Supported Palladium Nanoparticles Catalyzed *α*-Alkylation of Ketones using Alcohols as Alkylating Agents

C. Bal Reddy,[†,‡] Richa Bharti,[†,‡] Sandeep Kumar,[†,‡] Pralay Das[*,†,‡]

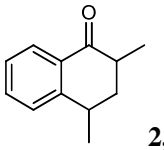
[†]Natural Product Chemistry & Process Development Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur 176061, HP, India

[‡]Academy of Scientific & Innovative Research, New Delhi 110025, India

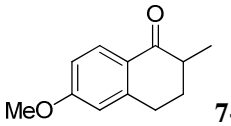
*Corresponding author: E-mail: pdas@ihbt.res.in, pdas_nbu@yahoo.com

CONTENTS

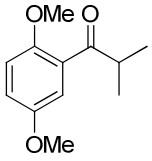
General procedure for alkylation of ketones with methanol



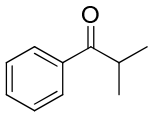
2,4-Dimethyl-3,4-dihydronaphthalen-1(2H)-one (3b); Prepared as described for **3a** starting from 4-methyltetralone (0.62 mmol), for 48 h, after workup, column chromatography (hexane) afforded **3b** (d.r = 51:49) as colourless liquid (81 mg) in 75% of yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.25-1.27 (m, 6H), 1.40-1.42 (m, 6H), 1.59-1.66 (m, 1H), 1.98-2.01 (m, 1H), 2.08-2.17 (m, 2H), 2.59-2.63 (m, 1H), 2.83-2.85 (m, 1H), 3.11-3.18 (m, 2H), 7.25-7.27 (m, 1H), 7.28-7.32 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.46-7.53 (m, 2H), 8.00 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 15.3, 15.6, 20.2, 21.6, 31.6, 33.0, 37.2, 37.8, 40.9, 42.8, 126.3, 126.4, 127.3, 127.4, 128.2, 131.2, 132.2, 133.2, 133.3, 148.2, 148.8, 200.8, 200.9; GC-MS m/z = 174.



7-Methoxy-2-methyl-3,4-dihydronaphthalen-1(2H)-one (3c): Prepared as described for **3a** starting from 7-methoxytetralone (0.57 mmol), for 48 h, after workup, column chromatography (hexane) afforded **3c** as colourless liquid (66 mg) in 61 % of yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.28 (d, *J* = 6.8 Hz, 3H), 1.86-1.90 (m, 1H), 2.17-2.22 (m, 1H), 2.55-2.60 (m, 1H), 2.93-2.98 (m, 2H), 3.85 (s, 3H), 7.03-7.07 (dd, *J* = 8.4 Hz, 1H), 7.14-7.17 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.4, 27.9, 31.6, 42.4, 55.4, 109.5, 121.3, 129.8, 133.2, 136.7, 158.3, 200.6; GC-MS m/z = 190.



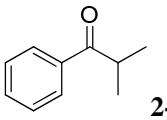
1-(2,5-Dimethoxyphenyl)-2-methylpropan-1-one (3d): Prepared as described for **3a** starting from 2,5-dimethoxyacetophenone (0.55 mmol), for 72 h, after workup, column chromatography (hexane) afforded **3d** as liquid (78 mg) in 68% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.14 (d, *J* = 6.8 Hz, 6H), 3.46-3.55 (m, 1H), 3.78 (s, 1H), 3.83 (s, 1H), 6.87-6.91 (m, 1H), 6.96-7.00 (m, 1H), 7.08 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 18.4, 39.9, 55.7, 56.1, 112.9, 114.3, 118.5, 129.4, 152.0, 153.5, 207.5; GC-MS m/z = 208.



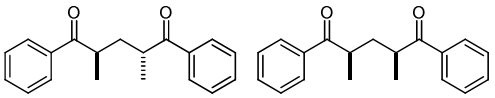
2-Methyl-1-phenylpropan-1-one (3e): Prepared as described for **3a** starting from acetophenone (0.68 mmol), for 36 h, after workup, column chromatography (hexane) afforded **3e** as liquid (61 mg) in 50% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.21-1.24 (m, 6H), 3.55-3.57 (m, 1H),

7.46-7.47 (m, 2H), 7.53-7.56 (m, 1H), 7.95-7.96 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 19.1, 35.7, 128.3, 128.5, 132.7, 136.2, 204.5; GC-MS m/z = 148.

2,4-Dimethyl-1,5-diphenylpentane-1,5-dione (3e'): Obtained in the reaction of 3e as another product 3e' (liquid, 28 mg) in 30% yield. Same as compound 3g'

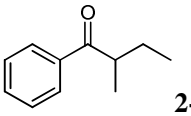


2-Methyl-1-phenylpropan-1-one (3g): Prepared as described for **3a** starting from propiophenone (0.37 mmol), for 48 h, after workup, column chromatography (hexane) afforded **3g** as liquid (30 mg) in 55% yield; NMR same as described for **3e**.

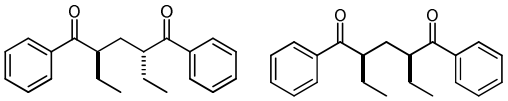


anti *syn*

2,4-Dimethyl-1,5-diphenylpentane-1,5-dione (3g')[5]: Obtained in the reaction of 3g as another product 3g' (liquid, 20 mg) in 40% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.16 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.48-1.50 (m, 1H), 2.00-2.02 (t, J = 7.0 Hz, 2H), 2.43-2.45 (m, 1H), 3.49-3.52 (m, 2H), 3.60-3.63 (m, 2H), 7.31-7.33 (t, *J* = 7.5 Hz, 4H), 7.44-7.47 (t, *J* = 7.2 Hz, 2H), 7.49-7.51 (t, *J* = 7.4 Hz, 4H), 7.57-7.59 (t, *J* = 7.2 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 4H), 8.04 (d, *J* = 7.7 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 17.5, 18.6, 36.9, 37.2, 38.0, 38.5, 128.1, 128.4, 128.5, 128.7, 132.8, 133.0, 136.2, 136.4, 203.7, 204.2.



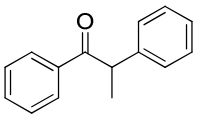
2-Methyl-1-phenylbutan-1-one (3f)[6]: Prepared as described for **3a** starting from butyrophenone (0.67 mmol), for 48 h, after workup, column chromatography (hexane) afforded **3f** as liquid (70 mg) in 65% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.90-0.92 (t, *J* = 7.4 Hz, 3H), 1.18-1.19 (d, *J* = 7 Hz, 3H), 1.46-1.51 (m, 1H), 1.81-1.85 (m, 1H), 3.38-3.41(m, 1H), 7.43-7.46 (t, *J* = 7.6 Hz, 2H), 7.52-7.54 (t, *J* = 7.4 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 11.6, 16.6, 26.5, 42.0, 128.1, 128.4, 128.5, 132.6, 136.7, 204.3.



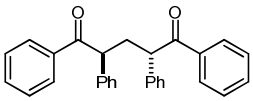
anti *syn*

2,4-Diethyl-1,5-diphenylpentane-1,5-dione (3f'): Obtained in the reaction of 3f as another product 3f' (liquid, 21 mg) in 20% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.79-0.81 (t, *J* = 7.4 Hz, 3H), 0.85-0.88 (t, *J* = 7.4 Hz, 3H), 1.15-1.18 (m, 1H), 1.51-1.54 (m, 2H), 1.64-1.66 (m, 1H), 1.71-1.77 (m, 2H), 2.05-2.08 (m, 1H), 2.30-2.32 (m, 1H), 3.30-3.32 (m, 1H), 3.44-3.46 (m, 1H), 7.26-7.28 (m, 2H), 7.41-7.43 (t, *J* = 7.4 Hz, 1H), 7.48-7.50 (t, *J* = 7.7 Hz, 2H), 7.56-7.58 (t, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 8.00 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 11.5, 11.7, 25.2, 27.0, 33.1, 33.3, 45.0, 45.3, 128.0, 128.3, 128.4, 128.7, 132.8,

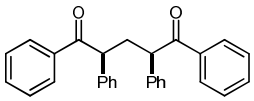
133.0, 137.2, 137.5, 203.7, 204.6; ESI-MS m/z calcd for $C_{21}H_{25}O_2$ $[M + H]^+$ 309.1855, found 309.1838.



1,2-Diphenylpropan-1-one (3h): Prepared as described for **3a** starting from 2-phenylacetophenone (0.51 mmol), for 48 h, after workup, column chromatography (hexane) afforded **3h** as liquid (66 mg) in 62% yield;^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.54 (d, *J* = 6.8 Hz, 3H), 4.68-4.72 (m, 1H), 7.20-7.22 (m, 1H), 7.30 (m, 4H), 7.37-7.46 (t, *J* = 7.7 Hz, 2H), 7.46-7.49 (t, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 19.4, 47.8, 126.8, 127.7, 128.4, 128.7, 128.9, 132.7, 136.4, 141.4, 200.2.

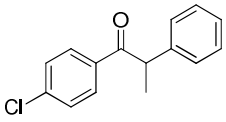


anti

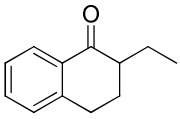


syn

1,2,4,5-Tetraphenylpentane-1,5-dione (3h'): Obtained in the reaction of 3h as another product 3h' (liquid, 32 mg) in 30% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.41-2.44 (m, 1H), 2.70-2.72 (t, *J* = 7.2 Hz, 2H), 2.98-3.00 (m, 1H), 4.51-4.53 (t, *J* = 7.5 Hz, 2H), 4.56-4.58 (t, *J* = 7.2 Hz, 2H), 7.17-7.18 (m, 4H), 7.19-7.21 (m, 2H), 7.23-7.25 (m, 5H), 7.28-7.31(m, 4H), 7.32-7.34 (m, 6H), 7.35-7.38 (m, 5H), 7.40-7.42 (m, 2H), 7.46-7.49 (m, 4H), 7.79 (d, *J* = 7.3 Hz, 4H), 7.89 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 37.7, 38.0, 50.9, 51.1, 127.2, 127.3, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 132.8, 132.9, 136.5, 136.6, 138.9, 139.1, 199.5, 199.6; ESI-MS m/z calcd for $C_{29}H_{25}O_2$ $[M + H]^+$ 405.1855, found 405.1837.

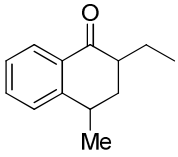


1-(4-Chlorophenyl)-2-phenylpropan-1-one (3i): Prepared as described for **3a** starting from 4-chloro-2-phenylacetophenone (0.43 mmol), for 48 h, after workup, column chromatography (hexane) afforded **3i** as liquid (63 mg) in 60% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.56 (d, *J* = 6.8 Hz, 3H), 4.68-4.75 (m, 1H), 7.21-7.25 (m, 1H), 7.31-7.32 (m, 3H), 7.38-7.43 (t, *J* = 7.7 Hz, 2H), 7.47-7.52 (m, 1H), 7.98 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 19.4, 47.8, 126.8, 127.7, 128.4, 128.7, 128.9, 132.7, 136.5, 141.4, 200.3.

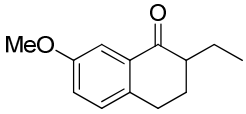


2-Ethyl-2,4-dihydronaphthalen-1(2H)-one (6a): Tetralone (0.34 mmol, 1 equiv.), KO^{t}Bu (1.02 mmol, 3 equiv.) and Pd@PS (229 mg, 3 mol%, 0.03 equiv.) were charged in a 30 mL reaction tube and ethanol (2.5 mL), toluene (0.5 mL) was added to it. The reaction tube was closed with the teflon screw cap and heated at 110 ^{o}C for 48 h under air (traces) present in the vial. The complition of the reaction was monitered by TLC, the reaction mixture was allow to cool to room

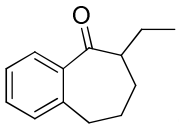
temperature and diluted with water 2 mL and extracted with EtOAc. The crude was concentrated under vacuum and purified by column chromatography on silica gel (hxane) affording the desired product **6a** as liquid (48 mg) in 82 % of yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.99-1.01 (t, *J* = 7.4 Hz, 3H), 1.55-1.61 (m, 2H), 1.87-2.00 (m, 2H), 2.22-2.25 (m, 1H), 2.39-2.42 (m, 1H), 2.98-3.01 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.28-7.30 (t, *J* = 7.5 Hz, 1H), 7.43-7.46 (m, 1H), 8.02 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 11.4, 22.4, 27.7, 28.3, 48.9, 126.5, 127.4, 128.6, 132.6, 133.0, 143.9, 200.2; GC-MS m/z = 174.



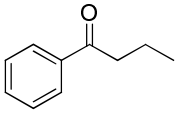
2-Ethyl-4-methyl-3,4-dihydronaphthalen-1(2H)-one (6b): Prepared as described for **3a** starting from 4-methyltetralone (0.62 mmol) for 48 h, after workup, column chromatography (hexane/ethylacetate = 98/2) afforded **6b** (d.r = 51:49) as colourless liquid (85 mg) in 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.99-1.04 (m, 6H), 1.41-1.47 (m, 6H), 1.53-1.67 (m, 3H), 1.93-2.14 (m, 4H), 2.16-2.23 (m, 1H), 2.43-2.47 (m, 1H), 2.61-2.65 (m, 1H), 3.07-3.19 (m, 2H), 7.28-7.35 (m, 3H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.47-7.53 (m, 2H), 8.01-8.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.1, 11.4, 20.2, 21.4, 22.5, 22.7, 31.1, 33.1, 34.6, 37.5, 44.3, 49.2, 126.2, 126.3, 126.4, 127.3, 127.9, 131.6, 132.7, 133.1, 133.2, 148.0, 148.5, 200.1, 200.2; GC-MS m/z = 188.



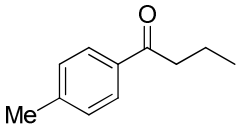
2-Ethyl-7-methoxy-3,4-dihydronaphthalen-1(2H)-one (6c): Prepared as described for **3a** starting from 7-methoxytetralone (0.56 mmol) for 48 h, after workup, column chromatography (hexane: ethylacetate = 95:5) afforded **6c** as liquid (69 mg) in 60% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.24-1.26 (m, 5H), 1.82-1.88 (m, 1H), 2.13-2.20 (m, 1H), 2.50-2.56 (m, 1H), 2.93-2.99 (m, 2H), 3.84 (s, 3H), 6.67 (s, 1H), 6.79-6.83 (dd, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.5, 29.1, 29.6, 31.4, 42.2, 55.3, 112.5, 113.0, 126.1, 129.8, 146.4, 163.3, 199.4.



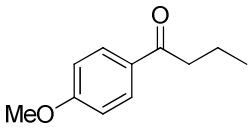
6-Ethyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (6d): Prepared as described for **3a** starting from benzoseburone (0.62 mmol) for 36 h, after workup, column chromatography (hexane: ethylacetate = 98:2) afforded **6d** as liquid (83 mg) in 71% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88-0.92 (m, 3H), 1.50-1.75 (m, 3H), 1.86-2.18 (m, 3H), 2.77-2.79 (m,1H), 2.93-2.98 (m, 2H), 7.20-7.23 (t, *J* = 6.6 Hz, 1H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.35-7.38 (t, *J* = 6.4 Hz, 1H), 7.63 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.8, 24.1, 25.3, 30.0, 33.6, 51.5, 126.3, 127.9, 129.7, 131.0, 140.4, 141.7, 207.8; GC-MS m/z = 188.



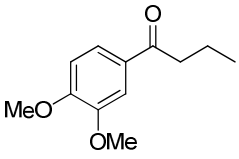
1-Phenylbutan-1-one (6e): Prepared as described for **3a** starting from acetophenone (0.82 mmol), after workup for 48 h, column chromatography (hexane) afforded **6e** as liquid (89 mg) in 73% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.99-1.02 (t, *J* = 7.4 Hz, 3H), 1.76-1.79 (m, 2H), 2.93-2.96 (t, *J* = 7.3 Hz, 2H), 7.44-7.47 (t, *J* = 7.5 Hz, 2H), 7.53-7.56 (t, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 13.8, 17.7, 40.4, 128.0, 128.5, 132.8, 137.1, 200.3; GC-MS m/z = 148.



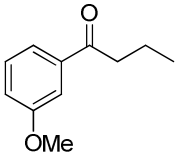
1-(*p*-Tolyl)butan-1-one (6f): Prepared as described for **3a** starting from 4-methylacetophenone (0.74 mmol) for 48 h, after workup, column chromatography (hexane) afforded **6f** as liquid (79 mg) in 66% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.99-1.01 (t, *J* = 7.4 Hz, 3H), 1.74-1.78 (m, 2H), 2.41 (s, 3H), 2.91-2.93 (t, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 13.8, 17.8, 21.5, 40.4, 128.1, 129.2, 134.6, 143.5, 200.1; GC-MS m/z = 162.



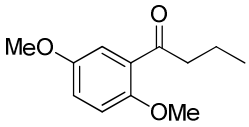
1-(4-Methoxyphenyl)butan-1-one (6g): Prepared as described for **3a** starting from 4-methoxyacetophenone (0.66 mmol) for 48 h, after workup, column chromatography (hexane) afforded **6g** as liquid (83 mg) in 70 yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.97-1.01 (t, *J* = 7.4 Hz, 3H), 1.78-1.79 (m, 2H), 2.86-2.91 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 6.91-6.94 (dd, *J* = 7.0 Hz, 2H), 7.93-7.95 (dd, *J* = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.8, 17.9, 40.1, 55.3, 113.5, 130.2, 163.2, 198.9.



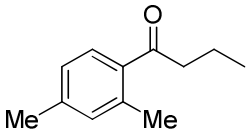
1-(3,4-Dimethoxyphenyl)butan-1-one (6h): Prepared as described for **3a** starting from 3,4-dimethoxyacetophenone (0.55 mmol) for 48 h, after workup, column chromatography (hexane) afforded **6h** as liquid (77 mg) in 68% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.97-0.99 (t, *J* = 7.3 Hz, 3H), 1.73-1.76 (m, 2H), 2.87-2.90 (t, *J* = 7.0 Hz, 2H), 3.92 (s, 6H), 6.86 (d, *J* = 8.2 Hz, 1H), 7.52 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 13.8, 18.0, 39.9, 55.9, 109.9, 110.1, 122.6, 130.3, 148.9, 153.0, 199.0; GC-MS m/z = 208.



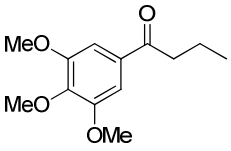
1-(3-methoxyphenyl)butan-1-one (6i): Prepared as described for **3a** starting from 3-methoxy acetophenone (0.66 mmol) for 48 h, after workup, column chromatography (hexane) afforded **6i** as liquid (89 mg) in 77% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.99-1.01 (t, *J* = 7.4 Hz, 3H), 1.74-1.78 (m, 2H), 2.92-2.94 (t, *J* = 7.3 Hz, 2H), 3.85 (s, 3H), 7.08-7.10 (dd, *J* = 8.2 Hz, 1H), 7.35-7.37 (t, *J* = 7.9 Hz, 1H), 7.49 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.8, 17.8, 40.6, 55.4, 112.3, 119.2, 120.6, 129.4, 138.5, 159.8, 200.2.



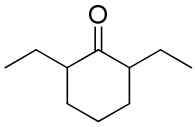
1-(2,5-Dimethoxyphenyl)butan-1-one (6j): Prepared as described for **3a** starting from 2,5-dimethoxyacetophenone (0.55 mmol) for 72 h, after workup, column chromatography (hexane) afforded **6j** as liquid (96 mg) in 82% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.94-0.96 (t, *J* = 7.4 Hz, 3H), 1.67-1.71 (m, 1H), 2.92-2.95 (t, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.84 (s, 3H), 6.88 (d, *J* = 8.9 Hz, 1H), 6.97-6.99 (m, 1H), 7.20 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 13.8, 17.7, 45.6, 55.7, 56.0, 113.0, 113.8, 119.4, 128.9, 152.8, 153.4, 202.6.



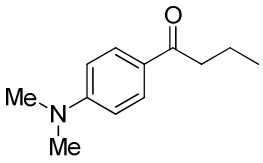
1-(2,4-Dimethylphenyl)butan-1-one (6k): Prepared as described for **3a** starting from 2,4-dimethylacetophenone (0.33 mmol) for 48 h, after workup, column chromatography (hexane) afforded **3k** as liquid (44 mg) in 76% yield;^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.97-0.99 (t, *J* = 7.4 Hz, 3H), 1.69-1.74 (m, 2H), 2.35 (s, 3H), 2.48 (s, 3H), 2.84-2.87 (t, *J* = 7.1 Hz, 2H), 7.05 (bs, 2H), 7.56 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 13.8, 18.0, 21.3, 21.4, 43.2, 126.2, 128.8, 132.8, 135.3, 138.3, 141.5, 204.1; GC-MS m/z = 176.



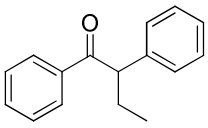
1-(3,4,5-Trimethoxyphenyl)butan-1-one (6l): Prepared as described for **3a** starting from 3,4,5-trimethoxy acetophenone (0.23 mmol) for 48 h, after workup, column chromatography (hexane) afforded **6l** as liquid (26 mg) in 50% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.99-1.01 (t, *J* = 7.4 Hz, 3H), 1.74-1.78 (m, 2H), 2.89-2.92 (t, *J* = 7.3 Hz, 2H), 3.90 (s, 3H), 3.91 (s, 6H), 7.92 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.8, 17.8, 40.2, 56.2, 60.8, 105.5, 132.4, 142.3, 153.0, 199.1; GC-MS m/z = 238.



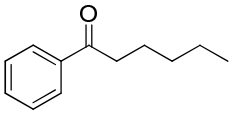
2,6-Diethylcyclohexanone (6m): Prepared as described for **3a** starting from cyclohexanone (1 mmol) for 48 h, after workup, column chromatography (hexane) afforded **6m** as colourless liquid (60 mg) in 39% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.82-0.85 (m, 6H), 1.14-1.17 (m, 2H), 1.22-1.24 (m, 3H), 1.69-1.77 (m, 4H), 2.11-2.15 (m, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.7, 22.0, 25.5, 35.0, 52.7, 213.9; GC-MS m/z = 154.



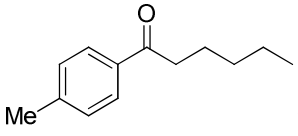
1-(4-(Dimethylamino)phenyl)butan-1-one (6n): Prepared as described for **3a** starting from 1-(4-(dimethylamino)phenyl)butan-1-one (0.30 mmol), for 48h, after workup, column chromatography (hexane) afforded **6n** as liquid (44 mg) in 76% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.98-1.00 (t, *J* = 7.2 Hz, 3H), 1.73-1.76 (m, 2H), 2.83-2.85 (t, *J* = 7.2 Hz, 2H), 3.04 (s, 6H), 6.64 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 13.9, 18.3, 39.8, 39.9, 110.5, 125.1, 130.1, 153.2, 198.6; ESI-MS m/z calcd for $C_{12}H_{18}NO$ $[M + H]^{+}$192.1388, found 192.1366.



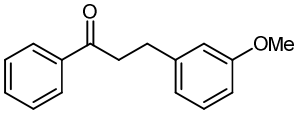
1,2-Diphenylbutan-1-one (6o): Prepared as described for **3a** starting from 1,2-diphenylbutan-1-one (0.51 mmol), after workup, column chromatography (hexane) afforded **6o** as liquid (87 mg) in 78% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.91-0.93 (t, *J* = 7.4 Hz, 3H), 1.85-1.90 (m, 1H), 2.19-2.24 (m, 1H), 4.44-4.17 (t, *J* = 7.2 Hz, 1H), 7.19-7.22 (m, 1H), 7.26-7.33 (m, 4H), 7.38-7.40 (t, *J* = 7.7 Hz, 2H), 7.47-7.49 (t, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 12.2, 27.1, 55.4, 126.9, 128.2, 128.4, 128.6, 128.8, 132.7, 137.0, 139.6, 200.0.



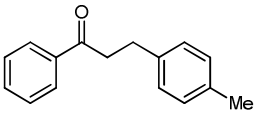
1-Phenylhexan-1-one (9a): Prepared as described for **3a** starting from acetophenone (0.42 mmol), for 24 h, after workup, column chromatography (hexane) afforded **9a** as colour less liquid (58 mg) in 79% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.90-0.92 (t, *J* = 7.0 Hz, 3H), 1.35-1.38 (m, 4H), 1.72-1.75 (m, 2H), 2.94-2.97 (t, *J* = 7.4 Hz, 2H), 7.43-7.46 (t, *J* = 7.6 Hz, 2H), 7.52-7.55 (t, *J* = 7.3 Hz, 1H), 7.95 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 13.8, 22.4, 24.0, 31.5, 38.5, 128.0, 128.4, 132.7, 137.1, 200.5; GC-MS m/z = 176.



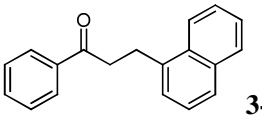
1-(*p*-Tolyl)hexan-1-one (9b): Prepared as described for **3a** starting from 4-methylacetophenone (0.37 mmol), for 24 h, after workup, column chromatography (hexane) afforded **9b** as colourless liquid (60 mg) in 86% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.90-0.92 (t, *J* = 6.8 Hz, 3H), 1.36-1.37 (m, 4H), 1.72-1.74 (m, 2H), 2.41 (s, 3H), 2.92-2.94 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 13.9, 21.5, 22.5, 24.1, 31.5, 38.4, 128.1, 129.1, 134.6, 143.5, 200.2; GC-MS m/z = 190.



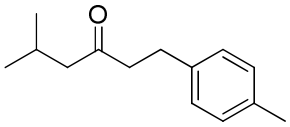
3-(3-Methoxyphenyl)-1-phenylpropan-1-one (9c): Prepared as described for **3a** starting from acetophenone (0.42 mmol), 3-methoxybenzylalcohol (1.25 mmol), toluene (2 mL) for 24 h, after workup, column chromatography (hexane/ethylacetate = 98/2) afforded **9c** as liquid (78 mg) in 78% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 3.04-3.07 (t, *J* = 7.7 Hz, 2H), 3.29-3.32 (t, *J* = 7.7 Hz, 2H), 3.80 (s, 3H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.81 (s, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 7.21-7.24 (t, *J* = 7.8 Hz, 1H), 7.45-7.47 (m, 2H), 7.55-7.57 (t, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 30.1, 40.3, 55.1, 111.4, 114.2, 120.7, 128.0, 128.5, 129.4, 133.0, 136.8, 142.9, 159.7, 199.1; GC-MS m/z = 240.



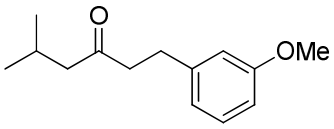
1-Phenyl-3-(p-tolyl)propan-1-one (9d): Prepared as described for **3a** starting from acetophenone (0.42 mmol), 4-methylbenzylalcohol (1.25 mmol), toluene (2 mL) for 24 h, after workup, column chromatography (hexane/ethylacetate = 98/2) afforded **9d** as colour less liquid (71 mg) in 75% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.33 (s, 3H), 3.03-3.06 (t, *J* = 7.7 Hz, 2H), 3.28-3.30 (t, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.45-7.47 (t, *J* = 7.7 Hz, 2H), 7.55-7.57 (t, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 20.9, 29.7, 40.5, 128.0, 128.2, 128.5, 129.1, 132.9, 135.5, 136.8, 138.1, 199.3; GC-MS m/z = 224.



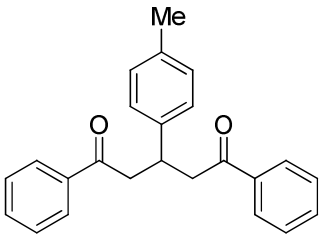
3-(Naphthalen-1-yl)-1-phenylpropan-1-one(9e): Prepared as described for **3a** starting from acetophenone (0.42 mmol), 1-napthalenemethanol (1.25 mmol), toluene (2 mL) for 24 h, after workup, column chromatography (hexane/ethylacetate = 98/2) afforded **9e** as colour less liquid (89 mg) in 82% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 3.43-3.47 (m, 2H), 3.55-3.57 (m, 2H), 7.42-7.46 (m, 4H), 7.49-7.57 (m, 3H), 7.75-7.76 (m, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 7.3 Hz, 2H), 8.07 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 27.1, 39.7, 123.4, 125.5, 125.6, 126.0, 126.1, 126.9, 128.0, 128.5, 128.8, 131.6, 133.0, 133.9, 136.8, 137.3, 199.2; GC-MS m/z = 260.



5-Methyl-1-(p-tolyl)hexan-3-one (9f): Prepared as described for **3a** starting from 4-methylpentan-2-one (1 mmol), 4-methylbenzylalcohol (3 mmol), toluene (3 mL), for 36 h, after workup, column chromatography (hexane/ethylacetate = 98/2) afforded **9f** as colour less liquid (90 mg) in 44% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.92 (d, *J* = 6.6 Hz, 6H), 2.16 (m, 1H), 2.29 (d, *J* = 7 Hz, 2H), 2.34 (s, 3H), 2.70-2.72 (t, *J* = 7.9 Hz, 2H), 2.87-2.89 (t, *J* = 7.9 Hz, 2H), 7.09-7.12 (m, 4H), ^{13}C NMR (150 MHz, $CDCl_3$) δ = 20.9, 22.6, 24.5, 29.3, 44.9, 52.0, 128.1, 129.1, 135.5, 138.0, 210.0.

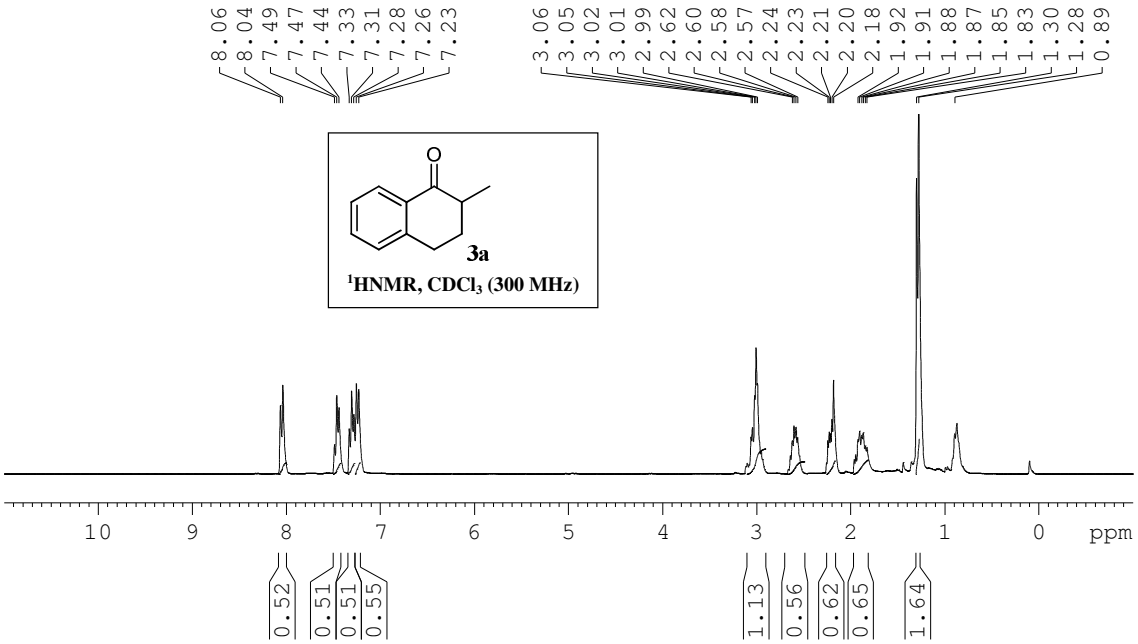


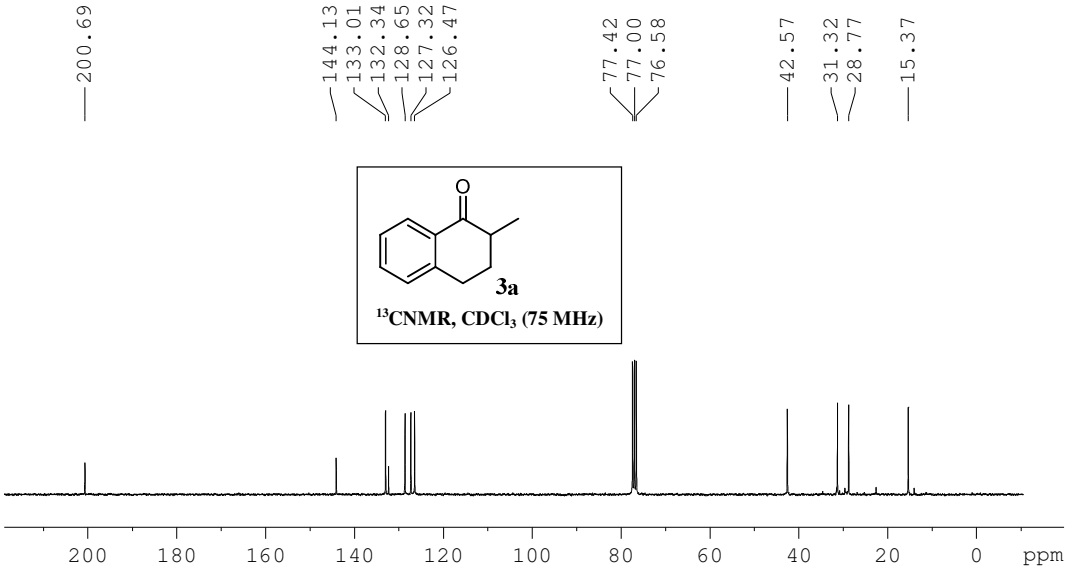
1-(3-Methoxyphenyl)-5-methylhexan-3-one (9g): Prepared as described for **3a** starting from 4-methylpentan-2-one (1 mmol), 3-methoxylbenzylalcohol (3 mmol), toluene (3 mL), for 36 h, after workup, column chromatography (hexane/ethylacetate = 98/2) afforded **9f** as colour less liquid (98 mg) in 46% yield;^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.89 (d, *J* = 6.6 Hz, 6H), 2.12 (m, 1H), 2.26 (d, *J* = 7.0 Hz, 2H), 2.68-2.71 (t, *J* = 7.6 Hz, 2H), 2.85-2.87 (t, *J* = 7.6 Hz, 2H), 3.78 (s, 3H), 6.72-6.73 (m, 2H), 6.76 (d, *J* = 7.4 Hz, 1H), 7.19 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 22.6, 24.5, 29.7, 44.6, 52.0, 55.1, 111.3, 114.0, 120.6, 129.4, 142.8, 159.6, 209.8.

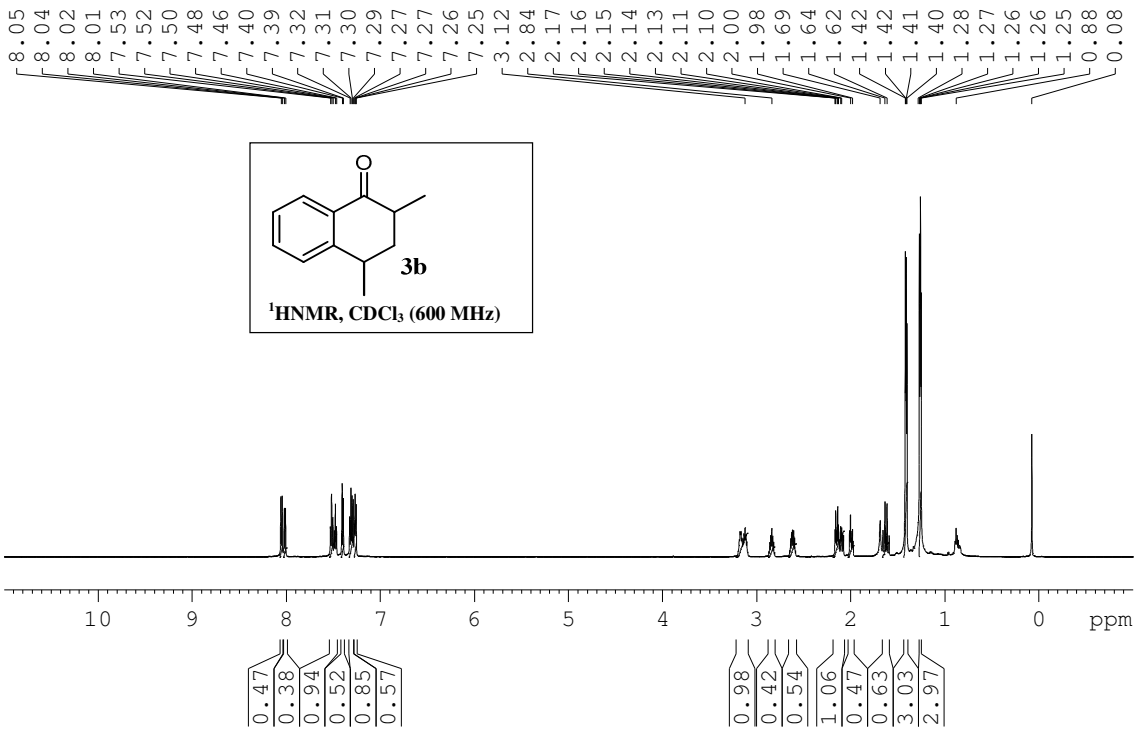


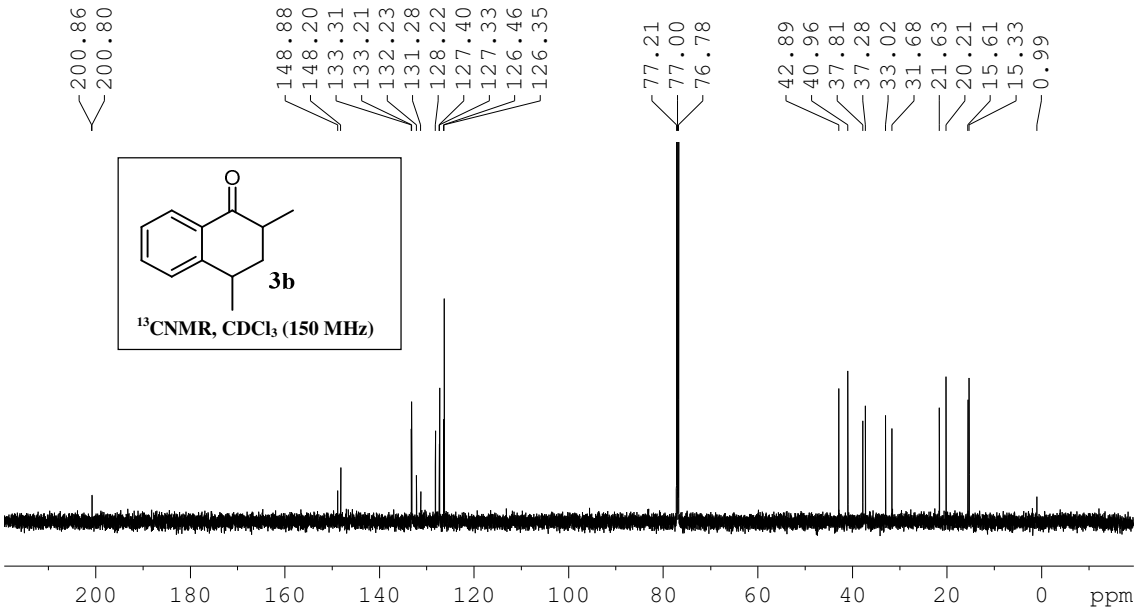
1,5-diphenyl-3-(p-tolyl)pentane-1,5-dione (9da): Compound was obtained as semi solid in the reaction of acetophenone (0.42 mmol, 1 equiv.), 4-methylbenzyl alcohol (1.28 mmol, 3 equiv.), KOtBu (3 equiv.) and Pd@PS (3 mol%) in toluene (2 ml) at 110 ^{o}C for 24 h. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.29 (s, 3H), 3.32-3.36 (dd, *J* = 7.1 Hz, *J* = 16.0 Hz, 2H), 3.46-3.50 (dd, *J* = 7.0 Hz, *J* = 16.0 Hz, 2H), 4.03-4.05 (m, 1H), 7.08 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.43-7.36 (t, *J* = 7.7 Hz, 4H), 7.53-7.56 (t, *J* = 7.4 Hz, 2H), 7.95 (d, *J* = 7.6 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 20.9, 36.8, 45.0, 127.2, 128.1, 128.5, 129.2, 132.9, 136.1, 136.9, 140.7, 198.6.

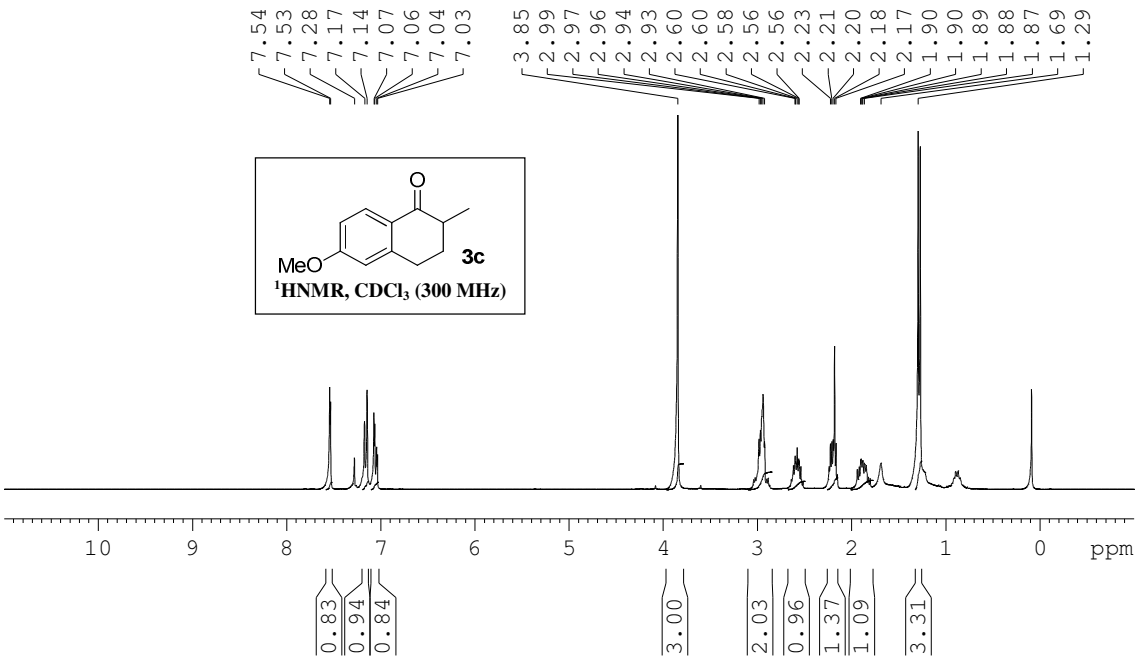
^{1}H, ^{13}C NMR and GC-MS spectra for syntheised compounds

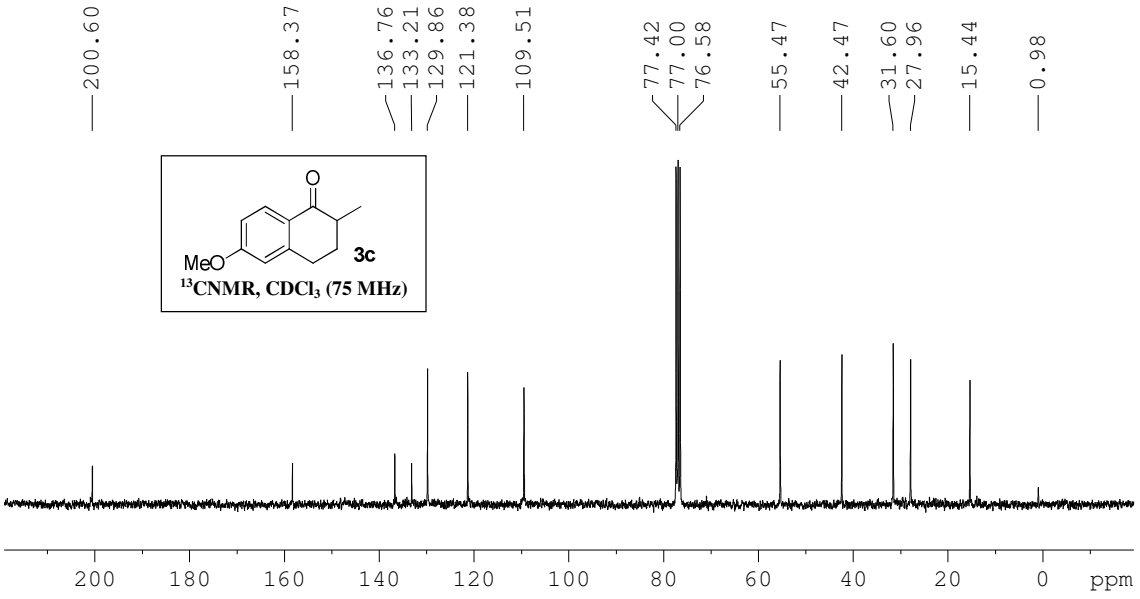


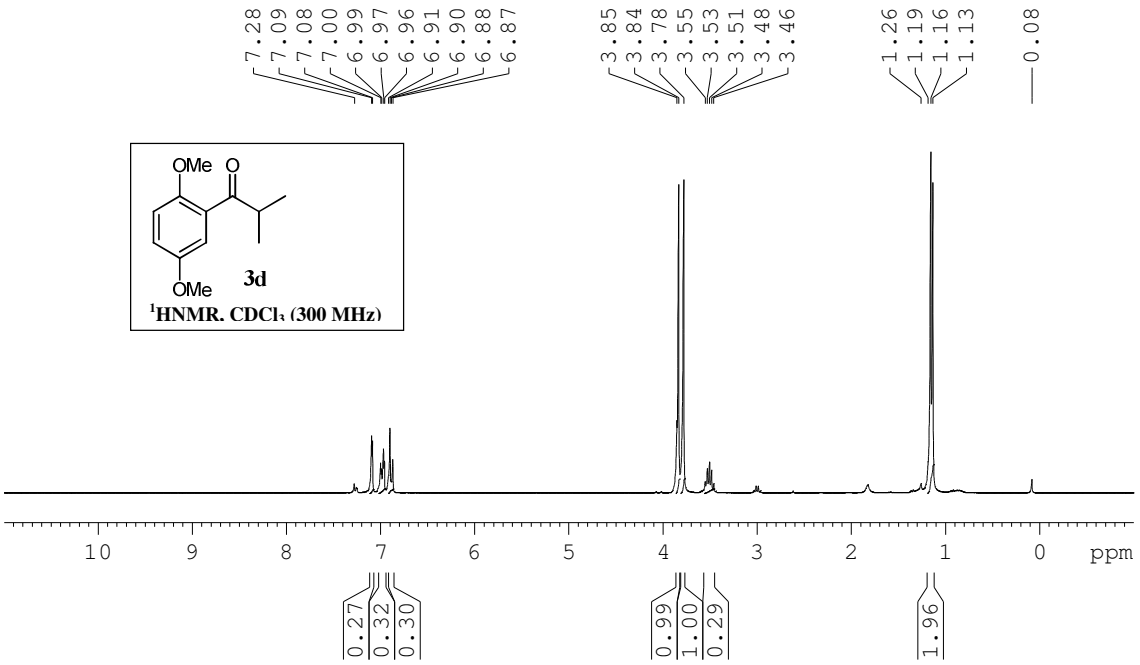


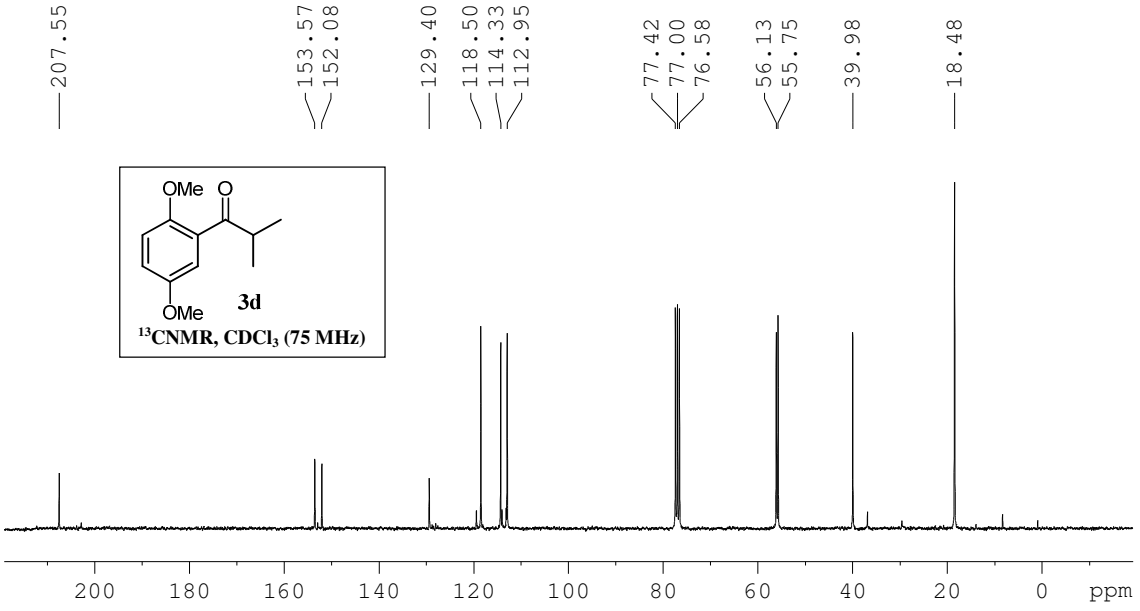

8.05 8.04 8.02 8.01 7.53 7.52 7.50 7.48 7.46 7.40 7.39 7.32 7.31 7.30 7.29 7.27 7.27 7.26 7.25
3.12 2.84 2.17 2.16 2.15 2.14 2.13 2.11 2.10 2.00 1.98 1.69 1.64 1.62 1.42 1.42 1.41 1.40 1.28 1.27 1.26 1.26 1.25 0.88 0.08
O
3b
¹HNMR, CDCl₃ (600 MHz)
10 9 8 7 6 5 4 3 2 1 0 ppm
0.47 0.38 0.94 0.52 0.85 0.57
0.98 0.42 0.54 1.06 0.47 0.63 3.03 2.97

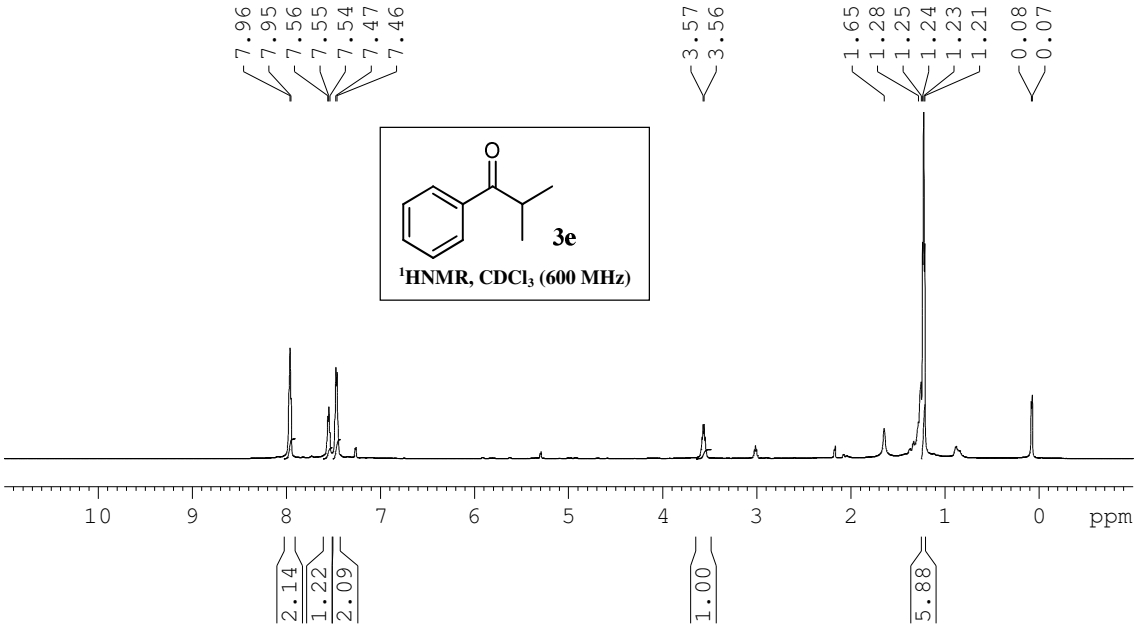

200.86 200.80
148.88 148.20 133.31 133.21 132.23 131.28 128.22 127.40 127.33 126.46 126.35
77.21 77.00 76.78
42.89 40.96 37.81 37.28 33.02 31.68 21.63 20.21 15.61 15.33 0.99
O
3b
¹³CNMR, CDCl₃ (150 MHz)
200 180 160 140 120 100 80 60 40 20 0 ppm

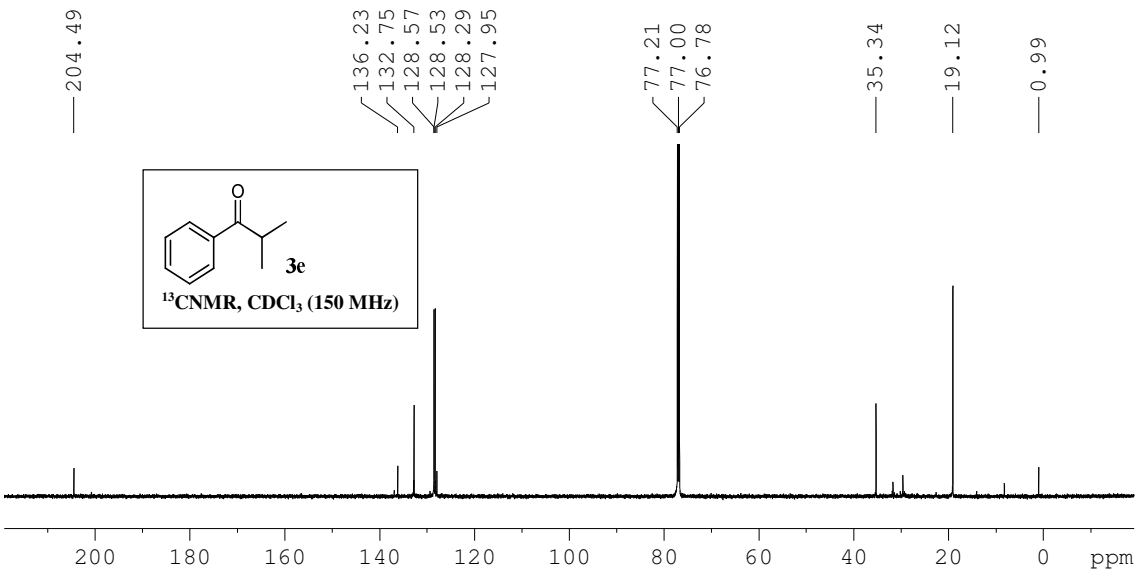

7.54
7.53
7.28
7.17
7.14
7.07
7.06
7.04
7.03
3.85
2.99
2.97
2.96
2.94
2.93
2.60
2.60
2.58
2.56
2.56
2.23
2.21
2.20
2.18
2.17
1.90
1.90
1.89
1.88
1.87
1.69
1.29
MeO
3c
1HNMR, CDCl3 (300 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.83
0.94
0.84
3.00
2.03
0.96
1.37
1.09
3.31

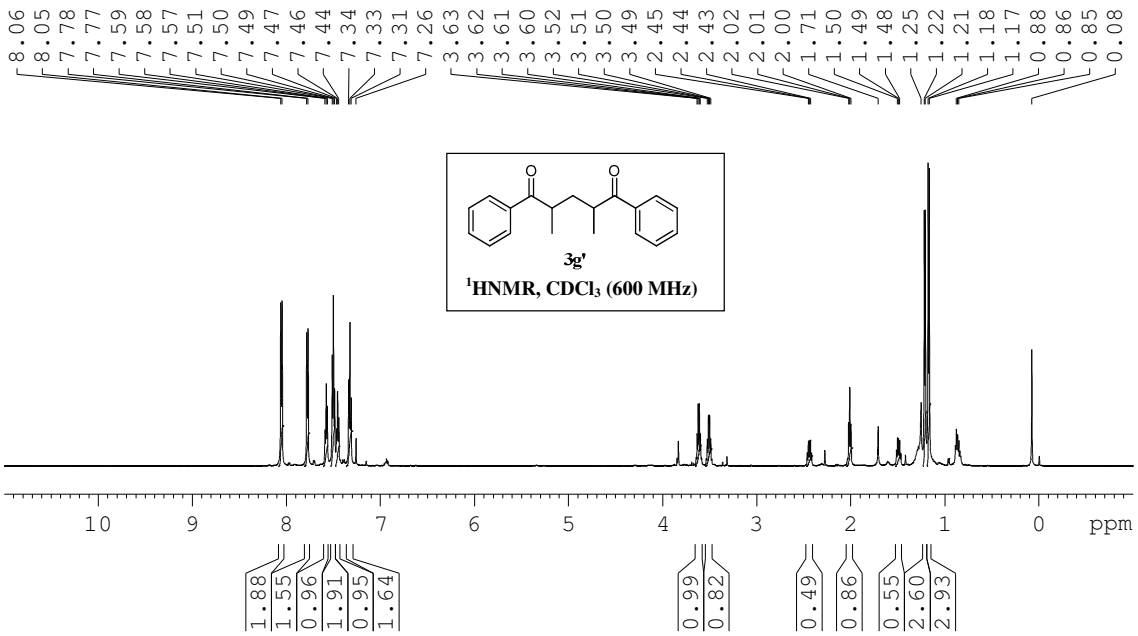

200.60
158.37
136.76
133.21
129.86
121.38
109.51
77.42
77.00
76.58
55.47
42.47
31.60
27.96
15.44
0.98
MeO
3c
13CNMR, CDCl3 (75 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

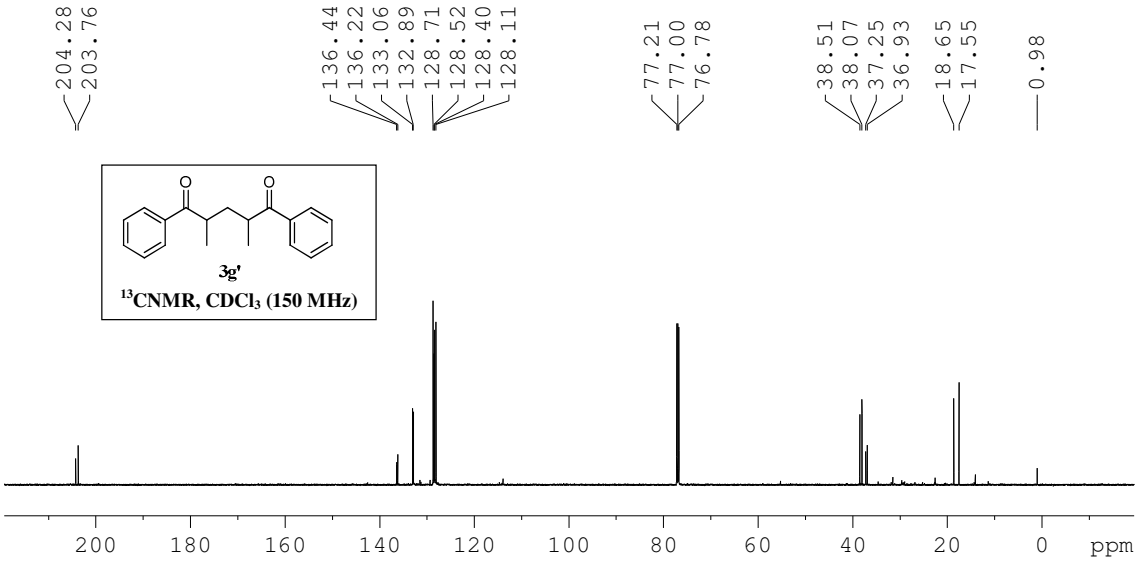

7.28
7.09
7.08
7.00
6.99
6.97
6.96
6.91
6.90
6.88
6.87
3.85
3.84
3.78
3.55
3.53
3.51
3.48
3.46
1.26
1.19
1.16
1.13
0.08
OMe
O
OMe
3d
¹HNMR. CDCl₃ (300 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.27
0.32
0.30
0.99
1.00
0.29
1.96

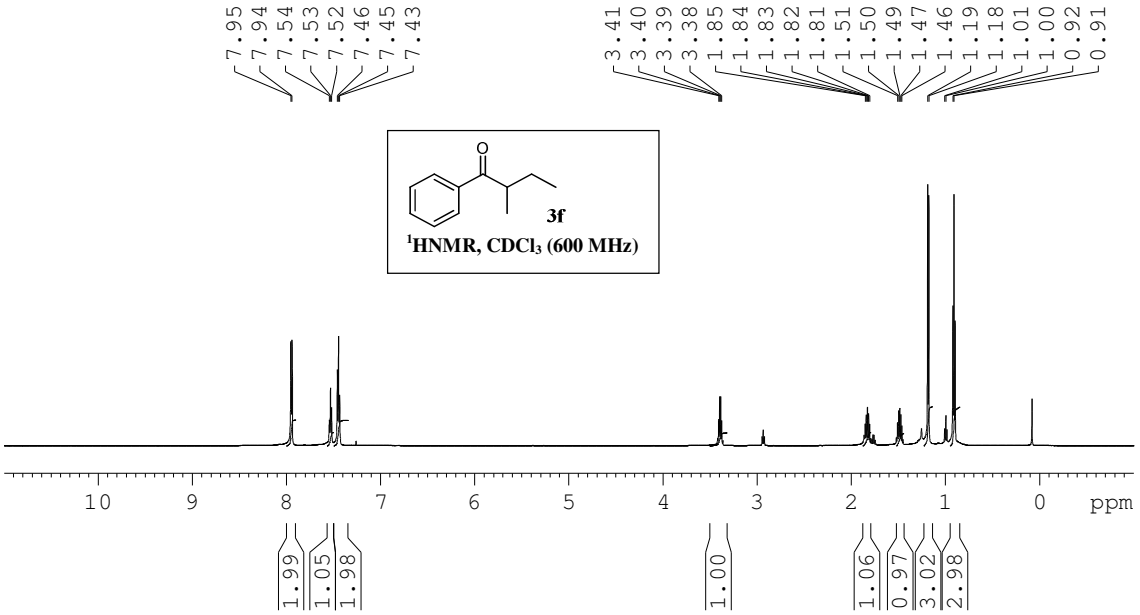

207.55
153.57
152.08
129.40
118.50
114.33
112.95
77.42
77.00
76.58
56.13
55.75
39.98
18.48
OMe
O
OMe
3d
¹³CNMR, CDCl₃ (75 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

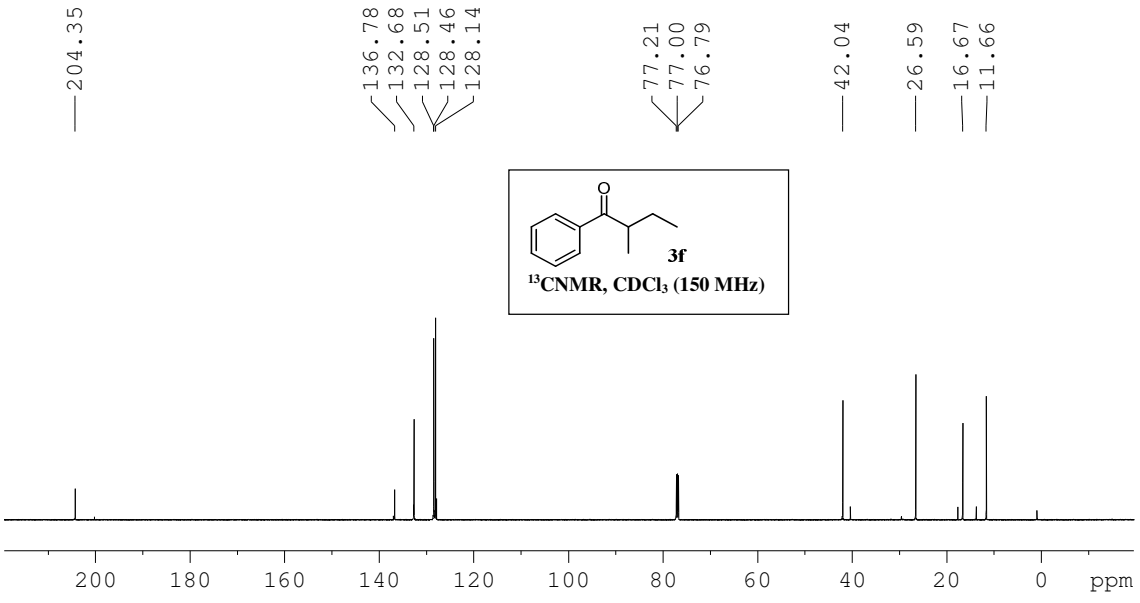

7.96
7.95
7.56
7.55
7.54
7.47
7.46
3.57
3.56
1.65
1.28
1.25
1.24
1.23
1.21
0.08
0.07
3e
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.14
1.22
2.09
1.00
5.88

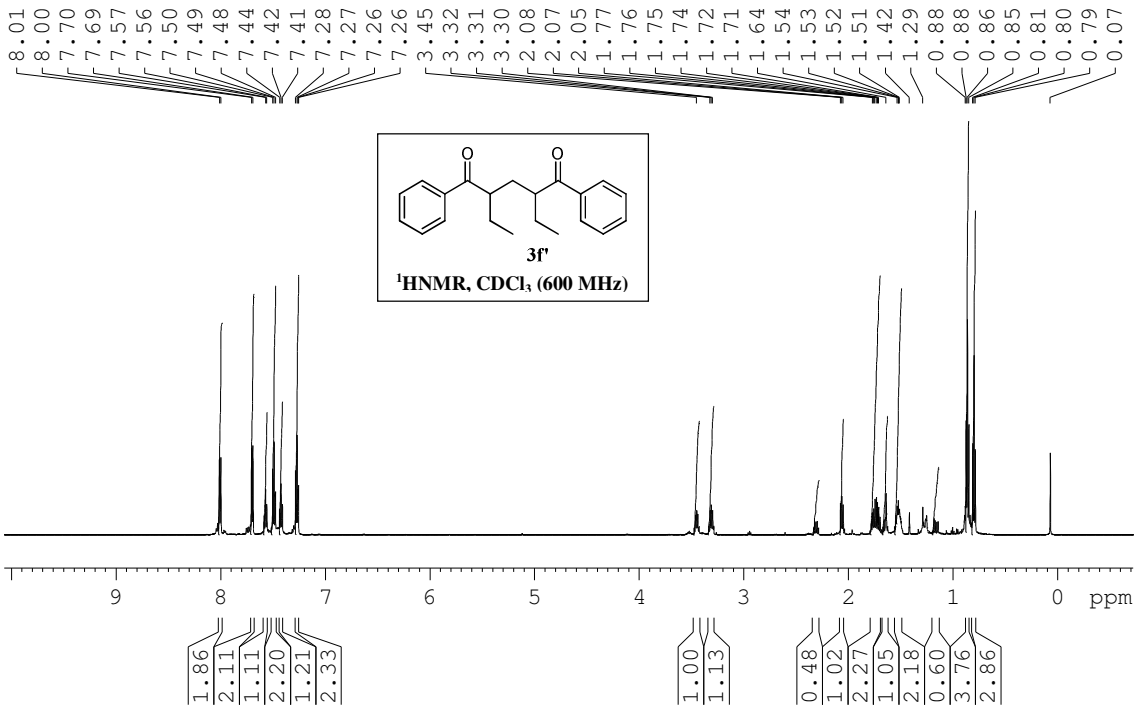

204.49
136.23
132.75
128.57
128.53
128.29
127.95
77.21
77.00
76.78
35.34
19.12
0.99
3e
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

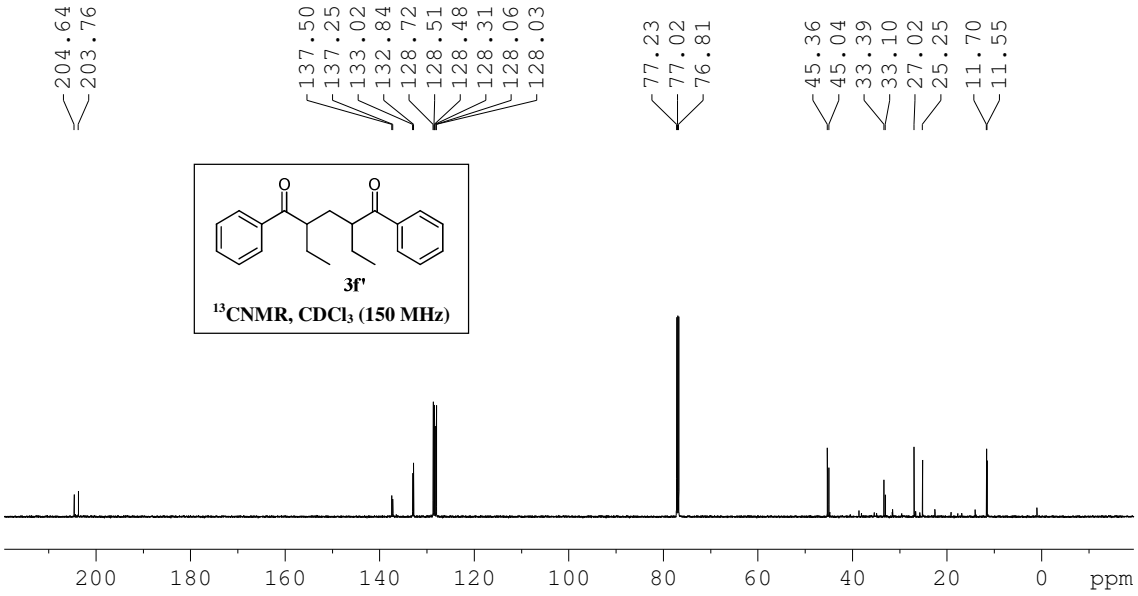

8.06
8.05
7.78
7.77
7.59
7.58
7.57
7.51
7.50
7.49
7.47
7.46
7.44
7.34
7.33
7.31
7.26
3.63
3.62
3.61
3.60
3.52
3.51
3.50
3.49
2.45
2.44
2.43
2.02
2.01
2.00
1.71
1.50
1.49
1.48
1.25
1.22
1.21
1.18
1.17
0.88
0.86
0.85
0.08
3g'
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.88
1.55
0.96
1.91
0.95
1.64
0.99
0.82
0.49
0.86
0.55
2.60
2.93

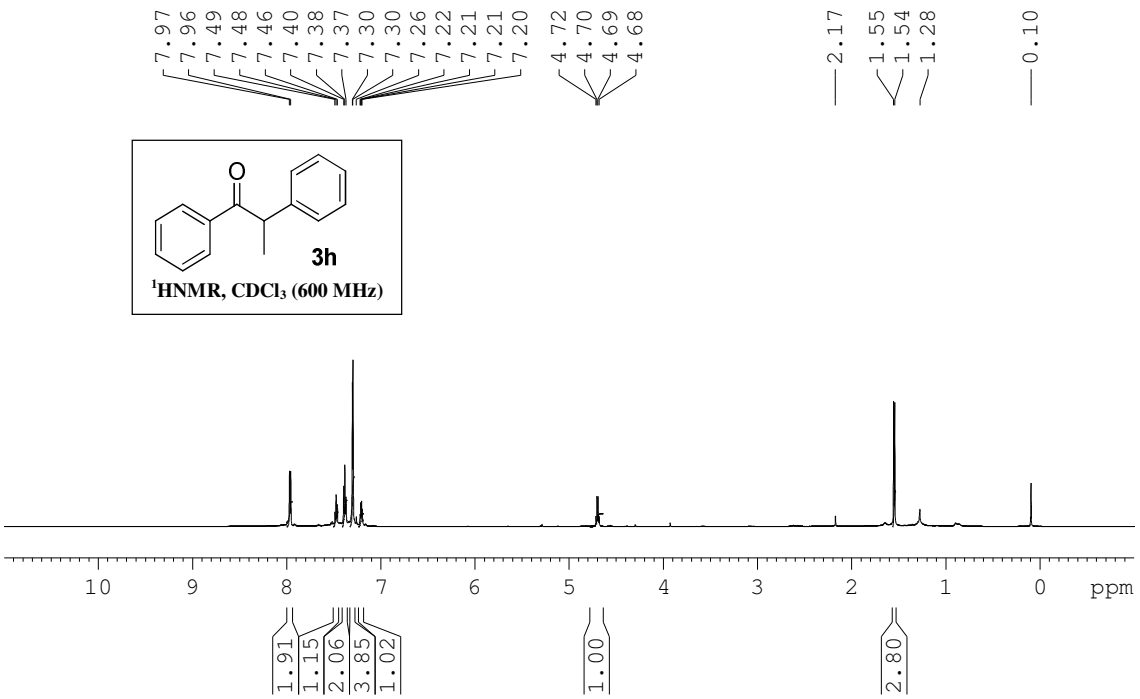

204.28
203.76
136.44
136.22
133.06
132.89
128.71
128.52
128.40
128.11
77.21
77.00
76.78
38.51
38.07
37.25
36.93
18.65
17.55
0.98
3g'
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

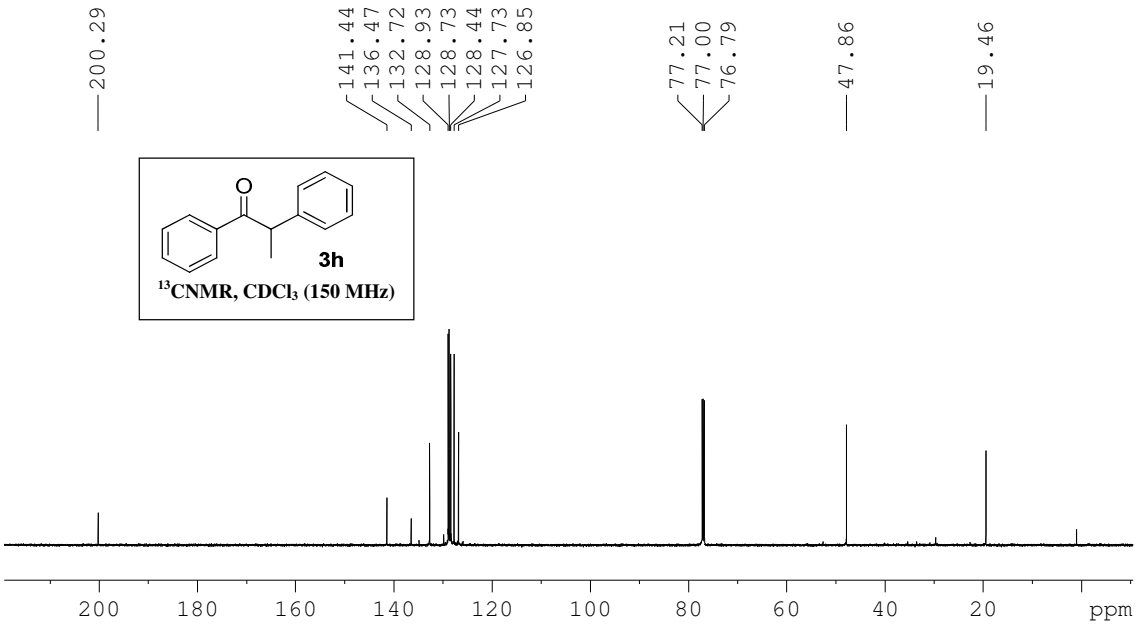

7.95
7.94
7.54
7.53
7.52
7.46
7.45
7.43
3.41
3.40
3.39
3.38
1.85
1.84
1.83
1.82
1.81
1.51
1.50
1.49
1.47
1.46
1.19
1.18
1.01
1.00
0.92
0.91
3f
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.99
1.05
1.98
1.00
1.06
0.97
3.02
2.98

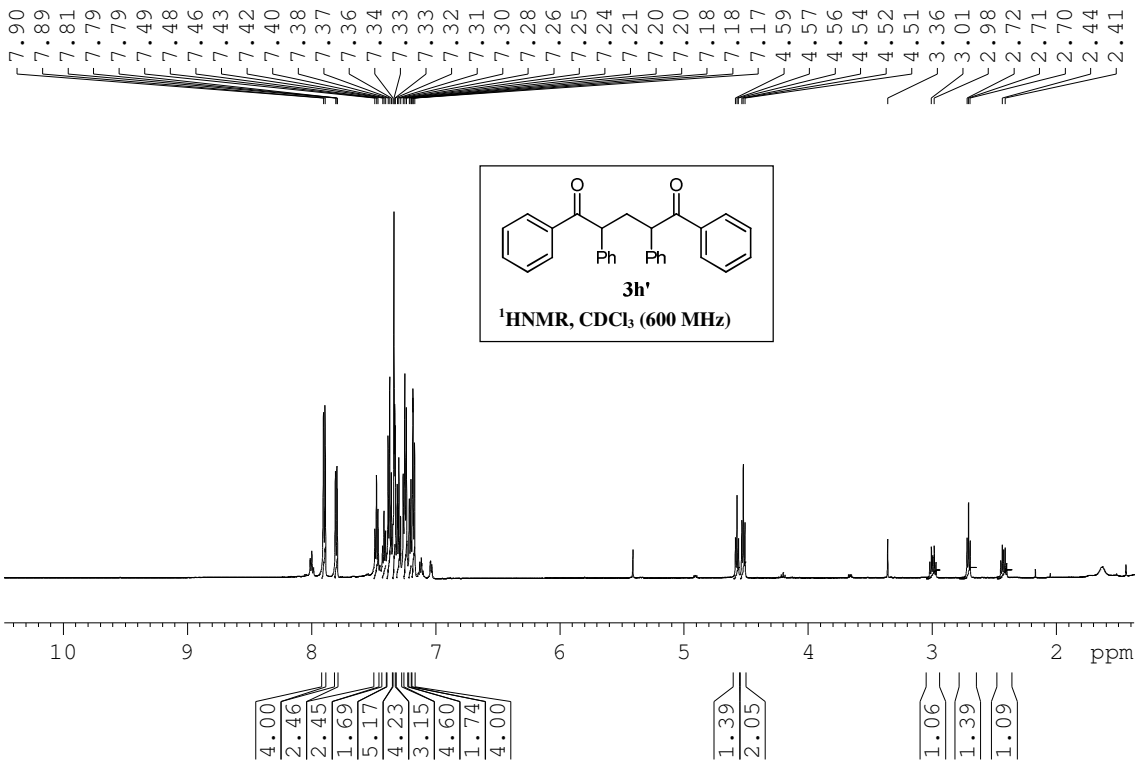

204.35
136.78
132.68
128.51
128.46
128.14
77.21
77.00
76.79
42.04
26.59
16.67
11.66
3f
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

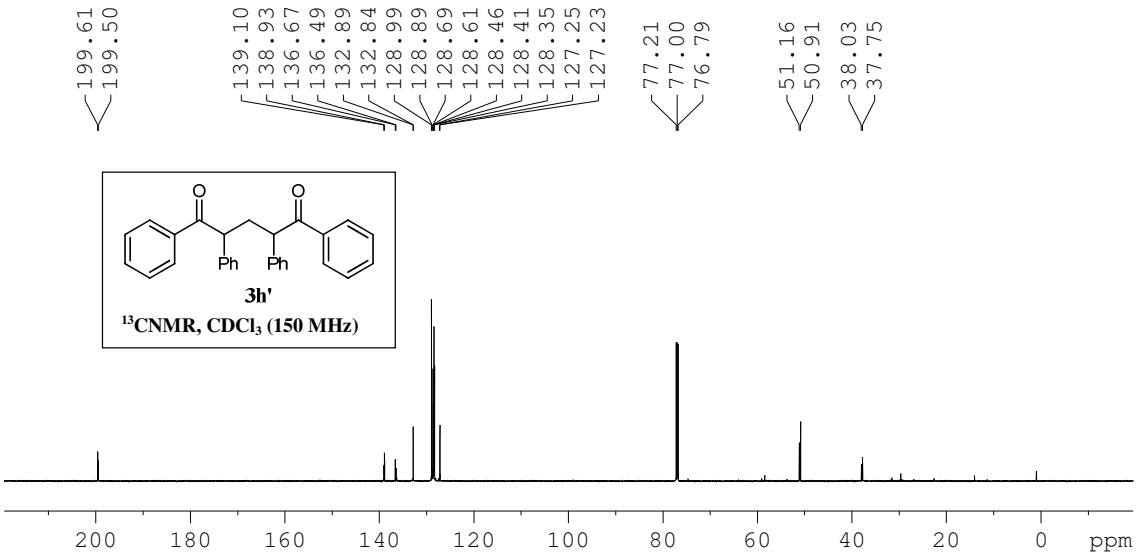

8.01
8.00
7.70
7.69
7.57
7.56
7.50
7.49
7.48
7.44
7.42
7.41
7.28
7.27
7.26
7.26
3.45
3.32
3.31
3.30
2.08
2.07
2.05
1.77
1.76
1.75
1.74
1.72
1.71
1.64
1.54
1.53
1.52
1.51
1.42
1.29
0.88
0.86
0.85
0.81
0.80
0.79
0.07
3f'
1HNMR, CDCl3 (600 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.86
2.11
1.11
2.20
1.21
2.33
1.00
1.13
0.48
1.02
2.27
1.05
2.18
0.60
3.76
2.86

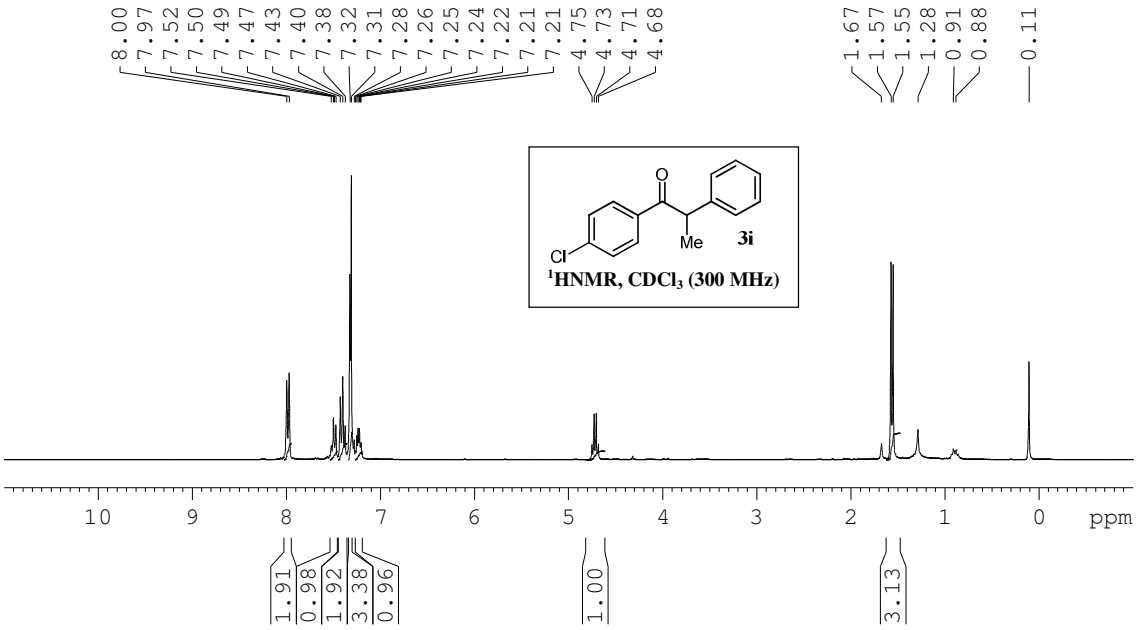

204.64
203.76
137.50
137.25
133.02
132.84
128.72
128.51
128.48
128.31
128.06
128.03
77.23
77.02
76.81
45.36
45.04
33.39
33.10
27.02
25.25
11.70
11.55
3f'
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

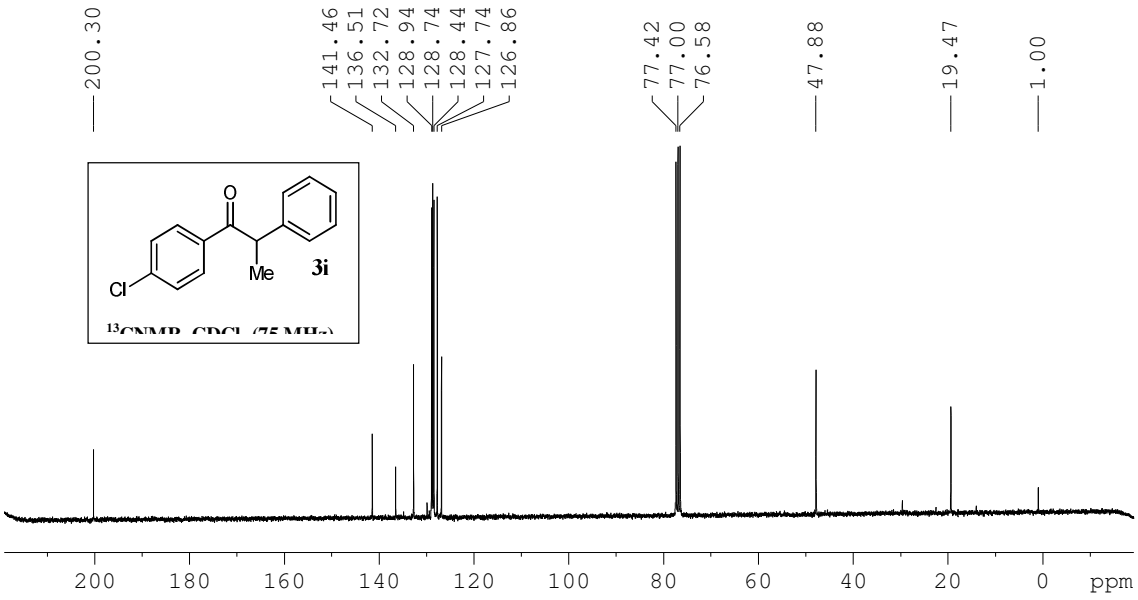

7.97
7.96
7.49
7.48
7.46
7.40
7.38
7.37
7.30
7.30
7.26
7.22
7.21
7.21
7.20
4.72
4.70
4.69
4.68
2.17
1.55
1.54
1.28
0.10
3h
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.91
1.15
2.06
3.85
1.02
1.00
2.80

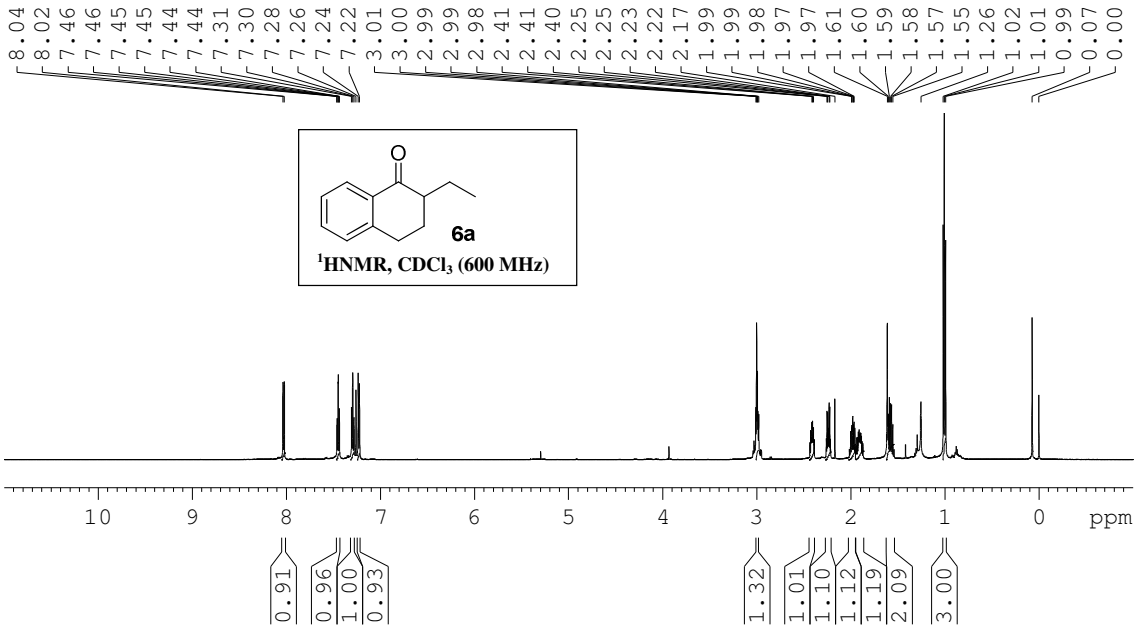

200.29
141.44
136.47
132.72
128.93
128.73
128.44
127.73
126.85
77.21
77.00
76.79
47.86
19.46
3h
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
ppm

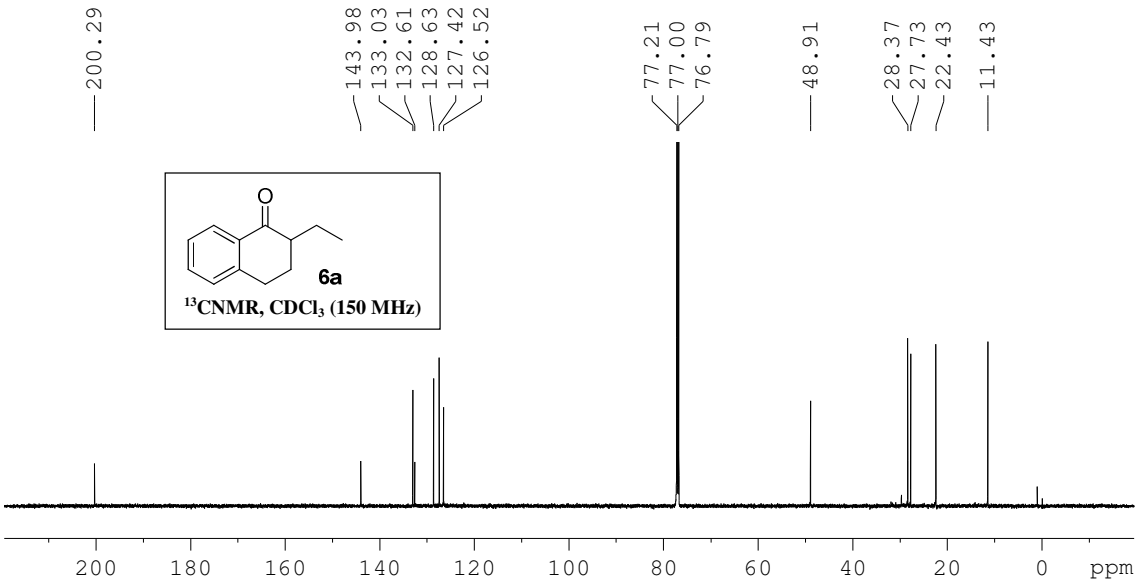

7.90 7.89 7.81 7.79 7.79 7.49 7.48 7.46 7.43 7.42 7.40 7.38 7.37 7.36 7.34 7.33 7.33 7.32 7.31 7.30 7.28 7.26 7.25 7.24 7.21 7.20 7.20 7.18 7.18 7.17 4.59 4.57 4.56 4.54 4.52 4.51 3.36 3.01 2.98 2.72 2.71 2.70 2.44 2.41
Ph Ph
3h'
1HNMR, CDCl3 (600 MHz)
10 9 8 7 6 5 4 3 2 ppm
4.00 2.46 2.45 1.69 5.17 4.23 3.15 4.60 1.74 4.00
1.39 2.05
1.06 1.39 1.09

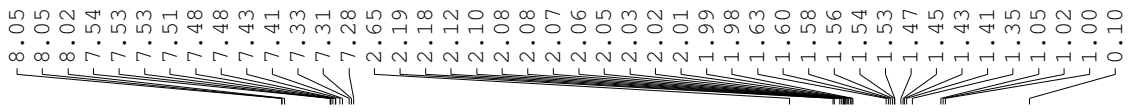

199.61 199.50
139.10 138.93 136.67 136.49 132.89 132.84 128.99 128.89 128.69 128.61 128.46 128.41 128.35 127.25 127.23
77.21 77.00 76.79
51.16 50.91
38.03 37.75
Ph Ph
3h'
13CNMR, CDCl3 (150 MHz)
200 180 160 140 120 100 80 60 40 20 0 ppm

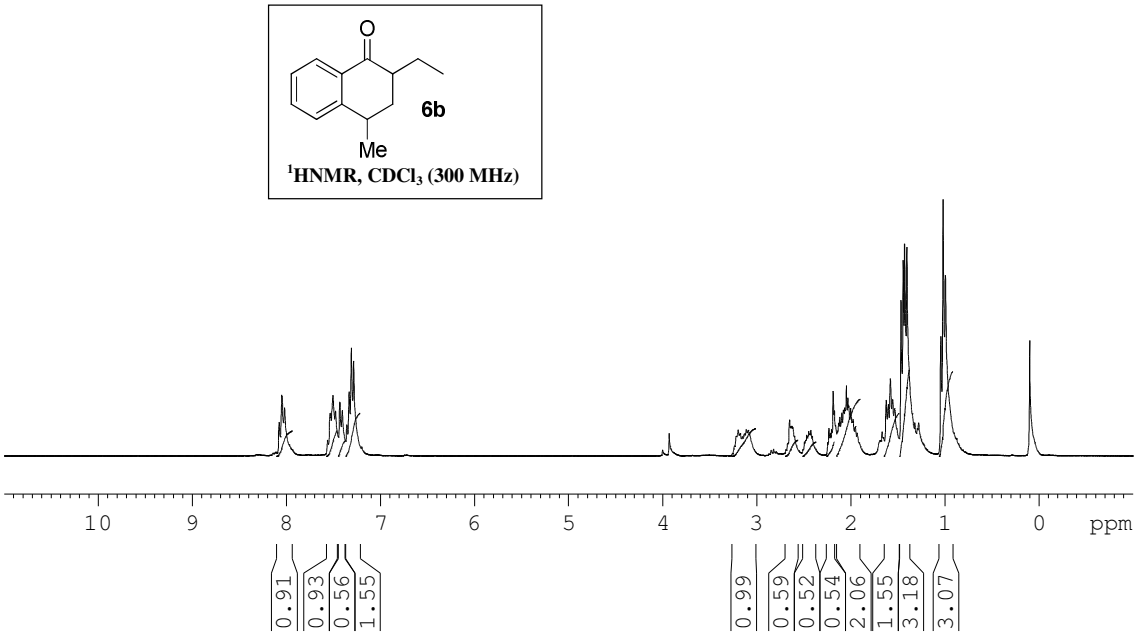

8.00
7.97
7.52
7.50
7.49
7.47
7.43
7.40
7.38
7.32
7.31
7.28
7.26
7.25
7.24
7.22
7.21
7.21
4.75
4.73
4.71
4.68
1.67
1.57
1.55
1.28
0.91
0.88
0.11
O
Me
3i
Cl
1HNMR, CDCl3 (300 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.91
0.98
1.92
3.38
0.96
1.00
3.13

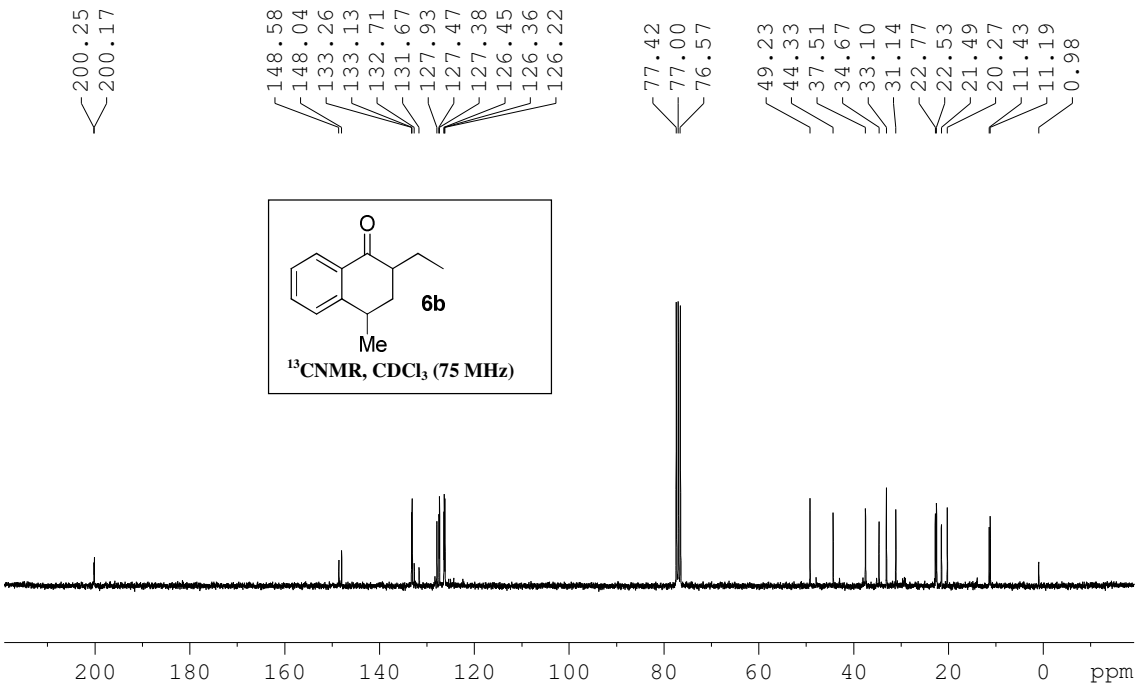

200.30
141.46
136.51
132.72
128.94
128.74
128.44
127.74
126.86
77.42
77.00
76.58
47.88
19.47
1.00
O
Me
3i
Cl
13CNMR, CDCl3 (75 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

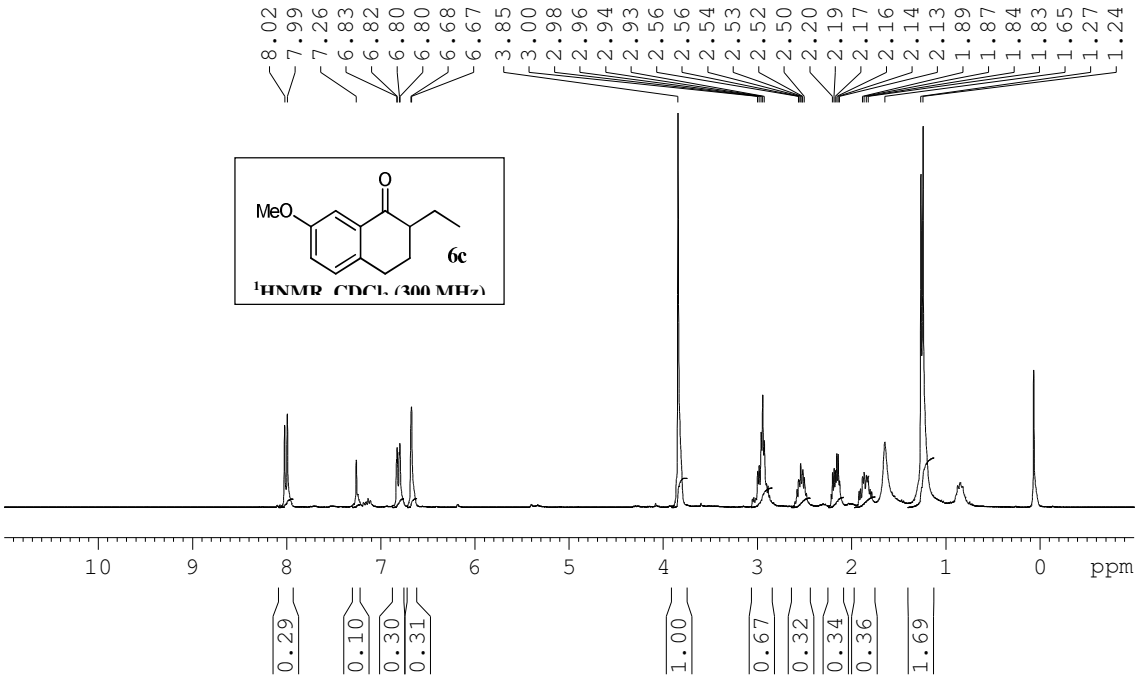

8.04
8.02
7.46
7.46
7.45
7.45
7.44
7.44
7.31
7.30
7.28
7.26
7.24
7.22
3.01
3.00
2.99
2.99
2.98
2.41
2.41
2.40
2.25
2.25
2.23
2.22
2.17
1.99
1.99
1.98
1.97
1.97
1.61
1.60
1.59
1.58
1.57
1.55
1.26
1.02
1.01
0.99
0.07
0.00
O
6a
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.91
0.96
1.00
0.93
1.32
1.01
1.10
1.12
1.19
2.09
3.00

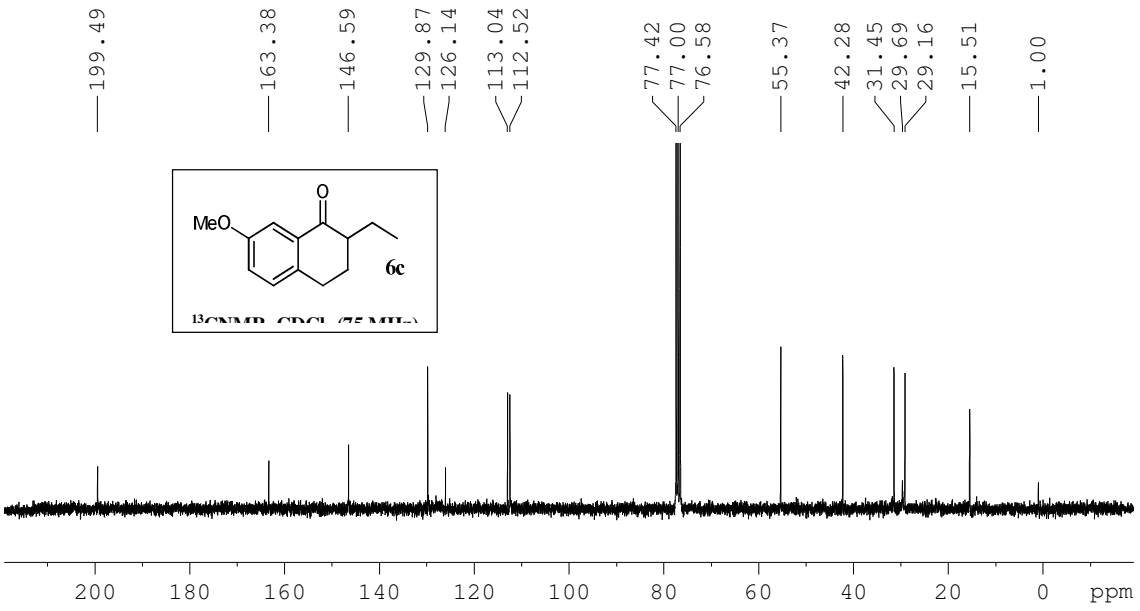

200.29
143.98
133.03
132.61
128.63
127.42
126.52
77.21
77.00
76.79
48.91
28.37
27.73
22.43
11.43
O
6a
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

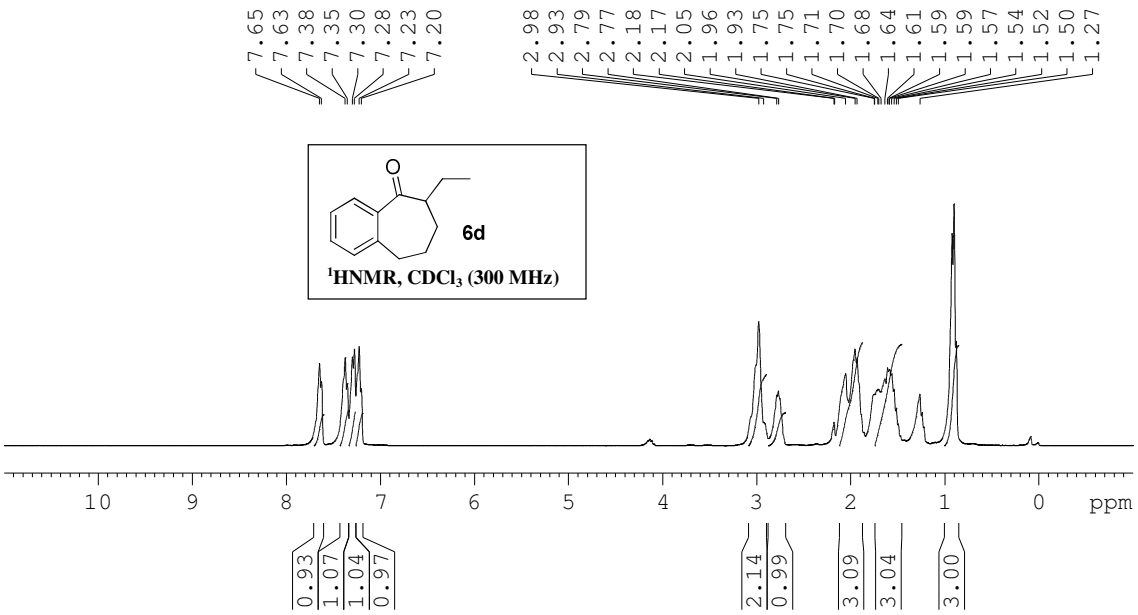

8.05
8.05
8.02
7.54
7.53
7.53
7.51
7.48
7.48
7.43
7.41
7.33
7.31
7.28
2.65
2.19
2.18
2.12
2.10
2.08
2.08
2.07
2.06
2.05
2.03
2.02
2.01
1.99
1.98
1.63
1.60
1.58
1.56
1.54
1.53
1.47
1.45
1.43
1.41
1.35
1.05
1.02
1.00
0.10

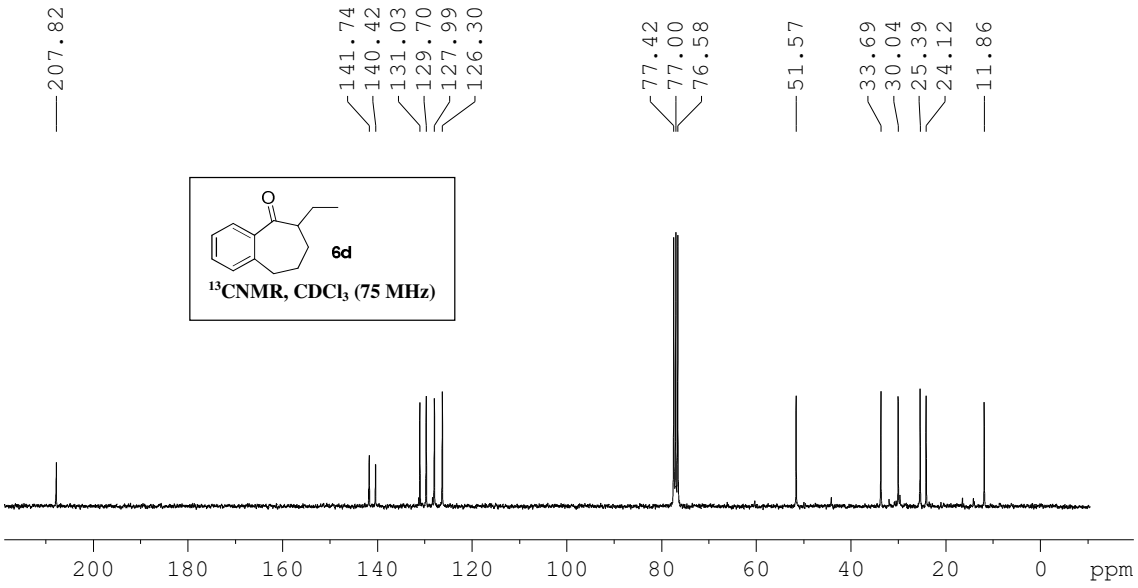

O
6b
Me
¹HNMR, CDCl₃ (300 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.91
0.93
0.56
1.55
0.99
0.59
0.52
0.54
2.06
1.55
3.18
3.07

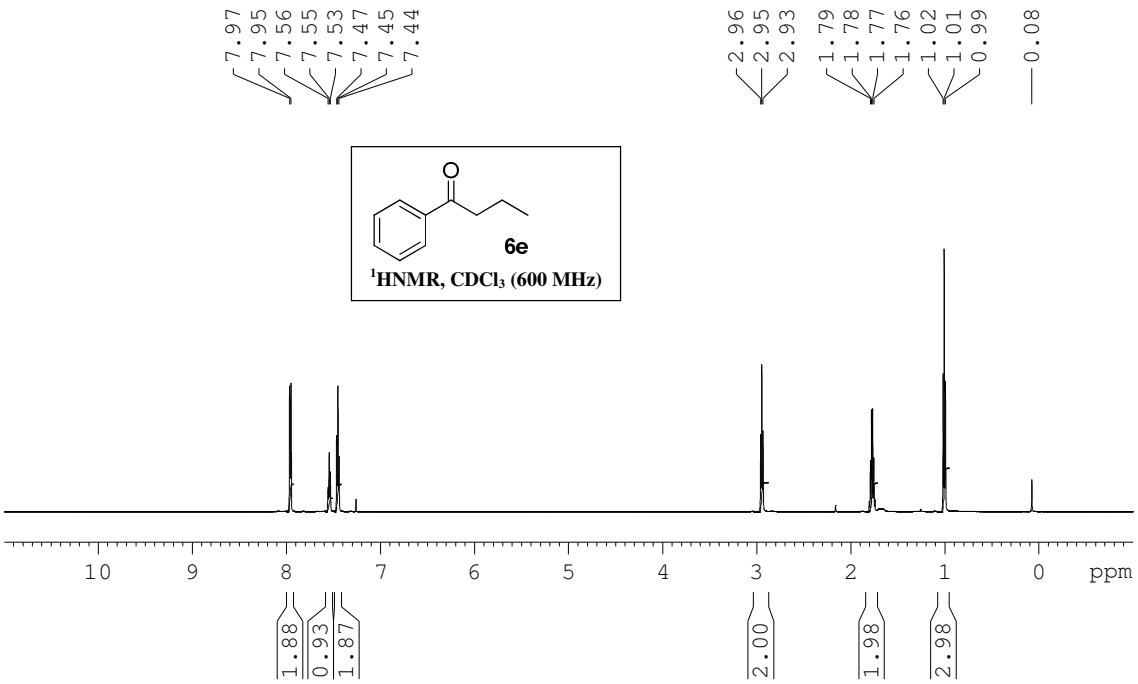

200.25
200.17
148.58
148.04
133.26
133.13
132.71
131.67
127.93
127.47
127.38
126.45
126.36
126.22
77.42
77.00
76.57
49.23
44.33
37.51
34.67
33.10
31.14
22.77
22.53
21.49
20.27
11.43
11.19
0.98
O
6b
Me
¹³CNMR, CDCl₃ (75 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

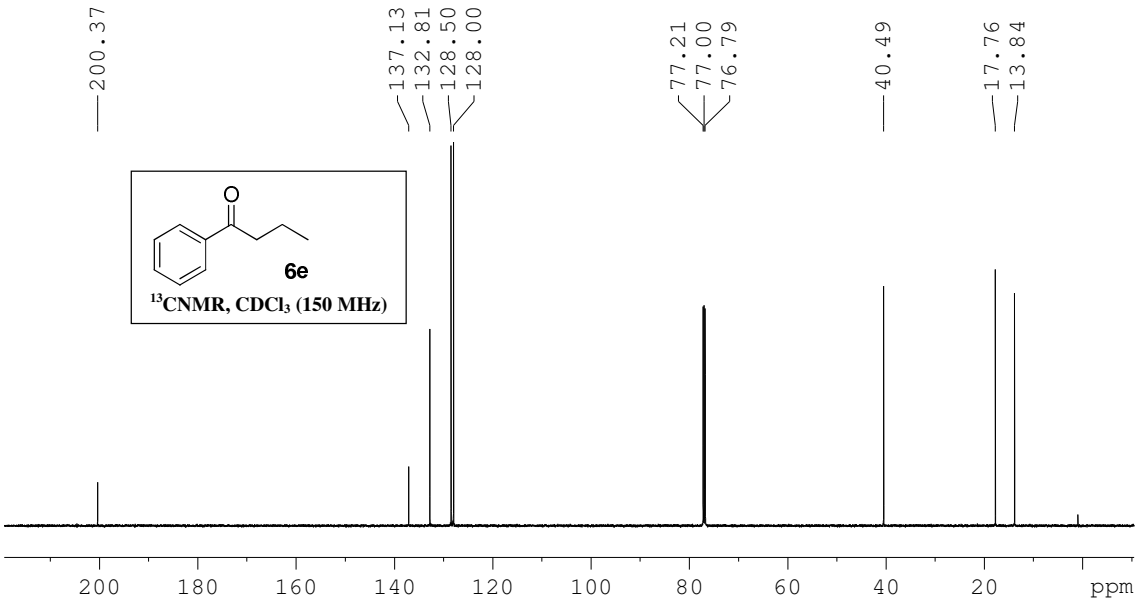

8.02
7.99
7.26
6.83
6.82
6.80
6.80
6.68
6.67
3.85
3.00
2.98
2.96
2.94
2.93
2.56
2.56
2.54
2.53
2.52
2.50
2.20
2.19
2.17
2.16
2.14
2.13
1.89
1.87
1.84
1.83
1.65
1.27
1.24
MeO
O
6c
10
9
8
7
6
5
4
3
2
1
0
ppm
0.29
0.10
0.30
0.31
1.00
0.67
0.32
0.34
0.36
1.69

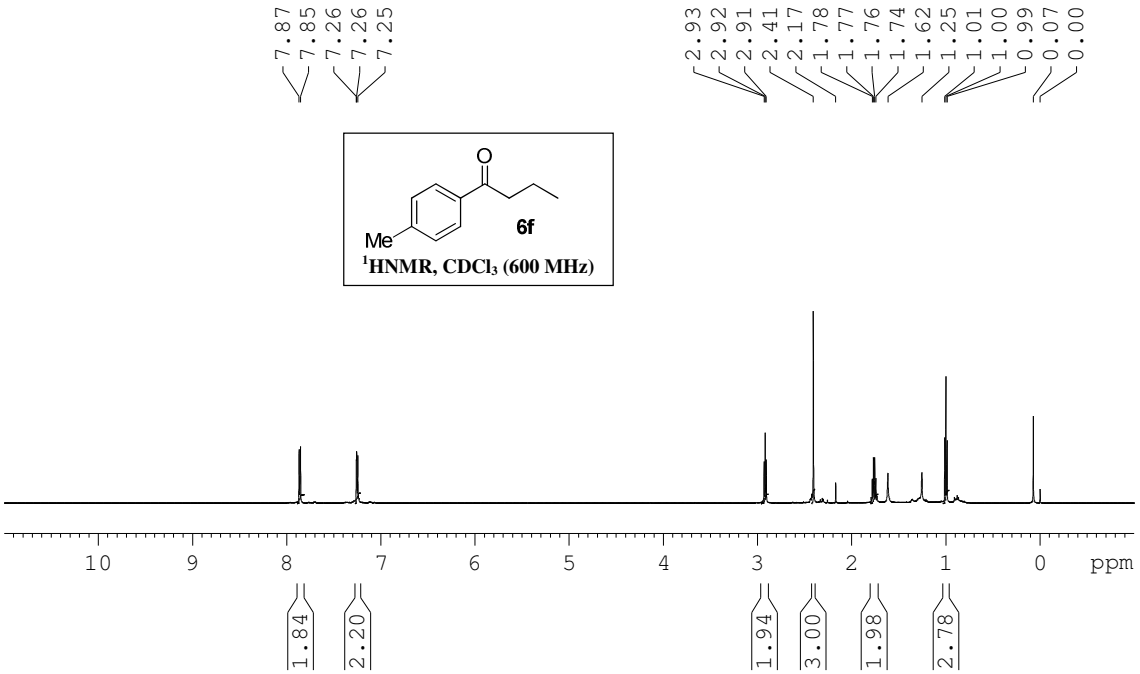

199.49
163.38
146.59
129.87
126.14
113.04
112.52
77.42
77.00
76.58
55.37
42.28
31.45
29.69
29.16
15.51
1.00
MeO
O
6c
200
180
160
140
120
100
80
60
40
20
0
ppm

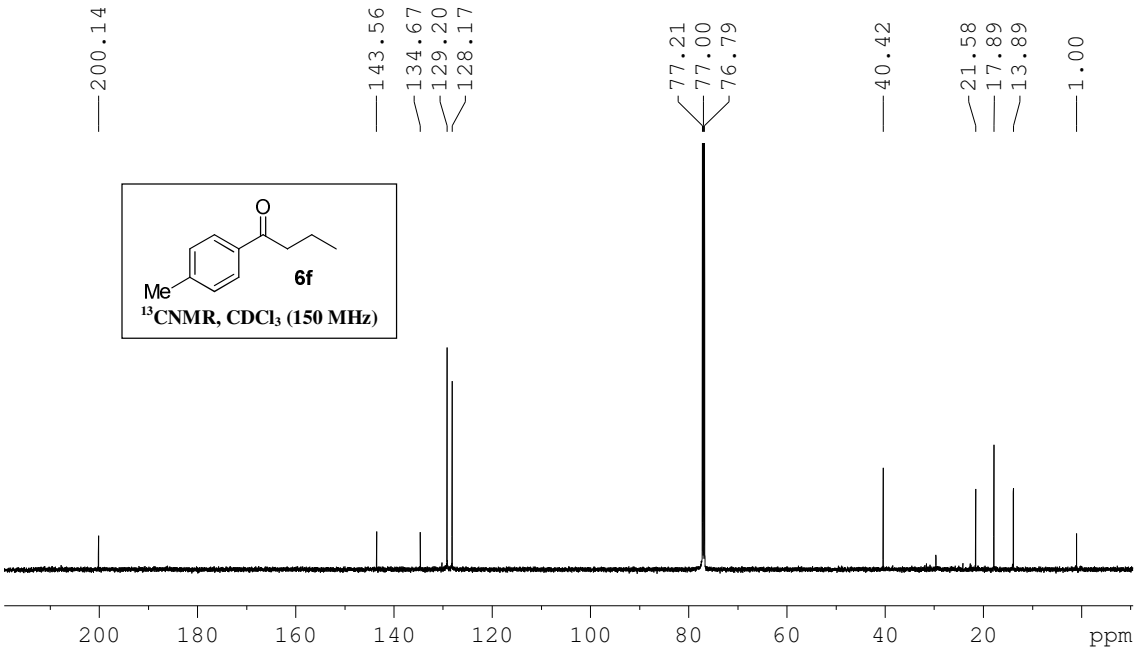

7.65
7.63
7.38
7.35
7.30
7.28
7.23
7.20
2.98
2.93
2.79
2.77
2.18
2.17
2.05
1.96
1.93
1.75
1.75
1.71
1.70
1.68
1.64
1.61
1.59
1.59
1.57
1.54
1.52
1.50
1.27
6d
1HNMR, CDCl3 (300 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
1.07
1.04
0.97
2.14
0.99
3.09
3.04
3.00

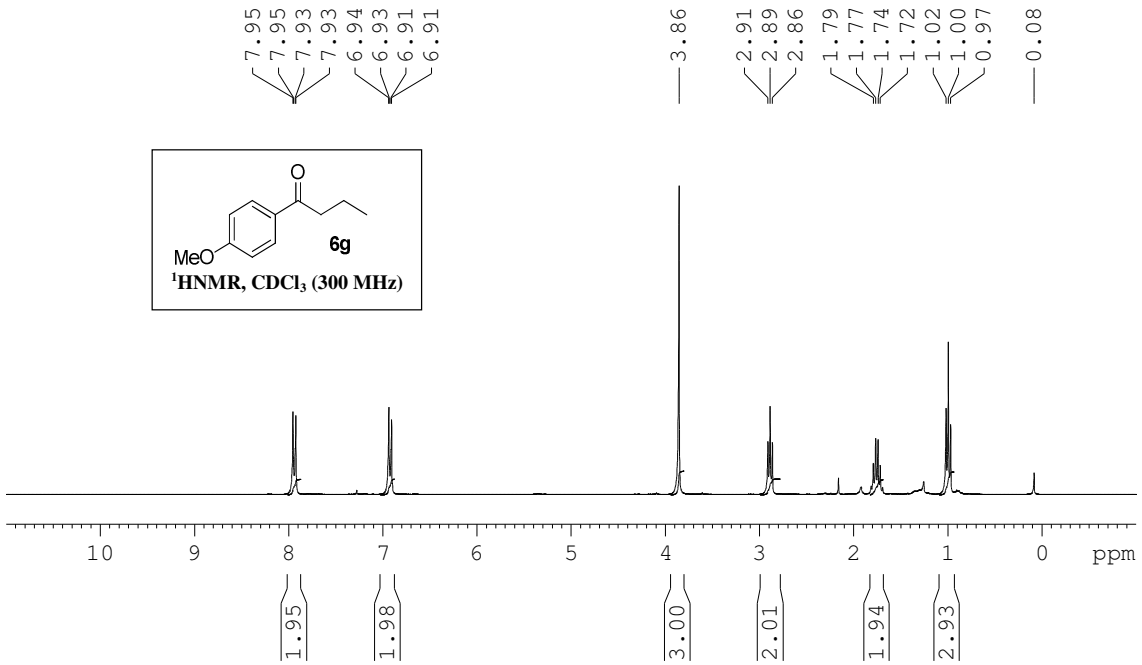

207.82
141.74
140.42
131.03
129.70
127.99
126.30
77.42
77.00
76.58
51.57
33.69
30.04
25.39
24.12
11.86
6d
13CNMR, CDCl3 (75 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

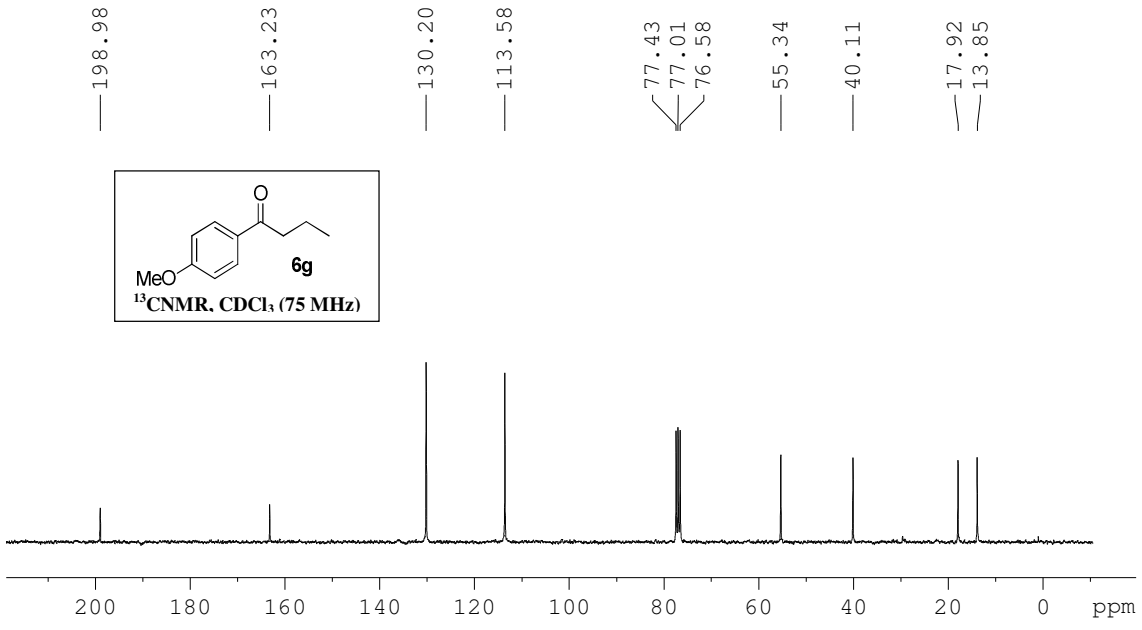

7.97
7.95
7.56
7.55
7.53
7.47
7.45
7.44
2.96
2.95
2.93
1.79
1.78
1.77
1.76
1.02
1.01
0.99
0.08
6e
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.88
0.93
1.87
2.00
1.98
2.98

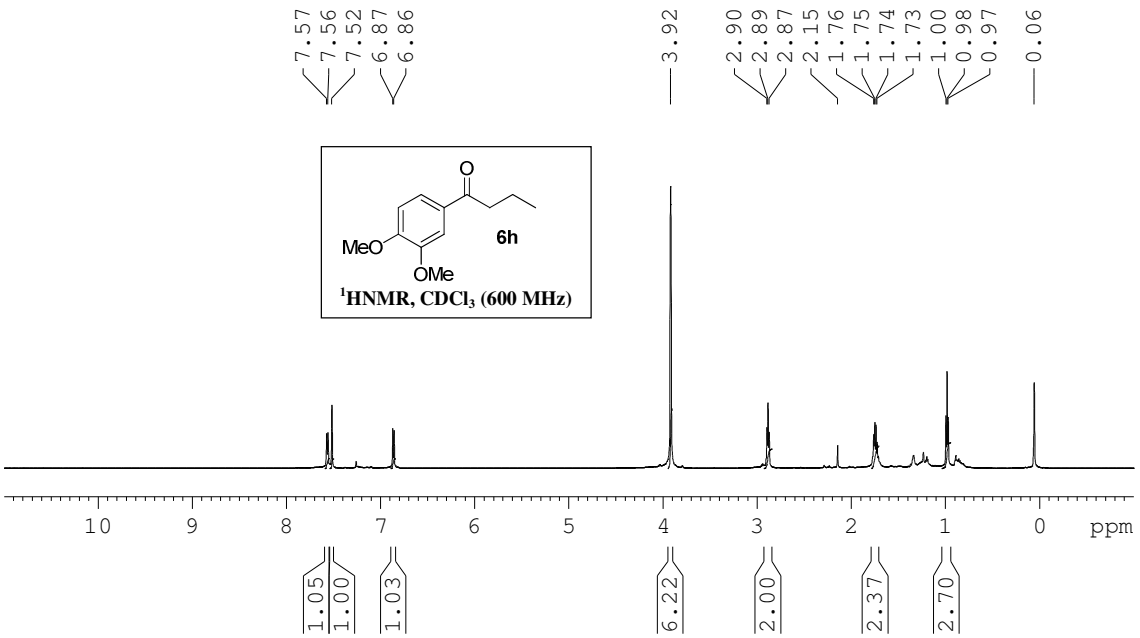

200.37
137.13
132.81
128.50
128.00
77.21
77.00
76.79
40.49
17.76
13.84
6e
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
ppm

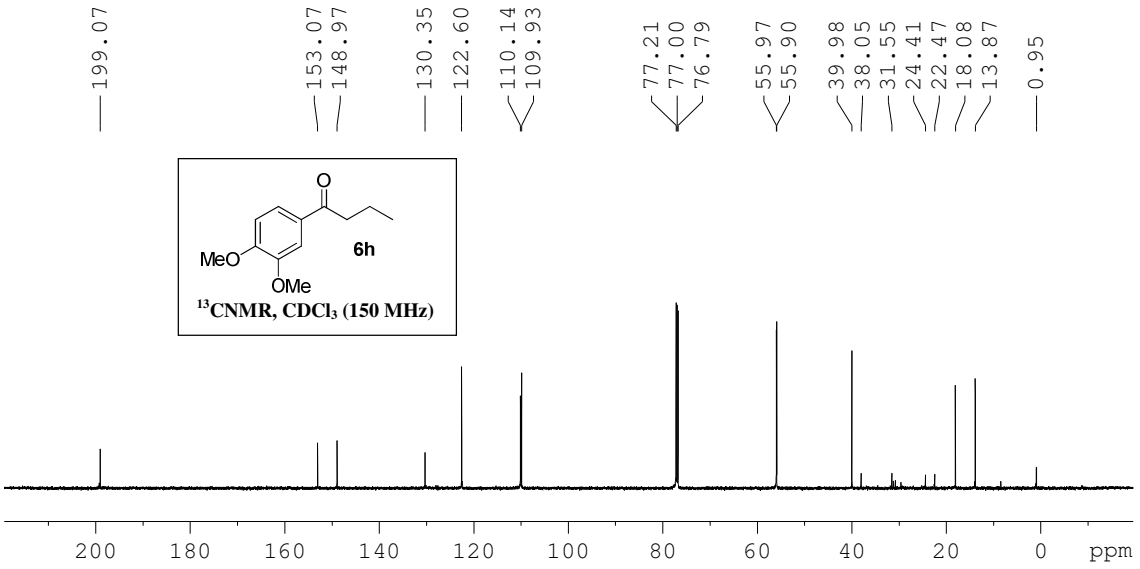

7.87
7.85
7.26
7.26
7.25
2.93
2.92
2.91
2.41
2.17
1.78
1.77
1.76
1.74
1.62
1.25
1.01
1.00
0.99
0.07
0.00
O
Me
6f
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.84
2.20
1.94
3.00
1.98
2.78

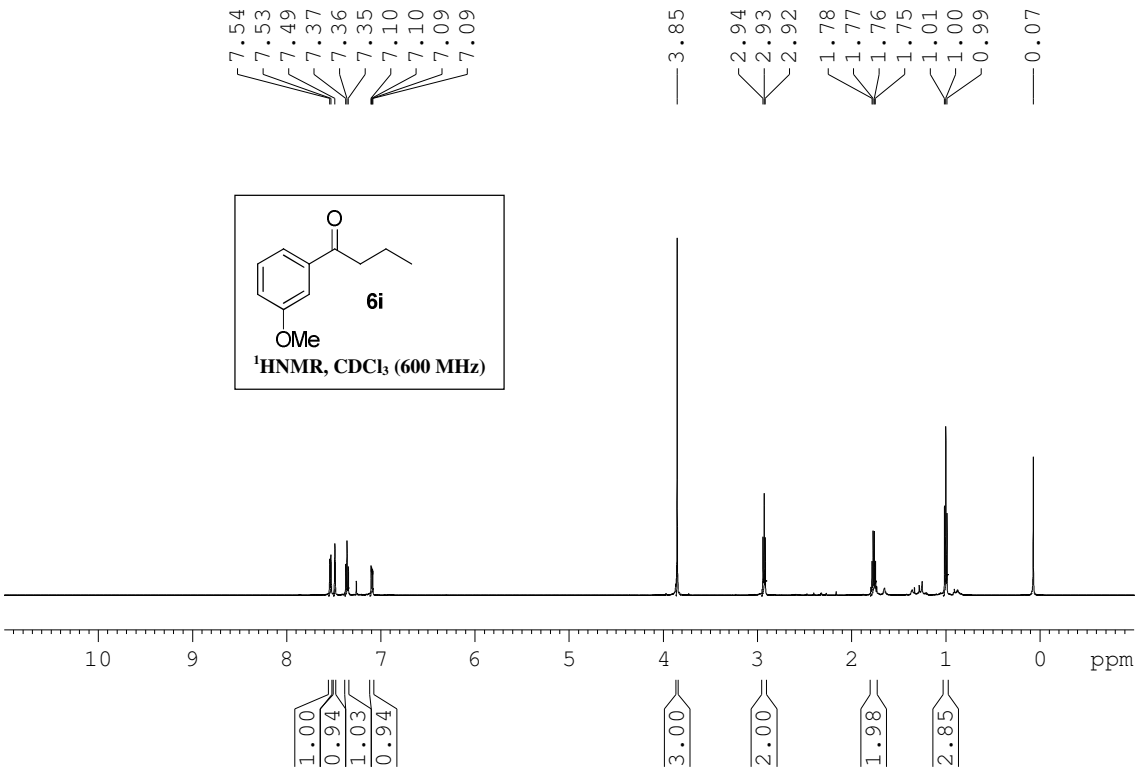

200.14
143.56
134.67
129.20
128.17
77.21
77.00
76.79
40.42
21.58
17.89
13.89
1.00
O
Me
6f
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
ppm

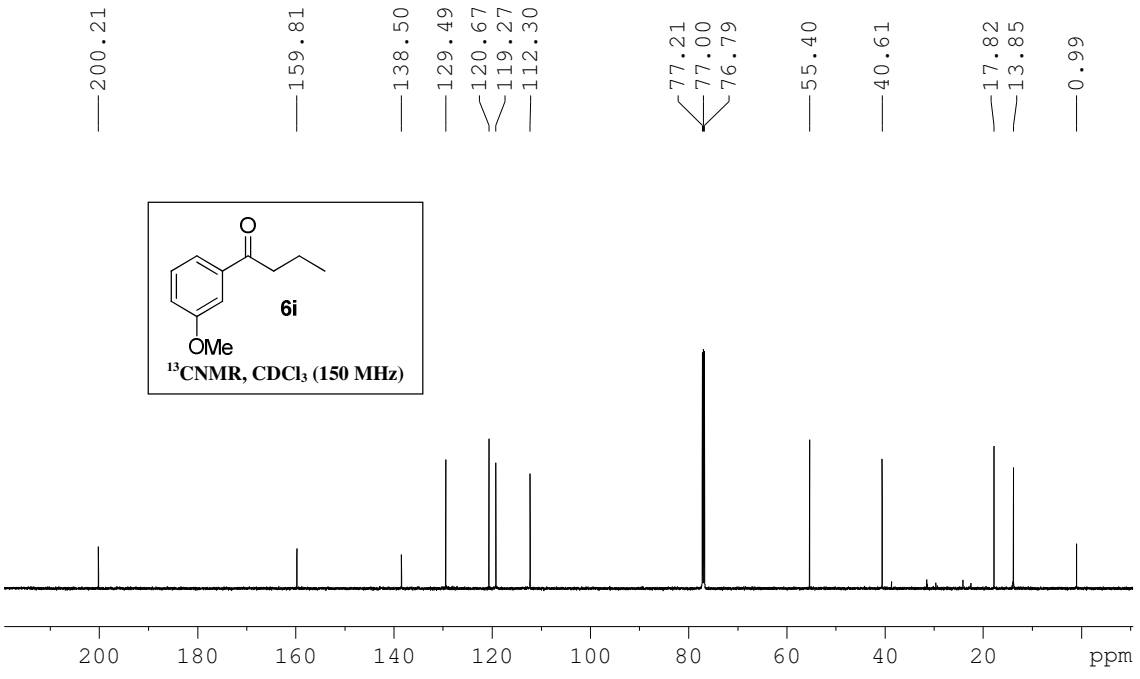

7.95
7.95
7.93
7.93
6.94
6.93
6.91
6.91
3.86
2.91
2.89
2.86
1.79
1.77
1.74
1.72
1.02
1.00
0.97
0.08
O
MeO
6g
¹HNMR, CDCl₃ (300 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.95
1.98
3.00
2.01
1.94
2.93

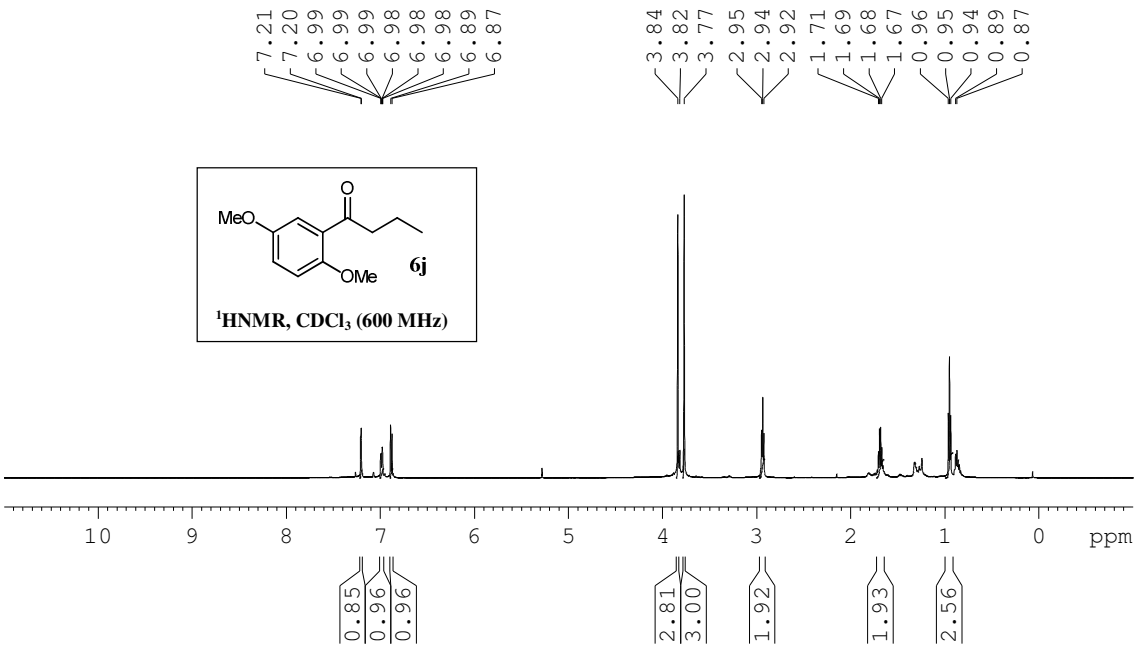

198.98
163.23
130.20
113.58
77.43
77.01
76.58
55.34
40.11
17.92
13.85
O
MeO
6g
¹³CNMR, CDCl₃ (75 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

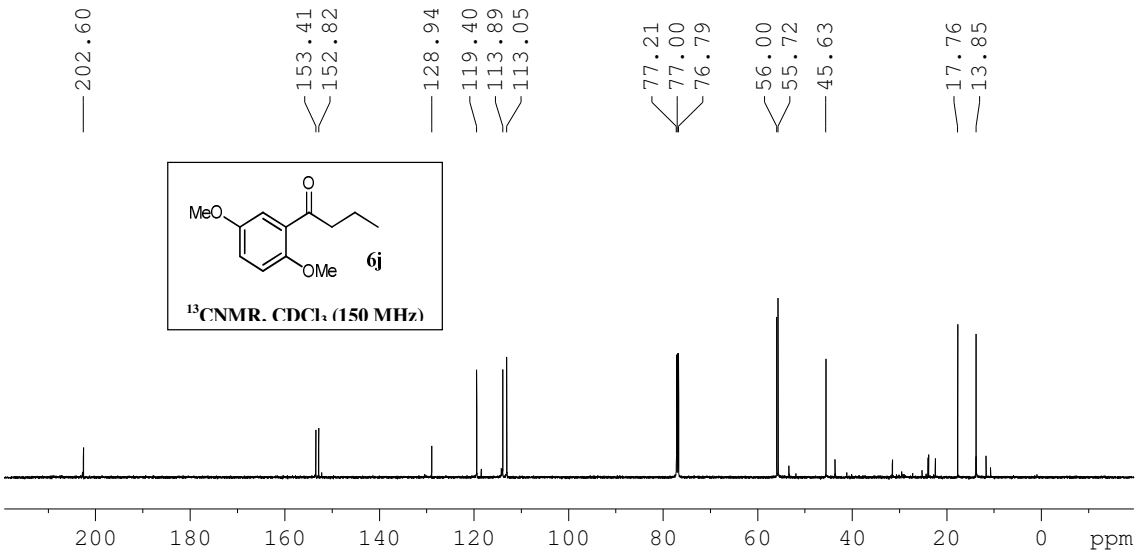

7.57
7.56
7.52
6.87
6.86
3.92
2.90
2.89
2.87
2.15
1.76
1.75
1.74
1.73
1.00
0.98
0.97
0.06
O
MeO
OMe
6h
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.00
1.03
6.22
2.00
2.37
2.70

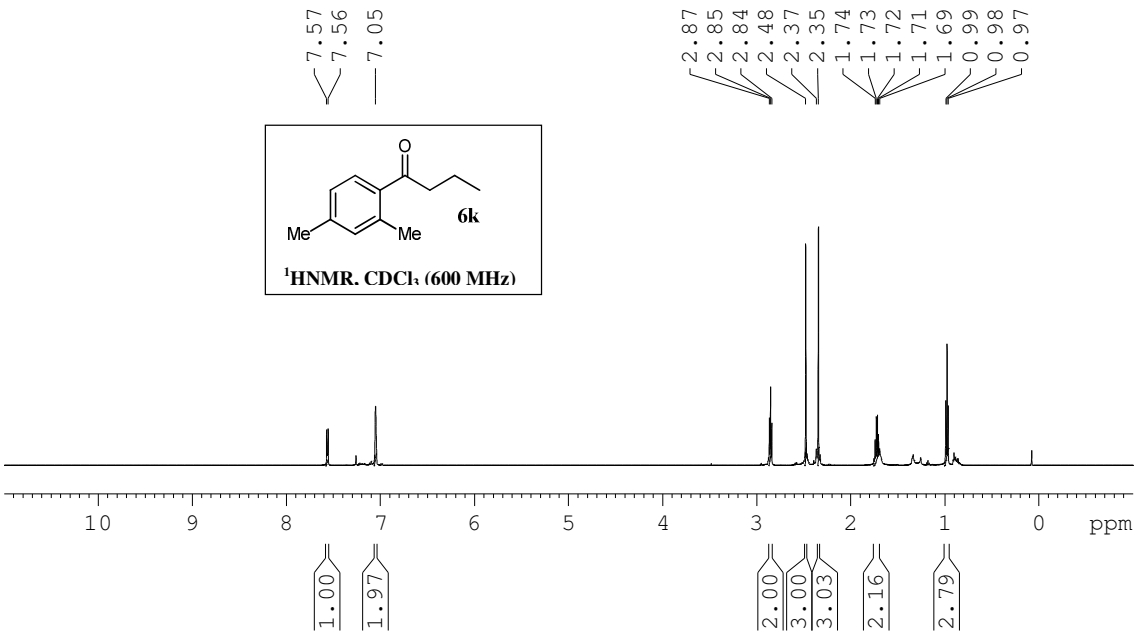

199.07
153.07
148.97
130.35
122.60
110.14
109.93
77.21
77.00
76.79
55.97
55.90
39.98
38.05
31.55
24.41
22.47
18.08
13.87
0.95
O
MeO
OMe
6h
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

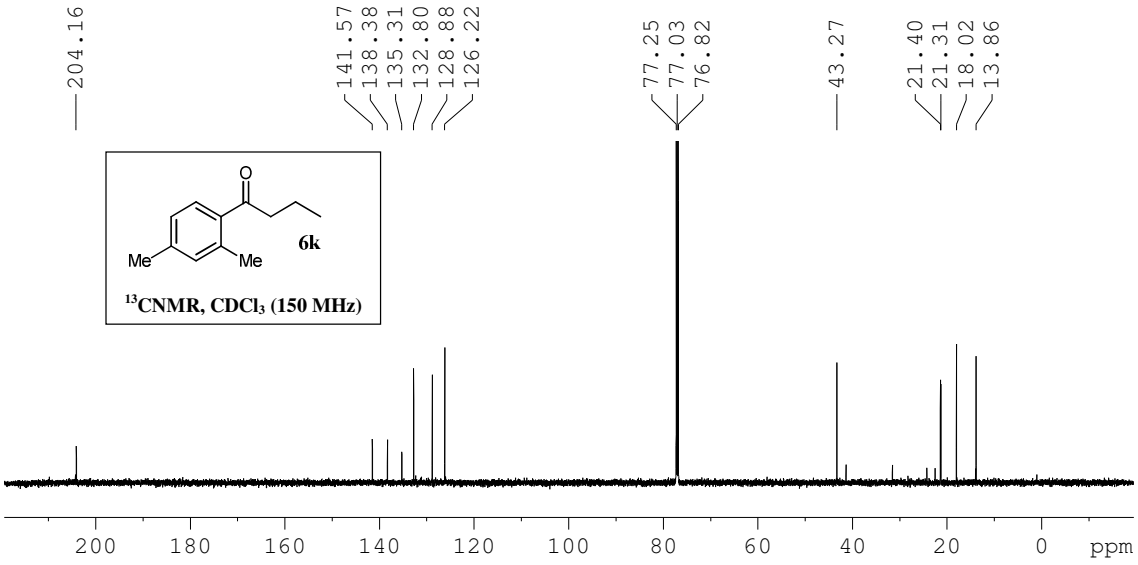

7.54
7.53
7.49
7.37
7.36
7.35
7.10
7.10
7.09
7.09
3.85
2.94
2.93
2.92
1.78
1.77
1.76
1.75
1.01
1.00
0.99
0.07
6i
OMe
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.94
1.03
0.94
3.00
2.00
1.98
2.85

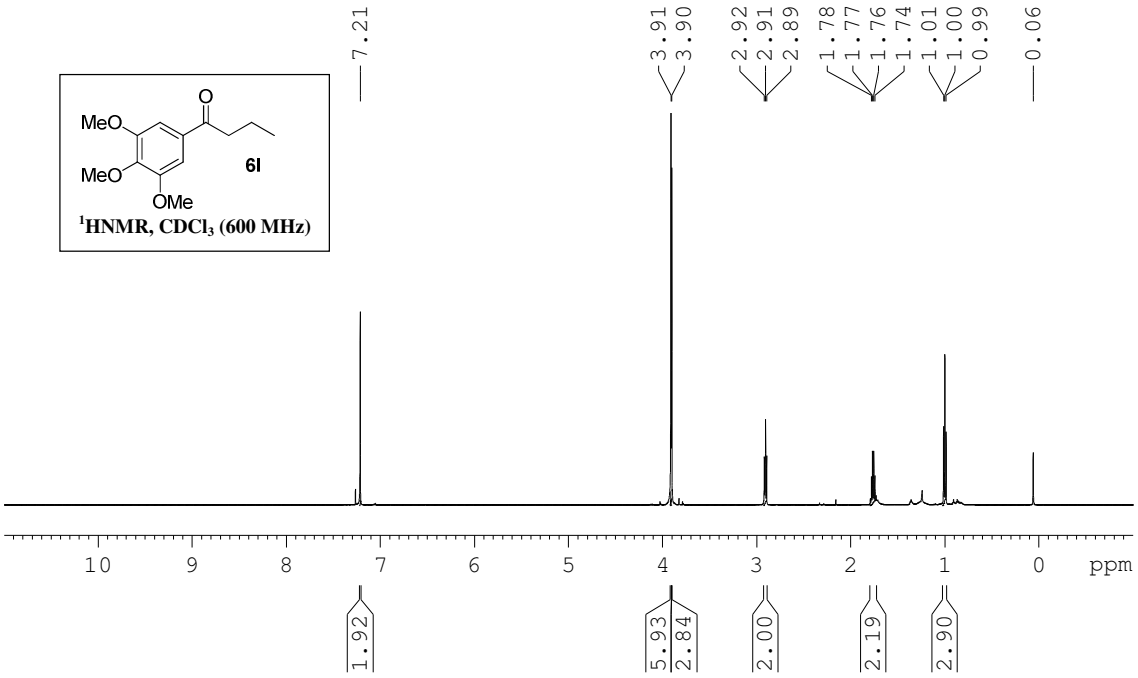

200.21
159.81
138.50
129.49
120.67
119.27
112.30
77.21
77.00
76.79
55.40
40.61
17.82
13.85
0.99
6i
OMe
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
ppm

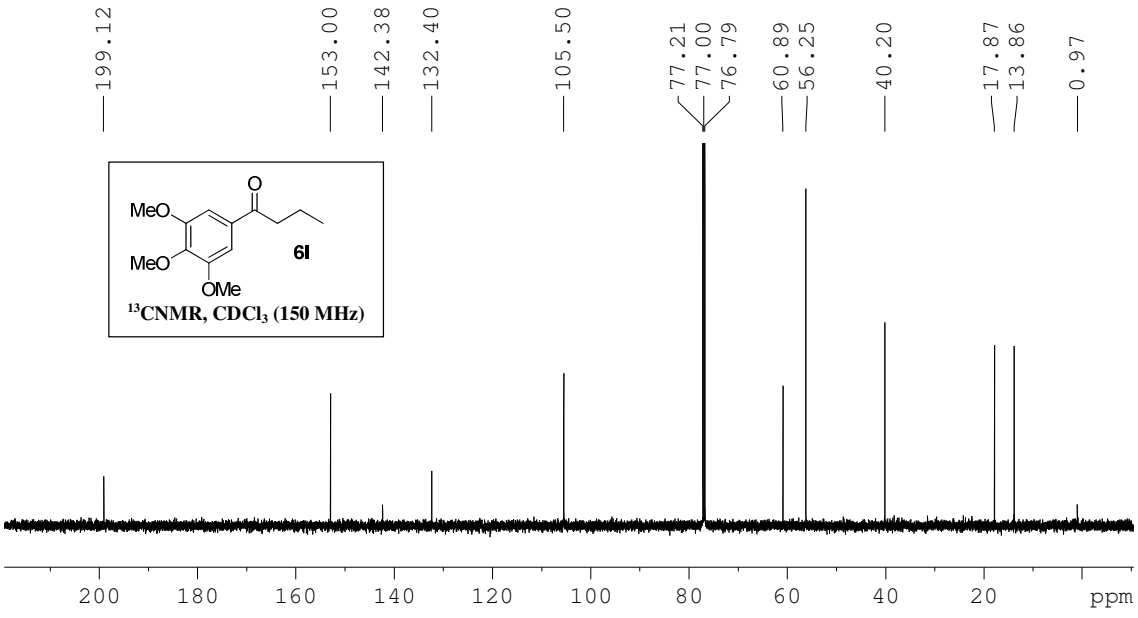

7.21
7.20
6.99
6.99
6.99
6.98
6.98
6.98
6.89
6.87
3.84
3.82
3.77
2.95
2.94
2.92
1.71
1.69
1.68
1.67
0.96
0.95
0.94
0.89
0.87
MeO
OMe
6j
¹HNMR, CDCl₃ (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.85
0.96
0.96
2.81
3.00
1.92
1.93
2.56

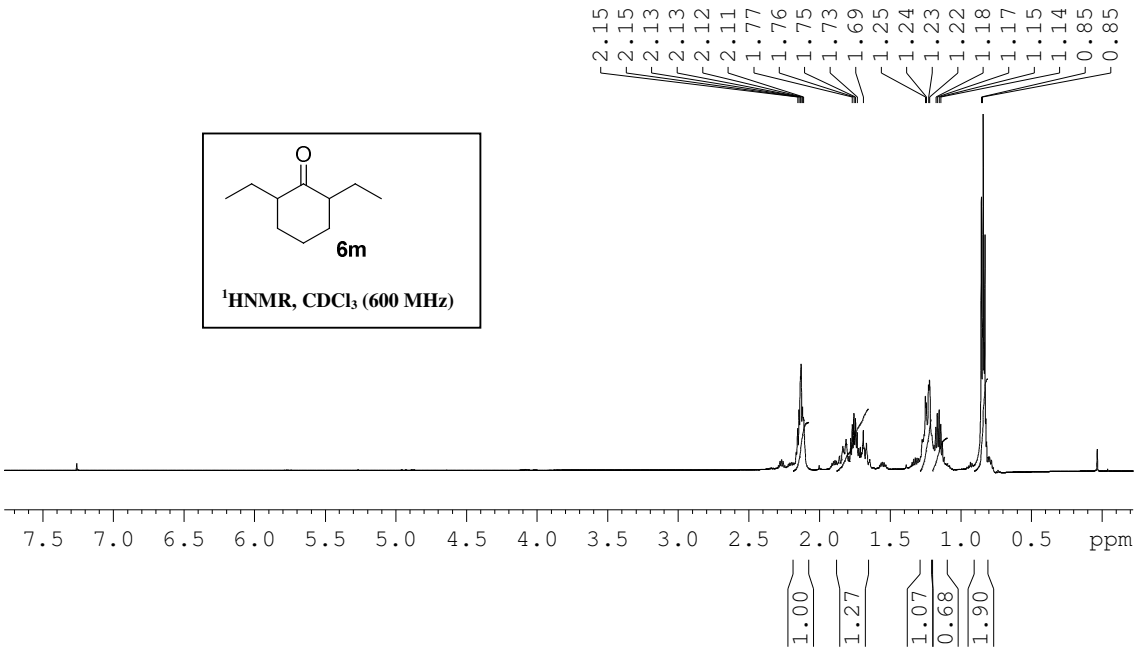

202.60
153.41
152.82
128.94
119.40
113.89
113.05
77.21
77.00
76.79
56.00
55.72
45.63
17.76
13.85
MeO
OMe
6j
¹³CNMR, CDCl₃ (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

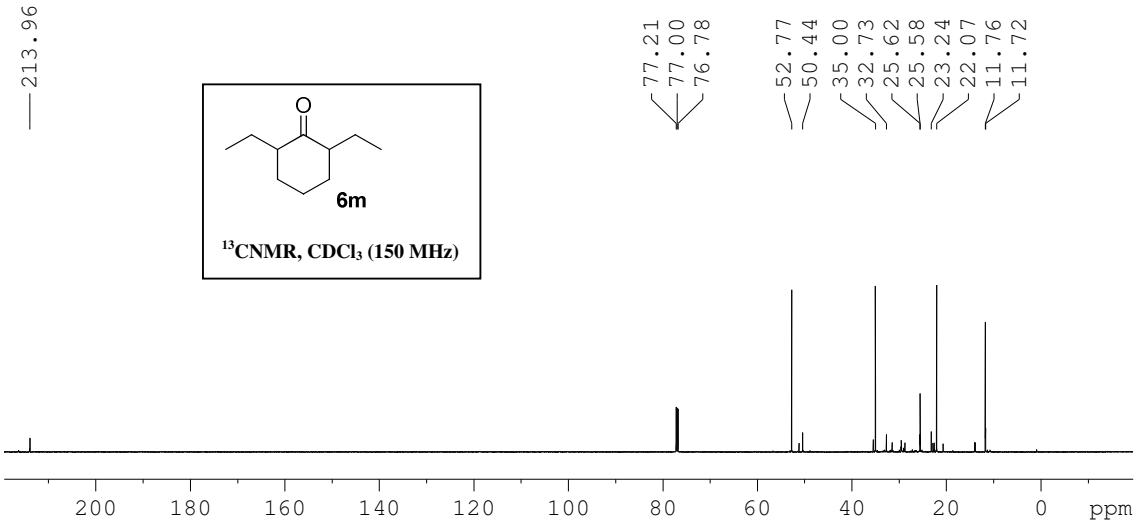

7.57
7.56
7.05
2.87
2.85
2.84
2.48
2.37
2.35
1.74
1.73
1.72
1.71
1.69
0.99
0.98
0.97
O
Me
Me
6k
1HNMR. CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.97
2.00
3.00
3.03
2.16
2.79

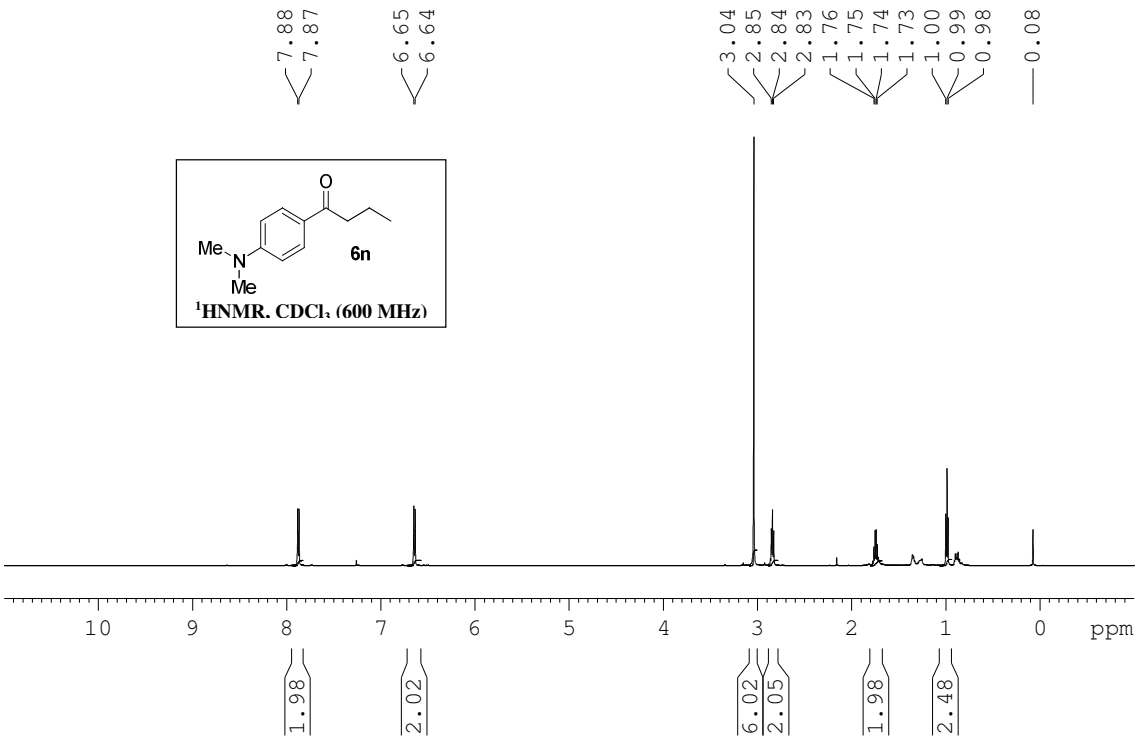

204.16
141.57
138.38
135.31
132.80
128.88
126.22
77.25
77.03
76.82
43.27
21.40
21.31
18.02
13.86
O
Me
Me
6k
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

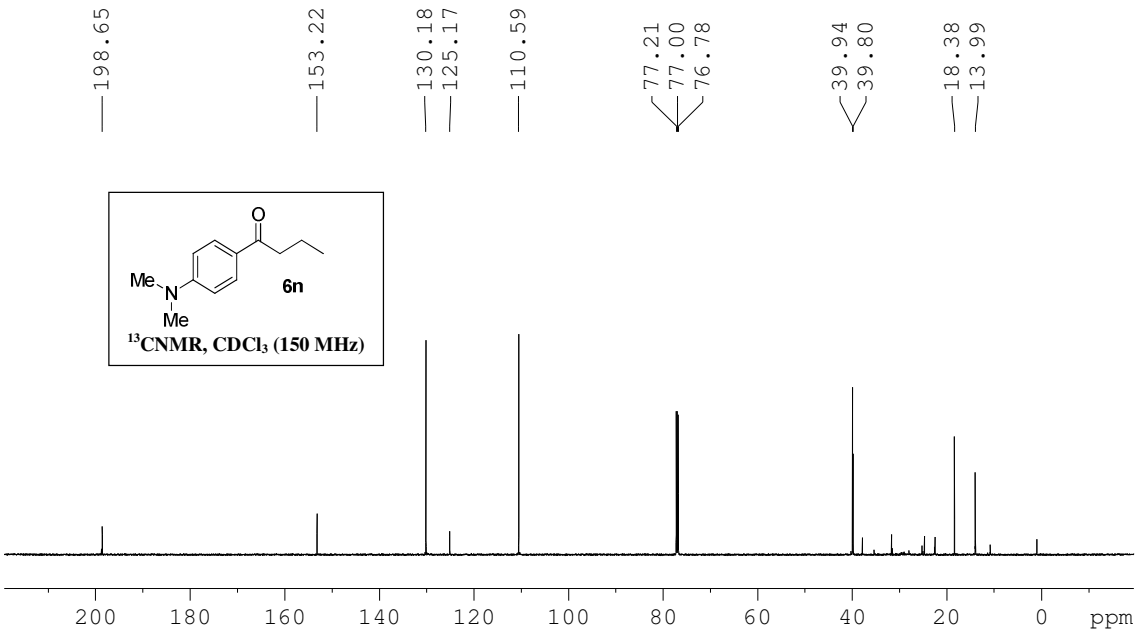

7.21
3.91
3.90
2.92
2.91
2.89
1.78
1.77
1.76
1.74
1.01
1.00
0.99
0.06
MeO
MeO
OMe
O
6l
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.92
5.93
2.84
2.00
2.19
2.90

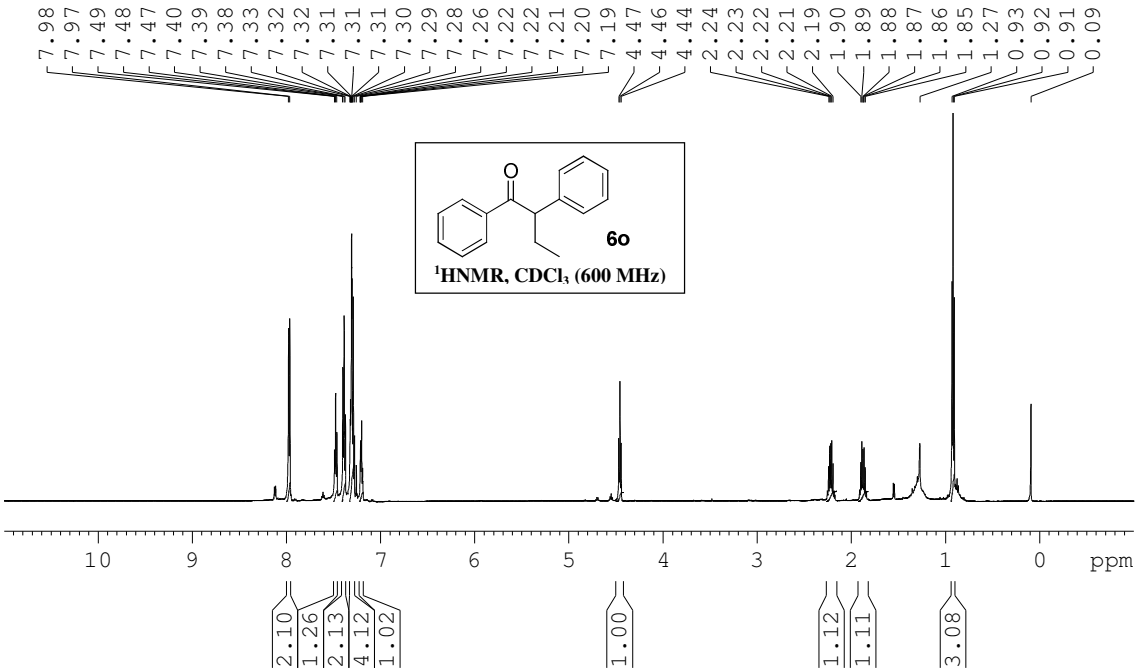

199.12
153.00
142.38
132.40
105.50
77.21
77.00
76.79
60.89
56.25
40.20
17.87
13.86
0.97
MeO
MeO
OMe
O
6l
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
ppm

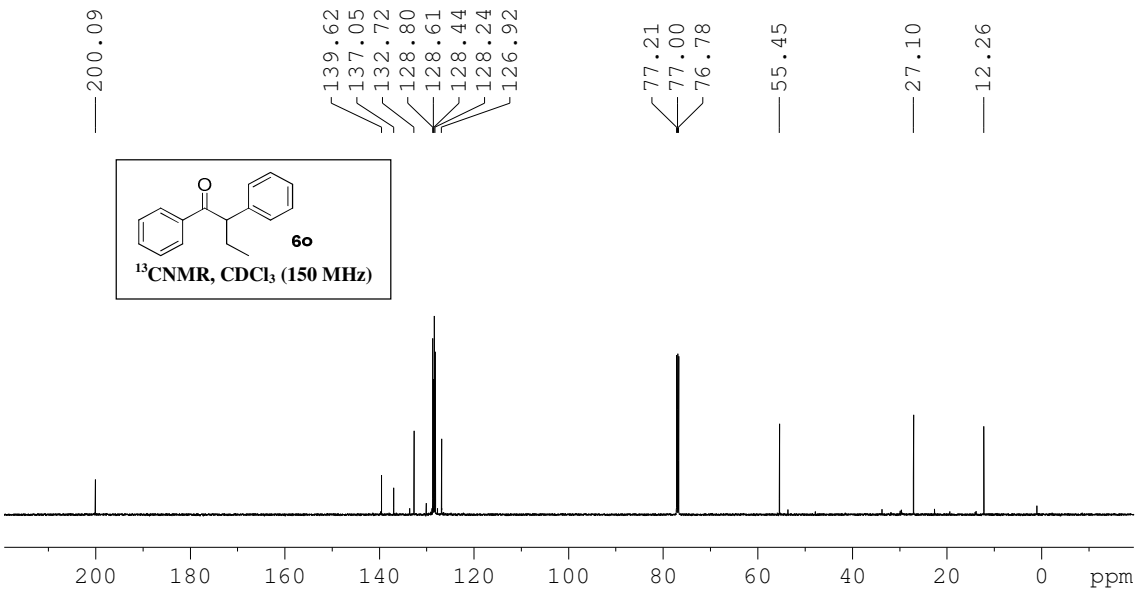

2.15
2.15
2.13
2.13
2.12
2.11
1.77
1.76
1.75
1.73
1.69
1.25
1.24
1.23
1.22
1.18
1.17
1.15
1.14
0.85
0.85
O
6m
1HNMR, CDCl3 (600 MHz)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.27
1.07
0.68
1.90

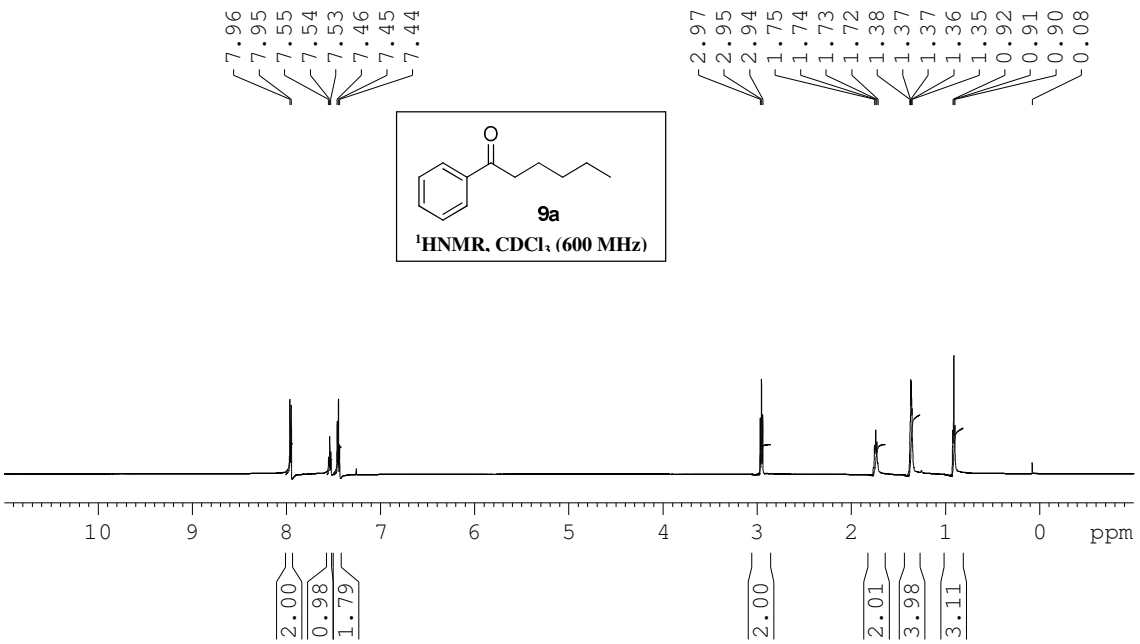

213.96
77.21
77.00
76.78
52.77
50.44
35.00
32.73
25.62
25.58
23.24
22.07
11.76
11.72
O
6m
13CNMR, CDCl3 (150 MHz)
200 180 160 140 120 100 80 60 40 20 0 ppm

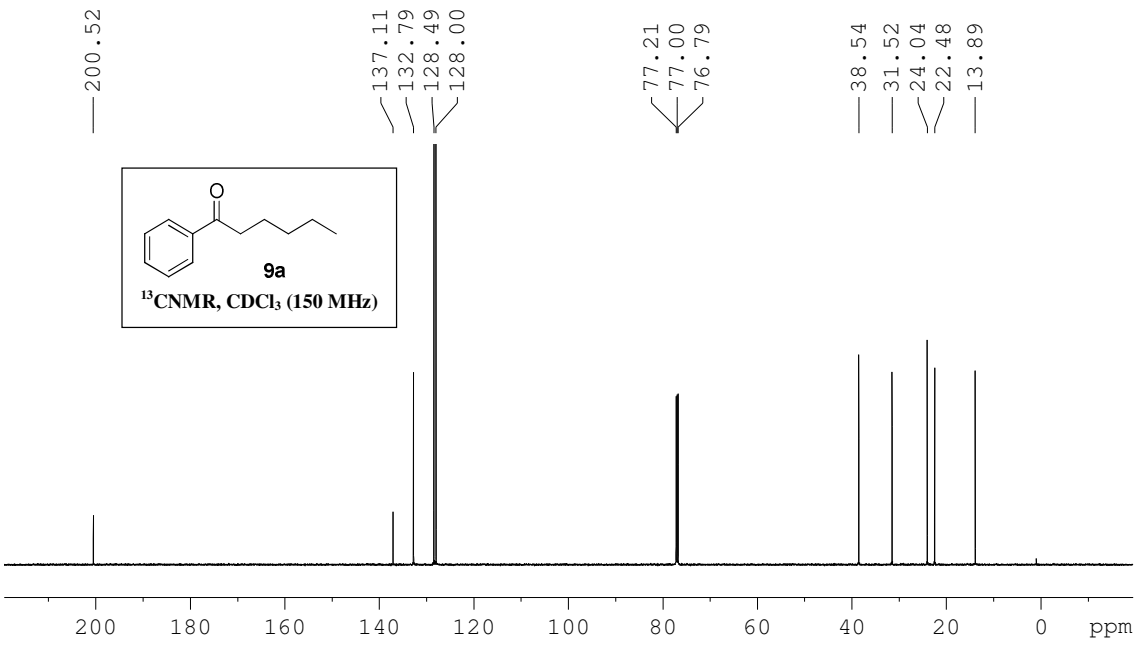

7.88
7.87
6.65
6.64
3.04
2.85
2.84
2.83
1.76
1.75
1.74
1.73
1.00
0.99
0.98
0.08
6n
^{1}HNMR. CDCl$_3$ (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.98
2.02
6.02
2.05
1.98
2.48

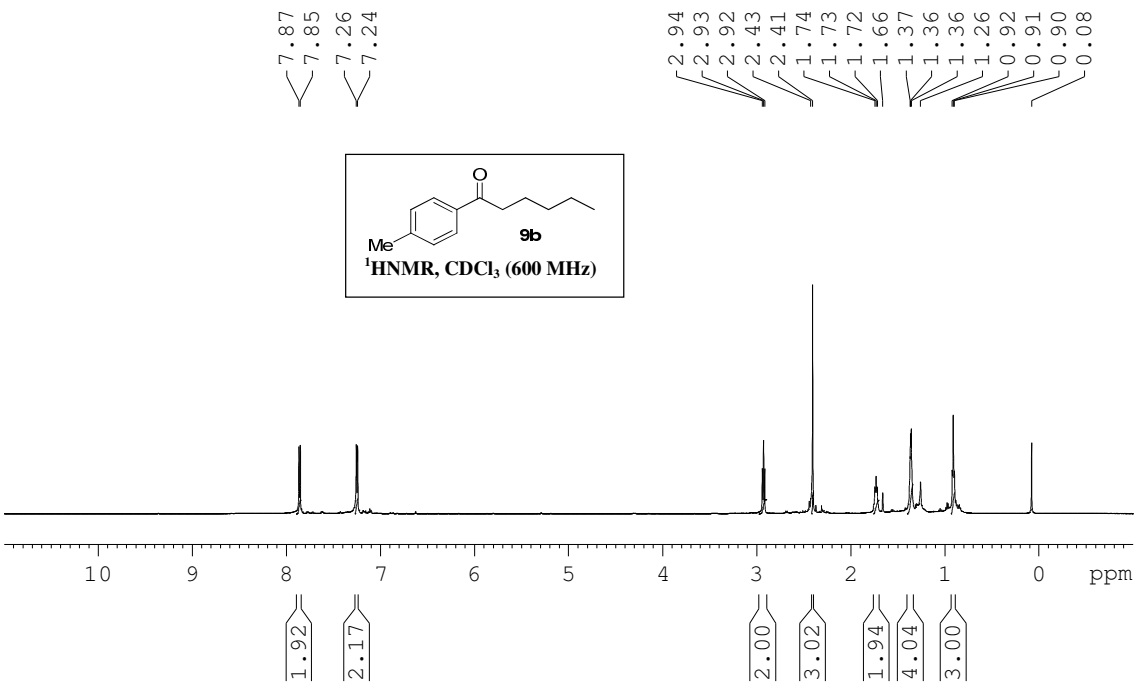

198.65
153.22
130.18
125.17
110.59
77.21
77.00
76.78
39.94
39.80
18.38
13.99
6n
^{13}CNMR, CDCl$_3$ (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

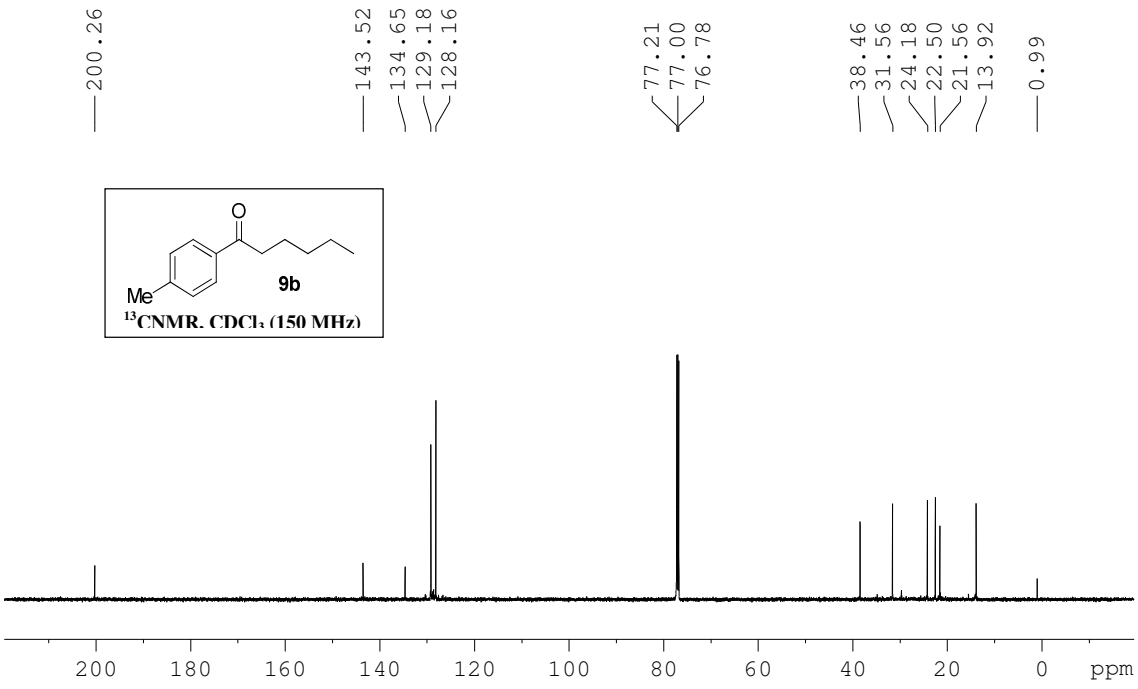

7.98
7.97
7.49
7.48
7.47
7.40
7.39
7.38
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.29
7.28
7.26
7.22
7.22
7.21
7.20
7.19
4.47
4.46
4.44
2.24
2.23
2.22
2.21
2.19
1.90
1.89
1.88
1.87
1.86
1.85
1.27
0.93
0.92
0.91
0.09
O
6o
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.10
1.26
2.13
4.12
1.02
1.00
1.12
1.11
3.08

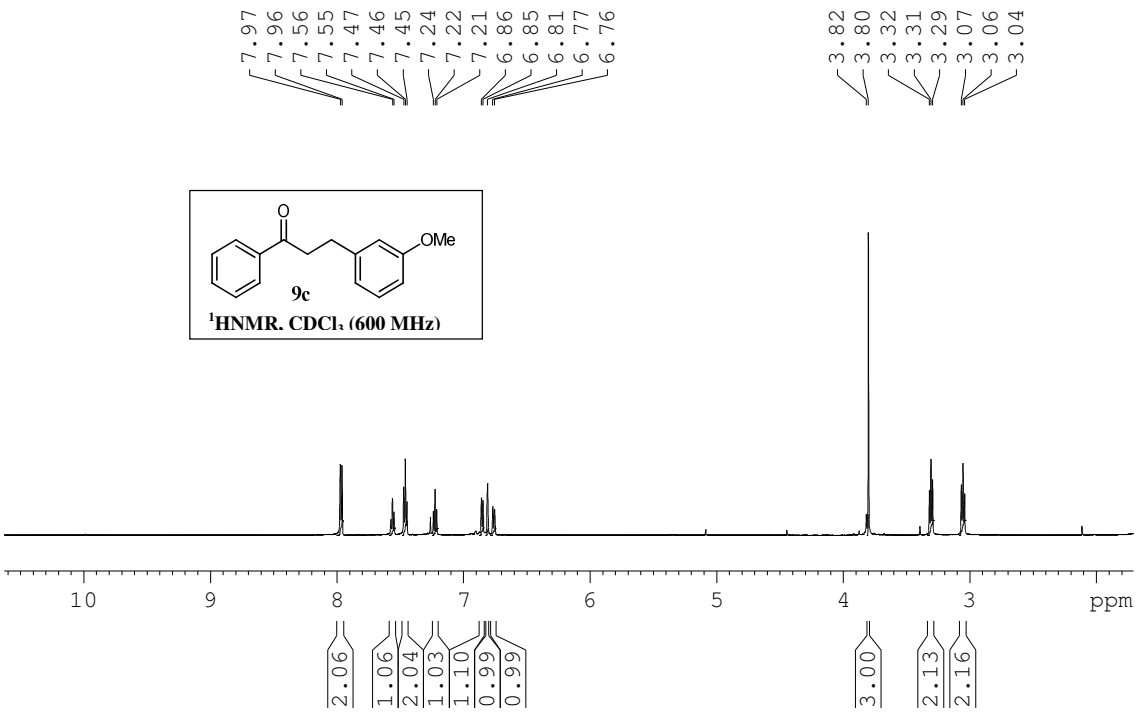

200.09
139.62
137.05
132.72
128.80
128.61
128.44
128.24
126.92
77.21
77.00
76.78
55.45
27.10
12.26
O
6o
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

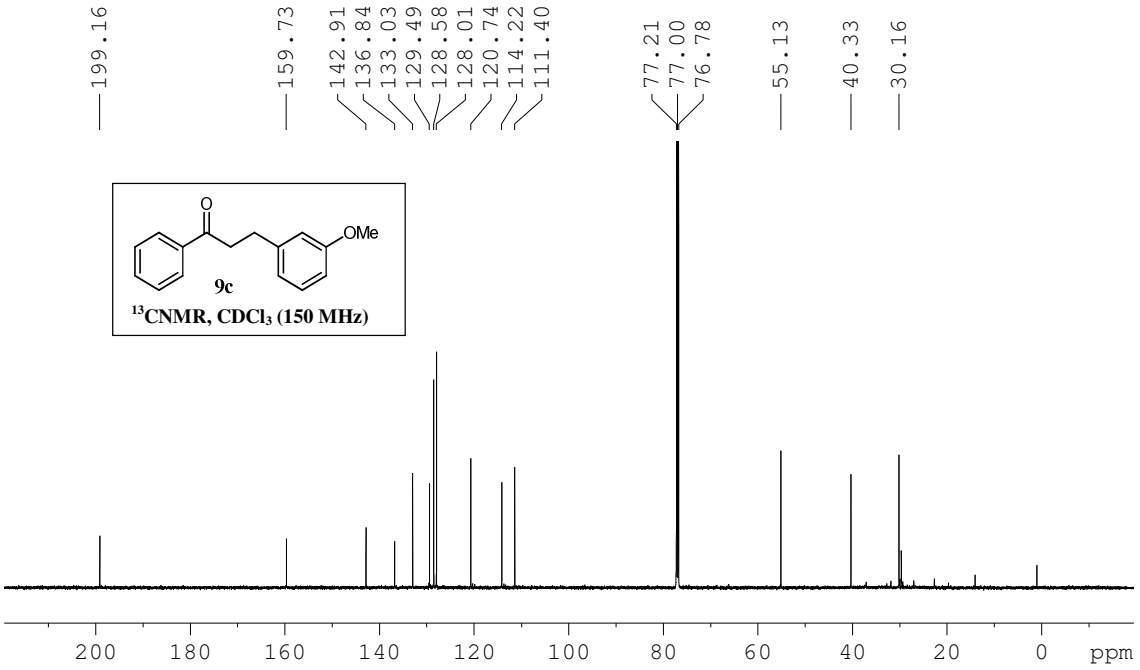

7.96
7.95
7.55
7.54
7.53
7.46
7.45
7.44
2.97
2.95
2.94
1.75
1.74
1.73
1.72
1.38
1.37
1.37
1.36
1.35
0.92
0.91
0.90
0.08
9a
¹HNMR, CDCl₃ (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
0.98
1.79
2.00
2.01
3.98
3.11

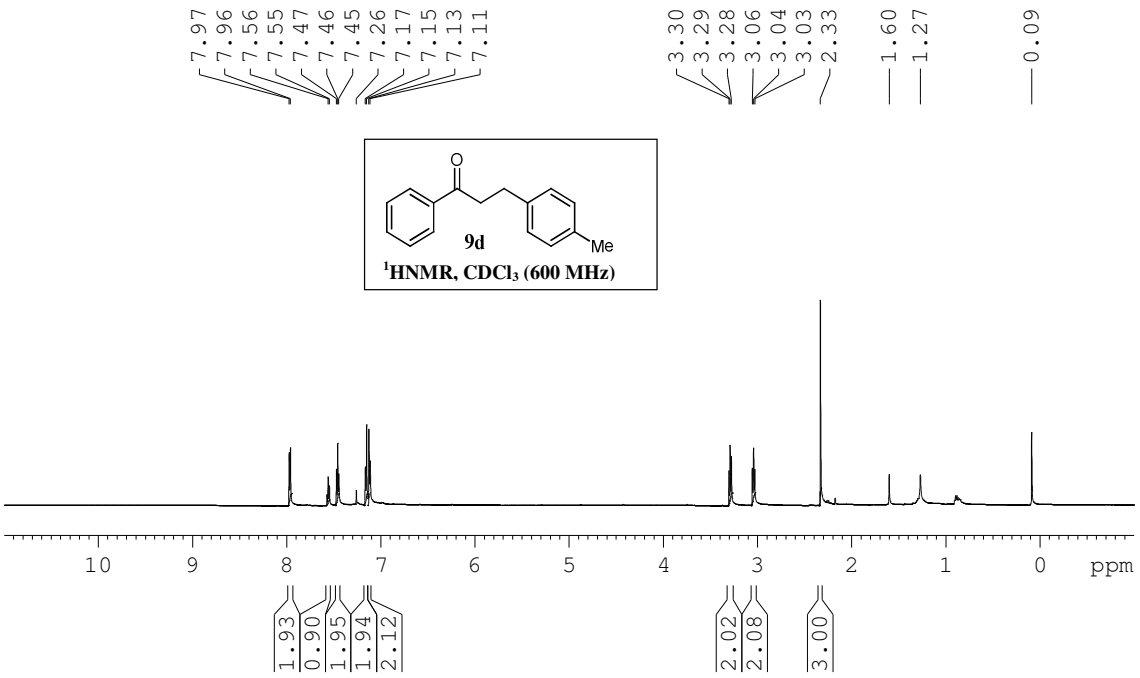

200.52
137.11
132.79
128.49
128.00
77.21
77.00
76.79
38.54
31.52
24.04
22.48
13.89
9a
¹³CNMR, CDCl₃ (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

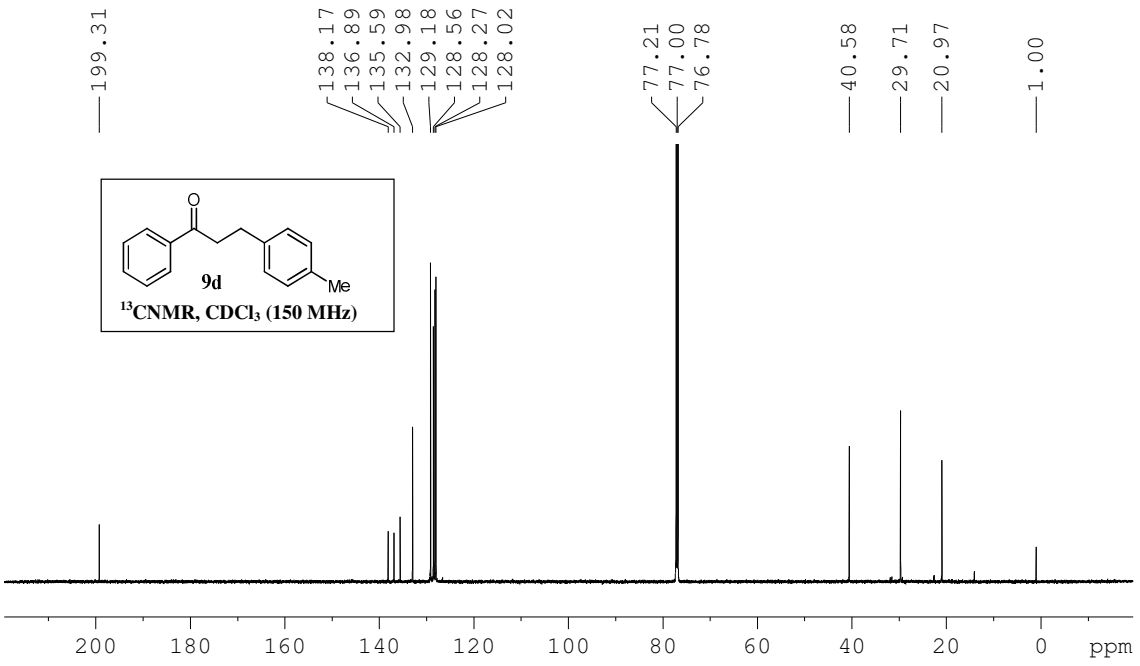

7.87
7.85
7.26
7.24
2.94
2.93
2.92
2.43
2.41
1.74
1.73
1.72
1.66
1.37
1.36
1.36
1.26
0.92
0.91
0.90
0.08
O
Me
9b
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.92
2.17
2.00
3.02
1.94
4.04
3.00

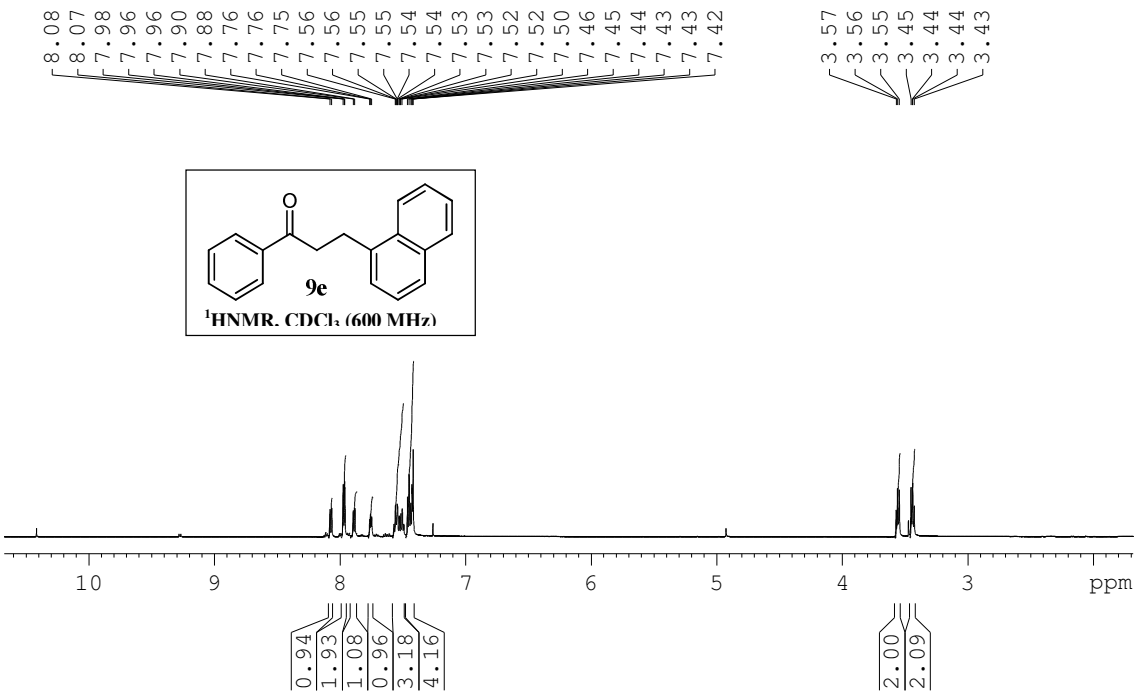

200.26
143.52
134.65
129.18
128.16
77.21
77.00
76.78
38.46
31.56
24.18
22.50
21.56
13.92
0.99
O
Me
9b
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

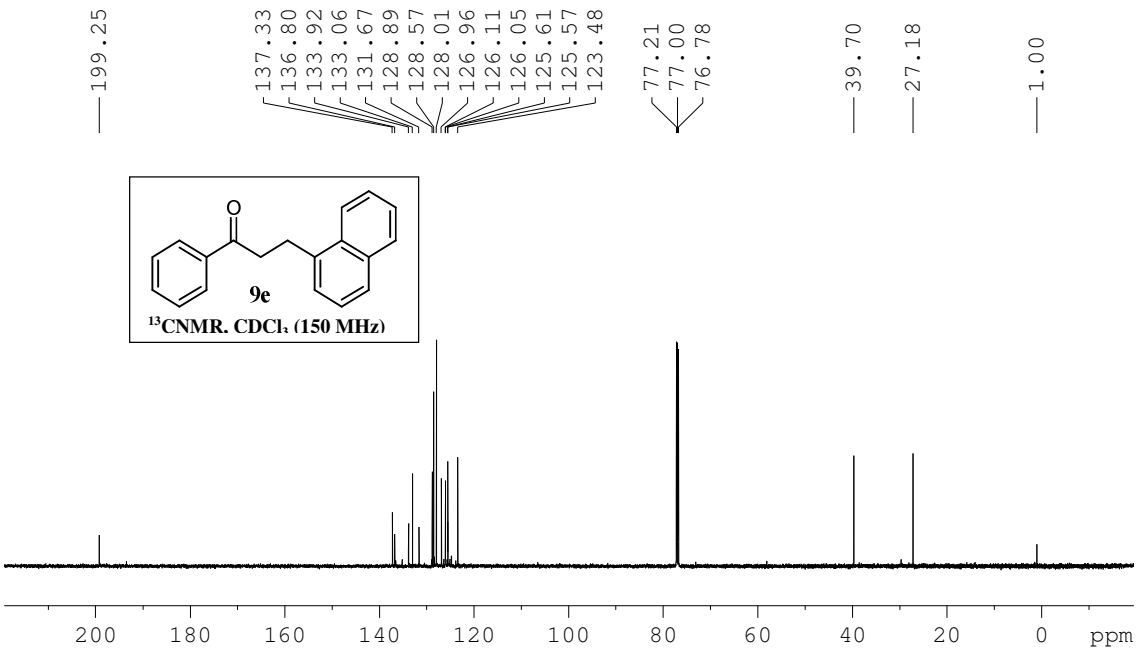

7.97
7.96
7.56
7.55
7.47
7.46
7.45
7.24
7.22
7.21
6.86
6.85
6.81
6.77
6.76
3.82
3.80
3.32
3.31
3.29
3.07
3.06
3.04
O
OMe
9c
¹HNMR. CDCl₃ (600 MHz)
10
9
8
7
6
5
4
3
ppm
2.06
1.06
2.04
1.03
1.10
0.99
0.99
3.00
2.13
2.16

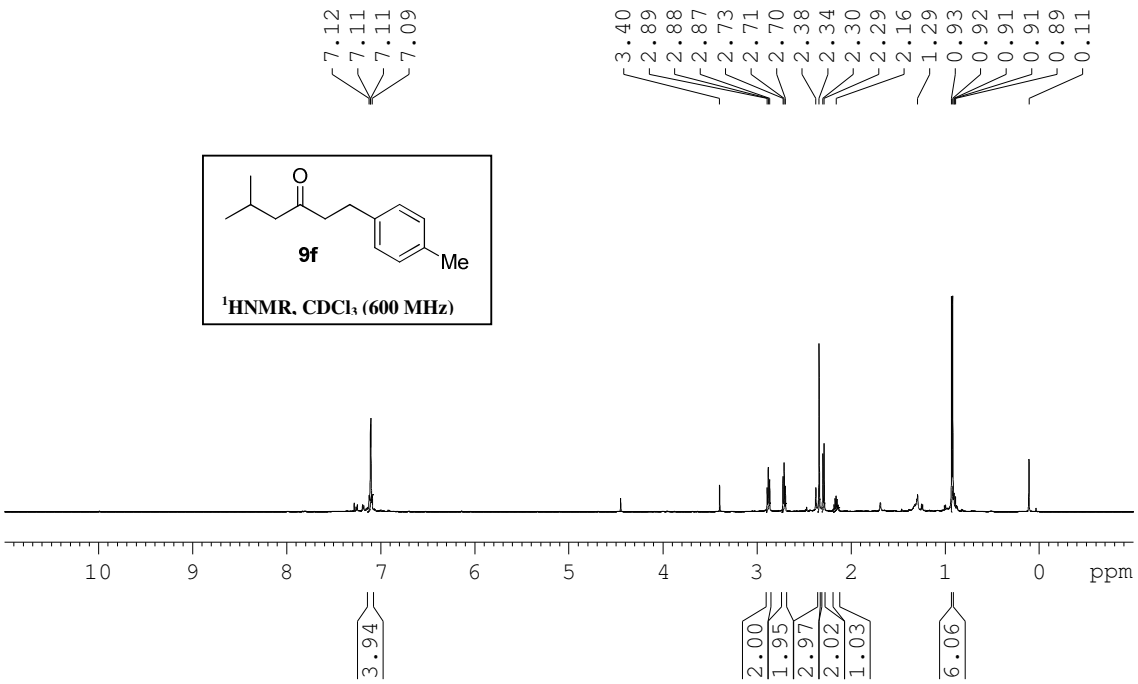

199.16
159.73
142.91
136.84
133.03
129.49
128.58
128.01
120.74
114.22
111.40
77.21
77.00
76.78
55.13
40.33
30.16
O
OMe
9c
¹³CNMR, CDCl₃ (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

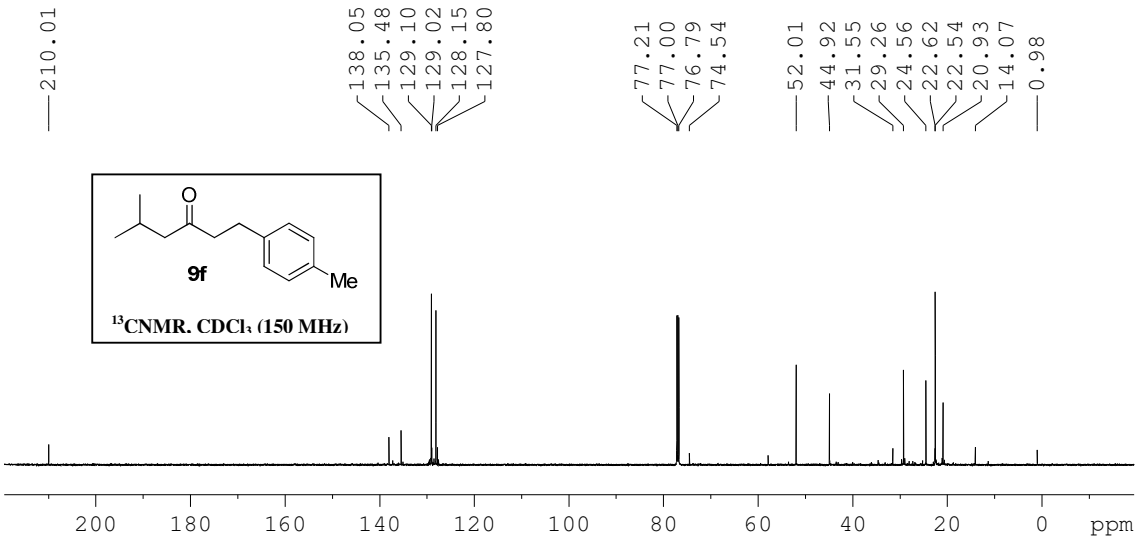

7.97
7.96
7.56
7.55
7.47
7.46
7.45
7.26
7.17
7.15
7.13
7.11
3.30
3.29
3.28
3.06
3.04
3.03
2.33
1.60
1.27
0.09
O
9d
Me
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.93
0.90
1.95
1.94
2.12
2.02
2.08
3.00

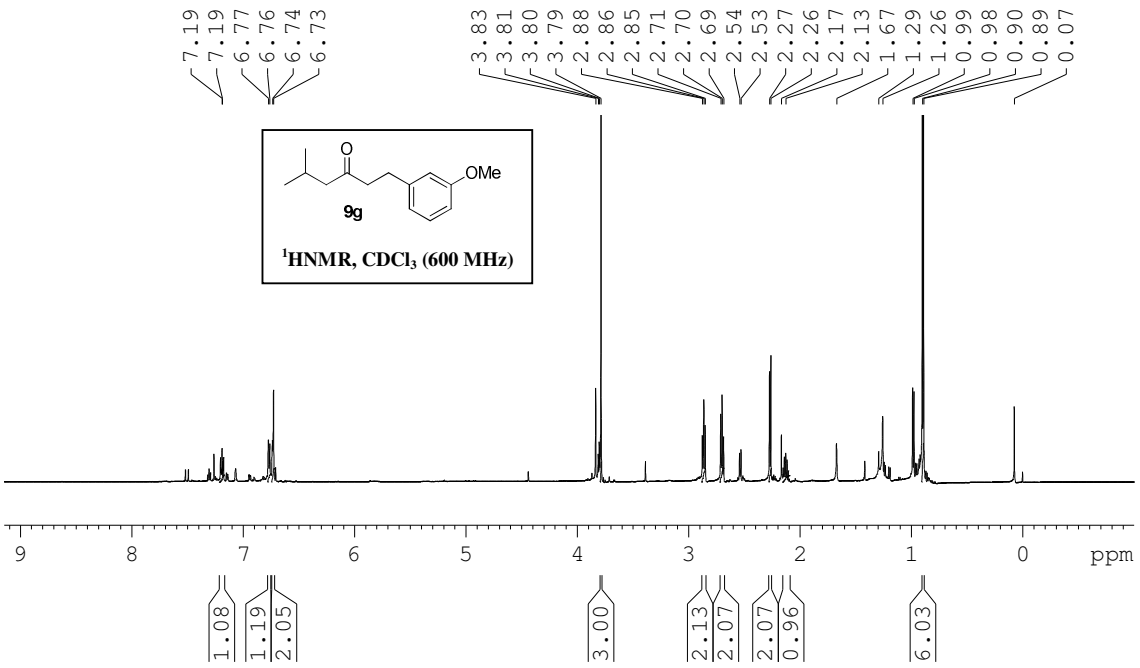

199.31
138.17
136.89
135.59
132.98
129.18
128.56
128.27
128.02
77.21
77.00
76.78
40.58
29.71
20.97
1.00
O
9d
Me
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

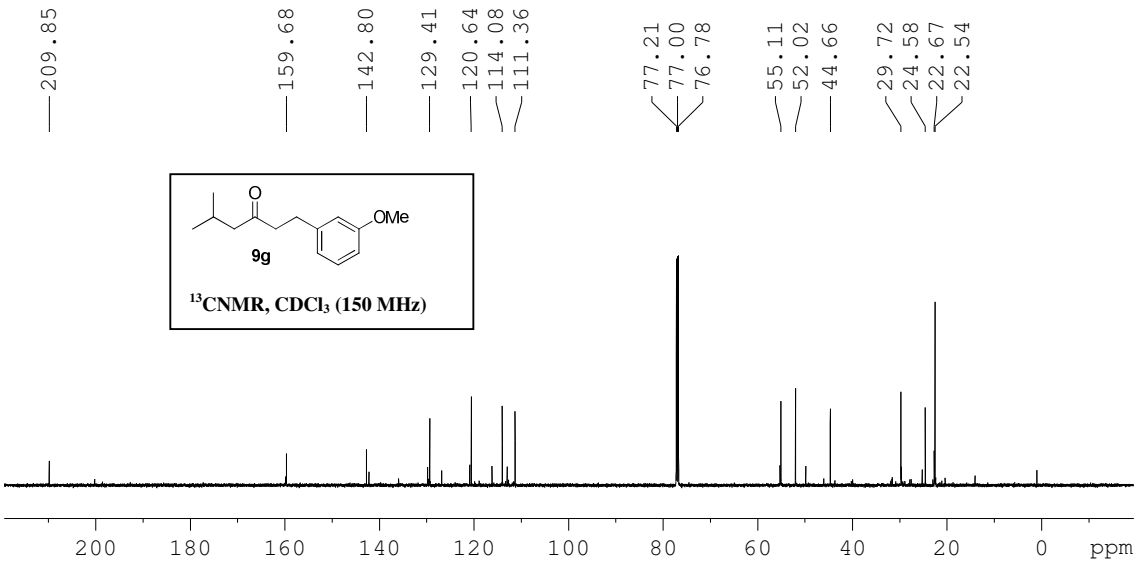

8.08
8.07
7.98
7.96
7.96
7.90
7.88
7.76
7.76
7.75
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.50
7.46
7.45
7.44
7.43
7.43
7.42
3.57
3.56
3.55
3.45
3.44
3.44
3.43
9e
10
9
8
7
6
5
4
3
ppm
0.94
1.93
1.08
0.96
3.18
4.16
2.00
2.09

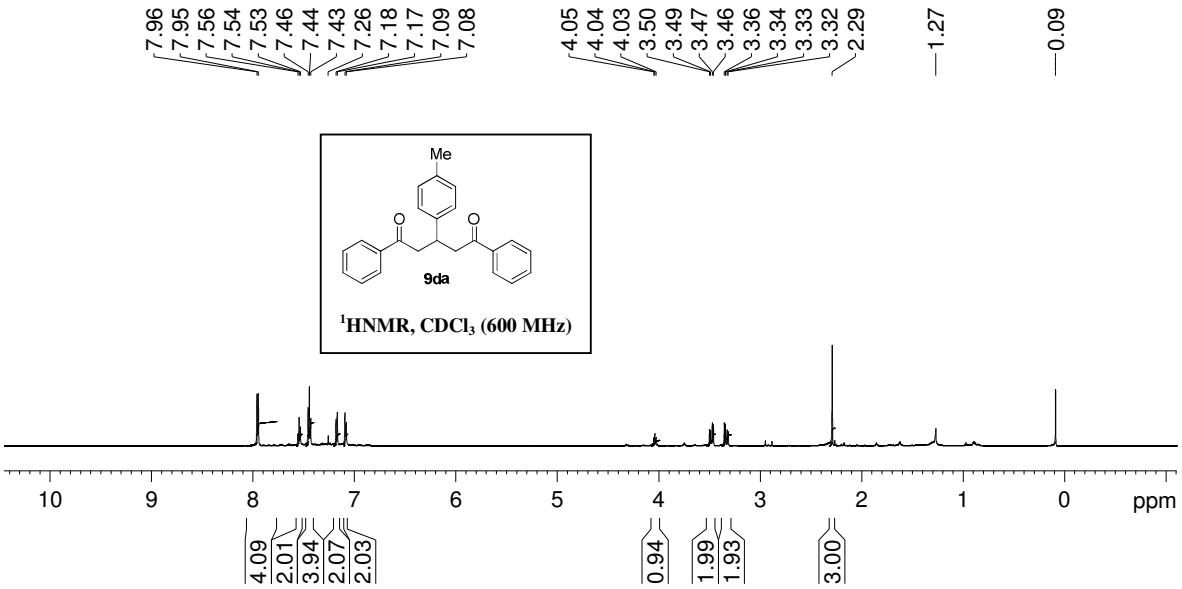

199.25
137.33
136.80
133.92
133.06
131.67
128.89
128.57
128.01
126.96
126.11
126.05
125.61
125.57
123.48
77.21
77.00
76.78
39.70
27.18
1.00
9e
200
180
160
140
120
100
80
60
40
20
0
ppm

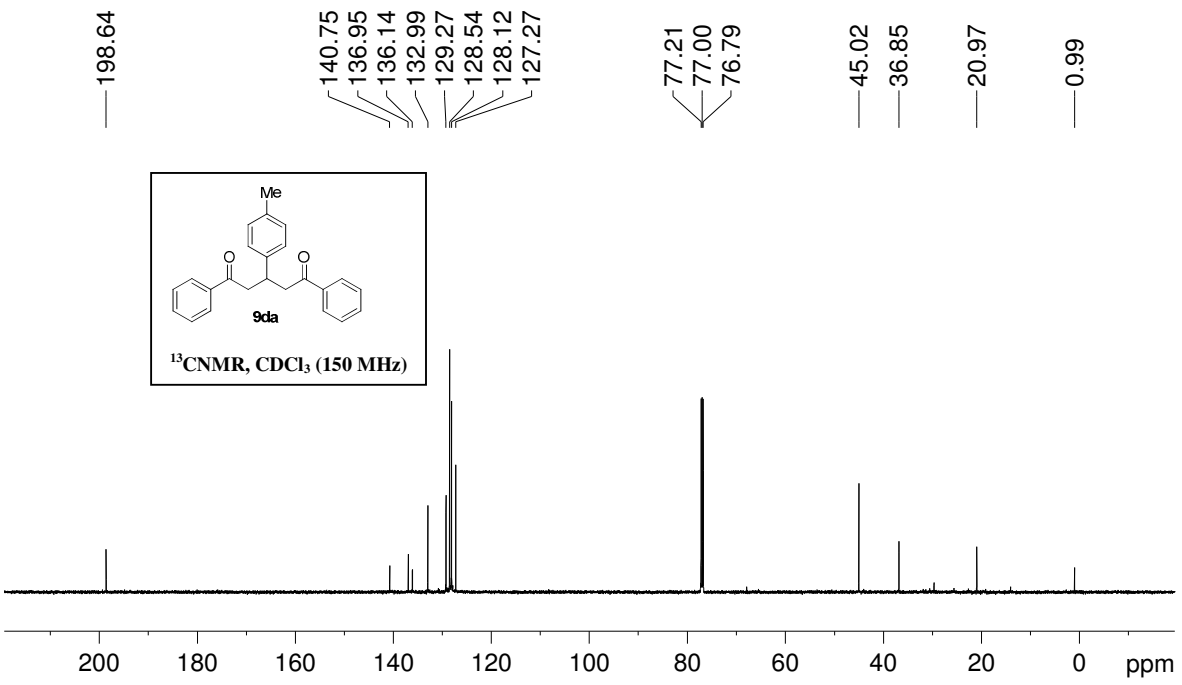

7.12
7.11
7.11
7.09
3.40
2.89
2.88
2.87
2.73
2.71
2.70
2.38
2.34
2.30
2.29
2.16
1.29
0.93
0.92
0.91
0.91
0.89
0.11
O
9f
Me
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
3.94
2.00
1.95
2.97
2.02
1.03
6.06

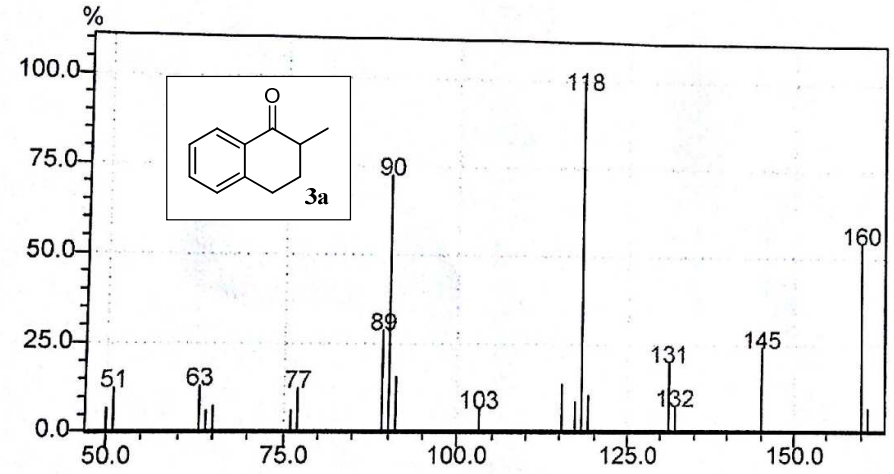

210.01
138.05
135.48
129.10
129.02
128.15
127.80
77.21
77.00
76.79
74.54
52.01
44.92
31.55
29.26
24.56
22.62
22.54
20.93
14.07
0.98
O
9f
Me
13CNMR. CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

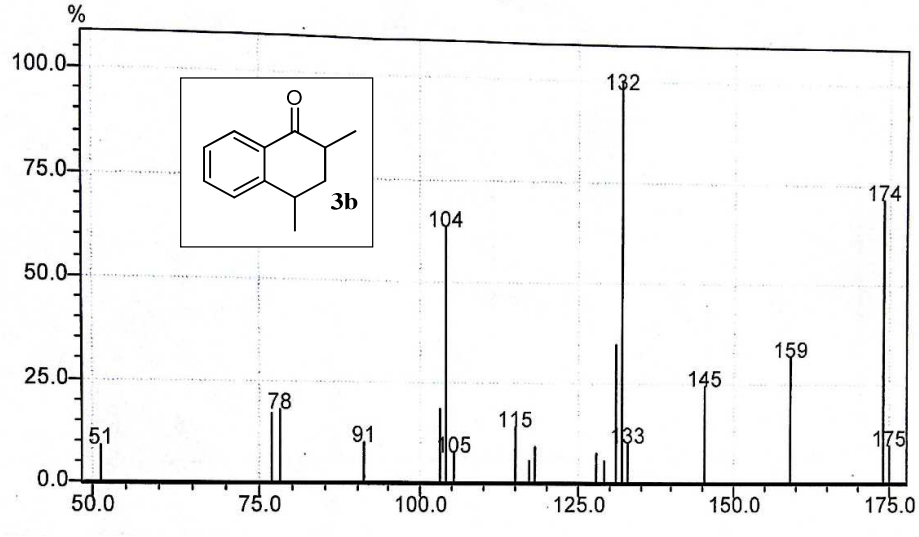

7.19
7.19
6.77
6.76
6.74
6.73
3.83
3.81
3.80
3.79
2.88
2.86
2.85
2.71
2.70
2.69
2.54
2.53
2.27
2.26
2.17
2.13
1.67
1.29
1.26
0.99
0.98
0.90
0.89
0.07
O
OMe
9g
1HNMR, CDCl3 (600 MHz)
9 8 7 6 5 4 3 2 1 0 ppm
1.08
1.19
2.05
3.00
2.13
2.07
2.07
0.96
6.03

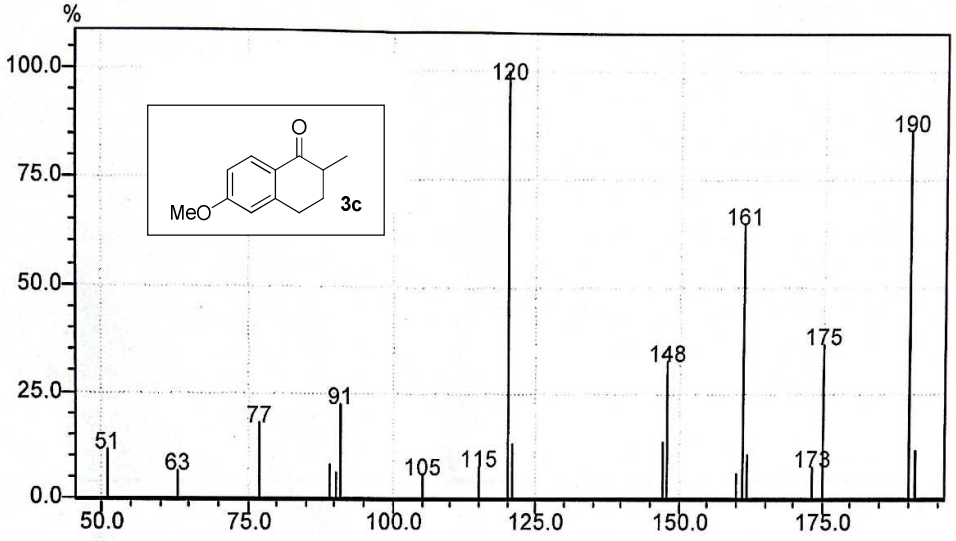

209.85
159.68
142.80
129.41
120.64
114.08
111.36
77.21
77.00
76.78
55.11
52.02
44.66
29.72
24.58
22.67
22.54
O
OMe
9g
13CNMR, CDCl3 (150 MHz)
200 180 160 140 120 100 80 60 40 20 0 ppm

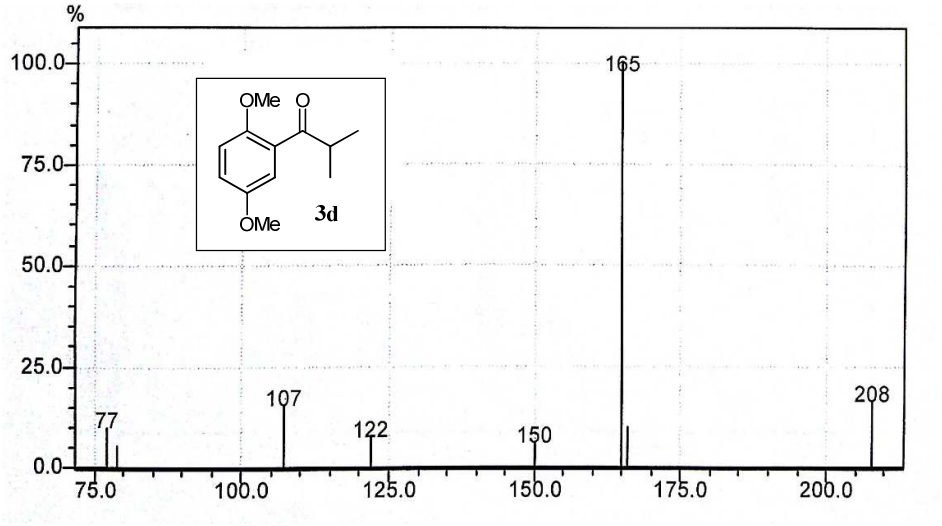

7.96
7.95
7.56
7.54
7.53
7.46
7.44
7.43
7.26
7.18
7.17
7.09
7.08
4.05
4.04
4.03
3.50
3.49
3.47
3.46
3.36
3.34
3.33
3.32
2.29
1.27
0.09
Me
O
O
9da
1HNMR, CDCl3 (600 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
4.09
2.01
3.94
2.07
2.03
0.94
1.99
1.93
3.00

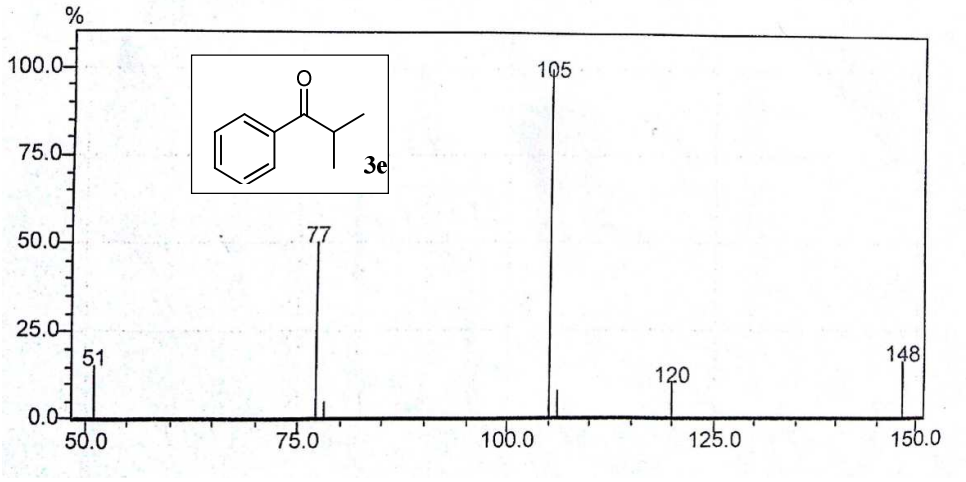

198.64
140.75
136.95
136.14
132.99
129.27
128.54
128.12
127.27
77.21
77.00
76.79
45.02
36.85
20.97
0.99
Me
O
O
9da
13CNMR, CDCl3 (150 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

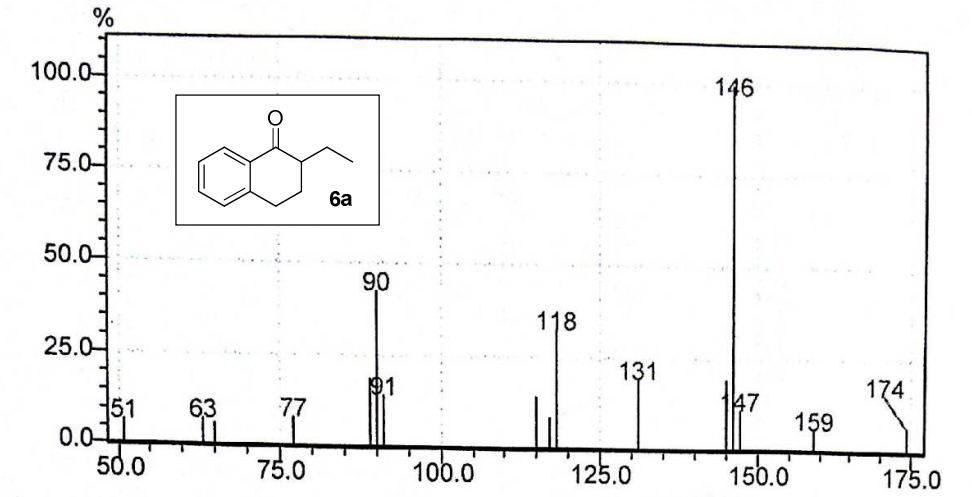

%
100.0
75.0
50.0
25.0
0.0
50.0
75.0
100.0
125.0
150.0
3a
118
90
160
89
131
145
51
63
77
103
132

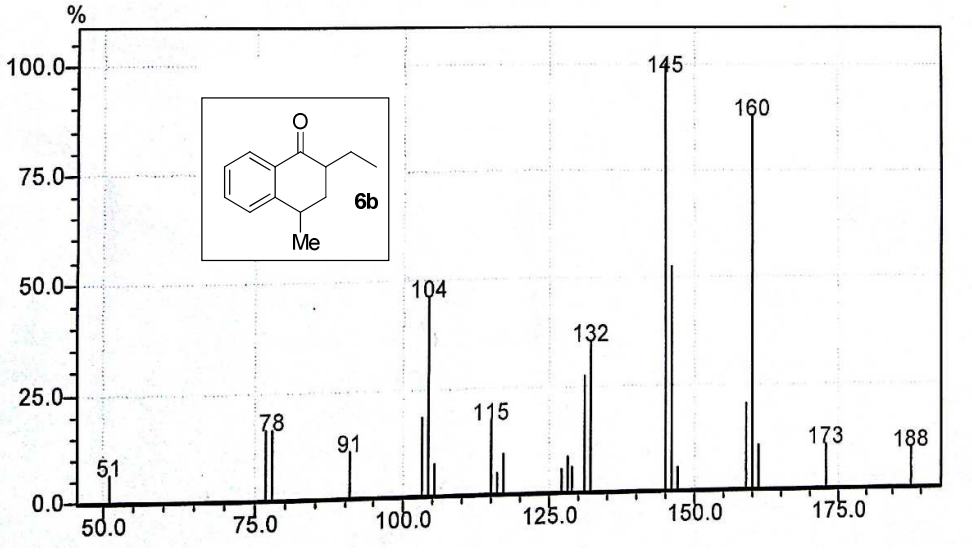

%
100.0
75.0
50.0
25.0
0.0
50.0
75.0
100.0
125.0
150.0
175.0
3b
132
174
104
159
145
78
115
51
91
105
133
175

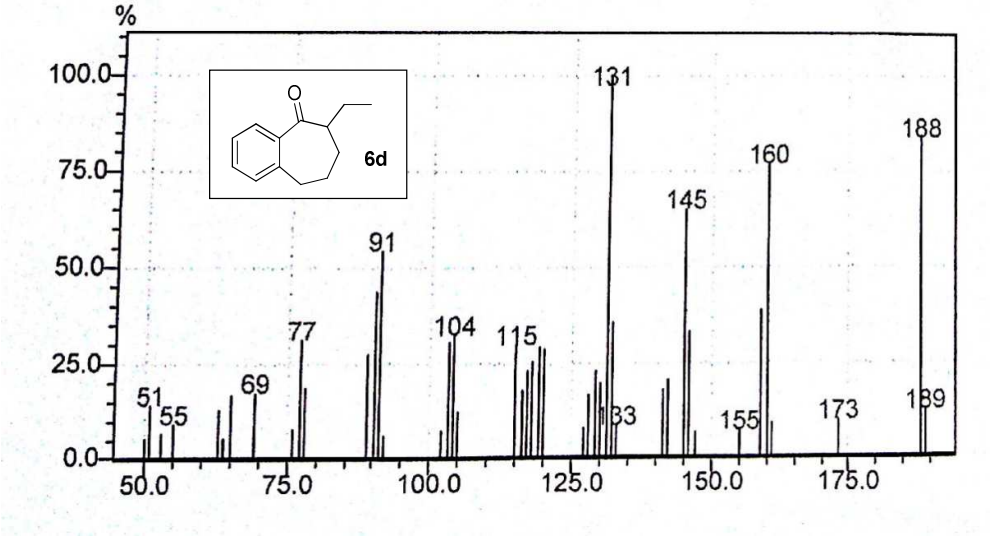

%
100.0
75.0
50.0
25.0
0.0
50.0
75.0
100.0
125.0
150.0
175.0
MeO
3c
120
190
161
148
175
77
91
51
63
105
115
173

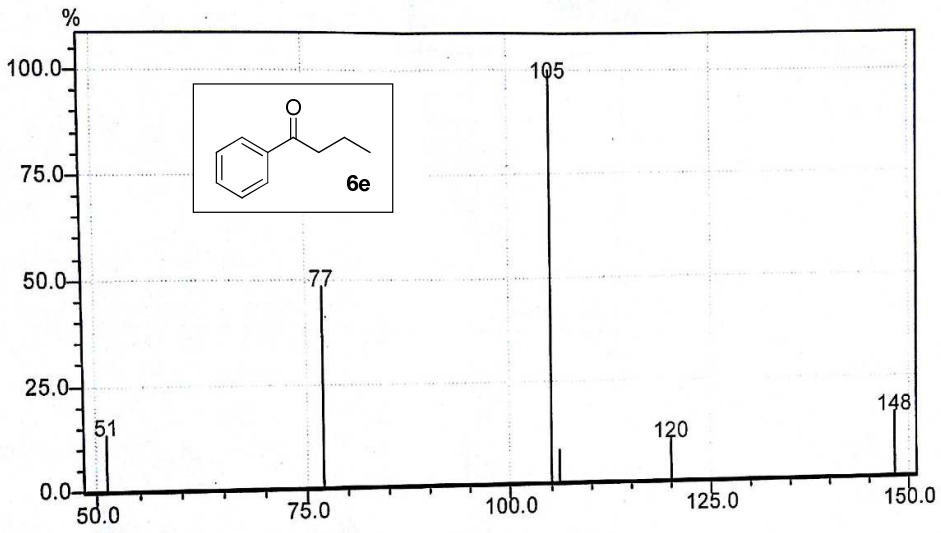

%
100.0
75.0
50.0
25.0
0.0
OMe
O
OMe
3d
165
107
208
77
122
150
75.0
100.0
125.0
150.0
175.0
200.0

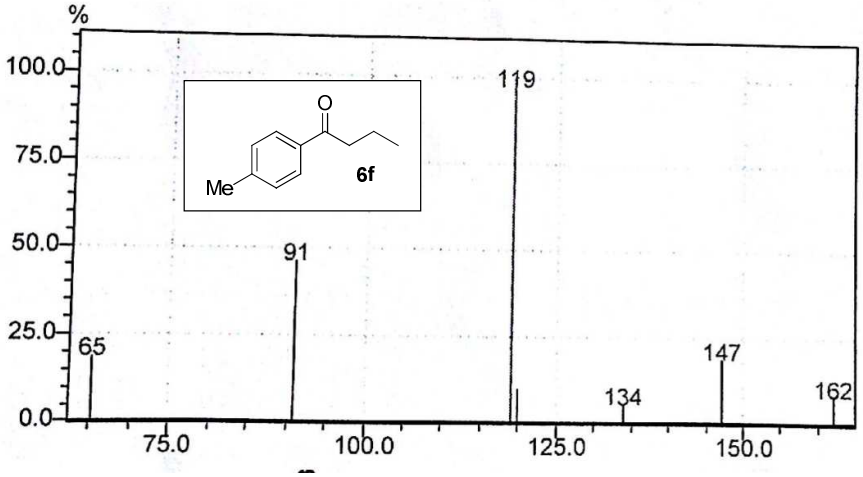

%
100.0
75.0
50.0
25.0
0.0
O
3e
105
77
51
120
148
50.0
75.0
100.0
125.0
150.0

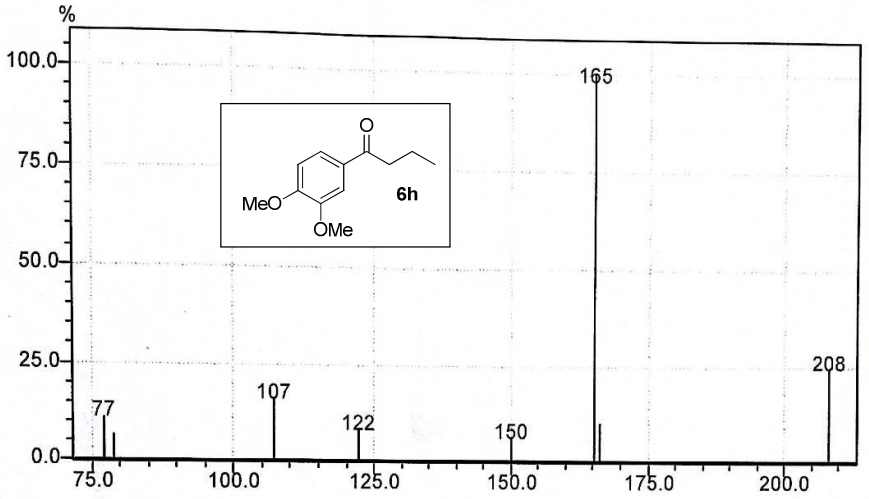

%
100.0
75.0
50.0
25.0
0.0
6a
146
90
118
131
91
174
51
63
77
147
159
50.0
75.0
100.0
125.0
150.0
175.0

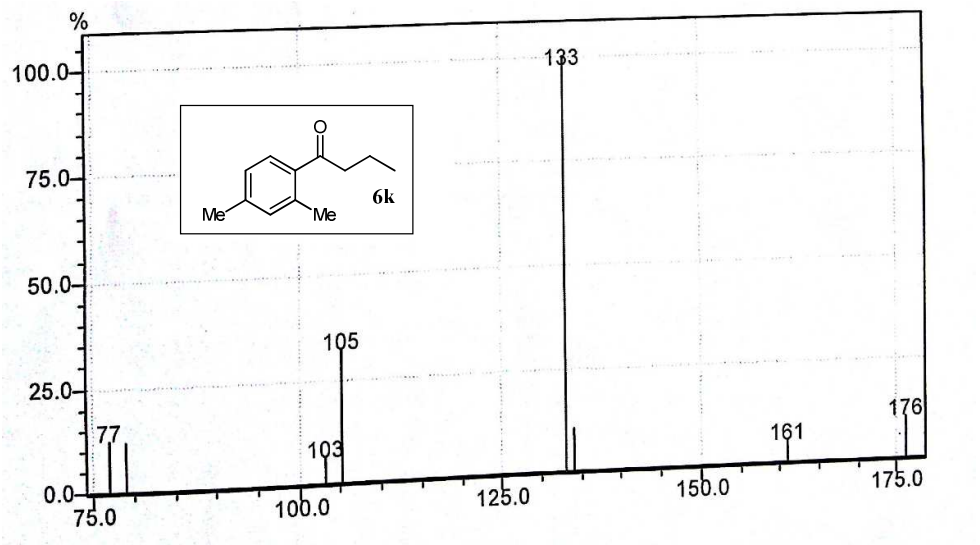

%
100.0
75.0
50.0
25.0
0.0
6b
Me
145
160
104
132
78
115
91
173
188
51
50.0
75.0
100.0
125.0
150.0
175.0

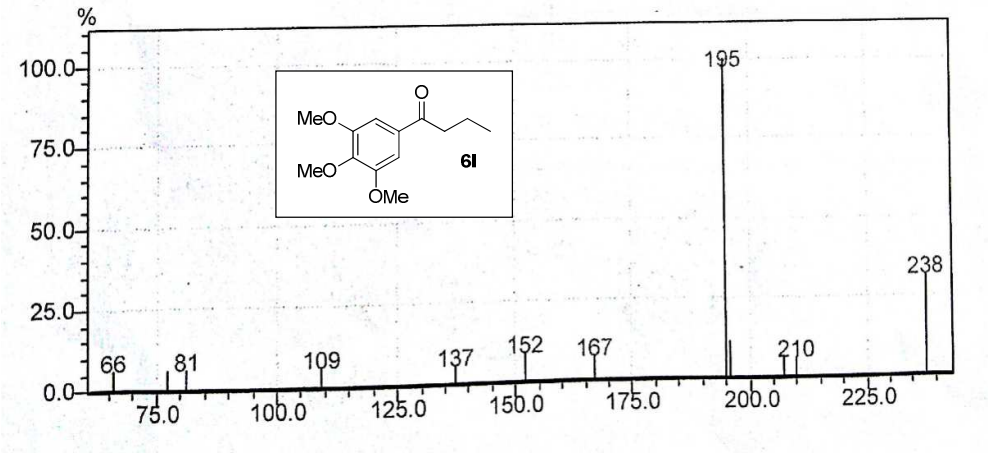

%
100.0
75.0
50.0
25.0
0.0
6d
131
188
160
145
91
77
104
115
69
51
55
133
155
173
189
50.0
75.0
100.0
125.0
150.0
175.0

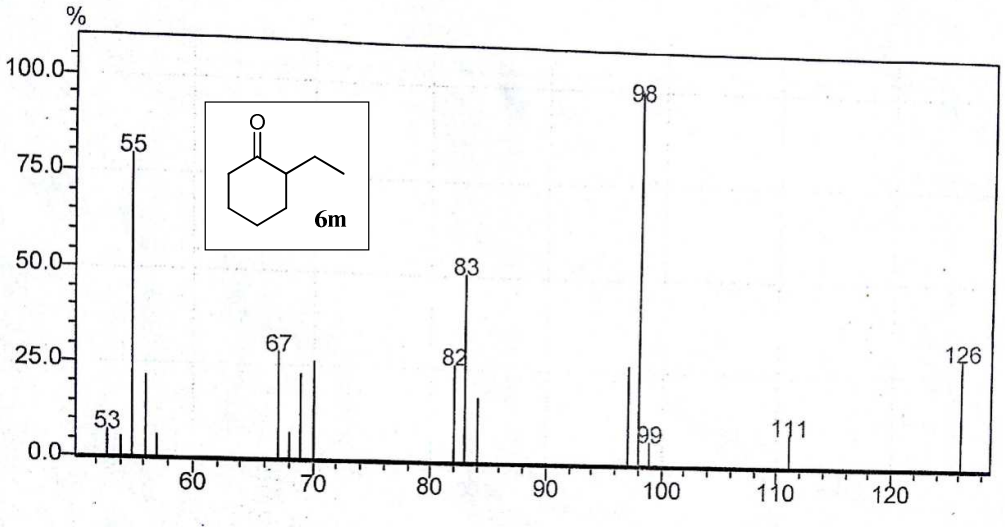

%
100.0
75.0
50.0
25.0
0.0
O
6e
105
77
51
120
148
50.0
75.0
100.0
125.0
150.0

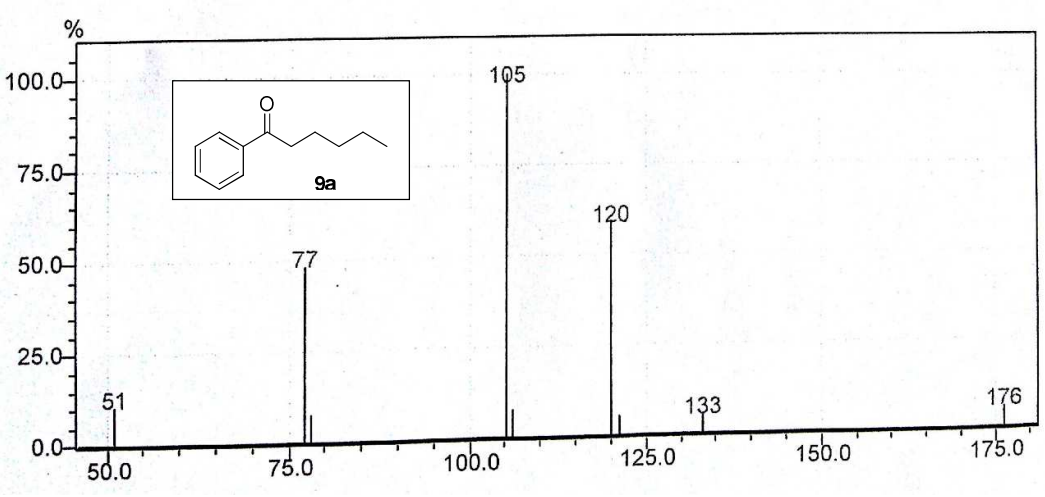

%
100.0
75.0
50.0
25.0
0.0
O
Me
6f
119
91
65
147
134
162
75.0
100.0
125.0
150.0

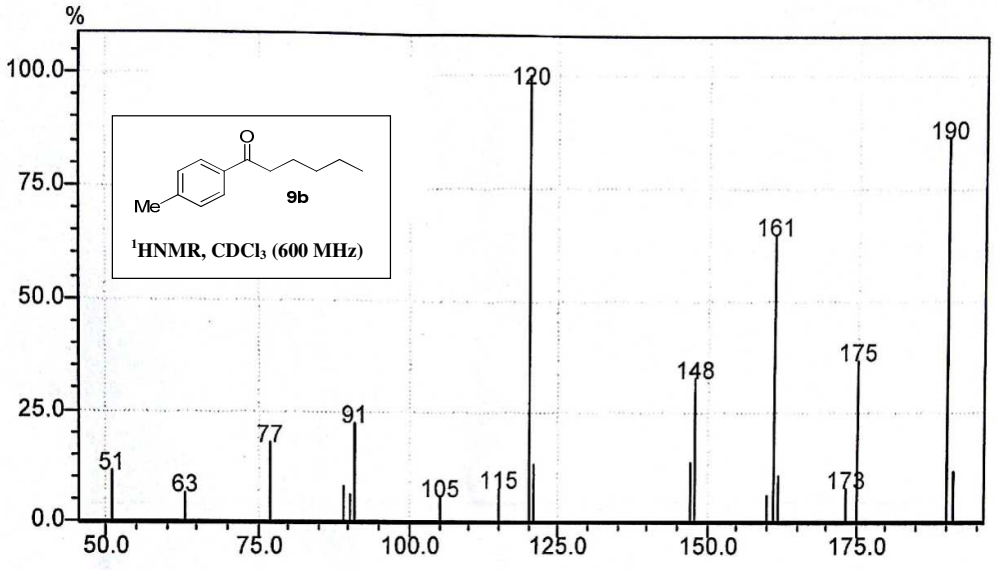

%
100.0
75.0
50.0
25.0
0.0
O
MeO
OMe
6h
165
208
107
77
122
150
75.0
100.0
125.0
150.0
175.0
200.0

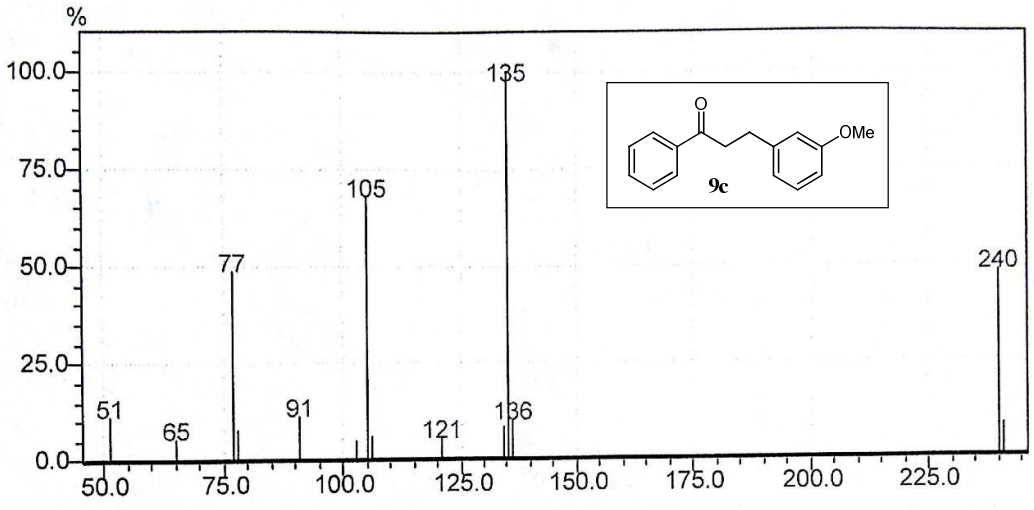

%
100.0
75.0
50.0
25.0
0.0
133
105
77
103
161
176
75.0
100.0
125.0
150.0
175.0
O
Me
Me
6k

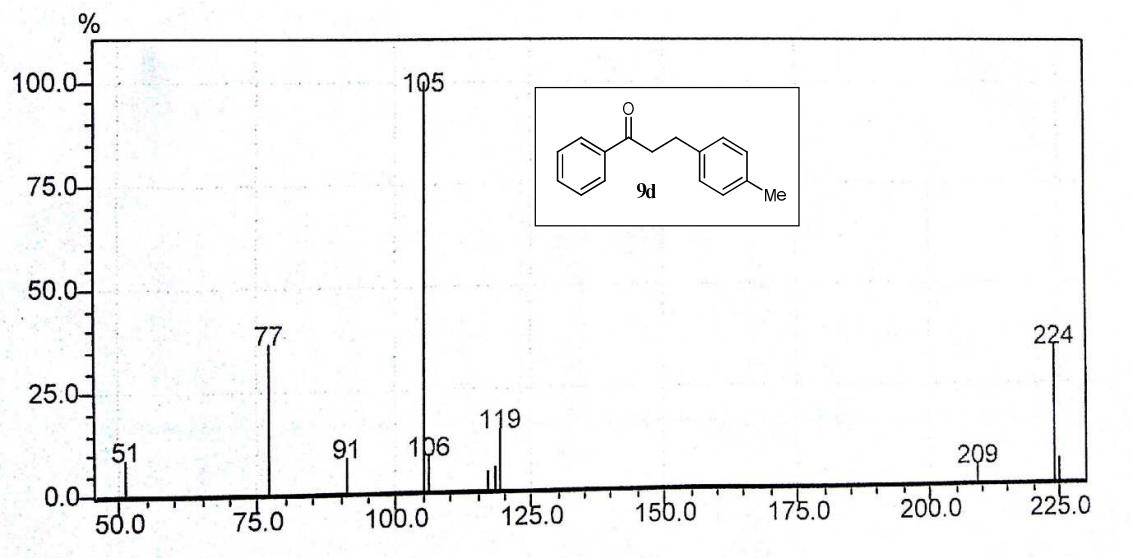

%
100.0
75.0
50.0
25.0
0.0
195
238
66
81
109
137
152
167
210
75.0
100.0
125.0
150.0
175.0
200.0
225.0
O
MeO
MeO
OMe
6l

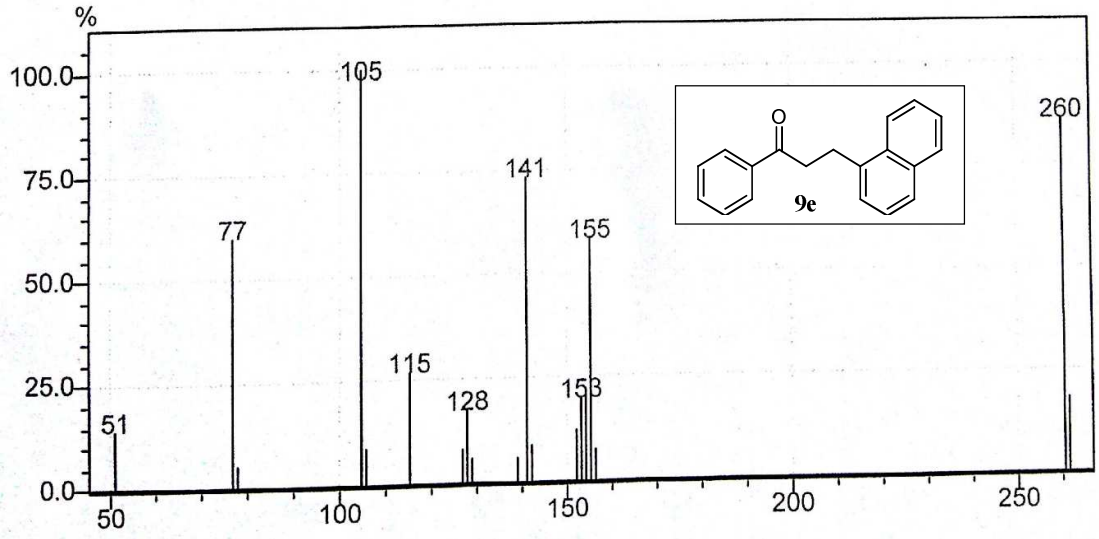

%
100.0
75.0
50.0
25.0
0.0
98
55
83
67
82
126
53
99
111
60
70
80
90
100
110
120
O
6m

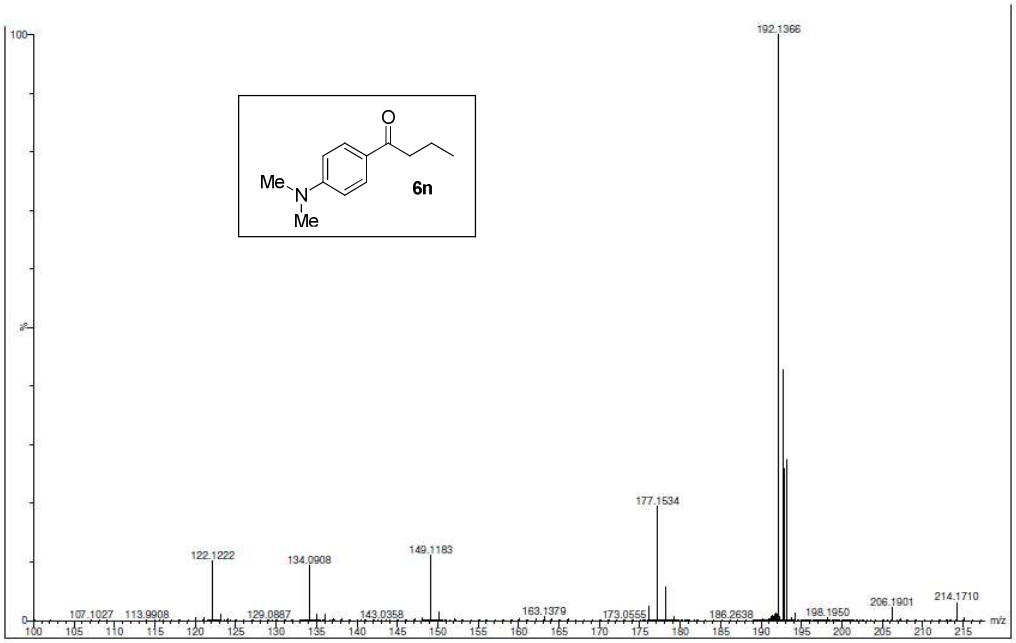

%
100.0
75.0
50.0
25.0
0.0
105
120
77
51
133
176
50.0
75.0
100.0
125.0
150.0
175.0
9a

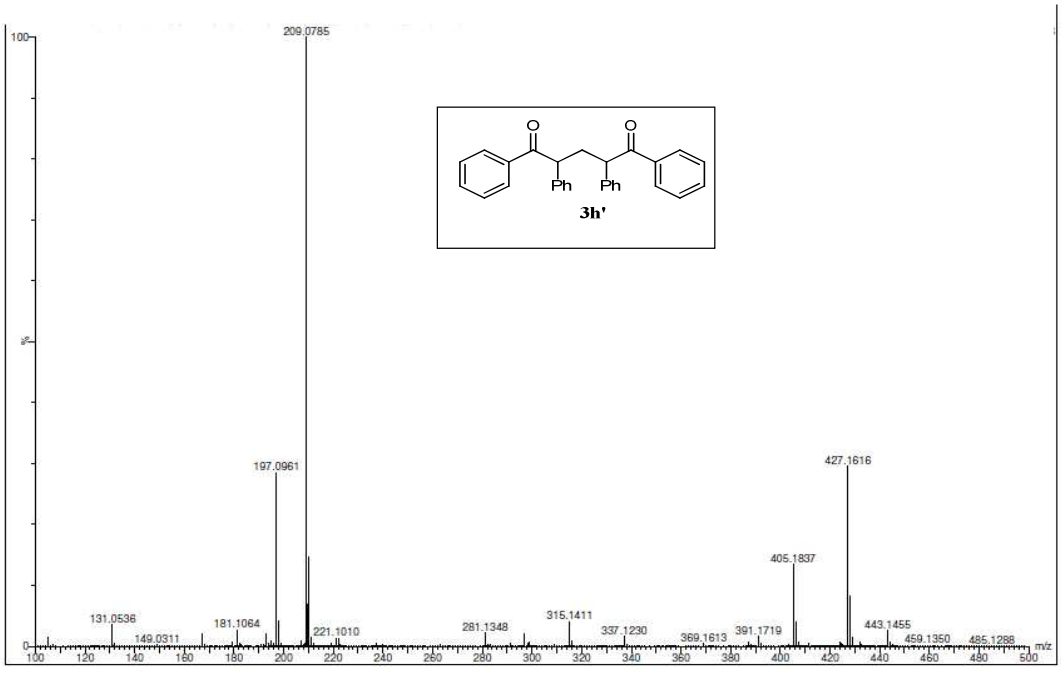

%
100.0
75.0
50.0
25.0
0.0
120
190
161
148
175
91
77
51
63
105
115
173
50.0
75.0
100.0
125.0
150.0
175.0
Me
9b
1HNMR, CDCl3 (600 MHz)

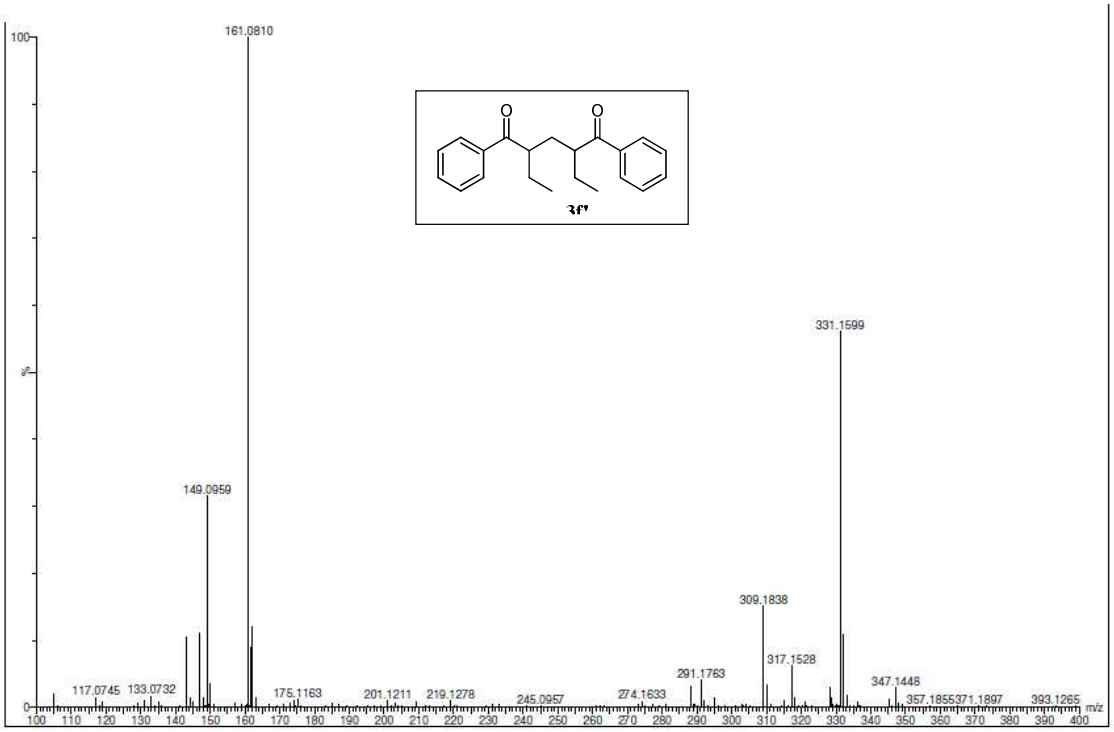

%
100.0
75.0
50.0
25.0
0.0
135
105
77
240
51
65
91
121
136
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
OMe
9c


%
100.0
75.0
50.0
25.0
0.0
105
77
51
91
106
119
209
224
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
O
9d
Me


%
100.0
75.0
50.0
25.0
0.0
105
77
51
115
128
141
155
153
260
50
100
150
200
250
O
9e


192.1366
177.1534
122.1222
134.0908
149.1183
107.1027
113.9908
129.0887
143.0358
163.1379
173.0555
186.2638
198.1950
206.1901
214.1710
m/z
6n


209.0785
197.0961
427.1616
405.1837
131.0536
149.0311
181.1064
221.1010
281.1348
315.1411
337.1230
369.1613
391.1719
443.1455
459.1350
485.1288
m/z
3h'



References

1. Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. Palladium(II)-Catalyzed Oxidation of Alcohols to Aldehydes and Ketones by Molecular Oxygen. *J. Org. Chem.* **1999,** *64,* 6750-6755.

2. Muzart, J. Palladium-catalysed oxidation of primary and secondary alcohols. *Tetrahedron.* **2003**, *59*, 5789–5816.

3. Bandna.; Aggarwal, N.; Das, P. Solid-supported Pd(0): an efficient heterogeneous catalyst for aerobic oxidation of benzyl alcohols into aldehydes and ketones. *Tetrahedron Lett.* **2011**, *52*, 4954–4956.

4. Karimi, B.; Abedi, S.; Clark, J. H.; Budarin, V. Highly Efficient Aerobic Oxidation of Alcohols Using a Recoverable Catalyst: The Role of Mesoporous Channels of SBA-

15 in Stabilizing Palladium Nanoparticles. *Angew. Chem. Int. Ed.* **2006**, *45*, 4776 – 4779.

5. Chan, L. K. M.; Poole, D. L.; Shen, D.; Healy, M. P.; Donohoe, T. J. Rhodium-Catalyzed Ketone Methylation Using Methanol Under Mild Conditions: Formation of a-Branched Products. *Angew. Chem., Int. Ed.* **2014**, *53*, 761.

1. Quan, X.; Kerdphon, S.; Andersson, P. G. C-C Coupling of Ketones with Methanol Catalyzed by a *N*-Heterocyclic Carbene–Phosphine Iridium Complex*Chem. - Eur. J.* **2015**, *21*, 3576.