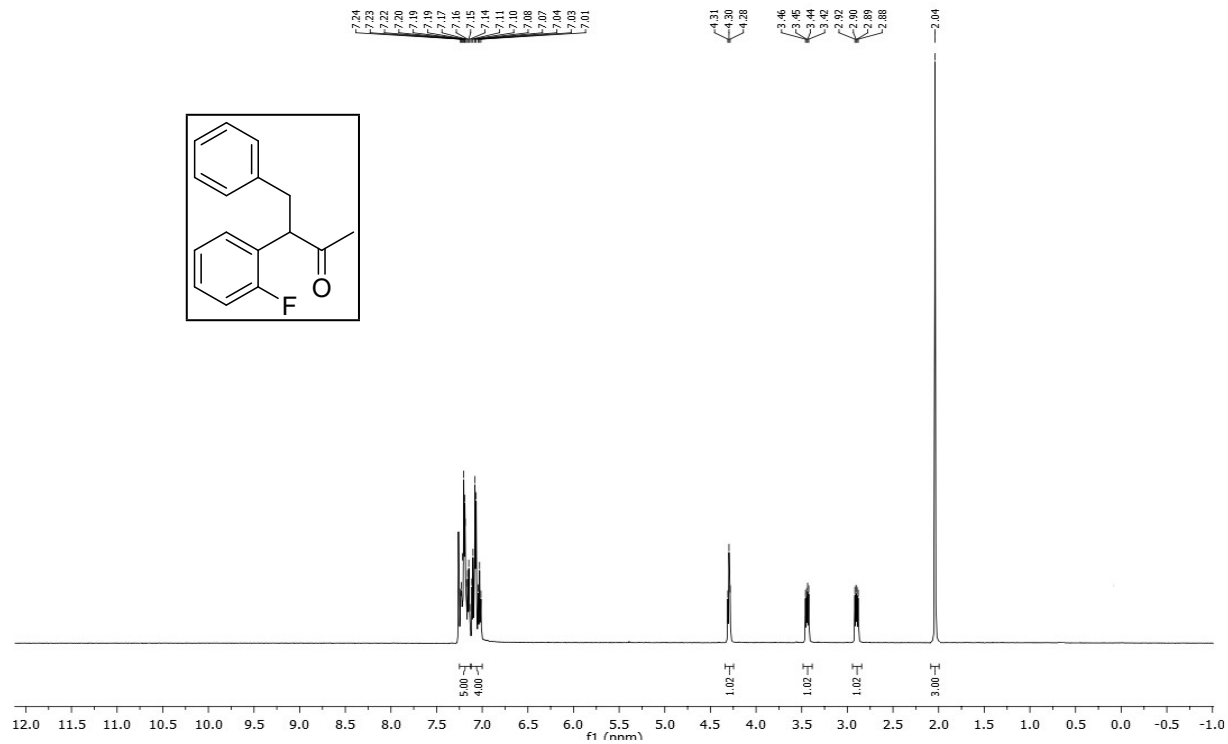


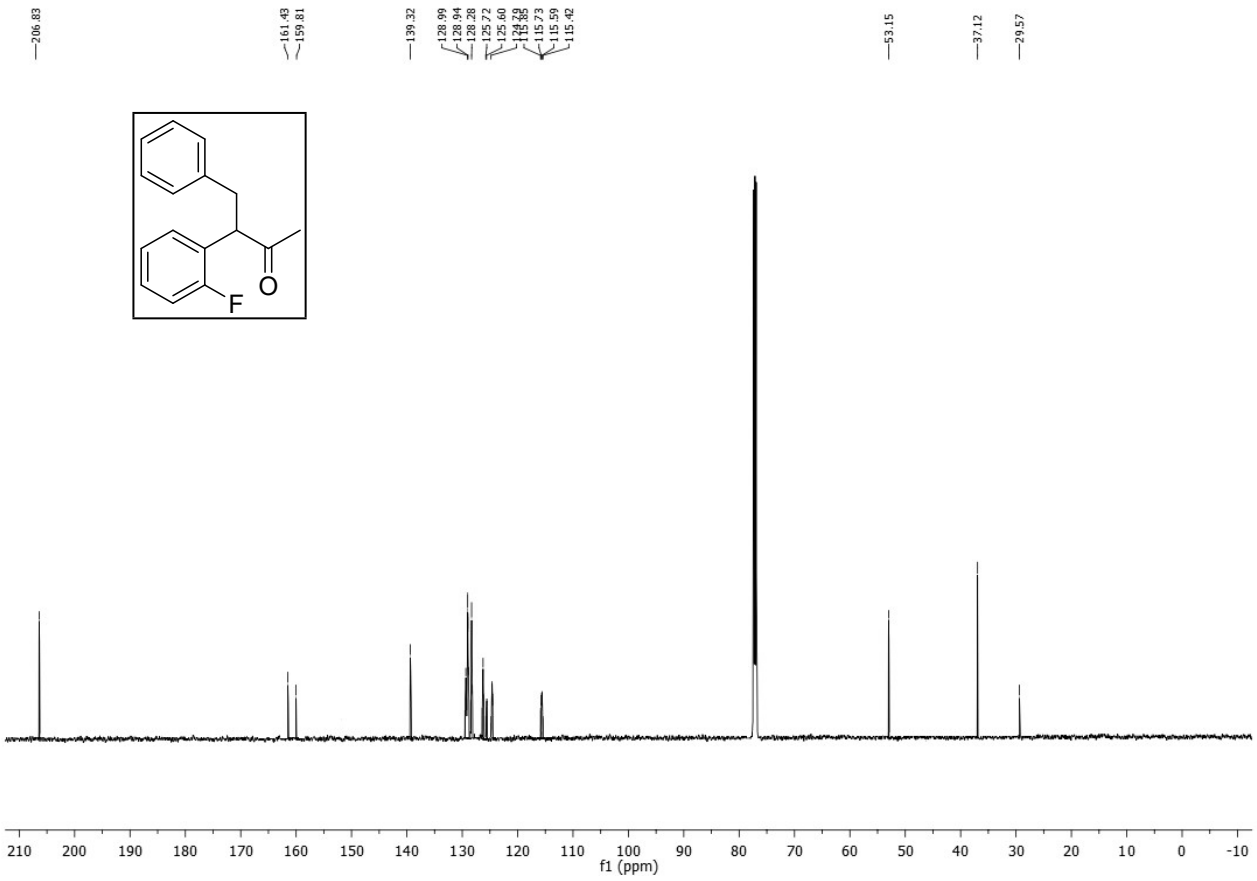
3-(2-Fluorophenyl)butan-2-one (3i)

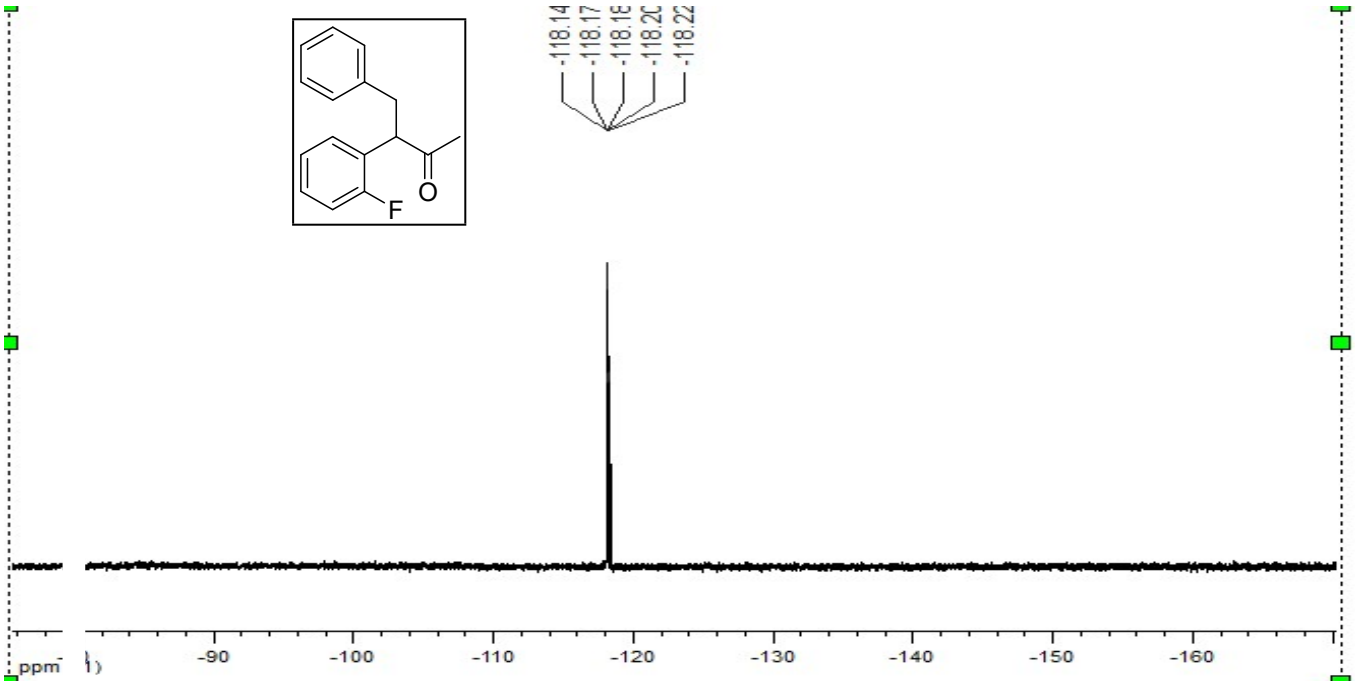


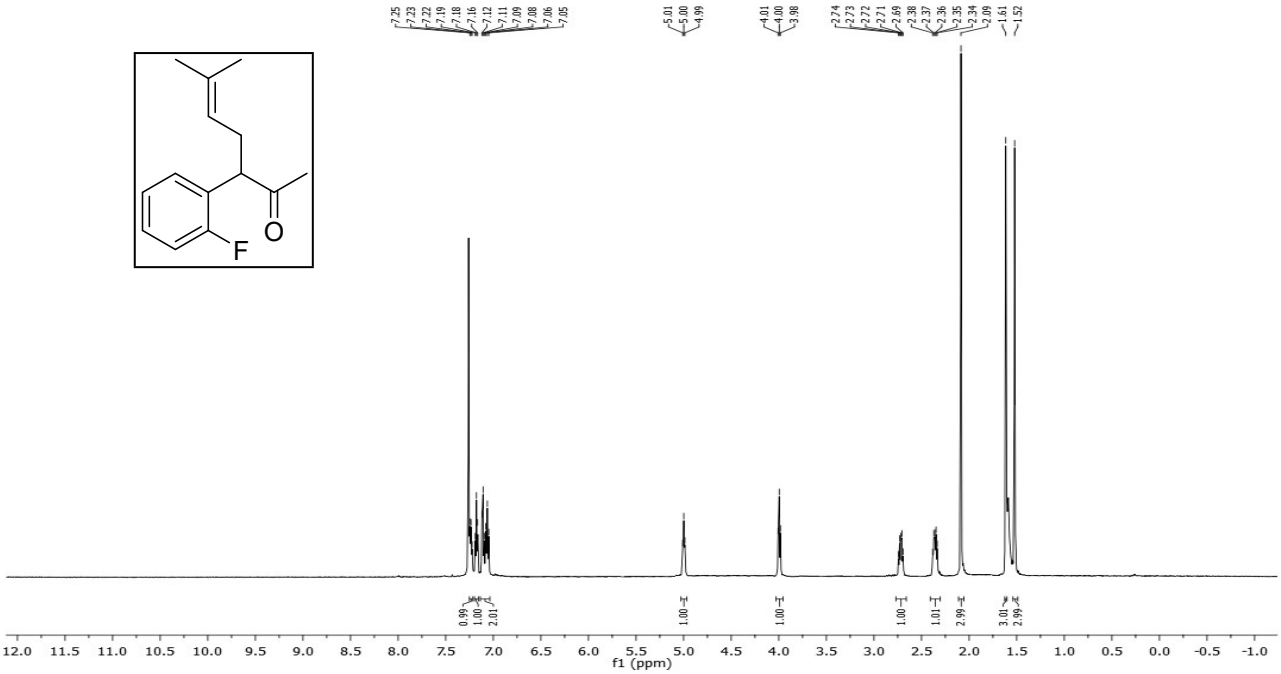


3-(2-Fluorophenyl)-4-phenylbutan-2-one (3j)

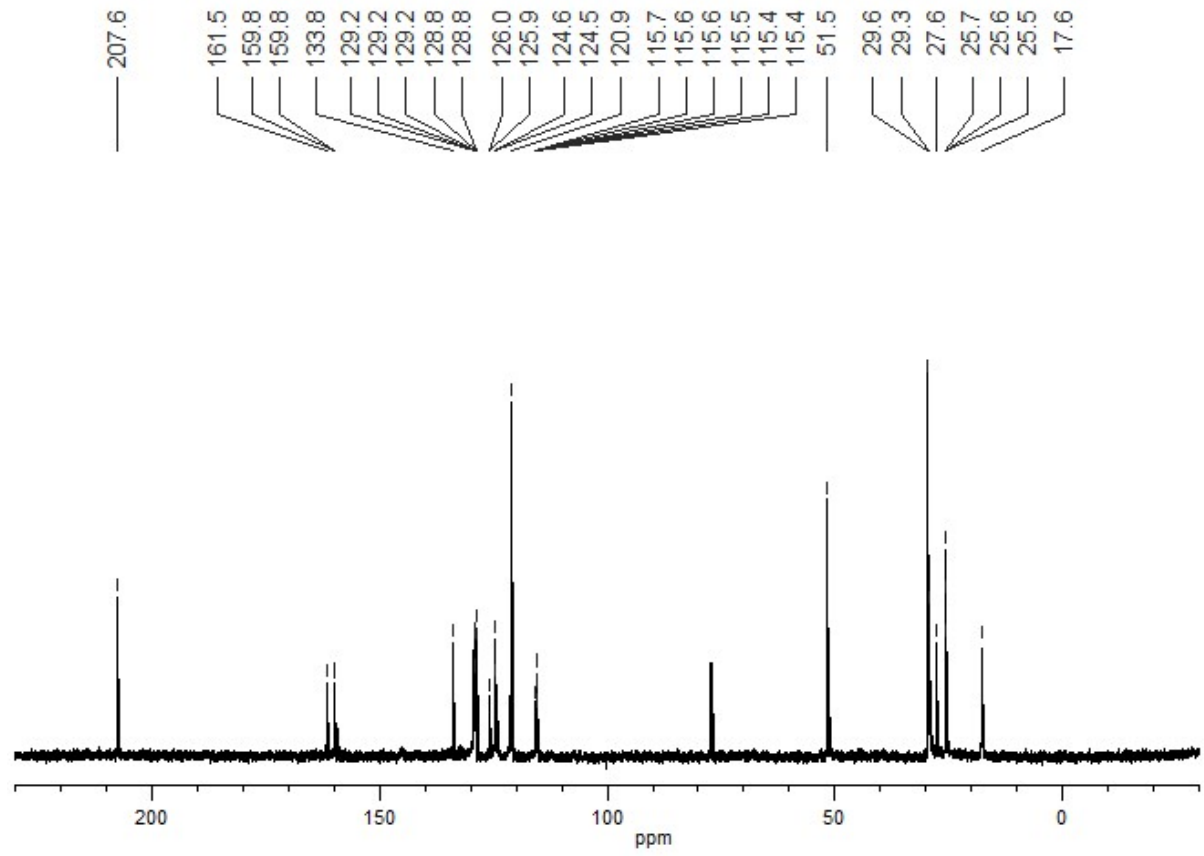


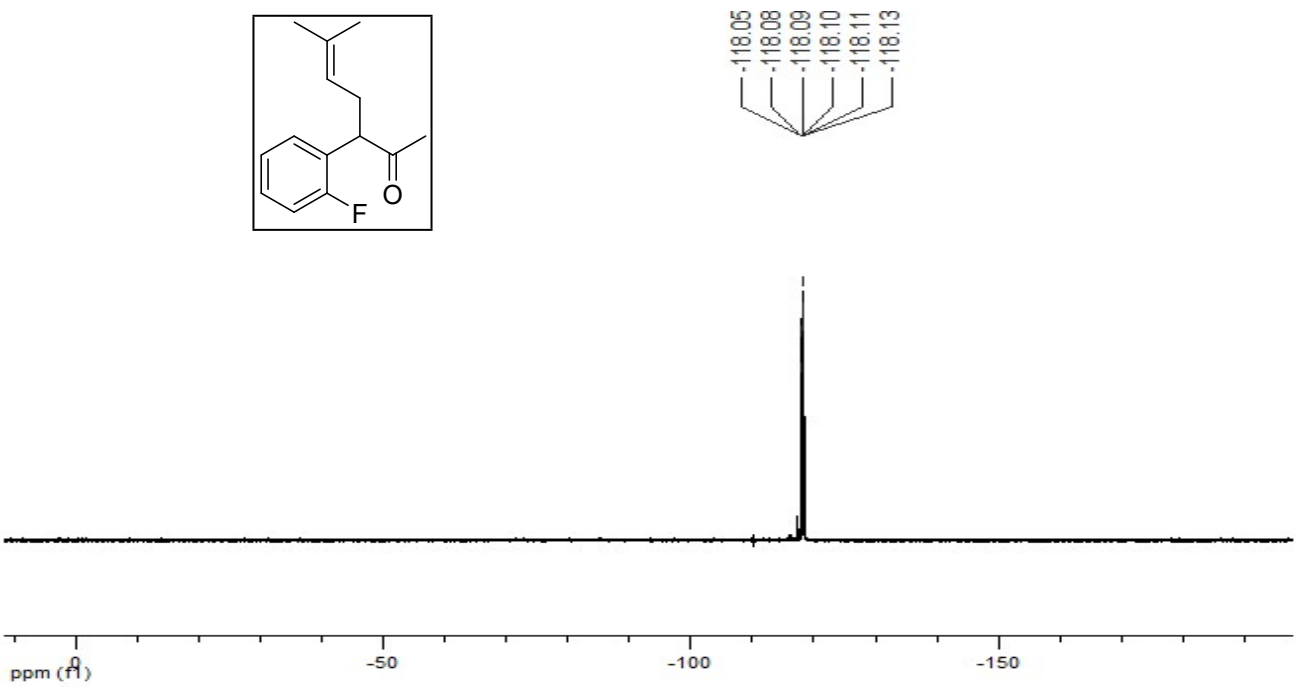

206.83
161.43
159.81
139.32
128.99
128.94
128.28
125.72
125.60
115.73
115.59
115.42
53.15
37.12
29.57
F
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-118.14
-118.17
-118.18
-118.20
-118.22
F
O
ppm
-90 -100 -110 -120 -130 -140 -150 -160

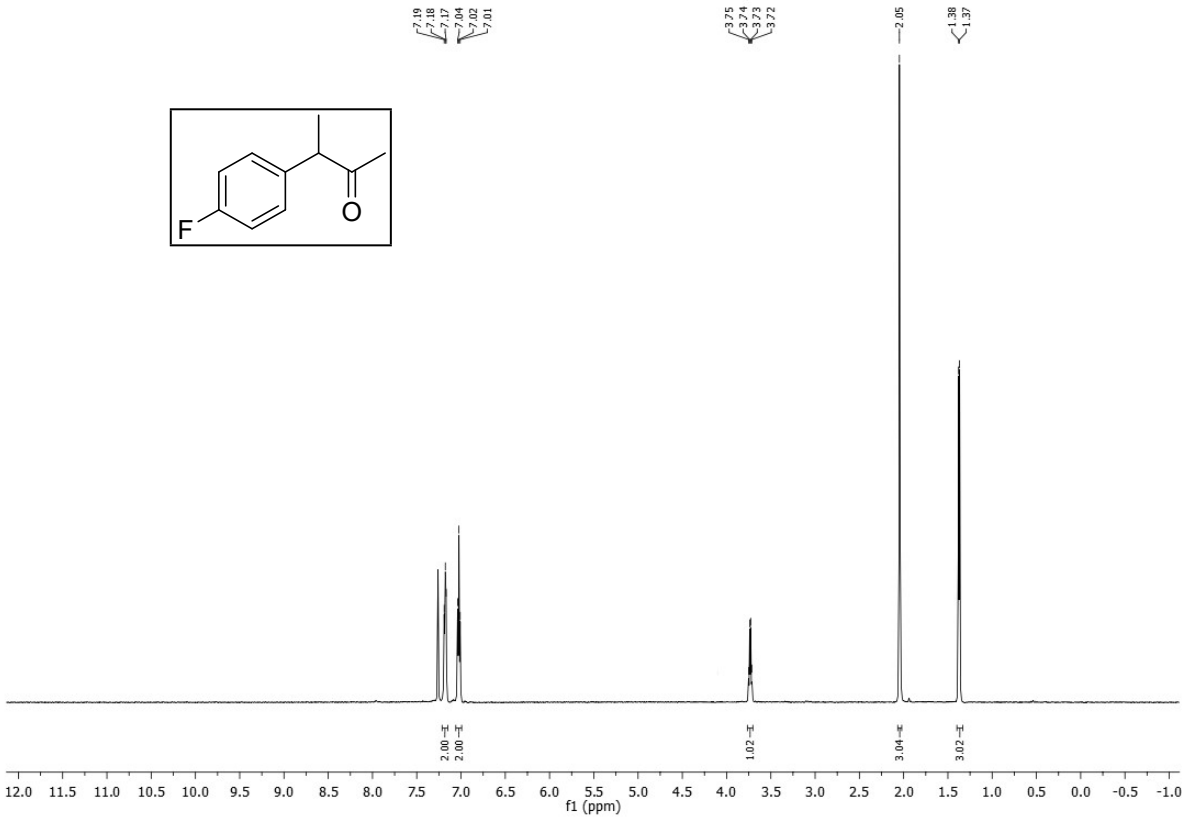


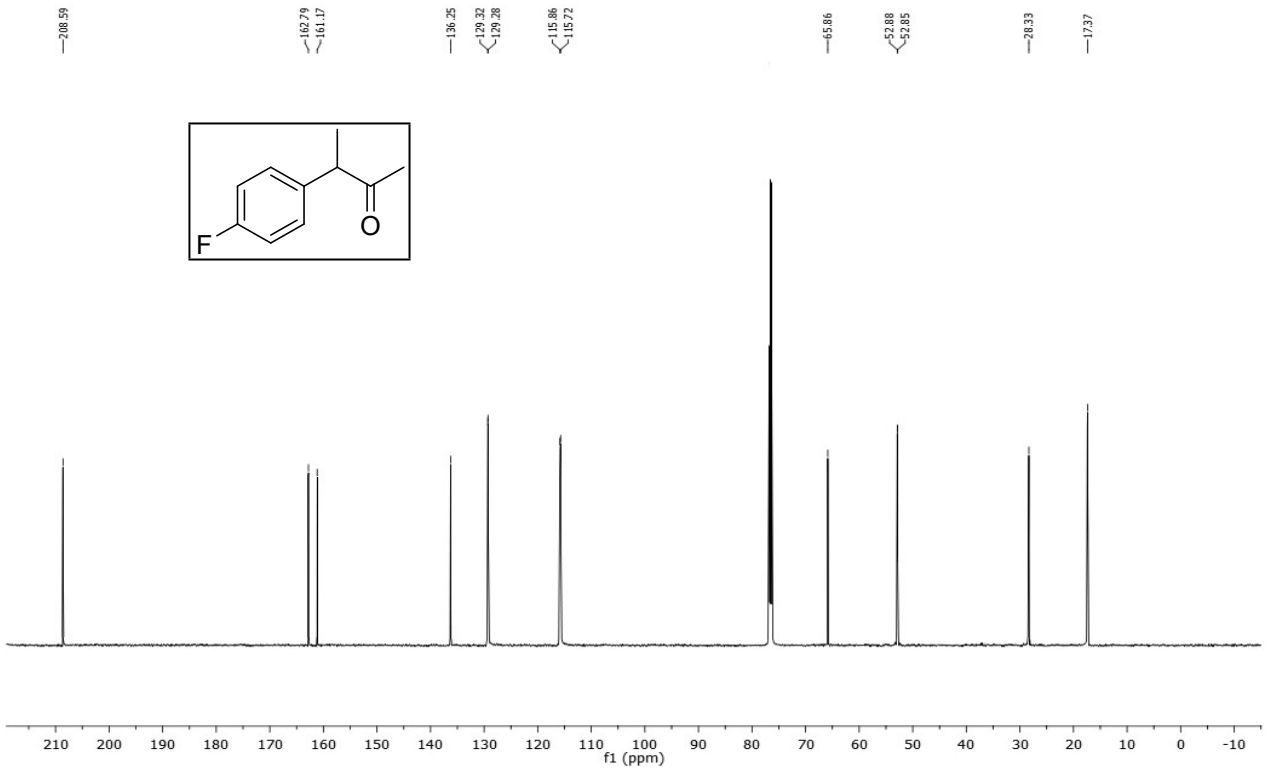
3-(2-Fluorophenyl)-6-methylhept-5-en-2-one (3k)

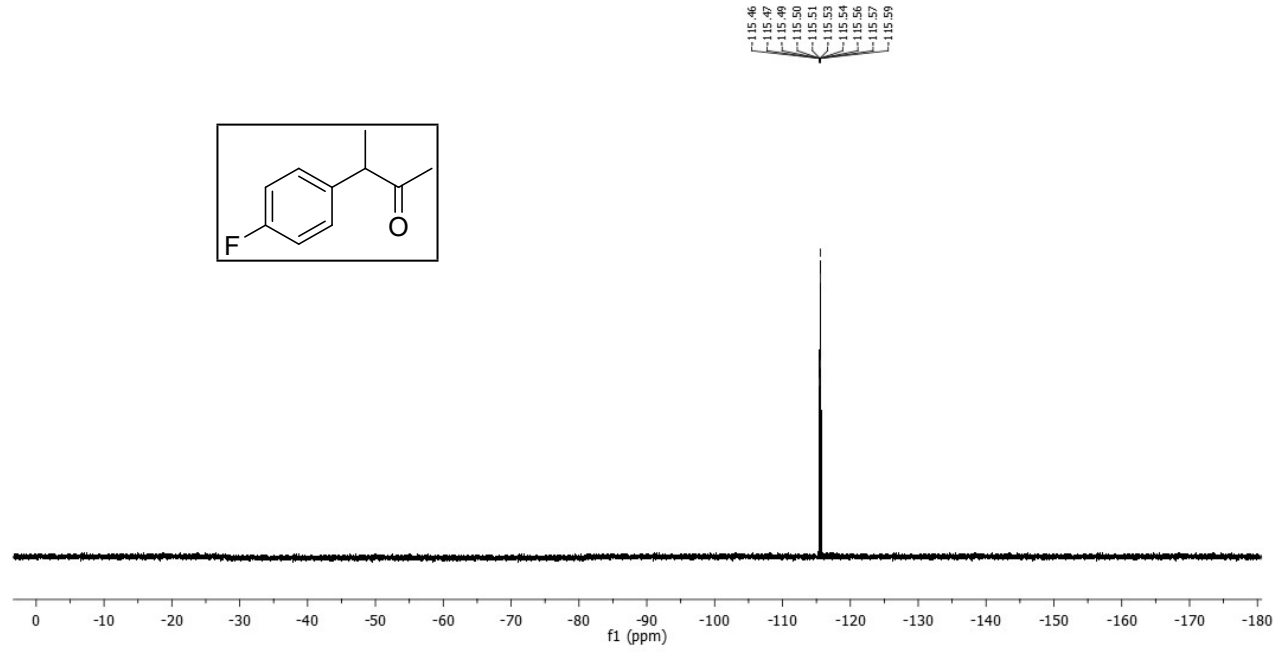




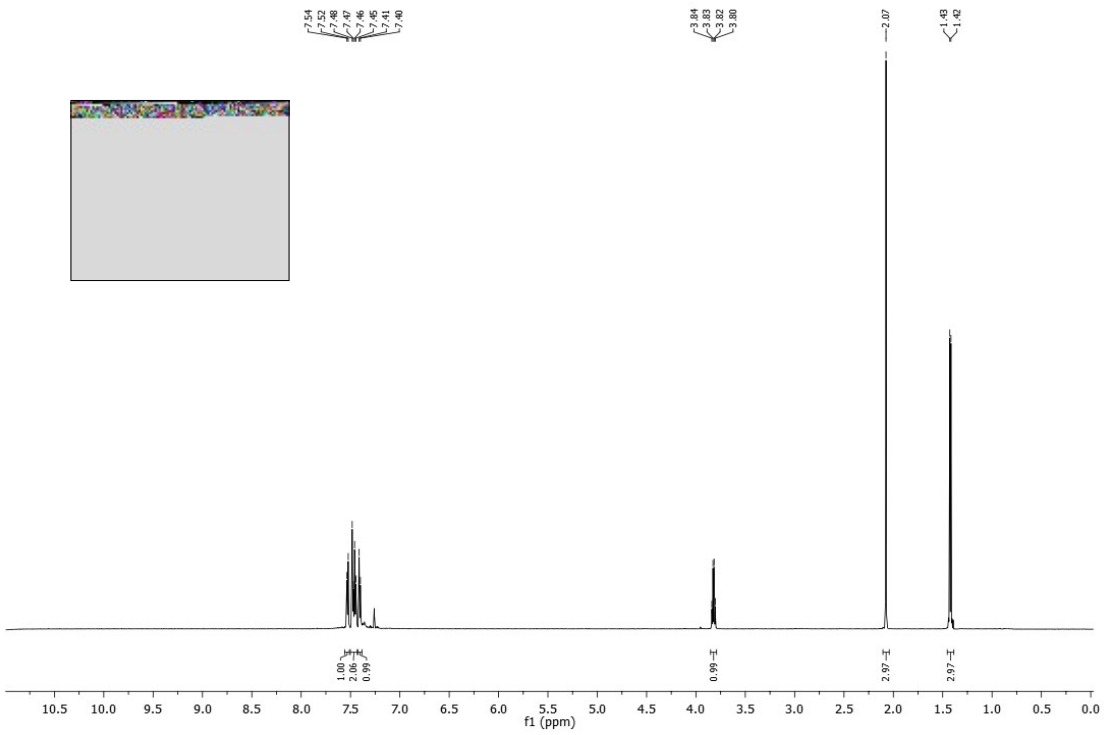
3-(4-Fluorophenyl)butan-2-one (3l)

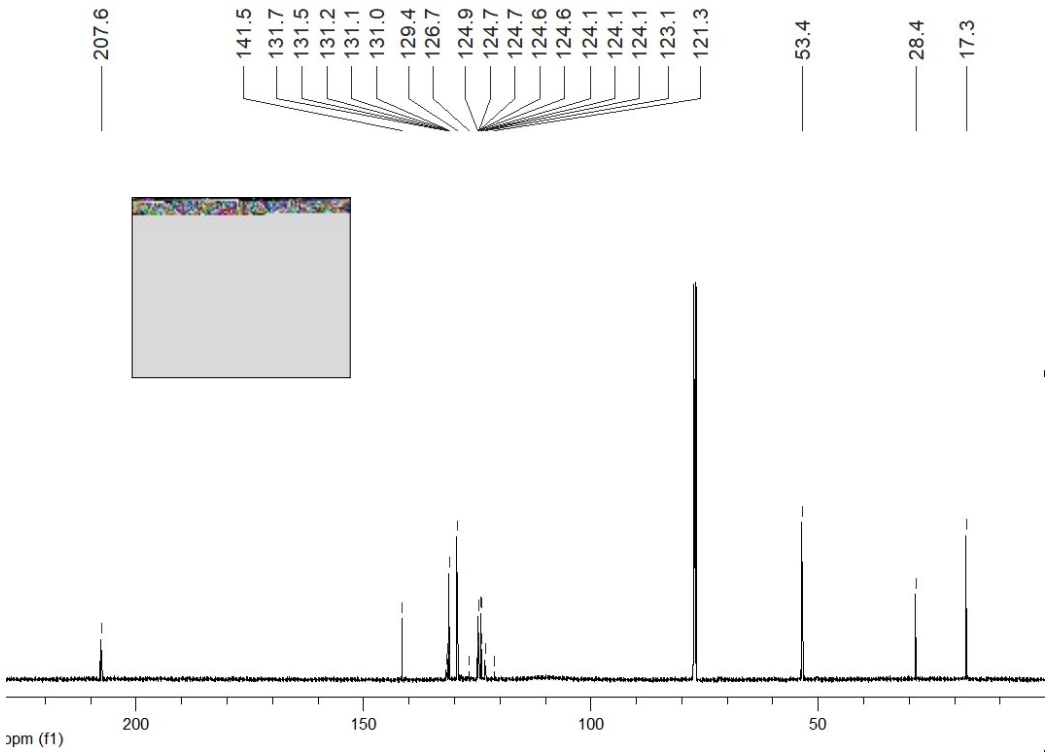



208.59
162.79
161.17
136.25
129.32
129.28
115.86
115.72
65.86
52.88
52.85
28.33
17.37
F
O
f1 (ppm)

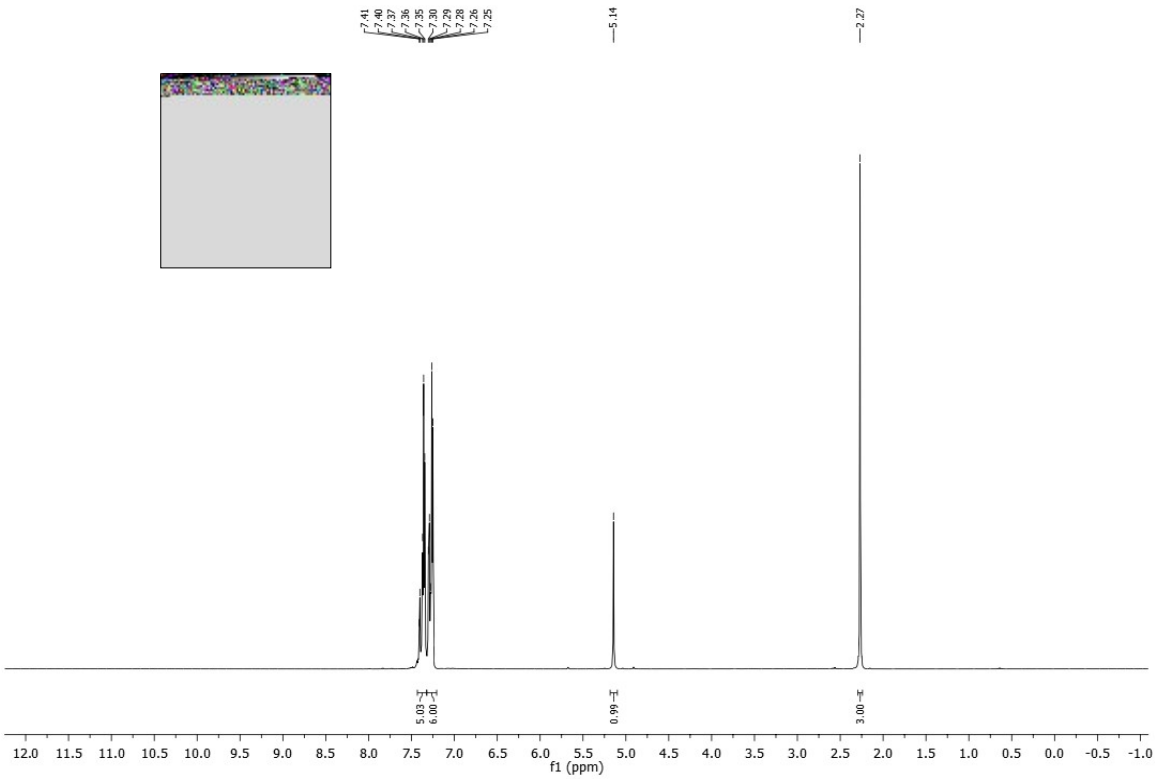

115.46
115.47
115.49
115.50
115.51
115.53
115.54
115.56
115.57
115.59
F
O
f1 (ppm)

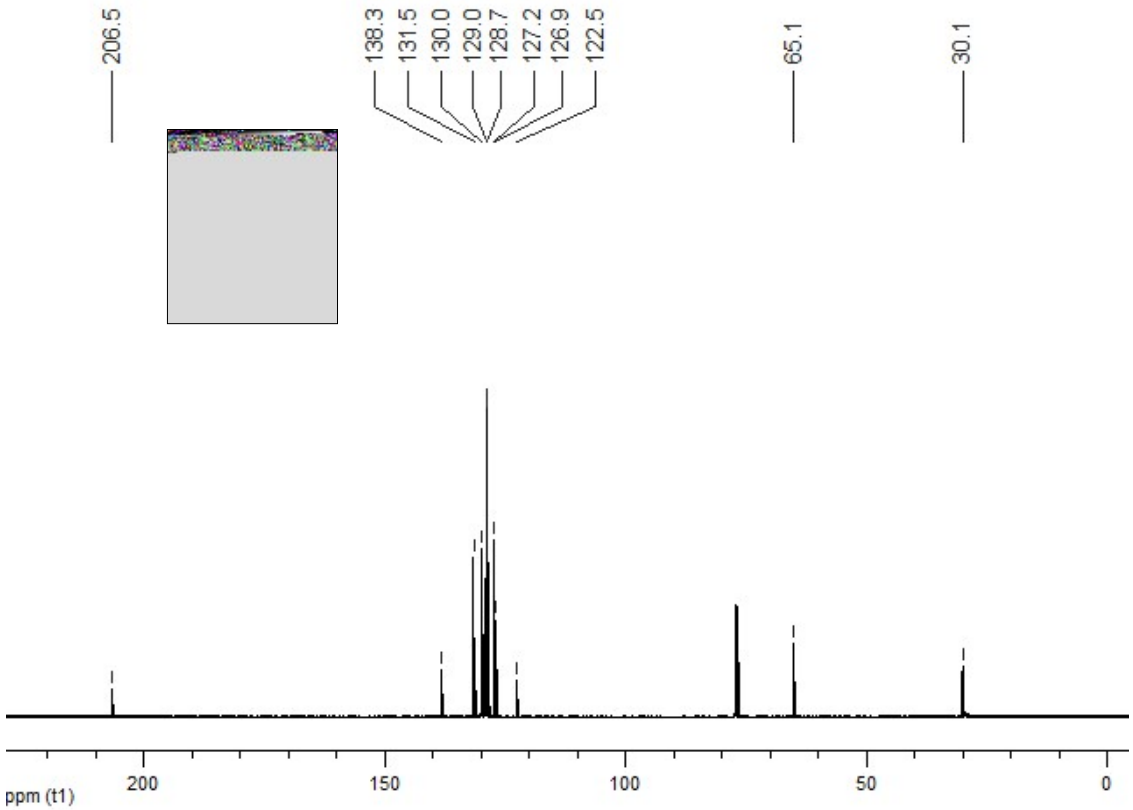
3-(3-(Trifluoromethyl)phenyl)butan-2-one (3m)



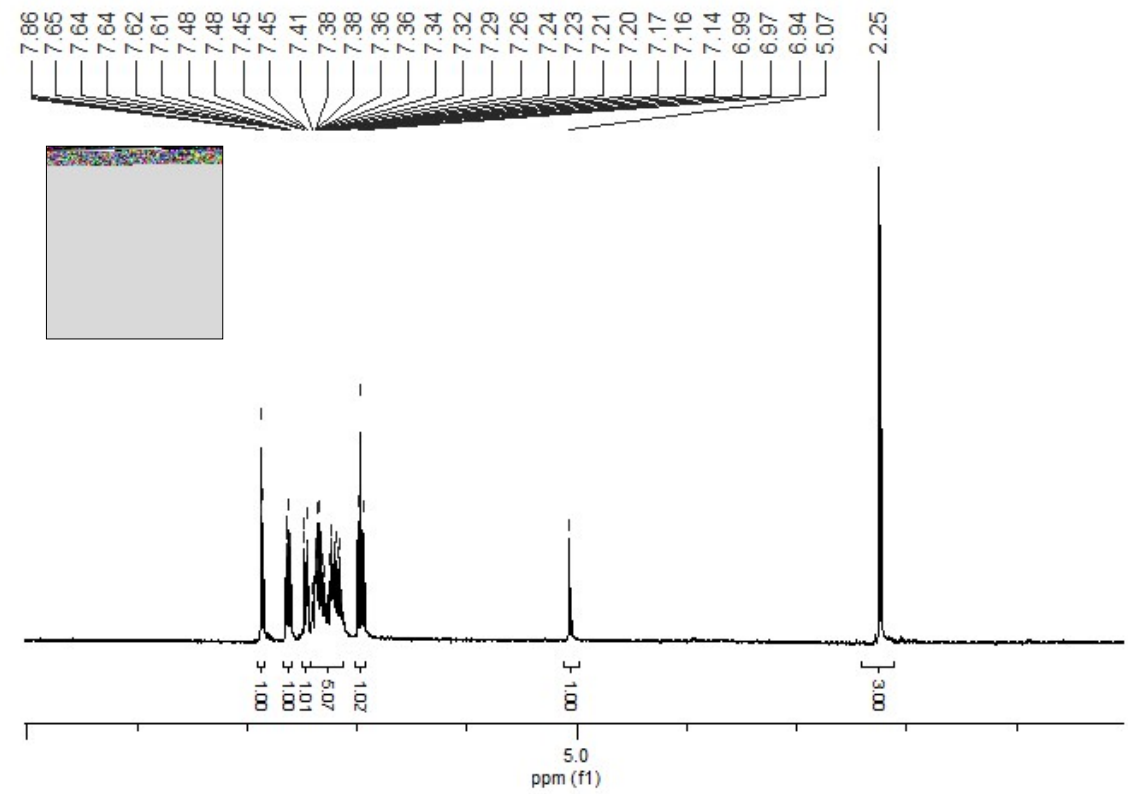


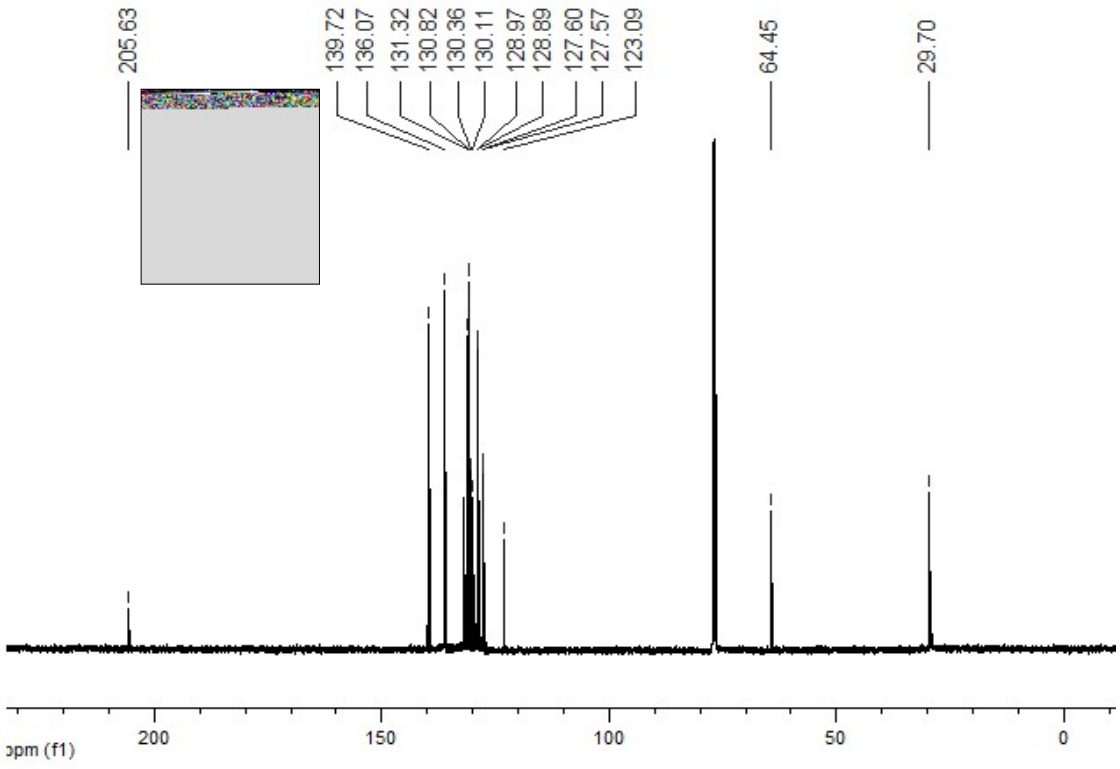
1,1-Diphenylpropan-2-one (3n)



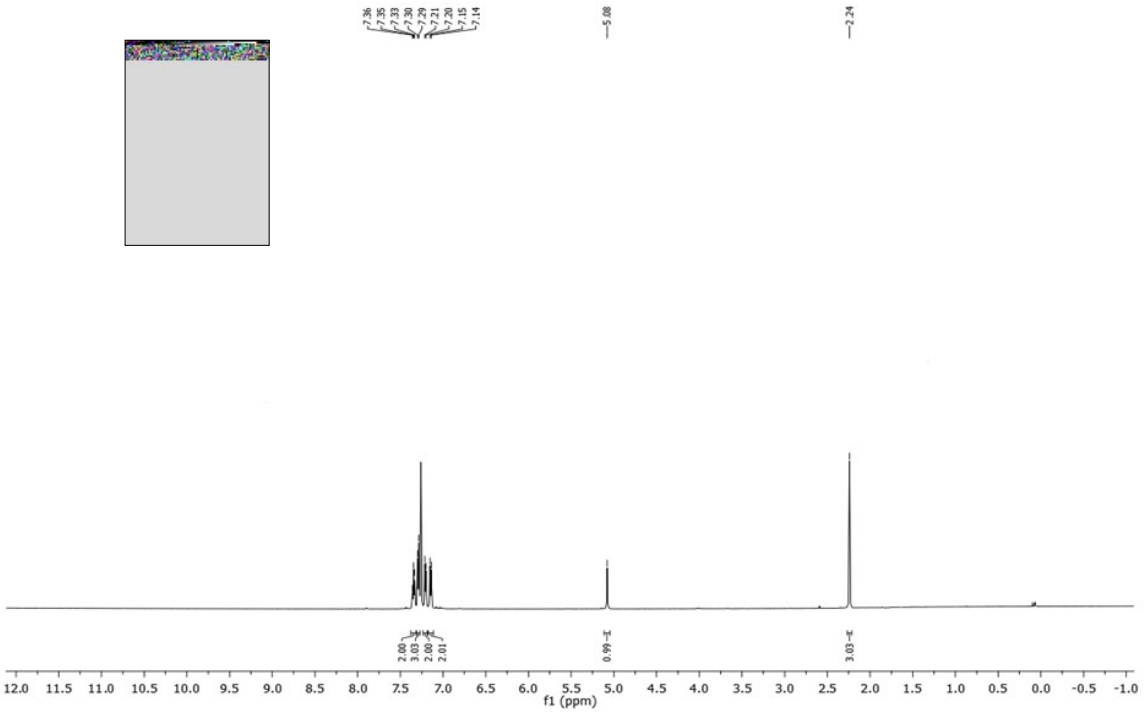


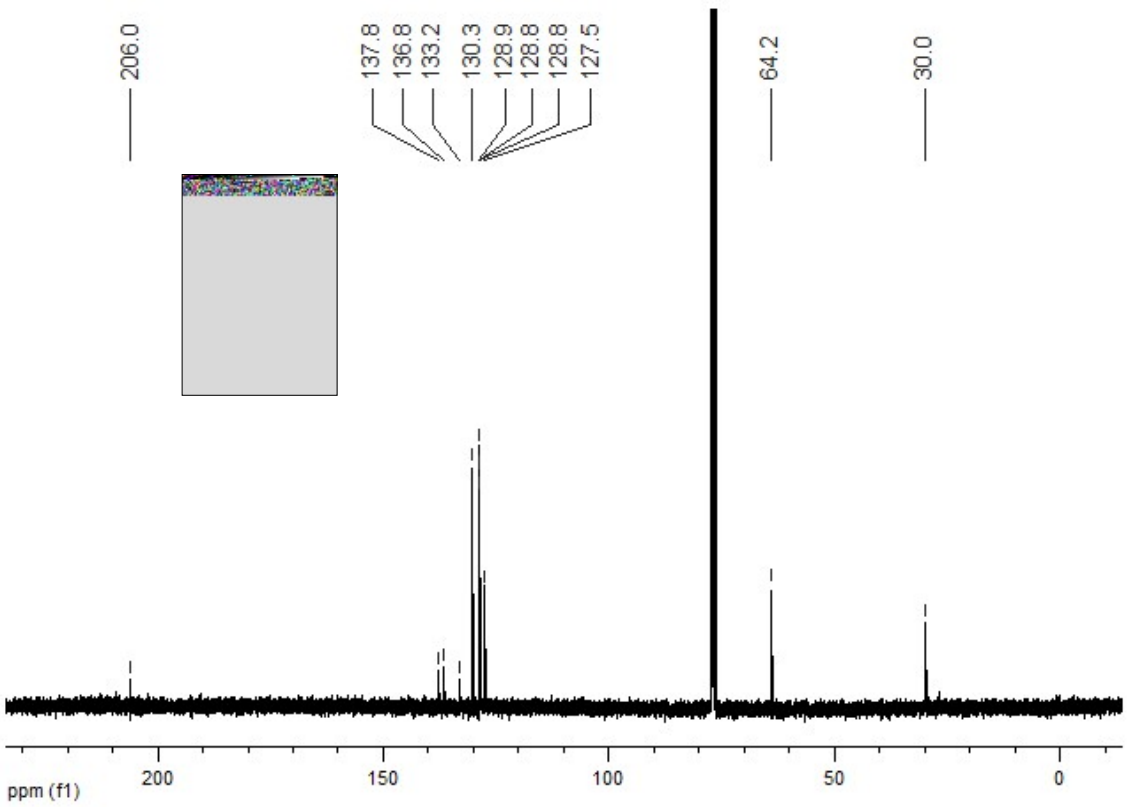
1-(3-Bromophenyl)-1-phenylpropan-2-one (3o)



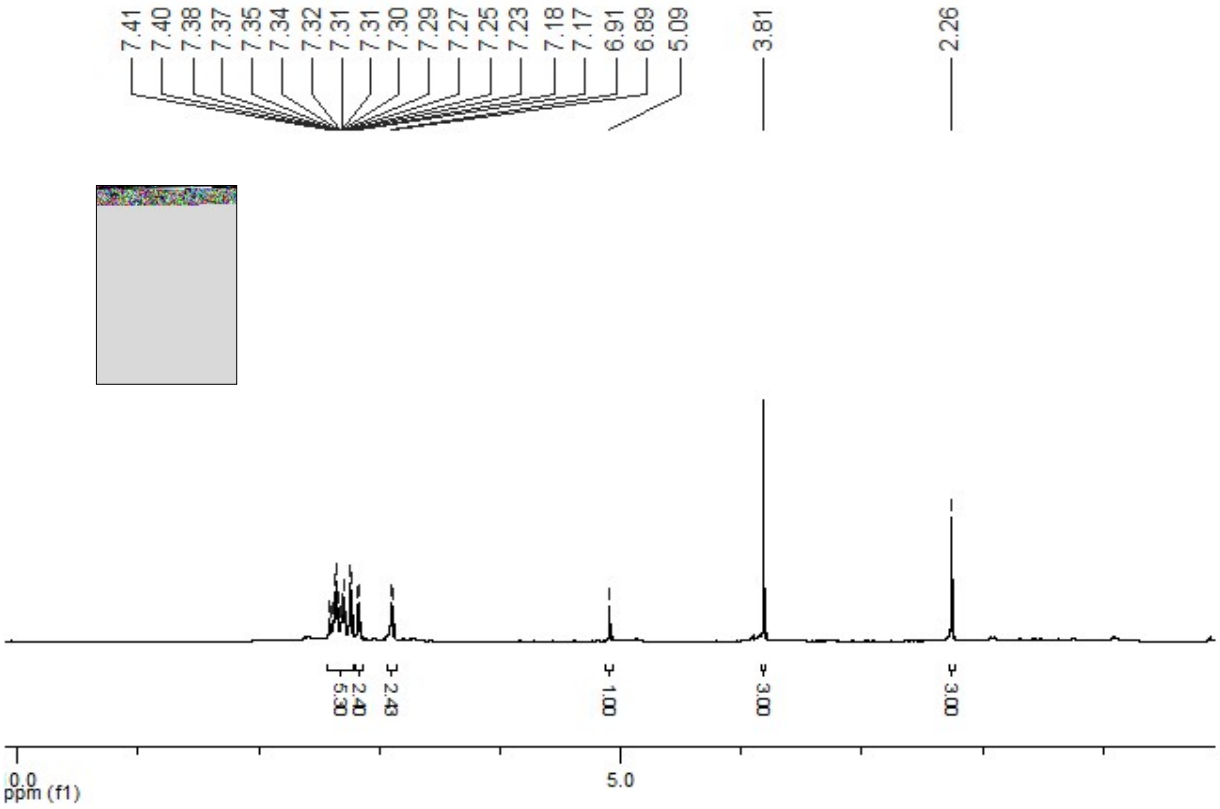


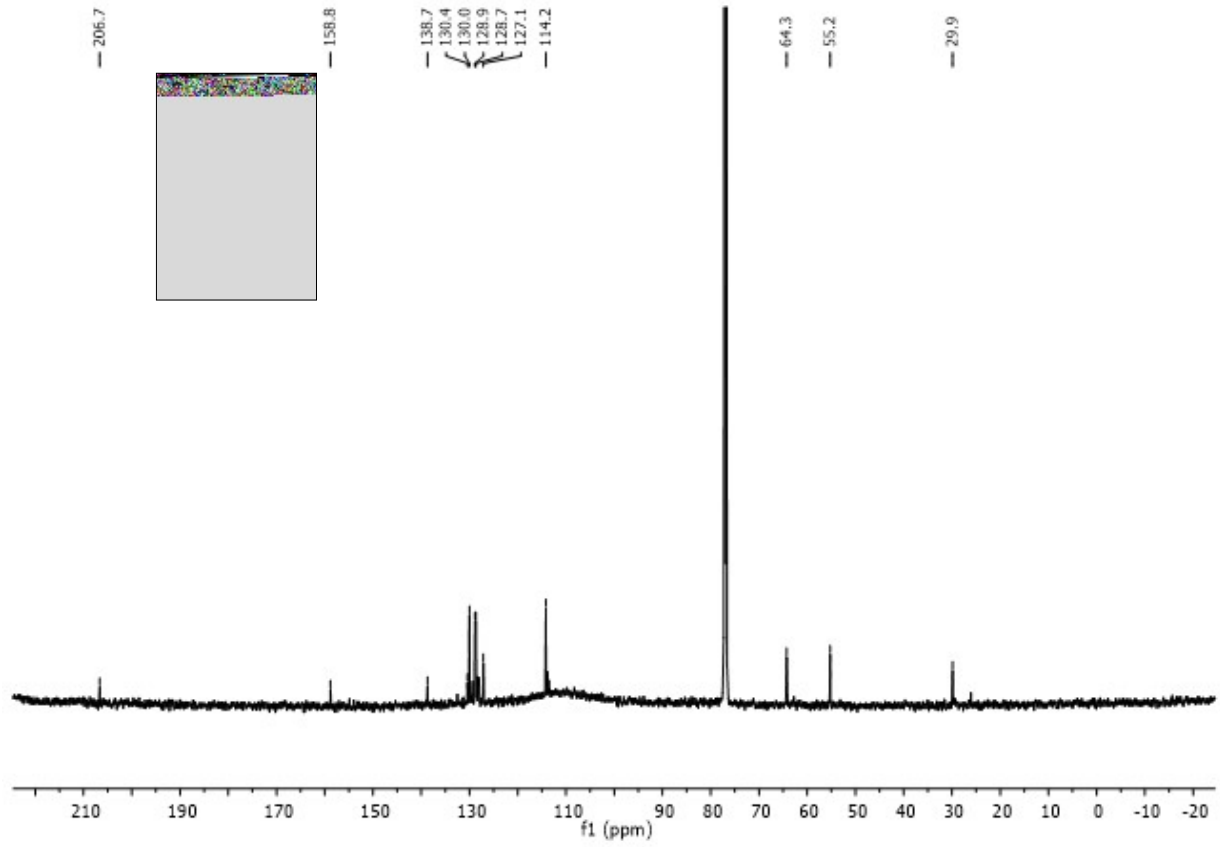
1-(4-chlorophenyl)-1-phenylpropan-2-one (3p)





1-(4-methoxyphenyl)-1-phenylpropan-2-one (3q)





1-(1-methyl-*1H*-indol-5-yl)-1-phenylpropan-2-one (3r)