Supporting Information

Nickel-Catalyzed Selective Oxidative Radical Cross-Coupling: An Effective Strategy for Inert Csp^3-H Functionalization

Dong Liu,[a] Yuxiu Li,[a] Xiaotian Qi,[b] Chao Liu,[a] Yu Lan,[b] and Aiwen Lei*[a,c]*

[a] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China
[b] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, P. R. China
[c] National Research Center for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang 330022, Jiangxi, P. R. China
E-mail: aiwenlei@whu.edu.cn; lanyu@cqu.edu.cn

General information

All reactions were isolated from moisture and oxygen by a nitrogen atmosphere in a sealed tube. All glassware was fully dried at 110 ^{o}C in oven for hours and cooled down under vacuum. Cyclohexane was purified by distillation with calcium hydride as the drying agent. Ni(acac)$_2$ was purchased from J&K Chemicals. Ph$_3$P and DTBP (Di-*tert*-butyl peroxide, Chemical Purity) was purchased from Sinopharm Chemical Reagent Co., Ltd. DPPB was purchased from Accela ChemBio Co., Ltd. K_3PO_4 was purchased from J&K Chemicals and dried in muffle furnace at 650 ^{o}C for 6 h. Unless otherwise noted, those materials were used without further purification. Substituted arylboronic acids derivatives were all purchased from commercial suppliers. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60-90 ^{o}C). Gas chromatographic analyses were performed on Varian GC 2000 gas chromatography instrument with a FID detector and dibenzofuran was added as an internal standard. ^{1}H and ^{13}C NMR data were recorded with Bruker ADVANCE III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.3 ppm, chloroform), respectively.

General procedure

1. General procedure for the nickel-catalyzed oxidative arylation of simple alkanes utilizing arylboronic acids as the coupling partners

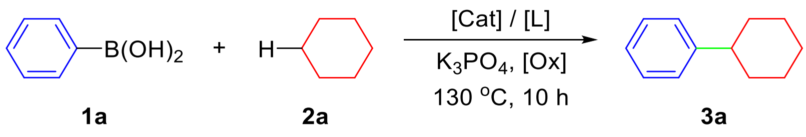
Ni(acac)$_2$ (12.9 mg, 0.05 mmol), Ph_3P (26.2 mg, 0.10 mmol), dppb (10.7 mg, 0.025 mmol) and K_3PO_4 (159.2 mg, 0.75 mmol) were added in a dried sealed tube in the glove box. Then the tube was sealed and transferred out. It was then filled with dry N_2. Under the protection of N_2, cyclohexane (5.0 mL) was injected into the tube *via* a syringe. After stirring for several minutes, *t*-BuOO*t*-Bu (146.2 mg, 1.0 mmol) was injected into the reaction tube by a microsyringe followed by the addition of arylboronic acid (0.5 mmol). The tube was then sealed and heated up to 130 ^{o}C and kept stirring for 10 hours. After completion of the reaction, the mixture was quenched with diluted hydrochloric acid. The solution was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel.

2. General procedure for the nickel-catalyzed oxidative arylation of simple alkanes utilizing arylboronic acid neopentyl glycol esters as the coupling partners

Ni(acac)$_2$ (12.9 mg, 0.05 mmol), dppb (21.3 mg, 0.05 mmol) and K_3PO_4 (159.2 mg, 0.75 mmol) were added in a dried sealed tube in the glove box. Then the tube was sealed and transferred out. It was then filled with dry N_2. Under the protection of N_2, cyclohexane (5.0 mL) was injected into the tube *via* a syringe. After stirring for several minutes, *t*-BuOO*t*-Bu (146.2 mg, 1.0 mmol) was injected into the reaction tube by a microsyringe followed by the addition of arylboronic acid neopentyl glycol ester (0.5 mmol). The tube was then sealed and heated up to 130 ^{o}C and kept stirring for 10 hours. After completion of the reaction, the mixture was quenched with diluted hydrochloric acid. The solution was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel.

Condition optimization

Table S1. Condition optimization for nickel-catalyzed selective radical cross-coupling of **2a** with **1a**[a]



Entry	[Cat]	[L]	[Ox]	Yield [%][b]
1	Ni(acac)$_2$	Ph$_3$P	DTBP	66
2	Fe(acac)$_3$	Ph$_3$P	DTBP	18
3	Co(acac)$_3$	Ph$_3$P	DTBP	0
4	Cu(acac)$_2$	Ph$_3$P	DTBP	2
5	Ni(acac)$_2$	bipy	DTBP	41
6	Ni(acac)$_2$	dppb	DTBP	48
7[c]	Ni(acac)$_2$	Ph$_3$P	TBHP	0
8	Ni(acac)$_2$	Ph$_3$P	DCP	61
9	Ni(acac)$_2$	Ph$_3$P	TBPB	3
10[d]	Ni(acac)$_2$	Ph$_3$P	DTBP	73(**66**)
11[d],[e]	Ni(acac)$_2$	Ph$_3$P	DTBP	49
12[d],[f]	Ni(acac)$_2$	Ph$_3$P	DTBP	21
13[d]	/	Ph$_3$P	DTBP	0
14	Ni(acac)$_2$	/	DTBP	6
15	/	/	DTBP	0

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (5 mL), [Cat] (10 mol%), [L] (20 mol% for monodentate ligand, 10 mol% for bidentate ligand), K_3PO_4 (0.75 mmol), [Ox] (1.0 mmol), 130 °C, 10 h. [b] Yield was determined by GC analysis, calibrated using dibenzofuran as the internal standard. Isolated yield in parentheses. [c] 70% in aqueous solution. [d] Extra addition of 5 mol% dppb. [e] K_2CO_3 as the base. [f] Cs_2CO_3 as the base. DTBP = di-*tert*-butyl peroxide. TBHP = *tert*-butyl hydroperoxide. DCP = dicumyl peroxide. TBPB = *tert*-butyl peroxybenzoate.

Complete reference for Gaussian 09

Gaussian 09, Revision A.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

B3LYP absolute calculation energies, enthalpies, and free energies

All the density functional theory (DFT) calculations were carried out with the GAUSSIAN 09 series of programs. DFT method B3LYP with a standard 6-31+G(d) basis set was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition structures and to derive the thermo chemical corrections for the enthalpies and free energies.

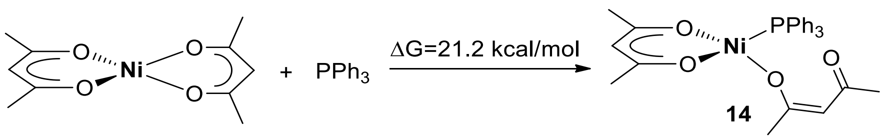


Figure S1. The free energy barrier for the coordination of one PPh_3 ligand.

In the theoretical study, we have also considered the transmetallation process, in which phenylboronic acid could replace one acac ligand, generating a σ–aryl nickel (II) complex. To test the possibility, the free energy barrier for the coordination of one PPh_3 ligand towards nickel, which would replaces one carbonyl group, is initially calculated (Figure S1). Not surprisingly, the value reaches as high as 21.2 kcal/mol.

Therefore, the barrier for following transmetallation transition state will be much higher. Consequently, the transmetallation process is supposed to be unfavorable.

Geometry	$E_{(B3LYP)}$	$H_{(B3LYP)}$	$G_{(B3LYP)}$	IF*
1a	-408.279654	-408.145902	-408.187772	-
2a	-235.872301	-235.694769	-235.731077	-
4	-233.013681	-233.883488	-233.920509	-
5-ts	-468.869742	-468.566012	-468.622399	-1648.58
6	-235.210648	-235.047919	-235.085866	-
7	-233.680210	-233.536786	-233.573536	-
8-ts	-641.283741	-641.019569	641.079546	-202.87
9	-231.567387	-231.474609	-231.507996	-
10	-409.749439	-409.577641	-409.622315	-
11-ts	-467.428629	-467.162453	-467.217638	-1337.89
12	-232.254405	-232.148457	-232.181271	-
13	-1096.702915	-1096.291444	-1096.374897	-
14	-1897.764925	-1897.225990	-1897.333872	

* IF: The imaginary frequencies for the transition states.

B3LYP geometries for all the optimized compounds and transition states

1a

B	1.74656700	-0.00192900	-0.00001400
O	2.54019300	1.12473300	0.00052700
H	2.05813800	1.96289000	0.00105900
O	2.38961800	-1.21211700	-0.00055800
H	3.35414000	-1.11169800	-0.00040700
C	0.17828000	0.01508500	-0.00003100
C	-0.56774900	1.20866200	-0.00030200
C	-0.53551100	-1.19977500	0.00024100
C	-1.96454200	1.19841600	-0.00028100
H	-0.06311700	2.17492700	-0.00061300

C	-1.93170300	-1.22088100	0.00030200
H	0.01867900	-2.13428100	0.00041000
C	-2.64967000	-0.02041700	0.00003800
H	-2.51628100	2.13522300	-0.00053100
H	-2.46060400	-2.17091200	0.00053600
H	-3.73690900	-0.03397700	0.00006400

2a

C	1.52926400	-0.00039400	-0.00020100
H	2.18917100	0.25480500	0.83978500
H	2.18813900	-0.25615400	-0.84083100
C	0.66632000	1.22868000	-0.38198400
H	0.45540900	1.21678800	-1.46100700
H	1.22335700	2.15480300	-0.19128800
C	-0.66578300	1.22885200	0.38220400
H	-1.22239600	2.15525400	0.19161900
H	-0.45508800	1.21655500	1.46125500
C	-1.52922800	0.00031800	-0.00018100
H	-2.18831800	0.25607200	-0.84063700
H	-2.18893700	-0.25500400	0.83992800
C	-0.66626100	-1.22869500	-0.38208100
H	-1.22330000	-2.15481400	-0.19139500
H	-0.45529900	-1.21678600	-1.46109500
C	0.66571600	-1.22878100	0.38227300
H	0.45473500	-1.21612100	1.46128200
H	1.22235700	-2.15527700	0.19220300

4

O	0.00000000	0.26199000	1.43337600
C	0.00000000	-0.02762700	0.08143800
C	0.00000000	1.39044600	-0.57873600
C	1.27845100	-0.79282000	-0.31550800
C	-1.27845100	-0.79281900	-0.31550800
H	-0.89143200	1.95223900	-0.28596500
H	0.89143200	1.95223900	-0.28596500
H	0.00000000	1.25743600	-1.66664700
H	1.30968900	-1.76317500	0.19277700
H	1.30929400	-0.97236200	-1.39684900
H	2.16834500	-0.22492100	-0.02519900
H	-1.30929400	-0.97236200	-1.39684900
H	-1.30968900	-1.76317500	0.19277700
H	-2.16834500	-0.22492000	-0.02519900

5-ts

C	1.50609100	1.36389900	-0.29785300

H	1.67796200	1.98477800	-1.18583700
H	0.79293200	1.91802300	0.32722600
C	2.83310600	1.17539600	0.48398900
H	2.62060900	0.99357400	1.54678600
H	3.41877400	2.10232600	0.44236400
C	3.63587400	-0.00468200	-0.08284400
H	4.61792600	-0.07268800	0.40168600
H	3.83136400	0.18564500	-1.14772300
C	2.86948100	-1.34256000	0.07900100
H	3.19551400	-1.85886700	0.99159400
H	3.11174000	-2.00904700	-0.75824900
C	1.32592800	-1.14239600	0.15240400
H	0.81920900	-2.06823600	-0.14262400
H	1.03839700	-0.94164700	1.19329600
C	0.90712700	0.02090000	-0.72610700
H	1.04497200	-0.19687000	-1.79255000
H	-0.37286600	0.17835100	-0.74137700
O	-1.58365800	0.48537300	-0.94977700
C	-2.46978800	-0.00740100	0.04472300
C	-2.51020300	-1.54646500	0.03797900
H	-3.26271900	-1.92684000	0.74027800
H	-2.75391100	-1.91327100	-0.96531600
H	-1.53942400	-1.96406800	0.32842500
C	-2.09469800	0.53053700	1.43762900
H	-2.05464200	1.62550000	1.42371400
H	-2.82753800	0.21943600	2.19260700
H	-1.11299600	0.15512000	1.75018300
C	-3.84213100	0.55652900	-0.38497700
H	-4.61888600	0.23091500	0.31799000
H	-3.81806400	1.65110800	-0.40084000
H	-4.10380500	0.20123700	-1.38707400

6

C	0.11731100	-1.48368400	-0.01811700
H	0.39625000	-2.15465900	0.80491200
H	-0.07357500	-2.13022100	-0.88477100
C	1.29904400	-0.53512800	-0.35151700
H	1.33097700	-0.35759800	-1.43481500
H	2.25138900	-1.01276100	-0.08869000
C	1.17615700	0.83440200	0.34753900
H	2.02731800	1.47641200	0.08162100
H	1.25297300	0.68616500	1.44279300
C	-0.12100300	1.49308500	-0.01562600
H	-0.20042200	2.57694700	-0.05187000
C	-1.30677200	0.63128300	-0.33368300

H	-2.24131300	1.13019300	-0.03966500
H	-1.39616200	0.46742500	-1.42593200
C	-1.18136300	-0.73406100	0.37004800
H	-1.19213100	-0.55732900	1.45416500
H	-2.05555000	-1.35994700	0.15039400

7

O	-0.01568500	-0.00128900	1.45610800
C	0.00543400	-0.00008300	0.01174000
C	-0.70480500	-1.25757600	-0.51309000
C	-0.67664300	1.27366100	-0.51094300
C	1.49125600	-0.01593700	-0.35608400
H	-0.23345400	-2.15889800	-0.10618700
H	-1.76317800	-1.26161200	-0.21850900
H	-0.66585000	-1.30827700	-1.60814200
H	-0.18430200	2.16364000	-0.10381400
H	-0.63756500	1.32454500	-1.60600600
H	-1.73427300	1.30183100	-0.21518800
H	1.62225000	-0.01510700	-1.44411400
H	1.99501400	0.86483700	0.05689700
H	1.97556000	-0.90931600	0.05308400
H	-0.94018000	0.00827400	1.75338100

8-ts

B	-0.18675200	1.50906500	0.10721500
O	-0.35825900	2.42484300	1.15962000
H	0.10459100	2.18782800	1.97378800
O	-0.66568500	1.96694300	-1.13001400
H	-1.12801500	2.80952900	-1.01042500
C	1.09279500	0.53396900	0.05505500
C	1.64759800	-0.05002700	1.21718700
C	1.74376800	0.28594000	-1.17461800
C	2.81985200	-0.80545800	1.16595600
H	1.14998200	0.08463600	2.17562500
C	2.91780000	-0.46347100	-1.23241700
H	1.32904900	0.72009400	-2.08001700
C	3.45908300	-1.01349900	-0.06137500
H	3.23181500	-1.23649800	2.07524800
H	3.41799300	-0.61875200	-2.18560700
H	4.37160100	-1.60304900	-0.10769900
O	-1.19321000	0.08428800	0.65455600
C	-2.01011700	-0.84802200	-0.01858500
C	-1.62691500	-1.01970600	-1.49960400
H	-0.62268400	-1.44832500	-1.58071400
H	-2.33472600	-1.70551200	-1.97957300

H	-1.63934700	-0.06074600	-2.02089900
C	-3.43178800	-0.21616800	0.08715000
H	-4.15230400	-0.90908000	-0.36312800
H	-3.70504000	-0.05079600	1.13355700
H	-3.46550900	0.73654200	-0.44769300
C	-1.95660000	-2.18633900	0.73467900
H	-2.23519900	-2.04821000	1.78501200
H	-2.64127700	-2.91461600	0.28390200
H	-0.94280500	-2.60027500	0.69868800

9

C	-1.21609400	0.63342000	-0.00000700
C	-1.22849600	-0.77332500	0.00002200
C	-0.00001100	-1.40026500	-0.00000900
C	1.22849900	-0.77331600	-0.00000900
C	1.21610700	0.63339400	0.00001900
C	-0.00000400	1.32653400	-0.00000500
H	-2.15707000	1.17950800	-0.00002700
H	-2.16476300	-1.32550800	-0.00000700
H	2.16473700	-1.32555000	-0.00002500
H	2.15706100	1.17952000	0.00001300
H	0.00002700	2.41337400	-0.00002000

10

B	-1.46444300	0.11686400	0.00002600
O	-1.65197000	-1.24717800	0.00006400
H	-2.59379300	-1.47320100	0.00006700
O	-2.58216500	0.92677400	0.00000200
H	-2.34483300	1.86581100	-0.00055900
O	-0.23218800	0.70001600	-0.00025100
C	1.06571400	0.04068500	-0.00004400
C	2.08017600	1.18950700	-0.00018200
H	1.94819600	1.81737100	0.88800900
H	3.10422800	0.79902000	-0.00064100
H	1.94768600	1.81799300	-0.88786300
C	1.21406800	-0.80967600	-1.26914900
H	2.21904700	-1.24590900	-1.31532400
H	0.48410200	-1.62384300	-1.28709500
H	1.07085400	-0.19002800	-2.16221100
C	1.21397400	-0.80904400	1.26954700
H	0.48349700	-1.62273300	1.28823000
H	2.21870200	-1.24581400	1.31546200
H	1.07151900	-0.18871200	2.16224600

11-ts

C	-1.73861900	-0.97692500	0.90993300
H	-1.78299300	-2.07151900	0.83893800
H	-1.06325500	-0.75209600	1.74762600
C	-3.14975600	-0.41683700	1.22714800
H	-3.06203300	0.54008600	1.76089900
H	-3.67590500	-1.09918800	1.90685400
C	-3.95640500	-0.20337900	-0.06237400
H	-4.98869400	0.08700000	0.17031300
H	-4.02121900	-1.16188400	-0.59712700
C	-3.29492000	0.86250900	-0.97433500
H	-3.74406100	1.84771900	-0.78980900
H	-3.49910900	0.62227500	-2.02578600
C	-1.76070900	0.96056300	-0.75069500
H	-1.27477600	1.37851800	-1.64078900
H	-1.55703600	1.66153800	0.07121700
C	-1.17584000	-0.39998400	-0.39798800
H	-1.25256700	-1.10121100	-1.23916700
H	0.07242000	-0.26769100	-0.27216200
C	1.51173300	-0.10914800	-0.12722200
C	2.33783700	-1.08222400	-0.67532500
C	2.01279600	0.99719300	0.54754700
C	3.72720500	-0.94015500	-0.54081900
H	1.92305900	-1.94097600	-1.19995300
C	3.40327100	1.13240600	0.67903900
H	1.34831500	1.74943700	0.96820900
C	4.25591200	0.16506700	0.13534700
H	4.39269400	-1.69058200	-0.96262500
H	3.81729100	1.99103000	1.20371800
H	5.33283200	0.27303500	0.23811800

12

C	0.70862800	-1.20614700	0.00000000
C	-0.69022600	-1.21669500	0.00000400
C	-1.39892000	-0.01060600	0.00000400
C	-0.70859400	1.20609200	0.00000000
C	0.69025600	1.21675100	-0.00000400
C	1.39884600	0.01060400	-0.00000400
H	1.25958100	-2.14346500	0.00000000
H	-1.22688300	-2.16233500	0.00000700
H	-1.25953100	2.14348500	0.00000000
H	1.22693800	2.16231300	-0.00000700
H	2.48614500	0.01885100	-0.00000700
H	-2.48619100	-0.01884800	0.00000700

13

C	-2.50797900	-1.50865600	-0.82286400
C	-3.39743900	-2.17087000	-1.85550600
H	-2.84462400	-2.97446600	-2.35619400
H	-4.31329100	-2.58079000	-1.42112600
H	-3.66326900	-1.43502800	-2.62388900
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H	-3.90129000	-1.88632300	0.74690800
C	-2.22882500	-0.86062000	1.58987200
C	-2.83767200	-0.89199300	2.97834900
H	-2.97324500	0.13578000	3.33573300
H	-3.80011000	-1.41030000	3.00539500
H	-2.14412100	-1.38413200	3.67032300
C	1.38492400	2.42221100	0.30931300
C	2.68863900	3.00355300	0.81903400
H	2.67953400	4.09676900	0.83761300
H	2.88339300	2.63054200	1.83168700
H	3.51644500	2.66462500	0.18459500
C	0.34862200	3.28638700	-0.06342200
H	0.52138400	4.35185000	0.03884700
C	-0.89390400	2.86768500	-0.59653600
C	-1.91355000	3.91190500	-1.00827600
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H	-1.56496700	4.93422200	-0.83638700
H	-2.15141100	3.78657000	-2.07124500
O	1.35708100	1.13779900	0.26074000
O	-1.23435100	1.65940100	-0.77558700
O	-1.40346500	-1.05466900	-1.27432500
O	-1.09168400	-0.28997100	1.51093100
Ni	-0.17150000	0.03483700	-0.21154600
C	1.00762400	-1.79805700	0.00315300
H	0.08947200	-2.36883500	0.14219400
C	1.89834100	-1.80841300	1.22602700
H	1.98024100	-2.87176700	1.52591900
H	1.39375400	-1.30962100	2.06244400
C	3.31470800	-1.24219100	1.02102300
H	3.25973800	-0.14983300	1.01318900
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H	3.50456200	-1.70539300	-2.43125500
H	2.93514200	-0.28288500	-1.55549400
C	3.94626400	-1.72080500	-0.29562600

H	4.93823400	-1.26730900	-0.42305800
H	4.10283400	-2.81111100	-0.26292300

14

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H	2.47516700	4.48158700	-1.70447700
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C	2.49718000	2.78258300	0.28362600
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H	3.77307400	3.40909400	2.50207500
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C	1.76256500	-4.10196700	0.82731400
H	2.62018600	-4.77964300	0.85325500
H	1.41324300	-3.92162900	1.85054100
H	0.93948400	-4.58555000	0.28767500
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H	4.11932000	-3.33424300	-0.24226300
C	3.74448900	-1.35360600	-0.99083600
C	5.13820400	-1.20270400	-1.56320300
H	5.62180300	-0.32768400	-1.11373400
H	5.75844800	-2.08643600	-1.38974600
H	5.07083500	-1.01631700	-2.64152400
O	1.11657200	-1.94986000	0.12801000
O	2.97731700	-0.35463700	-1.15776400
O	1.15332300	1.50824700	-1.27210100
O	1.94017600	0.83542200	1.54424300
Ni	1.19097000	-0.18986000	-0.49255800
P	-1.05230700	-0.06278500	-0.04442200
C	-1.78471300	1.62437600	0.04897000
C	-1.81676500	2.41868300	-1.11139200
C	-2.27388400	2.15671100	1.25079400
C	-2.34456600	3.70964900	-1.06956800
H	-1.42549600	2.02853000	-2.04584800
C	-2.79293300	3.45512200	1.29162500
H	-2.25416600	1.56195300	2.15833000
C	-2.83286500	4.23303700	0.13302300
H	-2.36967000	4.30957500	-1.97600900
H	-3.16779100	3.85308500	2.23127700
H	-3.23908400	5.24090900	0.16465600

C	-1.52800800	-0.87138900	1.54251200
C	-2.73808600	-1.56537400	1.69846100
C	-0.64467900	-0.77197300	2.63162200
C	-3.06818800	-2.14265600	2.92797900
H	-3.42423200	-1.66571900	0.86300100
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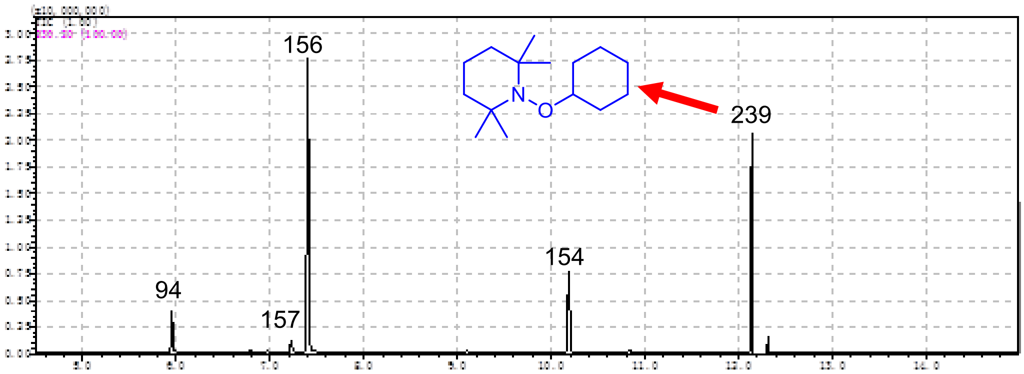
H	-1.76448900	-3.49970100	-3.54256100
H	-4.10450900	-2.82013100	-4.05709100

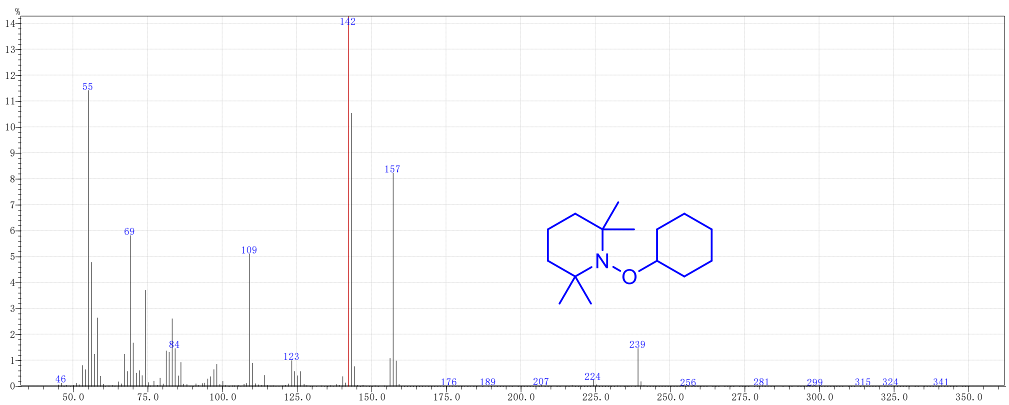
Radical-trapping experiment:

(1) TEMPO as the radical trapping reagent —— **General procedure**

Ni(acac)$_2$ (12.9 mg, 0.05 mmol), Ph$_3$P (26.2 mg, 0.10 mmol), dppb (10.7 mg, 0.025 mmol) and K$_3$PO$_4$ (159.2 mg, 0.75 mmol) were added in a dried sealed tube in the glove box. Then the tube was sealed and transferred out. It was then filled with dry N$_2$. Under the protection of N$_2$, cyclohexane (5.0 mL) was injected into the tube *via* a syringe. After stirring for several minutes, *t*-BuOO*t*-Bu (146.2 mg, 1.0 mmol) was injected into the reaction tube by a microsyringe followed by the addition of phenylboronic acid (0.5 mmol) and TEMPO (117.2 mg, 0.75 mmol). The tube was then sealed and heated up to 130 °C and kept stirring for 10 hours. After completion of the reaction, the mixture was quenched with diluted hydrochloric acid. The solution was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and dried over sodium sulfate, further detected by GC/MS analysis.

GC/MS Spectrum:

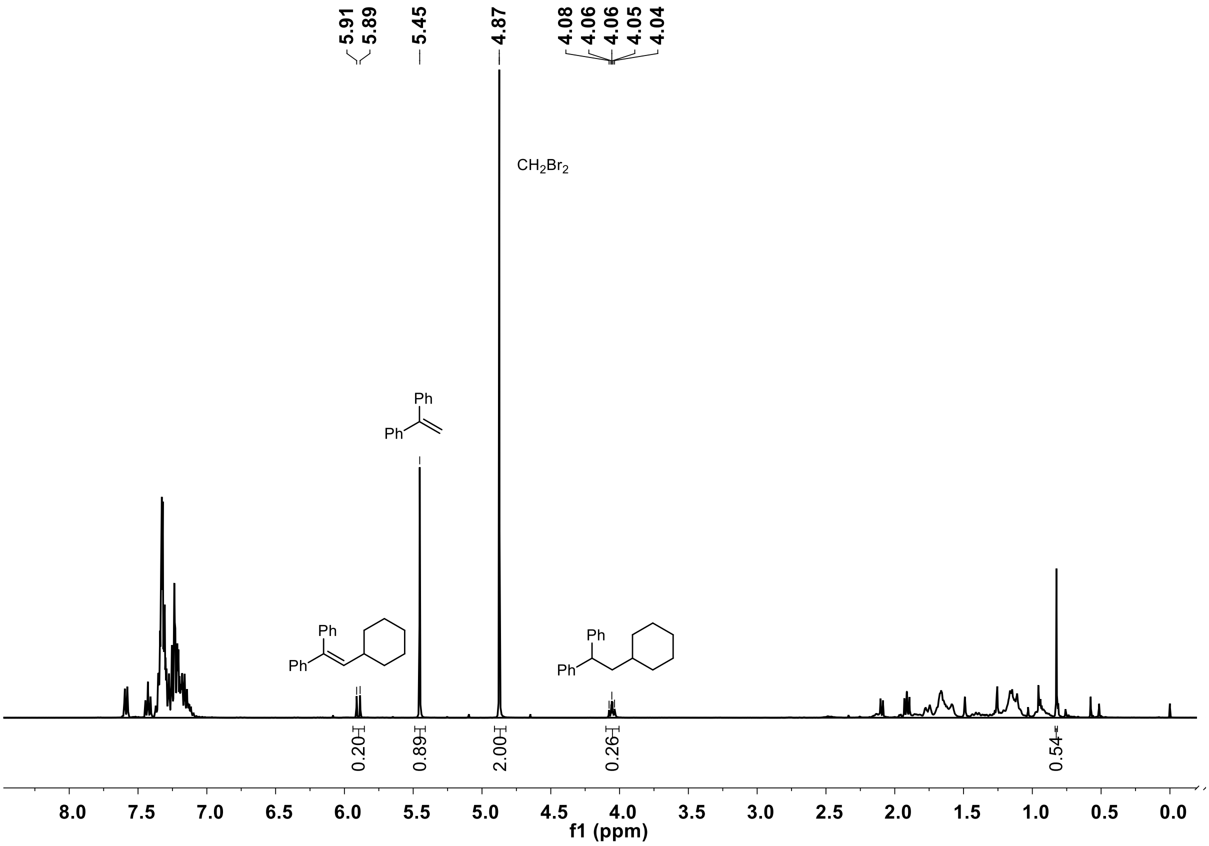




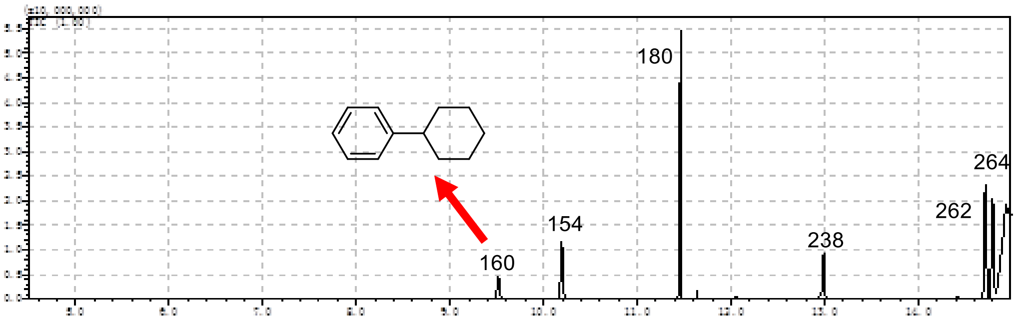
(2) 1,1-diphenylethene as the radical trapping reagent —— **General procedure**

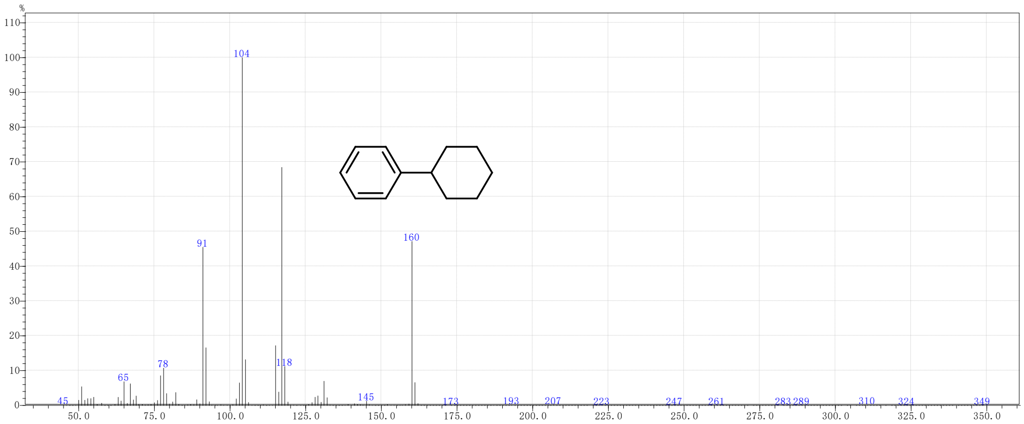
Ni(acac)$_2$ (12.9 mg, 0.05 mmol), Ph_3P (26.2 mg, 0.10 mmol), dppb (10.7 mg, 0.025 mmol) and K_3PO_4 (159.2 mg, 0.75 mmol) were added in a dried sealed tube in the glove box. Then the tube was sealed and transferred out. It was then filled with dry N_2. Under the protection of N_2, cyclohexane (5.0 mL) was injected into the tube *via* a syringe. After stirring for several minutes, *t*-BuOO*t*-Bu (146.2 mg, 1.0 mmol) was injected into the reaction tube by a microsyringe followed by the addition of phenylboronic acid (0.5 mmol) and 1,1-diphenylethene (135.2 mg, 0.75 mmol). The tube was then sealed and heated up to 130 ^{o}C and kept stirring for 10 hours. After completion of the reaction, the mixture was quenched with diluted hydrochloric acid. The solution was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and dried over sodium sulfate, further detected by GC/MS analysis and ^{1}H NMR analysis[1] using CH_2Br_2 (113.4 mg) as the internal standard.

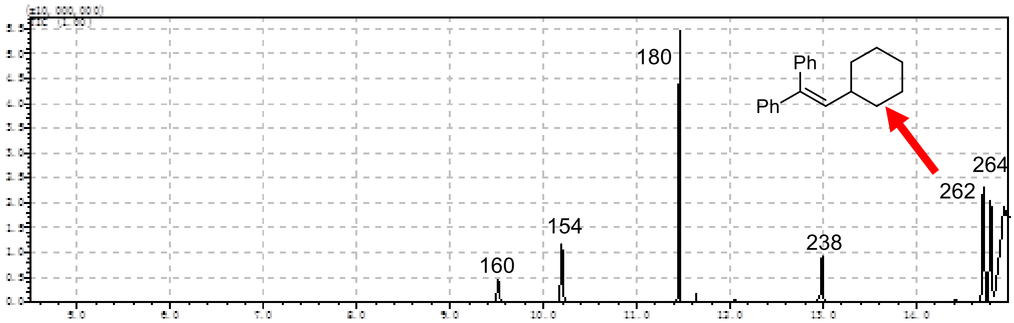
^{1}H NMR spectrum:

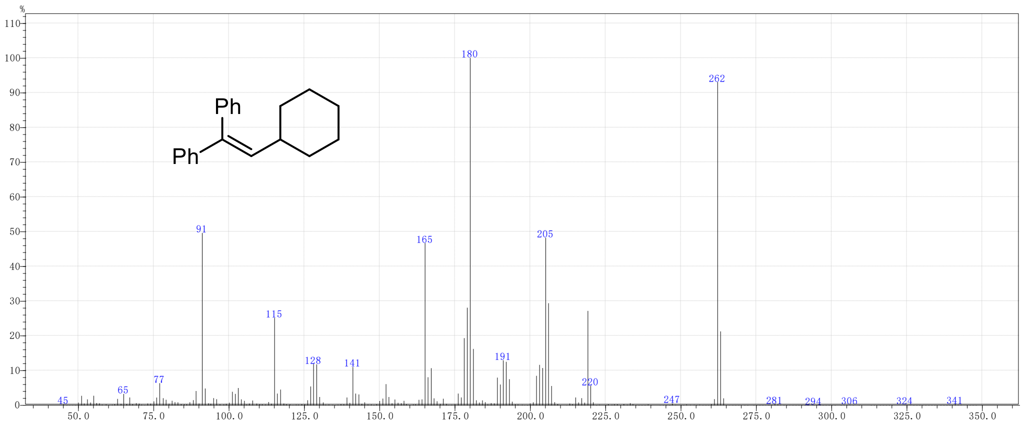


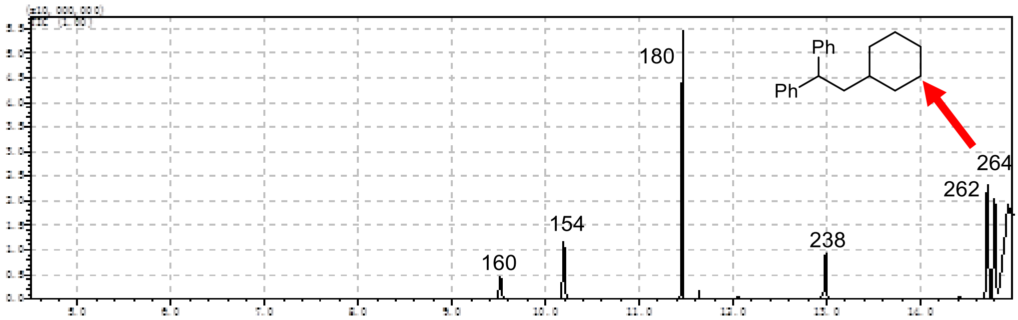
GC/MS spectrum:

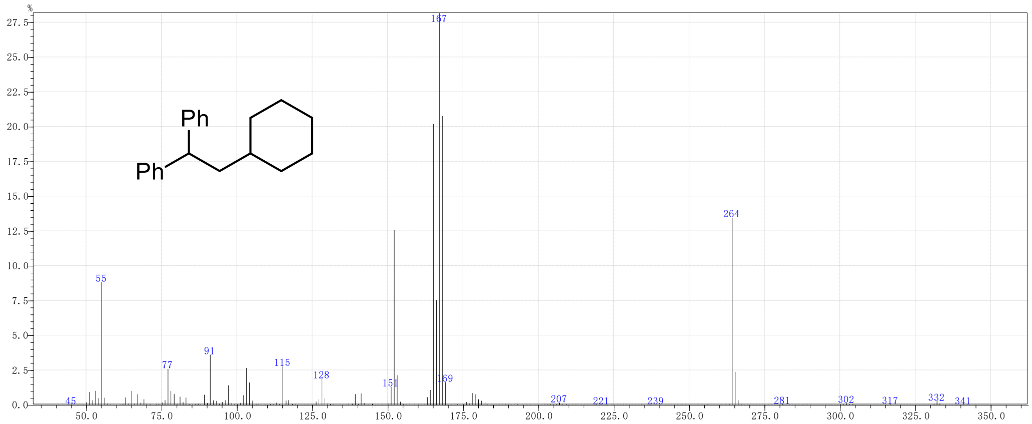









Ph
Ph
160
154
180
238
262
264

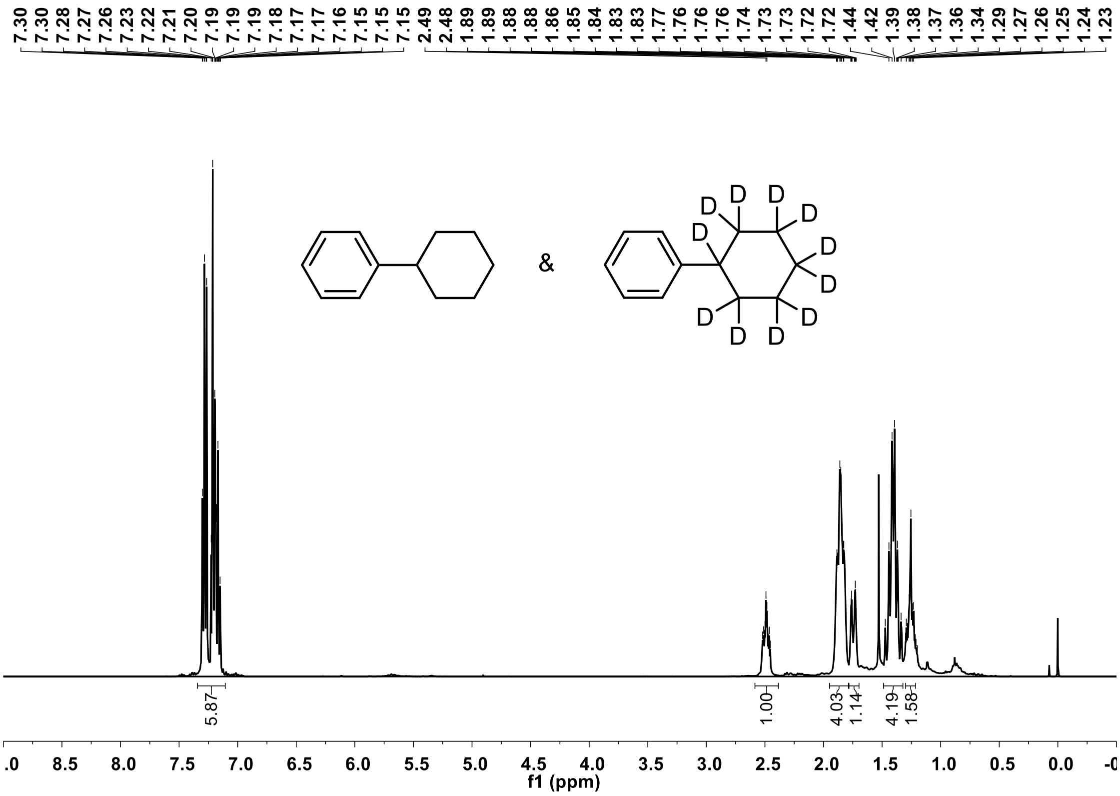

Ph
Ph
55
77
91
115
128
151
167
169
264

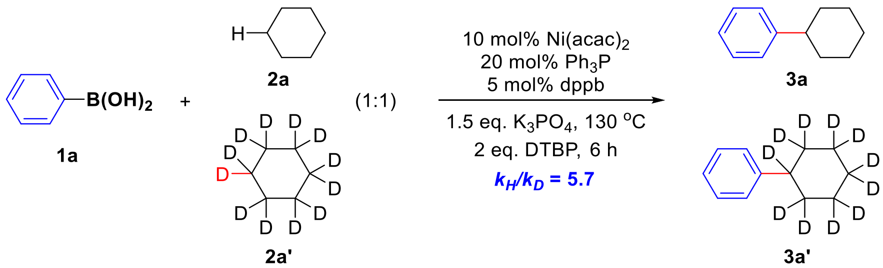
Deuteration experiment

1. Intermolecular Kinetic Isotopic Effect (KIE):

General procedure and characterization spectrum

Ni(acac)$_2$ (12.9 mg, 0.05 mmol), Ph$_3$P (26.2 mg, 0.10 mmol), dppb (10.7 mg, 0.025 mmol) and K$_3$PO$_4$ (159.2 mg, 0.75 mmol) were added in a dried sealed tube in the glove box. Then the tube was sealed and transferred out. It was then filled with dry N$_2$. Under the protection of N$_2$, cyclohexane (2.0 mL) and d_{12}-cyclohexane (2.0 mL) were injected into the tube *via* a syringe. After stirring for several minutes, *t*-BuOO*t*-Bu (146.2 mg, 1.0 mmol) was injected into the reaction tube by a microsyringe followed by the addition of phenylboronic acid (0.5 mmol). The tube was then sealed and heated up to 130 ^{o}C and kept stirring for 6 hours. After completion of the reaction, the mixture was quenched with diluted hydrochloric acid. The solution was extracted with ethyl acetate (3 x 5 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel (pure petroleum ether as the eluting agent) with a total yield of 38% and detected by ^{1}H NMR to determine the exact KIE value. From the following ^{1}H NMR spectrum, we can calculate the KIE value to be k_H/k_D = 5/(5.87-5) = 5.7.

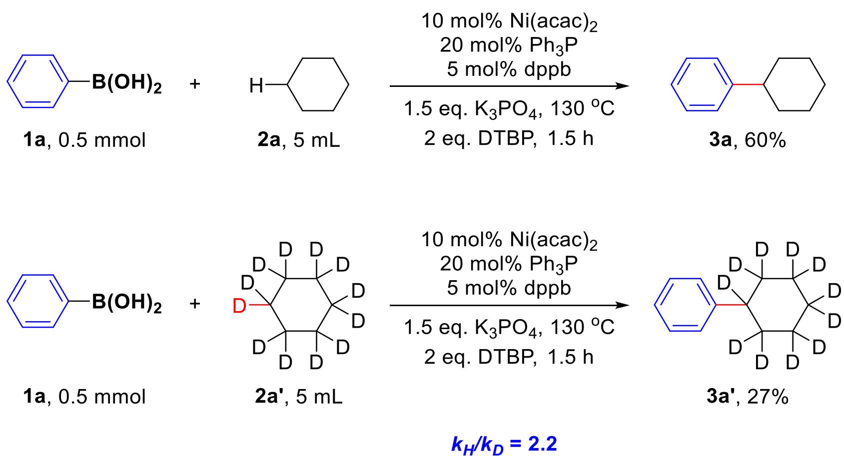




2. KIE Determined with Two Parallel Reactions:

General procedure and results:

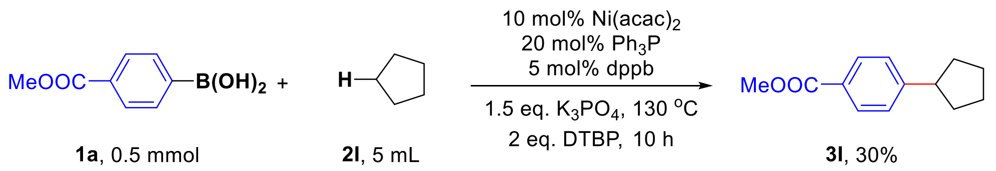
Ni(acac)$_2$ (12.9 mg, 0.05 mmol), Ph$_3$P (26.2 mg, 0.10 mmol), dppb (10.7 mg, 0.025 mmol) and K_3PO_4 (159.2 mg, 0.75 mmol) were added in two dried sealed tubes respectively in the glove box. Then the tubes were sealed and transferred out, further charged with dry N_2. Under the protection of N_2, cyclohexane (5.0 mL) and d_{12}-cyclohexane (5.0 mL) were injected respectively into the tubes *via* syringes. After stirring for several minutes, *t*-BuOO*t*-Bu (146.2 mg, 1.0 mmol) was injected into the two tubes by a microsyringe followed by the addition of phenylboronic acid (0.5 mmol). The tubes were then sealed and heated up to 130 °C and kept stirring for 1.5 hours. After completion of the reactions, the mixtures were quenched with diluted hydrochloric acid and detected by GC analysis with dibenzofuran as the internal standard. As a result, the desired coupling products were obtained in 60% and 27% yields, respectively, in which k_H/k_D = 2.2.

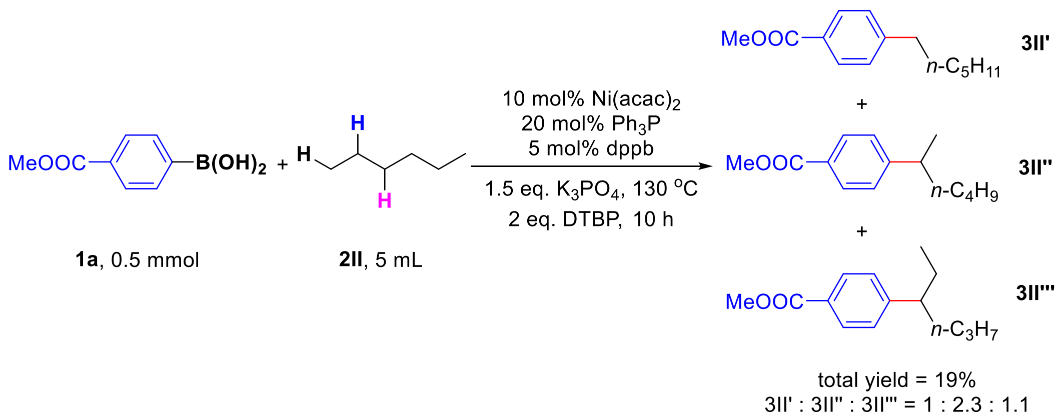


Reaction of simple alkanes

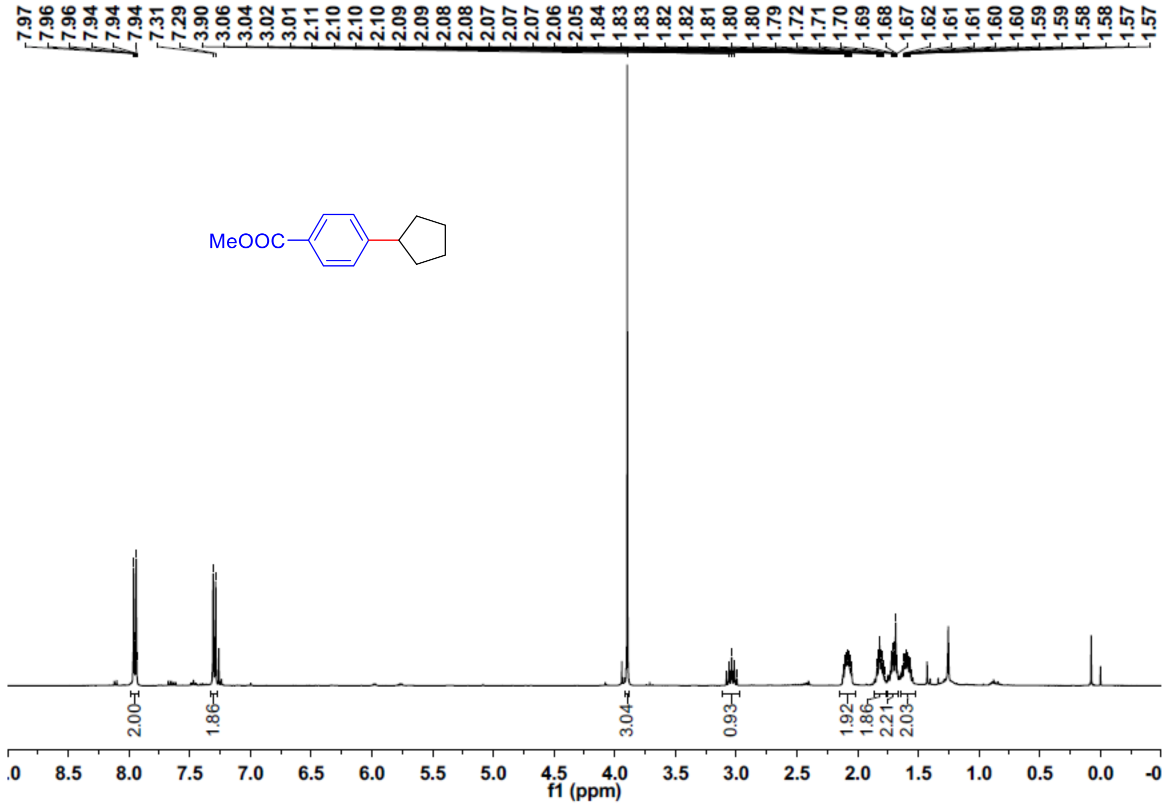
General procedure and results:

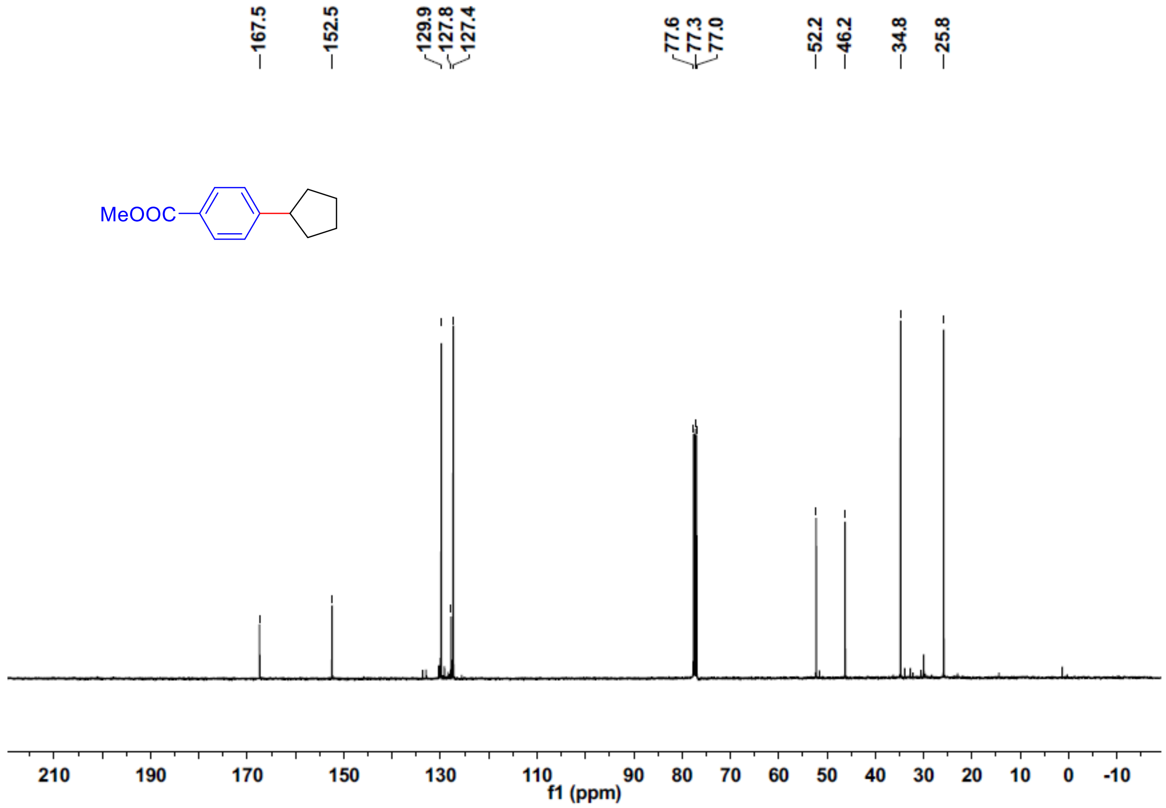
Ni(acac)$_2$ (12.9 mg, 0.05 mmol), Ph$_3$P (26.2 mg, 0.10 mmol), dppb (10.7 mg, 0.025 mmol) and K$_3$PO$_4$ (159.2 mg, 0.75 mmol) were added in a dried sealed tube in the glove box. Then the tube was sealed and transferred out. It was then filled with dry N$_2$. Under the protection of N$_2$, alkane (5.0 mL) was injected into the tube *via* a syringe. After stirring for several minutes, *t*-BuOO*t*-Bu (146.2 mg, 1.0 mmol) was injected into the reaction tube by a microsyringe followed by the addition of (4-(methoxycarbonyl)phenyl)boronic acid (0.5 mmol). The tube was then sealed and heated up to 130 °C and kept stirring for 10 hours. After completion of the reaction, the mixture was quenched with diluted hydrochloric acid. The solution was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel.

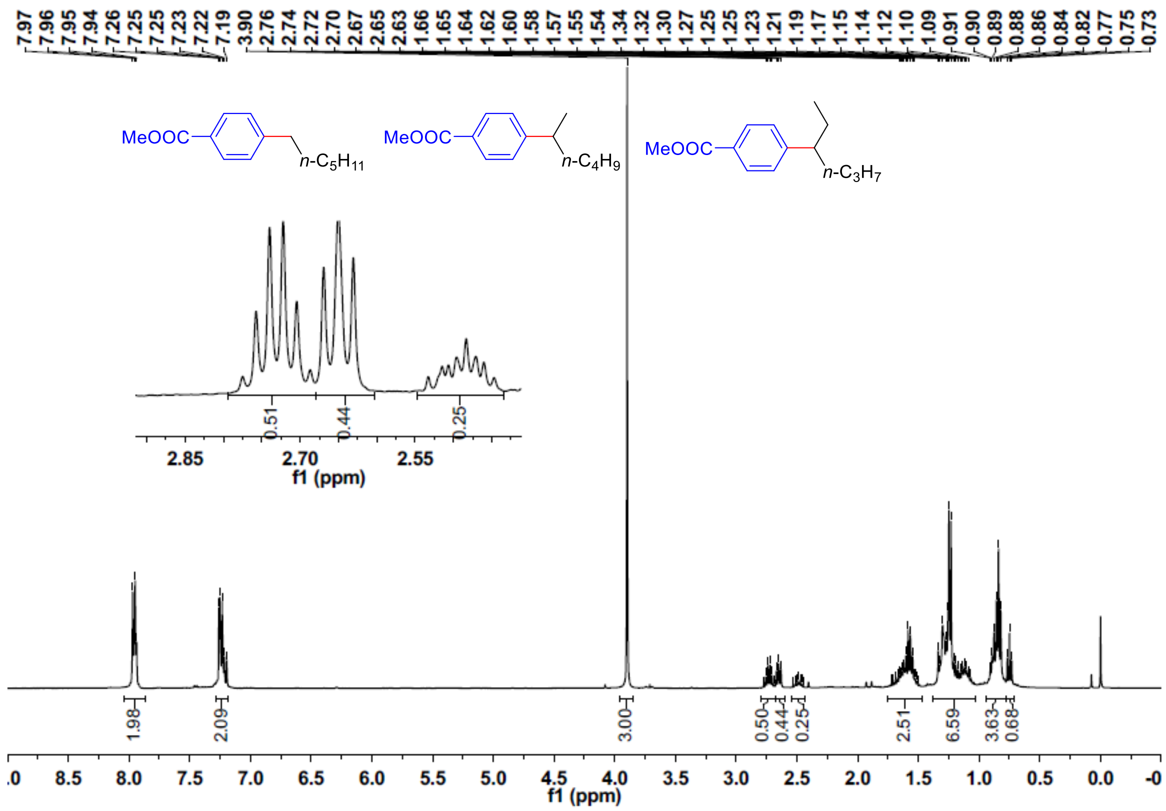


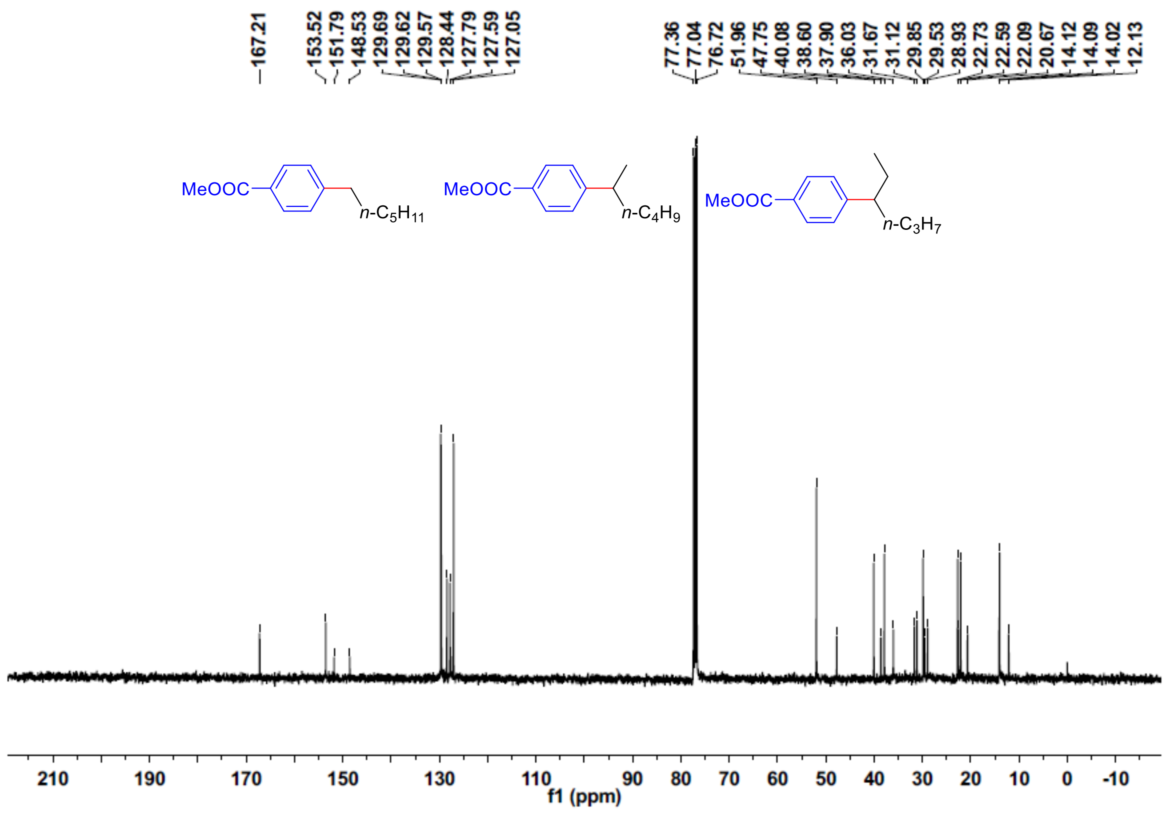


Spectrum Characterization:

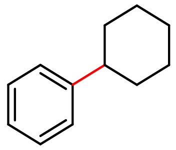








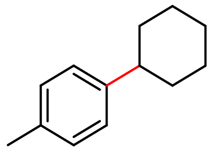
Detailed descriptions for products



Cyclohexylbenzene (3a)[2]: 52.8 mg. Isolated yield = 66%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.24 (m, 2H), 7.24 – 7.10 (m, 3H), 2.60 -2.36 (m, 1H), 1.92 – 1.79 (m, 4H), 1.78 – 1.70 (m, 1H), 1.48 – 1.31 (m, 4H), 1.31 – 1.19 (m, 1H).

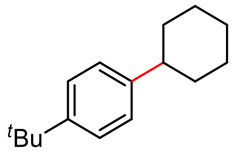
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 128.5, 127.1, 126.0, 44.9, 34.7, 27.2, 26.4.



1-Cyclohexyl-4-methylbenzene (3b)[2]: 53.1 mg. Isolated yield = 61%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 4H), 2.52 – 2.40 (m, 1H), 2.31 (s, 3H), 1.92 – 1.77 (m, 4H), 1.78 – 1.68 (m, 1H), 1.46 – 1.32 (m, 4H), 1.30 – 1.18 (m, 1H).

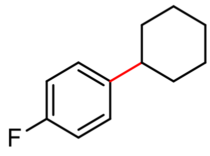
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 135.4, 129.2, 127.0, 44.4, 34.9, 27.2, 26.5, 21.3.



1-(*tert*-Butyl)-4-cyclohexylbenzene (3c)[3]: 55.1 mg. Isolated yield = 51%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.15 – 7.13 (m, 2H), 2.53 – 2.39 (m, 1H), 1.94 – 1.78 (m, 4H), 1.77 – 1.68 (m, 1H), 1.47 – 1.34 (m, 4H), 1.32 – 1.24 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 145.3, 126.7, 125.4, 44.3, 34.8, 34.6, 31.7, 27.3, 26.5.

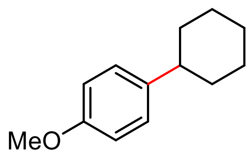


1-Cyclohexyl-4-fluorobenzene (3d)[2]: 53.4 mg. Isolated yield = 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.10 (m, 2H), 7.00 – 6.92 (m, 2H), 2.55 – 2.38 (m, 1H), 1.92 – 1.78 (m, 4H), 1.78 – 1.69 (m, 1H), 1.45 – 1.30 (m, 4H), 1.29 – 1.19 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1 (d, *J* = 243.0 Hz), 143.7 (d, *J* = 3.1 Hz), 128.1 (d, *J* = 7.7 Hz), 114.9 (d, *J* = 20.9 Hz), 44.1, 34.9, 27.1, 26.4.

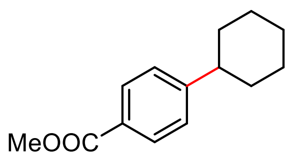
^{19}F NMR (377 MHz, $CDCl_3$) δ -117.95.



1-Cyclohexyl-4-methoxybenzene (3e)[2]: 39.9 mg. Isolated yield = 42%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.07 (m, 2H), 6.93 – 6.75 (m, 2H), 3.78 (s, 3H), 2.49 – 2.39 (m, 1H), 1.88 – 1.77 (m, 4H), 1.77 – 1.69 (m, 1H), 1.44 – 1.31 (m, 4H), 1.29 – 1.18 (m, 1H).

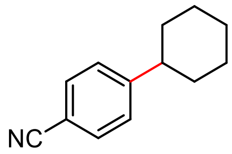
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 140.6, 127.9, 113.9, 55.5, 43.9, 35.0, 27.2, 26.4.



Methyl 4-cyclohexylbenzoate (3f)[4]: 65.4 mg. Isolated yield = 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 2H), 7.32 – 7.22 (m, 2H), 3.89 (s, 3H), 2.61 – 2.47 (m, 1H), 1.93 – 1.80 (m, 4H), 1.80 – 1.71 (m, 1H), 1.49 – 1.33 (m, 4H), 1.32 – 1.20 (m, 1H).

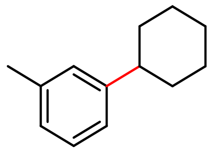
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 153.7, 129.9, 127.9, 127.1, 52.2, 44.9, 34.4, 27.0, 26.3.



4-Cyclohexylbenzonitrile (3g)[5]: 62.0 mg. Isolated yield = 67%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.31 – 7.29 (m, 2H), 2.62 – 2.47 (m, 1H), 1.86 (m, 4H), 1.80 – 1.73 (m, 1H), 1.47 – 1.34 (m, 4H), 1.31 – 1.22 (m, 1H).

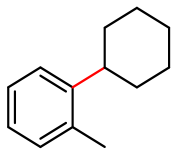
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 132.4, 127.9, 119.5, 109.7, 45.0, 34.2, 26.8, 26.2.



1-Cyclohexyl-3-methylbenzene (3h)[6]: 44.4 mg. Isolated yield = 51%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 1H), 7.06 – 6.93 (m, 3H), 2.50 – 2.40 (m, 1H), 2.33 (s, 3H), 1.93 – 1.78 (m, 4H), 1.79 – 1.69 (m, 1H), 1.48 – 1.30 (m, 4H), 1.30 – 1.19 (m, 1H).

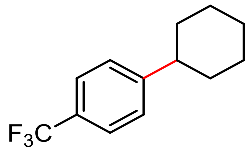
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 138.0, 128.4, 127.9, 126.8, 124.1, 44.8, 34.8, 27.2, 26.5, 21.8.



1-Cyclohexyl-2-methylbenzene (3i)[2]: 46.1 mg. Isolated yield = 53%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.10 (m, 3H), 7.09 – 7.05 (m, 1H), 2.78 – 2.62 (m, 1H), 2.33 (s, 3H), 1.88 – 1.71 (m, 5H), 1.49 – 1.34 (m, 4H), 1.34 – 1.21 (m, 1H).

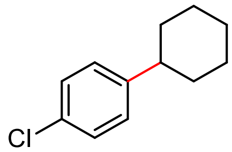
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 135.4, 130.4, 126.3, 125.7, 125.6, 40.3, 33.9, 27.5, 26.6, 19.6.



1-Cyclohexyl-4-(trifluoromethyl)benzene (3j)[7]: 78.7 mg. Isolated yield = 69%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.62 – 2.49 (m, 1H), 1.93 – 1.80 (m, 4H), 1.80 – 1.72 (m, 1H), 1.49 – 1.32 (m, 4H), 1.33 – 1.18 (m, 1H).

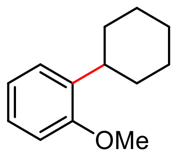
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 128.1 (q, *J* = 32.3 Hz), 127.2, 125.2 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272.7 Hz), 44.5, 34.2, 26.7, 26.0.



1-Chloro-4-cyclohexylbenzene (3k)[8]: 52.7 mg. Isolated yield = 54%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.23 (m, 2H), 7.14-7.12 (m, 2H), 2.58 – 2.34 (m, 1H), 1.85-1.83 (m, 4H), 1.76-1.73 (m, 1H), 1.45 – 1.29 (m, 4H), 1.29 – 1.16 (m, 1H).

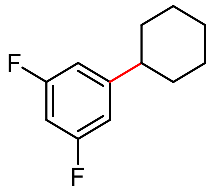
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 131.5, 128.6, 128.4, 44.2, 34.7, 27.1, 26.3.



1-Cyclohexyl-2-methoxybenzene (3l)[9]: 58.9 mg. Isolated yield = 62%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.12 (m, 2H), 6.92 (td, *J* = 7.4, 0.8 Hz, 1H), 6.85 – 6.83 (m, 1H), 3.81 (s, 3H), 2.99 – 2.92 (m, 1H), 1.87 – 1.79 (m, 4H), 1.79 – 1.70 (m, 1H), 1.49 – 1.31 (m, 4H), 1.30 – 1.21 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 136.5, 126.8, 126.7, 120.8, 110.6, 55.6, 37.0, 33.5, 27.4, 26.7.



1-Cyclohexyl-3,5-difluorobenzene (3m)[10]: 42.1 mg. Isolated yield = 43%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.67 (m, 2H), 6.60 (tt, *J* = 9.0, 2.3 Hz, 1H), 2.55 – 2.41 (m, 1H), 1.93 – 1.79 (m, 4H), 1.75 (d, *J* = 12.4 Hz, 1H), 1.45 – 1.29 (m, 4H), 1.29 – 1.19 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (dd, *J* = 247.1, 13.0 Hz), 152.3 (t, *J* = 8.4 Hz), 109.8 (dd, *J* = 18.2 Hz, 6.3 Hz), 101.3 (t, *J* = 25.5 Hz), 44.6 (t, *J* = 1.8 Hz), 34.3, 26.9, 26.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.90.

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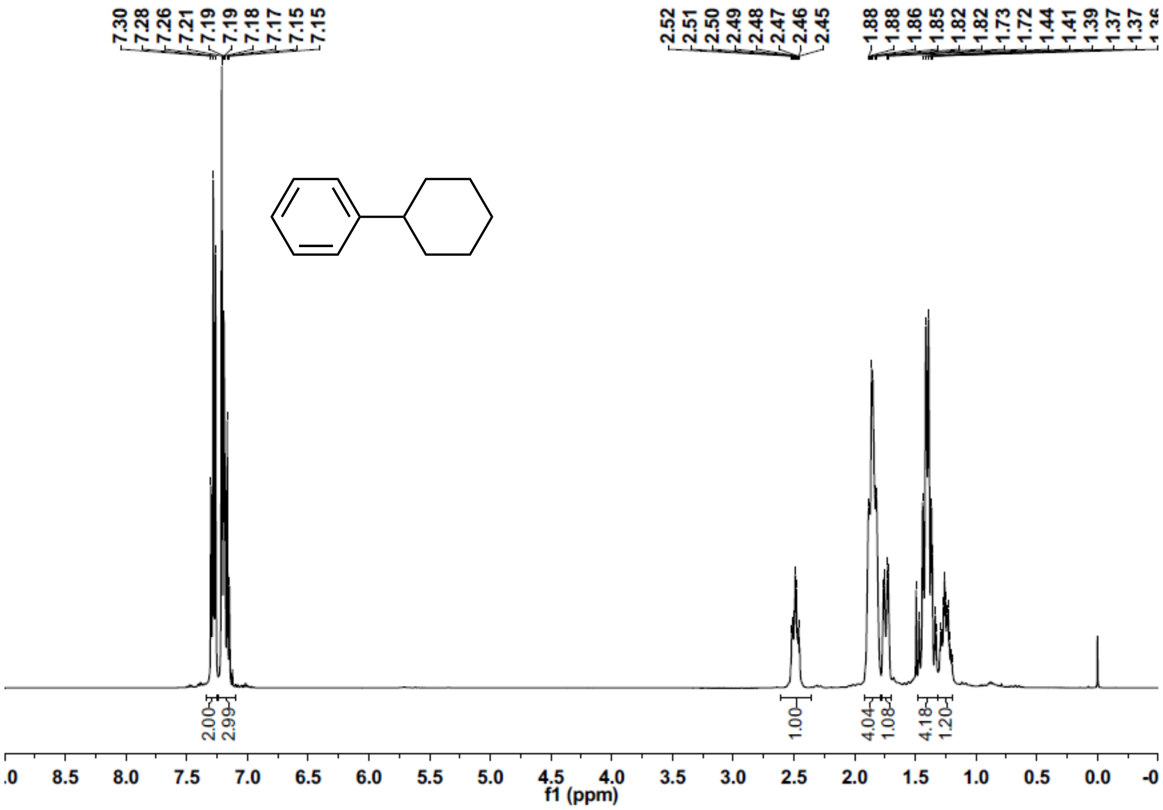
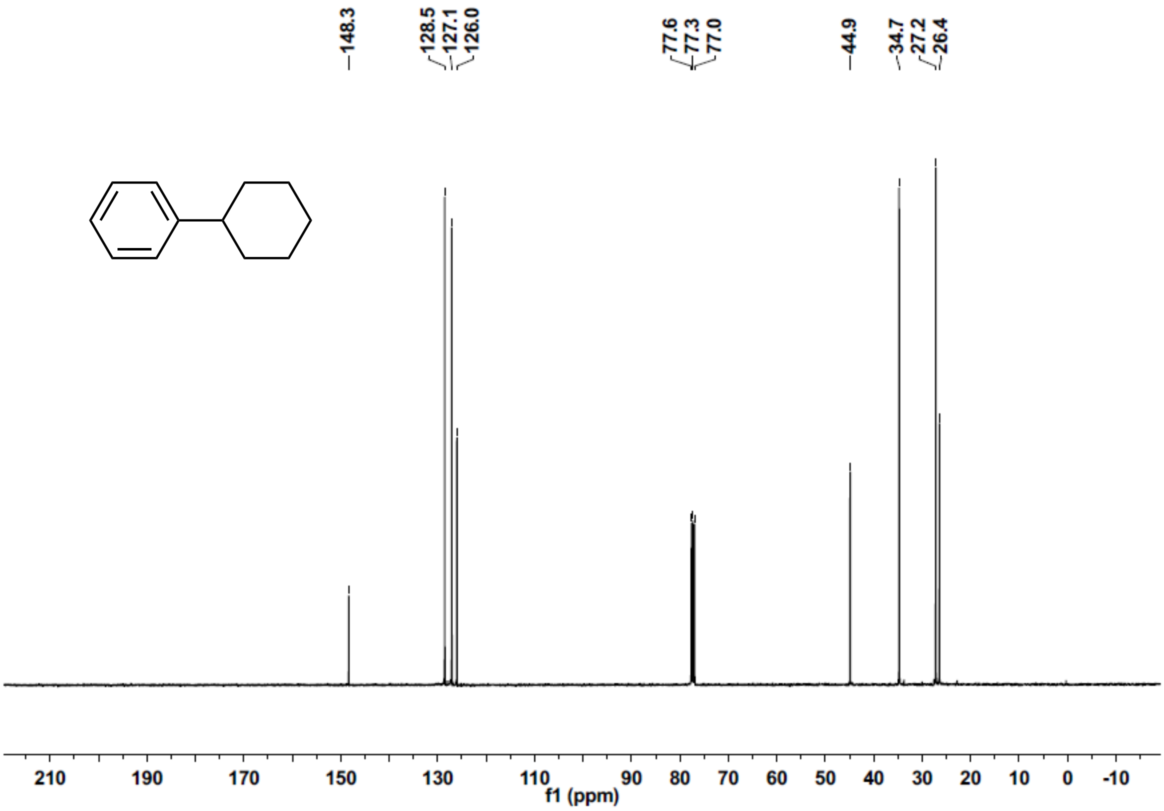
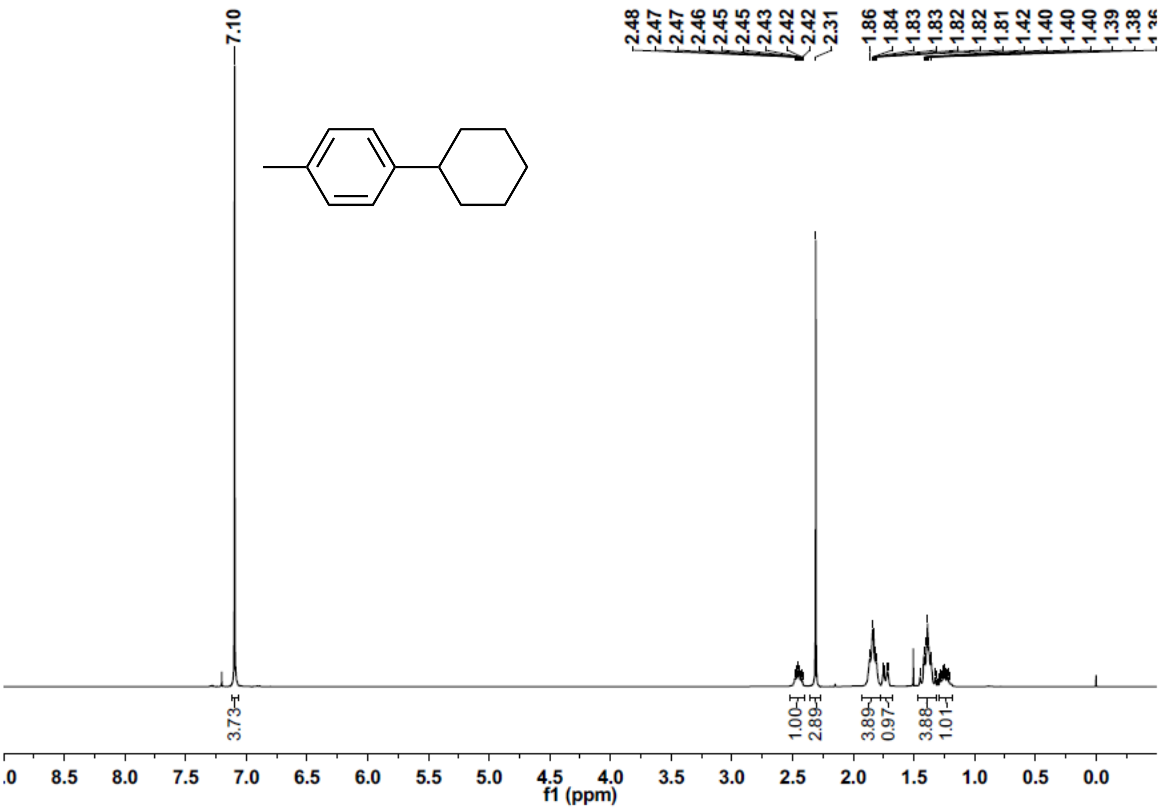
Copies of Products ^{1}H NMR and ^{13}C NMR:

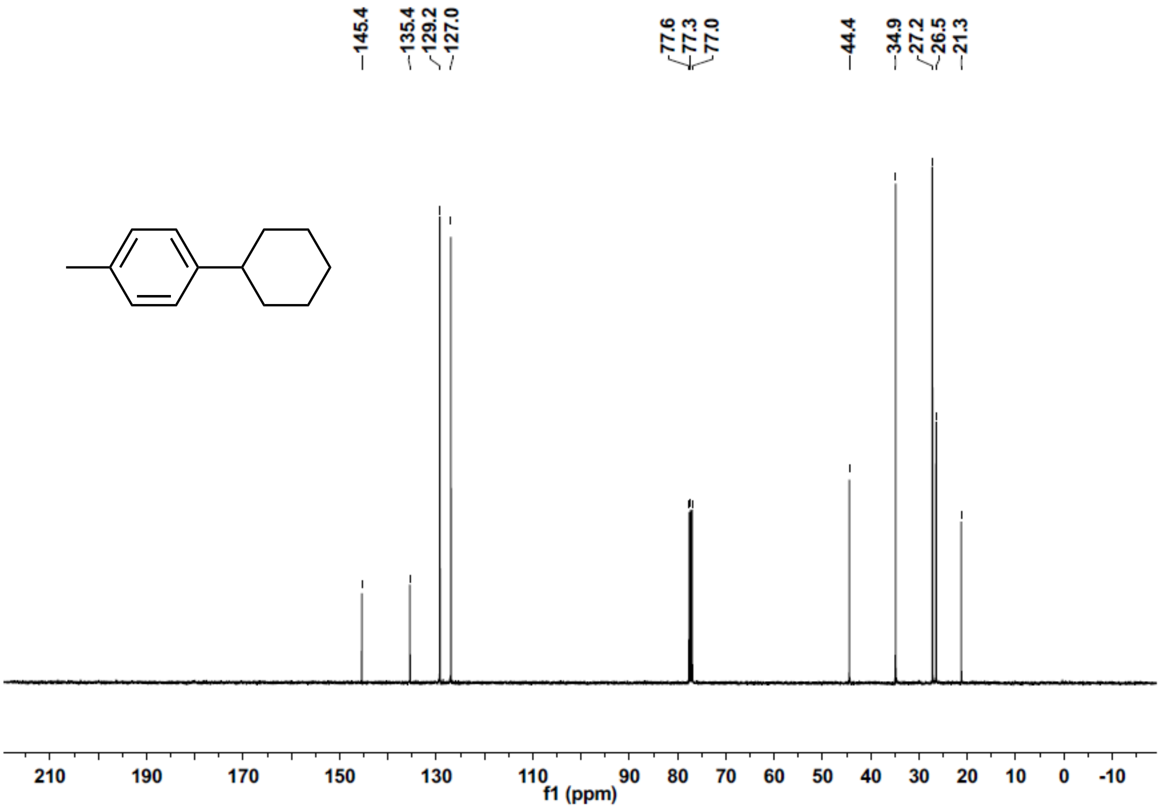
3a





3b





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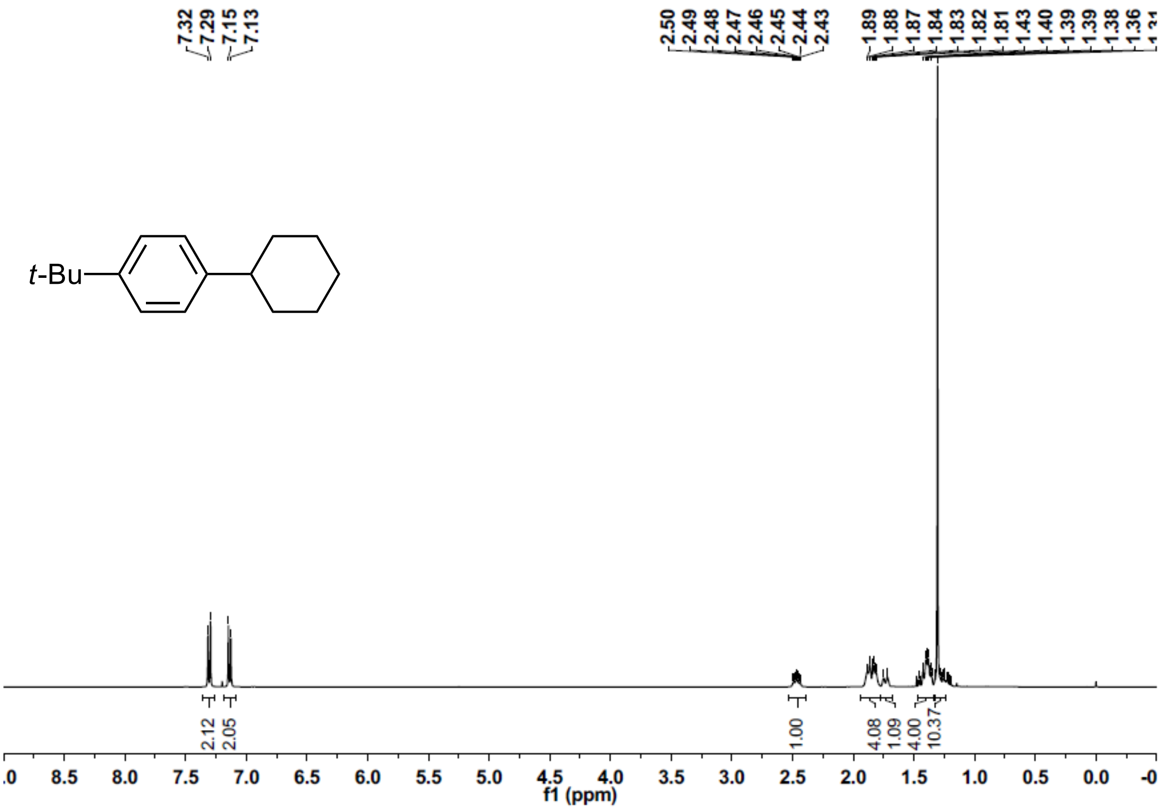
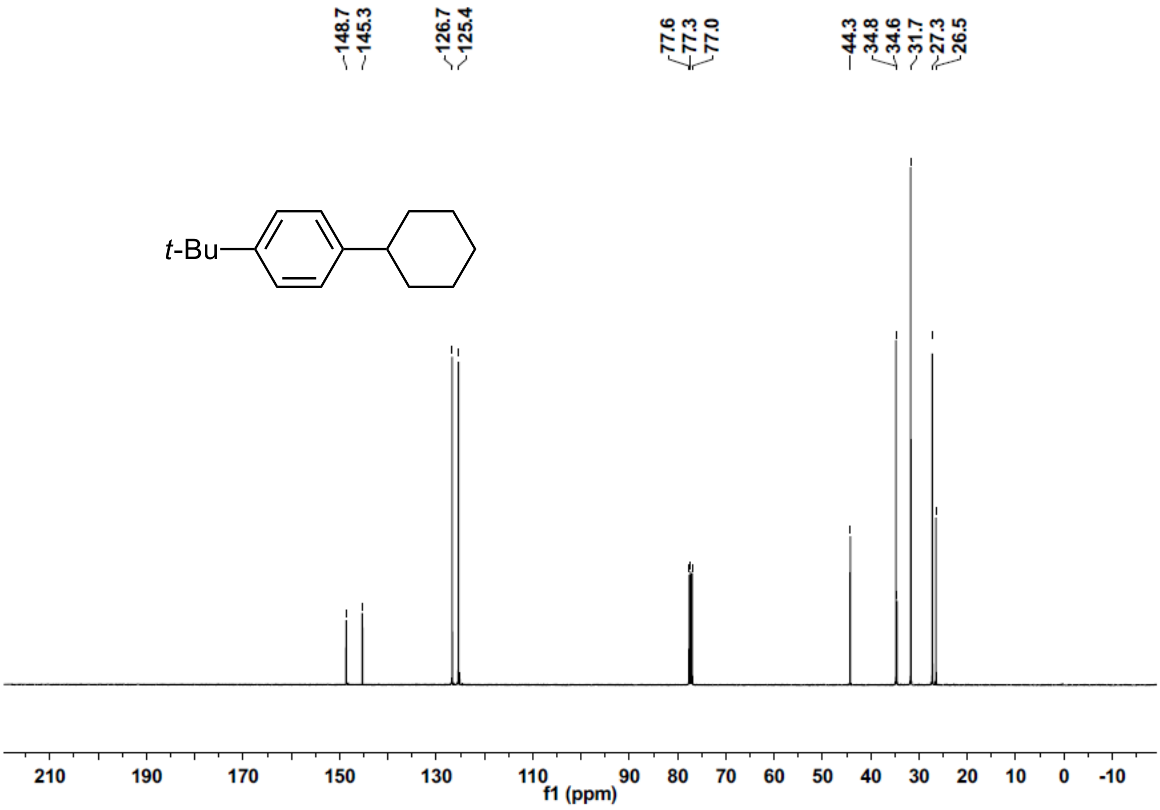
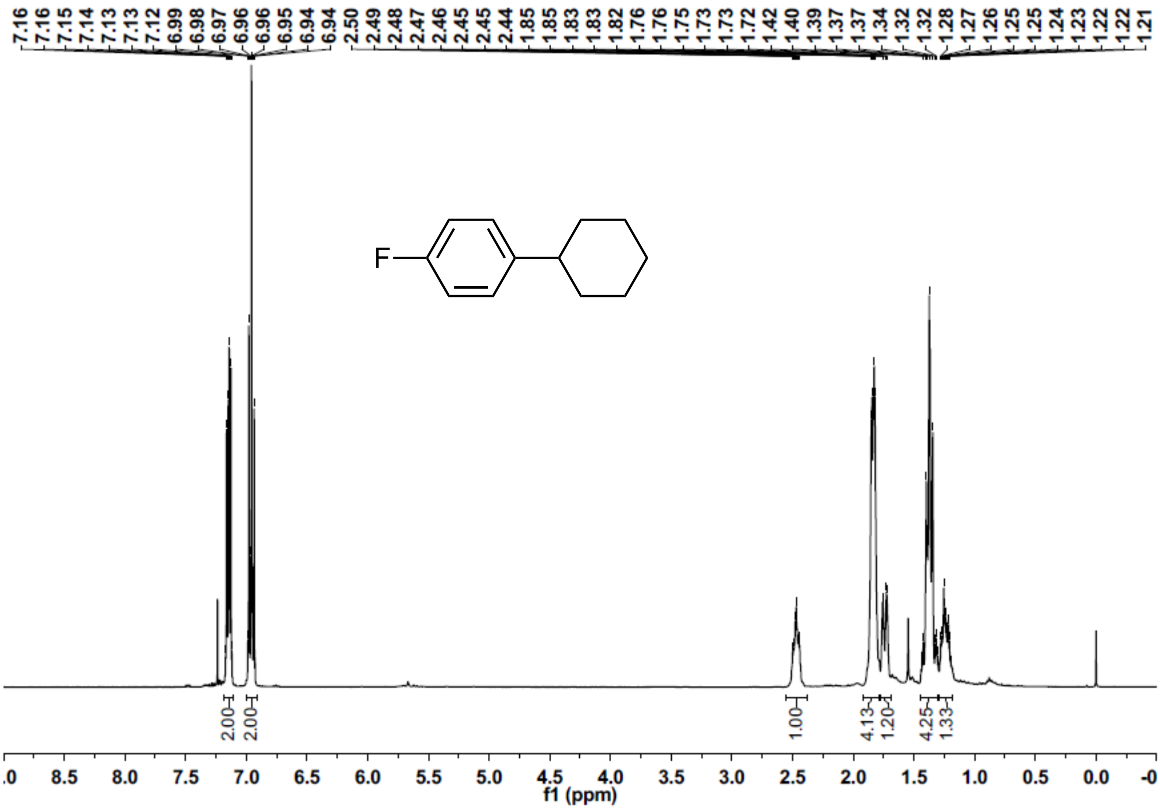


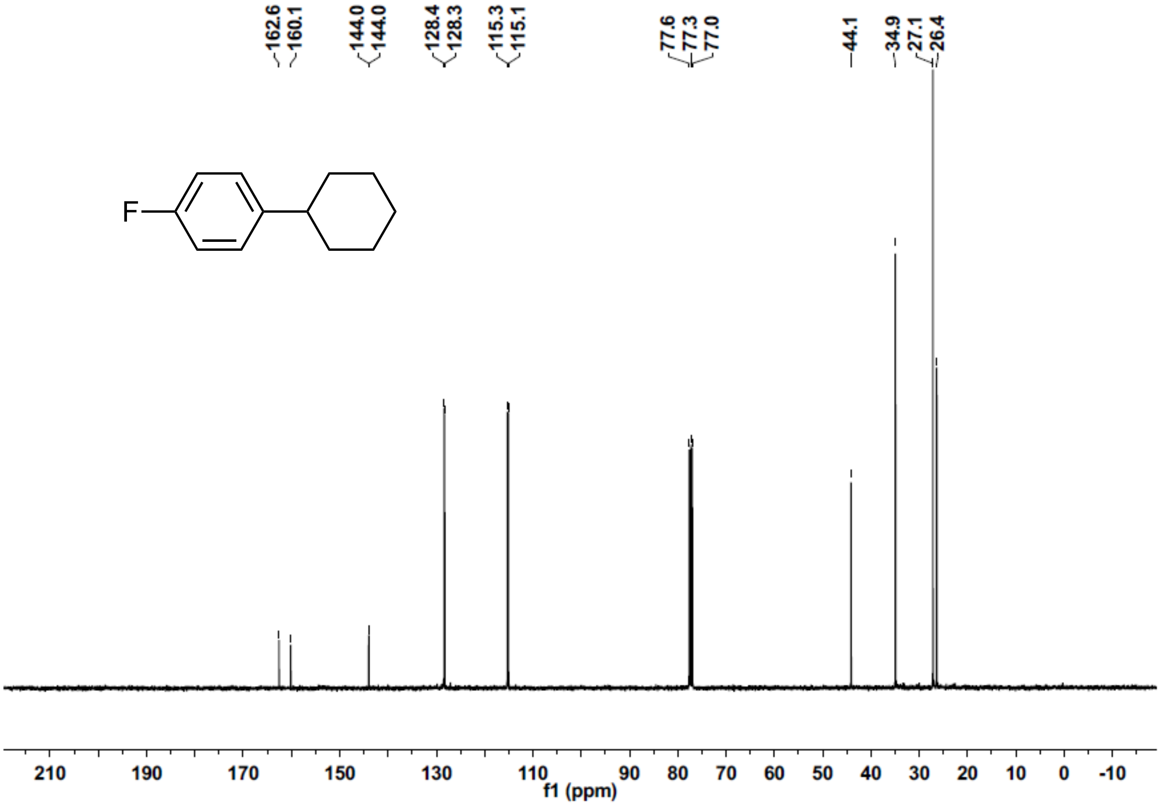
t-Bu
f1 (ppm)

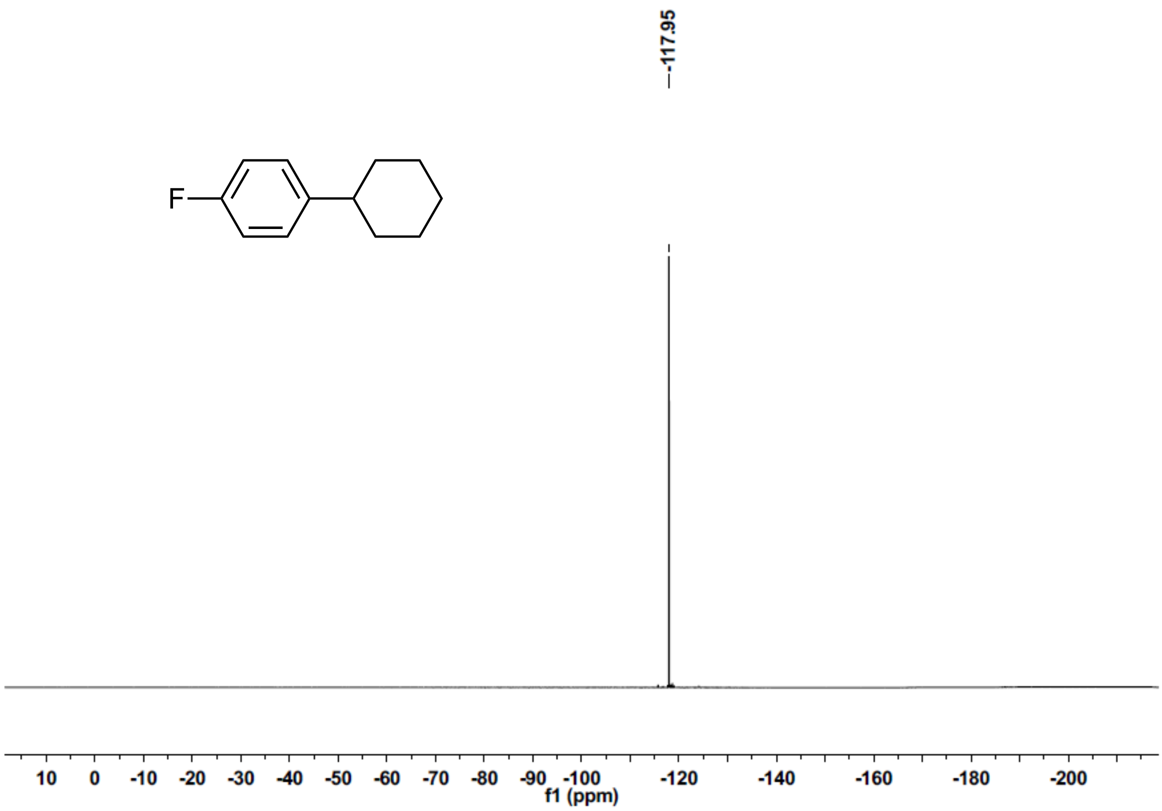


t-Bu
148.7
145.3
126.7
125.4
77.6
77.3
77.0
44.3
34.8
34.6
31.7
27.3
26.5
f1 (ppm)

3d







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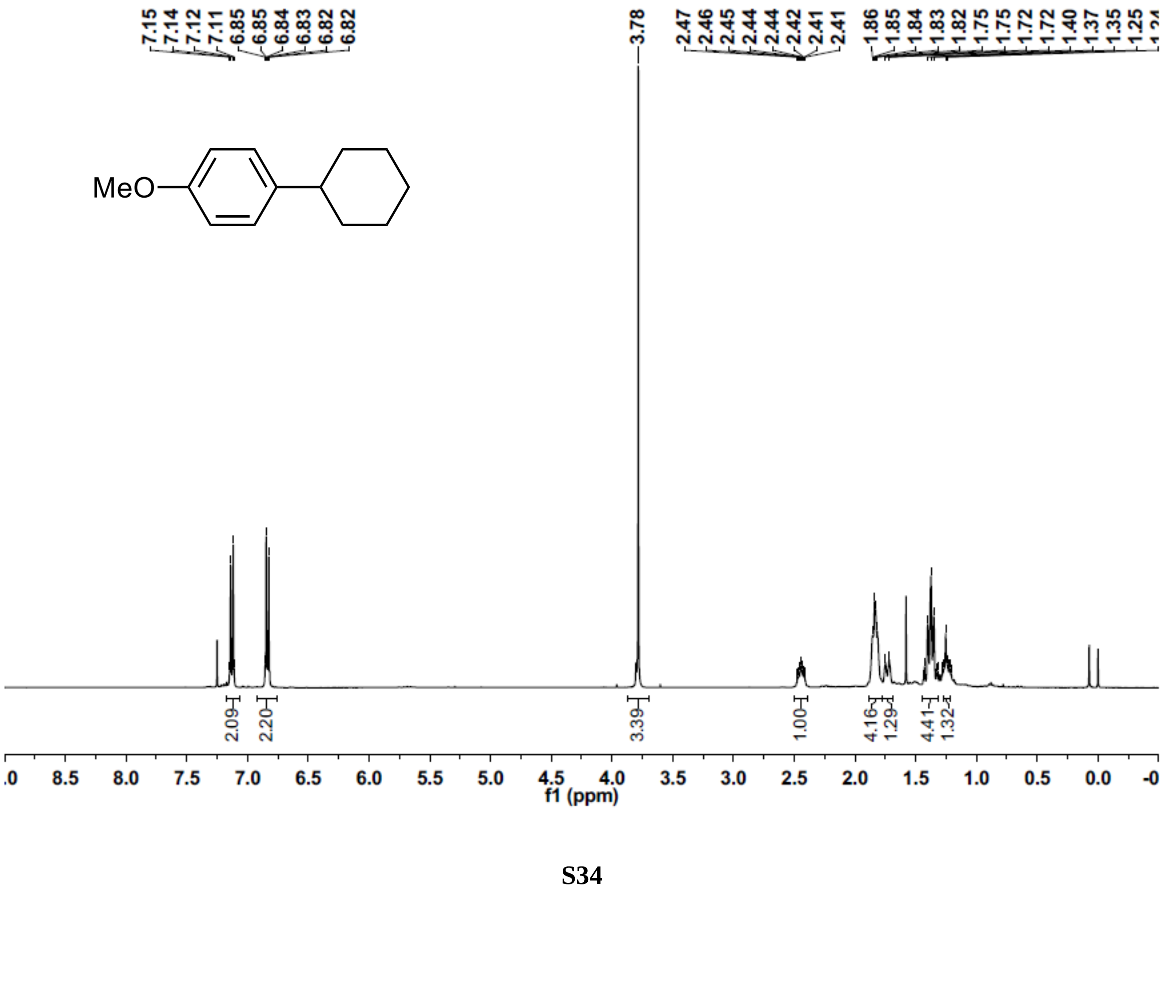

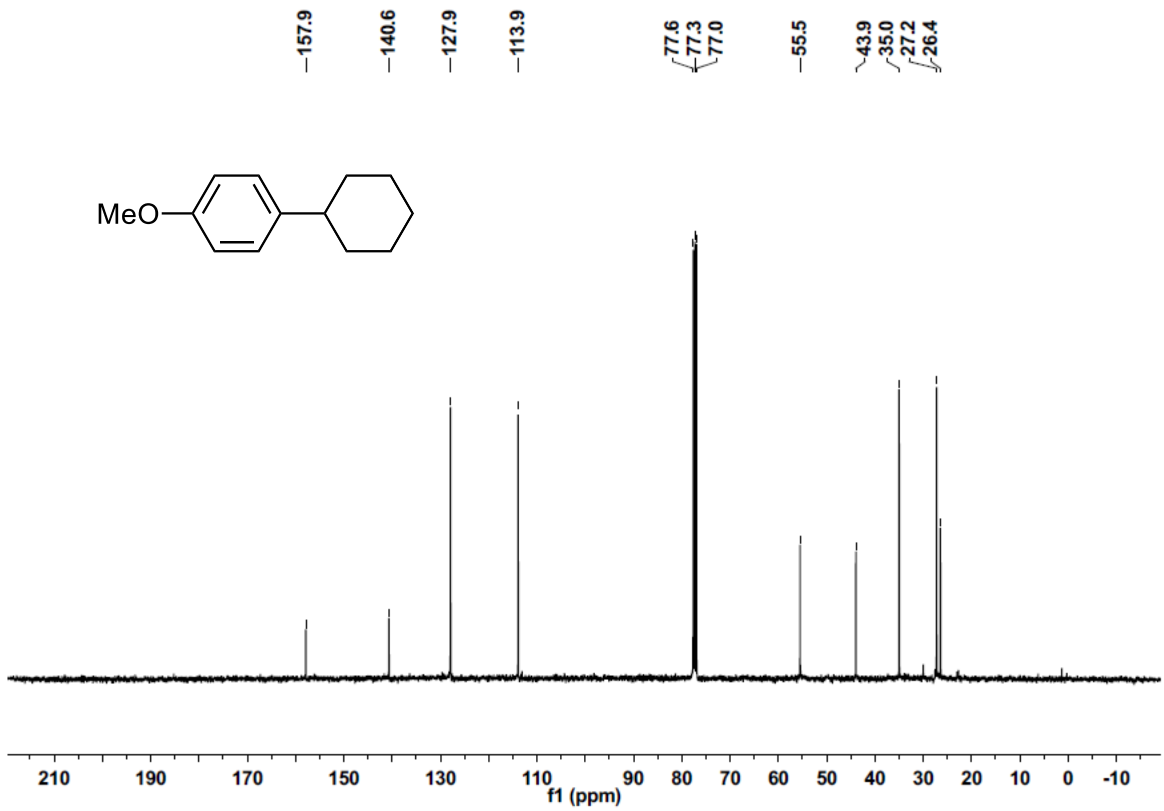

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113.9
77.6
77.3
77.0
55.5
43.9
35.0
27.2
26.4
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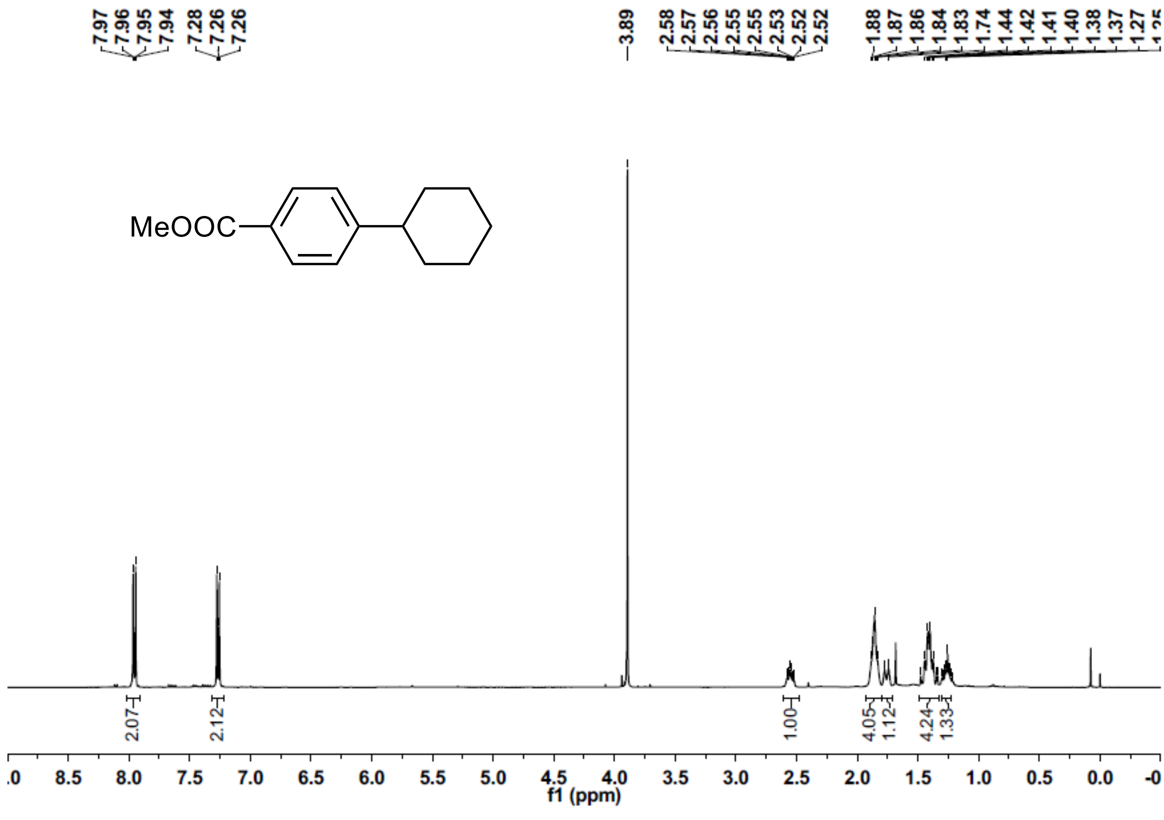
f1 (ppm)

3f



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2.55
2.53
2.52
2.52
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1.86
1.84
1.83
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1.44
1.42
1.41
1.40
1.38
1.37
1.27
2.07
2.12
1.00
4.05
1.12
4.24
1.33
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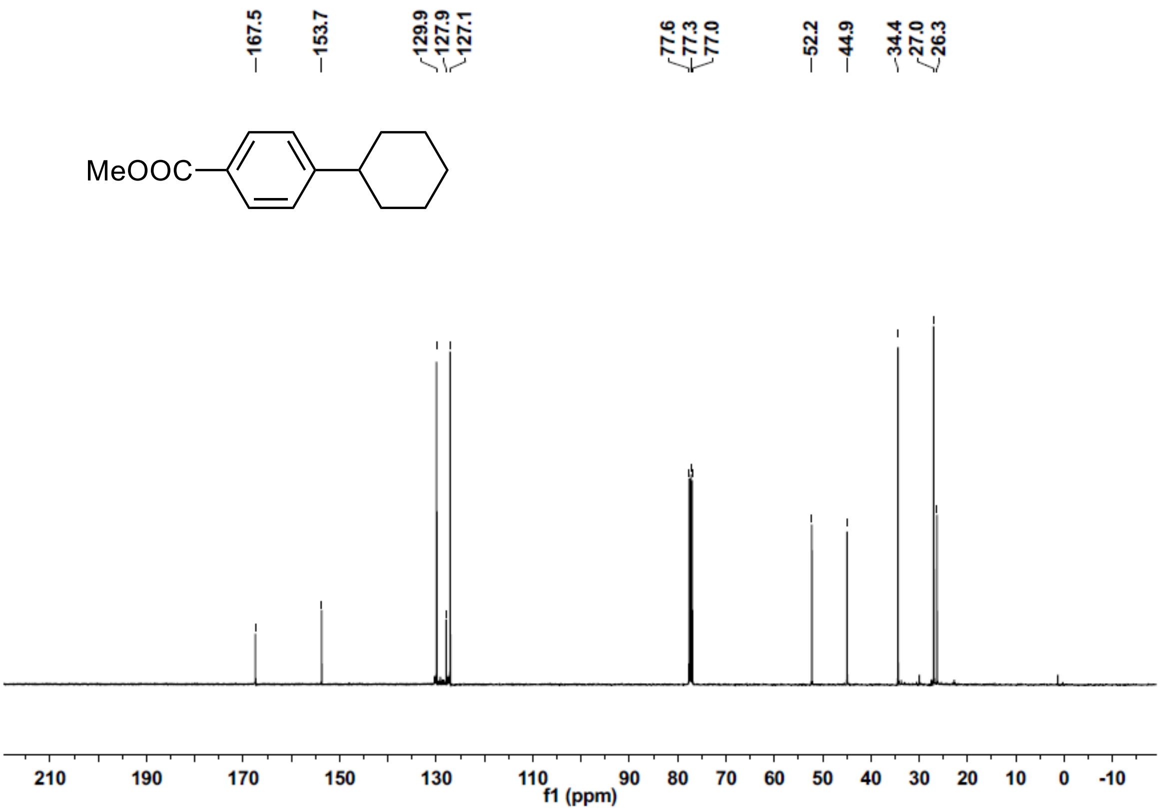
f1 (ppm)



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153.7
129.9
127.9
127.1
77.6
77.3
77.0
52.2
44.9
34.4
27.0
26.3
MeOOC
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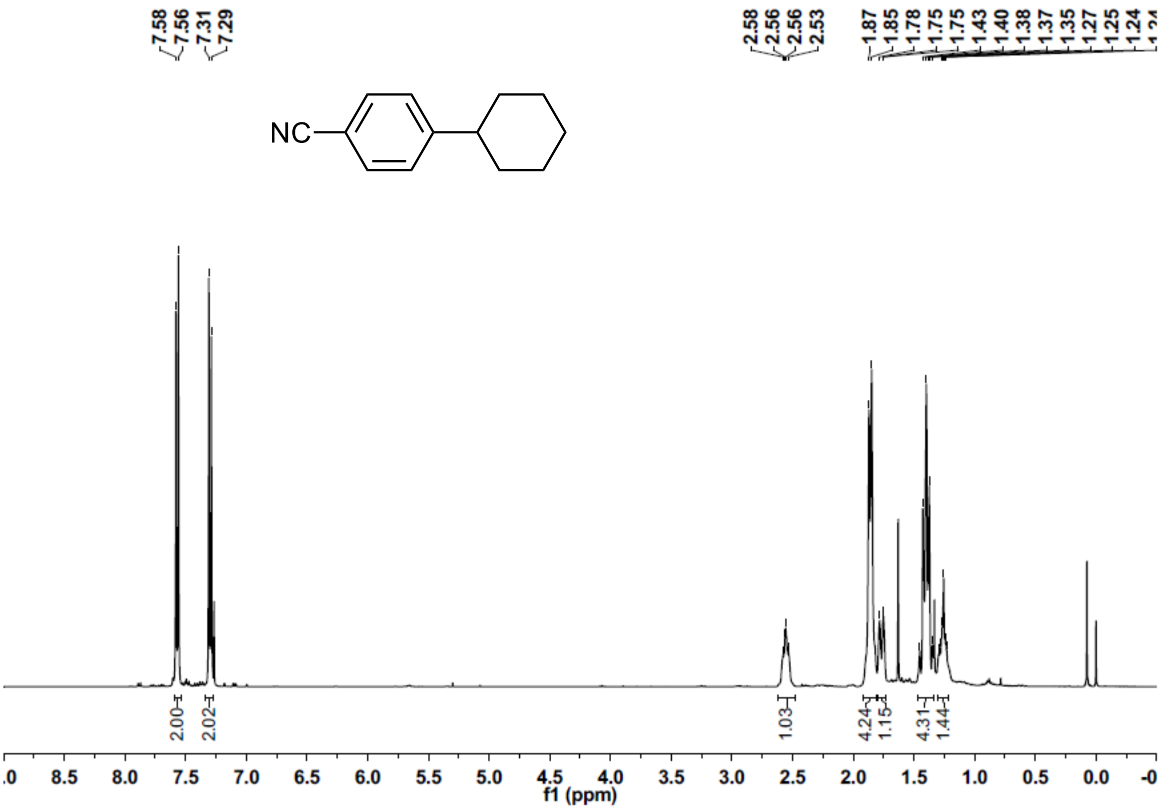
f1 (ppm)

3g



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1.40
1.38
1.37
1.35
1.27
1.25
1.24
NC
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2.02
1.03
4.24
1.15
4.31
1.44
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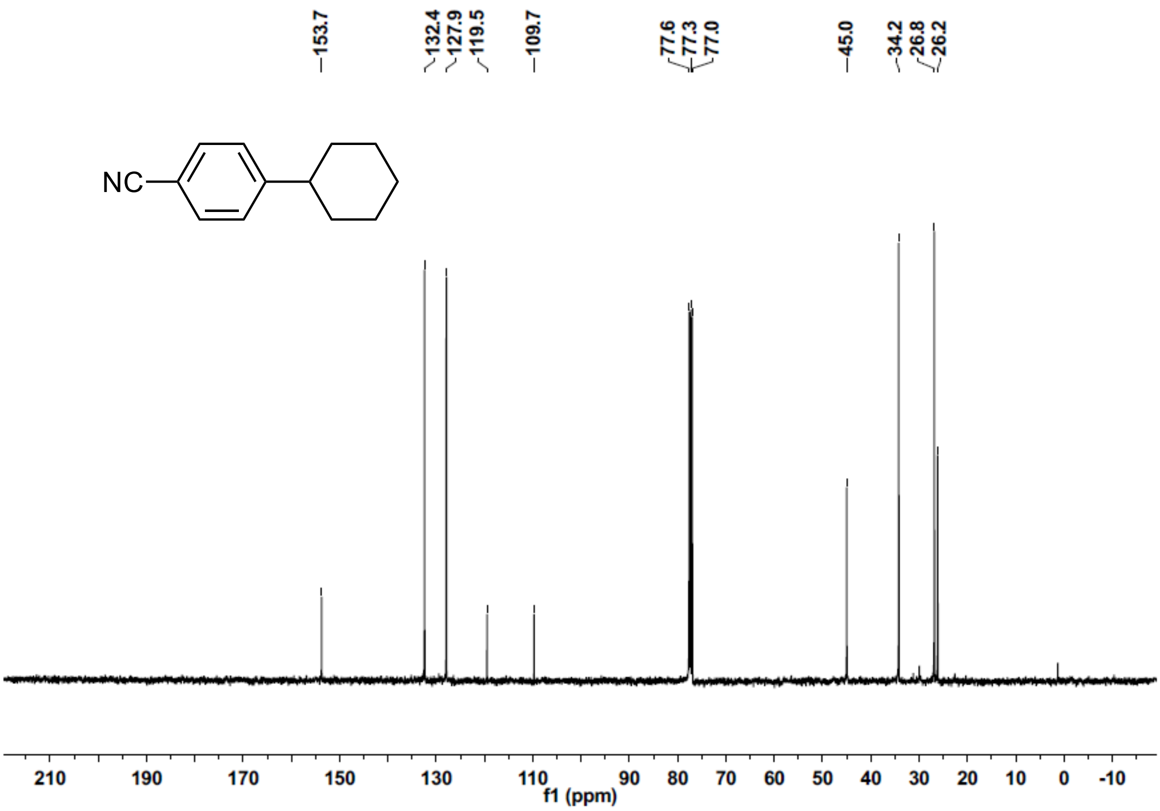
f1 (ppm)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127.9
119.5
109.7
77.6
77.3
77.0
45.0
34.2
26.8
26.2
NC
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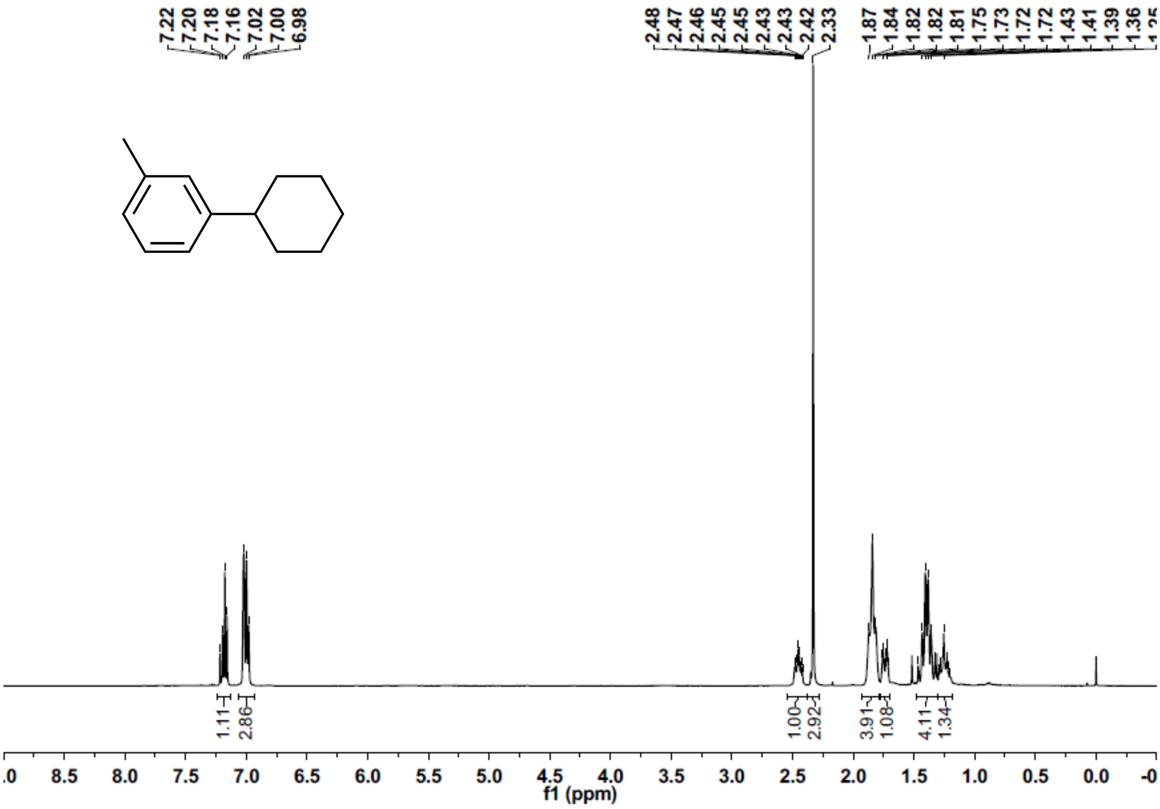
f1 (ppm)

3h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4.11
1.34
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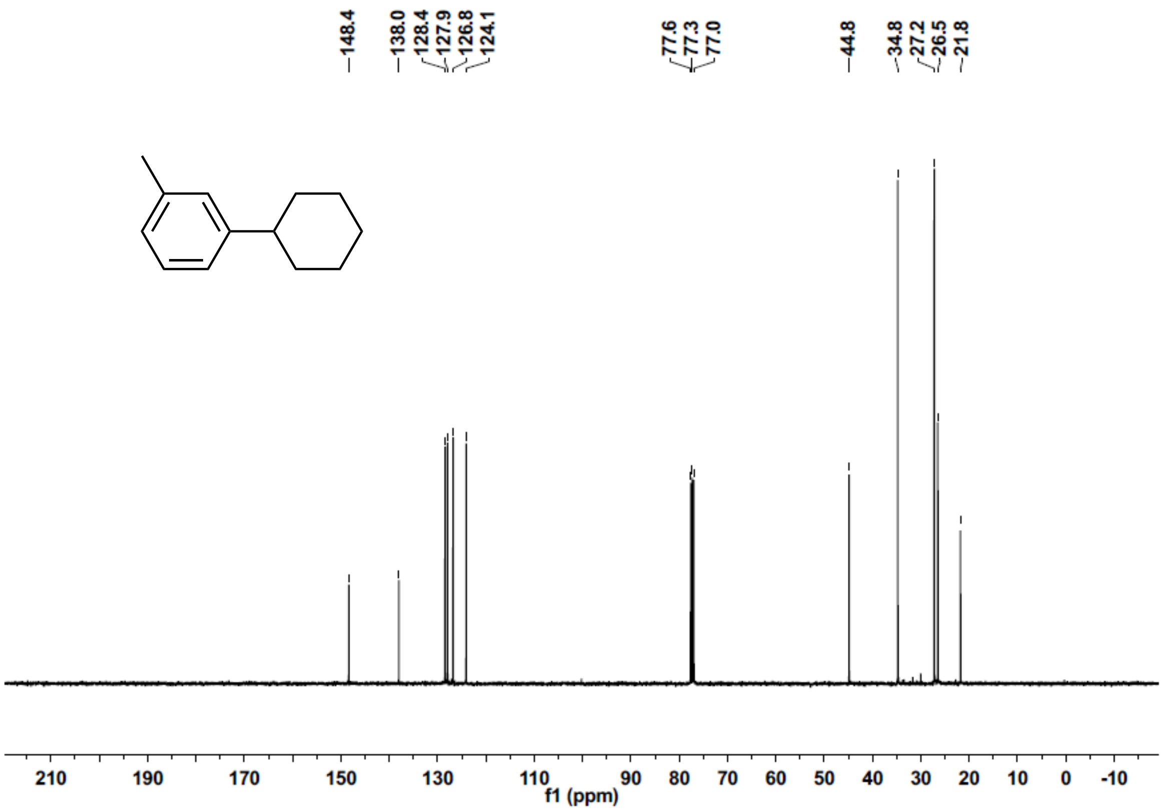
f1 (ppm)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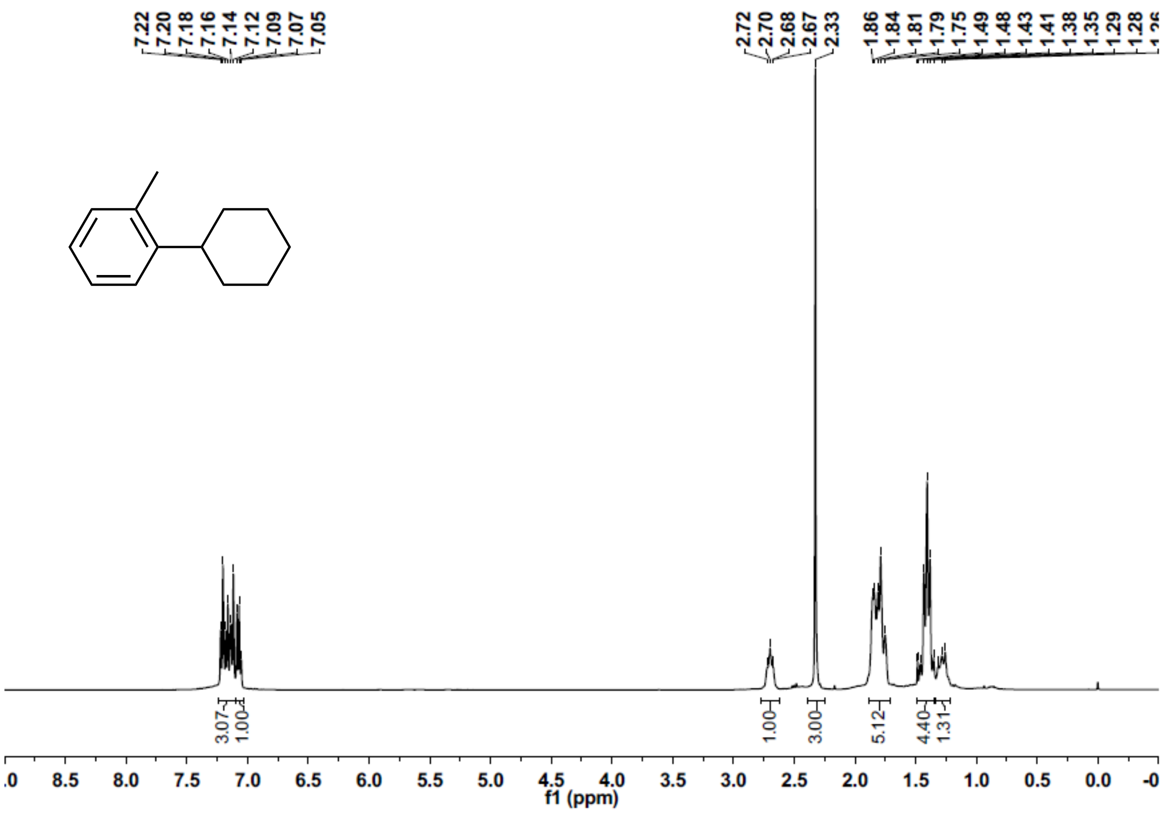
f1 (ppm)

3i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4.40
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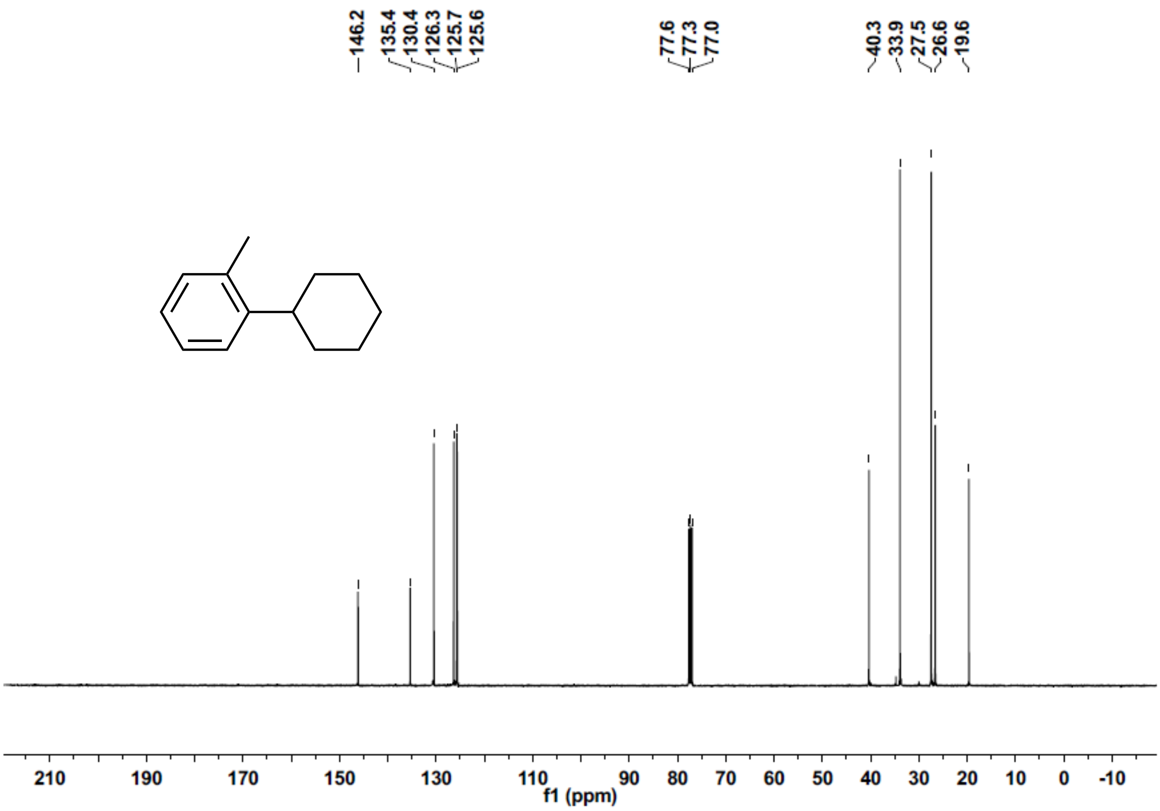
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27.5
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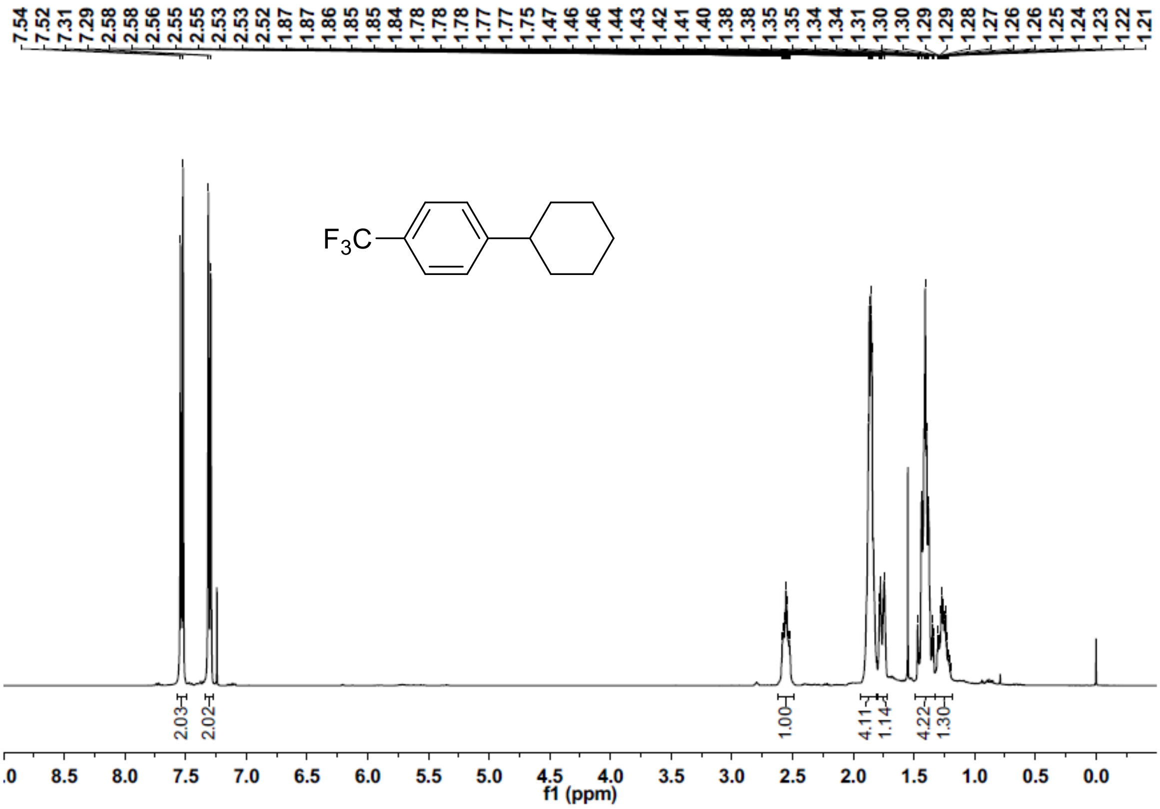
f1 (ppm)

3j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1.25
1.24
1.23
1.22
1.21
F3C
2.03
2.02
1.00
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1.14
4.22
1.30
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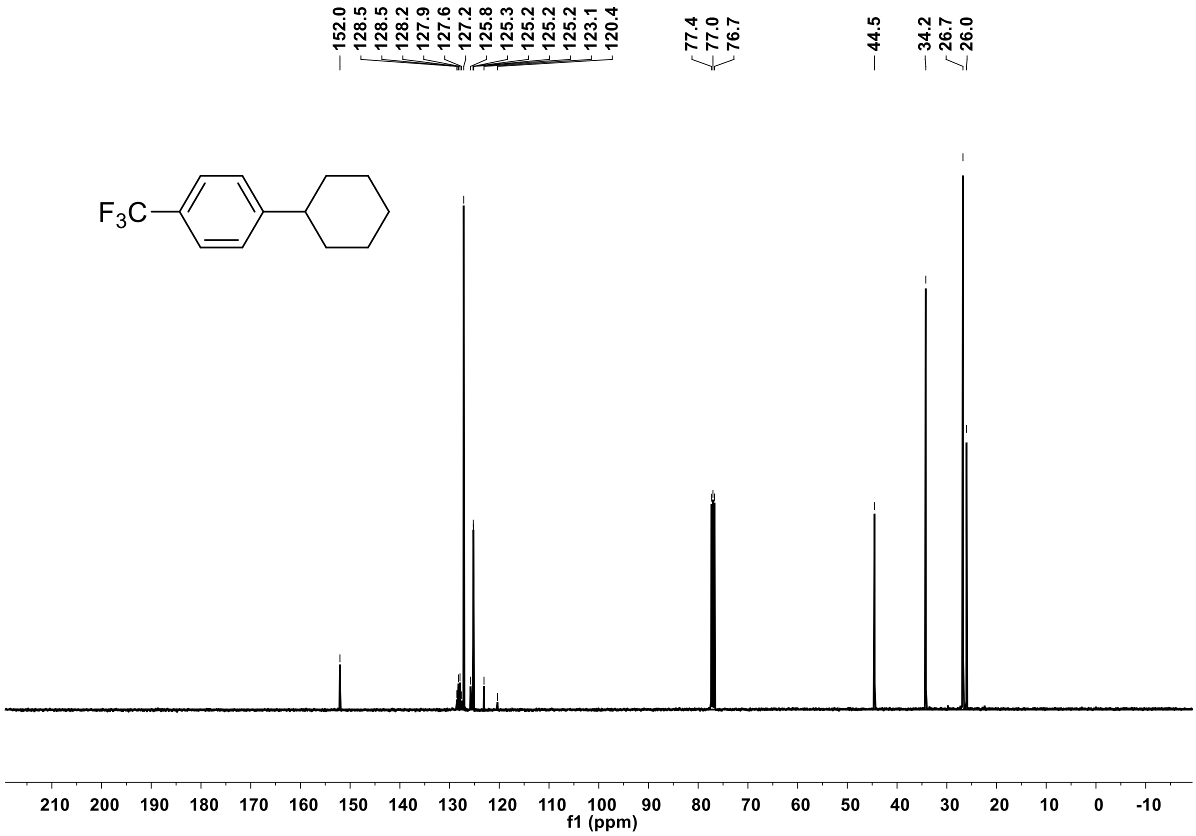
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125.8
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125.2
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123.1
120.4
77.4
77.0
76.7
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26.7
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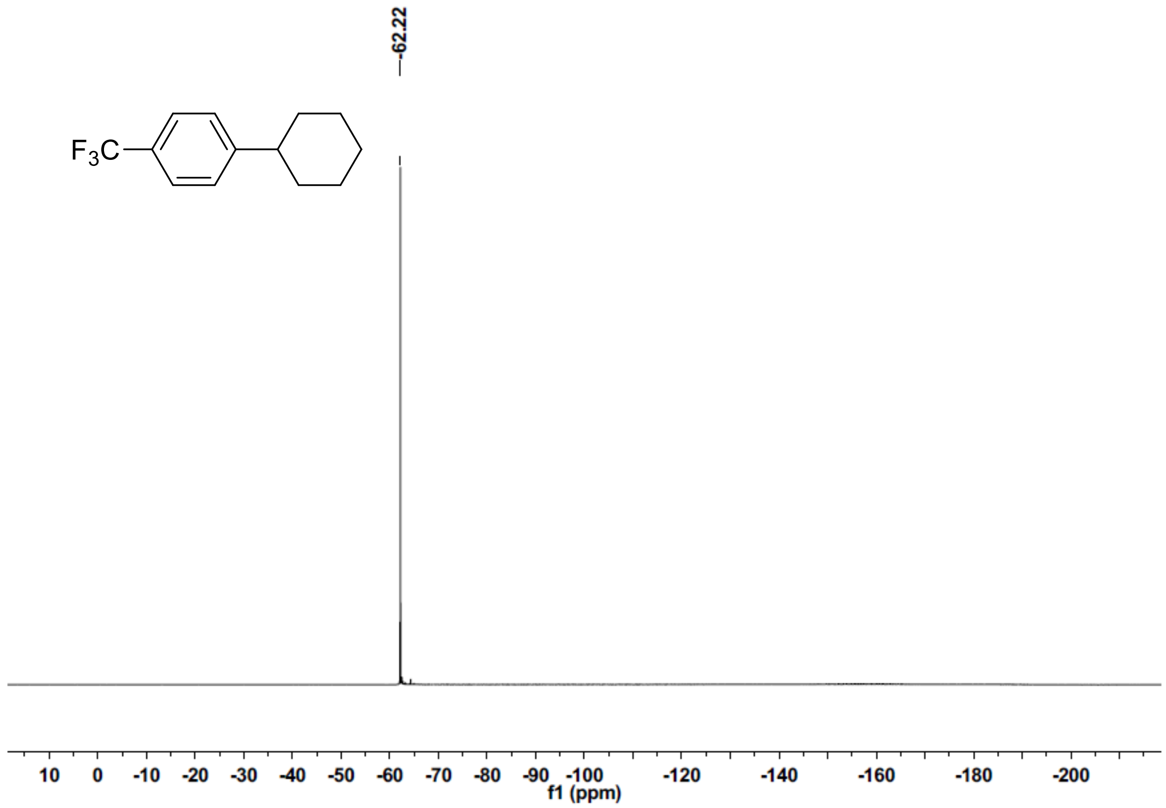
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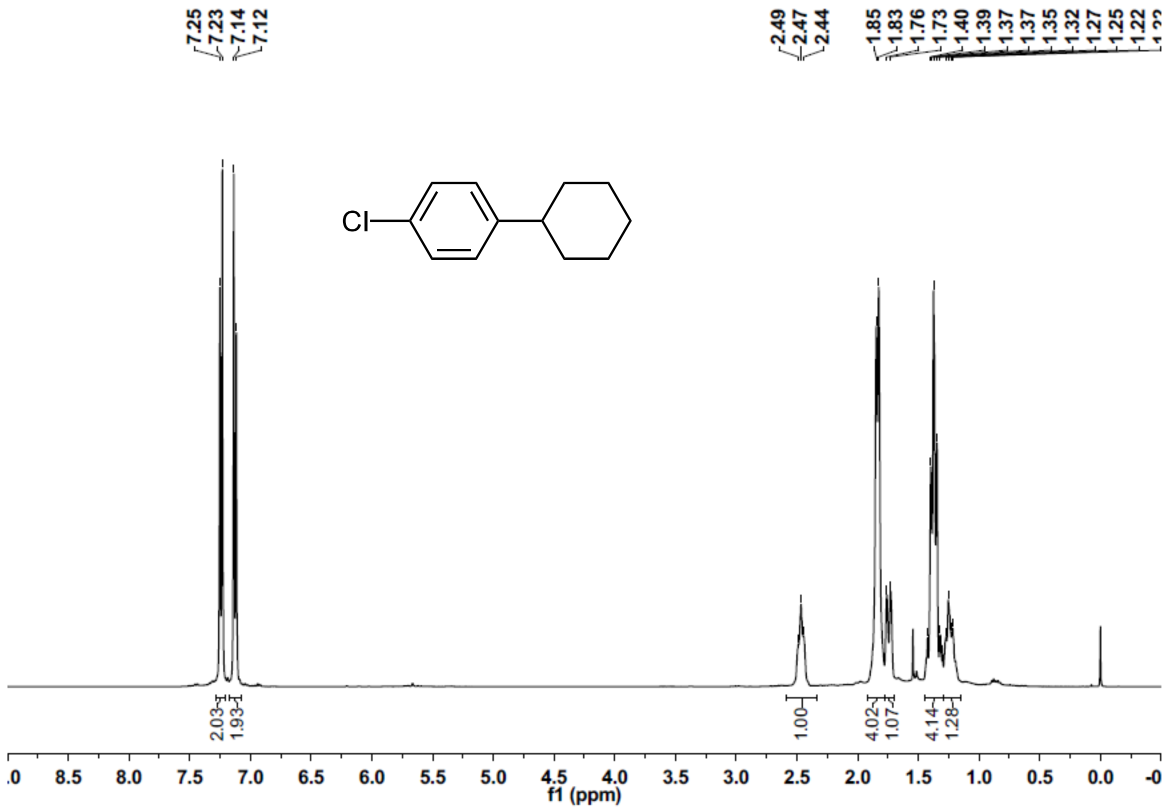

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Cl
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7.5
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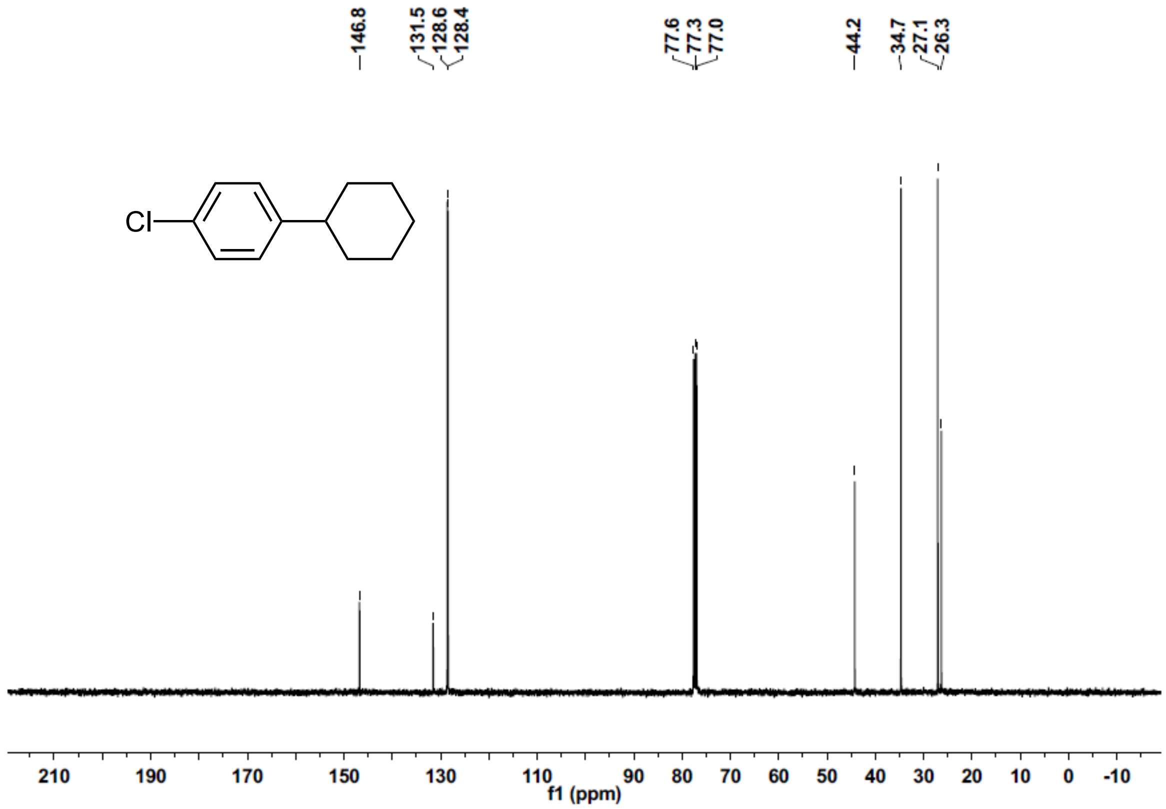
f1 (ppm)



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Cl
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110
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80
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60
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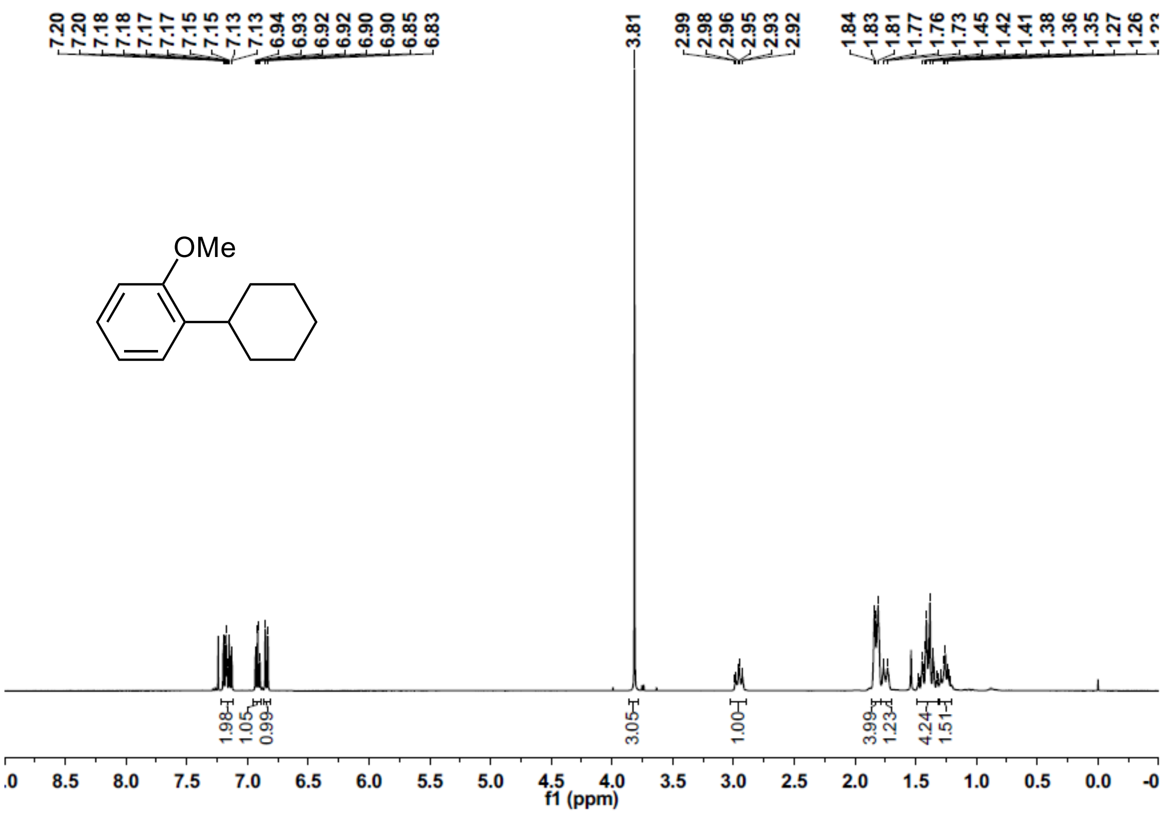
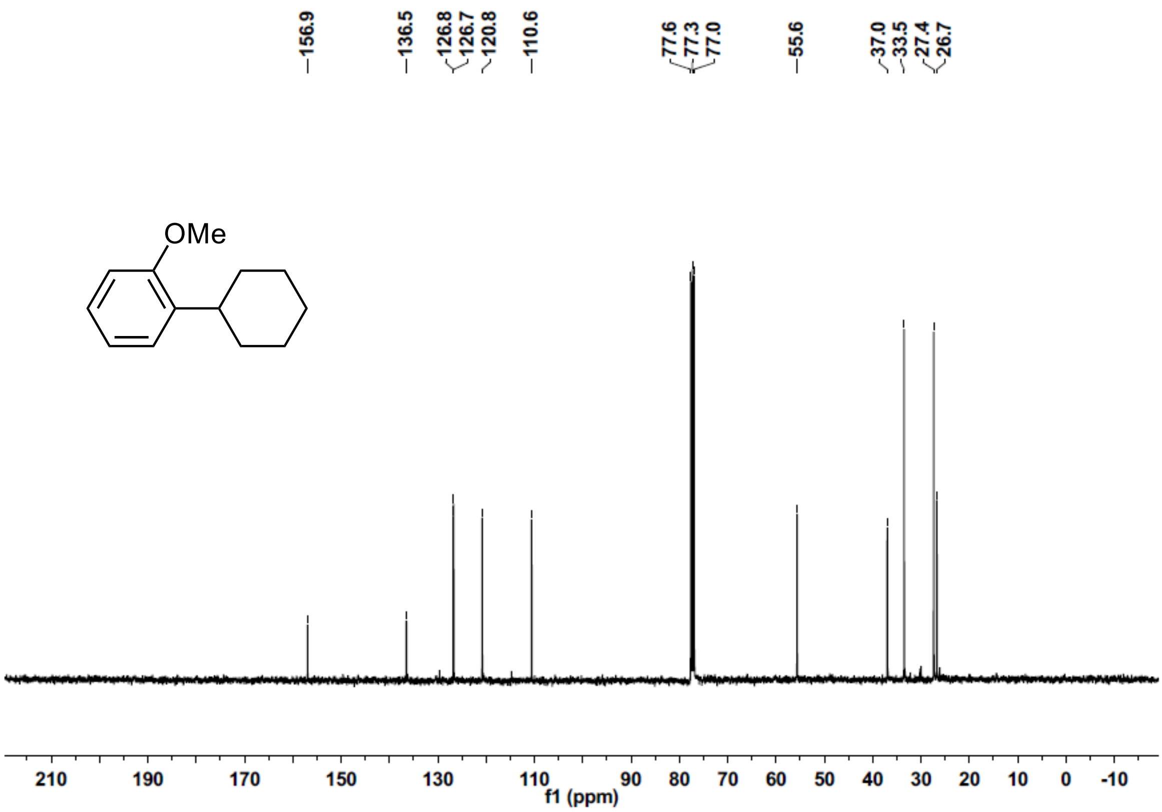
20
10
0
-10
f1 (ppm)

3l





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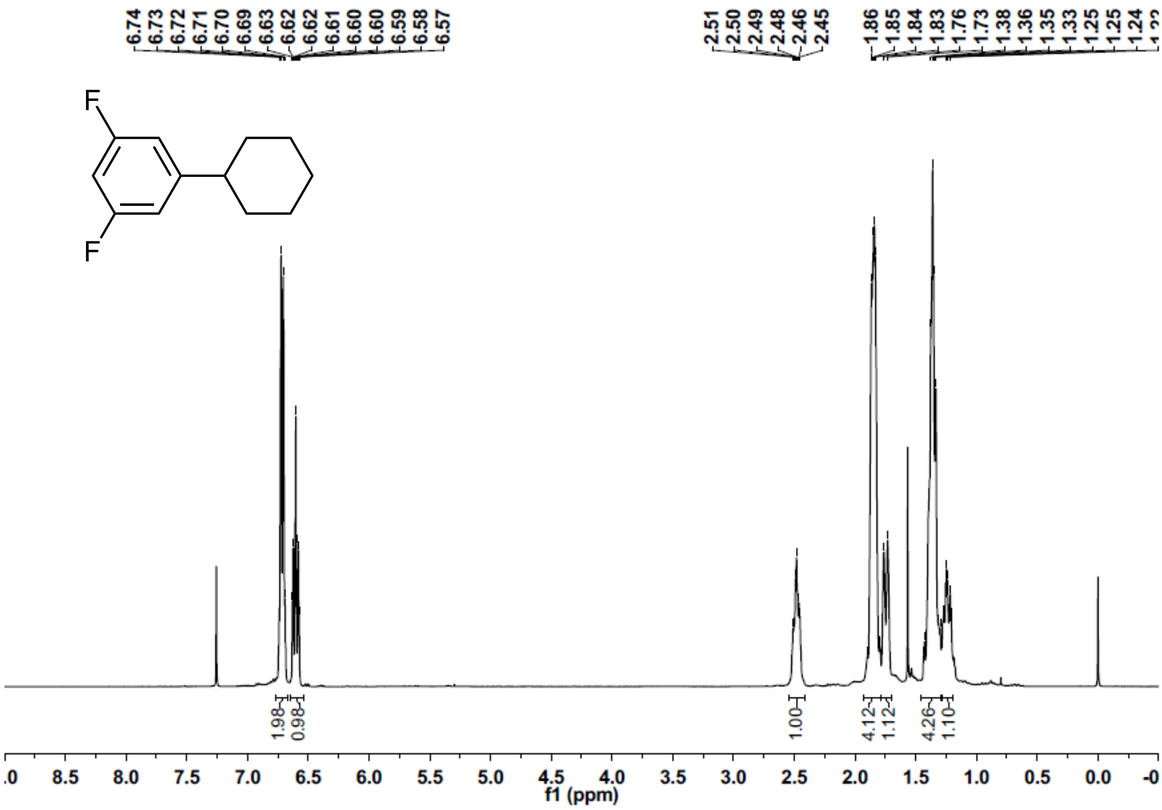

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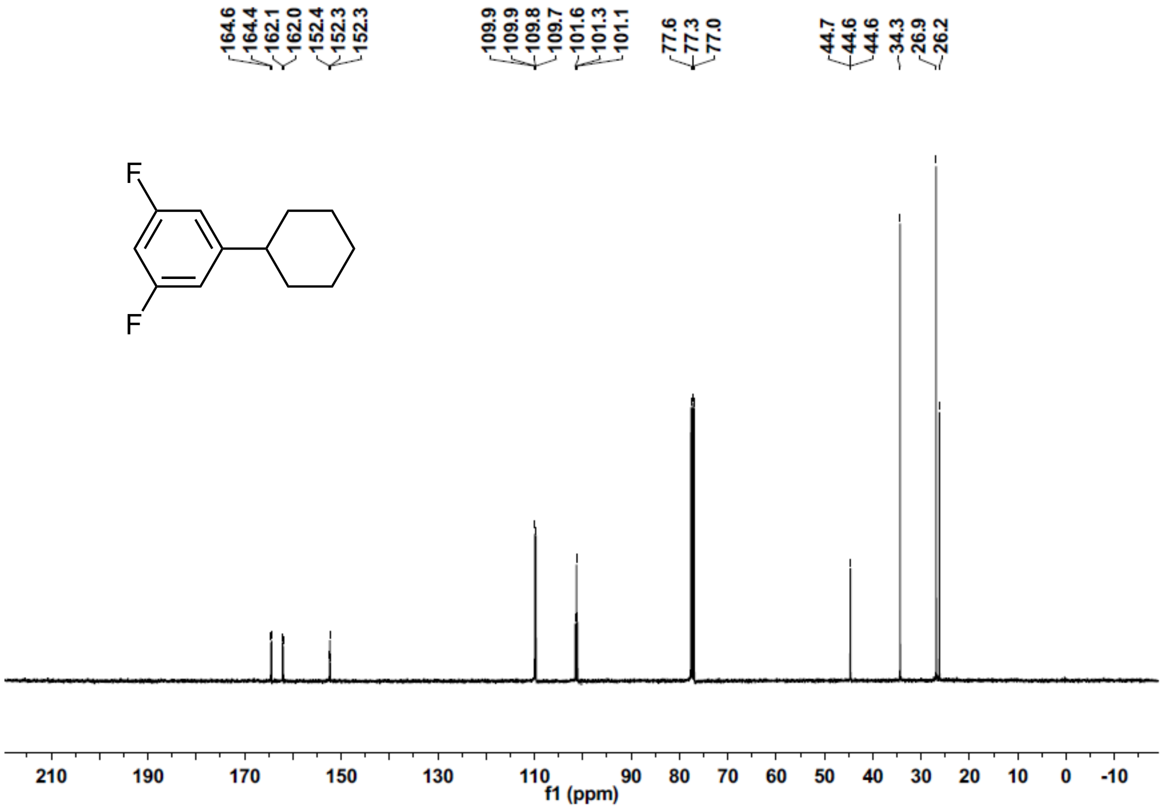
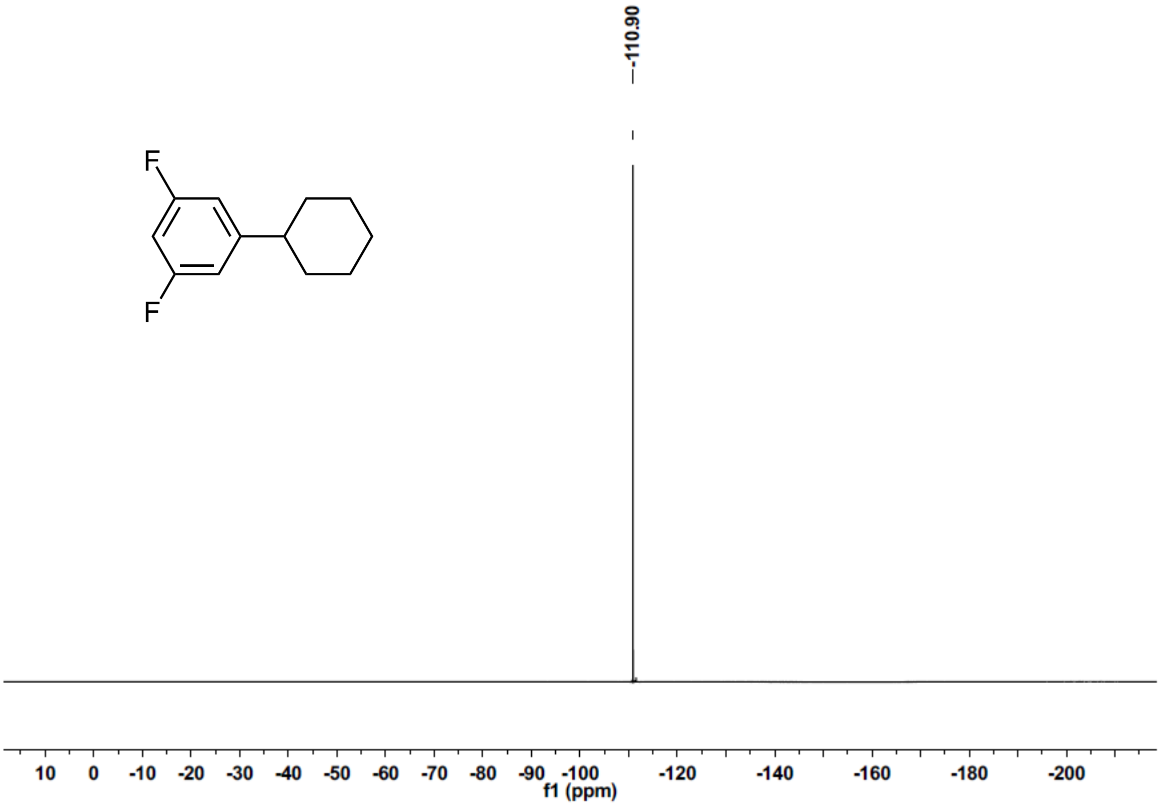
F
1.98
0.98
1.00
4.12
1.12
4.26
1.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



164.6
164.4
162.1
162.0
152.4
152.3
152.3
109.9
109.9
109.8
109.7
101.6
101.3
101.1
77.6
77.3
77.0
44.7
44.6
44.6
34.3
26.9
26.2
F
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



-110.90
F
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)