Supporting Information

Direct Conversion of Esters to Imines/Enamines and Applications to Polyester Waste Upcycling

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I. Materials and Methods

General procedural information. Reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise noted. Anhydrous toluene (PhMe) and anhydrous tetrahydrofuran (THF) were purchased from Fisher Chemical, stored in Apache Stainless solvent kegs, and dried by passage under argon pressure through columns packed with alumina and R3-15 (PhMe) or alumina (THF). Liquids and solutions were transferred via syringe. Bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) was purchased from Sigma Aldrich and stored in a desiccator. Schwartz's Reagent (Cp_2ZrHCl) was purchased from Strem Chemicals and stored in a nitrogen-atmosphere glovebox. Diethoxy(methyl)silane (DEMS) was purchased from TCI Chemicals and stored at 0 °C. Polymethylhydrosiloxane (PMHS) was purchased from Sigma Aldrich and stored at 0 °C. *n*-Butylamine was purchased from Oakwood Chemicals and distilled prior to use. Piperidine was purchased from Sigma Aldrich. All other commercially available materials were used as received. Medium pressure chromatography purifications were conducted with the assistance of a Teledyne NextGen 300 Chromatography System unless otherwise noted. Reusable cartridges (4g – 24g) were purchased from Biotage and disposable GOLD cartridges (4g – 24g) were purchased from Teledyne Isco. Manual packing of reusable cartridges was performed using P60 SiliaFlash silica gel (40-63 μm, 230-400 mesh). Activated neutral aluminum oxide (Brockmann Grade II, 58Å) was purchased from Thermo Fisher Scientific. Organic solutions were concentrated with the aid of a Buchi rotary evaporator equipped with a Buchi vacuum regulator. Isolated yields are reported for products of ≥96% purity, unless otherwise noted.

General analytical information. All reactions were monitored by thin-layer chromatography using Silicycle SiliaPlate pre-coated plates (0.25 mm) and visualized with UV light and/or $KMnO_4$ stain. All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD 600MHz, Bruker Avance III HD 400MHz, or Agilent VNMRS 500MHz instrument. ^1H and ^{13}C spectra were recorded in $CDCl_3$ or toluene-*d8* and chemical shifts are reported in δ units, parts per million (ppm), relative to residual chloroform or toluene in the deuterated solvent (for $CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR; for toluene-*d8*: 2.09 ppm for ^1H NMR). Coupling constants (*J*) are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Bruker Platinum-ATR IR spectrometer using a diamond window and reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectrometry (HRMS) data was obtained using electro-spray ionization (ESI) using a Thermo LTQ Orbitrap Q-Exactive instrument. Low-resolution mass spectrometry (LRMS) data was collected using an Agilent 8890 gas chromatography (GC) system equipped with a 5977B series inert mass selective detector. Analytical high performance liquid chromatography (HPLC) analysis was performed using an Agilent 1260 Infinity II instrument equipped with commercial columns obtained from Chiralcel (Daicel Corporation) with the following specifications: OD-H (4.6mm I.D. x 250 mm L, particle size 5 μm, and part no. 14325), and OJ-H (4.6mm I.D. x 250 mm L, particle size 5 μm, and part no. 17325).

II. General Procedures

General Procedure A: Reduction of Aryl and Alkenyl Esters

Cp_2ZrCl_2 (14.6 mg, 5.0 mol %) and solid starting materials (1.0 mmol) were weighed into a flame-dried 20 x 125 mm reaction tube equipped with a magnetic stir bar. The reaction tube was capped with an open top screw cap equipped with a Teflon-lined silicon septum and sealed with electrical tape. The reaction tube was then evacuated and backfilled with nitrogen (this process was repeated to a total of three times). The solids were dissolved in 2.5 mL of anhydrous PhMe (0.4 M). Liquid substrates were injected at this point. DEMS (480.6 µL, 3.0 equiv) was injected into the reaction mixture, followed by the injection of distilled *n*-butylamine[a] (168.0 µL, 1.7 equiv) using a Hamilton gastight glass microsyringe. The septum of the reaction tube was sealed with wax and the reaction solution was stirred at 400 rpm at 80 °C for 19 – 48 h. To obtain aldehyde products, the reaction mixture was then quenched with 5 mL of 1 M HCl and stirred at 80 °C for approx. 1 hour. The solution was diluted with ca. 5 mL of Et_2O and ca. 5 mL H_2O. The aqueous layer was washed three times with ca. 5 mL Et_2O. The combined organic washes were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator.

[a] *n*-Butylamine was stored at 0 °C and under an atmosphere of N_2 after distillation. The amine was distilled approx. every two weeks, or sooner if the solution was no longer colorless in appearance.

General Procedure B: Reduction of Aliphatic (Enamine-Forming) Esters

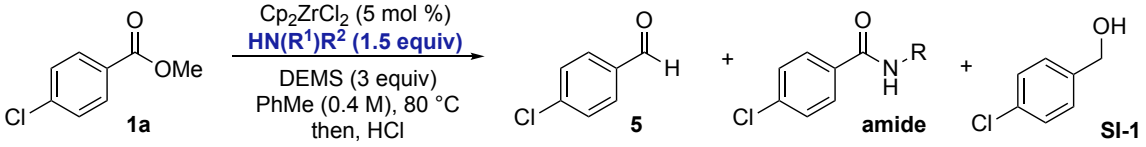
Cp_2ZrCl_2 (29.2 mg, 10.0 mol %) and solid starting materials (1.0 mmol) were weighed into a flame dried 20 x 125 mm reaction tube equipped with a magnetic stir bar. The reaction tube was capped with an open top screw cap equipped with a Teflon-lined silicon septum and sealed with electrical tape. The reaction tube was then evacuated and backfilled with nitrogen (this process was repeated to a total of three times). The solids were dissolved in 2.5 mL of anhydrous PhMe (0.4 M). Piperidine (148.1 µL, 1.5 equiv) was injected into the reaction mixture. Liquid starting materials were injected at this point, followed by the injection of DEMS (480.6 µL, 3.0 equiv) using a Hamilton gastight glass microsyringe. The septum of the reaction tube was sealed with wax and the reaction solution was stirred at 700 rpm at 80 °C for 17 – 24 h. To obtain aldehyde products, the reaction mixture was then quenched with 5 mL of 1 M HCl and stirred at 80 °C for approx. 1 hour. The solution was diluted with ca. 5 mL of Et_2O and ca. 5 mL H_2O. The aqueous layer was washed three times with ca. 5 mL Et_2O. The combined organic washes were dried over Na_2SO_4, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator.

III. Additional Optimization Data

General Procedure for Reaction Optimization (Using an Aryl Ester):

Cp_2ZrCl_2 (2.9 mg, 5.0 mol %) and methyl 4-chlorobenzoate (34.1 mg, 0.2 mmol) were weighed into a flame-dried 2-dram vial equipped with a magnetic stir bar. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum and sealed with electrical tape. The vial was then evacuated and backfilled with nitrogen (this process was repeated to a total of three times). The solids were dissolved in 0.5 mL of anhydrous PhMe (0.4 M). DEMS (95.9 µL, 3.0 equiv) was injected into the reaction mixture, followed by the injection of *n*-butylamine (33.7 µL, 1.7 equiv) using a Hamilton gastight glass microsyringe. The septum of the reaction tube was sealed with wax and the reaction solution was stirred at 700 rpm at 80 °C for 16 – 24 h. The reaction solution was quenched with ca. 1 mL of 1 M HCl and left to stir at 700 rpm at 80 °C for approx. 1 h. The solution was diluted with ca. 2 mL of CH_2Cl_2 and ca. 2 mL H_2O. The aqueous layer was washed three times with ca. 3 mL CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. A ^1H NMR yield was obtained using mesitylene (13.9 µL, 0.1 mmol) as an internal standard.

Table SI-1: Amine Screen for the Semi-Reduction of Methyl 4-Chlorobenzoate



Amine (equiv)	% Conv	% **5**	% **amide**	% **SI-1**
i-butylamine	96	77	7	<5
allylamine	87	45	19+3[a]	ND
n-butylamine	87	69	ND	<5
piperidine	87	46	ND	ND

[a] Proposed to have formed based on ^1H NMR analysis:

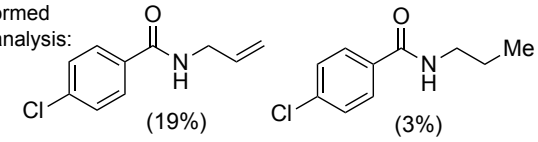
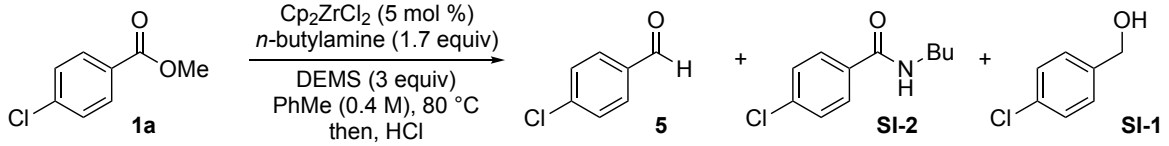
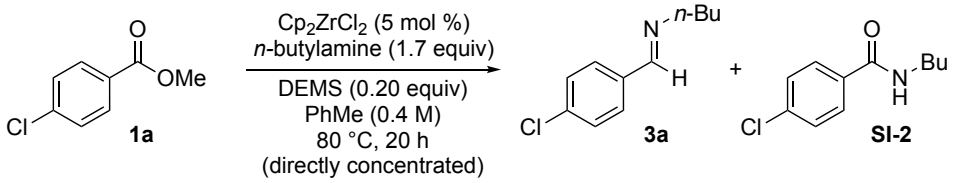


Table SI-2: Control Experiments for the Semi-Reduction of Methyl 4-Chlorobenzonate



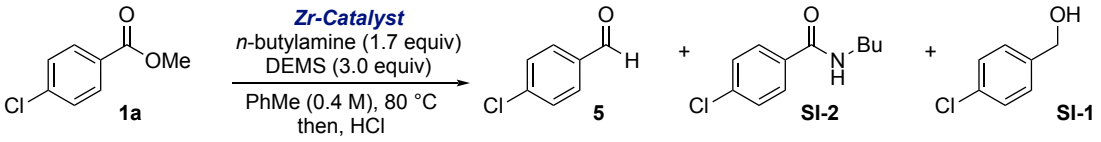
Temp (° C)	Catalyst (mol %)	Amine (equiv)	Silane (equiv)	% Conv	% **5**	% **SI-2**	% **SI-1**
80	—	*n*-butylamine (1.7)	DEMS (3)	0	ND	ND	ND
80	Cp_2ZrCl_2 (5)	*n*-butylamine (1.7)	—	24	ND	16	ND
80	$(Cp_2ZrCl)_2O$ (5)	*n*-butylamine (1.7)	—	18	ND	16	ND
80	Cp_2ZrHCl (5)	*n*-butylamine (1.7)	—	14	ND	14	ND
80	Cp_2ZrHCl (5)	—	DEMS (3)	100	ND	ND	98
80	Cp_2ZrCl_2 (2.5)	*n*-butylamine (1.7)	DEMS (3)	81	74	<5	<5
65	Cp_2ZrCl_2 (5)	*n*-butylamine (1.7)	DEMS (3)	75	62	<5	<5

Table SI-3: Testing Amidation in the Presence of 20 mol % DEMS



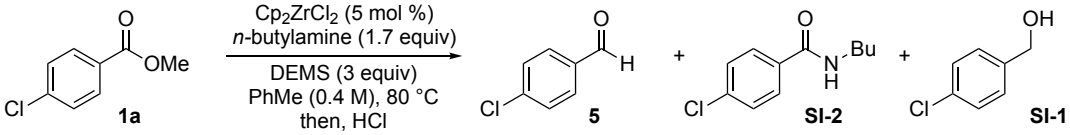
Temp (° C)	Catalyst (mol %)	Amine (equiv)	Silane (equiv)	% Conv	% **3a**	% **SI-2**
80	Cp_2ZrCl_2 (5)	*n*-butylamine (1.7)	DEMS (0.20)	49	4	18
80	$(Cp_2ZrCl)_2O$ (5)	*n*-butylamine (1.7)	DEMS (0.20)	36	5	32
80	Cp_2ZrHCl (5)	*n*-butylamine (1.7)	DEMS (0.20)	23	5	22

Table SI-4: Metallocene Screen for the Semi-Reduction of Methyl 4-Chlorobenzoate



Catalyst (mol %)	% Conv	% **5**	% **SI-2**	% **SI-1**
Cp_2ZrH_2 (5)	8	ND	ND	ND
$(Cp_2ZrCl)_2O$ (5)	100	87	ND	ND
Cp_2TiCl_2 (5)	81	27	52	ND
Cp_2HfCl_2 (5)	24	<5	12	ND
$Cp^*_2ZrCl_2$ (5)	52	ND	35	ND
$(n\text{-}BuC_5H_4)_2ZrCl_2$ (5)	100	52	46	ND
Cp_2ZrCl_2 (5) / NaOMe (5)	92	71	5	2
$Cp_2Zr(OTf)_2$	32	ND	12	ND

Table SI-5: Extended Optimization for Table 1

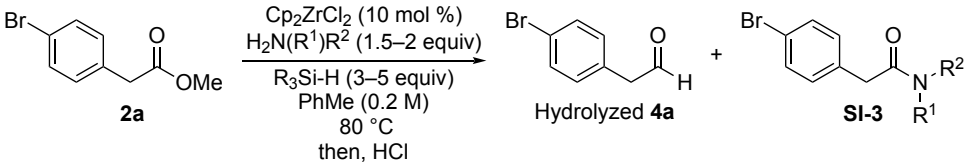


Temp (° C)	Catalyst (mol %)	Amine (equiv)	Silane (equiv)	% Conv	% **5**	% **SI-2**	% **SI-1**
80	Cp_2ZrCl_2 (5)	*n*-butylamine (1.5)	PMHS (5)	23	N.D.	19	N.D.
80	Cp_2ZrCl_2 (5)	*n*-butylamine (1.5)	DMMS (3)	61	44	<5	<5
80	Cp_2ZrCl_2 (5)	*n*-butylamine (1.5)	DEMS (3)	83	74	<5	<5
80	Cp_2ZrCl_2 (5)	*n*-butylamine (1.5)	DEMS (4)	100	90	<5	<5
80	Cp_2ZrCl_2 (5)	*n*-butylamine (1.7)	DEMS (3)	100	89	5	<5
80	Cp_2ZrHCl (5)	*n*-butylamine (1.7)	DEMS (3)	80	64	<5	<5

General Procedure for Reaction Optimization (Using an Aliphatic Ester):

Cp_2ZrCl_2 (5.8 mg, 10.0 mol %) was weighed into a flame-dried 2-dram vial equipped with a magnetic stir bar. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum and sealed with electrical tape. The vial was then evacuated and backfilled with nitrogen (this process was repeated to a total of three times). The catalyst was dissolved in 1.0 mL of anhydrous PhMe (0.2 M), followed by the injection of piperidine (33.3 µL, 0.34 mmol, 1.7 equiv) using a Hamilton gastight glass microsyringe. Methyl 4-bromophenylacetate (45.8 mg, 0.2 mmol, 1.0 equiv) and DEMS (95.9 µL, 3.0 equiv) were injected into the reaction mixture via microsyringe. The septum of the reaction vial was sealed with wax and the reaction solution was stirred at 700 rpm at 80 °C for 17 – 21 h. The reaction solution was quenched with ca. 1 mL of 1 M HCl and left to stir at 700 rpm at 80 °C for approx. 1 h. The solution was diluted with ca. 2 mL of CH_2Cl_2 and ca. 2 mL H_2O. The aqueous layer was washed three times with ca. 3 mL CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. A ^1H NMR yield was obtained using mesitylene (13.9 µL, 0.1 mmol) as an internal standard.

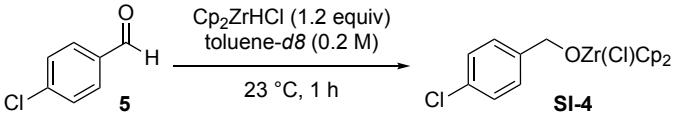
Table SI-6: Extended Optimization for the Semi-Reduction of Methyl 2-(4-Bromophenyl)acetate



Catalyst (mol %)	Amine (equiv)	Silane (equiv)	% Conv	% Hyd-**4a**	% **SI-3**
Cp_2ZrCl_2 (10)	*n*-Butylamine	DEMS (3)	100	12	ND
Cp_2ZrCl_2 (10)	Et_2NH (1.5)	DEMS (3)	58	29	ND
Cp_2ZrCl_2 (10)	Pyrrolidine (1.5)	DEMS (3)	97	6	62
Cp_2ZrCl_2 (10)	Morpholine (1.5)	DEMS (3)	92	50	ND
Cp_2ZrCl_2 (10)	*N*-methylpiperazine (1.5)	DEMS (3)	100	45	ND
Cp_2ZrCl_2 (10)	piperidine (2.0)	DEMS (3)	100	62	ND
Cp_2ZrCl_2 (10)	piperidine (1.7)	DMMS (5)	100	49	ND

IV. Additional Mechanistic Studies and Support

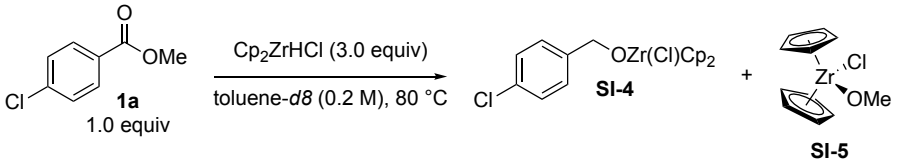
Scheme SI-1: *Preparation of zirconocene* ***SI-4***



4-chlorobenzaldehyde (**5**) (14.1 mg, 0.1 mmol, 1.0 equiv) was weighed into a flame-dried 1-dram vial equipped with a magnetic stir bar. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum, then evacuated and backfilled with nitrogen. The vial was brought into a nitrogen-filled glovebox and Cp_2ZrHCl (31.0 mg, 1.2 equiv) was added to the vial. The capped vial was removed from the glovebox and the solids were dissolved in 0.5 mL of toluene-*d8* (0.2 M) and the solution was stirred at 700 rpm for 1 h at 23 °C. The reaction solution was then transferred to an oven-dried reaction NMR tube under an atmosphere of N_2.

Diagnostic signal for SI-4: (600 MHz, Toluene-*d8*) δ 4.71 (s, $CH_2OZr(Cl)Cp_2$).

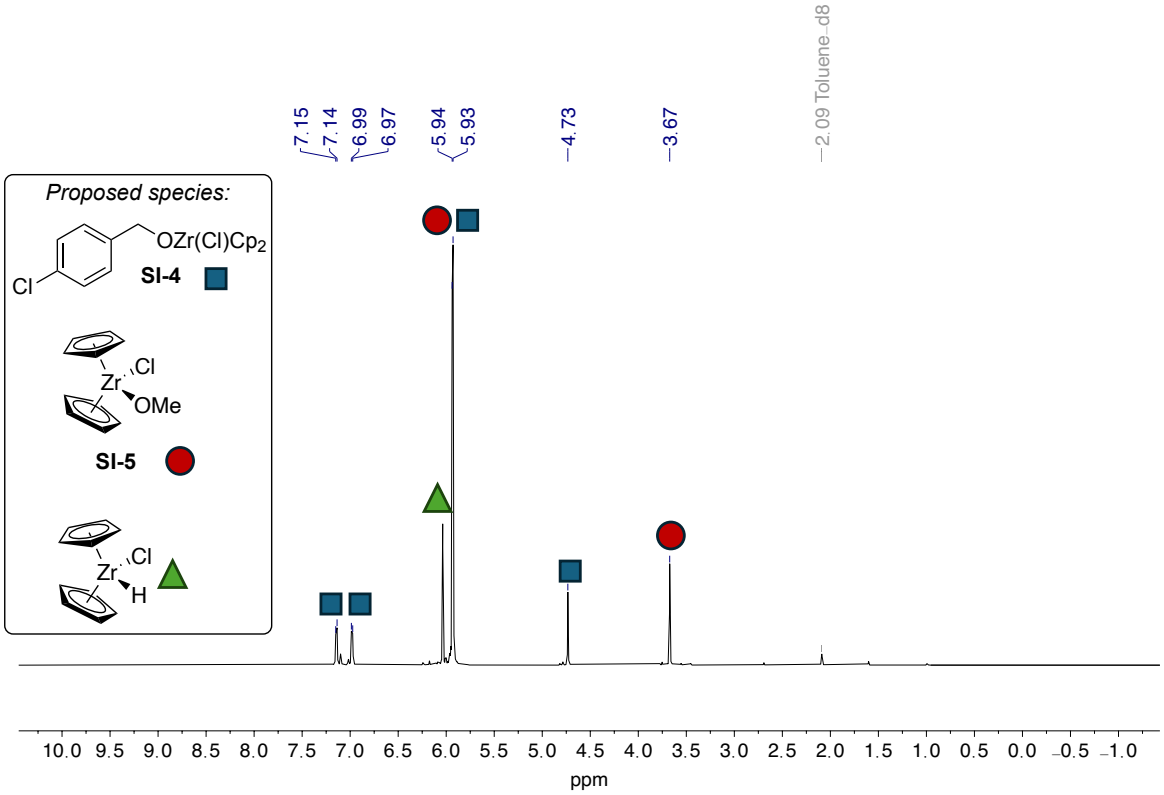
Scheme SI-2: *In situ* observation of **SI-4** and **SI-5**



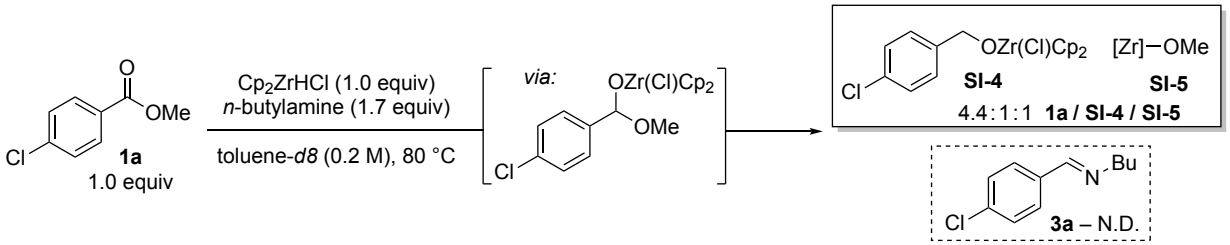
Methyl 4-chlorobenzoate (17.1 mg, 0.1 mmol, 1.0 equiv) was weighed into a flame-dried 1-dram vial equipped with a magnetic stir bar. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum, then evacuated and backfilled with nitrogen. The vial was brought into a nitrogen-filled glovebox and Cp_2ZrHCl (77.4 mg, 3.0 equiv) was added to the vial. The capped vial was removed from the glovebox and the solids were dissolved in 0.5 mL of toluene-*d8* (0.2 M). The solution was stirred at 700 rpm for 1.5 h at 80 °C. The reaction solution was cooled to room temperature and transferred to an oven-dried reaction NMR tube under an atmosphere of N_2.

Characterization of ***SI-4*** *was assigned analogously to the data provided in Scheme SI-1.* ***SI-5*** *was assigned analogously to Erker et. al, JACS, 1986, 108, 2257-2263.*

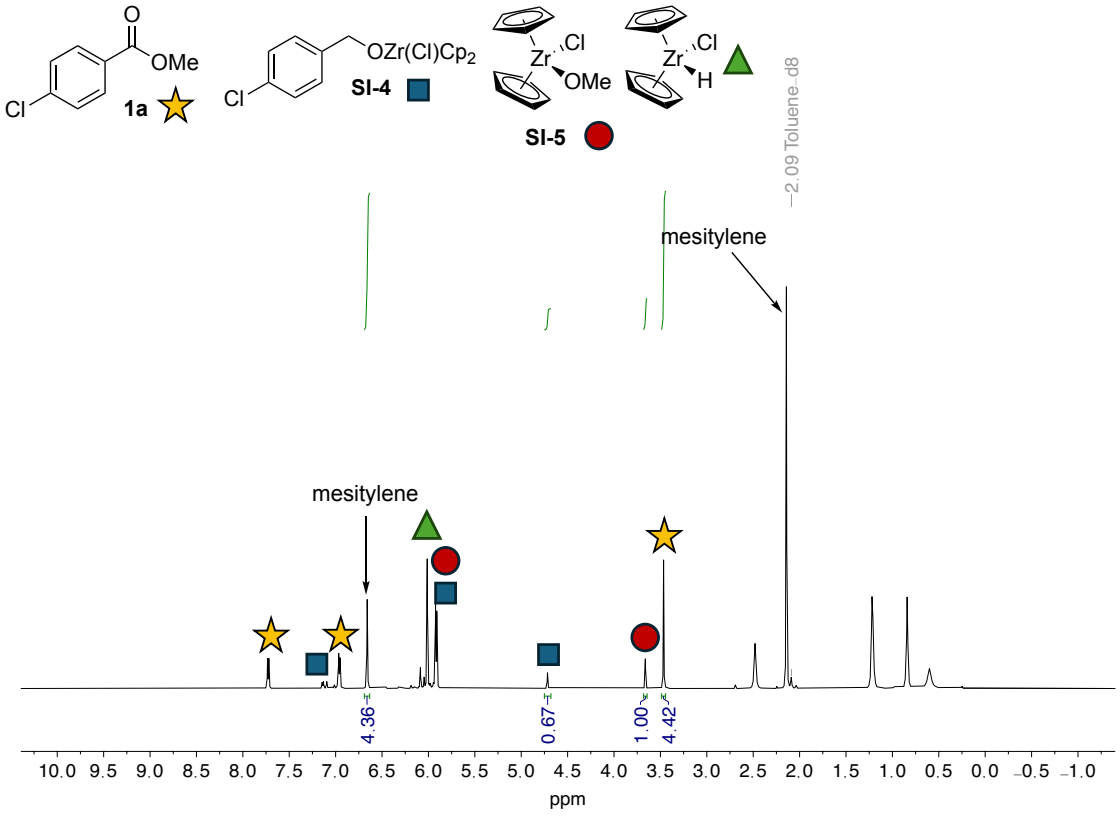
(1a) (600 MHz, Toluene-*d8*) δ 7.74 – 7.71 (m, 2H), 6.96 – 6.92 (m, 2H), 3.45 (s, 3H).
(SI-4) (600 MHz, Toluene-*d8*) δ 7.14 (d, J = 8.3 Hz, 2H), 6.98 (app d, 2H), 5.93 (s, 10H), 4.73 (s, 2H).
(SI-5) (600 MHz, Toluene-*d8*) δ 5.94 (s, 10 H), 3.67 (s, 3H).


Proposed species:
OZr(Cl)Cp2
Cl
SI-4
Zr
Cl
OMe
SI-5
Zr
Cl
H
7.15
7.14
6.99
6.97
5.94
5.93
4.73
3.67
2.09 Toluene-d8
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

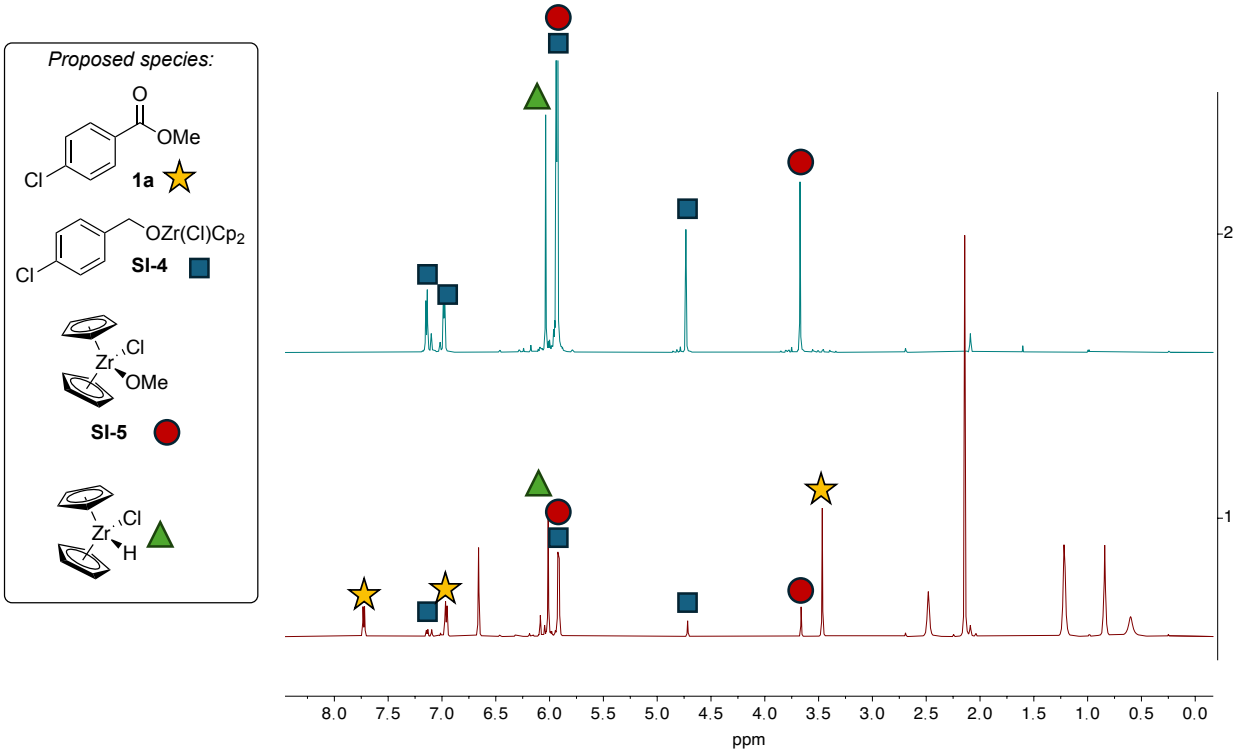
Scheme SI-3: Attempt to intercept zirconocene hemiacetal using exogeneous amine



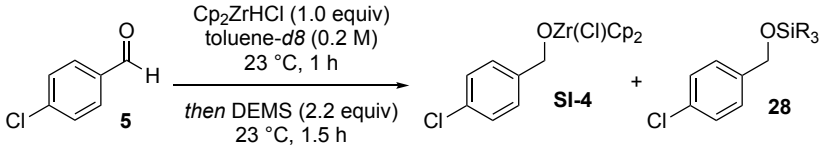
Methyl 4-chlorobenzoate (17.1 mg, 0.1 mmol, 1.0 equiv) was weighed into a flame-dried 1-dram vial equipped with a magnetic stir bar. The vial was brought into a nitrogen-filled glovebox and Cp_2ZrHCl (25.8 mg, 1.0 equiv) was added to the vial. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum and then removed from the glovebox. The solids were dissolved in 0.5 mL of toluene-*d8* (0.2 M). *n*-Butylamine (33.7 µL, 1.7 equiv) was immediately injected into the reaction solution using a Hamilton gastight glass microsyringe. The solution was stirred at 700 rpm at 80 °C for 1.5 h. The reaction solution was cooled to room temperature and mesitylene (13.9 µL, 0.1 mmol) was injected. The reaction solution was transferred to an oven-dried reaction NMR tube under an atmosphere of N_2.



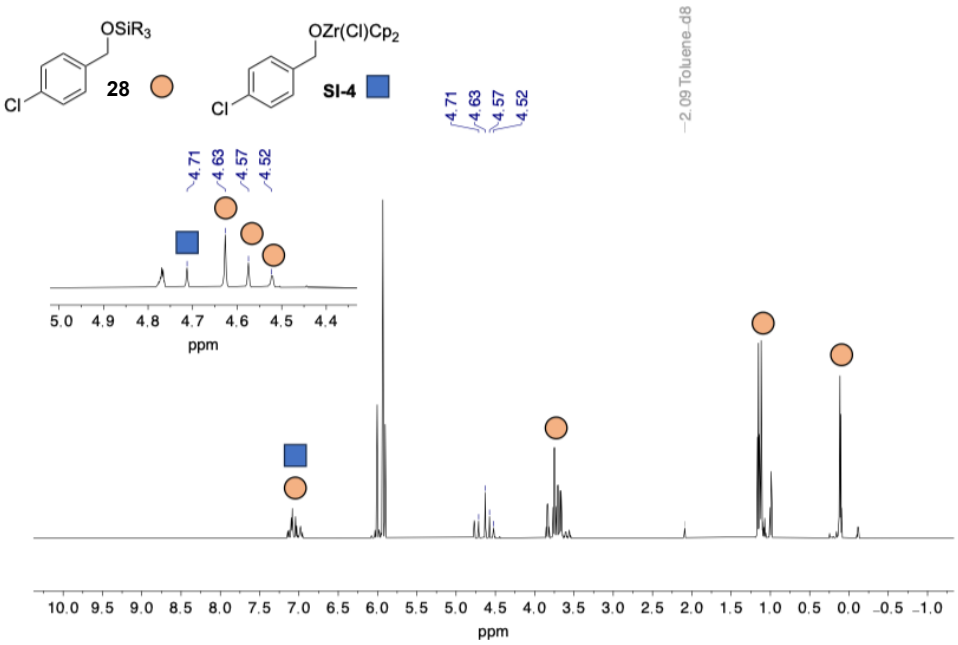
Stacked spectra of ***Cl*-25** and **SI-5** (top) versus attempt to intercept zirconocene hemiacetal with amine (bottom):



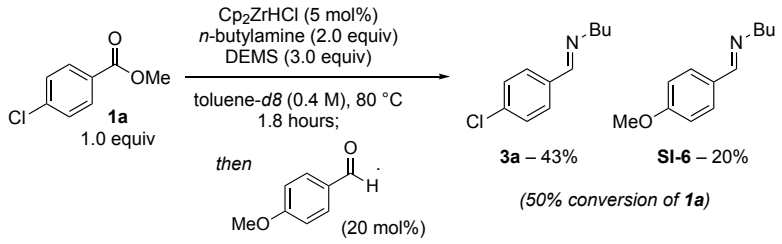
Scheme SI-4: *Preparation and characterization of silyl ethers* ***28***



4-chlorobenzaldehyde (**5**) (14.1 mg, 0.1 mmol, 1.0 equiv) was weighed into a flame-dried 1-dram vial equipped with a magnetic stir bar. The vial was brought into a nitrogen-filled glovebox and Cp_2ZrHCl (25.8 mg, 1.0 equiv) was added to the vial. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum and then removed from the glovebox. The solids were dissolved in 0.5 mL of toluene-*d8* (0.2 M) and the solution was stirred at 700 rpm for 1 h at 23 °C. Then, DEMS (35.2 µL, 2.2 equiv) was injected into the vial using a gastight microsyringe. After 1.5 h, mesitylene (13.9 µL, 0.1 mmol) was injected into the vial. The reaction solution was transferred to an oven-dried reaction NMR tube under an atmosphere of N_2.

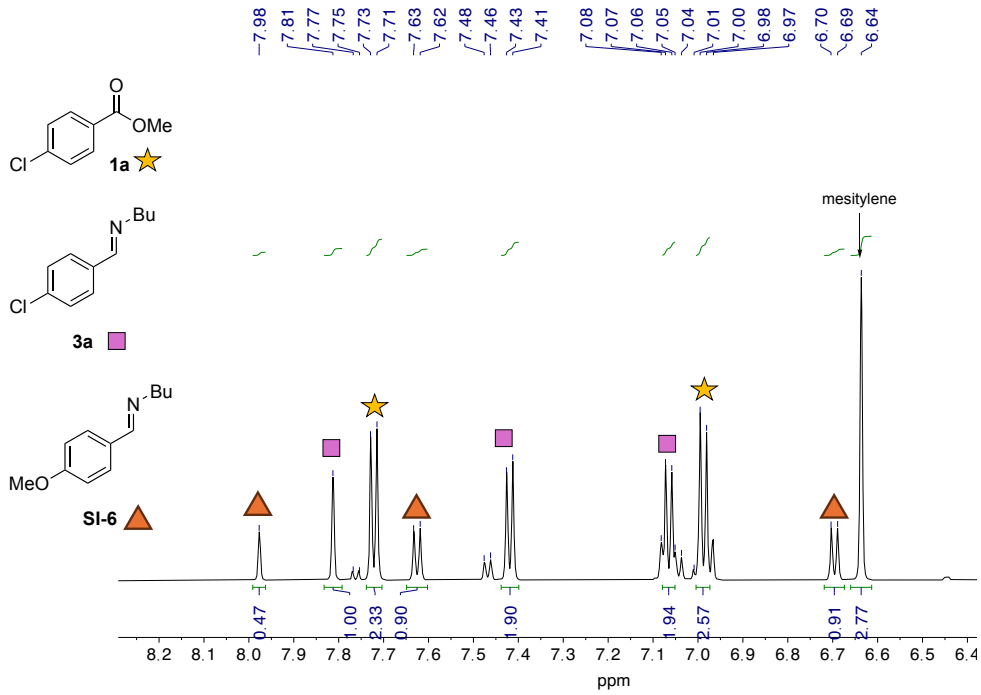


Scheme SI-5: Aldehyde doping experiment

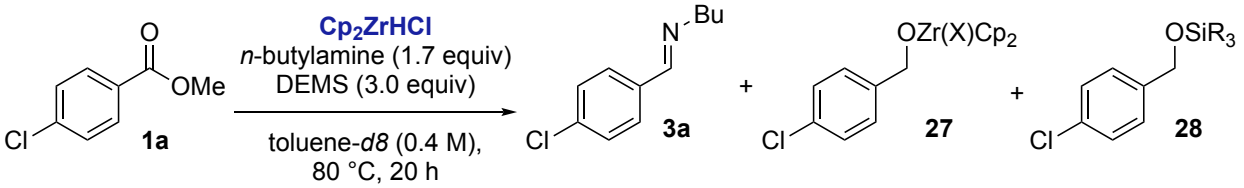


Cp_2ZrCl_2 (7.3 mg, 5 mol%) and methyl 4-chlorobenzoate (85.3 mg, 0.5 mmol, 1.0 equiv) was weighed into a flame-dried 2-dram vial equipped with a magnetic stir bar. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum. The atmosphere was evacuated and backfilled with nitrogen (this process was repeated to a total of 3 times). The solids were dissolved in 1.25 mL of toluene-*d8* (0.4 M). DEMS (240.3 µL, 3.0 equiv) and *n*-butylamine (84.0 µL, 1.7 equiv) were injected into the reaction solution sequentially using Hamilton gastight glass microsyringes. The solution was stirred for 1.8 hours at 80 °C, at which time anisaldehyde (12.1 µL, 20 mol%) was injected into the reaction. After approximately 20 hours, the reaction solution was cooled to room temperature and mesitylene (27.8 µL, 0.2 mmol) was added. The reaction solution was transferred to an NMR for analysis.

Authentic sample of 3a: (400 MHz, Toluene-*d8*): δ 7.79 (s, 1H), 7.44 – 7.38 (m, 2H), 7.08 – 7.03 (m, 2H), 3.42 (td, *J* = 6.9, 1.4 Hz, 2H), 1.67 – 1.56 (m, 2H), 1.41 – 1.30 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).
Authentic sample of SI-6: (600 MHz, Toluene-*d8*): δ 7.99 (s, 1H), 7.70 – 7.65 (m, 2H), 6.73 – 6.68 (m, 2H), 3.50 (td, *J* = 6.9, 1.4 Hz, 2H), 3.26 (s, 3H), 1.71 – 1.65 (m, 2H), 1.44 – 1.37 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).


7.98
7.81
7.77
7.75
7.73
7.71
7.63
7.62
7.48
7.46
7.43
7.41
7.08
7.07
7.06
7.05
7.04
7.01
7.00
6.98
6.97
6.70
6.69
6.64
O
OMe
Cl
1a
N
Bu
Cl
3a
mesitylene
N
Bu
MeO
SI-6
0.47
1.00
2.33
0.90
1.90
1.94
2.57
0.91
2.77
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
ppm

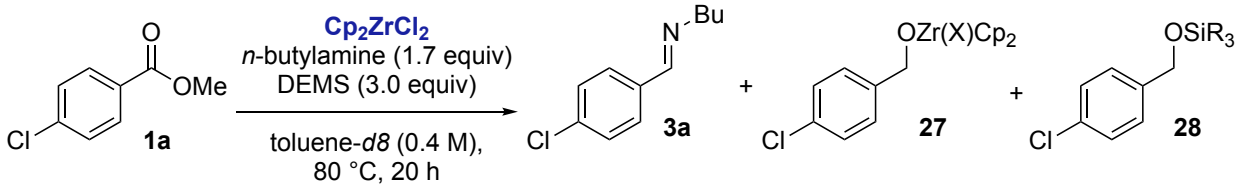
How do equivalents of Cp_2ZrHCl affect chemoselectivity?



Methyl 4-chlorobenzoate (1a) (34.1 mg, 0.2 mmol, 1.0 equiv) was weighed into a flame-dried 1-dram vial equipped with a magnetic stir bar. The vial was brought into a nitrogen-filled glovebox and Cp_2ZrHCl (51.6 – 5.2 mg, 1.0 – 0.10 equiv) was added to the vial. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum, sealed with electrical tape, and then removed from the glovebox. The solids were dissolved in 0.5 mL of toluene-*d8* (0.4 M). DEMS (95.9 µL, 3.0 equiv) was injected into the reaction mixture, followed by the injection of *n*-butylamine (33.7 µL, 1.7 equiv) using a Hamilton gastight glass microsyringe. The septum of the reaction vial was sealed with wax and the reaction solution was stirred at 700 rpm for 20 h at 80 °C. The reaction solution was then cooled to room temperature and filtered through a small celite plug. ^{1}H NMR yields were obtained using mesitylene (13.9 µL, 0.1 mmol) as an internal standard. The yield of silyl ethers **28** is a representative mixture of various species. Diagnostic CH_2–$OSiR_3$ peaks range from 4.63 – 4.52 ppm by ^{1}H NMR analysis.

mol % Cp_2ZrHCl	% Imine **3a**	% Zirconocene **27**	% Silyl Ethers **28**
100	0	15	79
50	2	6	89
30	9	2	74
25	68	≤1	23
20	82	≤1	9
10	95	≤1	4

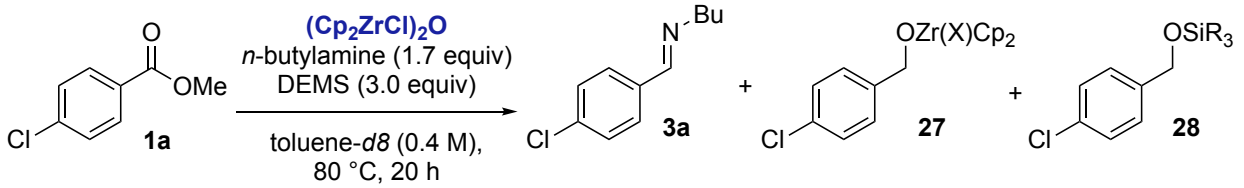
How do equivalents of Cp_2ZrCl_2 affect chemoselectivity?



Methyl 4-chlorobenzoate (1a) (34.1 mg, 0.2 mmol, 1.0 equiv) was weighed into a flame-dried 1-dram vial equipped with a magnetic stir bar and Cp_2ZrCl_2 (58.5 – 5.8 mg, 1.0 – 0.10 equiv). The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum and sealed with electrical tape. The reaction tube was then evacuated and backfilled with nitrogen (this process was repeated to a total of three times). The solids were dissolved in 0.5 mL of toluene-*d8* (0.4 M). DEMS (95.9 µL, 3.0 equiv) was injected into the reaction mixture, followed by the injection of *n*-butylamine (33.7 µL, 1.7 equiv) using a Hamilton gastight glass microsyringe. The vial was sealed with wax and the reaction solution was stirred at 700 rpm at 80 °C for 20 h. The reaction solution was cooled to room temperature and filtered through a small celite plug. ^{1}H NMR yields were obtained using mesitylene (13.9 µL, 0.1 mmol) as an internal standard. The yield of silyl ethers **28** is a representative mixture of various species. Diagnostic CH_2–$OSiR_3$ peaks range from 4.62 – 4.55 ppm by ^{1}H NMR analysis.

mol % Cp_2ZrCl_2	% Imine **3a**	% Zirconocene **27**	% Silyl Ethers **28**
100	≥99	0	0
50	≥99	0	0
30	97	0	≤1
25	97	0	≤1
20	89	0	≤1
10	97	0	≤1

How do equivalents of $(Cp_2ZrCl)_2O$ affect chemoselectivity?

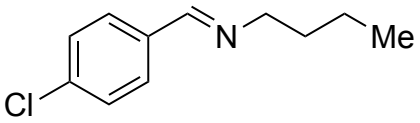


$(Cp_2ZrCl)_2O$ was synthesized according to the literature procedure.[1]

Methyl 4-chlorobenzoate (1a) (34.1 mg, 0.2 mmol, 1.0 equiv) was weighed into a flame-dried 2-dram vial equipped with a magnetic stir bar. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum. The vial was capped with an open top screw cap equipped with a Teflon-lined silicon septum, then evacuated and backfilled with nitrogen. The vial was brought into a nitrogen-filled glovebox and $(Cp_2ZrCl)_2O$ (105.9 – 10.6 mg, 1.0 – 0.10 equiv) was added to the vial. The capped vial was removed from the glovebox and sealed with electrical tape. The solids were dissolved in 0.5 mL of anhydrous PhMe (0.4 M). DEMS (95.9 µL, 3.0 equiv) was injected into the reaction mixture, followed by the injection of *n*-butylamine (33.7 µL, 1.7 equiv) using a Hamilton gastight glass microsyringe. The septum of the reaction vial was sealed with wax and the reaction solution was stirred at 700 rpm at 80 °C for 20 h. The reaction solution was cooled to room temperature and filtered through a small celite plug.^{1}H NMR yields were obtained using mesitylene (13.9 µL, 0.1 mmol) as an internal standard. The yield of silyl ethers **28** is a representative mixture of various species. Diagnostic CH_2–$OSiR_3$ peaks range from 4.62 – 4.55 ppm by ^{1}H NMR analysis.

mol % $(Cp_2ZrCl)_2O$	% Imine **3a**	% Zirconocene **27**	% Silyl Ethers **28**
100	≥99	0	0
50	≥99	0	0
30	96	2	≤1
25	97	0	≤1
20	91	0	2
10	93	0	≤1

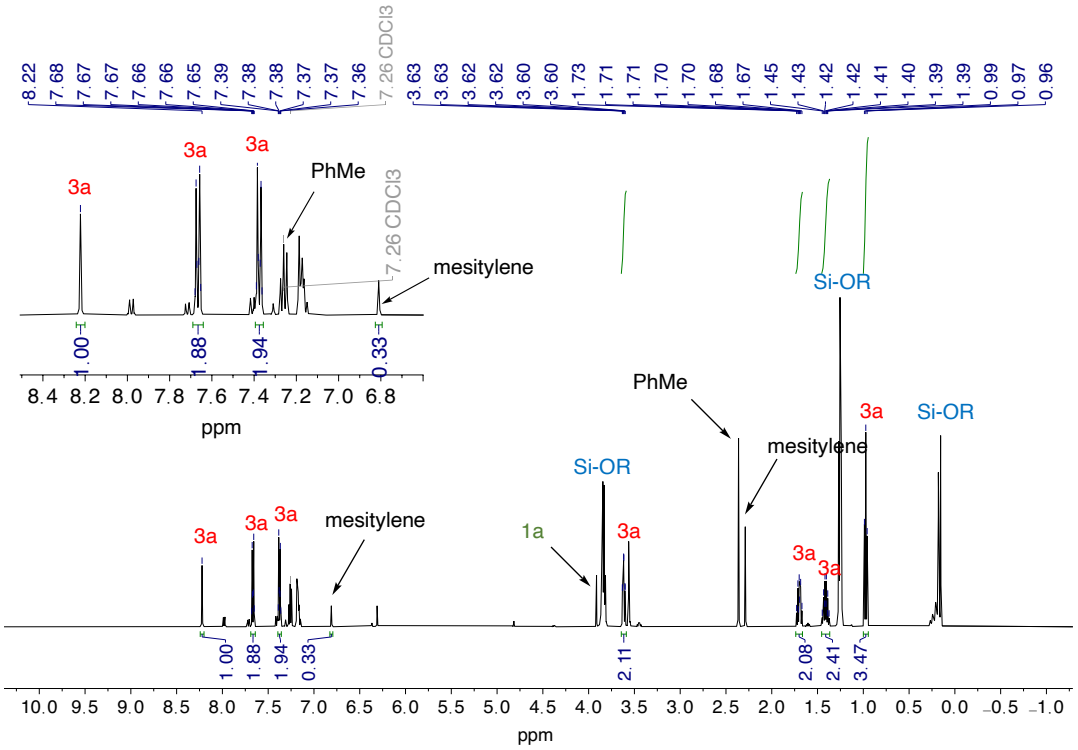
V) Characterization of Imines, Hydrazone, and Enamine Products (Table 2a)

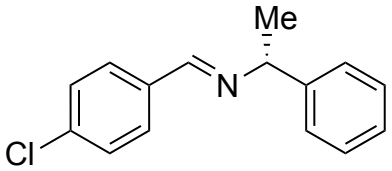


_N_-(4-chlorobenzylidene)butan-1-amine (3a)

Following general procedure A using methyl 4-chlorobenzoate (**1a**, 170.6 mg, 1.0 mmol), the reaction was carried out for 21 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (91% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[2]
Diagnostic signals identified in the ^{1}H NMR of the crude residue:
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.69 – 7.64 (m, 2H), 7.39 – 7.36 (m, 2H), 3.62 (td, *J* = 7.0, 1.4 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.45 – 1.37 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).



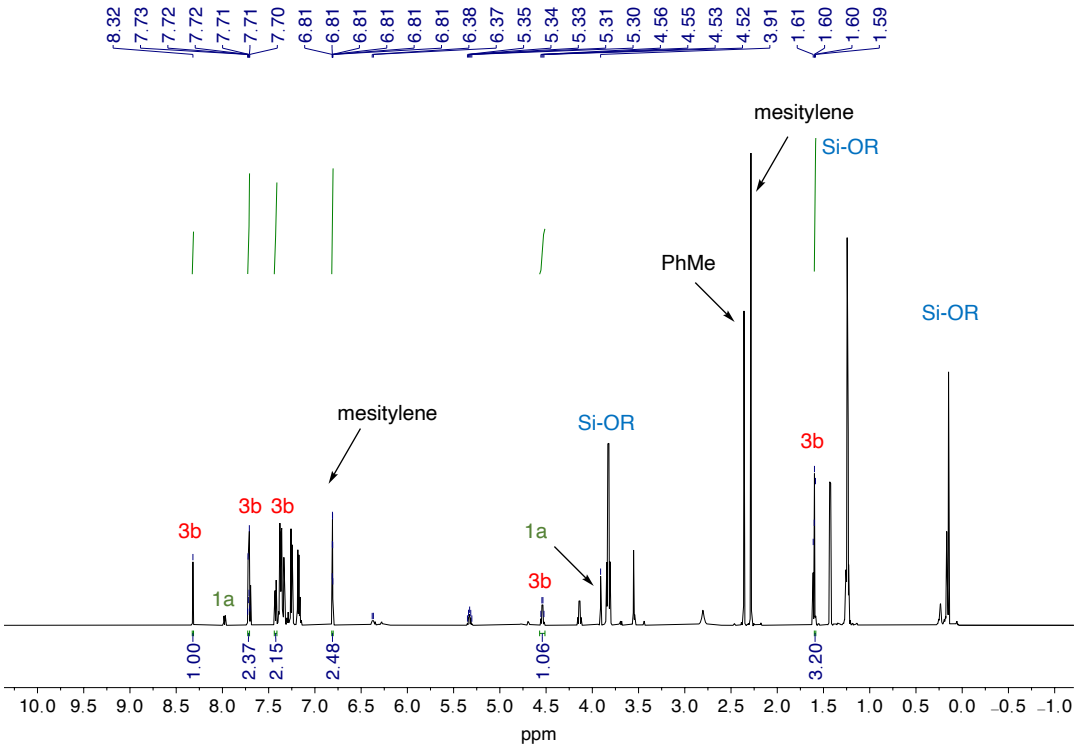


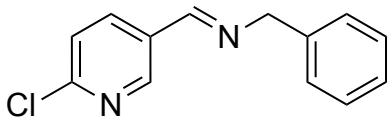
***(R)-N*-(4-chlorobenzylidene)-1-phenylethanamine (3b)**

Following general procedure A using methyl 4-chlorobenzoate (34.1 mg, 0.20 mmol) and (*R*)-α-methylbenzylamine (43.5 µL, 0.34 mmol, 1.7 equiv), the reaction was carried out for 22 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (60% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[3]
Diagnostic signals identified in the ^{1}H NMR of the crude residue:
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.73 – 7.71 (m, 2H), 7.44 – 7.41 (m, 2H), 4.54 (q, *J* = 6.6 Hz, 1H), 1.59 (d, *J* = 6.6 Hz, 3H).

Note: The formation of 4-chloro-*N*-(1-phenylethyl)benzamide was also apparent.[4]
Diagnostic signals identified in the ^{1}H NMR of the crude residue:
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.37 (br s, 1H), 5.33 (p, *J* = 7.1 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H).



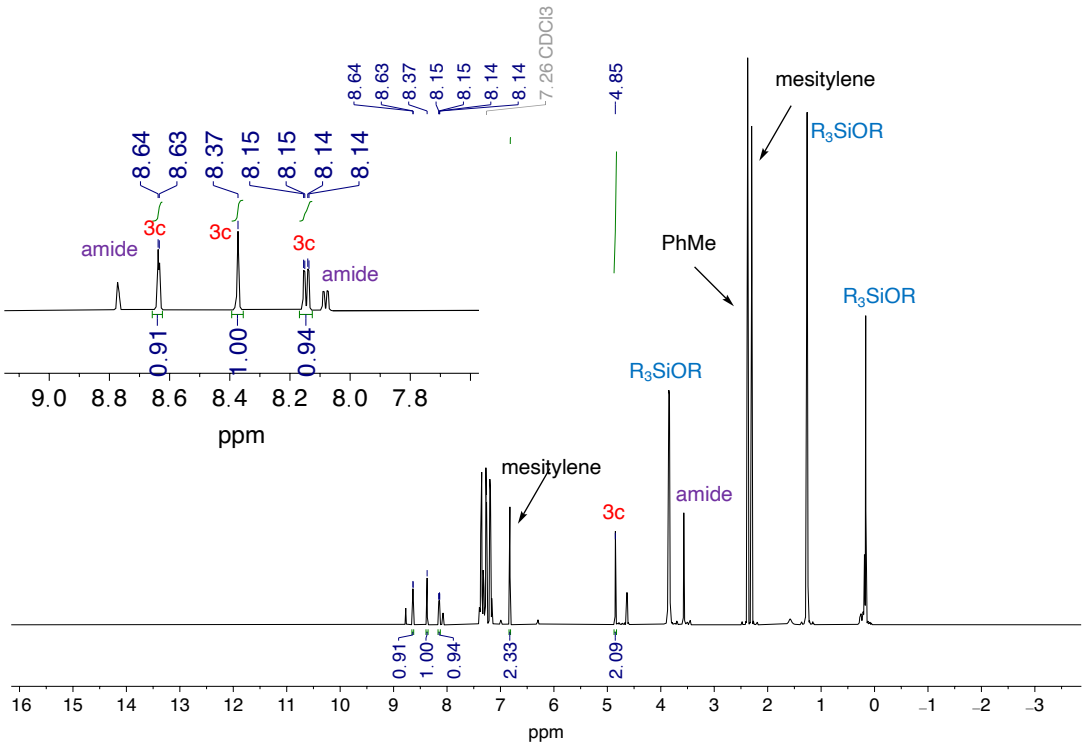


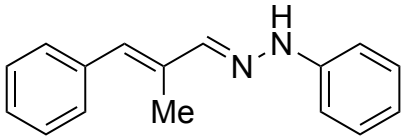
_N_-benzyl-1-(6-chloropyridin-3-yl)methanimine (3c)

Following general procedure A using methyl 6-chloronicotinate (34.3 mg, 0.20 mmol) and benzylamine (37.1 µL), the reaction was carried out for 18 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (64% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[5]
Diagnostic signals identified in the ^{1}H NMR of the crude residue (*excluding signals overlapping with residual PhMe*):
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.3 Hz, 1H), 8.37 (s, 1H), 8.15 (dd, *J* = 8.3, 2.4 Hz, 1H), 4.85 (s, 2H).

Note: The formation of *N*-benzyl-6-chloronicotinamide was also apparent.[6]
Diagnostic signals identified in the ^{1}H NMR of the crude residue:
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.6 Hz, 1H), 8.08 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.63 (d, *J* = 5.7 Hz, 2H).

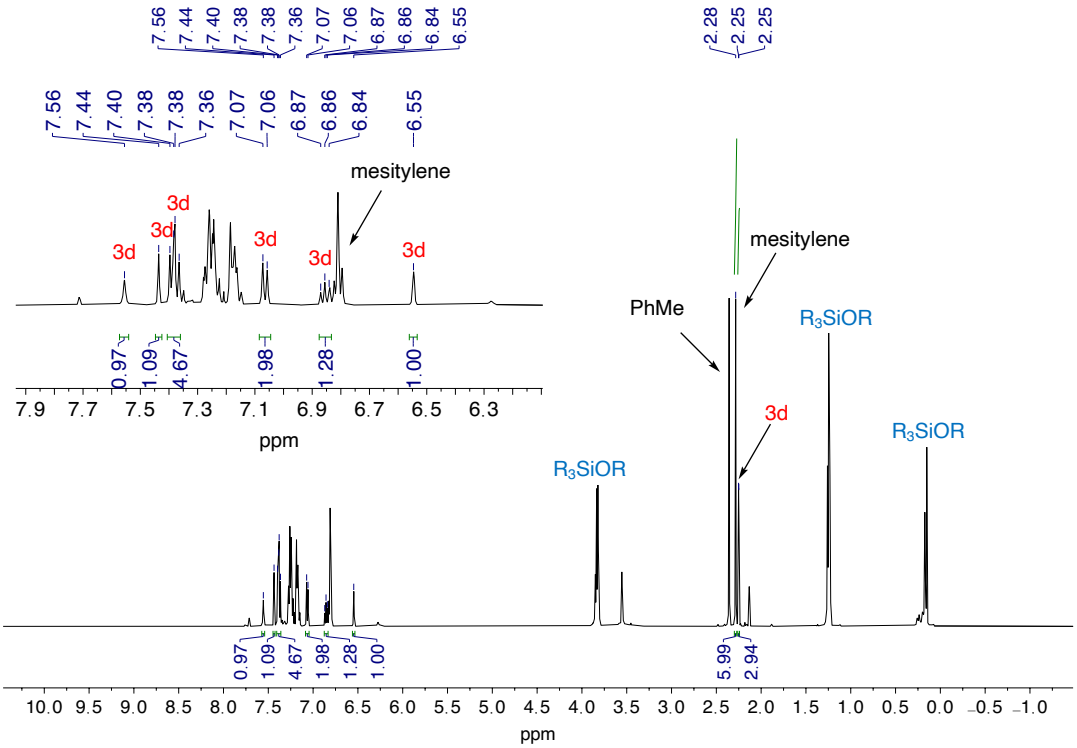


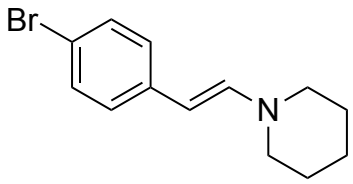


_(E)_-1-phenyl-2-((_E_)-2-methyl-3-phenylallyidene)hydrazone (3d)

Following general procedure A using methyl 3-methyl-3-phenylacrylate (35.2 mg, 0.20 mmol) and phenylhydrazine (36.8 mg, 0.34 mmol, 1.7 equiv), the reaction was carried out for 20 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (74% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[7] Diagnostic signals identified in the ^{1}H NMR of the crude residue (*excluding signals overlapping with residual PhMe*):
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (br s, 1H), 7.44 (s, 1H), 7.41 – 7.36 (m, 4H), 7.06 (d, J = 7.5 Hz, 2H), 6.86 (t, J = 7.3 Hz, 1H), 6.55 (s, 1H), 2.25 (d, J = 1.3 Hz, 3H).

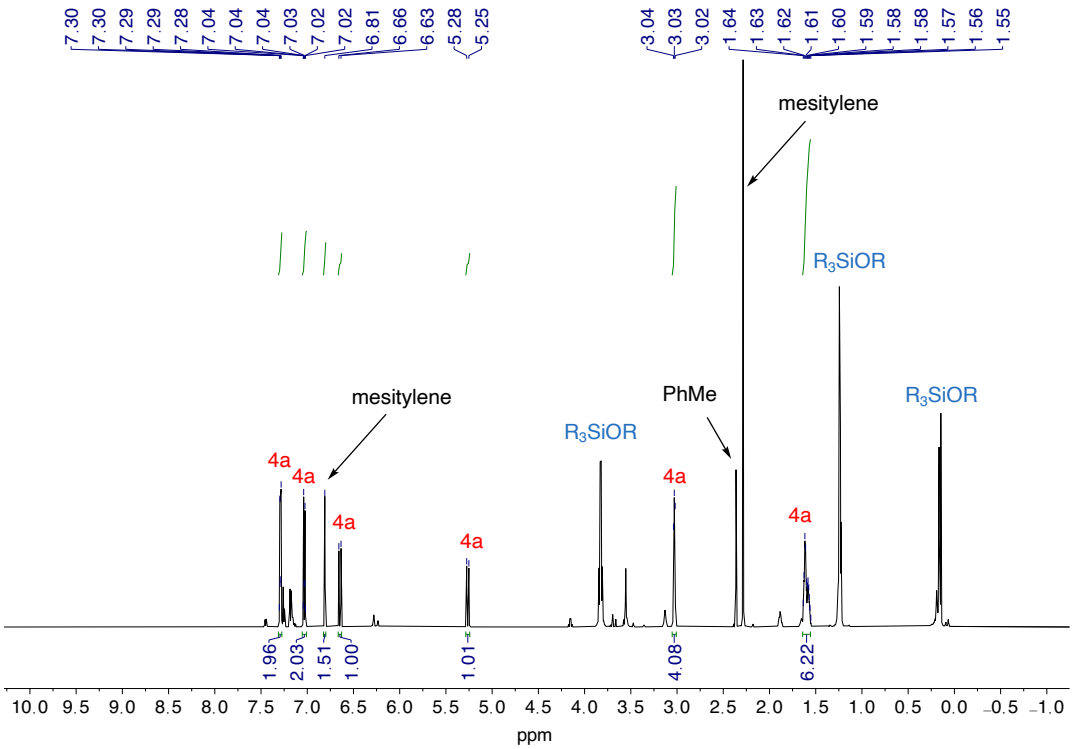




(*E*)-1-(4-bromostyryl)piperidine (4a)

0.2 mmol scale, crude ^{1}H NMR analysis:
Following general procedure B using methyl 2-(4-bromophenyl)acetate (45.8 mg, 0.2 mmol) the reaction was carried out for 23 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (≥99% ^{1}H NMR yield).

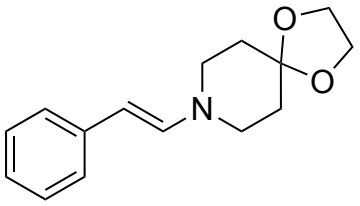
The spectroscopic data for this compound match those previously reported in the literature.[8]
Diagnostic signals identified in the ^{1}H NMR of the crude residue:
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.05 – 7.01 (m, 2H), 6.65 (d, *J* = 14.0 Hz, 1H), 5.26 (d, *J* = 14.0 Hz, 1H), 3.05 – 3.01 (m, 4H), 1.64 – 1.56 (m, 6H).



1.0 mmol scale, isolated yield of 4a:
Following general procedure B using methyl 2-(4-bromophenyl)acetate (229.1 mg, 1.0 mmol) the reaction was carried out for 22 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (27.8 µL, 0.20 mmol) as an internal standard (≥99% ^{1}H NMR yield). The crude residue was purified via flash column chromatography using activated aluminum oxide (neutral, Brockmann Grade I, 58 angstroms)

(elutes using 1% NEt_3 in Hex → 5% EtOAc/ 1% NEt_3 in Hex). The title compound was obtained as a white solid (179.6 mg, 67% yield).

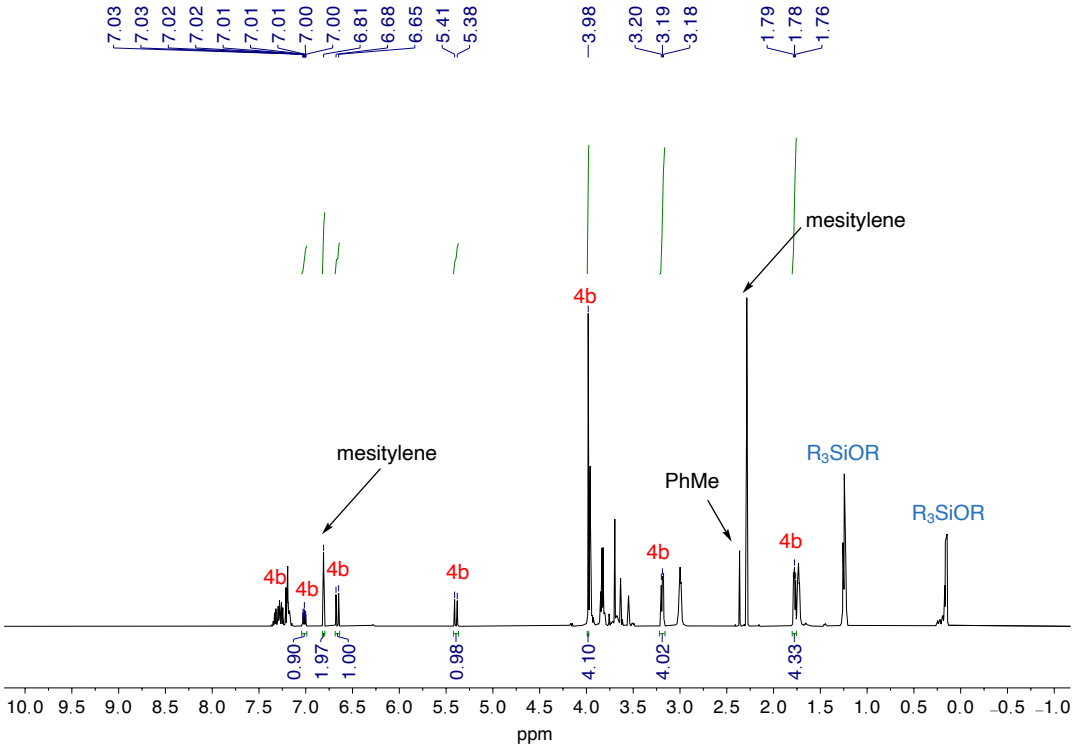
The spectroscopic data for this compound match those previously reported in the literature. [8]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.65 (d, *J* = 14.0 Hz, 1H), 5.26 (d, *J* = 14.0 Hz, 1H), 3.07 – 3.00 (m, 4H), 1.67 – 1.54 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8, 138.8, 131.5, 125.3, 116.5, 97.9, 49.7, 25.4, 24.4.

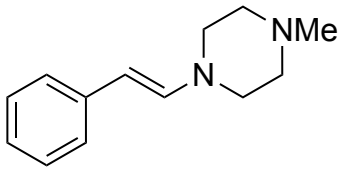


8-styryl-1,4-dioxa-8-aza-spiro[4,5]decane (4b)

Following general procedure B using methyl phenylacetate (28.2 µL, 0.20 mmol) and 1,4-dioxa-8-azaspiro[4.5]decane (51.3 µL, 0.40 mmol, 2.0 equiv), the reaction was carried out for 23 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (76% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[9]
Diagnostic signals identified in the ^{1}H NMR of the crude residue (*excluding signals overlapping with residual PhMe*):
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (tt, *J* = 6.8, 1.8 Hz, 1H), 6.66 (d, *J* = 14.1 Hz, 1H), 5.39 (d, *J* = 14.1 Hz, 1H), 3.98 (s, 4H), 3.22 – 3.16 (m, 4H), 1.80 – 1.76 (m, 4H).

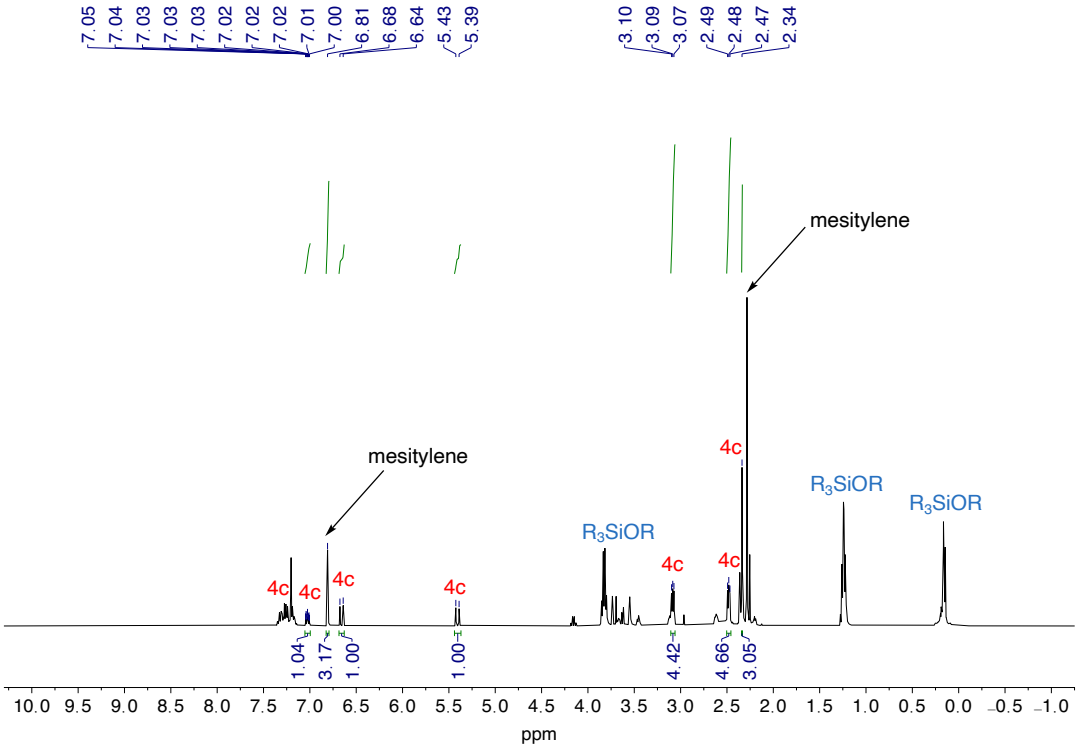


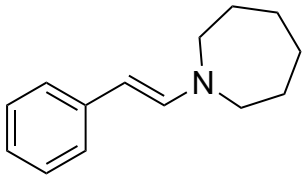


(*E*)-1-Methyl-4-styrylpiperazine (4c)

Following general procedure B using methyl phenylacetate (28.2 µL, 0.20 mmol) and *N*-methylpiperazine (33.3 µL, 0.30 mmol, 1.5 equiv), the reaction was carried out for 24 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (47% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[8] Diagnostic signals identified in the ^{1}H NMR of the crude residue (*excluding signals overlapping with residual PhMe*):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 7.00 (m, 1H), 6.66 (d, J = 14.1 Hz, 1H), 5.41 (d, J = 14.1 Hz, 1H), 3.11 – 3.06 (m, 4H), 2.50 – 2.46 (m, 4H), 2.34 (s, 3H).

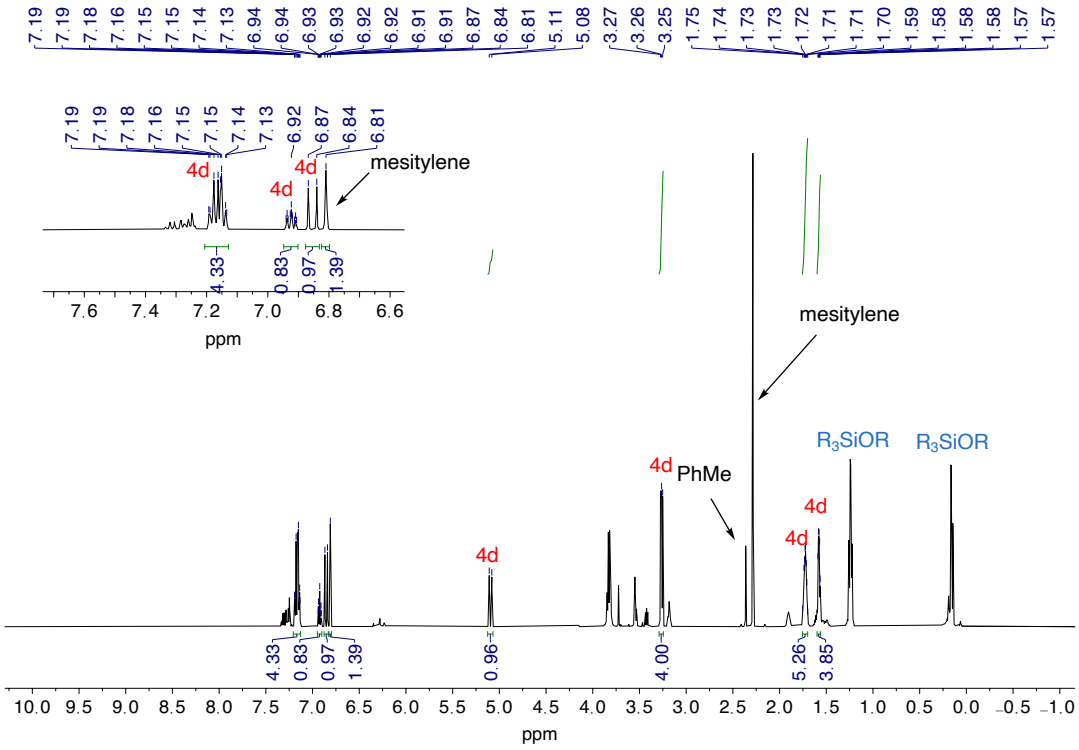


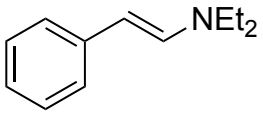


(*E*)-1-Styrylazepane (4d)

Following general procedure B using methyl phenylacetate (28.2 µL, 0.20 mmol) and azepane (33.8 µL, 0.30 mmol, 1.5 equiv), the reaction was carried out for 21 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (≥99% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[8]
Diagnostic signals identified in the ^{1}H NMR of the crude residue:
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 4H), 6.92 (tt, J = 6.9, 1.6 Hz, 1H), 6.85 (d, J = 13.8 Hz, 1H), 5.09 (d, J = 13.8 Hz, 1H), 3.29 – 3.24 (m, 4H), 1.76 – 1.70 (m, 4H, overlapping), 1.59 1.57 (m, 4H).



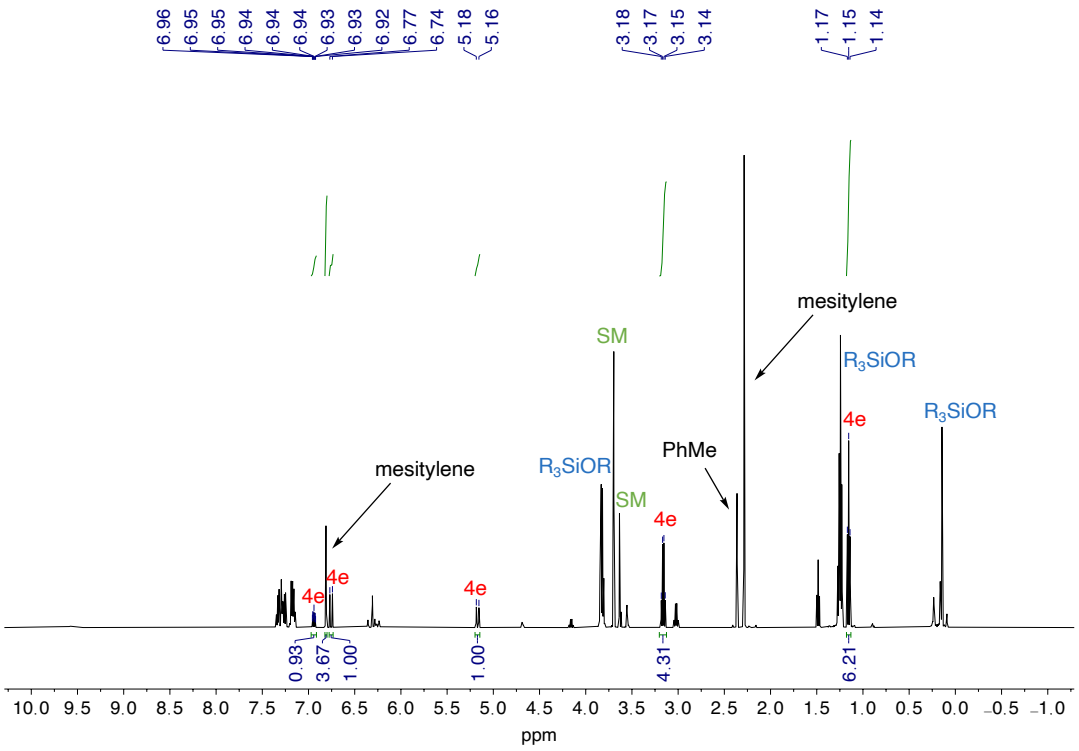


(*E*)- *N,N*-Diethylstyrylamine (4e)

0.2 mmol scale, crude ^{1}H NMR analysis:
Following general procedure B using methyl phenylacetate (28.2 µL, 0.20 mmol) and diethylamine (31.0 µL, 0.30 mmol, 1.5 equiv), the reaction was carried out for 21 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (41% ^{1}H NMR yield).

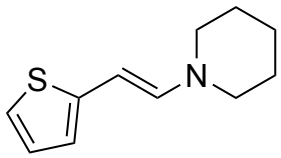
The spectroscopic data for this compound match those previously reported in the literature.[10] Diagnostic signals identified in the ^{1}H NMR of the crude residue (*excluding signals overlapping with residual PhMe*):

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (tt, *J* = 7.0, 1.6 Hz, 1H), 6.76 (d, *J* = 14.0 Hz, 1H), 5.17 (d, *J* = 14.0 Hz, 1H), 3.16 (q, *J* = 7.1 Hz, 4H), 1.15 (t, *J* = 7.1 Hz, 6H).



1.0 mmol scale, isolated yield of 4e:
Following general procedure B using methyl phenylacetate (141.0 µL, 1.0 mmol) the reaction was carried out for 22 h. In lieu of an acidic workup, the crude residue was directly purified via flash column chromatography using activated aluminum oxide (neutral, Brockmann Grade I, 58 angstroms) (elutes using 10% EtOAc/ 1% NEt_3 in Hex). The title compound was obtained as a colorless oil (69 mg, 39% yield).

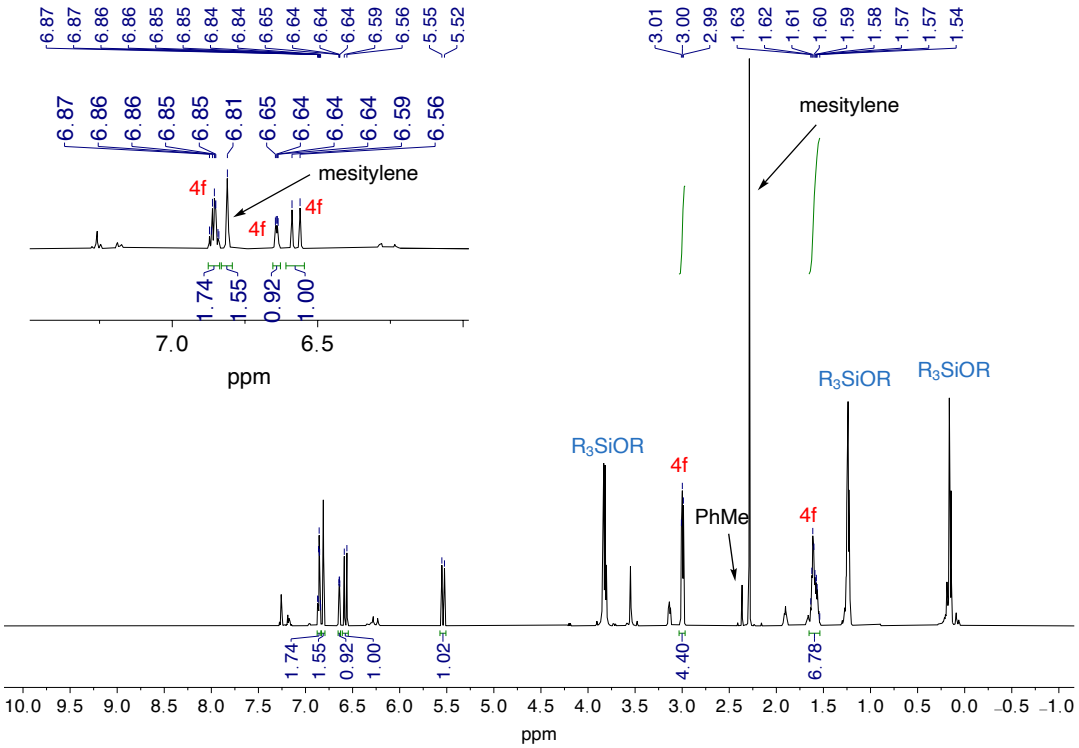
The spectroscopic data for this compound match those previously reported in the literature.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.18 (m, 2H), 7.16 – 7.14 (m, 2H), 6.94 (tt, *J* = 7.2, 1.5 Hz, 1H), 6.76 (d, *J* = 14.0 Hz, 1H), 5.17 (d, *J* = 14.0 Hz, 1H), 3.16 (q, *J* = 7.1 Hz, 4H), 1.16 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 137.8, 128.6, 123.3, 122.9, 96.2, 45.4, 13.3.

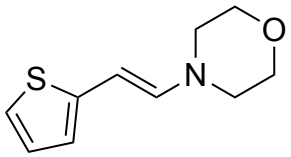


(*E*)-1-(2-(Thiophen-2-yl-vinyl)piperidine (4f)

Following general procedure B using methyl 2-thienylacetate (31.2 mg, 0.2 mmol), the reaction was carried out for 20 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (97% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[11]
Diagnostic signals identified in the ^{1}H NMR of the crude residue:
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 – 6.84 (m, 2H), 6.64 (dd, *J* = 3.3, 1.4 Hz, 1H), 6.57 (d, *J* = 13.9 Hz, 1H), 5.54 (d, *J* = 13.9 Hz, 1H), 3.03 – 2.97 (m, 4H), 1.65 – 1.54 (m, 6H).

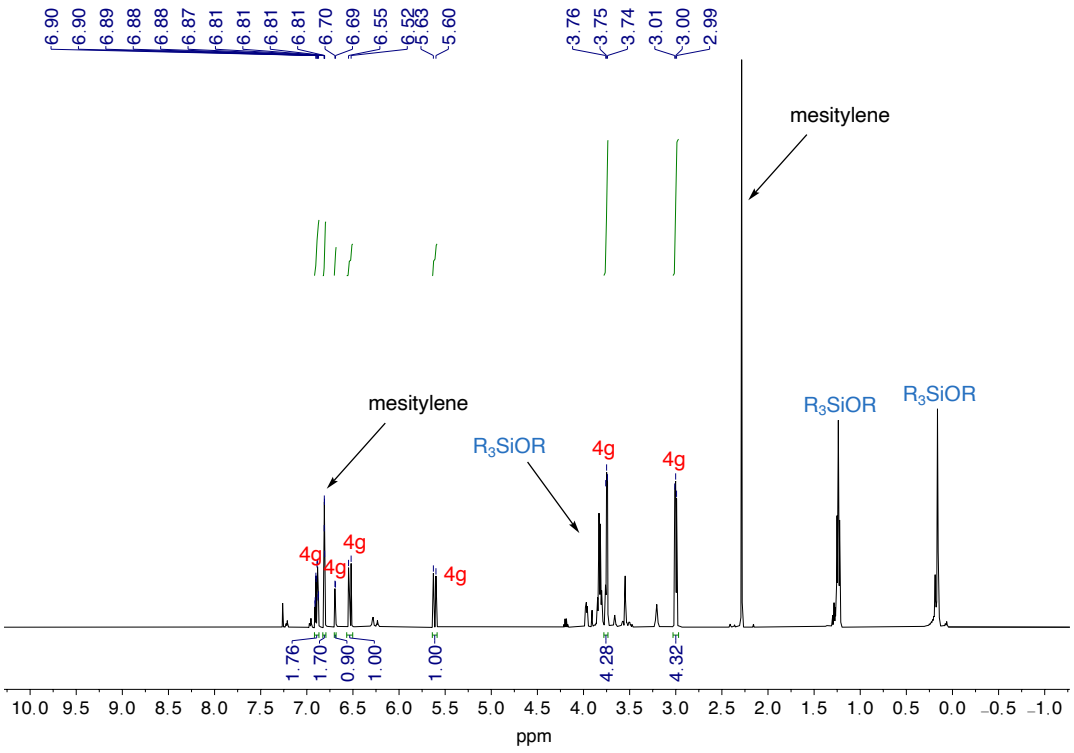


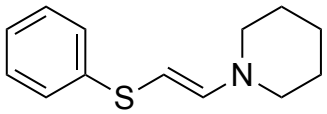


4-((*E*)-2-Thiophen-2-yl-vinyl)morpholine (4g)

Following general procedure B using methyl 2-thienylacetate (31.2 mg, 0.20 mmol) and morpholine (25.9 µL, 0.30 mmol, 1.5 equiv), the reaction was carried out for 20 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (88% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[12]
Diagnostic signals identified in the ^{1}H NMR of the crude residue:
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 – 6.87 (m, 2H), 6.69 (d, *J* = 3.3 Hz, 1H), 6.53 (d, *J* = 14.0 Hz, 1H), 5.61 (d, *J* = 13.9 Hz, 1H), 3.78 – 3.74 (m, 4H), 3.03 – 2.97 (m, 4H).



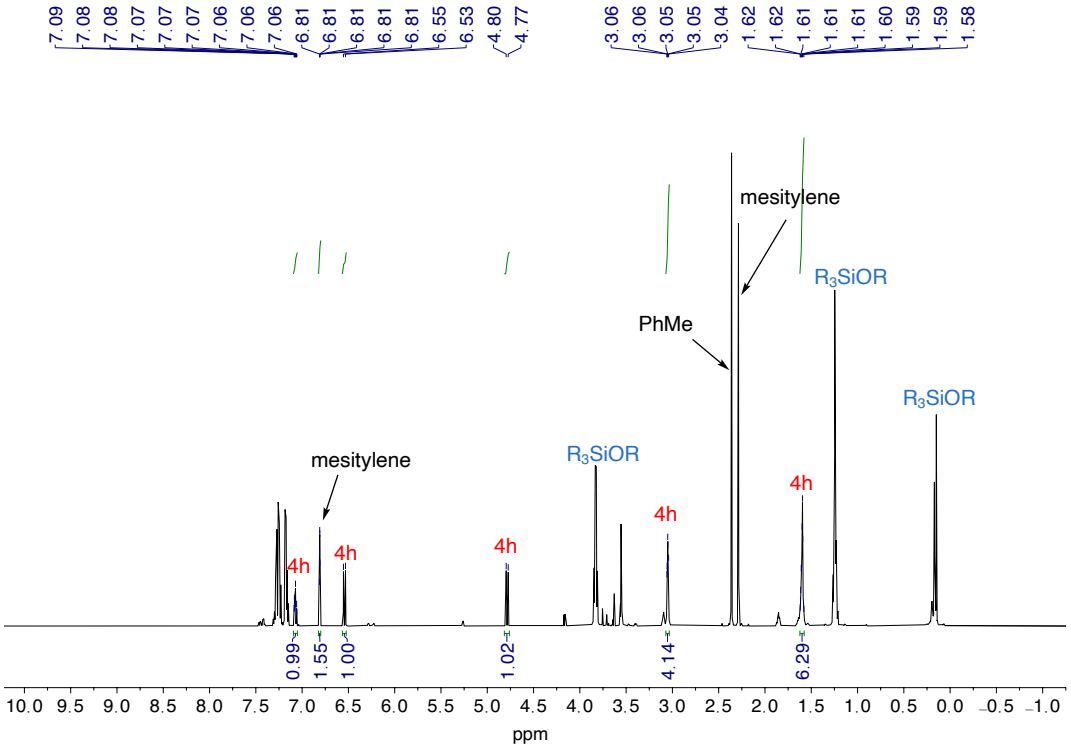


(*E*)-1-(2-(Phenylthio)vinyl)piperidine (4h)

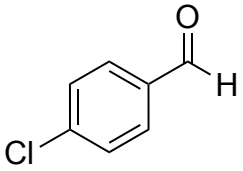
Following general procedure B using methyl 2-(phenylthiol)acetate (36.5 mg, 0.2 mmol), the reaction was carried out for 18 h. In lieu of an acidic workup, the crude residue was directly concentrated and a ^{1}H NMR yield was obtained using mesitylene (13.9 µL, 0.10 mmol) as an internal standard (97% ^{1}H NMR yield).

The spectroscopic data for this compound match those previously reported in the literature.[11] Diagnostic signals identified in the ^{1}H NMR of the crude residue (*excluding signals overlapping with residual PhMe*):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (tt, *J* = 7.4, 1.4 Hz, 1H), 6.81 (dt, *J* = 1.4, 0.7 Hz, 2H), 6.54 (d, *J* = 12.9 Hz, 1H), 4.78 (d, *J* = 12.9 Hz, 1H), 3.07 – 3.03 (m, 4H), 1.62 – 1.58 (m, 6H).



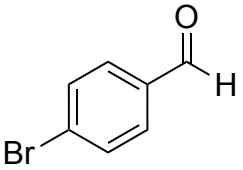
VI) Characterization Data for Aldehyde Products (Table 2a)



4-chlorobenzaldehyde (5)

Following general procedure A using methyl 4-chlorobenzoate (1a) (170.6 mg, 1.0 mmol), the reaction was carried for 23 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 2.5% Et_2O in Pentane 30 mL/min). The title compound was obtained as a white solid (107.6 mg, 76% yield).

The spectroscopic data for this compound match those previously reported in the literature.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.85 – 7.80 (m, 2H), 7.54 – 7.50 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 141.1, 134.9, 131.1, 129.6.



4-bromobenzaldehyde (6)

(**Using 1d**): Following general procedure A using methyl 4-bromobenzoate (1d) (215.05 mg, 1.0 mmol), the reaction was carried out for 21 h. A ^{1}H NMR yield was obtained using mesitylene as an internal standard (79% ^{1}H NMR yield).

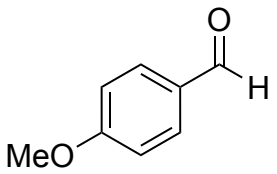
(**Using 1e**): Following general procedure A using ethyl 4-bromobenzoate (1e) (163.6 µL, 1.0 mmol), the reaction was carried out for 21.5 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% Et_2O in Pentane at 30 mL/min). To remove residual silicon-based impurities, the title compound was further purified by a second round of chromatography (12 g gold cartridge, elutes using 5% Et_2O in Pentane at 30 mL/min). The title compound was obtained as a crystalline white solid (138.5 mg, 75% yield).

The spectroscopic data for this compound match those previously reported in the literature.[14]
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.78 – 7.73 (m, 2H), 7.72 – 7.67 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 135.2, 132.6, 131.1, 129.9.

(**Using 1e, 10.0 mmol**): Following general procedure A using ethyl 4-bromobenzoate (1e) (1.65 mL, 10.0 mmol), the reaction was carried out for 48 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (100 gold cartridge, elutes using 2.5% Et_2O in Pentane at 30 mL/min). The title compound was obtained as a white solid (1.13 g, 61% yield).

(**Using 1f**): Following general procedure A using isopropyl 4-bromobenzoate (1f) (138.6 mg, 0.5 mmol), the reaction was carried out for 23 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 2.5% Et_2O in Hexane at 30 mL/min). The title compound was obtained as a white solid (38.9 mg, 42% yield).

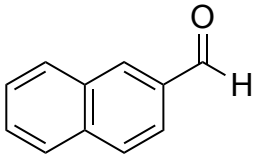
(**Using 1g**): Following general procedure A using phenyl 4-bromobenzoate (1g) (138.6 mg, 0.5 mmol), the reaction was carried out for 23 h. Crude ^{1}H NMR analysis showed full conversion of 1h to 4-bromo-*N*-butylbenzamide.



4-methoxybenzaldehyde (7)

Following general procedure A using methyl 4-methoxybenzoate (166.2 mg, 1.0 mmol), the reaction was carried out for 20 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 100% Et_2O at 30 mL/min). To remove residual silicon-based impurities, the title compound was further purified through a plug of neutral Brockmann grade alumina (approx. 2.0 g alumina, elutes using 100% Hex → 50% Et_2O/Hex). The title compound was obtained as a yellow oil (98.0 mg, 72% yield).

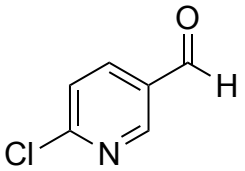
The spectroscopic data for this compound match those previously reported in the literature.[14]
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.84 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 164.7, 132.1, 130.1, 114.4, 55.7.



2-naphthaldehyde (8)

Following general procedure A using methyl 2-naphthoate (186.2 mg, 1.0 mmol), the reaction was carried out for 22.5 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 100% Hexanes at 30 mL/min). The title compound was obtained as a white solid (131.0 mg, 84% yield).

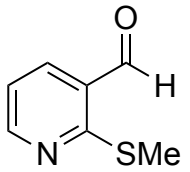
The spectroscopic data for this compound match those previously reported in the literature.[15]
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.31 (s, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.95 (m, 1H), 7.93 – 7.87 (m, 2H), 7.64 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.58 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 136.4, 134.6, 134.1, 132.6, 129.5, 129.1, 129.1, 128.1, 127.1, 122.7.



6-chloronicotinylaldehyde (9)

Following general procedure A using methyl 6-chloronicotinate (171.6 mg, 1.0 mmol), the reaction was carried out for 22 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% Et_2O in Pentane at 30 mL/min). The title compound was obtained as a white solid (83.1 mg, 59% yield).

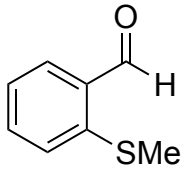
The spectroscopic data for this compound match those previously reported in the literature.[16]
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.87 (dd, *J* = 2.4, 0.7 Hz, 1H), 8.14 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.52 (dt, *J* = 8.2, 0.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 157.0, 152.5, 138.1, 130.5, 125.3.



2-(methylthio)nicotinylaldehyde (10)

Following general procedure A using methyl 2-(methylthio)nicotinate (171.6 mg, 1.0 mmol), the reaction was carried out for 22 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% Et_2O in Hexane at 30 mL/min). The title compound was obtained as a white solid (93.7 mg, 61% yield).

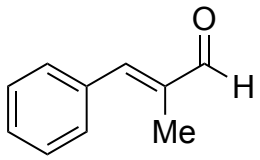
The ^{1}H NMR spectroscopic data for this compound match a previous literature report.[17]
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (dd, J = 7.0, 3.4 Hz, 1H), 8.60 – 8.54 (m, 1H), 7.99 – 7.93 (m, 1H), 7.13 (dtd, J = 7.7, 4.8, 2.5 Hz, 1H), 2.56 (dd, J = 6.4, 3.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 162.8, 153.6, 139.8, 128.5, 118.8, 13.1.
IR (neat): 2746, 1682, 1541, 1377, 1138, 1095, 1061, 801, 684 cm^{-1}.
HRMS (+ESI): Calculated for C_7H_7SNO $[M + H]^+$: 154.0321. Found: 154.0321.



2-(methylthio)benzaldehyde (11)

Following general procedure A using ethyl 2-thiomethylbenzoate (196.3 mg, 1.0 mmol), the reaction was carried out for 21.5 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% Et_2O in Pentane at 30 mL/min). To remove residual silicon-based impurities, the title compound was further purified by a second round of chromatography (12 g gold cartridge, elutes using 5% Et_2O in Pentane at 30 mL/min). The title compound was obtained as a yellow oil (120.2 mg, 79% yield).

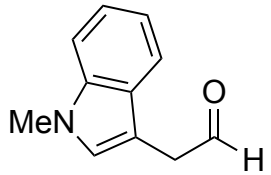
The spectroscopic data for this compound match those previously reported in the literature.[18]
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.80 (dd, J = 7.7, 1.3 Hz, 1H), 7.53 (tdd, J = 7.3, 1.6, 0.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 2.49 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 143.5, 134.1, 133.5, 133.0, 125.5, 124.5, 15.6.



***(E)*-2-methyl-3-phenylacrylaldehyde (12)**

Following general procedure A using *(E)*-methyl-2-methyl-3-phenylacrylate (176.2 mg, 1.0 mmol), the reaction was carried out for 19 h. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% Et_2O in Pentane at 30 mL/min). The title compound was obtained as a pale yellow oil (104.1 mg, 71% yield).

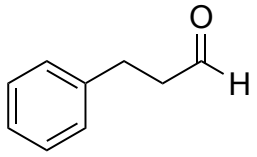
The spectroscopic data for this compound match those previously reported in the literature.[14]
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.57 – 7.50 (m, 2H), 7.49 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 7.28 (br s, 1H), 2.09 (d, J = 1.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 150.0, 138.5, 135.3, 130.2, 129.7, 128.9, 11.1.



2-(1-methyl-1H-indol-3-yl)acetaldehyde (13)

Following general procedure B using methyl *N*-methylindol-3-acetate (99.6 mg, 0.49 mmol) and PMHS (150 µL, 2.5 mmol), the reaction was carried out for 20 h. The crude residue was purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 15% Et_2O in Pentane at 30 mL/min). The title compound was obtained as a viscous, pale yellow oil (48.9 mg, 58% yield).

The spectroscopic data for this compound match those previously reported in the literature.[19, 20]
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 2.5 Hz, 1H), 7.53 (dt, J = 7.9, 1.0 Hz, 1H), 7.35–7.30 (m, 1H), 7.26 (ddd, J = 7.9, 6.8, 1.1 Hz, 1H), 7.14 (ddd, *J* = 8.0, 6.9, 1.1, 1H), 7.00 (s, 1H), 3.79 – 3.78 (m, 2H), 3.77 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 137.2, 128.2, 128.0, 122.2. 119.6, 118.7, 109.6, 104.4, 40.4, 32.9.

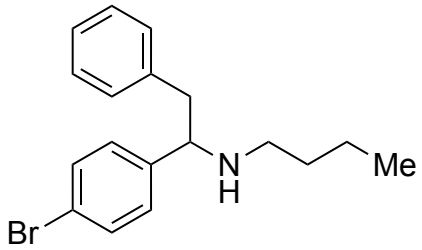


3-Phenyl-propionaldehyde (14)

In a nitrogen-filled glovebox Cp_2ZrCl_2 (29.2 mg, 10.0 mol %) was weighed into a flame dried 20 x 125 mm reaction tube equipped with a magnetic stir bar. Anhydrous PhMe (2.5 mL, 0.4 M) was injected into the reaction tube, followed by the injection of methyl 3-phenylpropionate (164.2 mg, 1.0 mmol), DMMS (733 µL, 6.0 mmol, 6.0 equiv), and *n*-butylamine 395 µL, 4.0 mmol, 4.0 equiv). The mixture was stirred for 3 minutes, then the tube was capped with an open top screw cap equipped with a Teflon-lined silicon septum and removed from the glovebox. The tube was connected to a N_2 flow and left to stir at 80 °C for 20 h. The reaction mixture was then quenched with 10 mL of 4 M HCl, diluted with 20 mL of H_2O, and stirred at room temperature. The solution was diluted with ca. 10 mL of brine and the aqueous layer was extracted with CH_2Cl_2 (ca. 3 x 10 mL). The combined organic washes were dried over Na_2SO_4, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was purified via flash column chromatography (elutes using 5% EtOAc in CH_2Cl_2). The title compound was obtained as a colorless oil (68.6 mg, 51% yield).

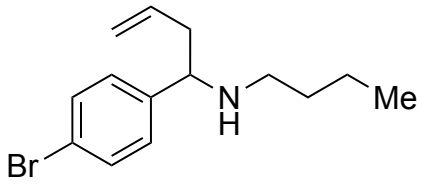
The spectroscopic data for this compound match those previously reported in the literature.[21]
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.83 (t, *J* = 1.4 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.22 – 7.19 (m, 3H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.79 (td, *J* = 7.6 Hz, 1.3 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 201.7, 140.4, 128.7, 128.4, 126.4, 45.4, 28.2.

VII) Characterization Data for Amines 15 & 16 (Table 2b)



15: Cp_2ZrCl_2 (14.6 mg, 5.0 mol %) was weighed into a flame-dried 20 x 125 mm reaction tube equipped with a magnetic stir bar. The reaction tube was capped with an open top screw cap equipped with a Teflon-lined silicon septum and sealed with electrical tape. The reaction tube was then evacuated and backfilled with nitrogen (this process was repeated to a total of three times). The catalyst was dissolved in 2.5 mL of anhydrous PhMe (0.4 M). Ethyl 4-bromo benzoate (163.3 µL, 1.0 mmol) was injected via microsyringe. DEMS (480.6 µL, 3.0 equiv) was injected into the reaction mixture, followed by the injection of *n*-butylamine (168.0 µL, 1.7 equiv) using a Hamilton gastight glass microsyringe. The septum of the reaction tube was sealed with wax and the reaction solution was stirred at 500 rpm at 80 °C. After 21 h, the reaction solution was cooled to 0 °C and diluted with 3.5 mL of anhydrous THF. Benzylmagnesium chloride (2.0 mL [2.0 M solution in THF], 4.0 equiv) was injected dropwise over approx. 5 min. After 40 min, the reaction mixture was warmed to 23 °C. After 5 h, the reaction solution was quenched with 5 mL of 1 M HCl. The aqueous layer was washed three times with ca. 10 mL Et_2O. The combined organic layers were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (10 g cartridge, elutes using 5% EtOAc/1% NEt_3/Hex at 30 mL/min). The desired product **15** was obtained as a pale yellow oil (254.7 mg, 94.3% purity, 72% yield).

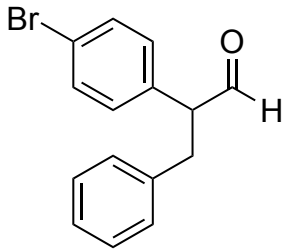
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.28 – 7.24 (m, 2H), 7.23 – 7.16 (m, 3H), 7.10 (d, J = 6.8 Hz, 2H), 3.81 (t, J = 7.1 Hz, 1H), 2.88 (d, J = 5.8 Hz, 2H), 2.41 – 2.29 (m, 2H), 1.34 (d, J = 7.8 Hz, 2H), 1.19 (dpd, J = 14.4, 7.3, 2.2 Hz, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 138.6, 131.5, 129.4, 129.2, 128.6, 126.6, 120.7, 64.5, 47.6, 45.4, 32.3, 20.4, 14.1.
IR (neat): 3027, 2925, 1602, 1484, 1454, 1117, 1070, 1009, 818, 745, 697, 555 cm^{-1}.
LRMS (LC-MS): Calculated for $C_{22}H_{23}BrN$ [M]: 332.28. Found: 332.27.
HRMS (+ESI): Calculated for $C_{22}H_{23}BrN$ $[M + H]^+$: 332.1008, 334.0988. Found: 332.0981, 334.0959.



16: Cp_2ZrCl_2 (14.6 mg, 5.0 mol %) was weighed into a flame-dried 20 x 125 mm reaction tube equipped with a magnetic stir bar. The reaction tube was capped with an open top screw cap equipped with a Teflon-lined silicon septum and sealed with electrical tape. The reaction tube was then evacuated and backfilled with nitrogen (this process was repeated to a total of three times). The catalyst was dissolved in 2.5 mL of anhydrous PhMe (0.4 M). Ethyl 4-bromo benzoate (163.3 µL, 1.0 mmol) was injected via microsyringe. DEMS (480.6 µL, 3.0 equiv) was injected into the reaction mixture, followed by the injection of *n*-butylamine (168.0 µL, 1.7 equiv) using a Hamilton gastight glass microsyringe. The septum of the reaction tube was sealed with wax and the reaction solution was stirred at 500 rpm at 80 °C. After 19.5 h, the reaction solution was cooled to 0 °C and diluted with 3.5 mL of anhydrous THF. Allylmagnesium bromide (4.0 mL [1.0 M solution in Et_2O], 4.0 equiv) was injected dropwise over approx. 5 min. After 45 min, the reaction mixture was warmed to 23 °C. After 5 h, the reaction solution was quenched with 5 mL of 1 M HCl. The aqueous layer was washed three times with ca. 10 mL Et_2O. The combined organic layers were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (10 g cartridge, elutes using 5% EtOAc/1% NEt_3/Hex at 30 mL/min). The desired product **16** was obtained as a pale yellow oil (161.6 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.22 – 7.16 (m, 2H), 5.69 (dddd, *J* = 16.7, 10.2, 7.9, 6.3 Hz, 1H), 5.11 – 5.01 (m, 2H), 3.60 (dd, *J* = 7.6, 5.9 Hz, 1H), 2.43 – 2.26 (m, 4H), 1.41 (p, *J* = 6.8 Hz, 3H), 1.28 (dpd, *J* = 14.2, 7.2, 2.0 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 135.3, 131.5, 129.1, 120.6, 118.0, 62.3, 47.6, 43.2, 32.4, 20.6, 14.1.
IR (neat): 3077, 2956, 2926, 1639, 1485, 1464, 1009, 916, 820 cm^{-1}.
HRMS (+ESI): Calculated for $C_{14}H_{20}BrN$ $[M + H]^+$: 282.0852, 284.0831. Found: 282.0849, 284.0829.

VIII) Characterization Data for Aldehyde 17 (Table 2c)

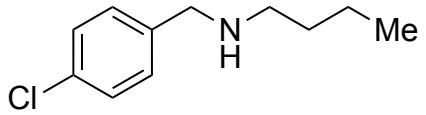


2-(4-bromophenyl)-3-phenylpropanal (17)

The title compound was obtained with slight procedural modification to general procedure B. PhMe (2.5 mL, 0.4 M), piperidine (148.1 µL, 1.5 equiv), methyl 2-(4-bromophenyl)acetate (2a) (229.0 mg, 1.0 mmol), and DEMS (480.6 µL, 3.0 equiv) were stirred at 80 °C for 23 h. Then, the reaction was cooled to 23 °C and benzyl bromide (0.48 mL, 4.0 equiv) was injected dropwise into the reaction tube. The reaction solution was re-heated to 80 °C for 24 hours. Following acidic workup, the crude residue was purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% Et_2O in Hexanes at 30 mL/min). The title compound was obtained as an orange oil (170.2 mg, 59% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.73 (d, *J* = 1.4 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.25 – 7.20 (m, 2H), 7.19 – 7.15 (m, 1H), 7.06 – 7.02 (m, 2H), 7.01 – 6.98 (m, 2H), 3.81 (ddd, *J* = 8.1, 6.4, 1.4 Hz, 1H), 3.45 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.94 (dd, *J* = 14.0, 8.3 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.4, 138.4, 134.8, 132.3, 130.8, 128.6, 129.1, 126.6, 122.0, 60.4, 36.3.
IR (neat): 3027, 2924, 1721, 1487, 1072, 1010, 698, 523 cm^{-1}.
HRMS (-ESI): Calculated for $C_{15}H_{13}BrO$ [M+H]: 289.0223, 291.0202. Found: 289.0058, 291.0202.

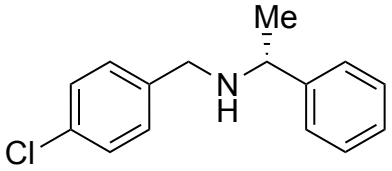
IX) Characterization Data for Amines 18–23 (Table 2d)



***N*-(4-chlorobenzyl)butan-1-amine (18)**

Following general procedure A using methyl 4-chlorobenzoate (170.6 mg, 1.0 mmol), the reaction was carried out for 18 h. The reaction solution was cooled to 0 °C and diluted with MeOH (2.5 mL). $NaBH_4$ (56.7 mg, 1.5 equiv) was added and the reaction solution stirred at 0 °C for 15 min. The mixture was warmed to room temperature, stirred for 15 min, then heated to 65 °C for 4 h [Caution: vigorous gas evolution was observed!]. The solution was cooled to room temperature and quenched with ca. 5 mL of saturated aqueous $NaHCO_3$. The aqueous layer was washed three times with ca. 5 mL Et_2O. The combined organic layers were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% EtOAc/1% NEt_3 in Hexanes at 30 mL/min). The title compound was obtained as a yellow oil (118.7 mg, 60% yield).

The spectroscopic data for this compound match those previously reported in the literature.[22]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 4H), 3.75 (s, 2H), 2.63 – 2.58 (m, 2H), 1.49 (dt, *J* = 14.4, 7.4 Hz, 2H), 1.40 (br s, 1H), 1.35 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2, 132.6, 129.5, 128.6, 53.5, 49.2, 32.3, 20.6, 14.1.



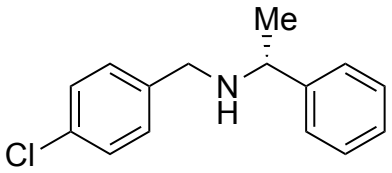
***N*-(4-chlorobenzyl)-1-phenylethanamine (19)**

Following general procedure A using methyl 4-chlorobenzoate (170.6 mg, 1.0 mmol) and (*R)*-1-phenylethanamine (216.4 µL, 1.7 mmol, 1.7 equiv), the reaction was carried out for 21 h. The reaction solution was cooled to 0 °C and diluted with MeOH (2.5 mL). $NaBH_4$ (56.7 mg, 1.5 equiv) was added, and the reaction solution stirred at 0 °C for 15 min. The mixture was warmed to room temperature, stirred for 15 min, then heated to 65 °C for 9 h [Caution: vigorous gas evolution was observed!]. The solution was cooled to room temperature and quenched with ca. 5 mL of saturated aqueous $NaHCO_3$. The aqueous layer was washed three times with ca. 5 mL Et_2O. The combined organic layers were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 10% EtOAc/1% NEt_3 in Hexanes at 30 mL/min). The title compound was obtained as a pale yellow oil (141.8 mg, 58% yield).

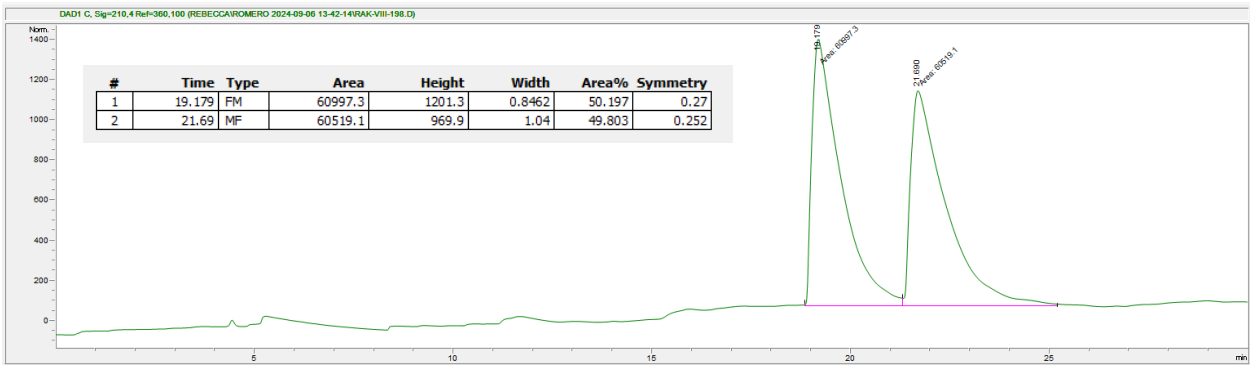
The spectroscopic data for this compound match those previously reported in the literature.[22]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 4H), 7.21 – 7.16 (m, 3H), 7.14 (app d, J = 8.3 Hz, 2H), 3.70 (q, J = 6.6 Hz, 1H), 3.57 – 3.44 (m, 2H), 1.50 (br s, 1H), 1.29 (d, J = 6.6, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 139.3, 132.6, 129.6, 128.6, 128.6. 127.1, 126.8, 57.6, 51.0, 24.6.
HPLC: Chiralcel OJ-H column (Hexane/*i*-PrOH 98/2, flow rate 0.7 mL/min, 5.00 µL injection, λ = 210 nm), t_R = 21.77 min.

Synthesis of ***rac*-19**: A flame-dried 50 mL 2-neck round bottom flask was equipped with a magnetic stir. The flask was charged with 4 Å molecular sieves (2.0 g) and 4-chlorobenzaldehyde (0.70 g, 5.0 mmol, 1.0 equiv) The flask and reflux apparatus were evacuated and backfilled with nitrogen (this process was repeated to a total of three times). PhMe (5.0 mL, 1.0 M) and rac-1-phenylethanamine (0.97 mL, 7.5 mL, 1.5 equiv) were injected and the reaction solution was heated to 65 °C for 19 h. Once the reaction was complete, the reaction solution was filtered over a pad of celite and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was added to a flame-dried 50 mL 2-neck round bottom flask equipped with a magnetic stir bar. MeOH (10.0 mL, 0.05 M) was injected into the flask and the solution was cooled to 0 °C. $NaBH_4$ (226.8 mg, 6.0 mmol, 1.2 equiv) was added to the flask. The reaction solution stirred at 0 °C for 15 min. The mixture was warmed to room temperature, stirred for 15 min, then heated to 50 °C for 9 h [Caution: vigorous gas evolution was observed!]. The solution was cooled to room temperature and quenched with ca. 10 mL of saturated aqueous $NaHCO_3$. The aqueous layer was washed three times with ca. 10 mL Et_2O. The combined organic layers were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 10% EtOAc/1% NEt_3 in Hexanes at 30 mL/min). The title compound was obtained as a colorless oil.

HPLC: Chiralcel OJ-H column (Hexane/*i*-PrOH 98:02, flow rate 0.7 mL/min, 5.00 µL injection, λ = 210 nm), t_R (left) = 19.18, t_R (right) = 21.70 min.

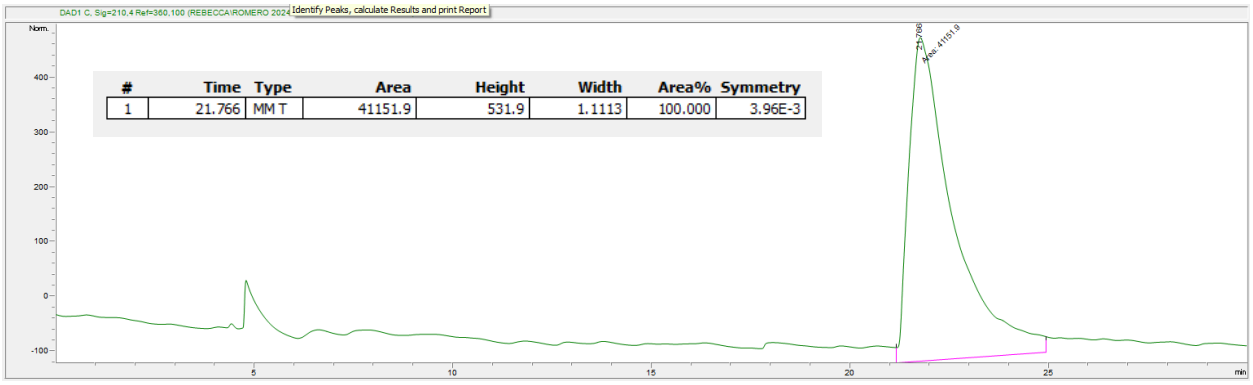


HPLC trace *rac*-19: Racemic, OJ-H column (Hexane/*i*-PrOH 98/2, flow rate 0.7 mL/min, 5.00 µL injection, λ = 210 nm), t_R (left) = 19.18, t_R (right) = 21.69 min.

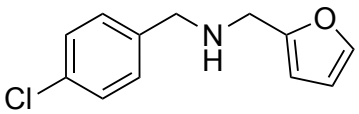


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.179	FM	60997.3	1201.3	0.8462	50.197	0.27
2	21.69	MF	60519.1	969.9	1.04	49.803	0.252

HPLC trace (*R*)-19: Single enantiomer, OJ-H column (Hexane/*i*-PrOH 98/2, flow rate 0.7 mL/min, 5.00 µL injection, λ = 210 nm), t_R = 21.77 min.



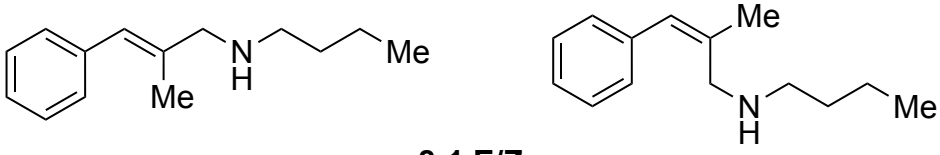
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.766	MM T	41151.9	531.9	1.1113	100.000	3.96E-3



***N*-(4-chlorobenzyl)-1-(furan-2-yl)methanamine (20)**

Following general procedure A using methyl 4-chlorobenzoate (170.6 mg, 1.0 mmol) and furfurylamine (157.2 µL, 1.7 mmol, 1.7 equiv) in lieu of *n*-butylamine, the reaction was carried out for 21 h. The reaction solution was cooled to 0 °C and diluted with MeOH (2.5 mL). $NaBH_4$ (56.7 mg, 1.5 equiv) was added and the reaction solution stirred at 0 °C for 15 min. The mixture was warmed to room temperature, stirred for 15 min, then heated to 65 °C for 4 h [Caution: vigorous gas evolution was observed!]. The solution was cooled to room temperature and quenched with ca. 5 mL of saturated aqueous $NaHCO_3$. The aqueous layer was washed three times with ca. 5 mL Et_2O. The combined organic layers were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5→10% EtOAc/1% NEt_3 in Hexanes at 30 mL/min). The title compound was obtained as a yellow oil (142.7 mg, 64% yield).

The spectroscopic data for this compound match those previously reported in the literature.[23]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.29 – 7.22 (m, 4H), 6.30 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.15 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.74 (s, 2H), 3.73 (s, 2H), 1.71 (br s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 142.0, 138.5, 132.8, 129.7, 128.6, 110.3, 107.3, 52.1, 45.4.



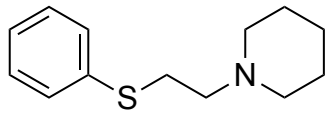
8:1 E/Z
***N*-butyl-*N*-[(*2E*)-2-methyl-3-phenylprop-2-enyl]amine (21)**
& *N*-butyl-*N*-[(*2Z*)-2-methyl-3-phenylprop-2-enyl]amine

Following general procedure A using methyl 3-methyl-3-phenylacrylate (88.1 mg, 0.5 mmol), the reaction was carried out for 20 h. The reaction solution was cooled to 0 °C and diluted with MeOH (2.5 mL). $NaBH_4$ (56.7 mg, 3.0 equiv) was added and the reaction solution stirred at 0 °C for 15 min. The mixture was warmed to room temperature, stirred for 15 min, then heated to 65 °C for 4 h [Caution: vigorous gas evolution was observed!]. The solution was cooled to room temperature and quenched with ca. 5 mL of saturated aqueous $NaHCO_3$. The aqueous layer was washed three times with ca. 5 mL Et_2O. The combined organic layers were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% EtOAc/1% NEt_3 in Hexanes at 30 mL/min). The title compound was obtained as a yellow oil (72.9 mg, 72% yield).

The spectroscopic data for *(E)*-**21** match those previously reported in the literature.[24a]
(Z)-**21** was assigned by analogy to *N*-**propyl**-*N*-[*(2E)*-2-methyl-3-phenylprop-2-enyl]amine.[24b]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.18 (m, 1H), 6.44 (s, 0.8 H), 6.42 (s, 0.2 H), 3.38 (s, 0.2H), 3.33 (s, 1.8H), 2.64 (t, *J* = 7.3, 1.8H), 2.54 (t, *J* =

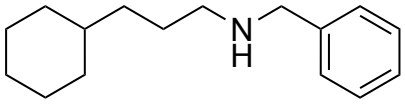
7.2 Hz, 0.2H), 1.95 (d, *J* = 1.6 Hz, 0.3H), 1.90 (d, *J* = 1.5 Hz, 2.6H), 1.56 – 1.48 (m, 2H), 1.45 – 1.29 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 2.6H), 0.89 (t, *J* = 7.3 Hz, 0.4H).
^{13}C NMR *trans* (major) (151 MHz, $CDCl_3$) δ 138.2, 137.3, 129.0, 128.2, 126.2, 125.6, 58.3, 49.1, 32.4, 20.7, 16.7, 14.2.
^{13}C NMR *cis* (minor) (151 MHz, $CDCl_3$) δ 138.0, 137.6, 128.8, 128.2, 127.9, 126.3, 50.6, 49.3, 32.3, 23.0, 20.6, 14.1.
HRMS (+ESI): Calculated for $C_{14}H_{21}N$ [M+H]: 204.1747. Found: 204.1724.
LRMS (GC-MS): Calculated for $C_{14}H_{21}N$: 203.17. Found: 203.15 (peak 1) and 203.15 (peak 2).



1-[2-(phenylthiol)ethyl]piperidine (22)

Following general procedure B using Methyl 2-(phenylthiol)acetate (182.2 mg, 1.0 mmol), the reaction was carried out for 24 h. The reaction solution was cooled to 0 °C and diluted with MeOH (2.5 mL). $NaBH_4$ (113.5 mg, 3.0 equiv) was added and the reaction solution stirred at 0 °C for 15 min. The mixture was warmed to room temperature, stirred for 15 min, then heated to 65 °C for 9 h. The solution was cooled to room temperature and quenched with ca. 5 mL of saturated aqueous $NaHCO_3$. The aqueous layer was washed three times with ca. 5 mL Et_2O. The combined organic layers were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% EtOAc/1% NEt_3 in Hexanes at 30 mL/min). The title compound was obtained as a yellow oil (144.3 mg, 65% yield).

The spectroscopic data for this compound are in good agreement with those previously reported in the literature.[25]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.23 – 7.17 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.04 – 2.95 (m, 2H), 2.58 – 2.49 (m, 2H), 2.35 (br s, 4H), 1.51 (p, *J* = 5.6 Hz, 4H), 1.34 – 1.38 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 136.7, 129.0, 129.0, 125.9, 58.6, 54.6, 30.8, 26.0, 24.4.
IR (neat): 2932, 2757, 1584, 1480, 1439, 1104, 735, 689, 474 cm^{-1}.
HRMS (+ESI): Calculated for $C_{13}H_{19}NS$ [M+H]: 222.1311. Found: 222.1295.



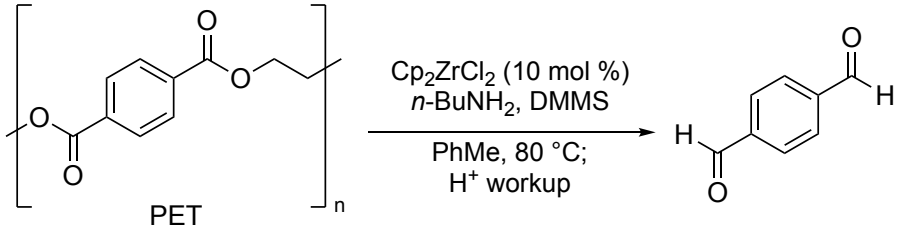
_N_-benzyl-3-cyclohexylpropylamine (23)

Amine **22** was obtained following general procedure A with the following modifications: using methyl 3-cyclohexylpropionate (170.3 mg, 1.0 mmol), *N*-benzylamine (327.7 μL, 3.0 equiv), and DMMS (0.74 mL, 6.0 equiv), the reaction was carried out for 22 h. The reaction solution was cooled to 0 °C and diluted with MeOH (2.5 mL). $NaBH_4$ (113.5 mg, 3.0 equiv) was added and the reaction solution stirred at 0 °C for 15 min. The mixture was warmed to room temperature, stirred for 15 min, then heated to 65 °C for 4 h. The solution was cooled to room temperature and quenched with ca. 5 mL of saturated aqueous $NaHCO_3$. The aqueous layer was washed three times with ca. 5 mL Et_2O. The combined organic layers were dried over $MgSO_4$, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was then purified with the aid of CombiFlash Nextgen 300 (12 g gold cartridge, elutes using 5% EtOAc/1% NEt_3 in Hexanes at 30 mL/min). The title compound was obtained as a viscous, pale yellow oil (169.9 mg, contaminated with ca. 3% *N,N*-dibenzylamine, 71% yield).

The spectroscopic data for this compound match those previously reported in the literature.[25]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 4H), 7.27 – 7.24 (m, 1H), 3.80 (s, 2H), 2.61 (t, *J* = 7.3 Hz, 2H), 1.87 (br s, 1H), 1.74 – 1.65 (m, 4H), 1.65 – 1.61 (m, 1H), 1.55 – 1.50 (m, 2H), 1.28 – 1.17 (m, 5H), 1.17 – 1.09 (m, 1H), 0.92 – 0.82 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 140.3, 128.5, 128.3, 127.1, 54.1, 49.9, 37.7, 35.2, 33.5, 27.4, 26.8, 26.5.

X) Depolymerization Reaction and Characterization Data (Scheme 2)



Synthesis of aldehyde 24 using a clear plastic bottle: The polyester (PET) starting material from a water bottle was cut into small pieces and ground with dry ice using an electrical grinder. The ground PET was then rinsed with acetone and dried under high vacuum at room temperature overnight. A 25 mL Schlenk flask with a magnetic stirring bar was dried in an oven (140 °C) overnight and then transferred into a glovebox with a stopper. PET (192.2 mg, ca. 1.0 mmol, 1.0 equiv), Cp_2ZrCl_2 (29.2 mg, 0.1 mmol, 0.1 equiv, 15.2 weight %) and PhMe (10 mL, 0.1 M) were added to the flask. DMMS (1.46 mL, 12.0 mmol, 12.0 equiv, 6.6 weight equiv) and *n*-butylamine (791 µL, 8.0 mmol, 8.0 equiv, 3.0 weight equiv) were slowly added to the mixture with stirring [gas evolution was observed]. The solution was left to stir for approx. 5 minutes until no obvious bubbles were observed. The flask was then sealed with a stopper and removed from the glovebox. It was connected to N_2 flow and stirred at 80 °C for 20 hours. After cooling to room temperature, the reaction solution was transferred to a 100 mL round bottom flask and rinsed with CH_2Cl_2. The solvents were evaporated *in vacuo*. The mixture was diluted with approx. 10 mL 4 M HCl and approx. 20 mL H_2O and stirred at room temperature. The mixture was diluted with brine and extracted with DCM (3 x 10 mL). The organic layer was collected and dried with anhydrous $MgSO_4$, followed by concentration *in vacuo* using a rotary evaporator. The crude residue was purified via silica gel chromatography (elutes using a 20% EtOAc/Hexane eluent). The dialdehyde was isolated as a white powder (111.3 mg, 83% yield).

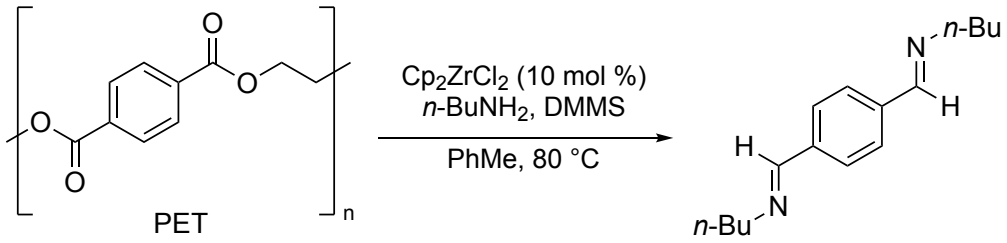
The spectroscopic data for this compound match those previously reported in the literature.[26]
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.14 (s, 2H), 8.06 (s, 4H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 191.6, 140.2, 130.3.

Synthesis of aldehyde 24 using a green beverage bottle: The polyester (PET) starting material from a green plastic bottle was cut into small pieces and ground with dry ice using an electrical grinder. The ground PET was then rinsed with acetone and dried under high vacuum at room temperature overnight. A 25 mL Schlenk flask with a magnetic stirring bar was dried in an oven (140 °C) overnight and then transferred into a glovebox with a stopper. PET (192.2 mg, ca. 1.0 mmol, 1.0 equiv), Cp_2ZrCl_2 (29.2 mg, 0.1 mmol, 0.1 equiv, 15.2 weight %) and PhMe (10 mL, 0.1 M) were added to the flask. DMMS (1.46 mL, 12.0 mmol, 12.0 equiv, 6.6 weight equiv) and *n*-butylamine (791 µL, 8.0 mmol, 8.0 equiv, 3.0 weight equiv) were slowly added to the mixture with stirring [gas evolution was observed]. The solution was left to stir for approx. 5 minutes until no obvious bubbles were observed. The flask was then sealed with a stopper and removed from the glovebox. It was connected to N_2 flow and stirred at 80 °C for 20 hours. After cooling to room temperature, the reaction solution was transferred to a 100 mL round bottom flask and rinsed with CH_2Cl_2. The solvents were evaporated *in vacuo*. The mixture was diluted with approx. 10 mL 4 M HCl and approx. 20 mL H_2O and stirred at room temperature. The mixture was diluted with

brine and extracted with DCM (3 x 10 mL). The organic layer was collected and dried with anhydrous $MgSO_4$, followed by concentration *in vacuo* using a rotary evaporator. The crude residue was purified via silica gel chromatography (elutes using a 20% EtOAc/Hexane eluent). The dialdehyde was rinsed with hexane and isolated as a white powder (85.4 mg, 64% yield).

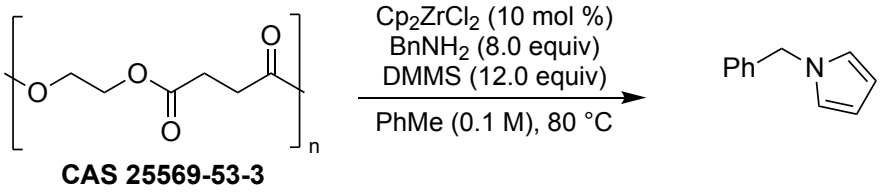
Synthesis of aldehyde 24 using a polyester T-shirt: The polyester (PET) fabric starting material from a T-shirt was cut into small pieces and ground with dry ice using an electrical grinder. The ground PET was then rinsed with acetone and dried under high vacuum at room temperature overnight. A 100 mL Schlenk flask with a magnetic stirring bar was dried in an oven (140 °C) overnight and then transferred into a glovebox with a stopper. PET (192.2 mg, ca. 1.0 mmol, 1.0 equiv), Cp_2ZrCl_2 (29.2 mg, 0.1 mmol, 0.1 equiv, 15.2 weight %) and PhMe (10 mL, 0.1 M) were added to the flask. DMMS (1.46 mL, 12.0 mmol, 12.0 equiv, 6.6 weight equiv) and *n*-butylamine (791 µL, 8.0 mmol, 8.0 equiv, 3.0 weight equiv) were slowly added to the mixture with stirring [gas evolution was observed]. The solution was left to stir for 5 minutes until no obvious bubbles were observed. The flask was then sealed with a stopper and removed from the glovebox. It was connected to N_2 flow and stirred at 80 °C for 20 hours. After cooling to room temperature, the reaction solution was quenched with approx. 10 mL 4 M HCl and approx. 20 mL H_2O and stirred at room temperature. The mixture was diluted with brine and extracted with DCM (3 x 10 mL). The organic layer was collected and dried with anhydrous $MgSO_4$, followed by concentration *in vacuo* using a rotary evaporator. The crude residue was purified via silica gel chromatography (elutes using a 20% EtOAc/Hexane eluent). The dialdehyde was isolated as a white powder (122.0 mg, 91% yield).

Synthesis of aldehyde 24 using a laptop screen protector: The polyester (PET) fabric starting material from screen protector was cut into small pieces and ground with dry ice using an electrical grinder. The ground PET was then rinsed with acetone and dried under high vacuum at room temperature overnight. A 100 mL Schlenk flask with a magnetic stirring bar was dried in an oven (140 °C) overnight and then transferred into a glovebox with a stopper. PET (192.2 mg, ca. 1.0 mmol, 1.0 equiv), Cp_2ZrCl_2 (29.2 mg, 0.1 mmol, 0.1 equiv, 15.2 weight %) and PhMe (10 mL, 0.1 M) were added to the flask. DMMS (1.46 mL, 12.0 mmol, 12.0 equiv, 6.6 weight equiv) and *n*-butylamine (791 µL, 8.0 mmol, 8.0 equiv, 3.0 weight equiv) were slowly added to the mixture with stirring [gas evolution was observed]. The solution was left to stir for 5 minutes until no obvious bubbles were observed. The flask was then sealed with a stopper and removed from the glovebox. It was connected to N_2 flow and stirred at 80 °C for 20 hours. After cooling to room temperature, the reaction solution was transferred to a 100 mL round bottom flask and rinsed with CH_2Cl_2. The solvents were evaporated *in vacuo*. The mixture was diluted with approx. 10 mL 4 M HCl and approx. 20 mL H_2O and stirred at room temperature. The mixture was diluted with brine and extracted with DCM (3 x 10 mL). The organic layer was collected and dried with anhydrous $MgSO_4$, followed by concentration *in vacuo* using a rotary evaporator. The crude residue was purified via silica gel chromatography (elutes using a 20% EtOAc/Hexane eluent). The dialdehyde was rinsed with hexane and isolated as a white powder (65.4 mg, 48% yield).



Synthesis of diimine 25 using a clear plastic bottle: The polyester (PET) starting material from a water bottle was cut into small pieces and ground with dry ice using an electrical grinder. The ground PET was then rinsed with acetone and dried under high vacuum at room temperature overnight. A 25 mL Schlenk flask with a magnetic stirring bar was dried in an oven (140 °C) overnight and then transferred into a glovebox with a stopper. PET (192.2 mg, ca. 1.0 mmol, 1.0 equiv), Cp_2ZrCl_2 (29.2 mg, 0.1 mmol, 0.1 equiv, 15.2 weight %) and PhMe (10 mL, 0.1 M) were added to the flask. DMMS (1.46 mL, 12.0 mmol, 12.0 equiv, 6.6 weight equiv) and *n*-butylamine (791 µL, 8.0 mmol, 8.0 equiv, 3.0 weight equiv) were slowly added to the mixture with stirring [gas evolution was observed]. The solution was left to stir for approx. 5 minutes until no obvious bubbles were observed. The flask was then sealed with a stopper and removed from the glovebox. It was connected to N_2 flow and stirred at 80 °C for 20 hours. After cooling to room temperature, the reaction solution was directly purified via flash column chromatography using activated aluminum oxide (neutral, Brockmann Grade I, 58 angstroms) (elutes using 5% EtOAc/ 1% NEt_3 in Hex). The title compound was obtained as a colorless oil (134 mg, 55% yield).

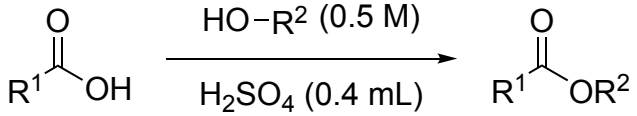
The spectroscopic data for this compound match those previously reported in the literature.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 2H), 7.75 (s, 4H), 3.62 (td, *J* = 7.0, 1.3 Hz, 4H), 1.73 – 1.65 (m, 4H), 1.39 (sex, *J* = 7.4 Hz, 4H), 0.98 – 0.91 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3, 138.2, 128.3, 61.7, 33.1, 20.6, 14.0.



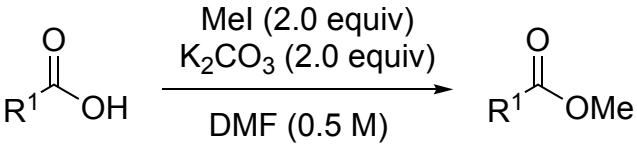
Synthesis of pyrrole 26: A 25 mL Schlenk flask with a magnetic stirring bar was dried in an oven (140 °C) overnight and then transferred into a glovebox with a stopper. Poly(ethylene succinate) (144 mg, ca. 1.0 mmol, 1.0 equiv), Cp_2ZrCl_2 (29.2 mg, 0.1 mmol, 0.1 equiv, 20.3 weight %) and PhMe (10 mL, 0.1 M) were added to the flask. DMMS (1.46 mL, 12.0 mmol, 12.0 equiv, 8.8 weight equiv) and *N*-benzylamine (874 µL, 8.0 mmol, 8.0 equiv, 6.0 weight equiv) were slowly added to the mixture with stirring [gas evolution was observed]. The solution was left to stir for 5 to 10 minutes until no obvious bubbles were observed. The flask was then sealed with a stopper and removed from the glovebox. It was connected to N_2 flow and stirred at 80 °C for 20 hours. The reaction solution was cooled to room temperature and directly concentrated *in vacuo*. The product was obtained by silica gel chromatography (flushed with ca. 100 mL 100% Hex, then elutes using a 5% EtOAc/Hexane eluent). The *N*-benzylpyrrole was isolated as a colorless oil (134.4 mg, 85% yield).

The spectroscopic data for this compound match those previously reported in the literature.[27]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.14 (d, J = 7.4 Hz, 2H), 6.72 – 6.71 (m, 2H), 6.24 – 6.20 (m, 2H), 5.09 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 128.8, 127.8, 127.1, 121.3, 108.6, 53.5.

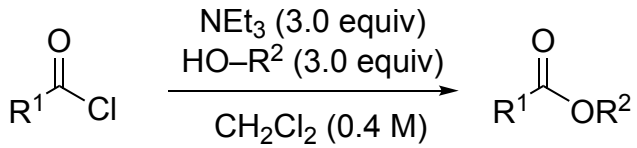
XI) Preparation of Starting Materials



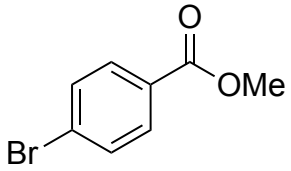
Starting Material General Procedure A: A flame-dried 50 mL 2-neck round bottom flask was equipped with a magnetic stir bar and reflux apparatus. The carboxylic acid (10.0 mmol) was added to the flask. The flask and reflux apparatus were evacuated and backfilled with nitrogen (this process was repeated to a total of three times). The alcohol (20 mL, 0.5 M) and H_2SO_4 (0.4 mL) were injected and the reaction solution was heated to reflux for 18–24 h. Once the reaction was complete, the reaction solution was quenched with H_2O (approx. 10 mL) and diluted with CH_2Cl_2 (approx. 10 mL). The aqueous layer was washed three times with CH_2Cl_2, dried over Na_2SO_4, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was purified by automated column chromatography to afford the desired ester.



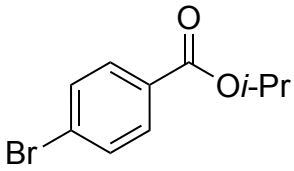
Starting Material General Procedure B: A flame-dried 50 mL 2-neck round bottom flask equipped with a magnetic stir bar was charged with carboxylic acid (10.0 mmol). The flask was evacuated and backfilled with nitrogen (this process was repeated to a total of three times). DMF (0.5 M), was injected into the flask. K_2CO_3 (2.0 equiv) was added to the flask, followed by the dropwise addition of MeI (2.0 equiv). The reaction was left to stir at room temperature. Once the reaction was complete, the reaction solution was quenched with H_2O (approx. 10 mL) and diluted with EtOAc (approx. 10 mL). The aqueous layer was washed with EtOAc, dried over Na_2SO_4, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was purified by automated column chromatography to afford the desired ester.



Starting Material General Procedure C: A flame-dried 50 mL round bottom flask was equipped with a magnetic stir bar. CH_2Cl_2 (0.4 M) was injected into the flask, followed by the injection of the alcohol (3.0 equiv). NEt_3 (3.0 equiv) was added to the flask, followed by the dropwise or portionwise addition of acid chloride (1.0 equiv). The reaction was left to stir at room temperature. Once the reaction was complete, the reaction solution was quenched with H_2O (approx. 10 mL) and diluted with CH_2Cl_2 (approx. 10 mL). The aqueous layer was washed with CH_2Cl_2, dried over Na_2SO_4, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was purified by automated column chromatography to afford the desired ester.

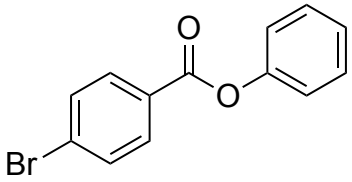


(1d) Methyl 4-bromobenzoate was obtained following the Starting Material General Procedure C. The spectroscopic data for this compound match those previously reported in the literature.[28]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.61 – 7.54 (m, 2H), 3.91 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 131.9, 131.3, 129.2, 128.2, 52.4.



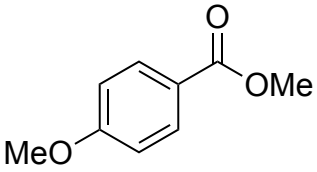
(1f) Isopropyl 4-bromobenzoate was obtained following the Starting Material General Procedure C. The spectroscopic data for this compound match those previously reported in the literature.[29]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.59 – 7.52 (m, 2H), 5.24 (hept, J = 6.3 Hz, 1H), 1.36 (d, J = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 131.7, 131.2, 129.9, 127.9, 68.9, 22.0.



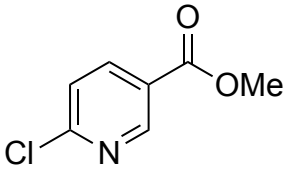
(1g) Phenyl 4-bromobenzoate was obtained following the Starting Material General Procedure C. The spectroscopic data for this compound match those previously reported in the literature.[30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.7 Hz, 2H), 7.70 – 7.63 (m, 2H), 7.48 – 7.39 (m, 2H), 7.32 – 7.26 (m, 1H), 7.24 – 7.17 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 150.9, 132.1, 131.8, 129.7, 129.0, 128.6, 126.2, 121.8.



Methyl 4-methoxybenzoate was obtained following the Starting Material General Procedure C. The spectroscopic data for this compound match those previously reported in the literature.[28]

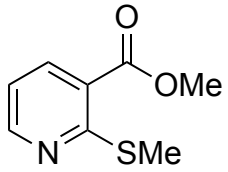
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 6.94 – 6.90 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 163.5, 135.5, 131.7, 122.8, 113.8, 55.6, 52.0.



Methyl 6-chloronicotinate was obtained following the Starting Material General Procedure B. The spectroscopic data for this compound match those previously reported in the literature.[31]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 1.7 Hz, 1H), 8.24 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.42 (d, *J* = 9.2 Hz, 1H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 155.8, 151.3, 139.7, 125.1, 124.3, 52.8.



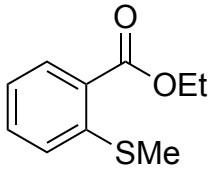
Methyl 2-(methylthio)nicotinate was obtained following the Starting Material General Procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.20 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.04 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.92 (s, 3H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 163.0, 152.1, 138.8, 123.0, 118.0, 52.4, 14.0.

IR (neat): 1711, 1553, 1277, 1233, 1129, 1057, 766 cm^{-1}.

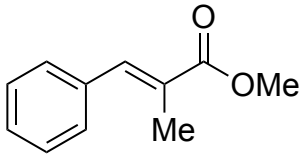
HRMS: Calculated for $C_8H_9NO_2S$ $[M + H]^+$: 184.0427. Found: 184.0407.



Ethyl 2-thiomethylbenzoate was obtained following the Starting Material General Procedure C. The spectroscopic data for this compound match those previously reported in the literature.[32]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.45 (ddd, *J* = 8.9, 7.3, 1.5 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.16 – 7.11 (m, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H).

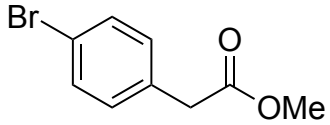
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 143.3, 132.5, 131.4, 127.3, 124.5, 123.5, 61.1, 15.7, 14.4.



Methyl 3-methyl-3-phenylacrylate was obtained following the Starting Material General Procedure C. The spectroscopic data for this compound match those previously reported in the literature.[33]

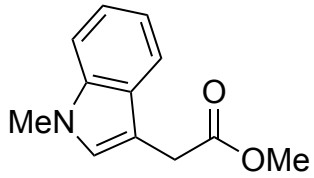
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.5 Hz, 1H), 7.40 (d, *J* = 4.5 Hz, 4H), 7.34 – 7.31 (m, 1H), 3.82 (s, 3H), 2.13 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 129.8, 128.5, 128.5, 52.2, 46.4, 14.2.



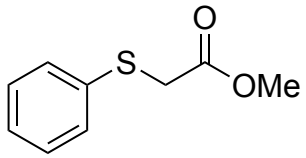
Methyl 2-(4-bromophenyl)acetate was obtained following the Starting Material General Procedure A. The spectroscopic data for this compound match those previously reported in the literature.[34]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.18 – 7.14 (m, 2H), 3.69 (s, 3H), 3.58 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 133.0, 131.8, 131.1, 121.3, 52.2, 40.6.

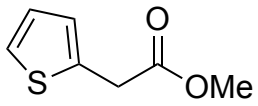


Methyl inodol-3-acetate was obtained following the Starting Material General Procedure A. Then, a 25 mL round-bottom flask was charged with NaH (2.0 equiv). Methyl inodol-3-acetate (1.0 equiv) was prepared as a solution in DMF (0.24 M). The solution was added dropwise to the round-bottom flask at 0 °C. After approx. 15 min, MeI (1.4 equiv) was added dropwise to the reaction solution. The solution was warmed to room temperature and left to stir. Upon completion by TLC, the reaction solution was quenched with H_2O (approx. 10 mL) and diluted with CH_2Cl_2 (approx. 10 mL). The aqueous layer was washed with CH_2Cl_2, dried over Na_2SO_4, vacuum filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude residue was purified by automated column chromatography to afford methyl-indole-(*N*-methyl)3-acetate. The spectroscopic data for this compound match those previously reported in the literature.[35]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.9 Hz, 1H), 7.52 (d, J = 8.2, Hz, 1H), 7.47 (s, 1H), 7.46 – 7.42 (m, 1H), 7.35 (t, J = 7.7 Hz, 1H), 3.99 (s, 2H), 3.98 (s, 3H), 3.92 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 137.0, 127.9, 127.8, 121.9, 119.3, 119.1, 109.4, 106.9, 52.1, 32.8, 31.2.



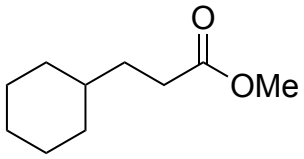
Methyl 2-(phenylthiol)acetate was obtained following the Starting Material General Procedure A. The spectroscopic data for this compound match those previously reported in the literature.[36]
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 3.72 (s, 3H), 3.66 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 135.0, 130.0, 129.2, 127.1, 52.7, 36.6.



Methyl 2-thienylacetate was obtained following the Starting Material General Procedure A. The spectroscopic data for this compound match those previously reported in the literature.[37]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, J = 5.1, 1.4 Hz, 1H), 6.97 – 6.93 (m, 2H), 3.85 (d, J = 0.9 Hz, 2H), 3.73 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.08, 135.12, 126.99, 126.96, 125.19, 52.41, 35.35.

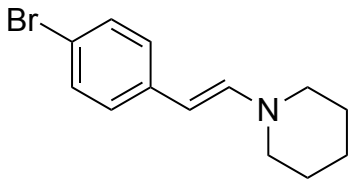


Methyl 3-cyclohexylpropionate was obtained following the Starting Material General Procedure C. The spectroscopic data for this compound match those previously reported in the literature.[38]

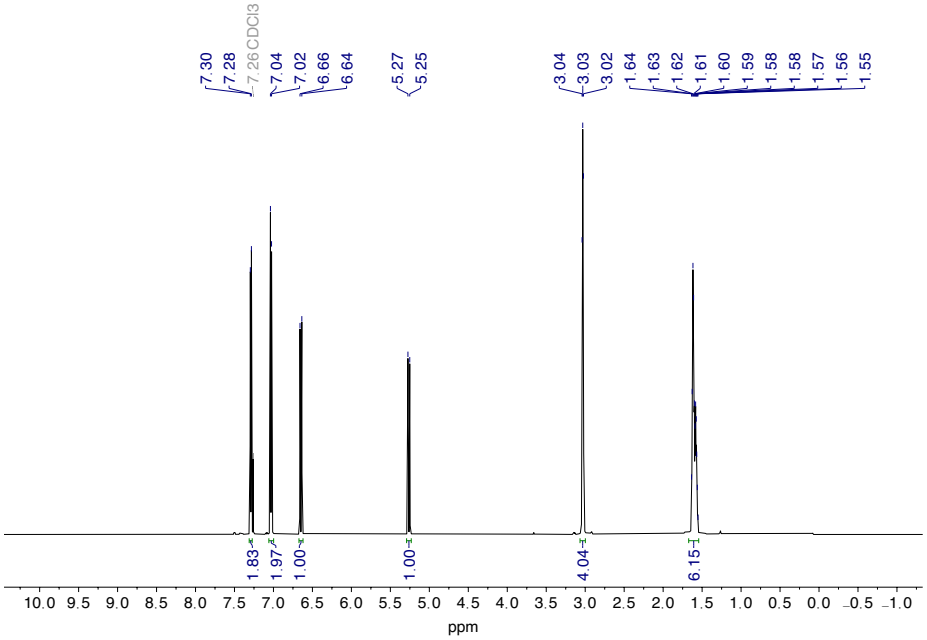
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.34 – 2.27 (m, 2H), 1.69 (d, *J* = 10.8 Hz, 4H), 1.64 (d, *J* = 12.2 Hz, 1H), 1.52 (q, *J* = 7.7 Hz, 2H), 1.26 – 1.18 (m, 3H), 1.18 – 1.09 (m, 1H), 0.93 – 0.83 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 51.6, 37.4, 33.1, 32.5, 31.8, 26.7, 26.4.

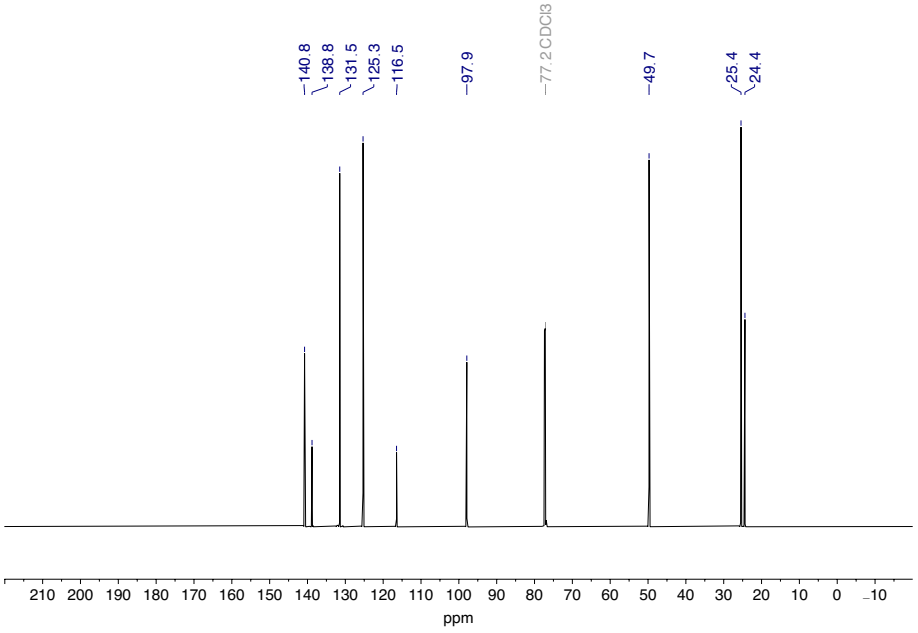
XII) NMR Spectra

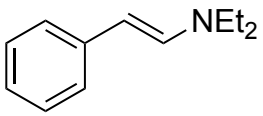


(4a) ^{1}H NMR (600 MHz, $CDCl_3$)

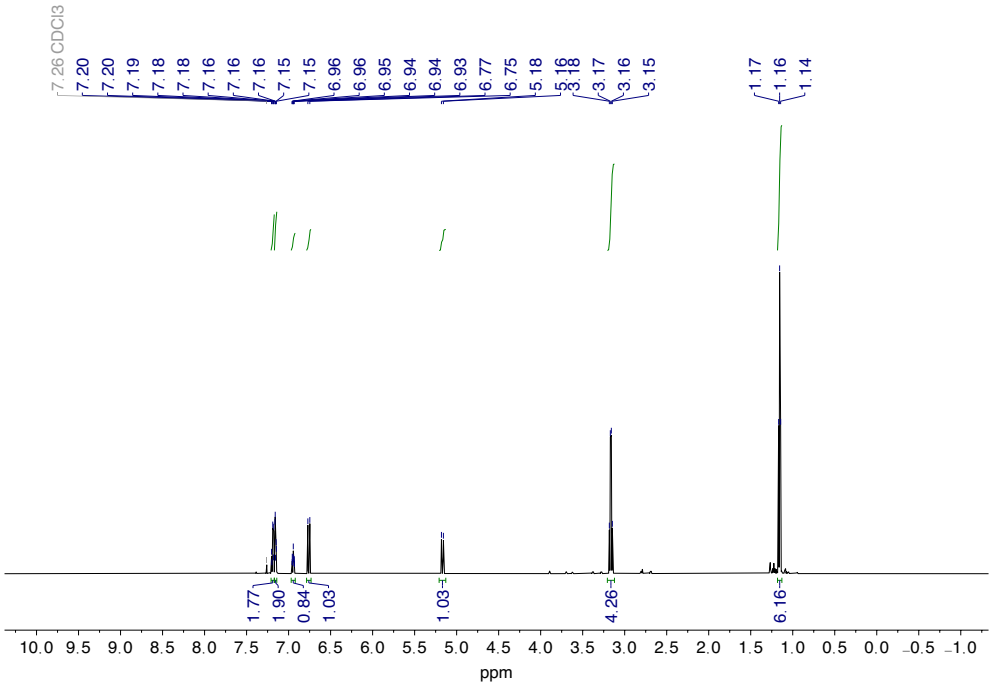


(4a) ^{13}C NMR (151 MHz, $CDCl_3$)

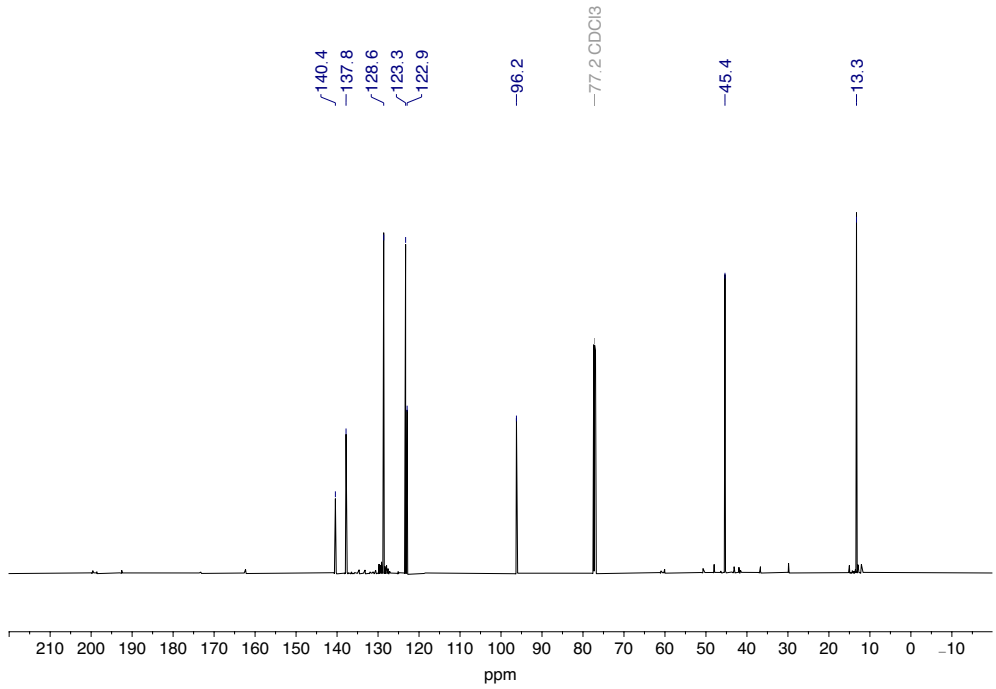


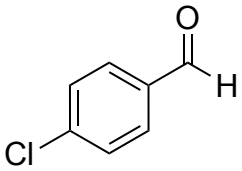


(4e) ^{1}H NMR (600 MHz, $CDCl_3$)

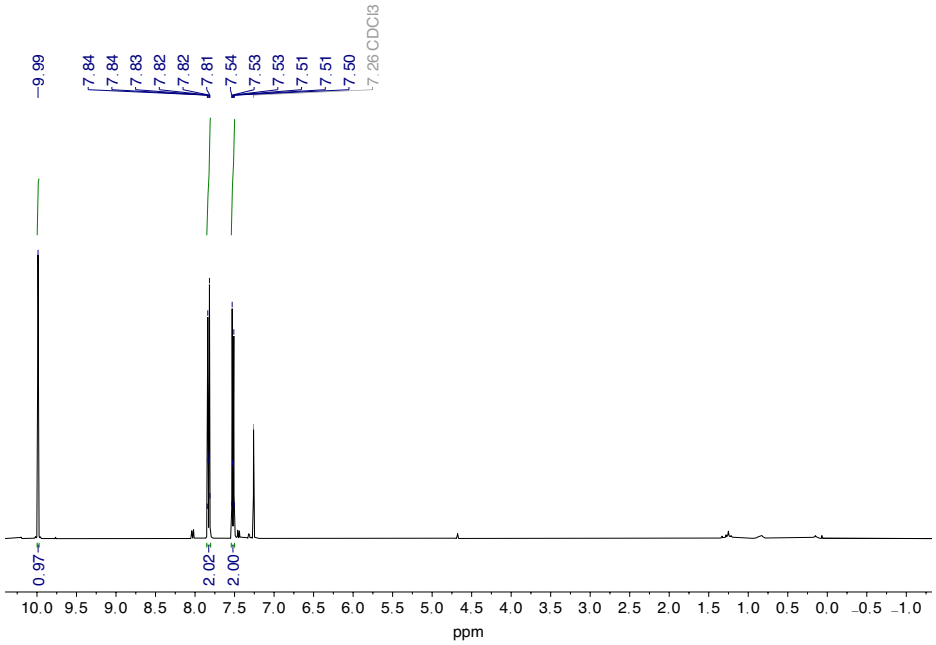


(4e) ^{13}C NMR (151 MHz, $CDCl_3$)

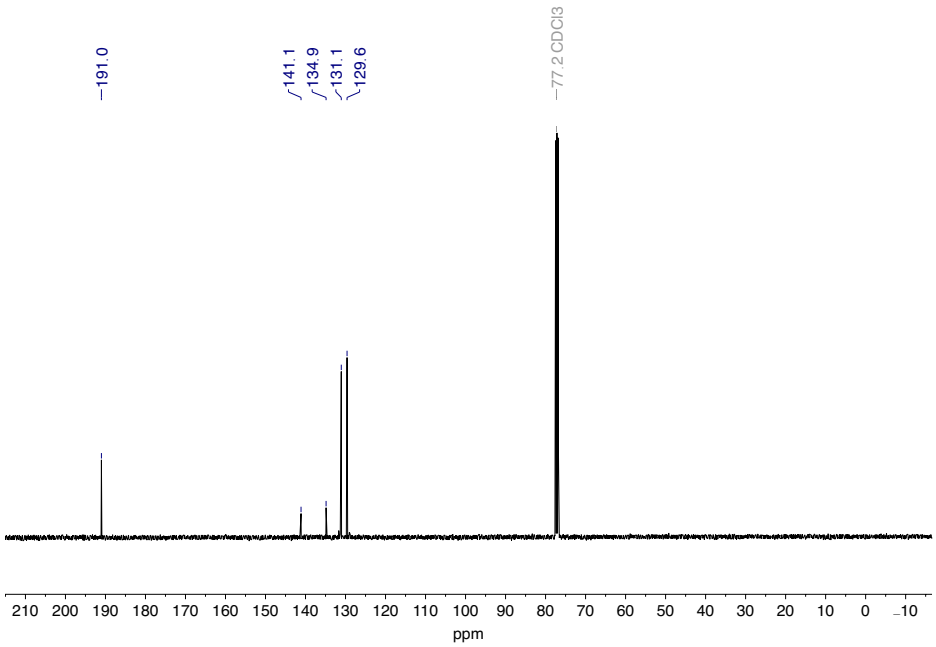


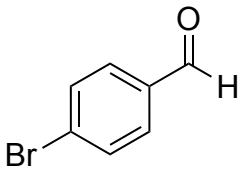


(5) ^{1}H NMR (400 MHz, $CDCl_3$)

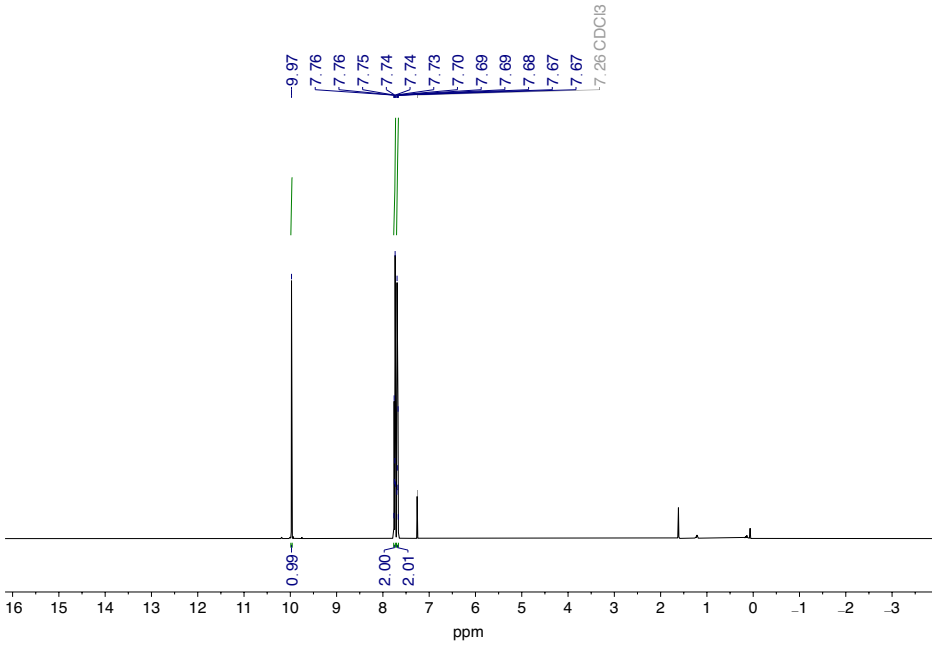


(5) ^{13}C NMR (101 MHz, $CDCl_3$)

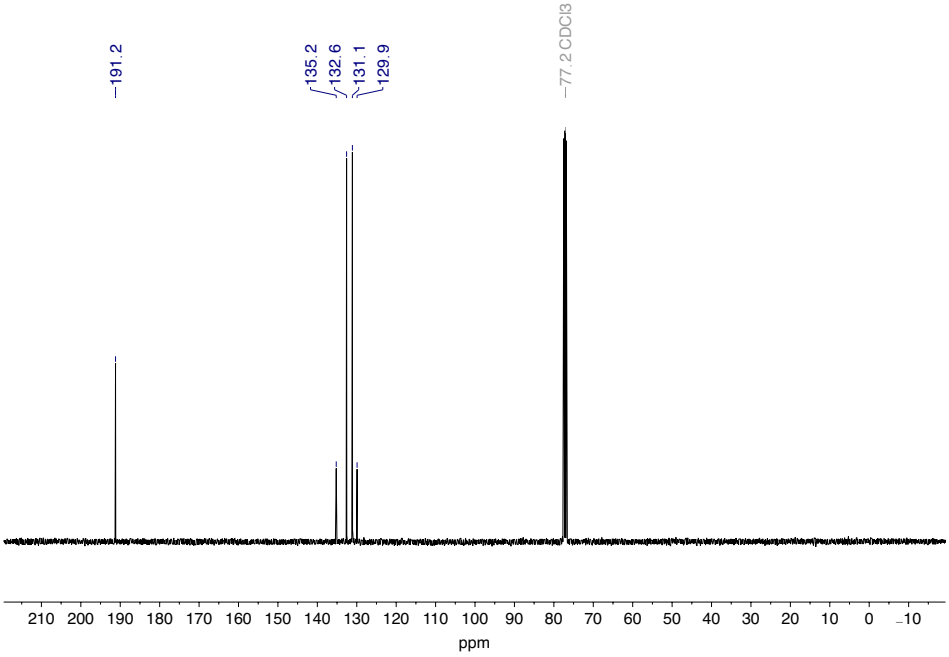


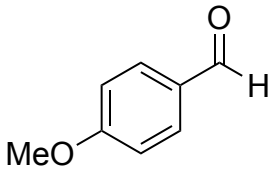


(6) ^{1}H NMR (400 MHz, $CDCl_3$)

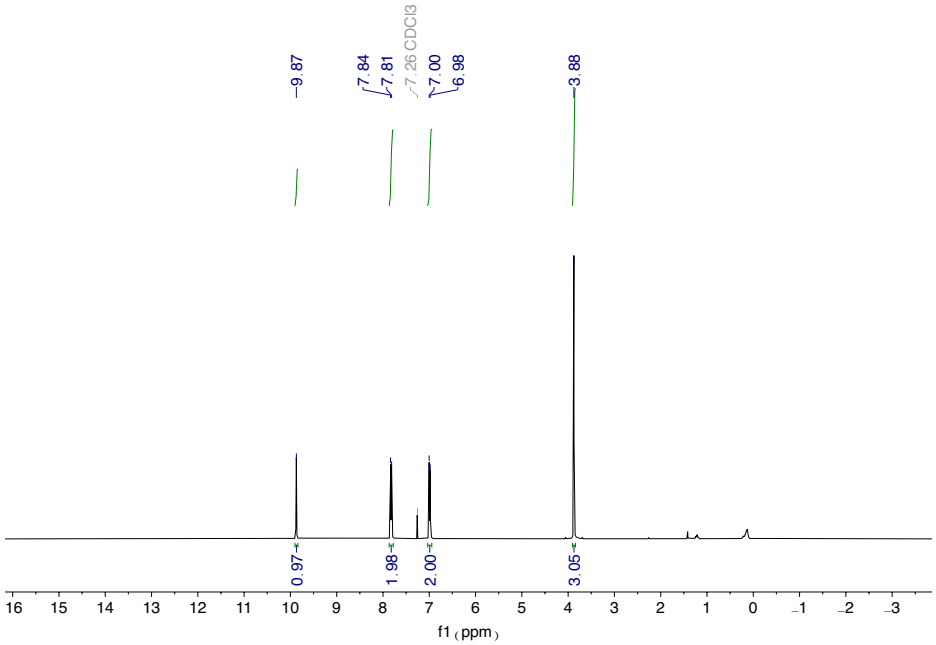


(6) ^{1}H NMR (101 MHz, $CDCl_3$)

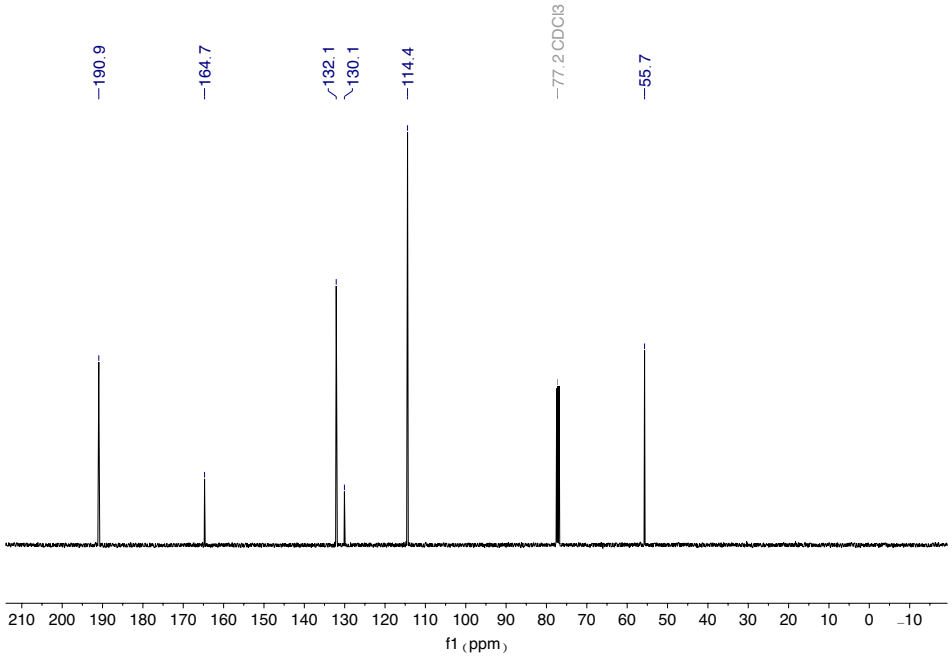


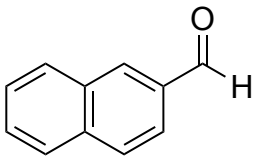


(7) ^{1}H NMR (400 MHz, $CDCl_3$)

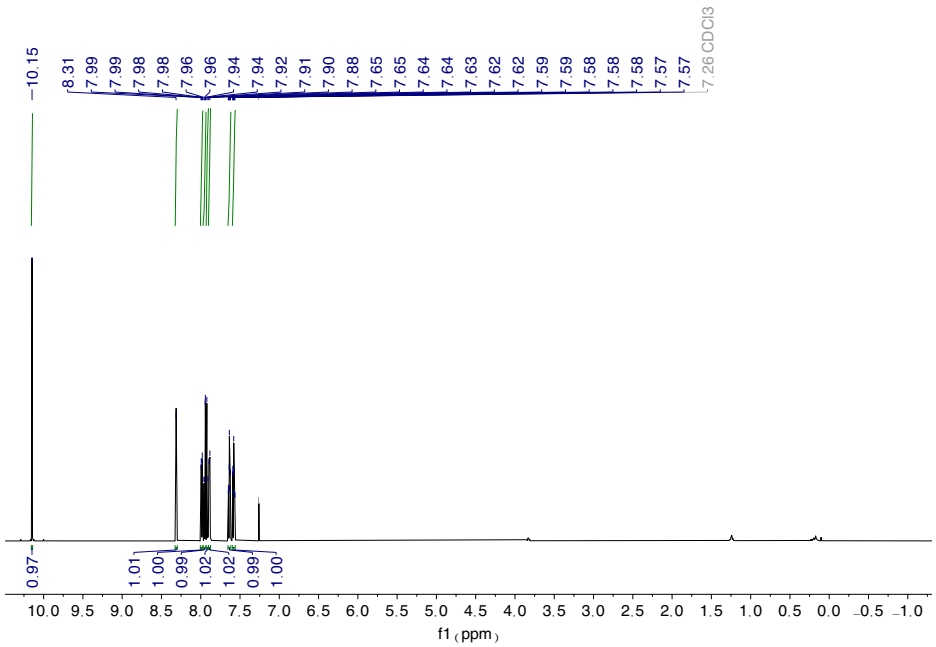


(7) ^{13}C NMR (101 MHz, $CDCl_3$)

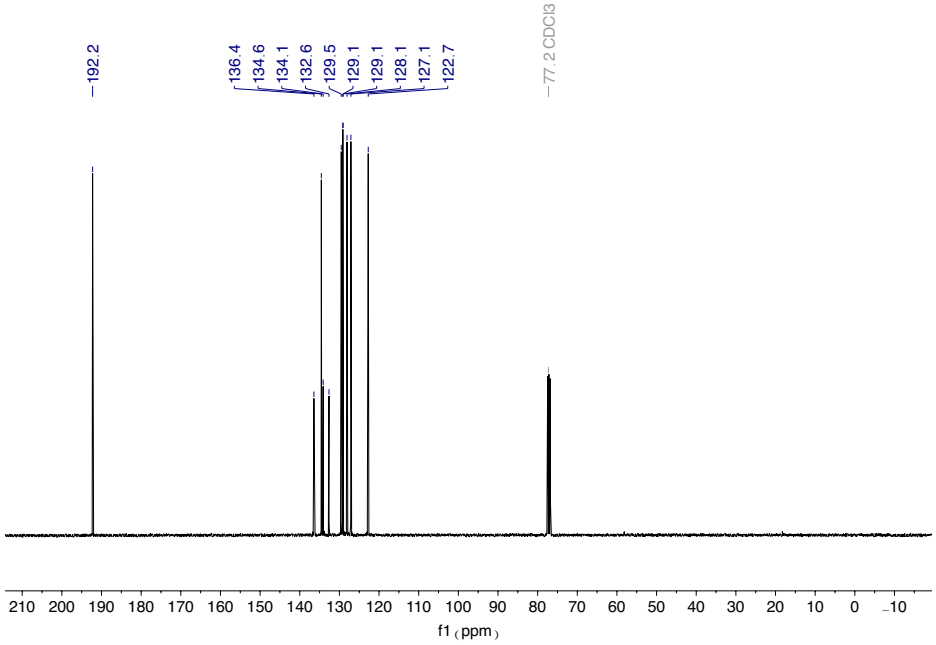


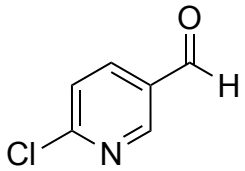


(8) ^{1}H NMR (600 MHz, $CDCl_3$)

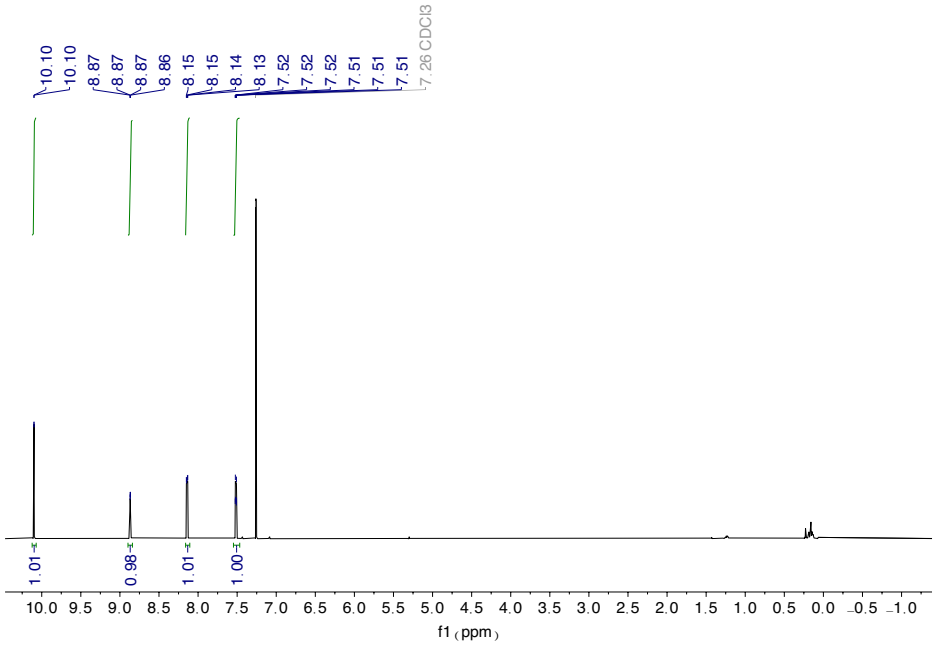


(8) ^{13}C NMR (101 MHz, $CDCl_3$)

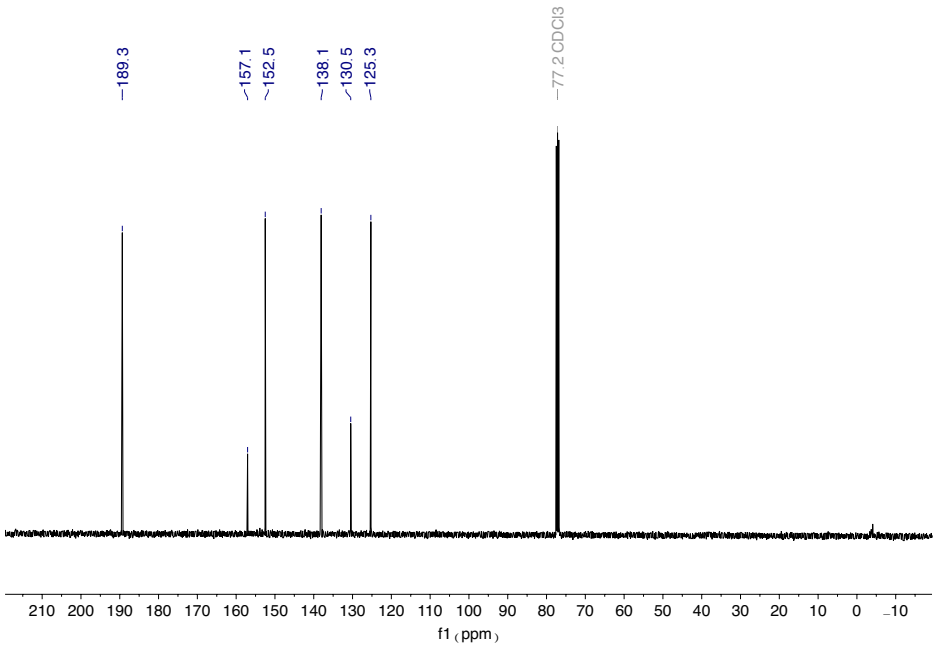


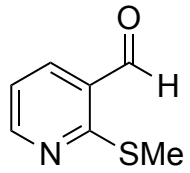


(9) ^{1}H NMR (600 MHz, $CDCl_3$)

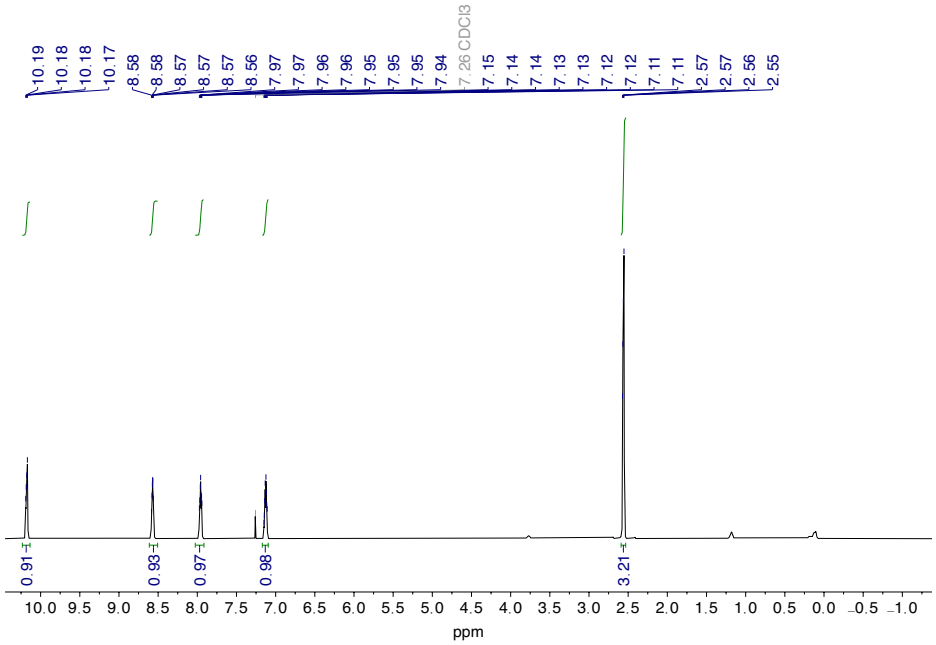


(9) ^{13}C NMR (101 MHz, $CDCl_3$)

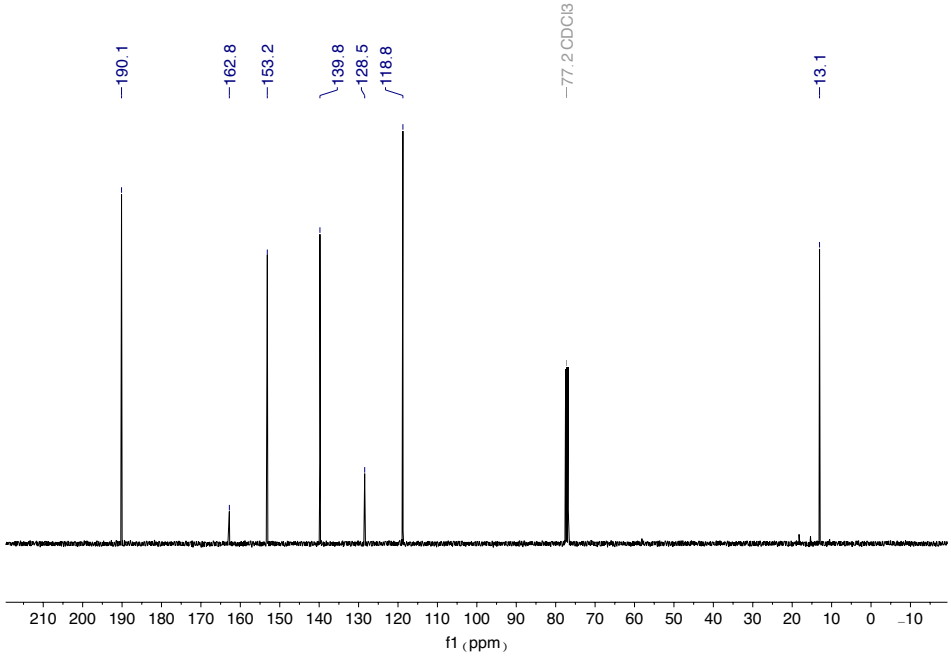


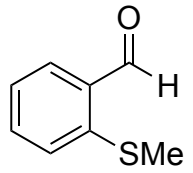


(10) ^{1}H NMR (500 MHz, $CDCl_3$)

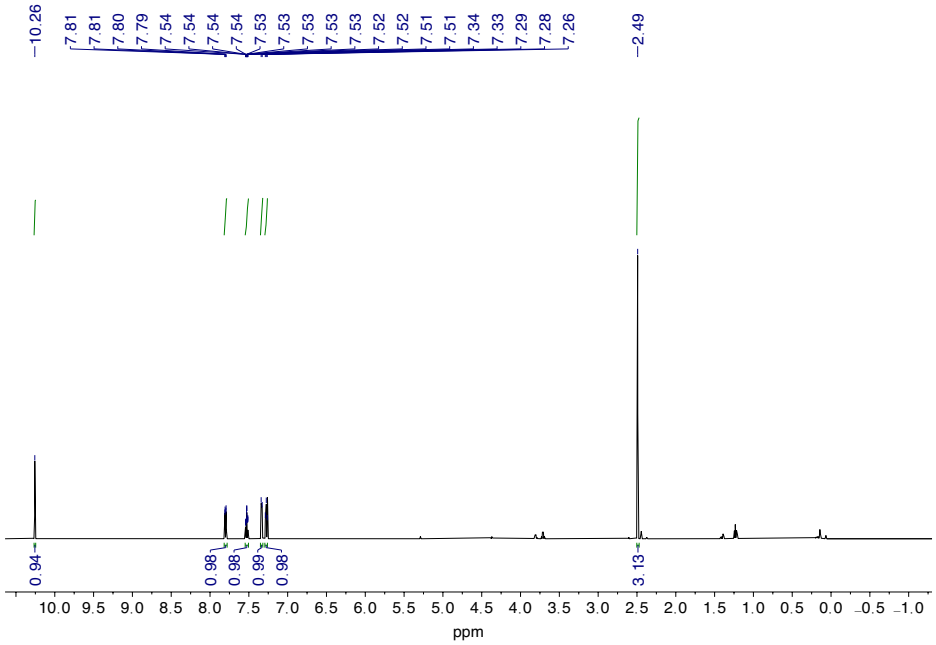


(10) ^{13}C NMR (101 MHz, $CDCl_3$)

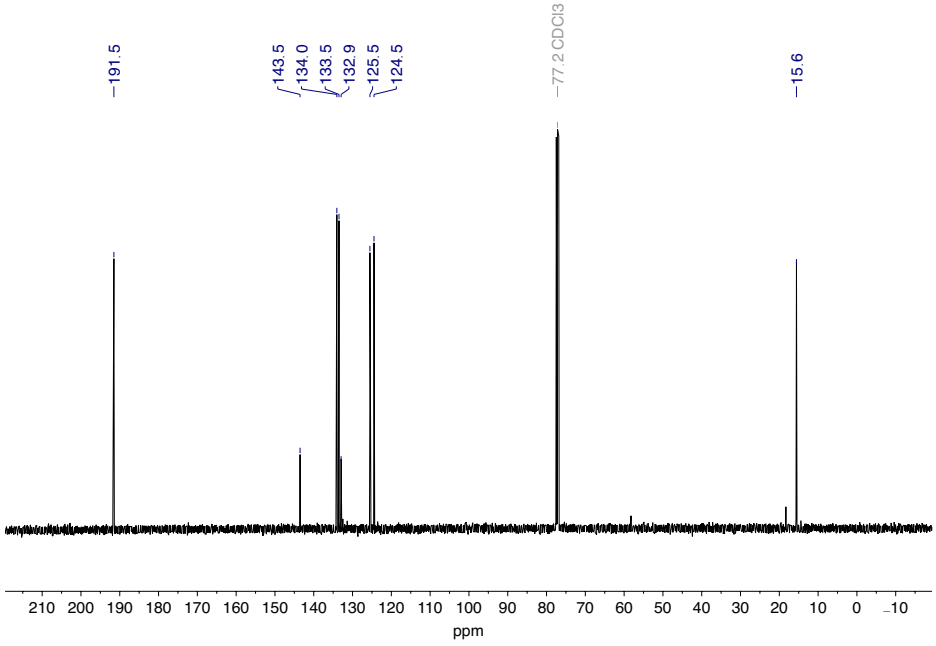


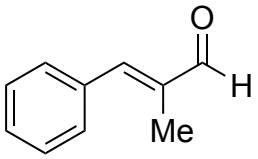


(11) ^{1}H NMR (600 MHz, $CDCl_3$)

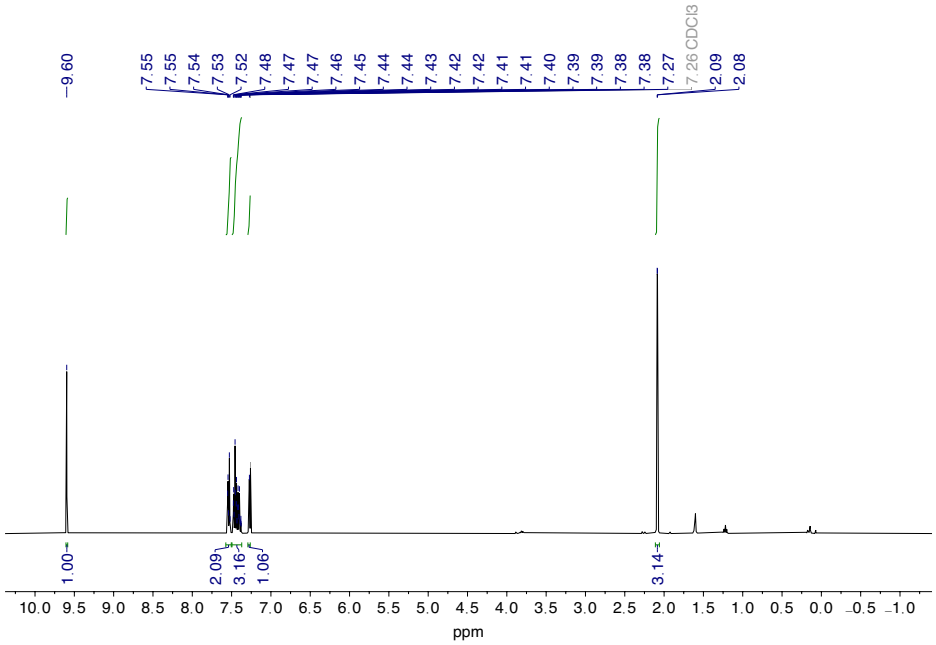


(11) ^{13}C NMR (101 MHz, $CDCl_3$)

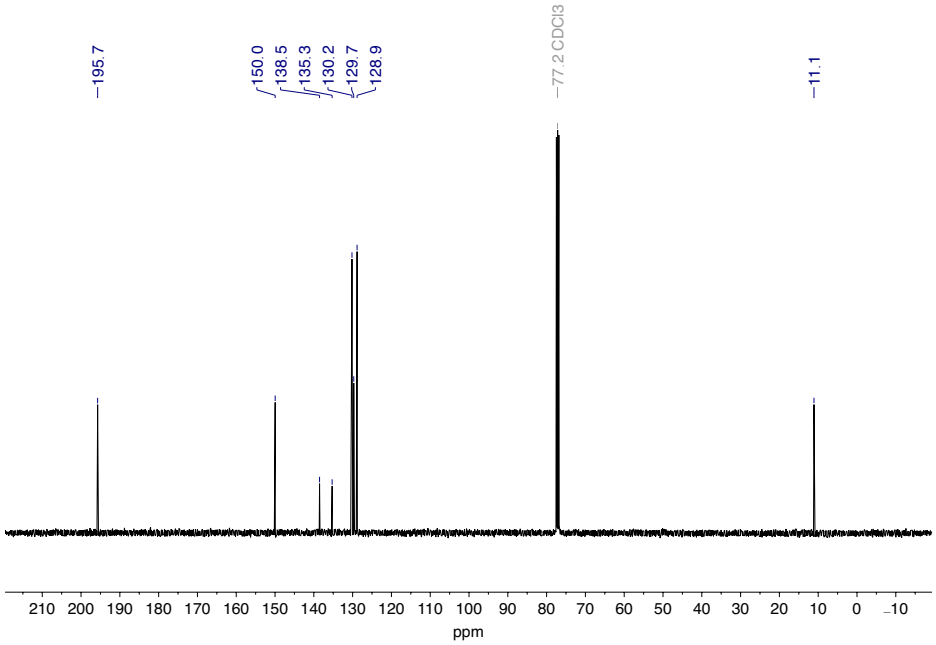


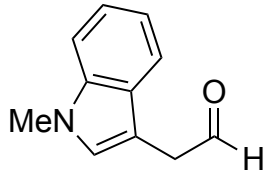


(12) ^{1}H NMR (400 MHz, $CDCl_3$)

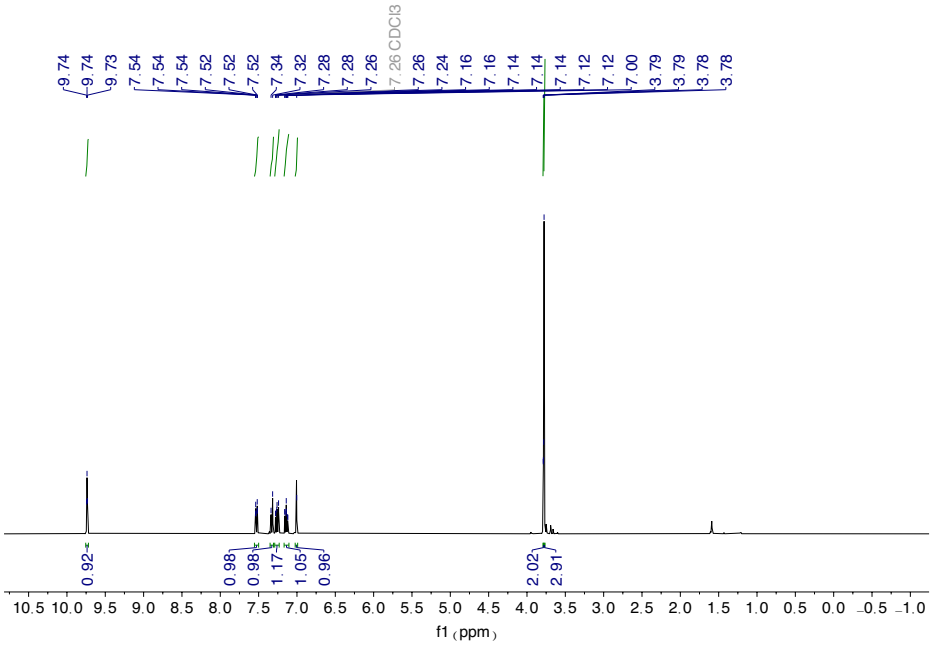


(12) ^{13}C NMR (101 MHz, $CDCl_3$)

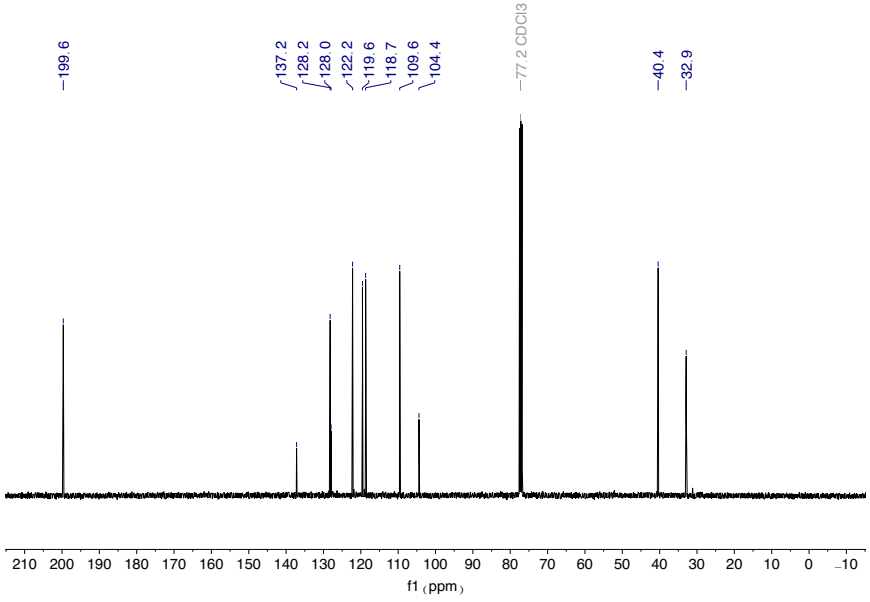


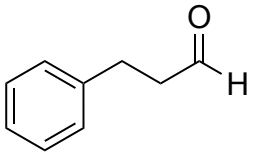


(13) ^{1}H NMR (400 MHz, $CDCl_3$)

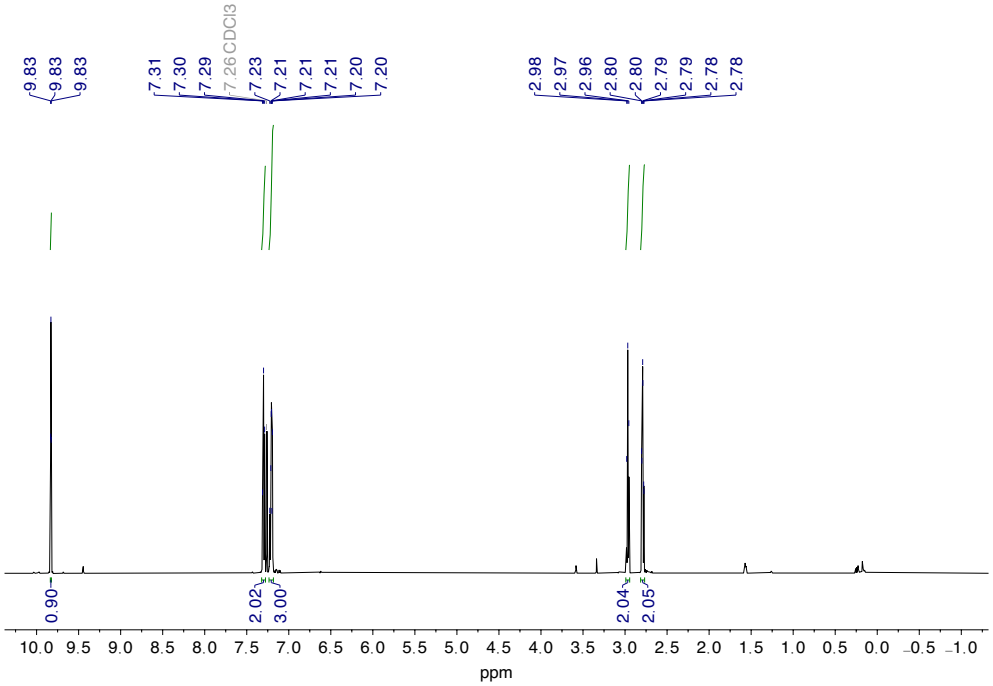


(13) ^{13}C NMR (101 MHz, $CDCl_3$)

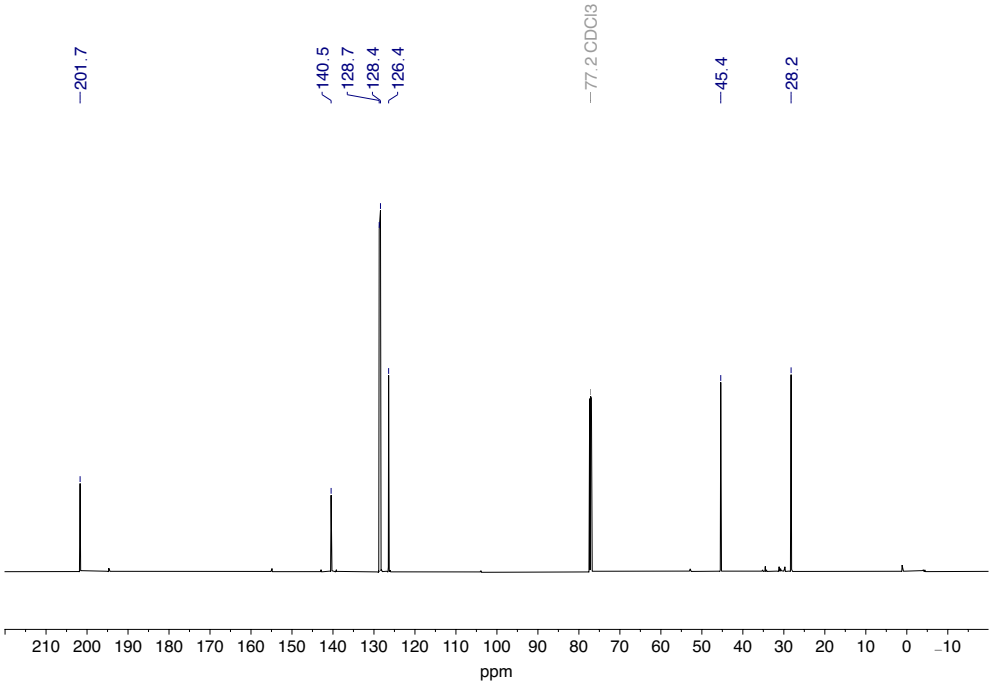


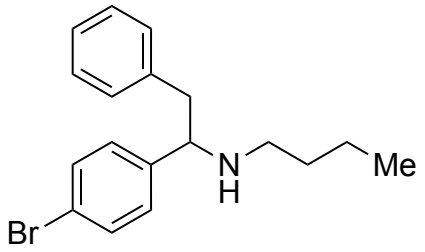


(14) ^{1}H NMR (600 MHz, $CDCl_3$)

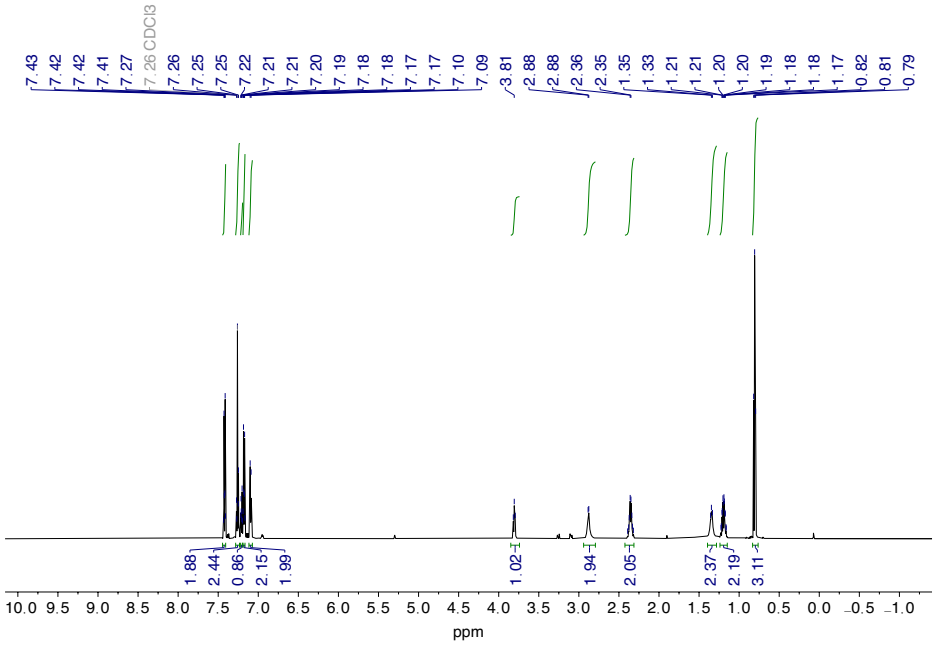


(14) ^{13}C NMR (151 MHz, $CDCl_3$)

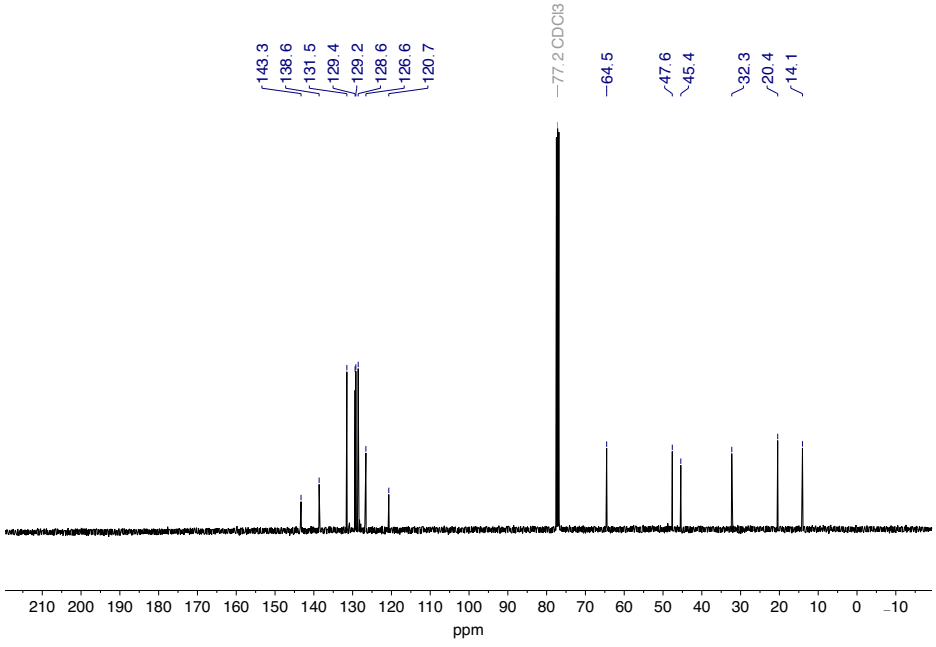


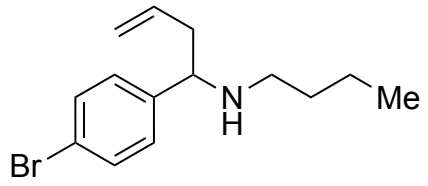


(15) ^{1}H NMR (400 MHz, $CDCl_3$)

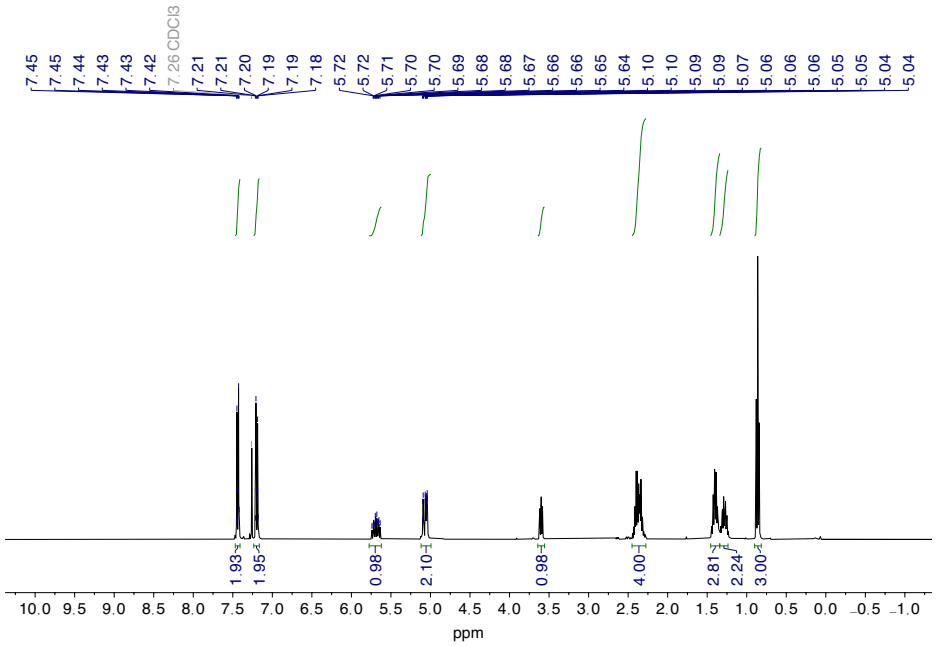


(15) ^{13}C NMR (101 MHz, $CDCl_3$)

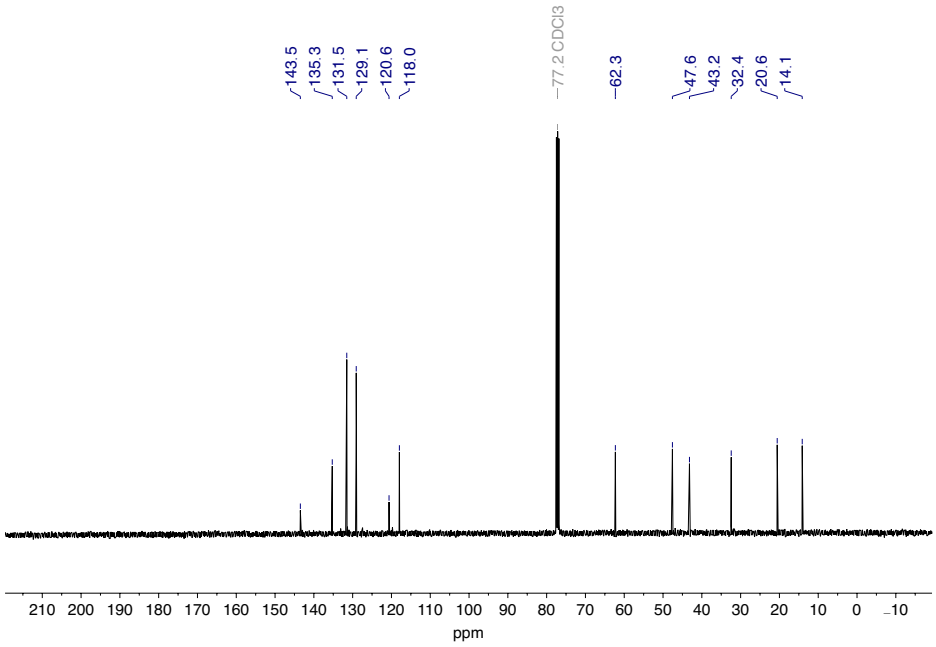


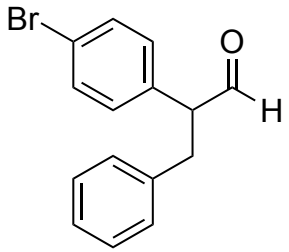


(16) ^{1}H NMR (400 MHz, $CDCl_3$)

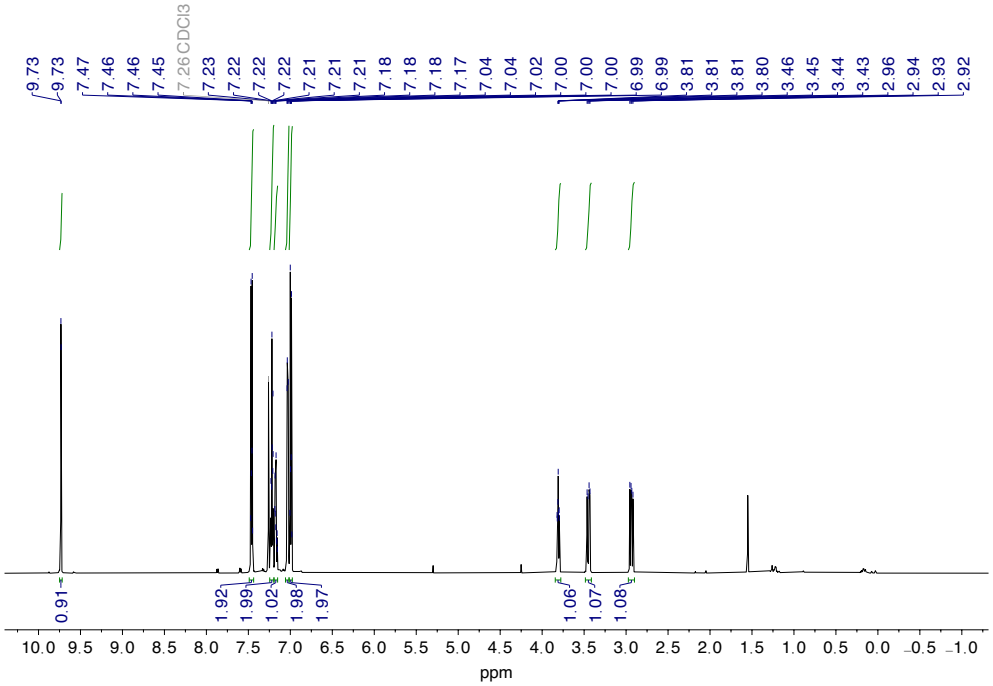


(16) ^{13}C NMR (101 MHz, $CDCl_3$)

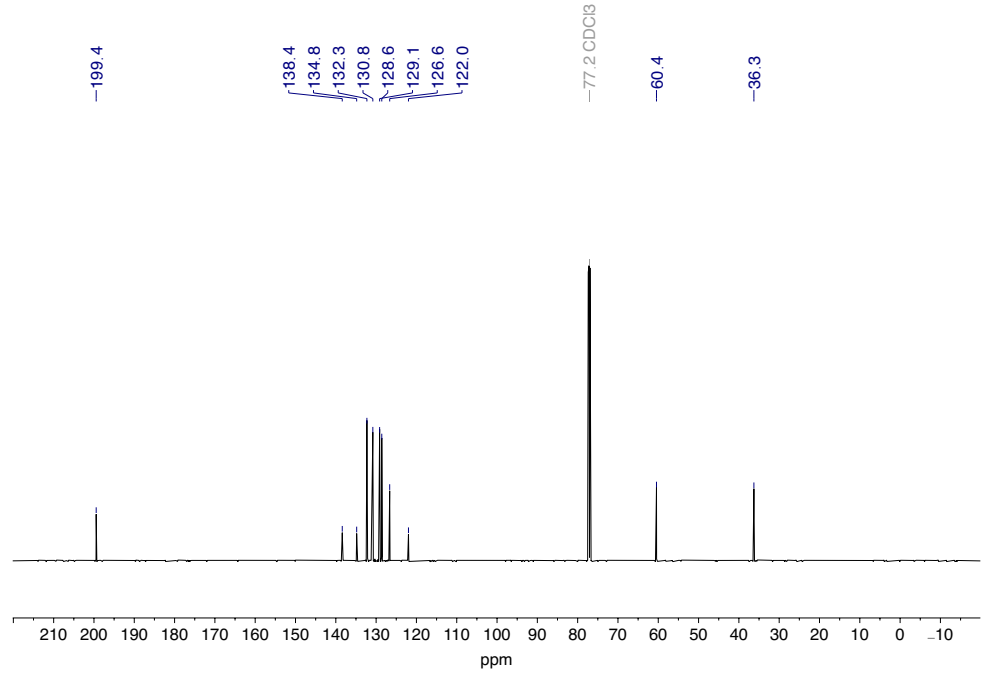


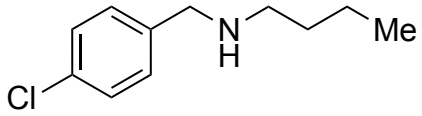


(17) ^{1}H NMR (600 MHz, $CDCl_3$)

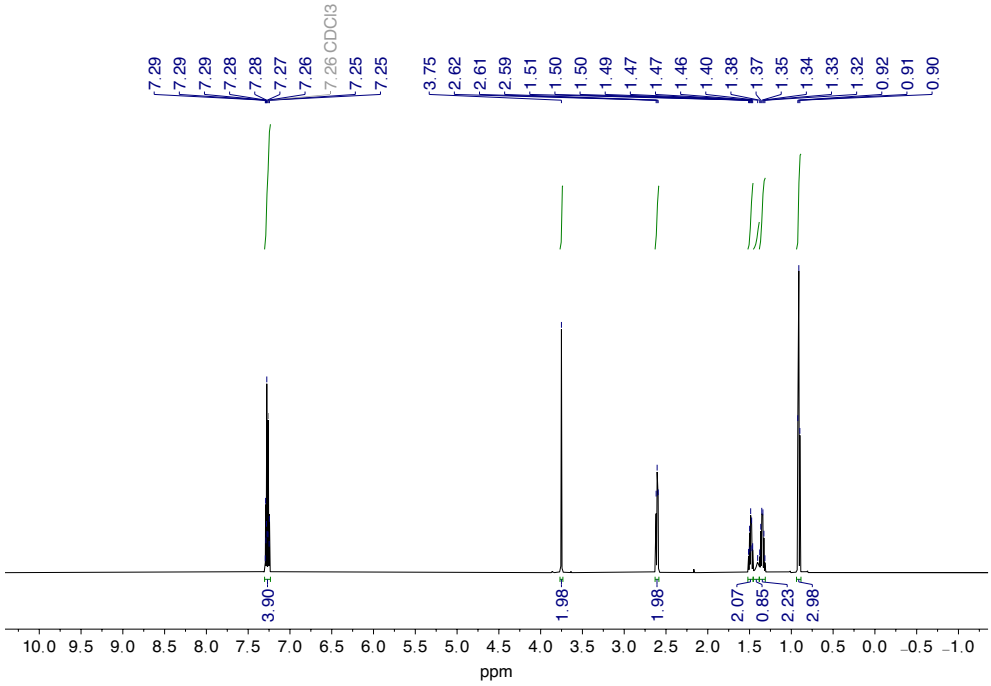


(17) ^{1}H NMR (151 MHz, $CDCl_3$)

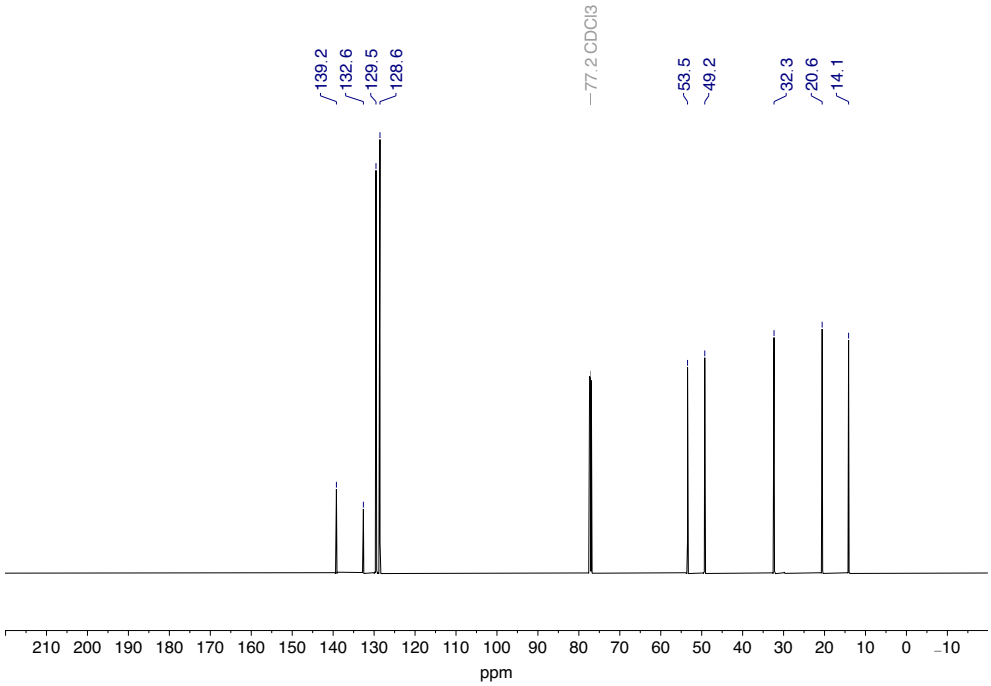


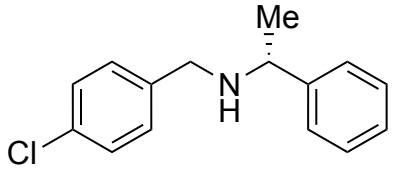


(18) ^{1}H NMR (600 MHz, $CDCl_3$)

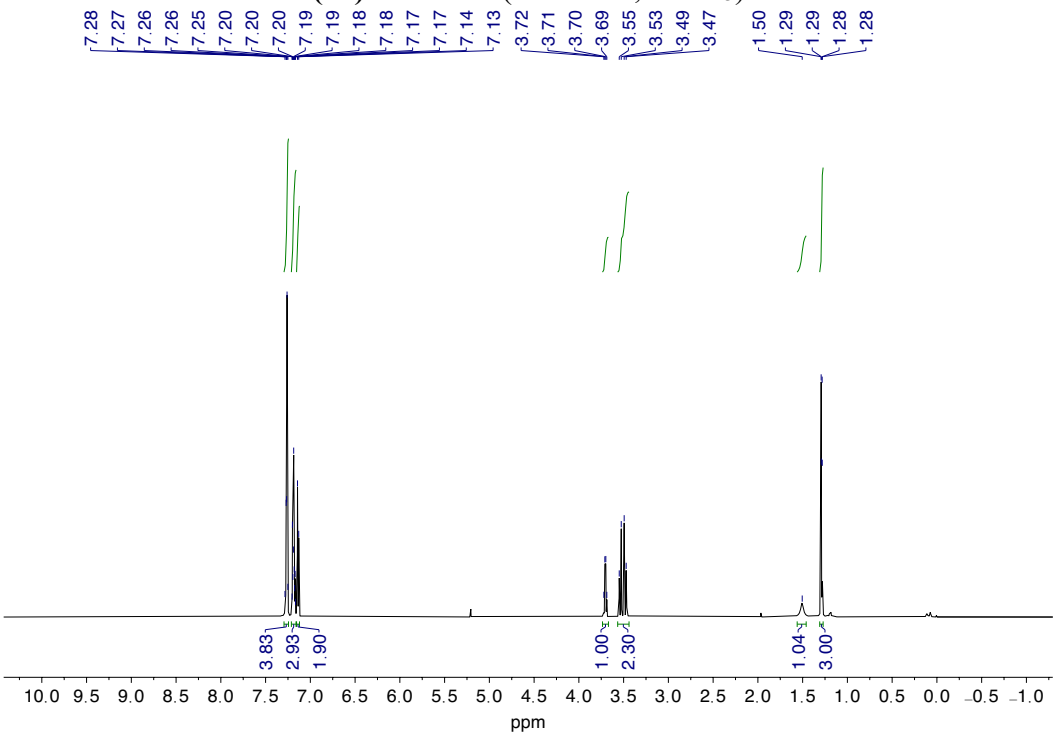


(18) ^{13}C NMR (151 MHz, $CDCl_3$)

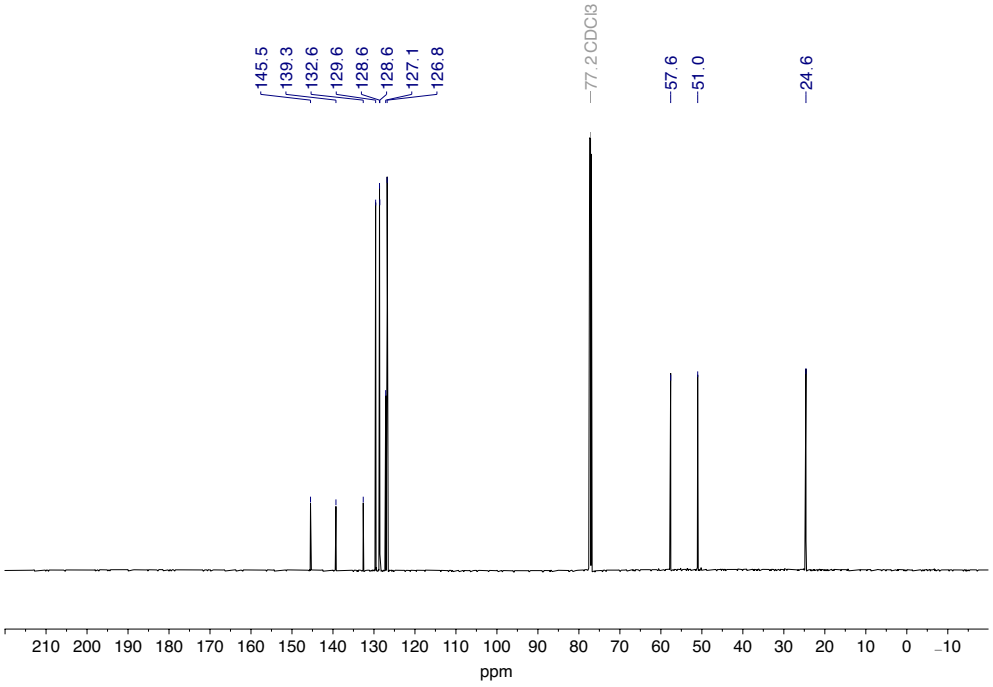


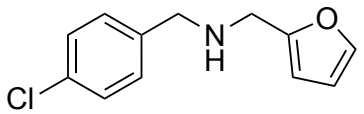


(19) ^{1}H NMR (600 MHz, $CDCl_3$)

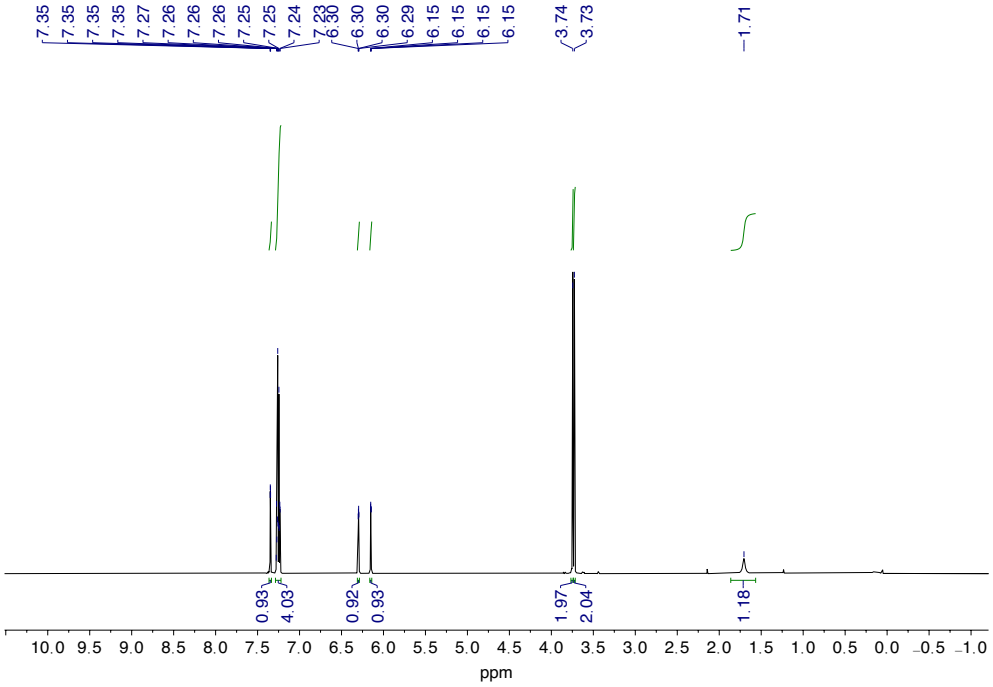


(19) ^{13}C NMR (151 MHz, $CDCl_3$)

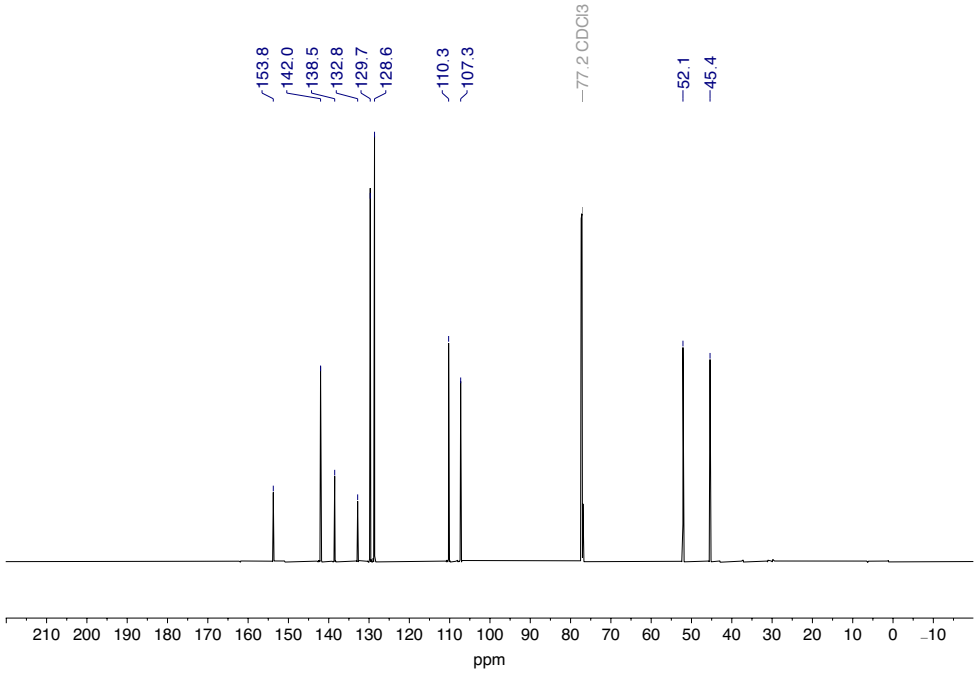


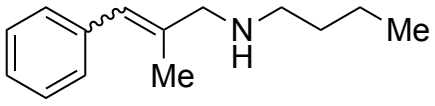


(20) ^{1}H NMR (600 MHz, $CDCl_3$)

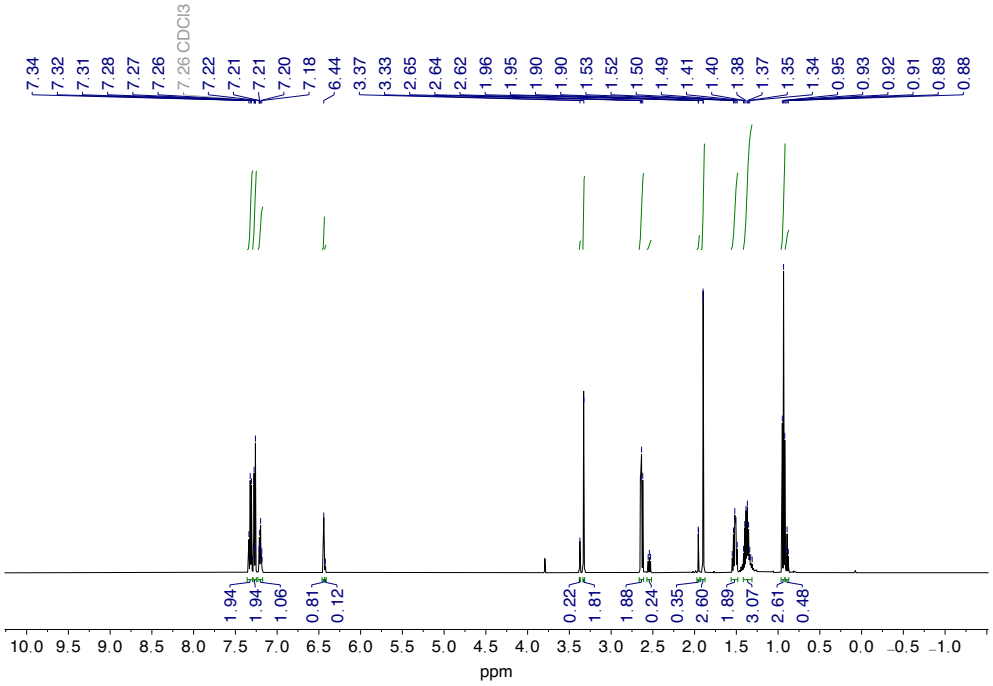


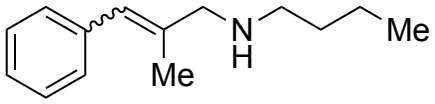
(20) ^{13}C NMR (151 MHz, $CDCl_3$)



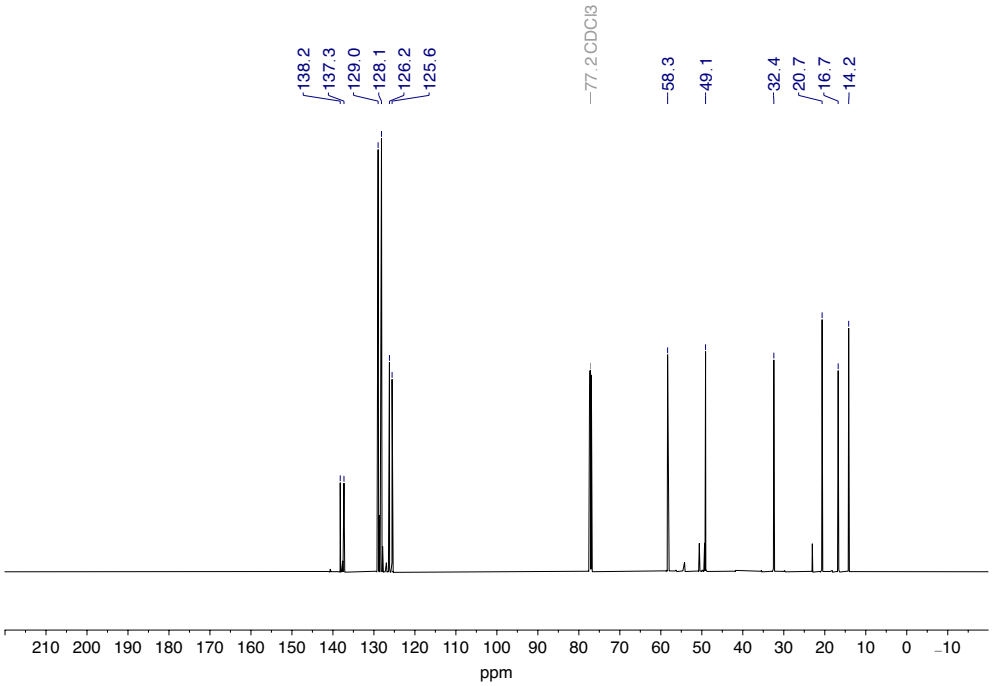


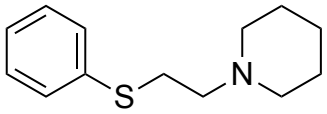
(21) ^{1}H NMR (500 MHz, $CDCl_3$)



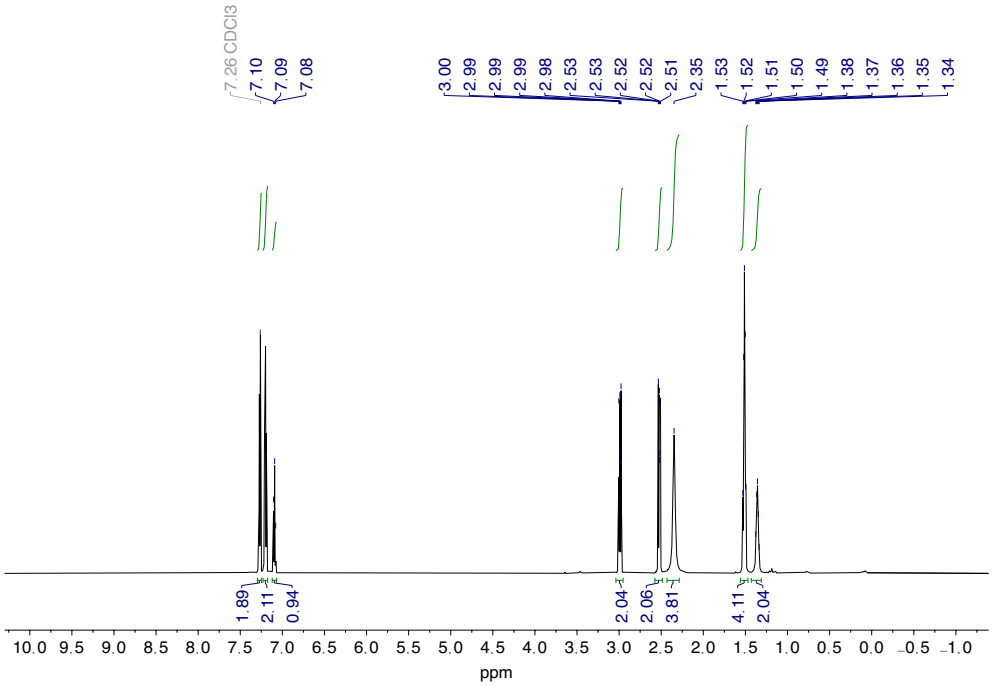


(21) ^{13}C NMR (151 MHz, $CDCl_3$) (peaks picked for *E* isomer)

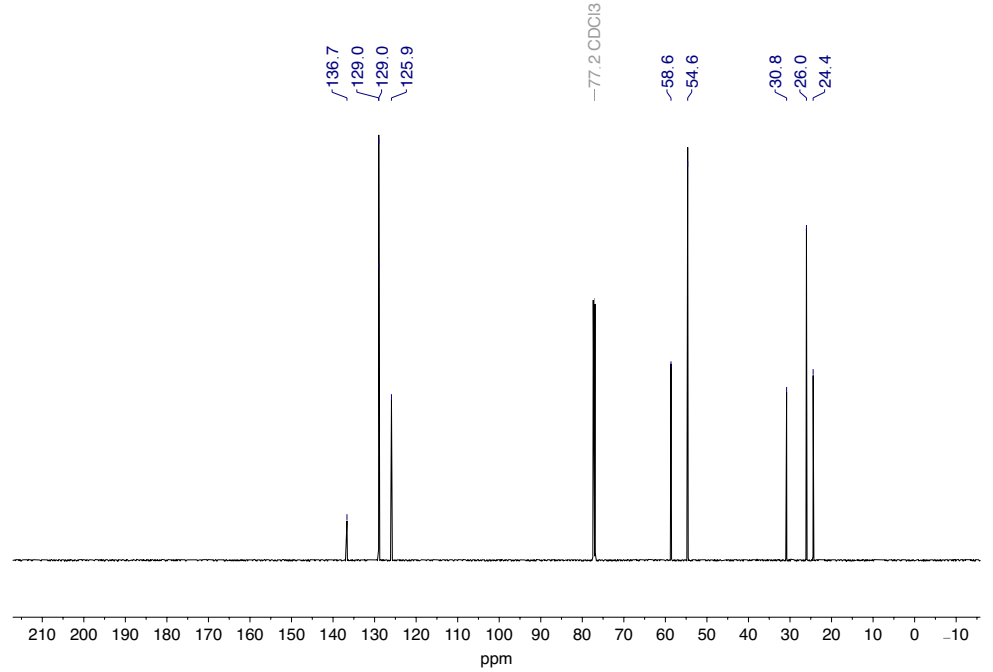


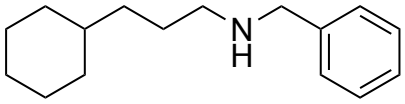


(22) ^{1}H NMR (600 MHz, $CDCl_3$)



(22) ^{13}C NMR (151 MHz, $CDCl_3$)





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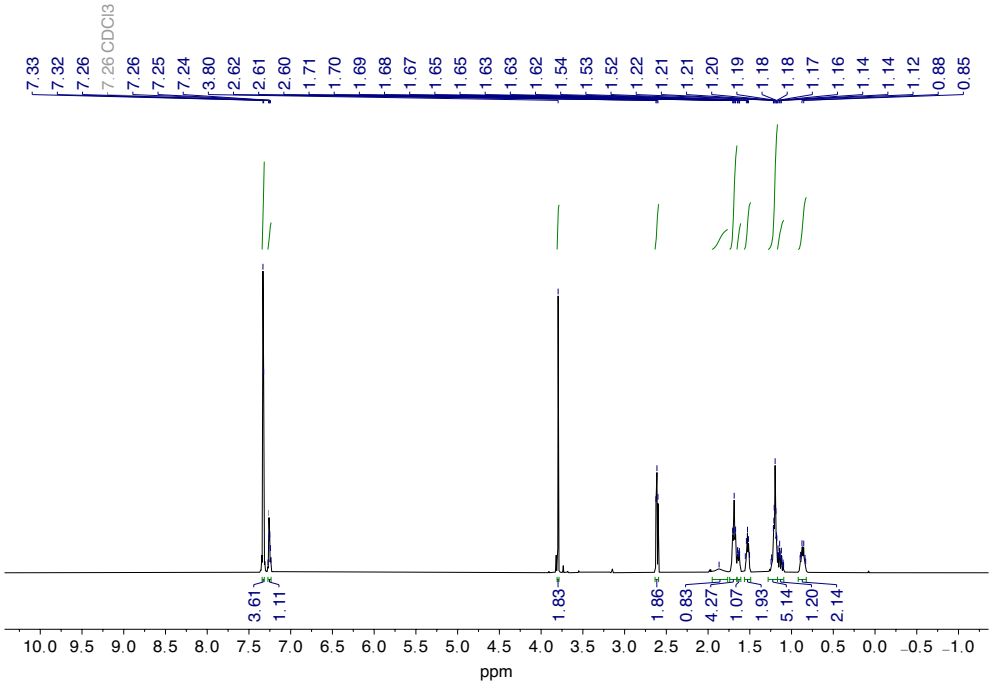

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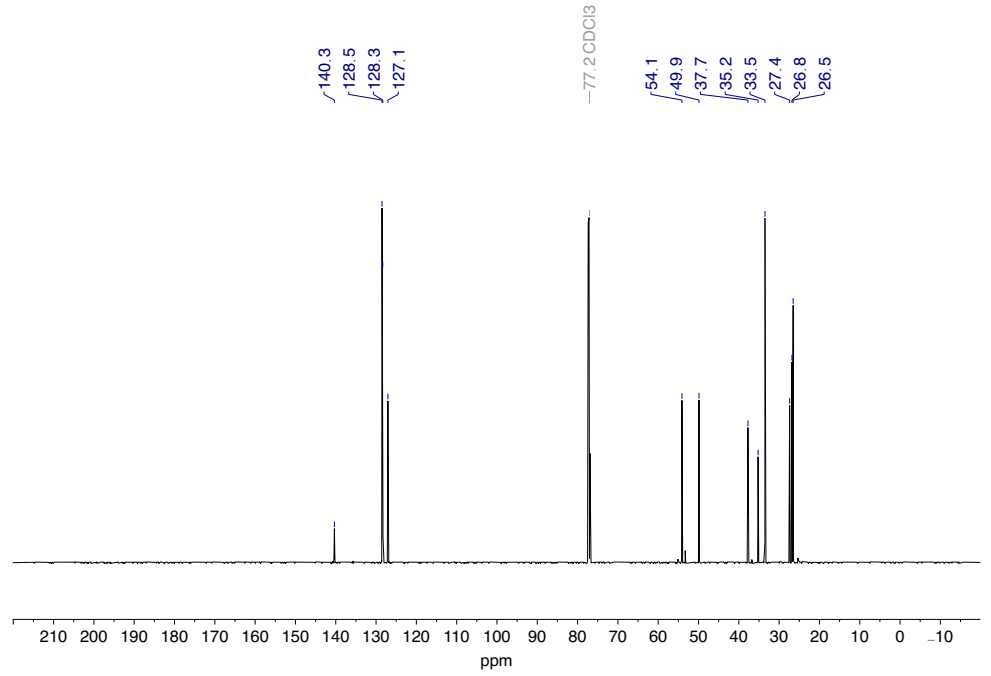

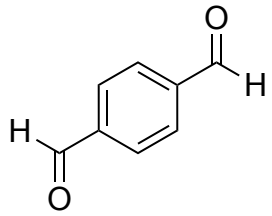

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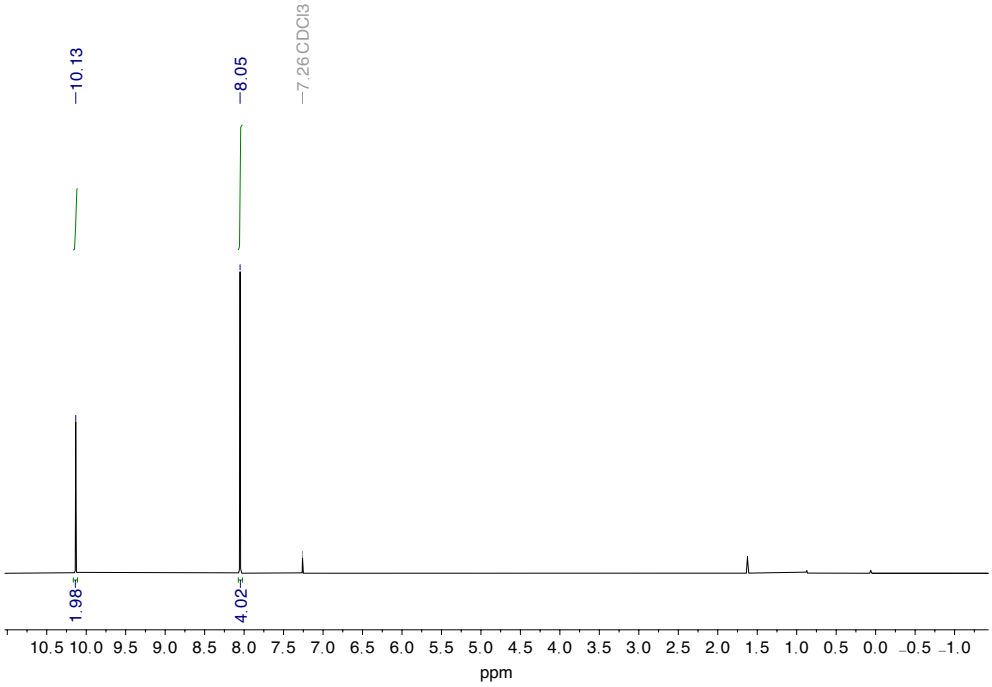

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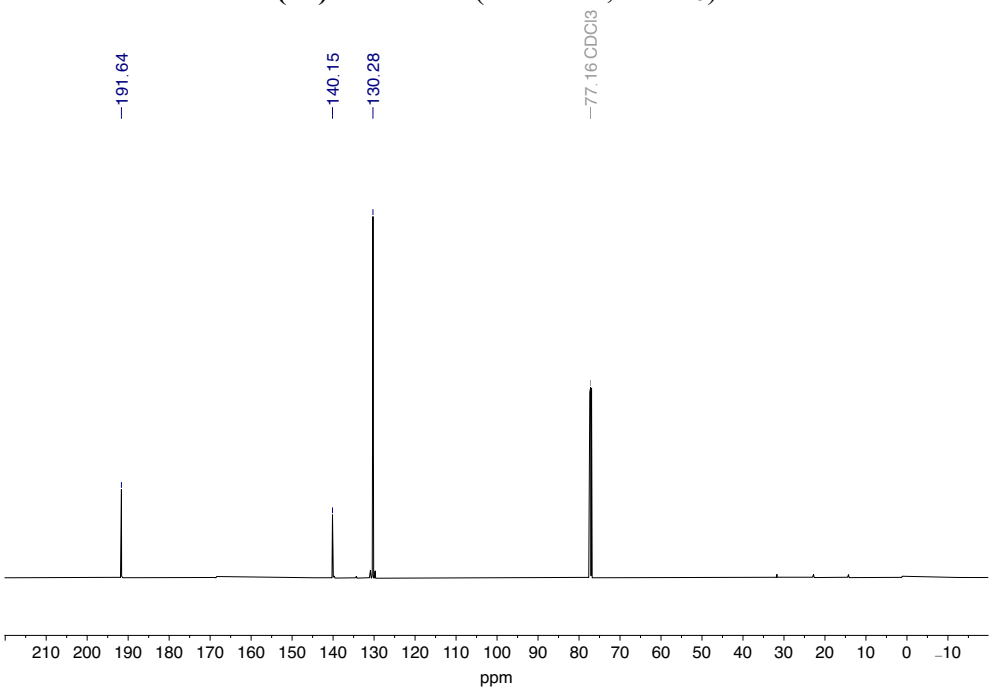

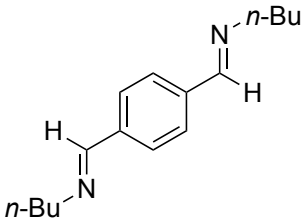

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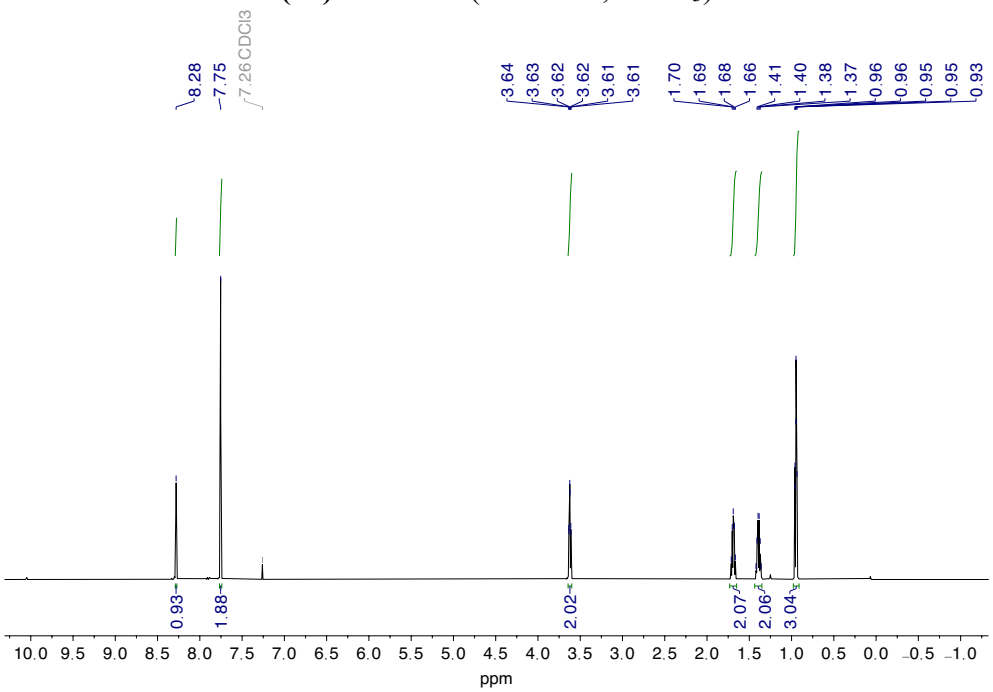

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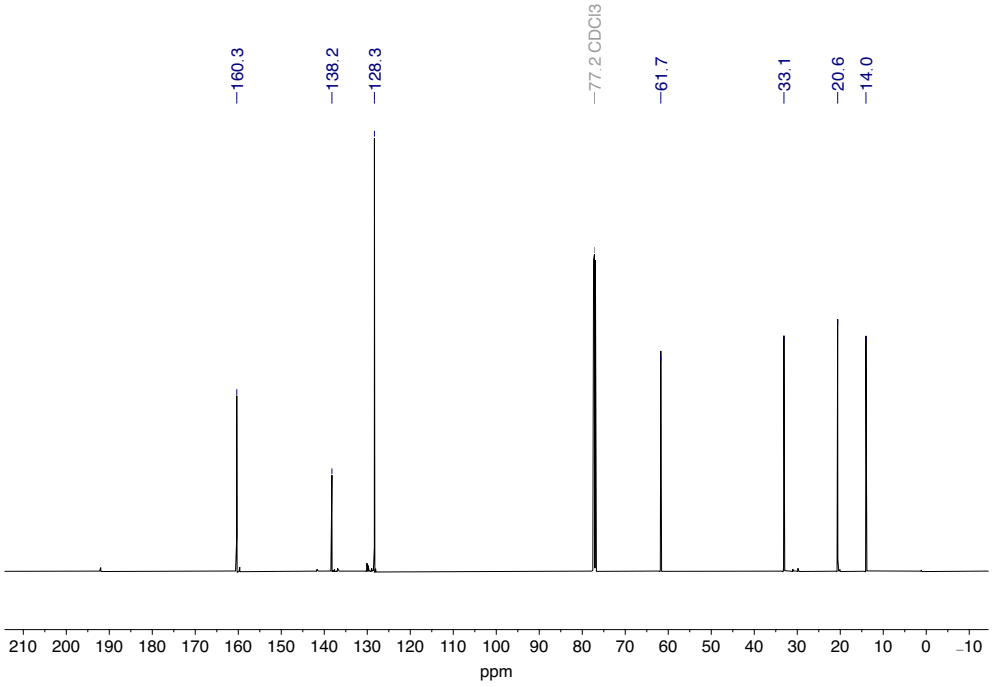

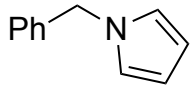

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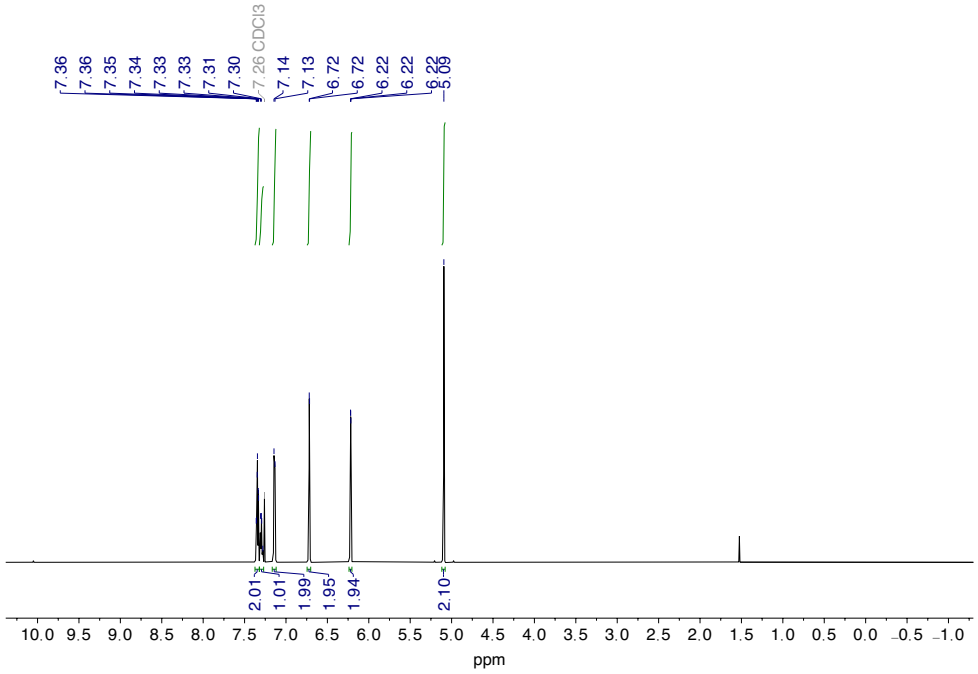

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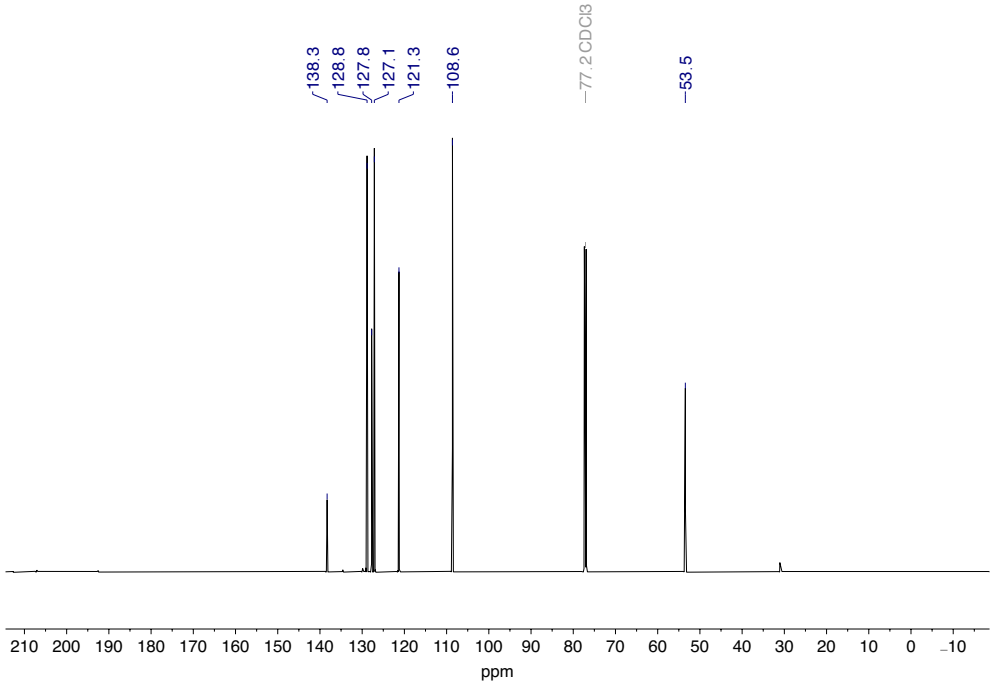

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