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Supporting Information

Thorpe–Ingold Effect in Branch-Selective Alkylation of Unactivated Aryl Fluorides

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Author Contributions

M.O. Conceptualization: Equal
T.R. Conceptualization: Equal.

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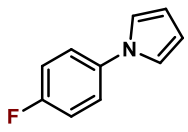
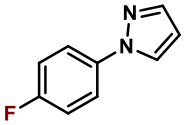
1. General Experimental Notes

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under dry argon in flame-dried glassware. Anhydrous solvents were distilled from appropriate drying agents and were transferred under Argon: THF, Et_2O (Mg/anthracene), CH_2Cl_2 (CaH_2), CH_3CN (CaH_2), hexane, toluene (Na/K), EtOH, MeOH (Mg), Et_3N (MS), DMF (MS). $Ni(acac)_2$ purchased from Alpha Aesar, azeotropically distilled from toluene to remove traces of water, and stored in a 2 neck-flask under argon. Small amounts were kept in a Teflon sealed vial, handled open to air, and placed under argon between uses. Fresh $Ni(acac)_2$ was used to replaced aged samples approximately every 3 weeks. Commercially available Grignard reagents were obtained from Sigma Aldrich. Flash chromatography: Merck silica gel 60 (40-63 µm). GC-MS (FID): GC-MS-QP2010 equipped (Shimadzu Europe Analytical Instriuments). MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker). Accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). NMR spectra were recorded using a Bruker Avance VIII-300, Bruker Avance III HD 400 MHz spectrometer, Bruker Avance III 500MHz spectrometer equipped with a 5mm BBFO probe. ^{1}H NMR spectra (300.13 MHz, 400.1 MHz, or 500 MHz) were referenced to the residual protons of the deuterated solvent used. $^{13}C\{1H\}$ NMR spectra (75.47 MHz. 101 MHz, or 125 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. All compounds purified by column chromatography are shown with the isomerized product in the same spectra, and the obtained selectivities were determined by the integration of the respective terminal methyl groups. Chemical shifts (δ) are given in ppm, relative to deuterated solvent residual peak, and coupling constants (J) are provided in Hz.

2. Starting Material Preparation



1-(4-fluorophenyl)-1H-pyrrole



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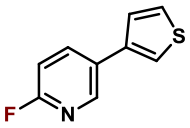
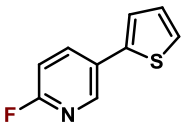


2-fluoro-5-(thiophen-3-yl)pyridine



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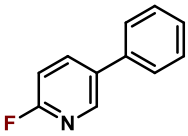

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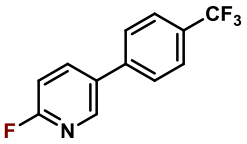
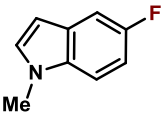
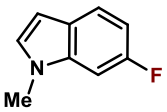


2-fluoro-5-(4-(trifluoromethyl)phenyl)pyridine



5-fluoro-1-methyl-1H-indole



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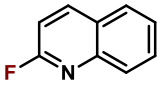
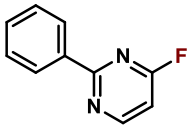
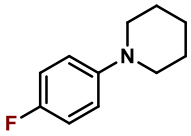


2-fluoroquinoline



4-fluoro-2-phenylpyrimidine



1-(4-fluorophenyl)piperidine

The above starting materials were prepared via cross-coupling, alkylation or fluorination according to general methods reported in the literature.

(a) *Via cross coupling:* 1-(4-fluorophenyl)-1H-pyrrole,[1] 1-(4-fluorophenyl)-1H-pyrazole,[1] 2-fluoro-5-(thiophen-3-yl)pyridine,[2] 2-fluoro-5-(thiophen-2-yl)pyridine,[2] 2-fluoro-5-phenylpyridine,[2] and 2-fluoro-5-(4-(trifluoromethyl)phenyl)pyridine,[2] and 1-(4-fluorophenyl)piperidine.[3]

(b) *Via alkylation*: 5-fluoro-1-methyl-1H-indole[4] and 6-fluoro-1-methyl-1H-indole.[4]

(c) *Fluorination via Hartwig's protocol*[5]: 2-fluoroquinoline and 4-fluoro-2-phenylpyrimidine.

2-chloro-3-fluoropyridine (**36**) and 4-chloro-3-fluoropyridine (**39**) were each synthesized from 3-fluoropyridine (**35**) according to Schlosser's literature precedent[6].

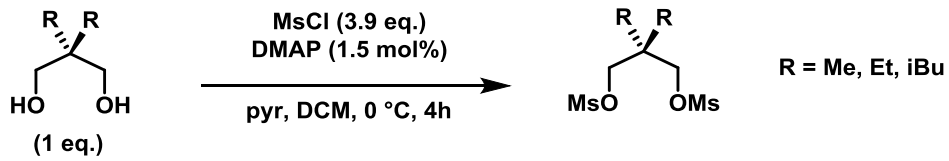
Cyclopropyl magnesium bromide in Et_2O was prepared from cyclopropyl bromide according to literature precedent[7].

(4-phenylbutan-2-yl)magnesium bromide in Et_2O was prepared from (3-bromobutyl)benzene according to literature precedent[8].

Spectroscopic analysis of each of the above compounds was in agreement with the respective literature report.

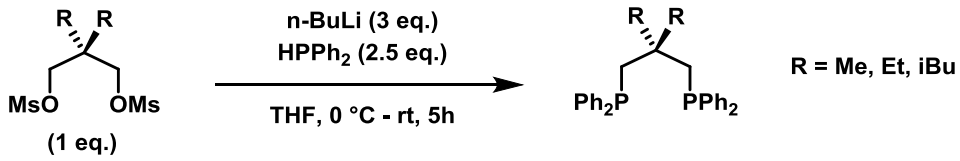
3. Synthesis of Ligands

Preparation of Mesylate



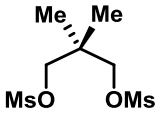
To a mixture of the respective diol (22 mmol, 1 eq.), DMAP (0.33 mmol, 40 mg, 0.015 eq.), DCM (10 mL) and pyridine (20 mL), was added methanesulfonylchloride (86.7 mmol, 6.7 mL, 4 eq.) at 0 °C. The resulting suspension was stirred for 4 h at the same temperature. Subsequently, the reaction mixture was poured onto ice-cold HCl (2M, 100 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with H_2O (50 mL) and with saturated aq $NaHCO_3$ solution (50 mL), dried over $MgSO_4$, concentrated, and purified by column chromatography (Hexanes/EtOAc).

Preparation of Diphosphines[9]



While rigorously stirring, n-BuLi (13 mL, 1.6 M, 3 eq.) was added dropwise to a solution of diphenylphosphine (3 mL, 17.3 mmol, 2.5 eq.) in THF (40 mL) at 0 °C. The deep-red solution was allowed to stir for 1 h at 25 °C. Subsequently, a solution prepared from the respective dimesylate (7 mmol, 1eq.) in THF (20 mL) was slowly added and stirred for an additional 4 h at the same temperature. The reaction was quenched with MeOH. The mixture was concentrated *in vacuo* and the crude product was partitioned between Et_2O (60 mL) and saturated aq NH_4Cl solution (32 mL). The aq phase was extracted under inert atmosphere with Et_2O (2 × 30 mL). The combined organic phases were dried over Na_2SO_4, and quickly filtered through a short plug of silica. The solution was concentrated and the product recrystallized.

Characterization of Mesylates and Phosphine Ligands



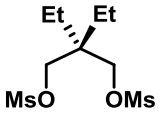
S1

2,2-Dimethylpropane-1,3-diyl dimethanesulfonate[10]

Prepared from 2,2-dimethylpropane-1,3-diol (22 mmol, 2.3 g, 1 eq.). The desired product was obtained as a pale-yellow solid (5.2 g, 91%) after purification by column chromatography with silica gel (6.0 g, 95%). NMR data are in accordance with the literature report.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02 (s, 4H), 3.04 (s, 6H), 1.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 73.2, 37.4, 35.6, 21.3.



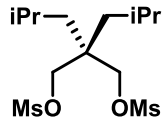
S2

2,2-Diethylpropane-1,3-diyl dimethanesulfonate[9]

Prepared from 2,2-diethylpropane-1,3-diol (22 mmol, 2.9 g, 1 eq.). The desired product was obtained as a white solid (6.0 g, 95%) after purification by column chromatography with silica gel (hexane/EtOAc = 4:1). NMR data are in accordance with the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (s, 4H), 3.04 (s, 6H), 1.38 (q, J = 7.5 Hz, 4H), 0.89 (t, J = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 69.9, 40.7, 37.4, 21.9, 6.8.



S3

2,2-Diisobutylpropane-1,3-diyldimethanesulfonate

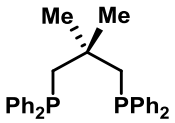
Prepared from 2,2-diisobutylpropane-1,3-diol (22 mmol, 4.1 g, 1 eq.). The desired product was obtained as a pale-yellow solid (4.5 g, 62%) after purification by column chromatography (hexane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 (s, 4H), 3.04 (s, 6H), 1.76 (hept, *J* = 6.3 Hz, 2H), 1.36 (d, *J* = 5.6 Hz, 4H), 0.98 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 71.0, 41.7, 39.7, 37.4, 25.3, 23.3.

HRMS (ESI): calc'd for $C_{13}H_{28}O_6S_2Na$ $[M+Na]^+$ 367.1220; found 367.1218.

M.P.: 64.4 °C.



L3

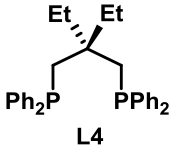
(2,2-Dimethylpropane-1,3-diyl)bis(diphenylphosphane)[11]

Prepared from 2,2-dimethylpropane-1,3-diyl dimethanesulfonate **S1** (1,9 mmol, 500 mg). The desired product was obtained after recrystallization from boiling MeOH as a white solid (250 mg, 30%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 - 7.40 (m, 8H), 7.33 – 7.27 (m, 12H), 2.34 (d, J_{H-P} = 3.1 Hz, 4H), 1.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.5 (d, *J* = 13.0 Hz), 133.4 (d, *J* = 20.1 Hz), 128.8 (d, *J* = 3.5 Hz), 128.7, 44.6 (dd, *J* = 16.6, 9.0 Hz), 35.6 (t, *J* = 14.2 Hz), 30.8 (t, *J* = 9.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ -24.5 (s).



L4

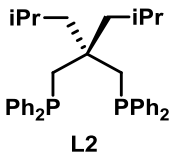
(2,2-Diethylpropane-1,3-diyl)bis(diphenylphosphane)[9]

Prepared from 2,2-diethylpropane-1,3-diyl dimethanesulfonate **S2** (7 mmol, 2 g). The desired product was obtained after recrystallization from boiling MeOH as a white solid (1.34 g, 41%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.37 (m, 8H), 7.33 – 7.22 (m, 12H), 2.37 (d, J_{H-P} = 4.6 Hz, 4H), 1.49 (q, *J* = 7.4 Hz, 4H), 0.55 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.6 (d, *J* = 4.3 Hz), 133.3 (d, *J* = 20.0 Hz), 128.9, 128.6 (m), 40.6 (t, *J* = 11.4 Hz), 37.5 (t, *J* = 11.8 Hz), 31.3 (t, *J* = 8.4 Hz), 7.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ -26.0 (s).



L2

(2,2-Diisobutylpropane-1,3-diyl)bis(diphenylphosphane)

Prepared from 2,2-diisobutylpropane-1,3-diyl dimethanesulfonate **S3** (0.7 mmol, 250 mg). The desired product was obtained after recrystallization from boiling MeOH as a white solid (242 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.37 (m, 8H), 7.31 – 7.26 (m, 12H), 2.36 (d, J_{H-P} = 3.6 Hz, 4H), 1.64 (hept, *J* = 6.6, 2H), 1.46 (d, *J* = 5.2 Hz, 4H), 0.83 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.5 (d, *J* = 12.6 Hz), 133.3 (d, *J* = 20.1 Hz), 128.5 (m), 128.4, 48.7 (t, *J* = 7.8 Hz), 42.6 (t, *J* = 12.3 Hz), 40.0 (dd, *J* = 16.3, 9.2 Hz), 25.7, 24.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ -25.8 (s).

HRMS (ESI): calc'd for $C_{35}H_{43}P_2$ 524.2762 $[M+H]^+$ 525.2835; found 525.2836.

M.P.: 83.6 °C.

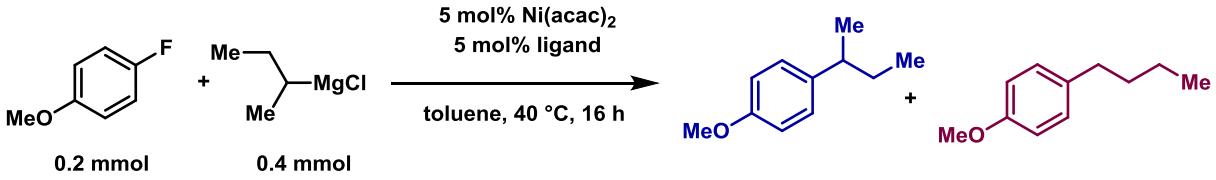
4. Optimization Studies

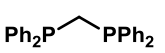
General Procedure for Early Optimization

A culture tube equipped with a stir bar was charged with $Ni(acac)_2$ (2.6 mg, 0.01 mmol) and phosphine ligand (0.01 mmol). A teflon cap was fitted, and the tube was evacuated for 15 min, refilled with argon, and then the atmosphere was recycled 2 times. 4-Fluoroanisole (0.2 mmol) was added, followed by toluene, ensuring to rinse any residual substrate from the walls of the vial. The mixture was vigorously stirred, and the Grignard nucleophile (0.2-0.4 mmol) was added with a *single* push of the syringe. The reaction was then stirred at the desired temperature for 24 h. The solution was diluted with MTBE (~10 mL) and quenched with saturated aq NH_4Cl or H_2O (1 mL). Tetradecane was added as an internal standard, and GC was used to confirm the branched/linear selectivity and yield.

*Moisture sensitive additives were added in an argon-filled glovebox before adding fluoroanisole.

Ligand Screening





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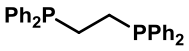

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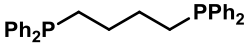
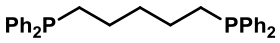
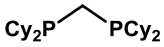
2%, 1.3 : 1



(L7)
42%, 1.7 : 1



(L8)
12%, 1.5 : 1



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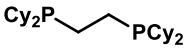

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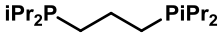

(L11)
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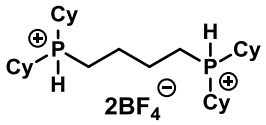
(L12)
26%, 1 : 1



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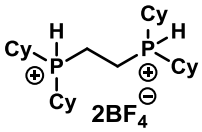

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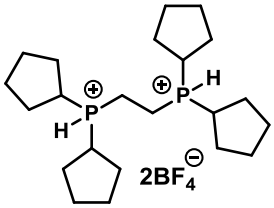

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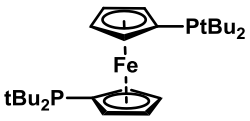

(L16)
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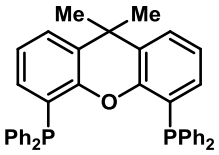

(L17)
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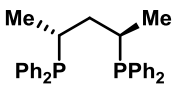
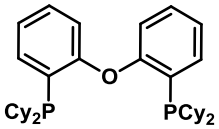


(L18)
50%, 18.5 : 1



(L19)
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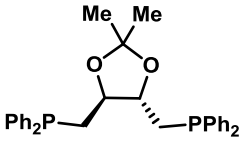

(L20)
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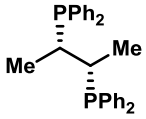
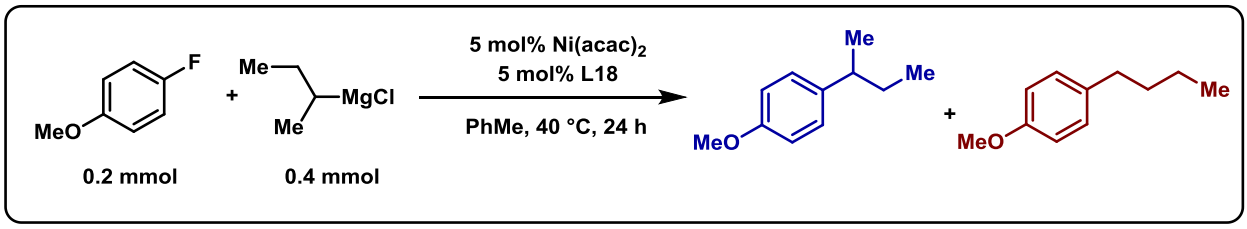


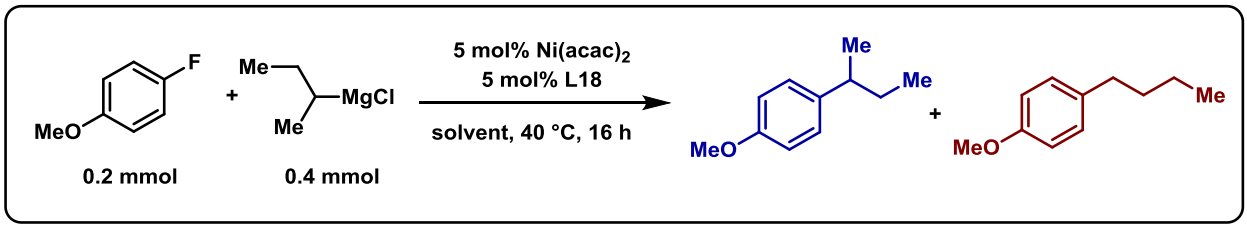
(L21)
20%, 6.3 : 1

Temperature Screening



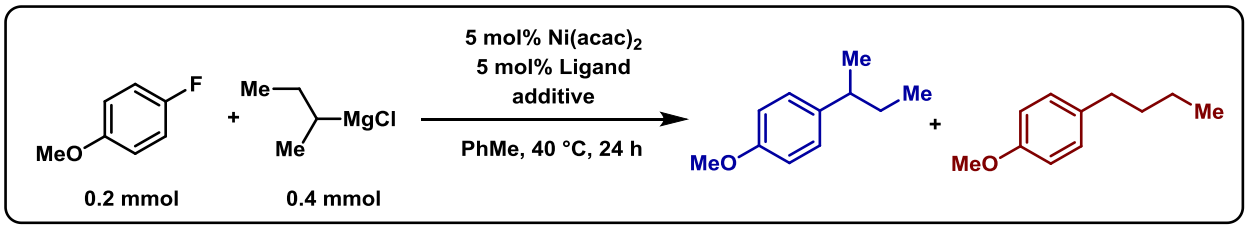
Temperature	Yield branched	Selectivity (b:l)
20 °C	40%	18.7 : 1
40 °C	83%	18.6 : 1
60 °C	70%	10.3 : 1

Solvent Screening



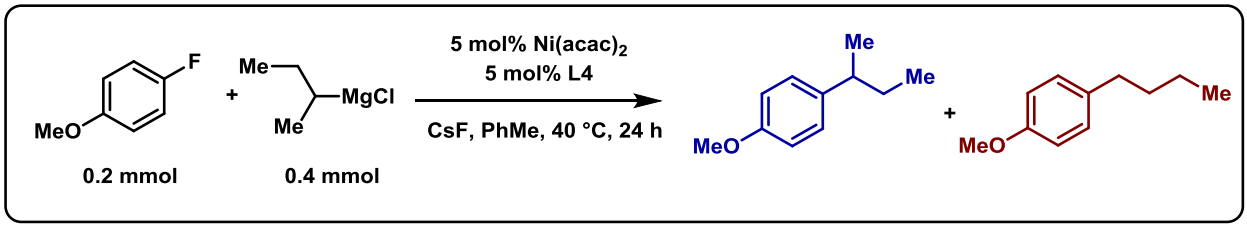
Solvent	Yield branched	Selectivity (b:l)
Toluene	50%	18.5 : 1
Diethylether	72%	17.8 : 1
Tetrahydrofuran	<5%	n.d.
Dioxane	<5%	n.d.

Additive Screening



Additive	Ligand	Additive Loading	Selectivity (b:l)
$NaBF_4$	L18	1 eq.	5.6 : 1
LiOTf	L18	1 eq.	6.4 : 1
LiI	L18	1 eq.	n.d.
$LiBF_4$	L18	1 eq.	1 : 1
LiF	L4	0.15 eq.	23:1
NaF	L4	0.15 eq.	20:1
CsF	L4	0.15 eq.	28:1

Additive and Concentration Dependency

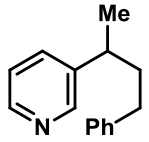


Reaction Volume	CsF	Selectivity (b:l)
0.5 mL	-	19:1
1.0 mL	-	23:1
0.5 mL	15%	24:1
1.0 mL	15%.	30:1

5. General Procedure

A culture tube equipped with a stir bar was charged with $Ni(acac)_2$ (2.6 mg, 0.01 mmol) and phosphine ligand **L4** (4.7 mg, 0.01 mmol), and additionally aryl fluoride if solid. A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and anhydrous CsF (6.0 mg, 0.04 mmol) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. Aryl fluoride (0.2 mmol) was added (if liquid), followed by toluene (1 mL), ensuring to rinse any residual aryl fluoride from the walls of the vial. The mixture was vigorously stirred, and the Grignard nucleophile (100-200 μL, 0.2 M, 0.2-0.4 mmol) was added with a *single* push of the syringe. The reaction was then stirred at the desired temperature (0 °C to 60 °C) until the reaction was judged complete by TLC or GC. The solution was diluted with EtOAc or MTBE (~10 mL) and quenched with saturated aq NH_4Cl or H_2O (3 mL) - depending on substrate sensitivity to acid. The aq phase was separated and extracted with MTBE (3 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The desired product was then purified by flash chromatography with a mixture of pentane/EtOAc, pentane/MTBE, or DCM/MeOH to afford the desired coupled product.

6. Characterization Data



5

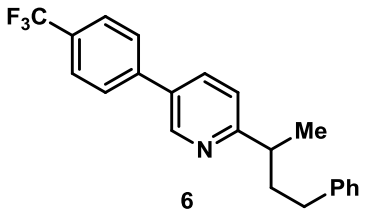
3-(4-Phenylbutan-2-yl)pyridine[12]

Following the general procedure at 0 °C, **5** was prepared from 3-fluoropyridine (171 µL, 2 mmol) yielding the above compound (29.9 mg, 1.42 mmol, 71% yield) as a viscous, pale oil after silica gel chromatography (pentane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (broad s, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.21 – 7.14 (m, 1H), 7.14 – 7.08 (m, 2H), 2.77 (q, J = 7.6 Hz, 1H), 2.52 (tt, J = 9.5, 5.2 Hz, 2H), 2.00 – 1.87 (m, 2H), 1.31 (d, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.8, 147.1, 142.8, 141.9, 134.9, 128.5, 128.4, 126.0, 123.8, 39.7, 37.1, 33.8, 22.3.

HRMS (ESI): calc'd for $C_{15}H_{17}N$ $[M+H]^+$ 212.1434; found 212.1434.



6

2-(4-Phenylbutan-2-yl)-5-(-(trifluoromethyl)phenyl)pyridine

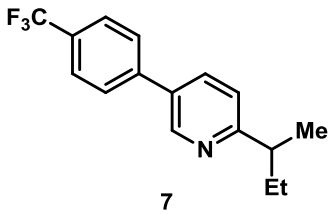
Following the general procedure at 0 °C, **6** was prepared from 2-fluoro-5-(4-(trifluoromethyl)phenyl)pyridine (48.1 mg, 0.2 mmol) yielding the above compound (62.5 mg, 0.176 mmol, 88% yield) as a viscous, colorless oil after silica gel chromatography (pentane/EtOAc = 15:1 to 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.95 – 7.88 (m, 1H), 7.79 – 7.66 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.16 (td, *J* = 5.3, 2.8 Hz, 3H), 3.13 (d, *J* = 8.4 Hz, 1H), 2.71 – 2.50 (m, 2H), 2.19 (dddd, *J* = 13.9, 9.5, 8.1, 6.0 Hz, 1H), 2.02 (ddt, *J* = 13.1, 9.7, 6.3 Hz, 1H), 1.41 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.0, 128.6, 128.5, 127.5, 126.5, 126.4, 126.3, 126.2, 125.9, 125.5, 122.9 – 122.7 (m), 40.7, 38.6, 34.0, 21.0.

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.6.

HRMS (ESI): calc'd for $C_{22}H_{21}F_3N$ $[M+H]^+$ 356.1621; found 356.1621.



7

2-(*sec*-Butyl)-5-(4-(trifluoromethyl)phenyl)pyridine

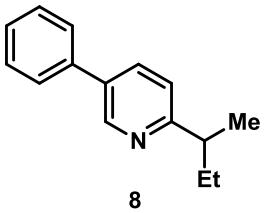
Following the general procedure at 0 °C, **7** was prepared from 2-fluoro-5-(4-(trifluoromethyl)phenyl)pyridine (48.1 mg, 0.2 mmol) yielding the above compound (41.9 mg, 0.15 mmol, 75% yield) as a viscous, colorless oil following silica gel chromatography (pentane/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.85 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.79 – 7.64 (m, 4H), 7.33 – 7.24 (m, 1H), 2.91 (h, *J* = 7.0 Hz, 1H), 1.82 (dt, *J* = 13.4, 7.5 Hz, 1H), 1.69 (ddd, *J* = 13.8, 7.5, 6.6 Hz, 1H), 1.34 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 147.1, 141.4, 135.5, 133.1, 130.2 (q, *J* = 32.6 Hz), 127.4, 126.2 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 272.0 Hz), 122.0, 43.3, 30.1, 20.5, 12.3.

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.6.

HRMS (ESI): calc'd for $C_{16}H_{17}F_3N$ $[M+H]^+$ 280.1308; found 280.1308.



8

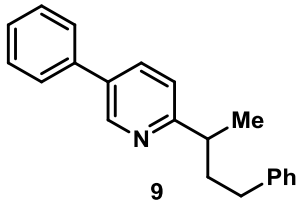
2-(*sec*-Butyl)-5-phenylpyridine

Following the general procedure at 0 °C, **8** was prepared from 2-fluoro-5-phenylpyridine (34.6 mg, 0.2 mmol) yielding the above compound (31.7 mg, 0.15 mmol, 75% yield) as a colorless oil after silica gel chromatography (pentane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (dd, *J* = 2.4, 0.9 Hz, 1H), 7.80 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.59-7.56 (m, 2H), 7.49 - 7.45 (m, 2H), 7.40 – 7.36 (m, 1H), 7.20 (dd, *J* = 8.0, 0.8 Hz, 1H), 2.85 (sext, *J* = 7.0 Hz, 1H), 1.87 - 1.74 (m, 1H), 1.72 - 1.64 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 147.7, 138.2, 134.8, 134.1, 129.1, 127.9, 127.1, 121.6, 43.5, 30.2, 20.6, 12.3.

HRMS (ESI): calc'd for $C_{15}H_{18}N$ $[M+H]^+$ 212.1434; found 212.1436.



9

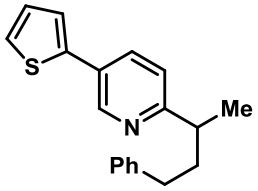
5-Phenyl-2-(4-phenylbutan-2-yl)pyridine

Following the general procedure at 0 °C, **9** was prepared from 2-fluoro-5-phenylpyridine (34.6 mg, 0.2 mmol) yielding the above compound (47.1 mg, 0.164 mmol, 82% yield) as a colorless oil after silica gel chromatography (pentane/EtOAc = 15:1 to 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.85 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.51 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 7.29 – 7.22 (m, 3H), 7.19 – 7.13 (m, 3H), 3.13 – 2.98 (m, 1H), 2.69 – 2.49 (m, 2H), 2.23 - 2.11 (m, 1H), 2.04 – 1.92 (m, 1H), 1.38 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.7, 147.0, 142.4, 137.7, 135.6, 134.6, 129.2, 128.5, 128.4, 128.1, 127.1, 125.8, 122.0, 41.1, 38.8, 34.0, 21.1.

HRMS (ESI): calc'd for $C_{21}H_{22}N$ 288.1747; found $[M+H]^+$ 288.1748.



10

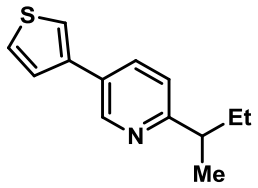
2-(4-Phenylbutan-2-yl)-5-(thiophen-2-yl)pyridine

Following the general procedure at 0 °C, **10** was prepared from 2-fluoro-5-(thiophen-3-yl)pyridine (35.8 mg, 0.2 mmol) yielding the above compound (25.2 mg, 0.086 mmol, 43% yield) as a colorless oil after silica gel chromatography (pentane/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.30 (td, *J* = 4.2, 3.6, 1.2 Hz, 2H), 7.21 – 7.14 (m, 4H), 7.12 – 7.04 (m, 5H), 3.04 (s, 1H), 2.51 (dddd, *J* = 29.4, 15.7, 8.6, 4.7 Hz, 2H), 2.09 (dddd, *J* = 13.9, 9.6, 8.2, 5.9 Hz, 1H), 1.92 (ddt, *J* = 13.2, 9.8, 6.3 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.0, 144.8, 144.6, 142.2, 135.2, 128.9, 128.8, 128.5, 128.4, 126.4, 125.9, 124.5, 122.5, 40.6, 38.7, 34.0, 21.0.

HRMS (ESI): calc'd for $C_{19}H_{20}NS$ $[M+H]^+$ 294.1311; found 294.1312.



11

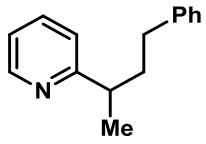
2-(*sec*-Butyl)-5-(thiophen-2-yl)pyridine

Following the general procedure at 0 °C, **11** was prepared from 2-fluoro-5-(thiophen-3-yl)pyridine (35.8 mg, 0.2 mmol) yielding the above compound (21.3 mg, 0.1 mmol, 49% yield) as a colorless oil after silica gel chromatography (pentane/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (dd, *J* = 2.4, 0.9 Hz, 1H), 7.81 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.49 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.45-7.41 (m, 1H), 7.38 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.19 (dd, *J* = 8.1, 0.9 Hz, 1H), 2.85 (p, *J* = 7.0 Hz, 1H), 1.85 – 1.73 (m, 1H), 1.72-1.60 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.1, 146.7, 139.0, 134.5, 129.3, 127.0, 126.1, 121.8, 121.1, 43.3, 30.1, 20.5, 12.3.

HRMS (ESI): calc'd for $C_{13}H_{16}NS$ $[M+H]^+$ 218.0998; found 218.0999.



12

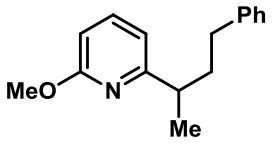
2-(4-Phenylbutan-2-yl)pyridine[13]

Following the general procedure at 0 °C, **12** was prepared from 3-fluoropyridine (171 µL, 2 mmol) yielding the above compound (40.1 mg, 0.19 mmol, 95% yield) as a viscous, colorless oil after silica gel chromatography (pentane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.54 (td, *J* = 7.7, 1.9 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.10 – 7.02 (m, 5H), 2.87 (dq, *J* = 8.2, 6.7 Hz, 1H), 2.55 – 2.38 (m, 2H), 2.10-1.98 (m, 1H), 1.90 – 1.78 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 149.1, 142.5, 136.8, 128.5, 128.4, 125.8, 122.0, 121.4, 41.5, 38.8, 33.4, 21.0.

HRMS (ESI): calc'd for $C_{15}H_{18}N$ $[M+H]^+$ 212.1434; found 212.1434.



13

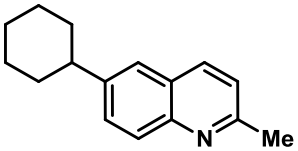
2-Methoxy-6-(4-phenylbutan-2-yl)pyridine[14]

Following the general procedure with 10% catalyst and ligand loading, **13** was prepared from 2-fluoro-6-methoxypyridine (25.4 mg, 0.2 mmol) yielding the above compound (31.3 mg, 0.13 mmol, 64% yield) as a colorless oil after silica gel chromatography (pentane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.20 – 7.12 (m, 3H), 6.69 (dd, *J* = 7.3, 0.7 Hz, 1H), 6.54 (dd, *J* = 8.2, 0.8 Hz, 1H), 3.93 (s, 3H), 2.87 – 2.73 (m, 1H), 2.60 – 2.43 (m, 2H), 2.19 – 2.07 (m, 1H), 1.92-1.80 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.0, 163.8, 142.9, 138.8, 128.5, 128.4, 125.7, 114.5, 107.6, 53.3, 41.2, 38.5, 34.0, 21.1.

HRMS (ESI): calc'd for $C_{16}H_{20}NO$ $[M+H]^+$ 242.1539; found 242.1539.



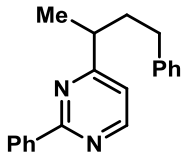
14

6-Cycloheyl-2-methylquinoline[15]

Following the general procedure at 40 °C, **14** was prepared from 6-fluoro-2-methylquinoline (32.2 mg, 0.2 mmol) yielding the above compound (39.2 g, 0.174 mmol, 87% yield) as a colorless oil after silica gel chromatography (pentane/EtOAc = 3:1).

^{1}H NMR (400 MHz, Chloroform-d): δ 8.02 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.60 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.28 (d, *J* = 2.8 Hz, 1H), 2.76 (s, 3H), 2.74 – 2.64 (m, 1H), 2.04 – 1.86 (m, 4H), 1.82 (ddd, *J* = 12.8, 3.1, 1.5 Hz, 1H), 1.61 – 1.39 (m, 4H), 1.40 – 1.24 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.1, 146.8, 145.6, 136.1, 129.9, 128.4, 126.7, 124.2, 122.0, 44.5, 34.6, 27.0, 26.3, 25.4.



15

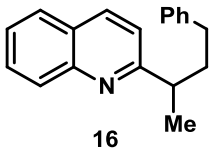
2-Phenyl-4-(4-phenylbutan-2-yl)pyrimidine

Following the general procedure at 0 °C, **15** was prepared from 4-fluoro-2-phenylpyrimidine (17.4 mg, 0.1 mmol) yielding the above compound (18.7 mg, 0.065 mmol, 65% yield) as a colorless oil after silica gel chromatography (pentane/MTBE = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 5.1 Hz, 1H), 8.51 - 8.48 (m, 2H), 7.51 – 7.48 (m, 3H), 7.29 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 7.02 (d, *J* = 5.1 Hz, 1H), 2.96 – 2.89 (m, 1H), 2.63 – 2.57 (m, 2H), 2.23 (dddd, *J* = 13.5, 9.2, 8.0, 6.2 Hz, 1H), 1.97 (dddd, *J* = 13.3, 9.4, 7.0, 6.2 Hz, 1H), 1.37 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.9, 164.4, 157.1, 142.2, 138.1, 130.7, 128.7, 128.5, 128.5, 128.4, 126.0, 117.4, 41.3, 38.0, 33.8, 20.5.

HRMS (ESI): calc'd for $C_{20}H_{21}N_2$ $[M+H]^+$ 289.1699; found 289.1700.



16

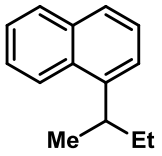
2-(4-Phenylbutan-2-yl)quinolone

Following the general procedure at 0 °C, **16** was prepared from 2-fluoroquinoline (29.4 mg, 0.2 mmol) yielding the above compound (36.5 mg, 1.4 mmol, 70% yield) as a colorless oil after silica gel chromatography (hexane/EtOAc = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.04 (m, 2H), 7.78 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.68 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.48 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.18 – 7.11 (m, 3H), δ 3.14 (dt, *J* = 8.2, 6.7 Hz, 1H), 2.64 (ddd, *J* = 13.7, 10.3, 6.2 Hz, 1H), 2.52 (ddd, *J* = 13.7, 10.4, 5.5 Hz, 1H), 2.20 (dddd, *J* = 13.6, 10.4, 8.2, 5.5 Hz, 1H), 2.00 (ddt, *J* = 13.4, 10.4, 6.3 Hz, 1H), 1.41 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 148.0, 142.6, 136.5, 129.4, 129.2, 128.5, 128.4, 127.6, 127.1, 125.8, 125.8, 119.9, 42.7, 38.9, 34.1, 21.4.

HRMS (ESI): calc'd for $C_{19}H_{20}N$ $[M+H]^+$ 262.1590; found 262.1593.



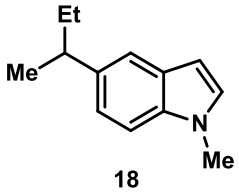
17

1-(*sec*-Butyl)napthalene[16]

Following the general procedure at 40 °C, **17** was prepared from fluoronapthalene (25.8 µL, 0.2 mmol) yielding the above compound (33.1 mg, 0.18 mmol, 90% yield) as a transparent oil after silica gel chromatography (pentane/EtOAc = 100:1 to 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 – 8.12 (m, 1H), 7.89 – 7.84 (m, 1H), 7.71 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.39 (dd, *J* = 7.3, 1.3 Hz, 1H), 3.53 (hept, *J* = 6.9 Hz, 1H), 1.95 – 1.80 (m, 1H), 1.79-1.67 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.9, 134.1, 131.9, 129.1, 126.3, 125.7, 125.7, 125.3, 123.4, 122.6, 35.5, 30.7, 21.4, 12.4.



18

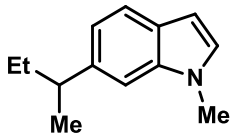
5-(*sec*-Butyl)-1-methyl-1*H*-indole

Following the general procedure at 40 °C, **18** was prepared from 5-fluoro-1-methyl-1H-indole (29.8 mg, 0.2 mmol) yielding the above compound (33.3 mg, 0.178 mmol, 89% yield) as a viscous, yellow oil after silica gel chromatography (pentane/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 1.6 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.00 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.93 (d, *J* = 3.1 Hz, 1H), 6.34 (d, *J* = 3.1 Hz, 1H), 3.68 (s, 3H), 2.61 (q, *J* = 7.0 Hz, 1H), 1.57 (tt, *J* = 8.1, 4.4 Hz, 2H), 1.21 (d, *J* = 6.9 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.8, 135.6, 128.9, 128.7, 121.3, 118.8, 109.0, 100.7, 41.9, 33.0, 31.8, 22.8, 12.6.

HRMS (ESI): calc'd for $C_{13}H_{18}N$ $[M+H]^+$ 188.1434; found 188.1435.



19

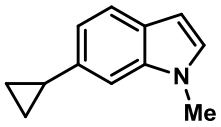
6-(*sec*-Butyl)-1-methyl-1*H*-indole

Following the general procedure at 40 °C, **19** was prepared from 6-fluoro-1-methyl-1H-indole (29.8 mg, 0.2 mmol) yielding the above compound (34.8 mg, 0.186 mmol, 93% yield) as a viscous, yellow oil after silica gel chromatography (pentane/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.01 – 6.94 (m, 2H), 6.44 (dd, *J* = 3.1, 0.9 Hz, 1H), 3.78 (s, 3H), 2.73 (q, *J* = 7.0 Hz, 1H), 1.67 (dd, *J* = 7.3, 4.3 Hz, 2H), 1.32 (d, *J* = 6.9 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.7, 137.1, 128.4, 126.8, 120.6, 119.2, 107.3, 100.7, 42.3, 32.9, 31.8, 22.7, 12.6.

HRMS (ESI): calc'd for $C_{13}H_{18}N$ $[M+H]^+$ 188.1434; found 188.1435.



20

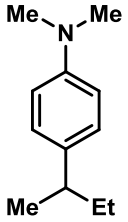
6-Cyclopropyl-1-methyl-1*H*-indole

Following the general procedure at 40 °C, **20** was prepared from 6-fluoro-1-methyl-1H-indole (29.8 mg, 0.2 mmol) yielding the above compound (27.7 mg, 0.162 mmol, 81% yield) as a viscous, yellow oil after silica gel chromatography (pentane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 1.7 Hz, 1H), 6.99 (d, *J* = 2.6 Hz, 1H), 6.89 (dd, *J* = 8.2, 1.6 Hz, 1H), δ 6.44 (d, *J* = 3.1 Hz, 1H), 3.77 (s, 3H), 2.07 (tt, *J* = 8.4, 5.1 Hz, 1H), 1.03 – 0.96 (m, 2H), 0.80 – 0.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.6, 137.2, 128.4, 126.7, 120.7, 118.1, 106.3, 101.2, 32.9, 16.1, 9.09.

HRMS (ESI): calc'd for $C_{12}H_{14}N$ $[M+H]^+$ 172.1126; found 172.1121.



21

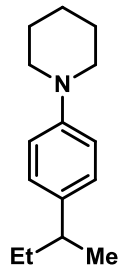
4-(*sec*-Butyl)-*N,N*-dimethylaniline

Following the general procedure at 60 °C, **21** was prepared from 4-fluoro-N,N-dimethylaniline (27.8 mg, 0.2 mmol) yielding the above compound (29.7 mg, mmol, 0.168 mmol, 84% yield) as a colorless oil after silica gel chromatography (pentane/MTBE = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8.8, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 2.92 (s, 6H), 2.51 (sext, *J* = 7.0 Hz, 1H), 1.56 (quint, *J* = 7.4 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.1, 136.1, 127.7, 113.0, 41.1, 40.8, 31.5, 22.1, 12.5.

HRMS (ESI): calc'd for $C_{12}H_{20}N$ $[M+H]^+$ 178.1590: found 178.1590.



22

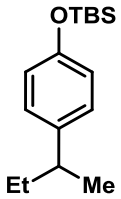
1-(4-(*sec*-Butyl)phenyl)piperidine

Following the general procedure at 60 °C, **22** was prepared from 1-(4-fluorophenyl)piperidine (35.8 mg, 0.2 mmol) yielding the above compound (31.2 mg, 0.144 mmol, 72% yield) as a colorless oil after silica gel chromatography (pentane/MTBE = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.14 – 3.11 (m, 4H), 2.53 (sext, *J* = 7.0 Hz, 1H), 1.75 – 1.70 (m, 4H), 1.60 – 1.53 (m, 4H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.6, 138.7, 127.6, 116.7, 51.2, 40.9, 31.5, 26.2, 24.5, 22.0, 12.4.

HRMS (ESI): calc'd for $C_{15}H_{24}N$ $[M+H]^+$ 218.1903; found 218.1905.



23

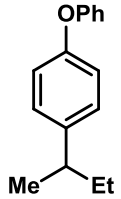
***tert*-Butyl(4-(*sec*-butyl)phenoxy)dimethylsilane**

Following the general procedure at 40 °C with the omission of CsF additive, **23** was prepared from *tert*-butyl(4-fluorophenoxy)dimethylsilane (45.2 mg, 0.2 mmol) yielding the above compound (44.8 mg, 0.17 mmol, 85% yield) as a pale-yellow oil after silica gel chromatography (pentane/MTBE = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 – 7.00 (m, 2H), 6.77 – 6.74 (m, 2H), 2.52 (sext, *J* = 7.0 Hz, 1H), 1.54 (quint, *J* = 7.3 Hz, 2H), 1.20 (d, *J* = 6.9 Hz, 3H), 0.98 (s, 9H), 0.80 (t, *J* = 7.4 Hz, 3H), 0.19 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.6, 140.5, 127.9, 119.8, 41.0, 31.5, 25.9, 22.1, 18.3, 12.4, -4.3.

HRMS (EI): calc'd for $C_{16}H_{28}OSi$ $[M]^+$ (264.1904); found 264.1902.



24

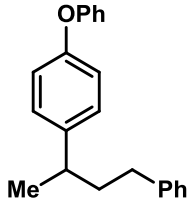
1-(*sec*-Butyl)-4-phenoxybenzene[17]

Following the general procedure at 40 °C, **24** was prepared from 1-fluoro-4-phenoxybenzene (37.6 mg, 0.2 mmol) yielding the above compound (30.7 mg, 0.136 mmol, 68% yield) as a colorless oil after silica gel chromatography (pentane/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 2H), 7.19 – 7.14 (m, 2H), 7.14 – 7.07 (m, 1H), 7.06 – 7.00 (m, 2H), 7.00 – 6.95 (m, 2H), 2.62 (q, *J* = 7.0 Hz, 1H), 1.62 (p, *J* = 7.4 Hz, 2H), 1.27 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.8, 155.1, 142.8, 129.8, 128.3, 123.0, 119.0, 118.7, 41.2, 31.5, 22.1, 12.4.

HRMS (EI): calc'd for $C_{16}H_{18}O$ $[M]^+$ 226.1358; found 226.1354.



25

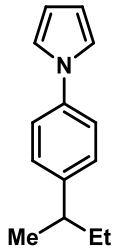
1-Phenoxy-4-(4-phenylbutan-2-yl)benzene

Following the general procedure at 40 °C, **25** was prepared from 1-fluoro-4-phenoxybenzene (37.6 mg, 0.2 mmol) yielding the above compound (38.7 mg, 0.128 mmol, 64% yield) as a transparent oil after silica gel chromatography (pentane/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.30 (m, 2 H), 7.28-7.24 (m, 2 H), 7.19-7.13 (m, 5 H), 7.10-7.05 (m, 1 H), 7.03-7.00 (m, 2 H), 6.98-6.95 (m, 2 H), 2.72 (q, *J* = 7.1 Hz, 1H), 2.53 (ddd, *J* = 8.7, 6.1, 2.1 Hz, 2H), 1.97 – 1.84 (m, 2H), 1.28 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.7, 155.3, 142.6, 142.4, 129.8, 128.5, 128.4, 128.4, 125.8, 123.1, 119.1, 118.7, 40.3, 39.0, 34.1, 22.7.

HRMS (EI): calc'd for $C_{22}H_{22}O$ $[M]^+$ 302.1671; found 302.1667.



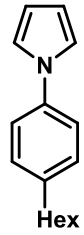
26

1-(4-(*sec*-Butyl)phenyl)-1*H*-pyrrole[18]

Following the general procedure, **26** was prepared from 1-(4-fluorophenyl)-1H-pyrrole (32.2 mg, 0.2 mmol) yielding the above compound (23.9 mg, 0.12 mmol, 60%) as a colorless oil after silica gel chromatography (pentane/EtOAc = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.08 (t, *J* = 2.1 Hz, 2H), 6.34 (t, *J* = 2.1 Hz, 2H), 2.68-2.60 (m, 1H), 1.65-1.59 (m, 2H), 1.26 (d, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 138.9, 128.2, 120.7, 119.5, 110.1, 41.3, 31.3, 22.0, 12.4.



27

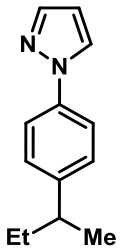
1-(4-Hexylphenyl)-1H-pyrrole

Following the general procedure, **27** was prepared from 1-(4-fluorophenyl)-1H-pyrrole (32.2 mg, 0.2 mmol) yielding the above compound (38.1 mg, 0.168 mmol, 84% yield) as a colorless oil after silica gel chromatography (pentane/EtOAc = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 2H), 7.25 – 7.21 (m, 2H), 7.07 (t, *J* = 2.2 Hz, 2H), 6.34 (t, *J* = 2.2 Hz, 2H), 2.67 – 2.60 (m, 2H), 1.64 (s, 2H), 1.42 – 1.29 (m, 6H), 0.94 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.6, 138.8, 129.5, 120.7, 119.5, 110.2, 35.5, 31.9, 31.6, 29.1, 22.8, 14.3.

HRMS (ESI): calc'd for $C_{16}H_{22}N$ $[M+H]^+$ 228.1747; found 228.1746.



28

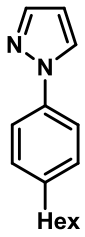
1-(4-(*sec*-Butyl)phenyl-1*H*-pyrazole

Following the general procedure, **28** was prepared from 1-(4-fluorophenyl)-1H-pyrazole (32.4 mg, 0.2 mmol) yielding the above compound (22.8 mg, 0.11 mmol, 57%) as a colorless oil after silica gel chromatography (pentane/EtOAc = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dt, *J* = 2.1, 1.0 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.62-7.57 (m, 2H), 7.28 – 7.23 (m, 2H), 6.45 (dd, *J* = 2.4, 1.8 Hz, 1H), 2.71 – 2.59 (m, 1H), 1.68 – 1.56 (m, 2H), 1.26 (d, *J* = 7.0 Hz, 3H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.2, 140.9, 129.4, 128.1, 126.8, 119.4, 107.4, 41.4, 31.3, 22.0, 12.3.

HRMS (ESI): calc'd for $C_{13}H_{17}N_2$ $[M+H]^+$ 201.1386; found 201.1388.



29

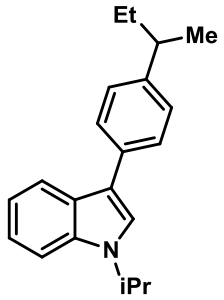
1-(4-Hexylphenyl)-1H-pyrazole

Following the general procedure, **29** was prepared from 1-(4-fluorophenyl)-1H-pyrazole (32.4 mg, 0.2 mmol) yielding the above compound (38.8 mg, 0.17 mmol, 85% yield) as a pale yellow residue after silica gel chromatography (pentane/EtOAc = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 2.4 Hz, 1H), 7.70 (d, *J* = 1.7 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.25 (dd, *J* = 7.2, 1.5 Hz, 2H), 6.47 – 6.41 (m, 1H), 2.68 – 2.59 (m, 2H), 1.69 – 1.56 (m, 2H), 1.42 – 1.24 (m, 6H), 0.88 (td, *J* = 5.9, 4.8, 2.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.5, 140.9, 138.3, 129.4, 126.8, 119.4, 107.4, 35.5, 31.8, 31.5, 29.0, 22.8, 14.2.

HRMS (ESI): calc'd for $C_{15}H_{21}N_2$ $[M+H]^+$ 229.1699; found 229.1701.



30

3-(4-(*sec*-Butyl)phenyl)-1-isopropyl-1*H*-indole

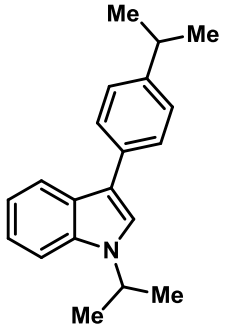
Small Scale: Following the general procedure at 40 °C, **30** was prepared from 3-(4-fluorophenyl)-1-methyl-1H-indole (**32**) (52.6 mg, 0.2 mmol) yielding the above compound (48.3 mg, 0.166 mmol, 83% yield) as a viscous, yellow oil after silica gel chromatography (pentane/EtOAc = 25:1).

Large Scale: A 100-mL Schlenk flask equipped with a stirring bar was charged 3-(4-fluorophenyl)-1-methyl-1H-indole (**32**) (1.267 g, 5 mmol), $Ni(acac)_2$ (128 mg, 0.5 mmol), and phosphine ligand (**L4)** (234 mg, 0.5 mmol). Anhydrous CsF (150 mg, 1 mmol) was added, followed by toluene (25 mL). After stirring for 10 min, *sec*-butylmagnesium chloride (5 mL, 2 M) was added in a *single* fast push, and the flask was immediately subjected to a heating bath preheated to 40 °C. The reaction was stirred for 24 h, at which point H_2O (20 mL) was added to the flask. The phases were separated, and the aq phase extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography to afford **31** as a yellow, viscous oil (1.253 g, 4.27 mmol, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.36 – 7.26 (m, 2H), 7.21 – 7.12 (m, 3H), 7.08 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 4.62 (hept, *J* = 6.7 Hz, 1H), 2.55 (p, *J* = 7.0 Hz, 1H), 1.64 – 1.48 (m, 2H), 1.47 (d, *J* = 6.7 Hz, 6H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.2, 136.4, 133.5, 127.5, 127.3, 126.5, 121.7, 121.3, 120.3, 119.8, 117.0, 109.8, 47.2, 41.5, 31.4, 23.0, 22.0, 12.5.

HRMS (ESI): calc'd for $C_{21}H_{26}N$ $[M+H]^+$ 292.2060; found 292.2060.



31

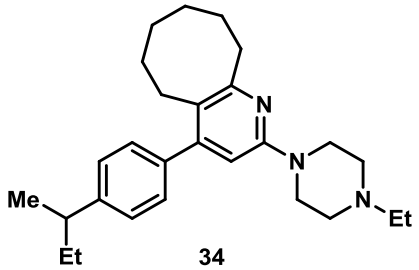
1-Isopropyl-3-(4-isopropylphenyl)-1*H*-indole

Following the general procedure at 40 °C, **31** was prepared from 3-(4-fluorophenyl)-1-isopropyl-1H-indole (50.6 mg, 0.2 mmol) yielding the above compound (49 mg, 0.178 mmol, 89% yield) as a pale-yellow oil after silica gel chromatography (pentane/MTBE = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.92 (m, 1H), 7.63 – 7.57 (m, 2H), 7.42 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.36 (s, 1H), 7.34 – 7.29 (m, 2H), 7.29 – 7.22 (m, 2H), 7.19-7.18 (d, *J* = 1.1 Hz, 1H), 4.72 (hept, *J* = 6.7 Hz, 1H), 3.02 – 2.91 (m, 1H), 1.57 (d, *J* = 6.7 Hz, 6H), 1.31 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.4, 136.4, 133.5, 127.4, 126.9, 126.5, 121.7, 121.4, 120.2, 119.8, 117.0, 109.8, 47.2, 33.4, 24.2, 23.0.

HRMS (ESI): calc'd for $C_{20}H_{24}N$ $[M+H]^+$ 278.1903; found 278.1903.



34

4-(4-(sec-Butyl)phenyl)-2-(4-ethylpiperazin-1-yl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine

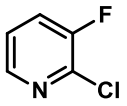
34 was prepared from blonanserin (**33**) (9.2 mg, 0.025 mmol) following the general procedure at 60°C with 10% metal and catalyst until the point of purification. The crude white solid obtained after standard aq workup was purified by preparative HPLC, which afforded **34** as an off white solid (4.2 mg, 42% yield single isomer, 46% yield of mix).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (q, *J* = 8.2 Hz, 4H), 6.35 (s, 1H), 3.56 (s, 4H), 2.92–2.84 (m, 2H), 2.63 (dt, *J* = 18.5, 6.6 Hz, 4H), 1.77 (d, *J* = 12.4 Hz, 2H), 1.67–1.58 (m, 2H), 1.50 – 1.05 (m, 14 H), 0.86 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): 159.8, 151.8, 146.7, 138.8, 128.3, 126.6, 123.3, 106.3, 52.6, 52.4, 45.5, 41.4, 35.5, 31.6, 31.2, 30.6, 29.7, 26.6, 26.5, 25.9, 21.7, 12.3.

HRMS (**ESI**): calc'd for $C_{27}H_{40}N_3$ $[M+H]^+$ 406.3217; found 406.3125.

By ^{13}C NMR three carbon peaks were not effectively resolved. The product identity was confirmed spectroscopically by mass spec and 2D HMBC.

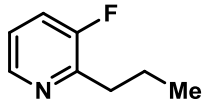


36

2-Chloro-3-fluoropyridine

Prepared according to Schlosser's protocol[6]. A Schlenk flask equipped with a stir bar was charged with DABCO (561 mg, 5 mmol), Et_2O (25 mL) and hexane (3 mL). The flask was cooled to -20 °C, at which point n-BuLi (3.13 mL, 1.6 M, 5 mmol) was added dropwise. The solution stirred for 1 h at -20 °C, was cooled to -60 °C, and then charged dropwise with 3-fluoropyridine (0.43 mL, 5 mmol). The solution stirred for an additional hour at the same temperature, and then hexachloroethane (1.184 g, 5 mmol) was added all at once. The cooling bath was removed and the flask was warmed to rt. Then H_2O (15 mL) was added. The phases were separated, and the aq layer extracted with Et_2O (3 × 15). The combined organic layers were dried over Na_2SO_4, concentrated, and purified by flash chromatography (pentane/EtOAc = 3:1) to yield **36** as an off yellow oil (348 mg, 2.65 mmol, 53% yield). Purity was in accordance with commercially available **36**.

CAS: 17282-04-1



37

3-Fluoro-2-propylpyridine

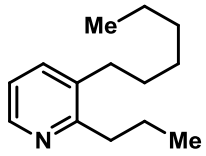
Prepared according to Fürstner's protocol[19]. A Schlenk flask was charged with 2-chloro-3-fluoropyridine **36** (260 mg, 2 mmol), $Fe(acac)_3$ (35.3 mg, 0.1 mmol) , THF (10 mL), and NMP (1 mL). Then, n-PrMgBr (1.2 mL, 0.2 M, 0.24 mmol) was added to the flask in a *single* push. The reaction was stirred at room temperature for 30 min, and then quenched with H_2O. The layers were partitioned, and the aq layer extracted with MTBE (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated *in vacuo*, and purified by column chromatography (pentane/EtOAc = 5:1), to afford **37** (255 mg, 1.84 mmol, 92% yield) as an off yellow, viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (dt, *J* = 4.7, 1.5 Hz, 1H), 7.30 (ddd, *J* = 9.6, 8.2, 1.4 Hz, 1H), 7.11 (dt, *J* = 8.5, 4.4 Hz, 1H), 2.82 (ddd, *J* = 7.8, 6.8, 2.5 Hz, 2H), 1.82 – 1.70 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 156.6, 150.7 (d, *J* = 15.5 Hz), 144.9 (d, *J* = 5.4 Hz), 122.8 – 121.9 (m), 33.6 (d, *J* = 2.4 Hz), 21.9, 13.9.

^{19}F NMR (282 MHz, $CDCl_3$): δ 125.8.

HRMS (ESI): calc'd for $C_8H_{11}FN$ $[M+H]^+$ 140.0870; found 140.0871.



38

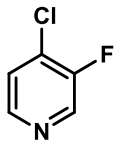
3-Hexyl-2-propylpyridine

Following the general procedure with 10 mol% metal and ligand, **38** was prepared from 3-fluoro-2-propylpyridine **37** (13.9 mg, 0.1 mmol) yielding the above compound (11.5 mg, 0.056 mmol, 56% yield) as a colorless oil following flash chromatography (pentane/EtOAc = 6:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.40 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.03 (dd, *J* = 7.6, 4.7 Hz, 1H), 2.81 – 2.73 (m, 2H), 2.64 – 2.55 (m, 2H), 1.82 – 1.68 (m, 2H), 1.57 (tt, *J* = 7.8, 6.2 Hz, 2H), 1.41 – 1.28 (m, 6H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.92 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.3, 146.7, 136.7, 135.7, 121.1, 37.1, 32.4, 31.8, 30.8, 29.4, 23.1, 22.8, 14.4, 14.2.

HRMS (ESI): calc'd for $C_{14}H_{24}N$ $[M+H]^+$ 206.1903; found 206.1903.

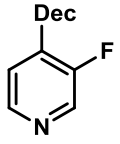


39

4-Chloro-3-fluoropyridine

Prepared according to Schlosser's protocol[6]. A Schlenk flask equipped with a stir bar was charged with n-BuLi (3.13 mL, 1.6 M, 5 mmol), THF (7 mL), and hexanes (3 mL) and cooled in a dry ice/MeOH bath. Diisopropyl amine (0.70 mL, 5 mmol) was added dropwise, stirred at -20 °C for 20 min, and cooled at -75 °C. Then 3-fluoropyridine (0.43 mL, 5 mmol) was added dropwise, and the mixture was aged for 2 h at -75 °C. Hexachloroethane (1.184 g, 5 mmol) was added all at once. The cooling bath was removed and the flask was warmed to rt. Then H_2O (15 mL) was added. The phases were separated, and the aq layer extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and purified by flash chromatography (pentane/EtOAc = 3:1) to yield **40** as an off yellow oil (375 mg, 2.85 mmol, 57% yield). Purity was in accordance with commercially available **40**.

CAS: 2546-56-7



40

3-Fluoro-4-hexylpyridine

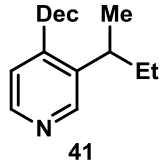
Prepared according to Fürstner's protocol[19]. A Schlenk flask was charged with 4-chloro-3-fluoropyridine **39** (260 mg, 2 mmol), $Fe(acac)_3$ (35.3 mg, 0.1 mmol) , THF (10 mL), and NMP (1 mL). Then, DecylMgBr (1.2 mL, 2.0 M, 2.4 mmol) was added to the flask in a *single* push. The reaction was stirred at room temperature for 30 min, and then quenched with H_2O. The layers were partitioned, and the aq layer extracted with MTBE (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and purified by column chromatography (pentane/EtOAc = 5:1), to afford **40** (465 mg, 1.98 mmol, 96% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 1.7 Hz, 1H), 8.29 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.13 (dd, *J* = 6.4, 4.9 Hz, 1H), 2.70 – 2.62 (m, 2H), 1.68 – 1.57 (m, 2H), 1.35 – 1.24 (m, 14H), 0.92 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6 (d, *J* = 253.9 Hz), 145.6 (d, *J* = 5.0 Hz), 138.5 (d, *J* = 14.0 Hz), 137.8 (d, *J* = 25.0 Hz), 125.2 (d, *J* = 2.5 Hz), 32.0, 28.4 (d, *J* = 2.0 Hz), 22.8, 14.3.

^{19}F NMR (282 MHz, $CDCl_3$): δ -133.5.

HRMS (ESI): calc'd for $C_{15}H_{25}FN$ $[M+H]^+$ 238.1966; found 238.1966.



41

3-(*sec*-butyl)-4-hexylpyridine

Following the general procedure at 40 °C with 10 mol% catalyst and ligand loading, **41** was prepared from 3-fluoro-4-hexylpyridine **40** (19 mg, 0.1 mmol) yielding the above compound (16 mg, 0.057 mmol, 57%) as a colorless oil following flash chromatography (pentane/MTBE = 1:1).

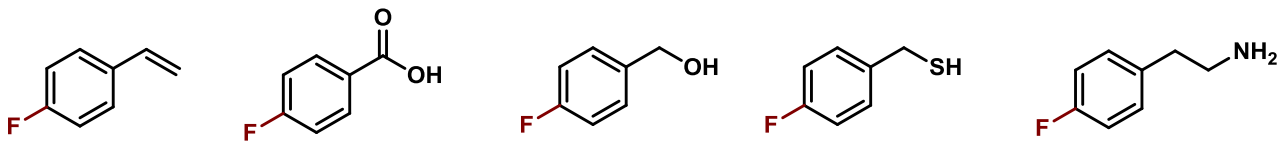
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 – 8.27 (m, 3H), 7.03 (dd, *J* = 8.0, 5.1 Hz, 1H), 2.88 (q, *J* = 7.1 Hz, 1H), 2.69 – 2.52 (m, *J* = 7.8 Hz, 4H), 1.73 – 1.51 (m, 6H), 1.45 – 1.22 (m, 25H), 0.98 – 0.83 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.3, 148.9, 148.0, 147.2, 146.7, 123.9, 34.3, 33.2, 32.1, 31.9, 31.8. 30.7, 30.6, 30.2, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 22.7, 21.8, 14.1, 13.9, 12.3.

HRMS (ESI): calc'd for $C_{19}H_{33}N$ $[M+H]^+$ 276.2684; found 276.2686.

7. Additional Results/Observations

Example Unsuccessful Substrates



Some substrates did not afford alkylated product under our catalytic protocol or proved recalcitrant to facile purification. For example, 4-fluorostyrene failed to show any conversion from the starting material. Molecules with functionality at the benzylic position also proved incompatible, and did not provide an indication of reactivity. Primary amines were also problematic, and no product was detected.

Grignard reagents prepared with solutions of THF were also found to perform poorly, and THF employed as solvent was found to preclude observable reaction progress. We propose that this detrimental effect arises through formation of an adduct with the Grignard, but thus far, only speculation has been put forth.

Additional Experiments and Considerations

After optimization, control reactions showed the requirement of the nickel catalyst and ligand to obtain couple product. Furthermore, control experiments for all electron deficient compounds that might experience competing S_NAr pathways of the Grignard without participation of the catalyst were completed. In each case, no product was observed when the catalyst was excluded.

An attempt to expand the scope to tertiary nucleophiles led to rearrangement of the nucleophile *t*-BuMgCl, with several distinct isomers identified by GC. Therefore, further attempts to expand beyond *t*-BuMgCl were not explored. Experiments utilizing chiral nucleophiles were not attempted for utilization herein.

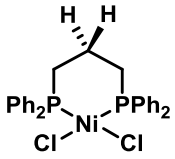
While Grignard nucleophiles were consistently added in a single push, the relevance of an exotherm does not seem to strongly influence the reaction. This is demonstrated by compound **30**, as the scale up had only a slight influence on the reaction outcome, despite the expected distinct exotherm profiles.

8. X-ray Crystallography Data

General Procedure

To obtain crystals suitable for X-ray study, NiCl2·6 H_2O (63.3 mg, 0.121 mmol) was dissolved in EtOH (1 mL). A solution of phosphine ligand (0.121 mmol) in DCM (0.8 mL) was added to the solution. The resulting red/orange solid was washed with Et_2O (3 × 1 mL). The solid was then dried *in vacuo*. Afterwards, the solid was dissolved in DCM (24 mL) and layered with Et_2O to obtain crystals. X-ray analysis was subsequently completed.

X-Ray Data for Compound $NiCl_2$·**L1**



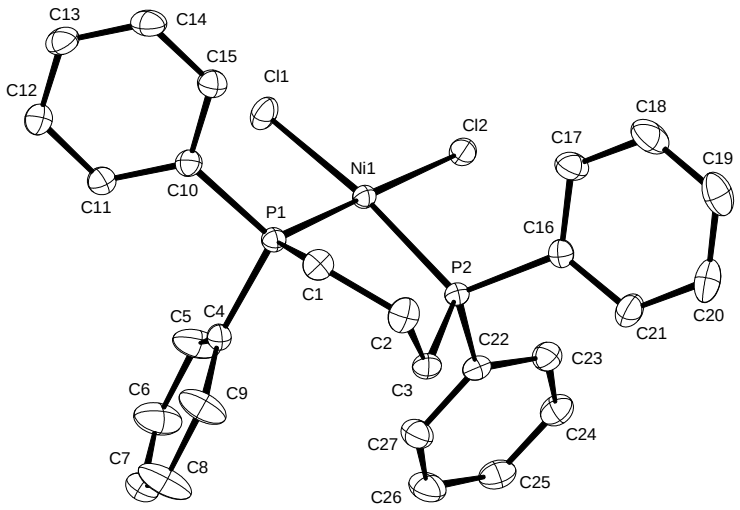


Table SX. Crystal data and structure refinement.

Identification code	11120
Empirical formula	$C_{27}H_{26}Cl_2NiP_2$
Color	red
Formula weight	542.03 g · mol^{-1}
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	TRICLINIC
Space group	**$P\bar{1}$, (no. 2)**
Unit cell dimensions	a = 8.4067(11) Å α= 88.217(16)°.

	b = 10.4499(14) Å	β= 79.904(19)°.
	c = 14.456(4) Å	γ = 73.186(14)°.
Volume	1196.6(4) $Å^3$	
Z	2	
Density (calculated)	1.504 $Mg \cdot m^{-3}$	
Absorption coefficient	1.182 mm^{-1}	
F(000)	560 e	
Crystal size	0.14 x 0.13 x 0.13 mm^3	
θ range for data collection	2.716 to 33.200°.	
Index ranges	$-12 \le h \le 12$, $-16 \le k \le 16$, $-22 \le l \le 22$	
Reflections collected	43081	
Independent reflections	9123 [R_{int} = 0.0454]	
Reflections with I>2σ(I)	7206	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.90 and 0.87	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9123 / 0 / 289	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2σ(I)]	R_1 = 0.0378	wR^2 = 0.0864
R indices (all data)	R_1 = 0.0558	wR^2 = 0.0959
Largest diff. peak and hole	0.6 and -0.9 e $\cdot Å^{-3}$	

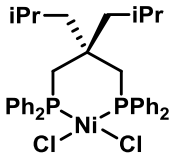
Table SX. Bond lengths [Å] and angles [°].

Ni(1)-Cl(1)	2.2062(6)	Ni(1)-Cl(2)	2.2138(5)	Ni(1)-P(1)	2.1737(5)	Ni(1)-P(2)	2.1690(6)
P(1)-C(1)	1.8444(17)	P(1)-C(4)	1.8195(16)	P(1)-C(10)	1.8200(16)	P(2)-C(3)	1.8350(17)
P(2)-C(16)	1.8155(17)	P(2)-C(22)	1.8174(17)	C(1)-C(2)	1.538(2)	C(2)-C(3)	1.532(2)
C(4)-C(5)	1.385(2)	C(4)-C(9)	1.391(3)	C(5)-C(6)	1.393(3)	C(6)-C(7)	1.365(3)
C(7)-C(8)	1.380(3)	C(8)-C(9)	1.388(3)	C(10)-C(11)	1.392(2)	C(10)-C(15)	1.401(2)
C(11)-C(12)	1.397(2)	C(12)-C(13)	1.390(3)	C(13)-C(14)	1.383(3)	C(14)-C(15)	1.395(2)
C(16)-C(17)	1.390(2)	C(16)-C(21)	1.395(2)	C(17)-C(18)	1.389(3)	C(18)-C(19)	1.392(3)
C(19)-C(20)	1.383(3)	C(20)-C(21)	1.392(3)	C(22)-C(23)	1.396(2)	C(22)-C(27)	1.399(2)
C(23)-C(24)	1.393(2)	C(24)-C(25)	1.379(3)	C(25)-C(26)	1.390(3)	C(26)-C(27)	1.395(3)

Cl(1)-Ni(1)-Cl(2)	91.96(2)	P(1)-Ni(1)-Cl(1)	90.58(2)	P(1)-Ni(1)-Cl(2)	176.329(18)	P(2)-Ni(1)-Cl(1)	170.017(19)
P(2)-Ni(1)-P(1)	91.03(2)	C(4)-P(1)-Ni(1)	109.44(6)	C(4)-P(1)-C(1)	106.28(8)	C(4)-P(1)-C(10)	106.19(7)
C(10)-P(1)-C(1)	101.10(8)	C(16)-P(2)-Ni(1)	115.66(6)	C(16)-P(2)-C(3)	115.30(6)	C(16)-P(2)-C(22)	107.44(8)
C(22)-P(2)-C(3)	103.74(8)	C(3)-C(2)-C(1)	115.31(14)	C(5)-C(4)-P(1)	118.74(13)	C(9)-C(4)-P(1)	122.56(13)
C(7)-C(6)-C(5)	120.41(19)	C(7)-C(8)-C(9)	120.9(2)	C(11)-C(10)-P(1)	121.84(12)		

C(10)-C(15)	119.53(15)	C(15)-C(10)-P(1)	118.61(13)	C(10)-
C(11)-C(12)	120.14(16)	C(13)-C(12)-C(11)	119.89(17)	C(14)-
C(13)-C(12)	120.35(16)	C(13)-C(14)-C(15)	120.05(16)	C(14)-
C(15)-C(10)	120.03(16)	C(17)-C(16)-P(2)	120.49(13)	C(17)-
C(16)-C(21)	119.33(16)	C(21)-C(16)-P(2)	120.00(13)	C(18)-
C(17)-C(16)	119.97(18)	C(17)-C(18)-C(19)	120.45(19)	C(20)-
C(19)-C(18)	119.83(18)	C(19)-C(20)-C(21)	119.83(18)	C(20)-
C(21)-C(16)	120.59(18)	C(23)-C(22)-P(2)	121.44(13)	C(23)-
C(22)-C(27)	119.32(15)	C(27)-C(22)-P(2)	119.08(13)	C(24)-
C(23)-C(22)	120.03(16)	C(25)-C(24)-C(23)	120.43(17)	C(24)-
C(25)-C(26)	120.18(17)	C(25)-C(26)-C(27)	119.88(17)	C(26)-
C(27)-C(22)	120.16(17)			

X-Ray Data for Compound $NiCl_2$·**L2**



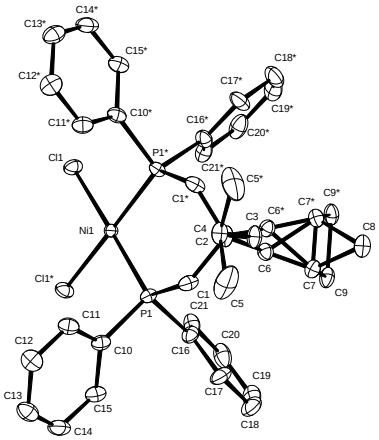


Table SX. Crystal data and structure refinement.

Identification code	11182	
Empirical formula	$C_{35}H_{40}Cl_2NiP_2$	
Color	orange	
Formula weight	652.22 g · mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	TETRAGONAL	
Space group	**I4/m, (no. 87)**	
Unit cell dimensions	a = 19.534(3) Å	α= 90°.
	b = 19.534(3) Å	β= 90°.

	c = 17.501(4) Å γ = 90°.
Volume	6678(2) Å^3
Z	8
Density (calculated)	1.298 Mg · m^{-3}
Absorption coefficient	0.859 mm^{-1}
F(000)	2736 e
Crystal size	0.11 x 0.045 x 0.04 mm^3
θ range for data collection	2.606 to 31.075°.
Index ranges	-28 ≤ h ≤ 28, -28≤ k ≤ 28, -20 ≤ l ≤ 25
Reflections collected	61097
Independent reflections	5522 [R_{int} = 0.0767]
Reflections with I>2σ(I)	4132
Completeness to θ = 25.242°	99.8 %
Absorption correction	Gaussian
Max. and min. transmission	0.96830 and 0.93116
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5522 / 0 / 213
Goodness-of-fit on F^2	1.107
Final R indices [I>2σ(I)]	R_1 = 0.0467 wR^2 = 0.0965
R indices (all data)	R_1 = 0.0752 wR^2 = 0.1078
Remarks	**SQUEEZE was applied**
Largest diff. peak and hole	0.8 and -0.4 e · Å^{-3}

Table SX. Bond lengths [Å] and angles [°].

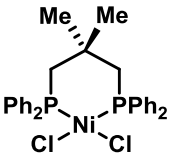
Ni(1)-Cl(1)*	2.1910(6)	Ni(1)-Cl(1)	2.1910(6)	Ni(1)-P(1)*	2.1650(6)
Ni(1)-P(1)	2.1650(6)	P(1)-C(1)	1.845(2)	P(1)-C(10)	1.828(2)
P(1)-C(16)	1.824(2)	C(1)-C(2)	1.534(3)	C(2)-C(3)	1.552(4)
C(2)-C(6)*	1.575(5)	C(2)-C(6)	1.575(5)	C(11)-C(10)	1.391(3)
C(11)-C(12)	1.395(3)	C(8)-C(7)*	1.581(5)	C(8)-C(7)	1.581(5)
C(3)-C(4)	1.545(4)	C(10)-C(15)	1.401(3)	C(14)-C(15)	1.383(3)
C(14)-C(13)	1.381(4)	C(12)-C(13)	1.388(4)	C(17)-C(16)	1.389(3)
C(17)-C(18)	1.401(3)	C(21)-C(16)	1.399(3)	C(21)-C(20)	1.397(3)
C(18)-C(19)	1.391(4)	C(4)-C(5)*	1.521(3)	C(4)-C(5)	1.521(3)
C(20)-C(19)	1.373(4)	C(7)-C(7)*	1.294(9)	C(7)-C(9)	1.527(6)
C(7)-C(6)	1.277(6)	C(7)-C(6)*	1.551(6)	C(9)-C(9)*	1.614(10)
C(6)-C(6)*	0.599(7)				

Cl(1)*-Ni(1)-Cl(1)	91.41(3)	P(1)*-Ni(1)-Cl(1)	86.14(2)	P(1)*-Ni(1)-Cl(1)*	176.93(3)
P(1)-Ni(1)-Cl(1)*	86.14(2)	P(1)*-Ni(1)-P(1)	176.93(3)	P(1)*-Ni(1)-P(1)	96.25(3)
C(1)-P(1)-Ni(1)	119.37(7)	C(10)-P(1)-Ni(1)	112.53(7)	C(10)-P(1)-C(1)	100.00(10)
C(16)-P(1)-Ni(1)	112.77(8)	C(16)-P(1)-C(10)	105.57(10)	C(16)-P(1)-C(1)	104.98(10)
C(2)-C(1)-P(1)	109.9(2)	C(1)*-C(2)-C(1)	119.66(17)	C(1)-C(2)-C(3)	107.26(16)
C(1)-C(2)-C(6)	107.27(16)	C(1)*-C(2)-C(6)*	100.97(19)	C(1)*-C(2)-C(6)	100.96(19)
C(1)-C(2)-C(6)*	120.1(2)	C(3)-C(2)-C(6)	110.6(3)	C(6)-C(2)-C(6)*	120.4(2)
C(7)-C(8)-C(6)*	21.9(3)	C(11)-C(10)-C(15)	117.5(2)	C(11)-C(10)-P(1)	119.3(2)
C(15)-C(10)-P(1)	121.2(2)	C(14)-C(15)-C(10)	119.9(2)	C(18)-C(17)-C(16)	119.7(2)

C(16)	120.2(2)	C(16)-C(21)-C(20)	119.8(2)	C(17)-C(18)-
C(19)	120.0(2)	C(5)*-C(4)-C(3)	110.3(2)	C(5)-C(4)-
C(3)	110.3(2)	C(5)-C(4)-C(5)*	111.2(4)	C(19)-C(20)-
C(21)	120.6(2)	C(14)-C(13)-C(12)	119.6(2)	C(17)-C(16)-
P(1)	120.28(18)	C(21)-C(16)-P(1)	120.49(17)	C(21)-
C(16)-C(17)	119.2(2)	C(20)-C(19)-C(18)	120.1(2)	C(7)*-C(7)-
C(8)	65.85(16)	C(7)*-C(7)-C(9)	96.0(2)	C(7)*-C(7)-
C(6)*	52.4(2)	C(9)-C(7)-C(8)	108.8(3)	C(9)-C(7)-
C(6)*	108.5(3)	C(6)*-C(7)-C(8)	109.3(3)	C(6)-C(7)-
C(8)	126.4(4)	C(6)-C(7)-C(7)*	74.2(3)	C(6)-C(7)-
C(9)	109.7(4)	C(6)-C(7)-C(6)*	21.8(3)	C(7)-C(9)-
C(9)*	84.0(2)	C(7)*-C(6)-C(2)	116.2(3)	C(7)-C(6)-
C(2)	136.8(4)	C(7)-C(6)-C(7)*	53.4(4)	C(6)*-C(6)-
C(2)	79.04(14)	C(6)*-C(6)-C(7)	105.8(3)	C(6)*-C(6)-
C(7)*	52.4(2)			

Symmetry transformations used to generate equivalent atoms: * x,y,-z+1

X-Ray Data for Compound $NiCl_2$·**L3**



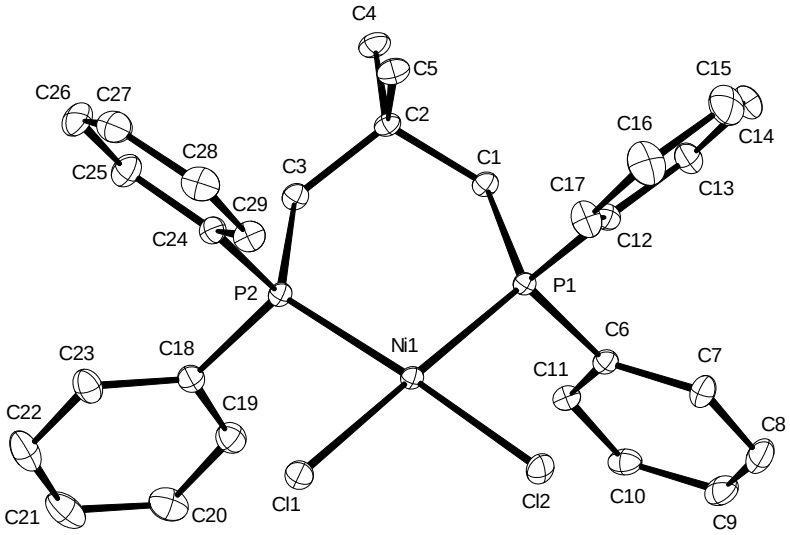


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Table SX. Crystal data and structure refinement.

Identification code	11121	
Empirical formula	$C_{29}H_{30}Cl_2NiP_2$	
Color	orange	
Formula weight	570.08 g · mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 11.2173(14) Å	α= 90°.
	b = 17.533(2) Å	β= 92.921(2)°.

	c = 13.6391(16) Å	γ = 90°.
Volume	2678.9(6) $Å^3$	
Z	4	
Density (calculated)	1.413 $Mg \cdot m^{-3}$	
Absorption coefficient	1.060 mm^{-1}	
F(000)	1184 e	
Crystal size	0.132 x 0.032 x 0.032 mm^3	
θ range for data collection	1.818 to 35.213°.	
Index ranges	$-18 \leq h \leq 18$, $-28 \leq k \leq 28$, $-22 \leq l \leq 22$	
Reflections collected	99600	
Independent reflections	11933 [R_{int} = 0.0850]	
Reflections with I>2σ(I)	8635	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98 and 0.89	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11933 / 0 / 309	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2σ(I)]	R_1 = 0.0393	wR^2 = 0.0920
R indices (all data)	R_1 = 0.0703	wR^2 = 0.1084
Largest diff. peak and hole	0.7 and -0.9 $e \cdot Å^{-3}$	

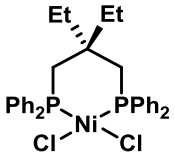
Table SX. Bond lengths [Å] and angles [°].

Ni(1)-Cl(1)	2.1924(5)	Ni(1)-Cl(2)	2.2056(5)	Ni(1)-P(1)	2.1659(5)
Ni(1)-P(2)	2.1591(5)	P(1)-C(1)	1.8334(15)	P(1)-C(6)	1.8140(15)
P(1)-C(12)	1.8140(17)	P(2)-C(3)	1.8271(16)	P(2)-C(18)	1.8205(17)
P(2)-C(24)	1.8225(16)	C(1)-C(2)	1.534(2)	C(2)-C(3)	1.536(2)
C(2)-C(4)	1.537(2)	C(2)-C(5)	1.532(2)	C(6)-C(7)	1.395(2)
C(6)-C(11)	1.396(2)	C(7)-C(8)	1.387(2)	C(8)-C(9)	1.387(3)
C(9)-C(10)	1.383(3)	C(10)-C(11)	1.393(2)	C(12)-C(17)	1.398(2)
C(12)-C(13)	1.395(2)	C(13)-C(14)	1.386(3)	C(14)-C(15)	1.384(3)
C(15)-C(16)	1.382(3)	C(16)-C(17)	1.388(3)	C(18)-C(23)	1.396(2)
C(18)-C(19)	1.395(2)	C(19)-C(20)	1.387(3)	C(20)-C(21)	1.386(3)
C(21)-C(22)	1.385(3)	C(22)-C(23)	1.391(3)	C(24)-C(29)	1.401(2)
C(24)-C(25)	1.392(2)	C(25)-C(26)	1.390(2)	C(26)-C(27)	1.387(3)
C(27)-C(28)	1.379(3)	C(28)-C(29)	1.395(2)		

Cl(1)-Ni(1)-Cl(2)	92.276(17)	P(1)-Ni(1)-Cl(1)	179.183(18)	P(1)-Ni(1)-Cl(2)	87.218(17)
P(2)-Ni(1)-Cl(1)	84.040(17)	P(2)-Ni(1)-Cl(2)	176.270(18)	P(2)-Ni(1)-P(1)	96.472(17)
C(1)-P(1)-Ni(1)	120.66(5)	C(6)-P(1)-C(1)	110.05(5)	C(6)-P(1)-Ni(1)	101.20(7)
C(6)-P(1)-C(12)	107.25(7)	C(12)-P(1)-Ni(1)	112.87(5)	C(12)-P(1)-C(1)	103.54(8)
C(3)-P(2)-Ni(1)	119.41(5)	C(18)-P(2)-Ni(1)	110.75(5)	C(18)-P(2)-C(3)	99.69(7)
C(18)-P(2)-C(24)	108.50(8)	C(24)-P(2)-Ni(1)	112.88(6)	C(24)-P(2)-C(3)	104.45(7)
C(2)-C(1)-P(1)	118.08(10)	C(1)-C(2)-C(4)	107.18(12)	C(1)-C(2)-C(3)	109.57(13)
C(3)-C(2)-C(4)	106.50(13)	C(5)-C(2)-C(1)	111.43(13)	C(5)-C(2)-C(3)	112.16(13)
C(7)-C(6)-C(4)	109.77(13)	C(7)-C(6)-P(1)	118.20(11)	C(11)-C(6)-C(4)	121.62(12)
C(7)-C(6)-C(11)	119.49(14)	C(11)-C(6)-P(1)			

P(1)	118.77(12)	C(8)-C(7)-C(6)	119.64(16)	C(9)-C(8)-
C(7)	120.62(16)	C(10)-C(9)-C(8)	120.20(15)	C(9)-C(10)-
C(11)	119.57(16)	C(10)-C(11)-C(6)	120.47(15)	C(13)-C(12)-
P(1)	120.61(12)	C(17)-C(12)-P(1)	120.23(13)	C(17)-C(12)-
C(13)	119.09(15)	C(14)-C(13)-C(12)	120.46(16)	C(15)-C(14)-
C(13)	119.79(17)	C(16)-C(15)-C(14)	120.37(18)	C(15)-C(16)-
C(17)	120.16(17)	C(16)-C(17)-C(12)	120.13(17)	C(19)-C(18)-
P(2)	116.44(13)	C(23)-C(18)-P(2)	124.08(13)	C(23)-C(18)-
C(19)	119.47(16)	C(20)-C(19)-C(18)	120.30(17)	C(21)-C(20)-
C(19)	120.08(17)	C(22)-C(21)-C(20)	119.85(18)	C(21)-C(22)-
C(23)	120.58(18)	C(22)-C(23)-C(18)	119.67(17)	C(25)-C(24)-
P(2)	120.89(13)	C(29)-C(24)-P(2)	120.08(12)	C(29)-C(24)-
C(25)	118.96(15)	C(26)-C(25)-C(24)	120.48(17)	C(27)-C(26)-
C(25)	119.77(17)	C(28)-C(27)-C(26)	120.36(16)	C(27)-C(28)-
C(29)	120.14(17)	C(24)-C(29)-C(28)	120.28(16)	

X-Ray Data for Compound $NiCl_2$·**L4**



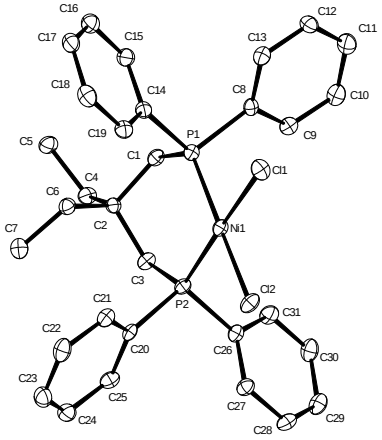


Table SX. Crystal data and structure refinement.

Identification code	11157	
Empirical formula	$C_{31}H_{34}Cl_2NiP_2$	
Color	orange	
Formula weight	598.13 g · mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/n$, (no. 14)**	
Unit cell dimensions	a = 11.201(8) Å	α= 90°.
	b = 19.982(12) Å	β= 110.304(18)°.
	c = 13.383(10) Å	γ = 90°.

Volume	2809(3) $Å^3$	
Z	4	
Density (calculated)	1.414 $Mg \cdot m^{-3}$	
Absorption coefficient	1.014 mm^{-1}	
F(000)	1248 e	
Crystal size	0.14 x 0.03 x 0.02 mm^3	
θ range for data collection	2.814 to 31.096°.	
Index ranges	$-16 \leq h \leq 16$, $-28 \leq k \leq 29$, $-19 \leq l \leq 19$	
Reflections collected	52505	
Independent reflections	9005 [R_{int} = 0.1251]	
Reflections with I>2σ(I)	5304	
Completeness to θ = 25.242°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98 and 0.88	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9005 / 0 / 327	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2σ(I)]	R_1 = 0.0608	wR^2 = 0.0853
R indices (all data)	R_1 = 0.1328	wR^2 = 0.1046
Largest diff. peak and hole	0.6 and -0.7 e $\cdot Å^{-3}$	

Table SX. Bond lengths [Å] and angles [°].

Ni(1)-Cl(1)	2.2189(13)	Ni(1)-Cl(2)	2.2015(16)	Ni(1)-
P(1)	2.1596(16)	Ni(1)-P(2)	2.1728(13)	P(1)-
C(1)	1.839(3)	P(1)-C(8)	1.824(3)	P(1)-C(14)
1.828(3)	P(2)-C(3)	1.847(3)	P(2)-C(20)	1.824(3)
P(2)-C(26)	1.829(3)	C(1)-C(2)	1.535(4)	C(2)-C(3)
1.541(4)	C(2)-C(4)	1.553(4)	C(2)-C(6)	1.543(4)
C(4)-C(5)	1.521(4)	C(6)-C(7)	1.531(4)	C(8)-C(9)
1.404(4)	C(8)-C(13)	1.390(4)	C(9)-C(10)	
1.382(5)	C(10)-C(11)	1.390(5)	C(11)-C(12)	
1.391(5)	C(12)-C(13)	1.385(4)	C(14)-C(15)	
1.393(4)	C(14)-C(19)	1.396(4)	C(15)-C(16)	
1.391(4)	C(16)-C(17)	1.385(4)	C(17)-C(18)	
1.389(5)	C(18)-C(19)	1.391(4)	C(20)-C(21)	
1.399(4)	C(20)-C(25)	1.396(4)	C(21)-C(22)	
1.389(5)	C(22)-C(23)	1.377(5)	C(23)-C(24)	
1.391(5)	C(24)-C(25)	1.387(4)	C(26)-C(27)	
1.396(4)	C(26)-C(31)	1.399(4)	C(27)-C(28)	
1.391(4)	C(28)-C(29)	1.382(4)	C(29)-C(30)	
1.386(5)	C(30)-C(31)	1.384(4)		

Cl(2)-Ni(1)-Cl(1)	92.46(5)	P(1)-Ni(1)-Cl(1)	85.67(5)	P(1)-Ni(1)-
Cl(2)	177.92(4)	P(1)-Ni(1)-P(2)	95.45(5)	P(2)-Ni(1)-
Cl(1)	178.64(4)	P(2)-Ni(1)-Cl(2)	86.43(5)	C(1)-P(1)-
Ni(1)	120.27(11)	C(8)-P(1)-Ni(1)	110.71(10)	C(8)-
P(1)-C(1)	100.57(14)	C(8)-P(1)-C(14)	106.59(14)	C(14)-
P(1)-Ni(1)	113.34(10)	C(14)-P(1)-C(1)	103.88(14)	C(3)-
P(2)-Ni(1)	121.47(11)	C(20)-P(2)-Ni(1)	112.93(11)	C(20)-
P(2)-C(3)	102.49(14)	C(20)-P(2)-C(26)	106.02(14)	C(26)-
P(2)-Ni(1)	111.29(11)	C(26)-P(2)-C(3)	101.00(14)	C(2)-
C(1)-P(1)	118.9(2)	C(1)-C(2)-C(3)	107.9(2)	C(1)-C(2)-
C(4)	106.8(2)	C(1)-C(2)-C(6)	111.5(2)	C(3)-C(2)-
C(4)	106.6(2)	C(3)-C(2)-C(6)	112.4(2)	C(6)-C(2)-
C(4)	111.2(2)	C(2)-C(3)-P(2)	118.4(2)	C(5)-C(4)-

C(2)	115.7(3)	C(7)-C(6)-C(2)	115.7(3)	C(9)-C(8)-
P(1)	117.8(2)	C(13)-C(8)-P(1)	123.4(2)	C(13)-C(8)-
C(9)	118.8(3)	C(10)-C(9)-C(8)	120.8(3)	C(9)-C(10)-
C(11)	119.9(3)	C(10)-C(11)-C(12)	119.6(3)	C(13)-C(12)-
C(11)	120.5(3)	C(12)-C(13)-C(8)	120.4(3)	C(15)-C(14)-
P(1)	119.6(2)	C(15)-C(14)-C(19)	119.4(3)	C(19)-C(14)-
P(1)	121.0(2)	C(16)-C(15)-C(14)	120.6(3)	C(17)-C(16)-
C(15)	119.9(3)	C(16)-C(17)-C(18)	119.8(3)	C(17)-C(18)-
C(19)	120.6(3)	C(18)-C(19)-C(14)	119.7(3)	C(21)-C(20)-
P(2)	120.0(2)	C(25)-C(20)-P(2)	120.9(2)	C(25)-C(20)-
C(21)	119.0(3)	C(22)-C(21)-C(20)	120.0(3)	C(23)-C(22)-
C(21)	120.4(3)	C(22)-C(23)-C(24)	120.3(3)	C(25)-C(24)-
C(23)	119.6(3)	C(24)-C(25)-C(20)	120.7(3)	C(27)-C(26)-
P(2)	121.0(2)	C(27)-C(26)-C(31)	119.0(3)	C(31)-C(26)-
P(2)	119.9(2)	C(28)-C(27)-C(26)	120.1(3)	C(29)-C(28)-
C(27)	120.5(3)	C(28)-C(29)-C(30)	119.6(3)	C(31)-C(30)-
C(29)	120.6(3)	C(30)-C(31)-C(26)	120.1(3)	

9. References

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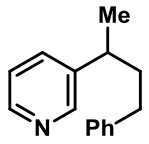
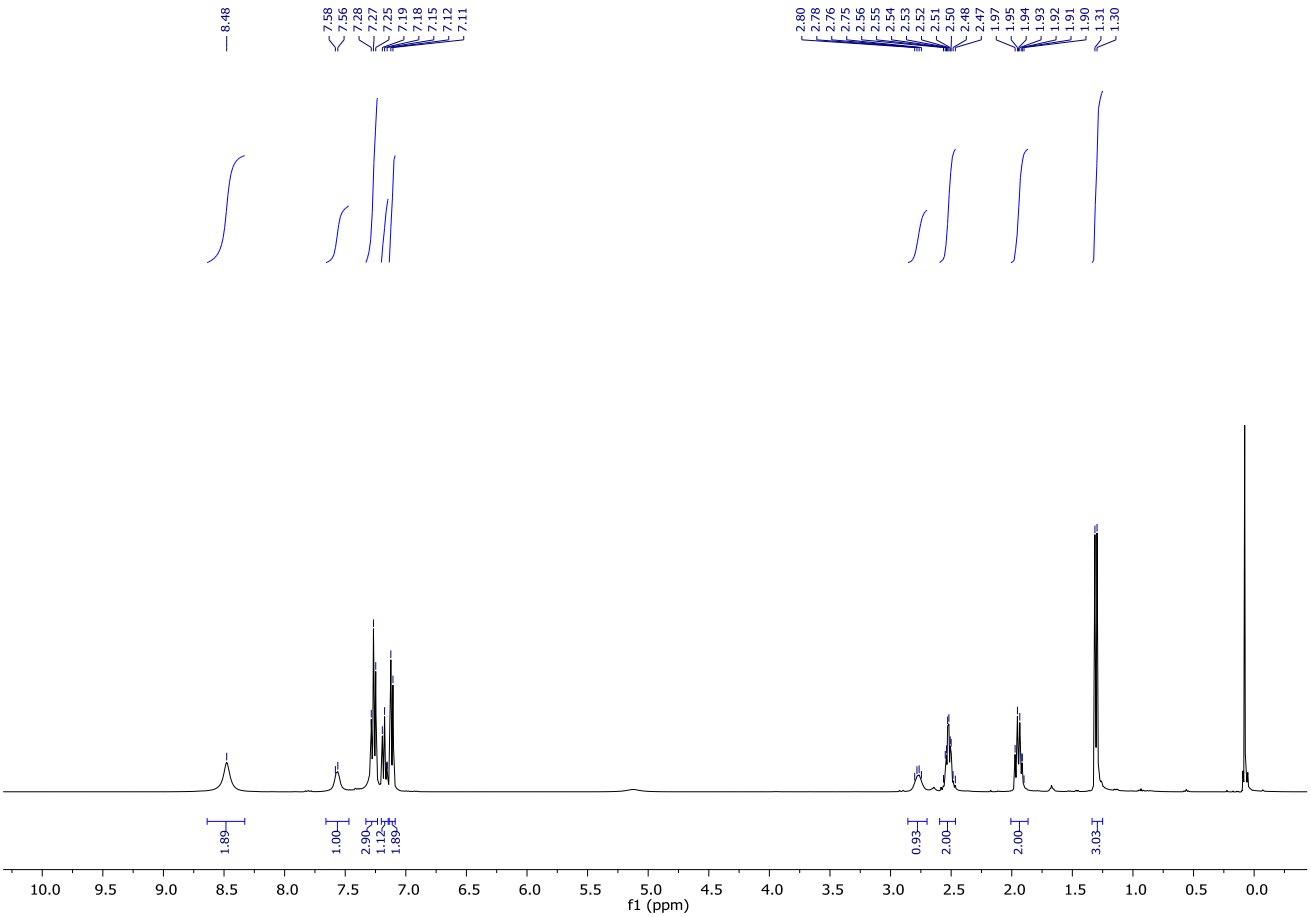
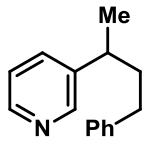
10. Experimental Spectra



5

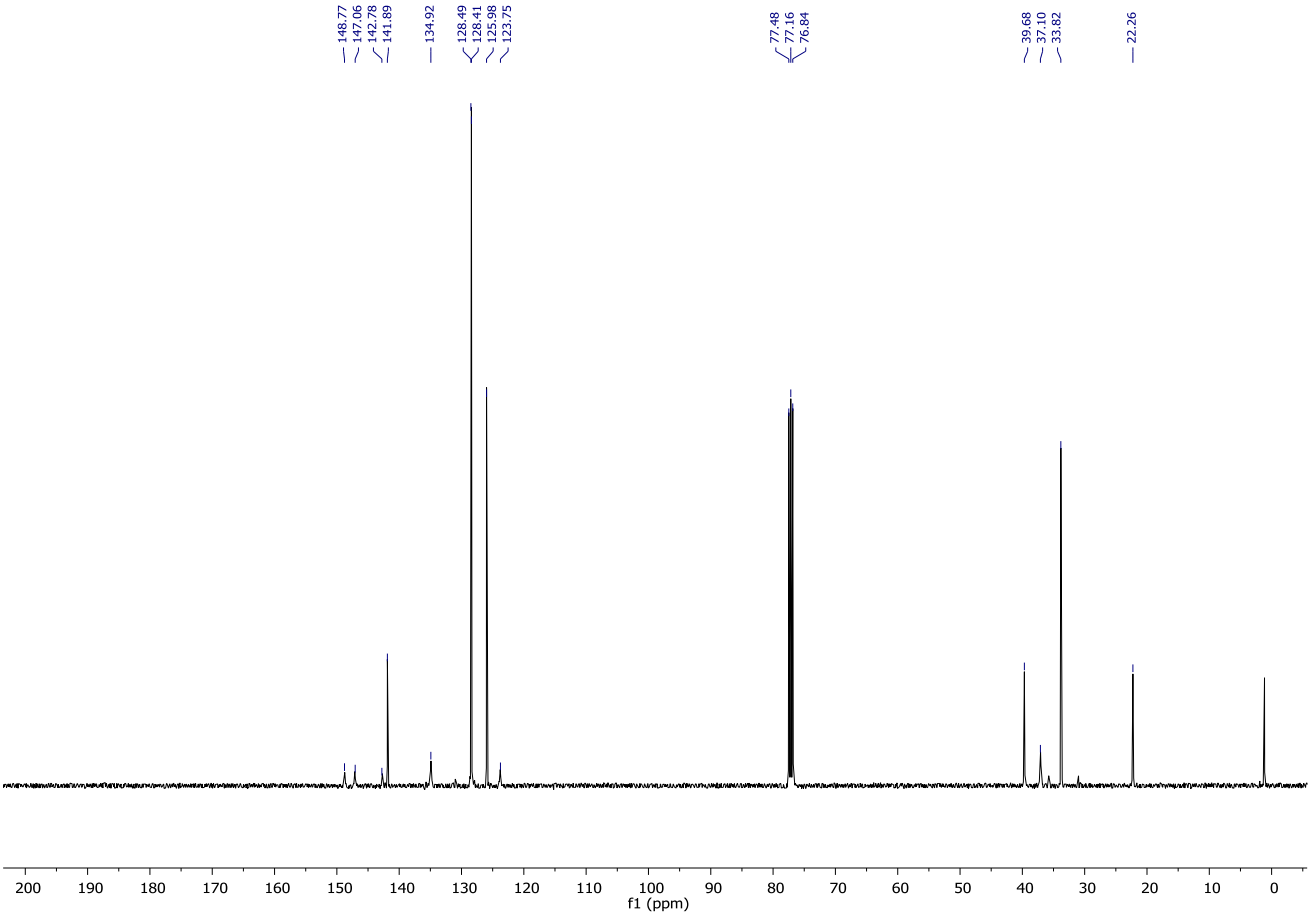
^{1}H Spectra

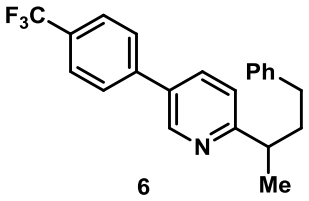




5

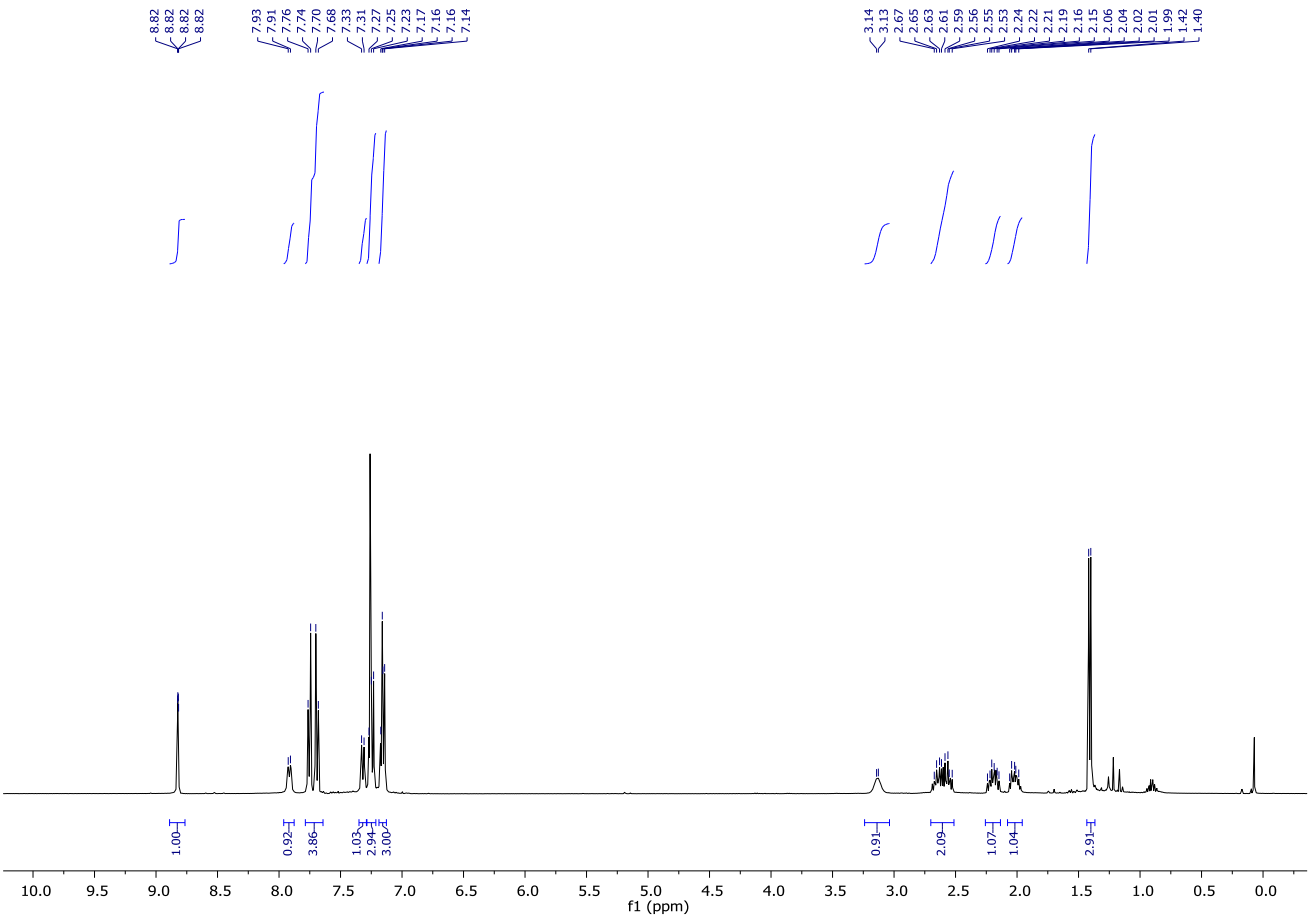
^{13}C Spectra




F3C
Ph
N
Me

6

^{1}H Spectra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8.82
8.82
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7.70
7.68
7.33
7.31
7.27
7.25
7.23
7.17
7.16
7.14
3.14
3.13
2.67
2.65
2.63
2.61
2.59
2.56
2.55
2.53
2.24
2.22
2.21
2.19
2.16
2.15
2.06
2.04
2.02
2.01
1.99
1.42
1.40
1.00
0.92
3.86
1.03
2.94
3.00
0.91
2.09
1.07
1.04
2.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
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2.5
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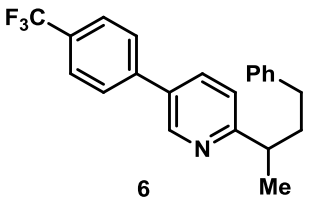
0.0
f1 (ppm)



6

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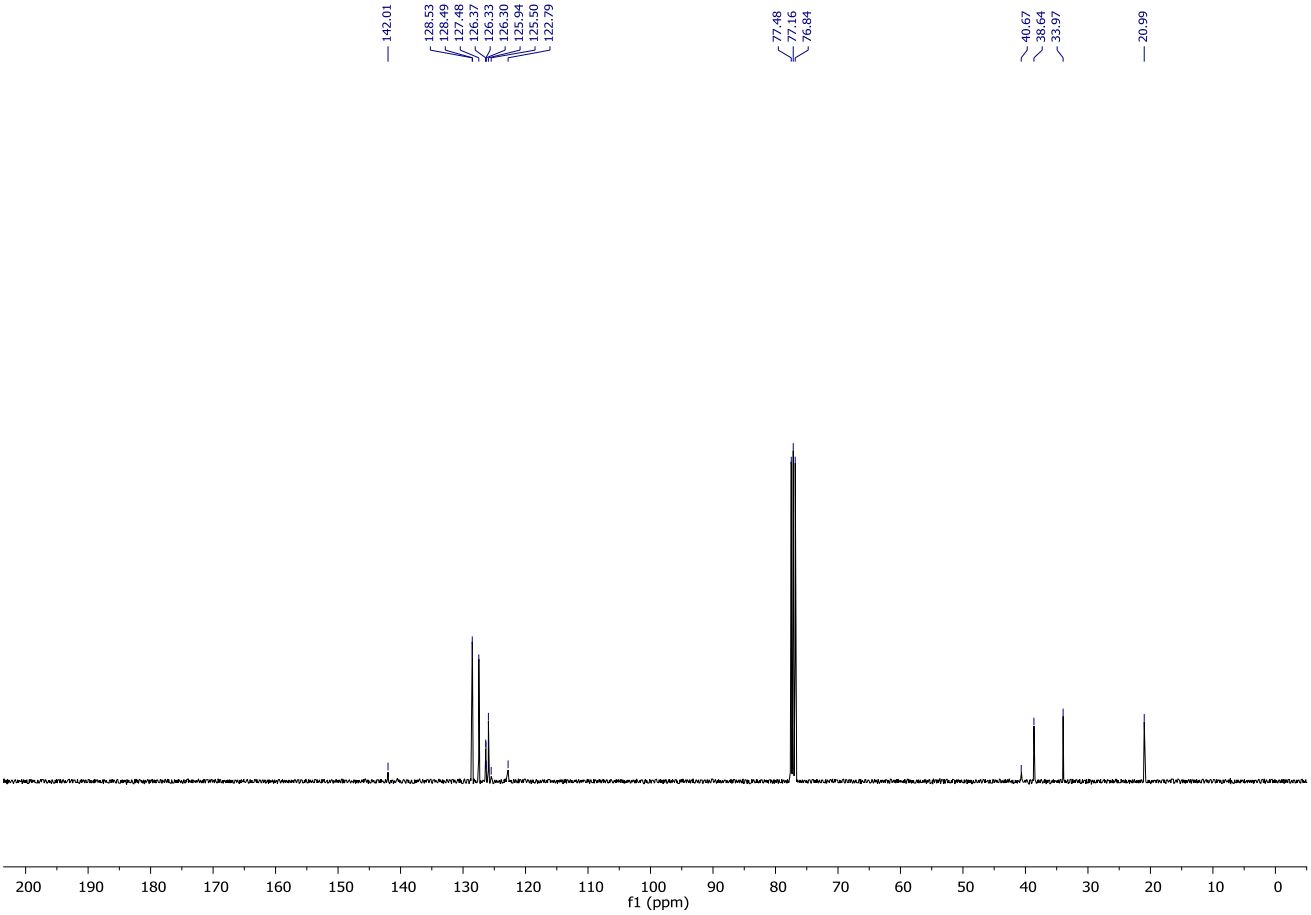
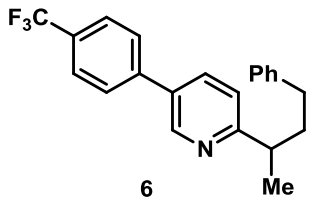
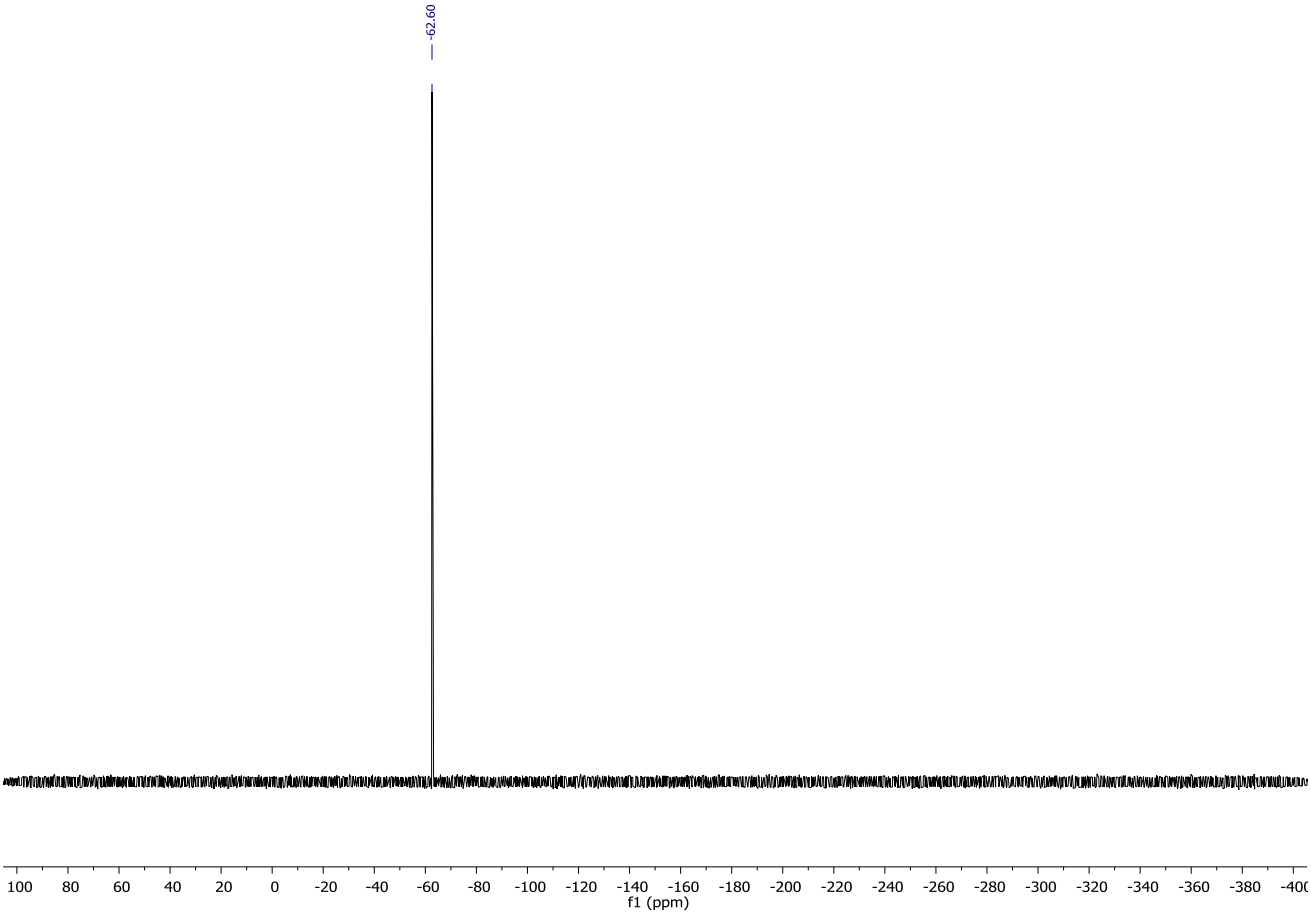
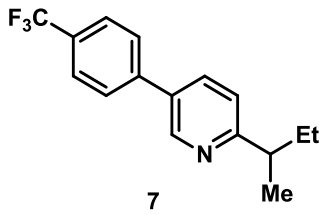




6

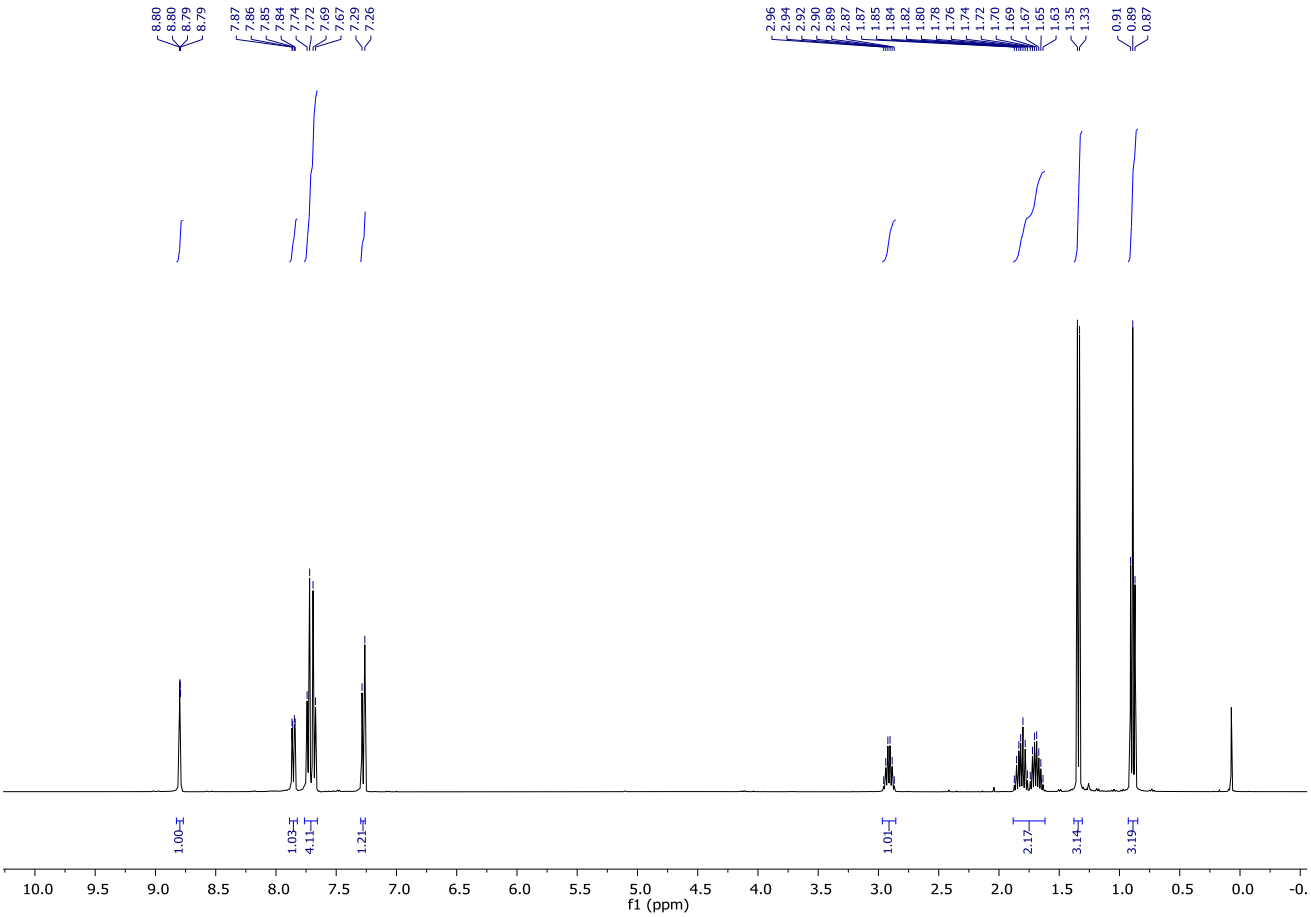
^{19}F Spectra




F3C
N
Et
Me

7

^{1}H Spectra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7.72
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7.26
2.96
2.94
2.92
2.90
2.89
2.87
1.87
1.85
1.84
1.82
1.80
1.78
1.76
1.74
1.72
1.70
1.69
1.67
1.65
1.63
1.35
1.33
0.91
0.89
0.87
1.00
1.03
4.11
1.21
1.01
2.17
3.14
3.19
10.0
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8.5
8.0
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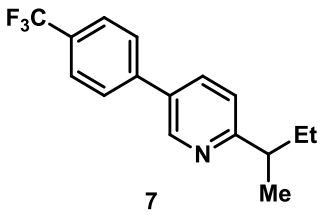
f1 (ppm)



7

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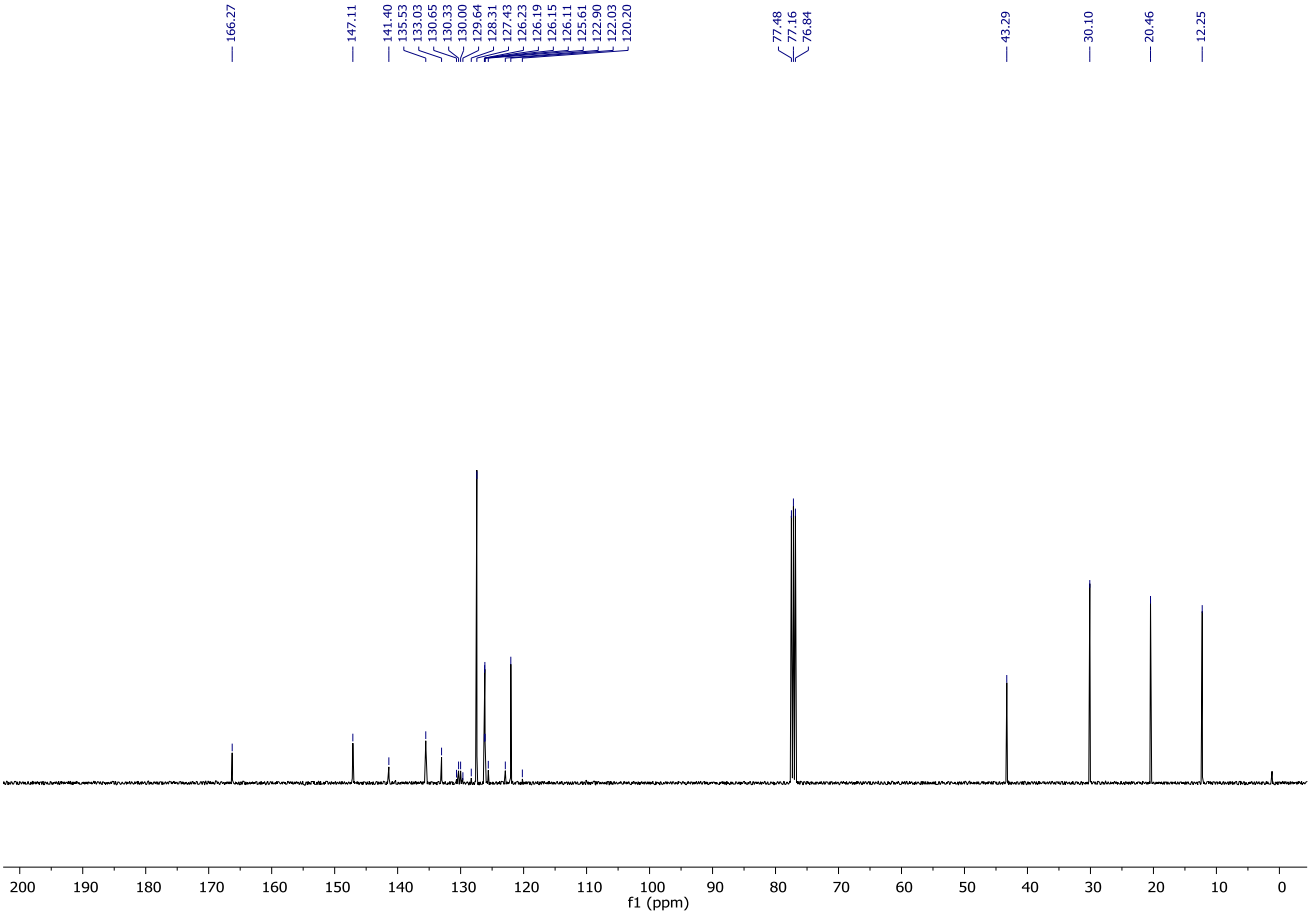
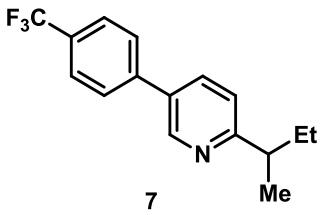
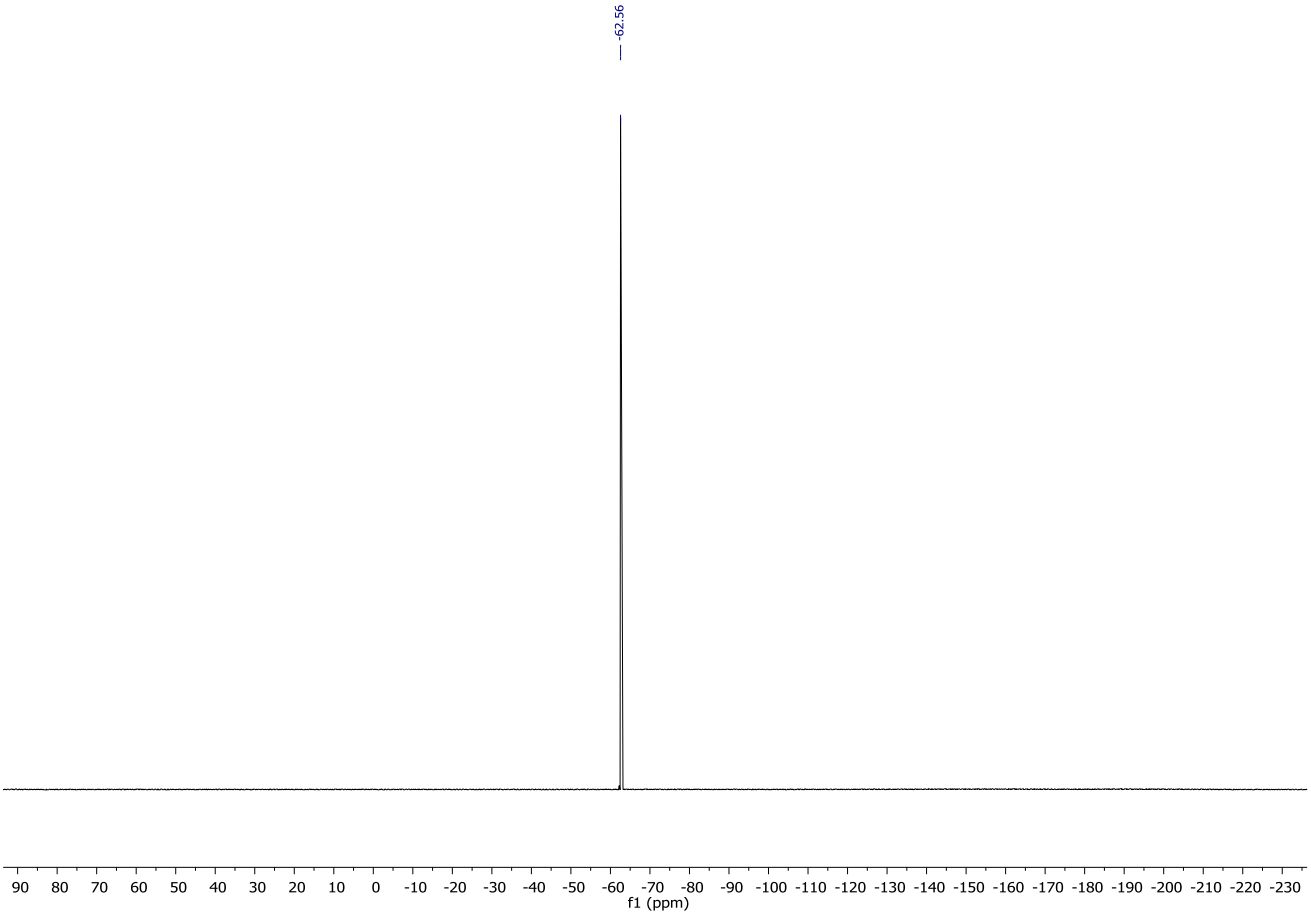
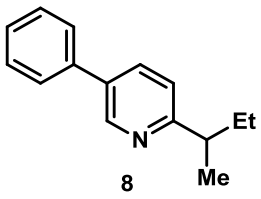




7

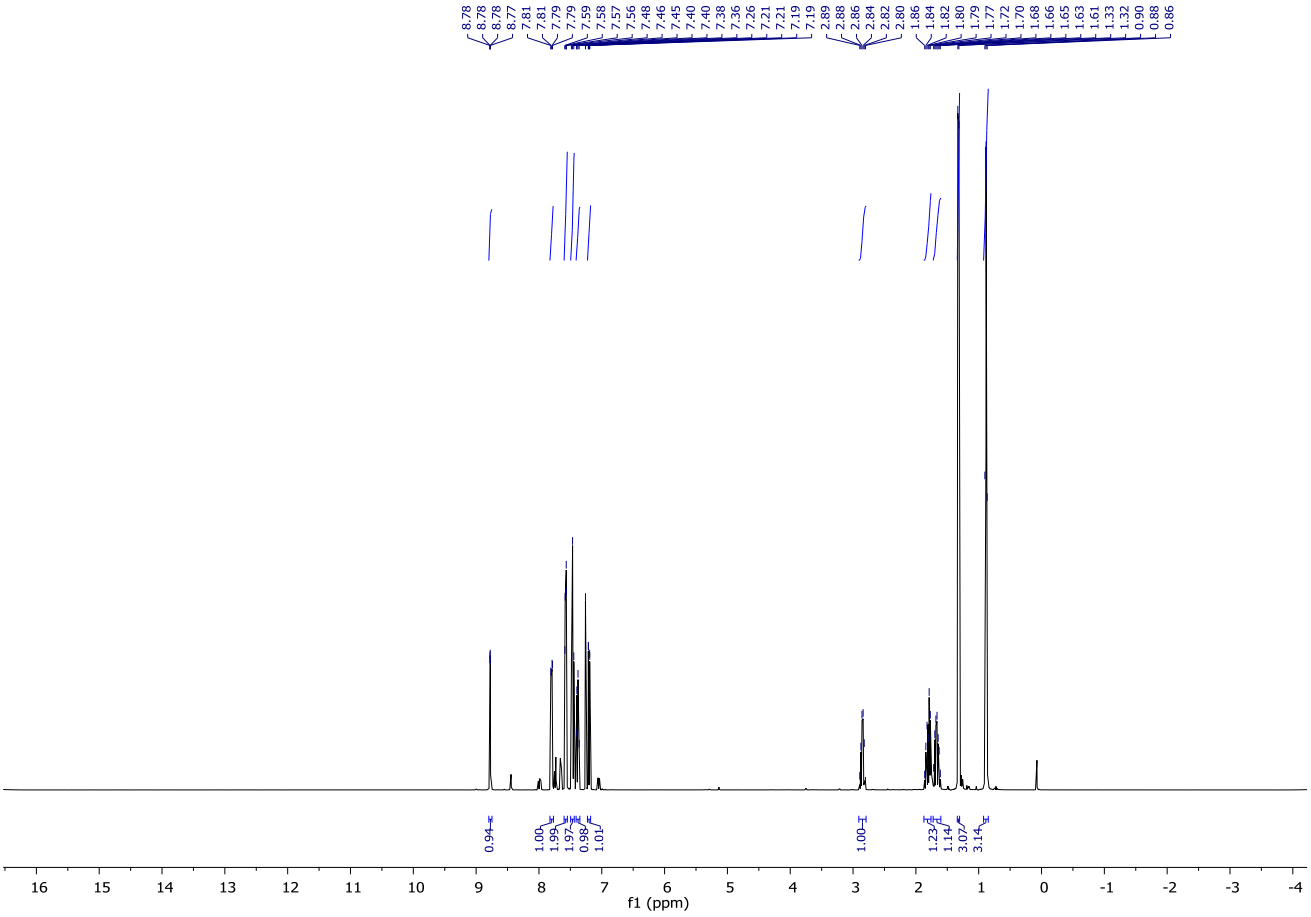
^{19}F Spectra




Et
N
Me

8

^{1}H Spectra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7.79
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7.58
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7.48
7.46
7.45
7.40
7.40
7.38
7.36
7.26
7.21
7.21
7.19
7.19
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2.88
2.86
2.84
2.82
2.80
1.86
1.84
1.82
1.80
1.79
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1.72
1.70
1.68
1.66
1.65
1.63
1.61
1.33
1.32
0.90
0.88
0.86
0.94
1.00
1.99
1.97
0.98
1.01
1.00
1.23
1.14
3.07
3.14
16
15
14
13
12
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10
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8
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6
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4
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2
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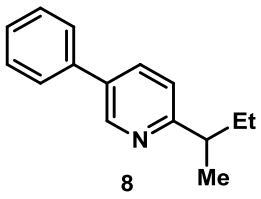
0
-1
-2
-3
-4
f1 (ppm)



8

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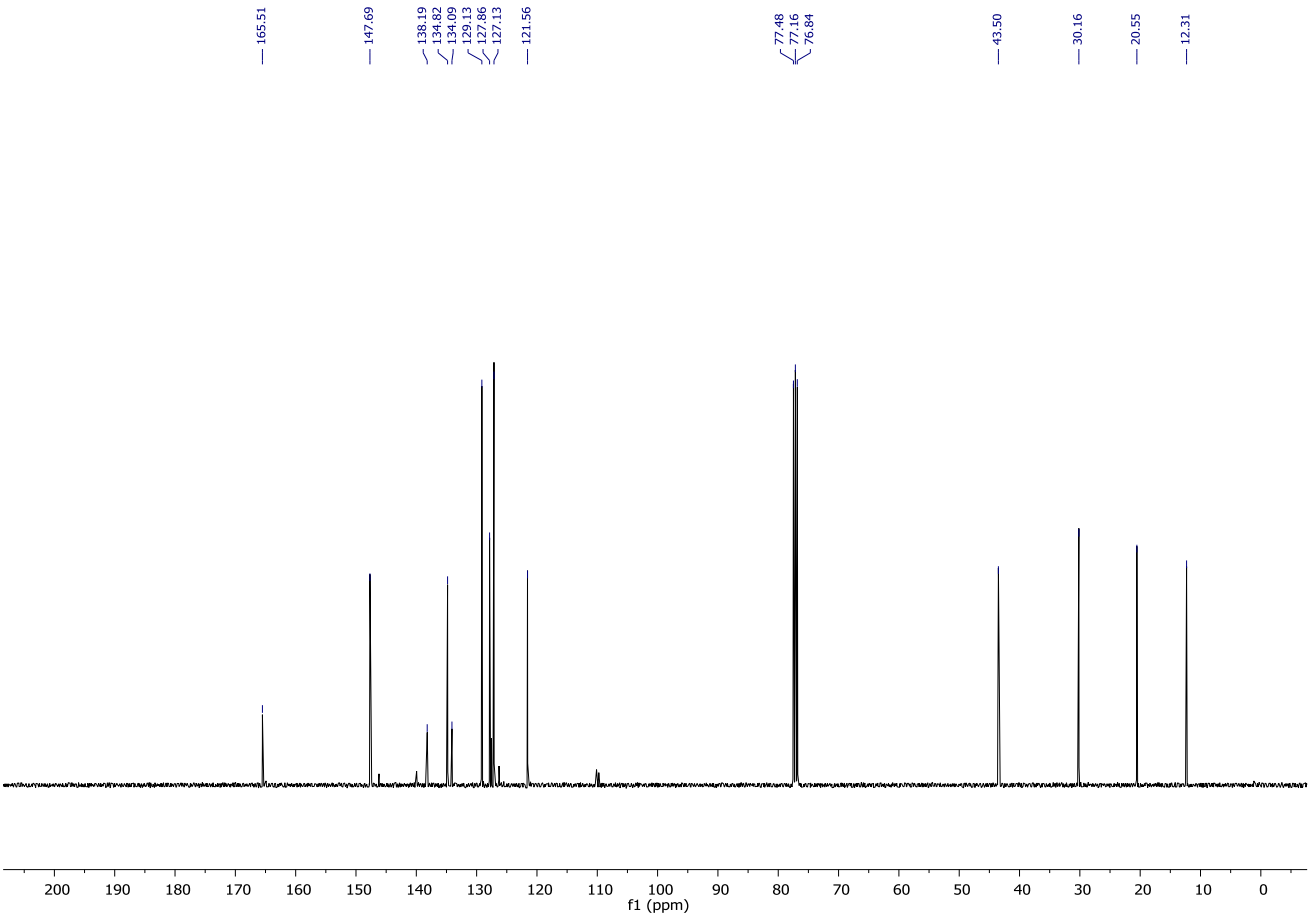
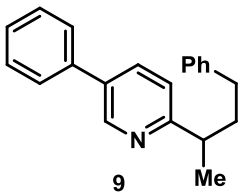
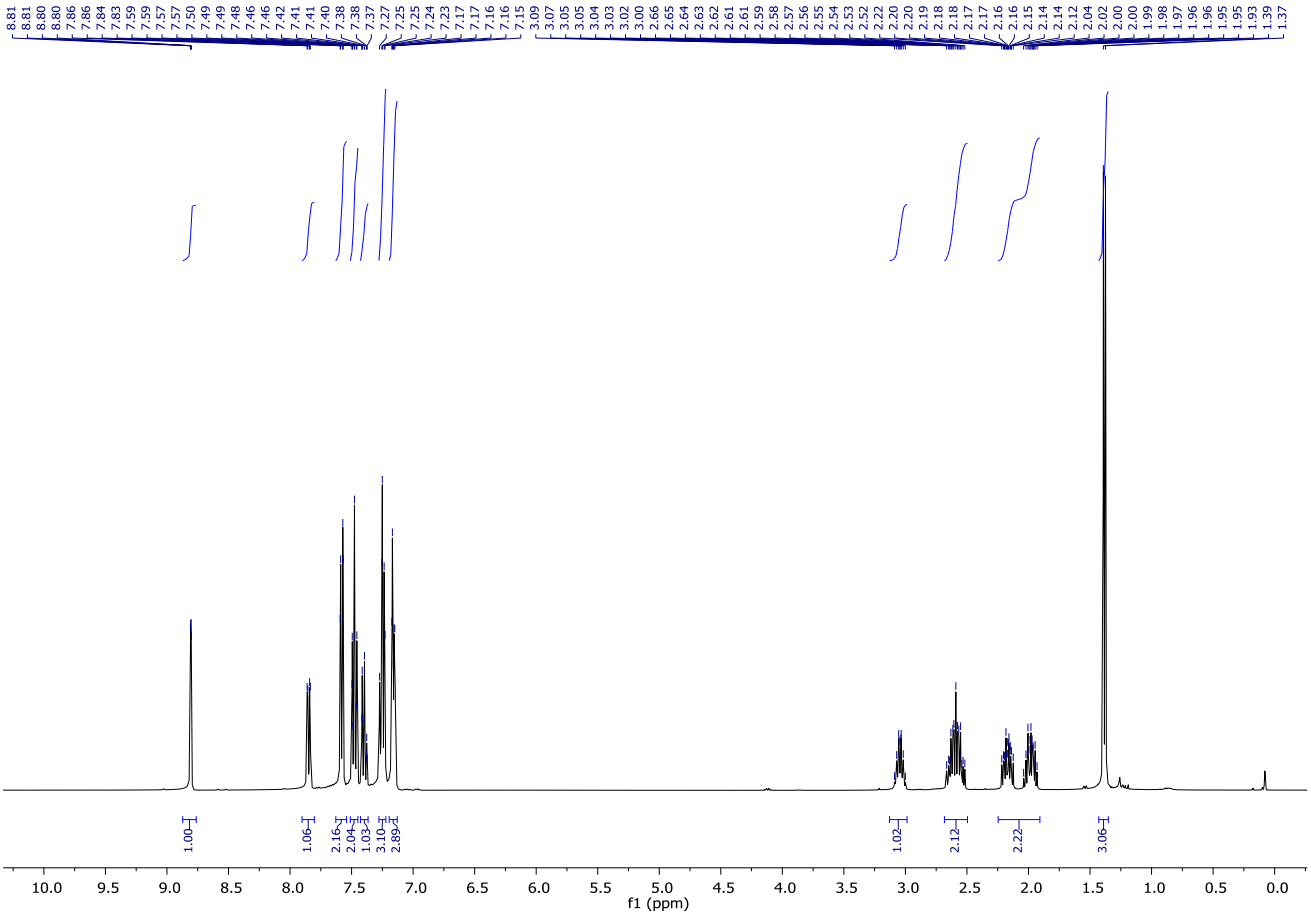



Ph
N
Me

9

^{1}H Spectra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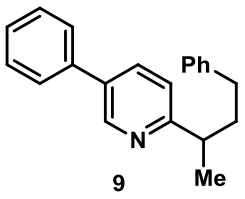
1.00
1.06
2.16
2.04
1.03
3.10
2.89
1.02
2.12
2.22
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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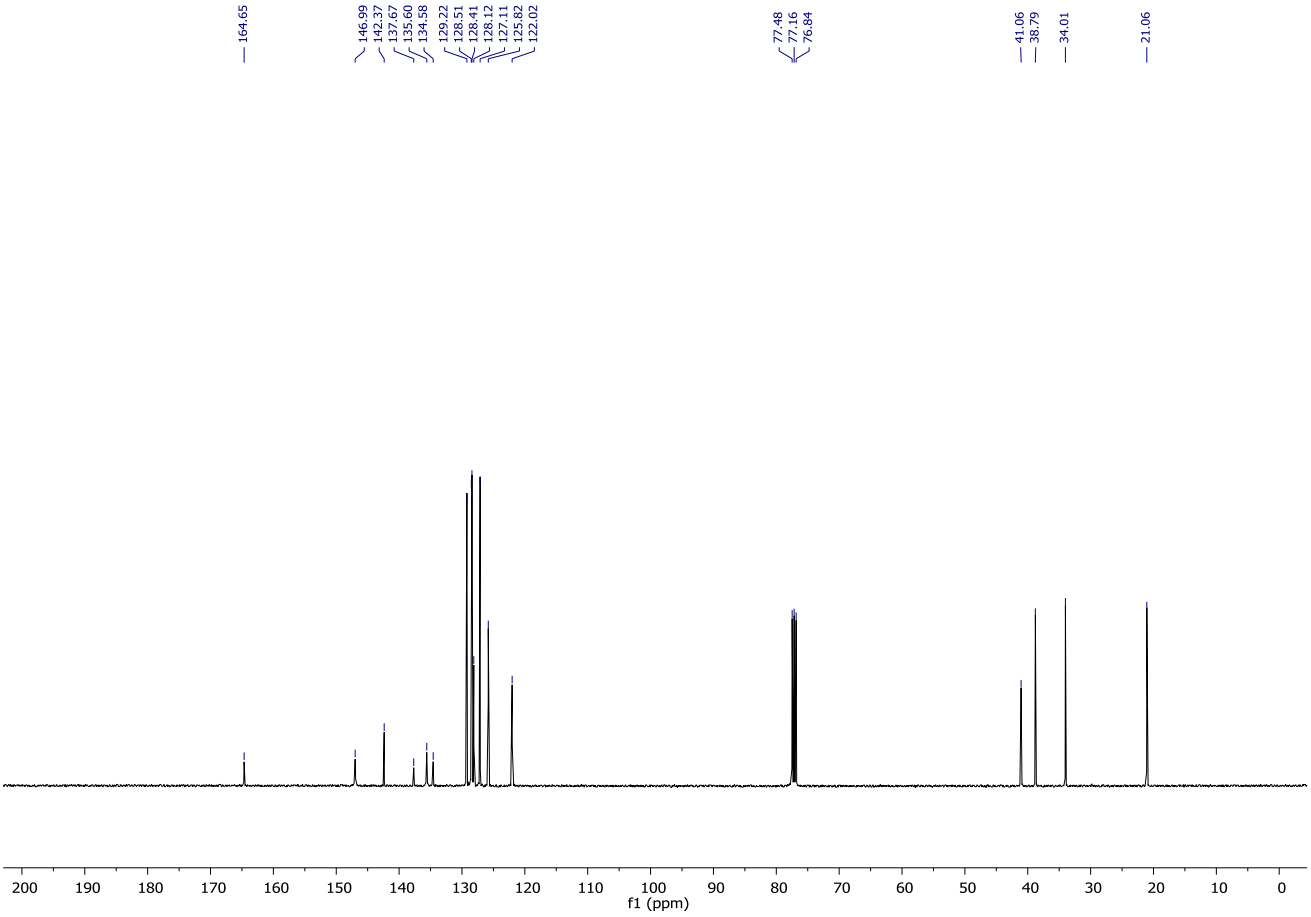

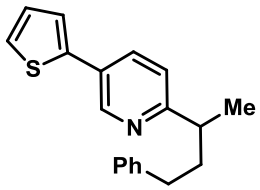

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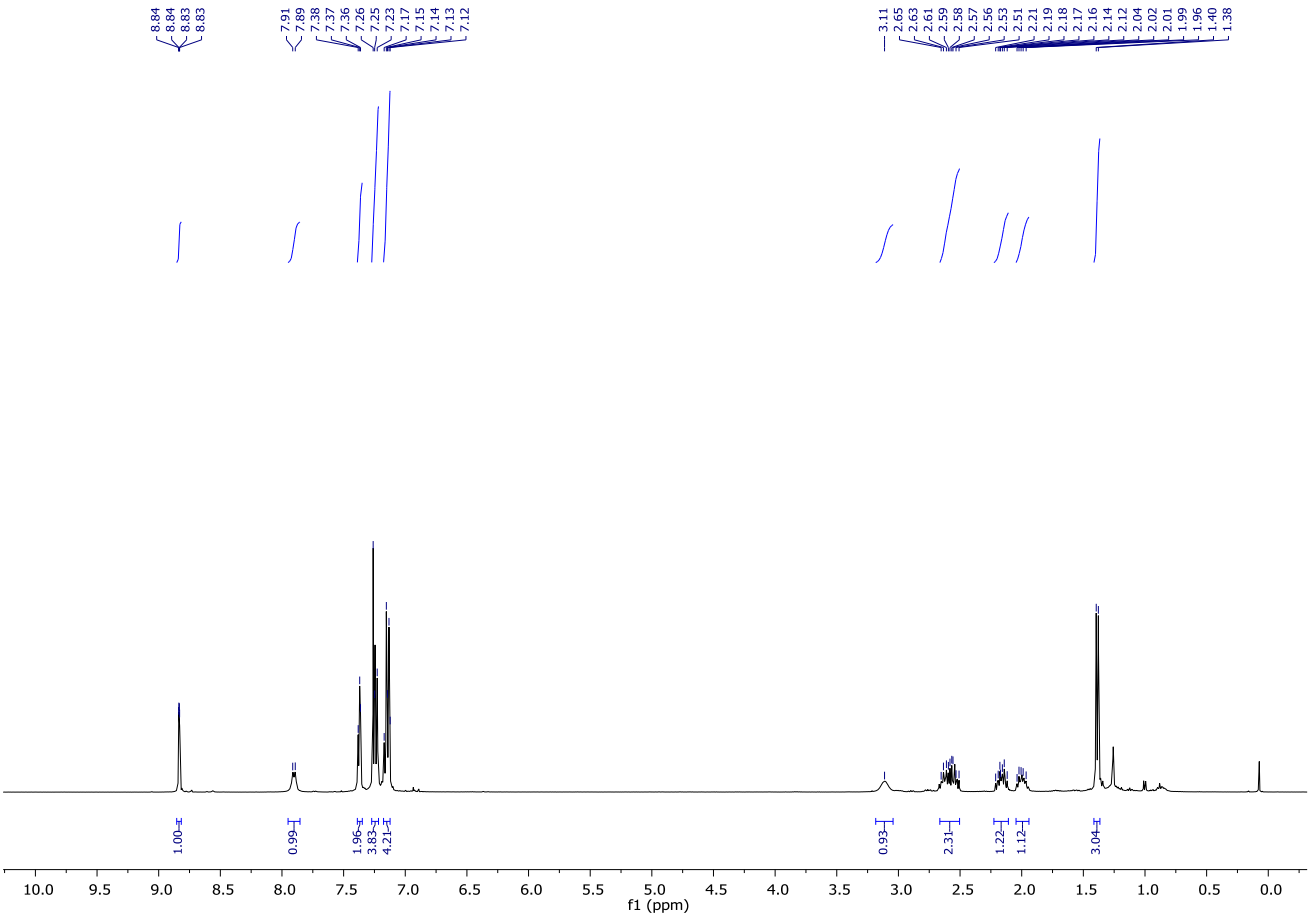

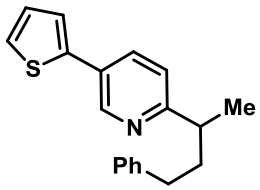

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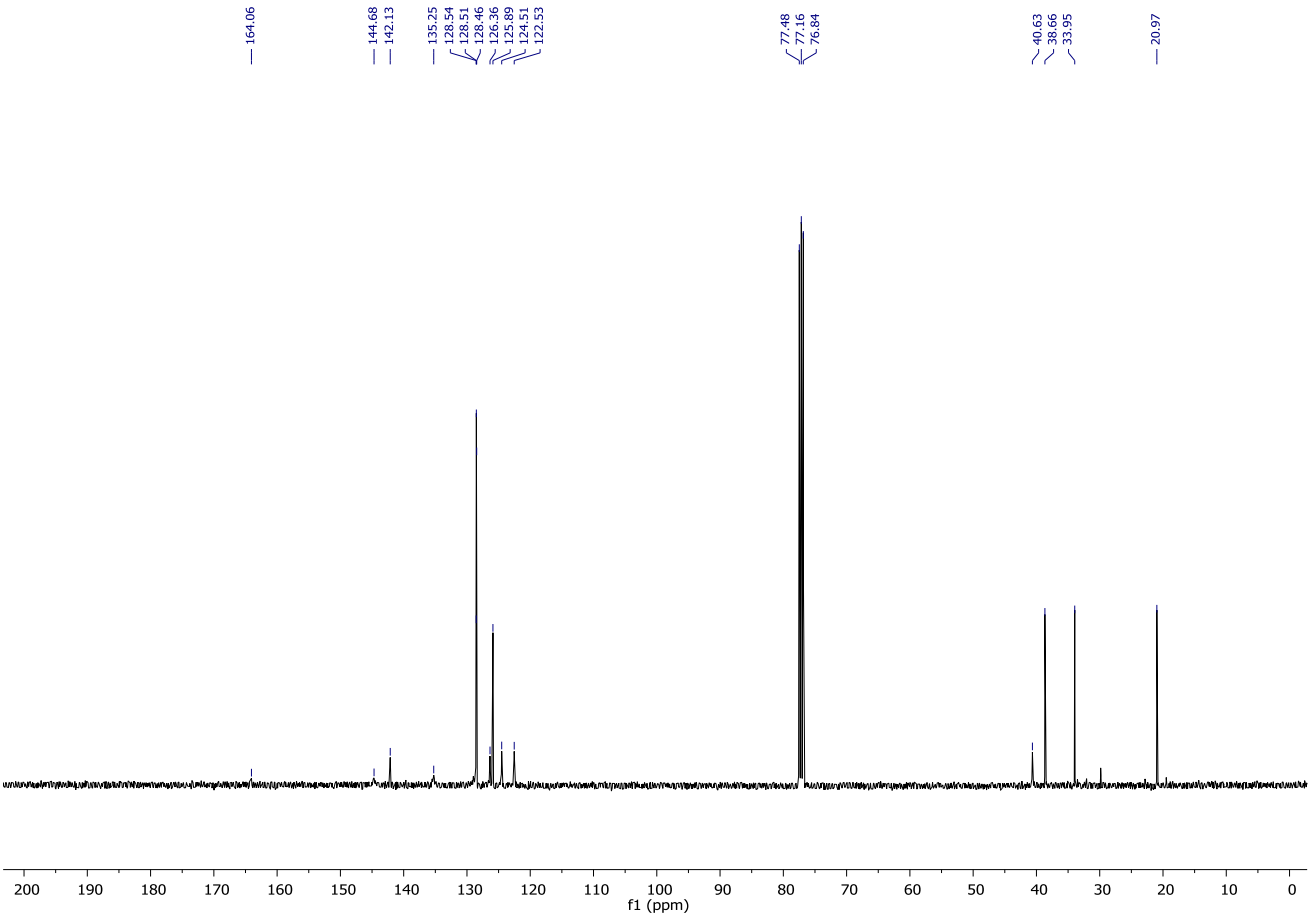

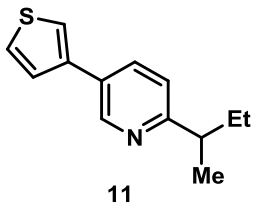

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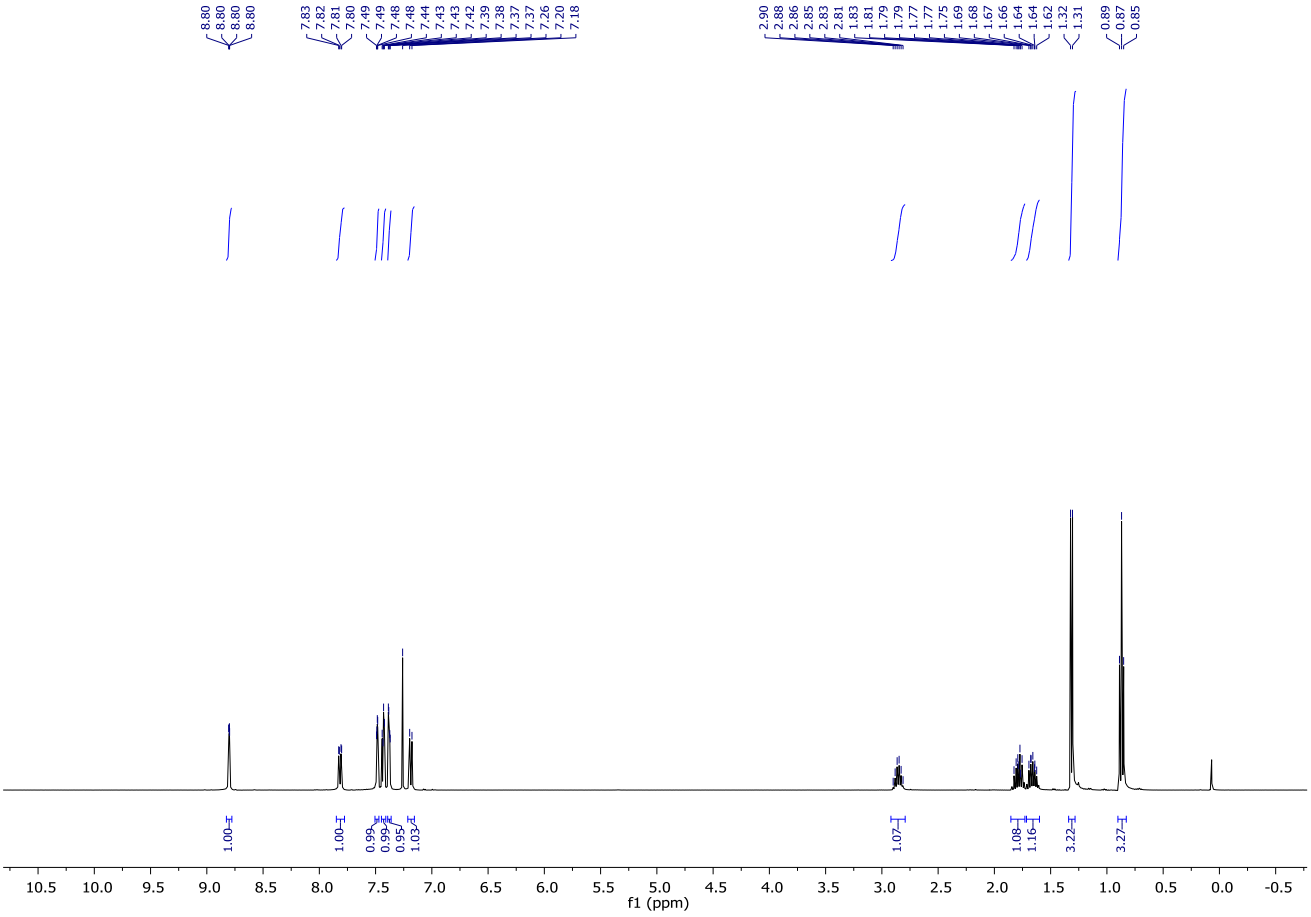

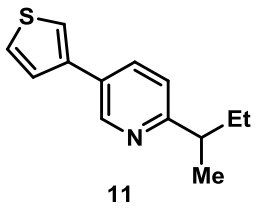

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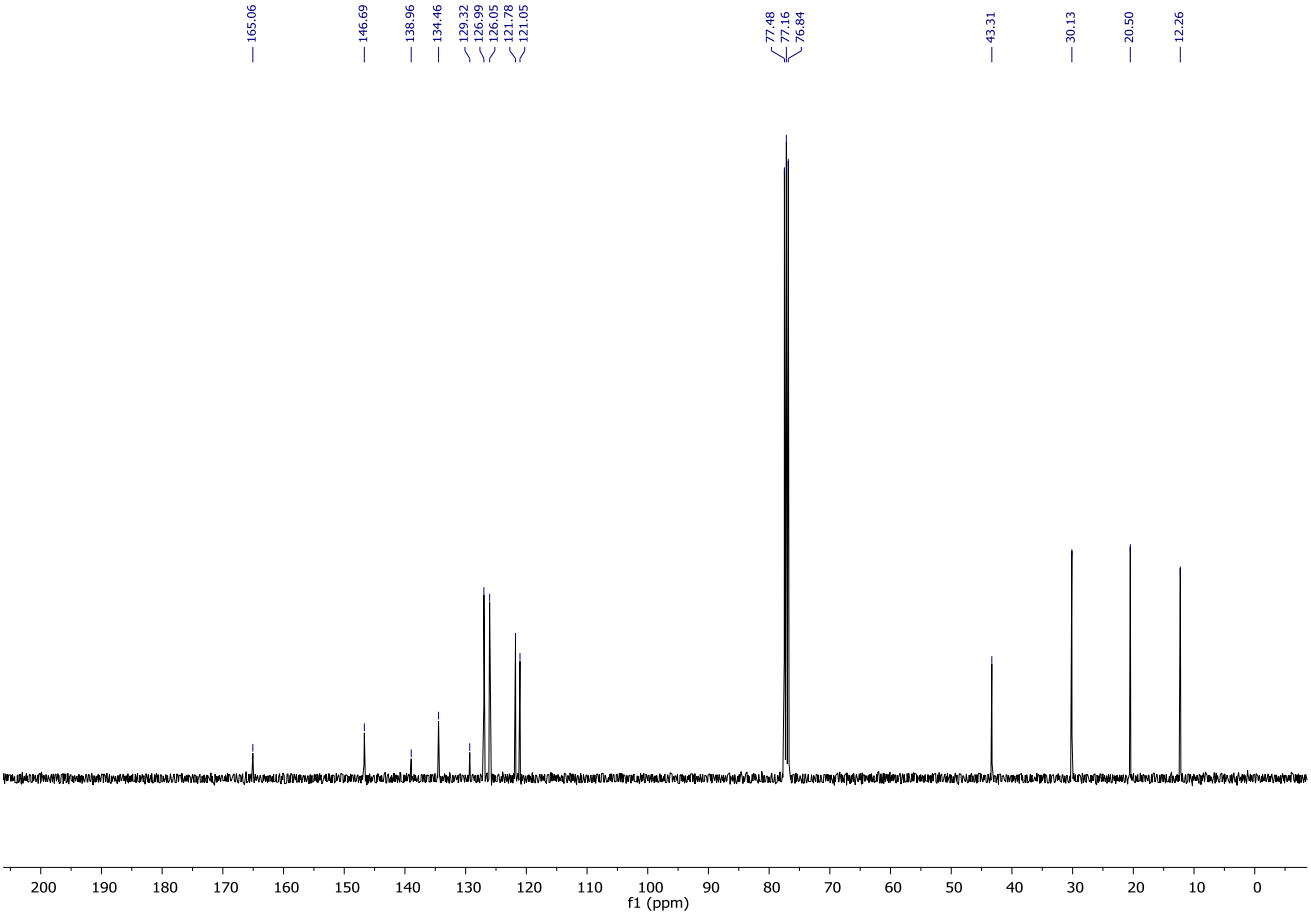

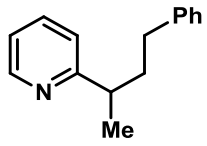

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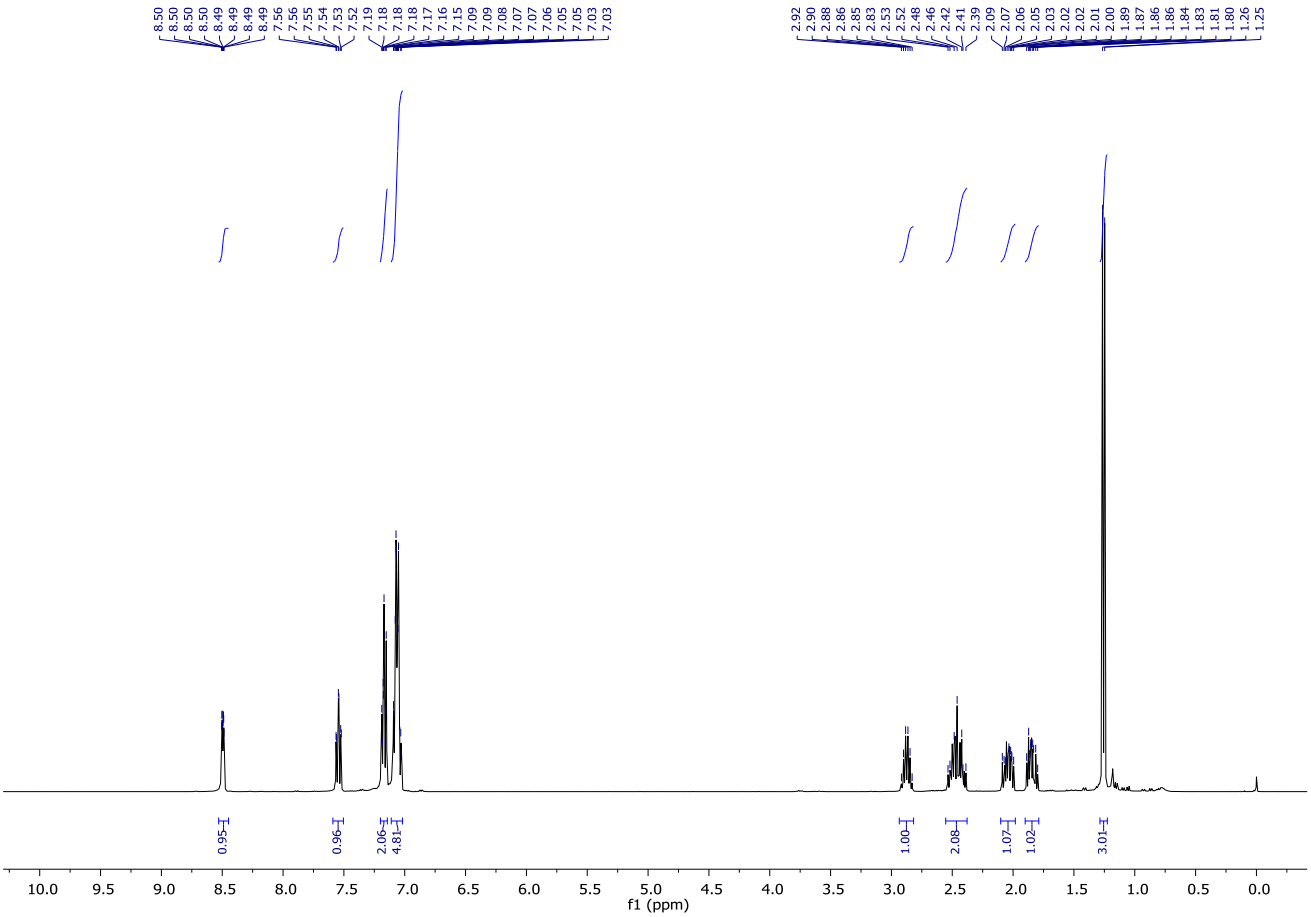

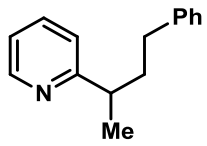

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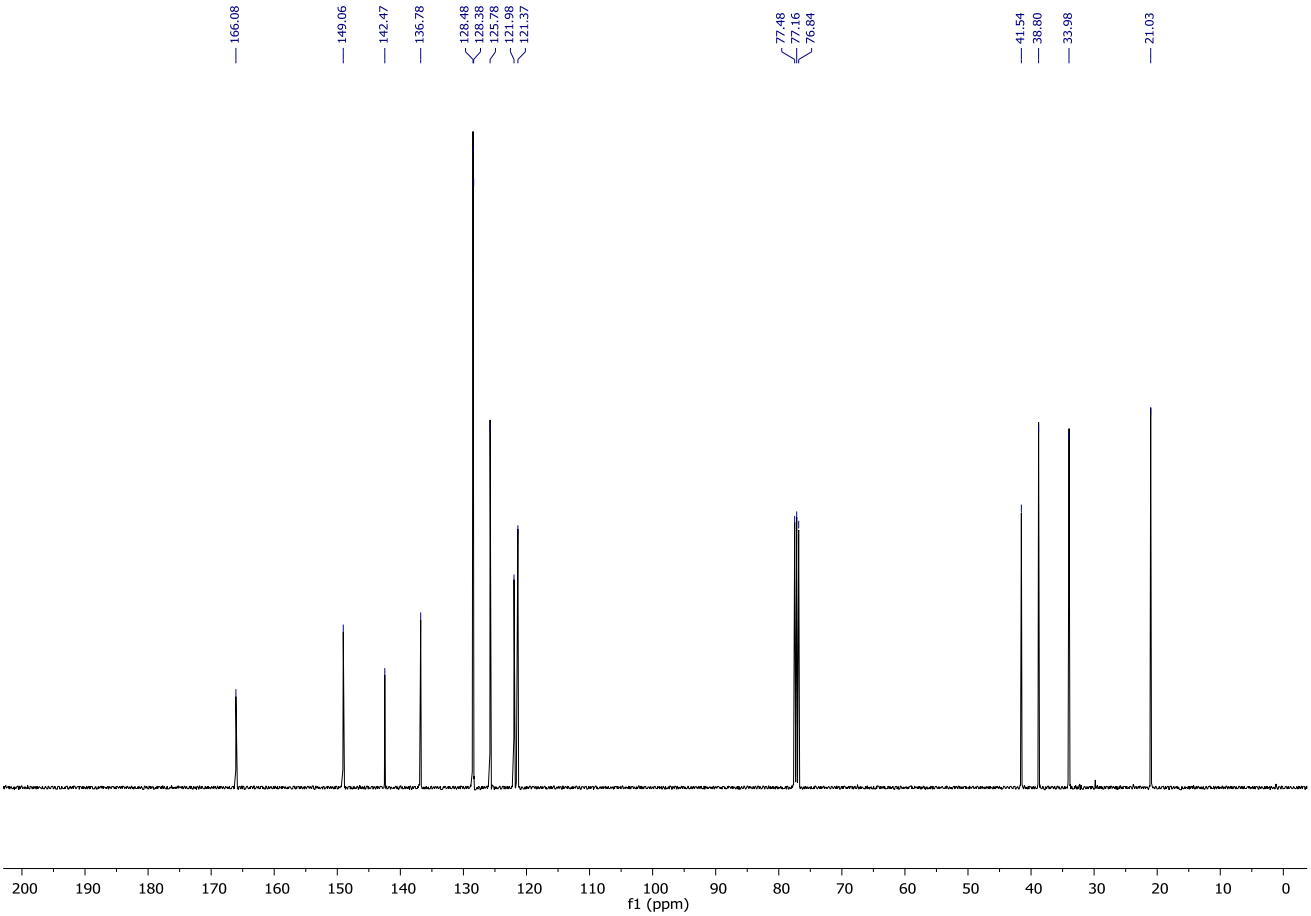
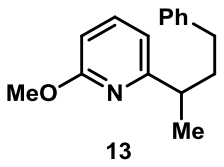
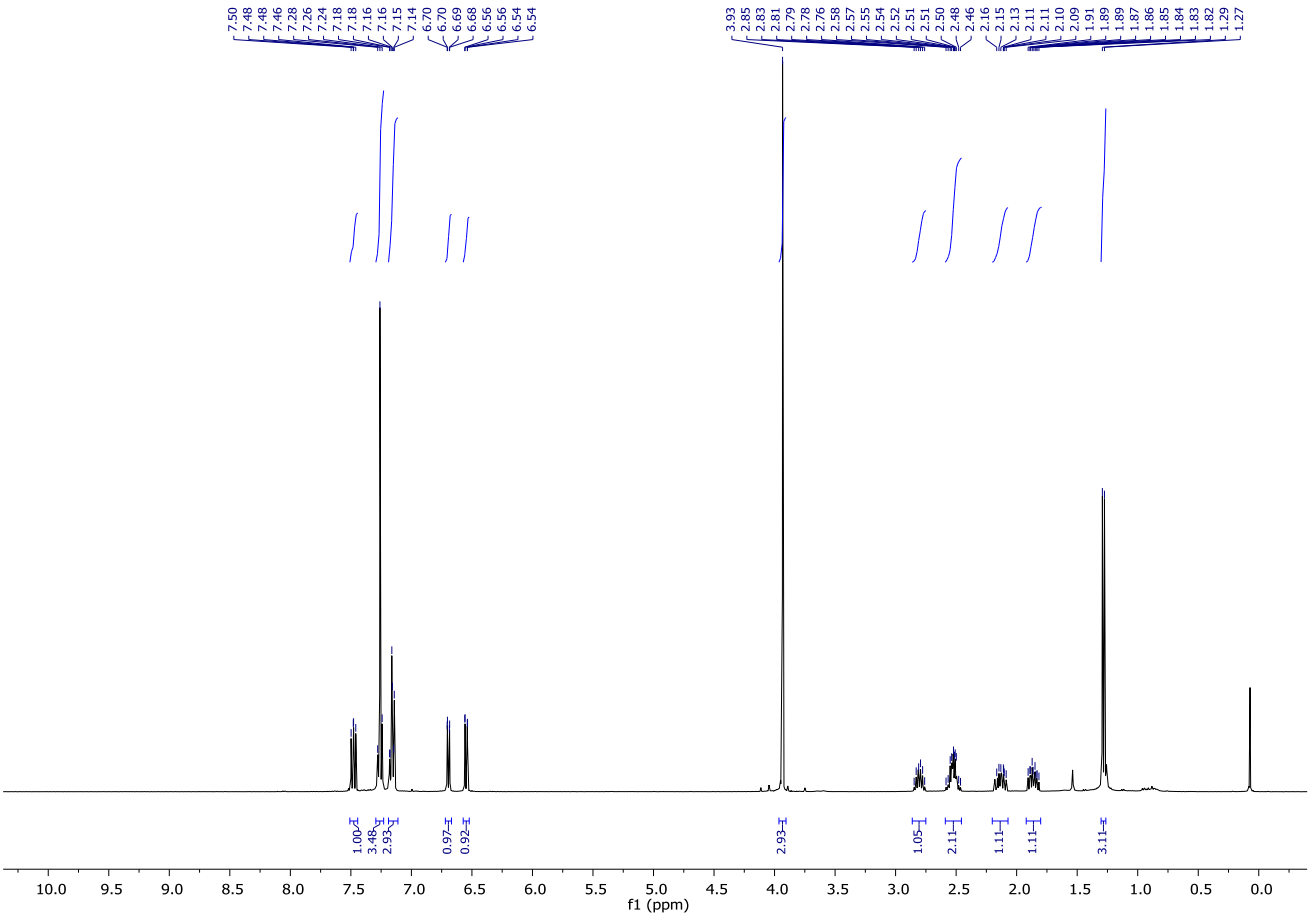
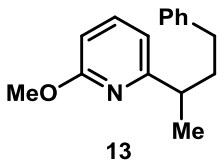




13

^{1}H Spectra





13

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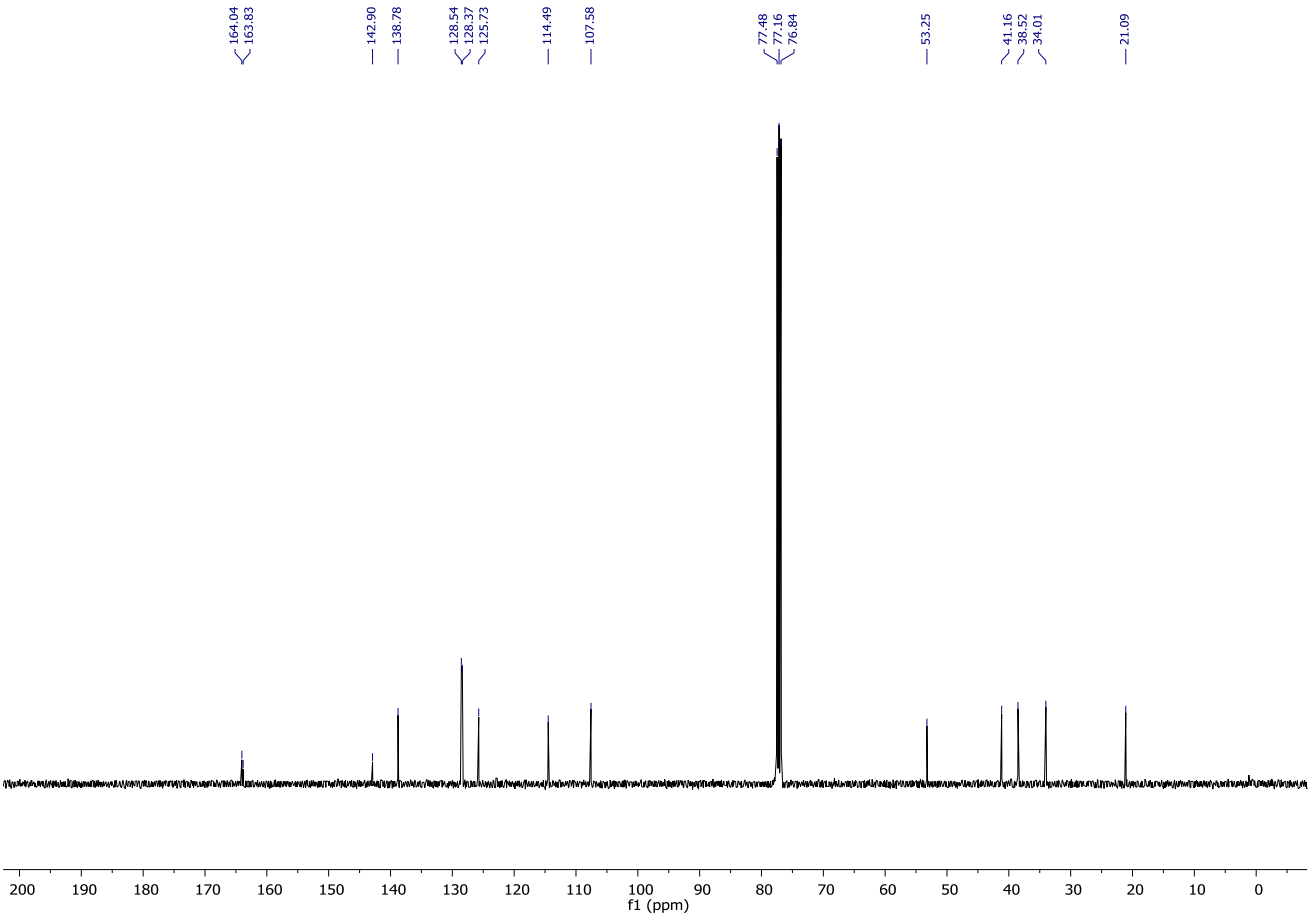

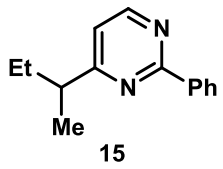

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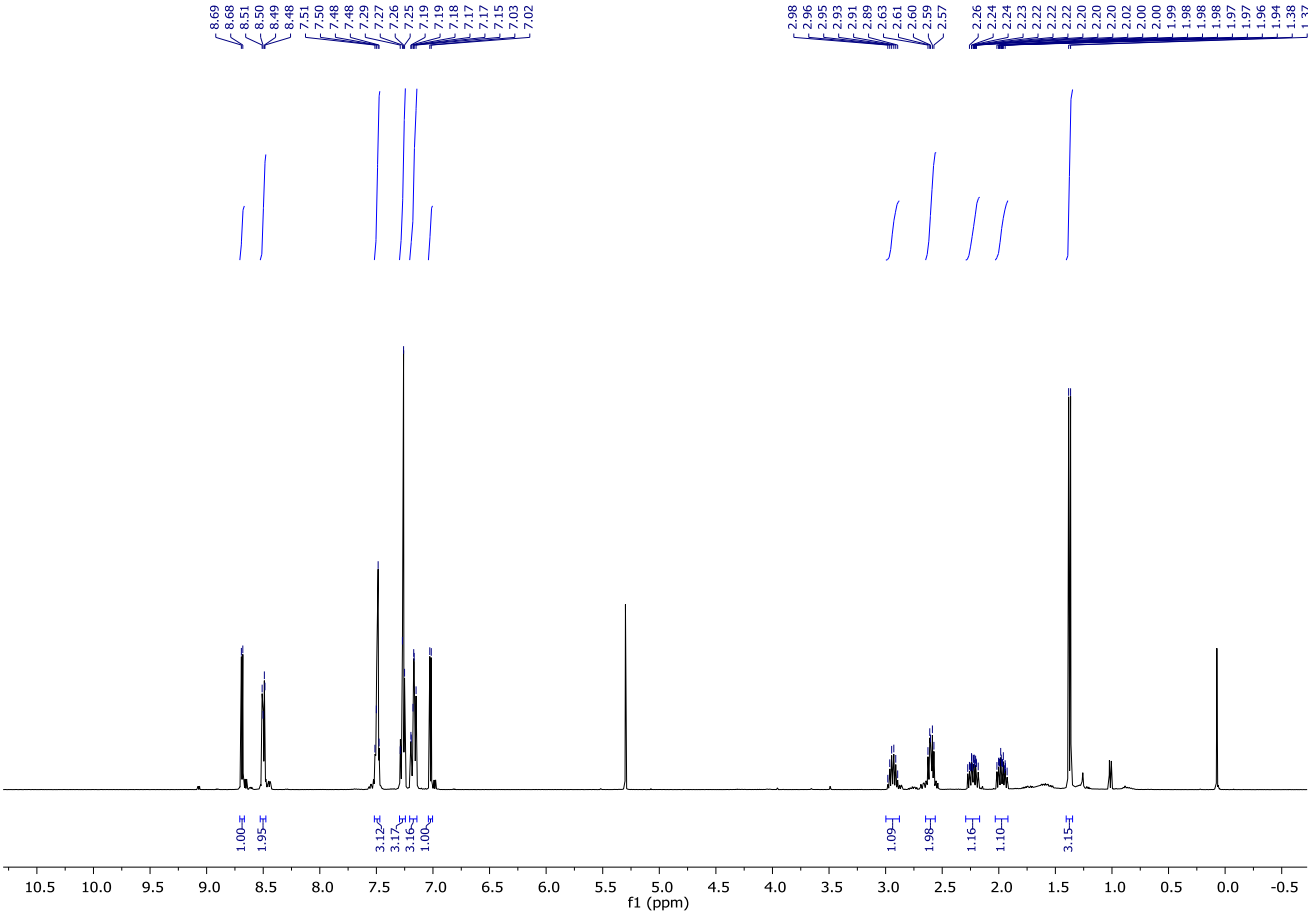

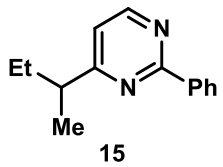

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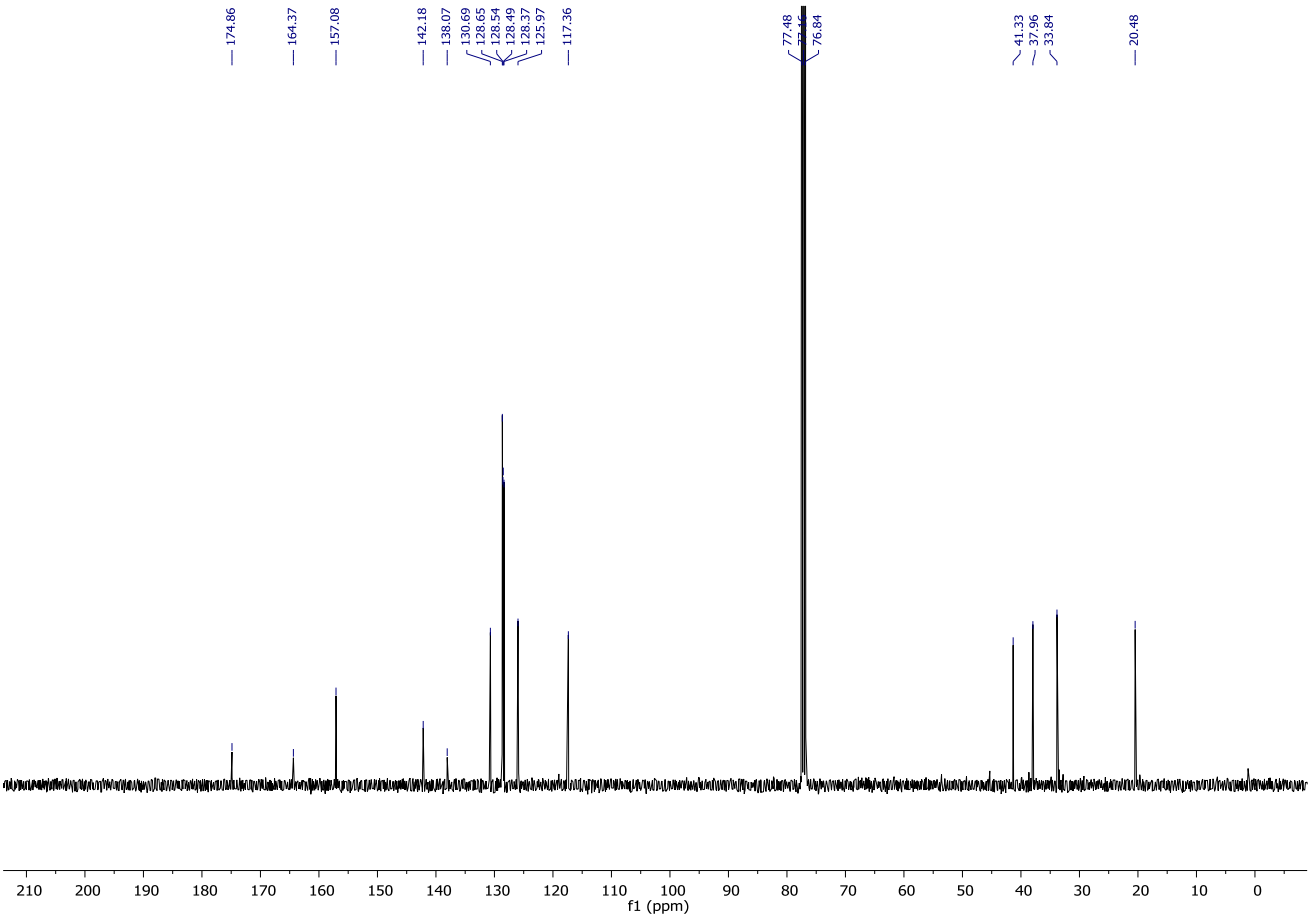

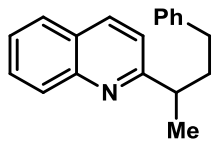

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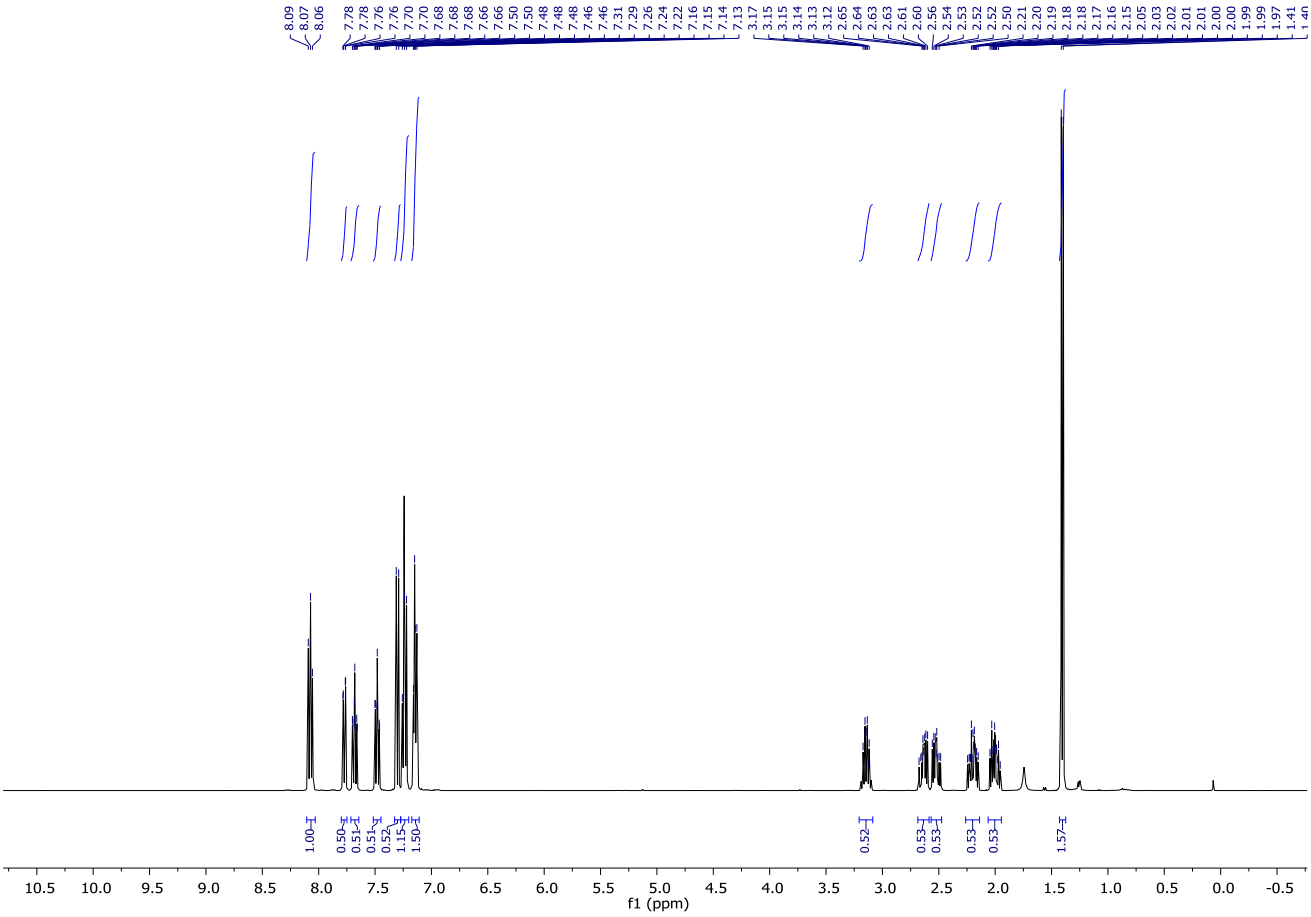

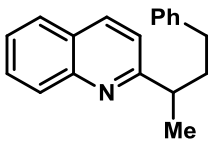

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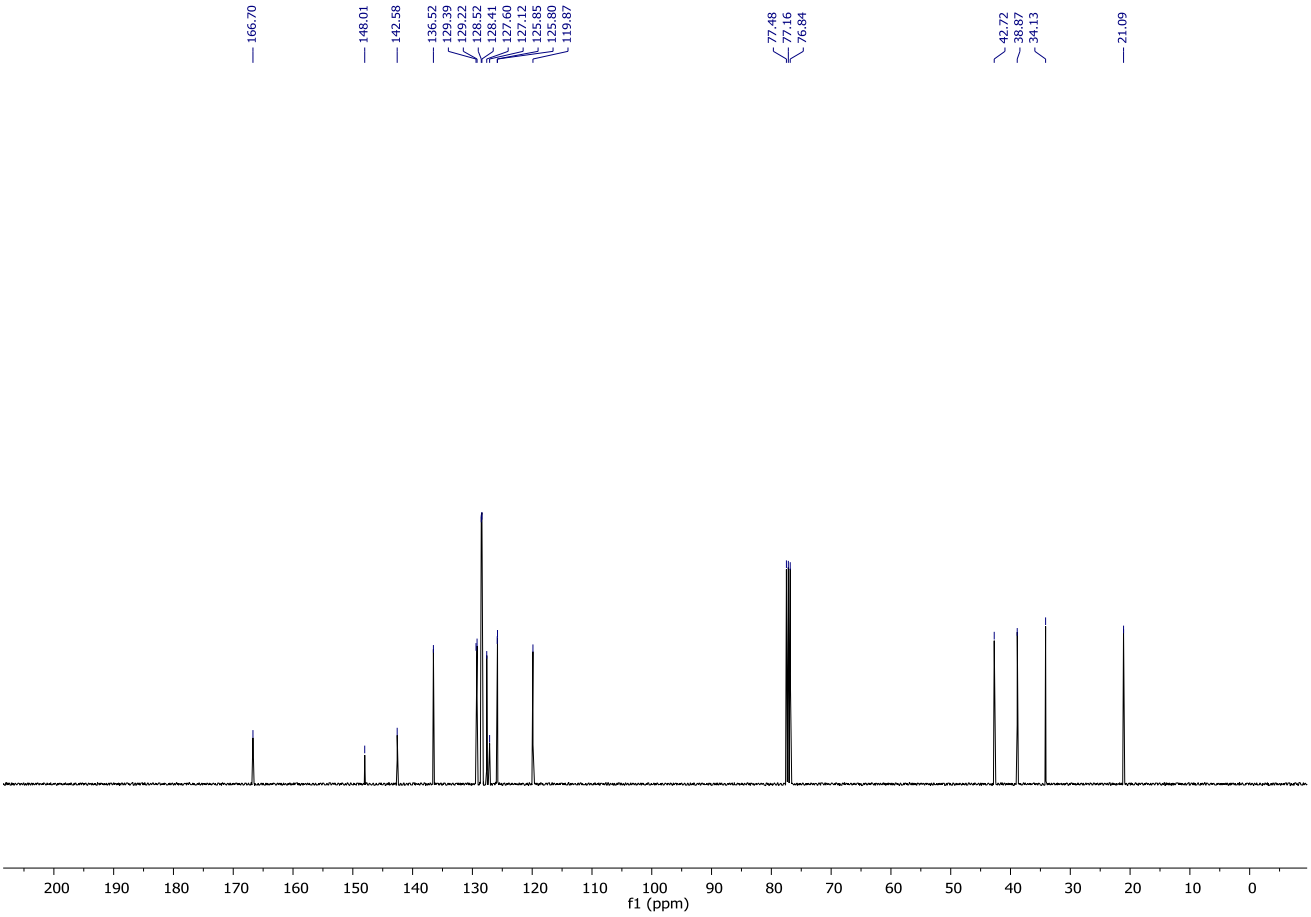

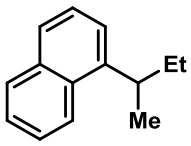

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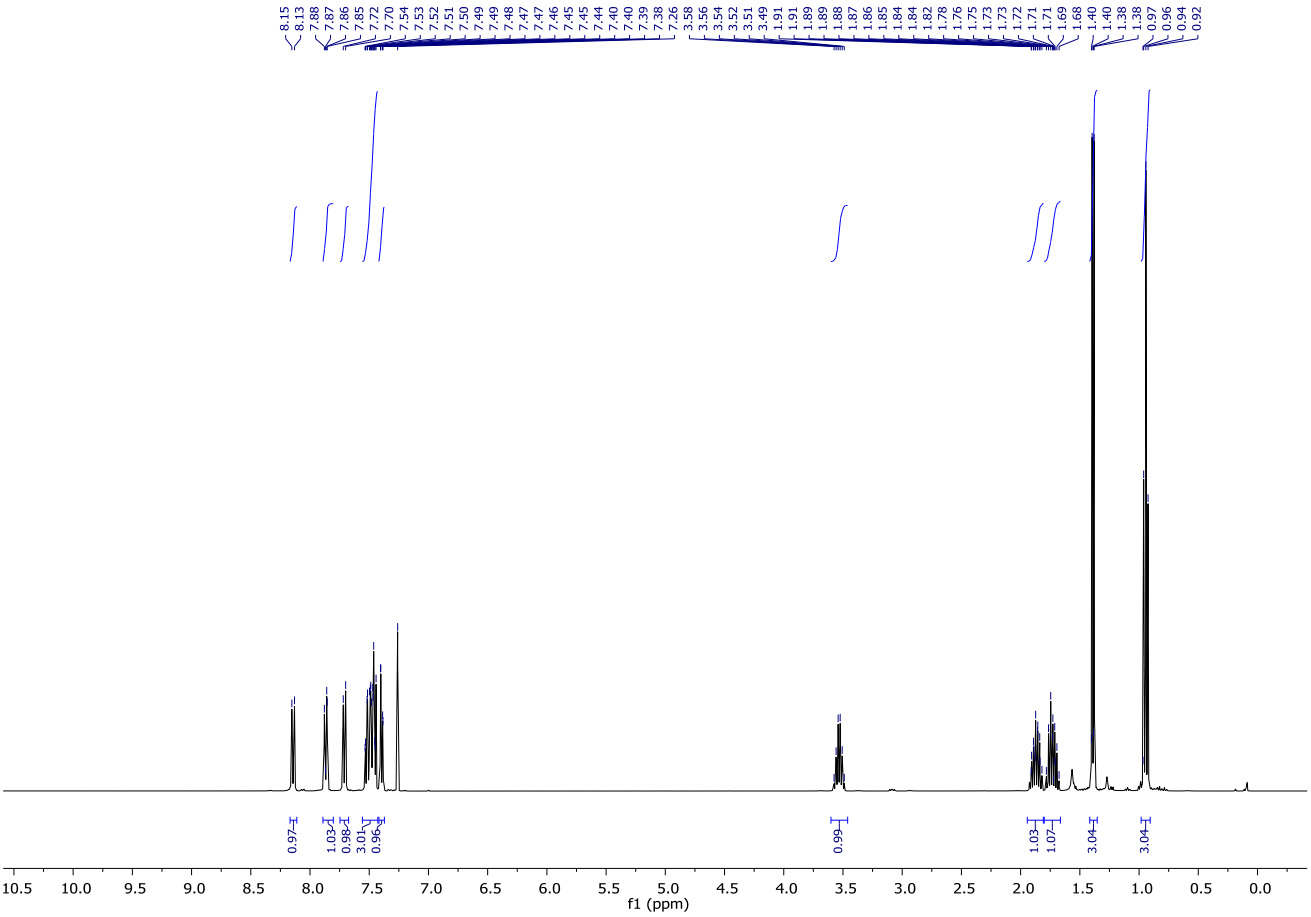

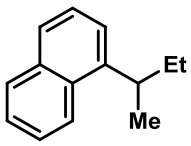

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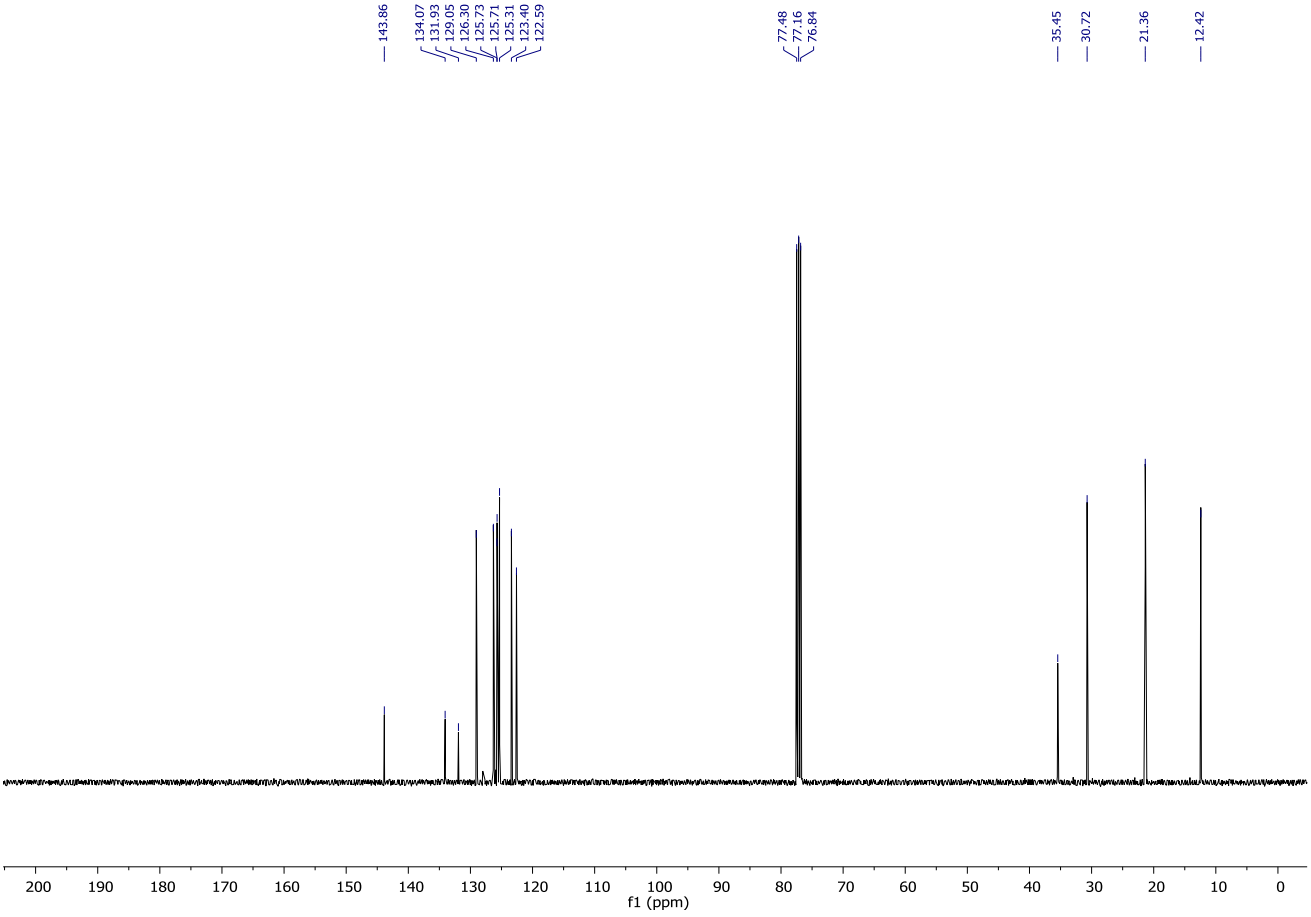

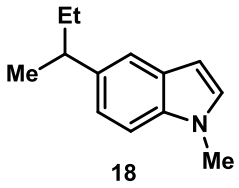

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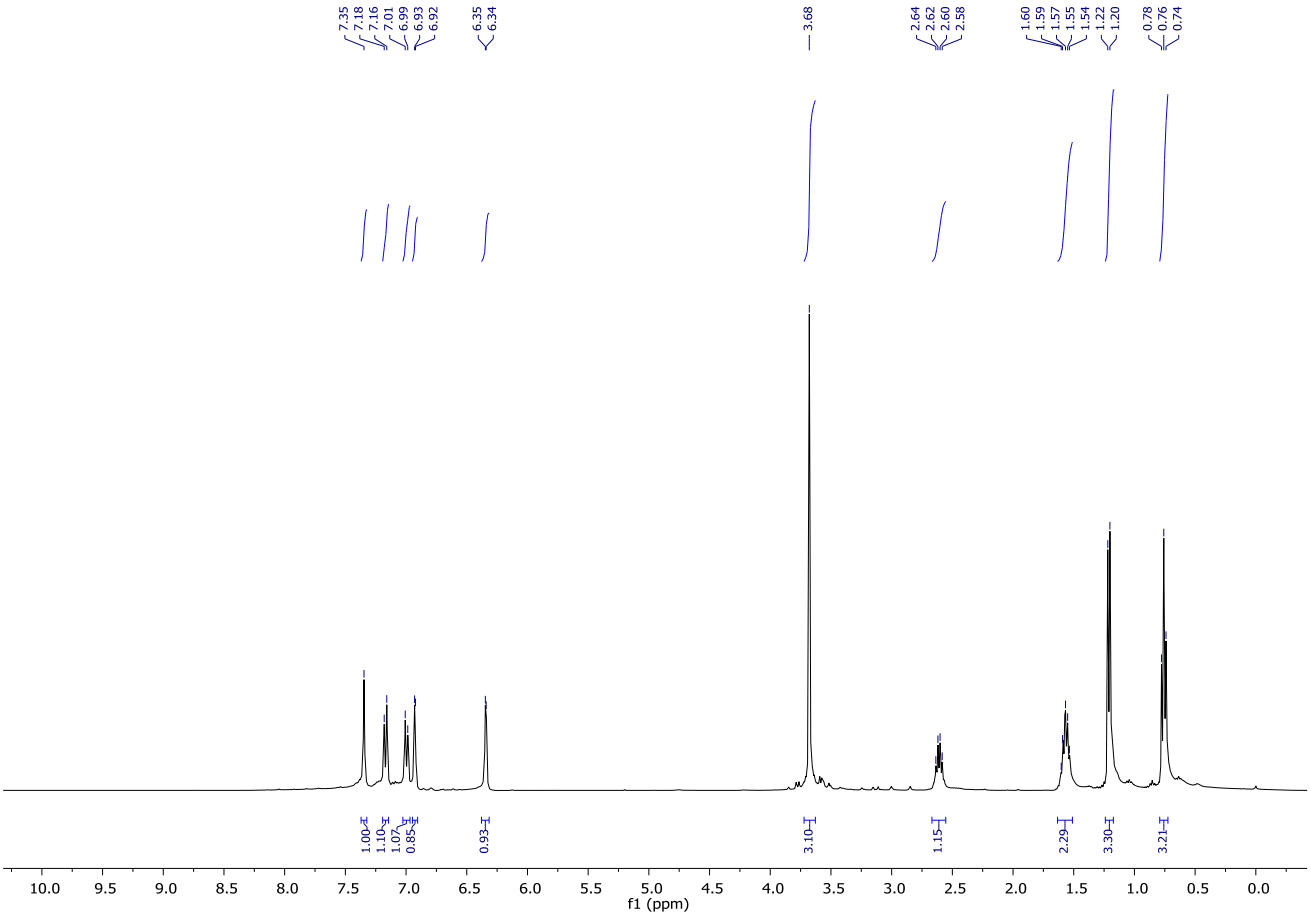

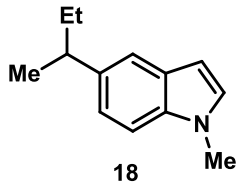

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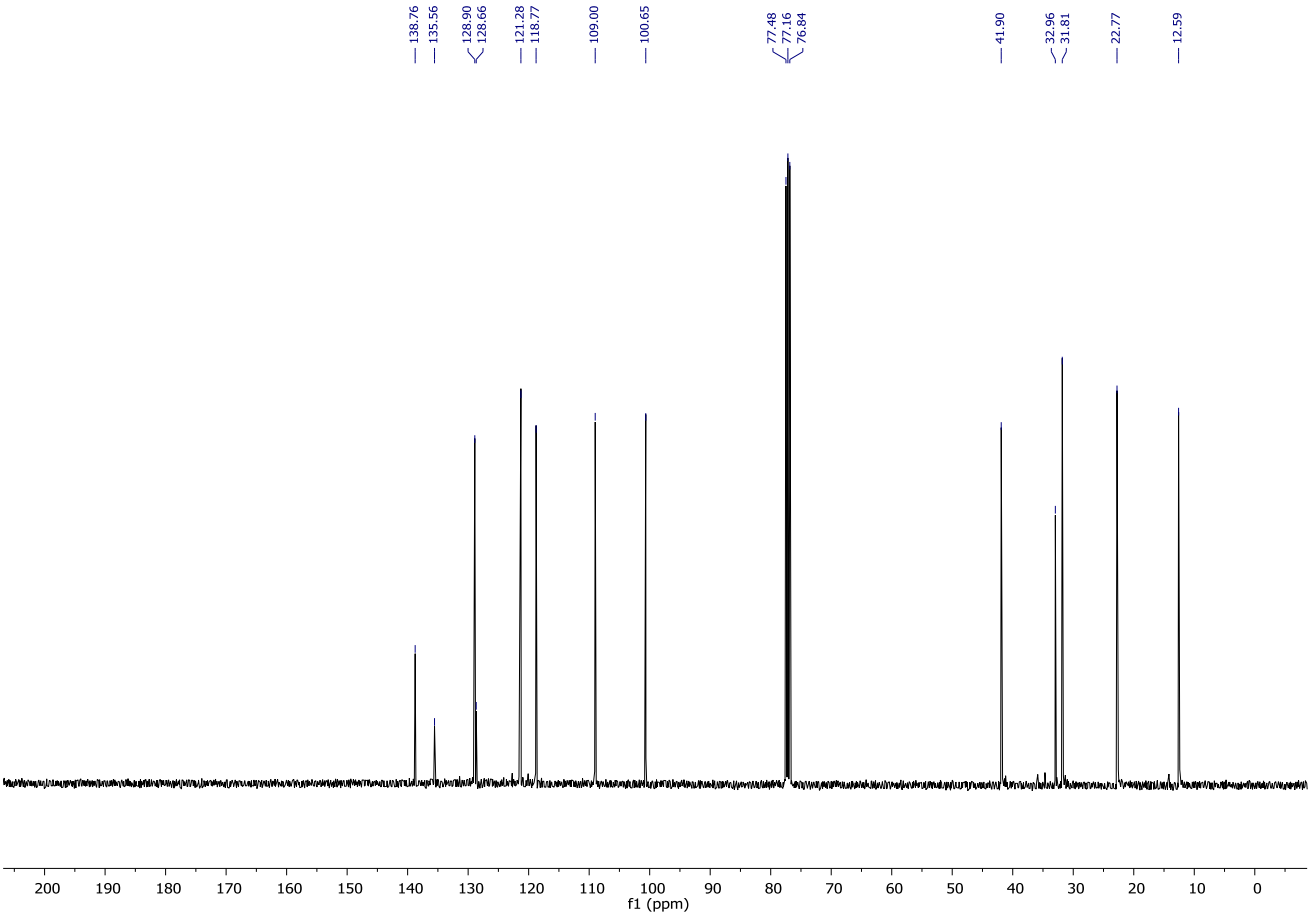

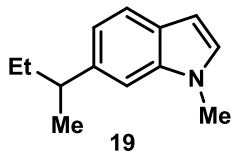

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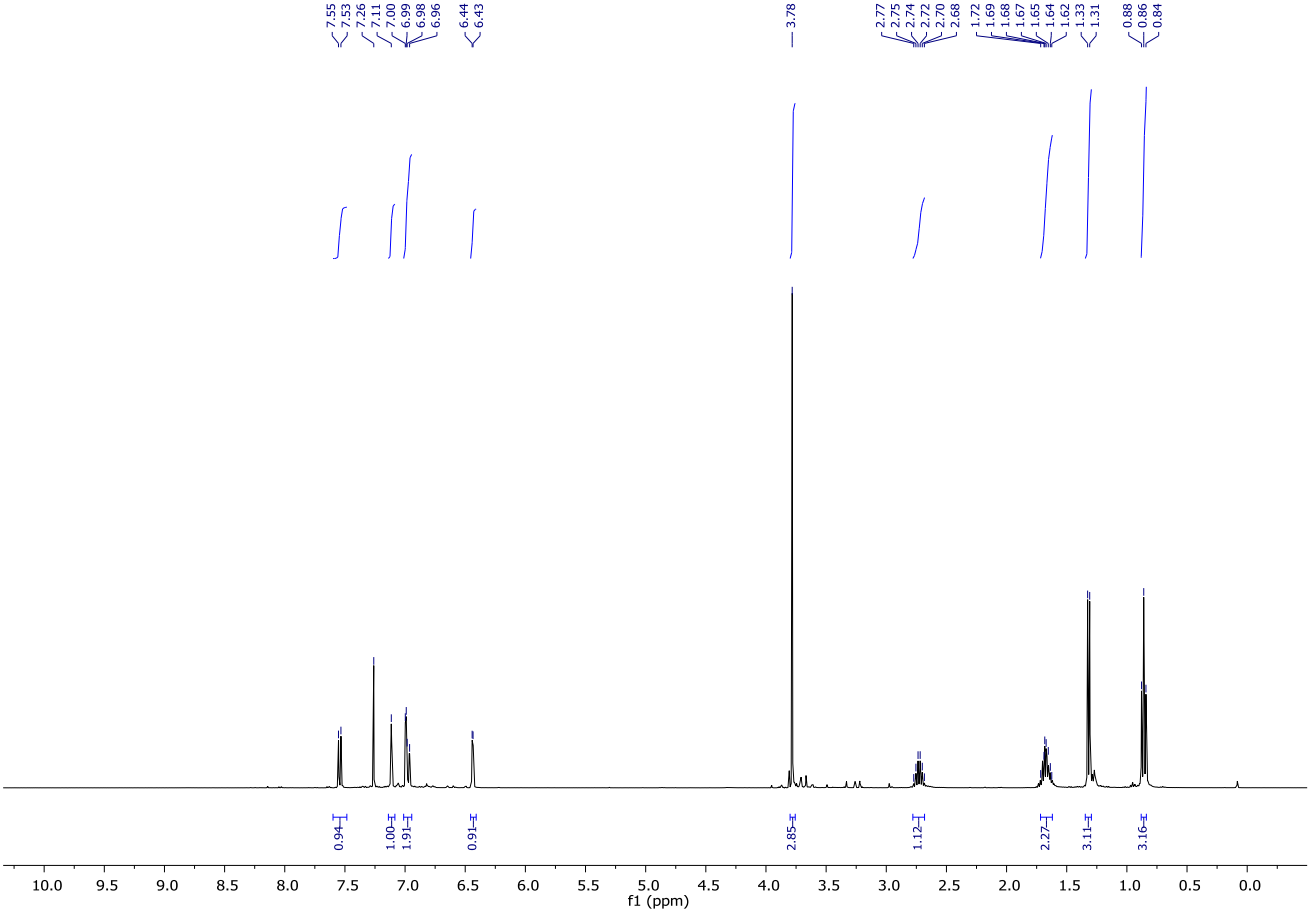

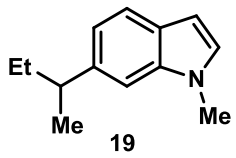

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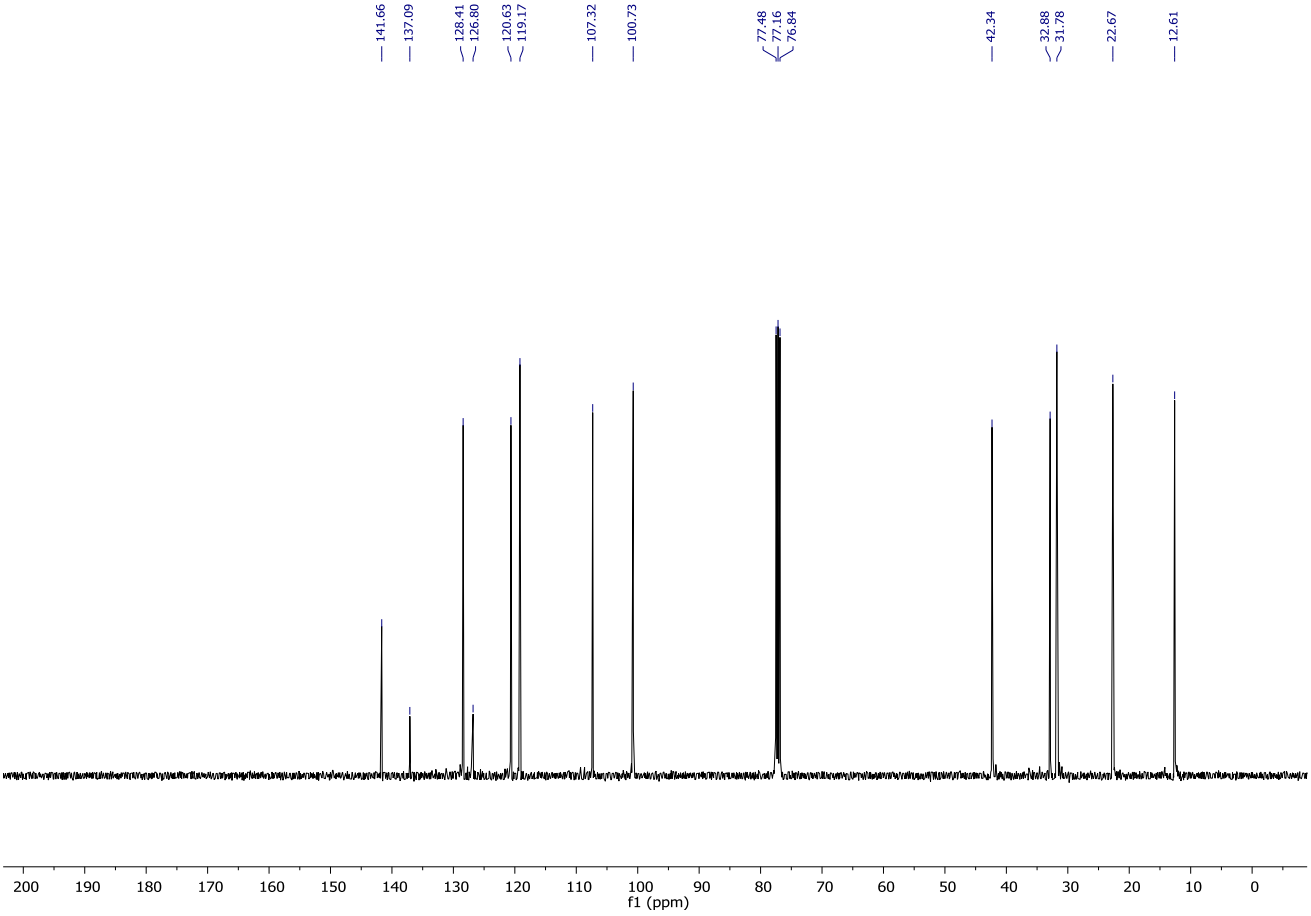

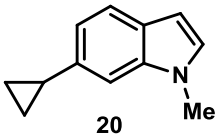

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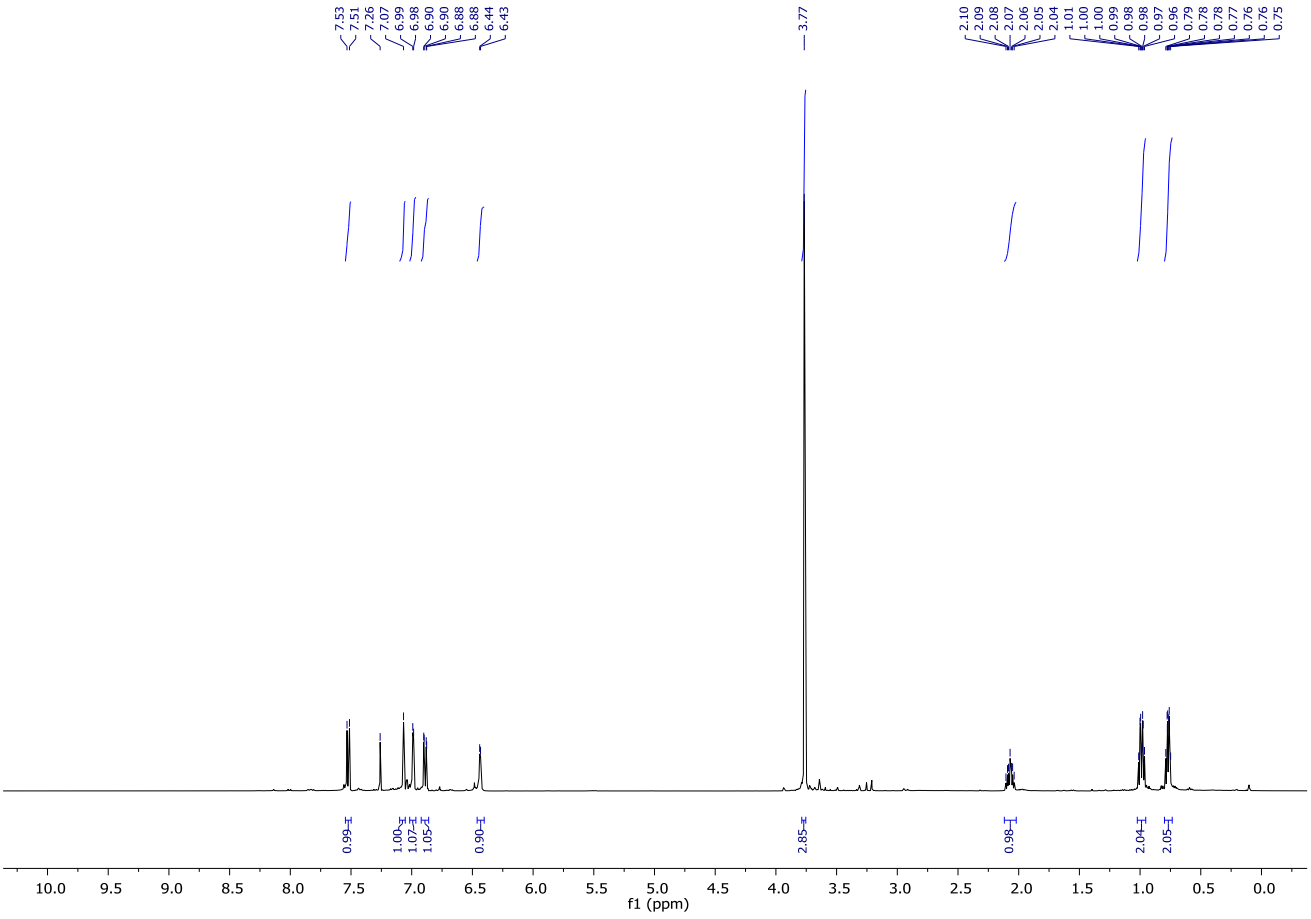

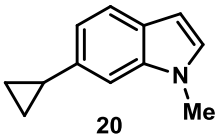

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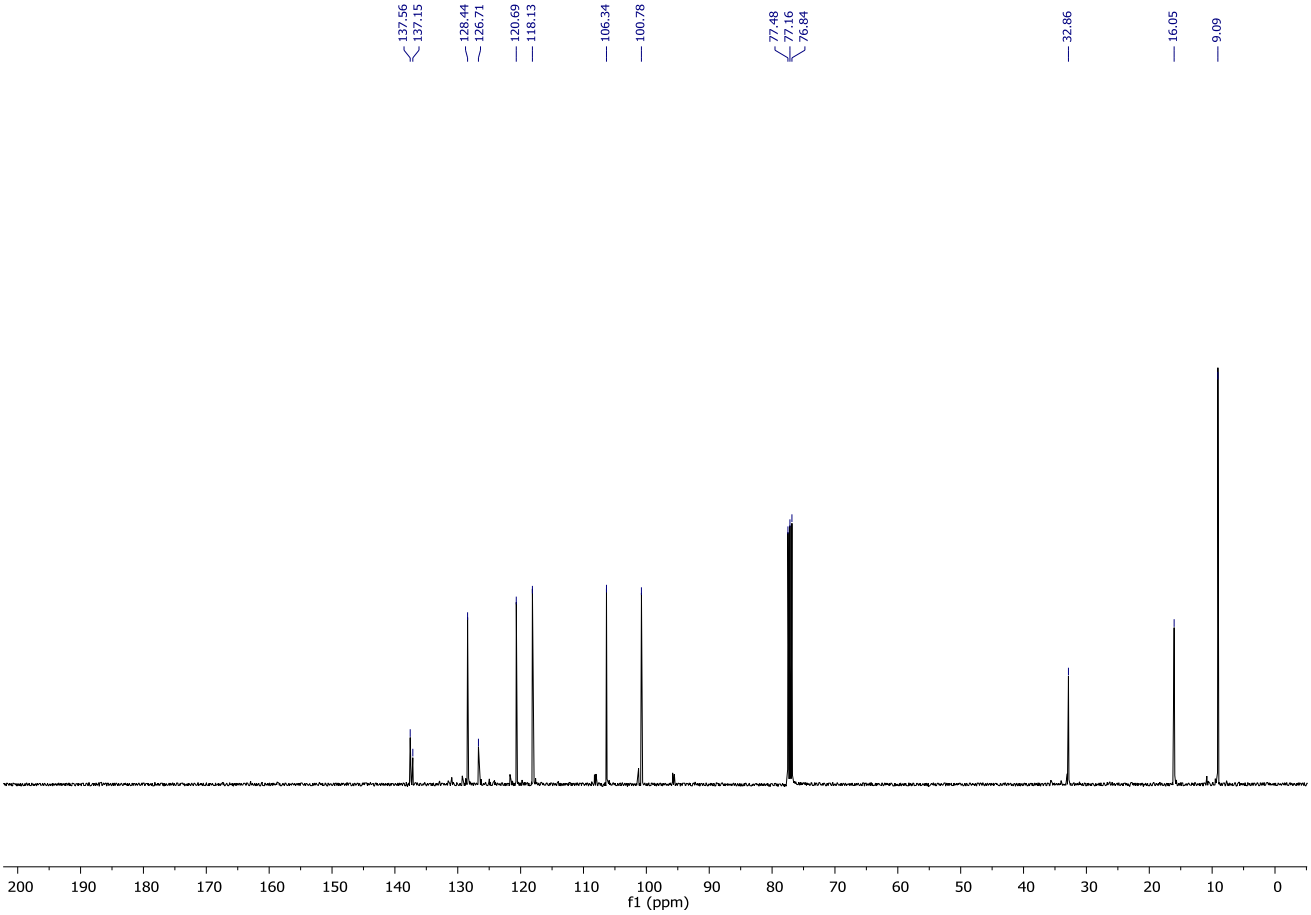

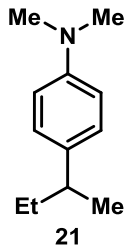

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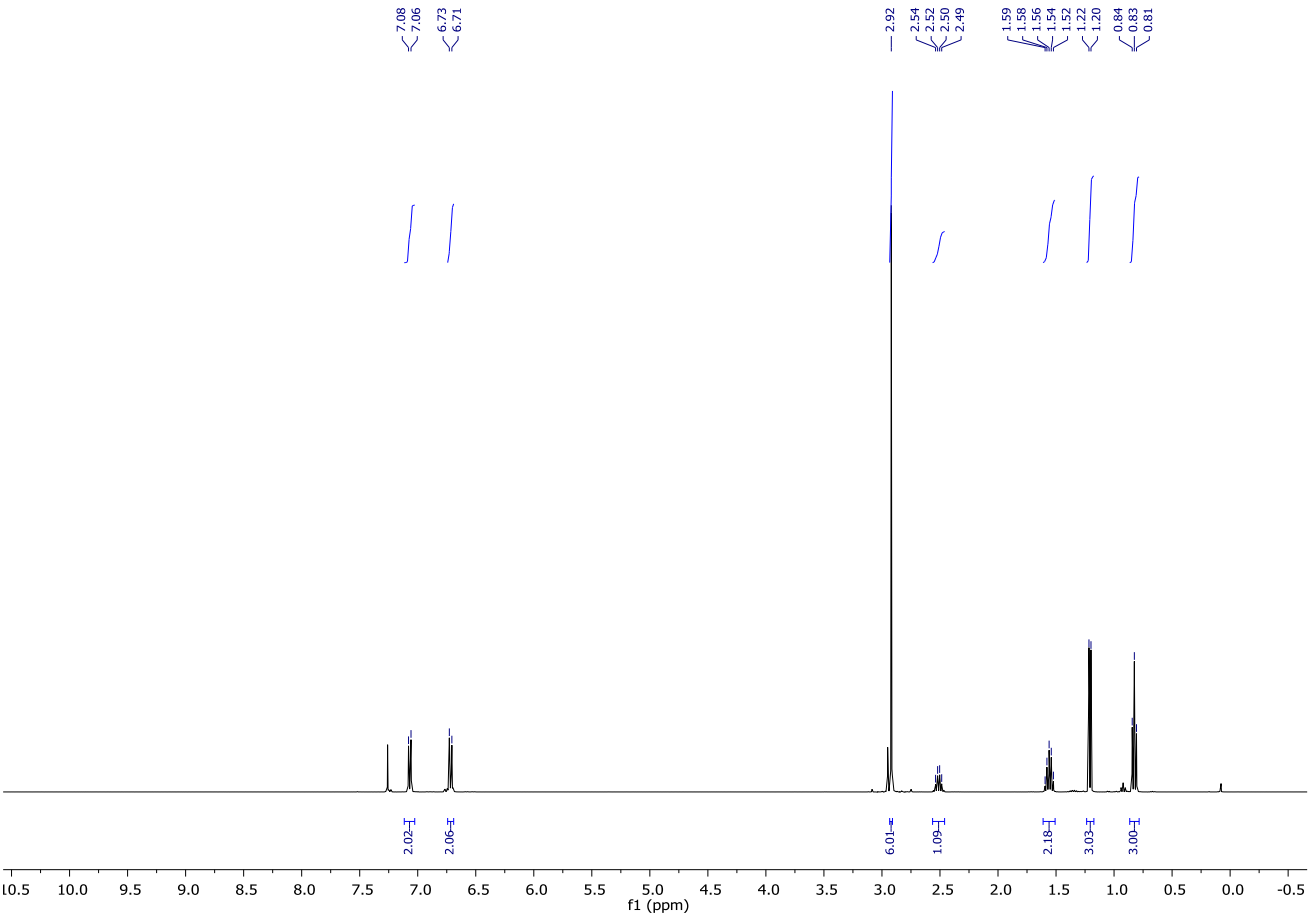

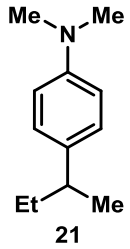

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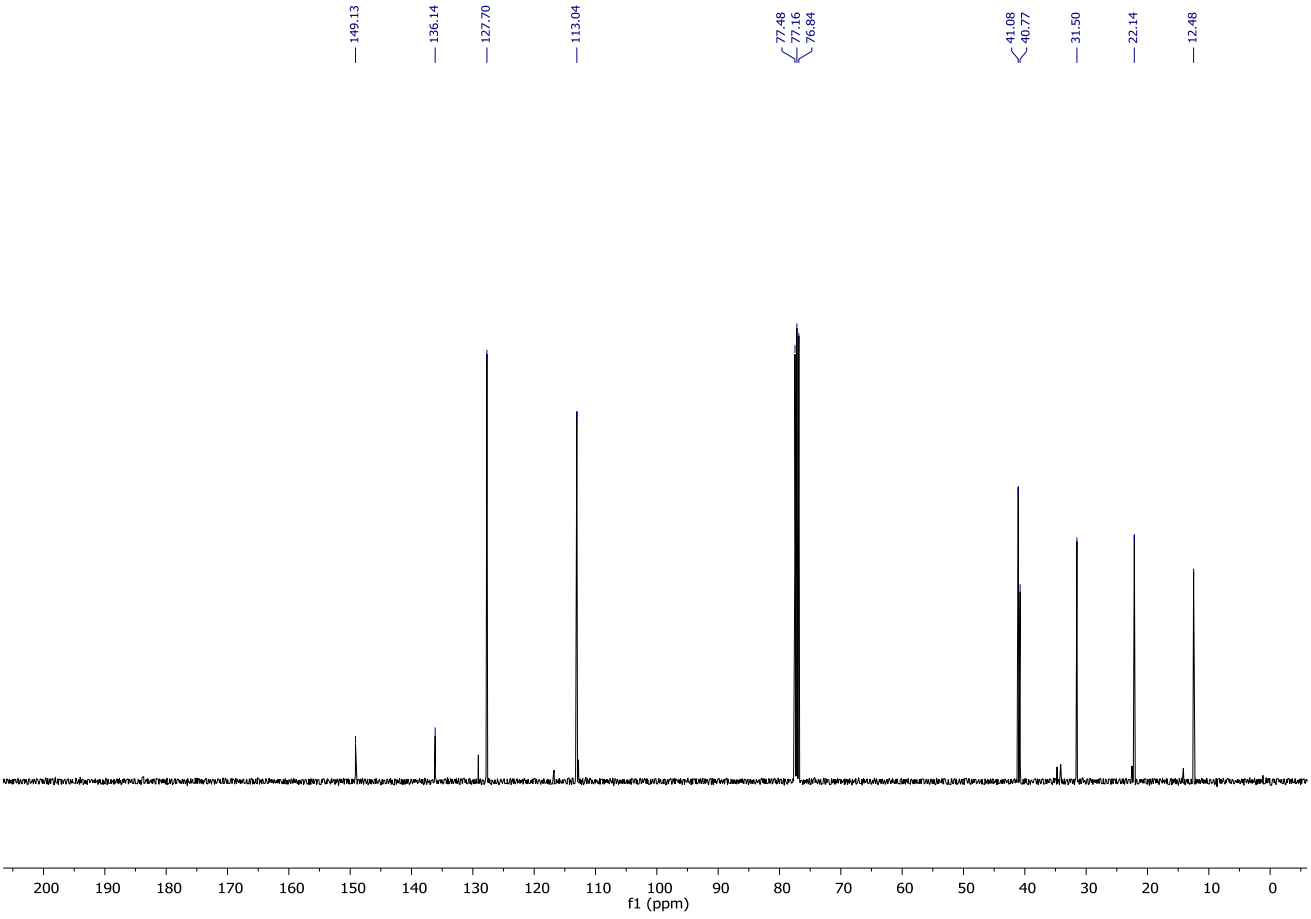

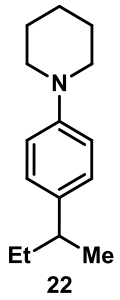

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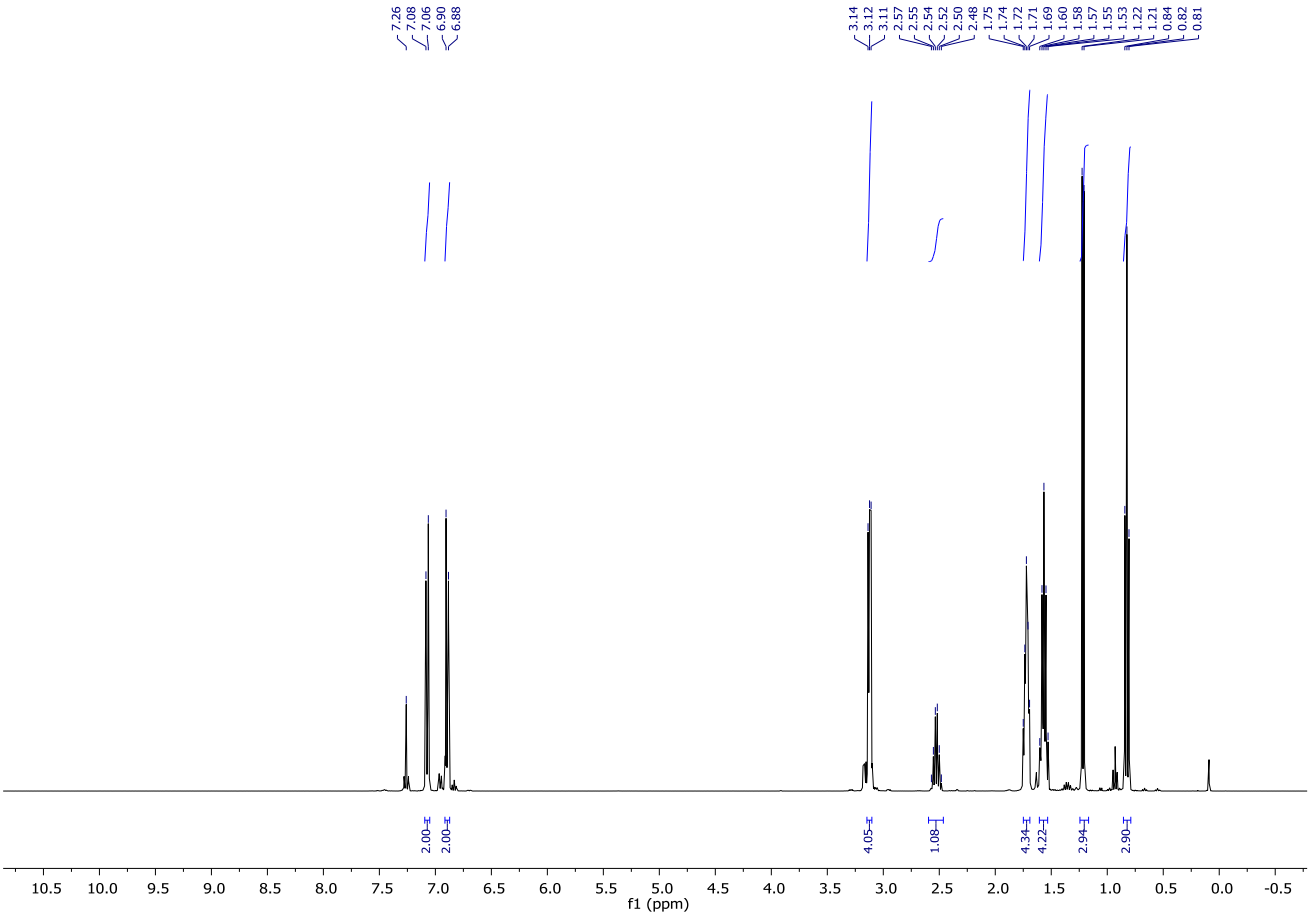

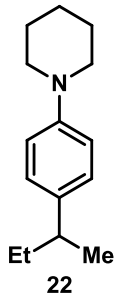

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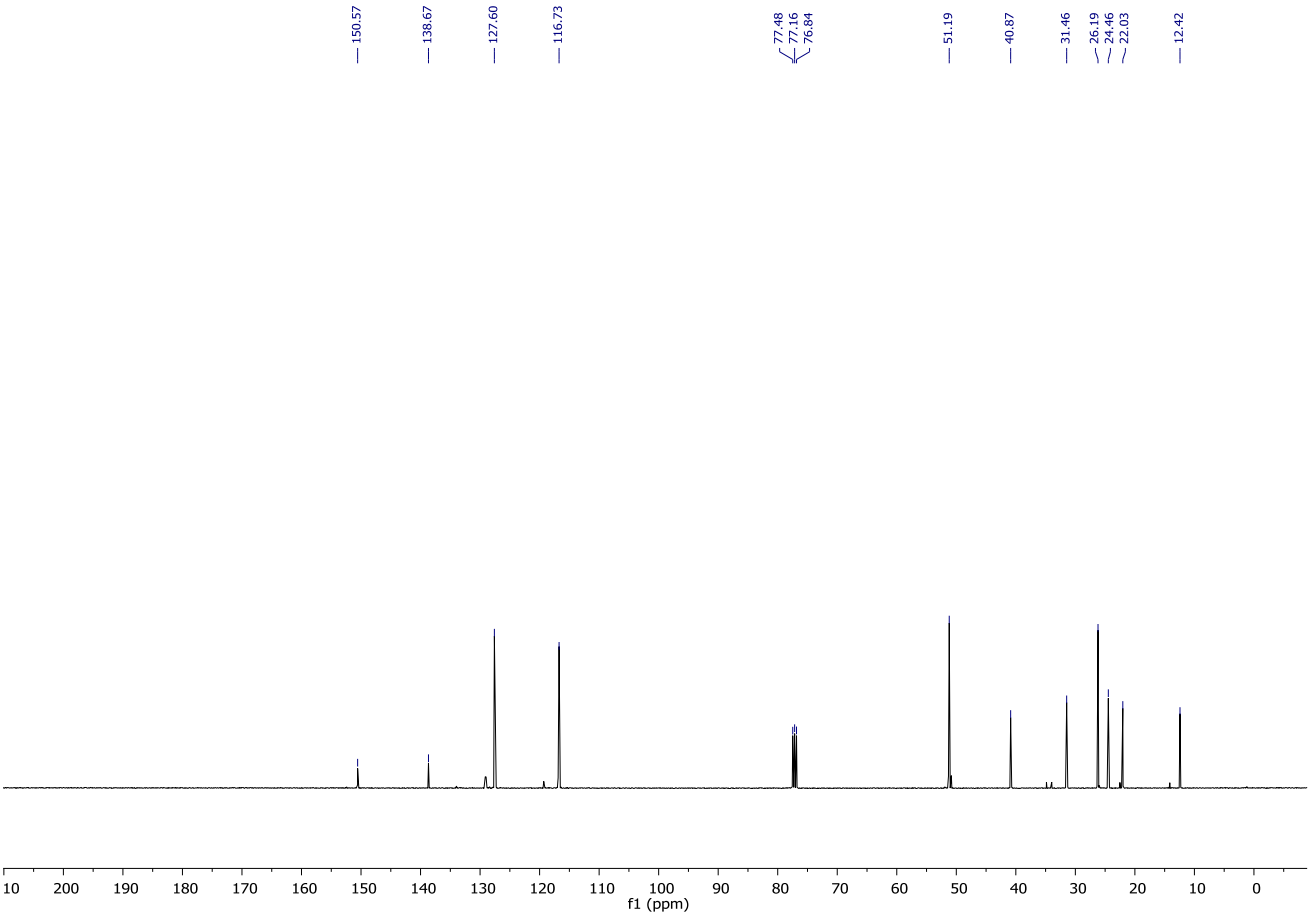

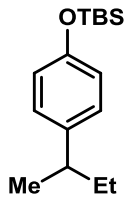

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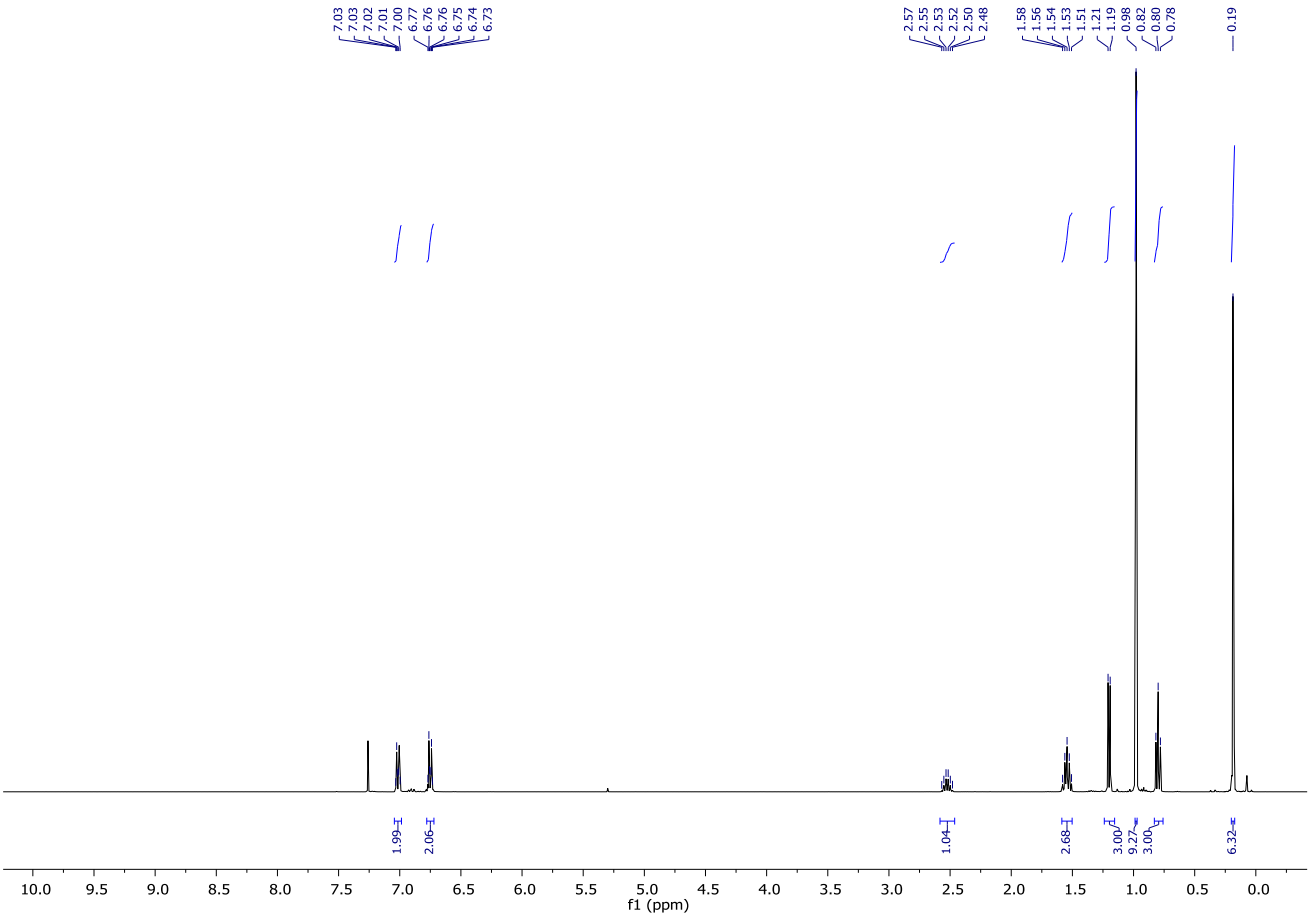

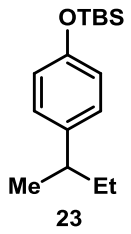

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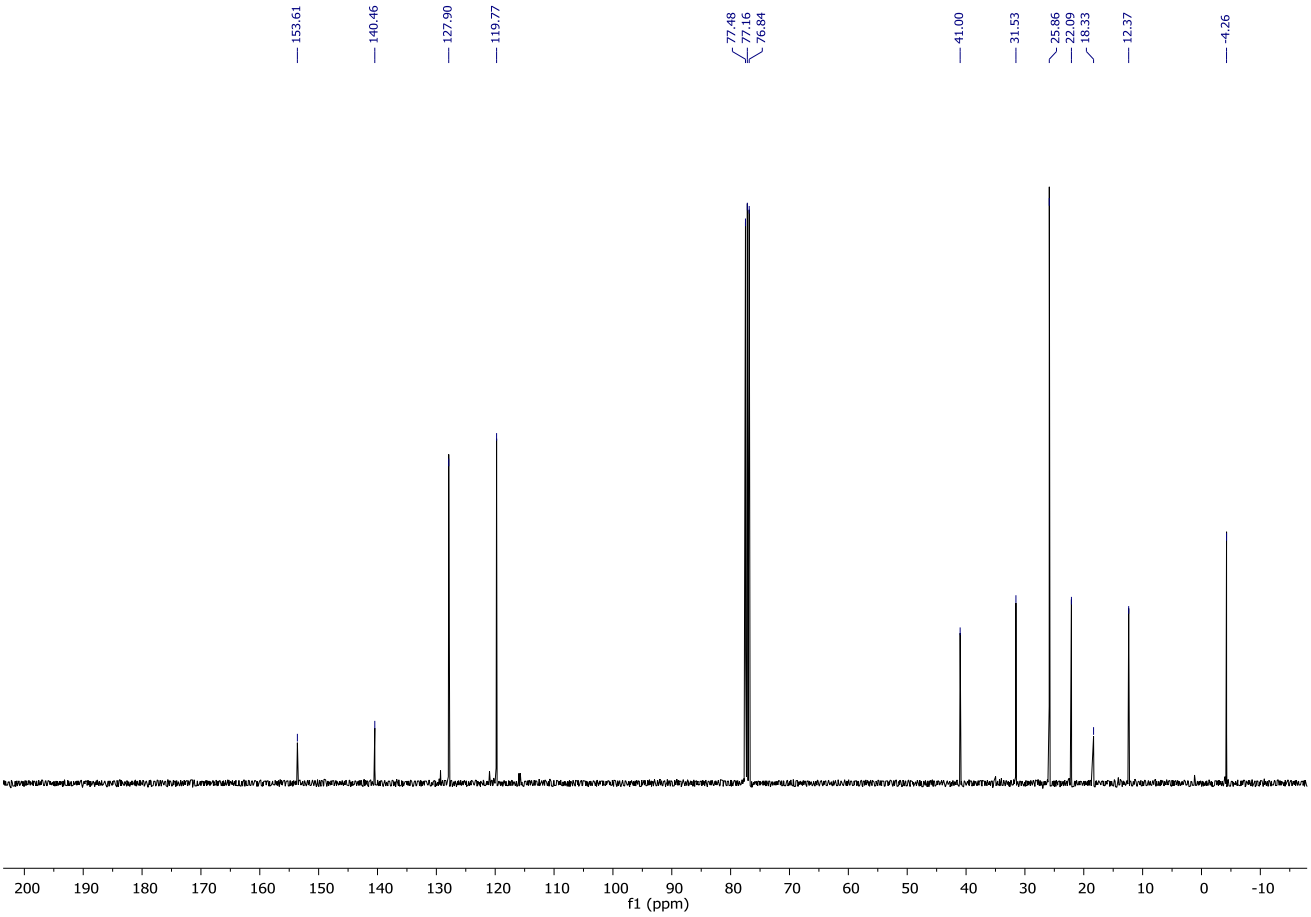

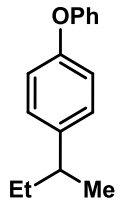

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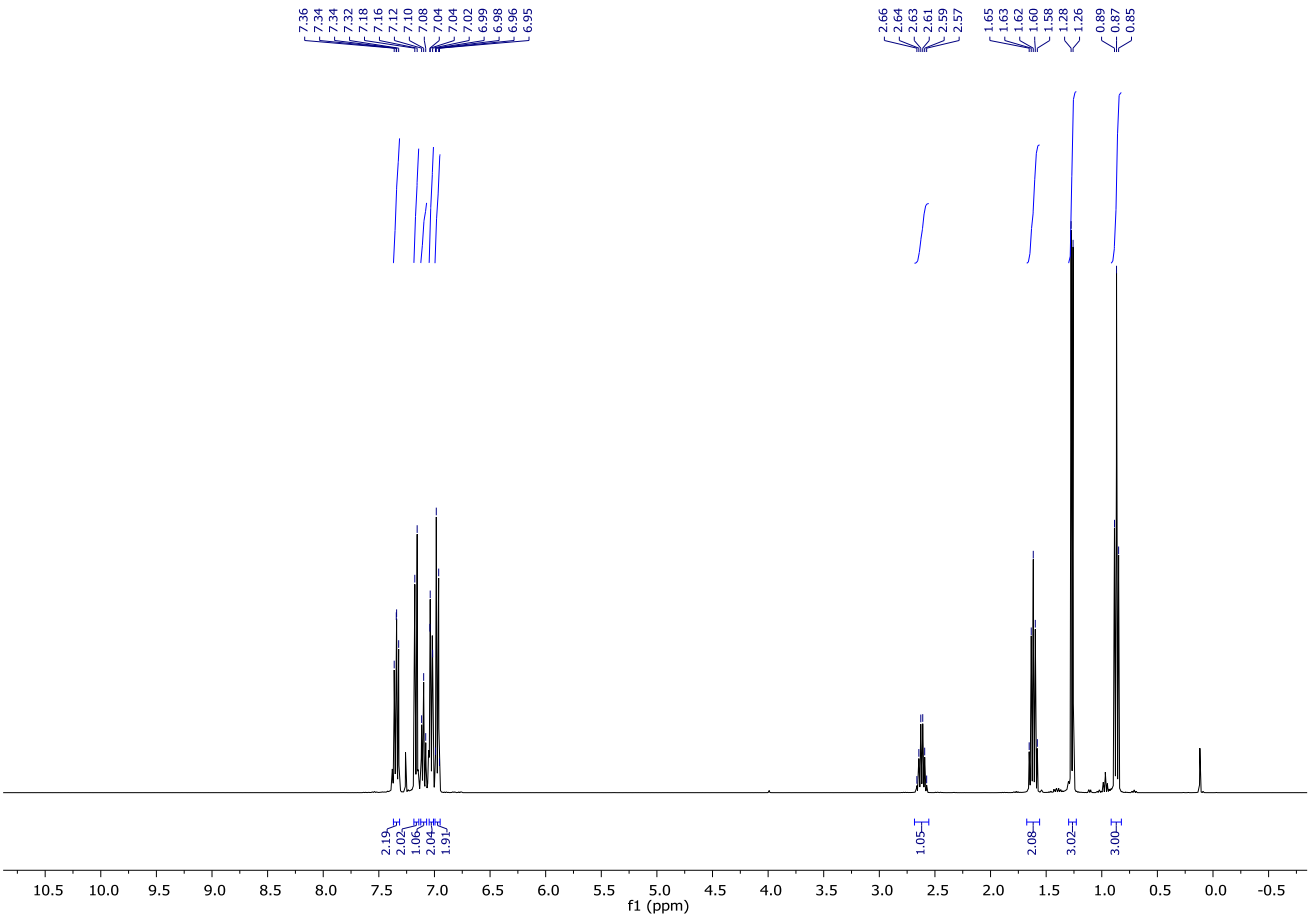

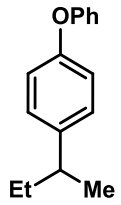

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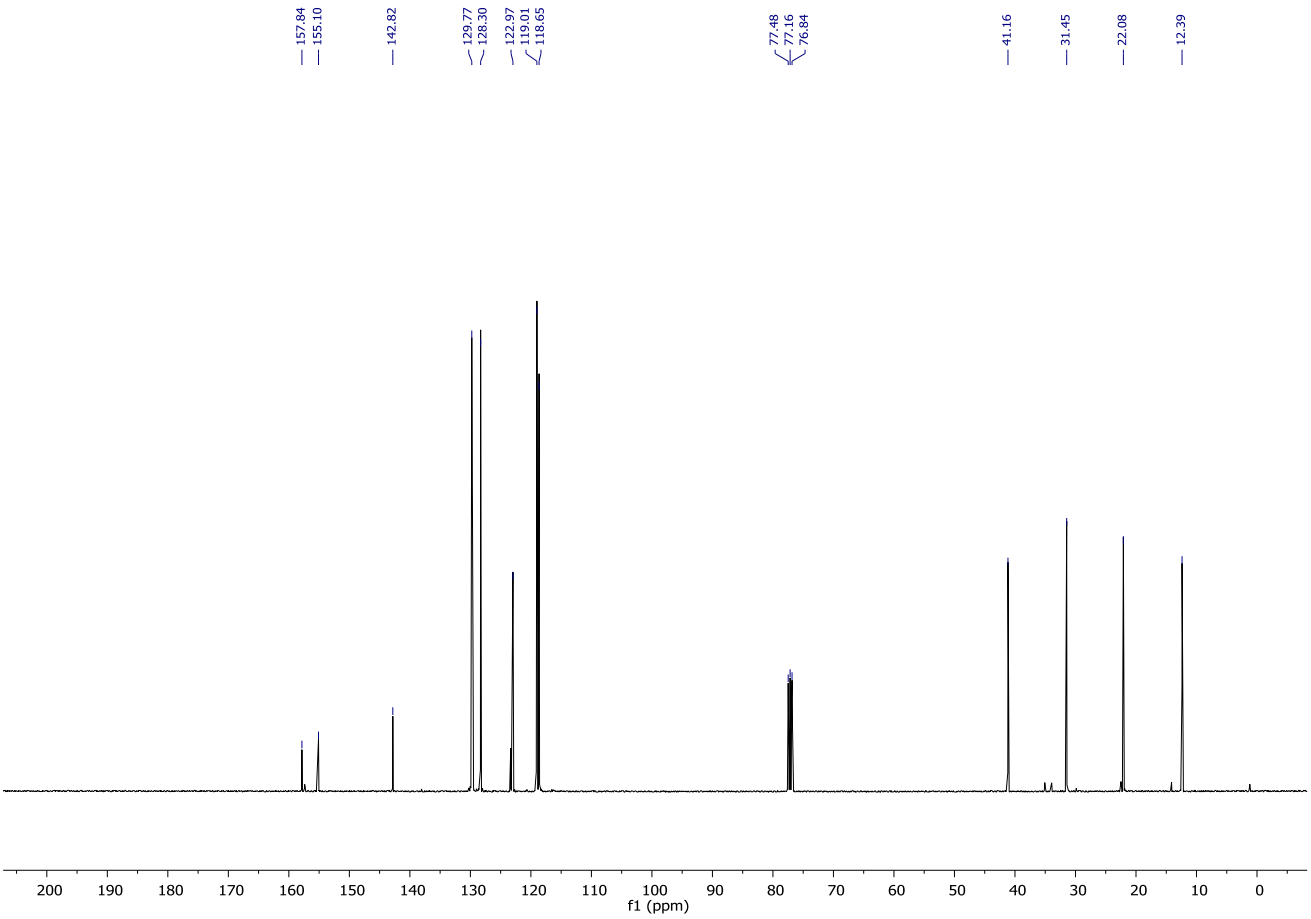

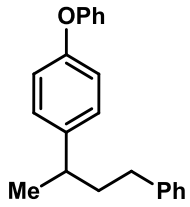

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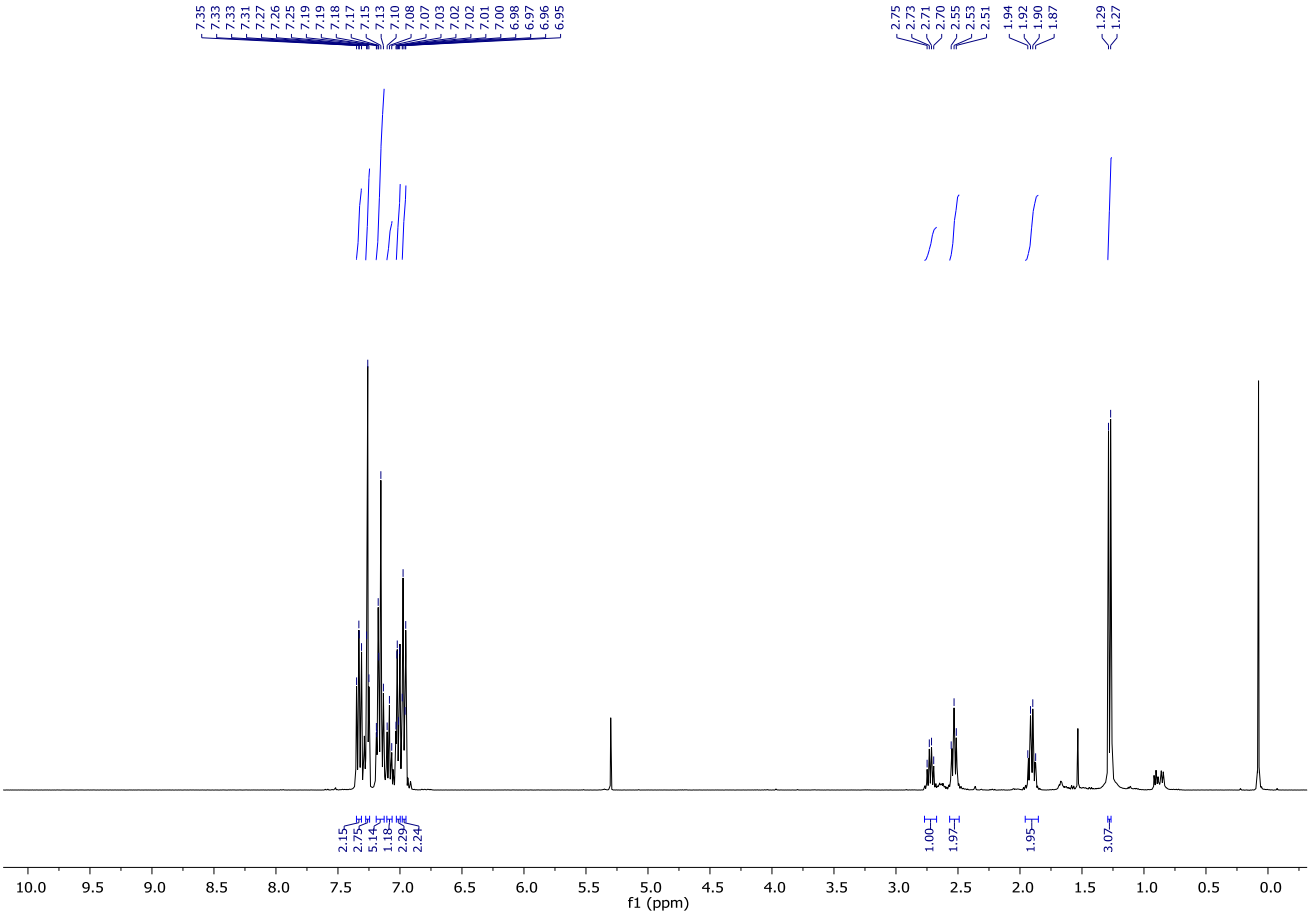

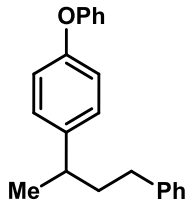

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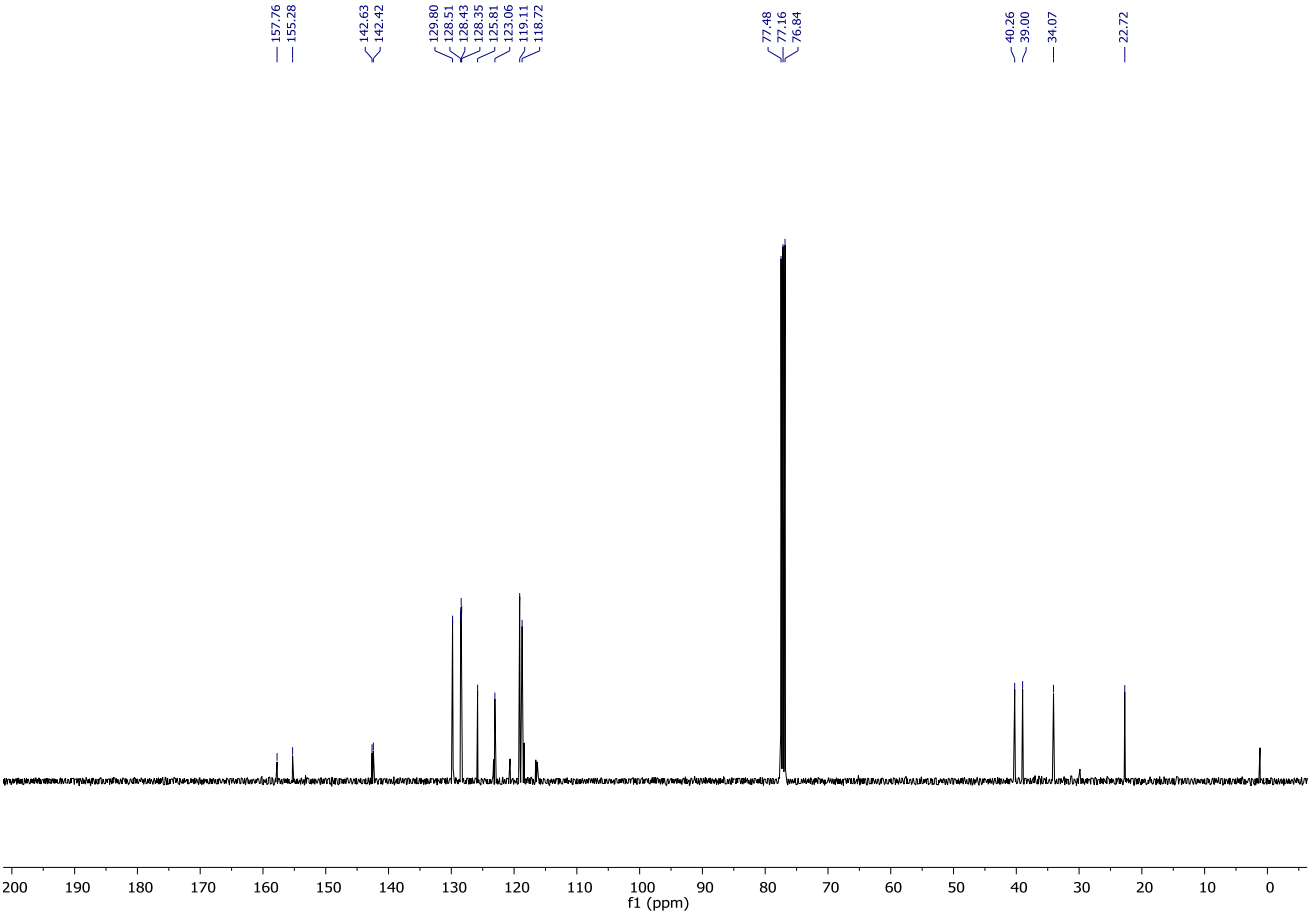

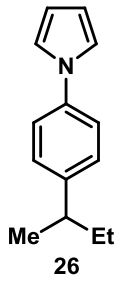

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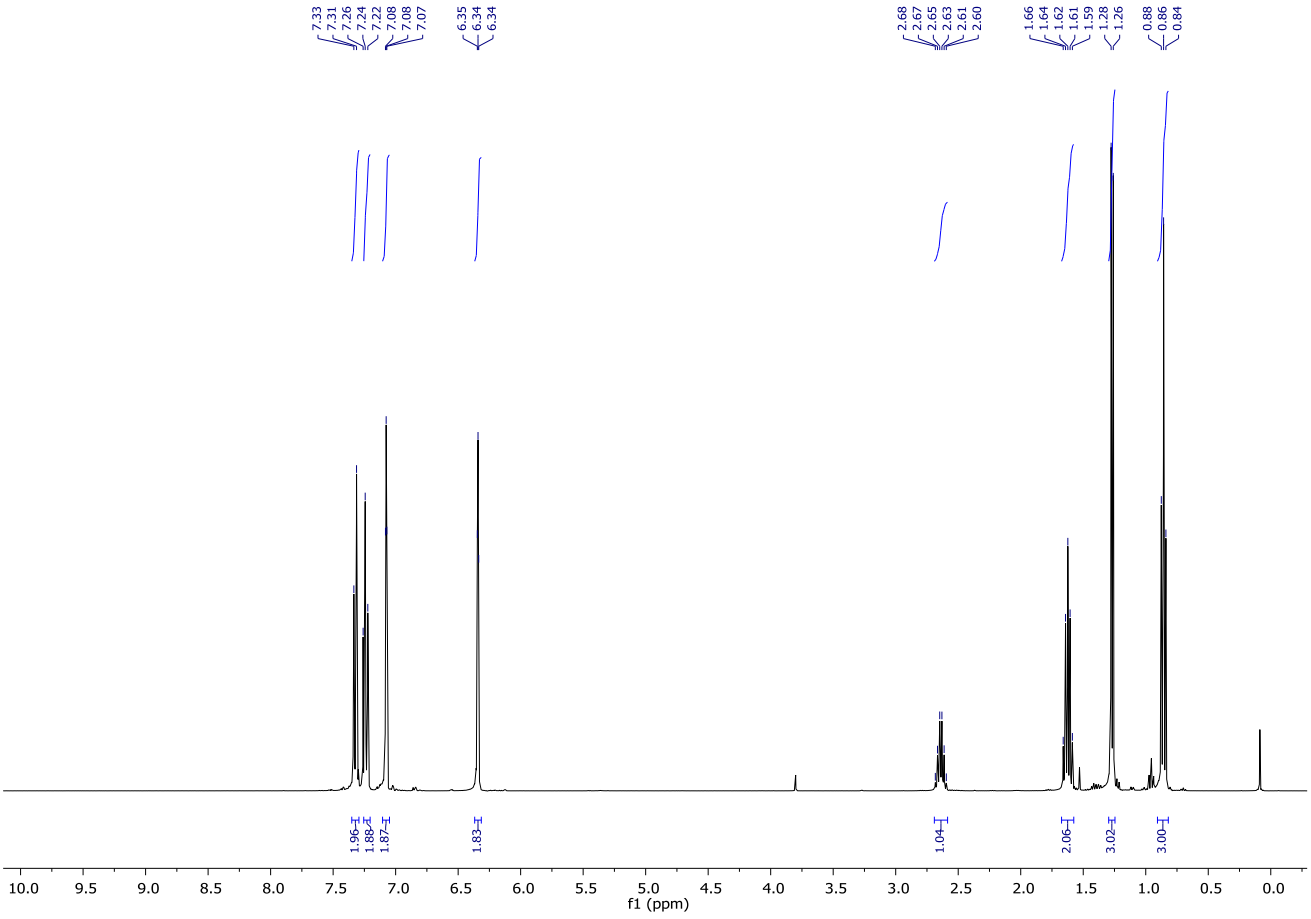

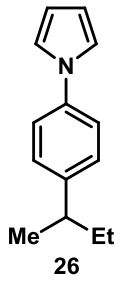

26

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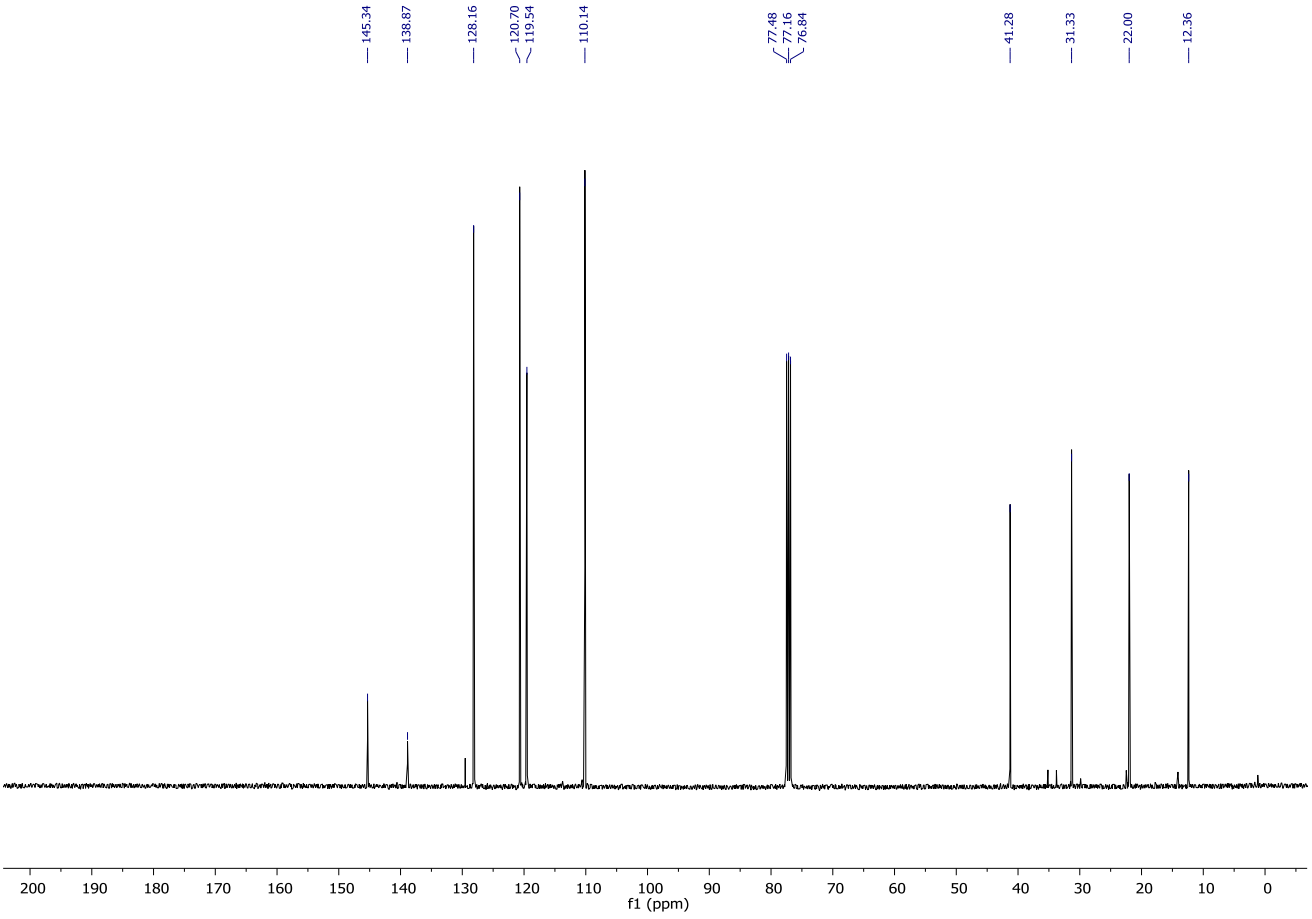

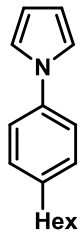

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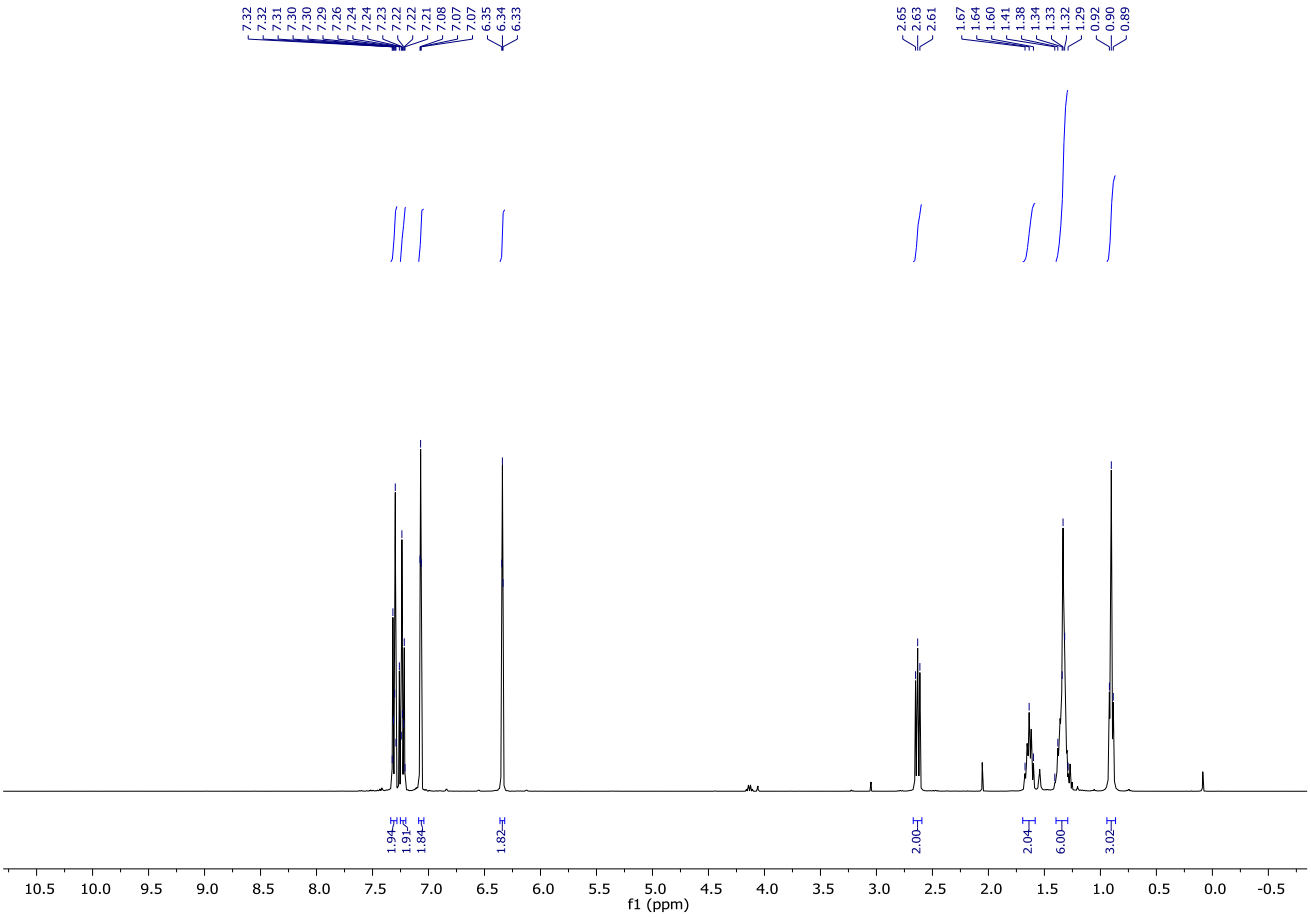

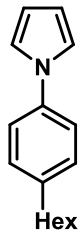

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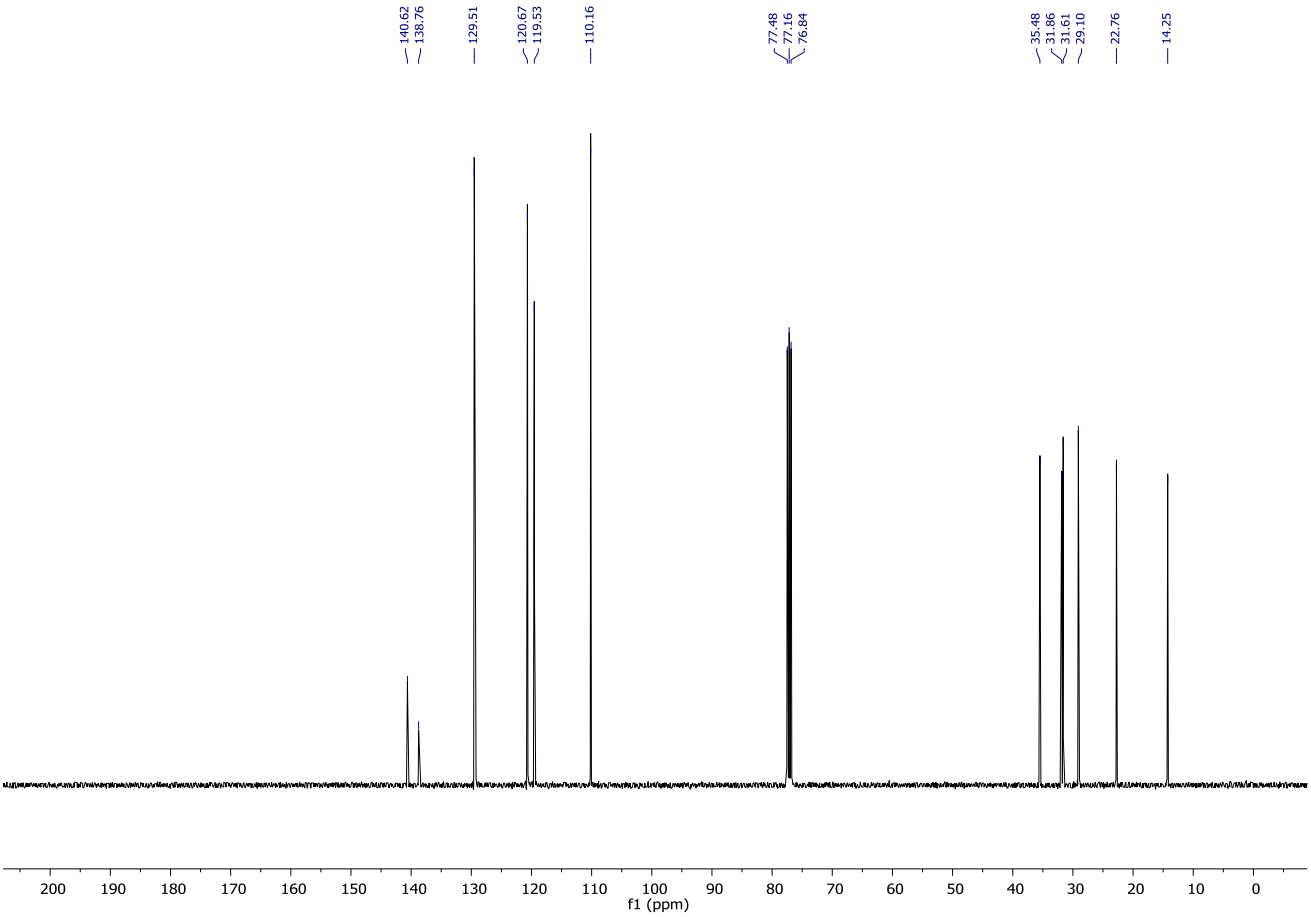
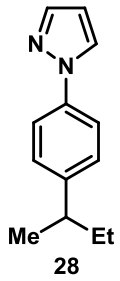
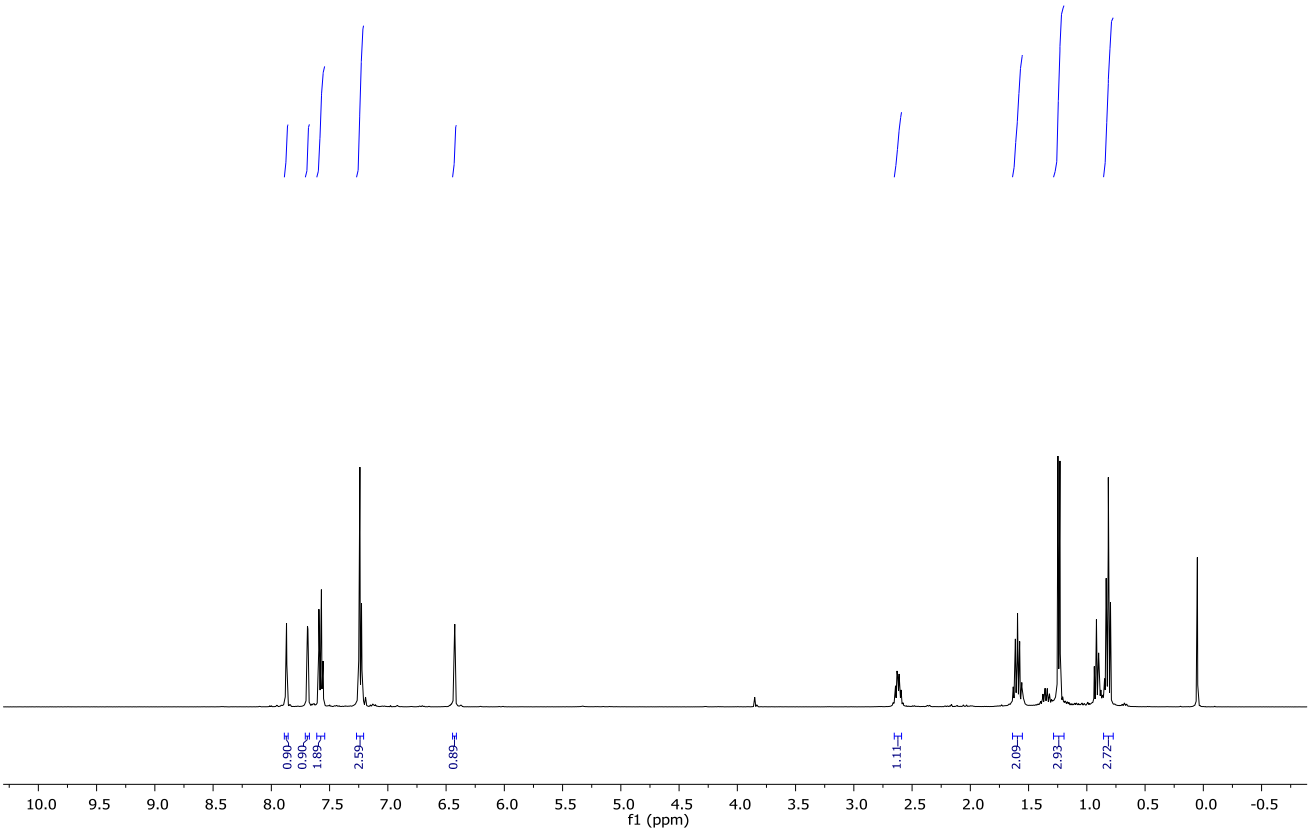
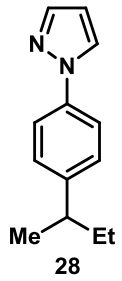




28

^{1}H Spectra





28

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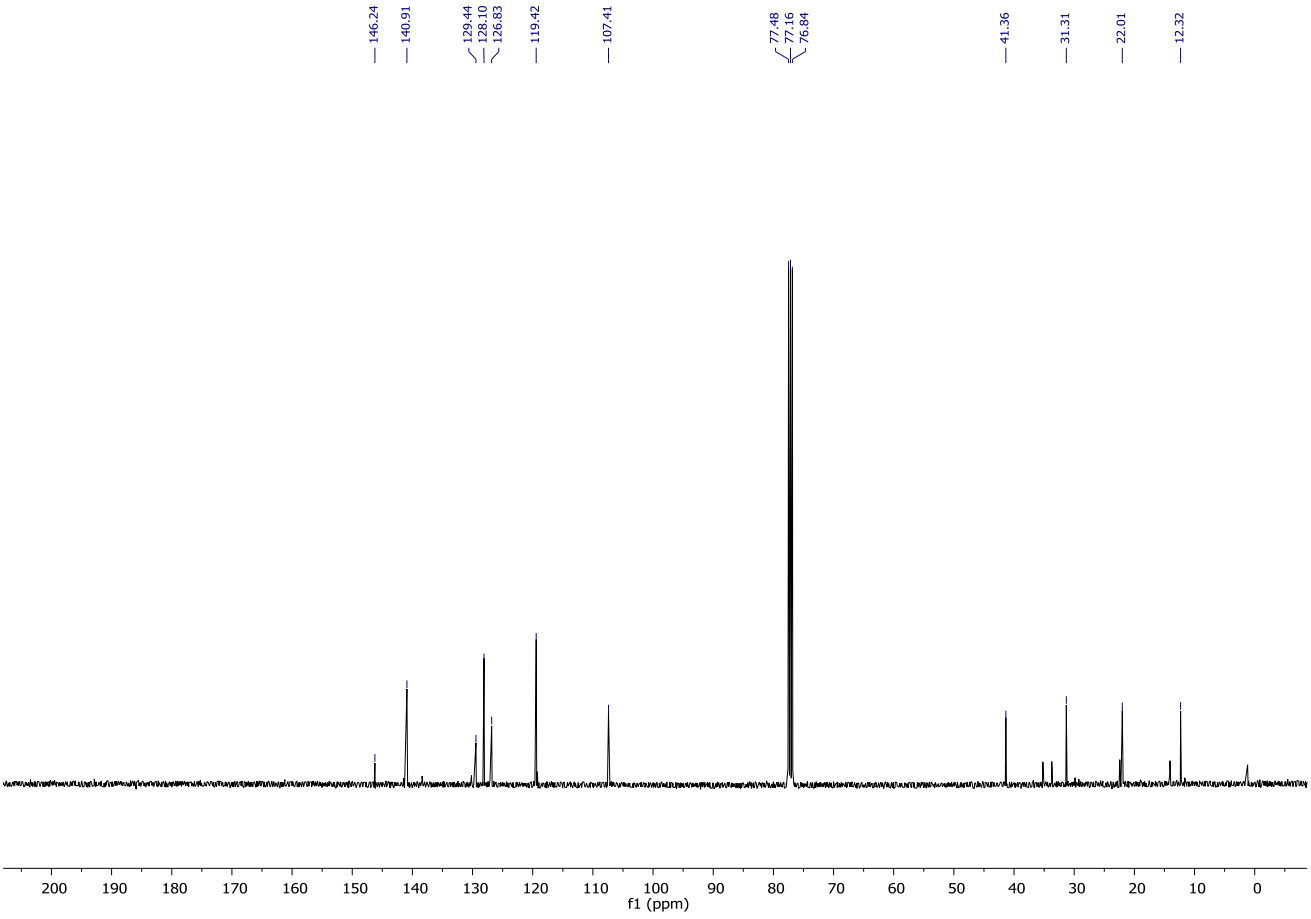

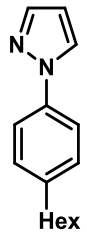

29

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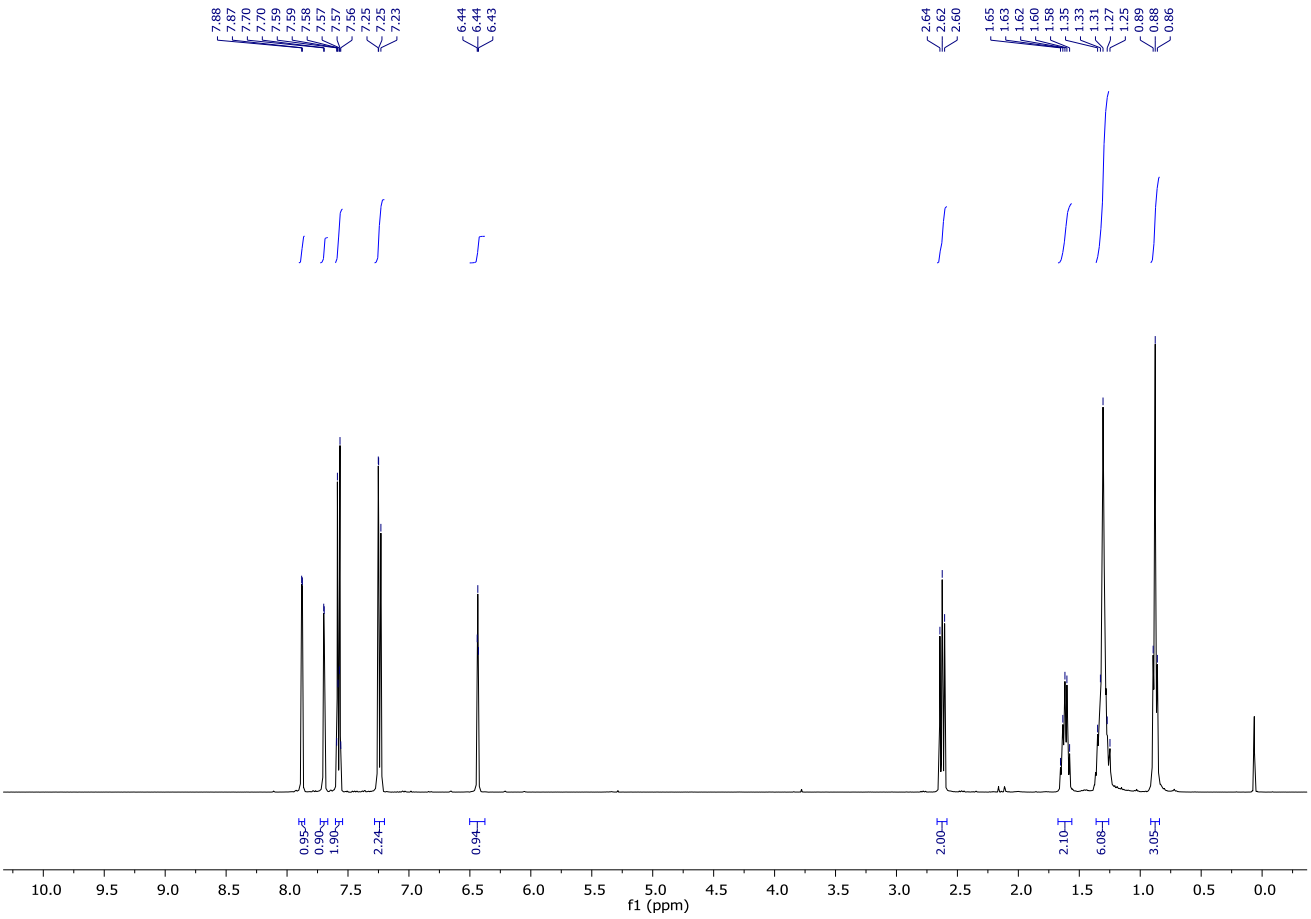

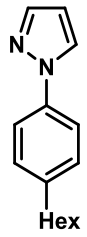

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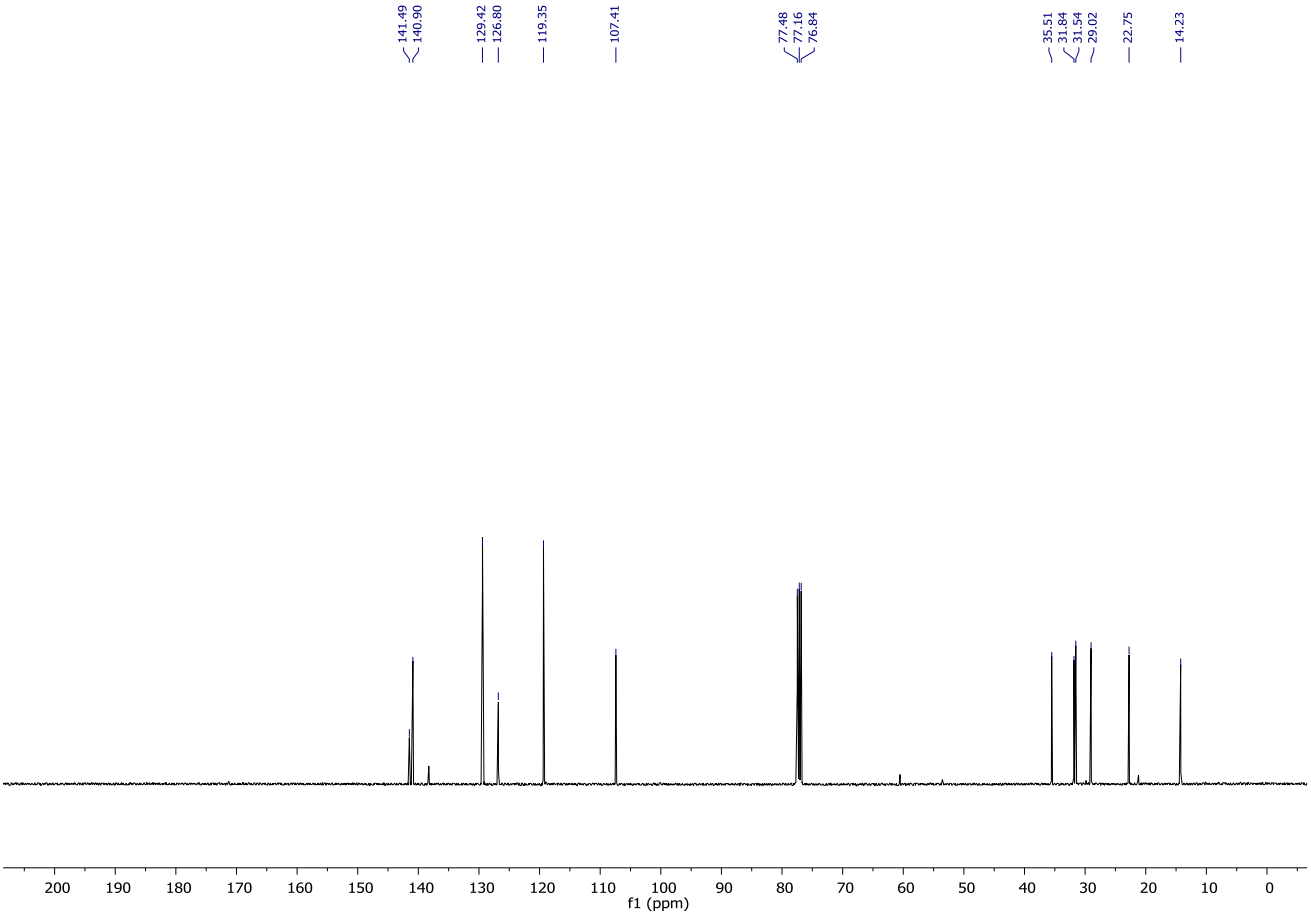

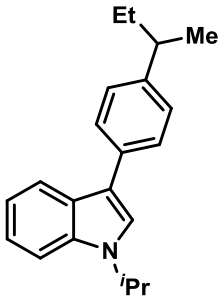

30

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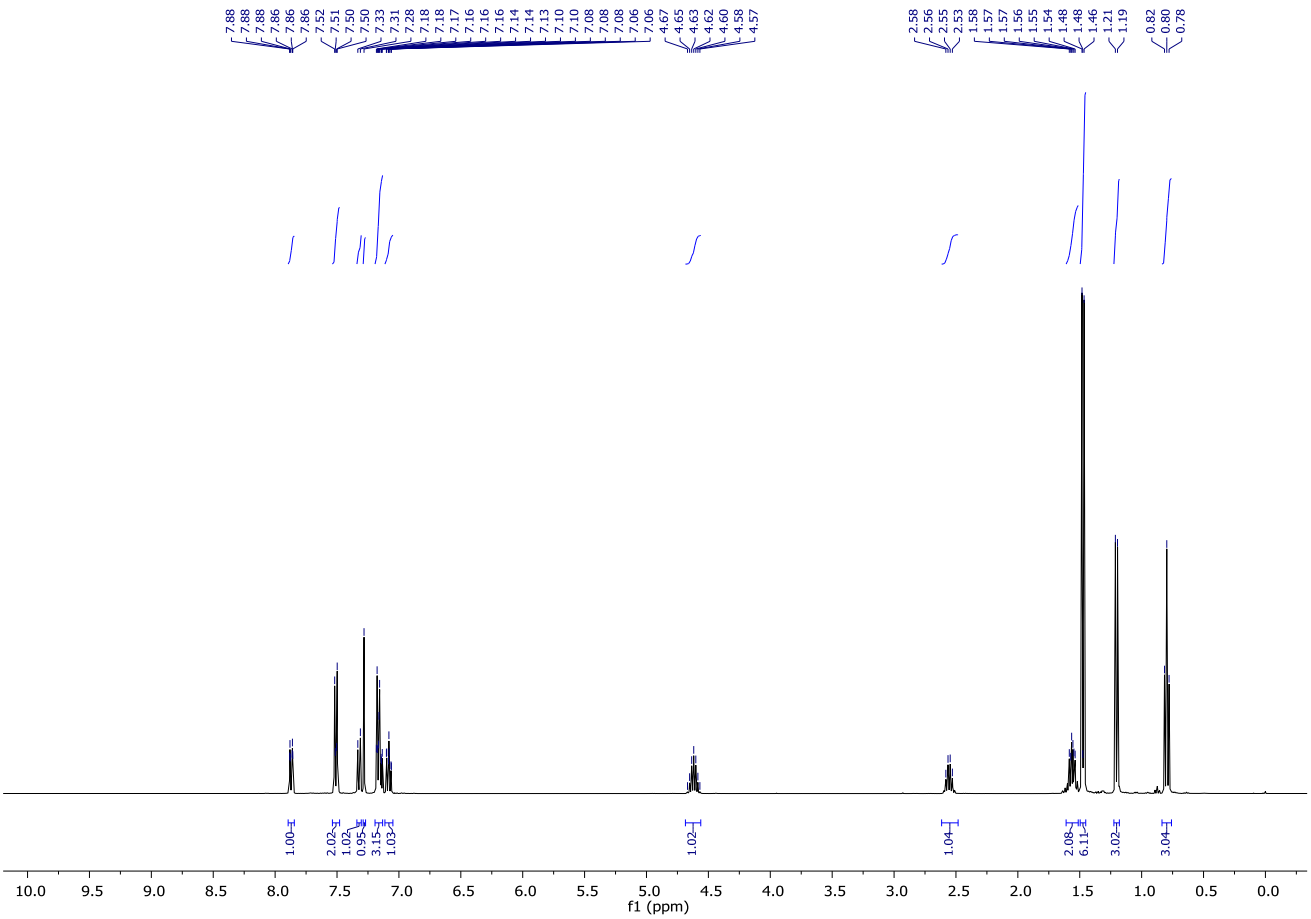

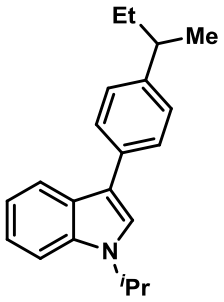

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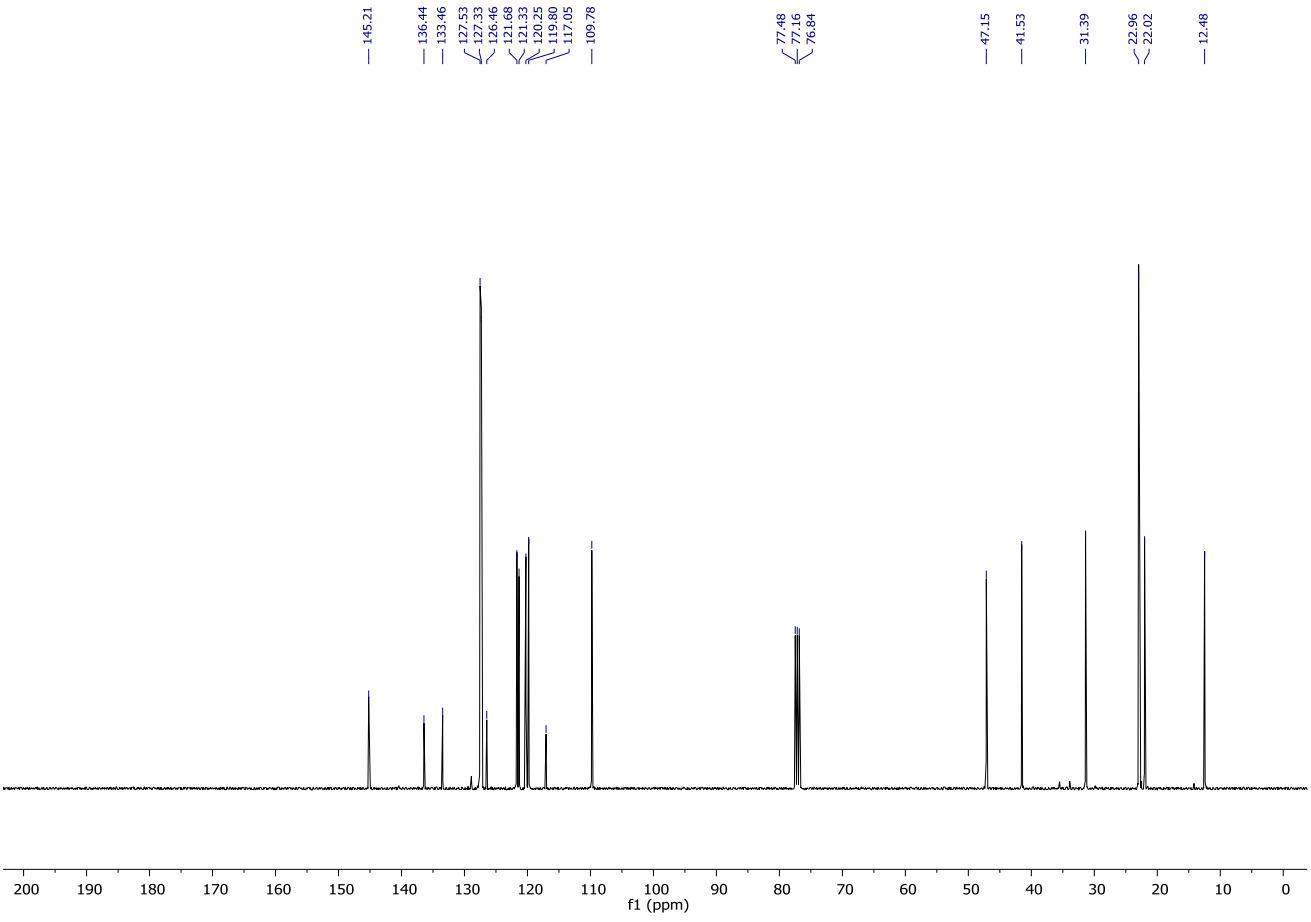

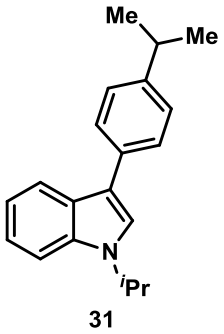

31

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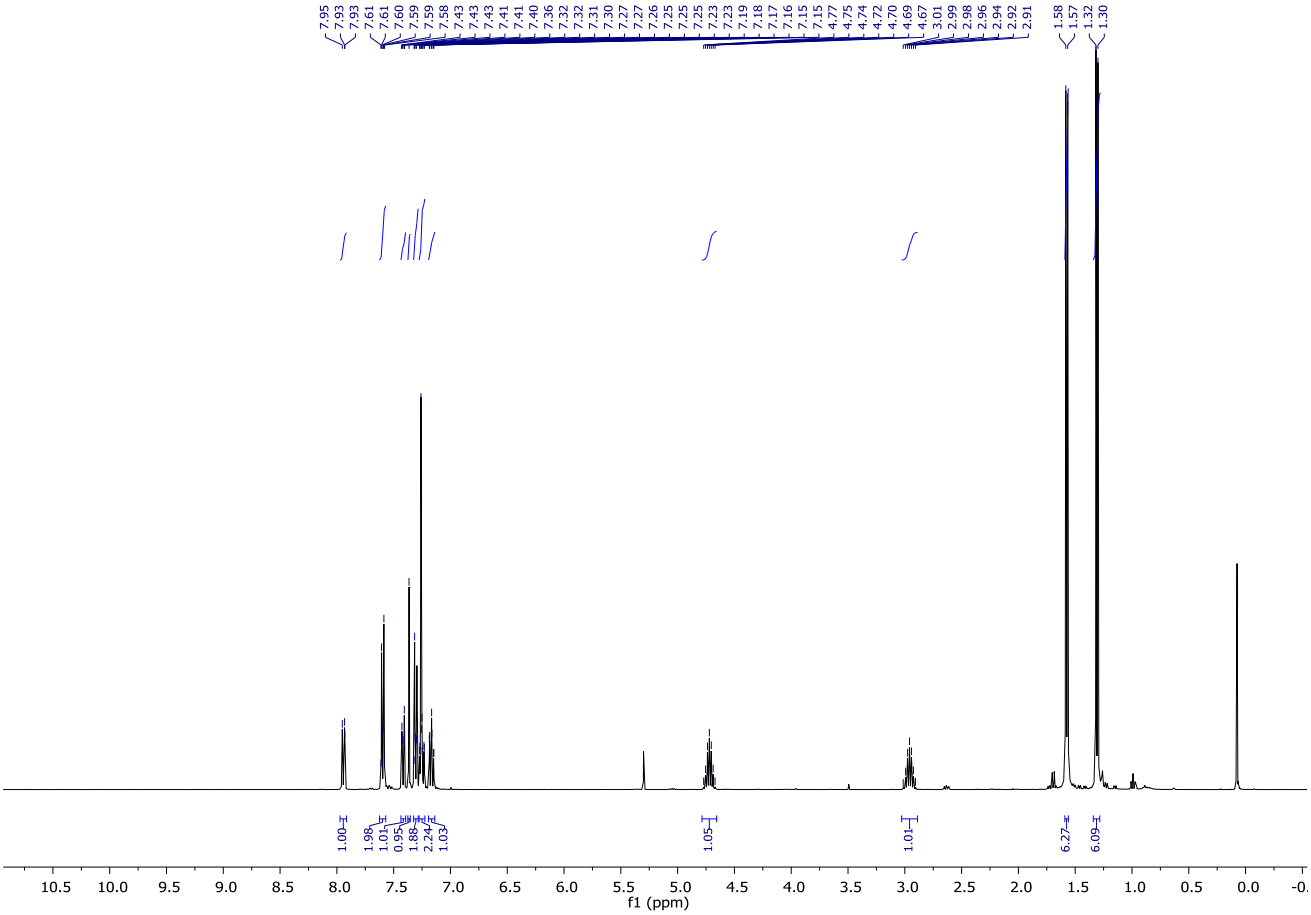

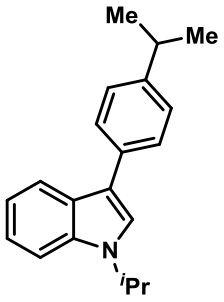

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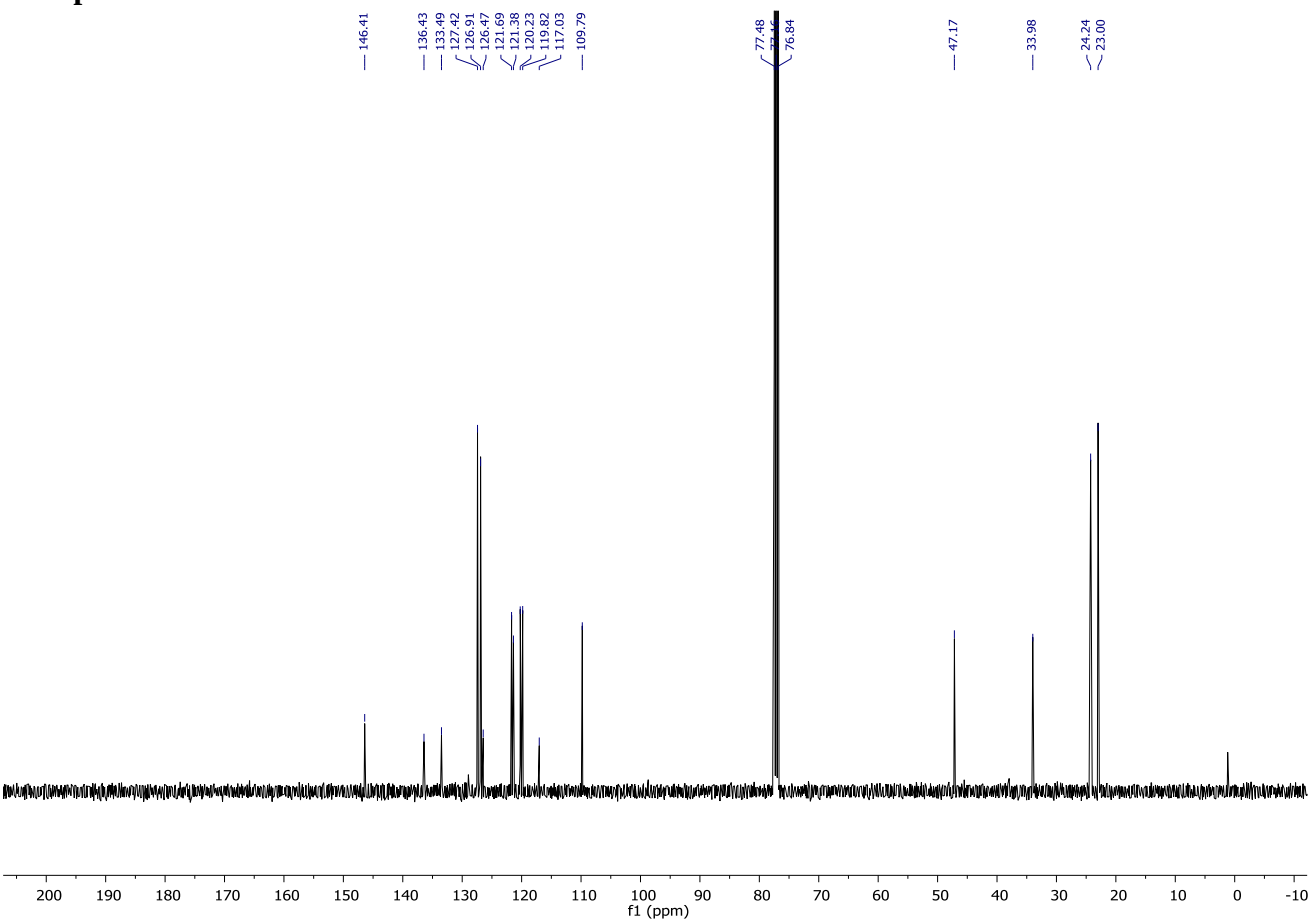

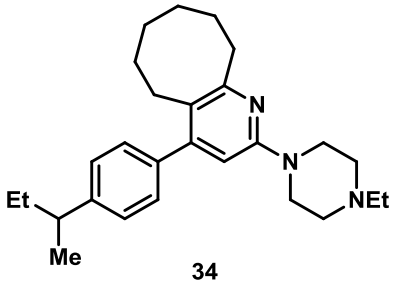

34

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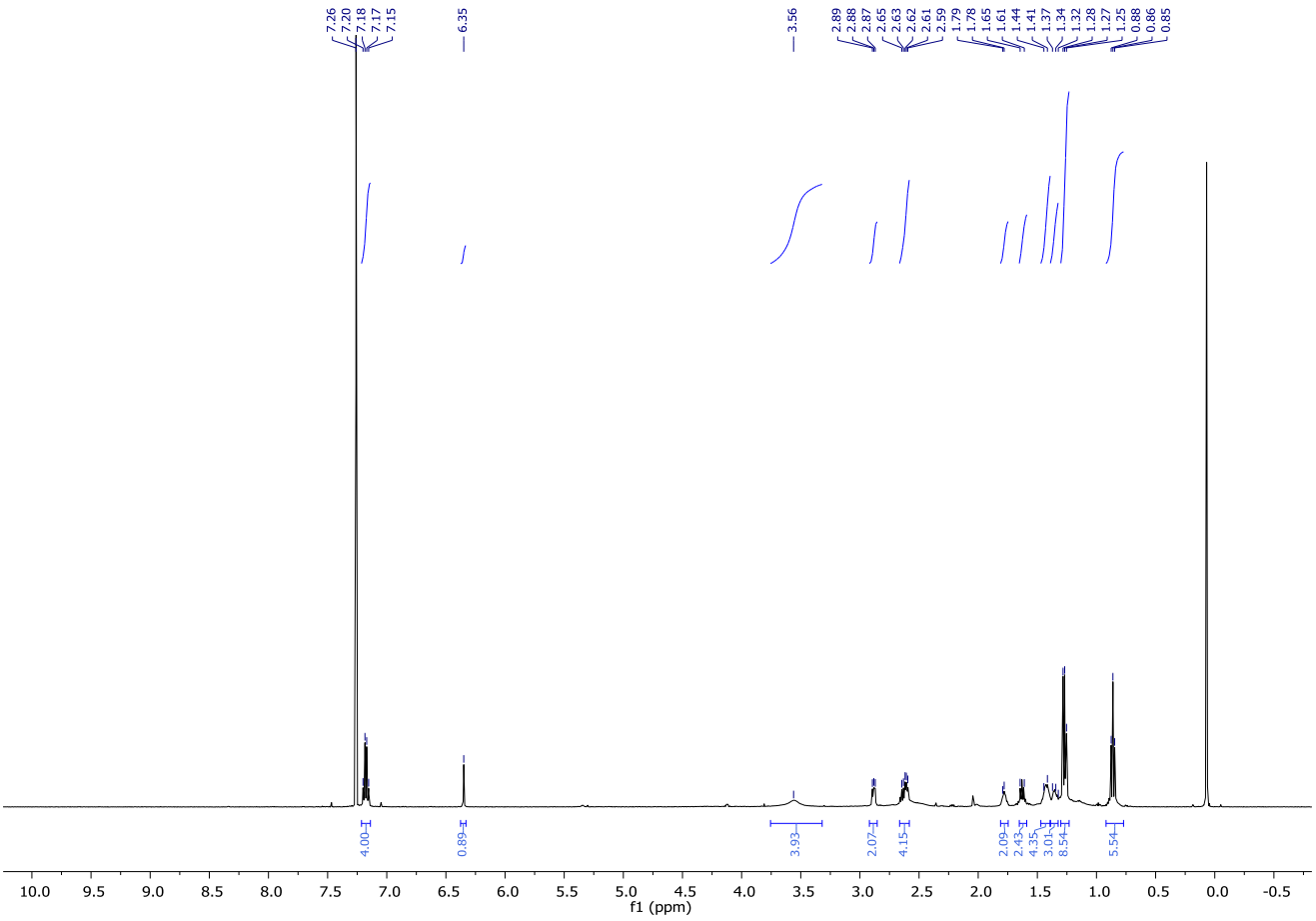

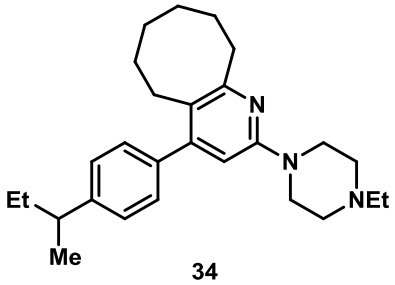

34

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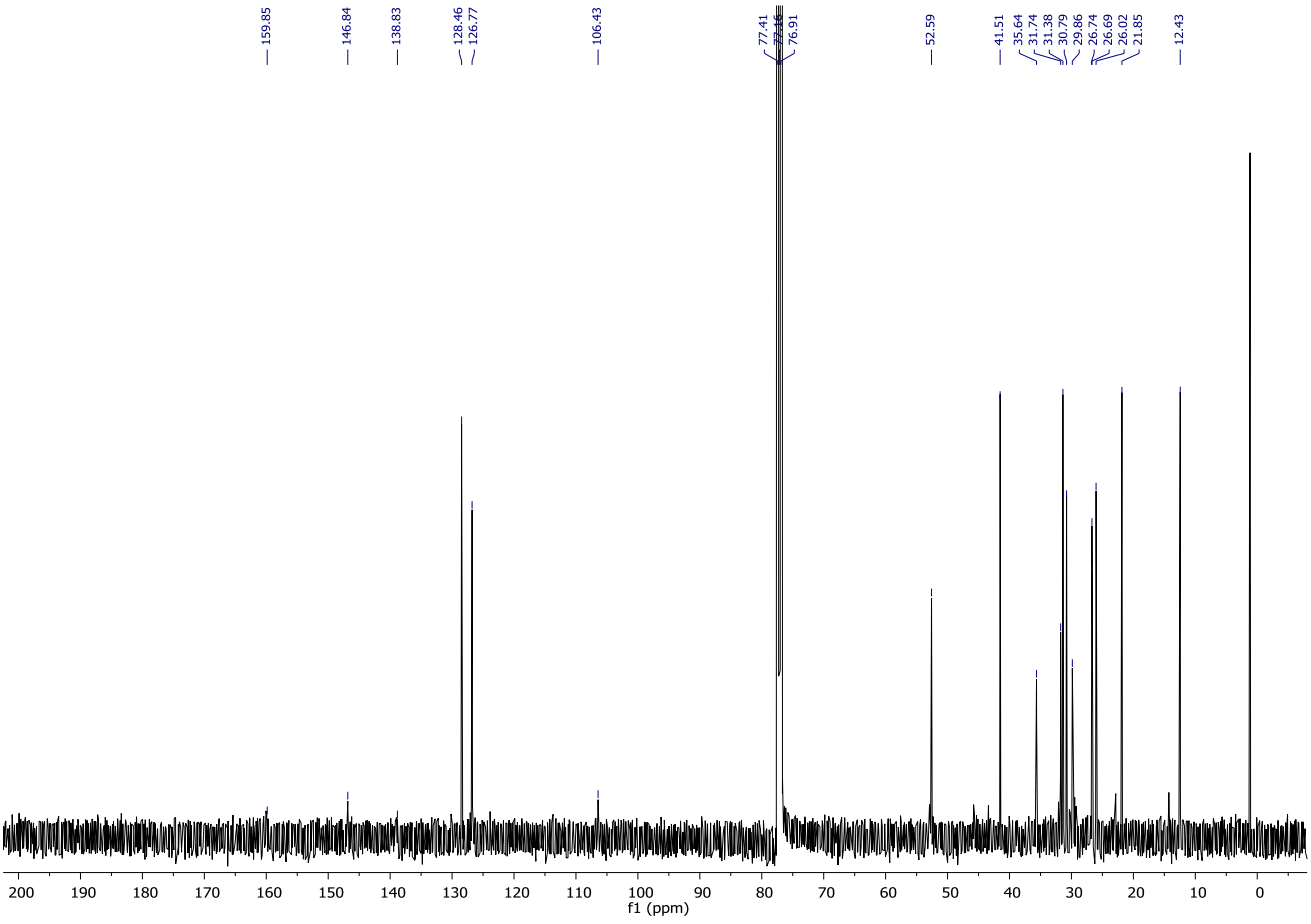
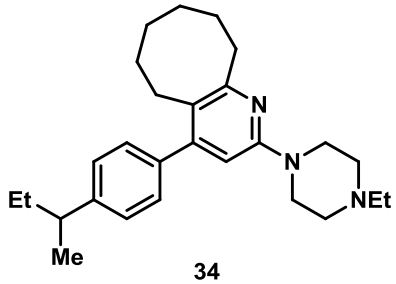
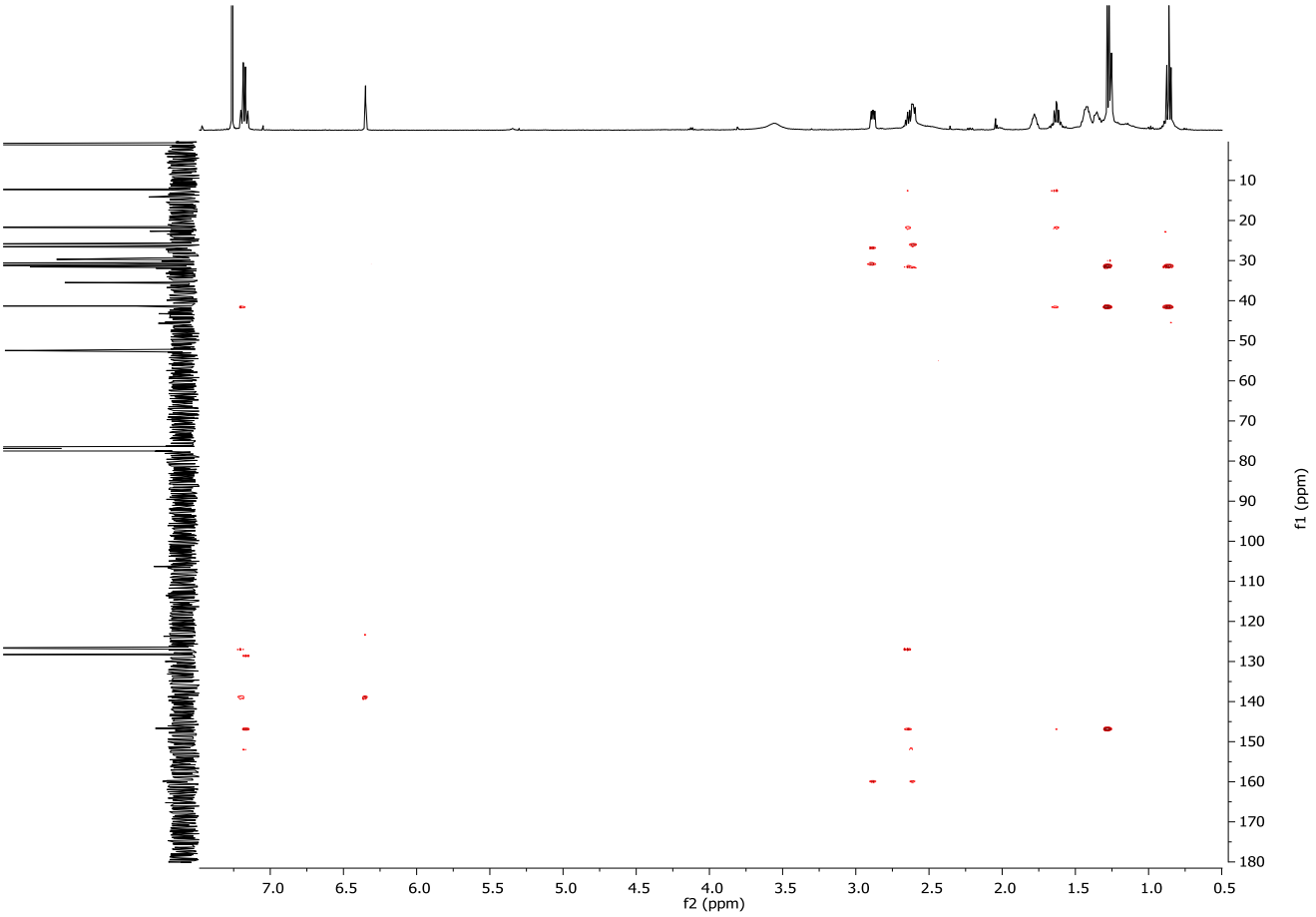


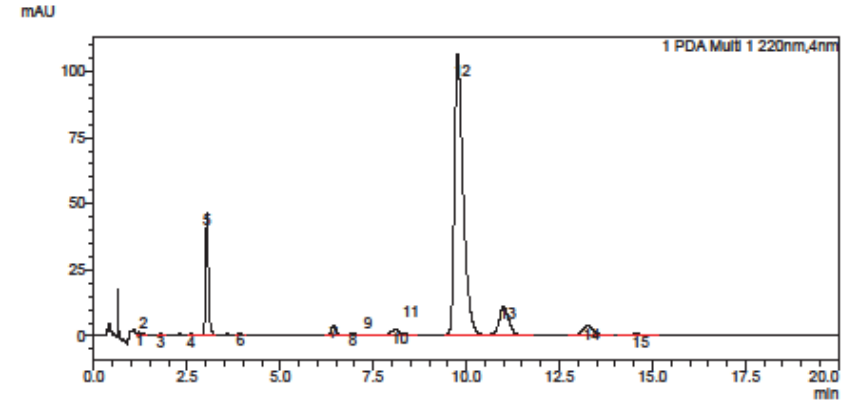


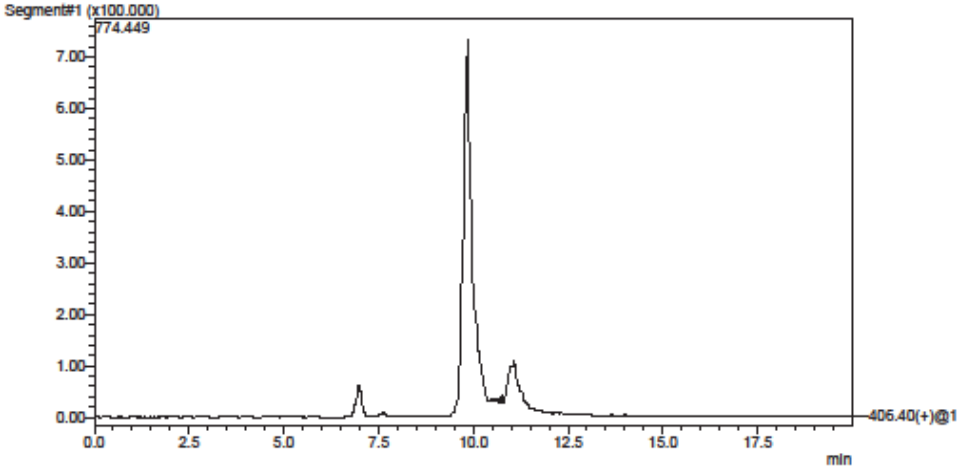
34

HMBC Spectra



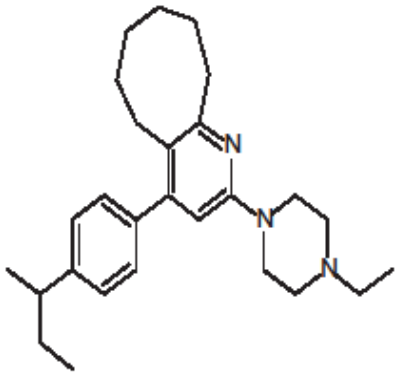
Analytical HPLC Data for 34





PDA Ch1 220nm

Peak#	Ret. Time	Area%	
1	1.22	0.11	
2	1.33	0.06	
3	1.78	0.12	
4	2.61	0.23	
5	3.03	9.96	starting material
6	3.93	0.29	
7	6.43	1.76	
8	6.94	0.64	
9	7.36	0.48	
10	8.10	1.80	
11	8.39	0.28	
12	9.77	72.02	product
13	11.00	8.53	isomer
14	13.25	3.16	
15	14.57	0.57	
Total		100.00	



M = 405

m/z 406: M + H

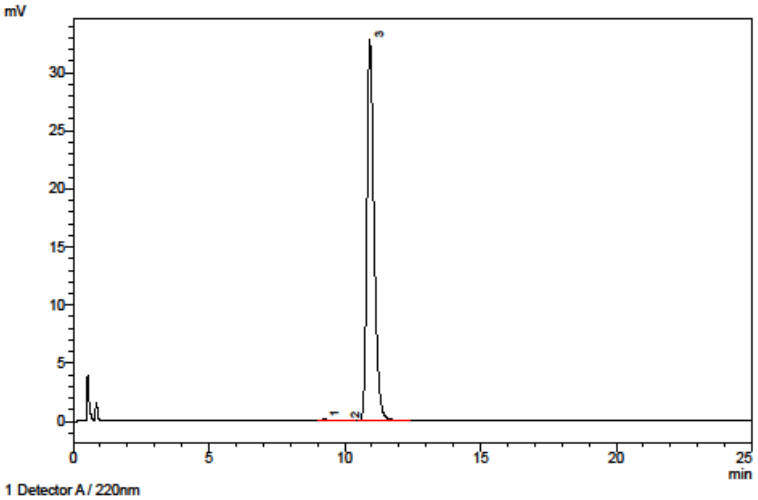
Preparative HPLC Data for 34

Gerät : ANA01

Operator : Br
Sample Name : OMN-OA-135-10
Vial # : 63
Injection Volume : 10 uL
Data File Name : OMN-OA-135-10-002.lcd
Method File Name : ONM-OA-135-01.lcm

Data Acquired: 26.01.2018 15:08:33

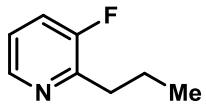
10 µl OMN-OA-135-10 komplette Probe
150 mm YMC-Pack Triart C18, 5 µm, 4.6 mm
Acetonitril/20 mmol Ammoniumhydrogencarbonat pH9 = 80:20
1.0 mL/min, 10.5 MPa MPa, 308 K
UV, 220 nm, Semimicro



1 Detector A / 220nm

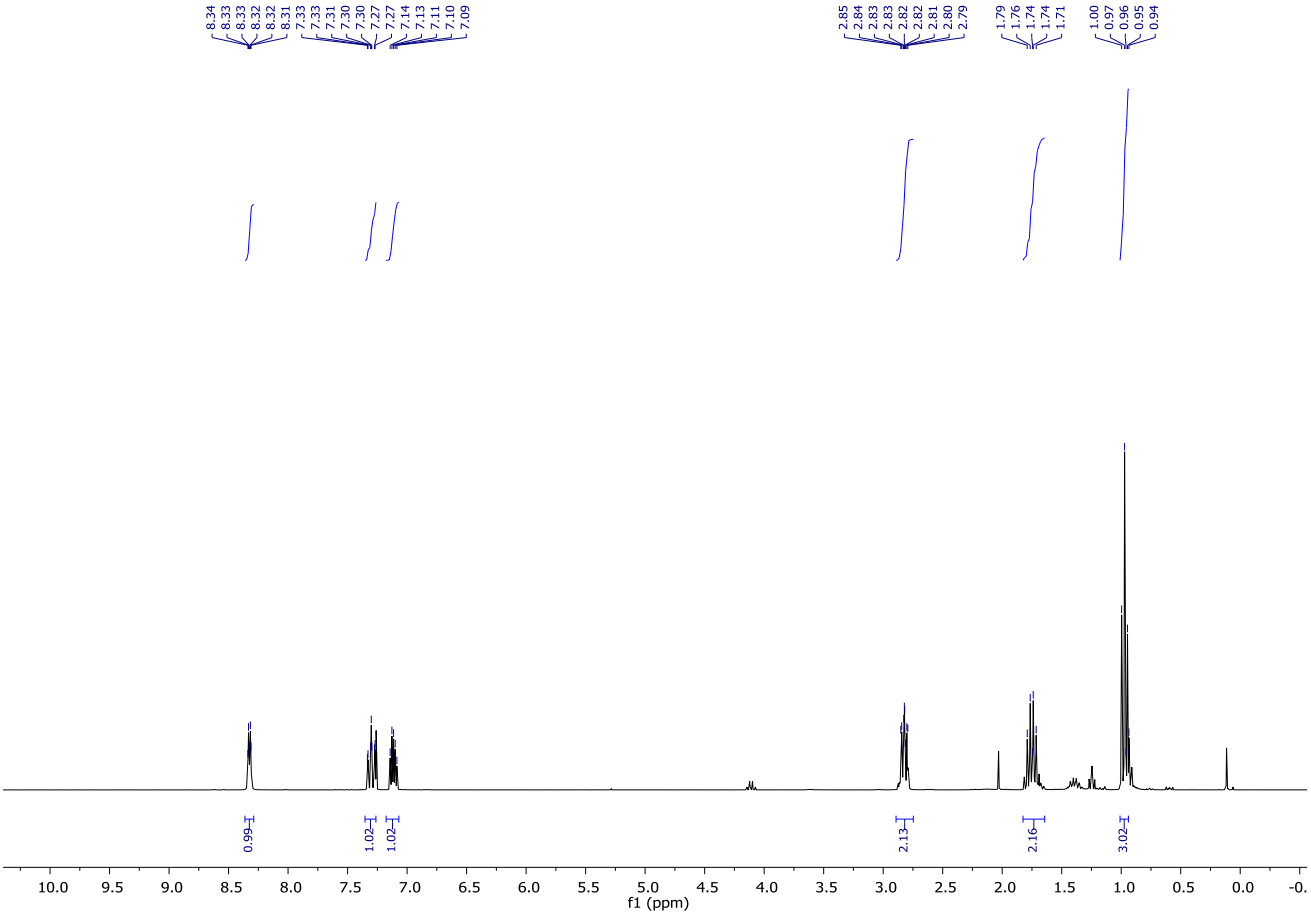
Detector A 220nm

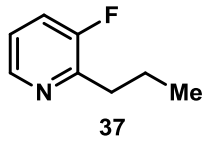
Peak #	Ret. Time	Area %
1	9,27	0,36
2	10,05	0,07
3	10,93	99,56
Total		100,00



37

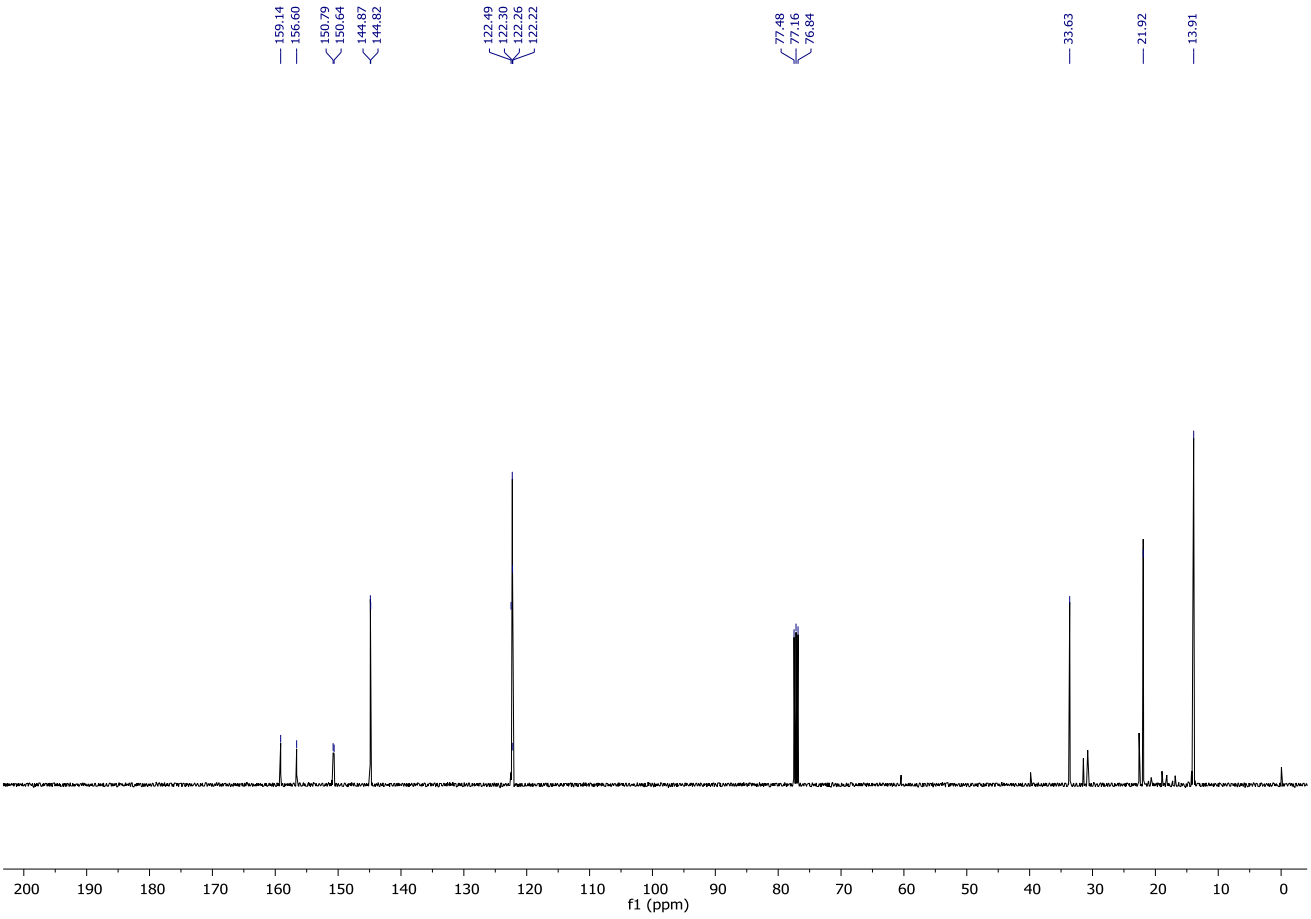
^{1}H Spectra

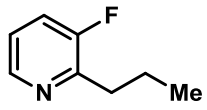




37

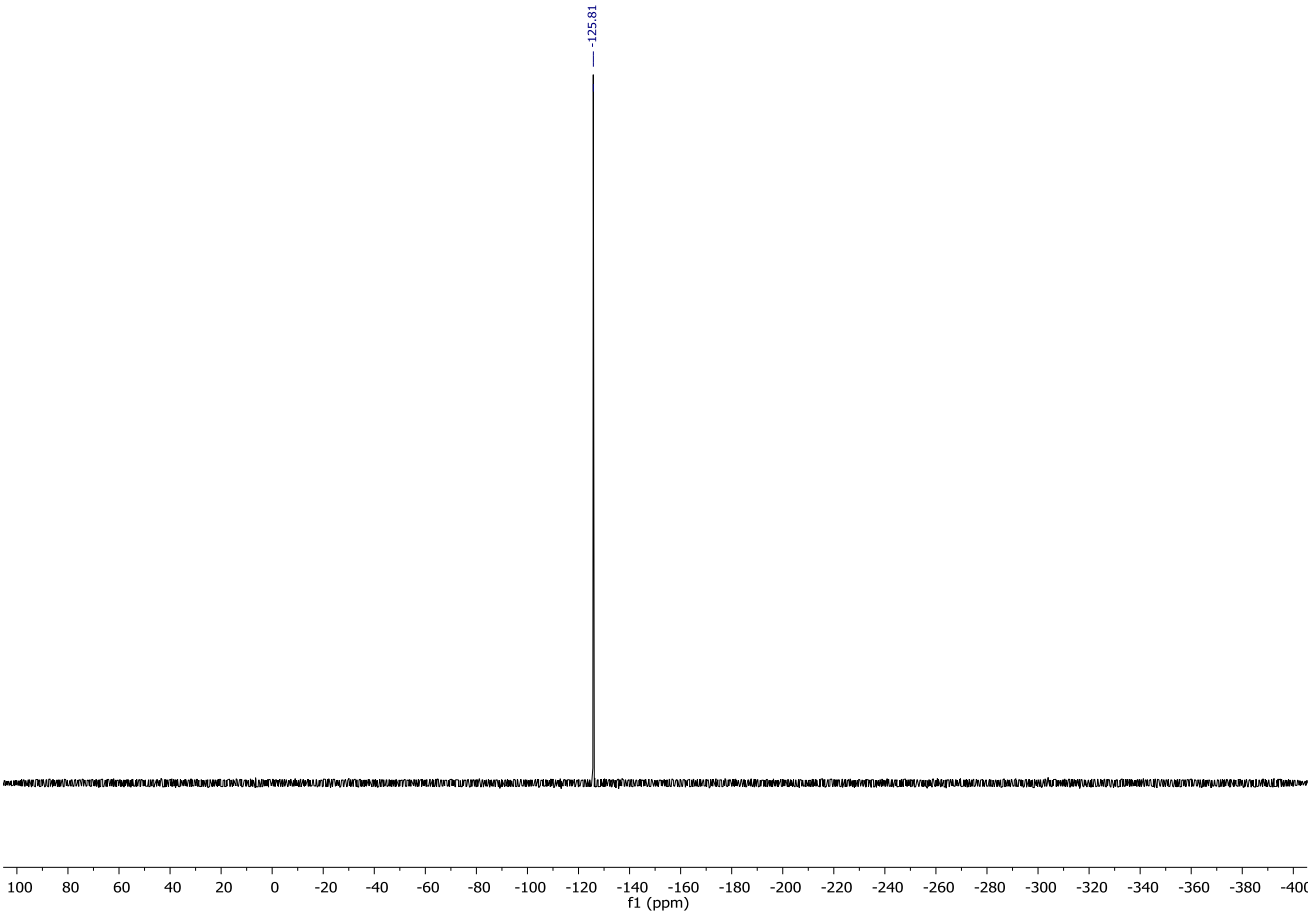
^{13}C Spectra

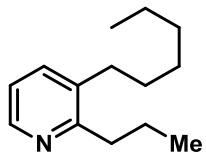




37

^{19}F Spectra





38

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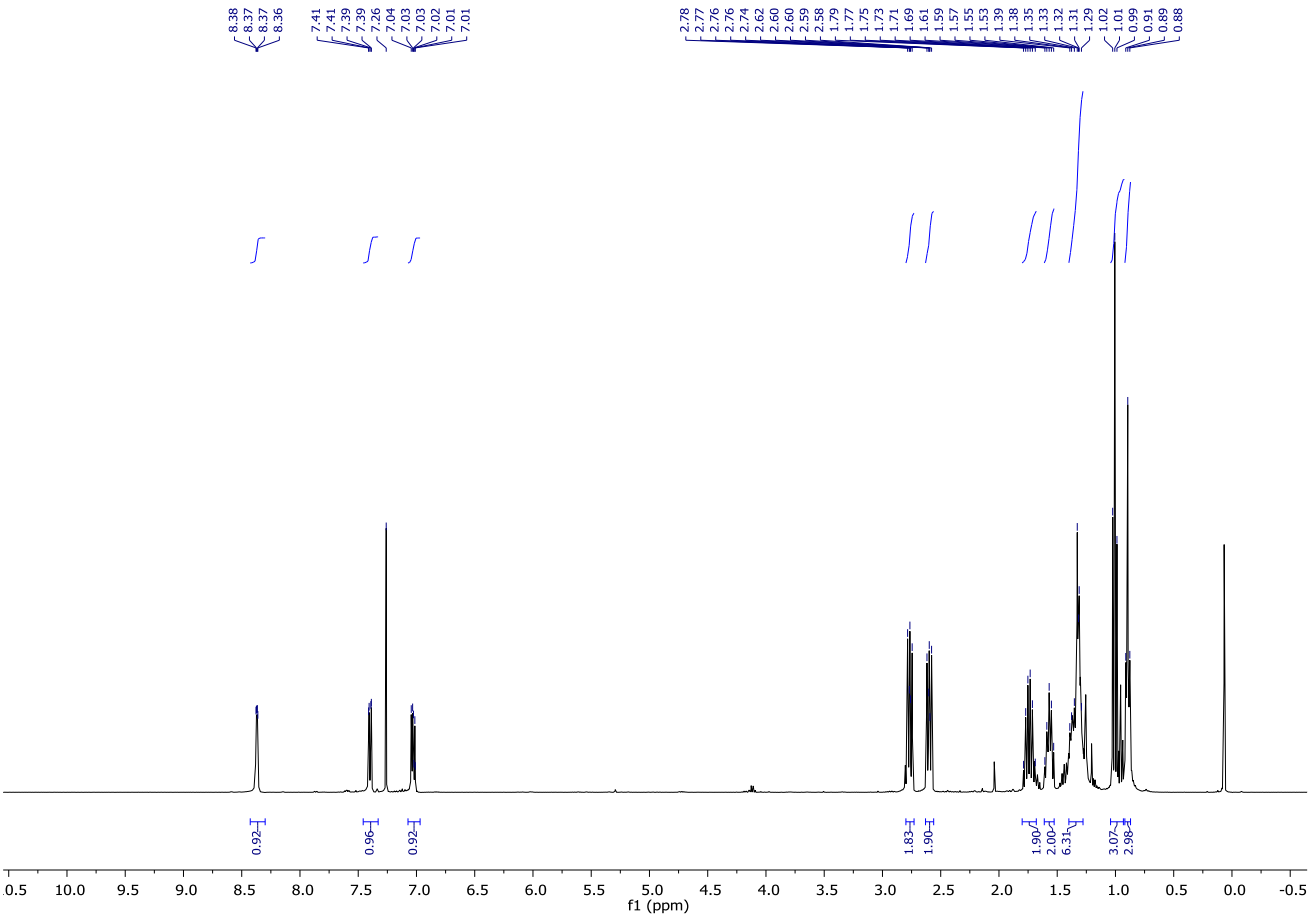

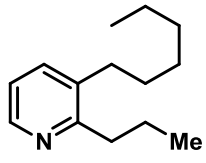

38

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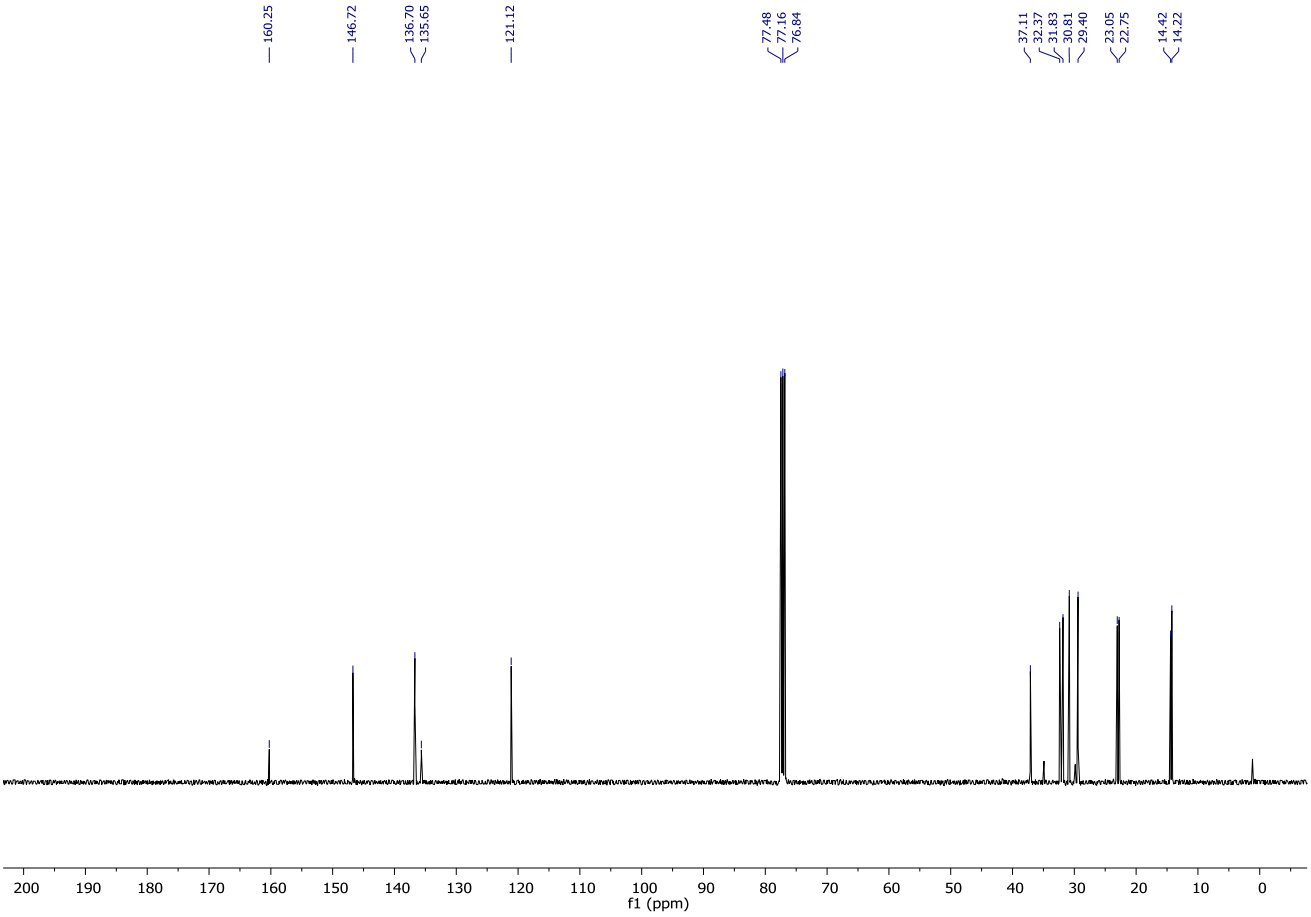

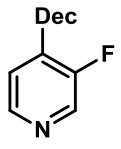

40

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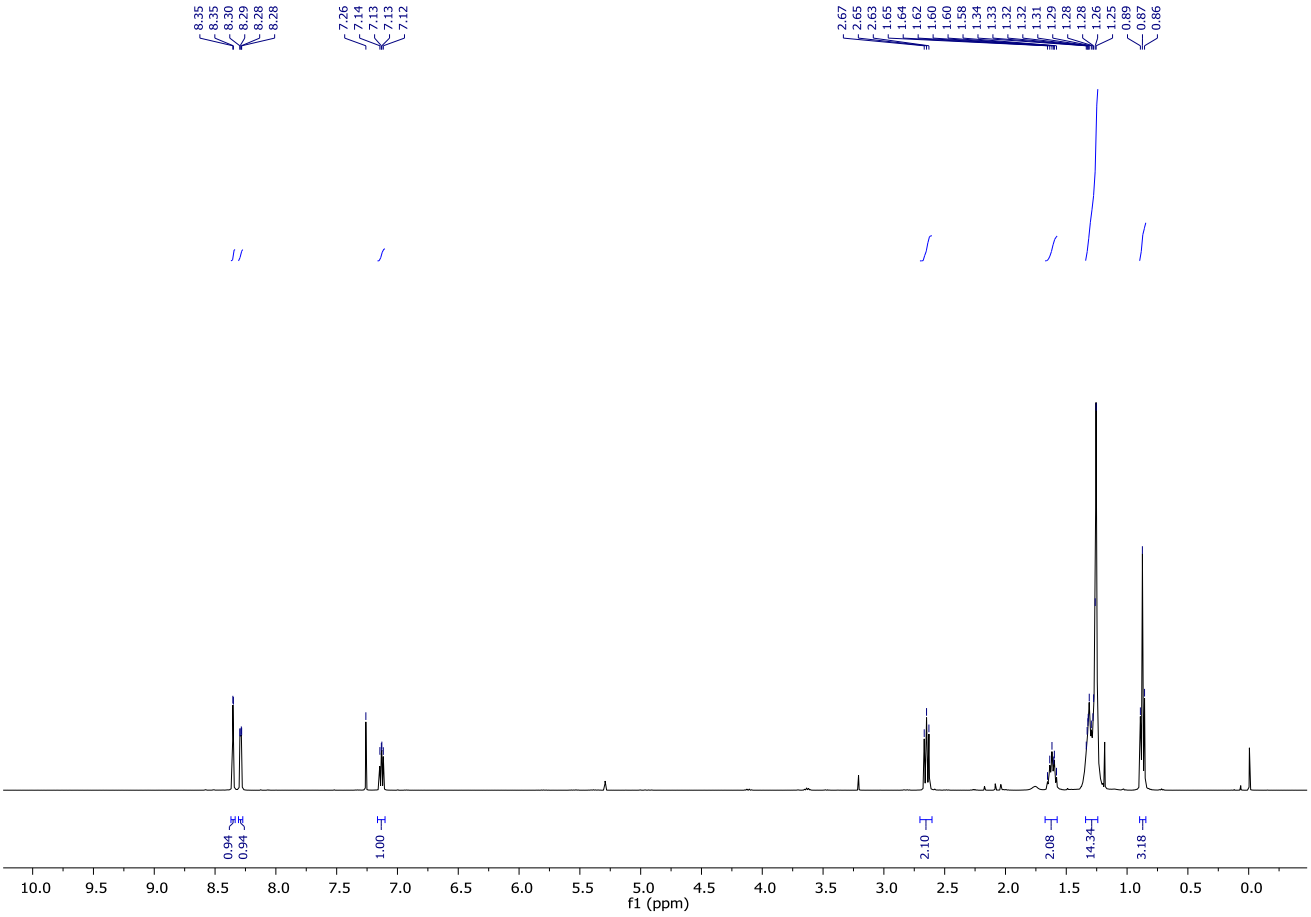

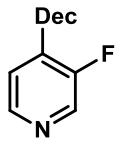

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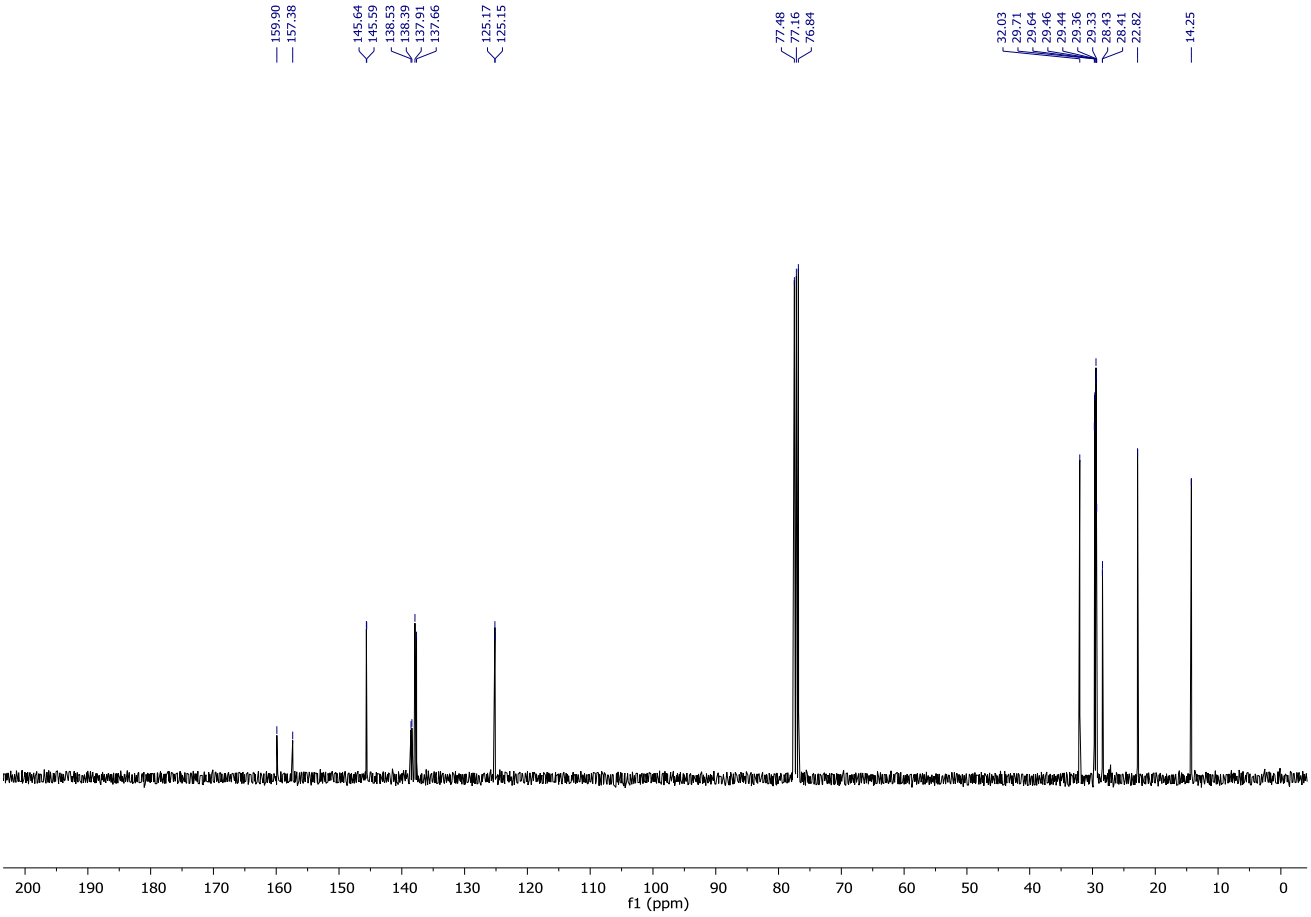
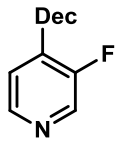
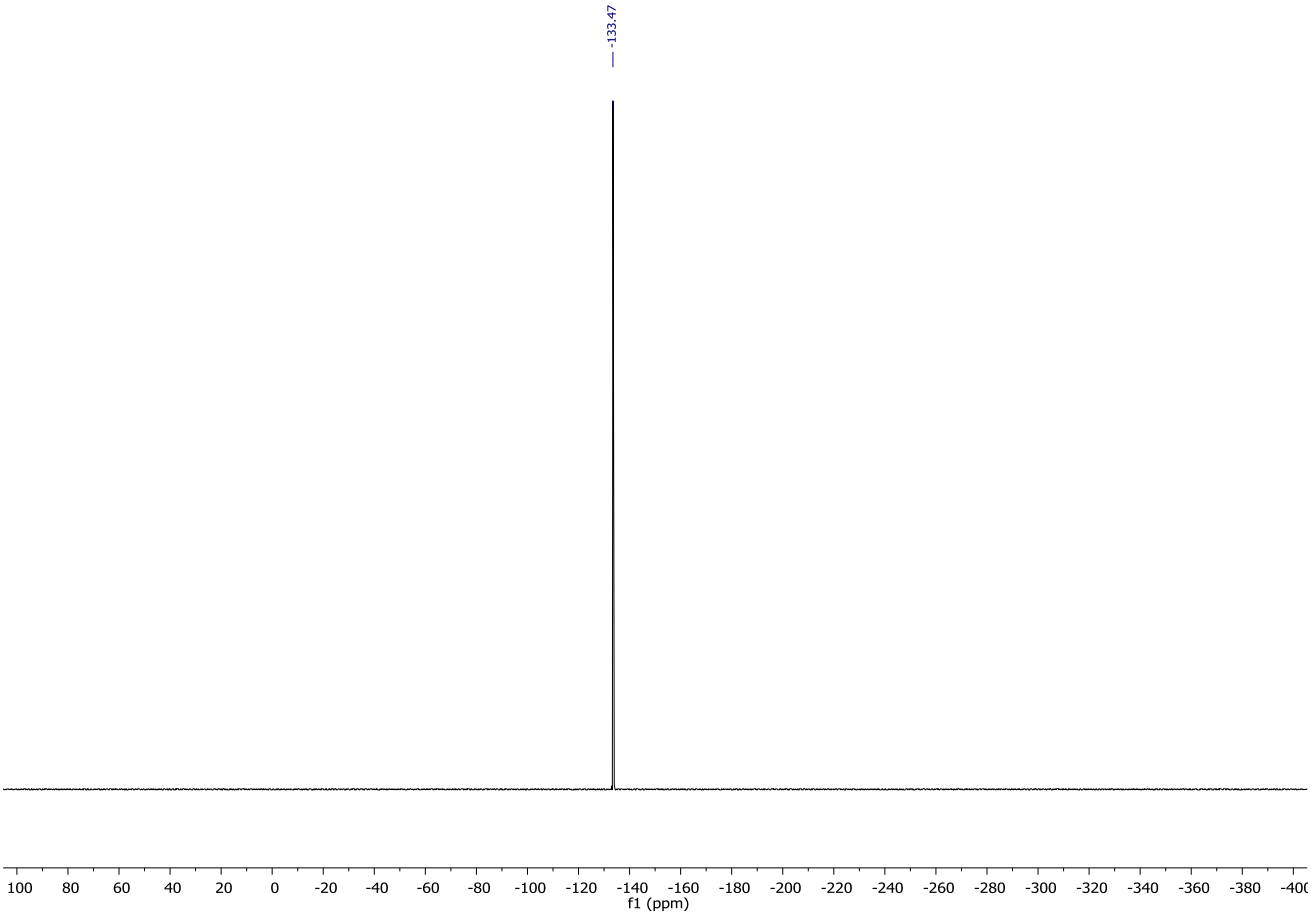
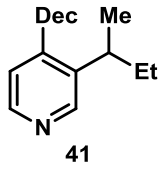




40

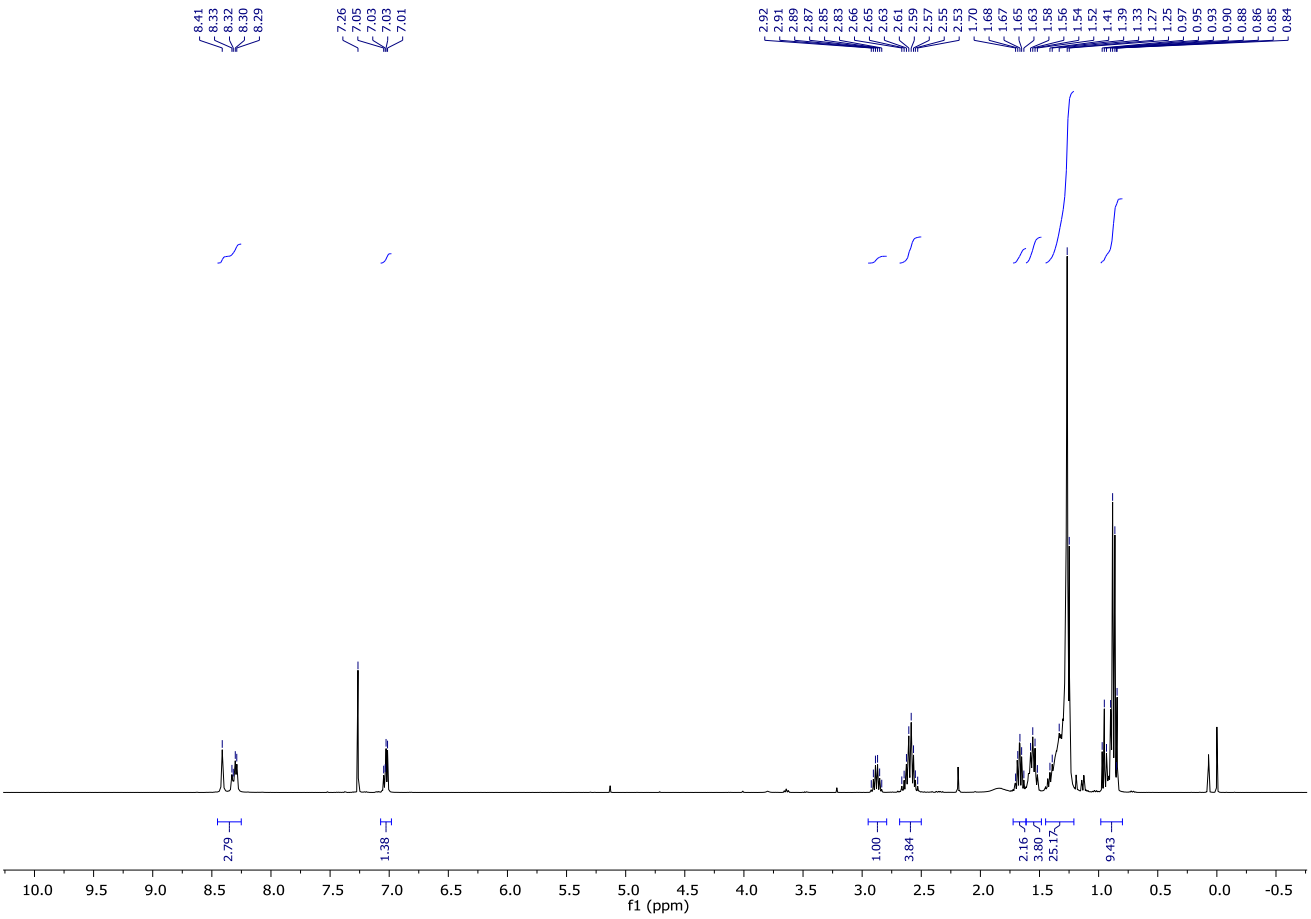
^{19}F Spectra

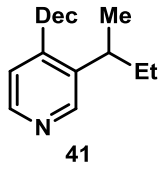




41

^{1}H Spectra





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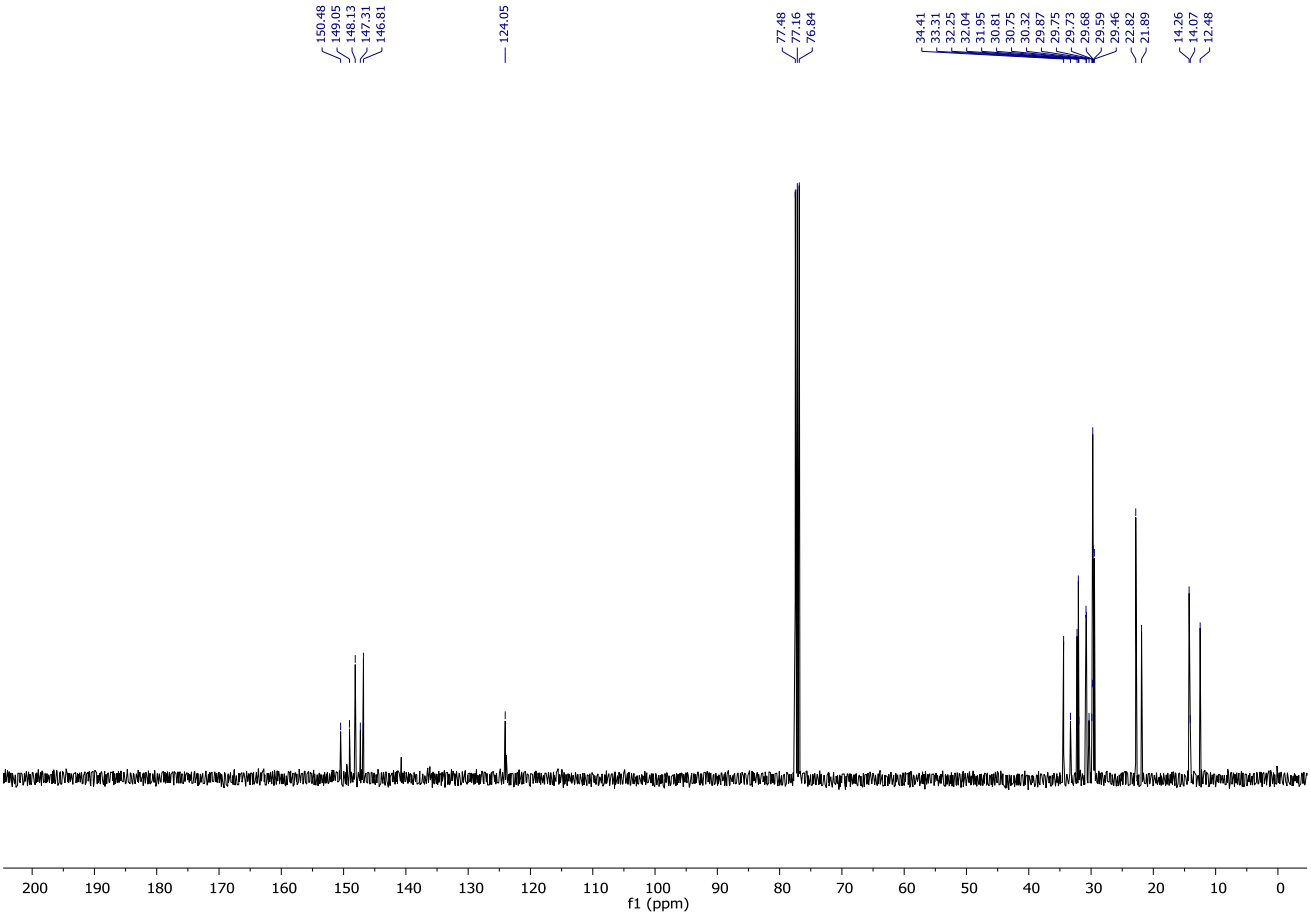
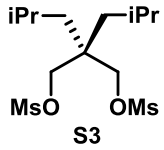
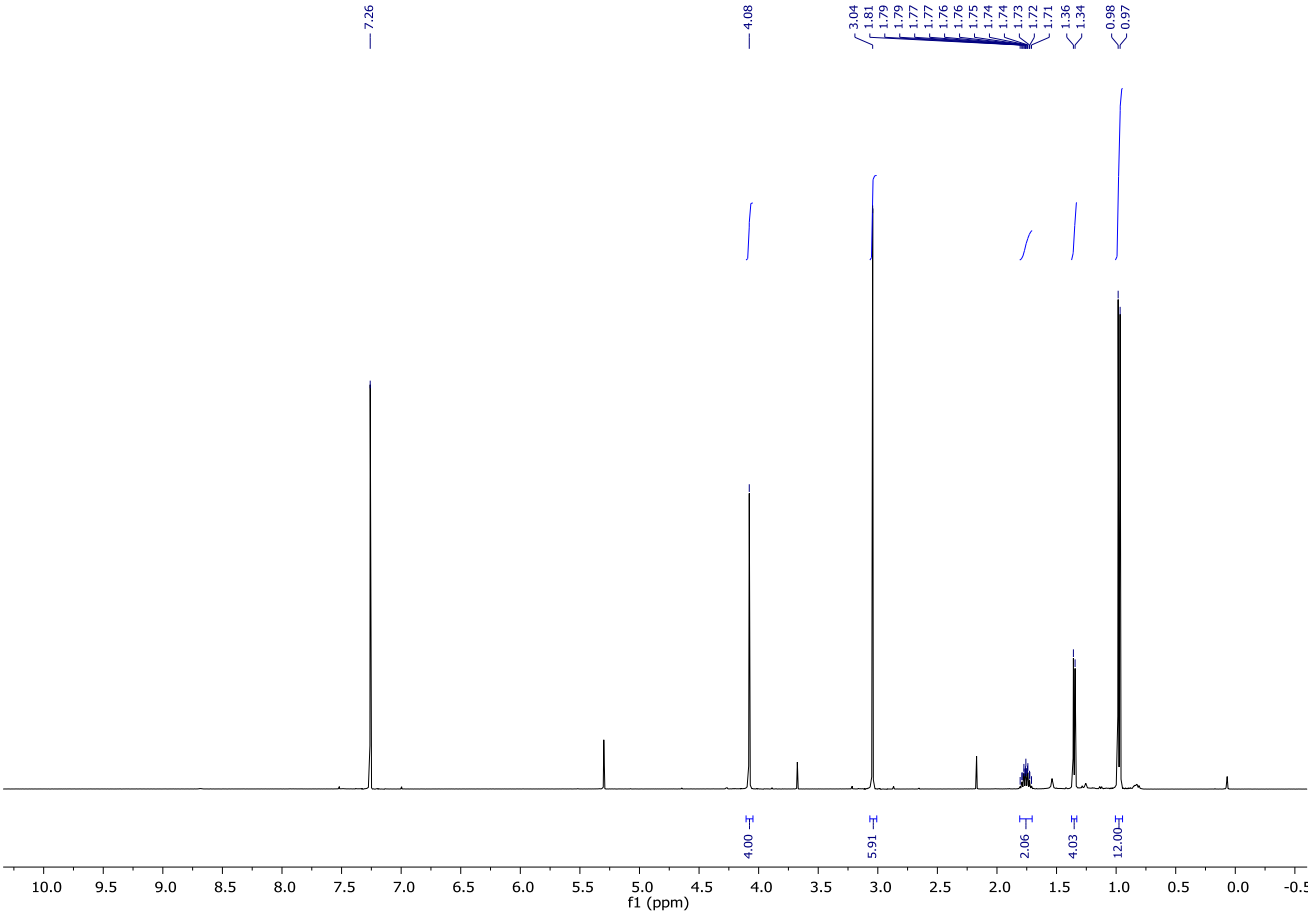
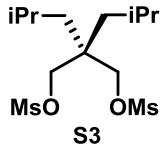




S3

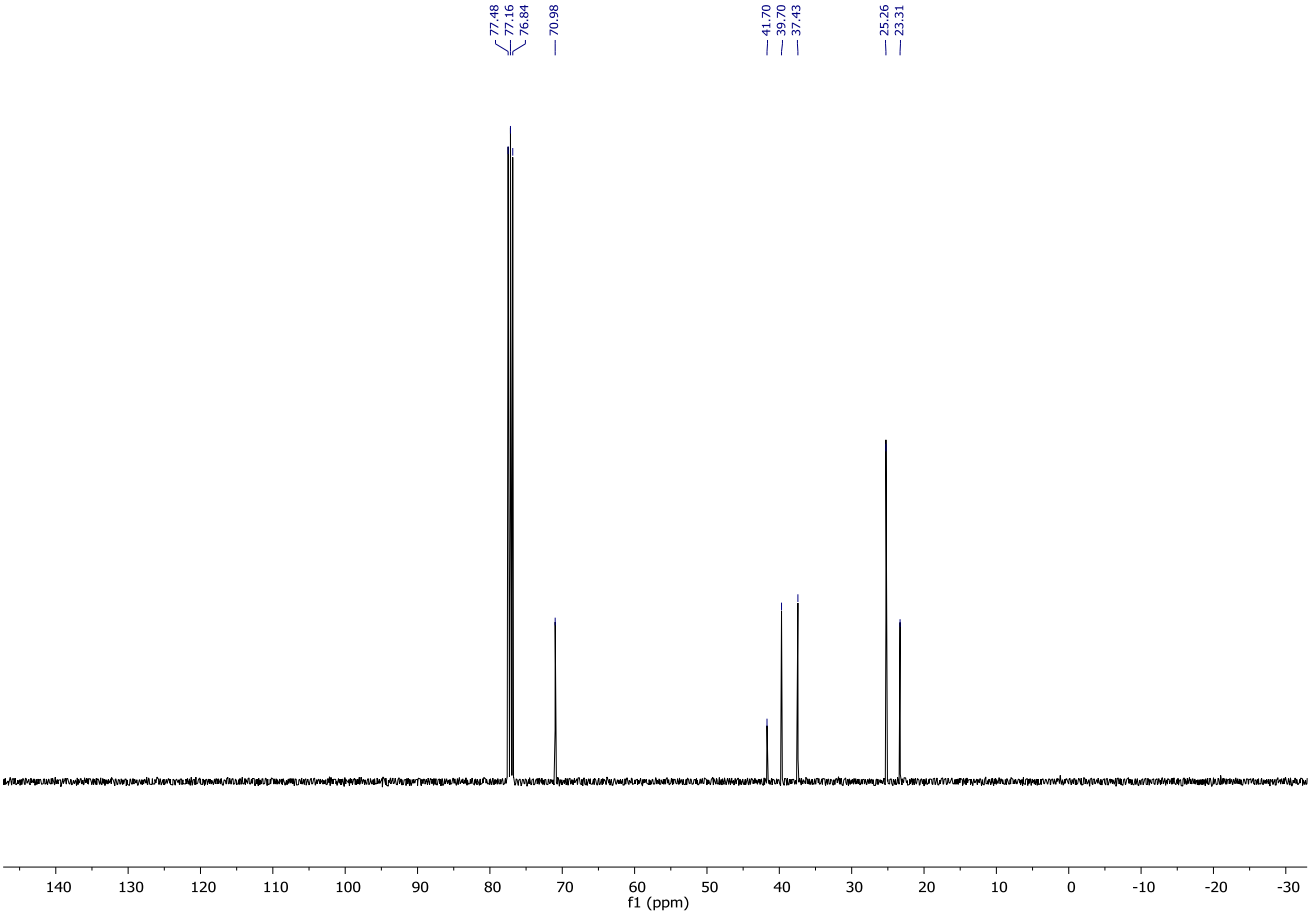
^{1}H Spectra

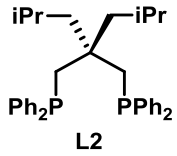




S3

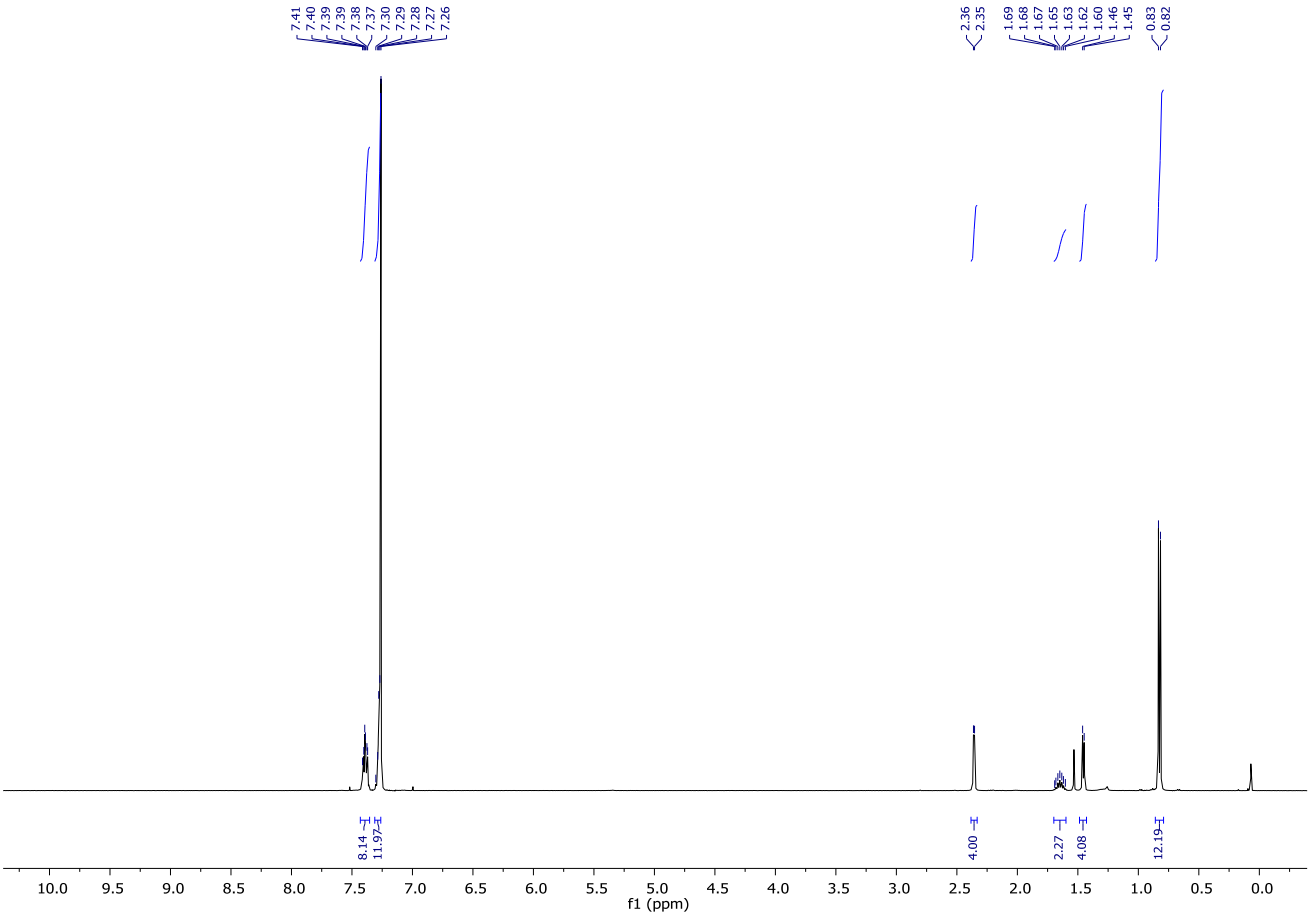
^{13}C Spectra

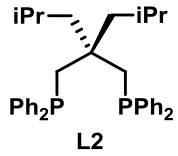




L2

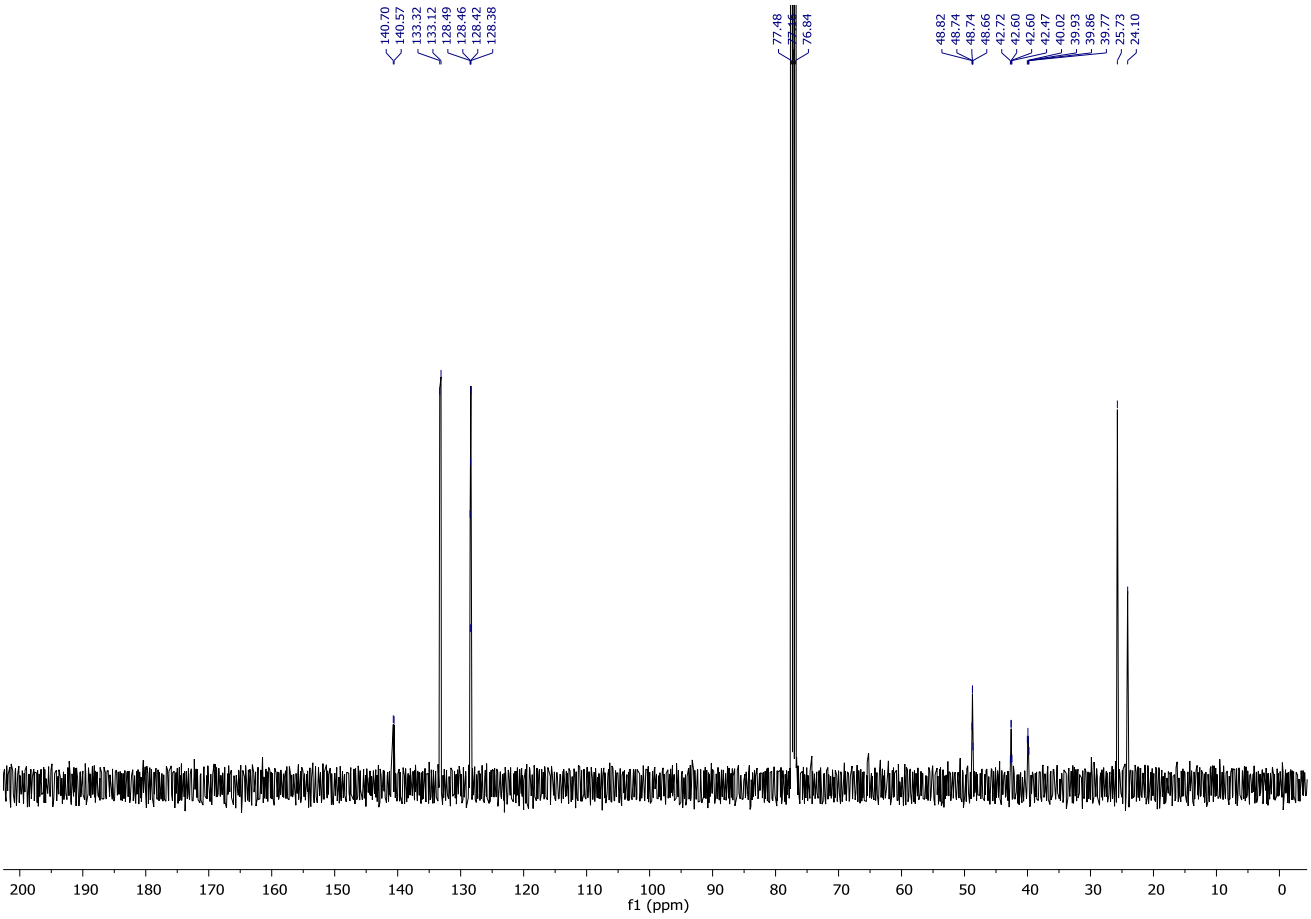
^{1}H Spectra

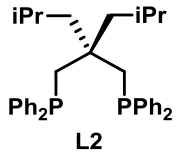




L2

^{13}C Spectra





L2

^{31}P Spectra