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Supporting Information

Cross Coupling of Alkylsilicates with Acylchlorides via Photoredox/Nickel Dual Catalysis. A New Synthesis of Ketones

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Table of content

I. General informations

Unless otherwise noted, reactions were carried out under an argon atmosphere in oven-dried glassware. Methanol was distillated over CaH_2, THF, acetonitrile and diethyl ether were distillated over sodium/benzophenone, triethylamine over potassium hydroxide. Catechol was purchased from commercial source and purified by crystallization from toluene followed by sublimation. Reagents and chemicals were purchased from commercial sources and used as received. Infrared (IR) spectra were recorded on a Bruker Tensor 27 (ATR diamond) spectrophotometer. Melting points were determined on a melting point apparatus SMP3 (Stuart scientific) and are uncorrected. ^{1}H, ^{19}F, ^{13}C NMR spectra were recorded at room temperature at 400, 377 and 100 MHz respectively, on a Bruker AVANCE 400 spectrometer. ^{29}Si NMR spectra were recorded at 119 MHz on a Bruker AVANCE II 400, 600 spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are given in Hertz (Hz). Abbreviations used for peak multiplicity are: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); quint (quintet); sept (septet); m (multiplet). Thin layer chromatographies (TLC) were performed on Merck silica gel 60 F 254 and revealed with a UV lamp (λ = 254 nm) and $KMnO_4$ staining. Flash Column Chromatographies were conducted on silica Geduran® Si 60 Å (40 – 63 µm). High resolution mass spectrometries were performed on a microTOF (ESI). Photocatalysts were synthesized as described.[1],[2] Silicates **2a-2h and 2j** were synthesized as described.[3]

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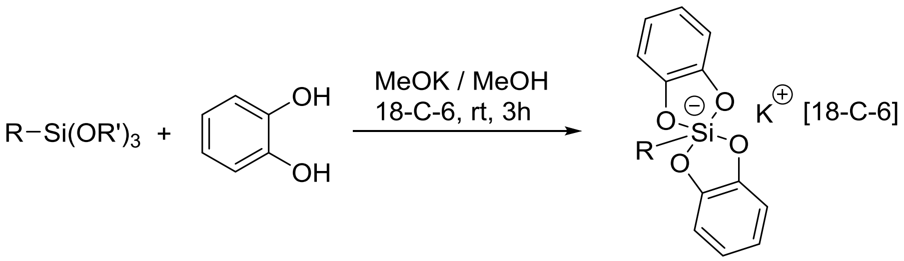
[1] D. Hanss, J. C. Freys, G. Bernardinelli and O. S. Wenger, *Eur. J. Inorg. Chem.*, 2009, **2009**, 4850

[2] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, ***17***, 5712

[3] V. Corcé, L.-M. Chamoreau, E. Derat, J.-P. Goddard, C. Ollivier and L. Fensterbank, *Angew. Chem. Int. Ed.* 2015, **54**, 11414

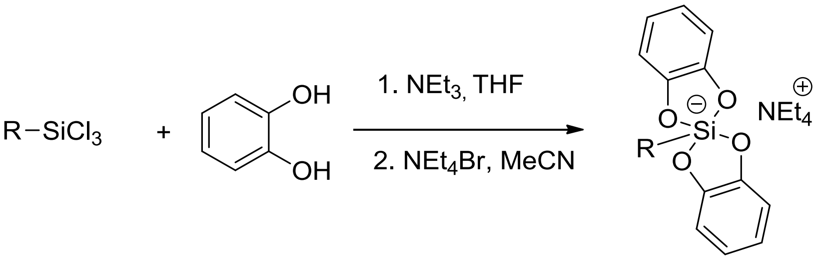
II. General procedures

1. General procedure A1 for silicate synthesis



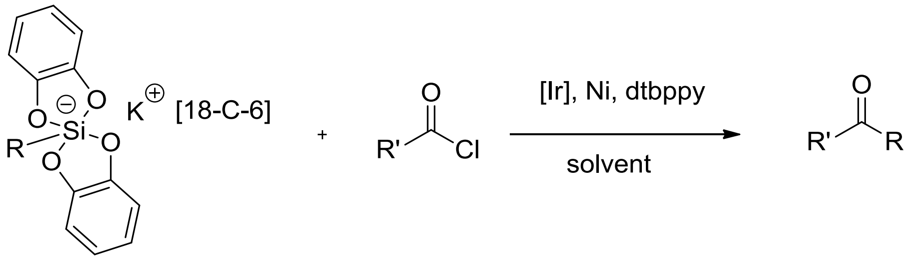
To a stirred solution of catechol (2 equiv) in dry methanol (0.25 M) was added 18-C-6 (1 equiv). After dissolution of the crown ether, the trialkoxy organosilane (1 equiv) was added, followed by a solution of potassium methoxide in methanol (1 equiv). The reaction mixture was stirred for 3 hours and the solvent was removed under reduced pressure. The residue was dissolved in the minimum volume of acetone and diethyl ether was added until a cloudy solution was obtained (scrapping on the edge of the flask could be done to induce crystallization). The flask was placed at -20°C overnight. The crystals were collected by filtration, washed with diethyl ether and dried under vacuum to afford [18-C-6] silicate.

2. General procedure A2 for the synthesis of triethylammonium bis(catecholato) 5-(bicycloheptenyl)silicate



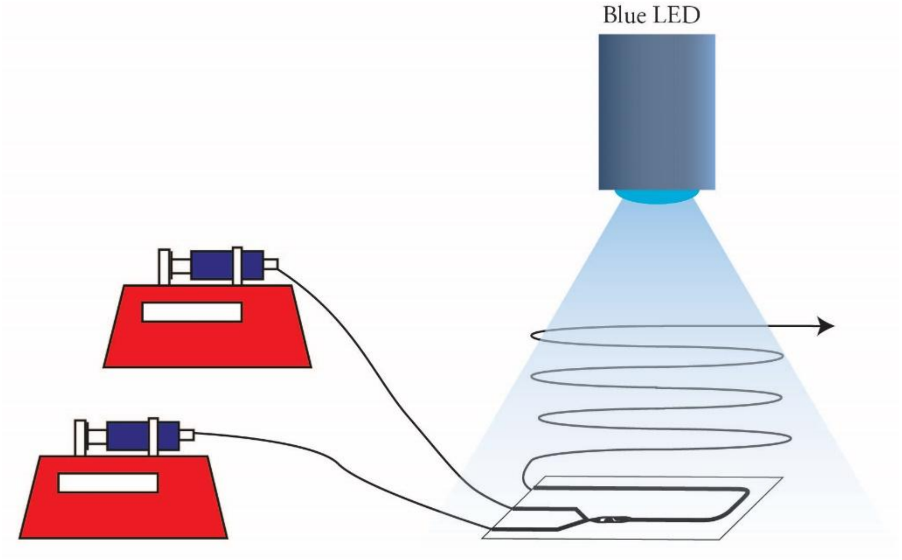
To a stirred solution of catechol (2 equiv) in dry THF (0.1 M) was added triethylamine (4 equiv). The reaction mixture was cooled to 0°C with an ice bath and the corresponding trichlorosilane (1 equiv) was added dropwise. The reaction mixture was stirred for one hour at 0°C and an additional hour at room temperature. The triethylamine hydrochloride salts were filtered off and the filtrate was evaporated under reduced pressure. The residue was taken up in acetonitrile (0.3 M) and tetraethylammonium bromide (1 equiv) was added. The reaction mixture was stirred for one hour then the mixture was evaporated under reduced mixture. The solid was taken up in water, filtered and washed again with water then dried *in vacuo* to give the corresponding triethylammonium silicate.

4. General procedure B for the photoredox/nickel cross-coupling dual catalysis



To a Schlenk flask was added the appropriate silicate (1.5 equiv), [Ir] (2 mol %), 4,4'-di-tert-butyl-2,2'-dipyridyl (4 mol %) and $NiCl_2$.dme (4 mol %). The Schlenk flask was sealed with a rubber septum and evacuated / purged with vacuum / argon three times. Then degassed THF (0.1 M) was introduced followed by addition of the electrophile **2** (1 equiv) and the reaction mixture was irradiated with blue LED (477 nm) at room temperature for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether, washed with aqueous saturated K_2CO_3 solution (2 times), brine (2 times), dried over MgSO4 and evaporated under reduced pressure. The crude residue was purified by flash chromatography.

5. General procedure B2 for the continuous flow photoredox/nickel cross-coupling dual catalysis

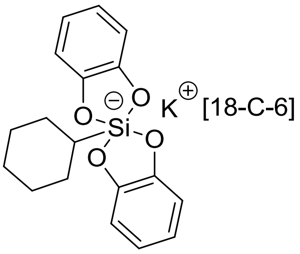


A solution of silicate with catalysts (1.5 equiv of the appropriate silicate, 2 mol% [Ir], 4 mol% 2,2’-bipyridine, prepared in glovebox) in degassed THF (0.2 M) and a solution of the appropriate electrophile (1 equiv) in degassed THF(0. 2M) were pumped by two syringe pumps (AL-300, World Precision Instruments, USA) with a flow rate of 22 µL/min respectively. They were mixed within a glass milli-mixer (LTF-MX, 0.2 mL at room temperature, Little Things Factory, Germany) under blue LED irradiation (477 nm), and the mixture then flowed through a PTFE tubing (1/16” tubing, 134 cm, 0.67 mL at room temperature) under blue LED irradiation (477 nm). The mixer and the PTFE tubing were rinsed with degassed THF prior to use. The reaction time was calculated with the total reaction volume and the total flow rate, which gave a reaction time of 20 min. The reaction mixture was then collected, diluted with diethyl ether, washed with an aqueous saturated K_2CO_3 solution (2 times), brine (2 times), dried over MgSO4 and evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the product. The reaction time is calculated as the total reaction volume (0.87 mL) divided by the total flowrate (44 µL/min), which is around 20 minutes.

III. Compound characterizations

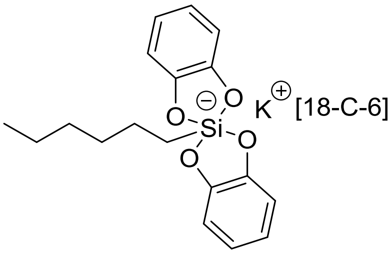
Synthesis and caracterisation of the silicates

Potassium [18-Crown-6] bis(catecholato)-cyclohexylsilicate (2a)



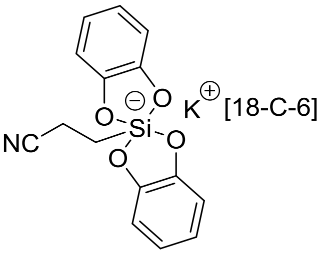
Silicate **2a** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[3]

Potassium [18-Crown-6] bis(catecholato)-hexylsilicate (2b)



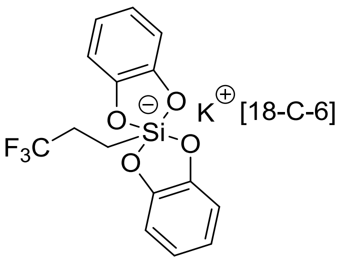
Silicate **2b** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[3]

Potassium [18-Crown-6] bis(catecholato)-2-cyanoethylsilicate (2c)



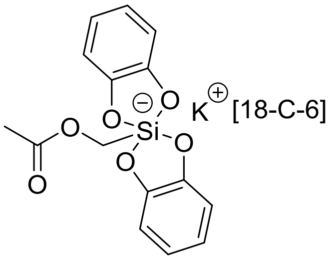
Silicate **2c** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[3]

Potassium [18-Crown-6] bis(catecholato)-3,3,3-trifluoropropylsilicate (2d)



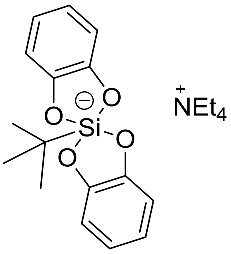
Silicate **2d** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[3]

Potassium [18-Crown-6] bis(catecholato)-acetoxymethylsilicate (2e)



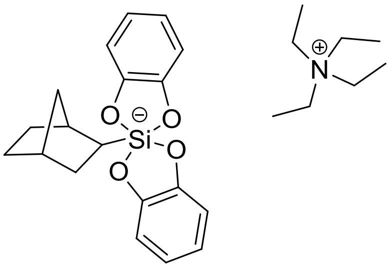
Silicate **2e** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[3]

Tetraethylammonium bis(catecholato)-*tert*-butylsilicate (2f)



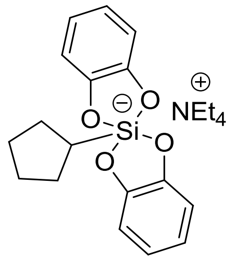
Silicate **2f** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[3]

Triethylammonium exo-2-bicyclo[2.2.1]heptylbis(catecholato)silicate (2g)



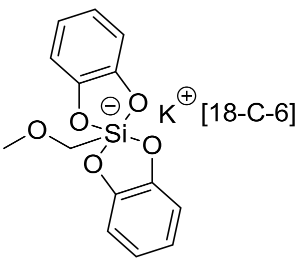
Silicate **2g** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[4]

Cyclopentylsilicate triethylammonium (2h)



Silicate **2h** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[3]

Potassium [18-Crown-6] bis(catecholato)-methoxymethylsilicate (2i)



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[4] M. Jouffroy, D.N. Primer and G. A. Molander, *J. Am. Chem. Soc.*, 2016, **138**, 475

Chloromethyltrimethoxysilane (4 mmol, 0.6 mL) was added to a stirred solution of potassium methoxyde 3.56 M in MeOH (4.4 mL). The resultant mixture was stirred for two days then the solvent was removed *in vacuo*. After that catechol (8 mmol, 880.8 mg) and 18-C-6 (1.056 g, 4.0 mmol) were added in 10 mL of MeOH. Then a solution of potassium methoxide in methanol 3.56 M (3.70 mmol, 1.04 mL) was added. The reaction mixture was stirred for 2 hours and the solvent was removed under reduced pressure. The residue was dissolved in the minimum volume of acetone and diethyl ether was added until a cloudy solution was obtained (scrapping on the edge of the flask could be done to induce crystallization). The flask was placed at – 20°C overnight. The crystals were collected to afford potassium [18-Crown-6] bis(catecholato)-methoxymethylsilicate **2i** (1.508 g, 64%)

^{1}H NMR (400 MHz, MeOD): δ 6.76-6.67 (m, 4H), 6.62-6.55 (m, 4H), 3.62 (s, 24H), 3.21 (s, 2H), 3.19 (s, 3H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ 150.9 (4C), 118.0 (4C), 110.6 (4C), 70.1 (12C), 66.2, 61.8.

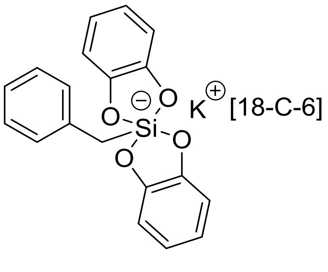
^{29}Si NMR (79 MHz, CD_2Cl_2) δ – 82.2.

HRMS calc. for $[C_{14}H_{13}O_5Si\text{-}]^-$ 289.0538, found 289.0539.

M.P. 161.9°C.

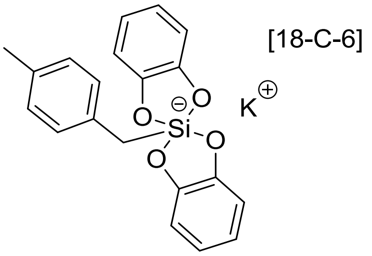
IR (neat): 2900, 1484, 1352, 1284, 1243, 1224, 1179, 1012, 956, 913, 885, 867, 834, 583 cm^{-1}.

Potassium [18-Crown-6] bis(catecholato)-benzylsilicate (2j)



Silicate **2j** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[3]

Potassium [18-Crown-6] bis(catecholato)-4-methylbenzylsilicate (2k)



To a stirred solution of dried THF were added 4-methylbenzyl bromide (5.00 mmol, 925 mg) and magnesium (6.00 mmol, 145.8 mg). The resultant mixture was heated under reflux for one hour then tetramethoxysilane (25.0 mmol, 3.70 mL) was added dropwise. The mixture was then heated under reflux for 16 additional hours before being concentrated under reduced pressure. 20 mL of pentane were added and the mixture was filtrated. The filtrate was concentrated *in vacuo* then catechol (7.39 mmol, 814 mg) and 18-C-6 (3.70 mmol, 978 mg).were added in 10 mL of dried MeOH. Then a solution of potassium methoxide in methanol 3.56 M (3.70 mmol, 1.04 mL) was added. The reaction mixture was stirred for 3 hours and the solvent was removed under reduced pressure. The residue was dissolved in the minimum volume of acetone and diethyl ether was added until a cloudy solution was obtained (scrapping on the edge of the flask could be done to induce crystallization). The flask was placed at -20°C overnight. The crystals were collected to afford potassium [18-Crown-6] bis(catecholato)-4-methylbenzylsilicate **2k** (400 mg, 12%).

^{1}H NMR (300 MHz, Methanol-*d*4): δ 6.80-6.72 (m, 4H), 6.70-6.60 (m, 4H), 6.60-6.50 (m, 4H), 3.62 (s, 24H), 2.15 (s, 3H), 2.09 (s, 2H).

^{13}C NMR (75 MHz, Methanol-*d*4): δ 149.5 (4C), 128.3 (2C), 127.5 (2C), 118.9, 117.9 (4C), 114.8, 110.1 (4C), 69.9 (12C), 25.8, 19.5.

^{29}Si NMR (79 MHz, Methanol-*d*4) δ 80.6.

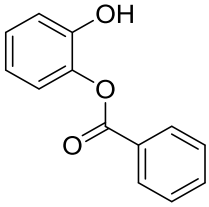
HRMS calc. for $[C_{20}H_{17}O_4Si]^-$ 349.0902, found 349.0902.

M.P. 218°C.

IR (neat): 2892, 1488, 1352, 1248, 1105, 1013, 964, 826, 767, 739, 708 cm^{-1}.

Characterisation of the byproducts

2-hydroxyphenyl benzoate (5a)

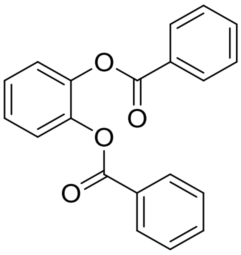


The spectroscopic data are in agreement with those reported in the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.15 (m, 2H), 7.72-7.64 (m, 1H), 7.58-7.51 (m, 2H), 7.23-7.16 (m, 2H), 7.11-7.04 (m, 1H), 7.01-6.95 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 147.4, 139.0, 134.2, 130.6 (2C), 129.0, 128.9 (2C), 127.3, 122.7, 121.4, 118.3.

1,2-phenylene dibenzoate (5b)



The spectroscopic data are in agreement with those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-8.04 (m, 4H), 7.58-7.50 (m, 2H), 7.44-7.32 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (2C), 142.8 (2C), 133.8 (2C), 130.3 (4C), 129.0 (2C), 128.6 (4C), 126.8 (2C), 123.7 (2C).

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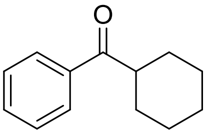
[5] N. Wakita and S. Hara, *Tetrahedron*, 2010, **66**, 7939

[6] W. Ren, A. Emi and M. Yamane, *Synthesis*, 2011, **14**, 2303

Synthesis and characterisation of ketones

Cyclohexyl(phenyl)methanone (3a)

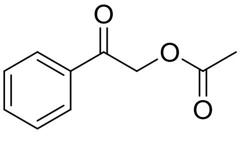


Following the general procedure B with benzoylchloride (0.417 mmol, 48 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and cyclohexyl silicate (0.626 mmol, 394 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3a** (50.0 mg, 64%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.95 (m, 2H), 7.60-7.55 (m, 1H), 7.51-7.54 (m, 2H), 3.30-3.20 (m, 1H), 2.00-1.20 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 136.5, 132.7, 128.5 (2C), 128.2 (2C), 45.7, 29.5 (2C), 26.0, 25.9 (2C).

2-Oxo-2-phenylethyl acetate (3e)



Following the general procedure B with benzoyl chloride (0.417 mmol, 48 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and acetoxysilicate (0.626 mmol, 388 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3e** (17.0 mg, 23%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[8]

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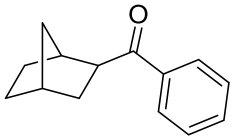
[7] T. Kondo, M. Akazome, Y. Tsuji and J. Watanabe, *J. Org. Chem.*, 1990, **55**, 1286

[8] J. Sheng, X. Li, M. Tang, B. Gao and G. Huang, *Synthesis*, 2007, **8**, 1165

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.80 (m, 2H), 7.60-7.50 (m, 1H), 7.46-7.37 (m, 2H), 5.27 (s, 2H), 2.17 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 170.5, 134.2, 133.9, 128.9 (2C), 127.8 (2C), 66.0, 20.6.

(1S,4R)-bicyclo[2.2.1]heptan-2-yl(phenyl)methanone (3g)

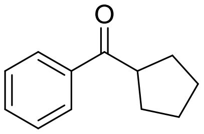


Following the general procedure B with benzoyl chloride (0.417 mmol, 48 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and 2-(bicycloheptyl) silicate (0.626 mmol, 294 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3g** (41.0 mg, 49%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[9]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04-7.92 (m, 2H), 7.57-7.51 (m, 1H), 7.49-7.42 (m, 2H), 3.25-3.19 (m, 1H), 2.55-2.51 (m, 1H), 2.37-2.33 (m, 1H), 2.06-1.99 (m, 1H), 168-1.09 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 136.8, 132.8, 128.6 (2C), 128.5 (2C), 49.7, 41.2, 36.4, 36.3, 33.8, 29.9, 29.2.

Cyclopentyl(phenyl)methanone (3h)



Following the general procedure B with benzoylchloride (0.417 mmol, 48 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and cyclopentylsilicate tetraethylammonium (0.626 mmol, 277 mg) in 4.2 mL of dry THF. The crude

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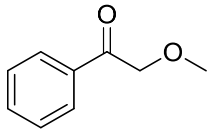
[9] K-M. Cha, E-A. Jun and C-H. J, *Synlett.*, 2009, **18**, 2939

product was purified according the general procedure to afford **3h** (21.0 mg, 27%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.96 (m, 2H), 7.60-7.51 (m, 1H), 7.49-7.43 (m, 2H), 3.79-3.65 (m, 1H), 1.92 (s, 4H), 1.75-1.50 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 137.0, 132.7, 128.5 (2C), 128.4 (2C), 46.3, 30.0 (2C), 26.3 (2C).

2-methoxy-1-phenylethanone (3i)

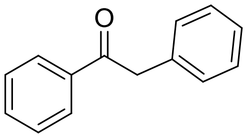


Following the general procedure B with benzoyl chloride (0.417 mmol, 48 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (16.7 µmol, 4.5 mg) and methoxymethyl silicate (0.626 mmol, 370 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3i** (40.0 mg, 64%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.90 (m, 2H), 7.63-7.55 (m, 1H), 7.50-7.44 (m, 2H), 4.72 (s, 2H), 3.55 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 134.9, 133.8, 128.8 (2C), 127.9 (2C), 73.4, 59.5.

1,2-Diphenylethanone (3j)



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[10] M. Li, C. Wang and H. Ge, *Org. Lett.*, 2011, **13**, 2062

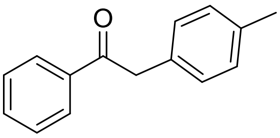
[11] D. L. Mo, L. X. Dai and X. L. Hou, *Tett. Lett.*, 2009, **50**, 5578

Following the general procedure B with benzoyl chloride (0.434 mmol, 50 µL), iridium (8.70 µmol, 8.7 mg), NiCl$_2$.dme (17.3 µmol, 3.8 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (17.3 µmol, 4.5 mg) and benzylsilicate (0.626 mmol, 416 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3j** (70.0 mg, 82%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[6]

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.00-7.90 (m, 2H), 7.55-7.45 (m, 1H), 7.42-7.35 (m, 2H), 7.30-7.10 (m, 5H), 4.21 (s, 2H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.6, 136.6, 134.6, 133.1, 129.5 (2C), 128.6 (6C), 126.9, 45.5.

1-Phenyl-2-(p-tolyl)ethanone (3k)



Following the general procedure B with benzoyl chloride (0.327 mmol, 38 µL), iridium (6.5 µmol, 6.6 mg), NiCl$_2$.dme (13.1 µmol, 2.9 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (13.1 µmol, 3.5 mg) and 4-methylbenzylsilicate (0.626 mmol, 388 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3k** (55.0 mg, 80%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[12]

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.00-7.89 (m, 2H), 7.51-7.45 (m, 1H), 7.42-7.33 (m, 2H), 7.12-7.00 (m, 4H), 4.17 (s, 2H), 2.25 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.8, 136.7, 136.6, 133.2, 131.3, 129.7 (2C), 129.5 (2C), 128.6 (4C), 45.1, 21.1.

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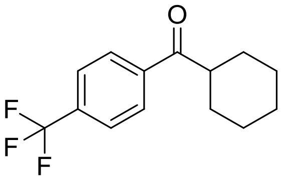
[12] B. Landers, C. Berini, C. Wang and O. Navarro, *J. Org. Chem.*, 2011, **76**, 1390

Cyclohexyl(4-(trifluoromethyl)phenyl)methanone (3l)



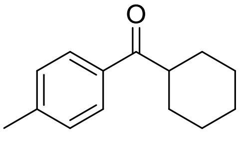
Following the general procedure B with 4-trifluoromethylbenzoyl chloride (0.834 mmol, 124 µL), iridium (16.7 µmol, 16.8 mg), $NiCl_2$.dme (33.4 µmol, 7.3 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (33.4 µmol, 7.0 mg) and cyclohexylsilicate (1.25 mmol, 788 mg) in 8.4 mL of dry THF. The crude product was purified according the general procedure to afford **3l** (20.0 mg, 8%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 3.27 (tt, J = 12 Hz and 3.6 Hz, 1H), 1.95-1.70 (m, 5H), 1.45-1.20 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 139.1, 134.1 (q, J=35 Hz, 2C), 128.6, 125.6 (q, J=5 Hz, 2C), 124.3 (q, J=267.2 Hz), 45.9, 29.3 (2C), 25.9 (2C), 25.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1.

Cyclohexyl(p-tolyl)methanone (3m)



Following the general procedure B with *p* toluoyl chloride (0.417 mmol, 57 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and cyclohexyl silicate (0.626 mmol , 394 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3m** (43.0 mg, 51%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[14]

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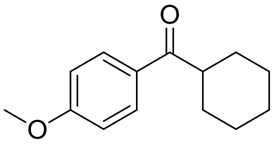
[13] A. Takemiya and J. F. Hartwig, *J. Am. Chem. Soc.*, 2006, **128**, 14800

[14] B. W. Fausett and L. S. Liebeskind, *J. Org. Chem.*, 2005, **70**, 4851

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 3.15-3.21 (m, 1H), 2.40 (s, 3H), 1.85-1.10 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 143.5, 133.7, 129.3 (2C), 128.4 (2C), 45.5, 29.5 (2C), 26.0, 25.9 (2C), 21.5.

Cyclohexyl(4-methoxyphenyl)methanone (3n)

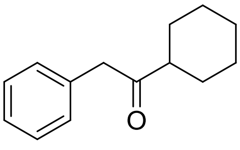


Following the general procedure B with *p* metoxy benzoylchloride (0.300 mmol, 41 µL), iridium (6.00 µmol, 6.0 mg), $NiCl_2$.dme (12.0 µmol, 2.6 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12 µmol, 1.9 mg) and cyclohexylsilicate (0.450 mmol, 280 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3n** (34.0 mg, 52%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J=9.2 Hz, 2H), 6.91 (d, J=9.2 Hz, 2H), 3.87 (s, 3H), 3.28-3.19 (m, 1H), 1.92-1.85 (m, 4H), 1.60-1.20 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 163.2, 130.5 (2C), 129.3, 113.7 (2C), 55.5, 45.3, 29.5 (2C), 26.0 (2C), 25.9.

1-Cyclohexyl-2-phenylethanone (3o)



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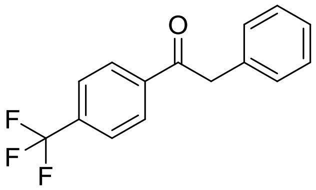
[15] H.Li,Y. Xu, E.o Shi, W. Wei, Xi. Suo and X. Wan, *Chem. Commun.*, 2011, **47**, 7880

Following the general procedure B with phenylacetylchloride (0.417 mmol, 55 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and cyclohexyl silicate (0.626 mmol, 394 mg) in 4.2mL of dry THF. The crude product was purified according the general procedure to afford **3o** (26.0 mg, 31%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[16]

^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.30-7.16 (m, 3H), 7.15-7.05 (m, 2H), 3.65 (s, 2H), 2.46-2.32 (m, 1H), 1.82-1.66 (m, 4H), 1.62-1.55 (m, 1H), 1.40-1.05 (m, 5H).

^{13}**C NMR** (75 MHz, $CDCl_3$) δ 210.2, 133.5, 128.5 (2C), 127.5 (2C), 125.7, 49.1, 46.8, 27.5 (2C), 24.7, 24.5 (2C).

2-Phenyl-1-(4-(trifluoromethyl)phenyl)ethanone (3q)



Following the general procedure B with 4-trifluoromethylbenzoyl chloride (0.417 mmol, 62 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzylsilicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3q** (18.0 mg, 16%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[17]

^{1}**H NMR** (300 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.40-7.23 (m, 5H), 4.31 (s, 2H).

^{13}**C NMR** (75 MHz, $CDCl_3$) δ 196.6, 139.2, 134.6 (q, J = 129.6 Hz, 2C), 133.8, 129.4 (2C), 128.9 (2C), 128.8, 127.2, 125.7 (q, J=5 Hz, 2C), 123.8 (q, J=295.7 Hz), 45.8.

^{19}**F NMR** (376 MHz, $CDCl_3$) δ -63.2.

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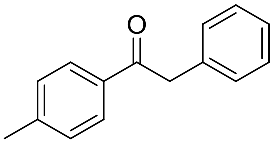
[16] S. Inaba and R. D. Rieke, *J. Org. Chem.*, 1985, **50**, 1373

[17] A. Battace, M. Feuerstein, M. Lemhadri, T. Zair, H. Doucet and M. Santelli, *Eur. Joc.*, 2007, **19**, 3122

2-Phenyl-1-(p-tolyl)ethanone (3r)

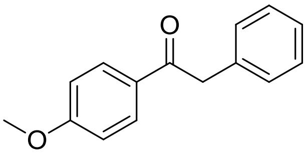


Following the general procedure B with 4-methylbenzylchloride (0.417 mmol, 57 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2mL of dry THF. The crude product was purified according the general procedure to afford **3r** (62.0 mg, 71%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.28-7.11 (m, 7H), 4.18 (s, 2H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.3, 144.0, 134.8, 134.1, 129.4 (2C), 129.3 (2C), 128.8 (2C), 128.6 (2C), 126.8, 45.4, 21.6.

1-(4-Methoxyphenyl)-2-phenylethanone (3s)



Following the general procedure B with 4-methoxybenzylchloride (0.417 mmol, 56 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3s** (76.4 mg, 81%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[19]

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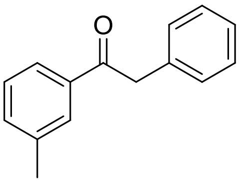
[18] T. Miao and G. W. Wang, *Chem. Commun.*, 2011, **47**, 9501

[19] J. Ruan, O. Saidi, J. A. Iggo and J. Xiao, *J. Am. Chem. Soc.*, 2008, **130**, 10510

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95-7.87 (m, 2H), 7.29-7.11 (m, 5H), 6.88-6.80 (m, 2H), 4.14 (s, 2H), 3.75 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 196.4, 163.6, 135.0, 131.0 (2C), 129.6, 129.4 (2C), 128.6 (2C), 126.8, 113.8 (2C), 55.5, 45.3.

2-Phenyl-1-(m-tolyl)ethanone (3t)

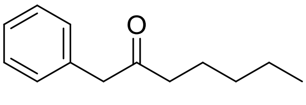


Following the general procedure B with *m* toluoyl chloride (0.417 mmol, 55 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3t** (62.0 mg, 71%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[20]

^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.72-7.69 (m, 2H), 7.15-7.32 (m, 7H), 4.18 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (CDCl3, 75 MHz): δ 197.7, 138.5, 136.7, 134.7, 133.9, 129.5 (2C), 129.1, 128.6 (2C), 128.5, 126.9, 125.9, 45.5, 21.4.

1-Phenylheptan-2-one (3u)



Following the general procedure B with hexanoylchloride (0.417 mmol, 58 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and

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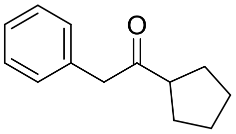
[20] R. C. Elderfield and K. L. Burges, *J. Am. Chem. Soc.*, 1960, **82**, 1975

benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3u** (71.0 mg, 89%) as a colorless oil.The spectroscopic data are in agreement with those reported in the literature.[21]

^{1}H-NMR (CDCl3, 300 MHz): δ 7.10-7.40 (m, 5H), 3.68 (s, 2H), 2.45 (t, J=7.4Hz, 2H), 1.52-1.63 (m, 2H), 1.16-1.36 (m, 4H), 0.88 (t, J = 6.9 Hz, 3H).

^{13}C NMR (CDCl3, 75 MHz): δ 208.6, 134.5, 129.5 (2C), 128.6 (2C), 127.0, 50.2, 42.0, 31.3, 23.5, 22.5, 14.0.

1-Cyclopentyl-2-phenylethanone (3v)



Following the general procedure B with cyclopentanecarbonyl chloride (0.417 mmol, 56µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (16.7 µmol, 4.5 mg) and benzylsilicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3v** (63.0 mg, 86%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[22]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.19 (m, 5H), 3.77 (s, 2H), 3.01-2.95 (m, 1H), 1.85-1.52 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 210.6, 134.5, 129.5 (2C), 128.6 (2C), 126.9, 50.6, 49.3, 29.1 (2C), 26.0 (2C).

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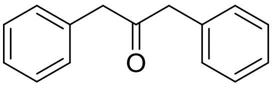
[21] H. Okada,T. Mori, Y. Saikawa and M. Nakata, *Tetrahedron Lett.*, 2009, **50**, 1276-1278

[22] F. Cadoret, P. Retailleau and Y. Six, *Tetrahedron. Lett.*, 2006, **47**, 7749-7753

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

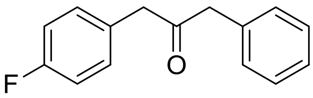


Following the general procedure B with phenylacetylchloride (0.417 mmol, 55 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3w** (84.0 mg, 88%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[16]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.25 (m, 6H), 7.22-7.15 (m, 4H), 3.76 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 205.6, 134.0 (2C), 129.5 (4C), 128.7 (4C), 127.0 (2C), 49.1 (2C).

1-(4-fluorophenyl)-3-phenylpropan-2-one (3x)



Following the general procedure B with 4-fluorophenylacetyl chloride (0.417 mmol, 57 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF The crude product was purified according the general procedure to afford **3x** (44.0 mg, 46 %) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature. [23]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.26 (m, 3H), 7.19-7.14 (m, 2H), 7.12-7.05 (m, 2H), 7.04-6.95 (m, 2H), 3.73 (s, 2H), 3.69 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 162.1 (d, J = 976 Hz), 134.0, 131.2 (d, J = 32 Hz, 2C), 129.7, 129.6 (2C), 128.9 (2C), 127.3, 115.7 (d, J = 85.2 Hz, 2C), 49.5, 48.1.

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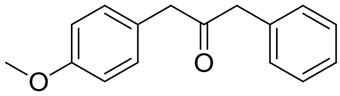
[23] N. Ishibe, S. Yutaka, J. Masui and N. Ihda, *J. Org. Chem.*, 1978, **43**, 2144

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7 Hz.

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

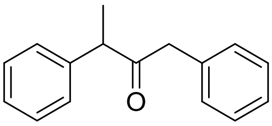


Following the general procedure B with 4-methoxyphenylacetyl chloride (0.417 mmol, 64 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3y** (39.0 mg, 38 %) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[24]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.24 (m, 3H), 7.23-7.14 (m, 2H), 7.13-7.04 (m, 2H), 6.94-6.87 (m, 2H), 3.83 (s, 3H), 3.75 (s, 2H), 3.69 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 206.1, 158.8, 134.2, 130.6 (2C), 129.6 (2C), 128.8 (2C), 127.1, 126.1, 114.3 (2C), 55.4, 49.0, 48.3.

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



Following the general procedure B with 2-phenylpropyonyl chloride (0.417 mmol, 62 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified

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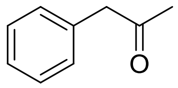
[24] L. Ackermann and P. M. Vaibhav, *Chem. Eur. Joc*, 2012, **18**, 10230

according the general procedure to afford **3z** (45.0 mg, 48 %) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[25]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.18 (m, 8H), 7.14-7.03 (m, 2H), 3.91 (q, J = 6.9 Hz, 1H), 3.66 (s, 2H), 1.41 (d, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.0, 140.5, 134.5, 129.6 (2C), 129.1 (2C), 128.6 (2C), 128.2 (2C), 127.3, 126.9, 52.2, 48.1, 17.8.

1-Phenylpropan-2-one (3za)

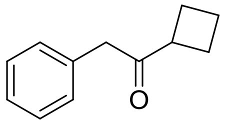


Following the general procedure B with acetyl chloride (0.834 mmol, 59 µL), iridium (16.68 µmol, 16.8 mg), $NiCl_2$.dme (33.4 µmol, 7.3 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (33.4 µmol, 8.9 mg) and benzyl silicate (1.67 mmol, 800 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3za** (54 mg, 48%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[26]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.42 (m, 3H), 7.25-7.20 (m, 2H), 3.72 (s, 2H), 2.18 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 206.4; 134.3, 129.5 (2C), 128.7 (2C), 127.1, 51.1, 29.3.

1-cyclobutyl-2-phenylethanone (3zb)



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[25] C. Gibb, A. K. Sundaresan, V. Ramamurthy and B. C. Gibb, *J. Am. Chem. Soc*, 2008, **130**, 4069

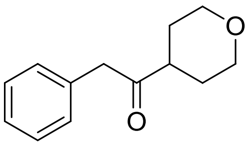
[26] J. M. Zimbron, M. Seigeer-Weibel, H. Hirt and F. Gallou, *Synthesis*, 2008, **8**, 1221-1226

Following the general procedure B with cyclobutane carbonyl chloride (0.417 mmol, 47 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3zb** (46 mg, 63%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature[27].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 2H), 7.30-7.26 (m, 1H), 7.24-7.18 (m, 2H), 3.66 (s, 2H), 3.42-3.30 (m, 1H), 2.31-2.21 (m, 2H), 2.15-2.04 (m, 2H), 2.00-1.90 (m, 1H), 1.87-1.77 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 134.5, 129.6 (2C), 128.8 (2C), 127.0, 47.8, 45.0, 24.7 (2C), 17.8.

2-phenyl-1-(tetrahydro-2H-pyran-4-yl)ethanone (3zc)



Following the general procedure B with tetrahydro-2H-pyran-4-carbonyl chloride (0.417 mmol, 52 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3zc** (70 mg, 82%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.21 (m, 5H), 4.08-3.93 (m, 2H),3.77 (s, 2H), 3.49-3.31 (m, 2H), 2.77-2.61 (m, 1H), 1.80-1.67 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 209.1, 134.0, 129.5 (2C), 128.8 (2C), 127.1, 67.2 (2C), 44.7, 46.9, 28.3 (2C).

HRMS calc. for [$C_{13}H_{16}O_2$] 205.1222, found 205.1223.

IR (neat): 2951, 2845, 1708, 1495, 1444, 1111, 1022, 704 cm^{-1}.

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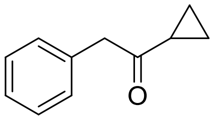
[27] J. Hye-Soo and K. Seung-Hoi, *Synlett*, 2015 , **26**, 666

1-cyclopropyl-2-phenylethanone (3zd)

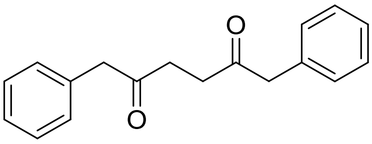


Following the general procedure B with cyclopropane carbonyl chloride (0.417 mmol, 37 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3zd** (60 mg, 90%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[28]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.21 (m, 5H), 3.85 (s, 2H), 2.09-1.91 (m, 1H), 1.11-1.01 (m, 2H), 0.93-0.81 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.5, 134.6, 129.6 (2C), 128.8 (2C), 127.0, 58.3, 20.2, 11.4 (2C).

1-cyclopropyl-2-phenylethanone (3ze)



Following the general procedure B with succinyl dichloride (0.417 mmol, 46 µL), iridium (8.34 µmol, 8.4 mg), $NiCl_2$.dme (16.7 µmol, 3.7 mg), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.7 µmol, 4.5 mg) and benzyl silicate (0.626 mmol, 400 mg) in 4.2 mL of dry THF. The crude product was purified according the general procedure to afford **3ze** (45 mg, 40%) as a colorless oil. The spectroscopic data are in agreement with those reported in the literature[29].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.17 (m, 10H), 3.75 (s, 4H), 2.72 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.0 (2C), 134.3 (2C), 129.6 (4C), 128.9 (4C), 127.2 (2C), 50.2 (2C), 35.8 (2C).

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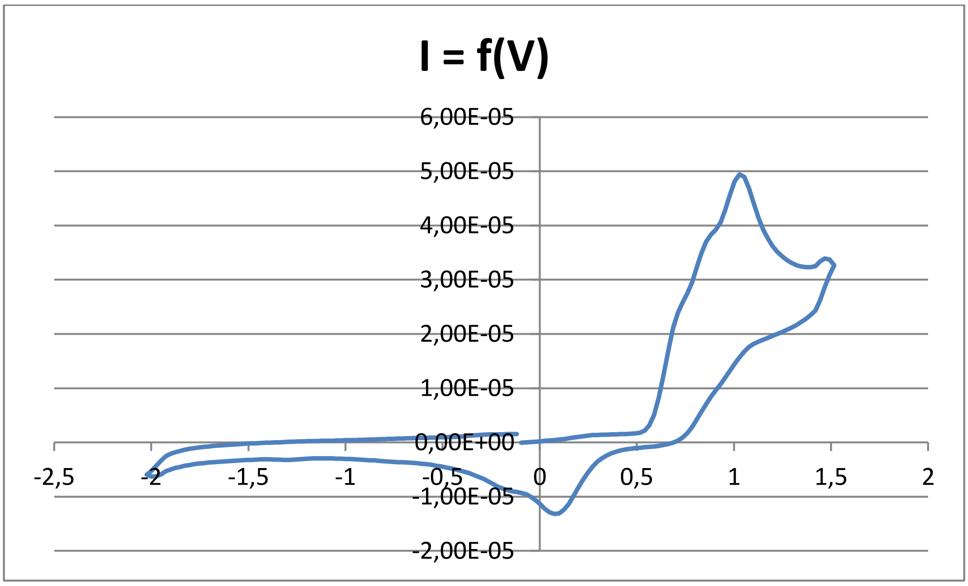
[28] X.-F. Fu, Y. Xiang and Z.-X. Yu, *Chem. Eur. J.*, 2015, **21**, 4242

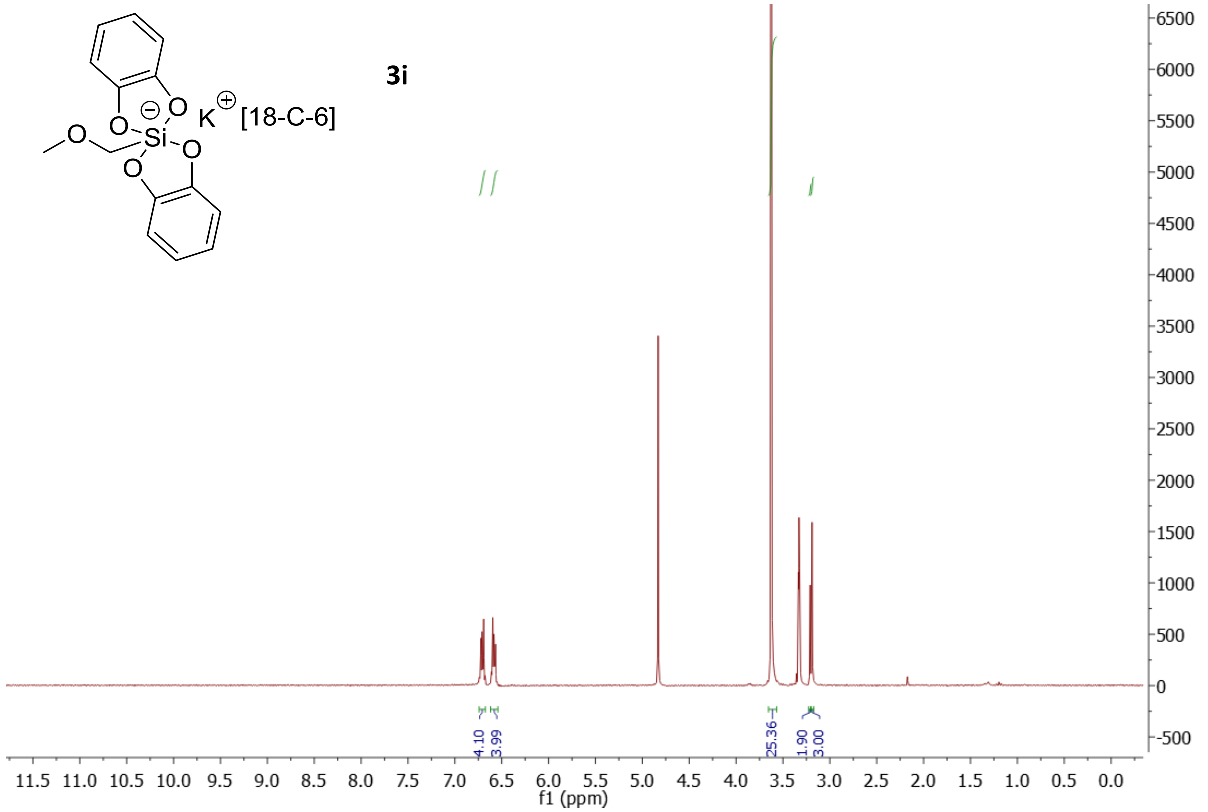
[29] S. Inaba and R. D. Rieke, *J. Org. Chem.*, 1985, **50**, 1363

IV. Electrochemical measurement

The voltammetric measurement was recorded with a three electrodes apparatus in degassed DMF with Bu_4NPF_6 (100 mM) as support electrolyte. Measurements were monitored on an AutoLab PSTAT10 electrochemical workstation. Cyclic voltammetry (CV) was used to estimate the redox potential. Glassy carbon, platinum plate, and saturated calomel were used as working, counter, and reference electrodes, respectively.



V. ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectra



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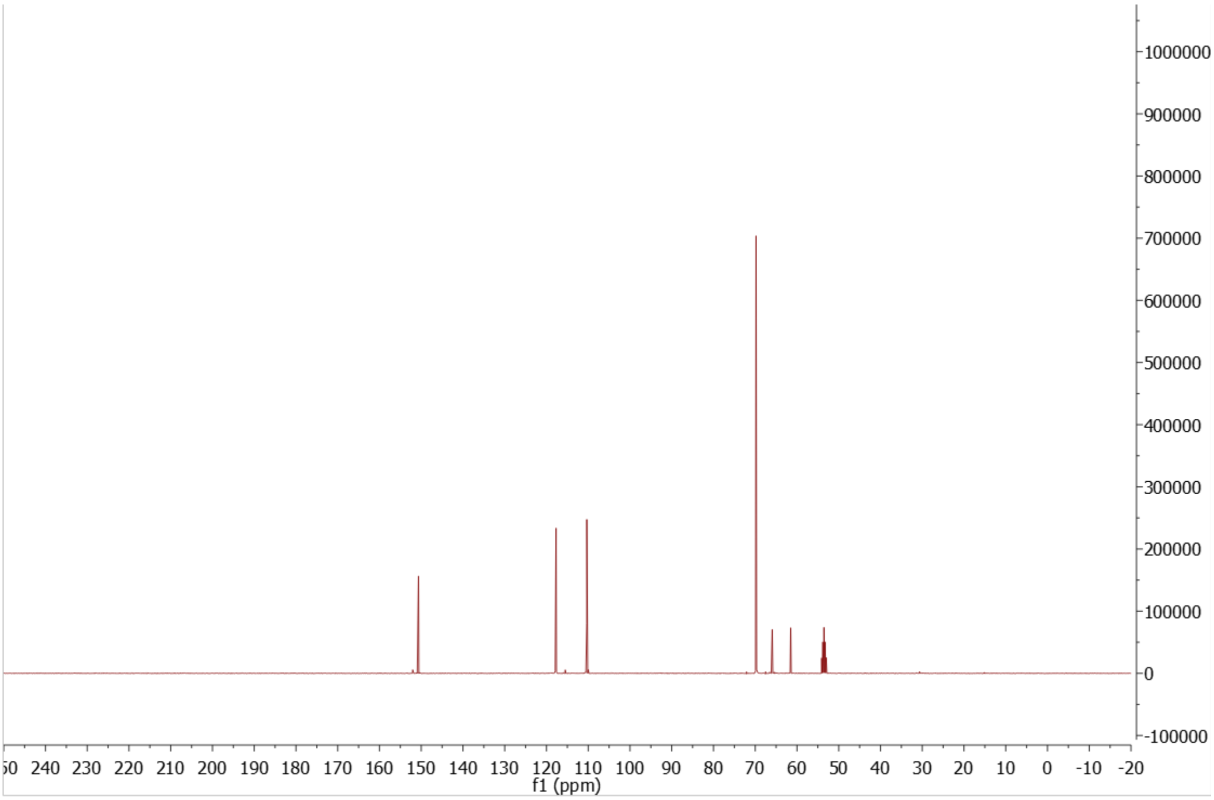

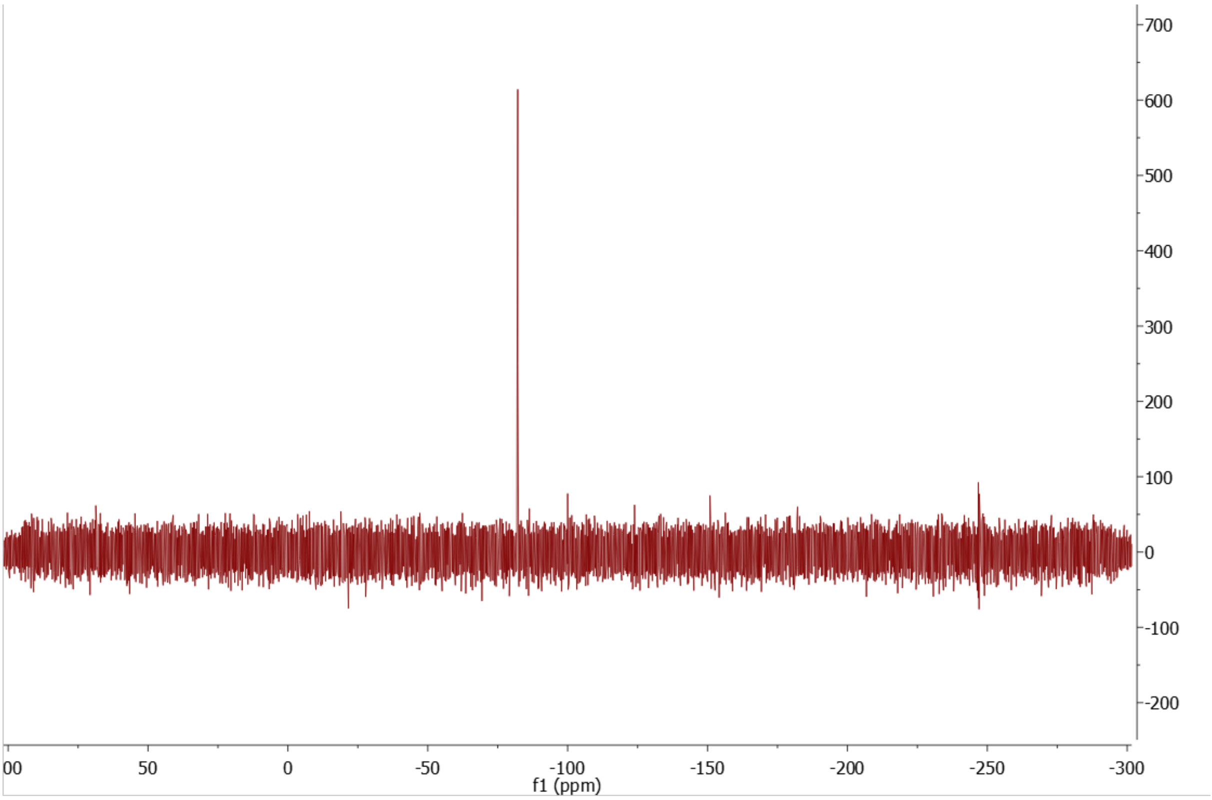
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-200
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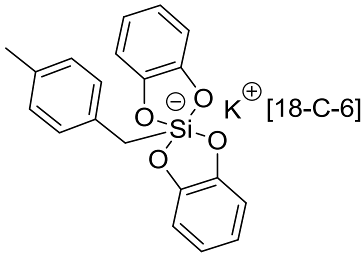
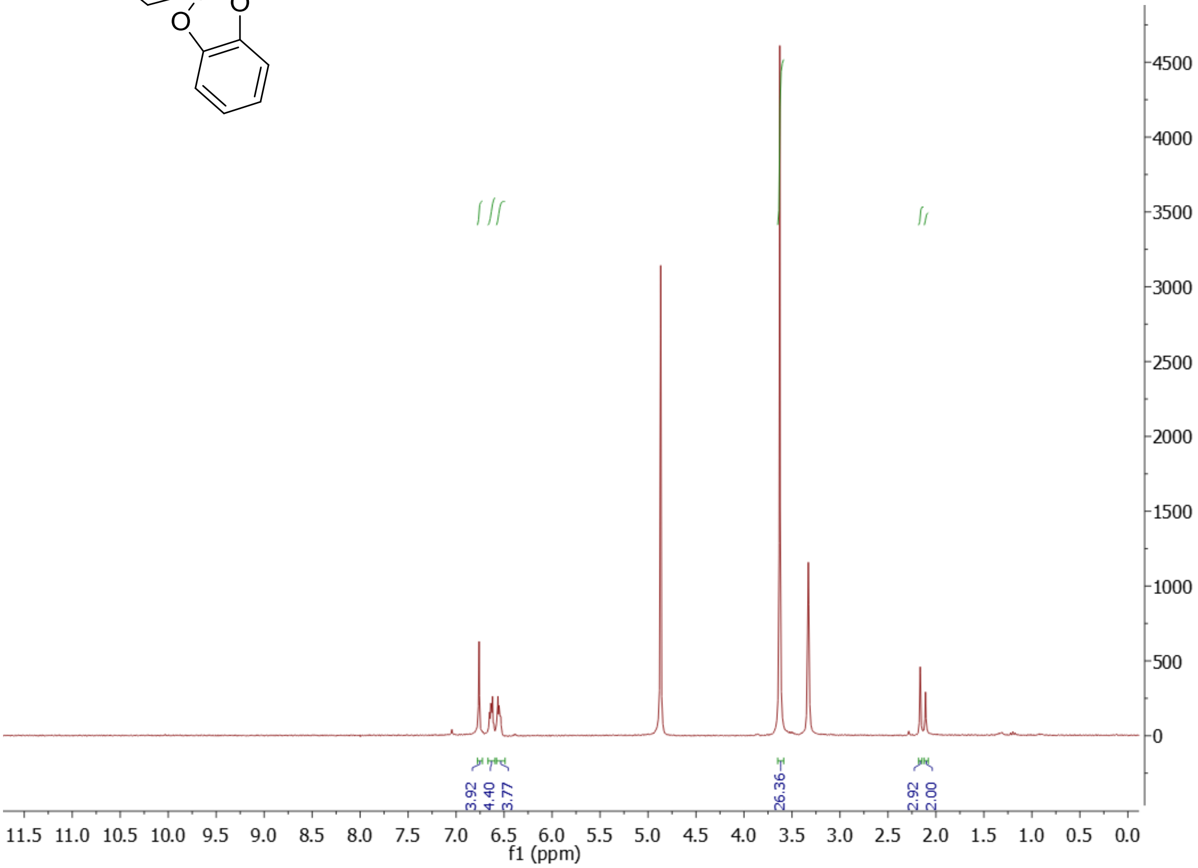
-250
-300
f1 (ppm)


O
O
Si
O
O
K⊕ [18-C-6]

3i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11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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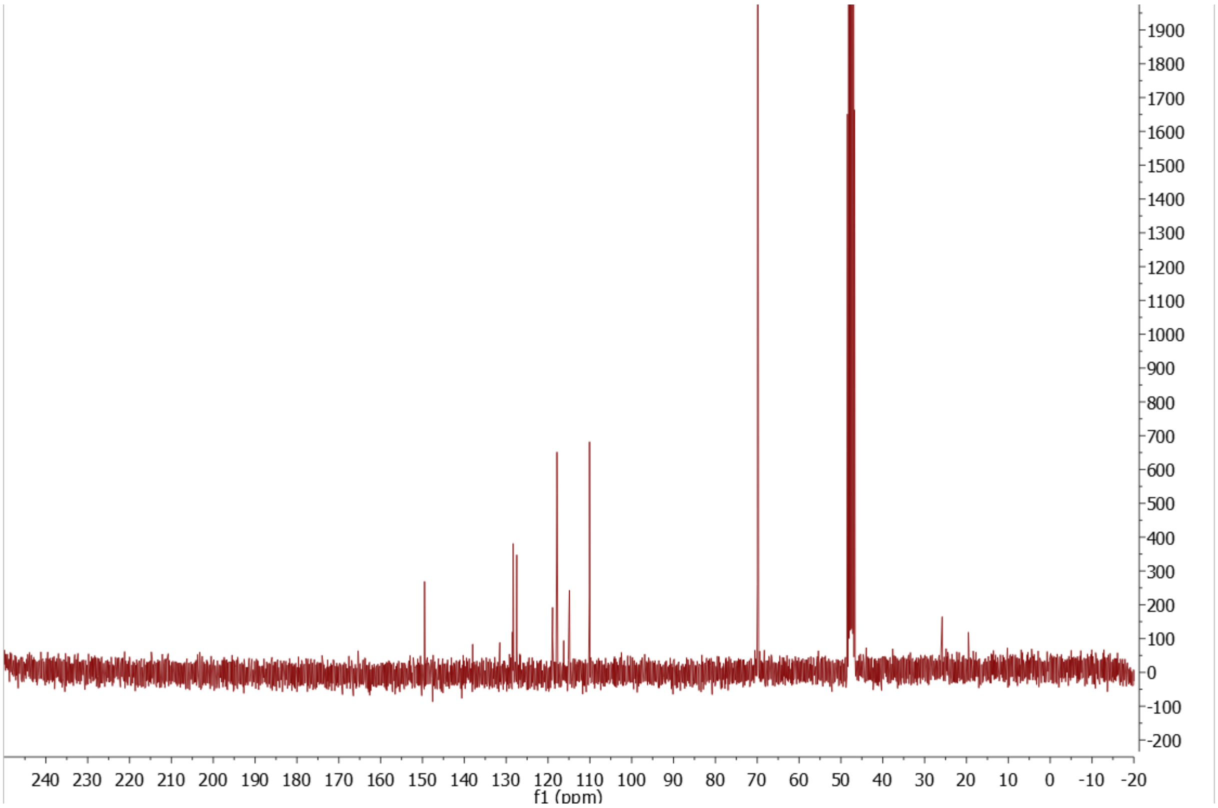
0.0
f1 (ppm)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400
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100
0
-100
-200
240
230
220
210
200
190
180
170
160
150
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30
20
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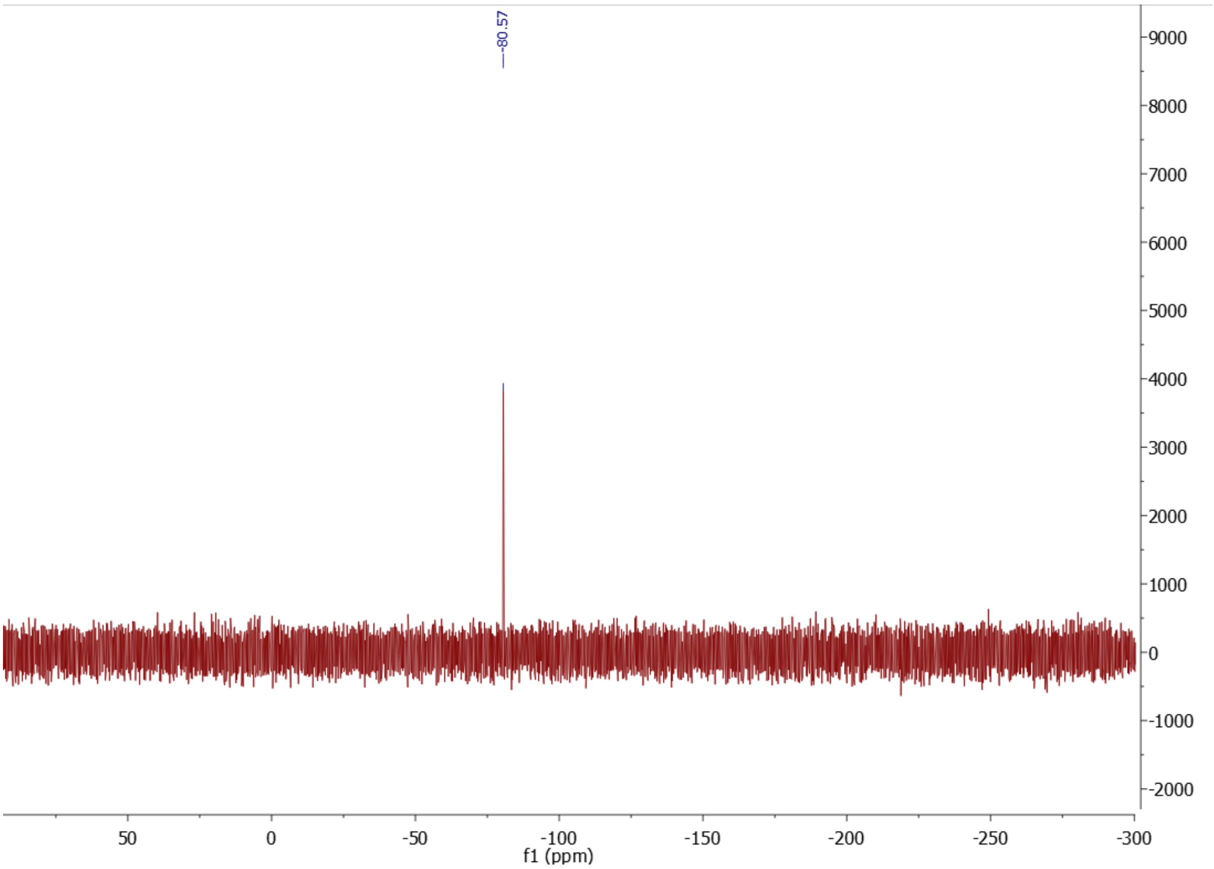
-20
f1 (ppm)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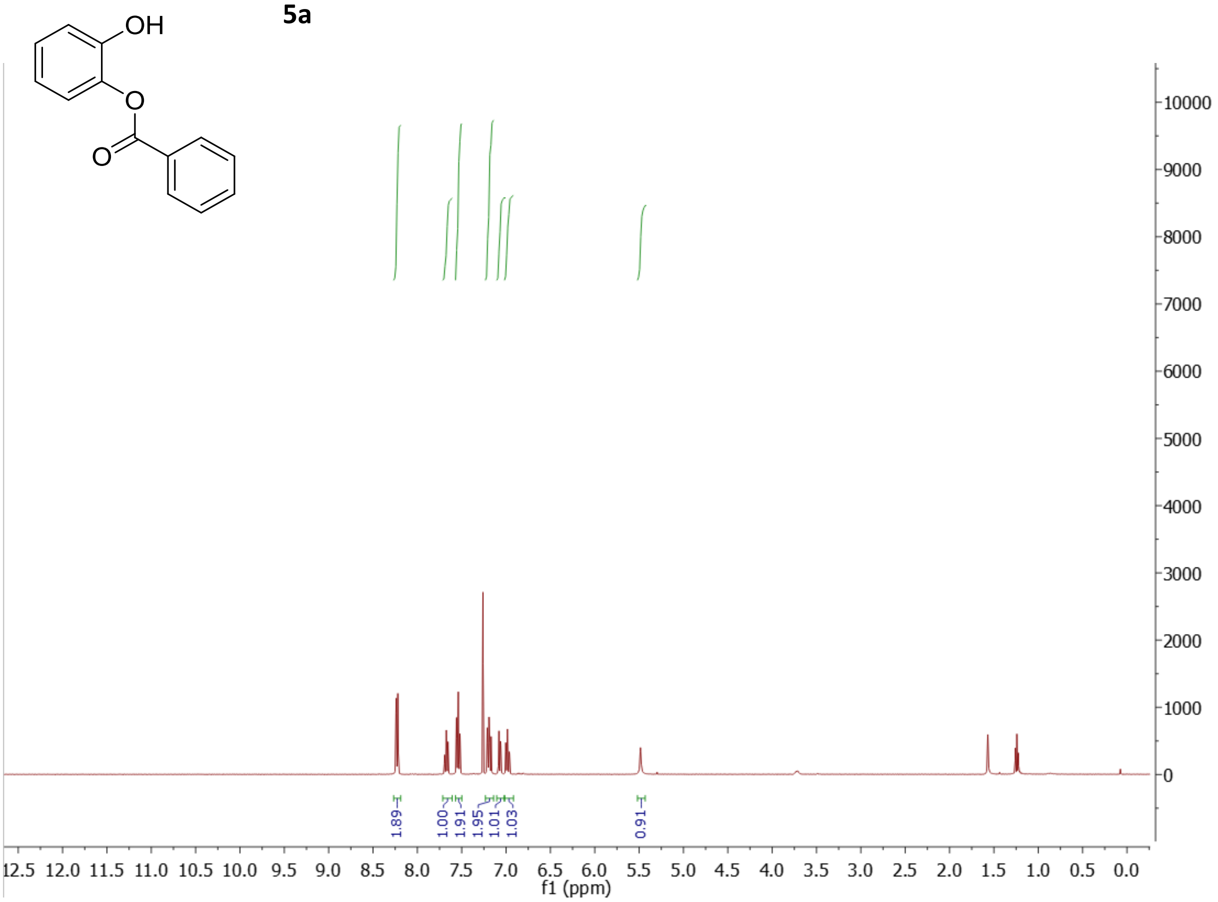
-200
-250
-300
f1 (ppm)

5a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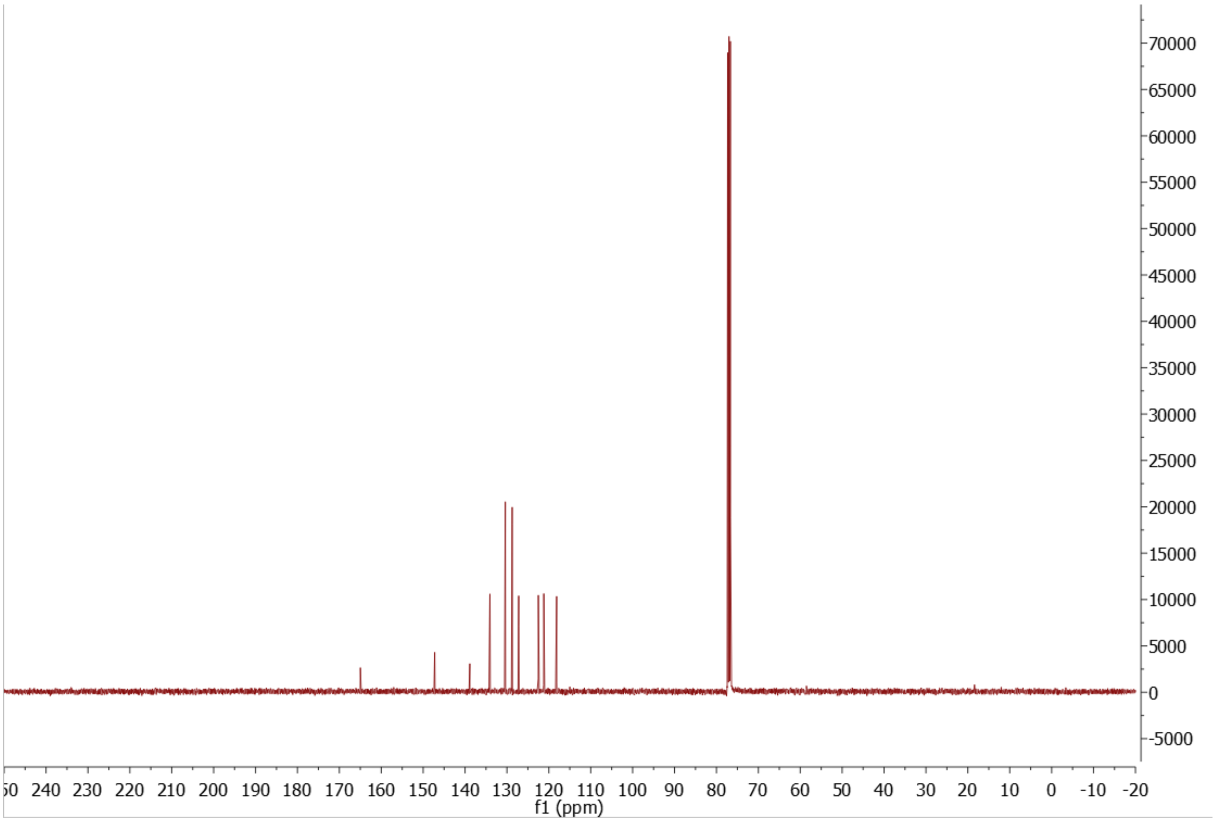
5000
4000
3000
2000
1000
0
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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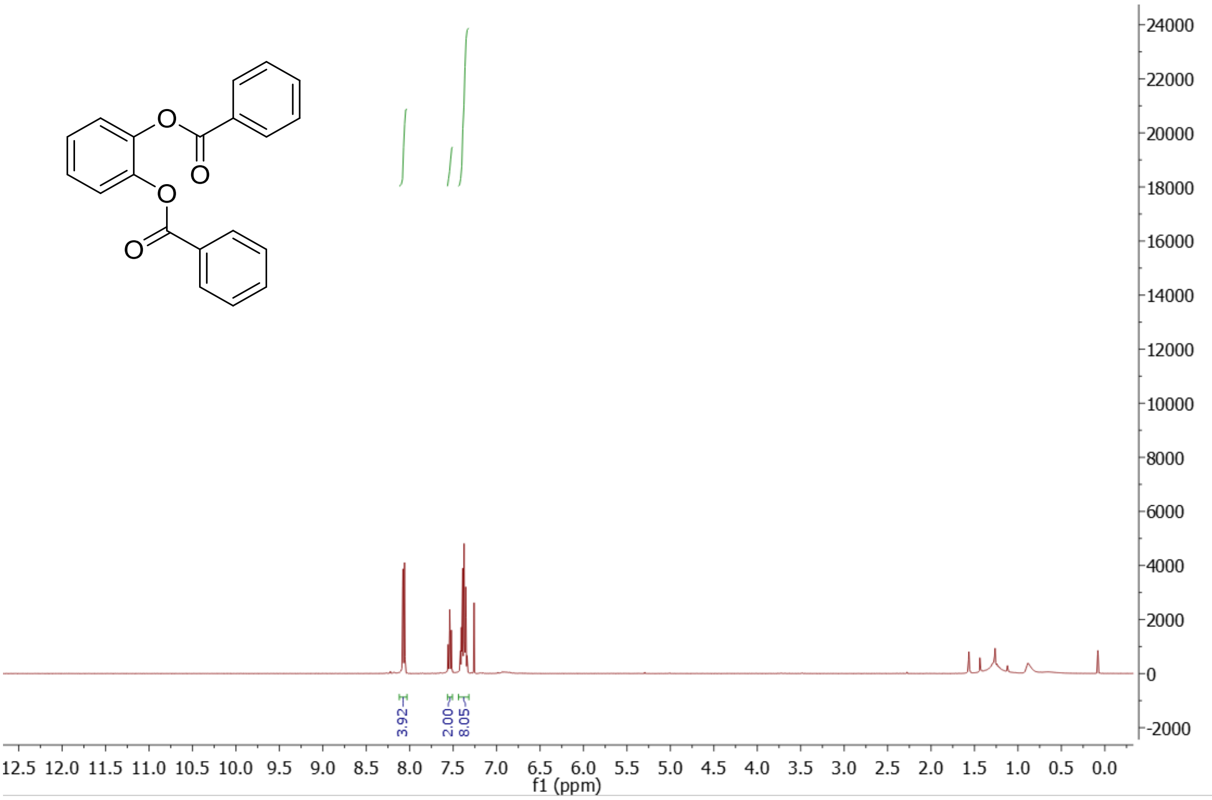
f1 (ppm)

5b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2000
0
-2000
12.5 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
f1 (ppm)
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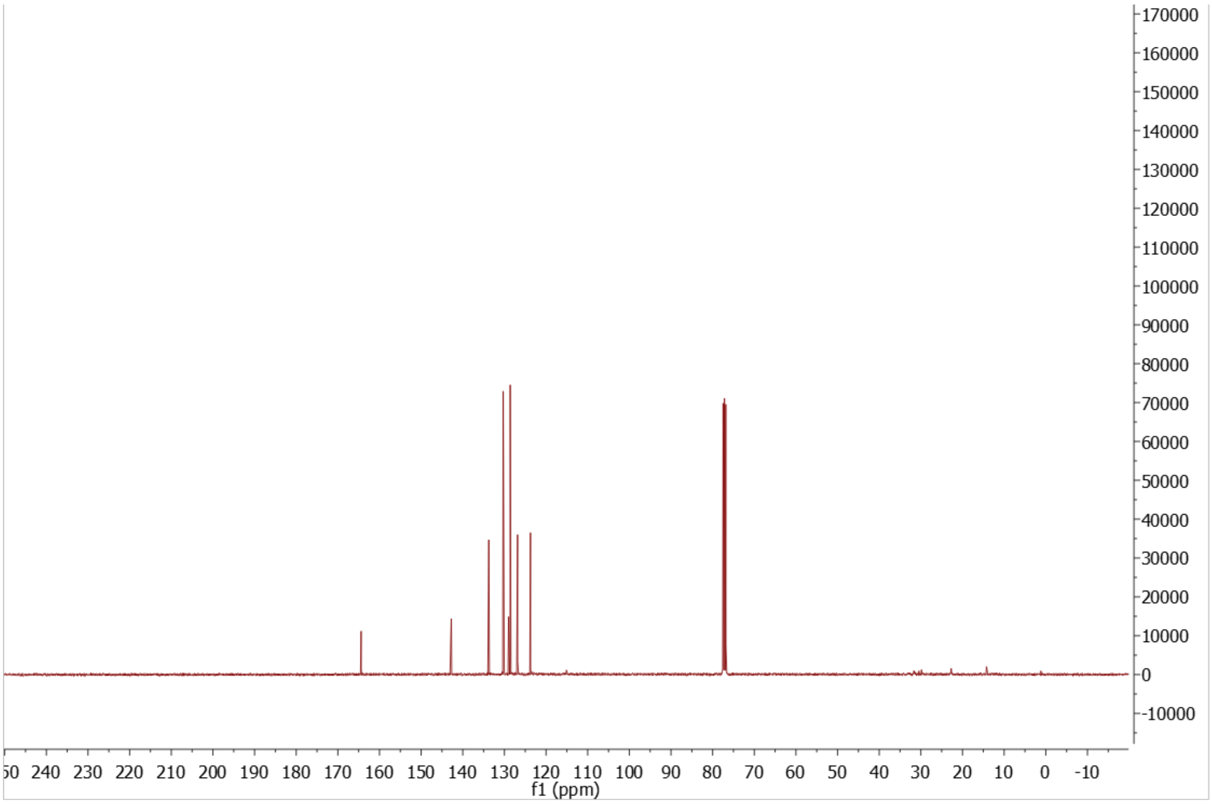
O
O
O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80000
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60000
50000
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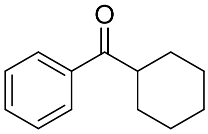
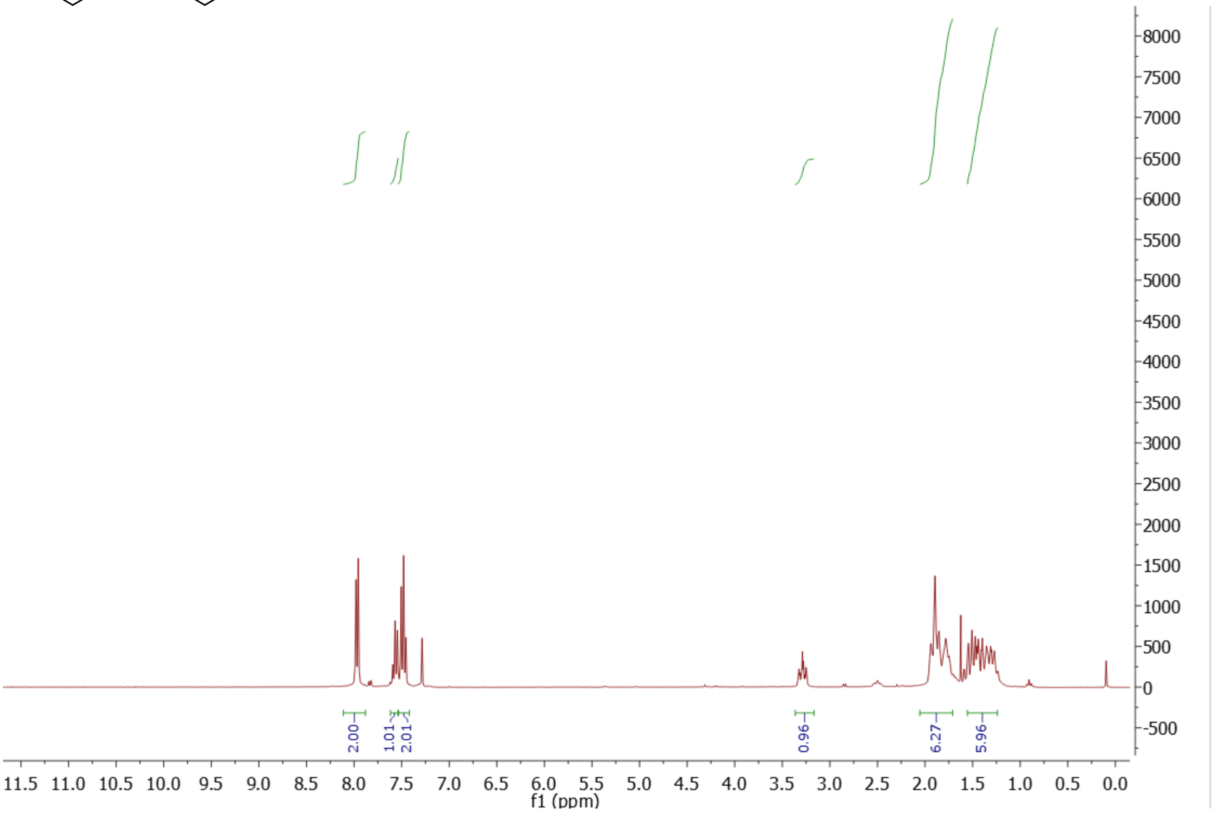
10000
0
-10000
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O

3a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3000
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1500
1000
500
0
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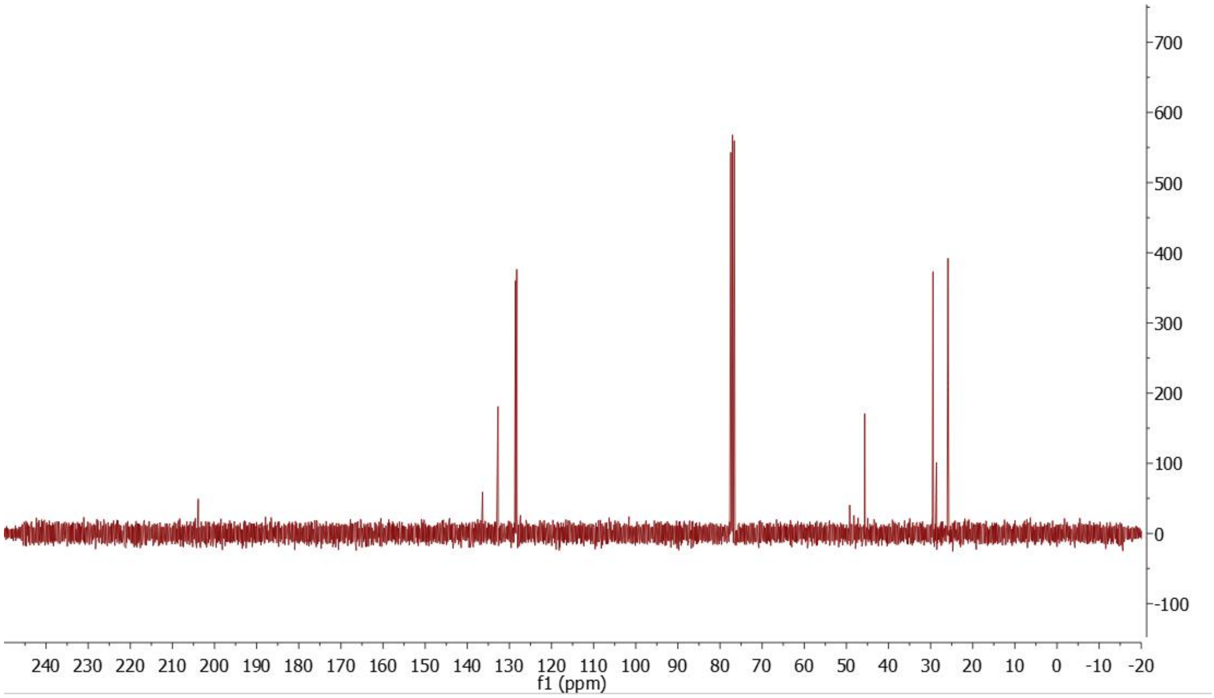
2.00
1.01
2.01
0.96
6.27
5.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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-100
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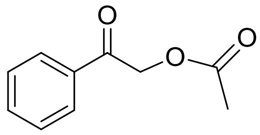
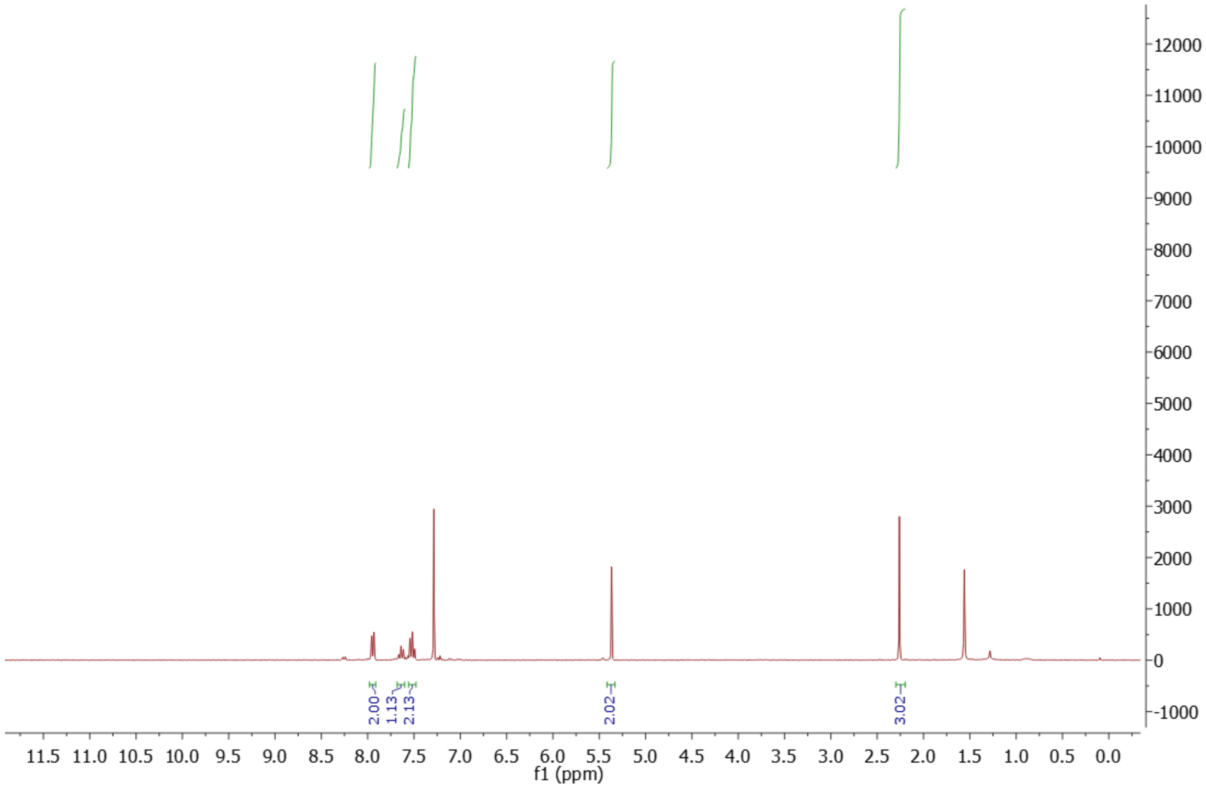
f1 (ppm)



3e



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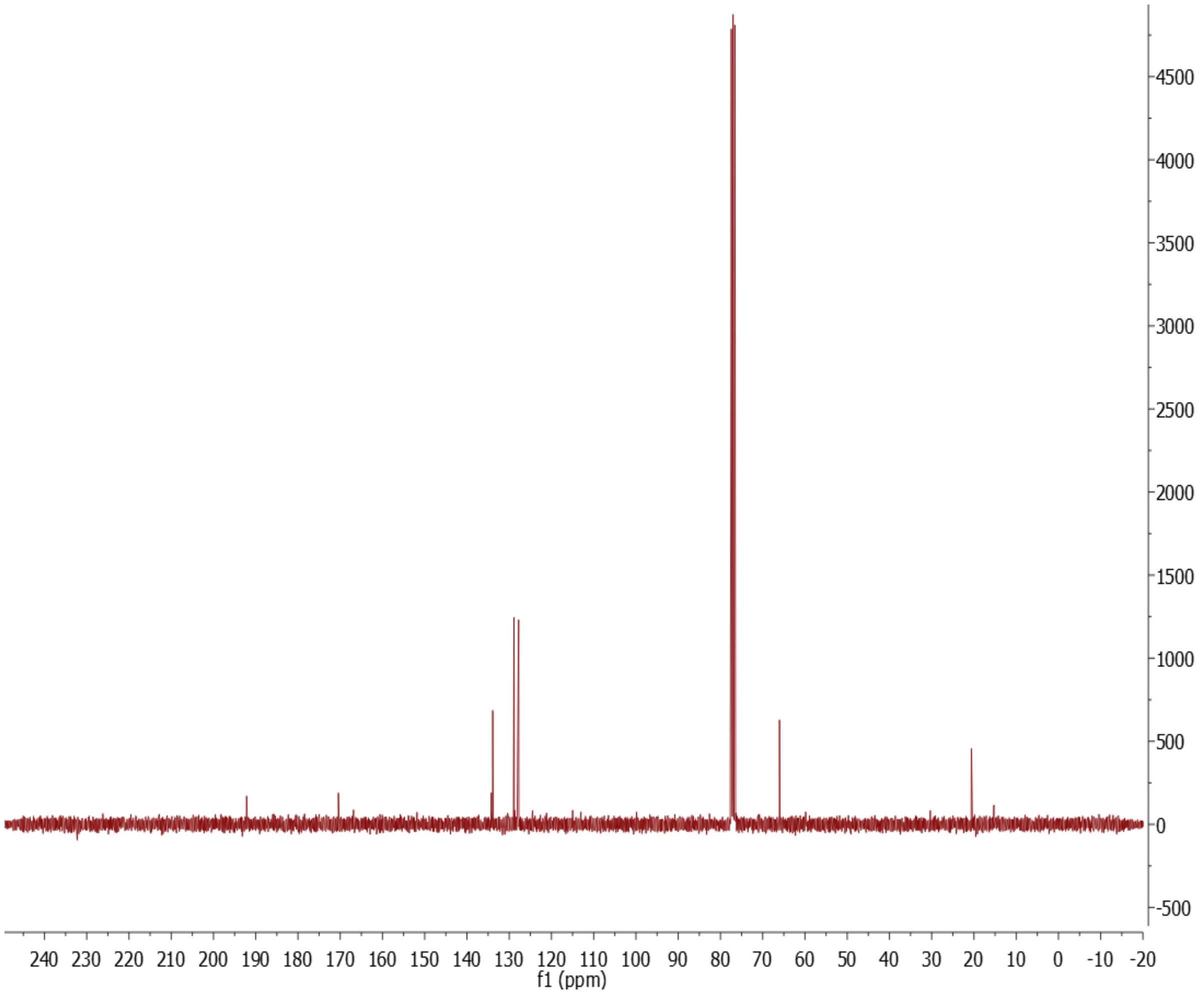
2.13
2.02
3.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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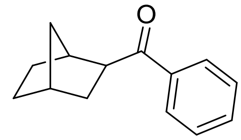
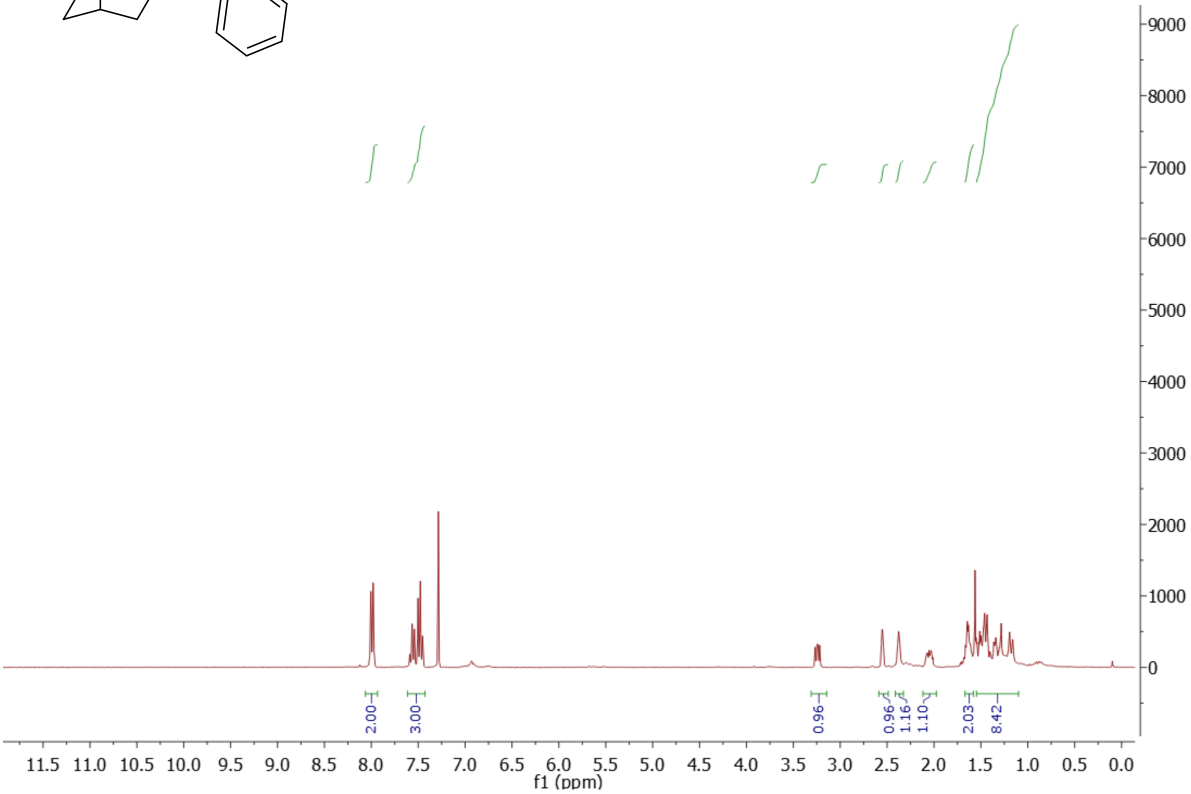
f1 (ppm)


O

3g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2.03
8.42
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
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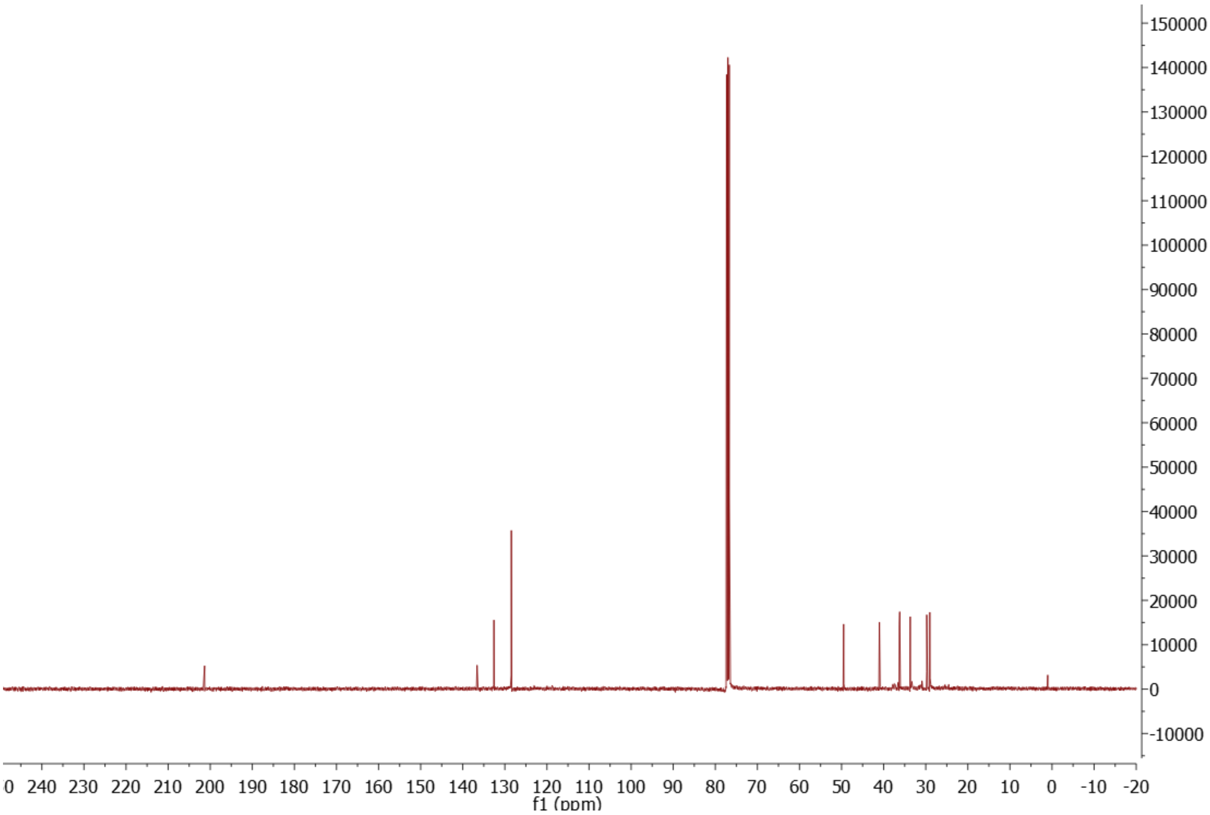
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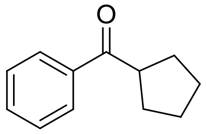
f1 (ppm)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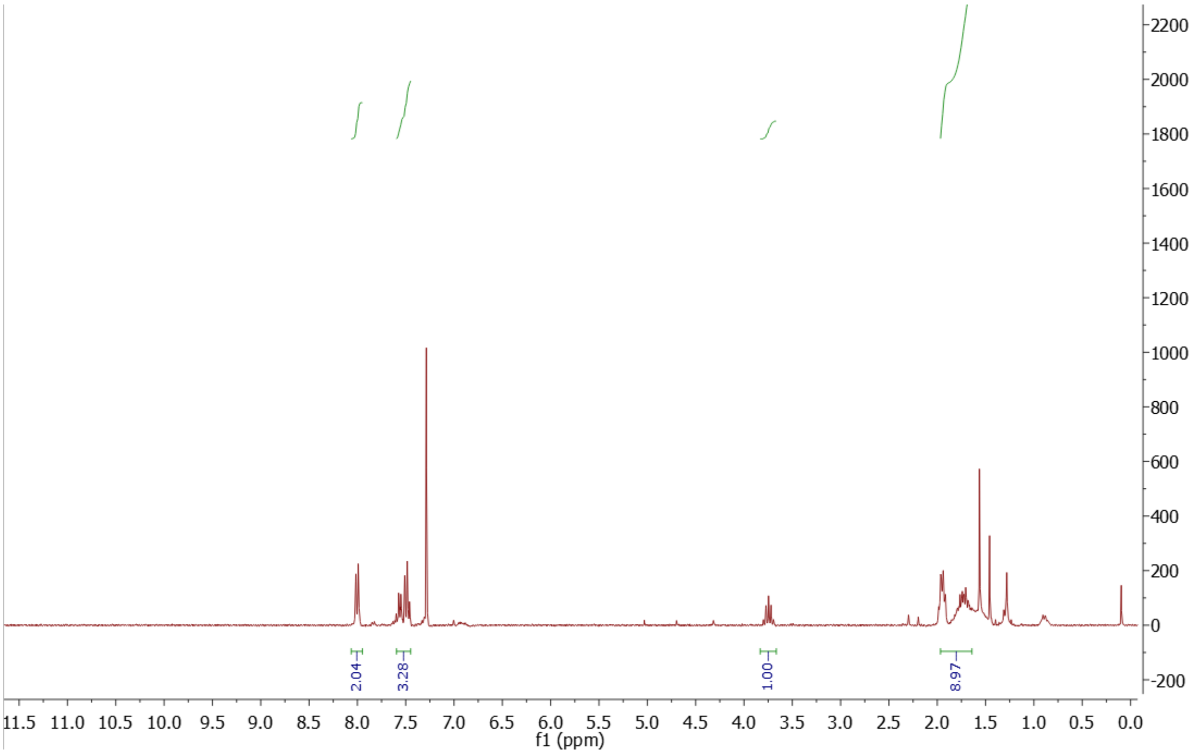
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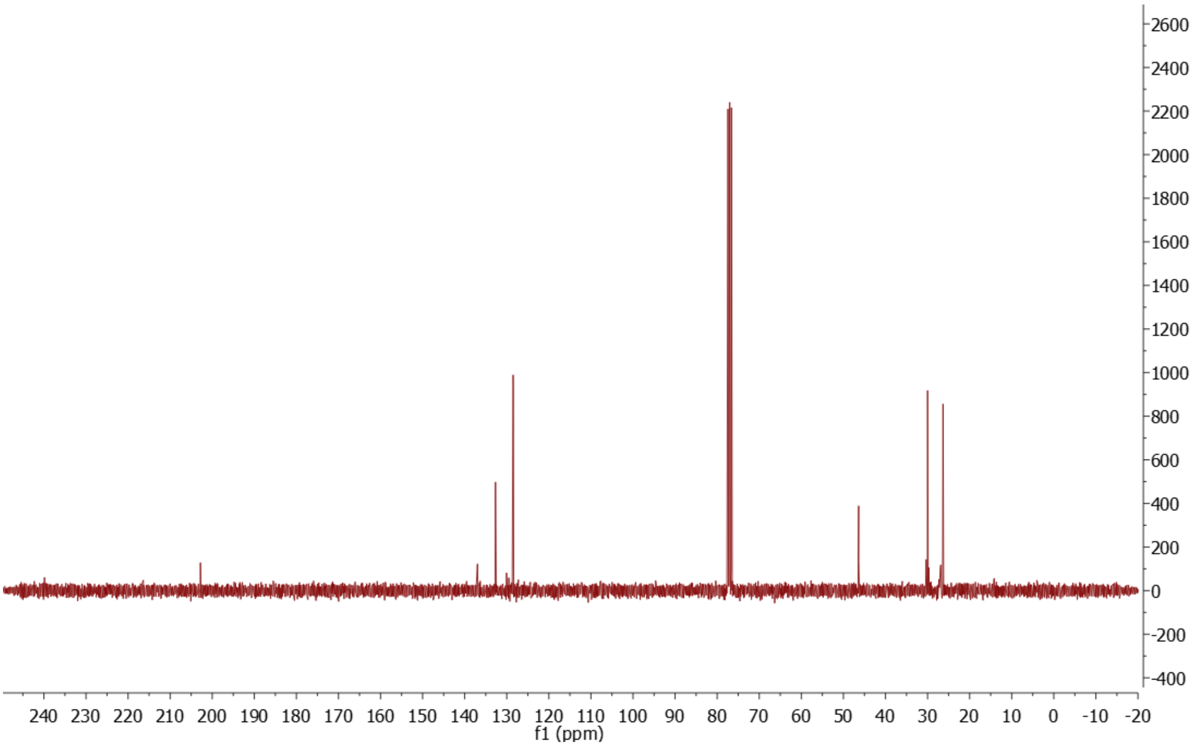
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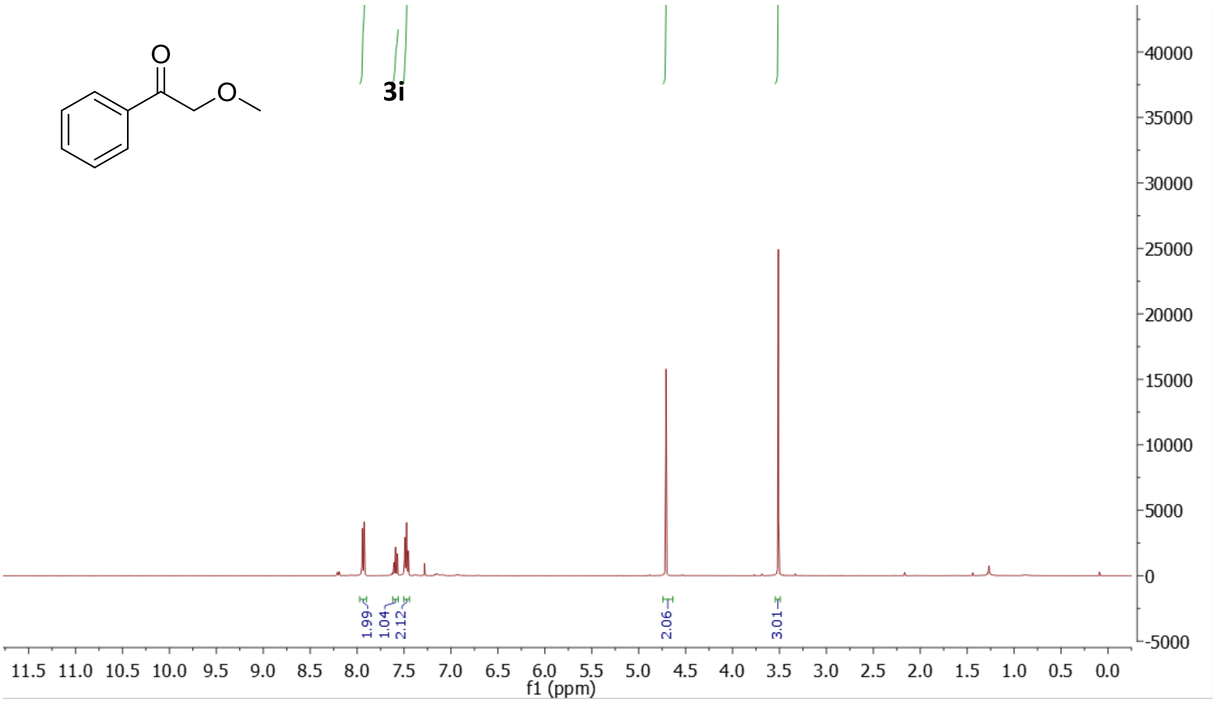

3i

O
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2.12
2.06
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35000
30000
25000
20000
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10000
5000
0
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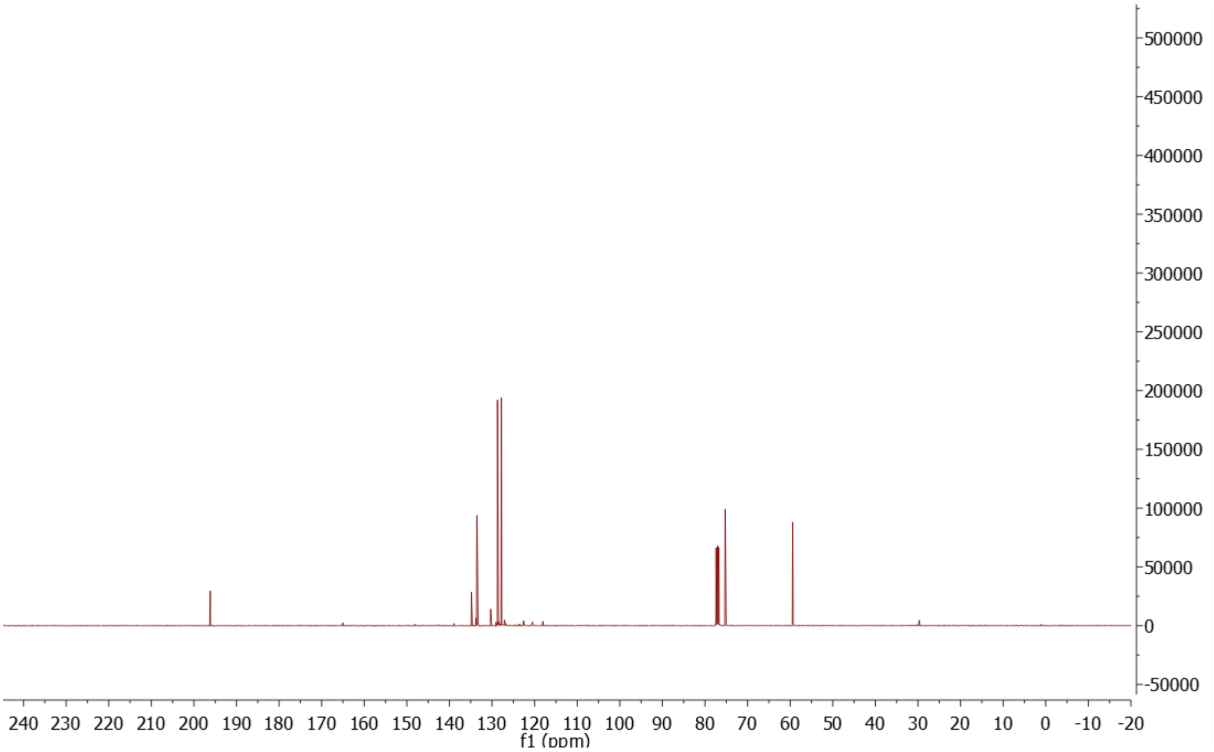

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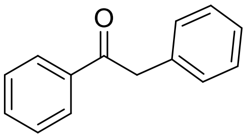
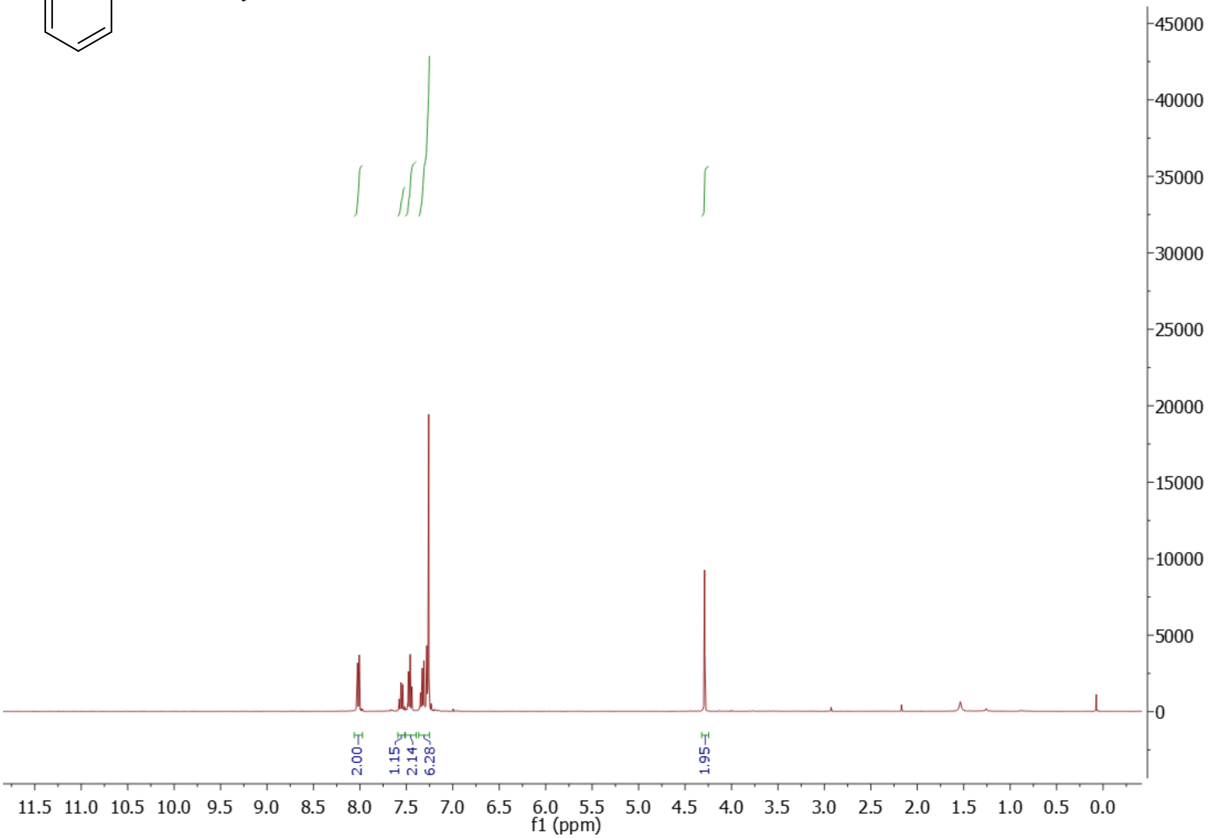
f1 (ppm)



3j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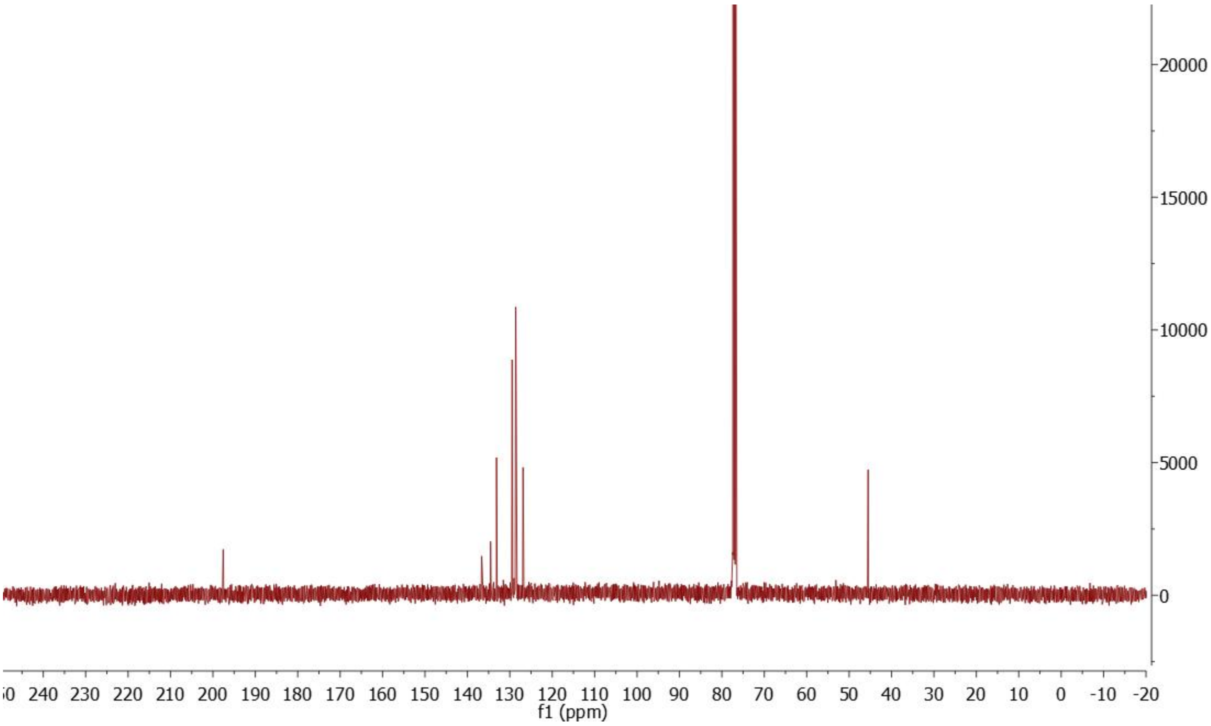
f1 (ppm)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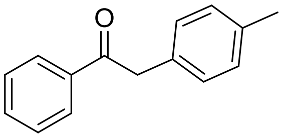
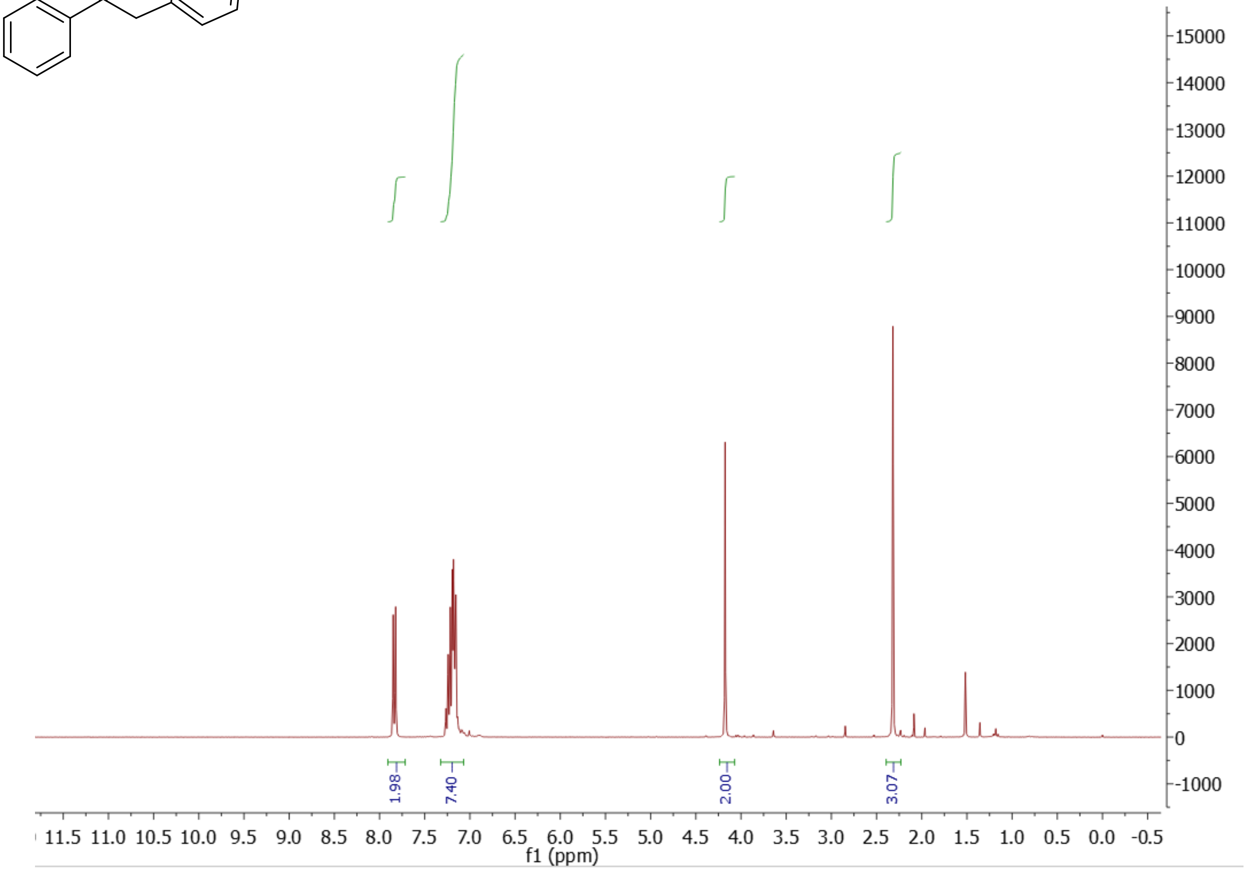


3k



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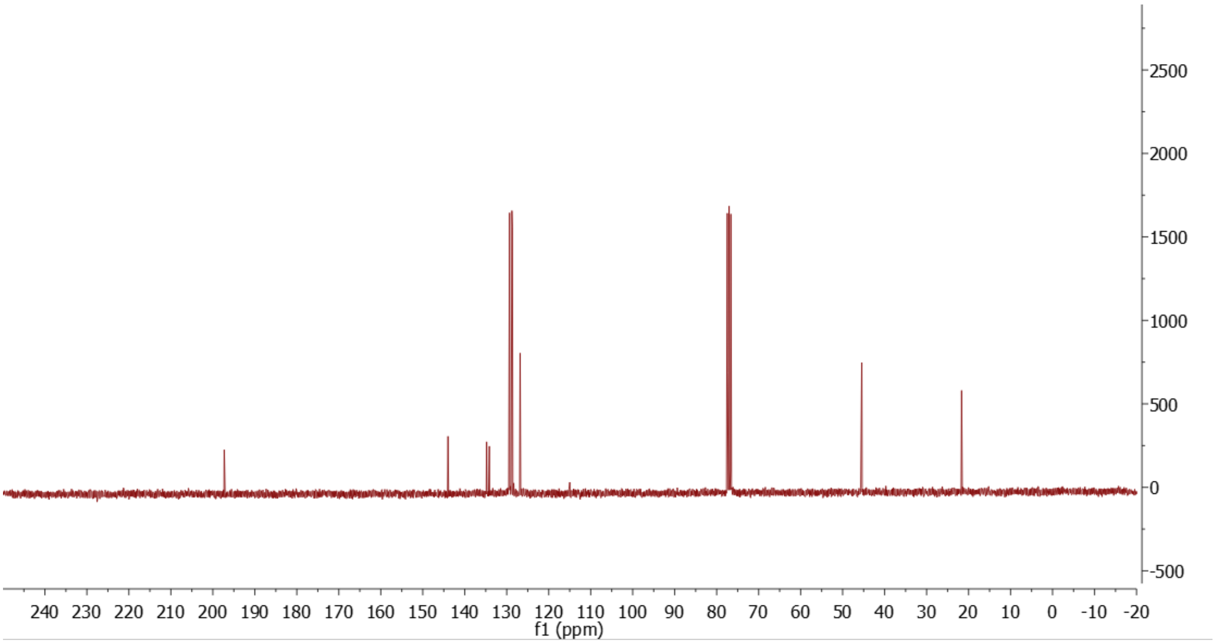
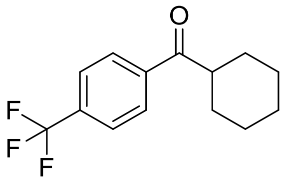
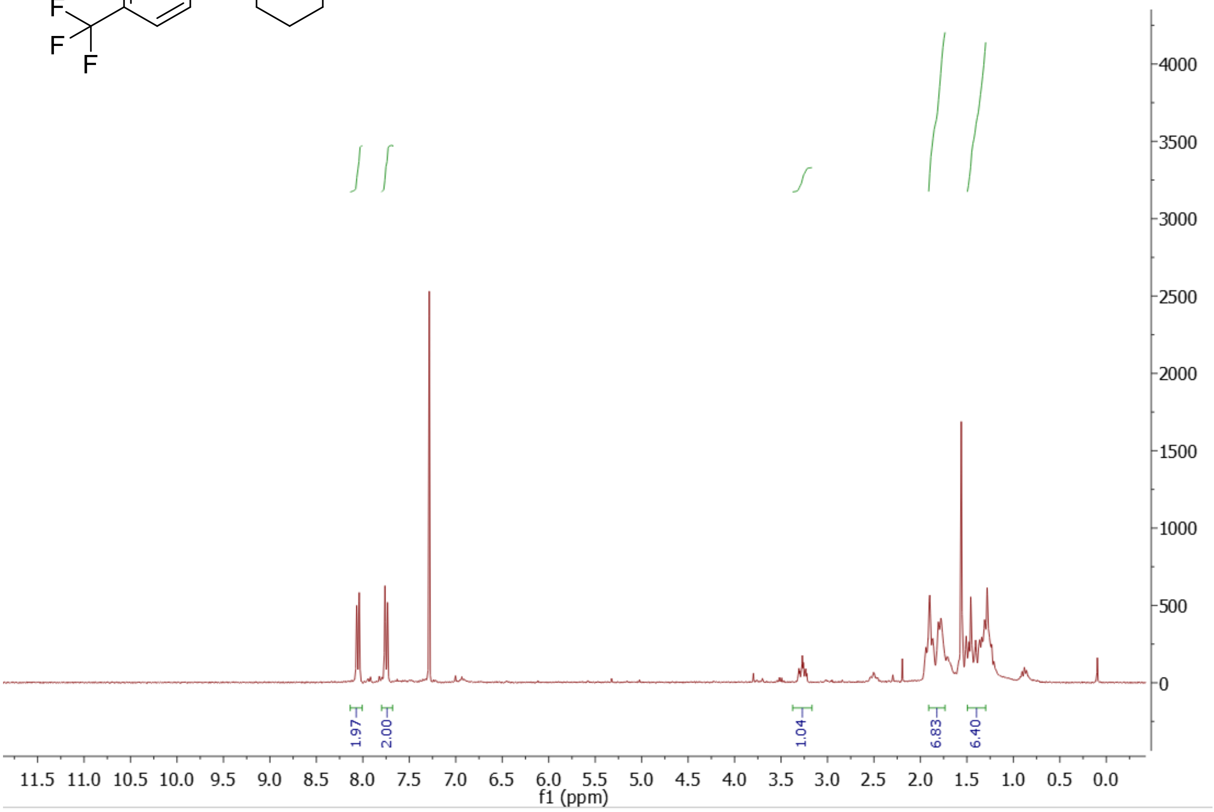
7.40
2.00
3.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

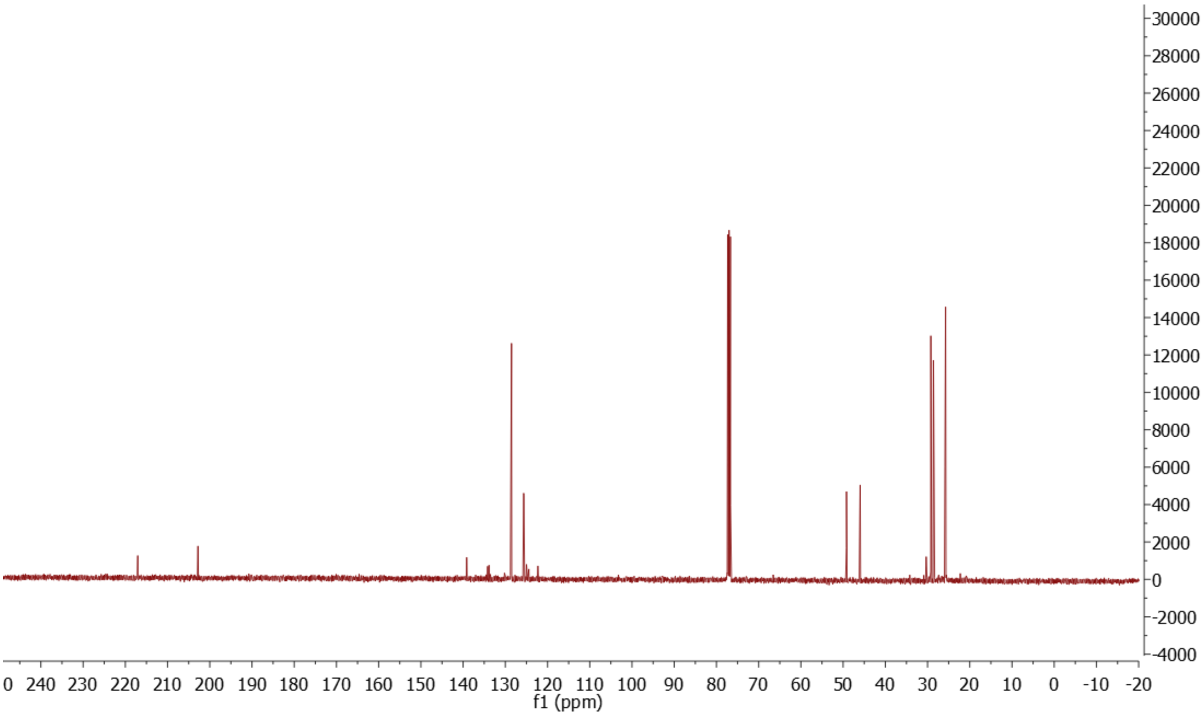


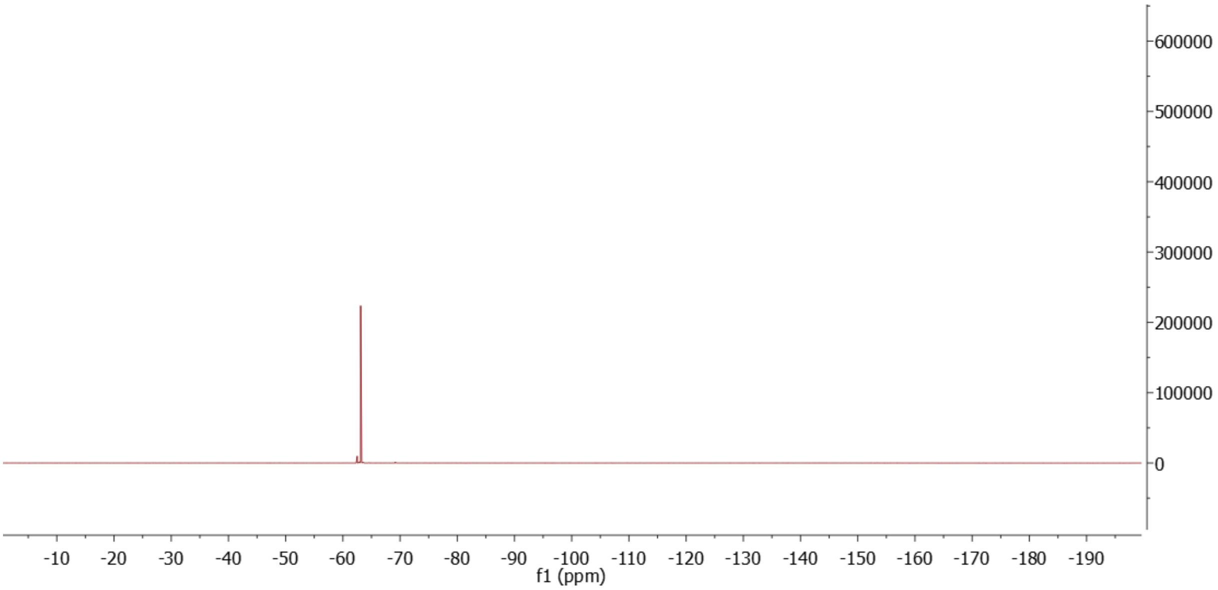
2500
2000
1500
1000
500
0
-500
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

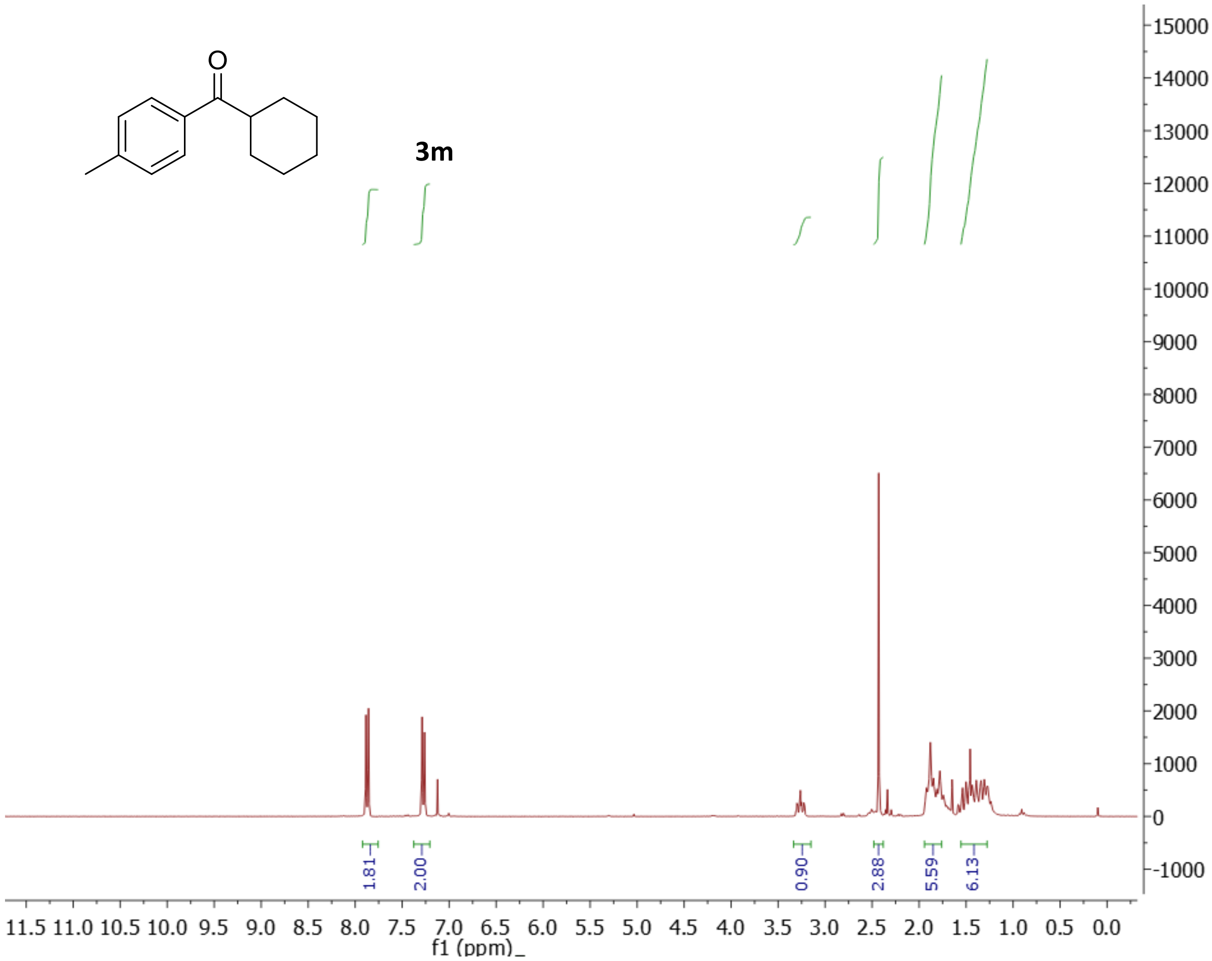


3l


1.97
2.00
1.04
6.83
6.40
4000
3500
3000
2500
2000
1500
1000
500
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
f1 (ppm)

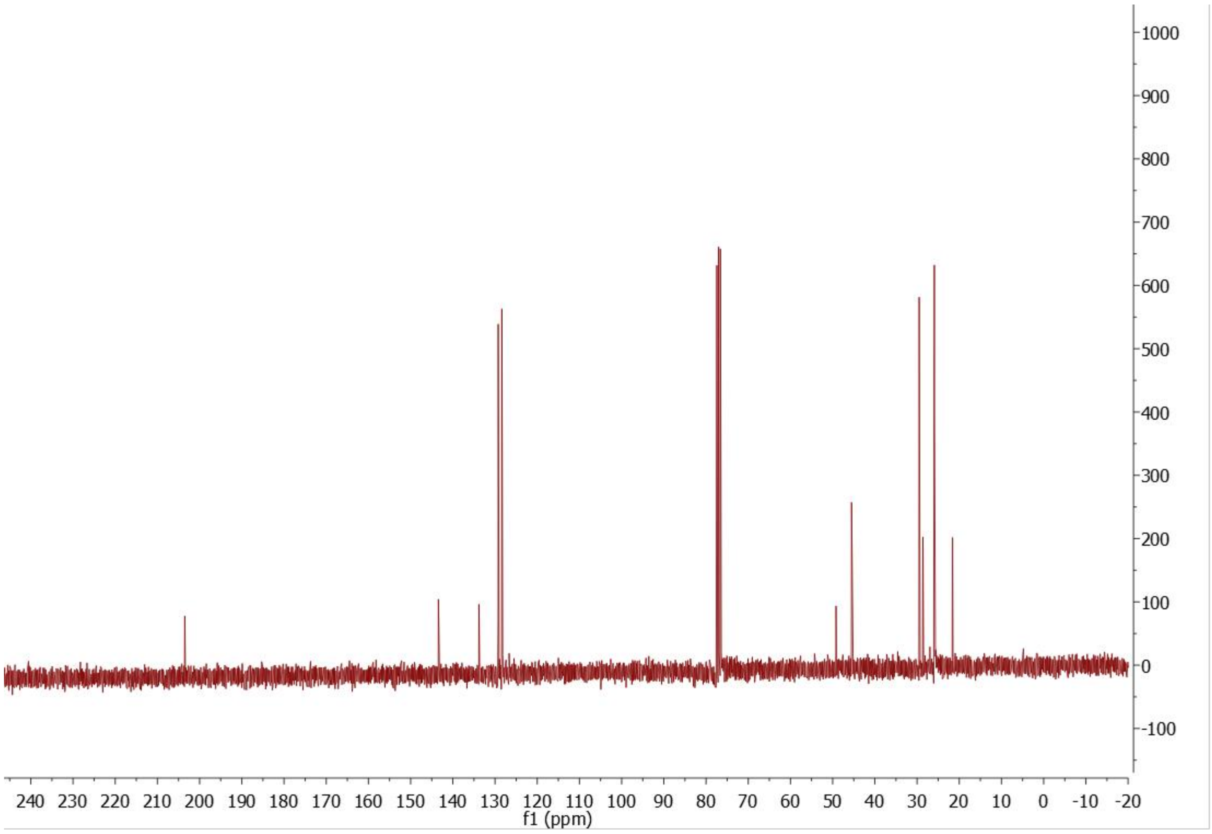

30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
0 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


600000
500000
400000
300000
200000
100000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

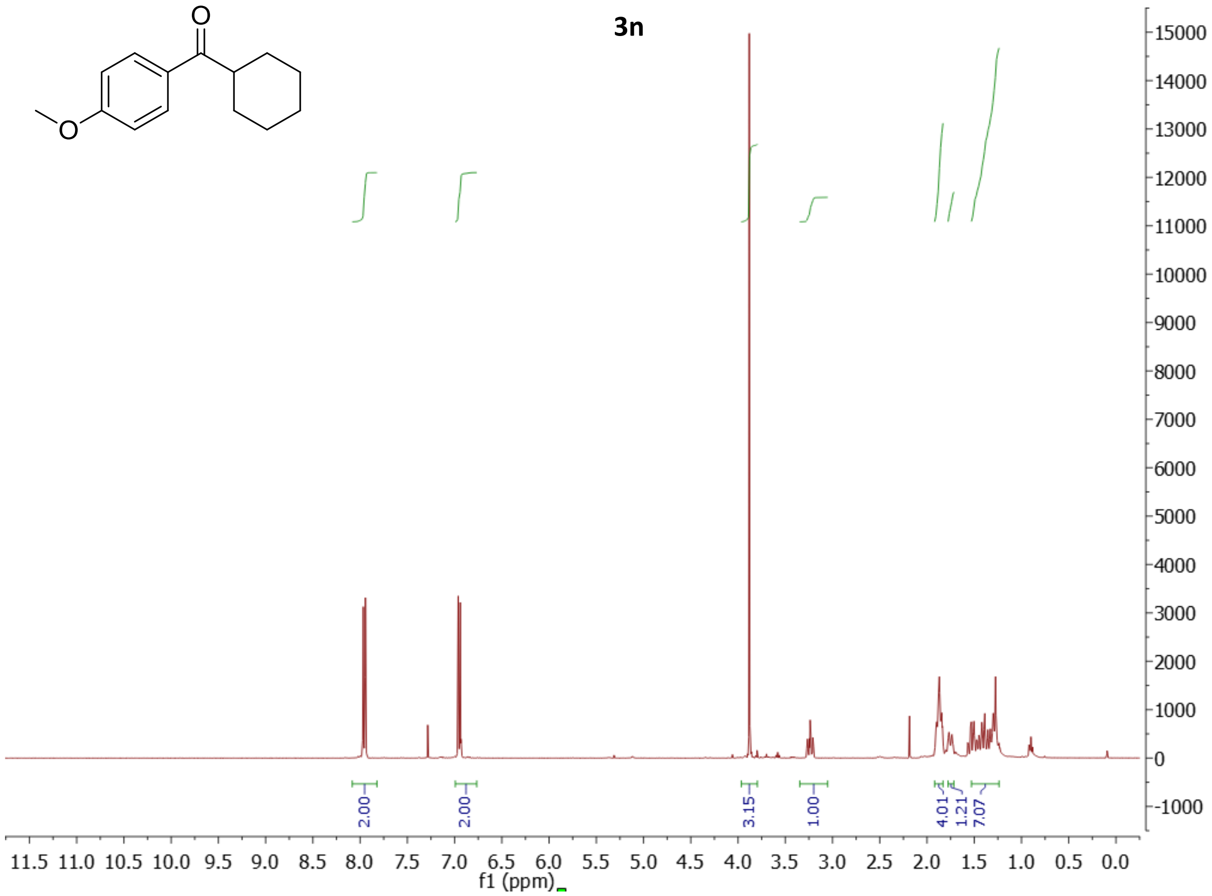


3m

1.81
2.00
0.90
2.88
5.59
6.13
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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
f1 (ppm)
O

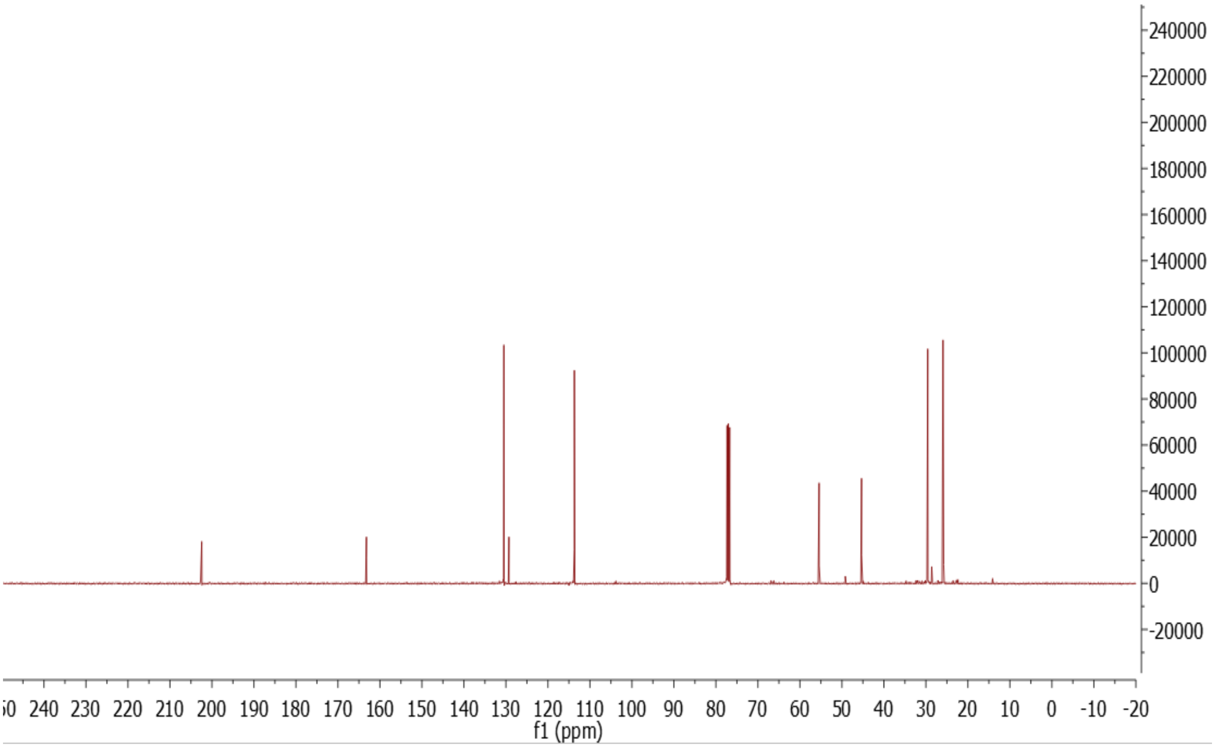


1000
900
800
700
600
500
400
300
200
100
0
-100
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

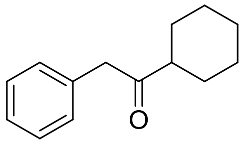


3n

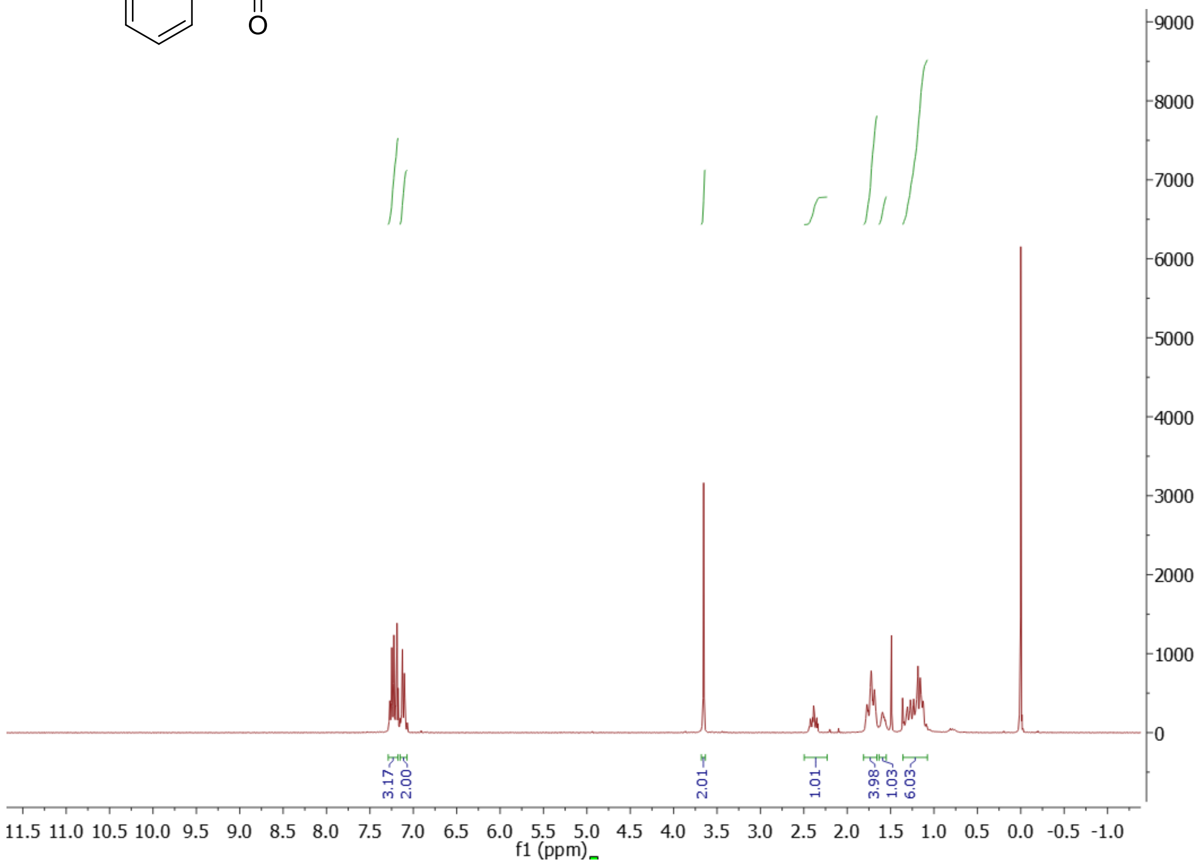
O
O
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.00
2.00
3.15
1.00
4.01
1.21
7.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

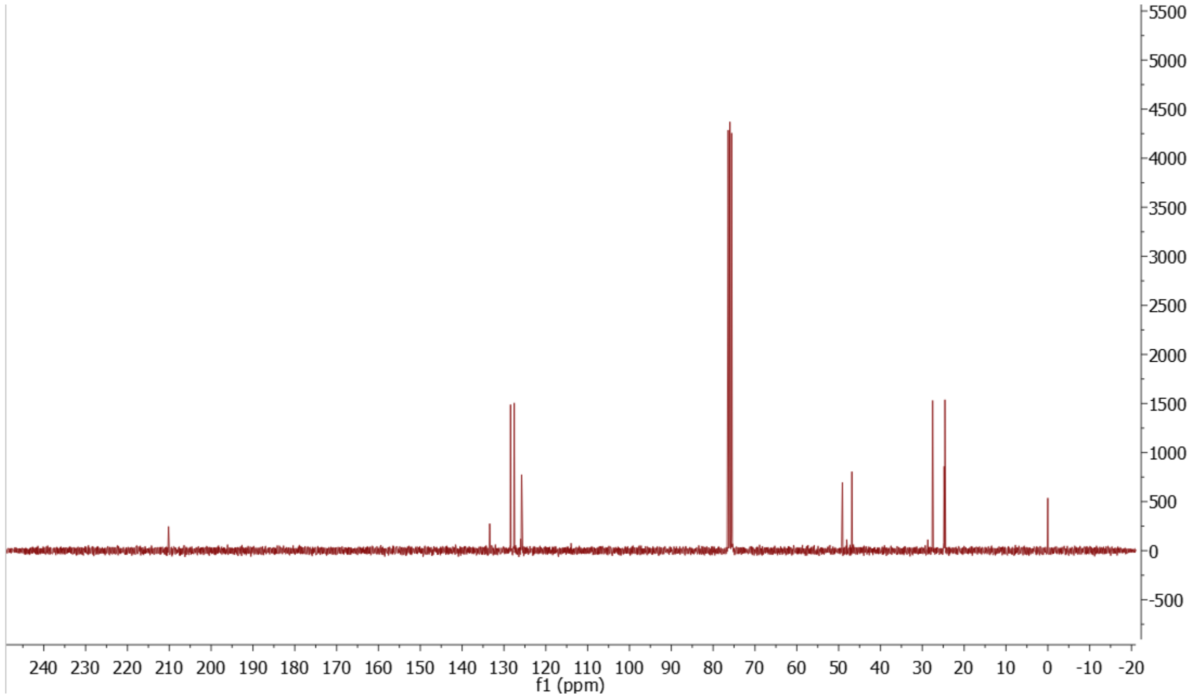


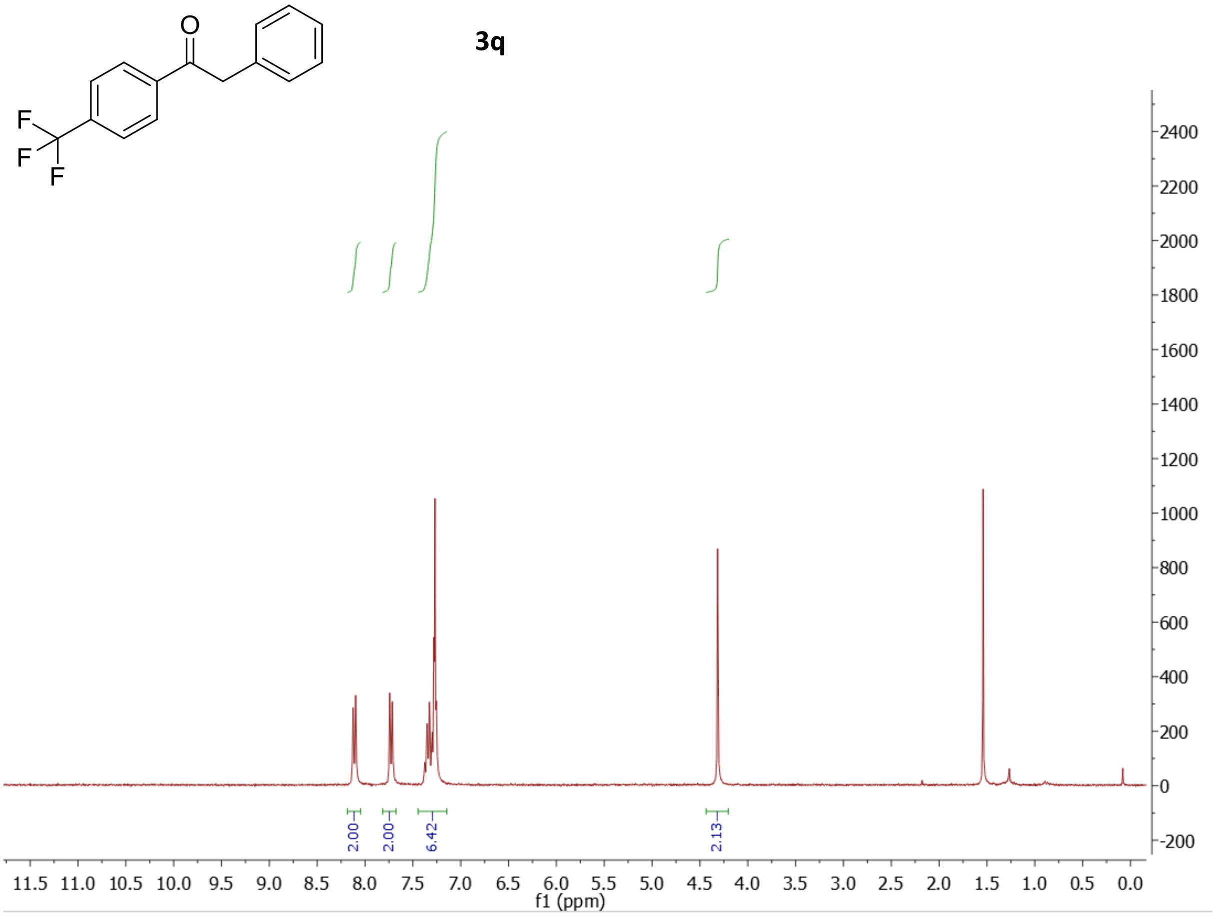
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
0 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O

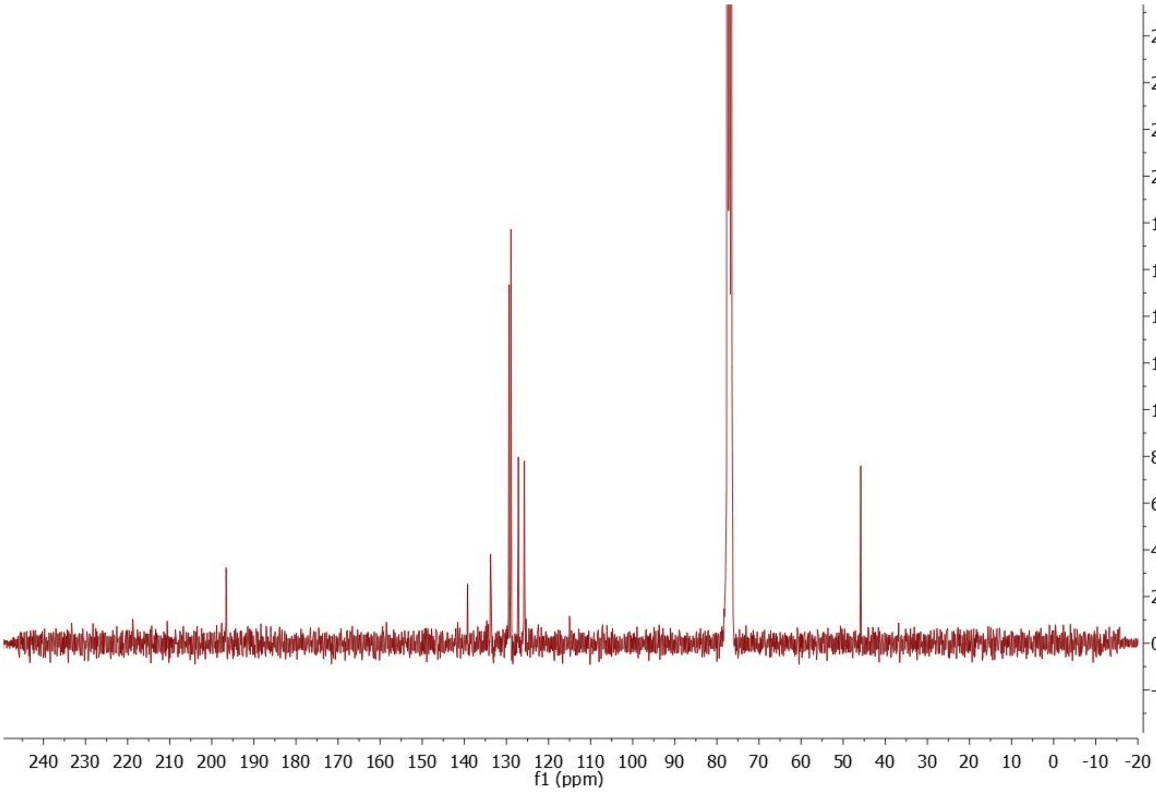
3o

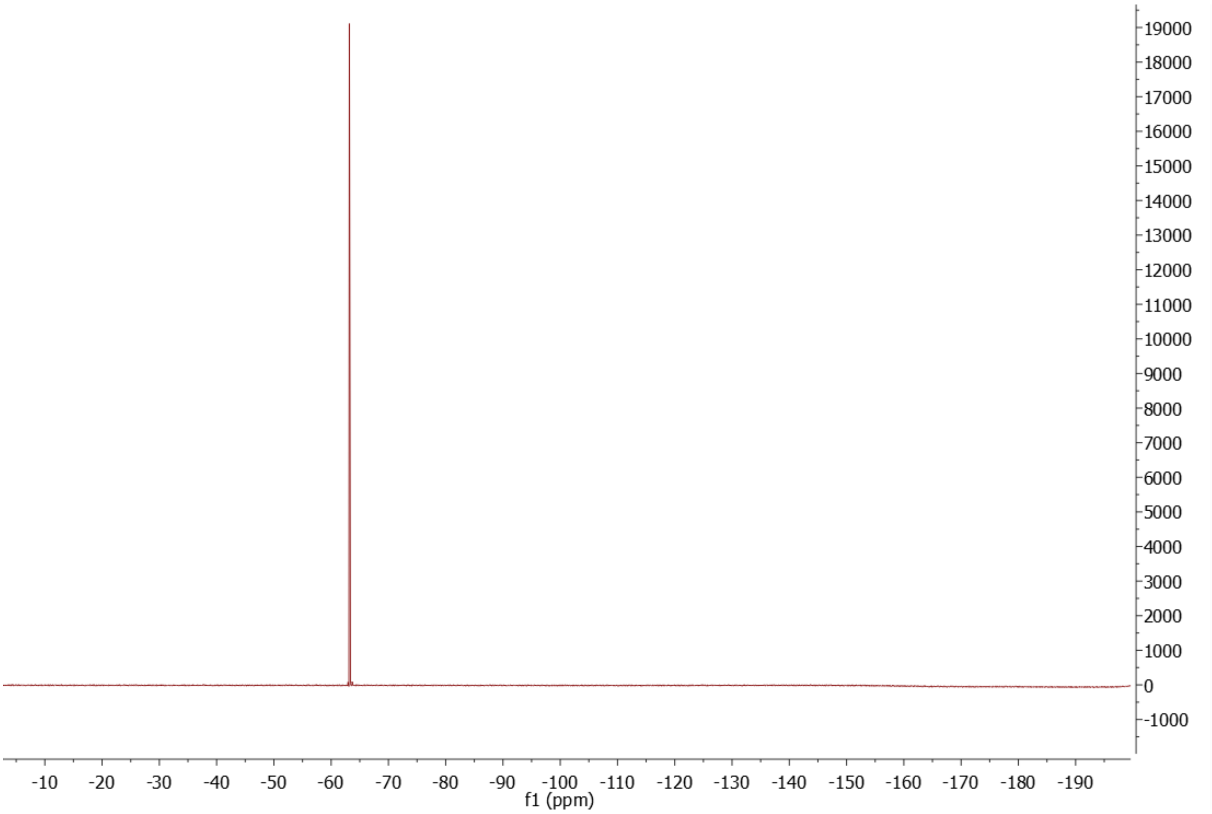

3.17
2.00
2.01
1.01
3.98
1.03
6.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

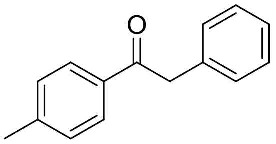

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


O
F
F
F
2.00
2.00
6.42
2.13
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
f1 (ppm)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

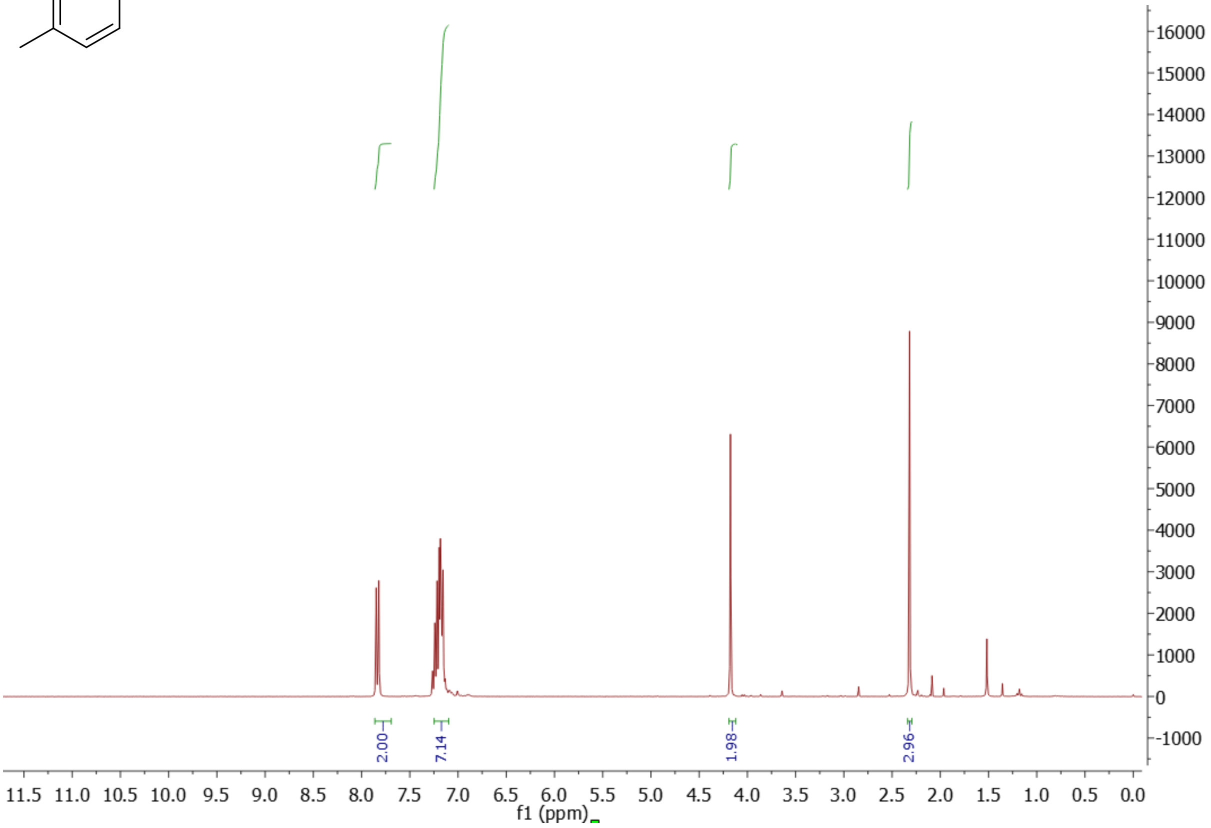
3q

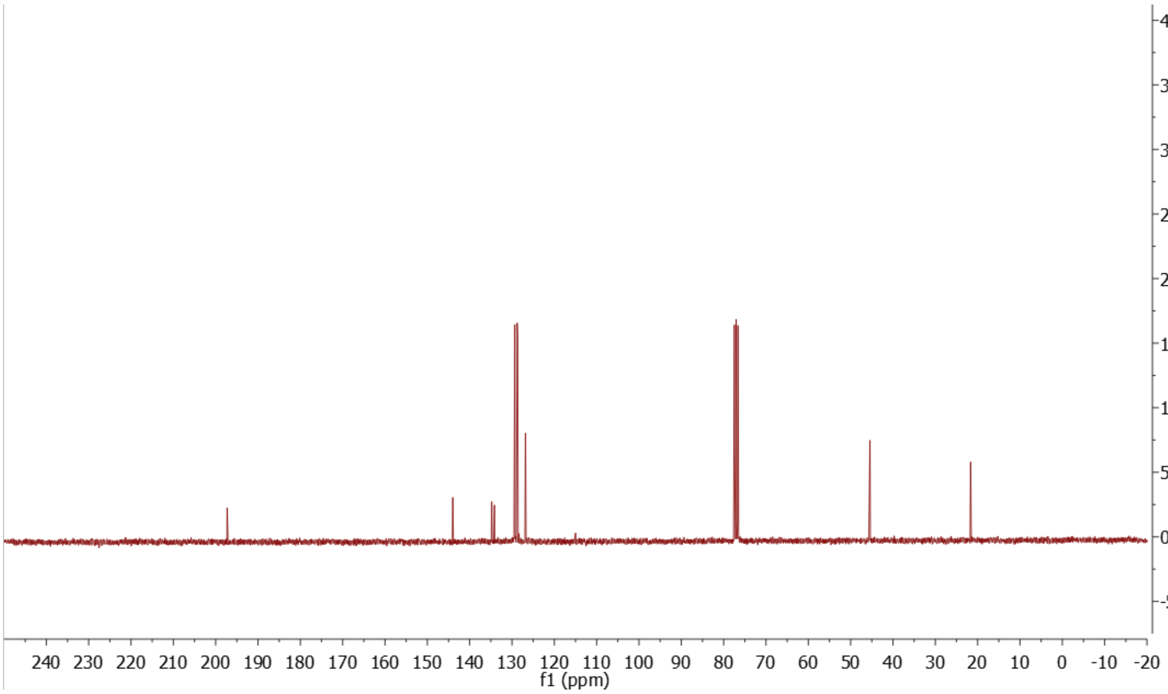

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

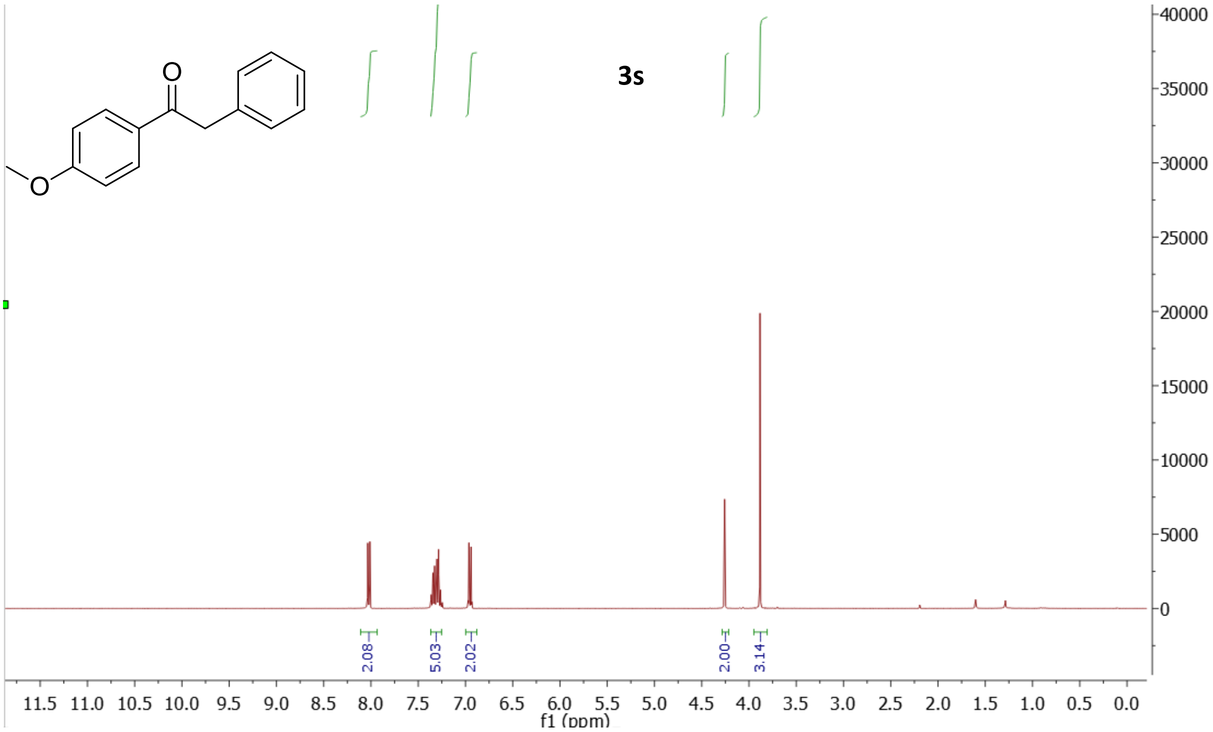

19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

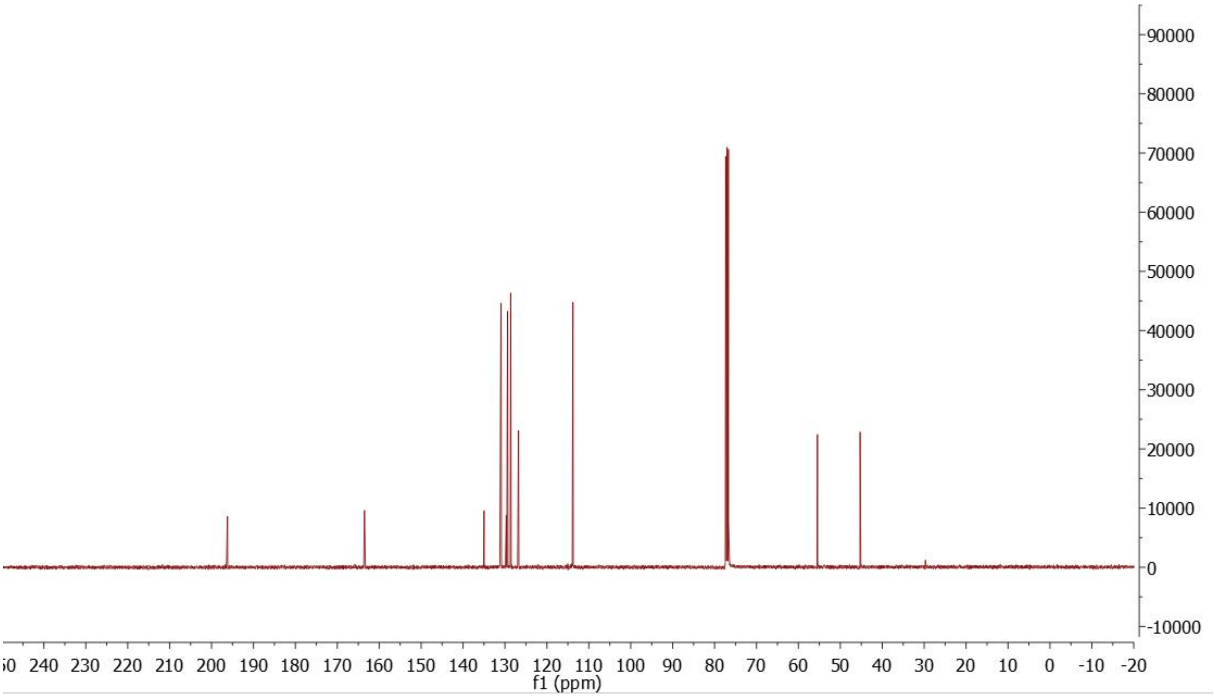


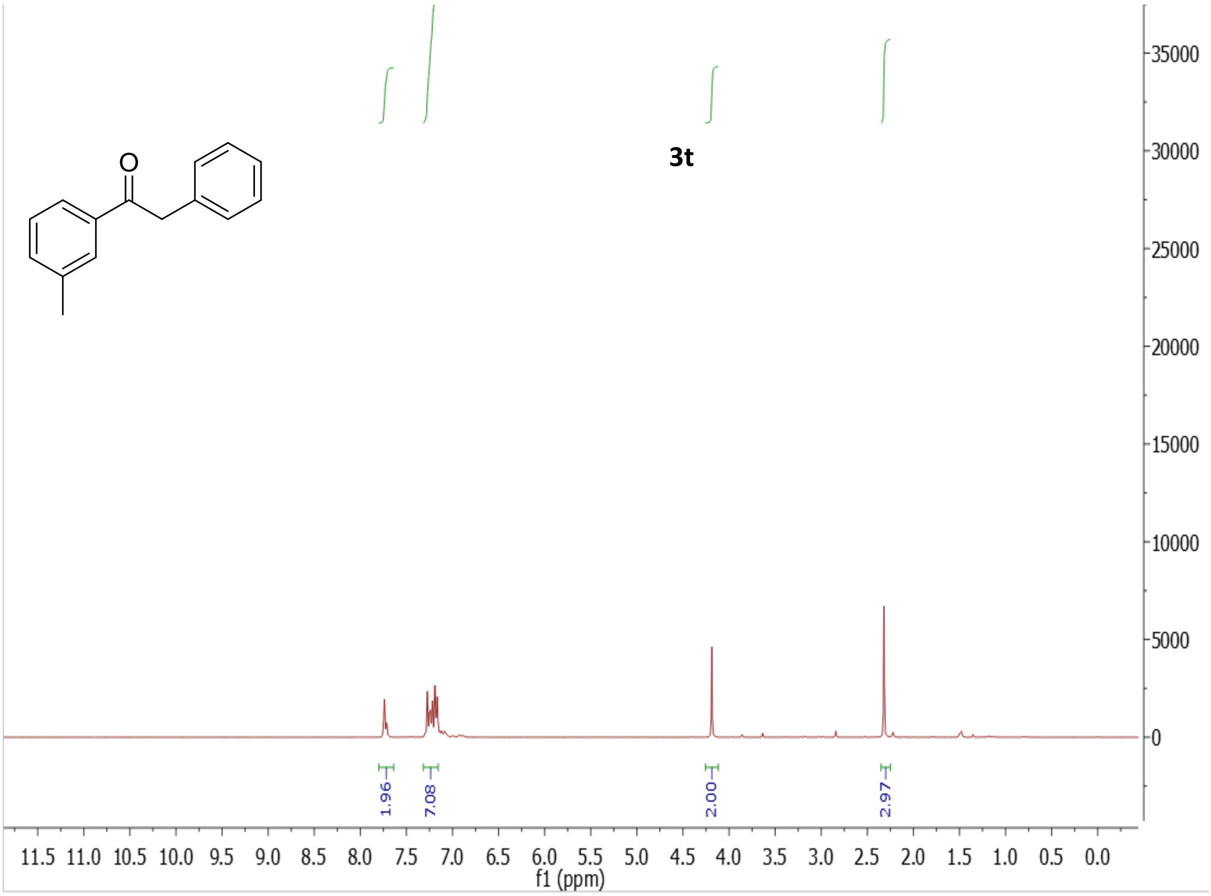
3r

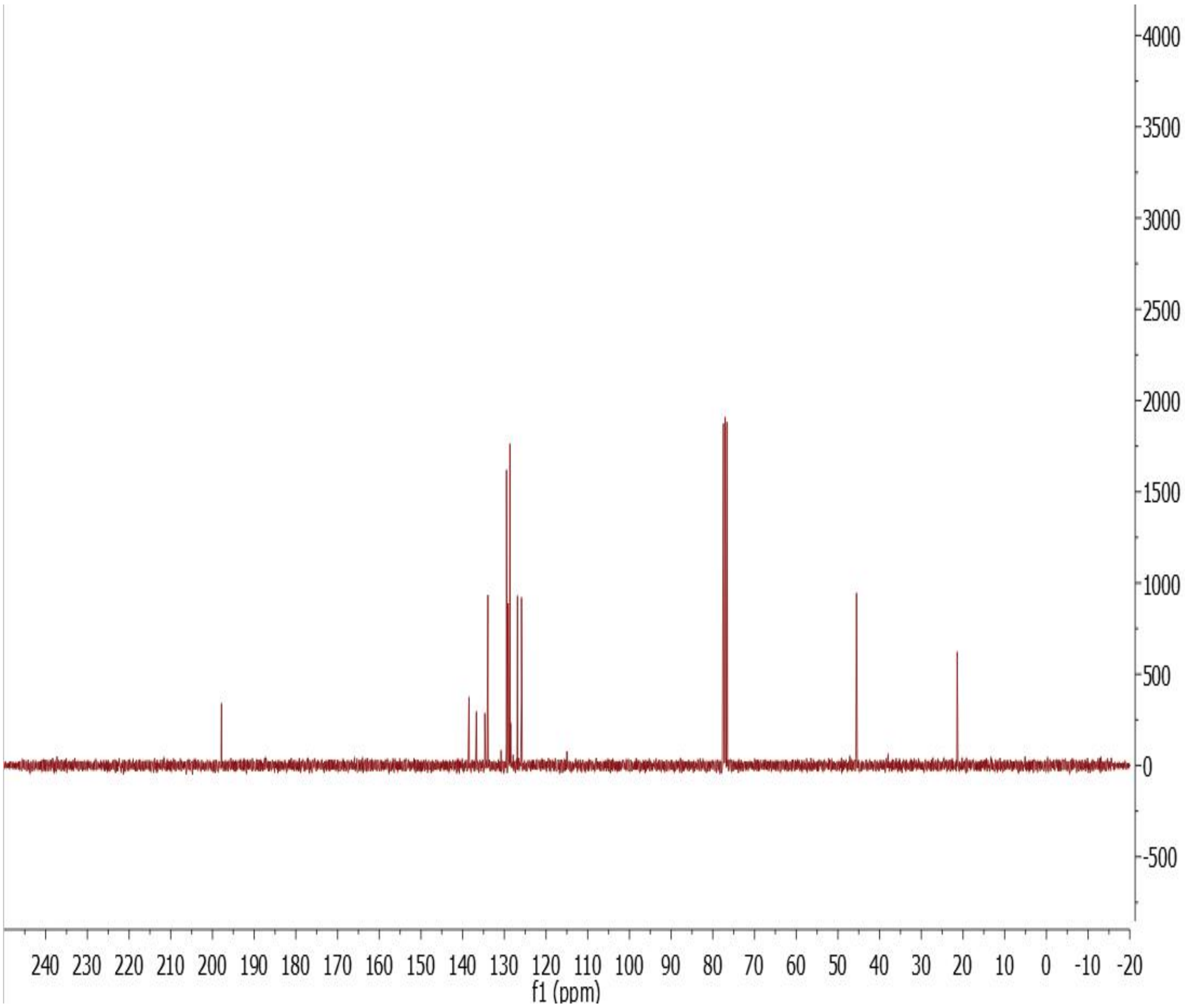

16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.00
7.14
1.98
2.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

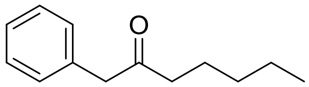

4000
3500
3000
2500
2000
1500
1000
500
0
-500
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


3s
O
O
2.08
5.03
2.02
2.00
3.14
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
f1 (ppm)
40000
35000
30000
25000
20000
15000
10000
5000
0

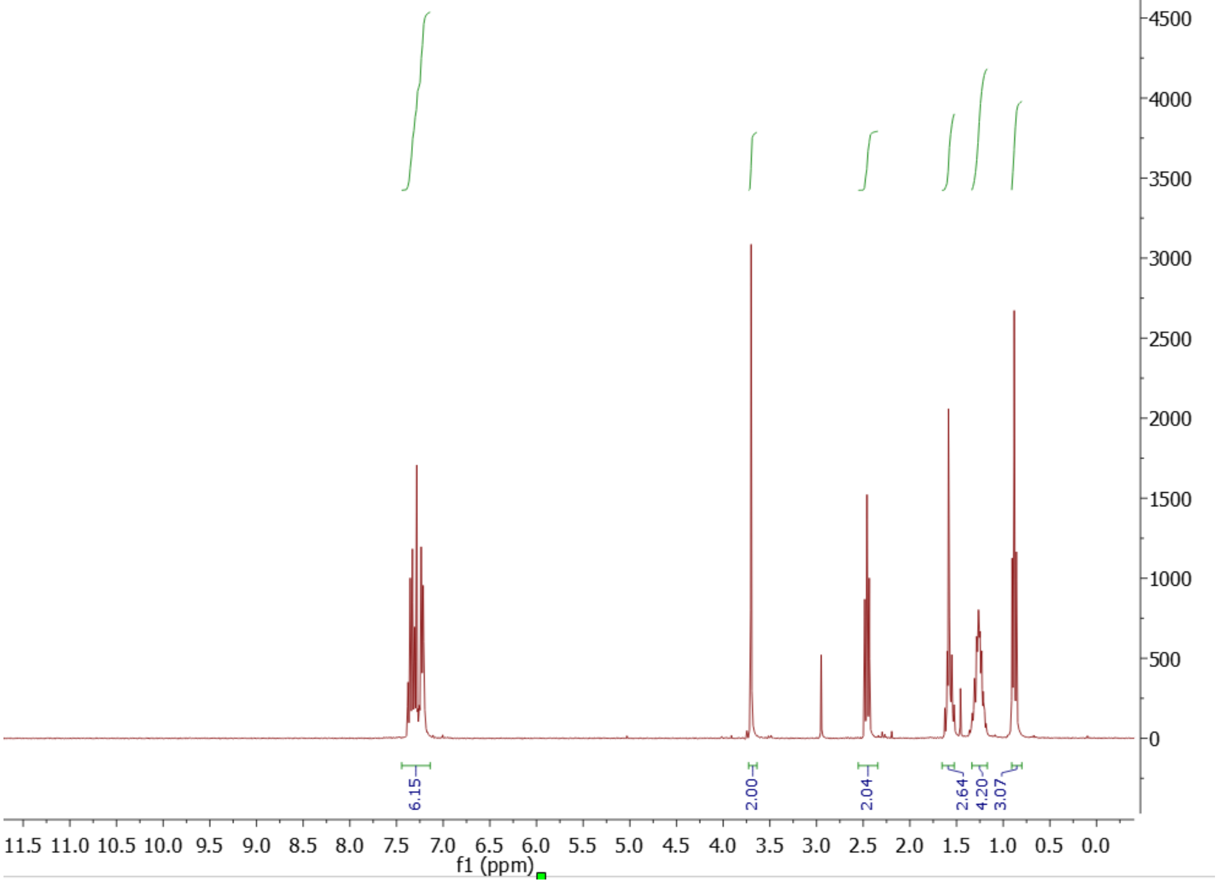

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000


O
3t
35000
30000
25000
20000
15000
10000
5000
0
1.96
7.08
2.00
2.97
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
f1 (ppm)

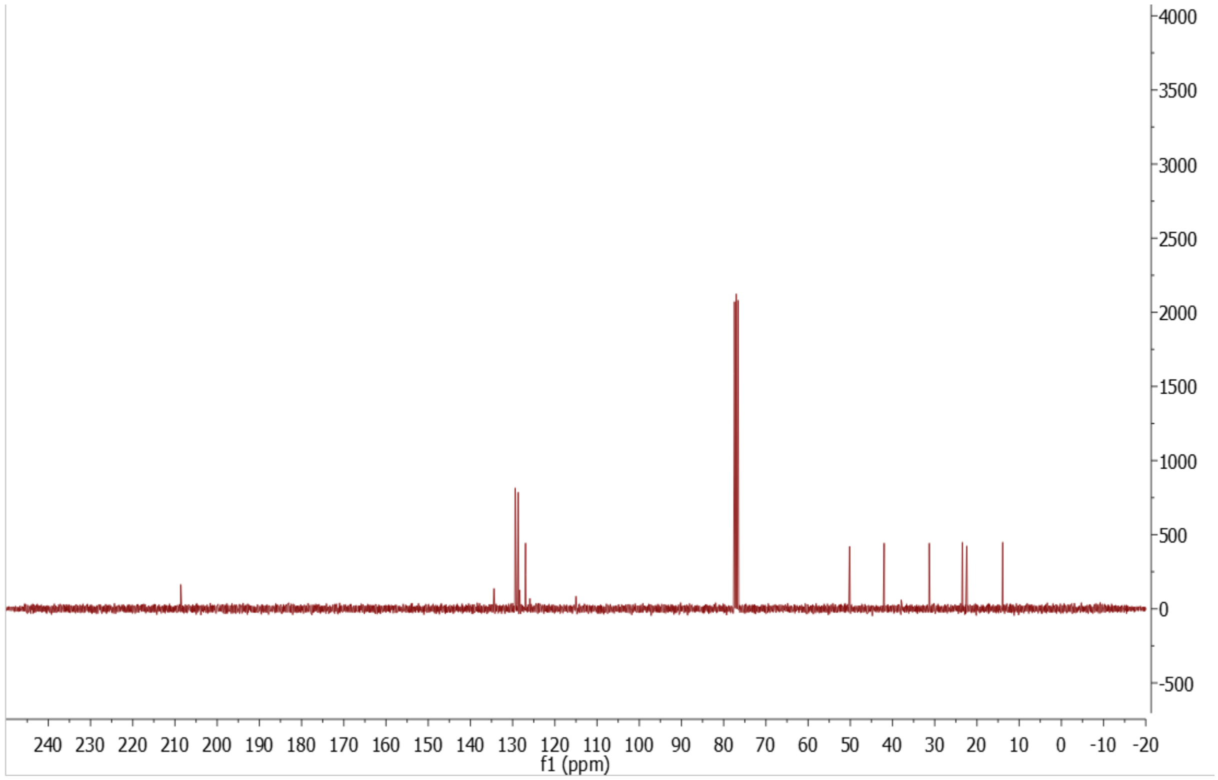

4000
3500
3000
2500
2000
1500
1000
500
0
-500
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



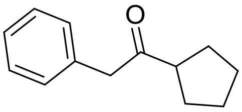
3u



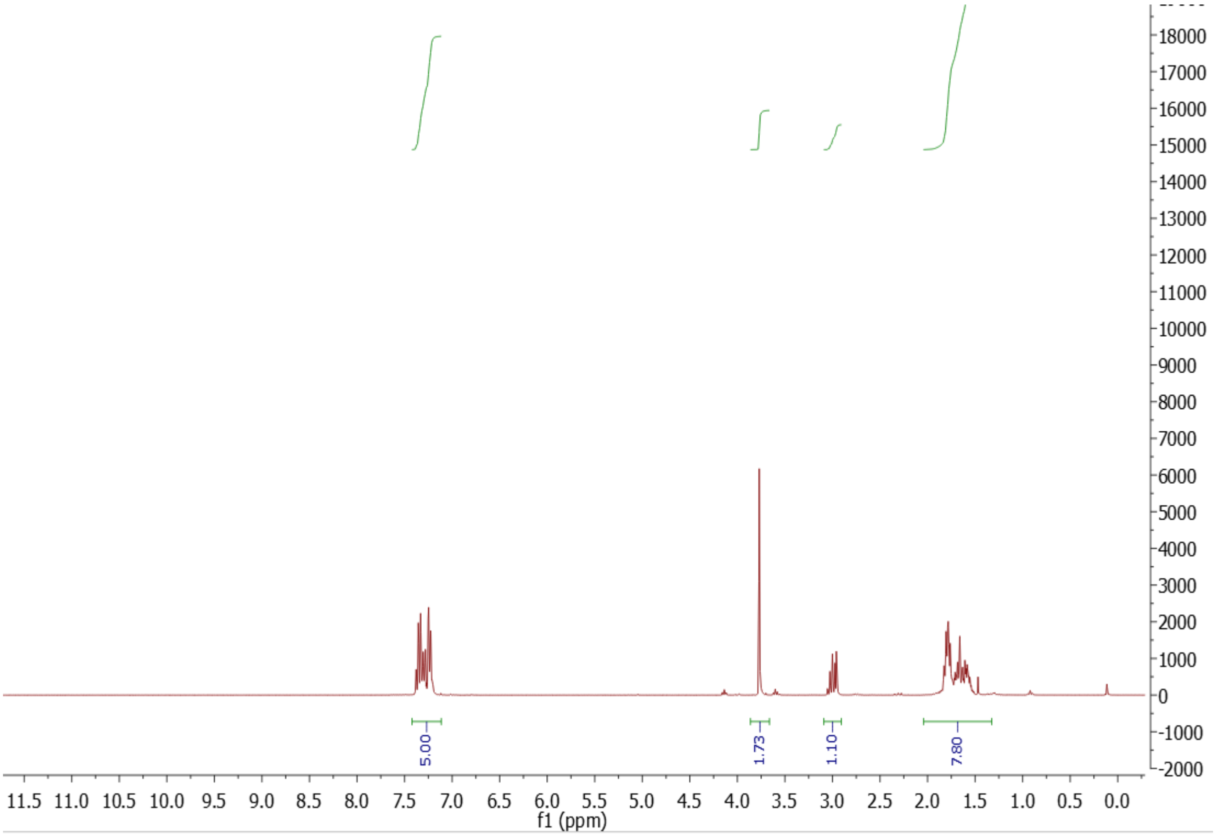
4500
4000
3500
3000
2500
2000
1500
1000
500
0
6.15
2.00
2.04
2.64
4.20
3.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

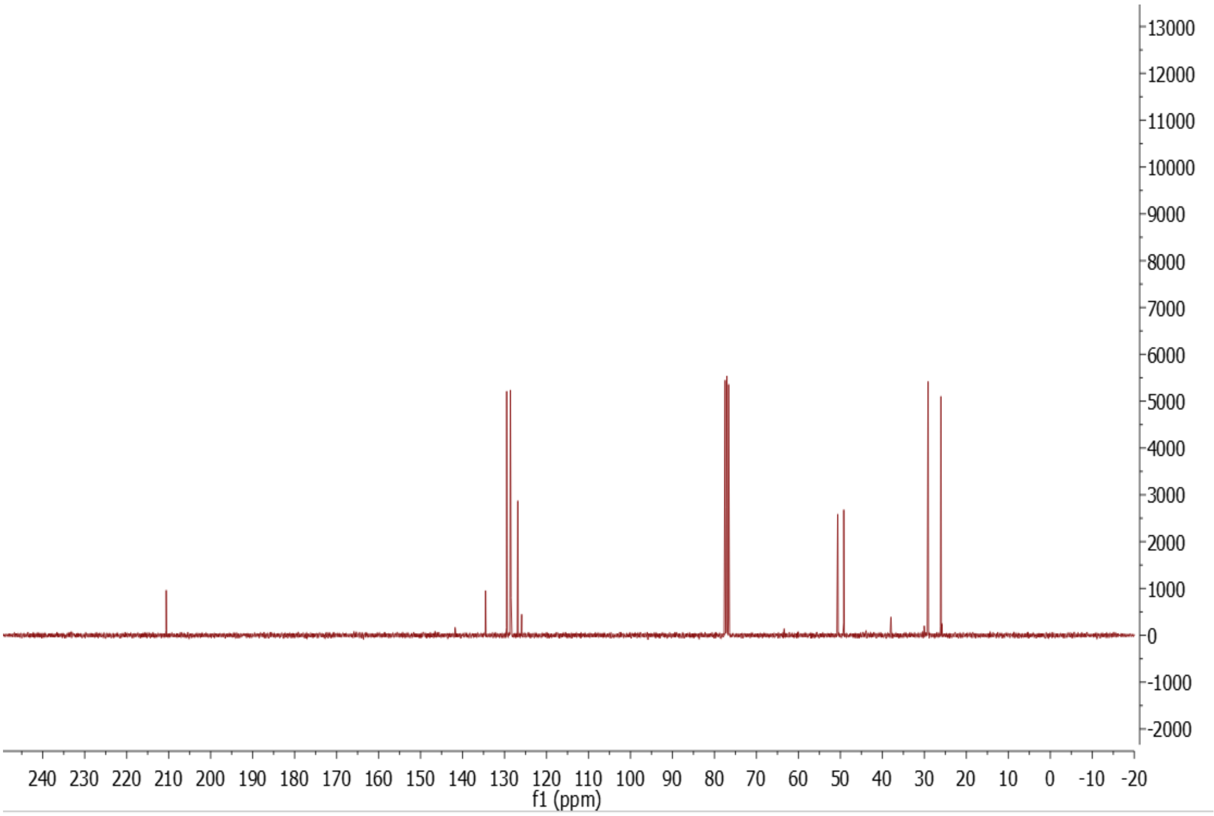


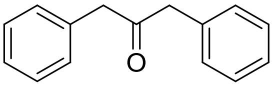
4000
3500
3000
2500
2000
1500
1000
500
0
-500
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



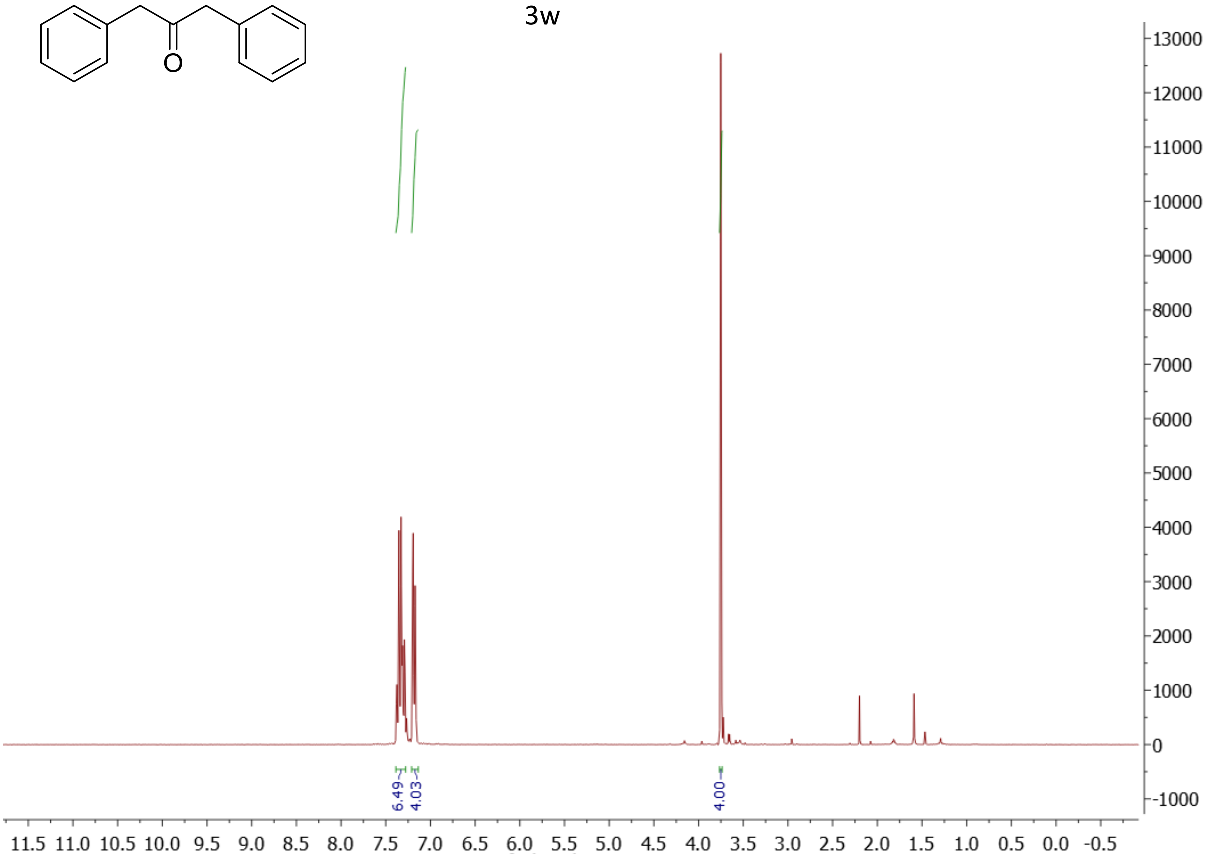
3v

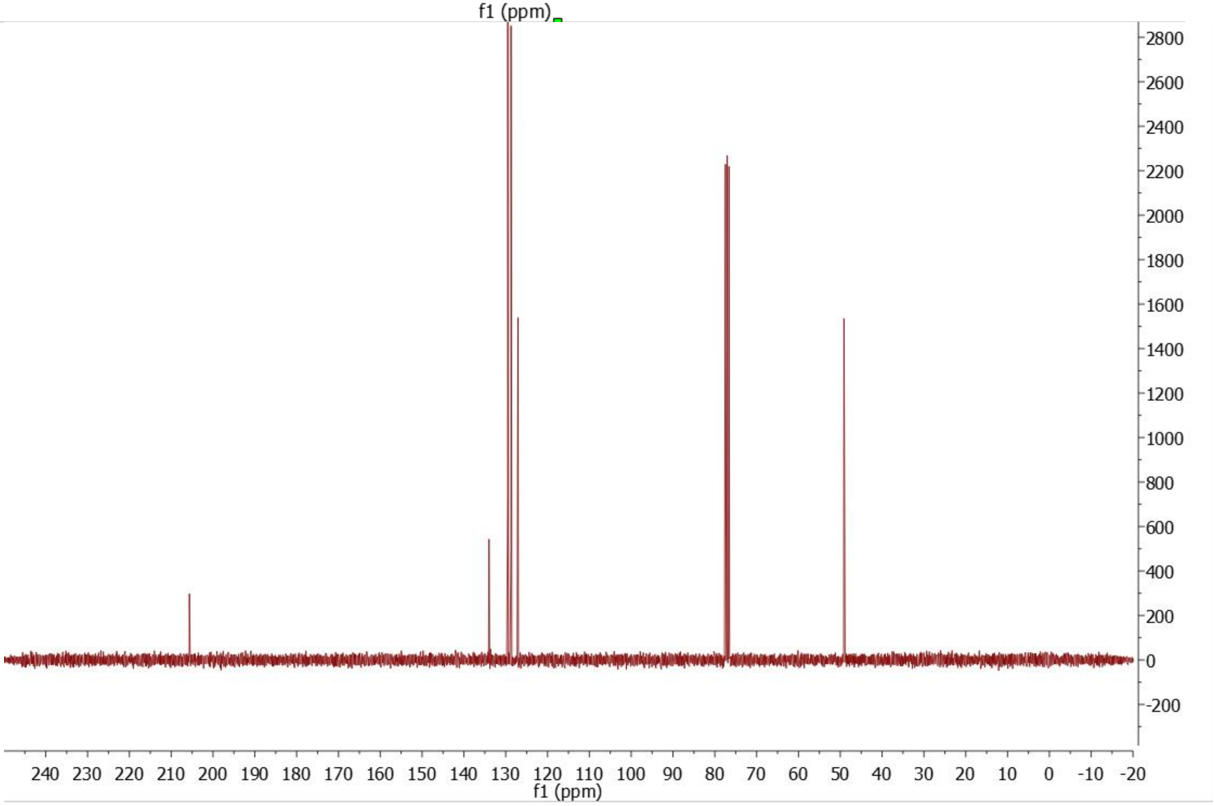

5.00
1.73
1.10
7.80
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000 -2000

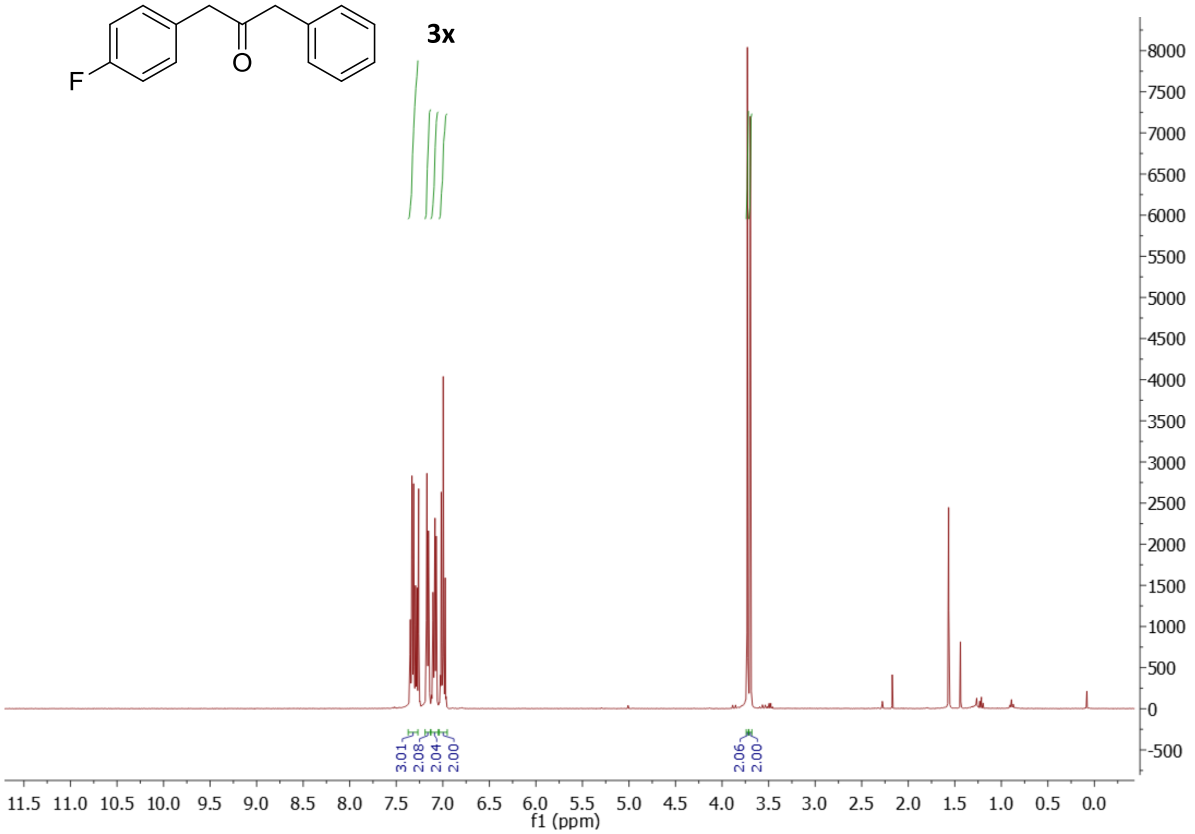

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000 -2000


O

3w

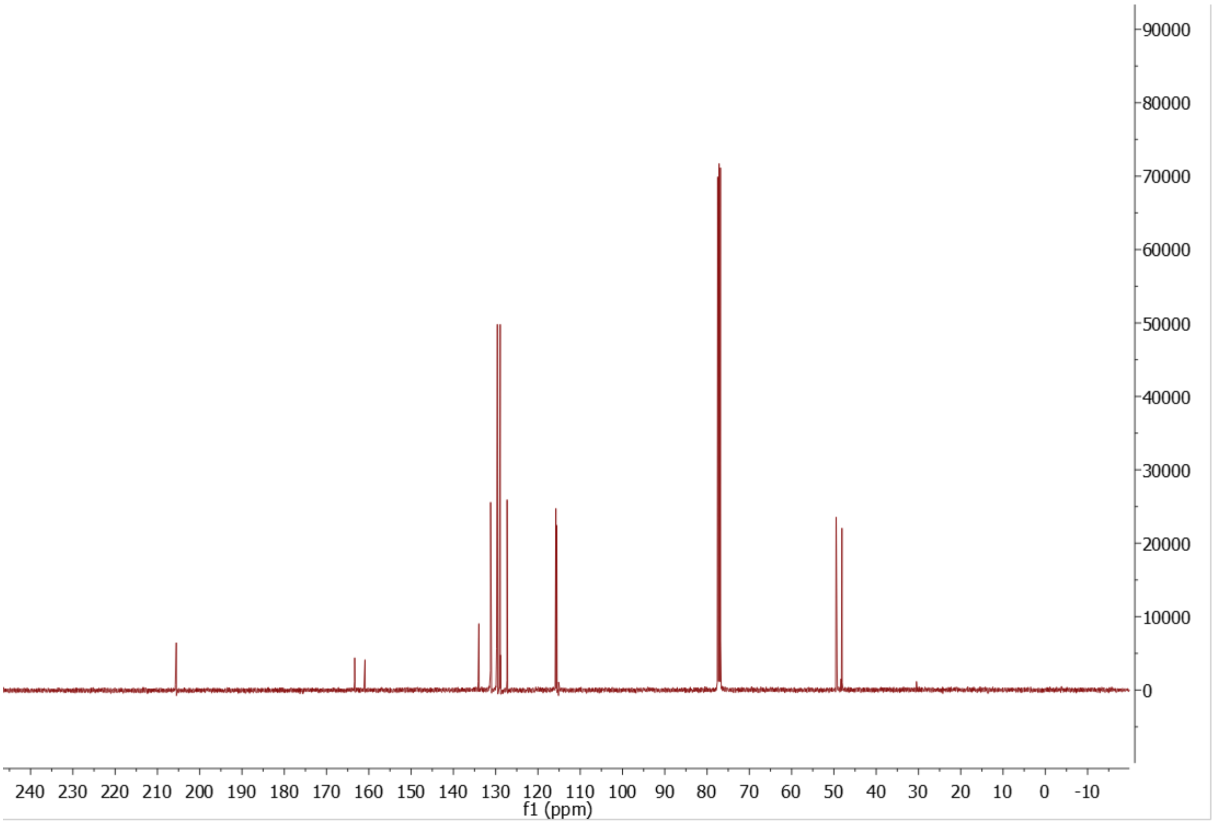

13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
6.49
4.03
4.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

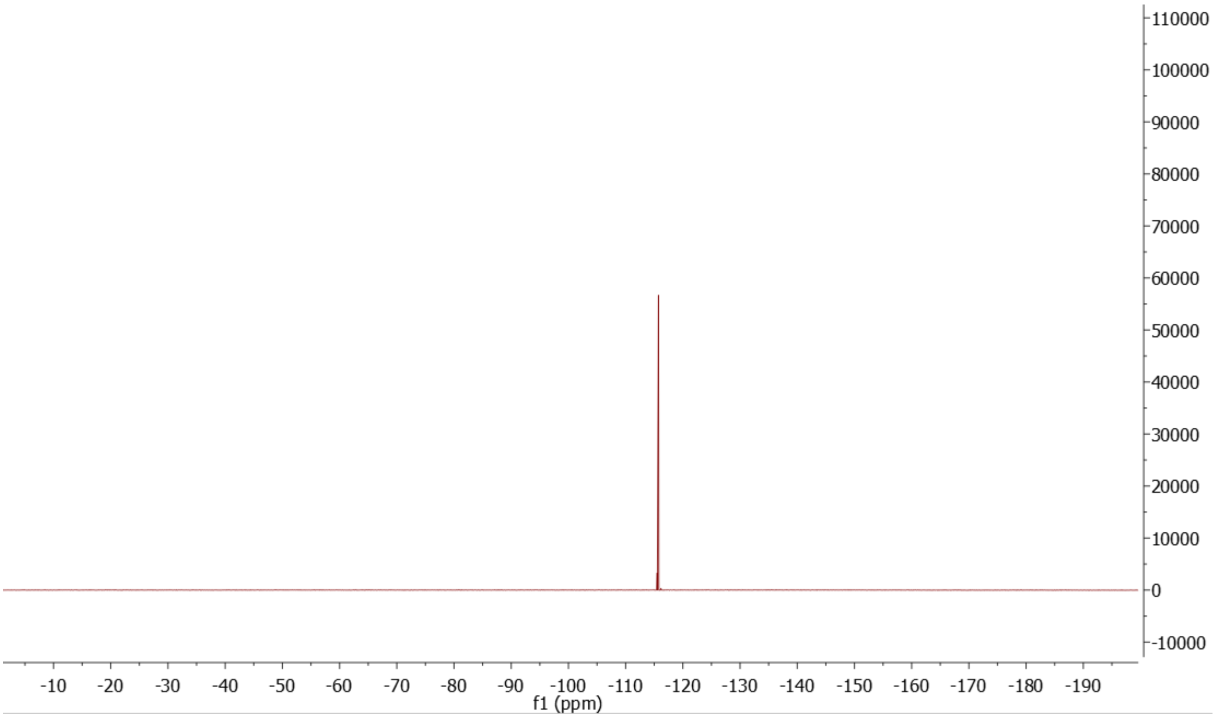


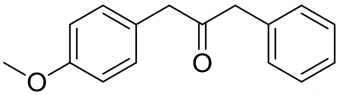
3x

3.01
2.08
2.04
2.00
2.06
2.00
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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
f1 (ppm)

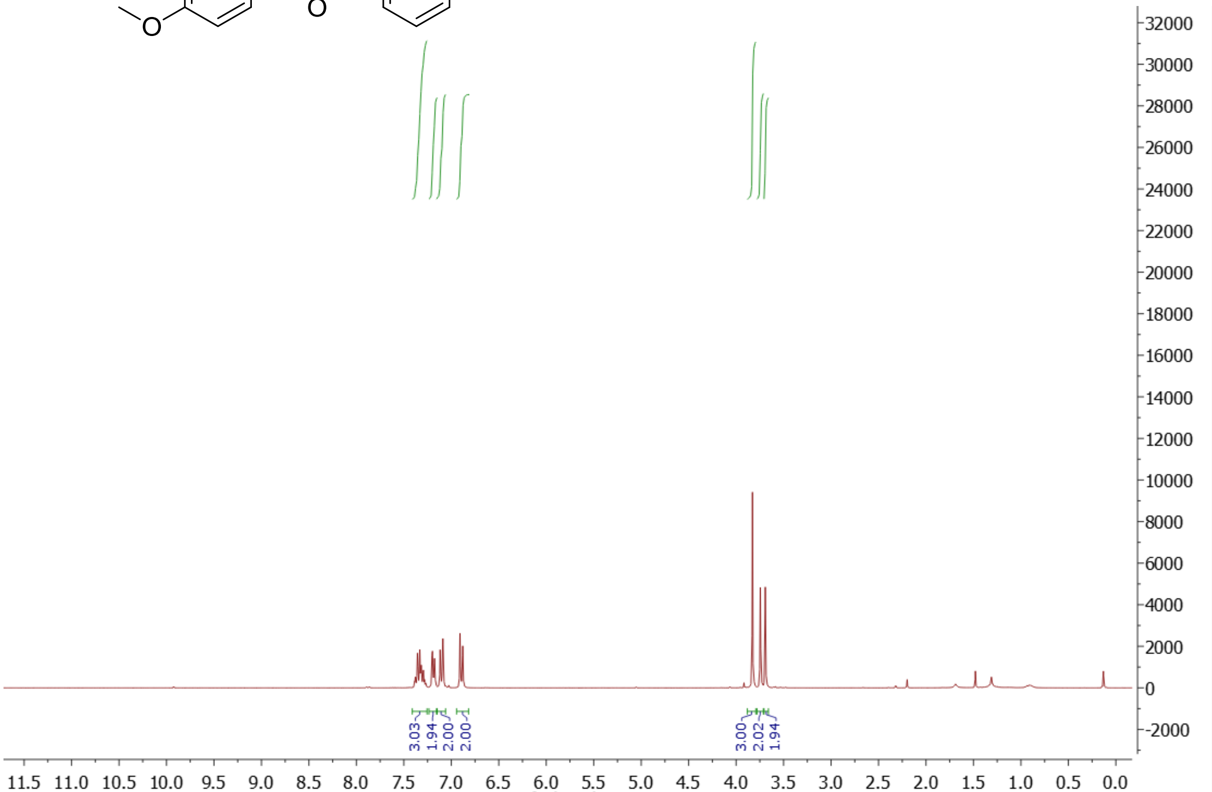


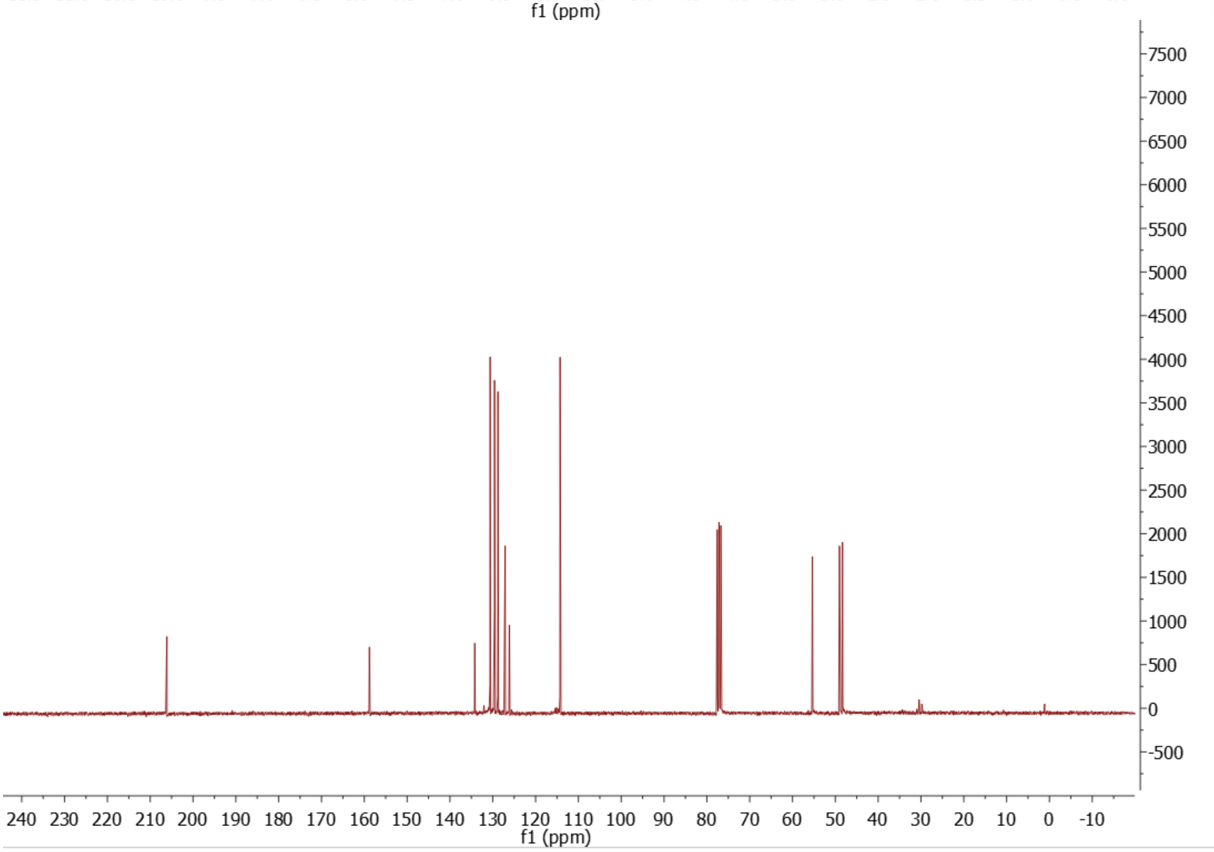
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

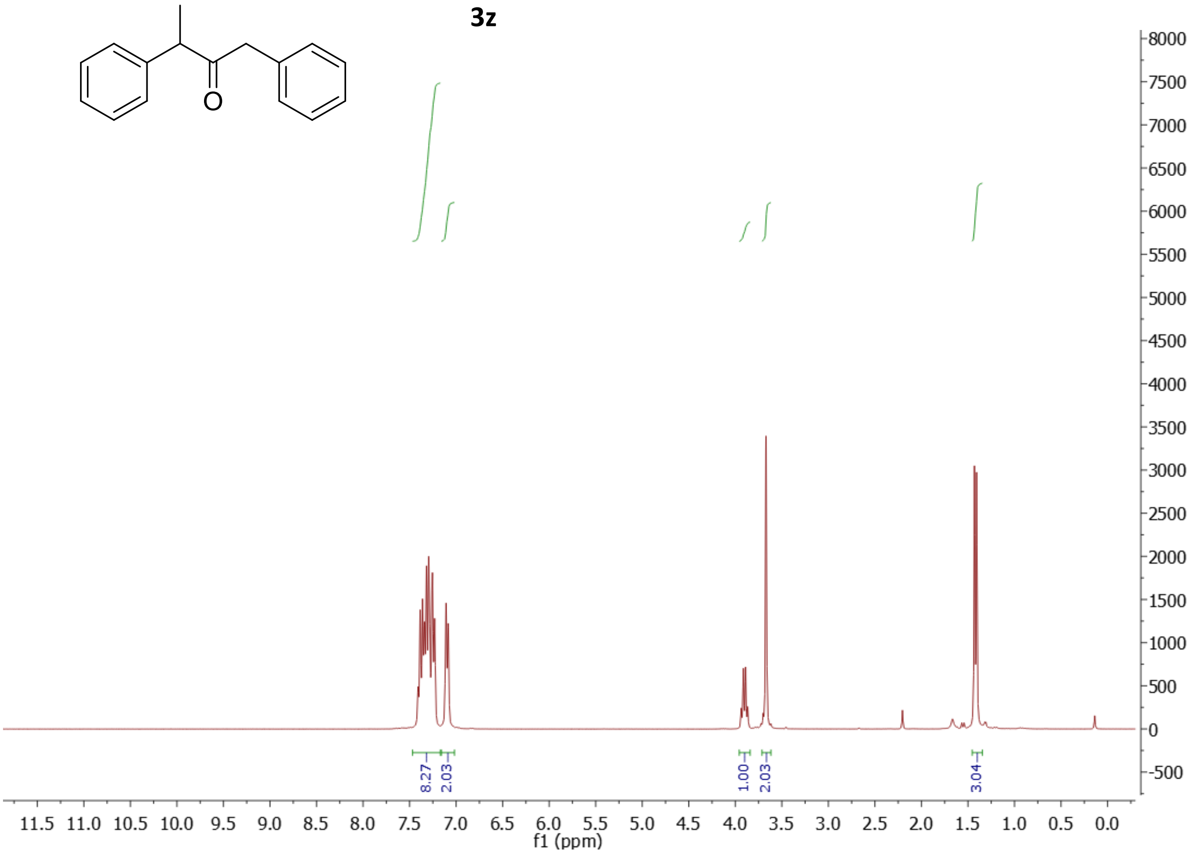

O
O

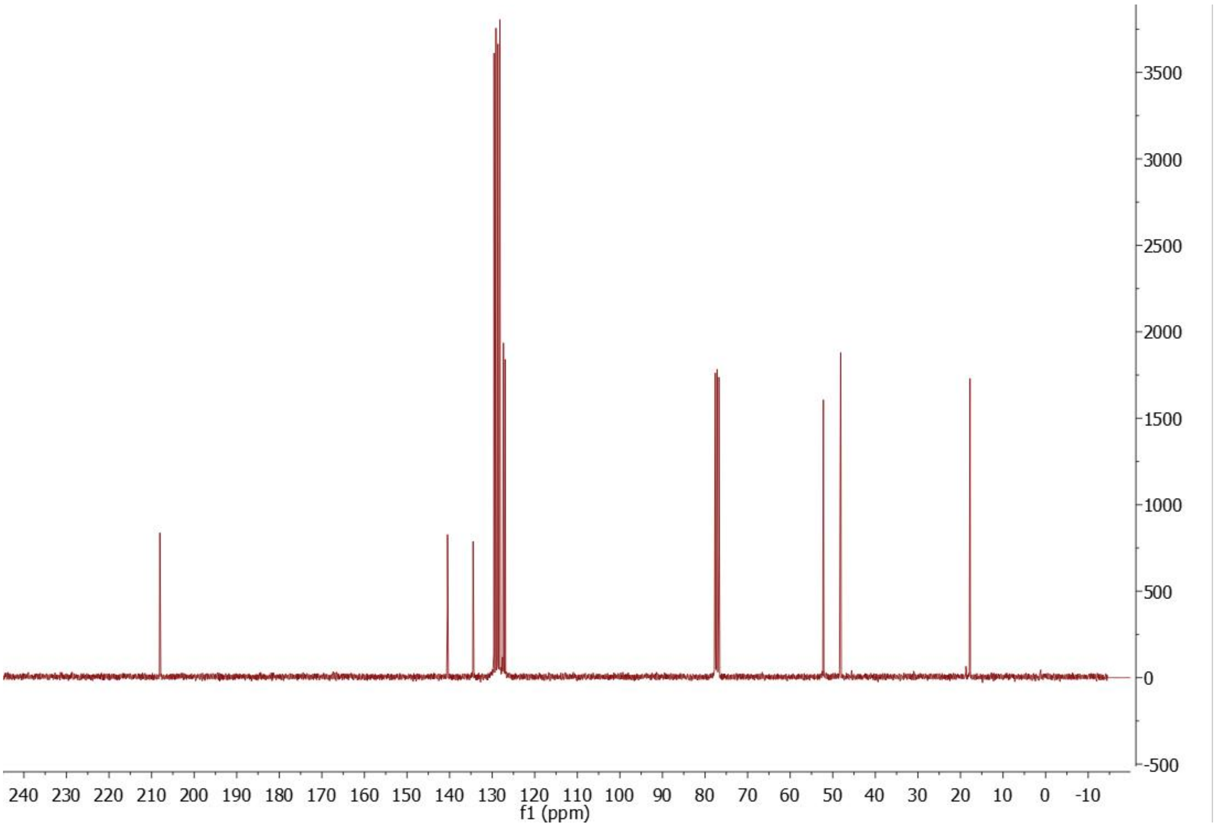
3y


32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
3.03
1.94
2.00
2.00
3.00
2.02
1.94
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
f1 (ppm)

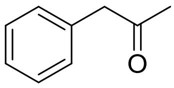

7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

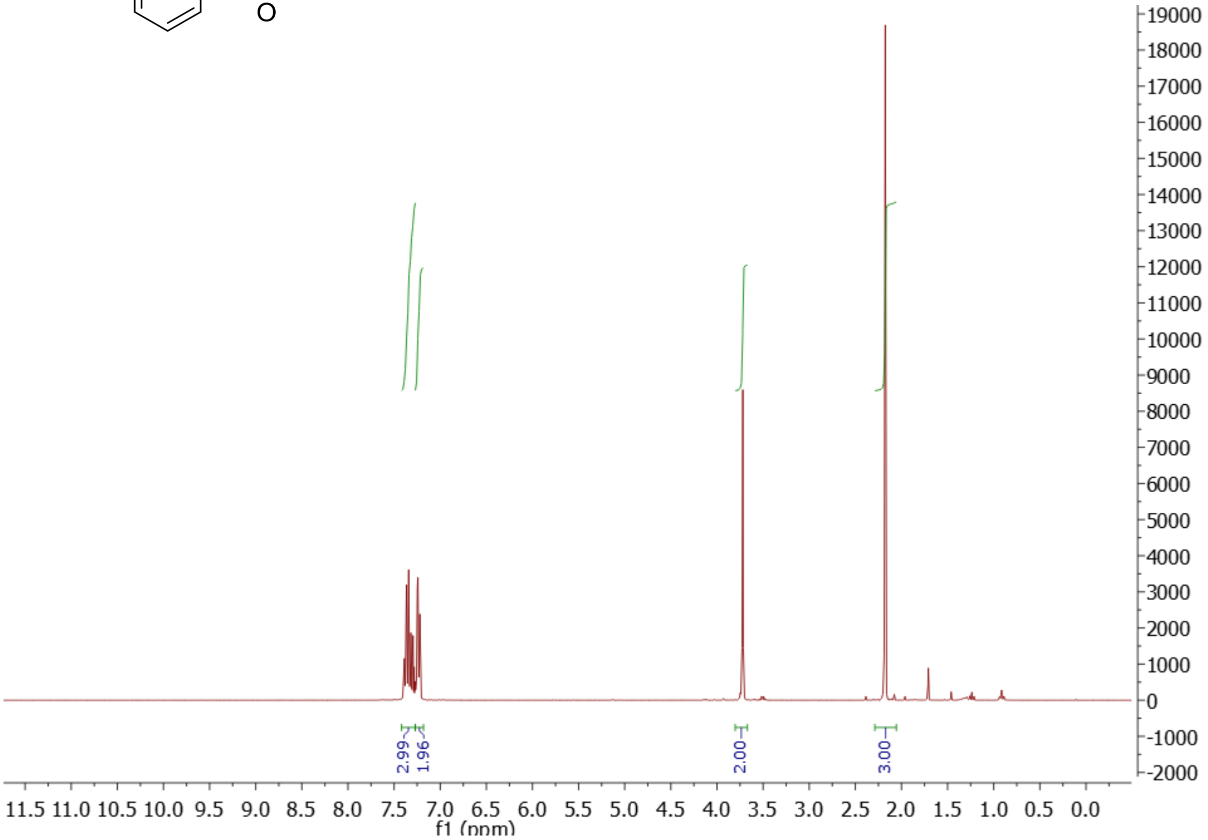
3z


O
8.27
2.03
1.00
2.03
3.04
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
f1 (ppm)
8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
3500 3000 2500 2000 1500 1000 500 0 -500

3za


O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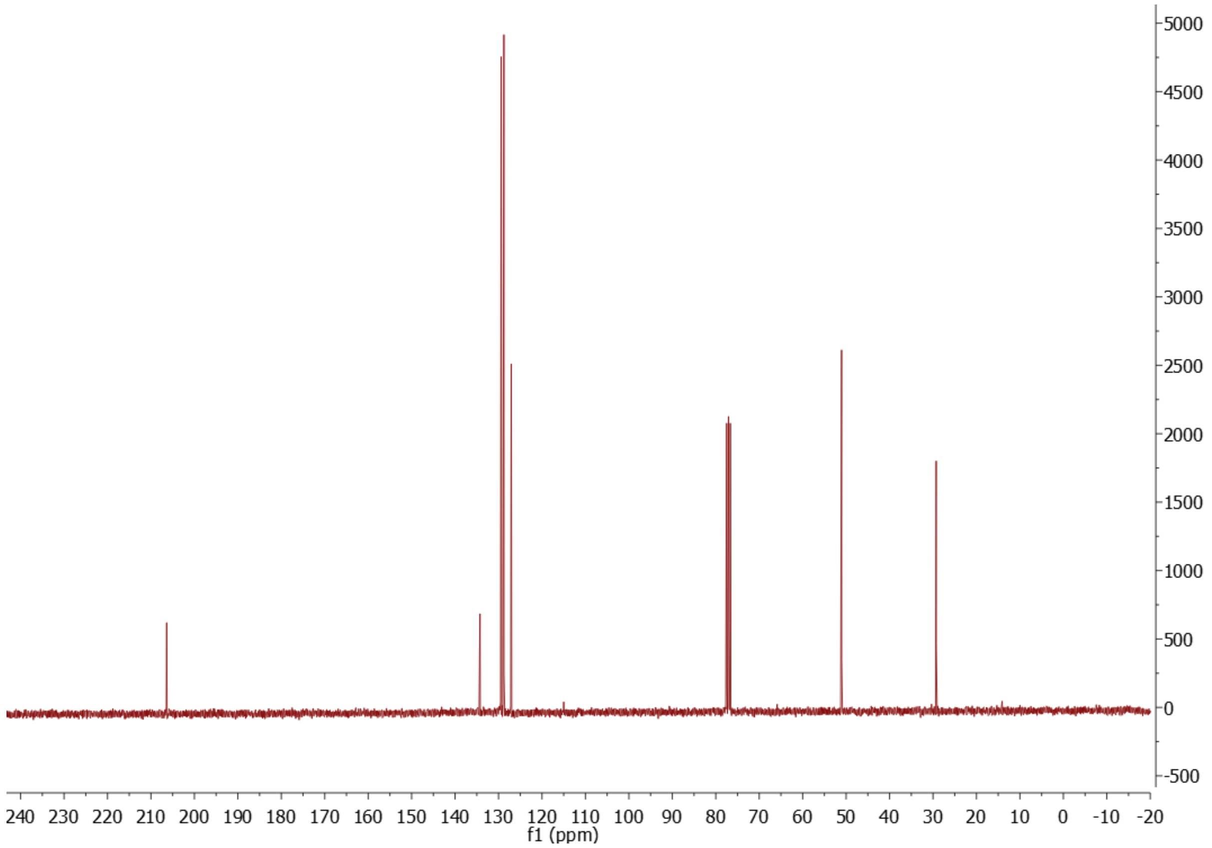
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
2.99
1.96
2.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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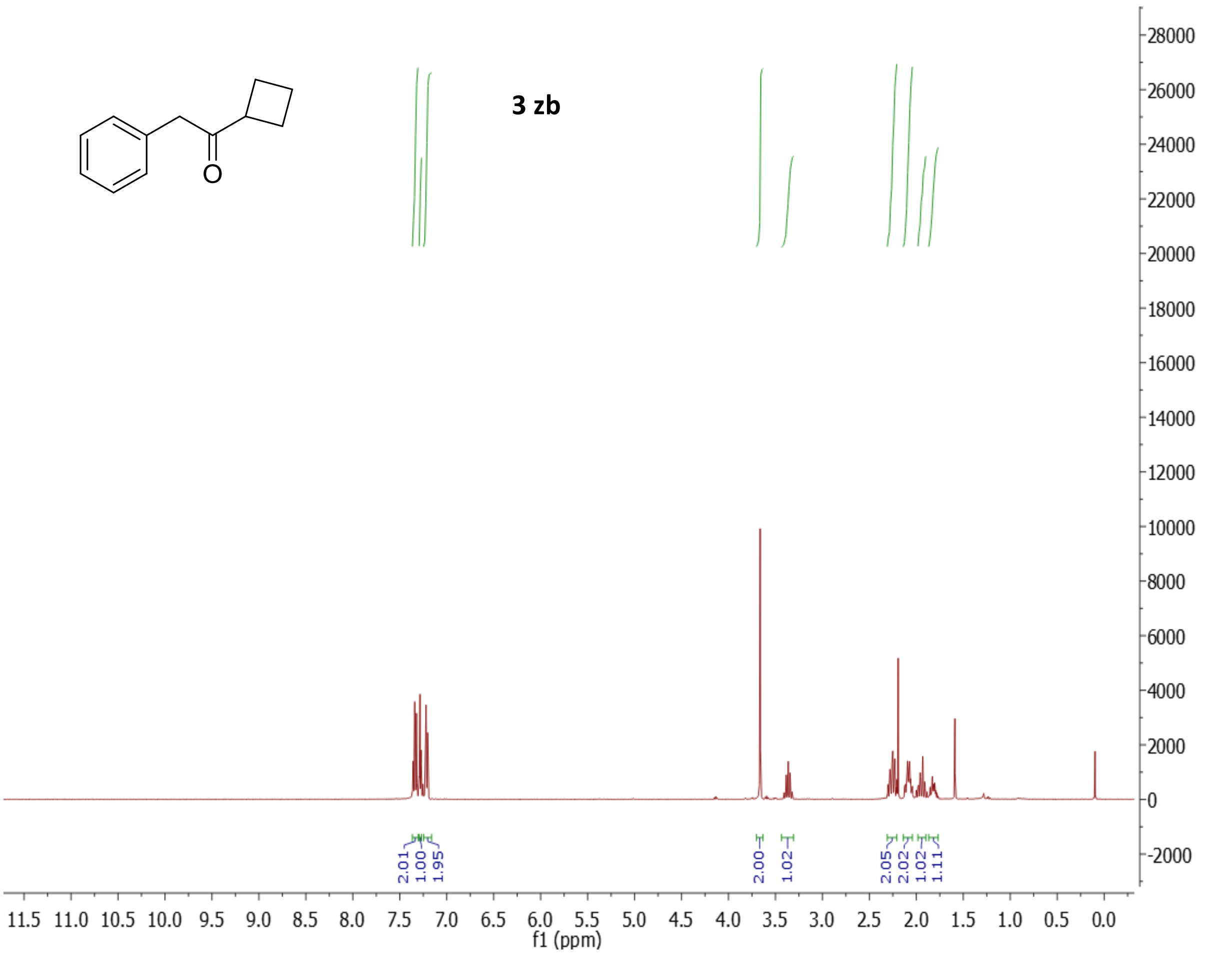
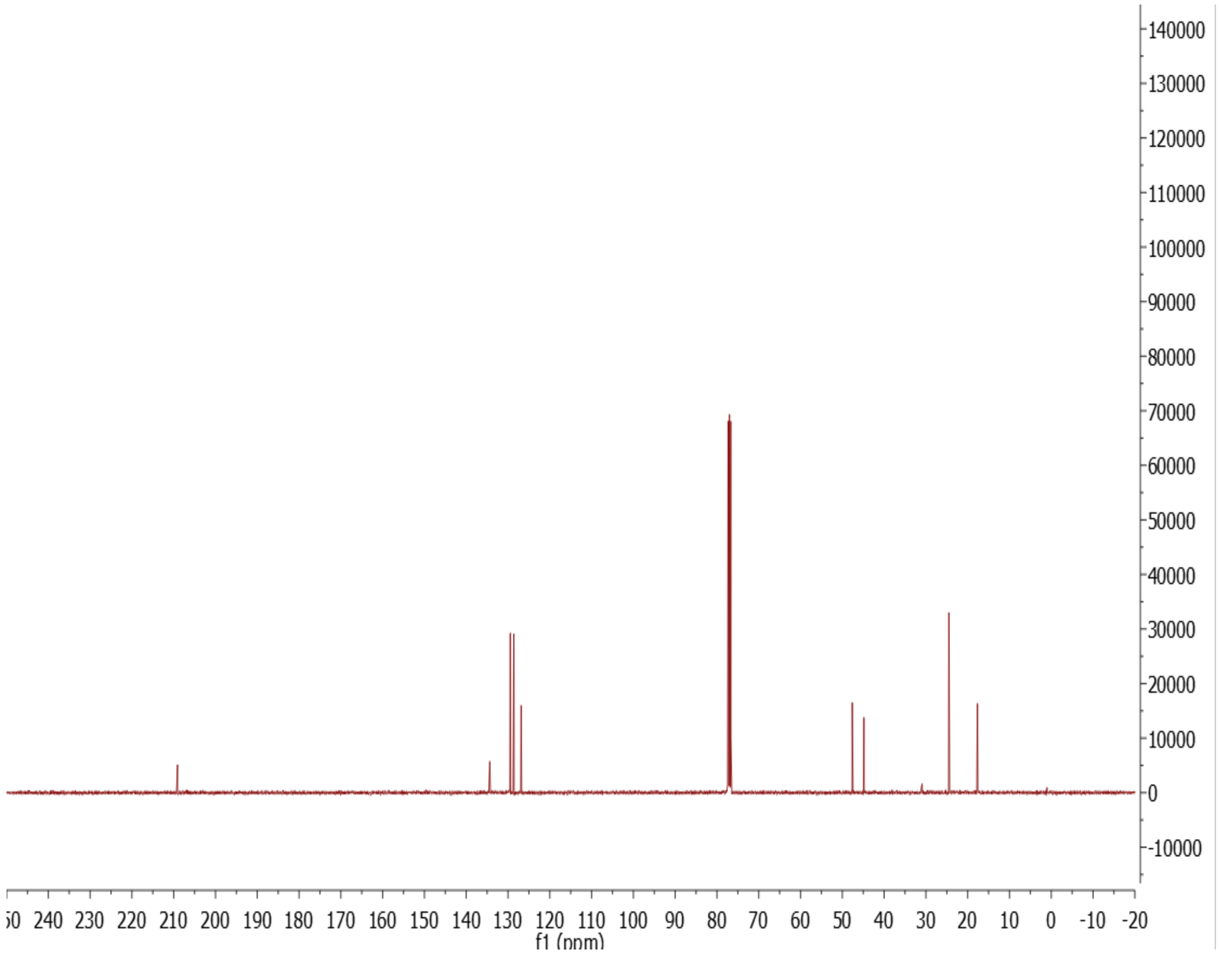
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

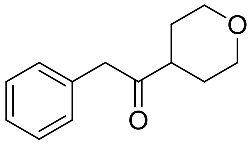


3 zb

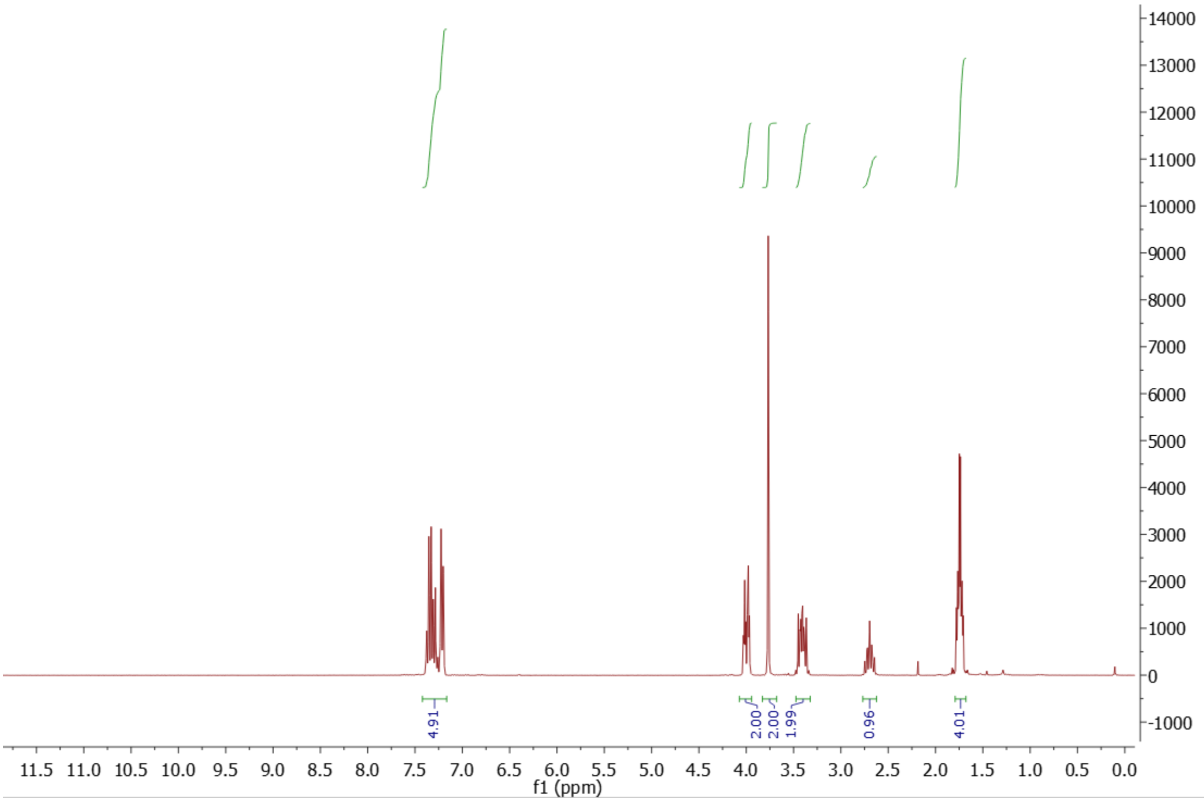
2.01
1.00
1.95
2.00
1.02
2.05
2.02
1.02
1.11
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
O



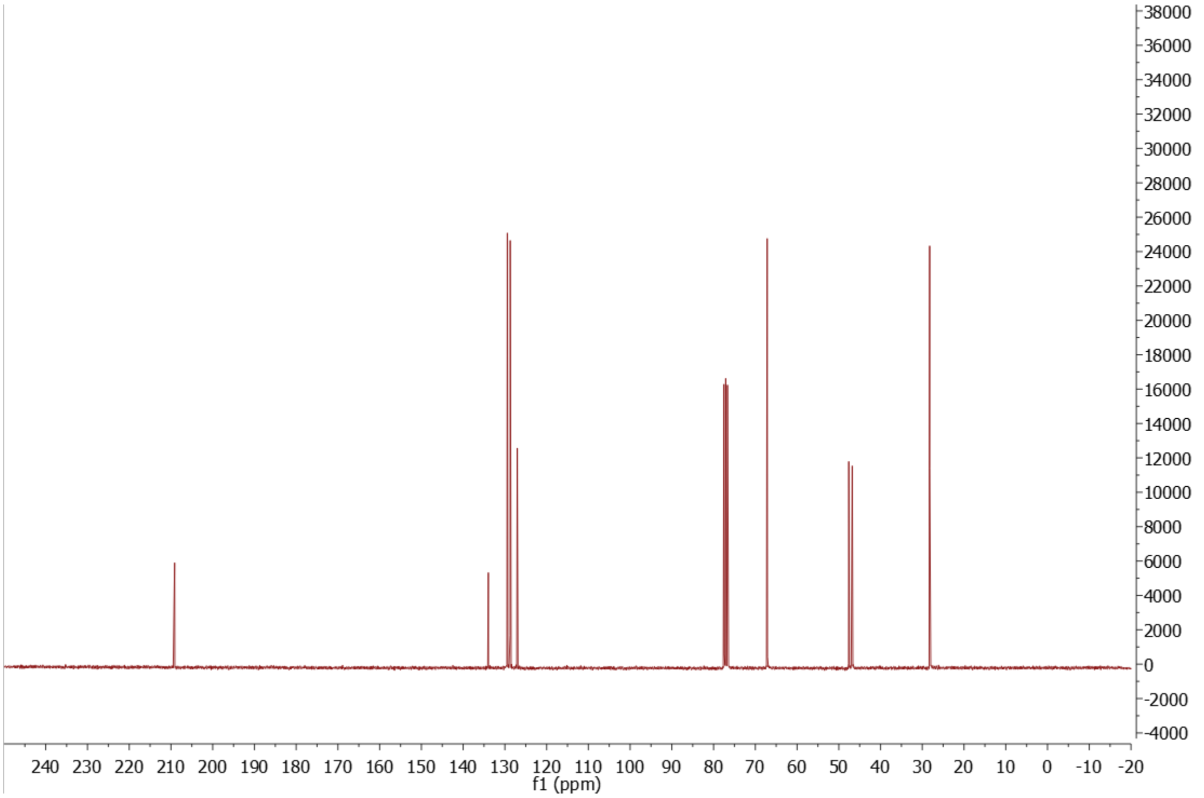
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000



3 zc



14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
4.91
2.00
2.00
1.99
0.96
4.01
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
f1 (ppm)



38000
36000
34000
32000
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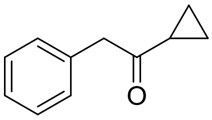
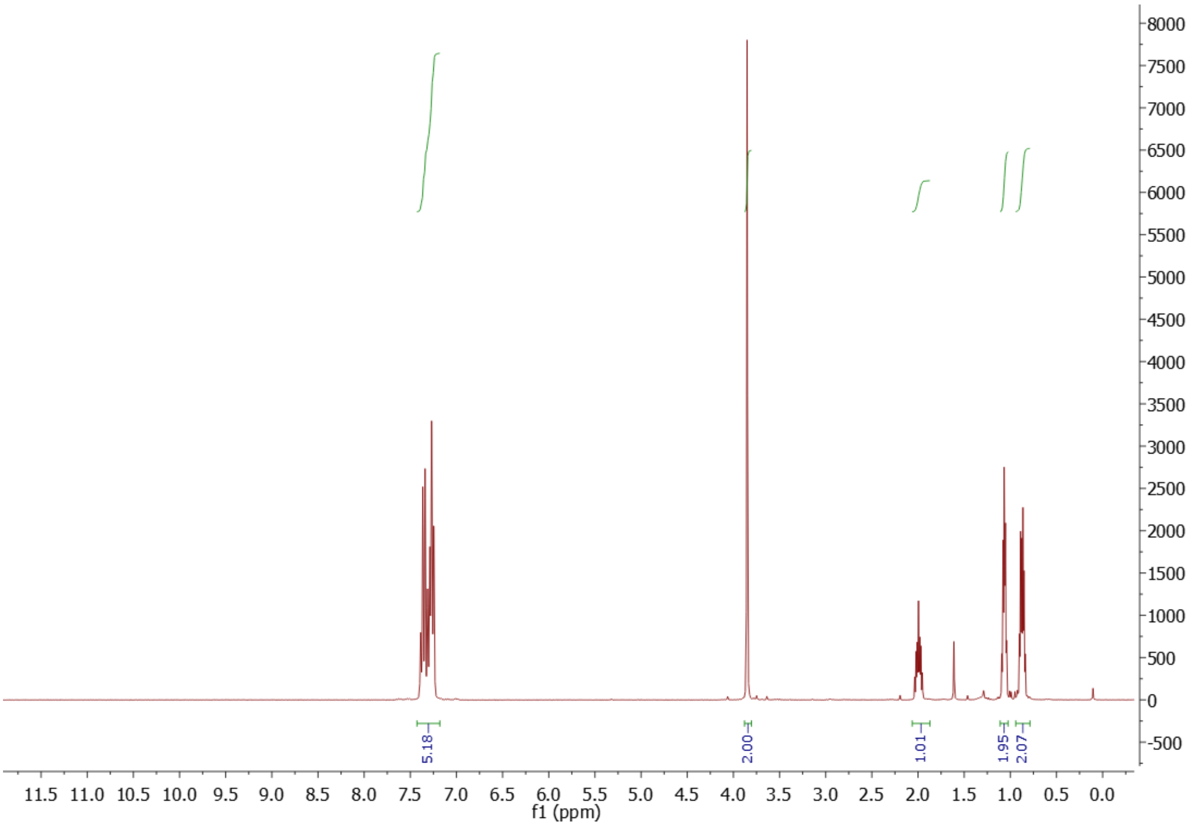
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



3 zd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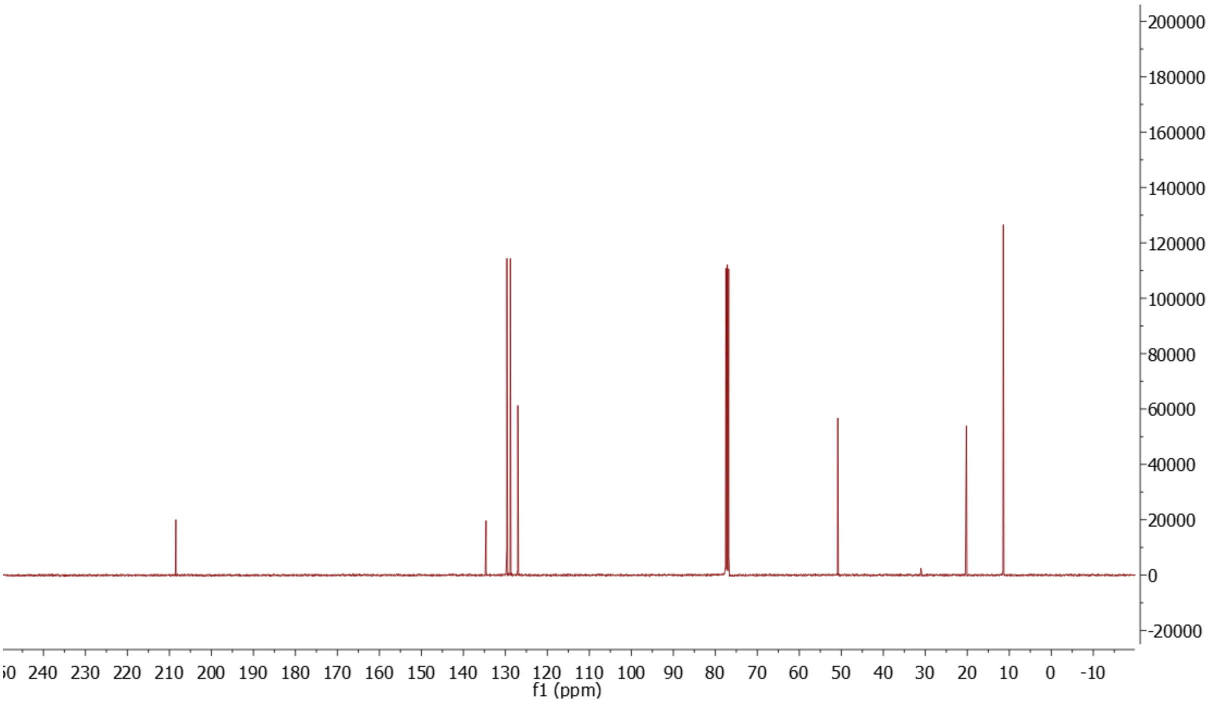
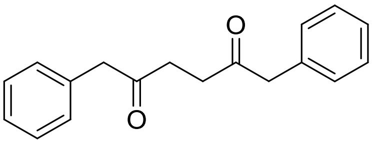
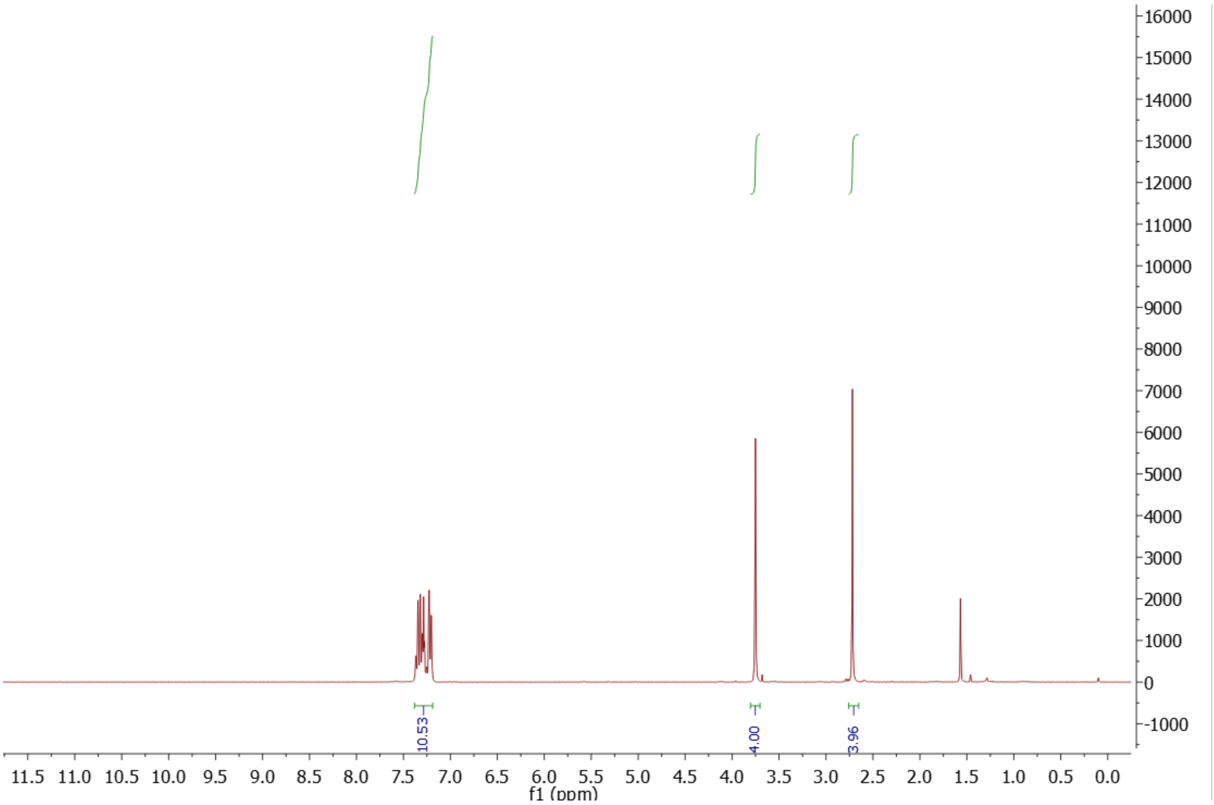
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
5.18
2.00
1.01
1.95
2.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

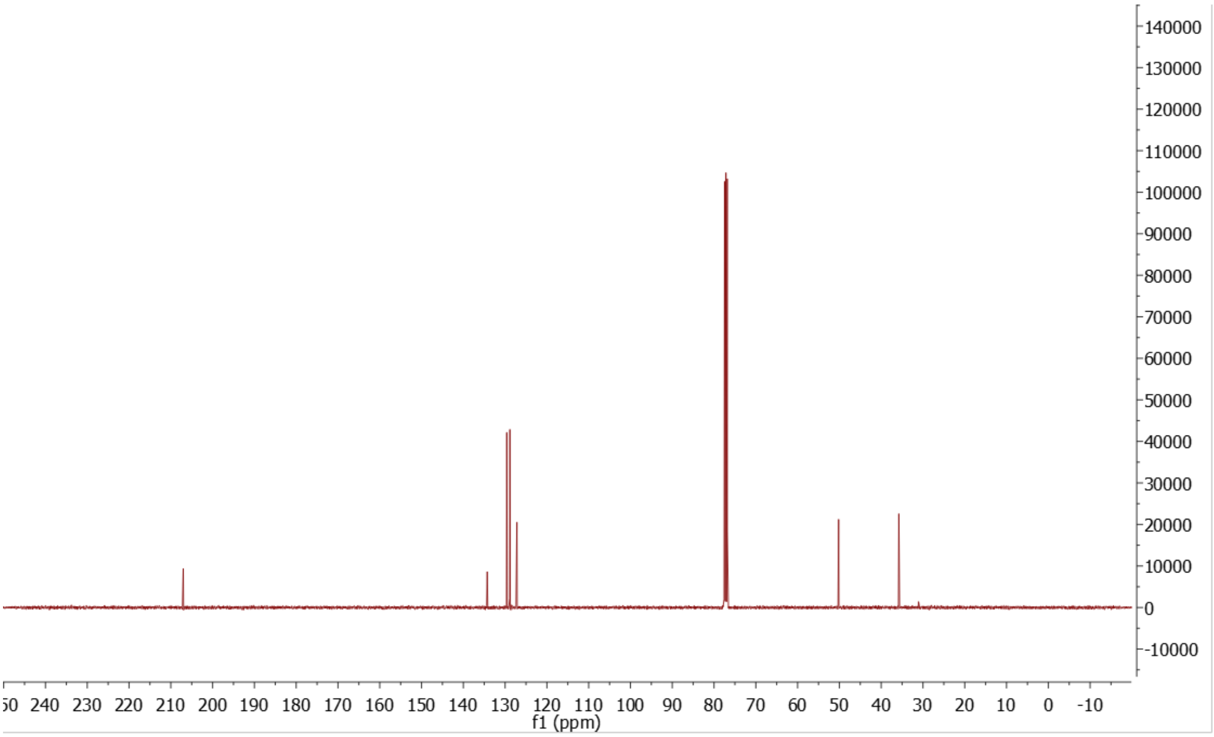

200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3ze



16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.53
4.00
3.96
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
f1 (ppm)



140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)