Phenol Derivatives as Coupling Partners with Alkylsilicates in Photoredox/Nickel Dual Catalysis

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Supporting Information

Key to Abbreviated Terms:

bpy: 2,2'-bipyridyl
CFL: Compact fluorescent light
LED: Light-emitting diode
dtbbpy: 4,4'-di-*tert*-butyl-2,2'-dipyridyl

General Considerations

All chemical transformations requiring inert atmospheric conditions utilized Schlenk line techniques with a 5-port dual-bank manifold. Argon was used to provide such an atmosphere. NMR Spectra (^{1}H, ^{13}C $\{^{1}H\}$, ^{19}F) were performed at 298 K. ^{1}H NMR spectra obtained in $CDCl_3$ were referenced to residual non-deuterated chloroform (δ 7.26) in the deuterated solvent. ^{13}C $\{^{1}H\}$ NMR spectra obtained in $CDCl_3$ were referenced to chloroform (δ 77.2). Reactions were monitored by GC/MS, HPLC, ^{1}H NMR, and/or by TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluant and visualized using permanganate stain and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 μm). Flash chromatography was accomplished using an automated system (visualizing at 254 nm, monitoring at 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). Solvents were purified either by distillation over sodium or CaH_2 or by use of drying cartridges through a solvent delivery system. Irradiation of reaction vessels was accomplished either using standard 26 W CFLs or LEDs (blue or white). The choice of light source did not appear to have any effect on reaction success. A fan was employed to ensure reactions remained at or near rt when using either CFLs or LEDs.

Chemicals:

Deuterated NMR solvents, $MgSO_4$, CH_2Cl_2, pentane, hexanes, and Et_2O were used as purchased. Et_3N and *i*-Pr_2NH were purchased from commercial suppliers and distilled from CaH_2 prior to use. THF was purchased from commercial suppliers and dried *via* a solvent delivery system. Catechol was purchased and recrystallized from refluxing hexanes or heptanes. DMF (99.8%, extra dry) was stored over 4 Å molecular sieves. $NiCl_2$•dme (min. 97%) and $RuCl_3$•$3H_2O$ were purchased commercially. Phenol derivatives were either purchased from commercial suppliers or prepared in-house. The aryl triflates **2a**, **2b**, **2c**, **2d**, and **2e** were purchased from commercial suppliers and used without further purification. The following aryl triflates, -tosylates, and -mesylates were prepared according to literature procedures: 4-cyanophenyl

trifluoromethanesulfonate (**2f**),[1] 4-(trifluoromethyl)phenyl trifluoromethanesulfonate (**2g**),[2] 3-(trifluoromethyl)phenyl trifluoromethanesulfonate (**2h**),[1] 4-fluorophenyl trifluoromethanesulfonate (**2n**),[2] 4-formylphenyl trifluoromethanesulfonate (**2o**),[3] 4-benzoylphenyl trifluoromethanesulfonate (**2p**),[4] 3-cyanophenyl trifluoromethanesulfonate (**2q**),[1] 3-fluorophenyl trifluoromethanesulfonate (**2r**),[5] 4-bromophenyl trifluoromethanesulfonate (**2s**),[6] 4-acetylphenyl 4-methylbenzenesulfonate (**2i**),[7] naphthalen-1-yl 4-methylbenzenesulfonate (**2j**),[6] 3-(trifluoromethyl)phenyl 4-methylbenzenesulfonate (**2k**),[8] 4-acetylphenyl methanesulfonate (**2l**),[6] naphthalen-1-yl methanesulfonate (**2m**).[6] $Ru(bpy)_3(PF_6)_2$ was prepared in-house by the procedure outlined in our previous reports.[9] Silicates were prepared from their corresponding alkyltrimethoxysilanes. Information (preparation protocols, characterization etc.) for all silicates can be found in our previous reports.[10]

[1] Lee, D-Y.; Hartwig, J. F. *Org. Lett*, **2005**, *7*, 1169.

[2] Mori, A.; Mizusaki, T.; Ikawa, T.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Chem. Eur. J.* **2007**, *13*, 1432.

[3] Maegawa, T.; Kitamura, Y.; Sako, S.; Udzo, T.; Sakurai, A.; Tanaka, A.; Kobayashi, Y.; Endo, K.; Bora, U.; Kurita, T.; Kozaki, A.; Monguchi, Y.; Sajiki, H. *Chem. Eur. J.* **2007**, *13*, 5937.

[4] Zhao, B.; Lu, X. *Org. Lett*. **2006**, *8*, 5987.

[5] Stang, P. J.; Anderson, A. G. *J. Org. Chem*. **1976**. *41*, 781.

[6] Chung, C. W. Y.; Toy, P. H. *Tetrahedron* **2005**, *61*, 709.

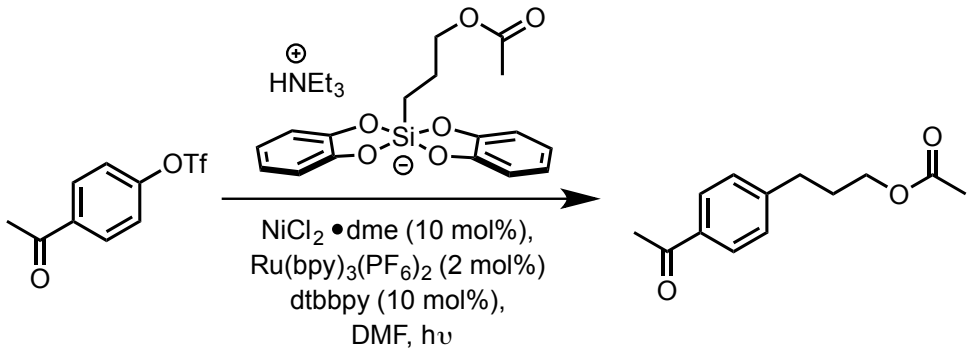
[7] Kuroda, J.; Inamoto, K.; Hiroya, K.; Doi, T. *Eur. J. Org. Chem*. **2009**, 2251.

[8] Munday, R. H.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc*. **2008**, *130*, 2754.

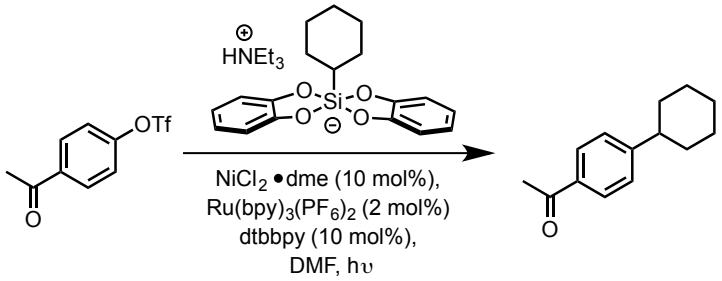
[9] Mabrouk, P.A.; Wrighton, M. S. *Inorg. Chem*. **1986**, *25*, 526.

[10] (a) Jouffroy, M.; Primer, D.; Molander, G. A. *J. Am. Chem. Soc.,* **2016**, 138, 475. (b) Patel, N. R., Kelly, C. B., Jouffroy, M., Molander, G. A. *Org Lett*. **2016**, 18, 764.

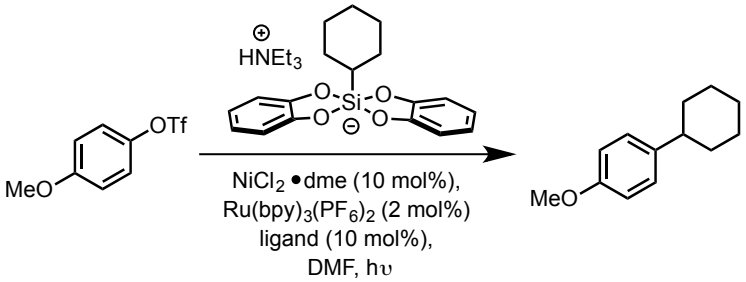
Reaction Optimization and Control Studies for Aryl Triflate Cross-Coupling



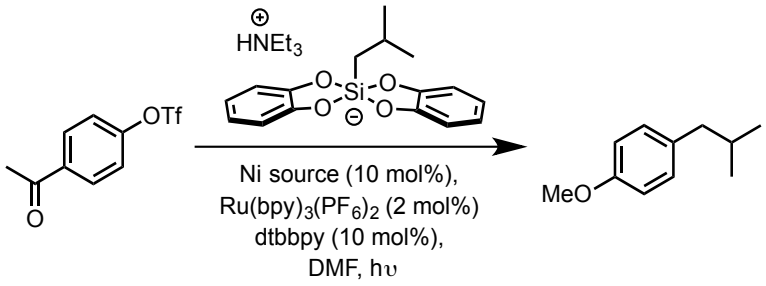
experiment #	conditions	conversion (determined by HPLC)
1	5 mol % $NiCl_2$·dme, 5 mol % dtbbpy 1.2 equiv alkylsilicate (not preforming Ni-ligand complex) (24 h)	84%
2	5 mol% $NiCl_2$·dme, 5 mol % dtbbpy 1.2 equiv alkylsilicate (preforming Ni-ligand complex) (24 h)	87%
3	10 mol % $NiCl_2$·dme, 10 mol % dtbbpy 1.2 equiv alkylsilicate (24 h)	95%
4	5 mol % $NiCl_2$·dme, 5 mol % dtbbpy 1.5 equiv alkylsilicate (24 h)	87%
5	10 mol % $NiCl_2$·dme, 10 mol % dtbbpy 1.5 equiv alkylsilicate (24 h)	98%
6	10 mol % $NiCl_2$·dme, 10 mol % dtbbpy 1.5 equiv alkylsilicate (36 h)	100%



experiment #	conditions	yield (determined by HPLC)
1	no light	0%
2	no Ru photocatalyst	10%
3	no $NiCl_2$·dme	0%

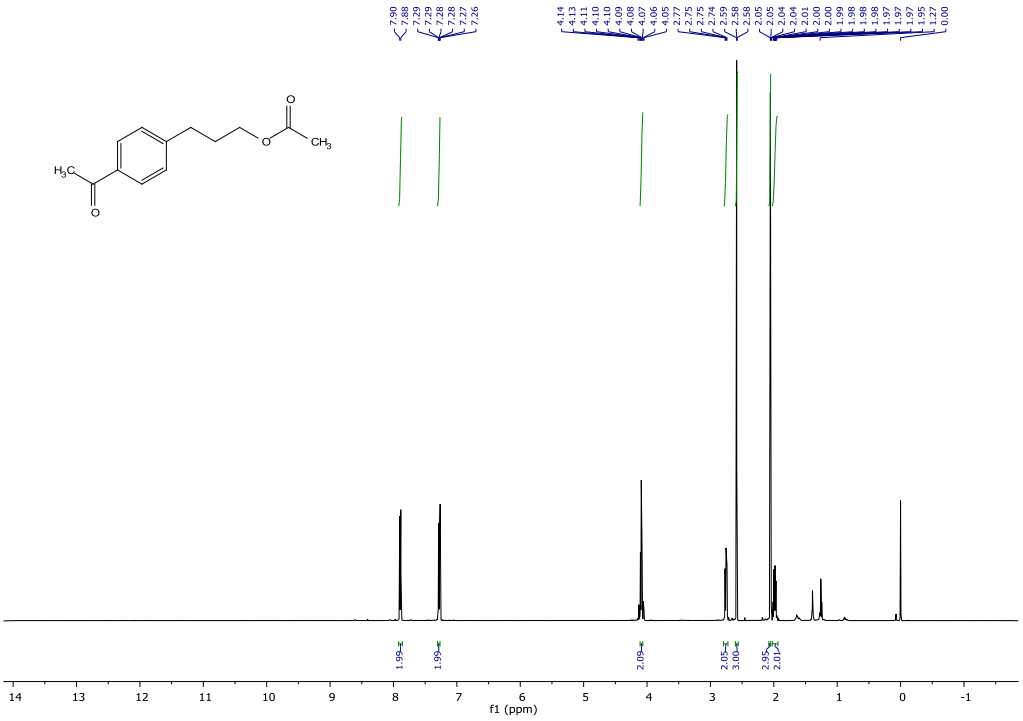


experiment #	ligand	yield (determined by HPLC)
1	2,2′:6′,2″-terpyridine	0%
2	2,2’-bis(2-oxazoline)	0%
3	neocuproine	0%

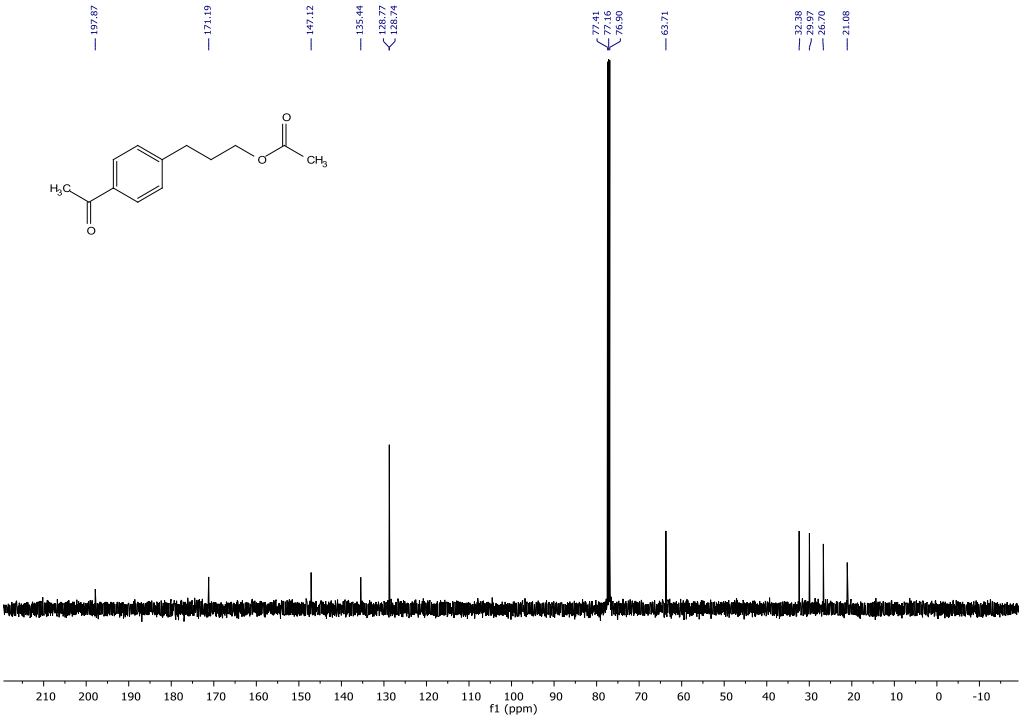


experiment #	Ni source	yield
1	$Ni(COD)_2$	60% (isolated yield)
2	$Ni(OTf)_2$	0% (determined by HPLC)

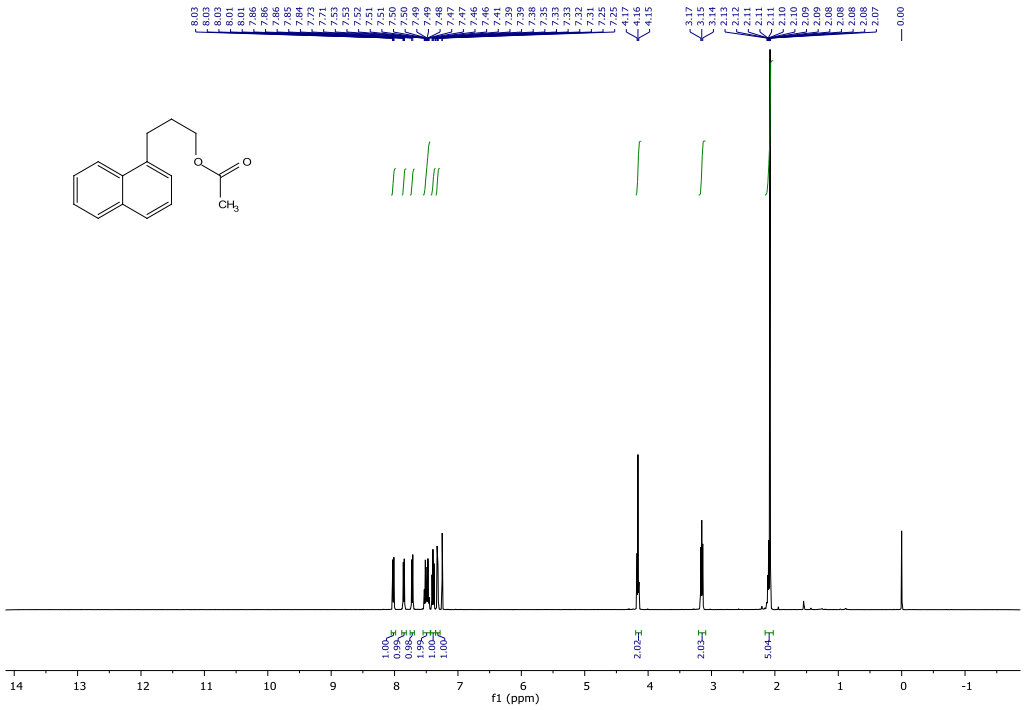
^{1}H, ^{13}C, and ^{19}F NMR Spectra of Synthesized Compounds



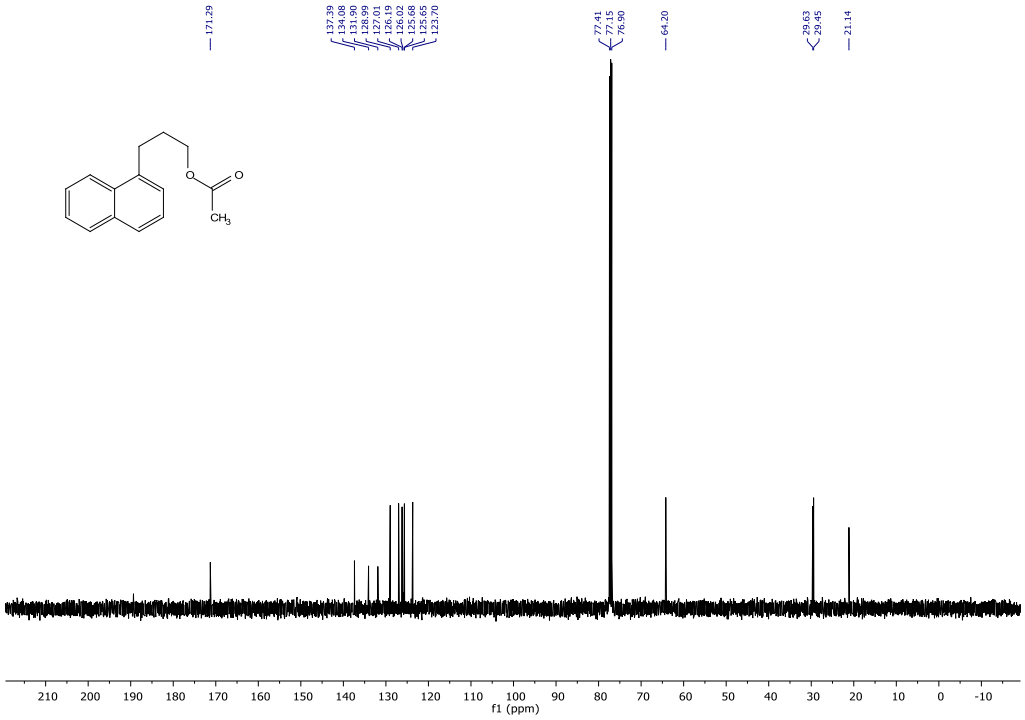
^{1}H NMR spectrum of 3-(4-acetylphenyl)propyl acetate (**3a**)



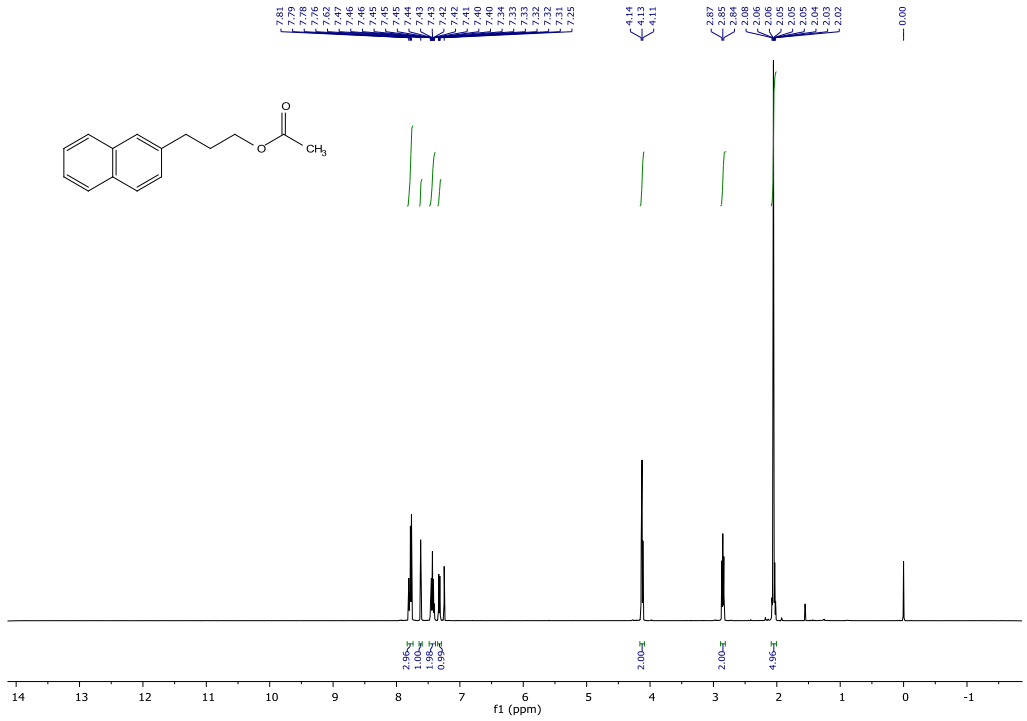
^{13}C {^{1}H} NMR spectrum of 3-(4-acetylphenyl)propyl acetate (**3a**)



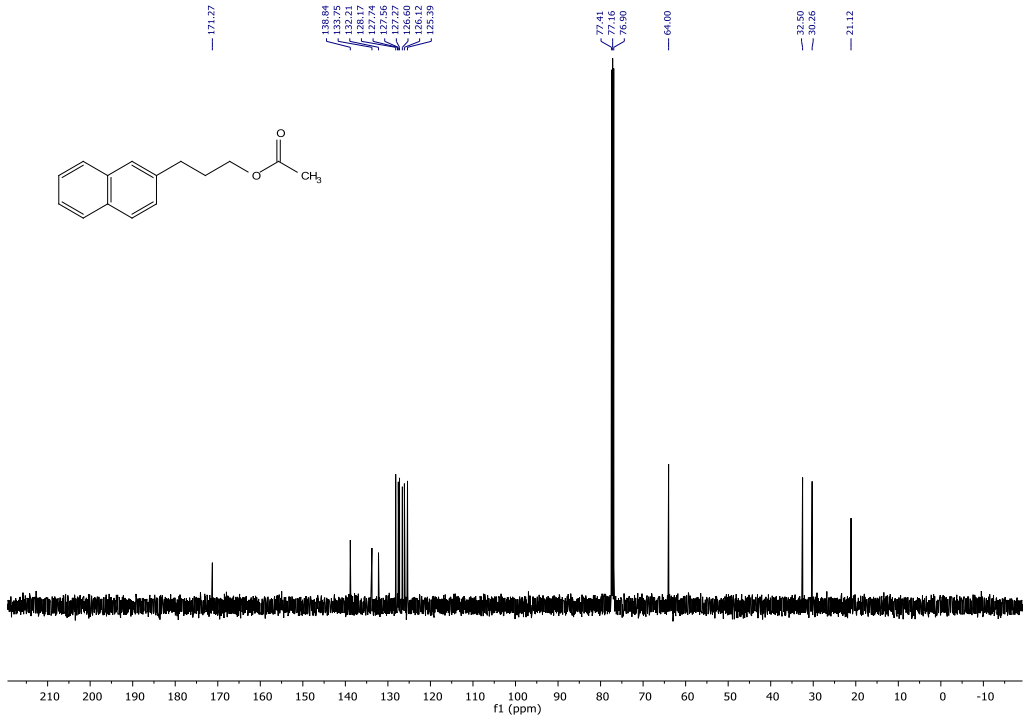
^{1}H NMR spectrum of 3-(naphthalene-1-yl)propyl acetate (**3c**)



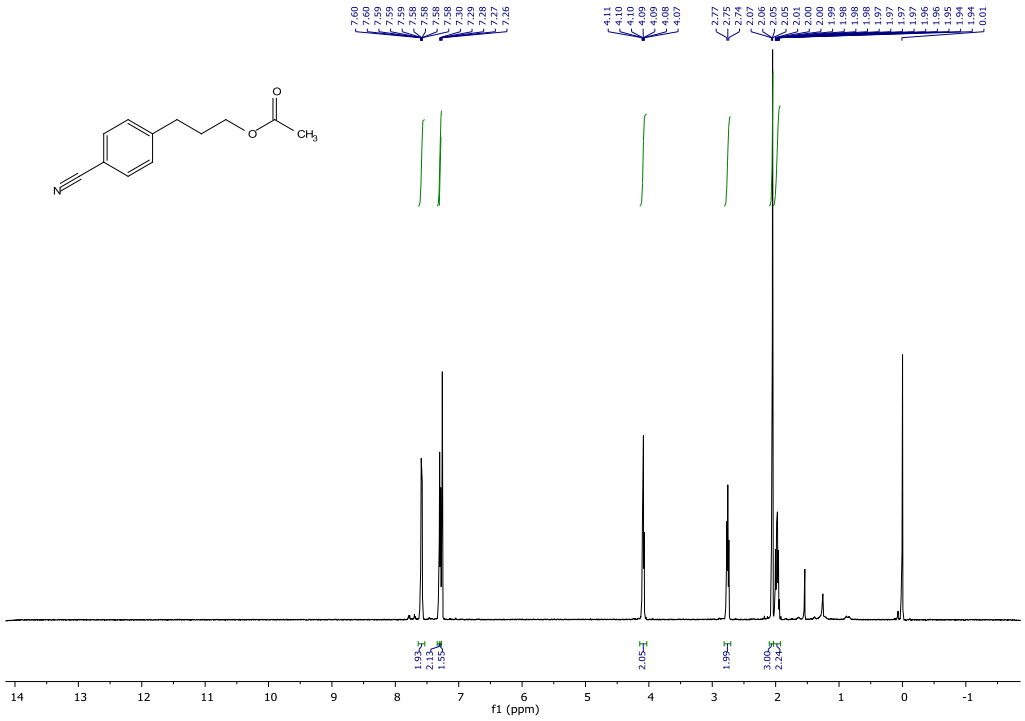
^{13}C {^{1}H} NMR spectrum of 3-(naphthalene-1-yl)propyl acetate (**3c**)



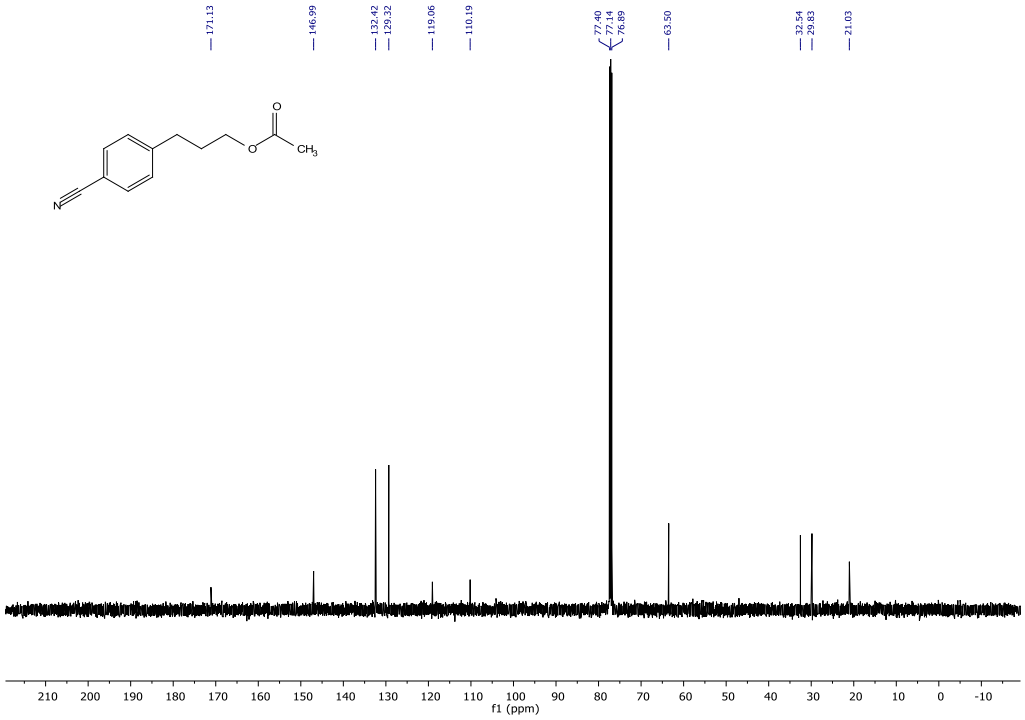
^{1}H NMR spectrum of 3-(naphthalene-2-yl)propyl acetate (**3d**)



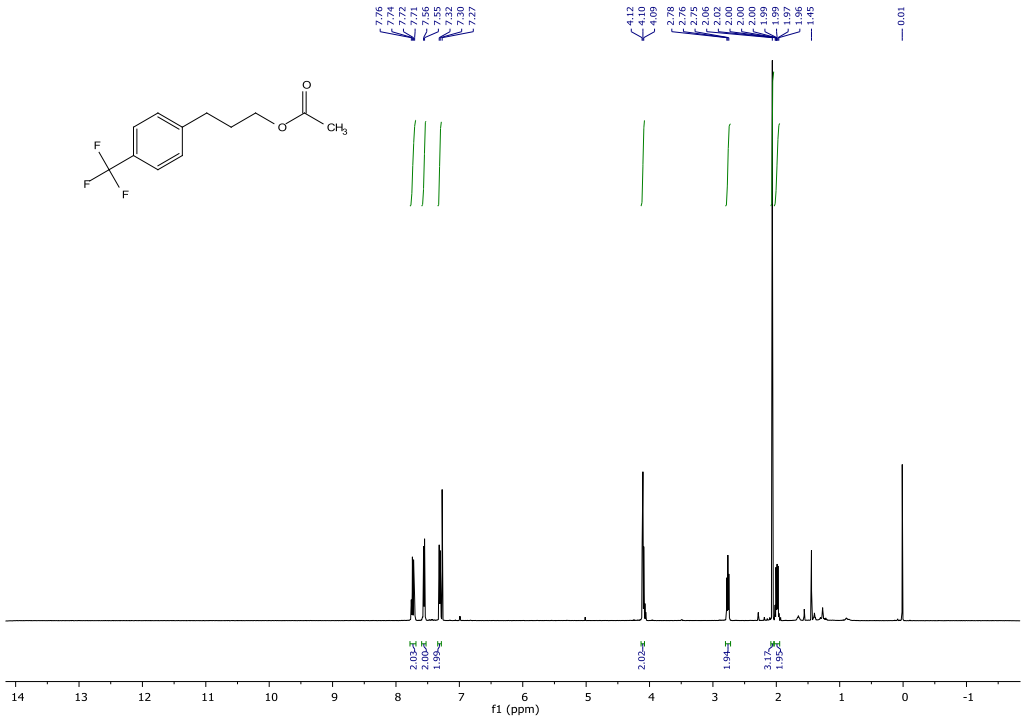
^{13}C {^{1}H} NMR spectrum of 3-(naphthalene-2-yl)propyl acetate (**3d**)



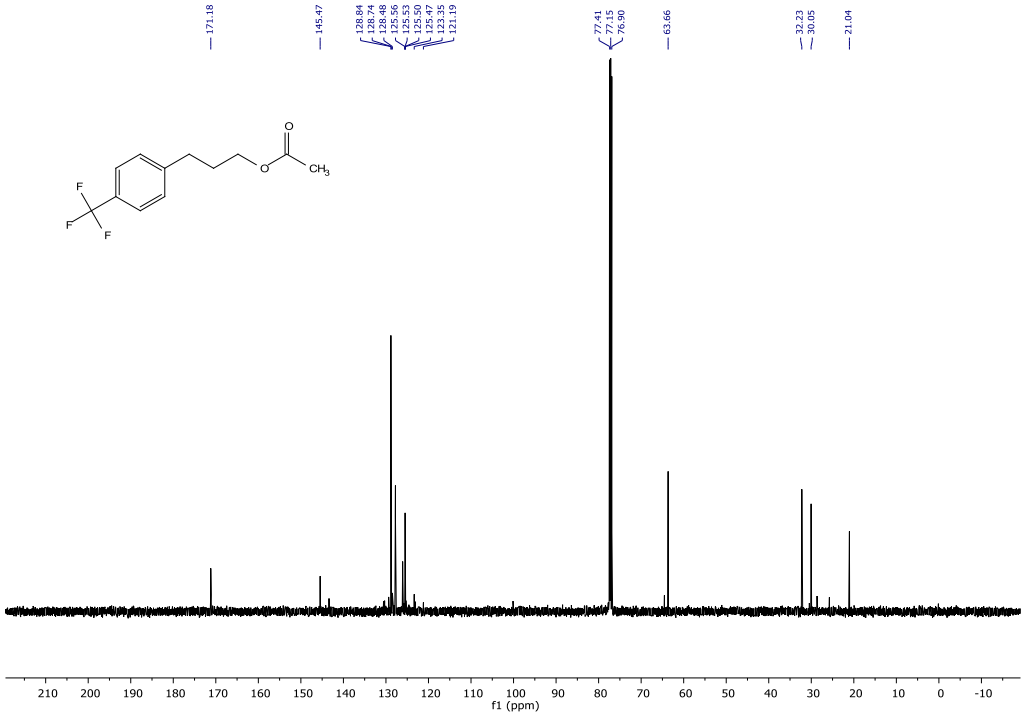
^{1}H NMR spectrum of 3-(4-cyanophenyl)propyl acetate (**3f**)



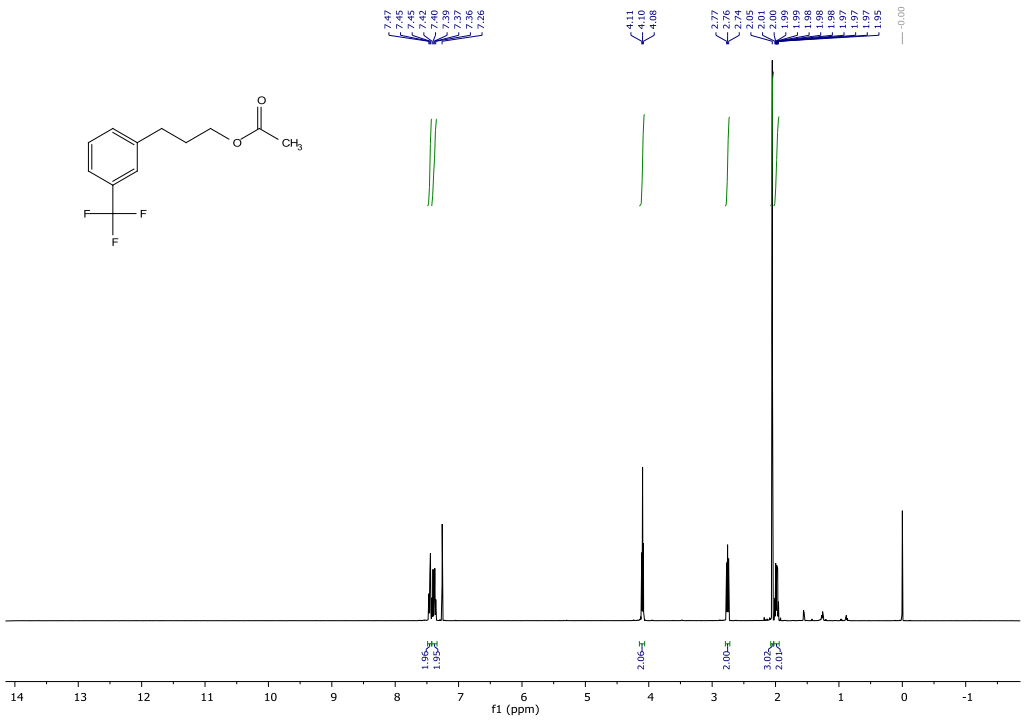
^{13}C {^{1}H} NMR spectrum of 3-(4-cyanophenyl)propyl acetate (**3f**)



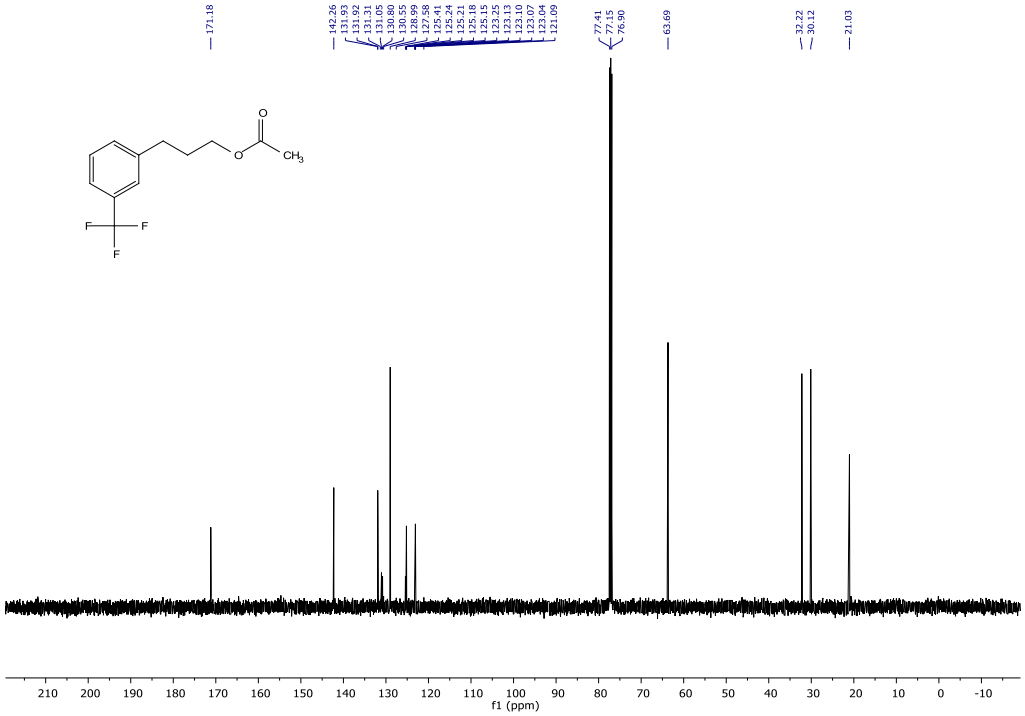
^{1}H NMR spectrum of 3-(4-(trifluoromethyl)phenyl)propyl acetate (**3g**)



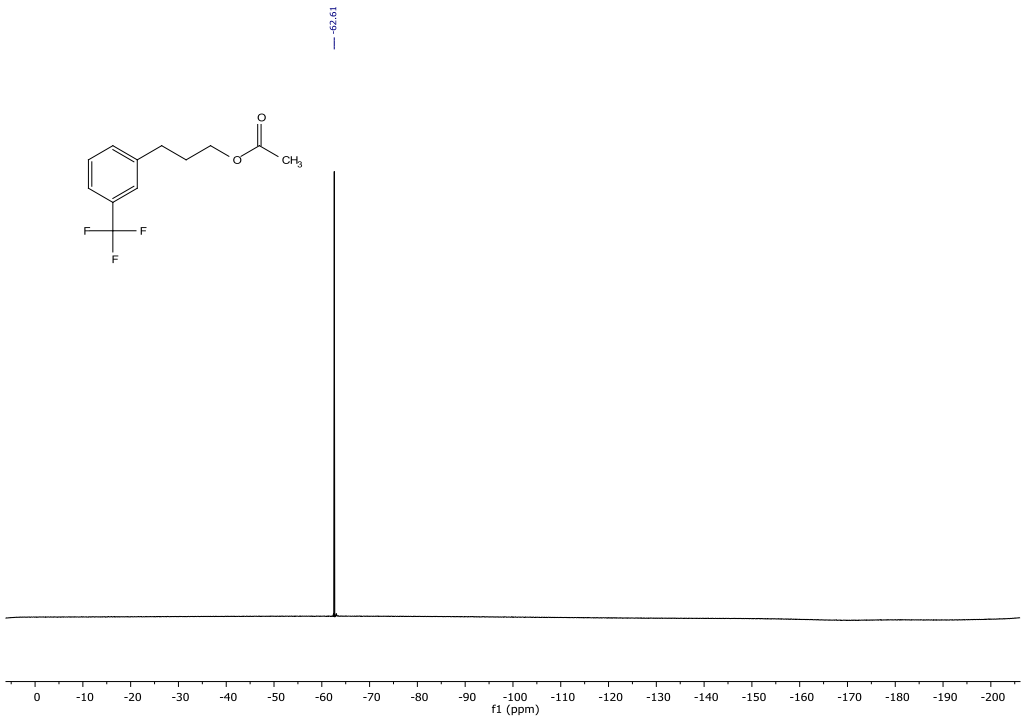
^{13}C {^{1}H} NMR spectrum of 3-(4-(trifluoromethyl)phenyl)propyl acetate (**3g**)



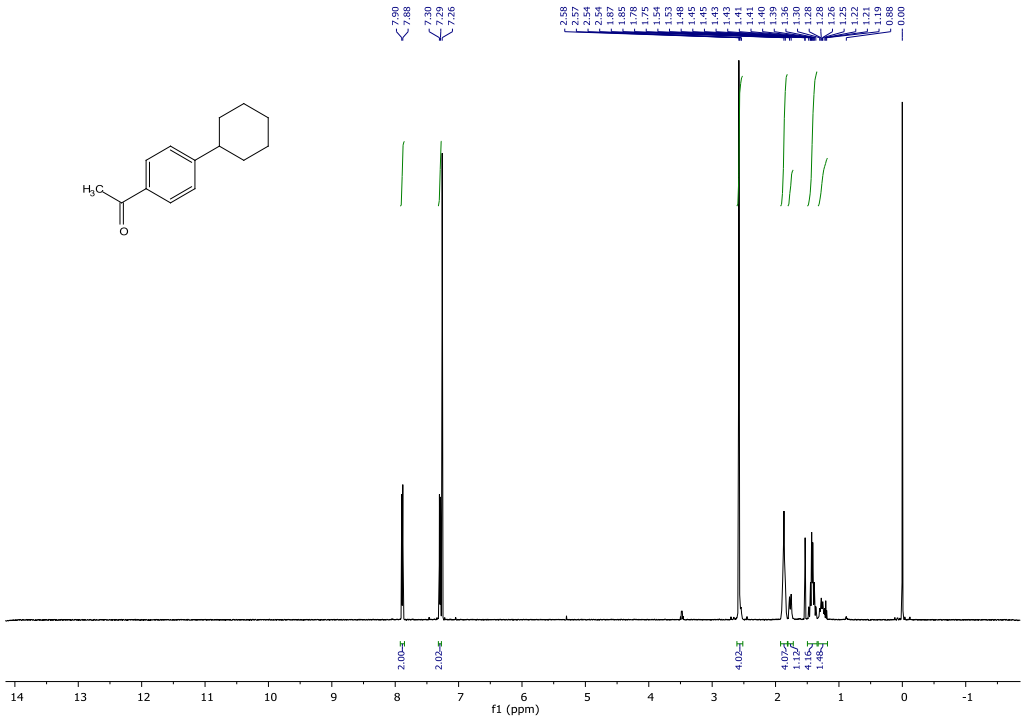
^{1}H NMR spectrum of 3-(3-(trifluoromethyl)phenyl)propyl acetate (**3h**)



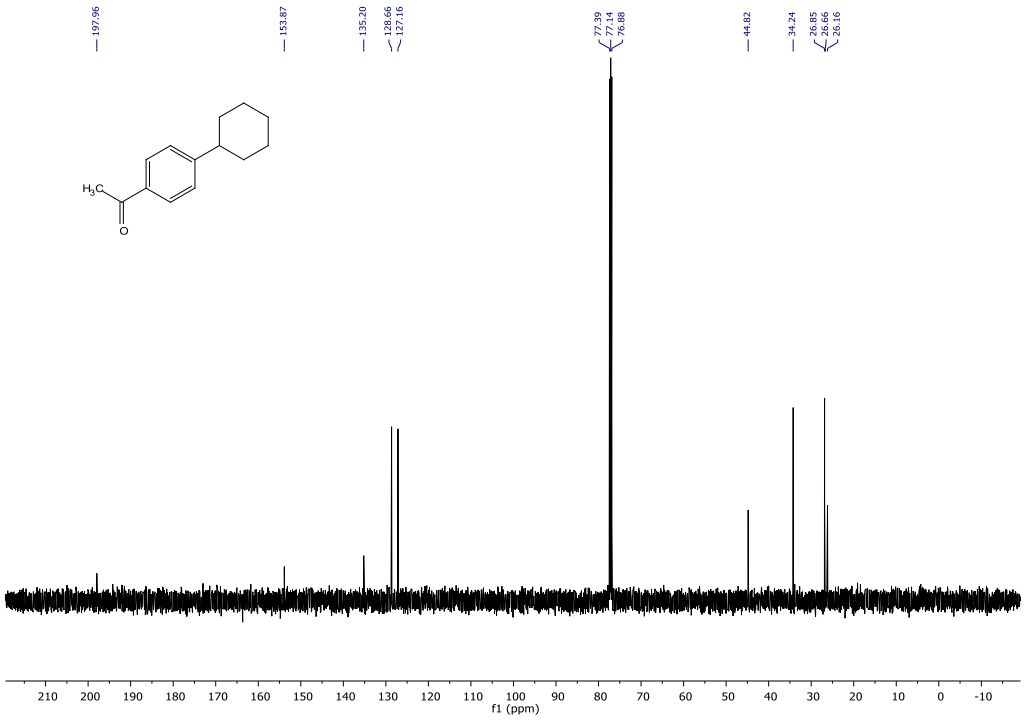
^{13}C {^{1}H} NMR spectrum of 3-(3-(trifluoromethyl)phenyl)propyl acetate (**3h**)



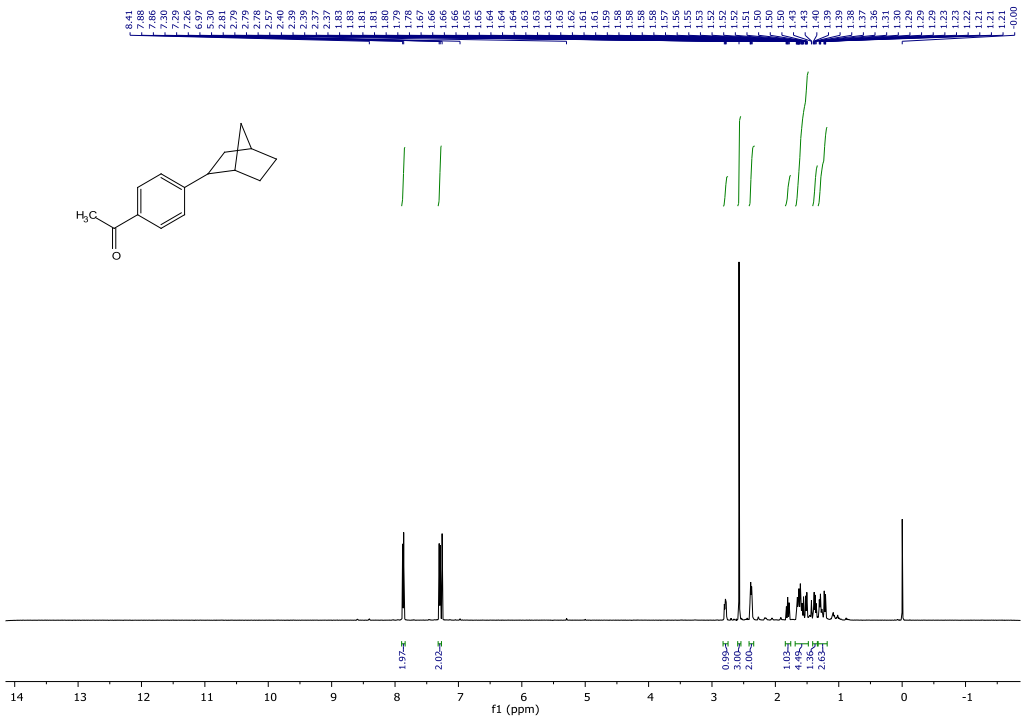
^{19}F NMR spectrum of 3-(3-(trifluoromethyl)phenyl)propyl acetate (**3h**)



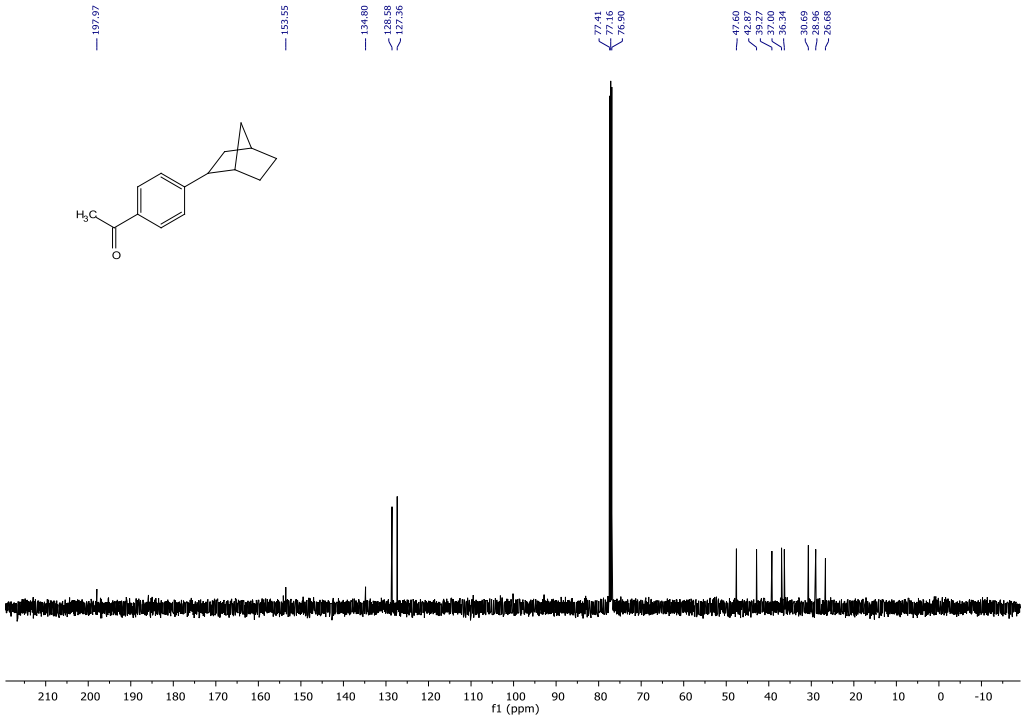
^{1}H NMR spectrum of 1-(4-cyclohexylphenyl)ethanone (**3i**)



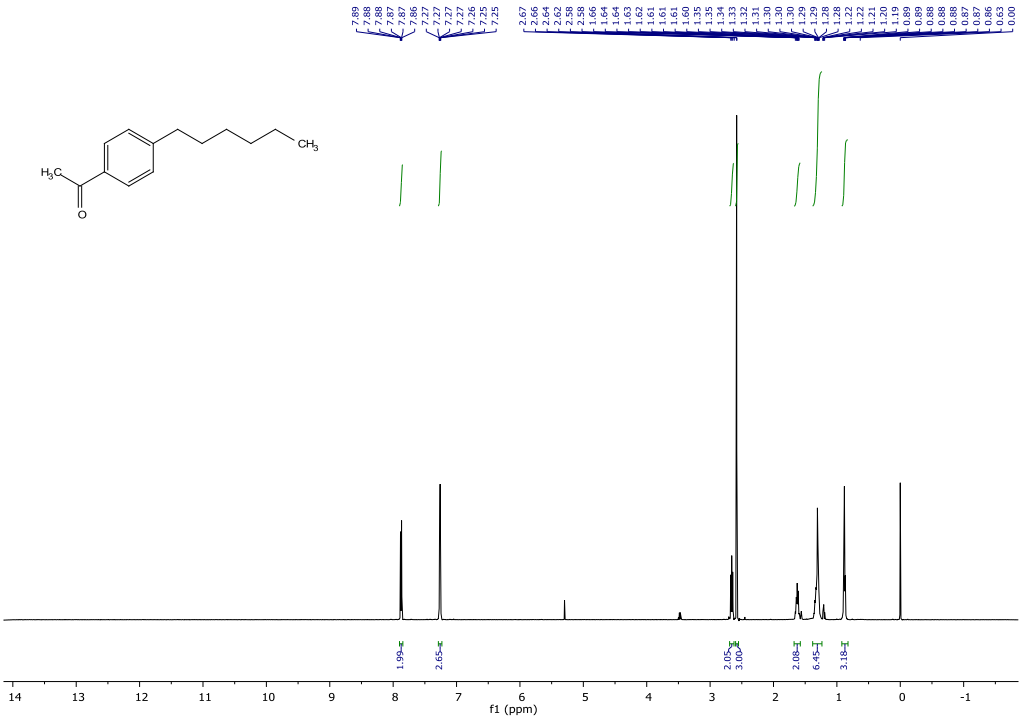
^{13}C {^{1}H} NMR spectrum of 1-(4-cyclohexylphenyl)ethanone (**3i**)



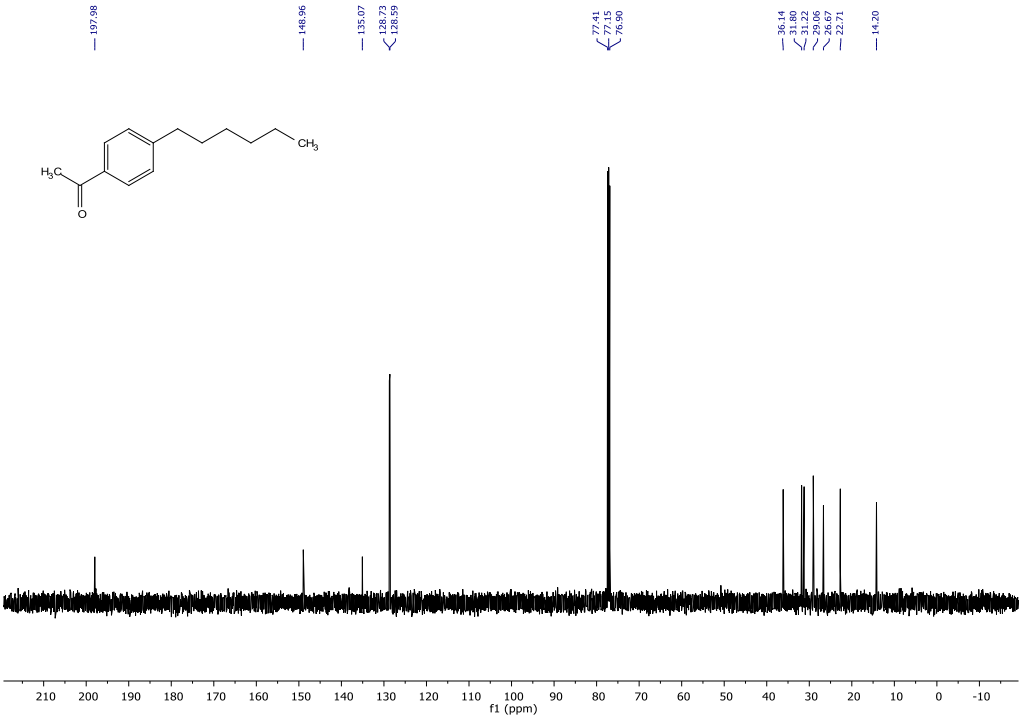
^{1}H NMR spectrum of (±)-1-(4-(bicyclo[2.2.1]heptan-2-yl)phenyl)ethanone (**3j)**



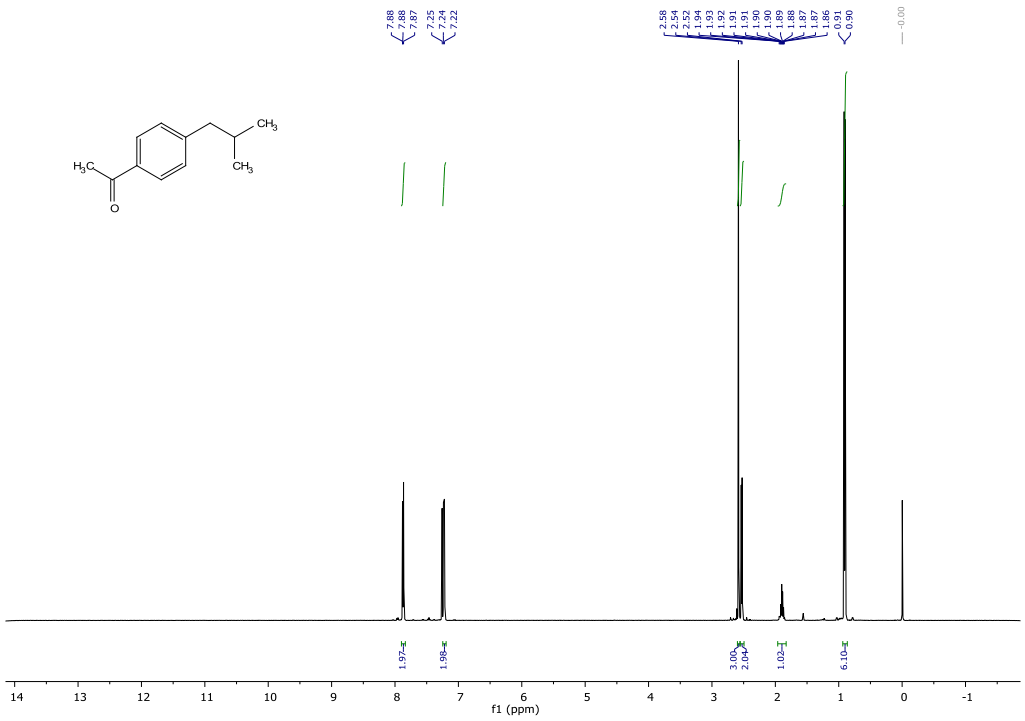
^{13}C {^{1}H} NMR spectrum of (±)-1-(4-(bicyclo[2.2.1]heptan-2-yl)phenyl)ethanone (**3j)**



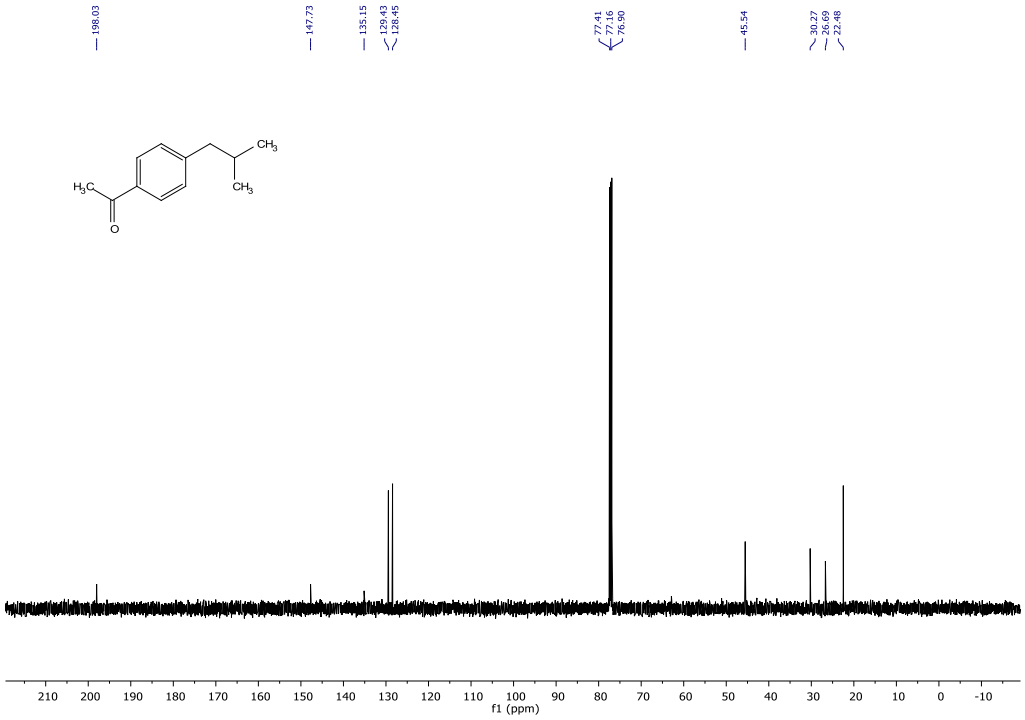
^{1}H NMR spectrum of 1-(4-hexylphenyl)ethanone (**3l)**



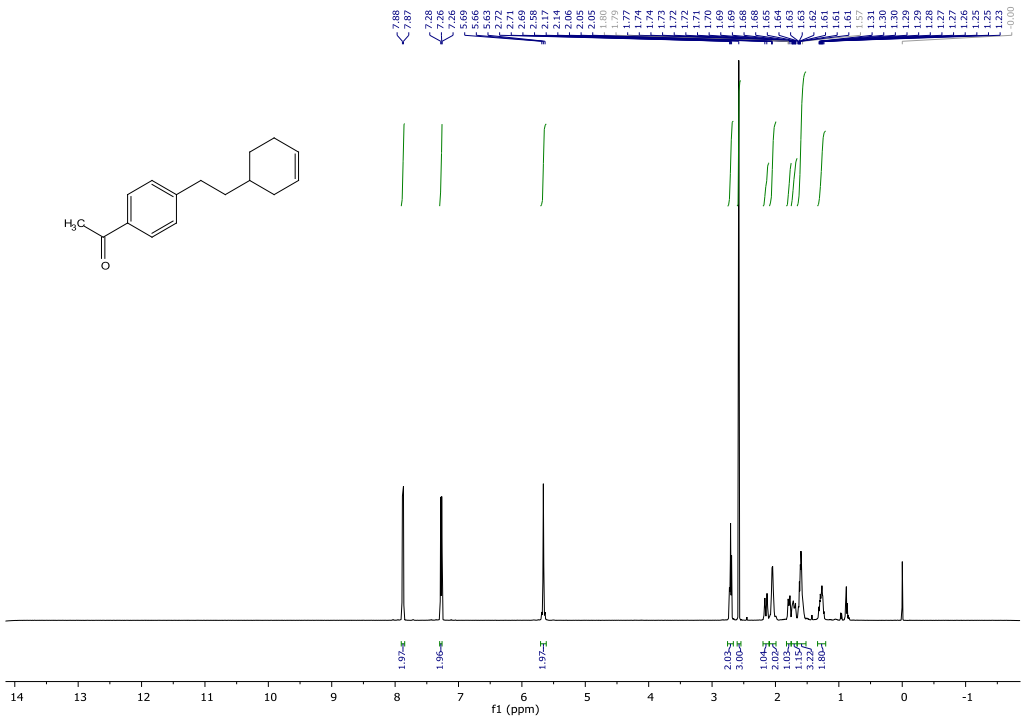
^{13}C {^{1}H} NMR spectrum of 1-(4-hexylphenyl)ethanone (**3l)**



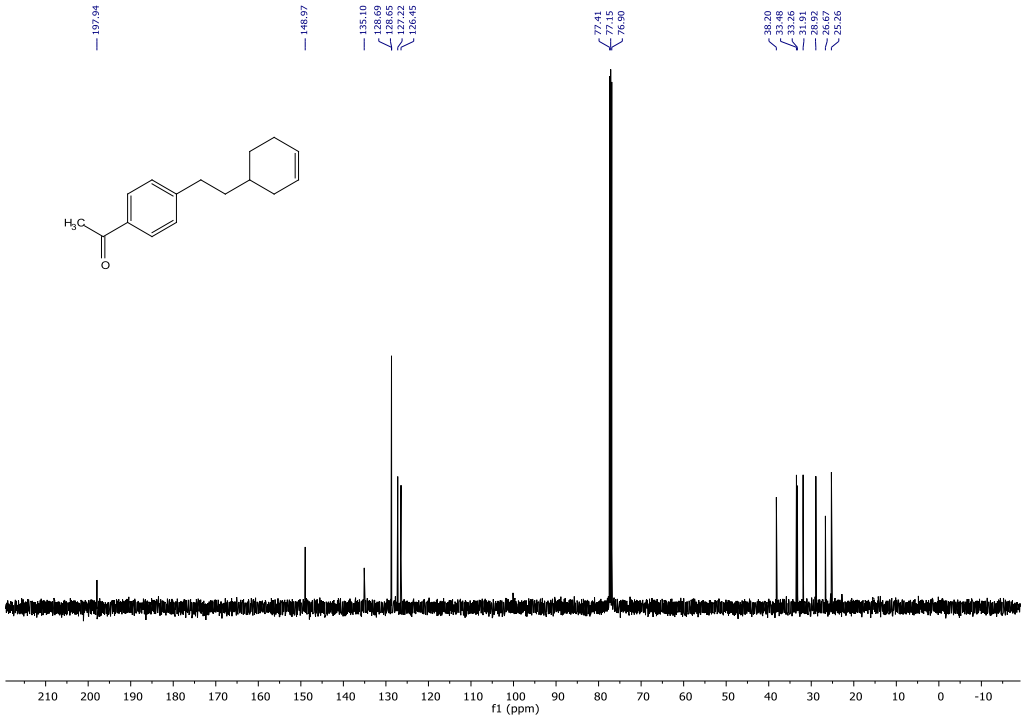
^{1}H NMR spectrum of 1-(4-isobutylphenyl)ethanone (**3m)**



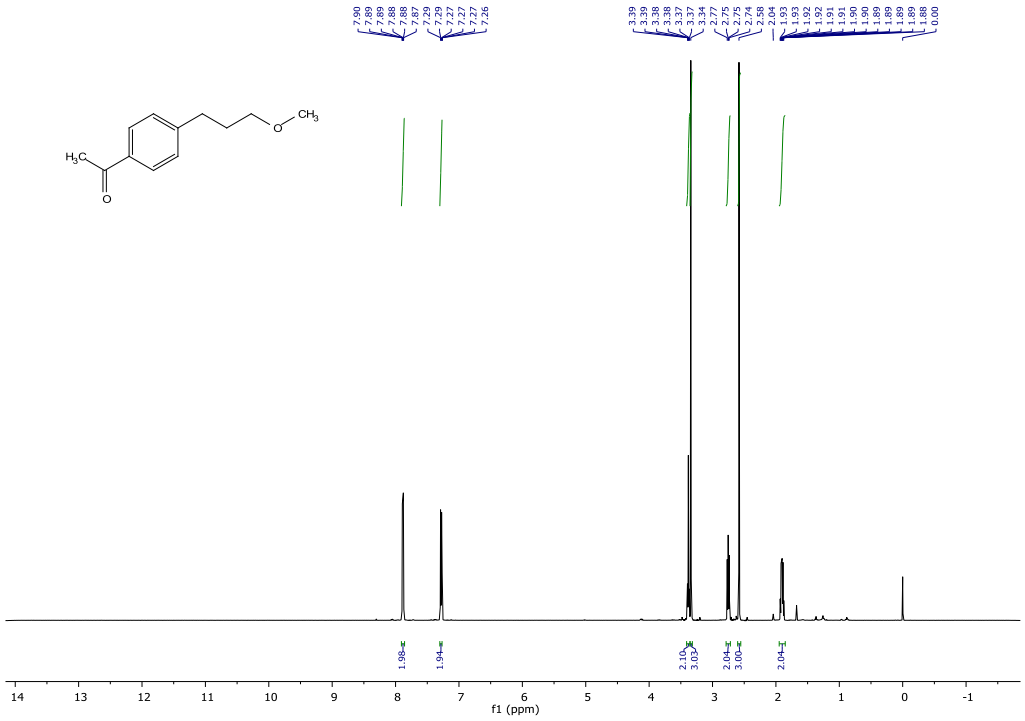
^{13}C {^{1}H} NMR spectrum of 1-(4-isobutylphenyl)ethanone (**3m)**



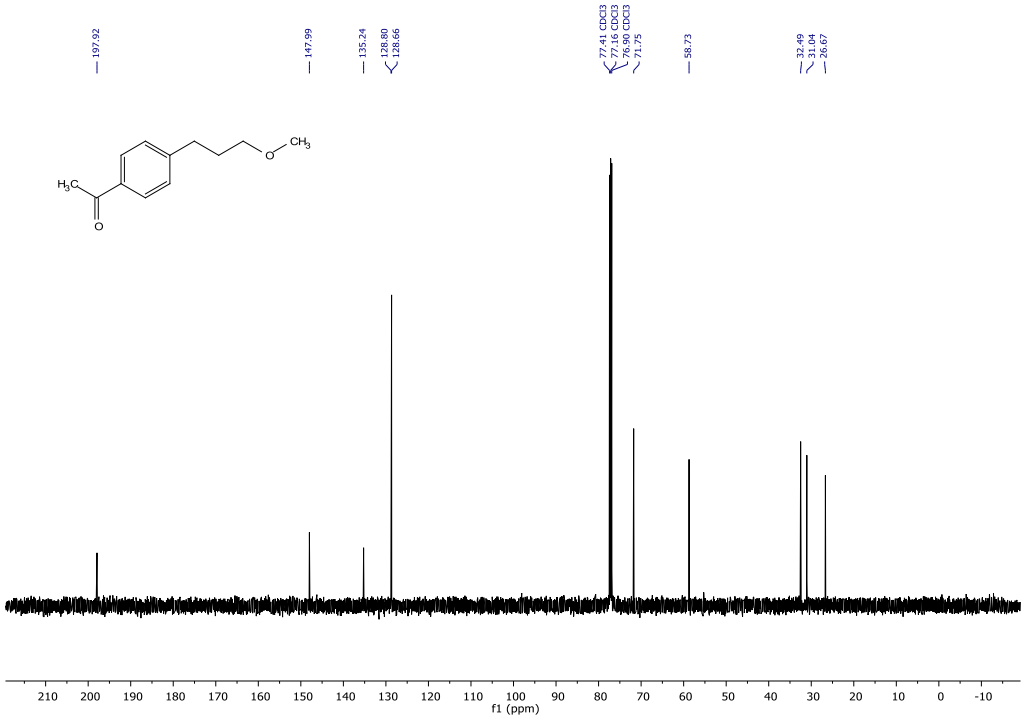
^{1}H NMR spectrum of 1-(4-(2-(cyclohex-3-en-1-yl)ethyl)phenyl)ethanone (**3n)**



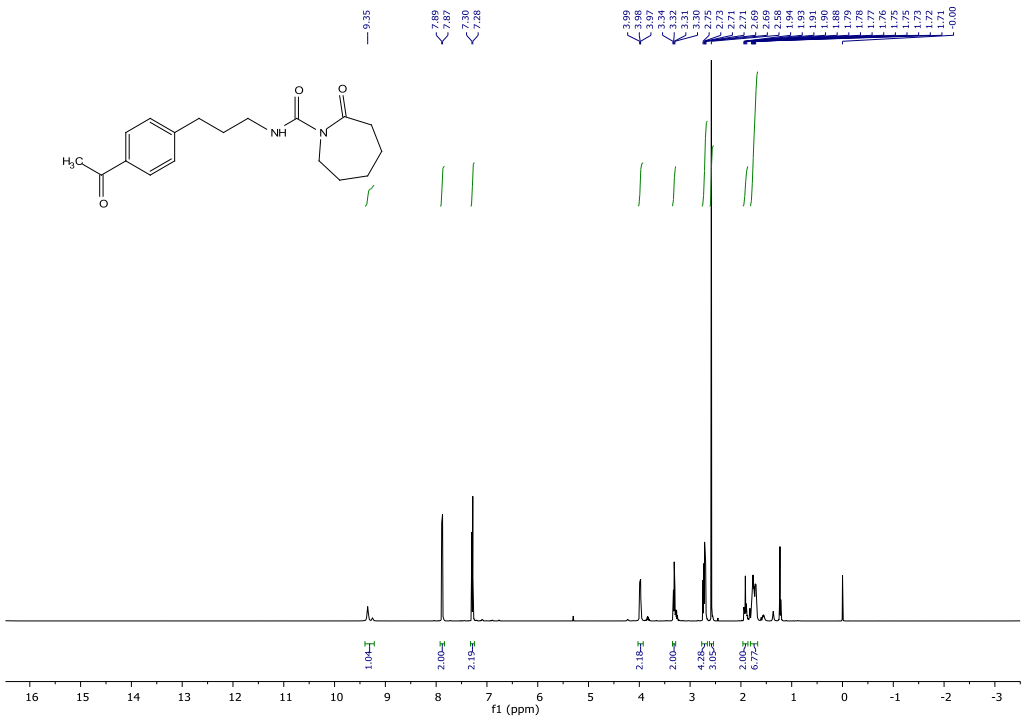
^{13}C {^{1}H} NMR spectrum of 1-(4-(2-(cyclohex-3-en-1-yl)ethyl)phenyl)ethanone (**3n)**



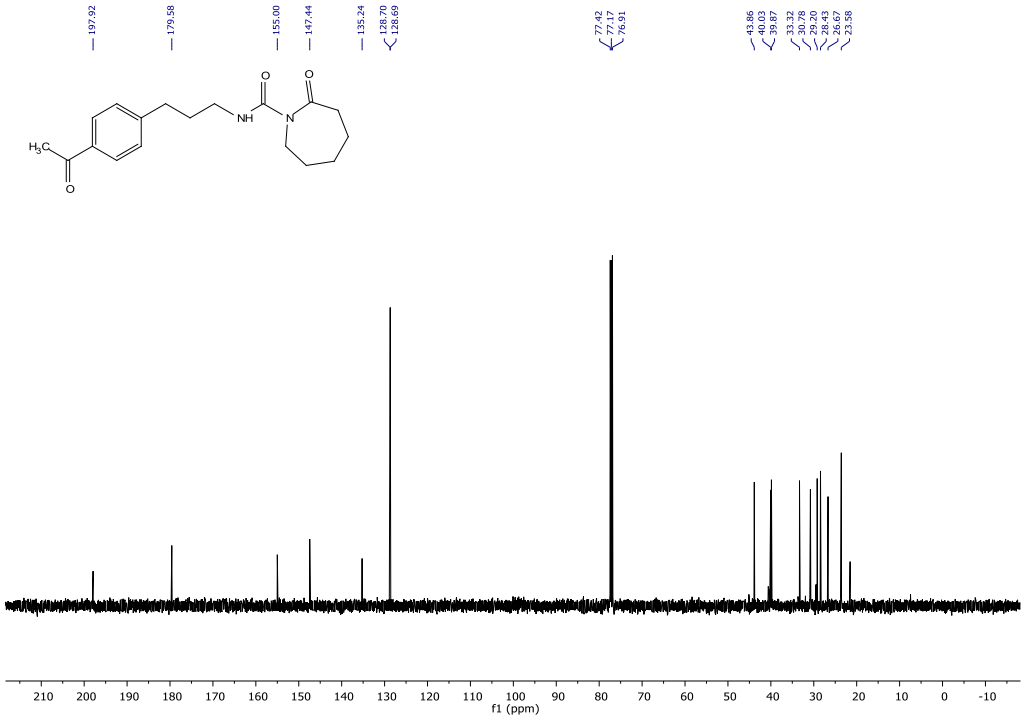
^{1}H NMR spectrum of 1-(4-(3-methoxypropyl)phenyl)ethanone (**3o)**



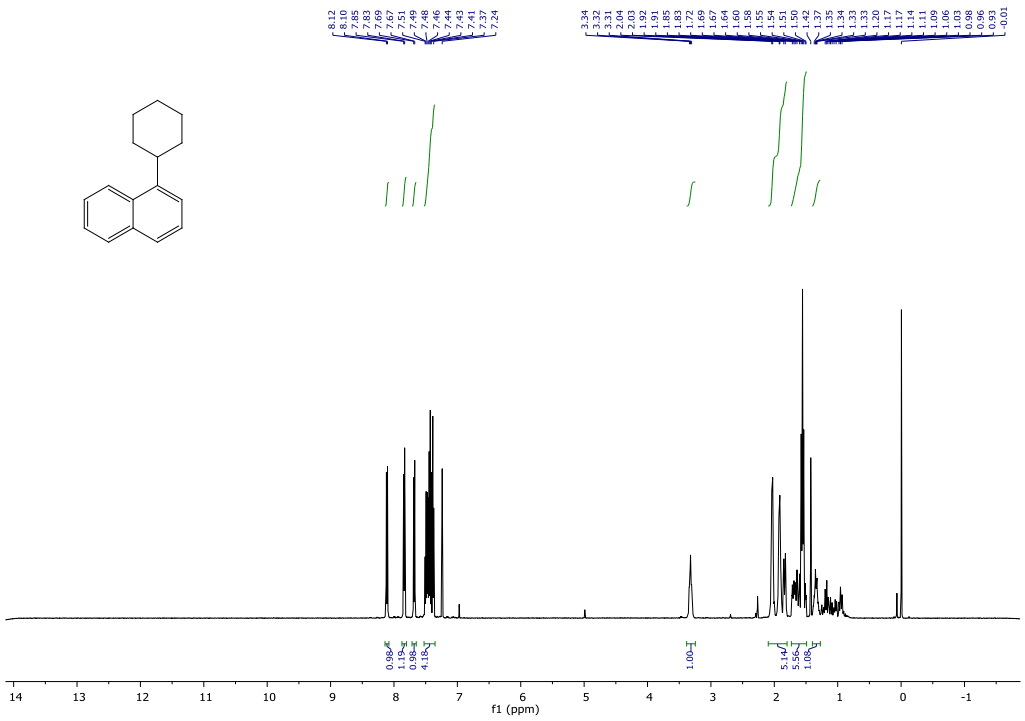
^{13}C {^{1}H} NMR spectrum of 1-(4-(3-methoxypropyl)phenyl)ethanone (**3o)**



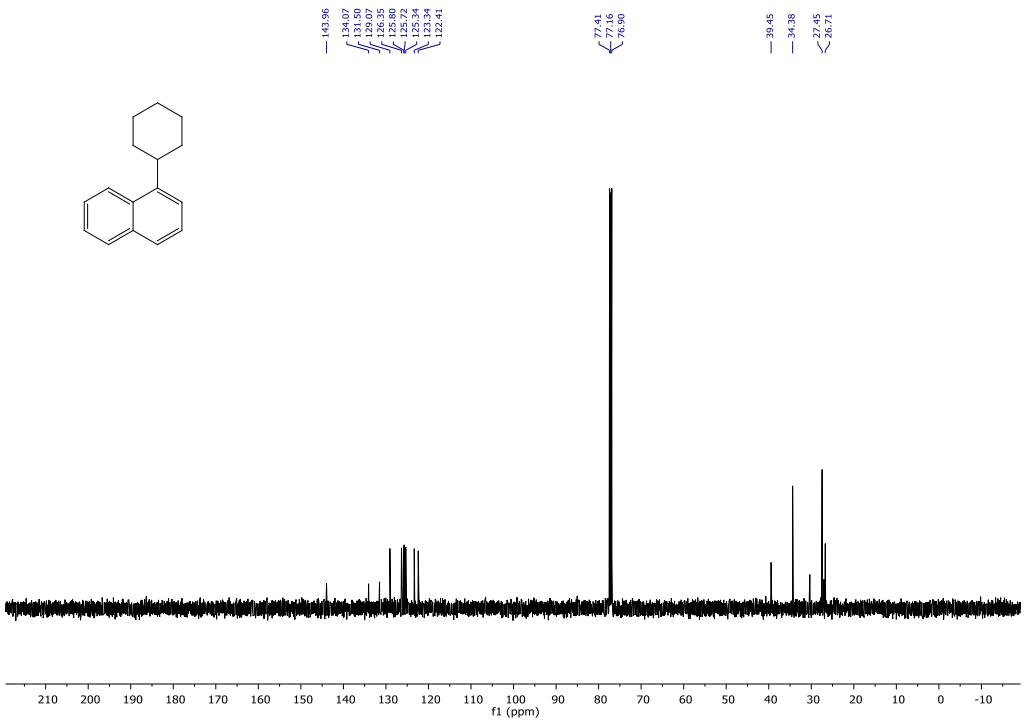
^{1}H NMR spectrum of N-(3-(4-acetylphenyl)propyl)-2-oxoazepane-1-carboxamide (**3p)**



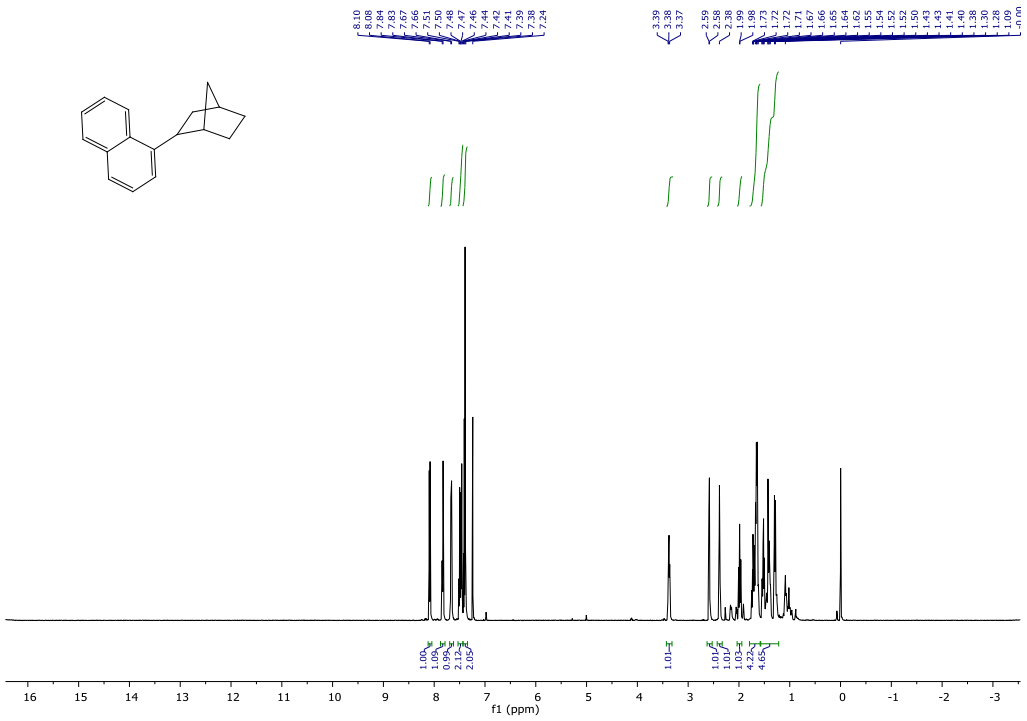
^{13}C {^{1}H} NMR spectrum of N-(3-(4-acetylphenyl)propyl)-2-oxoazepane-1-carboxamide (**3p)**



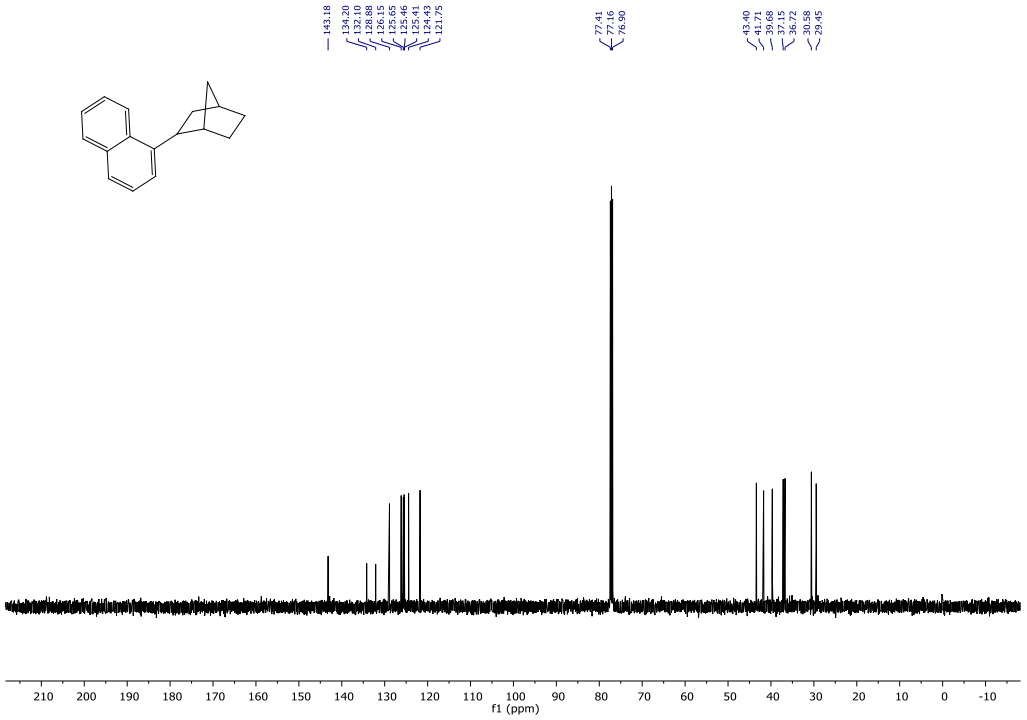
^{1}H NMR spectrum of 1-cyclohexylnaphthalene (**3q)**



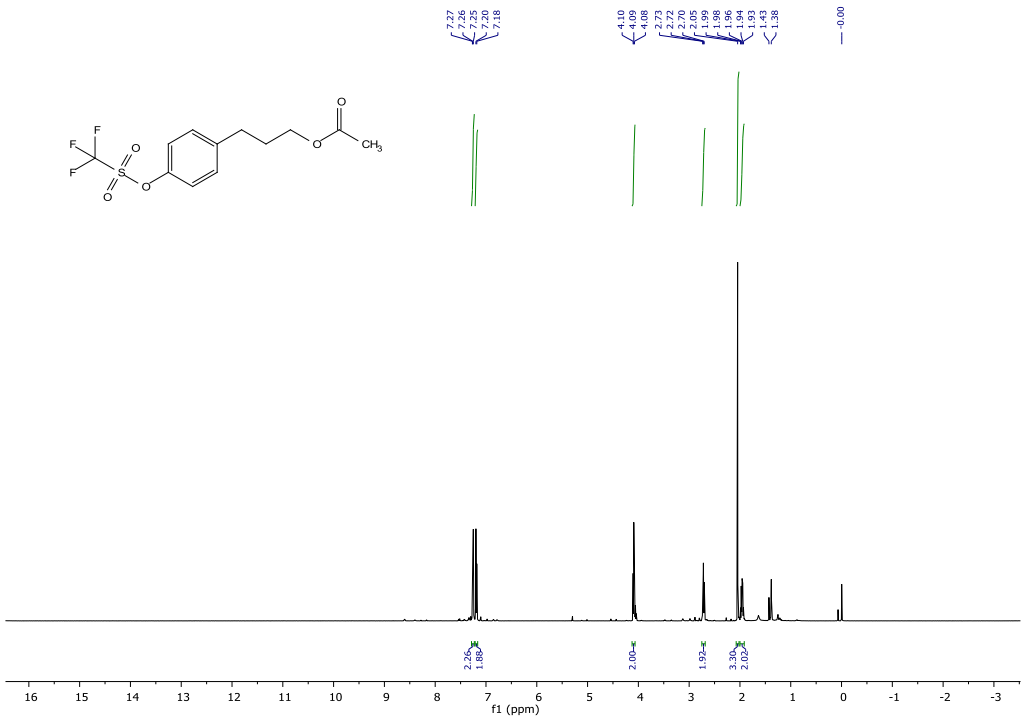
^{13}C {^{1}H} NMR spectrum of 1-cyclohexylnaphthalene (**3q)**



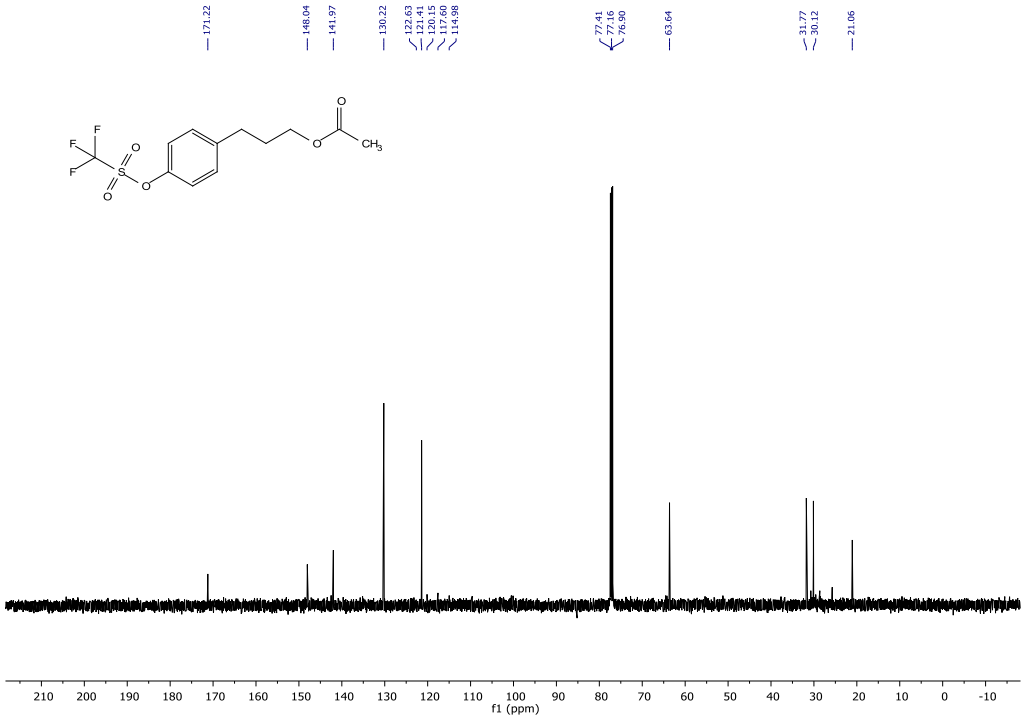
^{1}H NMR spectrum of (±)-1-bicyclo[2.2.1]heptan-2-yl)naphthalene (**3s)**



^{13}C {^{1}H} NMR spectrum of (±)-1-bicyclo[2.2.1]heptan-2-yl)naphthalene (**3s)**



^{1}H NMR spectrum of 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propyl acetate (**3t)**



^{13}C {^{1}H} NMR spectrum of 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propyl acetate (**3t)**

^{19}F NMR spectrum of 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propyl acetate (**3t)**