Chem, volume 9

Supplemental information

Iron-Mediated Modular Decarboxylative Cross-Nucleophile Coupling

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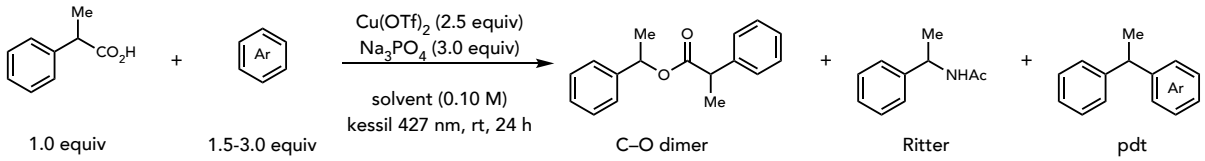
Supplemental Experimental Procedures

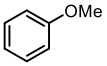
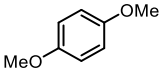
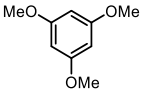
A. General Information

Dichloromethane, tetrahydrofuran, diethyl ether, toluene, and acetonitrile were dried by elution through alumina as described by Grubbs.[1] $Cu(OTf)_2$ was purchased from Oakwood Chemical and stored in a glovebox. $FeCl_3$ was purchased from Millipore-Sigma and stored in a glovebox. $Fe(OTf)_3$ was purchased from Ambeed Inc. and stored in a glovebox. 2-phenylethanol was distilled under atmospheric pressure and stored over 3 Å molecular sieves overnight prior to use. Pyridine was distilled over CaH_2. All other chemicals were purchased from commercial suppliers and used as received unless otherwise stated. 40 W PR160L 427 nm LEDs from Kessil Lights were used as light sources. Flash chromatography was performed with Sigma Aldrich 60 Å silica gel (230–400 mesh) and thin layer chromatography (TLC) was performed utilizing pre-coated silica gel F254 plates from SiliCycle Inc. containing a fluorescent indicator. Visualization of plates were accomplished with 254 nm UV lamp or staining with *p*-anisaldehyde or $KMnO_4$. Automated flash chromatography was performed with the use of a Biotage Selekt instrument using Biotage branded columns. All NMR spectra were obtained using a Bruker Avance-400, Avance-500 or Avance-600 spectrometer, and the spectra were internally referenced according to $CDCl_3$ chemical shifts (7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). The spectrometers used for this work are funded by the NSF (CHE-1048642), NIH (1S10 OD020022-1) and a generous gift from Paul J. and Margaret M. Bender. Mass spectrometry was performed with a Thermo Q Exactive™ Plus (electrospray ionization, time-of-flight analyzer or electron impact) and is funded by the NIH (1S10 OD020022-1). Melting points were obtained using a Stanford Research Systems DigiMelt apparatus.

B. Select Optimization Results

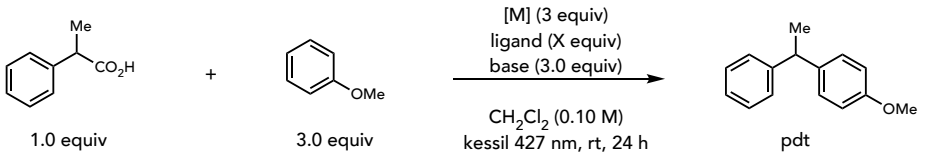
Table S1. Cu(II) for arylation.



entry	Ar Nuc	solvent	Nuc equivs	C–O dimer (%)	Ritter (%)	pdt (%)
1		CH_2Cl_2 (0.10 M) + *i*-PrCN	3	27	–	14
2		MeCN	3	0	52	15
3		CH_2Cl_2 (0.10 M) + *i*-PrCN	1.5	28	–	15
4		CH_2Cl_2 (0.10 M) + *i*-PrCN	3	27	–	23
5		MeCN	3	0	24	0
6		CH_2Cl_2 (0.10 M) + *i*-PrCN	1.5	28	–	18
7		CH_2Cl_2 (0.10 M) + *i*-PrCN	3	7	–	20
8		MeCN	3	0	2	6
9		CH_2Cl_2 (0.10 M) + *i*-PrCN	1.5	2	–	25

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (0.090 g, 2.5 equiv, 0.25 mmol), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol), the arene nucleophile (if solid), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), the arene nucleophile (if liquid), and *i*-PrCN (50 µL, 0.55 mmol, 5.5 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

Table S2. Metal mediator.

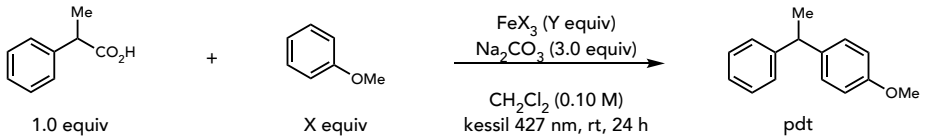


entry	[M]	base	Ligand	% recovered acid	% pdt	r.r.
1	$CeCl_3$	Na_3PO_4	20 mol% TBACl	97	0	-
2	$CeCl_3$	Na_3PO_4	3.0 equiv TBACl	100	0	-
3	$CeCl_3$	none	3.0 equiv Cs_2CO_3	77	0	-
4	$Ce(OTf)_4$	Na_3PO_4	–	100	0	-
5	$Ce(OH)_4$	Na_3PO_4	–	0	0	-
6	$Ce(OH)_4$	Cs_2CO_3	–	0	0	-
7	$Mn(OAc)_3$	Na_3PO_4	–	85	2	-
8	$Mn(OAc)_3$	Na_3PO_4	5.5 equiv *i*-PrCN	82	1	-
9	$NiCl_2$·dme	Na_3PO_4	–	100	0	-
10	$NiCl_2$·dme	Na_3PO_4	5.5 equiv *i*-PrCN	96	0	-
11	$CuCl_2$•H_2O	Na_3PO_4	–	27	0	-
12	$CuCl_2$•H_2O	Na_3PO_4	5.5 equiv *i*-PrCN	33	0	-
13	$CuCl_2$	Na_3PO_4	–	47	0	-
14	$CuBr_2$	Na_3PO_4	–	89	0	-
15	$CuBr_2$	Na_3PO_4	5.5 equiv *i*-PrCN	98	0	-
16	$Cu(OTf)_2$	Na_3PO_4	5.5 equiv *i*-PrCN	21	14	5:1
17	$CrCl_3$	Na_3PO_4	–	86	0	-
18	$CrCl_3$	Na_3PO_4	5.5 equiv *i*-PrCN	95	0	-
19	$FePO_4$	Na_2CO_3	–	84	0	-
20	$FePO_4$	Na_2CO_3	1.0 equiv NaCl	90	0	-
21	$FePO_4$	Na_2CO_3	3.0 equiv NaCl	89	0	-
22	$FePO_4$	Na_2CO_3	1.0 equiv TBACl	93	0	-
23	$FePO_4$	Na_2CO_3	3.0 equiv TBACl	87	0	-
24	$Fe_2(SO_4)_3$•$5H_2O$	Na_2CO_3	–	86	0	-
25	FeF_3	Na_2CO_3	–	99	0	-
26	$Fe(acac)_3$	Na_2CO_3	–	99	0	-
27	$Fe(OTf)_3$	Na_3PO_4	–	9	79	4:1
28	$Fe(OTf)_3$	Na_3PO_4	5.5 equiv *i*-PrCN	16	76	4:1
29	$FeCl_3$	Na_2CO_3	–	34	45	5:1
30	$FeCl_3$	Na_3PO_4	–	17	56	5:1

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with the metal salt (3.0 equiv), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol) or Na_2CO_3 (0.032 g, 3.0 equiv, 0.30 mmol), the ligand (if solid), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), anisole (32.6 µL, 3.0 equiv, 0.30 mmol), and the ligand (if liquid). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

Commentary on reactions with poor mass balance:
We observed significant decomposition of the starting materials with no identifiable major products present for entries 5 and 6. We believe in entries 11-13 the poor recovery of the acid is due to it strongly coordinating the copper. Under our standard workup conditions, most of the unreacted acid is in the aqueous layer. For entry 16, the C–O dimer was the major product (27% yield from ^{1}H NMR analysis of the crude reaction mixture) which is formed upon nucleophilic attack of another equivalent of the carboxylic acid.

Table S3. Fe loading.

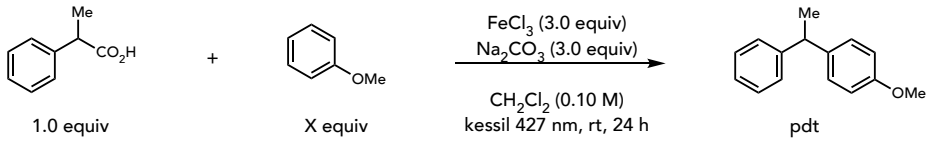


1.0 equiv X equiv pdt

entry	Fe salt	Fe equiv	anisole equiv	% pdt	r.r.
1	$FeCl_3$	2.0	5.0	50	4.8
2	$FeCl_3$	3.0	5.0	54	5.0
3	$FeCl_3$	4.0	5.0	53	4.9
4	$FeCl_3$	5.0	5.0	65	5.1
5	$FeCl_3$	7.0	5.0	28	4.2
6	$Fe(OTf)_3$	2.0	1.5	45	3.8
7	$Fe(OTf)_3$	3.0	1.5	53	3.9
8	$Fe(OTf)_3$	4.0	1.5	61	4.0
9	$Fe(OTf)_3$	5.0	1.5	61	4.1
10	$Fe(OTf)_3$	2.0	3.0	59	3.8
11	$Fe(OTf)_3$	3.0	3.0	74	3.9
12	$Fe(OTf)_3$	4.0	3.0	80	4.0
13	$Fe(OTf)_3$	5.0	3.0	83	4.0
14	$Fe(OTf)_3$	2.0	5.0	70	3.6
15	$Fe(OTf)_3$	3.0	5.0	90	3.8
16	$Fe(OTf)_3$	4.0	5.0	87	3.6
17	$Fe(OTf)_3$	5.0	5.0	89	3.6

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with the Fe salt (2.0 – 7.0 equiv), Na_2CO_3 (0.032 g, 3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), and anisole (1.5 – 5.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

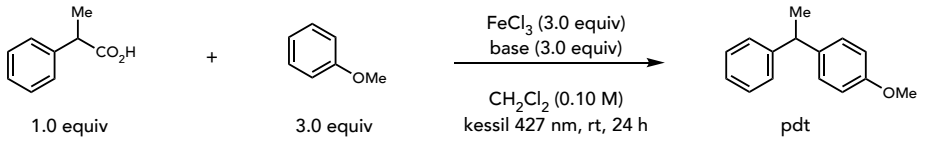
Table S4. Arene nucleophile loading.



entry	Nuc equivs	% recovered acid	% pdt	r.r.
1	1.5	0	54	4.8
2	3.0	0	52	5.2
3	5.0	0	54	5.0
4	20	0	61	4.8

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), Na_2CO_3 (0.032 g, 3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), and anisole (1.5 – 20 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

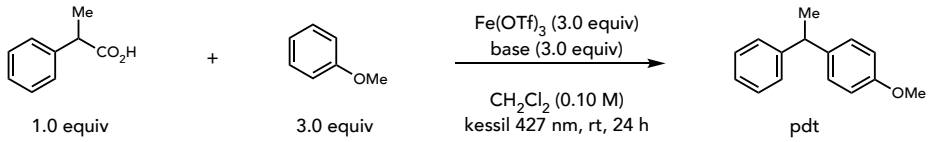
Table S5. Base with 3.0 equiv anisole and $FeCl_3$.



entry	base	% pdt	r.r.
1	Na_3PO_4	54	5.0
2	K_3PO_4	77	5.1
3	Na_2CO_3	41	4.9
4	K_2CO_3	26	4.6
5	Cs_2CO_3	3	6.7
6	Na_2HPO_4	5	5.1
7	K_2HPO_4	87	5.1
8	NaH_2PO_4	3	5.5
9	KH_2PO_4	1	6.6
10	NaOAc	88	5.0
11	Pyridine	37	4.7
12	DABCO	29	6.4

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), base (3.0 equiv), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), and anisole (32.6 µL, 3.0 equiv, 0.30 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

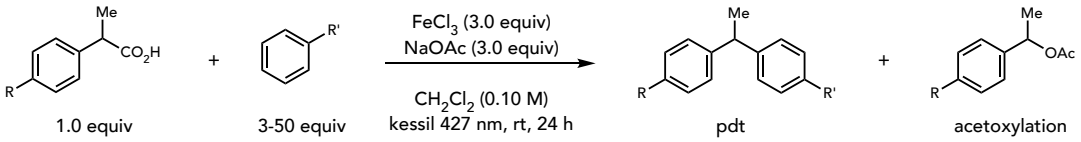
Table S6. Base with 3.0 equiv anisole and $Fe(OTf)_3$.



entry	base	% pdt	r.r.
1	Na_3PO_4	80	3.8
2	K_3PO_4	1	7.2
3	Na_2CO_3	76	3.9
4	K_2CO_3	68	3.9
5	Cs_2CO_3	2	0.5
6	Na_2HPO_4	64	3.8
7	K_2HPO_4	72	3.8
8	NaH_2PO_4	8	3.0
9	KH_2PO_4	4	2.6
10	NaOAc	79	3.8
11	Pyridine	47	4.4
12	DABCO	10	3.5

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Fe(OTf)_3$ (0.151 g, 3.0 equiv, 0.30 mmol), base (3.0 equiv), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), and anisole (32.6 µL, 3.0 equiv, 0.30 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

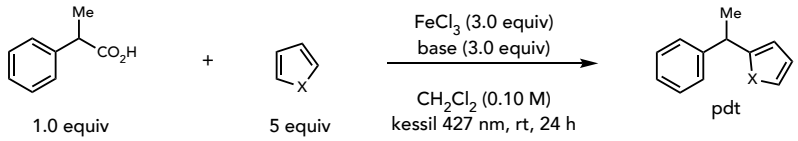
Table S7. Reactivity with less activated arenes.



entry	nuc	nuc equiv	R	% pdt	r.r.	% acetoxylation
1	toluene	3	Me	52	5:1	12
2	toluene	5	Me	62	5:1	6
3	toluene	10	Me	77	6:1	6
4	toluene	20	Me	75	5:1	0
5	toluene	3	H	61	6:1	12
6	toluene	5	H	72	6:1	10
7	toluene	10	H	82	6:1	9
8	toluene	20	H	78	6:1	8
9	benzene	3	Me	6	–	14
10	benzene	5	Me	8	–	11
11	benzene	10	Me	14	–	14
12	benzene	20	Me	16	–	9
13	benzene	3	H	12	–	21
14	benzene	5	H	18	–	15
15	benzene	10	H	25	–	16
16	benzene	20	H	41	–	22
17	fluorobenzene	5	H	9	5:1	31
18	fluorobenzene	10	H	15	5:1	33
19	fluorobenzene	20	H	21	5:1	31
20	fluorobenzene	50	H	43	6:1	37
21	bromobenzene	5	H	0	–	0
22	bromobenzene	10	H	0	–	0
23	bromobenzene	20	H	0	–	0
24	bromobenzene	50	H	0	–	49
25	chlorobenzene	5	H	0	–	0
26	chlorobenzene	10	H	0	–	0
27	chlorobenzene	20	H	0	–	0
28	chlorobenzene	50	H	15	–	30

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), NaOAc (0.025 g, 3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol) or 2-(*p*-tolyl)propanoic acid (0.016 g, 1.0 equiv, 0.10 mmol), and the arene nucleophile (1.0 – 20 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 μL) as an internal standard.

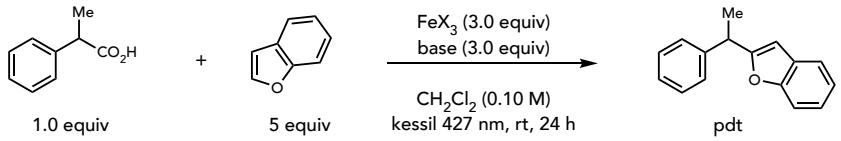
Table S8. Base screen with furan and thiophene.



entry	nuc	base	% pdt	r.r.
1	furan	Na_3PO_4	8	>20:1
2	furan	K_3PO_4	51	>20:1
3	furan	Na_2CO_3	9	>20:1
4	furan	K_2CO_3	18	>20:1
5	furan	NaOAc	22	>20:1
6	furan	K_2HPO_4	24	>20:1
7	furan	Na_2HPO_4	5	>20:1
8	furan	Pyridine	22	>20:1
9	thiophene	Na_3PO_4	32	5.0:1
10	thiophene	K_3PO_4	68	6.6:1
11	thiophene	Na_2CO_3	31	6.8:1
12	thiophene	K_2CO_3	10	4.5:1
13	thiophene	Cs_2CO_3	0	–
14	thiophene	Na_2HPO_4	0	–
15	thiophene	K_2HPO_4	27	6.6:1
16	thiophene	NaH_2PO_4	0	–
17	thiophene	KH_2PO_4	0	–
18	thiophene	NaOAc	60	4.5:1
19	thiophene	Pyridine	11	3.0:1
20	thiophene	DABCO	32	7.0:1

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), base (3.0 equiv), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), and the arene nucleophile (5.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

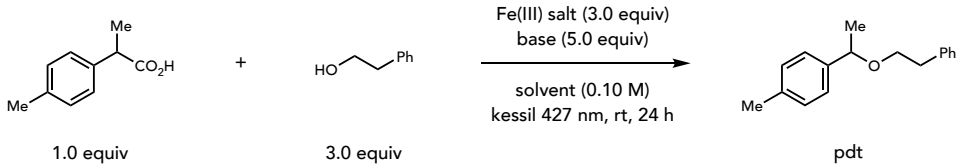
Table S9. Base screen with benzofuran.



entry	Fe salt	base	% pdt	r.r.
1	$FeCl_3$	K_3PO_4	trace	>20:1
2	$FeCl_3$	Pyridine	17	3.7:1
3	$Fe(OTf)_3$	Na_3PO_4	67	5.1:1
4	$Fe(OTf)_3$	K_3PO_4	3	1.6:1
5	$Fe(OTf)_3$	Na_2CO_3	41	3.6:1
6	$Fe(OTf)_3$	K_2CO_3	42	4.1:1
7	$Fe(OTf)_3$	NaOAc	56	3.6:1
8	$Fe(OTf)_3$	K_2HPO_4	37	4.6:1
9	$Fe(OTf)_3$	Na_2HPO_4	21	6.6:1
10	$Fe(OTf)_3$	Pyridine	67	3.8:1

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with the Fe salt (3.0 equiv), base (3.0 equiv), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), and benzofuran (53.9 µL, 5.0 equiv, 0.50 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

Table S10. Optimization of α,4-dimethylphenylacetic acid with 2-phenylethanol.

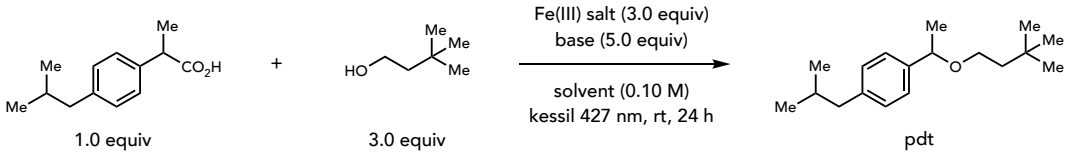


1.0 equiv 3.0 equiv pdt

entry	solvent	Fe(III) salt	base	pdt
1	CH_2Cl_2	$FeCl_3$	Na_3PO_4	39%
2	1,2-DCE	$FeCl_3$	Na_3PO_4	41%
3	MeCN	$FeCl_3$	Na_3PO_4	70%
4	toluene	$FeCl_3$	Na_3PO_4	18%
5	CH_2Cl_2	$FeCl_3$	K_3PO_4	37%
6	CH_2Cl_2	$FeCl_3$	K_2HPO_4	70%
7	CH_2Cl_2	$FeCl_3$	NaOAc	32%
8	CH_2Cl_2	$FeCl_3$	pyridine	17%
9	CH_2Cl_2	$Fe(acac)_3$	K_2HPO_4	61%
10	CH_2Cl_2	$Fe(NO_3)_3$	K_2HPO_4	0%
11	CH_2Cl_2	$Fe(OTf)_3$	K_2HPO_4	77%
15	1,2-DCE	$Fe(OTf)_3$	K_2HPO_4	74%

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with Fe(III) salt (3.0 equiv, 0.30 mmol), base (5.0 equiv, 0.50 mmol), solvent (1.0 mL, 0.10 M), α,4-dimethylphenylacetic acid (1.0 equiv, 0.10 mmol), and 2-phenylethanol (3.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

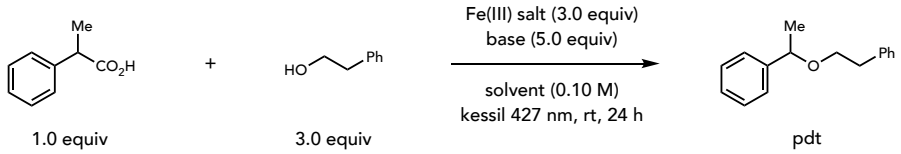
Table S11. Optimization of ibuprofen with 3,3-dimethyl-1-butanol.



entry	solvent	Fe(III) salt	base	pdt
1	CH_2Cl_2	$FeCl_3$	Na_3PO_4	60%
2	MeCN	$FeCl_3$	Na_3PO_4	77%
3	toluene	$FeCl_3$	Na_3PO_4	0%
4	CH_2Cl_2	$FeCl_3$	K_3PO_4	97%
5	CH_2Cl_2	$FeCl_3$	K_2HPO_4	80%
6	CH_2Cl_2	$FeCl_3$	Na_2CO_3	64%
7	CH_2Cl_2	$FeCl_3$	NaOAc	72%
8	CH_2Cl_2	$FeCl_3$	pyridine	72%
9	CH_2Cl_2	$Fe(acac)_3$	K_2HPO_4	0%
10	CH_2Cl_2	$Fe(NO_3)_3$	K_2HPO_4	0%
11	CH_2Cl_2	$Fe(OTf)_3$	K_2HPO_4	74%
12	1,2-DCE	$Fe(OTf)_3$	K_2HPO_4	99%
13	CH_2Cl_2	none	K_2HPO_4	0%
14*	CH_2Cl_2	$Fe(OTf)_3$	K_2HPO_4	0%
15	CH_2Cl_2	$Fe(OTf)_3$	none	0%

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with Fe(III) salt (3.0 equiv, 0.30 mmol), base (5.0 equiv, 0.50 mmol), solvent (1.0 mL, 0.10 M), ibuprofen (1.0 equiv, 0.10 mmol), and 3,3-dimethyl-1-butanol (3.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard. *Thermal control reaction. The reaction vial was wrapped in foil to block irradiation.

Table S12: Optimization of 2-phenylpropanoic acid with 2-phenylethanol.

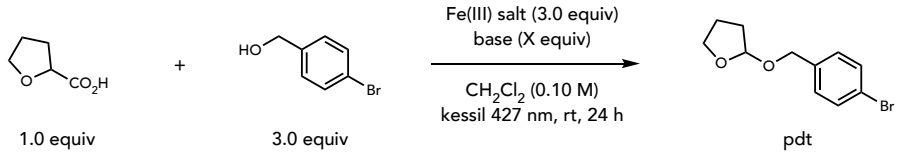


1.0 equiv 3.0 equiv pdt

entry	solvent	Fe(III) salt	base	pdt
1	CH_2Cl_2	$FeCl_3$	Na_3PO_4	64%
2	1,2-DCE	$FeCl_3$	Na_3PO_4	41%
3	MeCN	$FeCl_3$	Na_3PO_4	0%
4	toluene	$FeCl_3$	Na_3PO_4	16%
5	CH_2Cl_2	$FeCl_3$	K_3PO_4	23%
6	CH_2Cl_2	$FeCl_3$	K_2HPO_4	72%
7	CH_2Cl_2	$FeCl_3$	Na_2CO_3	54%
8	CH_2Cl_2	$FeCl_3$	NaOAc	35%
9	CH_2Cl_2	$FeCl_3$	pyridine	0%
10	CH_2Cl_2	$Fe(acac)_3$	K_2HPO_4	0%
11	CH_2Cl_2	$Fe(NO_3)_3$	K_2HPO_4	0%
12	CH_2Cl_2	$Fe(OTf)_3$	K_2HPO_4	89%
13	1,2-DCE	$Fe(OTf)_3$	K_2HPO_4	44%

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with Fe(III) salt (3.0 equiv, 0.30 mmol), base (5.0 equiv, 0.50 mmol), solvent (1.0 mL, 0.10 M), 2-phenylpropanoic acid (1.0 equiv, 0.10 mmol), and 2-phenylethanol (3.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

Table S13: Optimization of etherification with tetrahydro-2-furoic acid.

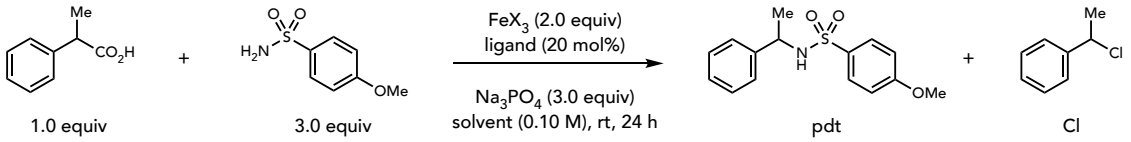


1.0 equiv 3.0 equiv pdt

entry	Fe(III) salt	base	base equiv	% pdt
1	$Fe(OTf)_3$	NaOAc	3	55
2	$Fe(OTf)_3$	pyridine	3	72
3	$Fe(OTf)_3$	K_2HPO_4	5	36
4	$FeCl_3$	NaOAc	3	0

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with Fe(III) salt (3.0 equiv, 0.30 mmol), base (X equiv), CH_2Cl_2 (1.0 mL, 0.10 M), tetrahydro-2-furoic acid (1.0 equiv, 0.10 mmol), and 4-bromobenzyl alcohol (3.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

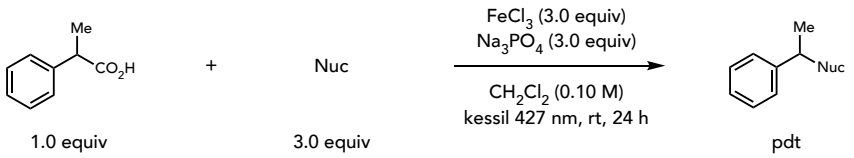
Table S14. Miscellaneous screens with a sulfonamide nucleophile.

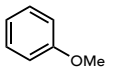
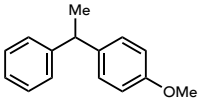
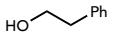
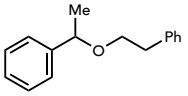
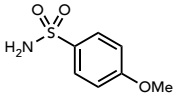
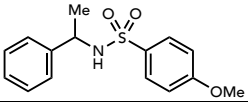


entry	FeX_3	solvent	ligand	% pdt	% Cl	% recovered acid
1	$Fe(OTf)_3$	CH_2Cl_2	(*t*-Bu)$_3$terpy	67	–	44
2	$Fe(OTf)_3$	CH_2Cl_2	bpy	70	–	24
3	$Fe(OTf)_3$	CH_2Cl_2	py	70	–	17
4	$Fe(OTf)_3$	CH_2Cl_2	KTp	80	–	13
5	$Fe(OTf)_3$	CH_2Cl_2	none	72	–	18
6	$FeCl_3$	CH_2Cl_2	none	66	0	14
7	$FeBr_3$	CH_2Cl_2	none	28	–	80
8	$FeCl_3$	MeCN	None	0	99	0
9*	$Fe(OTf)_3$	CH_2Cl_2	none	0	–	95
10*	$Fe(OTf)_3$	CH_2Cl_2	KTp	0	–	83

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with the Fe salt (2.0 equiv), the ligand (20 mol%), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol), the solvent (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), and 4-methoxybenzene sulfonamide (0.056 g, 3.0 equiv, 0.30 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard. *Thermal control reaction. The reaction vial was wrapped in foil to block irradiation.

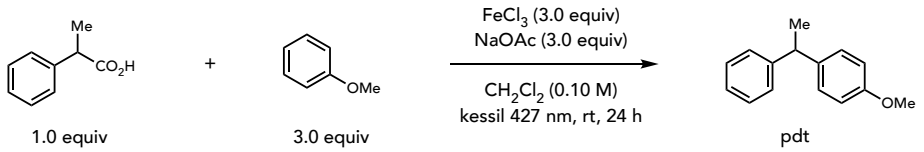
Table S15: Single set of reaction conditions across three nucleophile families.



entry	nuc	pdt	% pdt
1			53
2			64
3			99*

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (3.0 equiv, 0.30 mmol), Na_3PO_4 (3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (1.0 equiv, 0.10 mmol), and nucleophile (3.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard. *Isolated yield.

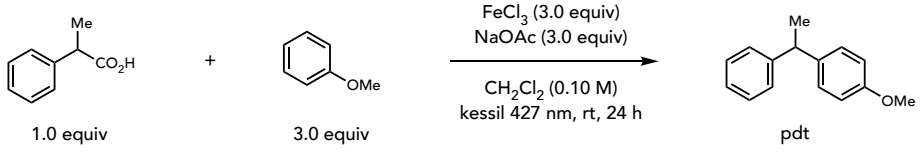
Table S16: Reaction conducted under air.



entry	deviation	% pdt
1	open to air	83

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (3.0 equiv, 0.30 mmol), NaOAc (3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (1.0 equiv, 0.10 mmol), and nucleophile (3.0 equiv). The vial removed from the glovebox, and remained open to air for 10 minutes. The vial was capped and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

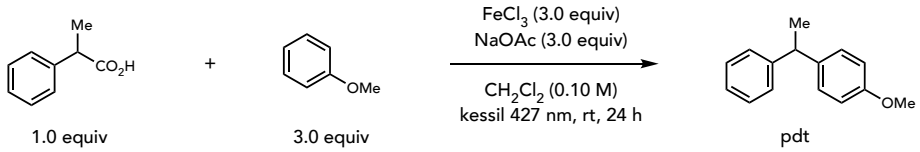
Table S17: Reaction sparged with N_2.



entry	deviation	% pdt
1	Everything massed outside glovebox	87

General procedure: An oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (3.0 equiv, 0.30 mmol), NaOAc (3.0 equiv, 0.30 mmol), 2-phenylpropanoic acid (1.0 equiv, 0.10 mmol), nucleophile (3.0 equiv), and CH_2Cl_2 (1.0 mL, 0.10 M). The vial is capped and sparged under N_2 for 5 minutes. The vial was wrapped in parafilm and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.
Note: We store $FeCl_3$ in the glovebox to increase its lifetime as it is very hygroscopic. For this reaction, we removed a vial of excess $FeCl_3$ and kept it capped on the benchtop for 24 h. After 24 h, we opened the vial of $FeCl_3$ and added all reagents to a new vial as detailed in the General Procedure. The purpose of this reaction was to demonstrate this robust protocol can be applied in laboratory settings that do not contain a glovebox.

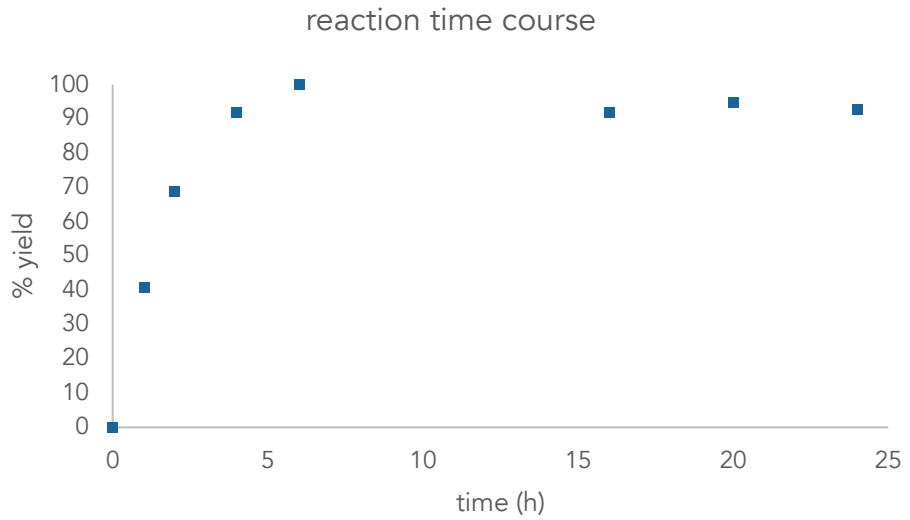
Table S18. Reaction time course.



entry	time (h)	% pdt
1	1	41
2	2	69
3	4	92
4	6	100
5	16	92
6	20	95
7	24	93

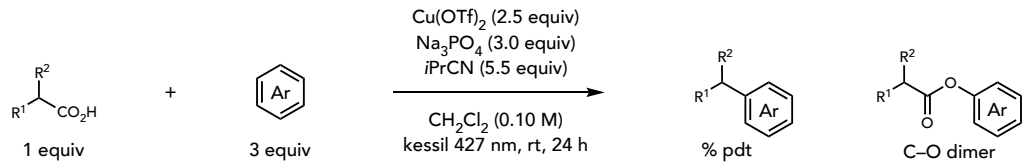
General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (3.0 equiv, 0.30 mmol), NaOAc (3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (1.0 equiv, 0.10 mmol), and anisole (3.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. Seven identical reactions were irradiated and removed from irradiation at the specified time point. The crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

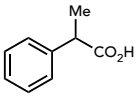
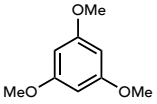
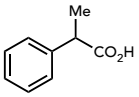
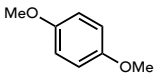
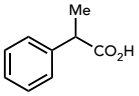
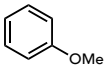
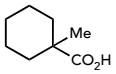
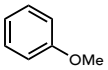
Figure S1. Plot of the reaction time course.



The reaction is complete after four hours and there is no degradation of the product over time. Small differences in the reaction yield (from 4–24 h) can be attributed to the slight variation in the set-up of seven reactions and the error in ^1H NMR analysis of crude reaction mixtures.

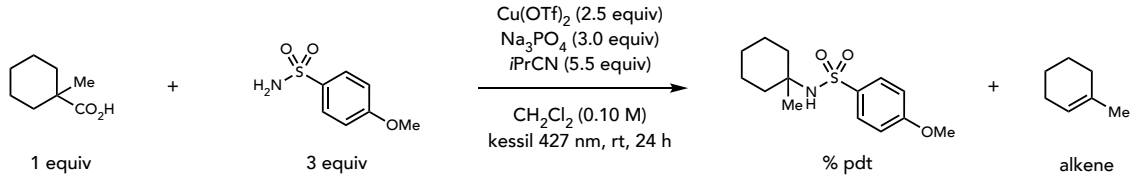
Table S19. Comparison to Cu(II) conditions with C- and O- nucleophiles.[16]



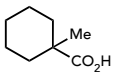
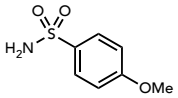
entry	acid	nuc	% pdt	C–O dimer
1			20%	7%
2			23%	27%
3			14%	27%
4			0%	0%

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (2.5 equiv, 0.25 mmol), Na_3PO_4 (3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), *i*-PrCN (5.5 equiv, 0.55 mmol), acid (1.0 equiv, 0.10 mmol), and nucleophile (3.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 μL) as an internal standard.

Table S20. Comparison to Cu(II) with a sulfonamide nucleophile.

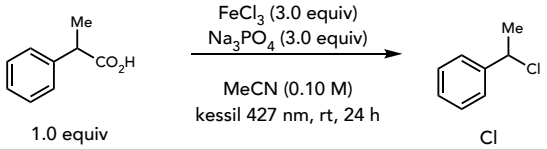


1 equiv | 3 equiv | % pdt | alkene

entry	acid	nuc	% pdt	alkene
1			0%	40%

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (2.5 equiv, 0.25 mmol), Na_3PO_4 (3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), *i*-PrCN (5.5 equiv, 0.55 mmol), acid (1.0 equiv, 0.10 mmol), and nucleophile (3.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 μL) as an internal standard.

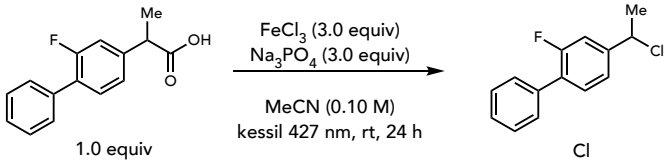
Table S21. Decarboxylative chlorination of 2-phenylpropanoic acid.



entry	deviation from rxn cond.	% Cl
1	none	99

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (3.0 equiv, 0.30 mmol), Na_3PO_4 (3.0 equiv, 0.30 mmol), MeCN (1.0 mL, 0.10 M), and 2-phenylpropanoic acid (1.0 equiv, 0.10 mmol) The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 μL) as an internal standard.

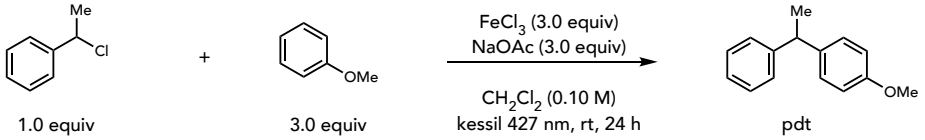
Table S22. Decarboxylative chlorination of flurbiprofen.



entry	deviation from rxn cond.	% Cl
1	none	92

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (3.0 equiv, 0.30 mmol), Na_3PO_4 (3.0 equiv, 0.30 mmol), MeCN (1.0 mL, 0.10 M), and flurbiprofen (1.0 equiv, 0.10 mmol) The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 μL) as an internal standard.

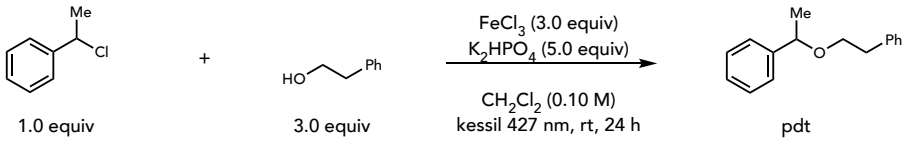
Table S23. Fe-mediated arylation from benzylic chloride.



entry	deviation from rxn cond.	% pdt	r.r.
1	none	94	5:1
2*	no light	84	8:1
3	no $FeCl_3$	no rxn	–
4	no $FeCl_3$, no light	no rxn	–

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (3.0 equiv, 0.30 mmol), NaOAc (3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), (1-chloroethyl)benzene (1.0 equiv, 0.10 mmol), and anisole (3.0 equiv, 0.30 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 μL) as an internal standard. *Thermal control reaction. The reaction vial was wrapped in foil to block irradiation.

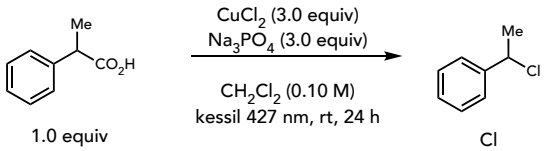
Table S24. Fe-mediated etherification from benzylic chloride.



entry	deviation from rxn cond.	% pdt
1	none	73

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (3.0 equiv, 0.30 mmol), K_2HPO_4 (5.0 equiv, 0.50 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), (1-chloroethyl)benzene (1.0 equiv, 0.10 mmol), and 2-phenylethanol (3.0 equiv, 0.30 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

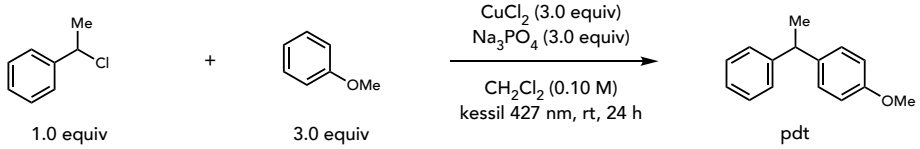
Table S25. Decarboxylative chlorination of 2-phenylpropanoic acid with $CuCl_2$.



entry	deviation from rxn cond.	% Cl	% RSM
1	none	0	96

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $CuCl_2$ (3.0 equiv, 0.30 mmol), Na_3PO_4 (3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), and 2-phenylpropanoic acid (1.0 equiv, 0.10 mmol) The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

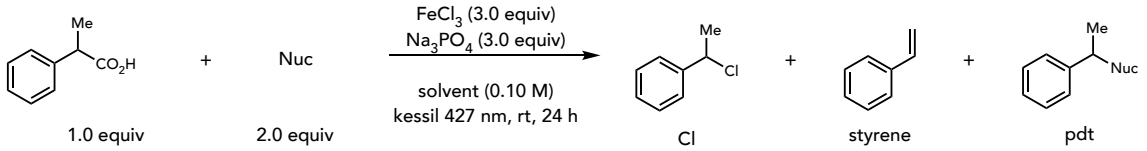
Table S26. Cu-mediated arylation from benzylic chloride.



entry	deviation from rxn cond.	% pdt	r.r.	% RSM
1	none	15	5:1	37%

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $CuCl_2$ (3.0 equiv, 0.30 mmol), Na_3PO_4 (3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), (1-chloroethyl)benzene (1.0 equiv, 0.10 mmol), and anisole (3.0 equiv, 0.30 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

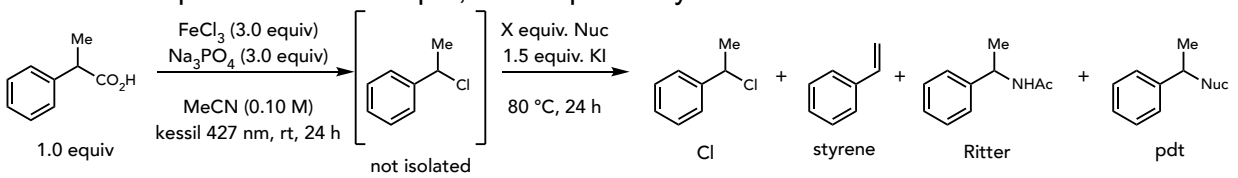
Table S27. One-pot, one-step decarboxylation with alkyl and aromatic amines.



entry	nucleophile	solvent	% Cl	% styrene	% pdt
1	morpholine	MeCN	59	20	0
2	morpholine	DMF	0	0	0
3	morpholine	DCM	54	1	0
4	*p*-toluidine	MeCN	31	1	4
5	*p*-toluidine	DMF	0	0	0
6	*p*-toluidine	DCM	0	0	20
7	*n*-butylamine	MeCN	66	10	0
8	*n*-butylamine	DMF	0	0	8
9	*n*-butylamine	DCM	0	1	21
10	2-methylimidazole	MeCN	41	0	0
11	2-methylimidazole	DMF	0	0	0
12	2-methylimidazole	DCM	15	1	14

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol), the solvent (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol), and the nucleophile (2.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

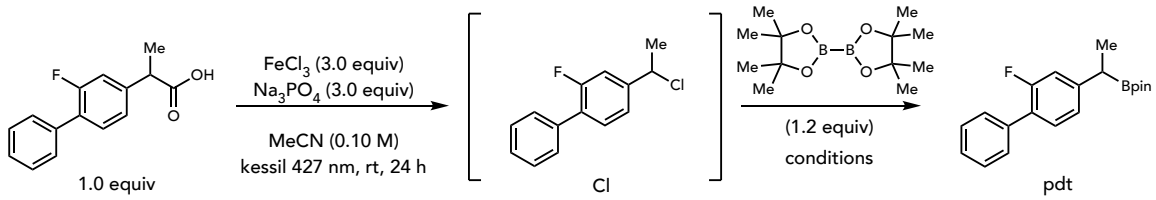
Table S28. Optimization of one-pot, two-step for alkyl and aromatic amines.



entry	nucleophile	workup	equiv nuc	Cl (%)	styrene (%)	Ritter (%)	pdt (%)
1	morpholine	celite plug	5.0	9	0	0	57
2	morpholine	silica plug	5.0	13	0	0	56
3	morpholine	no workup	3.0	0	47	0	29
4	morpholine	no workup	5.0	0	23	0	54
5	morpholine	no workup	7.0	0	20	0	58
6	morpholine	no workup	10	0	1	0	64
7	*p*-toluidine	no workup	2.0	0	0	8	37
8	*p*-toluidine	no workup	5.0	0	0	9	35
9	*p*-toluidine	no workup	10	0	0	6	45
10	*p*-toluidine	NH_4Cl wash	2.0	0	0	8	31
11	*p*-toluidine	K_2CO_3 wash	2.0	0	0	11	25
12	2-methylimidazole	no workup	3.0	0	0	36	1
13	2-methylimidazole	no workup	5.0	0	0	11	8
14	2-methylimidazole	no workup	7.0	4	0	6	31
15	2-methylimidazole	no workup	10	0	0	11	46
16	*n*-butylamine	no workup	3.0	0	4	16	11
17	*n*-butylamine	no workup	5.0	0	4	7	34
18	*n*-butylamine	no workup	7.0	0	2	10	51
19	*n*-butylamine	no workup	10	0	1	6	72

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol), MeCN (1.0 mL, 0.10 M), and 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is subjected to the corresponding workup (see below), charged with the nucleophile (3.0–10 equiv) and KI (0.025 g, 1.5 equiv, 0.15 mmol), and heated at 80 °C. After 16 h, the reaction is diluted with EtOAc and saturated aqueous K_2CO_3. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard. **Celite plug workup:** The crude reaction is pushed through a small pad of celite to remove the majority of the solids. The celite pad is rinsed with an additional 0.50 mL of MeCN. **Silica plug workup:** The crude reaction is pushed through a small pad of silica to remove the solids. The silica pad is rinsed with an additional 0.50 mL of MeCN. **NH_4Cl wash workup:** The crude reaction mixture is diluted with 1.5 mL diethyl ether and quenched with saturated aqueous NH_4Cl. The organic layer is carefully removed with a glass pipette. The aqueous layer is washed 3x 1 mL with diethyl ether. The combined organic layers are concentrated under reduced pressure. MeCN (1.0 mL, 0.10 M) is then added. **K_2CO_3 wash workup:** The crude reaction mixture is diluted with 1.5 mL diethyl ether and quenched with saturated aqueous K_2CO_3. The organic layer is carefully removed with a glass pipette. The aqueous layer is washed 3x1 mL with diethyl ether. The combined organic layers are concentrated under reduced pressure. MeCN (1.0 mL, 0.10 M) is then added. **No workup**: The crude reaction is directly charged with the nucleophile. No other manipulations performed.

Table S29. Optimization of one-pot, two-step for borylation.



entry	workup	borylation conditions	% pdt	% Cl
1	no workup	IPrCuCl (10 mol%), 1.2 equiv KOMe, THF (0.2 M), rt	0	78
2	NH_4Cl quench	IPrCuCl (10 mol%), 1.2 equiv KOMe, THF (0.2 M), rt	0	75
3	Celite filtration	IPrCuCl (10 mol%), 1.2 equiv KOMe, THF (0.2 M), rt	0	73
4	Celite filtration	IPrCuCl (10 mol%), 1.2 equiv KOMe, THF (0.2 M), 60 °C	0	61
5	Celite filtration	IPrCuCl (10 mol%), 1.2 equiv KOMe, THF (0.2 M), 80 °C	0	59
6	NH_4Cl quench	CuCl (10 mol%), Xantphos (10 mol%), 1.2 equiv KO*t*-Bu, THF (0.2 M), rt	0	0
7	NH_4Cl quench, then silica plug	CuCl (10 mol%), Xantphos (10 mol%) 1.2 equiv KO*t*-Bu, THF (0.2 M), rt	55	0
8	NH_4Cl quench, then silica plug	CuCl (10 mol%), Xantphos (10 mol%) 1.2 equiv KO*t*-Bu, THF (0.2 M), 60 °C	31	0

General procedure: An oven-dried 4-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol), flurbiprofen (0.024 g, 1.0 equiv, 0.10 mmol), and MeCN (1.0 mL, 0.10 M). The vial is sealed with a screwcap bearing a teflon septum, removed from the glovebox, and placed into a EvoluChem™ PhotoRedOx Box. Stirring at 800 rpm is engaged and the vial is irradiated at 427 nm with a 40 W Kessil™ lamp. After 24 h, the light is turned off, the vial is removed from the PhotoRedox Box, and subjected to the indicated workup to obtain the crude benzylic chloride intermediate.

A separate oven-dried 4-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with the Cu catalyst (10 mol%) and anhydrous THF (0.50 mL). The vial is next charged with bis(pinacolato)diboron (0.030 g, 1.2 equiv, 0.12 mmol) and the base (1.2 equiv) and swirled gently for ca. 5 min. Finally, the crude benzylic chloride from the first step is next added, the vial is sealed with a screwcap bearing a teflon septum, removed from the glovebox, and stirred at the indicated temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

C. Additional isolated substrate combinations

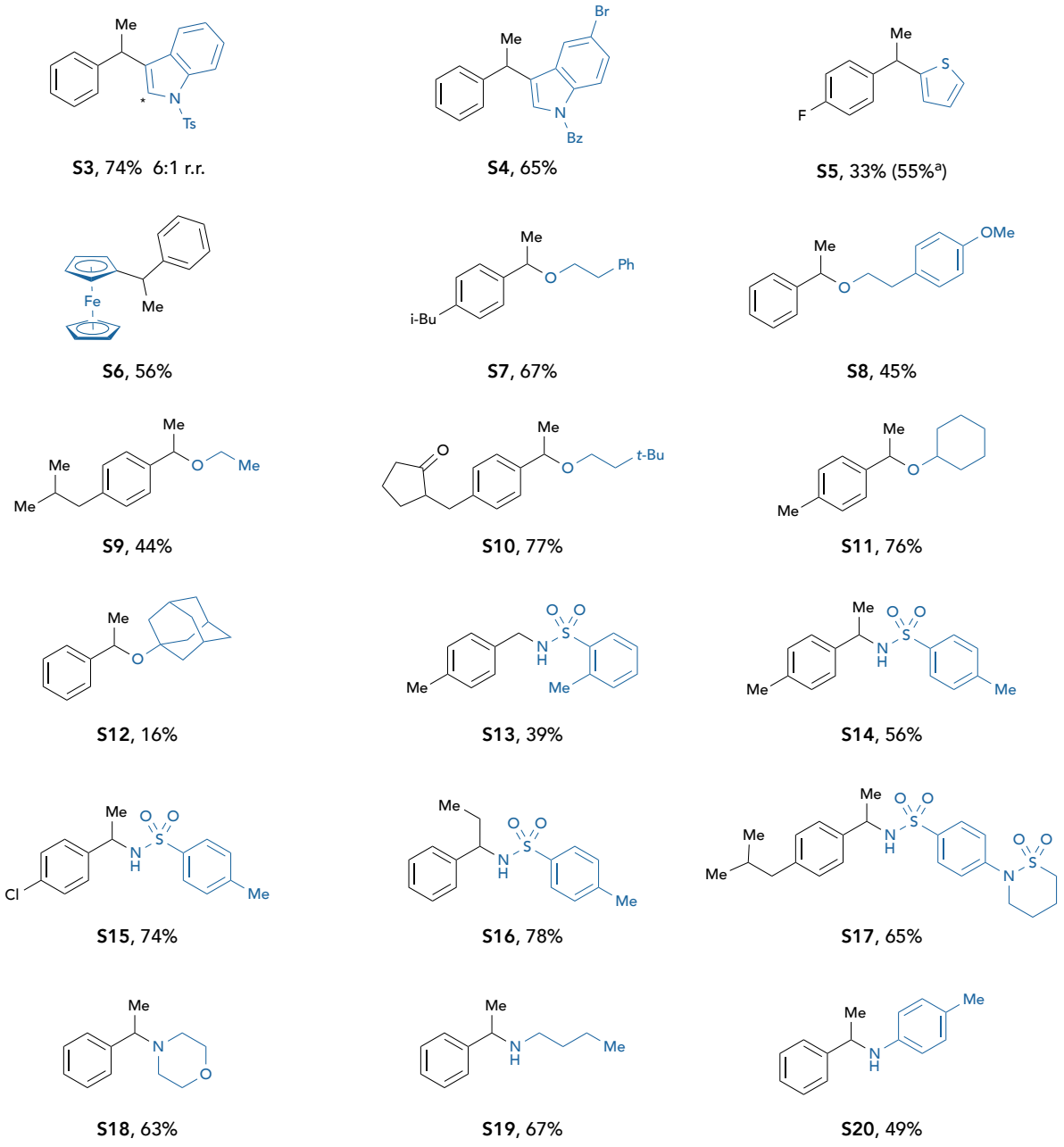
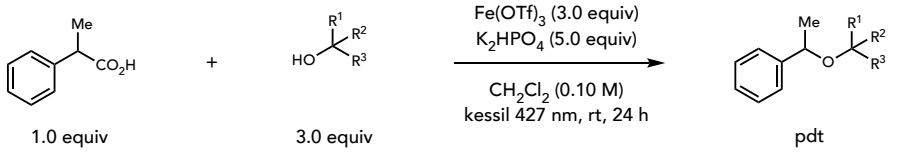
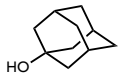
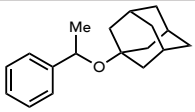
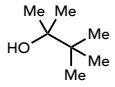
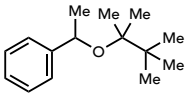


Figure S2. Additional cross-nucleophile products that were isolated and characterized. Reaction conditions are reported in the Experimental Procedures section of the SI. All yields are isolated unless otherwise noted. [a]Yields are determined by ^{1}H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

D. Substrate limitations

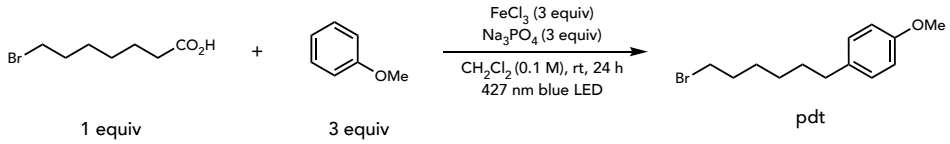
Table S30. Sterically hindered alcohols.



entry	nuc	pdt	% pdt
1			16*
2			0

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Fe(OTf)_3$ (3.0 equiv, 0.30 mmol), K_2HPO_4 (5.0 equiv, 0.50 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), 2-phenylpropanoic acid (1.0 equiv, 0.10 mmol), and alcohol (3.0 equiv). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and saturated aqueous NH_4Cl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard unless otherwise noted. *Isolated yield.

Table S31. Primary aliphatic carboxylic acid.



entry	% pdt	% RSM
1	0	100

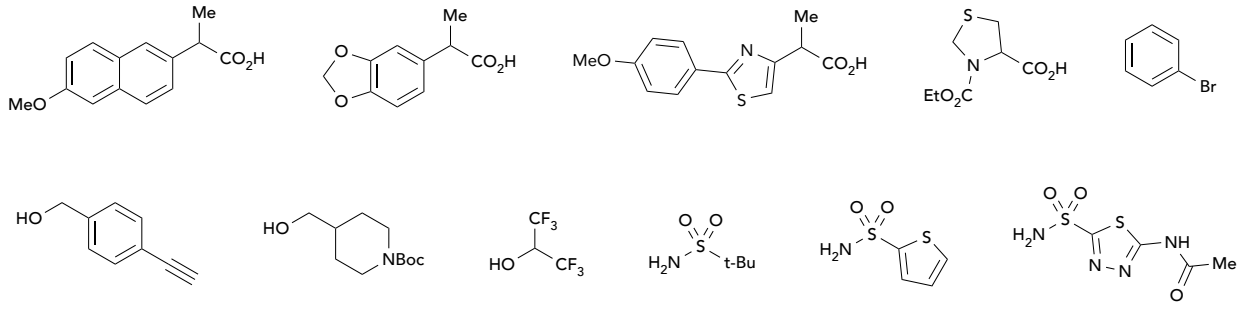
General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol), the dichloromethane (1.0 mL, 0.10 M), 7-bromoheptanoic acid (0.021 g, 1.0 equiv, 0.10 mmol), and the anisole (0.033 mL, 3.0 equiv, 0.3 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and 1M HCl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

Table S32. Secondary aliphatic carboxylic acid.

entry	% pdt	% RSM	% elimination
1	0	86	4

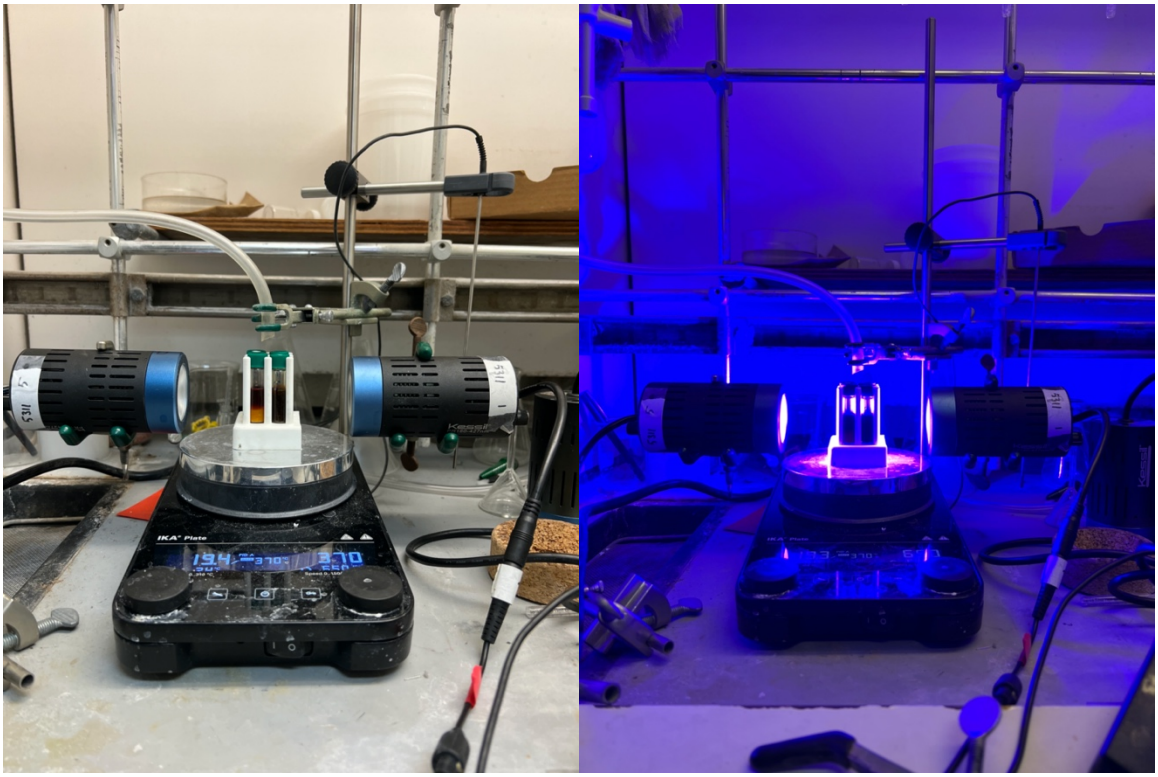
General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol), the dichloromethane (1.0 mL, 0.10 M), 4-(4-chlorophenyl)cyclohexane-1-carboxylic acid (0.024 g, 1.0 equiv, 0.10 mmol), and the anisole (0.033 mL, 3.0 equiv, 0.3 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with EtOAc and 1M HCl. Yields are determined by ^1H NMR analysis using 1-methylnaphthalene (10 µL) as an internal standard.

Figure S3. Other unsuccessful substrates.



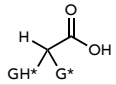
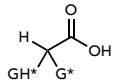
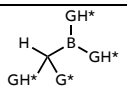
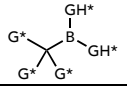
E. Photo of laboratory set up for isolation reactions:

Figure S4. Vials are irradiated at 427 nm with two 40 W Kessil Lamp PR160 lamps at a distance of 10 cm.



F. Analysis of alkyl building blocks from commercial vendors

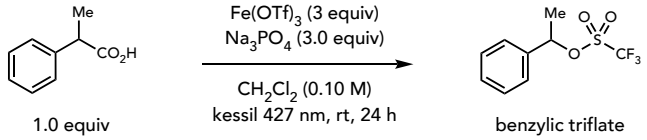
Table S33. The number of commercially available building blocks.

Structure of Fragment	Combi-Blocks	Alfa Chemistry	Ambeed
	18,873	17,109	15,624
	2,195	1,741	1,974
R–COOH sum	21,068	18,850	17,598
	16,611	20,498	14,775
	2,028	3,134	1,779
R–OH sum	18,639	23,632	16,6554
	16,556	11,048	15,224
	1,147	772	1,180
R–NH_2 sum	17,703	11,820	16,404
	5,253	4,667	5,214
	452	964	299
R–Cl sum	5,705	5,631	5,513
	3,564	2,927	3,861
	325	377	193
R–Br sum	3,889	3,304	4,054
	422	182	298
	47	3	18
R–I sum	469	185	316
	382	572	206
	9	63	11
R–[B]	391	635	217

The number of commercially available building blocks was analyzed with Reaxy based on the fragments drawn below. Under the Commercial Substances filter, the fragments were counted by vendor through the Commercial Suppliers tab. The number of compounds from Combi-Blocks, Alfa Chemistry, and Ambeed was recorded for each part structure. The search identified primary and secondary building blocks separate from tertiary, therefore, the sum of both searches was calculated and reported. Data collected on Dec. 8, 2022.

G. Evidence for decarboxylative triflation

Figure S5. GC-MS trace of proposed benzylic triflate intermediate.



Operational notes: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Fe(OTf)_3$ (3.0 equiv, 0.30 mmol), Na_3PO_4 (3.0 equiv, 0.30 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), and 2-phenylpropanoic acid (1.0 equiv, 0.10 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is filtered through a plug of celite and analyzed by gas chromatography-mass spectrometry using 1-methylnaphthalene (10 µL) as an internal standard.

Figure S6. Gas chromatogram of the reaction.

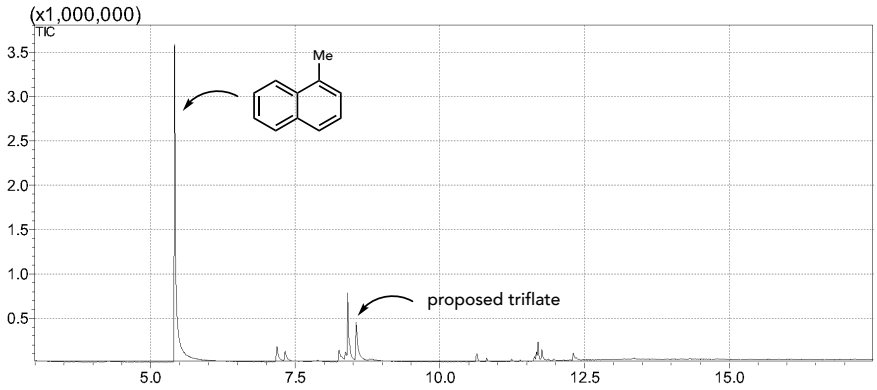
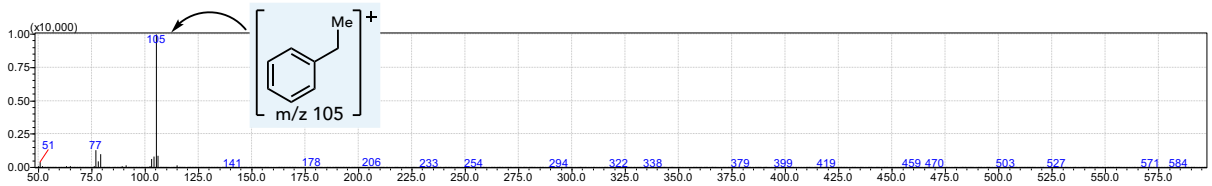
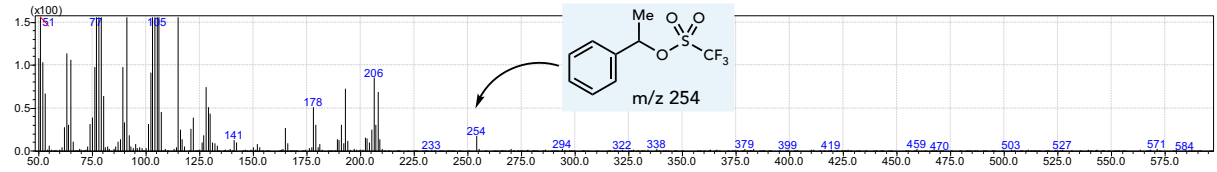


Figure S7. Mass spectrum of proposed triflate at a retention time of 8.5.



Comment: Major ion observed is the benzylic fragment.

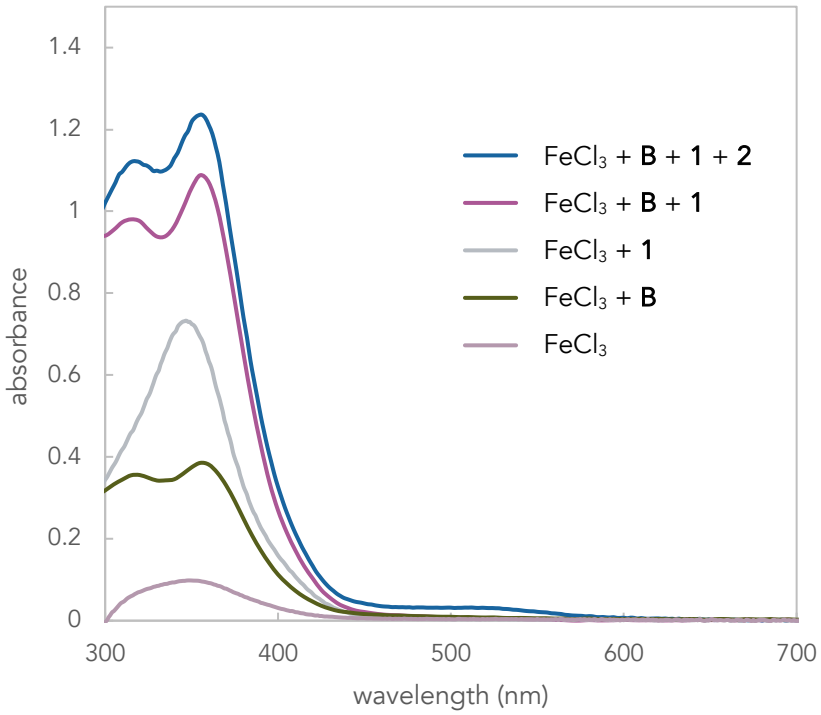
Figure S8. Zoomed mass spectrum of proposed triflate at a retention time of 8.5.



Comment: When zooming in significantly on the mass spectrum at 8.5, 254 is observed. The benzylic triflate is our best explanation for this peak as the retention time and fragmentation pattern do not match any of the known by-products commonly formed in the absence of the nucleophile. This is consistent with the instability of benzylic triflates, for which we propose rapid fragmentation to the benzyl fragment (m/z 105).

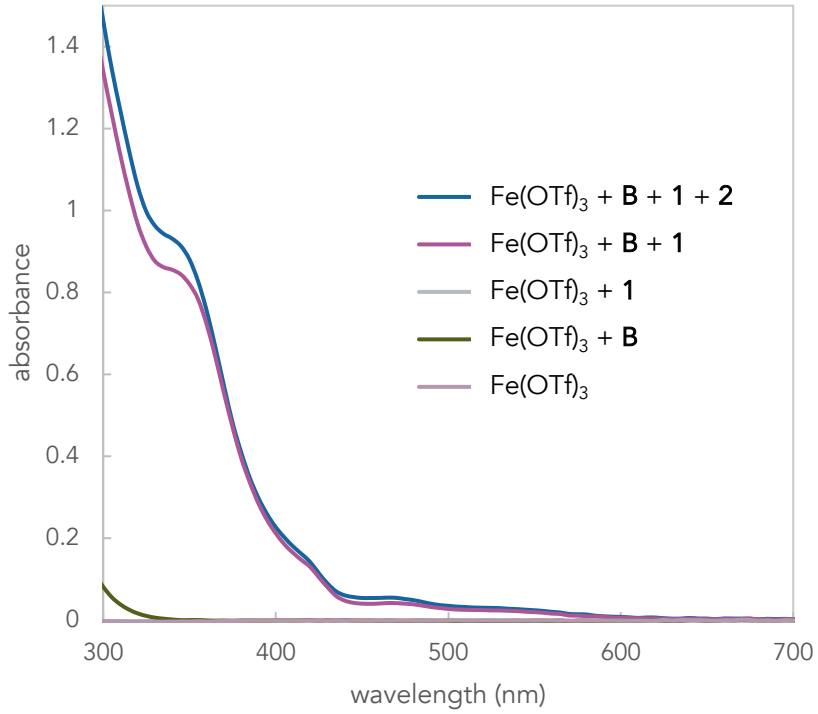
H. UV-Vis experiments

Figure S9. Absorption spectra of $FeCl_3$, 2-phenylpropanoic acid (**1**), anisole (**2**), and NaOAc (**B**) dissolved in CH_2Cl_2. The spectra were all recorded in quartz tubes under ambient conditions.



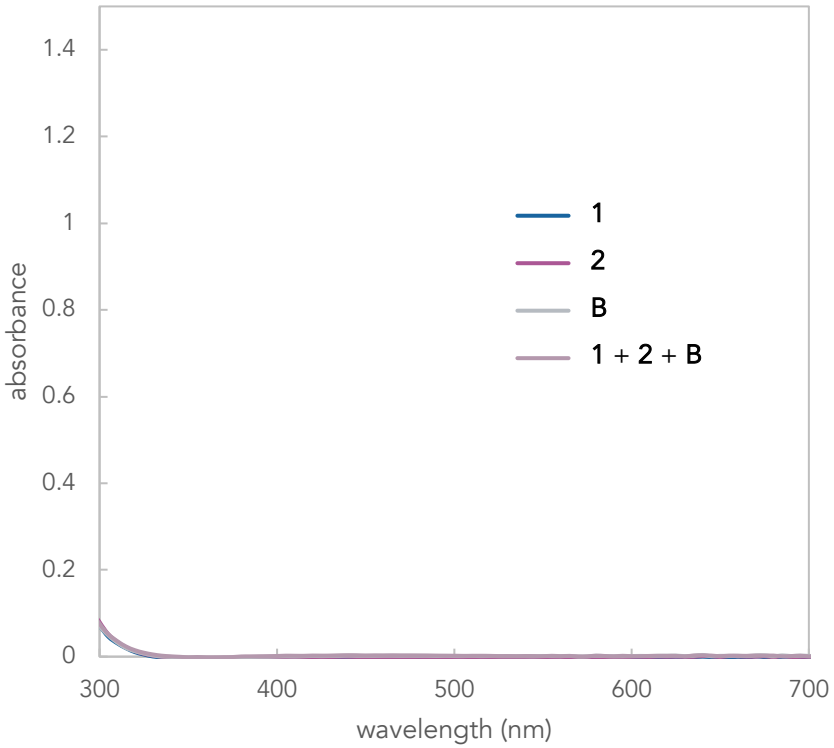
Operational notes: The solutions were prepared in a nitrogen-filled glovebox at reaction stoichiometry: $FeCl_3$ (0.049 g, 0.30 mmol), NaOAc (0.025 g, 0.30 mmol), dichloromethane (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 0.10 mmol), and anisole (0.033 mL, 0.30 mmol). The vials were sealed, removed from the glovebox, and stirred for 30 minutes. The solutions were filtered through a syringe filter to remove the undissolved iron and base. 0.070 mL of the filtered solution was added to a cuvette and diluted with 3.0 mL dichloromethane ($2 \cdot 10^{-3}$ M). To obtain the reported absorbance spectra, the prepared solution underwent a serial dilution where 1.0 mL of the solution was diluted to 3.0 mL with dichloromethane, three times. The approximate concentration of the analyzed solutions is $8 \cdot 10^{-5}$ M.

Figure S10. Absorption spectra of $Fe(OTf)_3$, 2-phenylpropanoic acid (**1**), anisole (**2**), and NaOAc (**B**) dissolved in CH_2Cl_2. The spectra were all recorded in quartz tubes under ambient conditions.



Operational notes: The solutions were prepared in a nitrogen-filled glovebox at reaction stoichiometry: $Fe(OTf)_3$ (0.151 g, 0.30 mmol), NaOAc (0.025 g, 0.30 mmol), dichloromethane (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 0.10 mmol), and anisole (0.033 mL, 0.30 mmol). The vials were sealed, removed from the glovebox, and stirred for 30 minutes. The solutions were filtered through a syringe filter to remove the undissolved iron and base. 0.070 mL of the filtered solution was added to a cuvette and diluted with 3.0 mL dichloromethane ($2 \cdot 10^{-3}$ M).

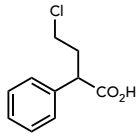
Figure S11. Absorption spectra of 2-phenylpropanoic acid (**1**), anisole (**2**), and NaOAc (**B**) dissolved in CH_2Cl_2. The spectra were all recorded in quartz tubes under ambient conditions.



Operational notes: The solutions were prepared in a nitrogen-filled glovebox at reaction stoichiometry: NaOAc (0.025 g, 0.30 mmol), dichloromethane (1.0 mL, 0.10 M), 2-phenylpropanoic acid (0.015 g, 0.10 mmol), and anisole (0.033 mL, 0.30 mmol). The vials were sealed, removed from the glovebox, and stirred for 30 minutes. The solutions were filtered through a syringe filter to remove the undissolved iron and base. 0.070 mL of the filtered solution was added to a cuvette and diluted with 3.0 mL dichloromethane ($2 \cdot 10^{-3}$ M).

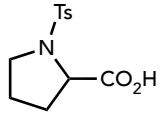
I. Substrate Preparation

4-chloro-2-phenylbutanoic acid[2] (S1)



A flame-dried round-bottomed flask was equipped with a stirbar and charged with phenyl acetic acid (0.681 g, 1 equiv, 5 mmol) and placed under N_2. Anhydrous THF (20 mL, 0.25 M) was added and the solution was cooled to –78 ºC. *n*-BuLi (2.5 M in hexane, 4 mL, 2 equiv, 10 mmol) was added dropwise to the solution. The mixture was allowed to warm to 0 ºC and was stirred for 1 h. 1-Bromo-2-chloroethane (0.42 mL, 1 equiv, 5 mmol) was added and the reaction was allowed to warm to room temperature over 16 hours. The reaction mixture was quenched with the addition of aqueous HCl (1 M, 25 mL). The aqueous phase was extracted with EtOAc (3 x 25 mL) and the combined organic fractions were dried over $MgSO_4$, filtered through a plug of celite, and concentrated under reduced pressure to give a pale yellow solid (0.815 g, 82% yield). The crude product was analytically pure and used without further purification. The spectral data matched those previously reported.[2] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H), 3.99 – 3.87 (m, 1H), 3.55 (dt, *J* = 11.5, 5.9 Hz, 1H), 3.37 (ddd, *J* = 11.1, 8.2, 5.3 Hz, 1H), 2.61 – 2.43 (m, 1H), 2.24 (dddd, *J* = 14.5, 8.3, 6.3, 5.3 Hz, 1H).

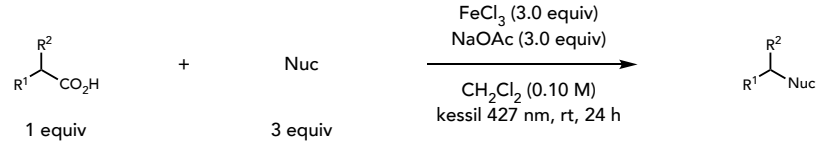
Tosylproline (S2)



L-Proline (0.460 g, 1 equiv, 4.0 mmol) was dissolved in 1.5 M aqueous NaOH (6.5 mL). Sulfonyl chloride (0.915 g, 1.2 equiv, 4.8 mmol) was added in Et2O (4 mL) and the resulting mixture was stirred overnight at room temperature. Concentrated HCl was added dropwise to the solution until the pH = 2. The organic layer was separated, and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was recrystallized (DCM/hexanes) to afford a white solid (0.932 g, 86% yield). The spectral data matched those previously reported.[3] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.25 (dd, *J* = 8.3, 3.5 Hz, 1H), 3.59 – 3.47 (m, 1H), 3.32 – 3.11 (m, 1H), 2.45 (s, 3H), 2.24 – 2.11 (m, 1H), 2.01 – 1.84 (m, 2H), 1.81 – 1.57 (m, 1H).

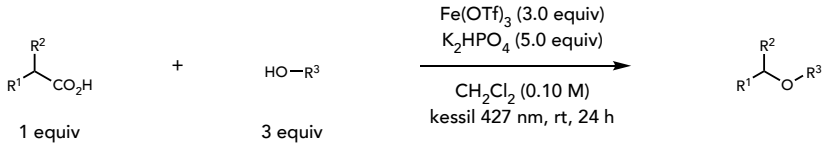
J. Experimental procedures, isolation, and characterization

General Procedure A:



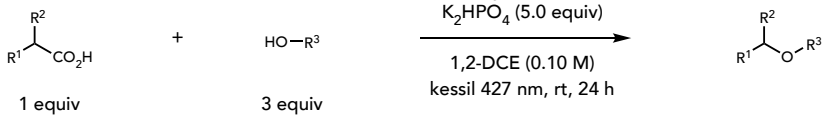
An oven-dried 6-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with $FeCl_3$ (3.0 equiv), NaOAc (3.0 equiv), the carbon nucleophile (3.0 equiv), the carboxylic acid (1.0 equiv), and methylene chloride (0.10 M). The vial is sealed with a screwcap bearing a teflon septum, removed from the glovebox, and placed on a stir plate. The vial is irradiated at 427 nm with two 40 W Kessil Lamp PR160 lamps at a distance of 10 cm with stirring at 800 rpm. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with 1.5 mL EtOAc and absorbed directly on diatomaceous earth (Celite®). The product is purified by flash chromatography.

General Procedure B:



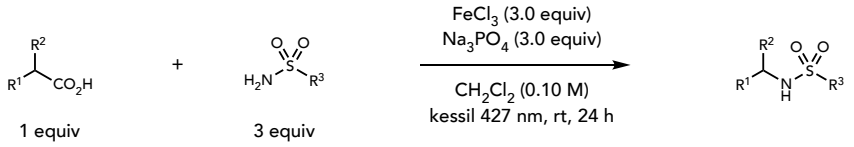
An oven-dried 6-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with $Fe(OTf)_3$ (0.453 g, 3.0 equiv, 0.9 mmol), K_2HPO_4 (0.261 g, 5.0 equiv, 1.5 mmol), the alcohol nucleophile (3.0 equiv, 0.9 mmol), the carboxylic acid (1.0 equiv, 0.3 mmol), and methylene chloride (3.0 mL, 0.10 M). The vial is sealed with a screwcap bearing a teflon septum, removed from the glovebox, and placed on a stir plate. The vial is irradiated at 427 nm with two 40 W Kessil Lamp PR160 lamps at a distance of 10 cm with stirring at 800 rpm. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with 1.5 mL EtOAc and absorbed directly on diatomaceous earth (Celite®). The product is purified by flash chromatography on silica gel.

General Procedure C:



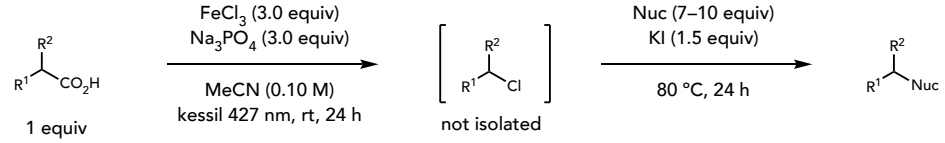
An oven-dried 6-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with $FeCl_3$ (0.146 g, 3.0 equiv, 0.9 mmol), K_2HPO_4 (0.261 g, 5.0 equiv, 1.5 mmol), the alcohol nucleophile (3.0 equiv, 0.9 mmol), the carboxylic acid (1.0 equiv, 0.3 mmol), and 1,2-dichloroethane (3.0 mL, 0.10 M). The vial is sealed with a screwcap bearing a teflon septum, removed from the glovebox, and placed on a stir plate. The vial is irradiated at 427 nm with two 40 W Kessil Lamp PR160 lamps at a distance of 10 cm with stirring at 800 rpm. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with 1.5 mL EtOAc and absorbed directly on diatomaceous earth (Celite®). The product is purified by flash chromatography on silica gel.

General Procedure D:



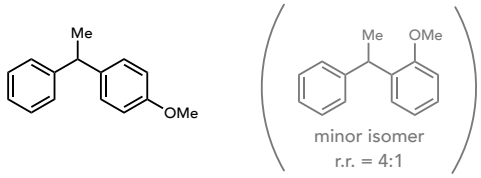
In a nitrogen-filled glovebox, an oven-dried 6-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.097 g, 3.0 equiv, 0.60 mmol), Na_3PO_4 (0.098 g, 3.0 equiv, 0.60 mmol), the carboxylic acid (1.0 equiv, 0.20 mmol), the sulfonamide (3.0 equiv, 0.60 mmol), and methylene chloride (2.0 mL, 0.10 M). The vial is sealed, removed from the glovebox, and irradiated at 427 nm with two 40 W Kessil Lamp PR160 lamps at a distance of 10 cm with stirring at 1000 rpm. A fan is used to maintain the vial at room temperature. After 24 h, the crude reaction mixture is diluted with 1.5 mL EtOAc and adsorbed directly on diatomaceous earth (Celite®). The product is purified by flash chromatography on silica gel, eluting with mixtures of ethyl acetate in hexanes.

General Procedure E:



In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol), MeCN (1.0 mL, 0.10 M), and the carboxylic acid (1.0 equiv, 0.10 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a Kessil® PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After 24 h, the cap is removed, and the crude mixture is directly charged with the amine nucleophile (7.0–10 equiv, 0.70–1.0 mmol) and KI (0.025 g, 1.5 equiv, 0.15 mmol). The vial is resealed and heated, with stirring, at 80 °C for 16 h. The crude reaction mixture is diluted with 1.5 mL EtOAc and adsorbed directly on diatomaceous earth (Celite®). The product is purified by flash chromatography on silica gel, eluting with mixtures of ethyl acetate in hexanes.

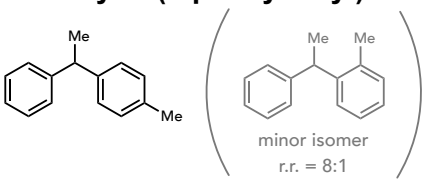
1-methoxy-4-(1-phenylethyl)benzene (3)



Prepared according to **General Procedure A** with anisole (65.1 µL, 3.0 equiv, 0.60 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 2.5% ethyl acetate in hexanes, afforded a mixture of the two isomeric products as a clear oil (40 mg, 94% yield, 4:1 *para*:*ortho*). The spectral data matched that previously reported.[4] *Where resolved, signals for the minor isomer are given in brackets.* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 2H), 7.24 – 7.18 (m, 3H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), [4.59 (q, *J* = 7.3 Hz, 0.25H)], 4.12 (q, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), [3.78 (s, 0.75H)], 1.63 (d, *J* = 7.3 Hz, 3H), [1.59 (d, *J* = 7.3 Hz, 0.75H)]. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.98, [156.98], 146.92, [146.53], 138.70, [135.06], 128.65, 128.47, [128.22], [127.86], [127.80], 127.67,

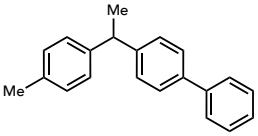
[127.18], 126.07, [125.80], [120.64], 113.87, [110.74], [55.57], 55.38, 44.08, [37.53], 22.20, [21.02]. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{15}H_{15}O$, 211.1117; found, 211.117.

1-methyl-4-(1-phenylethyl)benzene (4)



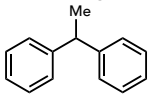
Prepared according to **General Procedure A** with toluene (213 µL, 10 equiv, 1.0 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 0–5% ethyl acetate in hexanes, afforded a mixture of the two isomeric products as a clear oil (30.9 mg, 79% yield, 8:1 *para*:*ortho*). The spectral data matched those previously reported.[5] *Where resolved, signals for the minor isomer are given in brackets.* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.04 (m, 11.62H), [4.32 (q, *J* = 7.2 Hz, 0.12H)], 4.12 (q, *J* = 7.2 Hz, 1H), [2.31 (s, 0.36H)], 2.31 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H), [1.61 (d, *J* = 7.2 Hz, 0.36H)]. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.75, [146.38], 143.56, [142.59], 135.63, 129.19, [128.89], [128.53], 128.47, [128.45], [127.82], [127.74], 127.71, 127.63, [126.90], [126.22], 126.08, [125.95], 44.51, [40.72], [24.01], 22.06, 21.11, [19.13]. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{15}H_{15}$, 195.1168; found, 195.1168.

4-(1-(*p*-tolyl)ethyl)-1,1'-biphenyl (5)



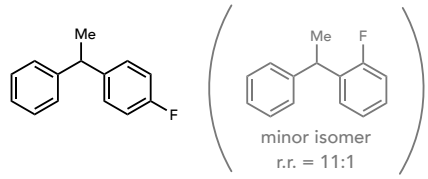
Prepared according to **General Procedure A** with biphenyl (0.463 g, 10 equiv, 3.0 mmol) and α-4-dimethylphenylacetic acid (0.049 g, 1.0 equiv, 0.30 mmol). Purification by flash chromatography on silica gel, eluting with 0–5% ethyl acetate in hexanes, afforded the product as a clear oil (60 mg, 74% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.58 – 7.53 (m, 2H), 7.53 – 7.48 (m, 2H), 7.43 – 7.39 (m, 2H), 7.34 – 7.26 (m, 3H), 7.18 – 7.08 (m, 4H), 4.16 (q, *J* = 7.2 Hz, 1H), 2.31 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.90, 143.46, 141.20, 139.03, 135.74, 129.26, 128.84, 128.10, 127.64, 127.24, 127.16, 127.16, 44.23, 22.07, 21.13. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{21}$, 273.1638; found, 273.1636.

1-methyl-4-(1-phenylethyl)benzene (6)



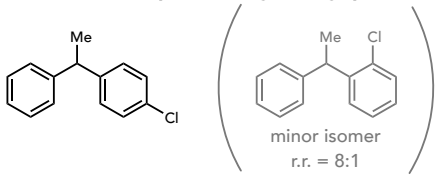
Prepared according to **General Procedure A** with benzene (357 µL, 20 equiv, 2.0 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica, eluting with a slow gradient of 0–100% with H_2O/MeOH. The product eluted at ~90% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the product as a clear oil (15.0 mg, 41% yield). The spectral data matched those previously reported.[5] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 7.25 – 7.21 (m, 4H), 7.21 – 7.13 (m, 2H), 4.16 (q, *J* = 7.3 Hz, 1H), 1.65 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.52, 128.50, 127.77, 126.16, 44.92, 22.00. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{14}H_{13}$, 181.1012; found, 181.1011.

1-fluoro-4-(1-phenylethyl)benzene (7)



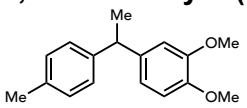
Prepared according to **General Procedure A** with fluorobenzene (942 µL, 50 equiv, 5.0 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica, eluting with a slow gradient of 0–100% with H_2O/MeOH. The product eluted at ~90% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford a mixture of the two isomeric products as a clear oil (19.2 mg, 48% yield, 11:1 *para*:*ortho*). The spectral data matched those previously reported.[5] *Where resolved, signals for the minor isomer are given in brackets.* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2.54H), 7.23 – 7.11 (m, 5.27H), 6.96 (t, *J* = 8.7 Hz, 2H), [4.48 (q, *J* = 7.3 Hz, 0.09H)], 4.14 (q, *J* = 7.3 Hz, 1H), [1.64 (d, *J* = 7.3 Hz, 0.27H)], 1.62 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.41 (d, *J* = 244.1 Hz), 146.32, 142.19 (d, *J* = 3.2 Hz), 129.12 (d, *J* = 7.8 Hz), 128.58, 127.66, 126.30, 115.21 (d, *J* = 21.1 Hz), 44.18, 22.15. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -117.52 (s, 1F), -117.88 (s, 0.09F). **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{14}H_{12}F$, 199.0918; found, 199.0917.

1-chloro-4-(1-phenylethyl)benzene (8)



Prepared according to **General Procedure A** with chlorobenzene (1.01 mL, 50 equiv, 5.0 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica, eluting with a slow gradient of 0–100% with H_2O/MeOH. The product eluted at ~90% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford a mixture of the two isomeric products as a clear oil (5.6 mg, 12% yield, 8:1 *para*:*ortho*). The spectral data matched those previously reported.[6] *Where resolved, signals for the minor isomer are given in brackets.* **^{1}H NMR** (500 MHz, $CDCl_3$) δ [7.37 – 7.32 (m, 0.52H)], 7.31 – 7.26 (m, 2.26H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.17 (m, 3.39H), 7.14 (d, *J* = 8.5 Hz, 2H), [4.65 (q, *J* = 7.2 Hz, 0.13H)], 4.12 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3.39H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.96, 145.02, 131.90, 129.13, 128.62, 128.60, 127.68, 126.39, 44.33, 21.93. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{14}H_{12}Cl$, 215.0622; found, 215.0621.

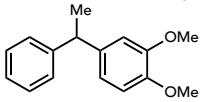
1,2-dimethoxy-4-(1-(*p*-tolyl)ethyl)benzene (9)



Prepared according to **General Procedure A** with 1,2-dimethoxybenzene (76.7 µL, 3.0 equiv, 0.6 mmol) and 2-(*p*-tolyl)propanoic acid (0.033 g, 1.0 equiv, 0.20 mmol). Na_2CO_3 (0.064 g, 3.0 equiv,

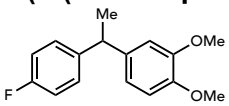
0.60 mmol) was used in place of NaOAc. Purification by flash chromatography on silica gel, eluting with 1–5% ethyl acetate in hexanes, afforded the product as a clear oil (50.2 mg, 98% yield). The spectral data matched those previously reported.[7] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.14 – 7.07 (m, 4H), 6.83 – 6.77 (m, 2H), 6.73 (d, *J* = 1.9 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 2.31 (s, 3H), 1.61 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.93, 147.42, 143.79, 139.40, 135.59, 129.17, 127.48, 120.98, 119.41, 111.36, 56.04, 55.96, 44.09, 22.28, 21.11. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{21}O_2$, 257.1536; found, 257.1533.

1,2-dimethoxy-4-(1-phenylethyl)benzene (10)



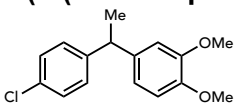
Prepared according to **General Procedure A** with 1,2-dimethoxybenzene (76.7 µL, 3.0 equiv, 0.6 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). Na_2CO_3 (0.064 g, 3.0 equiv, 0.60 mmol) was used in place of NaOAc. Purification by flash chromatography on silica gel, eluting with 1–5% ethyl acetate in hexanes, afforded the product as a clear oil (45.5 mg, 94% yield). The spectral data matched those previously reported.[7] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.24 – 7.15 (m, 3H), 6.86 – 6.76 (m, 2H), 6.72 (d, *J* = 1.8 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 1.63 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.95, 147.48, 146.76, 139.16, 128.49, 127.64, 126.13, 119.48, 111.41, 111.22, 56.04, 55.97, 44.48, 22.21. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{19}O_2$, 243.1380; found, 243.1378.

4-(1-(4-fluorophenyl)ethyl)-1,2-dimethoxybenzene (11)



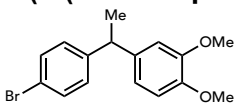
Prepared according to **General Procedure A** with 1,2-dimethoxybenzene (76.7 µL, 3.0 equiv, 0.6 mmol) and 2-(4-fluorophenyl)propanoic acid (0.034 g, 1.0 equiv, 0.20 mmol). Na_2CO_3 (0.064 g, 3.0 equiv, 0.60 mmol) was used in place of NaOAc. Purification by flash chromatography on silica gel, eluting with 1–5% ethyl acetate in hexanes, afforded the product as a clear oil (44.7 mg, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.8, 5.4, 2H), 6.96 (t, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.39 (d, *J* = 243.9 Hz), 149.02, 147.57, 142.44 (d, *J* = 3.1 Hz), 138.97, 129.01 (d, *J* = 7.7 Hz), 119.39, 115.19 (d, *J* = 21.2 Hz), 111.29, 111.25, 56.04, 55.98, 43.74, 22.35. ^{19}F NMR (377 MHz, $CDCl_3$) δ -117.54 (s, 1F). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{18}FO_2$, 261.1285; found, 261.1283.

4-(1-(4-chlorophenyl)ethyl)-1,2-dimethoxybenzene (12)



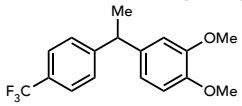
Prepared according to **General Procedure A** with 1,2-dimethoxybenzene (76.7 µL, 3.0 equiv, 0.6 mmol) and 2-(4-chlorophenyl)propanoic acid (0.037 g, 1.0 equiv, 0.20 mmol). Na_2CO_3 (0.064 g, 3.0 equiv, 0.60 mmol) was used in place of NaOAc. Purification by flash chromatography on silica gel, eluting with 1–5% ethyl acetate in hexanes, afforded the product as a clear oil (49.9 mg, 90% yield). The spectral data matched those previously reported.[7] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.04, 147.64, 145.28, 138.56, 131.83, 129.01, 128.58, 127.72, 119.42, 111.27, 56.04, 55.99, 43.88, 22.13. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{18}ClO_2$, 277.0990; found, 277.0987.

4-(1-(4-bromophenyl)ethyl)-1,2-dimethoxybenzene (13)



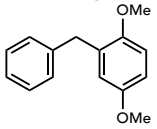
Prepared according to **General Procedure A** with 1,2-dimethoxybenzene (76.7 µL, 3.0 equiv, 0.6 mmol) and 2-(4-bromophenyl)propanoic acid (0.046 g, 1.0 equiv, 0.20 mmol). Na_2CO_3 (0.064 g, 3.0 equiv, 0.60 mmol) was used in place of NaOAc. Purification by flash chromatography on silica gel, eluting with 1–5% ethyl acetate in hexanes, afforded the product as a clear oil (55.9 mg, 87% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.05, 147.65, 145.81, 138.45, 131.53, 129.43, 128.57, 119.90, 119.42, 111.27, 56.04, 56.00, 43.95, 22.07. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{18}BrO_2$, 321.0485; found, 321.0481.

1,2-dimethoxy-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene (14)



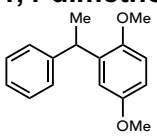
Prepared according to **General Procedure A** with 1,2-dimethoxybenzene (76.7 µL, 3.0 equiv, 0.6 mmol) and 2-(4-(trifluoromethyl)phenyl)propanoic acid (0.044 g, 1.0 equiv., 0.20 mmol). Na_2CO_3 (0.064 g, 3.0 equiv, 0.60 mmol) was used in place of NaOAc. Purification by flash chromatography on silica gel, eluting with 1–5% ethyl acetate in hexanes, afforded the product as a clear oil (18.0 mg, 29% yield). The spectral data matched those previously reported.[8] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.76 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.69 (d, *J* = 2.1 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.87, 149.12, 147.79, 137.99, 128.48 (q, *J* = 32.4 Hz), 127.96, 125.46 (q, *J* = 3.8 Hz), 124.47 (q, *J* = 271.9 Hz), 119.52, 111.34, 111.31, 56.06, 56.03, 44.38, 21.98. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.32 (s, 3F). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{18}F_3O_2$, 311.1253; found, 311.1251.

2-benzyl-1,4-dimethoxybenzene (15)



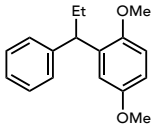
Prepared according to **General Procedure A** with 1,4-dimethoxybenzene (0.124 g, 3.0 equiv, 0.9 mmol) and phenylacetic acid (0.038 mL, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with a gradient of 1-5% ether in pentanes, afforded the product as a clear oil (14 mg, 21% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.23 – 7.14 (m, 3H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.71 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.65 (d, *J* = 3.1 Hz, 1H), 3.94 (s, 2H), 3.77 (s, 3H), 3.71 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.68, 151.85, 140.91, 131.10, 129.09, 128.43, 125.99, 117.01, 111.59, 111.40, 56.20, 55.78, 36.13. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{16}O_2H$, 229.1223; found, 229.1220.

1,4-dimethoxy-2-(1-phenylethyl)benzene (16)



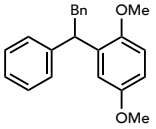
Prepared according to **General Procedure A** with 1,4-dimethoxybenzene (0.124 g, 3.0 equiv, 0.9 mmol) and 2-phenylpropanoic acid (0.045 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with a gradient of 1-10% ether in pentanes, afforded the product as a clear oil (41 mg, 54% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 5H), 7.17 – 7.13 (m, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 6.74 (d, *J* = 3.0 Hz, 1H), 6.68 (dd, *J* = 8.8, 3.1 Hz, 1H), 4.54 (q, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 1.56 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.78, 151.40, 146.25, 136.53, 128.27, 127.81, 125.89, 114.90, 111.82, 110.65, 56.34, 55.76, 37.71, 21.02. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{16}H_{18}O_2Na$, 265.1199; found, 265.1195.

1,4-dimethoxy-2-(1-phenylpropyl)benzene (17)



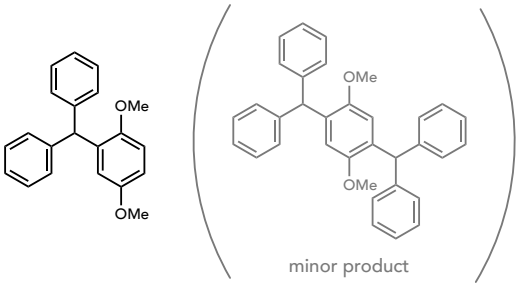
Prepared according to **General Procedure A** with 1,4-dimethoxybenzene (0.124 g, 3.0 equiv, 0.9 mmol) and 2-phenylbutyric acid (0.049 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 1% ether in pentanes, afforded the product as a clear oil (62 mg, 71% yield).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 5.7, 3.3 Hz, 4H), 7.16 – 7.10 (m, 1H), 6.82 (d, *J* = 3.1 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.67 (dd, *J* = 8.8, 3.1 Hz, 1H), 4.25 (t, *J* = 7.8 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.00 (p, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.80, 151.76, 145.03, 135.35, 128.30, 128.24, 125.89, 114.81, 111.94, 110.52, 56.41, 55.77, 45.33, 28.06, 12.87. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{17}H_{20}O_2Na$, 279.1355; found, 279.1353.

(1-(2,5-dimethoxyphenyl)ethane-1,2-diyl)dibenzene (18)



Prepared according to **General Procedure A** with 1,4-dimethoxybenzene (0.124 g, 3.0 equiv, 0.9 mmol) and 2,3-diphenylpropanoic acid (0.068 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with a gradient of 1-10% ether in pentanes, afforded the product as a clear oil (59 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 4H), 7.17 – 7.07 (m, 4H), 7.06 – 7.03 (m, 2H), 6.86 (d, *J* = 3.0 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 6.66 (dd, *J* = 8.8, 3.0 Hz, 1H), 4.70 (t, *J* = 7.8 Hz, 1H), 3.73 (s, 3H), 3.61 (s, 3H), 3.29 (dd, *J* = 7.8, 3.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.71, 151.52, 144.05, 140.73, 134.82, 129.19, 128.49, 128.21, 128.08, 126.07, 125.86, 115.18, 112.03, 110.86, 56.33, 55.79, 45.38, 41.36. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{22}H_{22}O_2H$, 319.1693; found, 319.1686.

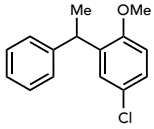
((2,5-dimethoxyphenyl)methylene)dibenzene (19)



Prepared according to **General Procedure A** with 1,4-dimethoxybenzene (0.124 g, 3.0 equiv, 0.9 mmol) and diphenylacetic acid (0.064 g, 1.0 equiv, 0.3 mmol). Purification by flash

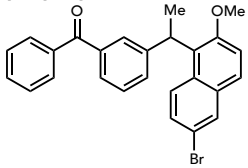
chromatography on silica gel, eluting with a gradient of 1-10% ether in pentanes, afforded the product as a clear oil (54 mg, 58% yield, 8:1). The spectral data matched those previously reported.[9] *Where resolved, signals for the minor product are given in brackets.* **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 5.21H), 7.22 – 7.15 (m, 2.53H), 7.13 – 7.05 (m, 5.11H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.72 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.46 (d, *J* = 3.0 Hz, 1H), [6.43 (s, 0.24H)], 5.89 (s, 1H), [5.87 (s, 0.24H)], 3.66 (s, 3H), 3.64 (s, 3H), [3.43 (s, 0.72H)]. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.53, 151.73, [151.22], [144.08], 143.81, 134.27, [131.54], 129.56, 128.28, [128.25], 126.22, [126.19], 117.57, [114.27], 111.99, 111.17, 56.51, 55.68, 49.91, [49.84].

4-chloro-1-methoxy-2-(1-phenylethyl)benzene (20)



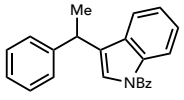
Prepared according to **General Procedure A** with 4-chloroanisole (0.128 g, 3.0 equiv, 0.9 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with <5% ethyl acetate in hexanes, afforded a mixture of the product and 4-chloroanisole. Fractions that eluted between 0–5% ethyl acetate in hexanes were recombined and purified by reverse phase flash chromatography over C18 functionalized silica, eluting with a slow gradient of 0–100% with H_2O/MeCN. The product eluted at ~65% MeCN. The product containing fractions were combined, concentrated under reduced pressure, diluted with CH_2Cl_2, filtered through a plug of $MgSO_4$, and concentrated under reduced pressure to afford the product as a clear oil (55 mg, 74% yield). The spectral data matched those previously reported.[10] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32 – 7.08 (m, 7H), 6.75 (d, *J* = 8.5 Hz, 1H), 4.52 (q, *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 1.56 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.60, 145.65, 136.95, 128.37, 127.85, 127.78, 126.85, 126.11, 125.66, 111.93, 55.88, 37.59, 20.90.

(3-(1-(6-bromo-2-methoxynaphthalen-1-yl)ethyl)phenyl)(phenyl)methanone (21)



Prepared according to **General Procedure A** with 2-bromo-6-methoxynaphthalene (0.213 g, 3.0 equiv, 0.9 mmol) and 2-(3-benzoylphenyl)propanoic acid (0.076 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 10% ethyl acetate in hexanes, afforded the product as a white solid (79 mg, 60% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 2.1 Hz, 1H), 7.73 – 7.63 (m, 5H), 7.59 – 7.50 (m, 2H), 7.45 – 7.39 (m, 1H), 7.40 – 7.35 (m, 3H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 9.1 Hz, 1H), 5.27 (q, *J* = 7.3 Hz, 1H), 3.81 (s, 3H), 1.83 (d, *J* = 7.3 Hz, 3H) **^{13}C NMR (126 MHz, $CDCl_{3z}$)** δ 197.09, 155.20, 146.18, 137.81, 137.49, 132.44, 131.36, 131.26, 130.96, 130.78, 130.21, 129.41, 128.60, 128.27, 128.10, 127.98, 127.55, 127.55, 126.25, 117.06, 115.32, 56.74, 34.61, 18.19. **mp**: 85 – 90 ºC **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{26}H_{21}BrO_2H$, 445.0798; found, 445.0791.

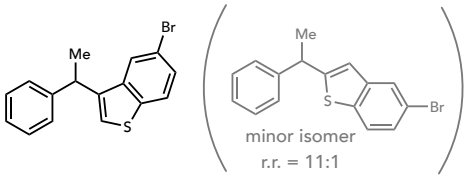
phenyl(3-(1-phenylethyl)-1H-indol-1-yl)methanone (22)



Prepared according to **General Procedure A** with 1-benzoylindole (0.066 g, 3.0 equiv, 0.3 mmol) and 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol). $Fe(OTf)_3$ (0.150 g, 3.0 equiv, 0.30 mmol) and Na_2CO_3 (0.032 g, 3.0 equiv, 0.30 mmol) were used in place of $FeCl_3$ and NaOAc,

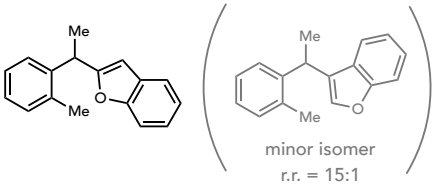
respectively. Purification by flash chromatography on silica gel, eluting with 0–2.5% ether in pentane, afforded the product as a white solid (24.9 mg, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.3 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.65 – 7.58 (m, 1H), 7.57 – 7.51 (m, 2H), 7.35 – 7.23 (m, 6H), 7.23 – 7.13 (m, 3H), 4.27 (q, *J* = 7.1 Hz, 1H), 1.62 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.62, 145.23, 136.91, 135.03, 131.96, 130.59, 129.28, 128.76, 128.67, 127.46, 126.97, 126.53, 125.07, 124.02, 123.75, 120.11, 116.54, 36.96, 22.08. **mp:** 101.6 – 102.7 °C. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{20}NO$, 326.1539; found, 326.1536.

5-bromo-3-(1-phenylethyl)benzo[b]thiophene (23)



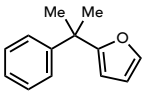
Prepared according to **General Procedure A** with 5-bromobenzo[b]thiophene (0.128 g, 3.0 equiv, 0.6 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). Na_2CO_3 (0.064 g, 3.0 equiv, 0.60 mmol) was used in place of NaOAc. Purification by flash chromatography on silica gel, eluting with 5–10% ethyl acetate in hexanes, afforded a mixture of the two isomeric products as a pale yellow oil (44.3 mg, 70% yield, 11:1 *r.r.*). *Where resolved, signals for the minor isomer are given in brackets.* **^{1}H NMR** (500 MHz, $CDCl_3$) δ [7.79 (d, *J* = 1.9 Hz, 0.09H)], 7.71 – 7.65 (m, 2H), [7.57 (d, *J* = 8.5 Hz, 0.09H)], 7.38 (dd, *J* = 8.5, 1.9 Hz, 1H), [7.35 – 7.32 (m, 0.27H)], 7.32 – 7.27 (m, 2.18H), 7.25 – 7.17 (m, 4.09H), [6.96 (m, 0.09H)], 4.38 (q, *J* = 7.1 Hz, 1.09H), [1.76 (d, *J* = 7.1 Hz, 0.27H)], 1.72 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ [153.83], [145.01], 144.93, [141.65], 140.42, 140.24, [139.51], 139.45, [138.23], [129.04], 128.80, [127.49], 127.44, 127.38, [127.06], [126.76], 126.66, [125.81], 125.34, 124.22, [123.60], 123.37, [119.45], 118.20, [41.62], 39.50, [22.80], 22.49. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{16}H_{12}BrS$, 314.9838; found, 314.9836.

2-(1-(*o*-tolyl)ethyl)benzofuran (24)



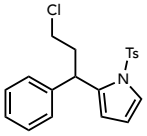
Prepared according to **General Procedure A** with benzofuran (64.6 µL, 3.0 equiv, 0.6 mmol) and 2-(*o*-tolyl)propanoic acid (0.033 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) and Na_3PO_4 (0.098 g, 3.0 equiv, 0.60 mmol) were used in place of $FeCl_3$ and NaOAc, respectively. The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica, eluting with a slow gradient of 0–100% with H_2O/MeOH. The product eluted at ~80% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford a mixture of the two isomeric products as a clear oil (34.9 mg, 74% yield, 15:1 *C2*:*C3*) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 1H), 7.39 (m, 1H), 7.21 – 7.11 (m, 6H), 6.39 (t, *J* = 1.1 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 1H), 2.43 (s, 3H), 1.68 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.39, 154.97, 141.44, 135.75, 130.66, 128.83, 126.85, 126.78, 126.48, 123.49, 122.57, 120.53, 111.10, 102.41, 35.60, 19.58, 19.55. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{17}O$, 237.1274; found, 237.1272.

2-(2-phenylpropan-2-yl)furan (25)



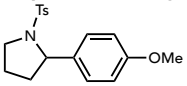
Prepared according to **General Procedure A** with furan (0.109 mL, 5.0 equiv, 1.5 mmol) and 2-methyl-2-phenylpropanoic acid (0.049 g, 1.0 equiv, 0.3 mmol). The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica with H_2O/MeOH. The product eluted around ~90% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered through a plug of celite, and concentrated under reduced pressure to afford the product as a clear oil (27 mg, 48% yield). The spectral data matched those previously reported.[11] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 3H), 7.24 – 7.16 (m, 3H), 6.30 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.11 (dd, *J* = 3.2, 0.9 Hz, 1H), 1.66 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.53, 148.04, 141.38, 128.31, 126.22, 126.08, 109.87, 104.53, 40.35, 28.67.

2-(3-chloro-1-phenylpropyl)-1-tosyl-1*H*-pyrrole (26)



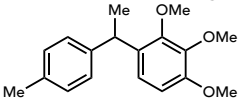
Prepared according to **General Procedure A** with 1-tosyl-*1H*-pyrrole (0.332 g, 5.0 equiv, 1.5 mmol) and **S1** (0.060 g, 1.0 equiv, 0.3 mmol). The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica with H_2O/MeOH. The product eluted around ~90% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered through a plug of celite, and concentrated under reduced pressure to afford the product as a clear oil (70 mg, 62% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 3H), 7.20 – 7.09 (m, 3H), 7.08 – 7.00 (m, 4H), 6.28 (t, *J* = 3.4 Hz, 1H), 6.24 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.74 (dd, *J* = 8.4, 6.9 Hz, 1H), 3.49 – 3.26 (m, 2H), 2.37–2.26 (m, 4 H), 2.21 (ddt, *J* = 14.3, 8.4, 6.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.52, 141.91, 136.85, 136.29, 129.77, 128.52, 128.10, 126.77, 126.60, 123.31, 112.73, 111.45, 42.75, 40.21, 39.98, 21.63. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{20}ClNO_2SH$, 374.0976; found, 374.0975.

2-(4-methoxyphenyl)-1-tosylpyrrolidine (27)



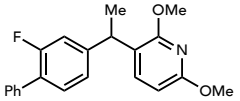
Prepared according to **General Procedure A** with anisole (0.163 mL, 5.0 equiv, 1.5 mmol) and **S2** (0.086 g, 1.0 equiv, 0.30 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a pale yellow oil (36 mg, 33% yield). The spectral data matched those previously reported.[12] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 2H), 7.27 (d, *J* = 9.6 Hz, 4H), 7.24 – 7.19 (m, 2H), 6.85 – 6.80 (m, 2H), 4.73 (dd, *J* = 7.9, 3.9 Hz, 1H), 3.79 (s, 3H), 3.63 – 3.55 (m, 1H), 3.46 – 3.37 (m, 1H), 2.42 (s, 3H), 2.02 – 1.74 (m, 3H), 1.71 – 1.59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.82, 143.30, 135.45, 135.28, 129.66, 127.65, 127.48, 113.85, 62.97, 55.44, 49.44, 35.93, 24.15, 21.66.

1,2,3-trimethoxy-4-(1-(*p*-tolyl)ethyl)benzene (28)



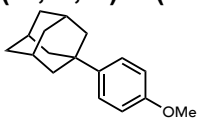
Prepared according to **General Procedure A** with 1,2,3-trimethoxybenzene (0.151 g, 3.0 equiv, 0.9 mmol) and 2-(*p*-tolyl)propanoic acid (0.049 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with a gradient of 0-15% ethyl acetate in hexanes, afforded the product as a clear oil (46 mg, 54% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 1H), 4.41 (q, *J* = 7.3 Hz, 1H), 3.84 (d, *J* = 9.4 Hz, 6H), 3.65 (s, 3H), 2.29 (s, 3H), 1.54 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.11, 151.64, 144.04, 142.42, 135.26, 132.90, 129.00, 127.53, 121.91, 107.17, 60.86, 60.77, 56.07, 37.48, 21.89, 21.10. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{22}O_3H$, 287.1642; found, 287.1637.

3-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)-2,6-dimethoxypyridine (29)



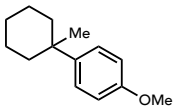
Prepared according to **General Procedure A** with 2,6-dimethoxypyridine (79.2 µL, 3.0 equiv, 0.6 mmol) and flurbiprofen (0.049 g, 1.0 equiv, 0.20 mmol). Na_3PO_4 (0.098 g, 3.0 equiv, 0.60 mmol) was used in place of NaOAc. After irradiation for 24 h, the lights were powered off, and the reaction was heated at 80 °C for an additional 16 h. The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica, eluting with a slow gradient of 0–100% with H_2O/MeOH. The product eluted at ~95% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the product as a clear oil (54.5 mg, 81% yield) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.06 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.00 (dd, *J* = 12.0, 1.8 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 1.57 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.59, 159.85, 159.79 (d, *J* = 247.4 Hz), 147.97 (d, *J* = 7.1 Hz), 138.79, 136.03, 129.08, 128.52, 127.54, 126.57, 126.46, 123.61 (d, *J* = 3.2 Hz), 119.04, 115.19 (d, *J* = 23.1 Hz), 100.44, 53.63, 53.47, 36.73, 20.65. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -118.59. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{21}FNO_2$, 338.1551; found, 338.1548.

(3*r*,5*r*,7*r*)-1-(4-methoxyphenyl)adamantane (30)



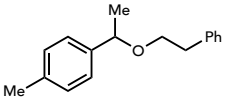
Prepared according to **General Procedure A** with anisole (0.098 mL, 3.0 equiv, 0.9 mmol) and (3*r*,5*r*,7*r*)-adamantane-1-carboxylic acid (0.054 g, 1.0 equiv, 0.3 mmol). The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica with H_2O/MeOH. The product eluted around ~95% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered through a plug of celite, and concentrated under reduced pressure to afford the product as an off-white solid (34 mg, 47% yield). The spectral data matched those previously reported.[13] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.13 – 2.06 (m, 3H), 1.91 – 1.86 (m, 6H), 1.83 – 1.69 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.49, 143.87, 125.93, 113.55, 55.36, 43.55, 36.97, 35.70, 29.16.

1-methoxy-4-(1-methylcyclohexyl)benzene (31)



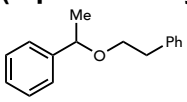
Prepared according to **General Procedure A** with anisole (65.1 µL, 3.0 equiv, 0.60 mmol) and 1-methylcyclohexane-1-carboxylic acid (0.028 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 5% ethyl acetate in hexanes, afforded the product as a pale yellow oil (21.1 mg, 52% yield). The spectral data matched those previously reported.[14] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.00 – 1.92 (m, 2H), 1.62 – 1.51 (m, 4H), 1.50 – 1.37 (m, 4H), 1.17 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.24, 142.27, 126.96, 113.62, 55.30, 38.19, 37.38, 30.72, 26.55, 22.79. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{14}H_{21}O$, 205.1587; found, 205.1586.

1-methyl-4-(1-phenethoxyethyl)benzene (**32**)



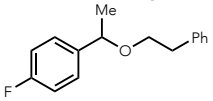
Prepared according to **General Procedure C** with 2-phenylethan-1-ol (0.108 mL, 3.0 equiv, 0.9 mmol) and 2-(*p*-tolyl)propanoic acid (0.049 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 2% ethyl acetate in hexanes, afforded the product as a clear oil (58 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.20 – 7.08 (m, 7H), 4.37 (q, *J* = 6.4 Hz, 1H), 3.54 – 3.44 (m, 2H), 2.93 – 2.79 (m, 2H), 2.32 (s, 3H), 1.41 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.04, 139.22, 137.07, 129.19, 129.07, 128.35, 126.23, 126.20, 78.03, 69.63, 36.71, 24.27, 21.24. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{17}H_{20}ONa$, 263.1406; found, 263.1403.

(1-phenethoxyethyl)benzene (33)



Prepared according to **General Procedure B** with 2-phenylethan-1-ol (0.108 mL, 3.0 equiv, 0.9 mmol) and 2-phenylpropanoic acid (0.045 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 2% ether in hexanes, afforded the product as a clear oil (45 mg, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.27 – 7.23 (m, 5H), 7.21 – 7.14 (m, 3H), 4.40 (q, *J* = 6.5 Hz, 1H), 3.51 (t, *J* = 7.3 Hz, 2H), 2.95 – 2.80 (m, 2H), 1.42 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.10, 139.19, 129.08, 128.51, 128.38, 127.47, 126.27, 126.24, 78.24, 69.75, 36.71, 24.26. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{16}H_{18}ONa$, 249.1250; found, 249.125.

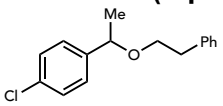
1-fluoro-4-(1-phenethoxyethyl)benzene (34)



Prepared according to **General Procedure B** with phenylethanol (0.108 mL, 3.0 equiv, 0.9 mmol) and 2-(4-fluorophenyl)propanoic acid (0.050 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 2% ether in hexanes, afforded the product as a clear oil (51 mg, 69% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 2H), 7.23 – 7.11 (m, 5H), 7.03 – 6.93 (m, 2H), 4.38 (q, *J* = 6.5 Hz, 1H), 3.55 – 3.39 (m, 2H), 2.87 (hept, *J* = 6.7 Hz, 2H), 1.40 (d, *J* = 6.5 Hz, 3H**). ^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.20, 161.25, 139.80 (d, *J* = 3.1 Hz), 139.14, 129.07, 128.41, 127.82 (d, *J* = 8.0 Hz), 126.29, 115.39, 115.22, 77.55, 69.69,

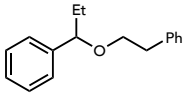
36.69, 24.24. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.57. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{16}H_{17}FONa$, 267.1155; found, 267.1152.

1-chloro-4-(1-phenethoxyethyl)benzene (**35**)



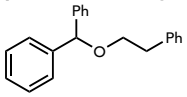
Prepared according to **General Procedure B** with 2-phenylethan-1-ol (0.108 mL, 3.0 equiv, 0.9 mmol) and 2-(4-chlorophenyl)propanoic acid (0.055 g, 1.0 equiv, 0.3 mmol). Reaction was irradiated for 48 h. Purification by flash chromatography on silica gel, eluting with 2% ether in hexanes, afforded the product as a clear oil (51 mg, 62% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 4H), 7.21 – 7.13 (m, 5H), 4.36 (q, *J* = 6.5 Hz, 1H), 3.57 – 3.42 (m, 2H), 2.92 – 2.78 (m, 2H), 1.39 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.66, 139.09, 133.07, 129.07, 128.67, 128.41, 127.62, 126.30, 77.55, 69.80, 36.68, 24.18. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{16}H_{17}ClONa$, 283.0860; found, 283.0858.

(1-phenethoxypropyl)benzene (36)



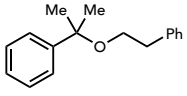
Prepared according to **General Procedure B** with 2-phenylethan-1-ol (0.108 mL, 3.0 equiv, 0.9 mmol) and 2-phenylbutanoic acid (0.049 g, 1.0 equiv, 0.3 mmol). Reaction was irradiated for 48 h. Purification by flash chromatography on silica gel, eluting with 2% ether in hexanes, afforded the product as a clear oil (50 mg, 69% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.32 – 7.29 (m, 2H), 7.27 – 7.20 (m, 5H), 7.20 – 7.15 (m, 3H), 4.12 (t, *J* = 6.6 Hz, 1H), 3.54 (ddd, *J* = 9.4, 8.0, 6.5 Hz, 1H), 3.46 (ddd, *J* = 9.3, 8.0, 6.4 Hz, 1H), 2.94 – 2.79 (m, 2H), 1.85 – 1.76 (m, 1H), 1.70 – 1.60 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.87, 139.31, 129.10, 128.37, 128.35, 127.44, 126.84, 126.19, 84.07, 69.86, 36.68, 31.26, 10.40. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{17}H_{20}OH$, 241.1587; found, 241.1585.

(phenethoxymethylene)dibenzene (37)



Prepared according to **General Procedure B** with 2-phenylethan-1-ol (0.108 mL, 3.0 equiv, 0.9 mmol) and 2,2-diphenylacetic acid (0.064 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 2% ether in hexanes, afforded the product as a clear oil (84 mg, 97% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 10H), 7.24 – 7.17 (m, 5H), 5.34 (s, 1H), 3.67 (t, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.51, 139.27, 129.19, 128.48, 128.41, 127.50, 127.06, 126.28, 83.91, 70.16, 36.69. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{21}H_{20}ONa$, 311.1406; found, 311.1402.

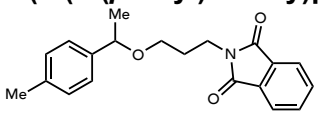
(2-phenethoxypropan-2-yl)benzene (38)



Prepared according to **General Procedure C** with 2-phenylethan-1-ol (0.108 mL, 3.0 equiv, 0.9 mmol) and 2-methyl-2-phenylpropanoic acid (0.049 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 2% ethyl acetate in hexanes, afforded the product as a clear oil (37 mg, 51% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.12 (m, 10H), 3.36 (t, *J* = 7.4 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 1.51 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.57, 139.37,

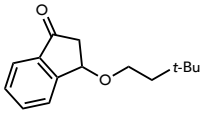
129.20, 128.32, 128.25, 126.87, 126.20, 125.81, 76.81, 64.23, 37.27, 28.50. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{17}H_{20}ONa$, 263.1406; found, 263.1405.

2-(3-(1-(*p*-tolyl)ethoxy)propyl)isoindoline-1,3-dione (39)



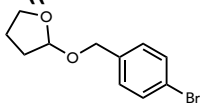
Prepared according to **General Procedure B** with 2-(3-hydroxypropyl)isoindoline-1,3-dione (0.185 g, 3.0 equiv, 0.9 mmol) and 2-(*p*-tolyl)propanoic acid (0.049 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 10% ethyl acetate in hexanes, afforded the product as a clear oil (64 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 4.31 (q, *J* = 6.4 Hz, 1H), 3.83 (dt, *J* = 13.8, 6.9 Hz, 1H), 3.75 (dt, *J* = 13.7, 6.9 Hz, 1H), 3.40 – 3.28 (m, 2H), 2.31 (s, 3H), 1.99 – 1.86 (m, 2H), 1.32 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.55, 140.94, 137.03, 133.89, 132.40, 129.15, 126.24, 123.22, 78.06, 66.22, 35.98, 28.82, 23.99, 21.22. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{20}H_{21}NO_3Na$, 346.1413; found, 346.1406.

3-(3,3-dimethylbutoxy)-2,3-dihydro-1*H*-inden-1-one (40)



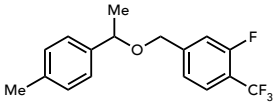
Prepared according to **General Procedure B** with 3,3-dimethylbutan-1-ol (0.109 mL, 3.0 equiv, 0.9 mmol) and 3-oxo-2,3-dihydro-1*H*-indene-1-carboxylic acid (0.053 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 10% ethyl acetate in hexanes, afforded the product as a clear oil (54 mg, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.50 – 7.45 (m, 1H), 5.08 (dd, *J* = 6.4, 2.9 Hz, 1H), 3.68 (t, *J* = 7.3 Hz, 2H), 3.01 (dd, *J* = 18.5, 6.4 Hz, 1H), 2.66 (dd, *J* = 18.6, 2.9 Hz, 1H), 1.67 – 1.51 (m, 2H), 0.96 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 203.33, 153.79, 136.88, 135.09, 129.51, 126.63, 123.35, 75.57, 67.52, 44.25, 43.33, 29.93, 29.87. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{20}O_2H$, 233.1536; found, 233.1532.

2-((4-bromobenzyl)oxy)tetrahydrofuran (41)



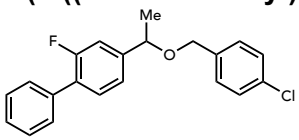
Prepared according to **General Procedure B** with (4-bromophenyl)methanol (0.168 g, 3.0 equiv, 0.9 mmol) and tetrahydrofuran-2-carboxylic acid (0.035 g, 1.0 equiv, 0.3 mmol). Pyridine (0.072 mL, 3.0 equiv, 0.9 mmol) was employed as the base in place of K_2HPO_4. The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica with H_2O/MeOH. The product eluted around ~60% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered through a plug of celite, and concentrated under reduced pressure to afford the product as a clear oil (53 mg, 71% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.19 (dd, *J* = 3.7, 2.6 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.42 (d, *J* = 12.2 Hz, 1H), 3.98 – 3.84 (m, 2H), 2.06 – 1.99 (m, , 1H), 1.98 – 1.91 (m, 2H), 1.89 – 1.80 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.61, 131.57, 129.58, 121.45, 103.34, 68.14, 67.24, 32.50, 23.59. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{11}H_{13}BrO_2H$, 257.0172; found, 257.0167.

2-fluoro-4-((1-(*p*-tolyl)ethoxy)methyl)-1-(trifluoromethyl)benzene (42)



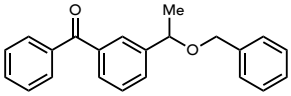
Prepared according to **General Procedure B** with (3-fluoro-4-(trifluoromethyl)phenyl)methanol (0.175 g, 3.0 equiv, 0.9 mmol) and 2-(*p*-tolyl)propanoic acid (0.049 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 1% ethyl acetate in hexanes, afforded the product as a clear oil (83 mg, 89% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.53 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.21 – 7.16 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 1H), 4.46 (q, *J* = 6.6 Hz, 1H), 4.43 (d, *J* = 13.2 Hz, 1H), 4.33 (d, *J* = 12.9 Hz, 1H), 2.36 (s, 3H), 1.50 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.05 (q, *J* = 2.1 Hz), 159.01 (q, *J* = 2.1 Hz), 146.40 (d, *J* = 7.1 Hz), 140.07, 137.70, 129.46, 127.14 (qd, *J* = 4.6, 1.8 Hz), 126.39, 122.50 (d, *J* = 3.5 Hz), 117.24 (qd, *J* = 32.9, 12.5 Hz), 115.49 (d, *J* = 21.0 Hz), 78.02, 68.87 (d, *J* = 1.6 Hz), 24.18, 21.27. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -61.23 (d, *J* = 12.7 Hz, 3F), -114.71 (q, *J* = 12.5 Hz, 1F). **HRSM** (FTMS + p ESI) m/z: $[M - C_8H_5F]^+$ calculated for $C_{17}H_{16}F_4O$, 119.0855; found, 119.0855.

4-(1-((4-chlorobenzyl)oxy)ethyl)-2-fluoro-1,1'-biphenyl (43)



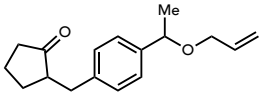
Prepared according to **General Procedure B** with (4-chlorophenyl)methanol (0.128 g, 3.0 equiv, 0.9 mmol) and 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (0.073 g, 1.0 equiv, 0.3 mmol). Reaction was irradiated for 48 h. Purification by flash chromatography on silica gel, eluting with 5% ethyl acetate in hexanes, afforded the product as a clear oil (53 mg, 51% yield). **^{1}H NM**R (500 MHz, Chloroform-*d*) δ 7.56 (dt, *J* = 8.1, 1.4 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.40 – 7.34 (m, 1H), 7.34 – 7.30 (m, 2H), 7.29 – 7.24 (m, 2H), 7.20 – 7.13 (m, 2H), 4.51 (q, *J* = 6.4 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 160.07 (d, J = 248.5 Hz), 145.44 (d, J = 6.9 Hz), 137.02, 135.75 (d, J = 1.1 Hz), 133.50, 131.02 (d, J = 3.8 Hz), 129.12 (d, J = 3.5 Hz), 128.67 (d, J = 14.2 Hz), 128.51, 128.42, 128.31, 127.82, 122.31 (d, J = 3.3 Hz), 113.97 (d, J = 23.3 Hz), 76.80 (d, J = 1.5 Hz), 69.92, 24.12. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -117.68. **HRSM** (FTMS + p ESI) m/z: $[M - C_7H_6ClO]^+$ calculated for $C_{21}H_{18}ClO$, 199.0918; found, 199.0916.

(3-(1-(benzyloxy)ethyl)phenyl)(phenyl)methanone (44)



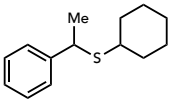
Prepared according to **General Procedure B** with phenylmethanol (0.093 mL, 3.0 equiv, 0.9 mmol) and 2-(3-benzoylphenyl)propanoic acid (0.076 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 5% ethyl acetate in hexanes, afforded the product as a clear oil (80 mg, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 3H), 7.74 – 7.71 (m, 1H), 7.64 – 7.56 (m, 2H), 7.50 – 7.46 (m, 3H), 7.36 – 7.24 (m, 5H), 4.58 (q, *J* = 6.5 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.35 (d, *J* = 11.8 Hz, 1H), 1.50 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.83, 144.34, 138.44, 137.98, 137.75, 132.58, 130.42, 130.18, 129.49, 128.69, 128.54, 128.44, 128.10, 127.81, 127.73, 77.01, 70.70, 24.25. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{22}H_{20}O_2H$, 317.1536; found, 317.1530.

2-(4-(1-(allyloxy)ethyl)benzyl)cyclopentan-1-one (45)



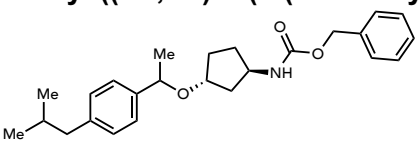
Prepared according to **General Procedure B** with prop-2-en-1-ol (0.061 mL, 3.0 equiv, 0.9 mmol) and 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoic acid (0.074 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 10% ethyl acetate in hexanes, afforded the product as a clear oil (45 mg, 60% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.96 – 5.85 (m, 1H), 5.24 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.44 (q, *J* = 6.5 Hz, 1H), 3.88 (dd, *J* = 12.9, 5.2 Hz, 1H), 3.79 (dd, *J* = 12.7, 6.0 Hz, 1H), 3.14 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.52 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.41 – 2.27 (m, 2H), 2.19 – 2.04 (m, 2H), 2.02 – 1.92 (m, 1H), 1.79 – 1.69 (m, 1H), 1.63 – 1.52 (m, 1H), 1.44 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.32, 141.74, 139.31, 135.21, 129.07, 126.47, 116.78, 77.11, 69.50, 51.16, 51.15, 38.32, 35.44, 29.40, 24.11, 24.10, 20.69. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{17}H_{22}O_2H$, 259.1693; found, 259.1690.

cyclohexyl(1-phenylethyl)sulfane (46)



Prepared according to **General Procedure B** with cyclohexanethiol (0.110 mL, 3.0 equiv, 0.9 mmol) and 2-phenylpropanoic acid (0.041 mL, 1.0 equiv, 0.3 mmol). The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica with H_2O/MeOH. The product eluted around ~75% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered through a plug of celite, and concentrated under reduced pressure to afford the product as a clear oil (35 mg, 53% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 4H), 7.24 – 7.18 (m, 1H), 4.04 (q, *J* = 7.0 Hz, 1H), 2.39 (tt, *J* = 10.5, 3.6 Hz, 1H), 2.02 – 1.87 (m, 1H), 1.77 – 1.69 (m, 2H), 1.70 – 1.61 (m, 1H), 1.55 (d, *J* = 7.0 Hz, 3H), 1.43 – 1.12 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.87, 128.56, 127.28, 126.99, 42.92, 42.61, 34.02, 33.45, 26.14, 26.00, 23.27. The spectral data matched those previously reported.[15]

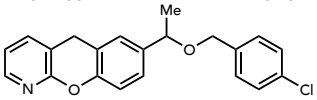
benzyl ((1*R*,3*R*)-3-(1-(4-isobutylphenyl)ethoxy)cyclopentyl)carbamate (47)



An oven-dried 4-mL vial equipped with a stir bar is charged with $Fe(OTf)_3$ (0.152 g, 3.0 equiv, 0.3 mmol), Na_3PO_4 (0.050 g, 3.0 equiv, 0.3 mmol), benzyl ((1*R*,3*R*)-3-hydroxycyclopentyl)carbamate (0.071 g, 3.0 equiv, 0.3 mmol), and ibuprofen (0.021 g, 1.0 equiv, 0.3 mmol). The vial was purged with nitrogen and the solids suspended in methylenechloride (2.0 mL, 0.05 M). The vial is irradiated at 427 nm with one 40 W Kessil Lamp PR160 lamp in a EvoluChem photoreactor box for 24 h at room temperature. After 24 h, the crude reaction mixture is diluted with 2.0 mL saturated aqueous NH4Cl and extracted with EtOAc (2 x 5 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel, eluting with a gradient of 0-20% EtOAc/heptane, to deliver the product as a clear oil (27 mg, 68% yield).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.20 – 4.99 (m, *J* = 7.0 Hz, 2H), 4.71 – 4.48 (m, 1H), 4.45 – 4.34 (m, 1H), 4.26 – 4.09 (m, 1H), 3.93 – 3.79 (m, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 2.24 – 1.96 (m, 2H), 1.95 – 1.77 (m, 2H), 1.66 – 1.44 (m, 2H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.35 – 1.19 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.30, 141.53, 141.49,

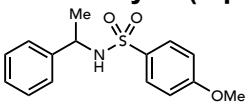
140.92, 140.90, 136.73, 129.39, 129.25, 129.24, 128.68, 128.66, 128.33, 128.25, 128.23, 126.14, 126.11, 77.36, 76.44, 75.67, 75.50, 45.29, 31.64, 30.55, 30.34, 24.64, 24.54, 22.57. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{25}H_{33}NO_3H$, 396.2533; found, 396.2525.

7-(1-((4-chlorobenzyl)oxy)ethyl)-5*H*-chromeno[2,3-*b*]pyridine (48)



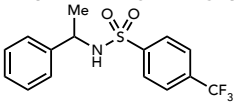
Prepared according to **General Procedure B** with (4-chlorophenyl)methanol (0.128 g, 3.0 equiv, 0.9 mmol) and 2-(*5H*-chromeno[2,3-b]pyridine-7-yl)propanoic acid (0.077 g, 1.0 equiv, 0.3 mmol). Pyridine (0.072 mL, 3.0 equiv, 0.9 mmol) was employed as the base in place of K_2HPO_4. Purification by flash chromatography on silica gel, eluting with gradient of 0-20% ethyl acetate in hexanes, afforded the product as a clear oil (54 mg, 48% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.22 – 8.14 (m, 1H), 7.55 (ddt, *J* = 7.3, 2.0, 1.1 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 7.19 – 7.13 (m, 3H), 7.04 (dd, *J* = 7.3, 4.8 Hz, 1H), 4.45 (q, *J* = 6.5 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.28 (d, *J* = 12.1 Hz, 1H), 4.12 (s, 2H), 1.47 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.64, 151.29, 146.89, 139.04, 138.52, 137.21, 133.40, 129.09, 128.67, 126.47, 126.31, 119.99, 119.77, 117.44, 115.52, 76.98, 69.65, 28.38, 24.23. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{18}ClNO_2H$, 352.1099; found, 352.1096.

4-methoxy-*N*-(1-phenylethyl)benzenesulfonamide (49)



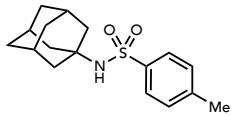
Prepared according to **General Procedure D** with 4-methoxybenzenesulfonamide (0.112 g, 3.0 equiv, 0.60 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a clear oil (57.6 mg, 99% yield). The spectral data matched those previously reported.[16] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.15 – 7.06 (m, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.73 (br m, 1H. N–H), 4.45 (p, *J* = 6.8 Hz, 1H), 3.84 (s, 3H), 1.43 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.83, 142.17, 132.41, 129.36, 128.73, 127.67, 126.27, 114.13, 55.73, 53.75, 23.73. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{15}H_{16}NO_3S$, 290.0856; found, 290.0858.

***N*-(1-phenylethyl)-4-(trifluoromethyl)benzenesulfonamide (50)**



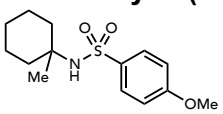
Prepared according to **General Procedure D** with 4-(trifluoromethyl)benzenesulfonamide (0.135 g, 3.0 equiv, 0.60 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a white solid (65.5 mg, 99% yield). The spectral data matched those previously reported.[16] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.10 (m, 3H), 7.07 – 6.96 (m, 2H), 4.97 (d, *J* = 7.0 Hz, 1H, N–H), 4.56 (m, 1H), 1.47 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.38, 141.27, 134.09 (q, *J* = 32.9 Hz), 128.77, 127.92, 127.64, 126.67, 125.98 (q, *J* = 3.7 Hz), 123.37 (q, *J* = 272.8 Hz), 54.24, 23.83. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -63.20 (s, 3F). **mp:** 117.8 – 118.6 °C (lit.[16] 118.7 – 120.1 °C). **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{15}H_{13}F_3NO_2S$, 328.0625; found, 328.0625.

***N*-(adamantan-1-yl)-4-methylbenzenesulfonamide (51)**



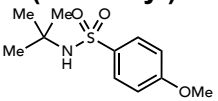
Prepared according to **General Procedure D** with *p*-toluenesulfonamide (0.051 g, 3.0 equiv, 0.60 mmol) and adamantane-1-carboxylic acid (0.036 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) and NaOAc (0.049 g, 3.0 equiv, 0.60 mmol) were used in place of $FeCl_3$ and Na_3PO_4, respectively. Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a white solid (42.5 mg, 70% yield). The spectral data matched those previously reported.[17] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 4.65 (s, 1H), 2.42 (s, 3H), 2.20 – 1.97 (m, 3H), 1.91 – 1.74 (m, 6H), 1.69 – 1.46 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.83, 141.27, 129.56, 127.06, 55.19, 43.20, 35.99, 29.62, 21.63. **mp:** 166.8 – 167.9 °C (lit.[18] 168 – 169.5 °C). **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{17}H_{22}NO_2S$, 304.1377; found, 304.1377.

4-methoxy-*N*-(1-methylcyclohexyl)benzenesulfonamide (52)



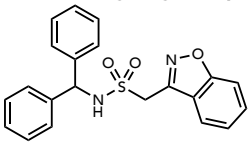
Prepared according to **General Procedure D** with 4-methoxybenzenesulfonamide (0.056 g, 3.0 equiv, 0.60 mmol) and 1-methylcyclohexane-1-carboxylic acid (0.028 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) and NaOAc (0.049 g, 3.0 equiv, 0.60 mmol) were used in place of $FeCl_3$ and Na_3PO_4, respectively. Purification by flash chromatography on silica gel, eluting with 20–30% ethyl acetate in hexanes, afforded the product as a clear oil (24.3 mg, 43% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.48 (s, 1H), 3.86 (s, 3H), 1.76 – 1.30 (m, 10H), 1.19 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.57, 135.64, 129.16, 114.10, 56.92, 55.70, 38.59, 35.53, 25.38, 21.99. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{14}H_{20}NO_3S$, 282.1169; found, 282.1169.

***N*-(*tert*-butyl)-4-methoxybenzenesulfonamide (53)**



Prepared according to **General Procedure D** with 4-methoxybenzenesulfonamide (0.056 g, 3.0 equiv, 0.90 mmol) and pivalic acid (0.031 g, 1.0 equiv, 0.30 mmol). NaOAc (0.074 g, 3.0 equiv, 0.90 mmol) was used in place of Na_3PO_4. Purification by flash chromatography on silica gel, eluting with 15% ethyl acetate in hexanes, afforded the product as a white solid (21 mg, 29% yield). The spectral data matched those previously reported.[19] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.58 (s, 1H), 3.79 (s, 3H), 1.14 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.60, 135.23, 129.22, 114.12, 55.70, 54.61, 30.28.

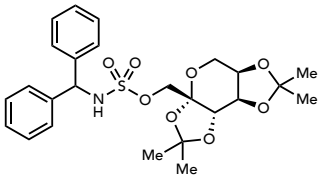
***N*-benzhydryl-1-(benzo[d]isoxazol-3-yl)methanesulfonamide (54)**



Prepared according to **General Procedure D** with zonisamide (0.042 g, 3.0 equiv, 0.60 mmol) and diphenylacetic acid (0.042 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) was used in place of $FeCl_3$. Purification by flash chromatography on silica gel, eluting with 20–30% ethyl acetate in hexanes, afforded the product as a white solid (55.9 mg, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.50 (m, 2H), 7.42 – 7.27 (m, 10H), 5.81 (d,

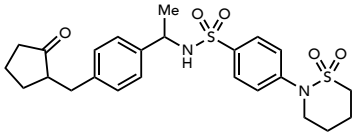
J = 7.2 Hz, 1H), 5.30 (d, *J* = 7.2 Hz, 1H), 4.45 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.72, 149.60, 140.31, 130.51, 129.01, 128.22, 127.68, 124.27, 122.47, 120.98, 110.04, 62.06, 50.72. **mp:** 172.6 – 173.0 °C. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{21}H_{17}N_2O_3S$, 377.0965; found, 377.0966.

((3aR,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl benzhydrylsulfamate (55)



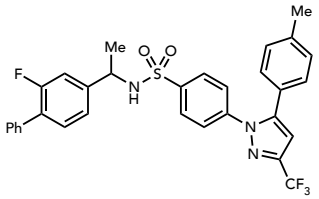
Prepared according to **General Procedure D** with topirimate (0.102 g, 3.0 equiv, 0.60 mmol) and diphenylacetic acid (0.042 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) was used in place of $FeCl_3$. Purification by flash chromatography on silica gel, eluting with 20–30% ethyl acetate in hexanes, afforded the product as a white solid (53.5 mg, 53% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 10H), 5.75 (d, *J* = 6.6 Hz, 1H), 5.20 (d, *J* = 6.6 Hz, 1H), 4.54 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.19 (dd, *J* = 7.9, 1.7 Hz, 1H), 4.16 (d, *J* = 2.6 Hz, 1H), 4.10 (d, *J* = 10.6 Hz, 1H), 4.02 (d, *J* = 10.6 Hz, 1H), 3.81 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.66 (dd, *J* = 13.0, 0.8 Hz, 1H), 1.48 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.69, 129.00, 128.14, 127.52, 109.32, 109.30, 100.97, 70.79, 70.53, 70.25, 70.06, 62.18, 61.45, 26.55, 26.03, 25.23, 24.22. **mp:** 123.0 – 125.0 °C. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{25}H_{30}NO_8S$, 504.1698; found, 504.1699.

4-(1,1-dioxido-1,2-thiazinan-2-yl)-*N*-(1-(4-((2-oxocyclopentyl)methyl)phenyl)ethyl)benzenesulfonamide (56)



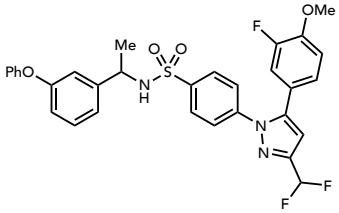
Prepared according to **General Procedure D** with sultiame (0.087 g, 3.0 equiv, 0.60 mmol) and loxoprofen (0.049 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) was used in place of $FeCl_3$. Purification by flash chromatography on silica gel, eluting with 70% ethyl acetate in hexanes, afforded the product as a white solid (51.0 mg, 52% yield, 1:1 *d.r.*). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.7, 3.4 Hz, 2H), 7.32 (dd, *J* = 8.7, 3.4 Hz, 2H), 7.07 – 6.97 (m, 4H), 4.77 (d, *J* = 6.9 Hz, 1H), 4.47 (td, *J* = 6.9, 3.5 Hz, 1H), 3.94 – 3.70 (m, 2H), 3.38 – 3.17 (m, 2H), 3.07 (ddd, *J* = 13.9, 4.3, 1.7 Hz, 1H), 2.47 (ddd, *J* = 14.1, 9.5, 1.4 Hz, 1H), 2.42 – 2.27 (m, 4H), 2.18 – 2.01 (m, 2H), 1.98 – 1.88 (m, 3H), 1.74 (m, 1H), 1.56 – 1.46 (m, 1H), 1.43 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.28, 144.33, 144.32, 139.77, 139.74, 139.73, 139.69, 138.91, 138.88, 129.26, 128.10, 126.36, 126.34, 53.67, 53.66, 53.25, 51.03, 51.01, 50.91, 38.29, 35.28, 35.26, 29.84, 29.40, 29.37, 24.55, 24.28, 23.70, 23.67, 20.66 (mixture of diastereomers). **mp:** 239 °C (decomp.). **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{24}H_{29}N_2O_5S_2$, 489.1523; found, 489.1522.

***N*-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)-4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (57)**



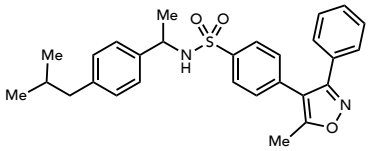
Prepared according to **General Procedure D** with celecoxib (0.114 g, 3.0 equiv, 0.60 mmol) and flurbiprofen (0.049 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (74.8 mg, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.7 Hz, 2H), 7.48 – 7.33 (m, 7H), 7.27 (t, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.97 – 6.87 (m, 2H), 6.72 (s, 1H), 4.85 (d, *J* = 6.8 Hz, 1H), 4.55 (p, *J* = 6.8 Hz, 1H), 2.35 (s, 3H), 1.47 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.72 (d, *J* = 249.2 Hz), 145.35, 144.26 (q, *J* = 38.6 Hz), 143.07 (d, *J* = 7.1 Hz), 142.54, 140.10, 139.93, 135.21, 131.17, 131.14, 129.86, 129.00 (d, *J* = 2.9 Hz), 128.84, 128.62, 128.18, 127.99, 125.87, 125.32, 122.21 (d, *J* = 3.4 Hz), 121.23 (q, *J* = 269.1 Hz), 114.09 (d, *J* = 23.8 Hz), 106.53 (d, *J* = 2.2 Hz), 53.31, 23.57, 21.44. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.37 (s, 3F), -117.00 (s, 1F). **mp:** 111.3 – 112.9 °C. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{31}H_{24}F_4N_3O_2S$, 578.1531; found, 578.1535.

4-(3-(difluoromethyl)-5-(3-fluoro-4-methoxyphenyl)-1H-pyrazol-1-yl)-*N*-(1-(3-phenoxyphenyl)ethyl)benzenesulfonamide (58)



Prepared according to **General Procedure D** with deracoxib (0.119 g, 3.0 equiv, 0.60 mmol) and fenoprofen (0.048 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (53.1 mg, 45% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 7.13 – 7.06 (m, 1H), 6.97 (dd, *J* = 11.5, 2.0 Hz, 1H), 6.94 – 6.89 (m, 3H), 6.89 – 6.84 (m, 2H), 6.82 – 6.76 (m, 2H), 6.70 (d, *J* = 54.8 Hz, 1H), 6.69 (m, 1H), 4.70 (d, *J* = 6.9 Hz, 1H), 4.49 (t, *J* = 6.9 Hz, 1H), 3.90 (s, 3H), 1.43 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.81, 156.76, 152.25 (d, *J* = 248.5 Hz), 148.72 (d, *J* = 10.4 Hz), 148.33 (d, *J* = 30.0 Hz), 143.84, 143.80, 142.46, 140.06, 130.19, 129.96, 128.24, 125.30 (d, *J* = 3.7 Hz), 125.06, 123.77, 121.90 (d, *J* = 7.0 Hz), 120.89, 119.21, 117.87, 116.76 (d, *J* = 19.8 Hz), 116.53, 113.71 (d, *J* = 2.3 Hz), 111.12 (t, *J* = 234.5 Hz), 105.98, 56.39, 53.70, 23.70. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -112.28 (s, 2F), -133.28 (s, 1F). **mp:** 115.9 – 117.8 °C. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{31}H_{25}F_3N_3O_4S$, 592.1523; found, 592.1528.

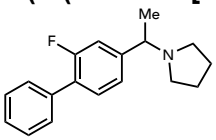
***N*-(1-(4-isobutylphenyl)ethyl)-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfonamide (59)**



Prepared according to **General Procedure D** with valdecoxib (0.094 g, 3.0 equiv, 0.60 mmol) and ibuprofen (0.041 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) was used in place of $FeCl_3$. Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a clear oil (87.8 mg, 92% yield). **^{1}H NMR** (500 MHz, $CDCl_3$)

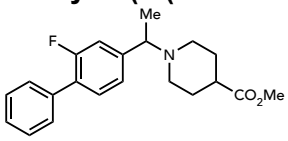
δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.30 (m, 5H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 4.86 (d, *J* = 5.1 Hz, 1H), 4.53 (m, 1H), 2.46 (s, 3H), 2.37 (d, *J* = 7.2 Hz, 2H), 1.86 – 1.68 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.24, 161.17, 141.41, 140.13, 139.24, 134.99, 130.14, 129.85, 129.41, 128.81, 128.65, 128.58, 127.59, 126.01, 114.67, 53.67, 45.08, 30.28, 23.69, 22.42, 11.84. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{28}H_{29}N_2O_3S$, 473.1904; found, 473.1905.

1-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)pyrrolidine (60)



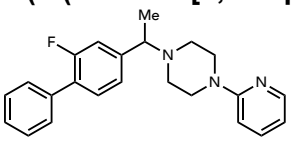
Prepared according to **General Procedure E** with pyrrolidine (81.9 µL, 10 equiv, 1.0 mmol) and flurbiprofen (0.024 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a clear oil (18.3 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.49 – 7.40 (m, 2H), 7.40 – 7.32 (m, 2H), 7.23 – 7.12 (m, 2H), 3.23 (q, *J* = 6.7 Hz, 1H), 2.75 – 2.48 (m, 2H), 2.47 – 2.29 (m, 2H), 1.95 – 1.69 (m, 4H), 1.42 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.90 (d, *J* = 247.6 Hz), 147.82, 136.02, 130.58 (d, *J* = 3.8 Hz), 129.11 (d, *J* = 3.0 Hz), 128.53, 127.59, 127.41, 123.18 (d, *J* = 3.2 Hz), 114.84 (d, *J* = 23.2 Hz), 65.39, 53.03, 23.60, 23.30. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -118.52 (s, 1F). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{21}FN$, 270.1652; found, 270.1647.

methyl 1-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)piperidine-4-carboxylate (61)



Prepared according to **General Procedure E** with methyl piperidine-4-carboxylate (94.4 µL, 7.0 equiv, 0.70 mmol) and flurbiprofen (0.024 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a clear oil (27.9 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.18 – 7.11 (m, 2H), 3.67 (s, 3H), 3.45 (q, *J* = 6.7 Hz, 1H), 3.08 – 2.91 (m, 1H), 2.87 – 2.76 (m, 1H), 2.27 (tt, *J* = 11.3, 4.1 Hz, 1H), 2.12 – 1.98 (m, 2H), 1.96 – 1.89 (m, 1H), 1.89 – 1.82 (m, 1H), 1.81 – 1.68 (m, 2H), 1.37 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.86, 159.88 (d, *J* = 247.6 Hz), 146.31 (d, *J* = 7.8 Hz), 135.96, 130.45 (d, *J* = 3.8 Hz), 129.10 (d, *J* = 3.0 Hz), 128.55, 127.63, 127.44 (d, *J* = 13.7 Hz), 123.55 (d, *J* = 3.2 Hz), 115.11 (d, *J* = 23.1 Hz), 64.04, 51.74, 50.53, 49.59, 41.41, 28.73, 19.17. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -118.45 (s, 1F). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{25}FNO_2$, 342.1864; found, 342.1857.

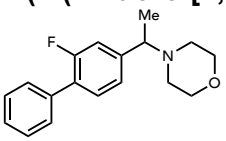
1-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)-4-(pyridin-2-yl)piperazine (62)



Prepared according to **General Procedure E** with 1-(2-pyridyl)piperazine (106.4 µL, 7.0 equiv, 0.70 mmol) and flurbiprofen (0.025 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a white solid (24.5 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.56 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.42 – 7.33 (m, 2H), 7.19 (d, *J* = 10.2 Hz, 2H), 6.74 –

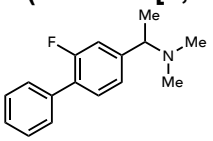
6.56 (m, 2H), 3.54 (ddd, *J* = 11.0, 6.9, 3.8 Hz, 4H), 3.46 (q, *J* = 6.7 Hz, 1H), 2.64 (td, *J* = 7.0, 3.4 Hz, 2H), 2.56 (td, *J* = 7.0, 3.4 Hz, 2H), 1.42 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.93 (d, *J* = 247.9 Hz), 159.73, 148.13, 146.09 (d, *J* = 7.1 Hz), 137.54, 135.91, 130.61 (d, *J* = 3.8 Hz), 129.11 (d, *J* = 3.0 Hz), 128.56, 127.68, 127.60, 123.65 (d, *J* = 3.1 Hz), 115.18 (d, *J* = 23.2 Hz), 113.35, 107.14, 64.31, 50.46, 45.62, 19.76. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -118.25 (s, 1F). **mp:** 109.3 – 110.8 °C. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{25}FN_3$, 362.2027; found, 362.2020.

4-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)morpholine (63)



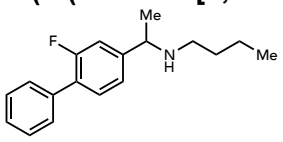
Prepared according to **General Procedure E** with morpholine (86.1 µL, 10 equiv, 1.0 mmol) and flurbiprofen (0.025 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a clear oil (25.7 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.47 – 7.41 (m, 2H), 7.40 – 7.32 (m, 2H), 7.18 – 7.12 (m, 2H), 3.72 (ddd, *J* = 5.9, 3.6, 2.4 Hz, 4H), 3.35 (q, *J* = 6.7 Hz, 1H), 2.66 – 2.48 (m, 2H), 2.49 – 2.35 (m, 2H), 1.37 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.93 (d, *J* = 247.8 Hz), 146.13 (d, *J* = 7.0 Hz), 135.89 (d, *J* = 1.3 Hz), 130.62 (d, *J* = 3.8 Hz), 129.09 (d, *J* = 3.0 Hz), 128.56, 127.68 (d, *J* = 13.7 Hz), 127.68, 123.65 (d, *J* = 3.3 Hz), 115.14 (d, *J* = 23.2 Hz), 67.38, 64.79, 51.35, 19.76. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -118.23 (s, 1F). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{21}FNO$, 286.1602; found, 286.1896.

1-(2-fluoro-[1,1'-biphenyl]-4-yl)-*N*,*N*-dimethylethan-1-amine (64)



Prepared according to **General Procedure E** with dimethylamine (1.5 mL, 2.0 M in THF, 10 equiv, 3.0 mmol) and flurbiprofen (0.073 g, 1.0 equiv, 0.30 mmol). Reaction was conducted on a 0.3 mmol scale. Purification by flash chromatography on silica gel, eluting with 40-60% ethyl acetate in hexanes, afforded the product as a clear oil (77 mg, 94% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 2H), 7.47 – 7.33 (m, 5H), 7.18 – 7.10 (m, 2H), 3.37 (q, *J* = 6.4 Hz, 1H), 2.26 (s, 6H), 1.41 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.84 (d, *J* = 247.9 Hz), 145.35 (d, *J* = 7.8 Hz), 135.85, 130.60 (d, *J* = 3.8 Hz), 129.10 (d, *J* = 2.9 Hz), 128.56, 127.83, 127.69, 123.70 (d, *J* = 3.2 Hz), 115.29 (d, *J* = 23.1 Hz), 65.29 (d, *J* = 1.5 Hz), 43.00, 19.83. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -118.24 (s, 1F). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{18}FNH$, 244.1496; found 244.1494.

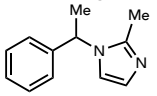
***N*-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)butan-1-amine (65)**



Prepared according to **General Procedure E** with butylamine (98.6 µL, 10 equiv, 1.0 mmol) and flurbiprofen (0.025 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a clear oil (21.9 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.51 – 7.41 (m, 2H), 7.41 – 7.32 (m, 2H), 7.20 – 7.11 (m, 2H), 3.79 (q, *J* = 6.6 Hz, 1H), 2.53 (dt, *J* = 11.3, 7.3 Hz, 1H), 2.47 (dt, *J* = 11.3, 7.3 Hz, 1H), 1.51 – 1.43 (m, 2H), 1.37 (d, *J* = 6.6 Hz, 3H), 1.36 – 1.30 (m, 2H), 0.90 (t, *J* = 7.3 Hz,

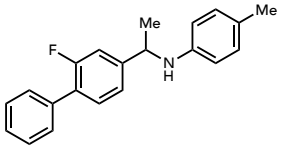
3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.05 (d, *J* = 247.7 Hz), 148.14 (d, *J* = 7.8 Hz), 136.02, 130.73 (d, *J* = 3.8 Hz), 129.12 (d, *J* = 2.9 Hz), 128.54, 127.61, 127.46 (d, *J* = 13.6 Hz), 122.63 (d, *J* = 3.2 Hz), 114.19 (d, *J* = 23.0 Hz), 58.01, 47.77, 32.59, 24.53, 20.64, 14.16. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -118.33 (s, 1F). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{23}FN$, 272.1809; found, 272.1804.

2-methyl-1-(1-phenylethyl)-1H-imidazole (66)



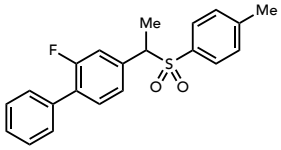
Prepared according to **General Procedure E** with 2-methylimidazole (0.082 g, 10 equiv, 1.0 mmol) and 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a white solid (10.9 mg, 59% yield). The spectral data matched those previously reported.[20] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.30 – 7.23 (m, 1H), 7.05 (dd, *J* = 7.8, 1.2 Hz, 2H), 6.98 (dd, *J* = 7.6, 1.4 Hz, 2H), 5.30 (q, *J* = 7.1 Hz, 1H), 2.27 (s, 3H), 1.80 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.90, 141.91, 128.98, 127.83, 127.33, 125.84, 116.54, 55.10, 22.43, 13.61. **mp:** 87.5 – 88.3 °C (lit.[20] 85 – 86 °C). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{12}H_{15}N_2$, 187.1230; found, 187.1228.

***N*-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)-4-methylaniline (67)**



Prepared according to **General Procedure E** with *p*-toluidine (0.107 g, 10 equiv, 1.0 mmol) and flurbiprofen (0.025 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a pale yellow oil (19.2 mg, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 2H), 7.47 – 7.41 (m, 2H), 7.40 – 7.31 (m, 2H), 7.22 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.18 (dd, *J* = 11.7, 1.7 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 8.4 Hz, 2H), 4.48 (q, *J* = 6.7 Hz, 1H), 3.93 (br s, 1H), 2.21 (s, 3H), 1.54 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.17 (d, *J* = 248.1 Hz), 147.62 (d, *J* = 6.6 Hz), 144.86, 135.92 (d, *J* = 1.3 Hz), 131.05 (d, *J* = 3.8 Hz), 129.82, 129.10 (d, *J* = 2.9 Hz), 128.53, 127.63, 127.53 (d, *J* = 13.7 Hz), 126.89, 121.90 (d, *J* = 3.2 Hz), 113.60 (d, *J* = 23.5 Hz), 113.58, 53.36, 25.14, 20.49. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -117.79 (s, 1F). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{21}FN$, 306.1652; found, 306.1646.

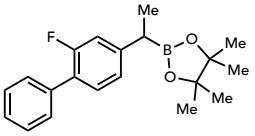
2-fluoro-4-(1-tosylethyl)-1,1'-biphenyl (68)



An oven-dried 4-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with $FeCl_3$ (0.049 g, 3.0 equiv, 0.30 mmol), Na_3PO_4 (0.049 g, 3.0 equiv, 0.30 mmol), flurbiprofen (0.024 g, 1.0 equiv, 0.10 mmol), and MeCN (1.0 mL, 0.10 M). The vial is sealed with a screwcap bearing a teflon septum, removed from the glovebox, and placed into a EvoluChem™ PhotoRedOx Box. Stirring at 800 rpm is engaged and the vial is irradiated at 427 nm with a 40 W Kessil™ lamp. After 24 h, the light is turned off, the vial is removed from the PhotoRedox Box, and diluted with 1.5 mL diethyl ether and 1.5 mL saturated aqueous NH_4Cl. The biphasic mixture is thoroughly shaken, and the organic layer is removed and filtered through a short pad of

diatomaceous earth to remove trace water. The remaining aqueous layer is washed 1x1.5 mL with diethyl ether, and the organic wash is pushed through the same filter pad. The solvent is removed from the combined organic layers to afford the crude benzylic chloride intermediate. To this vial is added DMF (0.50 mL, 0.20 M) and sodium *p*-toluenesulfinate (0.089 g, 5.0 equiv, 0.50 mmol). The vial is sealed with a screwcap bearing a teflon septum and stirred at 80 °C for 16 h. The reaction was quenched by the addition of 1.5 mL 0.5 M aqueous LiCl and is washed 3x1.5 mL ethyl acetate. The organic extracts are combined, and the solvent is removed under reduced pressure. Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a white solid (25.9 mg, 73% yield). The spectral data matched those previously reported.[21] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 4H), 7.41 – 7.36 (m, 2H), 7.35 – 7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 6.96 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.93 (dd, *J* = 11.4, 1.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 2.35 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.48 (d, *J* = 249.0 Hz), 144.97, 135.26 (d, *J* = 6.3 Hz), 135.22, 133.95, 130.64 (d, *J* = 3.9 Hz), 129.61, 129.49, 129.39, 129.09 (d, *J* = 3.0 Hz), 128.66, 128.12, 125.67 (d, *J* = 3.5 Hz), 117.22 (d, *J* = 24.3 Hz), 65.52, 21.78, 14.45. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -117.32 (s, 1F). **mp:** 137.2 – 138.5 °C. **HRMS** (FTMS + p ESI) m/z: $[M+NH_4]^+$ calculated for $[C_{21}H_{19}FO_2S][NH_4]^+$, 372.1428; found, 372.1422.

2-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69)



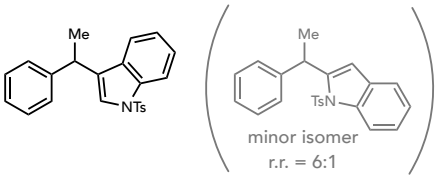
An oven-dried 6-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with $FeCl_3$ (0.097 g, 3.0 equiv, 0.60 mmol), Na_3PO_4 (0.098 g, 3.0 equiv, 0.60 mmol), flurbiprofen (0.049 g, 1.0 equiv, 0.20 mmol), and MeCN (2.0 mL, 0.10 M). The vial is sealed with a screwcap bearing a teflon septum, removed from the glovebox, and placed into a EvoluChem™ PhotoRedOx Box. Stirring at 800 rpm is engaged and the vial is irradiated at 427 nm with a 40 W Kessil™ lamp. After 24 h, the light is turned off, the vial is removed from the PhotoRedox Box, and diluted with 1.5 mL diethyl ether and 1.5 mL saturated aqueous NH_4Cl. The biphasic mixture is thoroughly shaken, and the organic layer is removed and filtered through a short pad of diatomaceous earth to remove trace water. The remaining aqueous layer is washed 1x1.5 mL with diethyl ether, and the organic wash is pushed through the same filter pad. The solvent is removed from the combined organic layers to afford the crude benzylic chloride intermediate.

A separate oven-dried 4-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with CuCl (0.002 g, 10 mol%), Xantphos (0.012 g, 10 mol%), and anhydrous THF (0.40 mL). The mixture is swirled gently to promote solvation. Once the majority of the CuCl is dissolved, the vial is next charged with bis(pinacolato)diboron (0.061 g, 1.2 equiv, 0.24 mmol) and KO*t*-Bu (0.027 g, 1.2 equiv, 0.24 mmol) and swirled gently for ca. 5 min. The crude benzylic chloride from the first step is next added as a solution in 1.0 mL anhydrous THF (total reaction concentration 0.40 M). The vial is sealed with a screwcap bearing a teflon septum, removed from the glovebox, and stirred at room temperature for 24 h. The reaction is quenched by addition of 1 mL saturated aqueous NH_4Cl, and the mixture is washed 3x1 mL Et_2O. The combined organic extracts are dried with $MgSO_4$, filtered, and the solvent is removed under reduced pressure. Purification by flash chromatography on silica, eluting with 5% ethyl acetate in hexanes, afforded the product as a clear oil (33.3 mg, 51% yield). The spectral data matched with those previously reported.[22] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.45 – 7.39 (m, 2H), 7.36 – 7.30 (m, 2H), 7.06 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.03 (dd, *J* = 12.1, 1.8 Hz, 1H), 2.48 (q, *J* = 7.5 Hz, 1H), 1.36 (d, *J* = 7.5 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.89 (d, *J* = 247.1 Hz), 146.96 (d, *J* = 7.7 Hz), 136.24 (d, *J* = 1.3 Hz), 130.50 (d, *J* = 4.0 Hz), 129.08 (d, *J* = 3.0 Hz),

128.49, 127.39, 125.74 (d, *J* = 13.6 Hz), 123.97 (d, *J* = 3.1 Hz), 115.37 (d, *J* = 22.8 Hz), 83.67, 24.97, 24.80, 24.76, 16.96. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -118.8. (s, 1F). **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.43 (s). **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{25}BFO_2$, 327.1926; found, 327.1922.

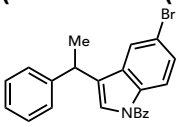
Extra Substrates

3-(1-phenylethyl)-1-tosyl-1H-indole (S3)



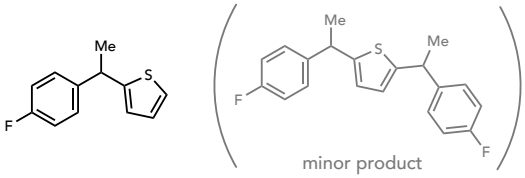
Prepared according to **General Procedure A** with 1-tosylindole (0.163 g, 3.0 equiv, 0.6 mmol) and 2-phenylpropanoic acid (0.030 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) and Na_2CO_3 (0.064 g, 3.0 equiv, 0.60 mmol) were used in place of $FeCl_3$ and NaOAc, respectively. Purification by flash chromatography on silica gel, eluting with 0–2.5% ether in pentane, enabled the separation of the two isomers, each isolated as a white solid (55.6 mg combined mass, 74% yield, 6:1 *r.r.*). Major isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 1.0 Hz, 1H), 7.29 – 7.20 (m, 5H), 7.20 – 7.14 (m, 4H), 7.07 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 4.22 (q, *J* = 7.7, 7.1 Hz, 1H), 2.35 (s, 3H), 1.66 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.07, 144.88, 135.85, 135.46, 130.60, 129.94, 128.66, 127.86, 127.42, 126.91, 126.54, 124.72, 123.14, 123.04, 120.48, 113.90, 37.01, 22.16, 21.71. **mp:** 121.0 – 122.6 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}NO_2SNa$, 398.1185; found, 398.1183. Minor isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.45 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.28 (t, *J* = 8.3 Hz, 3H), 7.25 – 7.15 (m, 6H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.54 (d, *J* = 1.0 Hz, 1H), 5.00 (q, *J* = 7.1 Hz, 1H), 2.28 (s, 3H), 1.66 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.20, 144.80, 144.44, 137.46, 136.15, 129.66, 129.62, 128.55, 127.92, 126.54, 126.48, 124.26, 123.62, 120.53, 115.27, 109.62, 38.45, 23.87, 21.60.

(5-bromo-3-(1-phenylethyl)-1H-indol-1-yl)(phenyl)methanone (S4)



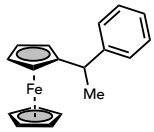
Prepared according to **General Procedure A** with 1-benzoyl-5-bromoindole (0.090 g, 3.0 equiv, 0.3 mmol) and 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol). $Fe(OTf)_3$ (0.150 g, 3.0 equiv, 0.30 mmol) and Na_2CO_3 (0.032 g, 3.0 equiv, 0.30 mmol) were used in place of $FeCl_3$ and NaOAc, respectively. Purification by flash chromatography on silica gel, eluting with 0–2.5% ether in pentane, afforded the product as a clear oil (26.3 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.81 – 7.71 (m, 2H), 7.68 – 7.59 (m, 1H), 7.62 – 7.51 (m, 2H), 7.45 – 7.38 (m, 2H), 7.35 – 7.24 (m, 2H), 7.24 – 7.11 (m, 4H), 4.22 (q, *J* = 7.1 Hz, 1H), 1.61 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.45, 144.67, 135.61, 134.51, 132.32, 132.24, 129.31, 128.85, 128.82, 127.98, 127.35, 126.77, 126.26, 125.09, 122.78, 117.98, 117.11, 36.79, 22.09. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{19}BrNO$, 404.0645; found, 404.0643.

2-(1-(4-fluorophenyl)ethyl)thiophene (S5)



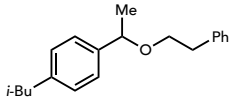
Prepared according to **General Procedure A** with thiophene (0.120 mL, 5.0 equiv, 1.5 mmol) and2-(4-fluorophenyl)propanoic acid (0.050 g, 1.0 equiv, 0.3 mmol). The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica with H_2O/MeOH. The product eluted around ~80% MeOH. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered through a plug of celite, and concentrated under reduced pressure to afford the product as a clear oil (20 mg, 33% yield, 10:1). *Where resolved, signals for the minor product are given in brackets.* **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 2.14H), 7.17 – 7.12 (m, 1H), 7.02 – 6.94 (m, 2.59H), 6.92 (dd, *J* = 5.2, 3.5 Hz, 1H), [6.85 (dd, *J* = 4.9, 1.3 Hz, 0.17H)], 6.81 – 6.76 (m, 1H), 4.33 (q, *J* = 7.1 Hz, 1H), [4.14 (q, *J* = 7.2 Hz, 0.19H)], 1.68 (d, *J* = 7.2 Hz, 3H), [1.61 (d, *J* = 7.2 Hz, 0.55H)]. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.64, [162.47], 160.70, [160.53], 150.65, [147.19], [142.10 (d, *J* = 3.0 Hz)], 141.92 (d, *J* = 3.1 Hz), [128.93 (d, *J* = 7.9 Hz)], 128.84 (d, *J* = 7.9 Hz), 127.84, 126.71, 125.70, 123.78, 123.76, 120.04, 115.45, [115.37], 115.29, [115.20], [40.20], 40.15, 23.60. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.74, [-117.29]. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{12}H_{11}FSH$, 207.0638; found, 207.0637.

1-ferrocenyl-1-phenylethane (S6)



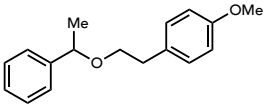
Prepared according to **General Procedure A** with ferrocene (0.059 g, 3.0 equiv, 0.3 mmol) and 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 0–5% ethyl acetate in hexanes, afforded the product as an orange oil (16.7 mg, 56% yield). The spectral data matched those previously reported.[23] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 7.19 – 7.11 (m, 3H), 4.20 (dt, *J* = 2.6, 1.3 Hz, 1H), 4.12 – 4.11 (m, 6H), 4.08 (td, *J* = 2.4, 1.3 Hz, 1H), 3.99 (dt, *J* = 2.5, 1.4 Hz, 1H), 3.86 (q, *J* = 7.2 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.69, 128.34, 127.24, 126.06, 94.47, 68.70, 68.04, 67.69, 67.06, 66.51, 39.95, 22.72. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{29}Fe$, 289.0877; found, 289.0874.

1-isobutyl-4-(1-phenethoxyethyl)benzene (**S7**)



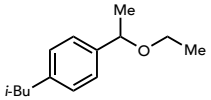
Prepared according to **General Procedure B** with 2-phenylethan-1-ol (0.108 mL, 3.0 equiv, 0.9 mmol) and 2-(4-isobutylphenyl)propanoic acid (0.062 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 2% ether in hexanes, afforded the product as a clear oil (57 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 2H), 7.20 – 7.12 (m, 5H), 7.08 – 7.07 (m, 2H), 4.38 (q, *J* = 6.4 Hz, 1H), 3.50 (td, *J* = 7.3, 2.9 Hz, 2H), 2.93 – 2.78 (m, 2H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.42 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.24, 140.90, 139.25, 129.21, 129.08, 128.36, 126.20, 126.06, 78.07, 69.63, 45.28, 36.72, 30.35, 24.14, 22.55. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{20}H_{26}ONa$, 305.1876; found, 305.1871.

1-methoxy-4-(2-(1-phenylethoxy)ethyl)benzene (S8)



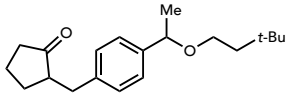
Prepared according to **General Procedure B** with 2-(4-methoxyphenyl)ethan-1-ol (0.137 g, 3.0 equiv, 0.9 mmol) and 2-phenylpropanoic acid (0.045 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 2% ether in hexanes, afforded the product as a clear oil (38 mg, 45% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.27 – 7.23 (m, 3H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.39 (q, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 3.50 – 3.44 (m, 2H), 2.87 – 2.75 (m, 2H), 1.42 (d, *J* = 6.5 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.16, 144.14, 131.27, 129.99, 128.51, 127.46, 126.27, 113.83, 78.22, 70.00, 55.39, 35.79, 24.26. **HRSM** (FTMS + p ESI) m/z: $[M + Na]^+$ calculated for $C_{17}H_{20}O_2Na$, 279.1355; found, 279.1351.

1-(1-ethoxyethyl)-4-isobutylbenzene (S9)



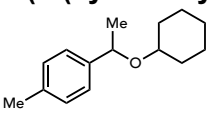
Prepared according to **General Procedure B** with ethanol (0.053 mL, 3.0 equiv, 0.9 mmol) and 2-(4-isobutylphenyl)propanoic acid (0.062 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 2% ethyl acetate in hexanes, afforded the product as a clear oil (27 mg, 44% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.38 (q, *J* = 6.5 Hz, 1H), 3.38 – 3.30 (m, 2H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.91 – 1.80 (m, 1H), 1.43 (d, *J* = 6.5 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.55, 140.88, 129.23, 126.03, 77.72, 63.93, 45.30, 30.37, 24.30, 22.56, 15.57. **HRSM** (FTMS + p ESI) m/z: $[M - H]^+$ calculated for $C_{14}H_{21}O$, 205.1587; found, 205.1586.

2-(4-(1-(3,3-dimethylbutoxy)ethyl)benzyl)cyclopentan-1-one (S10)



Prepared according to **General Procedure B** with 3,3-dimethylbutan-1-ol (0.109 mL, 3.0 equiv, 0.9 mmol) and 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoic acid (0.074 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 10% ethyl acetate in hexanes, afforded the product as a clear oil (71 mg, 77% yield, 1:1 d.r.). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.35 (q, *J* = 6.5 Hz, 1H), 3.39 – 3.28 (m, 2H), 3.14 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.53 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.41 – 2.28 (m, 2H), 2.15 – 2.04 (m, 2H), 2.01 – 1.89 (m, 1H), 1.78 – 1.69 (m, 1H), 1.62 – 1.45 (m, 3H), 1.41 (d, *J* = 6.5 Hz, 3H), 0.86 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.40, 142.29, 142.27, 139.08, 129.01, 126.35, 77.85, 77.84, 66.03, 51.15, 43.39, 38.36, 35.45, 29.86, 29.78, 29.38, 29.36, 24.26, 24.24, 20.70 (mixture of diastereomers). **HRSM** (FTMS + p ESI) m/z: $[M –C_6H_{13}O + H]^+$ calculated for $C_{14}H_{17}OH$, 201.1274; found, 201.1273.

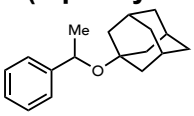
1-(1-(cyclohexyloxy)ethyl)-4-methylbenzene (S11)



Prepared according to **General Procedure B** with cyclohexanol (0.095 mL, 3.0 equiv, 0.9 mmol) and 2-(*p*-tolyl)propanoic acid (0.049 g, 1.0 equiv, 0.3 mmol). Purification by flash chromatography on silica gel, eluting with 5% ether in hexanes, afforded the product as a clear oil (67 mg, 76%

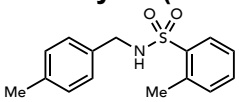
yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.56 (q, *J* = 6.5 Hz, 1H), 3.15 (tt, *J* = 9.7, 3.9 Hz, 1H), 2.34 (s, 3H), 2.00 – 1.91 (m, 1H), 1.80 – 1.63 (m, 3H), 1.53 – 1.45 (m, 1H), 1.39 (d, *J* = 6.5 Hz, 3H), 1.32 – 1.22 (m, 3H), 1.20 – 1.10 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.22, 136.80, 129.11, 126.18, 74.80, 74.14, 33.66, 31.94, 25.99, 25.08, 24.60, 24.37, 21.27. **HRSM** (FTMS + p ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{22}OH$, 219.1743; found, 219.1742.

1-(1-phenylethoxy)adamantane (S12)



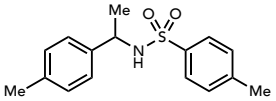
Prepared according to **General Procedure B** with (3*s*,*5s*,7*s*)-adamantan-1-ol (0.137 g, 3.0 equiv, 0.9 mmol) and 2-phenylpropanoic acid (0.041 mL, 1.0 equiv, 0.3 mmol). The crude reaction mixture was purified by reverse phase flash chromatography over C18 functionalized silica with H_2O/MeCN. The product eluted around ~50% MeCN. Product-containing fractions were combined, diluted with EtOAc, and washed with brine (1x). The aqueous layer was washed with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered through a plug of celite, and concentrated under reduced pressure to afford the product as a clear oil (12 mg, 16% yield). The spectral data matched those previously reported.[24] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.17 (m, 1H), 4.82 (q, *J* = 6.5 Hz, 1H), 2.11 – 2.05 (m, 3H), 1.78 – 1.65 (m, 6H), 1.66 – 1.50 (m, 6H), 1.36 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.89, 128.18, 126.57, 125.74, 73.58, 67.95, 42.75, 36.57, 30.74, 26.91.

2-methyl-*N*-(4-methylbenzyl)benzenesulfonamide (S13)



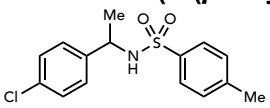
Prepared according to **General Procedure D** with *o*-toluenesulfonamide (0.051 g, 3.0 equiv, 0.60 mmol) and 2-(*p*-tolyl)acetic acid (0.030 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) was used in place of $FeCl_3$. Purification by flash chromatography on silica gel, eluting with 30–60% ethyl acetate in hexanes, afforded the product as a clear oil (21.0 mg, 38% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.47 (td, *J* = 7.4, 1.4 Hz, 1H), 7.32 (dd, *J* = 9.0, 7.4 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 4.62 (t, *J* = 6.1 Hz, 1H), 4.07 (d, *J* = 6.0 Hz, 2H), 2.62 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.95, 137.90, 137.20, 133.36, 132.96, 132.69, 129.85, 129.55, 128.04, 126.34, 47.10, 21.22, 20.44. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{15}H_{16}NO_2S$, 274.0907; found, 274.0909.

4-methyl-*N*-(1-(*p*-tolyl)ethyl)benzenesulfonamide (S14)



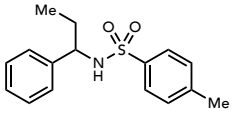
Prepared according to **General Procedure D** with *p*-toluenesulfonamide (0.051 g, 3.0 equiv, 0.60 mmol) and 2-(*p*-tolyl)propanoic acid (0.033 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20–30% ethyl acetate in hexanes, afforded the product as a white solid (32.4 mg, 56% yield). The spectral data matched those previously reported.[25] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.10 – 6.95 (m, 4H), 4.80 (d, *J* = 6.8 Hz, 1H), 4.41 (p, *J* = 6.8 Hz, 1H), 2.39 (s, 3H), 2.28 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.21, 139.22, 137.86, 137.37, 129.55, 129.32, 127.27, 126.18, 53.52, 23.59, 21.61, 21.13. **mp:** 113.9 – 115.0 °C (lit.[26] 114 – 115 °C). **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{16}H_{18}NO_2S$, 288.1064; found, 288.1064.

4-chloro-*N*-(1-(*p*-tolyl)ethyl)benzenesulfonamide (S15)



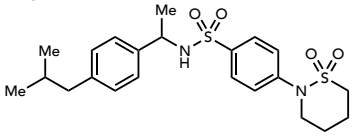
Prepared according to **General Procedure D** with *p*-toluenesulfonamide (0.051 g, 3.0 equiv, 0.60 mmol) and 2-(4-chlorophenyl)propanoic acid (0.037 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (45.7 mg, 74% yield). The spectral data matched those previously reported.[27] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 4.98 (d, *J* = 6.9 Hz, 1H), 4.44 (p, *J* = 6.9 Hz, 1H), 2.40 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.51, 140.65, 137.62, 133.37, 129.61, 128.73, 127.73, 127.22, 53.15, 23.60, 21.61. **mp:** 128.0 – 129.7 °C (lit.[28] 129 – 130 °C). **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{15}H_{15}ClNO_2S$, 308.0518; found, 308.0518.

4-methyl-*N*-(1-phenylpropyl)benzenesulfonamide (S16)



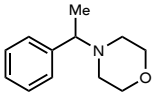
Prepared according to **General Procedure D** with *p*-toluenesulfonamide (0.051 g, 3.0 equiv, 0.60 mmol) and 2-phenylbutanoic acid (0.033 g, 1.0 equiv, 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (45.0 mg, 78% yield). The spectral data matched those previously reported.[25] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.14 (m, 3H), 7.11 (d, *J* = 8.3 Hz, 2H), 7.06 – 6.98 (m, 2H), 5.00 (d, *J* = 7.3 Hz, 1H), 4.19 (q, *J* = 7.3 Hz, 1H), 2.35 (s, 3H), 1.81 (dp, *J* = 13.9, 7.3 Hz, 1H), 1.71 (dp, *J* = 13.9, 7.3 Hz, 1H), 0.78 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.02, 140.81, 137.84, 129.37, 128.48, 127.40, 127.15, 126.67, 59.93, 30.70, 21.54, 10.54. **mp:** 107.2 – 108.2 °C (lit.[29] 107 – 108 °C). **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{16}H_{18}NO_2S$, 288.1064; found, 288.1064.

4-(1,1-dioxido-1,2-thiazinan-2-yl)-*N*-(1-(4-isobutylphenyl)ethyl)benzenesulfonamide (S17)



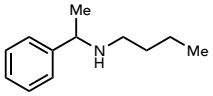
Prepared according to **General Procedure D** with sultiame (0.087 g, 3.0 equiv, 0.60 mmol) and ibuprofen (0.041 g, 1.0 equiv, 0.20 mmol). $Fe(OTf)_3$ (0.302 g, 3.0 equiv, 0.60 mmol) was used in place of $FeCl_3$. Purification by flash chromatography on silica gel, eluting with 70% ethyl acetate in hexanes, afforded the product as a white solid (58.6 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.07 – 6.95 (m, 4H), 4.73 (d, *J* = 6.8 Hz, 1H), 4.48 (p, *J* = 6.8 Hz, 1H), 3.88 – 3.69 (m, 2H), 3.44 – 3.14 (m, 2H), 2.40 (d, *J* = 7.2 Hz, 2H), 2.39 – 2.31 (m, 2H), 2.10 – 1.87 (m, 2H), 1.87 – 1.75 (m, 1H), 1.44 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 3H), 0.87 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.30, 141.41, 139.12, 138.95, 129.49, 128.12, 126.33, 126.01, 53.73, 53.21, 51.00, 45.08, 30.26, 24.53, 24.29, 23.68, 22.51, 22.49. **mp:** 121.0 – 123.3 °C. **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{22}H_{29}N_2O_4S_2$, 449.1574; found, 449.1576.

4-(1-phenylethyl)morpholine (S18)



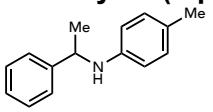
Prepared according to **General Procedure E** with morpholine (86.1 µL, 10 equiv, 1.0 mmol) and 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a clear oil (12.1 mg, 63% yield). The spectral data matched those previously reported.[30] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 4H), 7.28 – 7.20 (m, 1H), 3.69 (ddd, *J* = 5.5, 3.7, 1.4 Hz, 4H), 3.30 (q, *J* = 6.7 Hz, 1H), 2.61 – 2.42 (m, 2H), 2.40 – 2.32 (m, 2H), 1.35 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.11, 128.43, 127.77, 127.11, 67.39, 65.54, 51.46, 19.97. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{12}H_{18}NO$, 192.1383; found, 192.1382.

_N_-(1-phenylethyl)butan-1-amine (S19)



Prepared according to **General Procedure E** with butylamine (98.6 µL, 10 equiv, 1.0 mmol) and 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a clear oil (11.9 mg, 67% yield). The spectral data matched those previously reported.[31] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 4H), 7.27 – 7.19 (m, 1H), 3.75 (q, *J* = 6.6 Hz, 1H), 2.50 (ddd, *J* = 11.3, 8.0, 6.2 Hz, 1H), 2.42 (ddd, *J* = 11.3, 8.1, 6.8 Hz, 1H), 1.61 – 1.38 (m, 3H), 1.36 (d, *J* = 6.6 Hz, 3H), 1.34 – 1.21 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.12, 128.52, 126.93, 126.68, 58.55, 47.73, 32.60, 24.52, 20.64, 14.14. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{12}H_{20}N$, 178.1590; found, 178.1587.

4-methyl-_N_-(1-phenylethyl)aniline (S20)



Prepared according to **General Procedure E** with *p*-toluidine (0.107 g, 10 equiv, 1.0 mmol) and 2-phenylpropanoic acid (0.015 g, 1.0 equiv, 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 5-20% ethyl acetate in hexanes, afforded the product as a white solid (10.3 mg, 49% yield). The spectral data matched those previously reported.[32] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.45 (d, *J* = 8.3 Hz, 2H), 4.47 (q, *J* = 6.7 Hz, 1H), 3.91 (br s, 1H), 2.20 (s, 3H), 1.52 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.57, 145.17, 129.73, 128.74, 126.93, 126.50, 126.00, 113.56, 53.82, 25.18, 20.47. **mp:** 68.9 – 70.7 °C (lit.[33] 68 – 68.5 °C). **HRMS** (FTMS + p ESI) m/z: $[M-H]^-$ calculated for $C_{15}H_{16}N$, 210.1288; found, 210.1286.

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L. NMR spectra

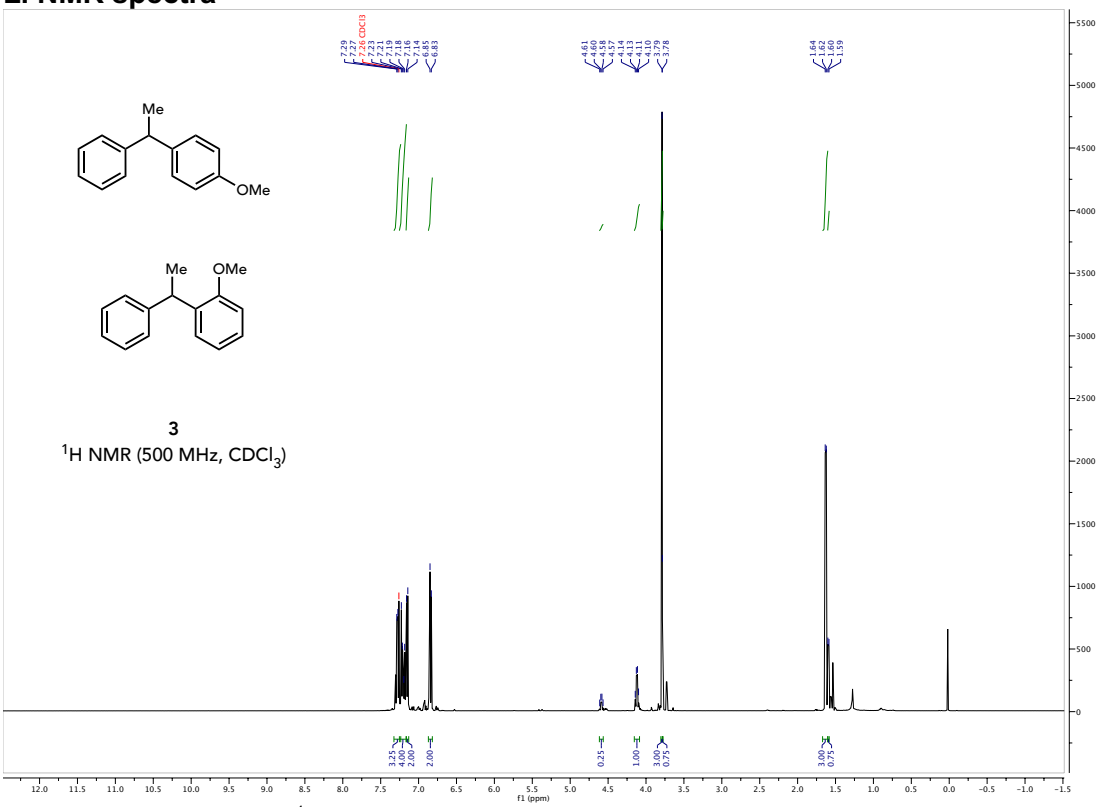


Figure S12. 500 MHz ^{1}H NMR spectrum of **3** in $CDCl_3$.

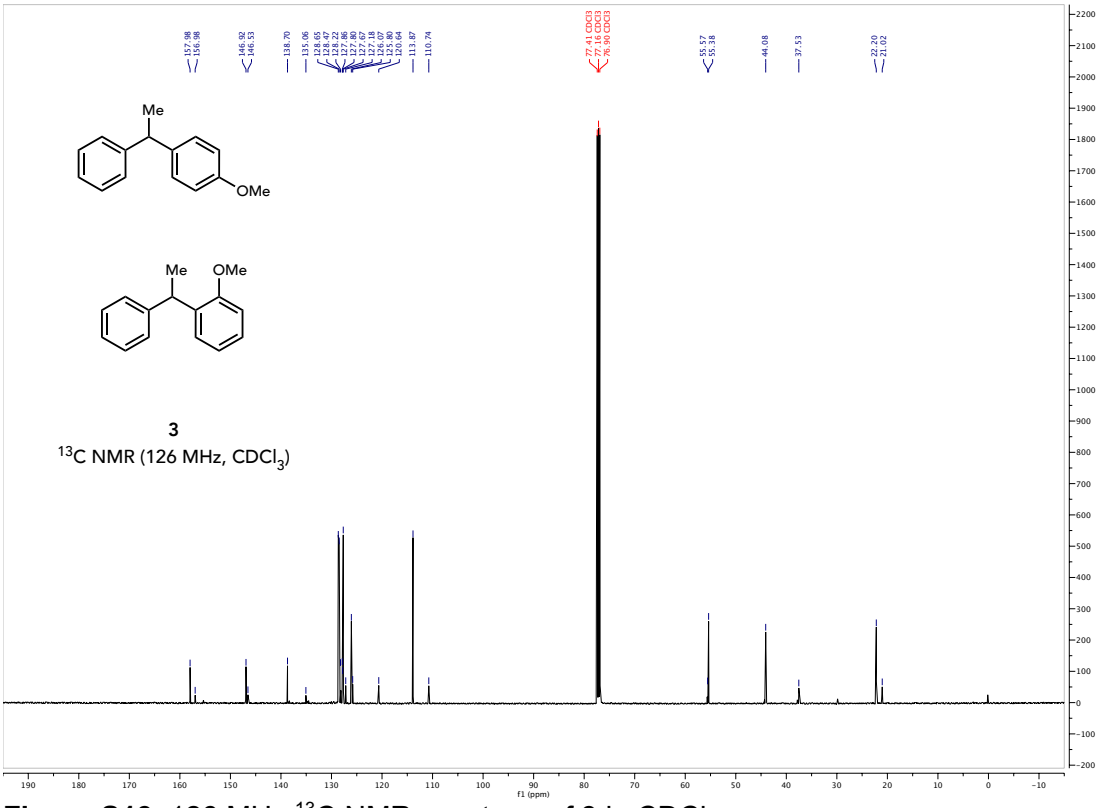


Figure S13. 126 MHz ^{13}C NMR spectrum of **3** in $CDCl_3$.

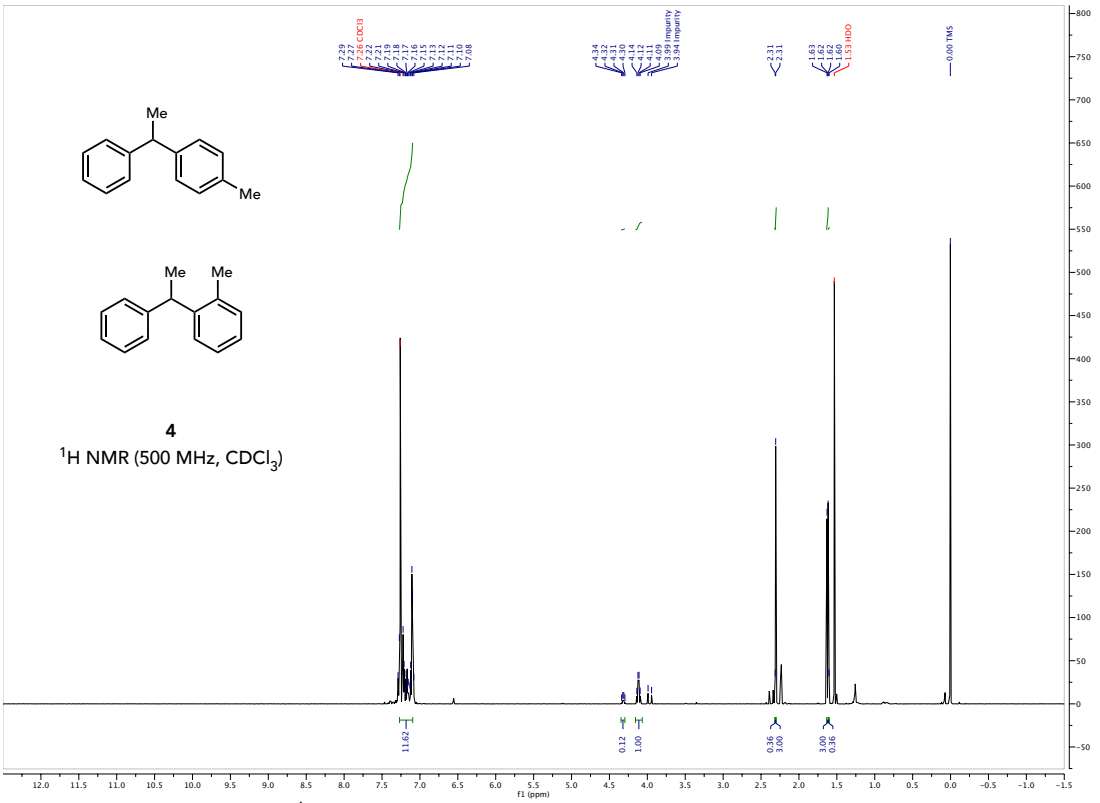


Figure S14. 500 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$.

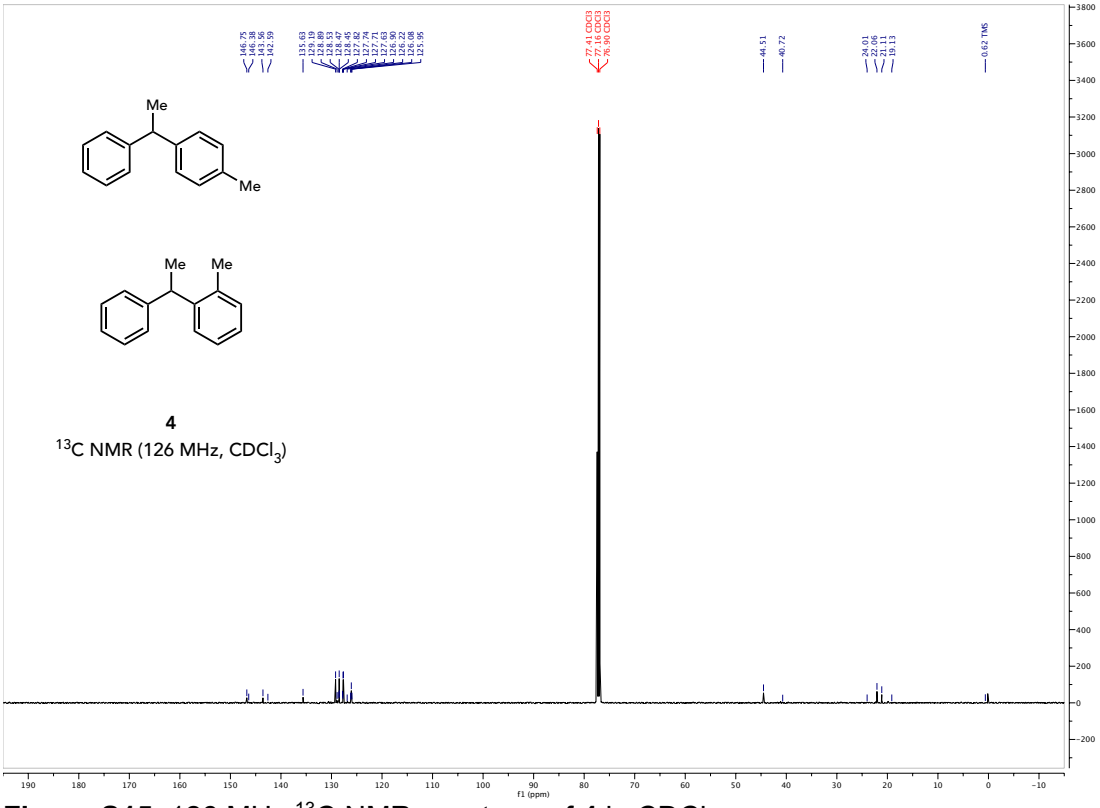


Figure S15. 126 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$.

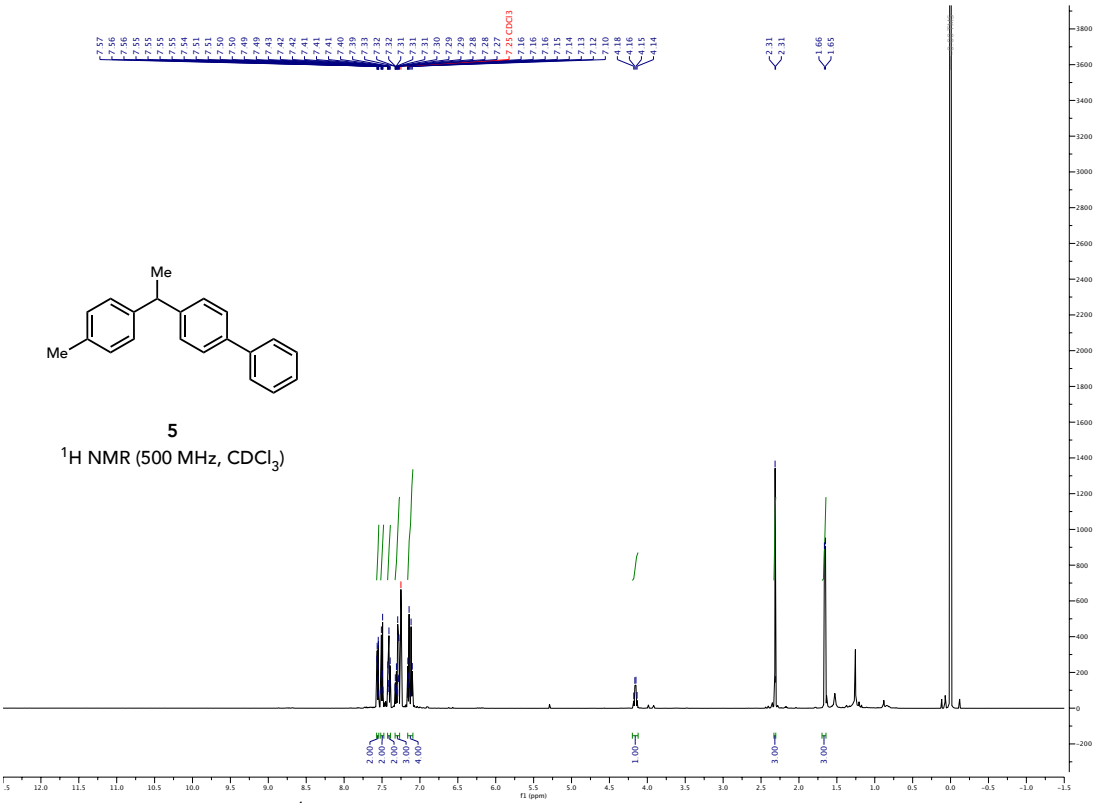


Figure S16. 500 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$.

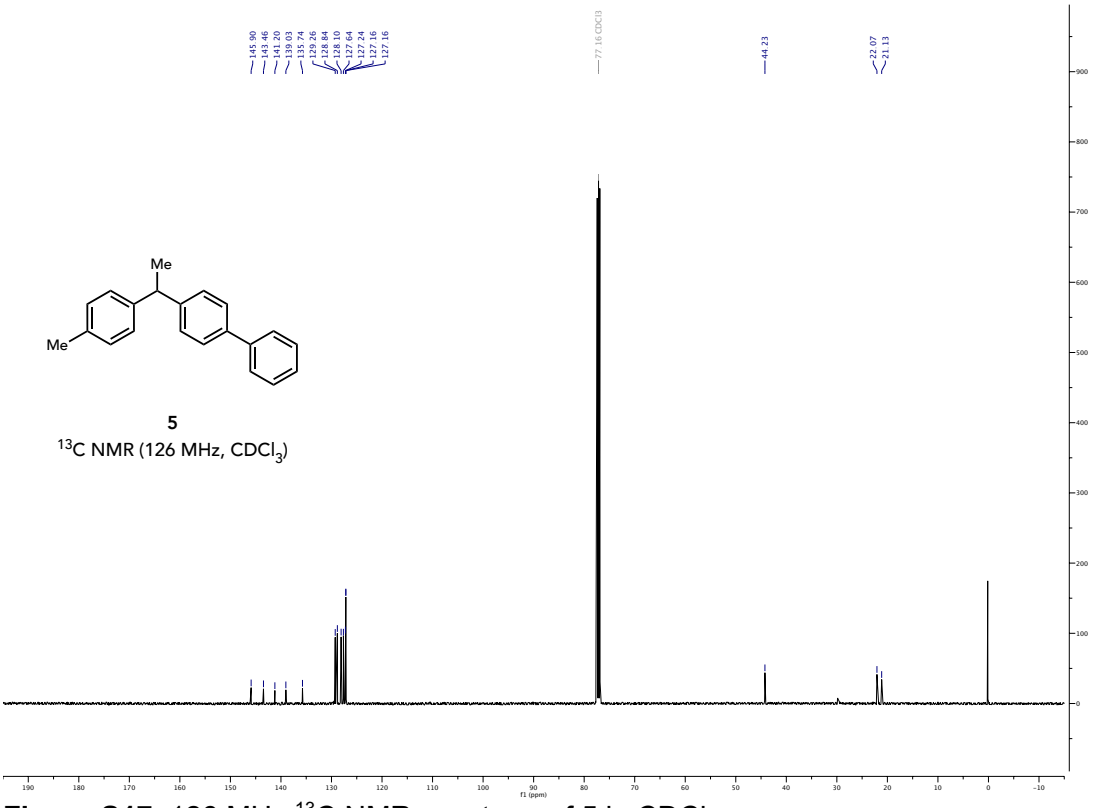


Figure S17. 126 MHz ^{13}C NMR spectrum of **5** in $CDCl_3$.

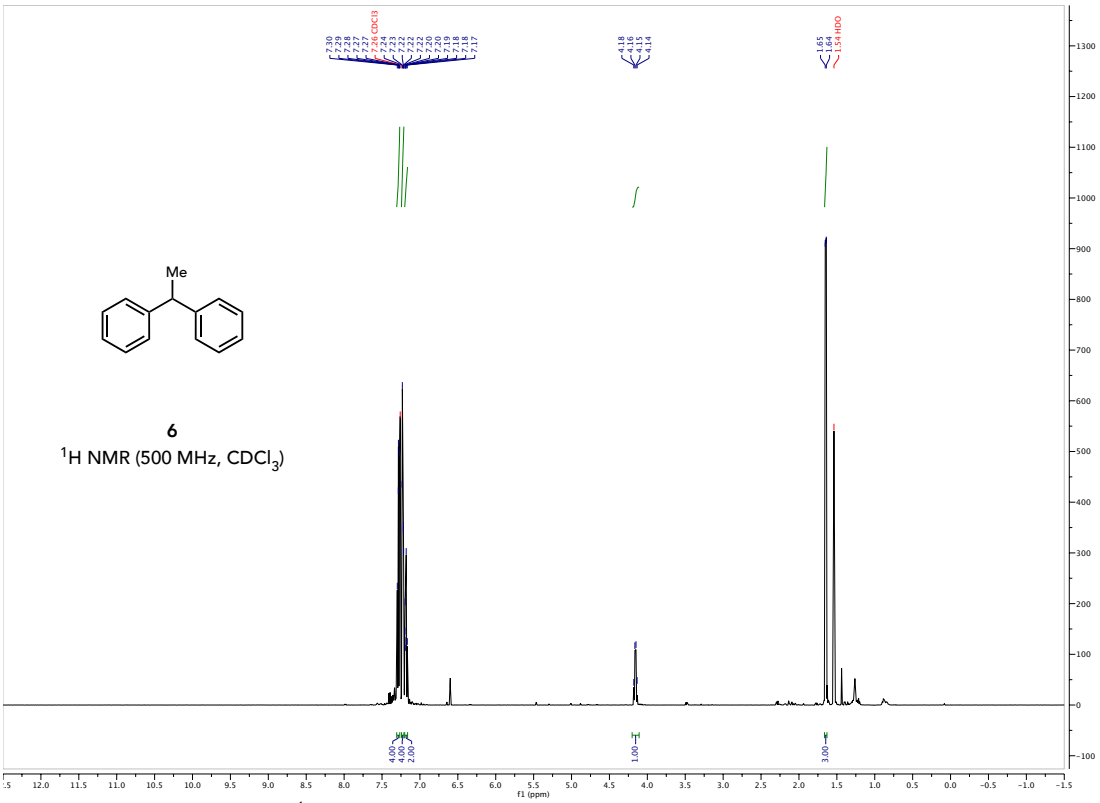


Figure S18. 500 MHz ^{1}H NMR spectrum of **6** in $CDCl_3$.

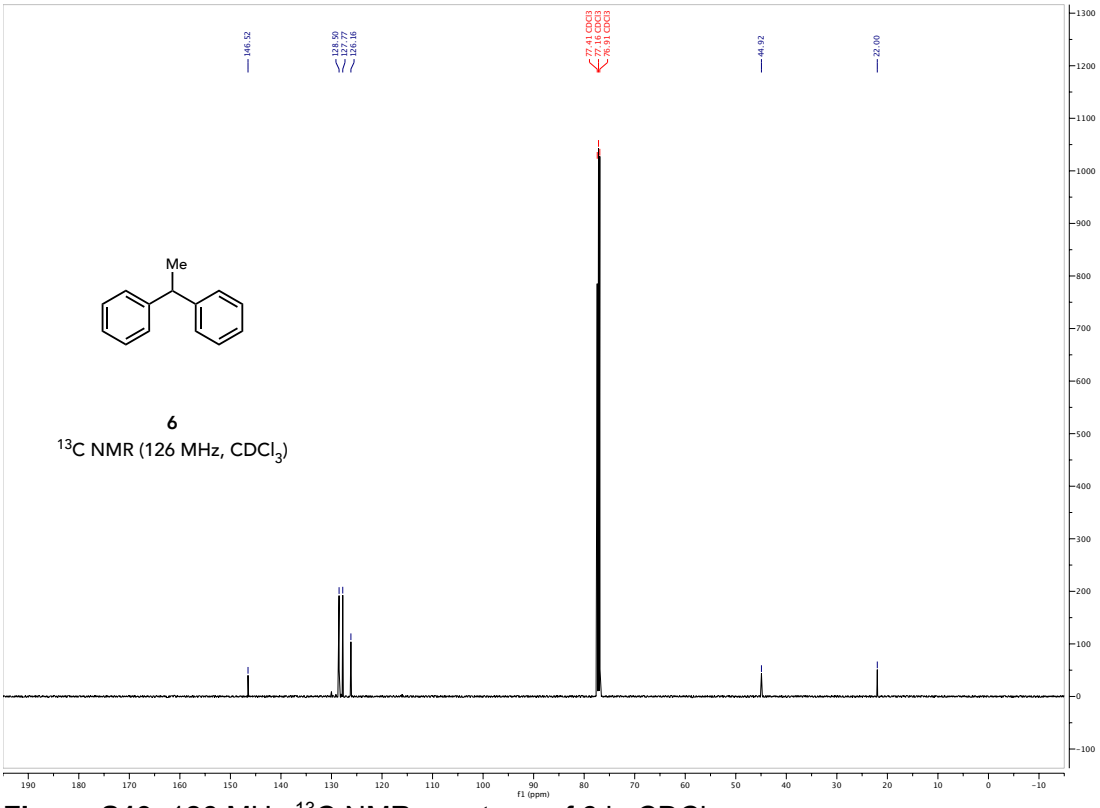


Figure S19. 126 MHz ^{13}C NMR spectrum of **6** in $CDCl_3$.

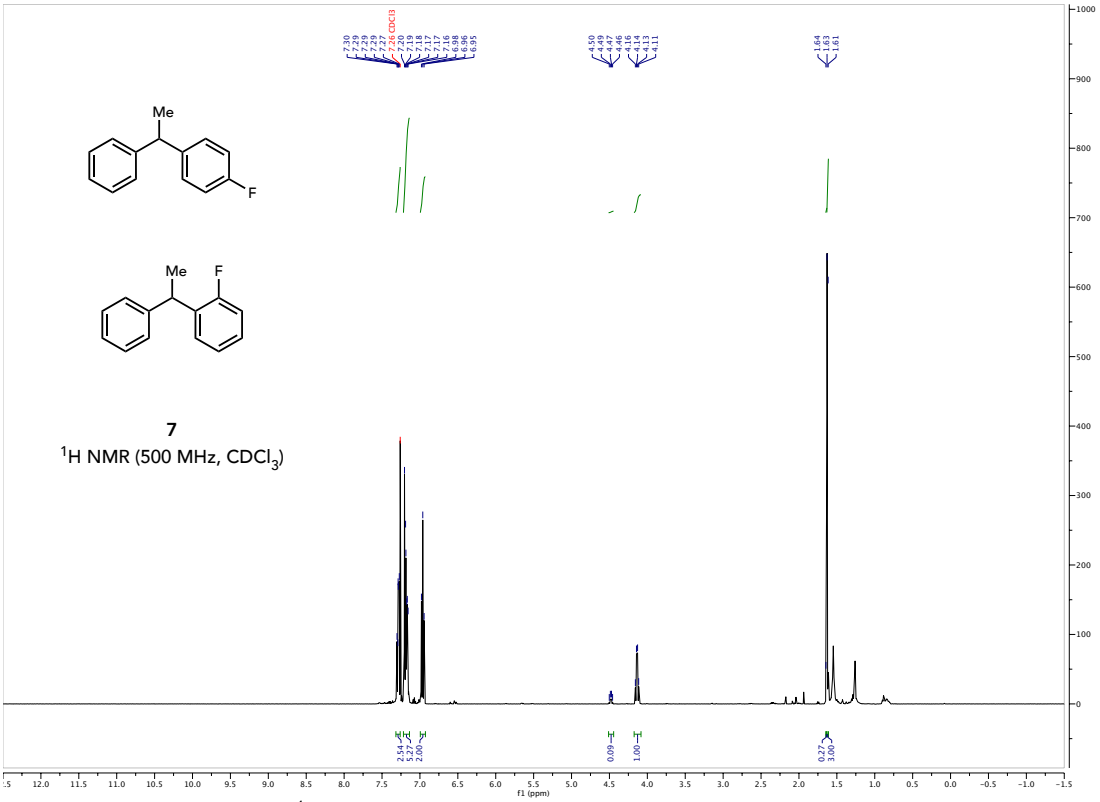


Figure S20. 500 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$.

Figure S21. 126 MHz ^{13}C NMR spectrum of **7** in $CDCl_3$.

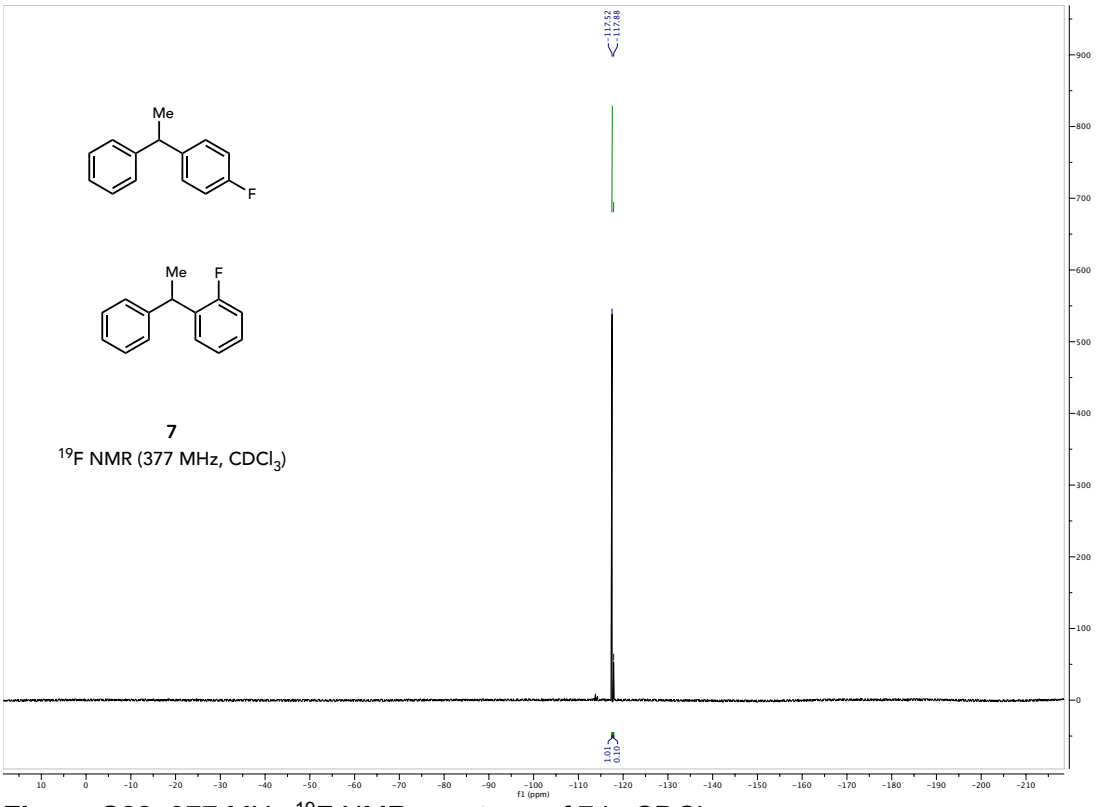


Figure S22. 377 MHz ^{19}F NMR spectrum of **7** in $CDCl_3$.

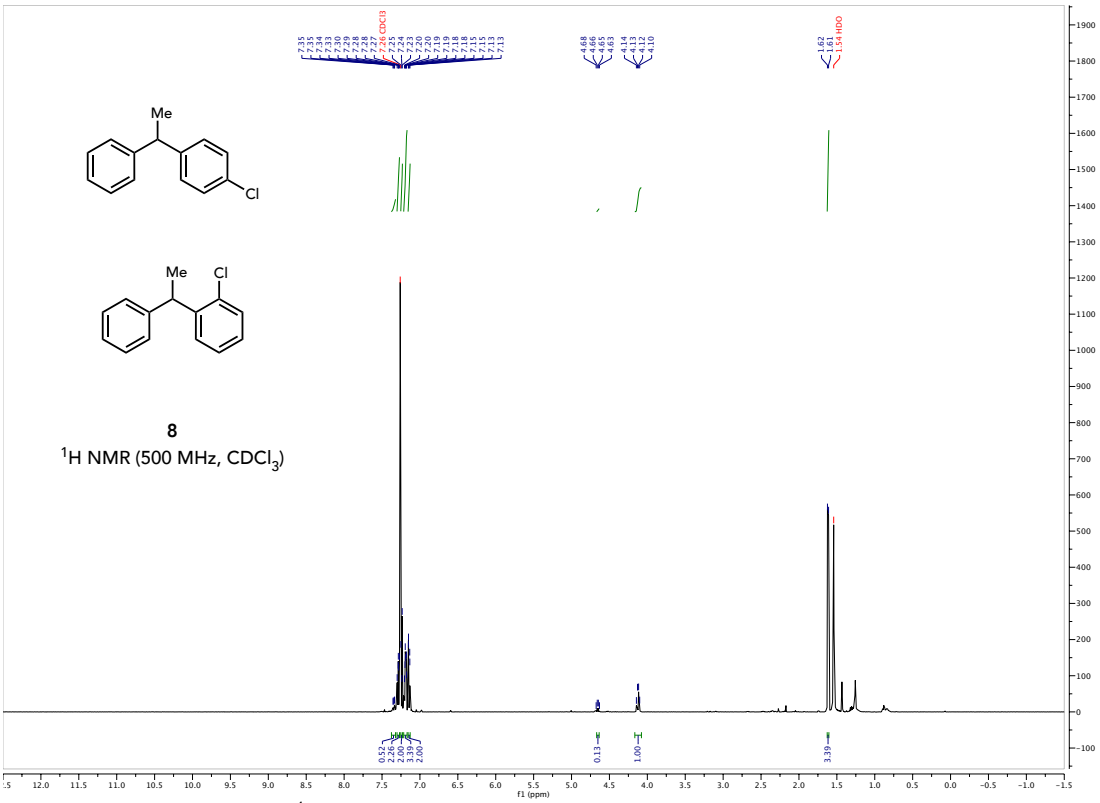


Figure S23. 500 MHz ^{1}H NMR spectrum of **8** in $CDCl_3$.

Figure S24. 126 MHz ^{13}C NMR spectrum of **8** in $CDCl_3$.

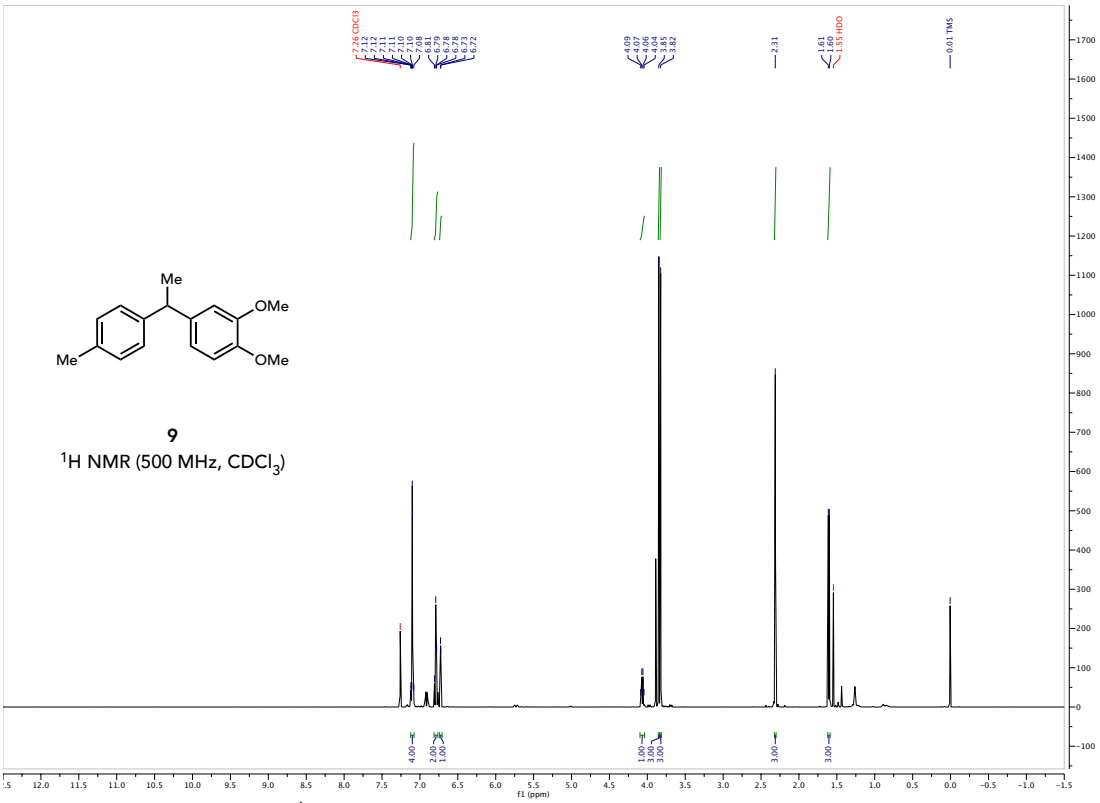


Figure S25. 500 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$.

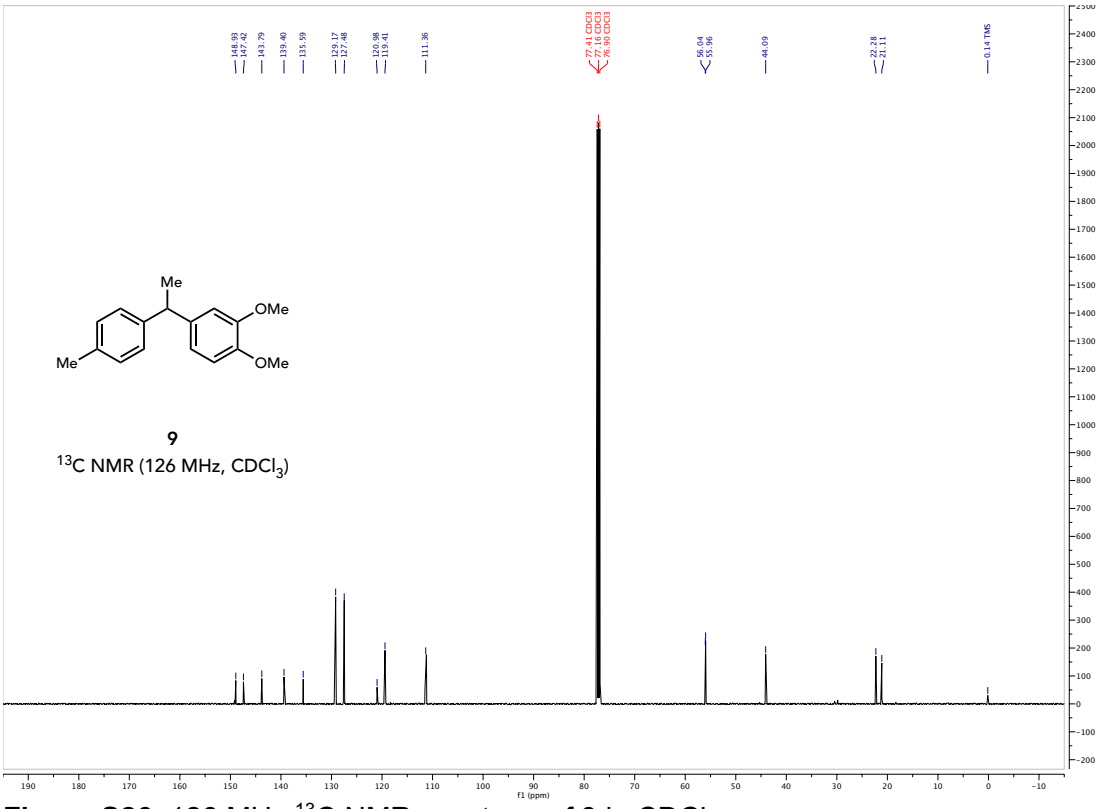


Figure S26. 126 MHz ^{13}C NMR spectrum of **9** in $CDCl_3$.

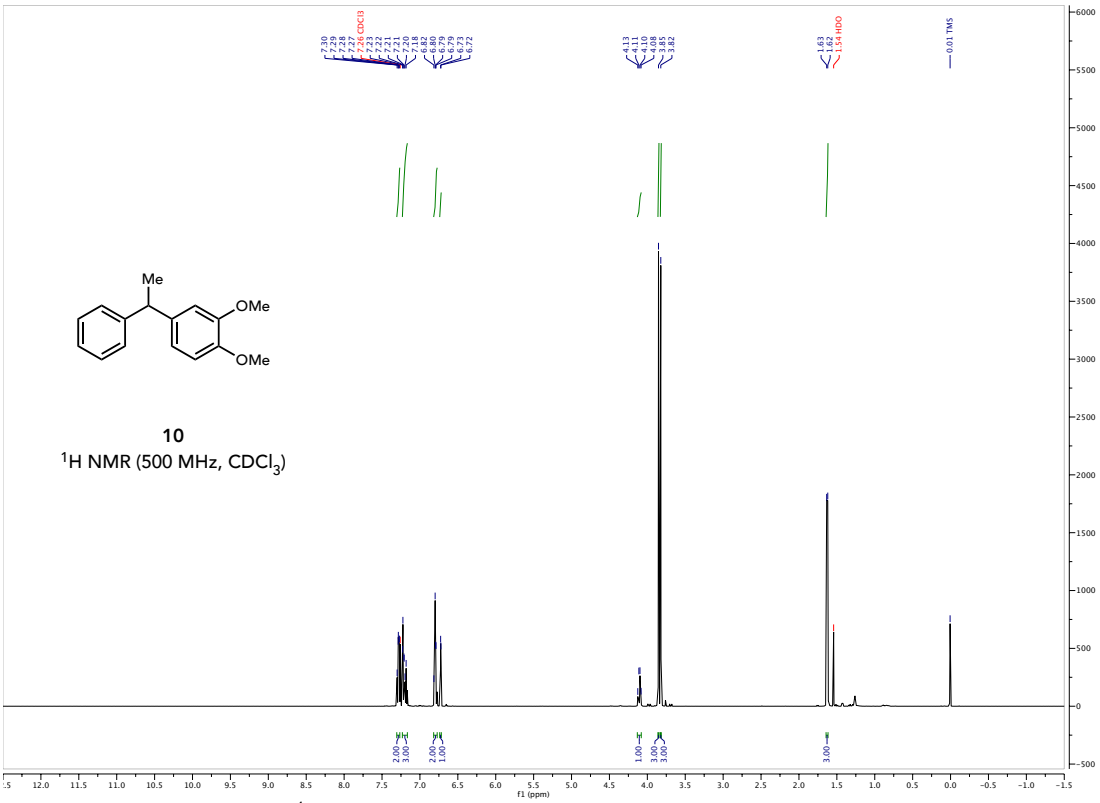


Figure S27. 500 MHz ^{1}H NMR spectrum of **10** in $CDCl_3$.

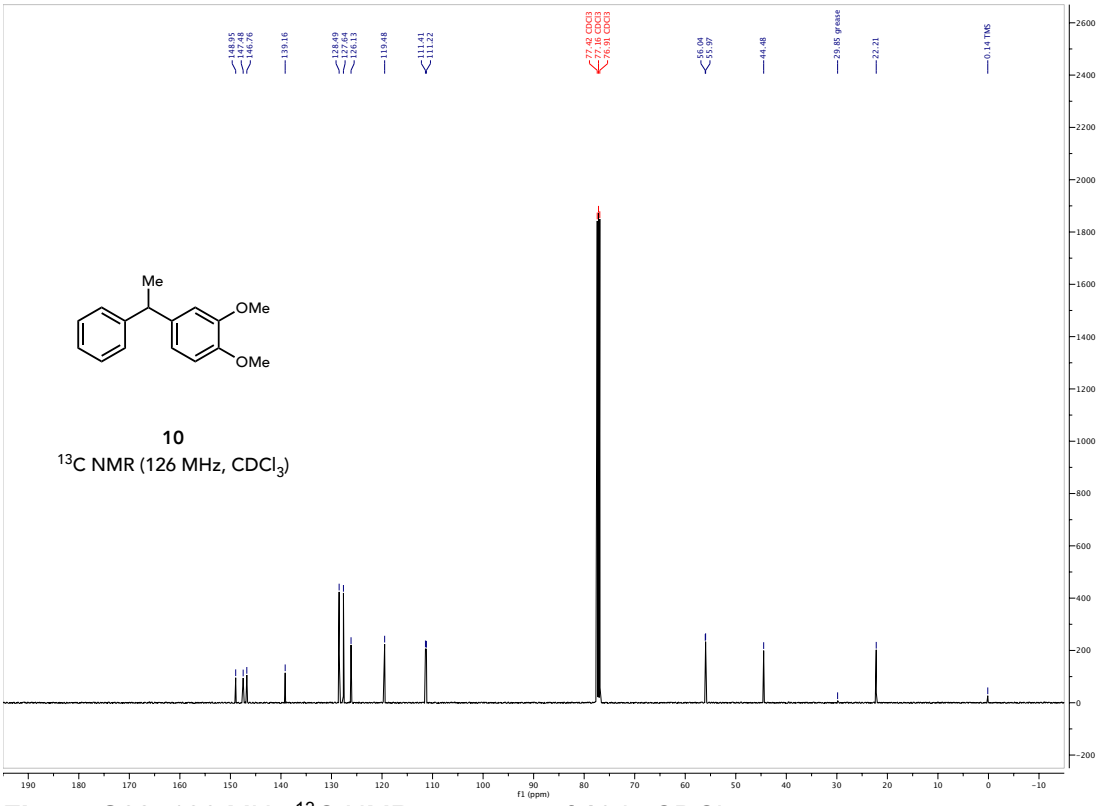


Figure S28. 126 MHz ^{13}C NMR spectrum of **10** in $CDCl_3$.

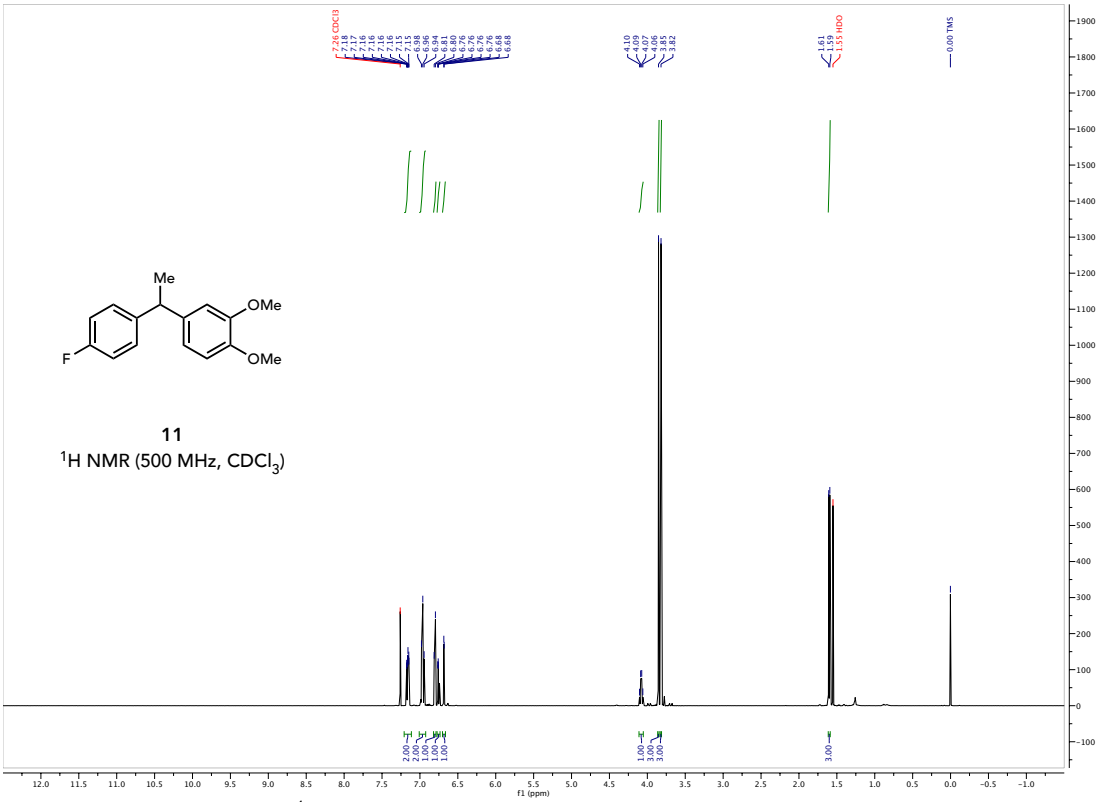


Figure S29. 500 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$.

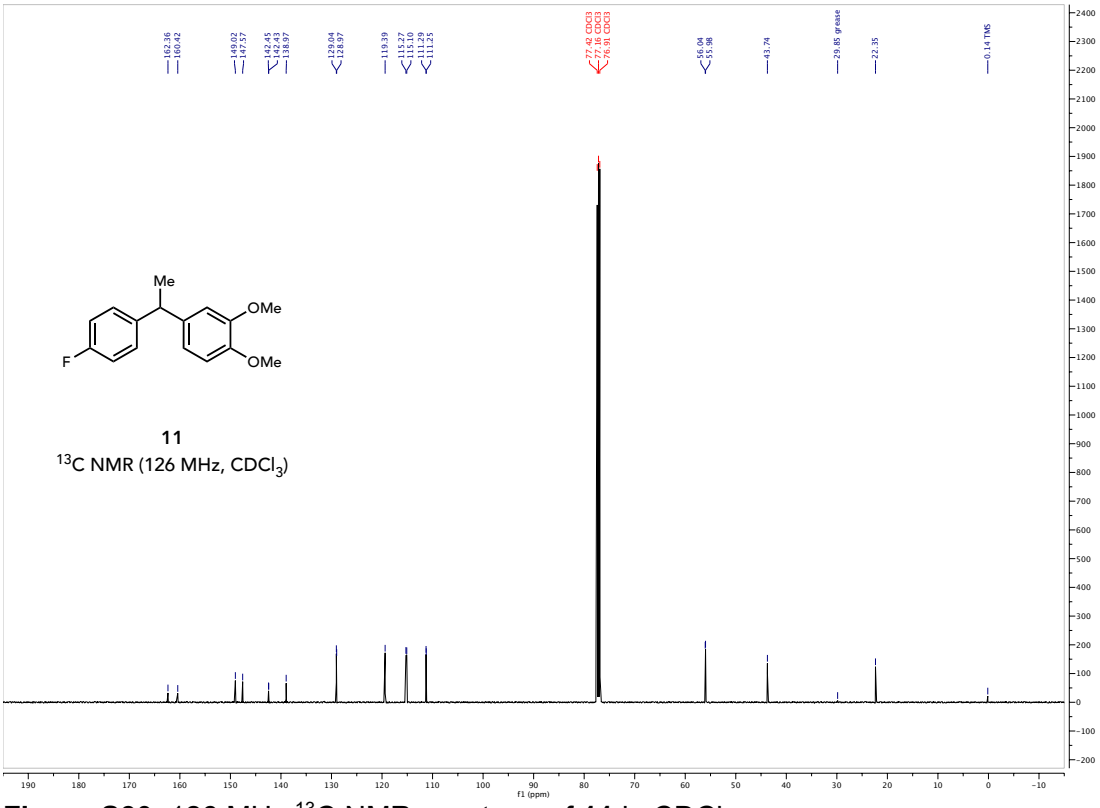


Figure S30. 126 MHz ^{13}C NMR spectrum of **11** in $CDCl_3$.

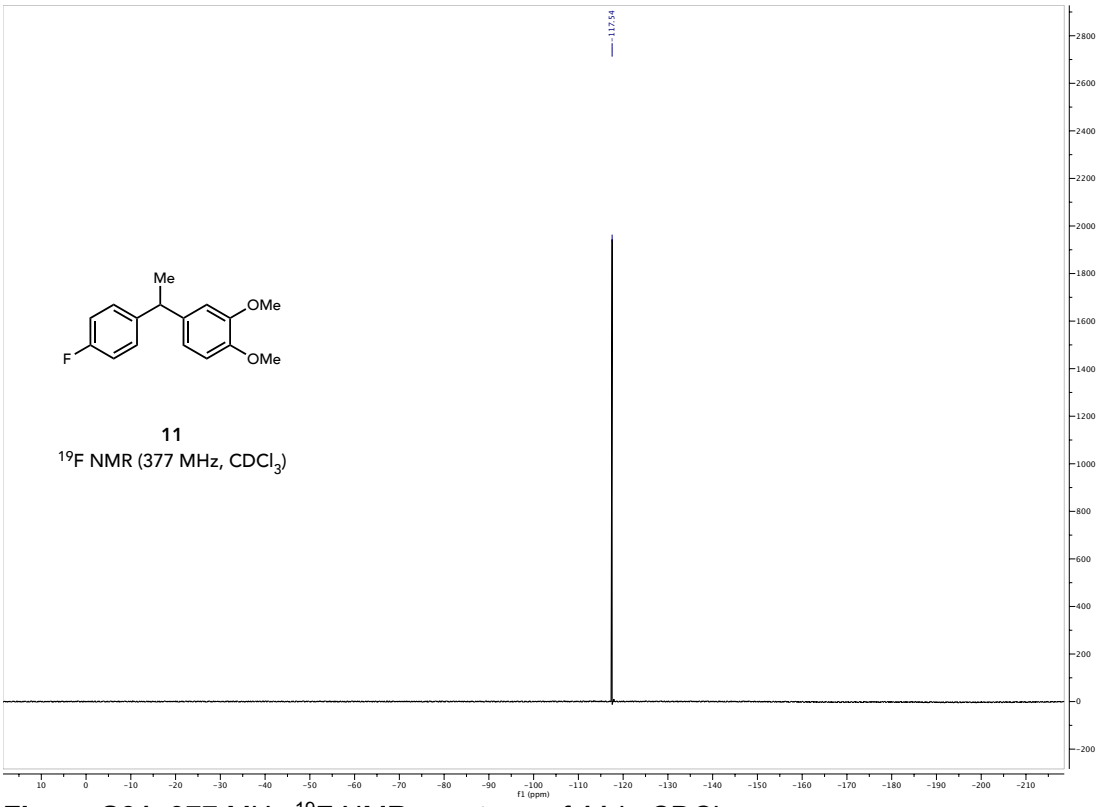


Figure S31. 377 MHz ^{19}F NMR spectrum of **11** in $CDCl_3$.

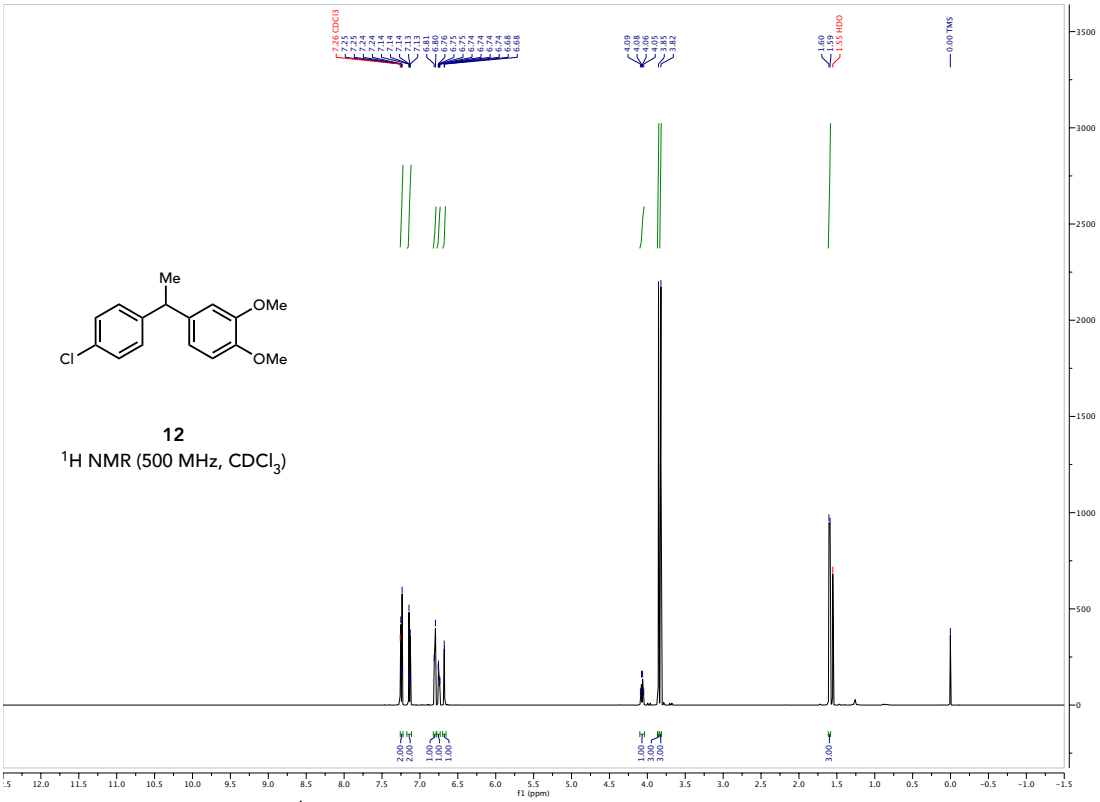


Figure S32. 500 MHz ^{1}H NMR spectrum of **12** in $CDCl_3$.

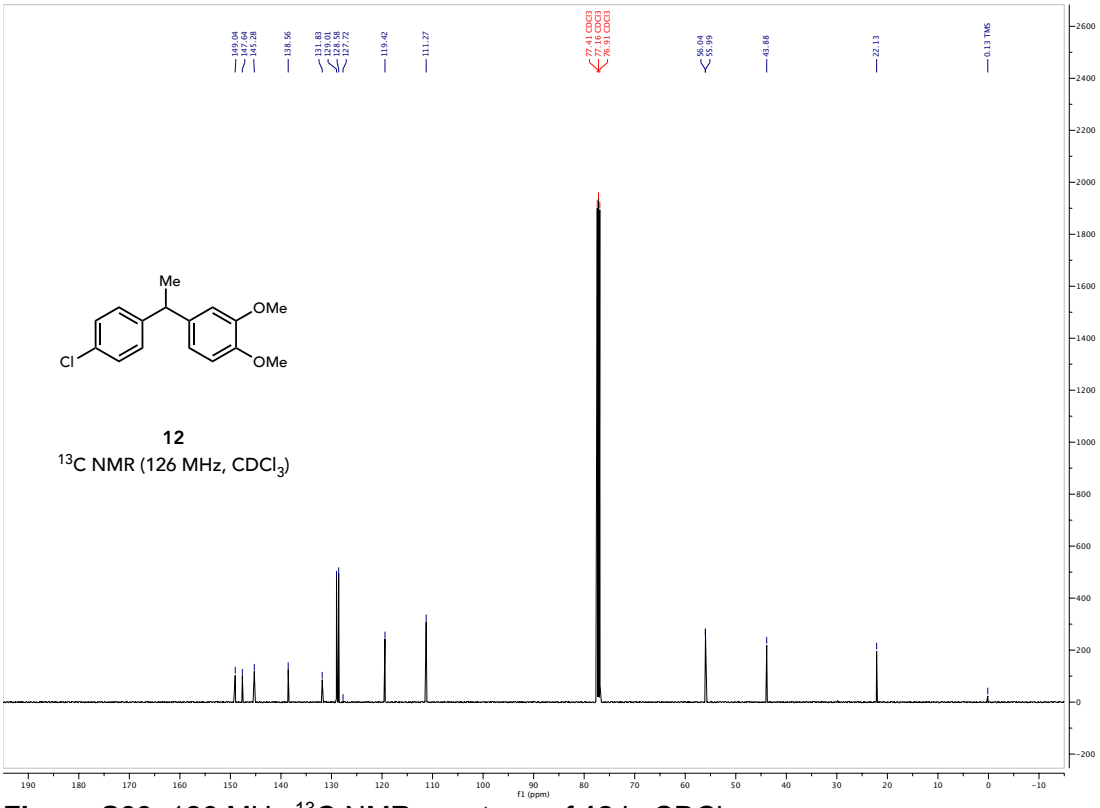


Figure S33. 126 MHz ^{13}C NMR spectrum of **12** in $CDCl_3$.

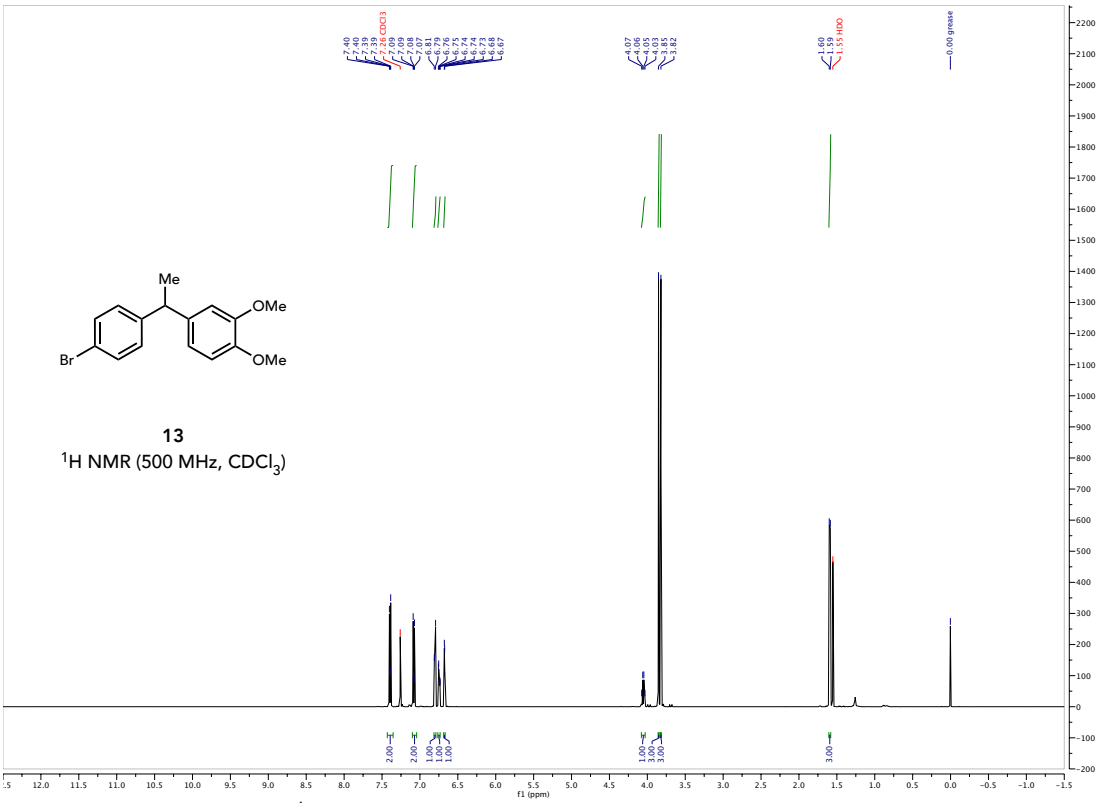


Figure S34. 500 MHz ^{1}H NMR spectrum of **13** in $CDCl_3$.

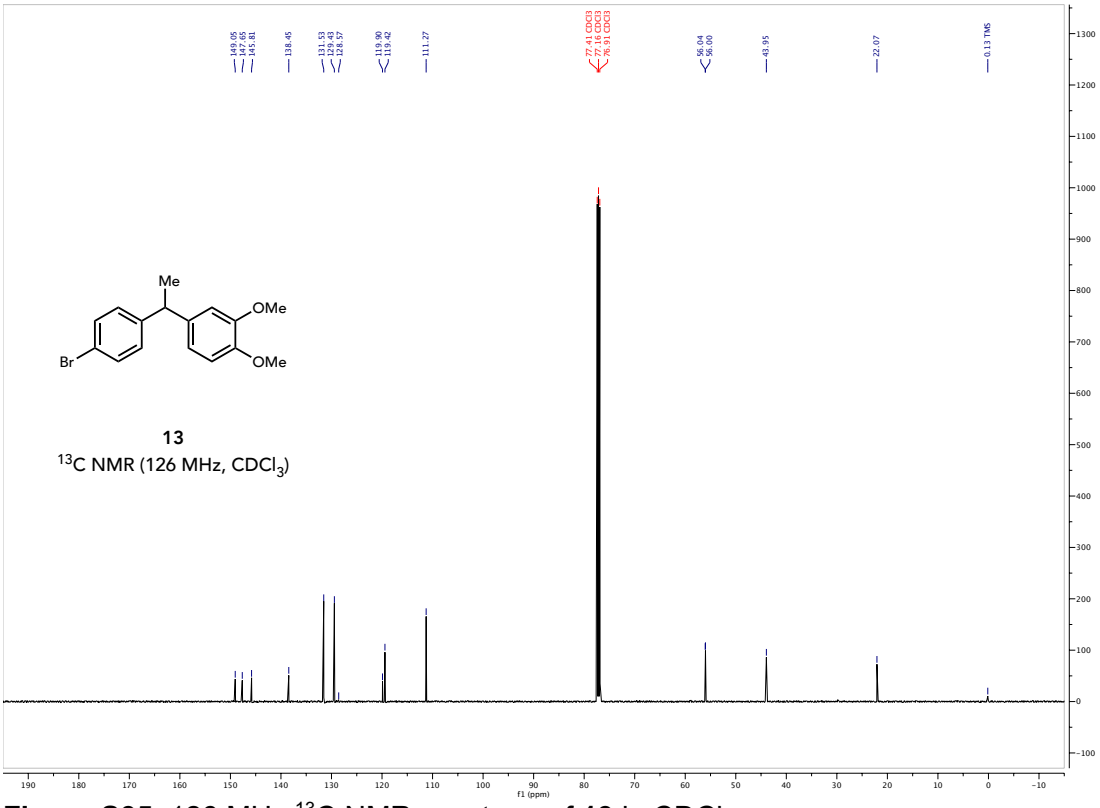


Figure S35. 126 MHz ^{13}C NMR spectrum of **13** in $CDCl_3$.

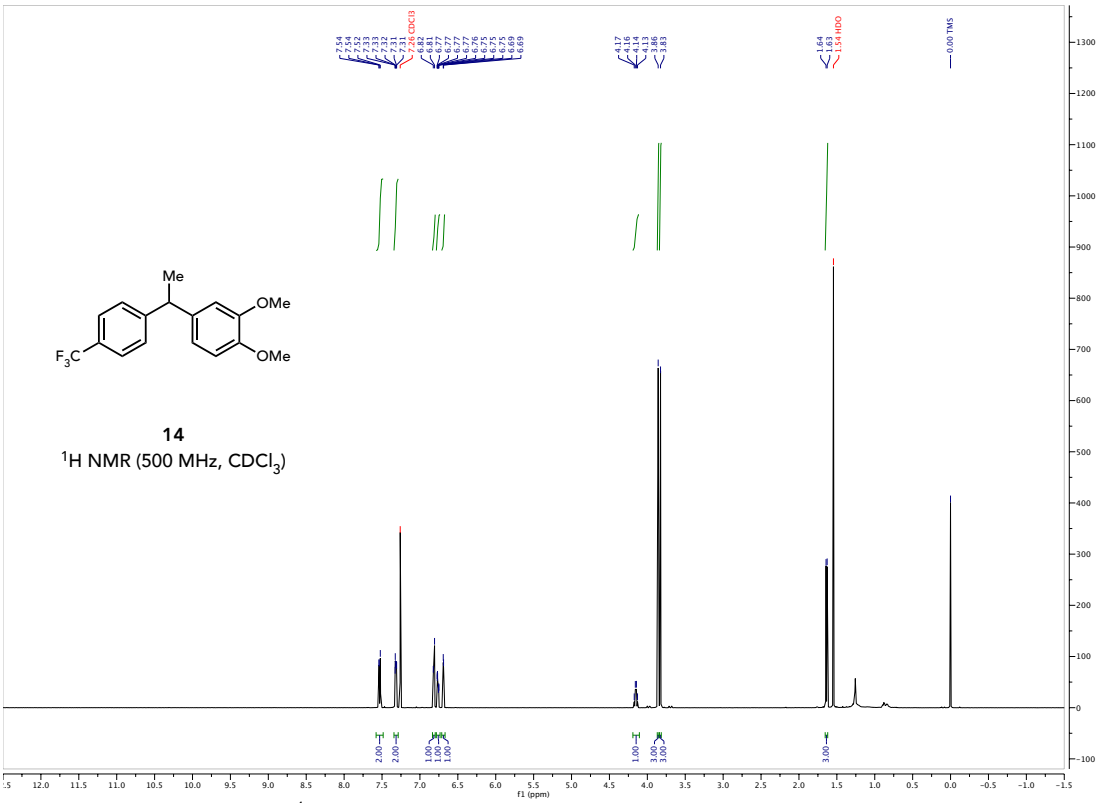


Figure S36. 500 MHz ^{1}H NMR spectrum of **14** in $CDCl_3$.

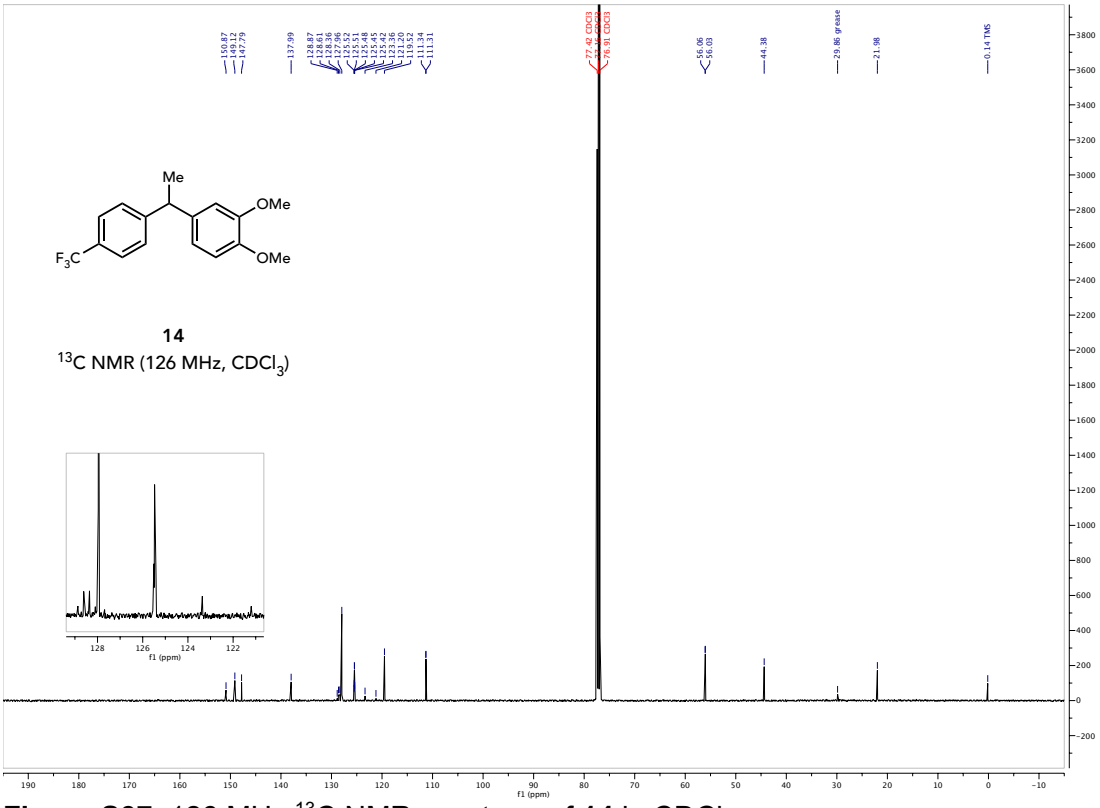


Figure S37. 126 MHz ^{13}C NMR spectrum of **14** in $CDCl_3$.

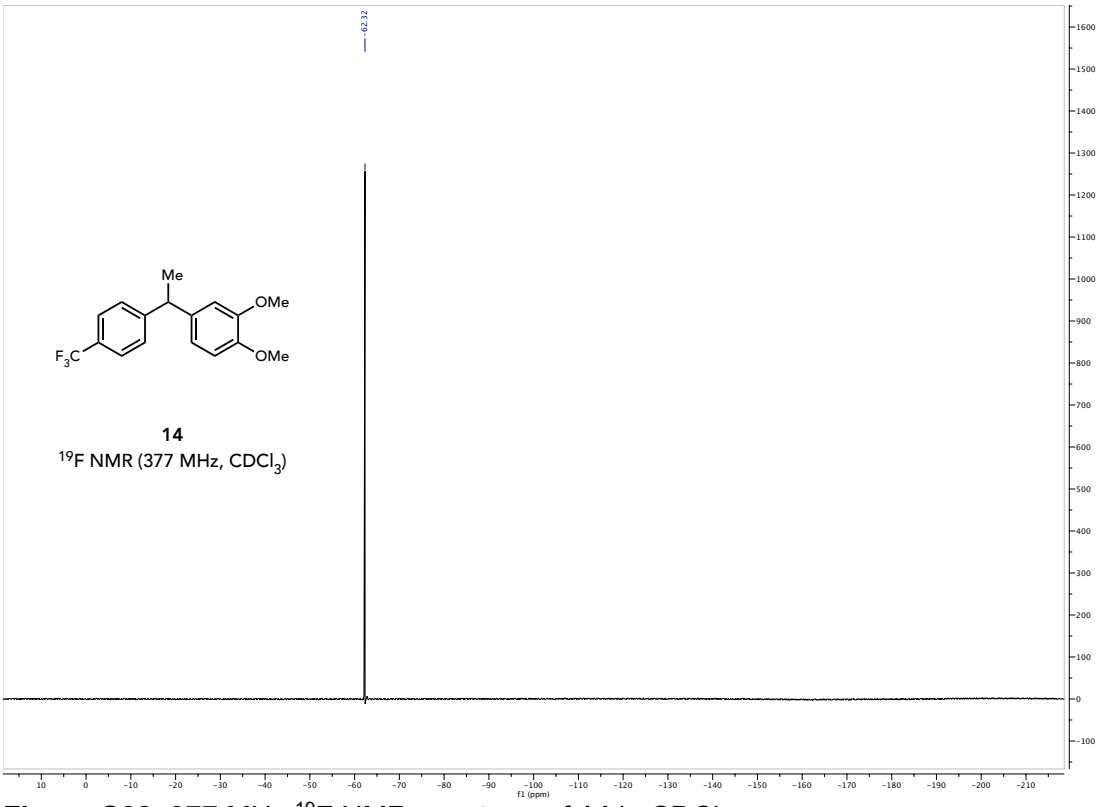


Figure S38. 377 MHz ^{19}F NMR spectrum of **14** in $CDCl_3$.

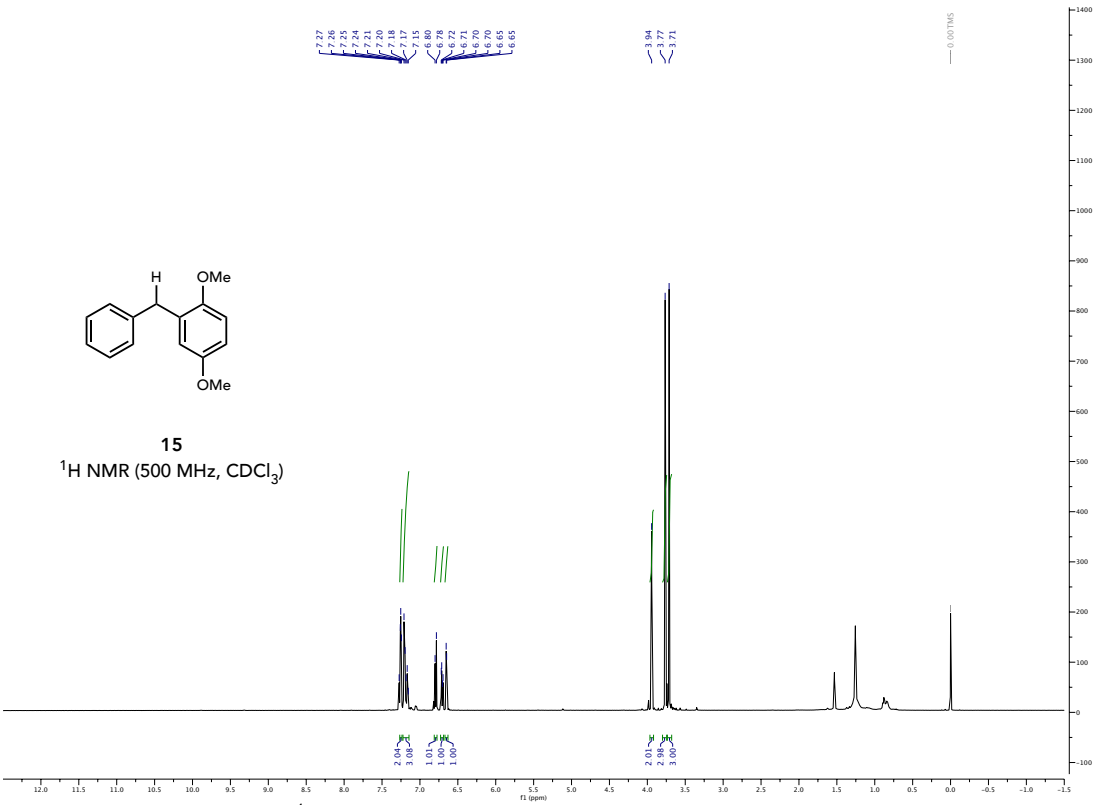


Figure S39. 500 MHz ^{1}H NMR spectrum of **15** in $CDCl_3$.

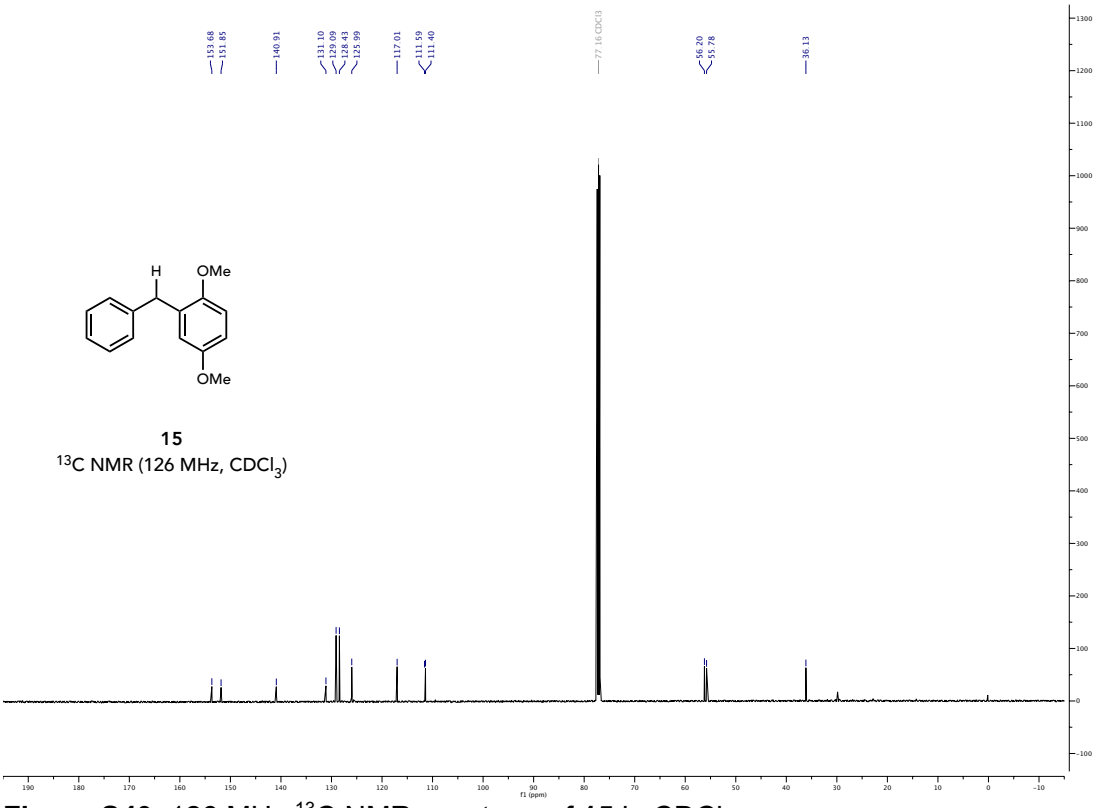


Figure S40. 126 MHz ^{13}C NMR spectrum of **15** in $CDCl_3$.

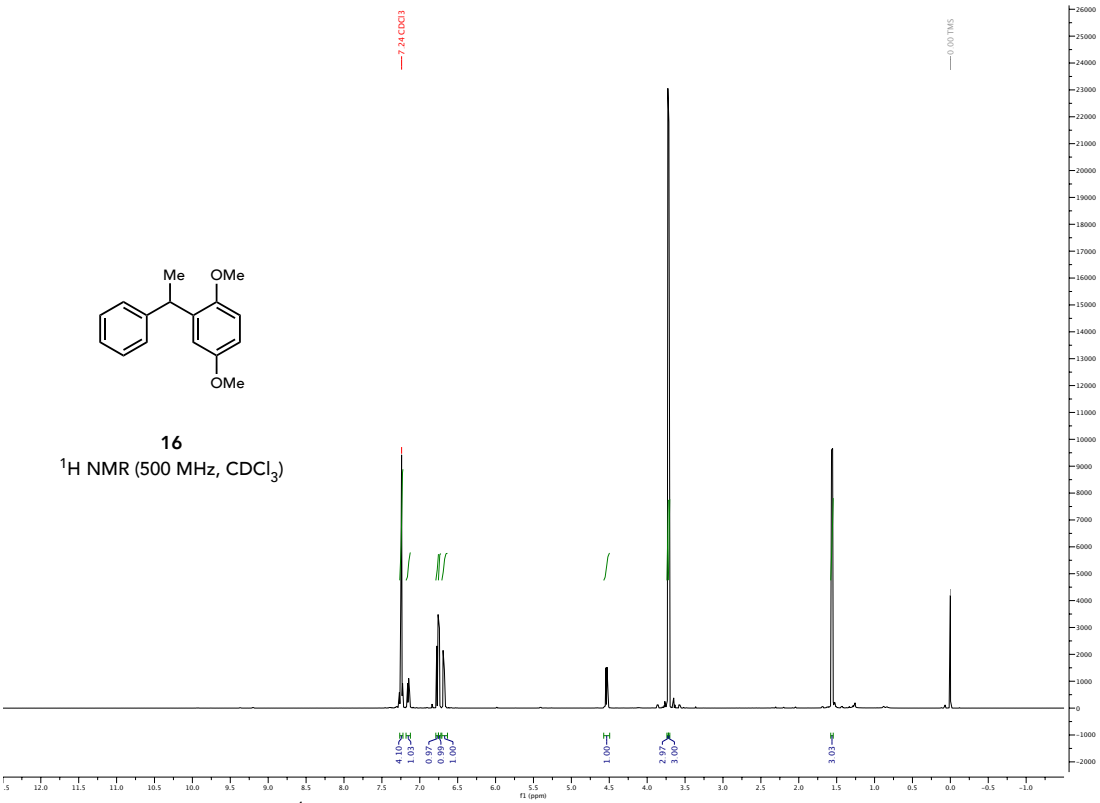


Figure S41. 500 MHz ^{1}H NMR spectrum of **16** in $CDCl_3$.

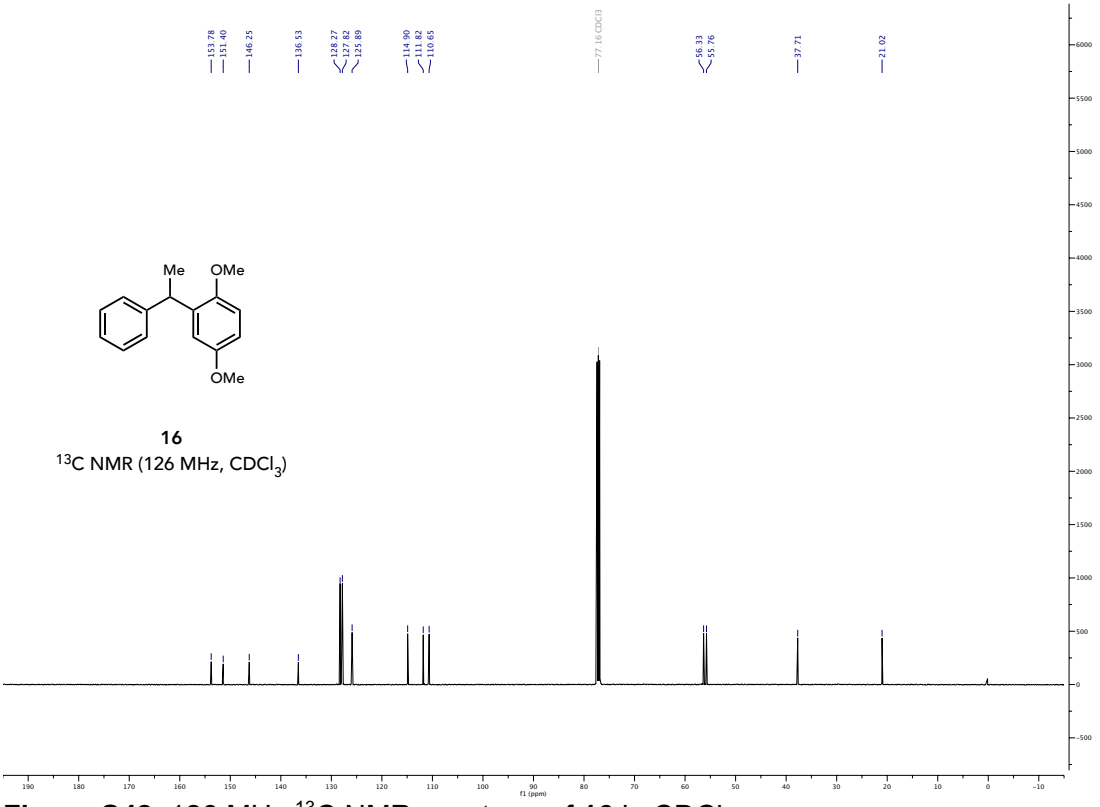


Figure S42. 126 MHz ^{13}C NMR spectrum of **16** in $CDCl_3$.

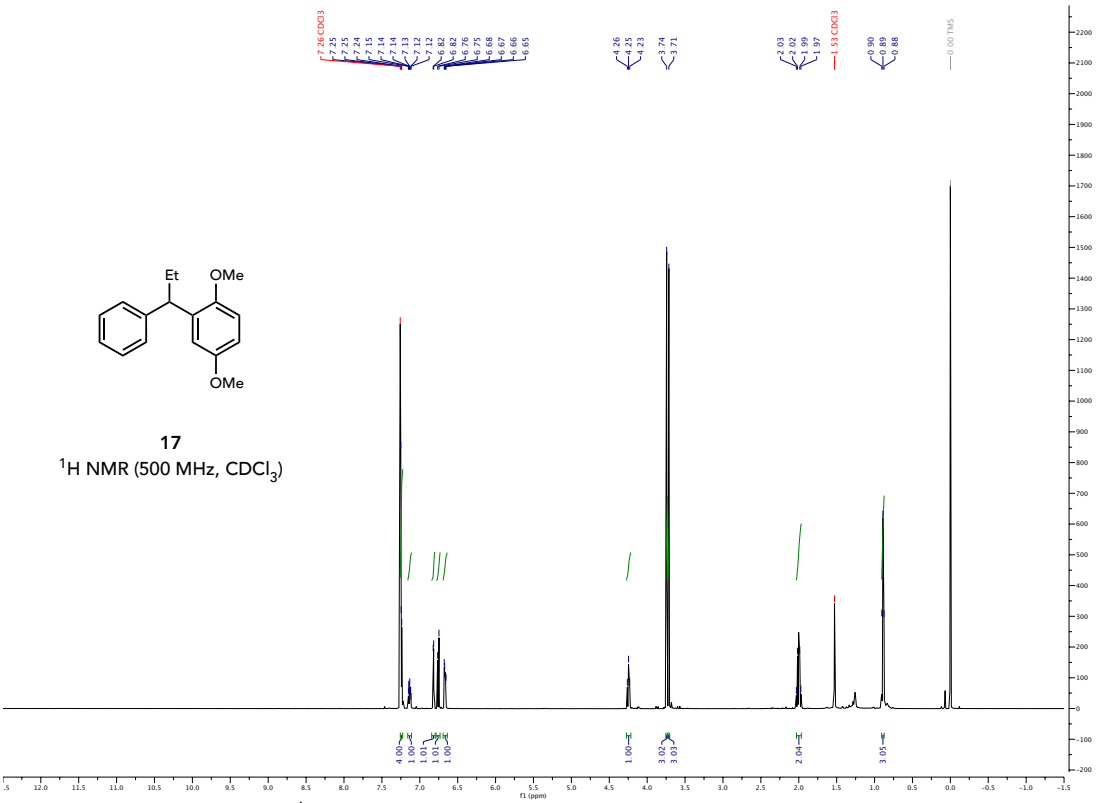


Figure S43. 500 MHz ^{1}H NMR spectrum of **17** in $CDCl_3$.

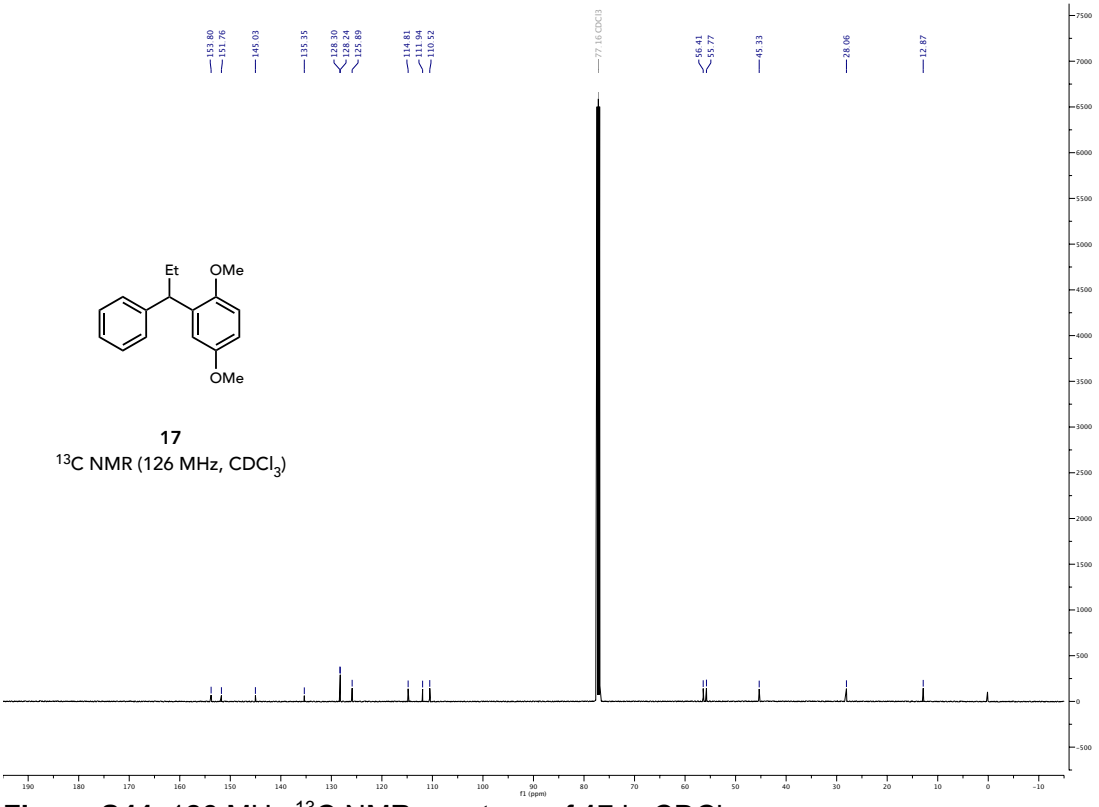


Figure S44. 126 MHz ^{13}C NMR spectrum of **17** in $CDCl_3$.

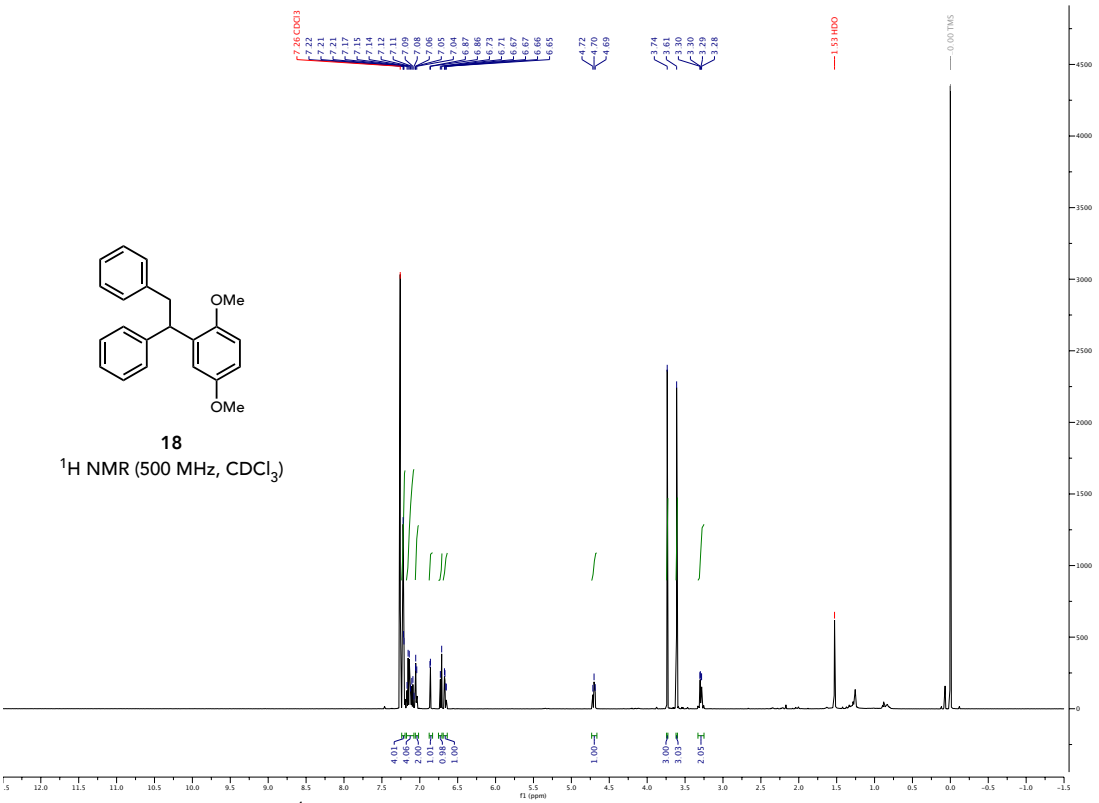


Figure S45. 500 MHz ^{1}H NMR spectrum of **18** in $CDCl_3$.

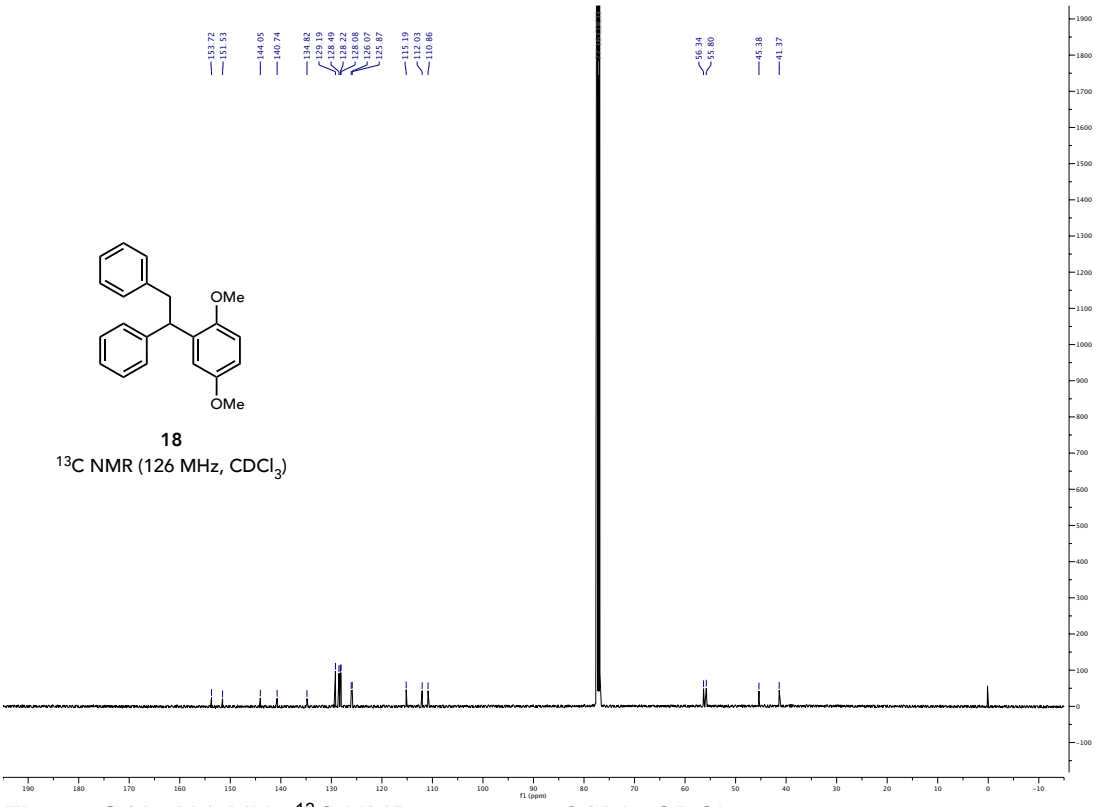


Figure S46. 126 MHz ^{13}C NMR spectrum of **18** in $CDCl_3$.

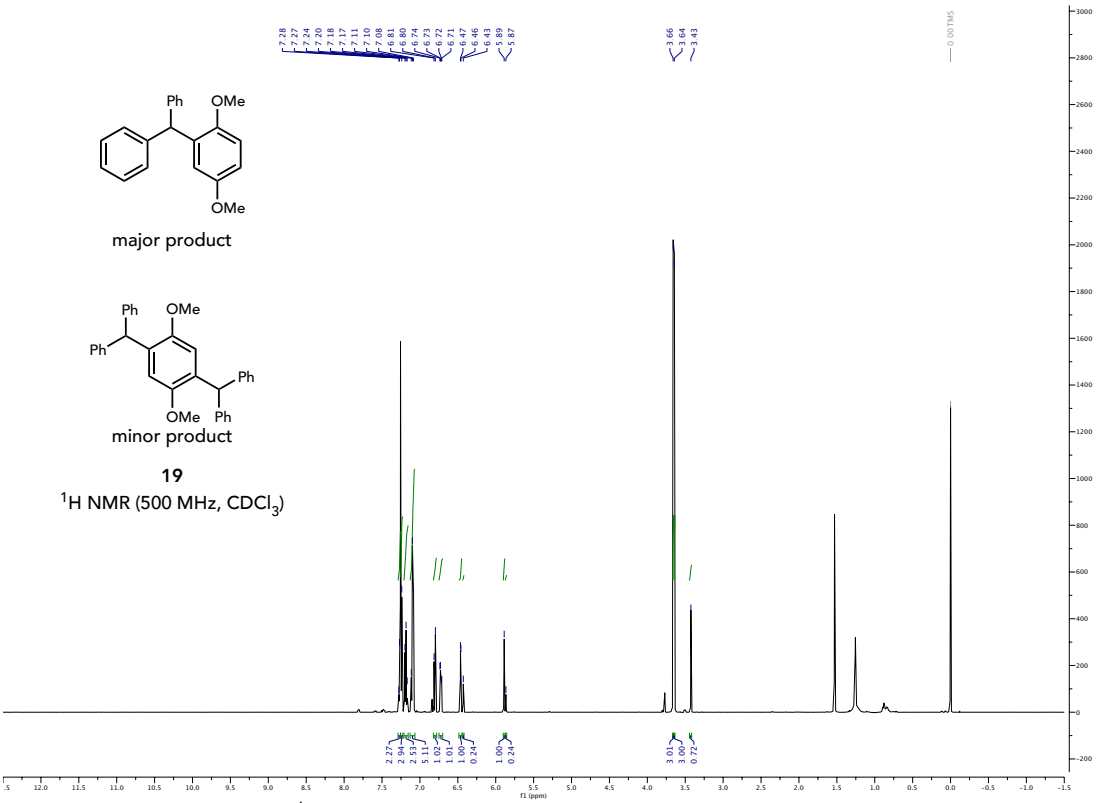


Figure S47. 500 MHz ^{1}H NMR spectrum of **19** in $CDCl_3$.

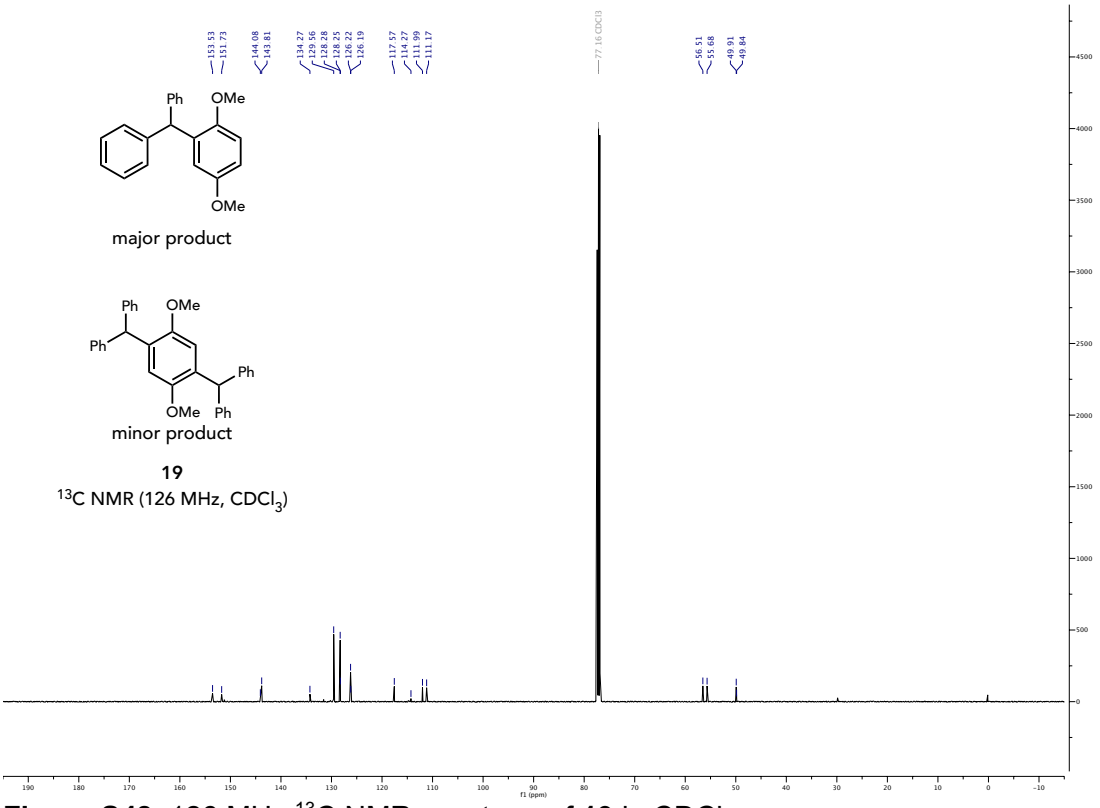


Figure S48. 126 MHz ^{13}C NMR spectrum of **19** in $CDCl_3$.

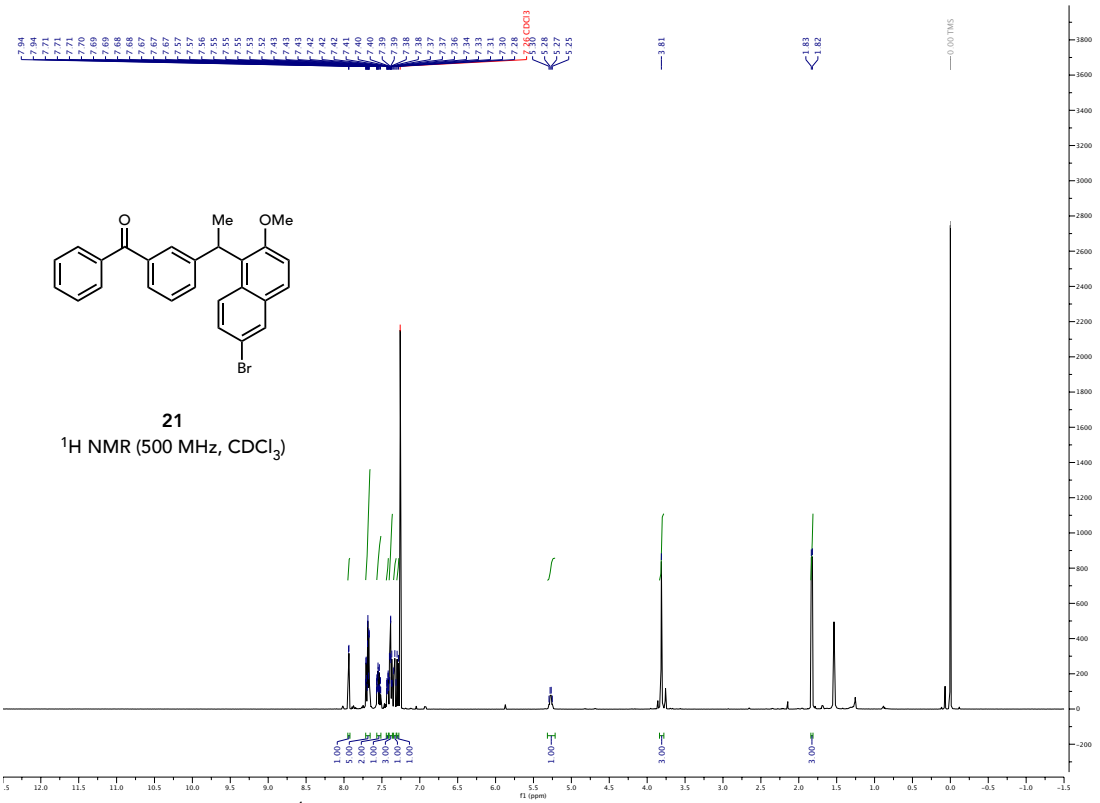


Figure S49. 500 MHz ^{1}H NMR spectrum of **21** in $CDCl_3$.

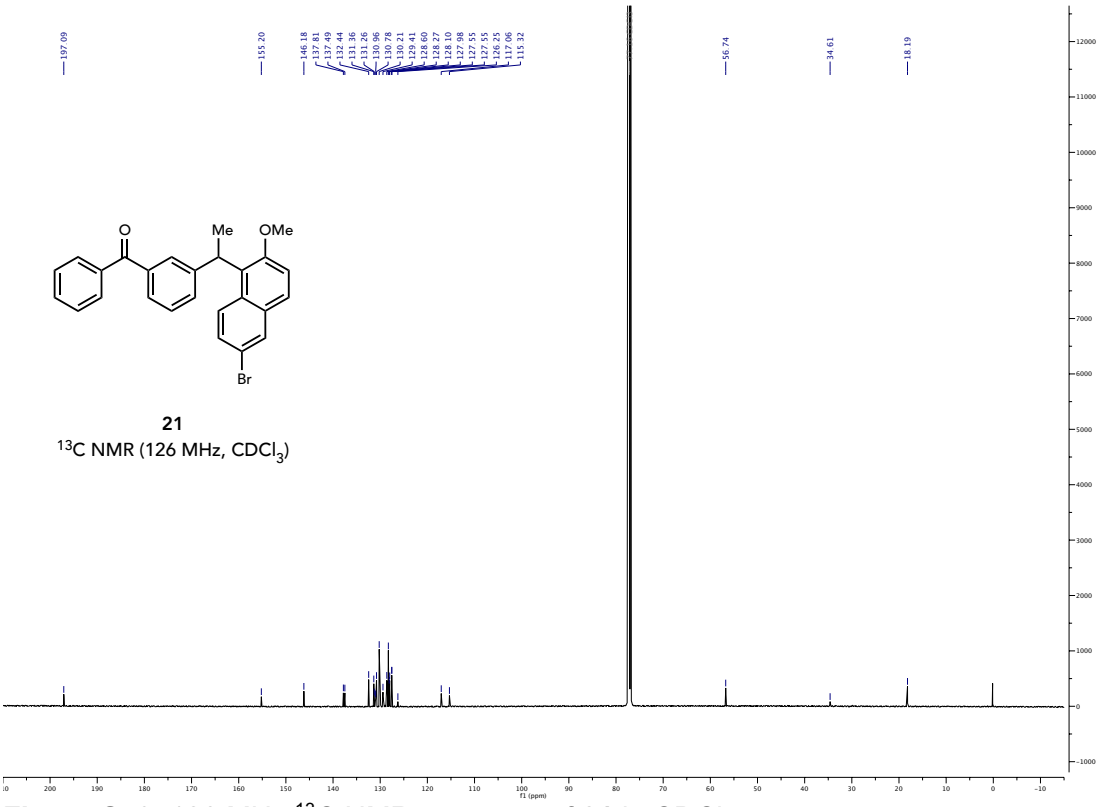


Figure S50. 126 MHz ^{13}C NMR spectrum of **21** in $CDCl_3$.

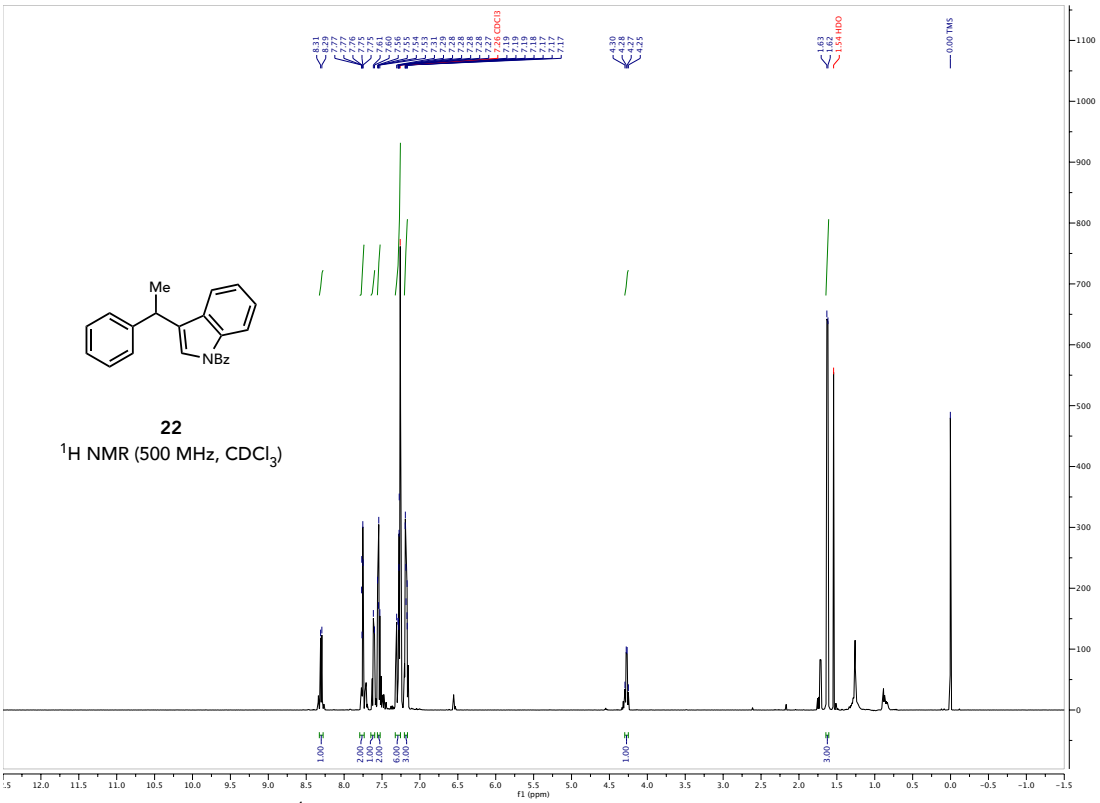


Figure S51. 500 MHz ^{1}H NMR spectrum of **22** in $CDCl_3$.

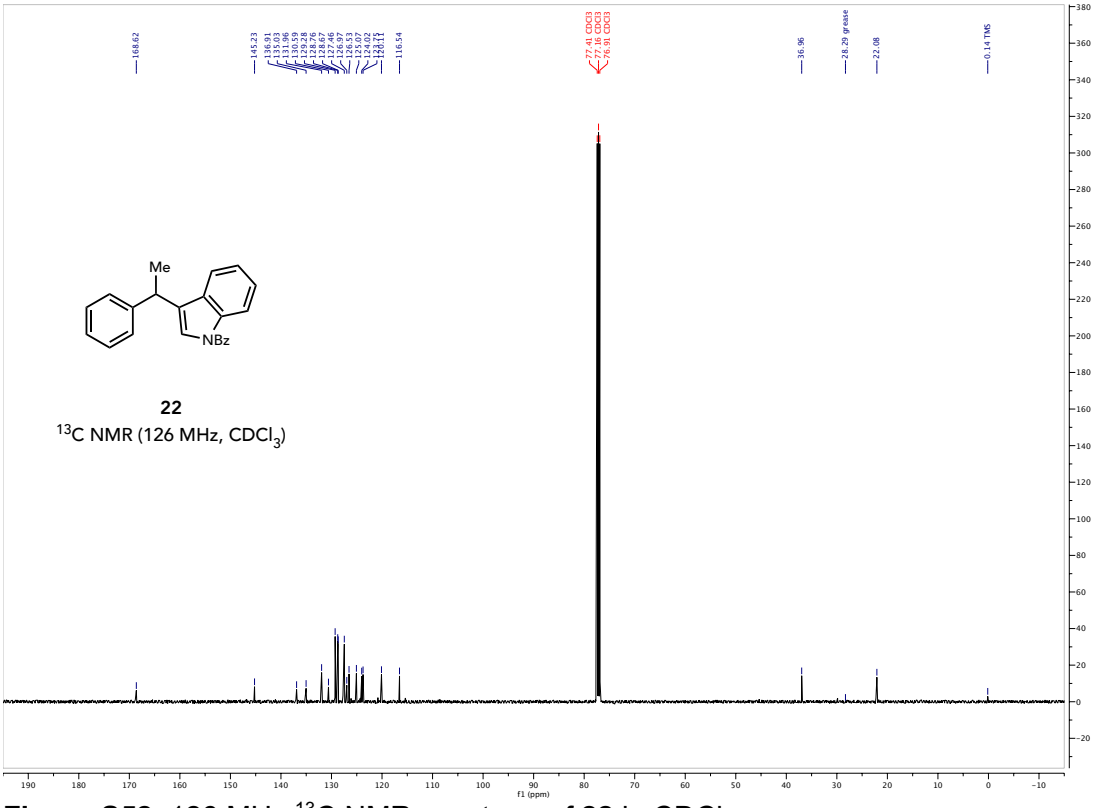


Figure S52. 126 MHz ^{13}C NMR spectrum of **22** in $CDCl_3$.

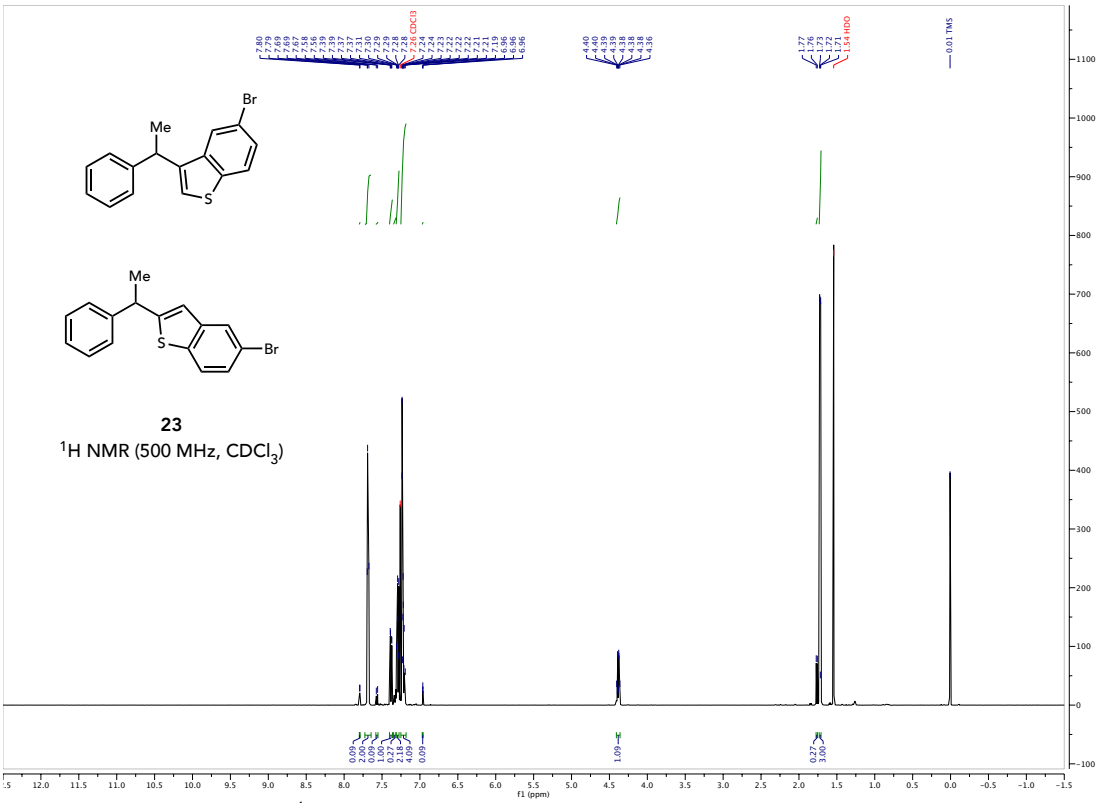


Figure S53. 500 MHz ^{1}H NMR spectrum of **23** in $CDCl_3$.

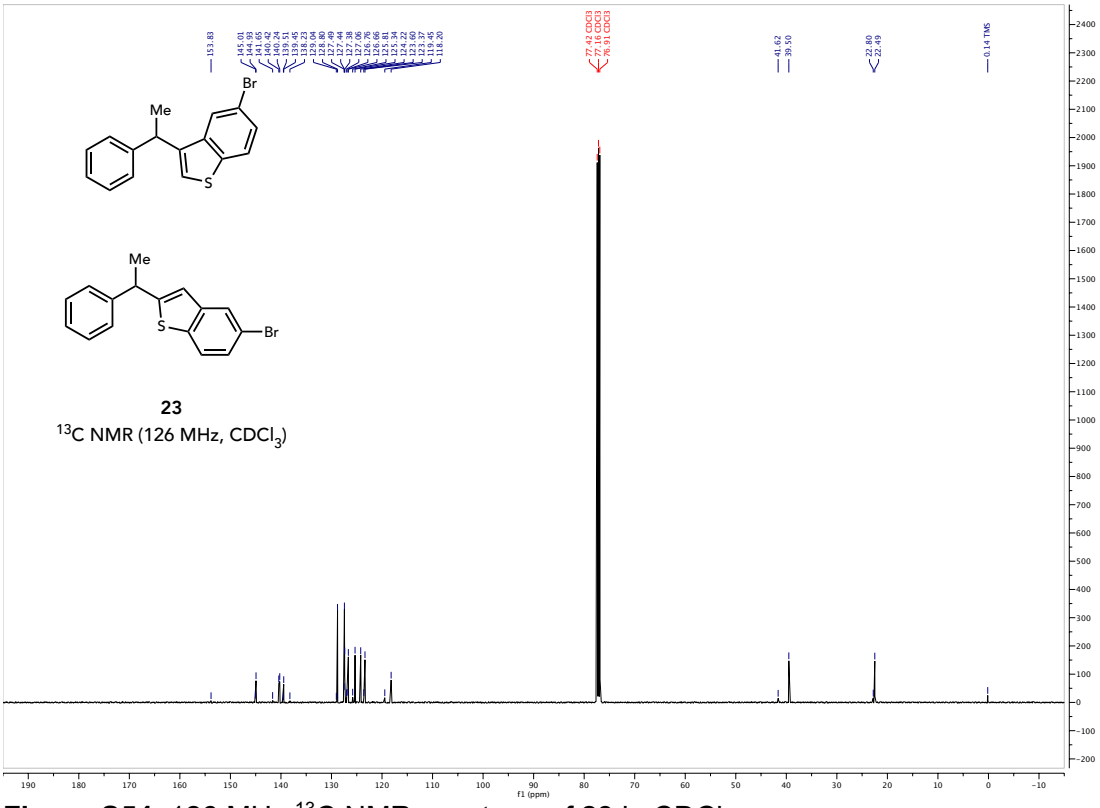


Figure S54. 126 MHz ^{13}C NMR spectrum of **23** in $CDCl_3$.

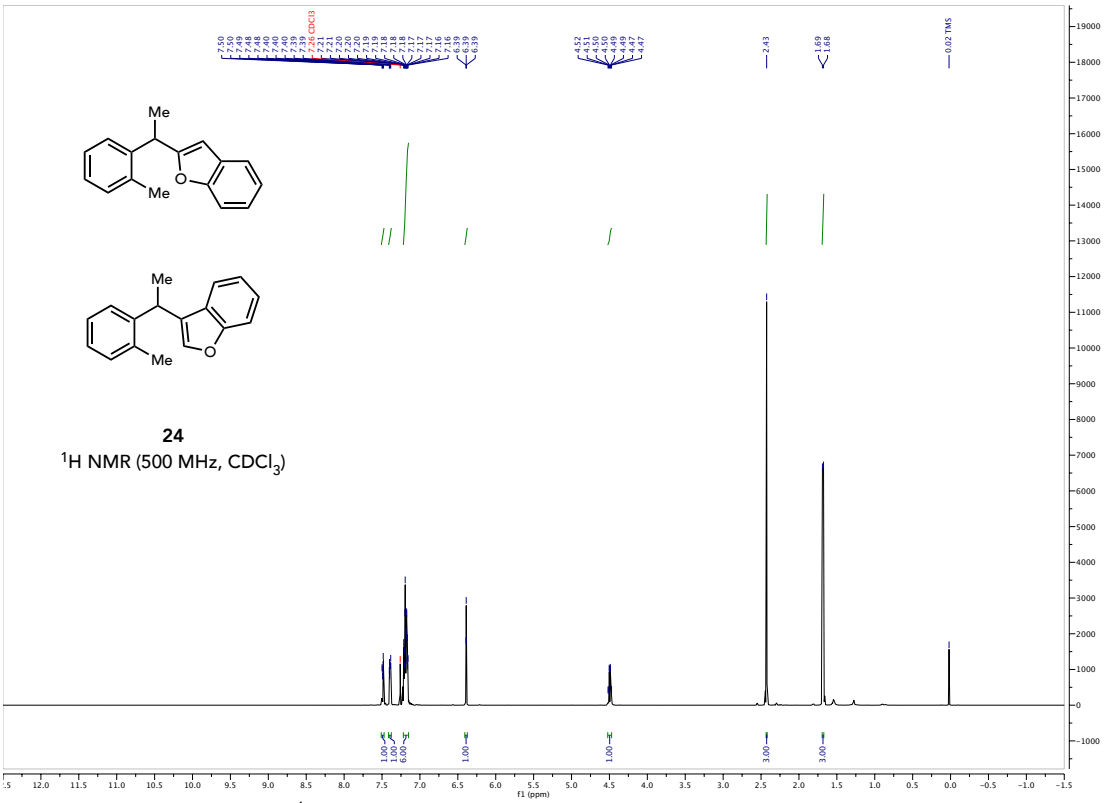


Figure S55. 500 MHz ^{1}H NMR spectrum of **24** in $CDCl_3$.

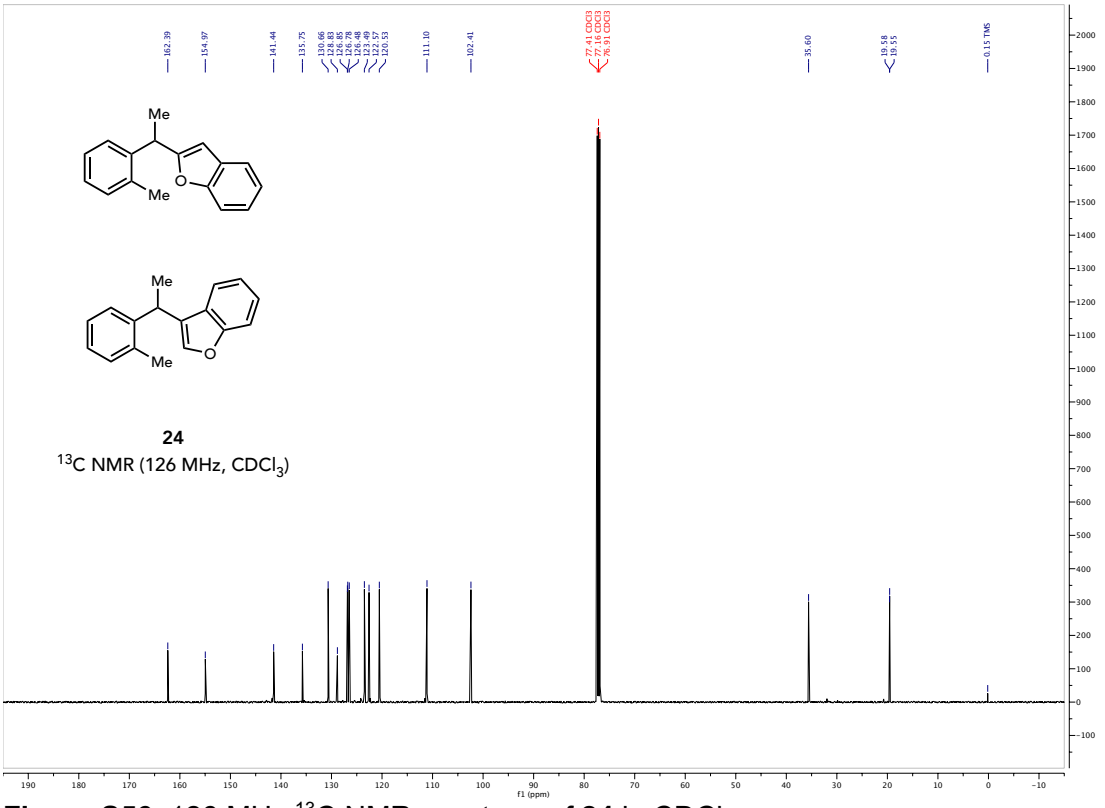


Figure S56. 126 MHz ^{13}C NMR spectrum of **24** in $CDCl_3$.

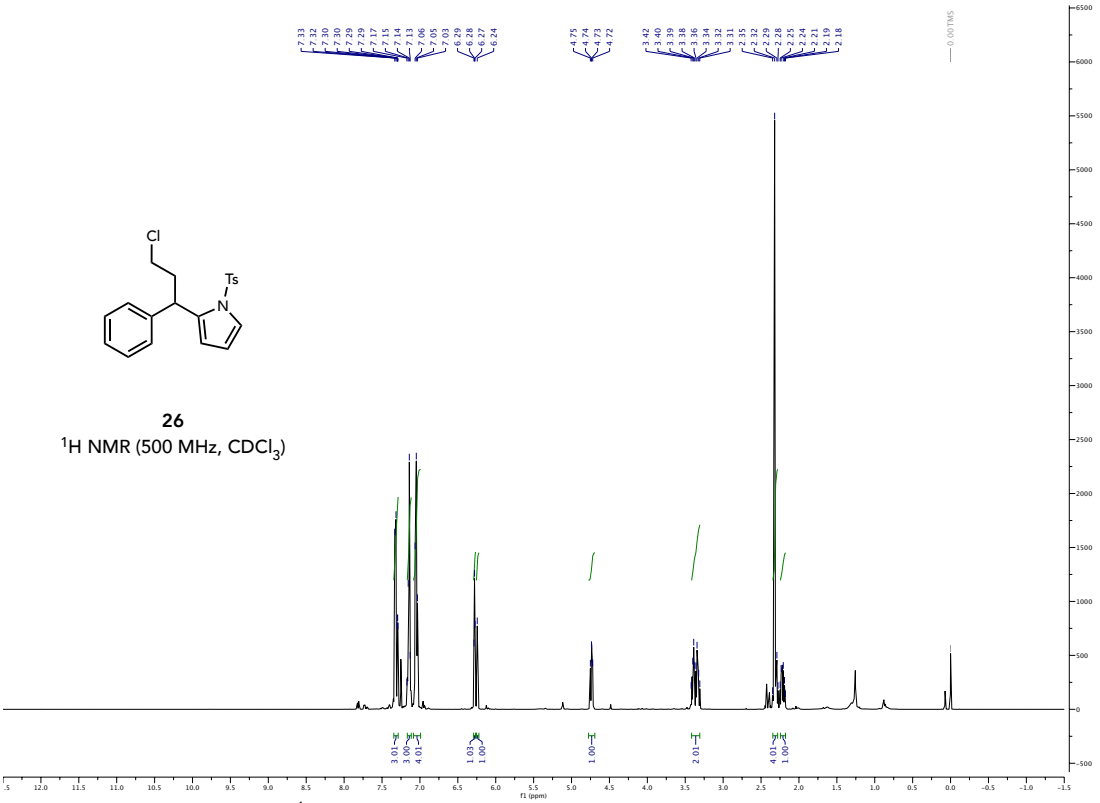


Figure S57. 500 MHz ^{1}H NMR spectrum of **26** in $CDCl_3$.

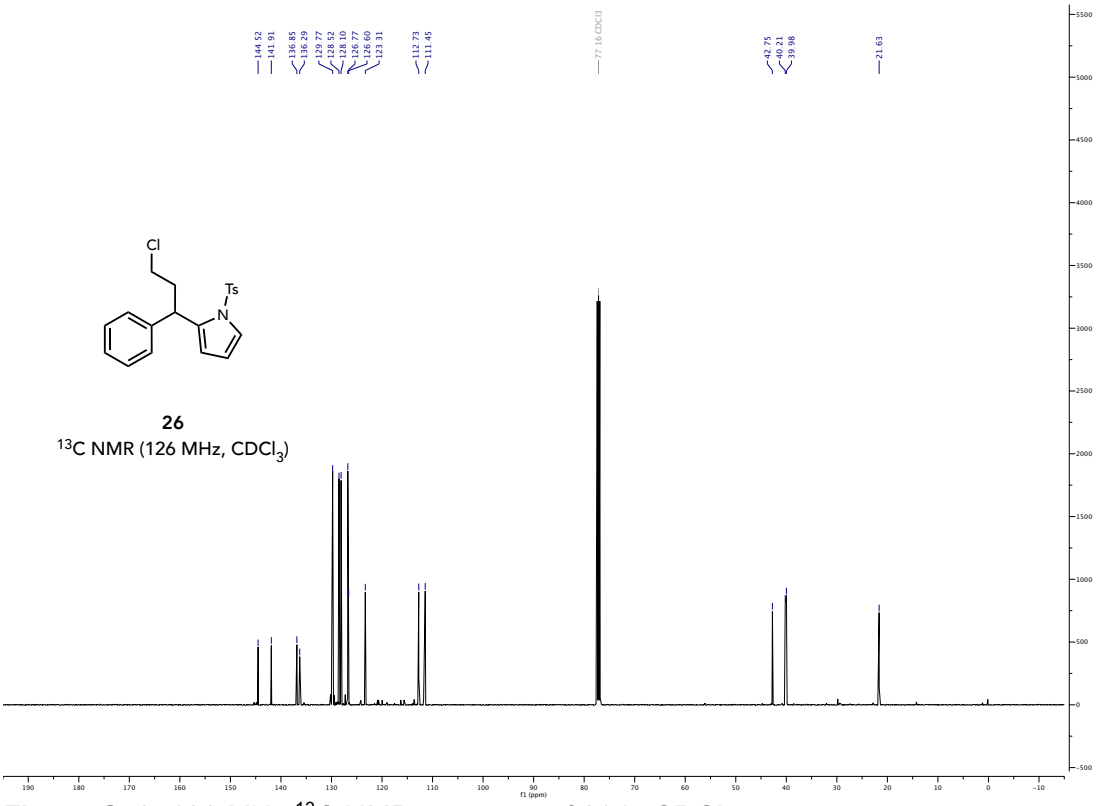


Figure S58. 126 MHz ^{13}C NMR spectrum of **26** in $CDCl_3$.

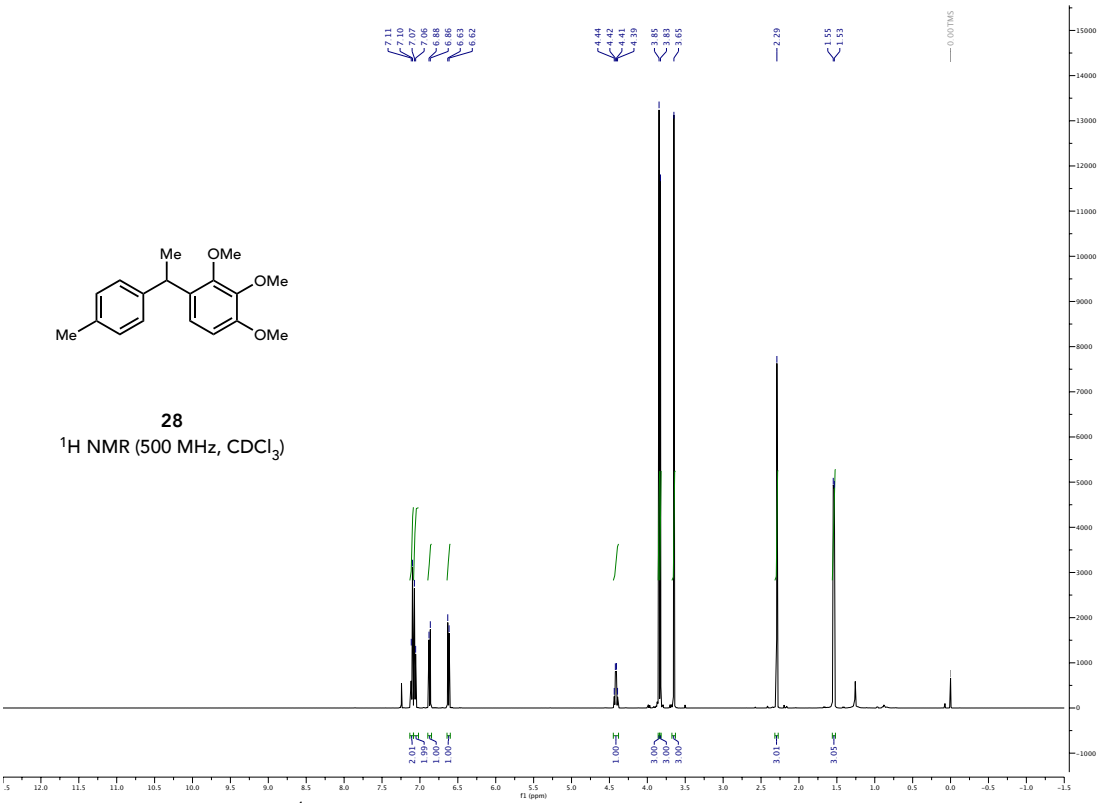


Figure S59. 500 MHz ^{1}H NMR spectrum of **28** in $CDCl_3$.

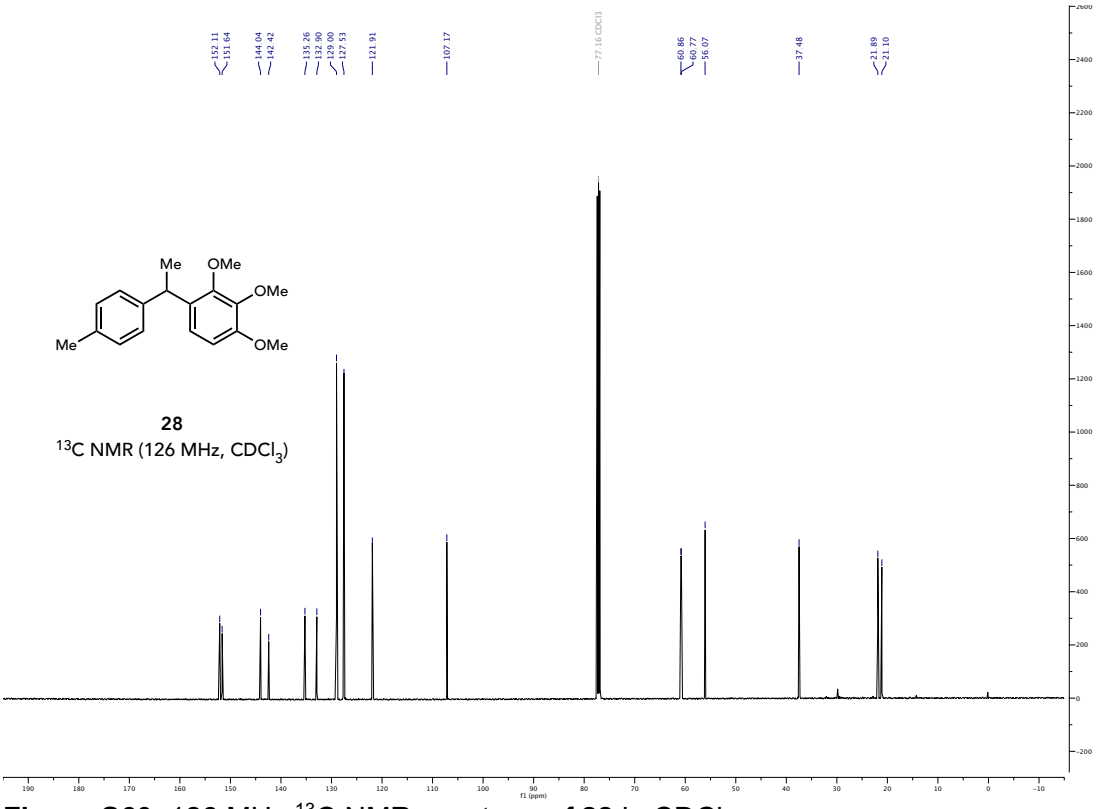


Figure S60. 126 MHz ^{13}C NMR spectrum of **28** in $CDCl_3$.

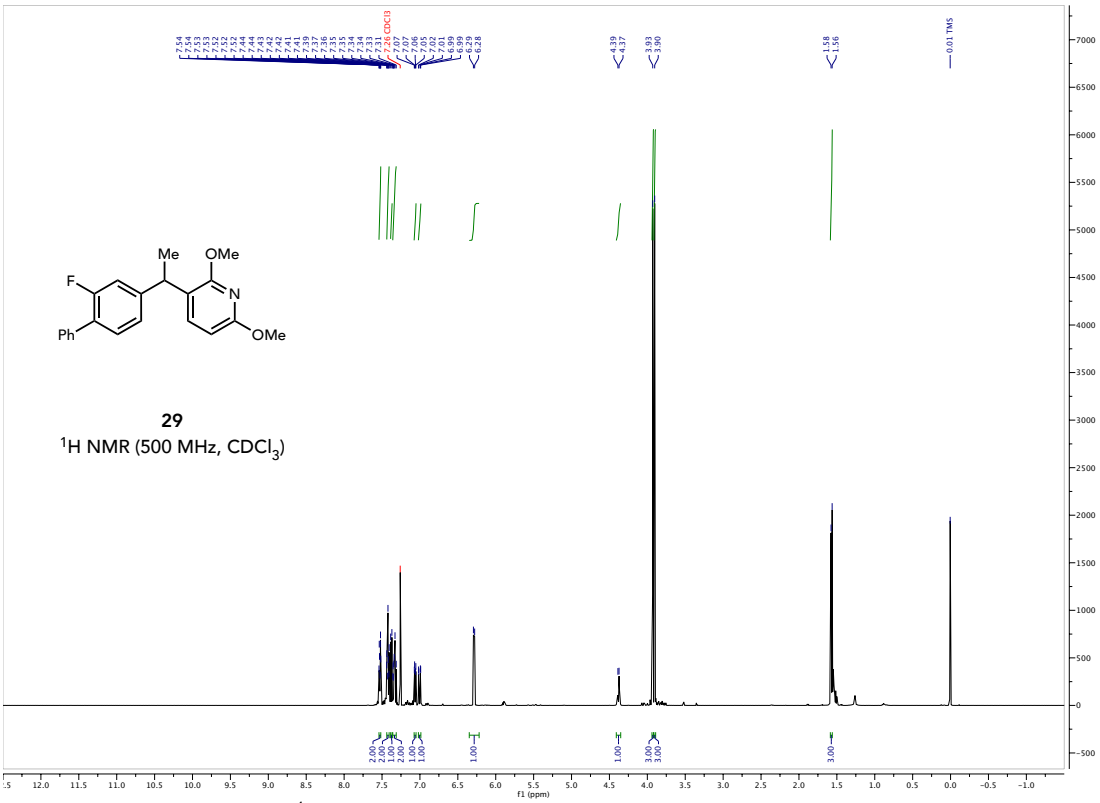


Figure S61. 500 MHz ^{1}H NMR spectrum of **29** in $CDCl_3$.

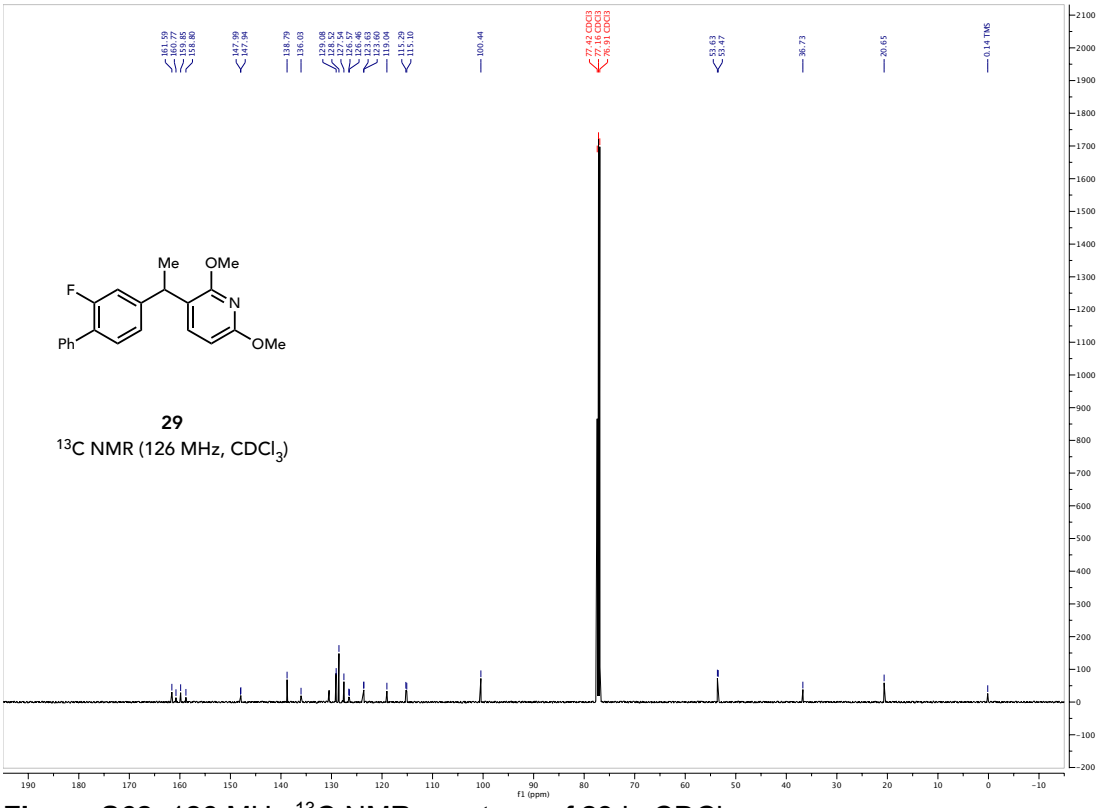


Figure S62. 126 MHz ^{13}C NMR spectrum of **29** in $CDCl_3$.

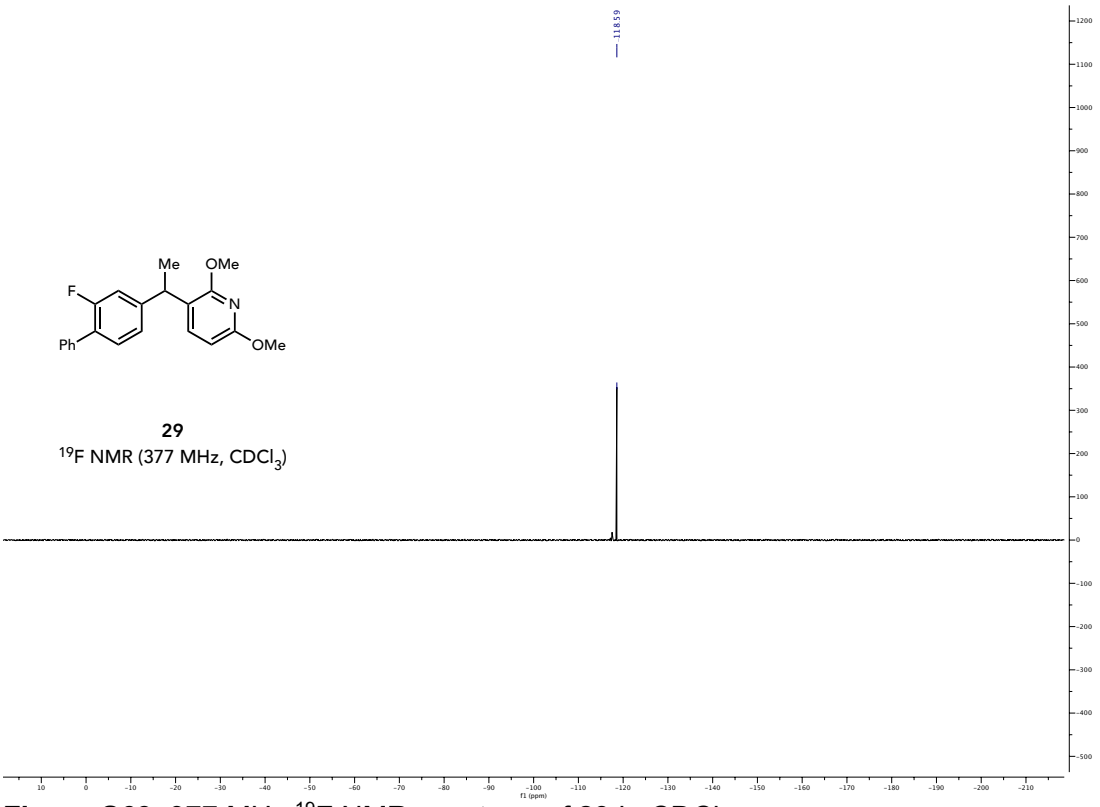


Figure S63. 377 MHz ^{19}F NMR spectrum of **29** in $CDCl_3$.

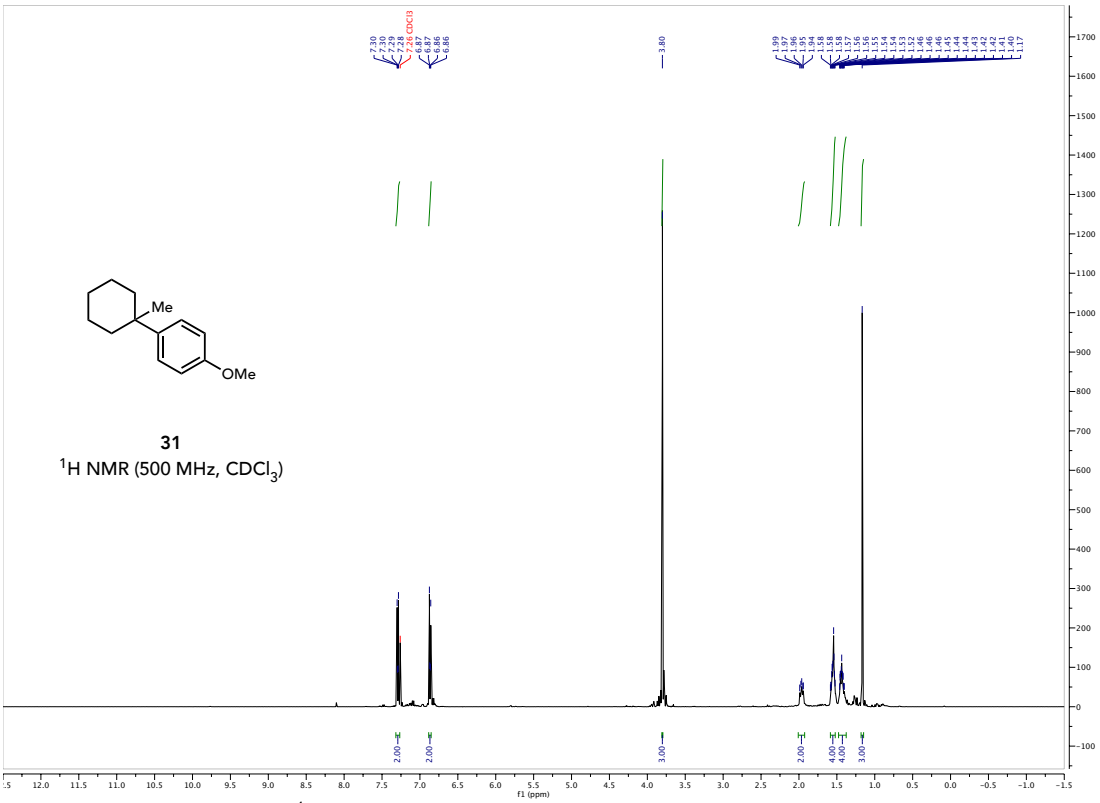


Figure S64. 500 MHz ^{1}H NMR spectrum of **31** in $CDCl_3$.

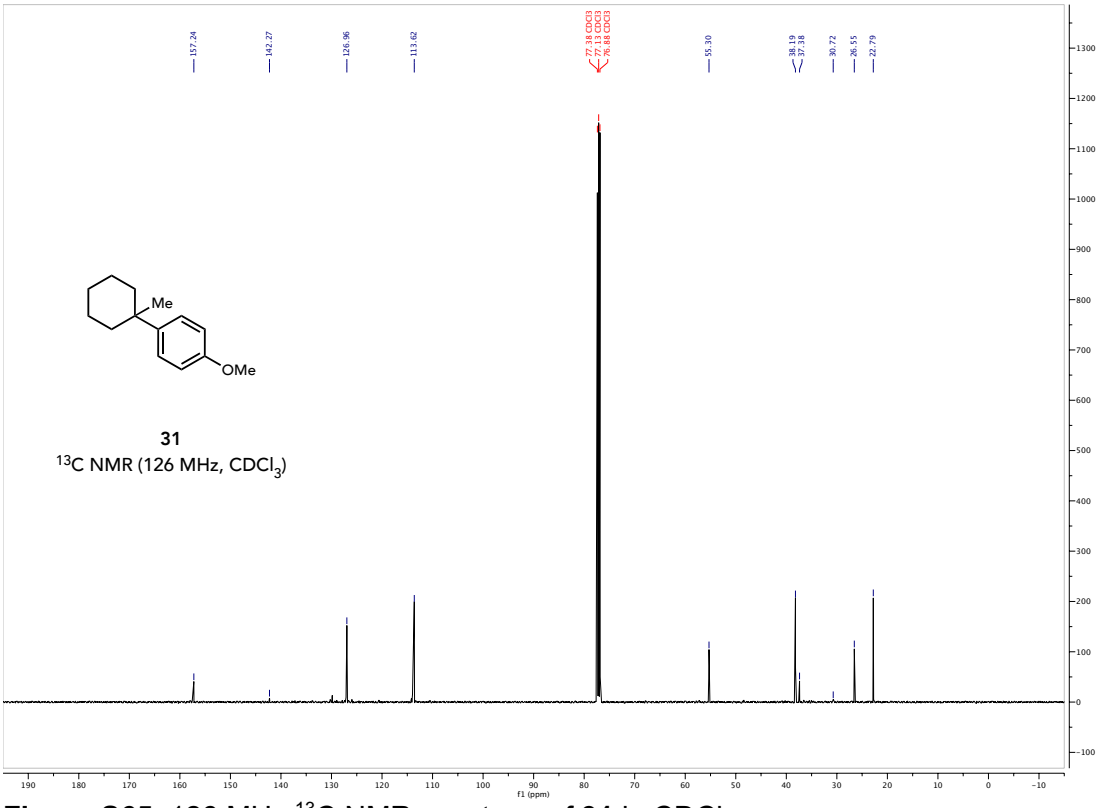


Figure S65. 126 MHz ^{13}C NMR spectrum of **31** in $CDCl_3$.

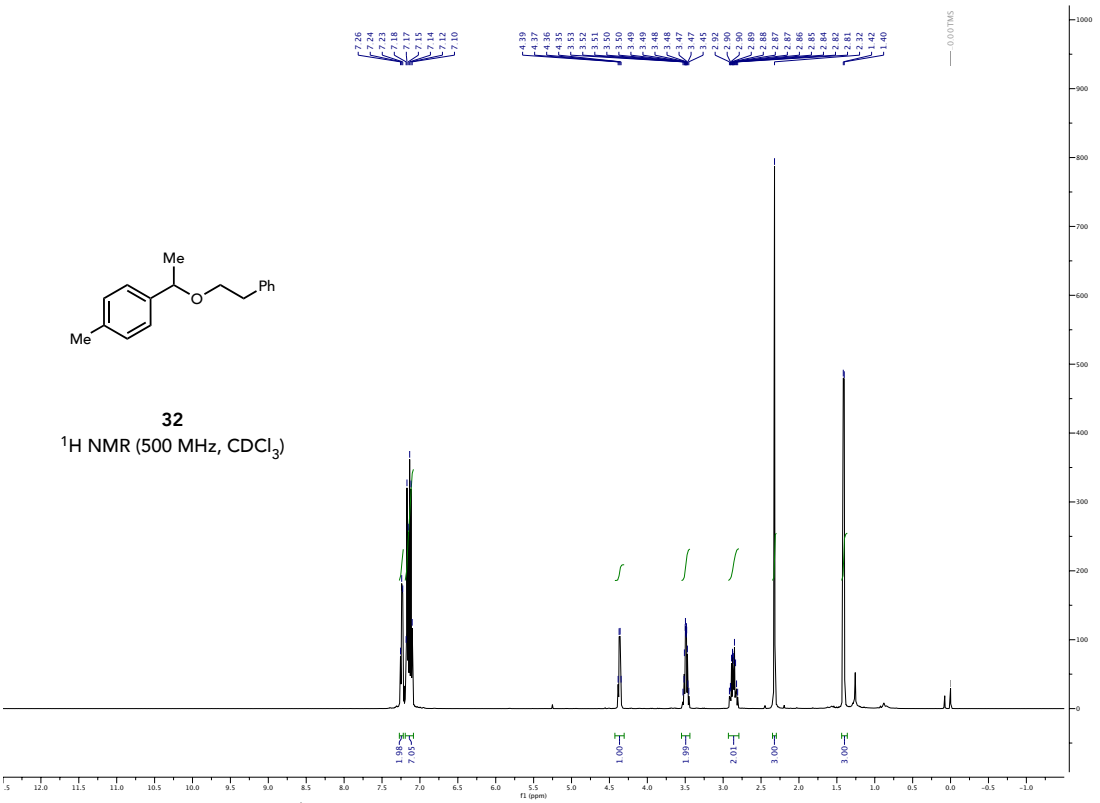


Figure S66. 500 MHz ^{1}H NMR spectrum of **32** in $CDCl_3$.

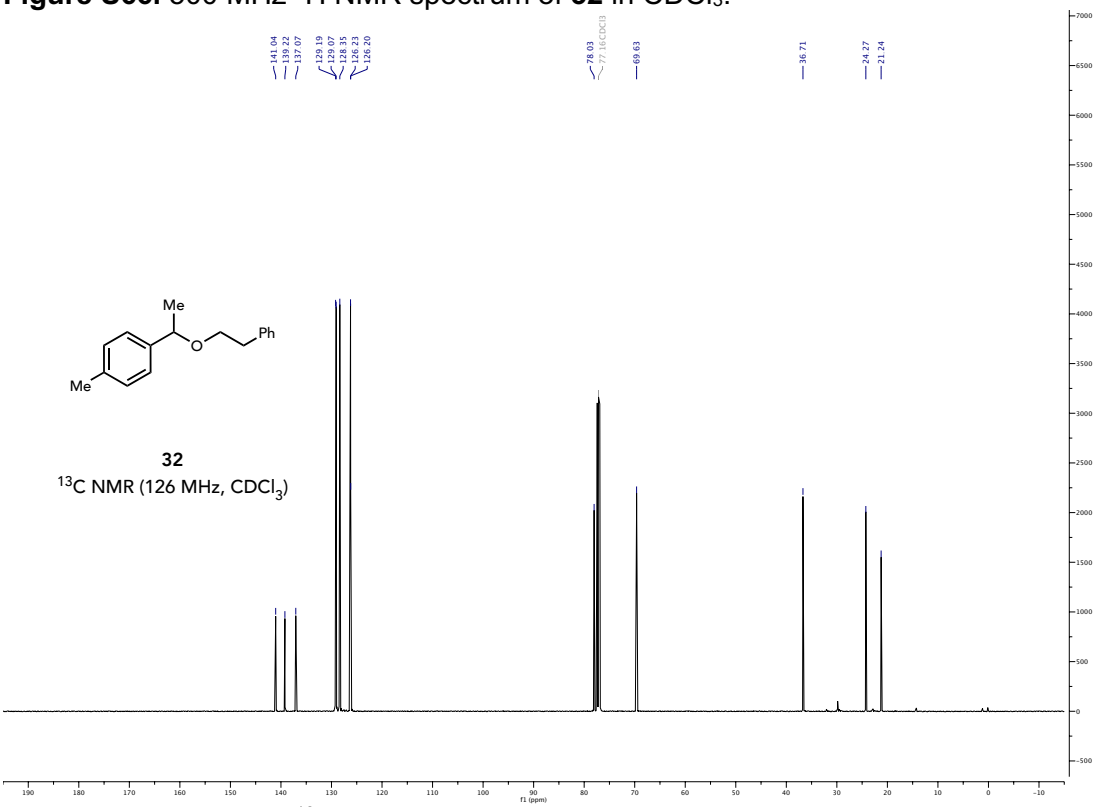


Figure S67. 126 MHz ^{13}C NMR spectrum of **32** in $CDCl_3$.

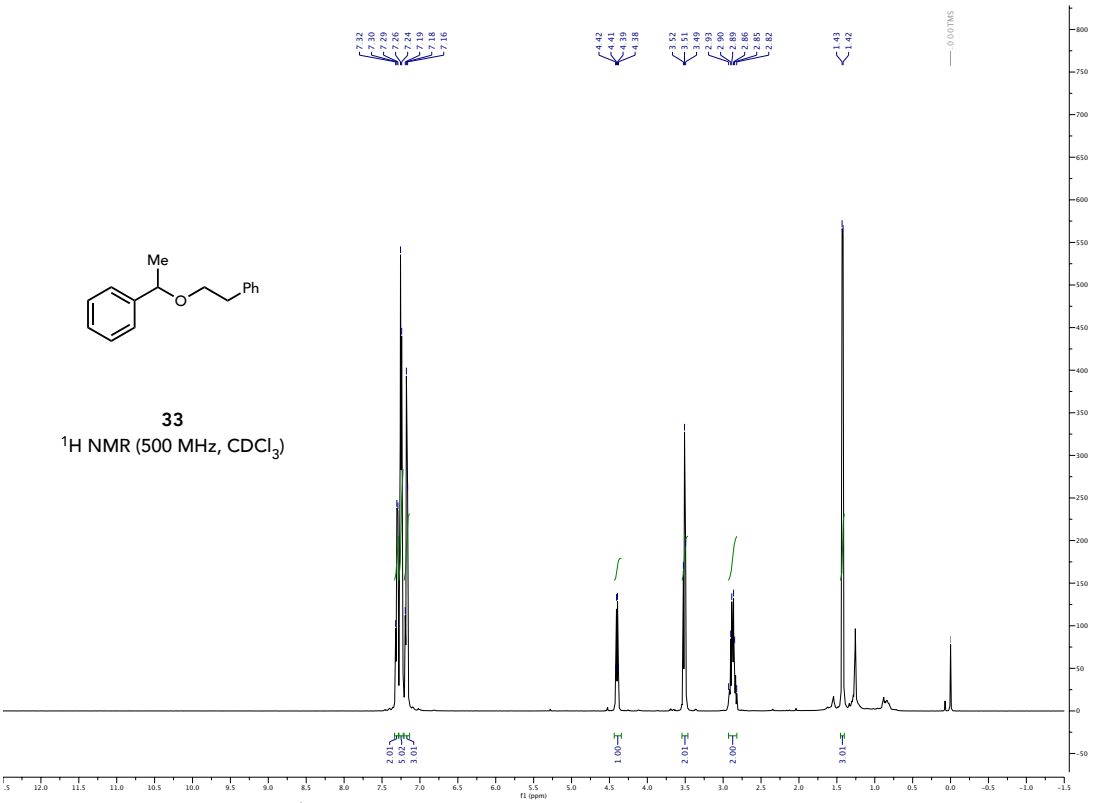


Figure S68. 500 MHz ^{1}H NMR spectrum of **33** in $CDCl_3$.

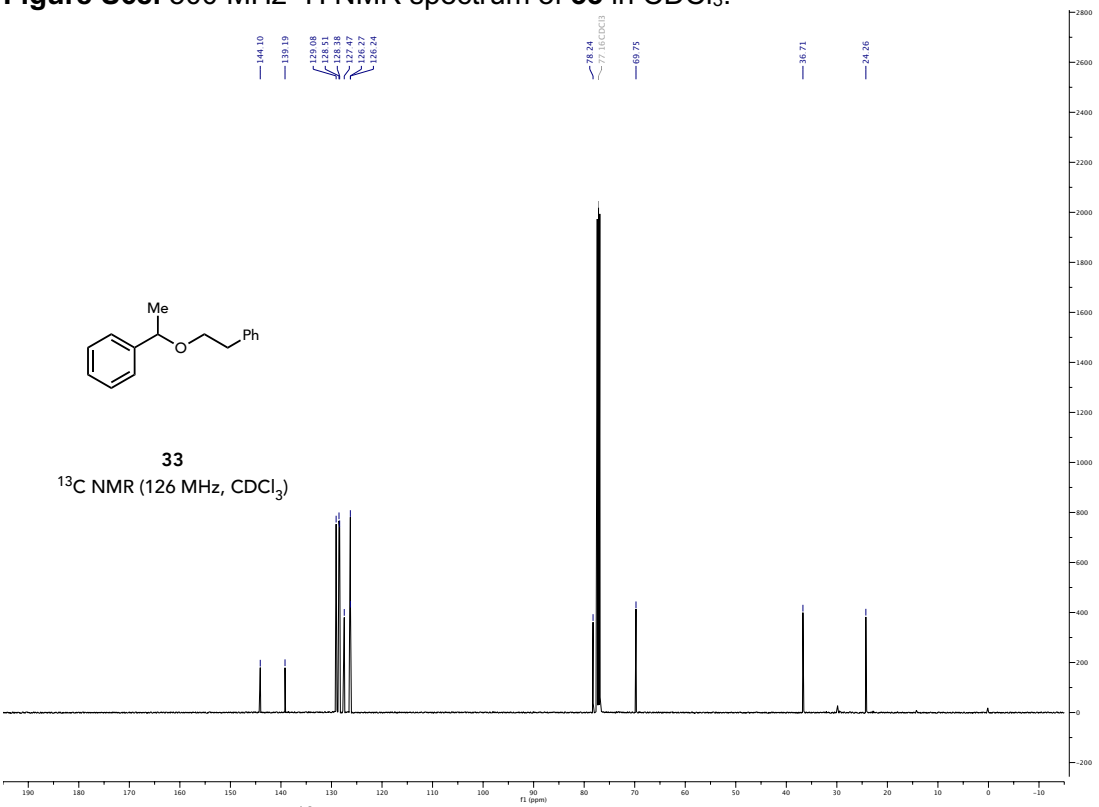


Figure S69. 126 MHz ^{13}C NMR spectrum of **33** in $CDCl_3$.

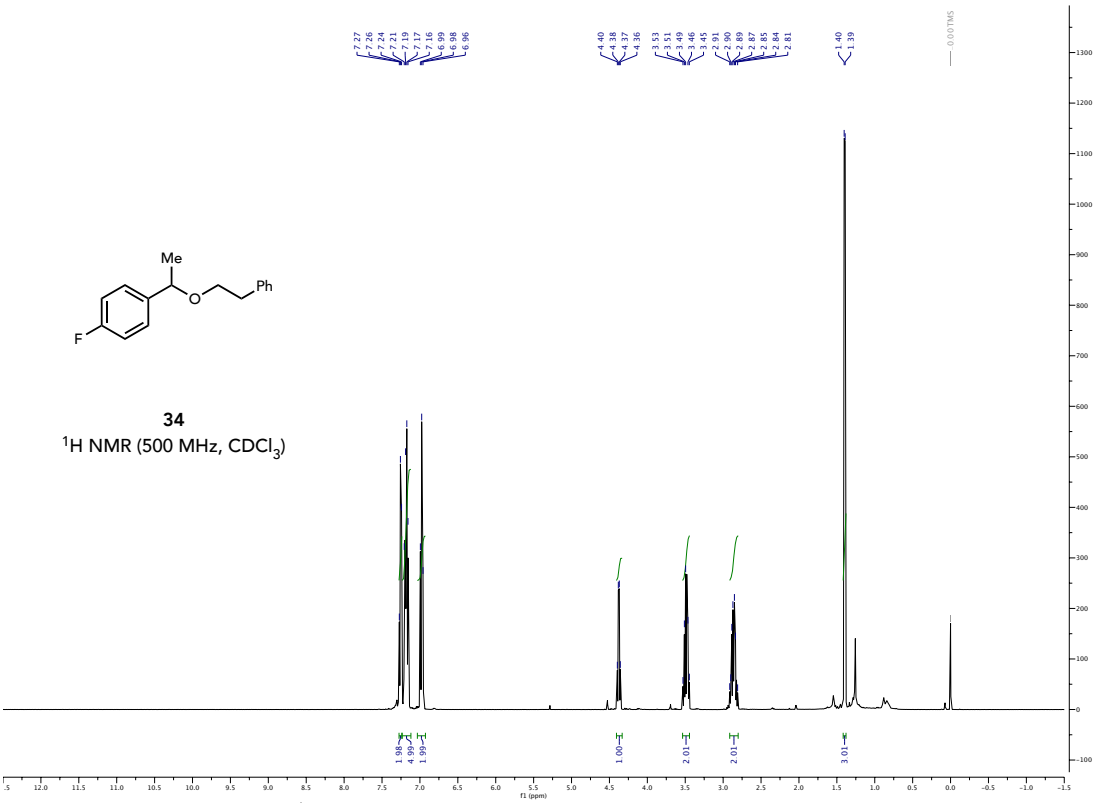


Figure S70. 500 MHz ^{1}H NMR spectrum of **34** in $CDCl_3$.

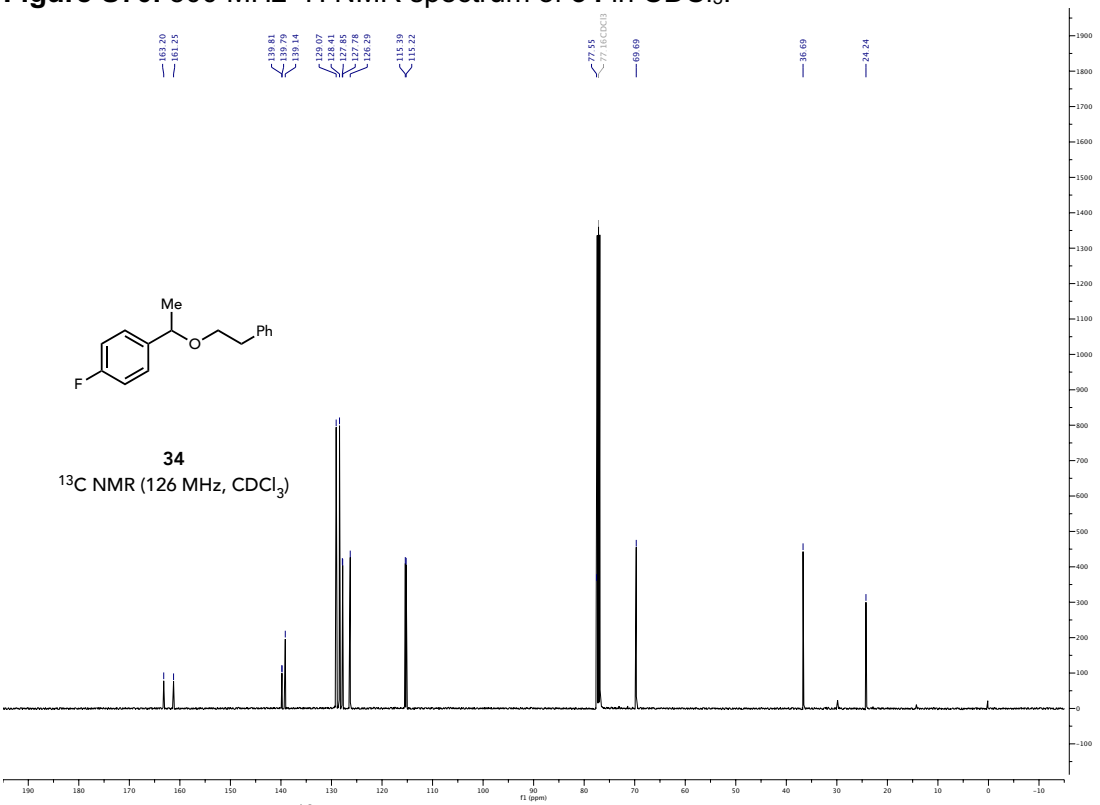
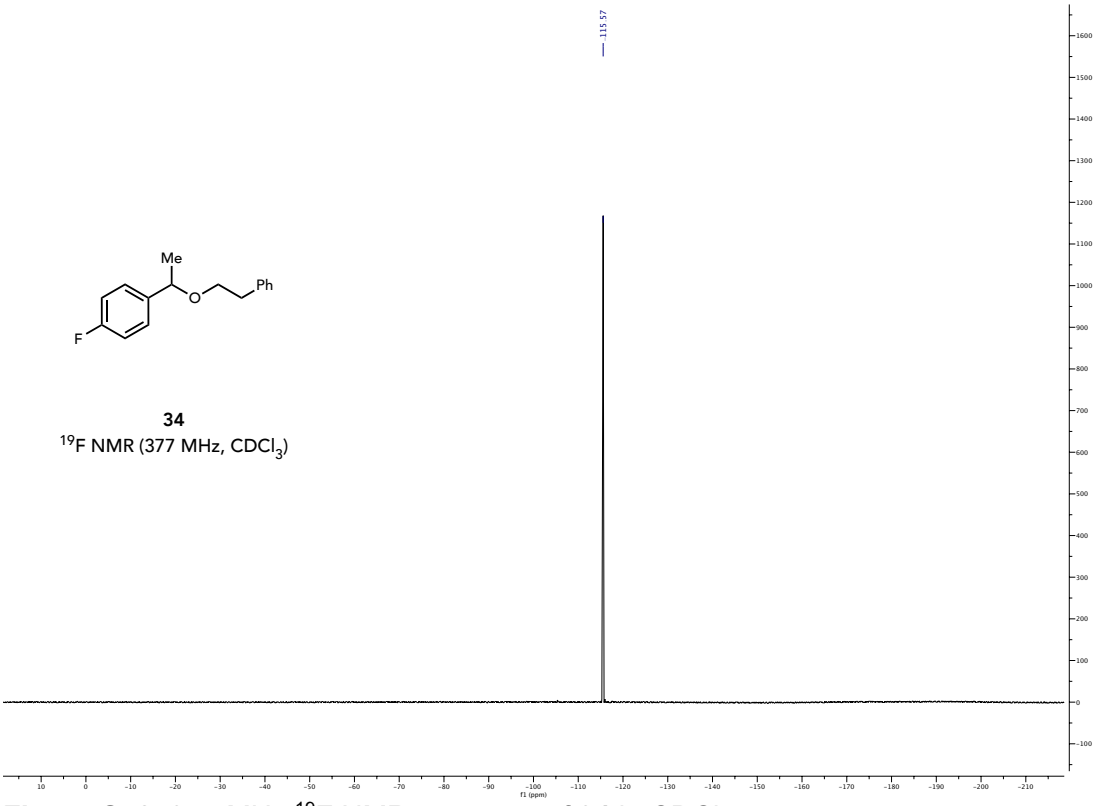


Figure S71. 126 MHz ^{13}C NMR spectrum of **34** in $CDCl_3$.



34
^{19}F NMR (377 MHz, $CDCl_3$)

Figure S72. 377 MHz ^{19}F NMR spectrum of **34** in $CDCl_3$.

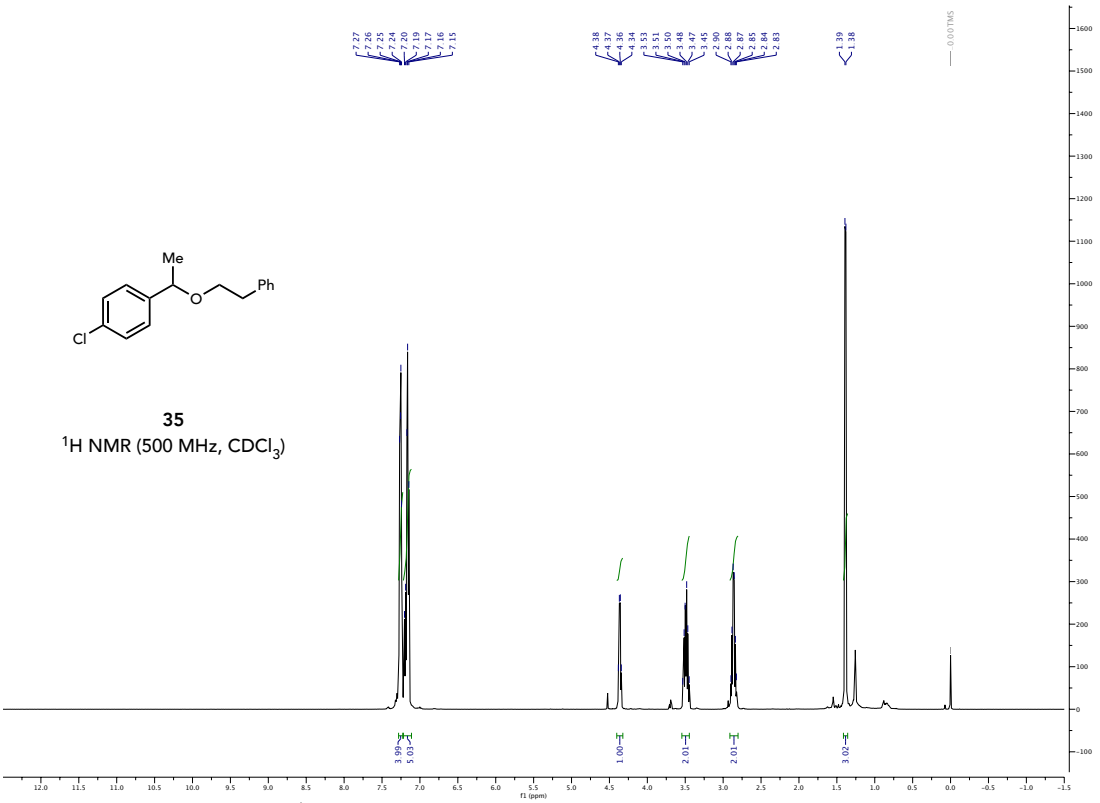


Figure S73. 500 MHz ^{1}H NMR spectrum of **35** in $CDCl_3$.

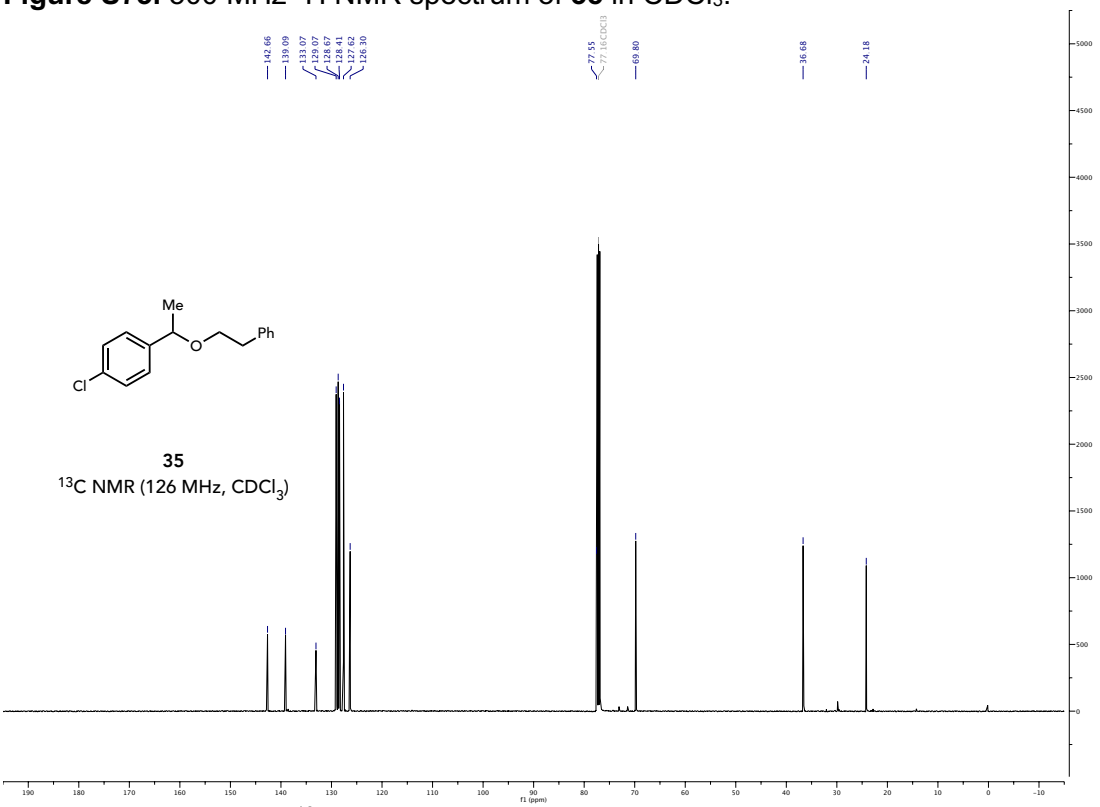


Figure S74. 126 MHz ^{13}C NMR spectrum of **35** in $CDCl_3$.

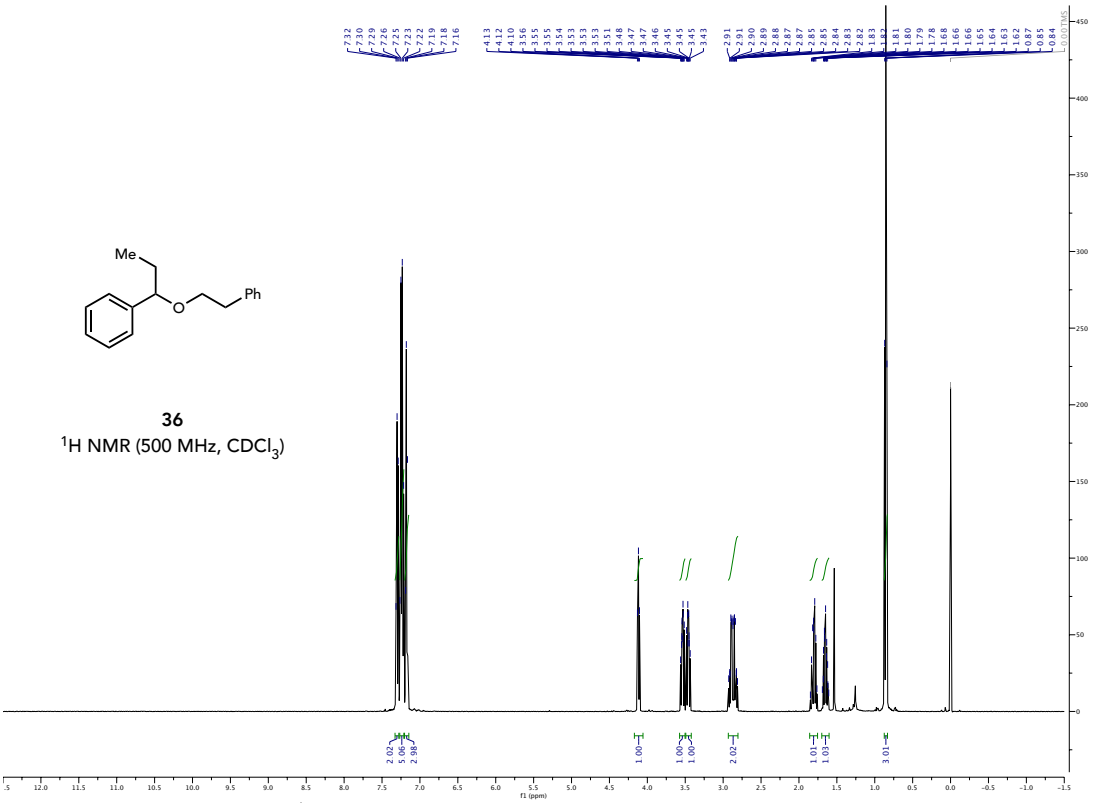


Figure S75. 500 MHz ^{1}H NMR spectrum of **36** in $CDCl_3$.

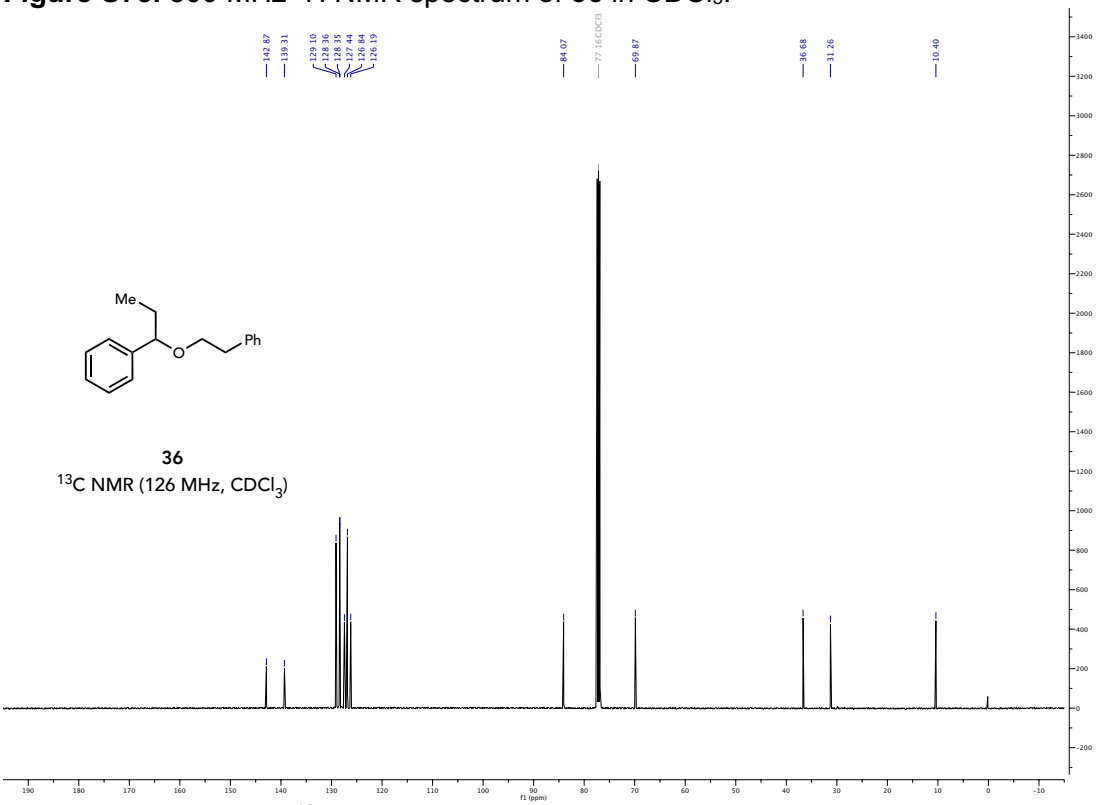


Figure S76. 126 MHz ^{13}C NMR spectrum of **36** in $CDCl_3$.

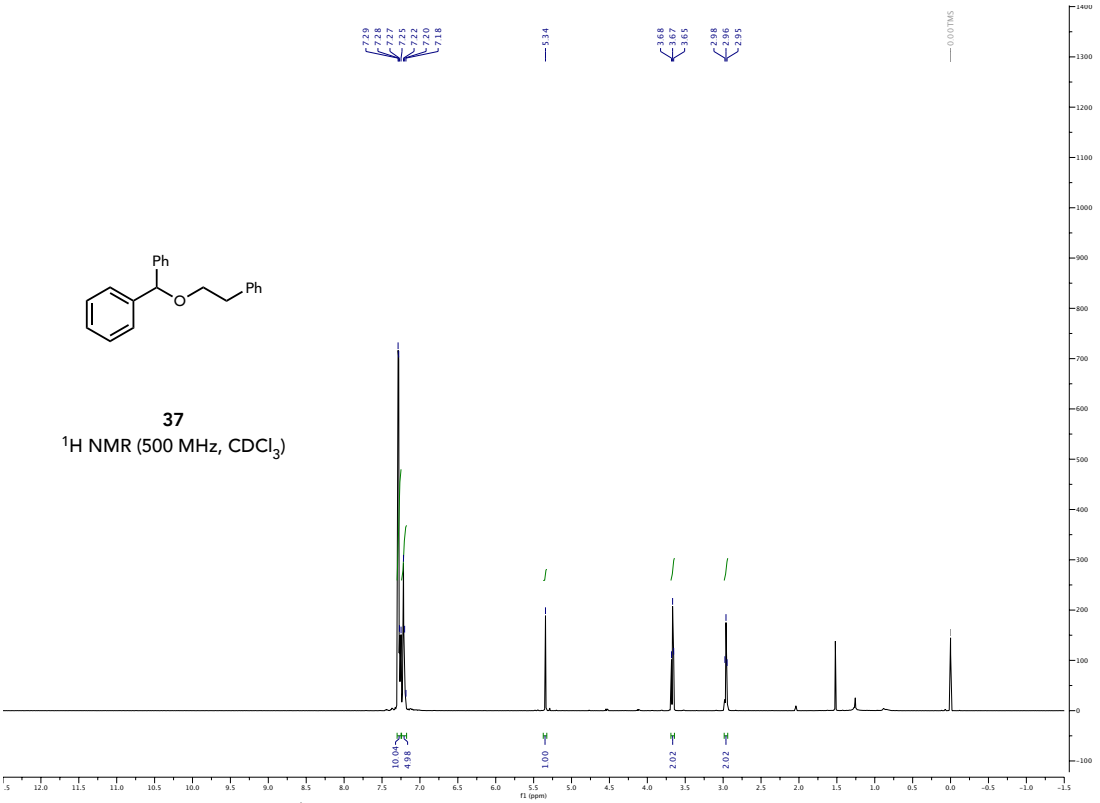


Figure S77. 500 MHz ^{1}H NMR spectrum of **37** in $CDCl_3$.

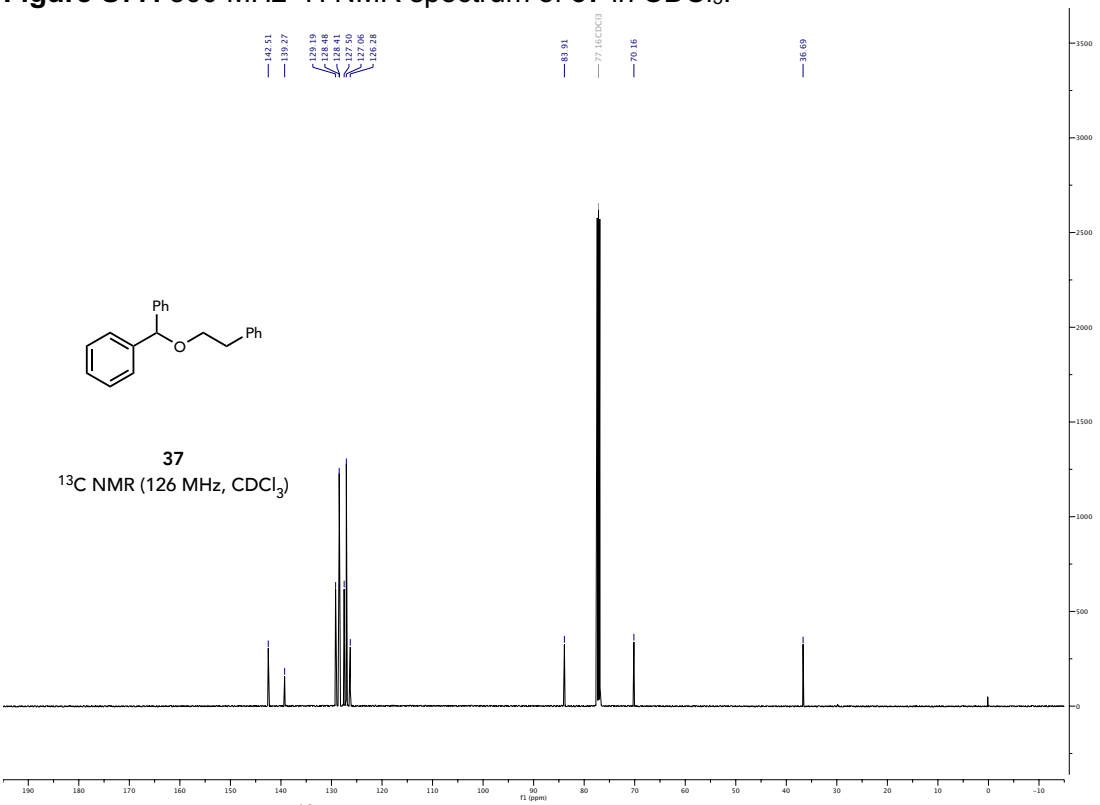


Figure S78. 126 MHz ^{13}C NMR spectrum of **37** in $CDCl_3$.

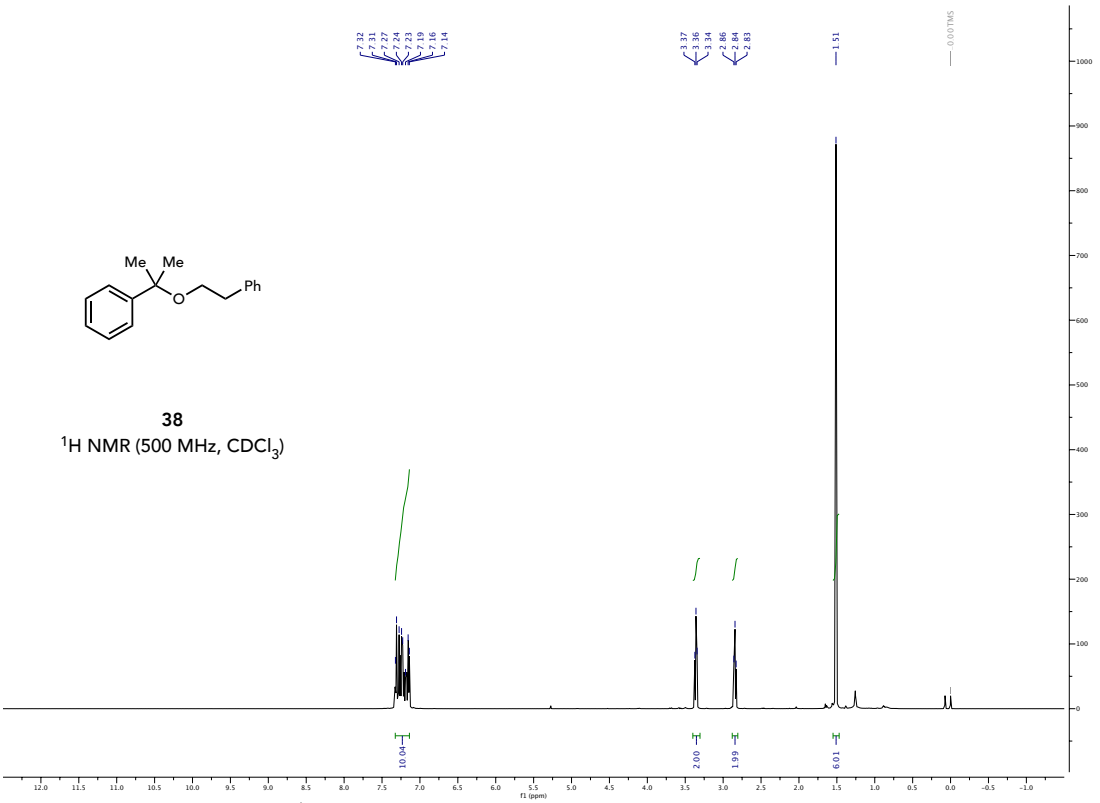


Figure S79. 500 MHz ^{1}H NMR spectrum of **38** in $CDCl_3$.

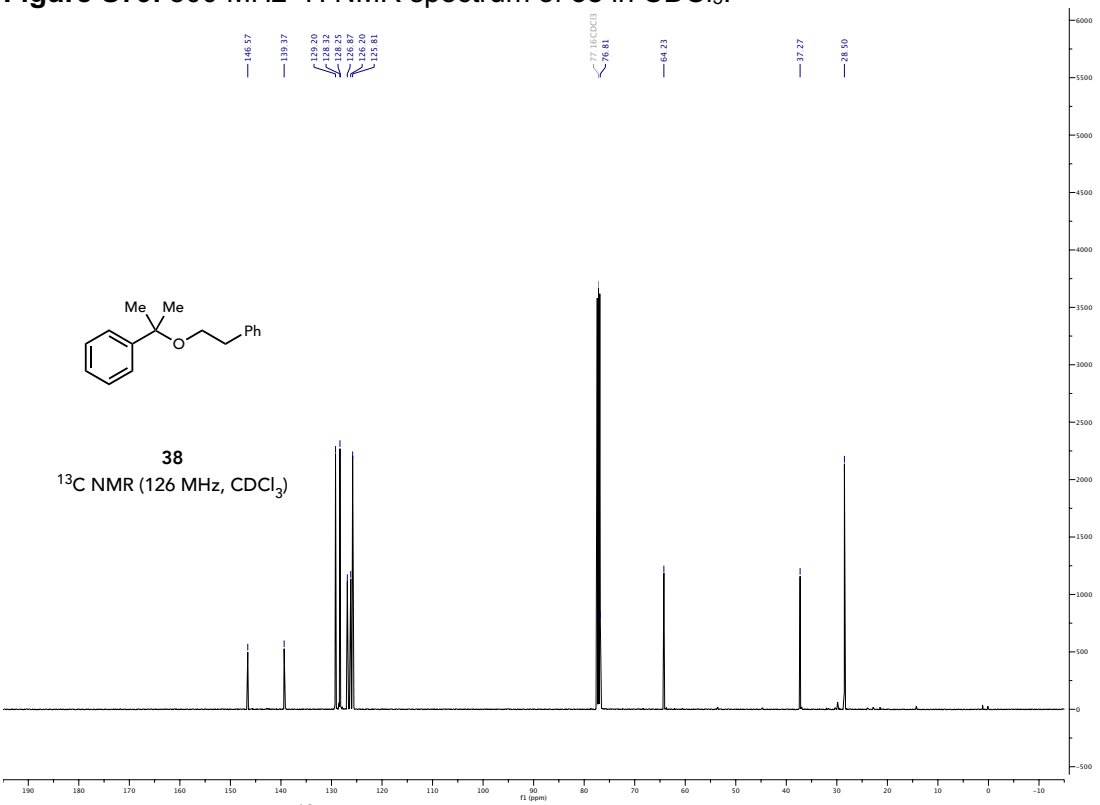


Figure S80. 126 MHz ^{13}C NMR spectrum of **38** in $CDCl_3$.

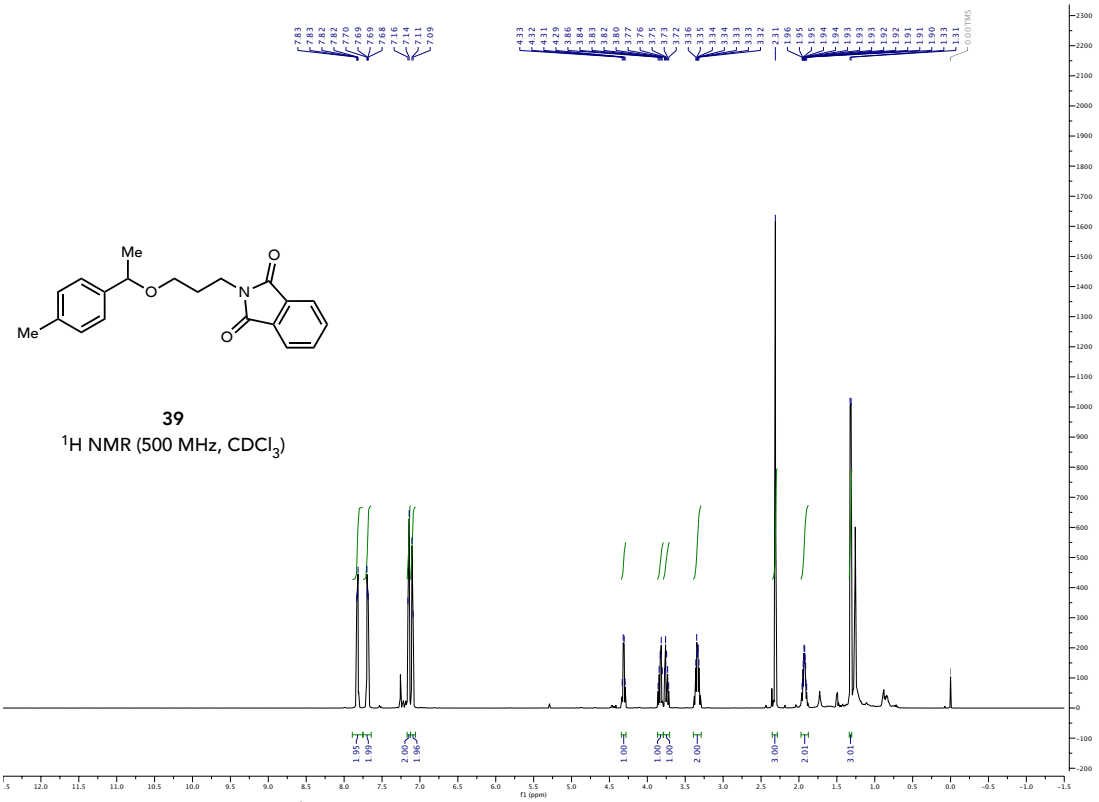


Figure S81. 500 MHz ^{1}H NMR spectrum of **39** in $CDCl_3$.

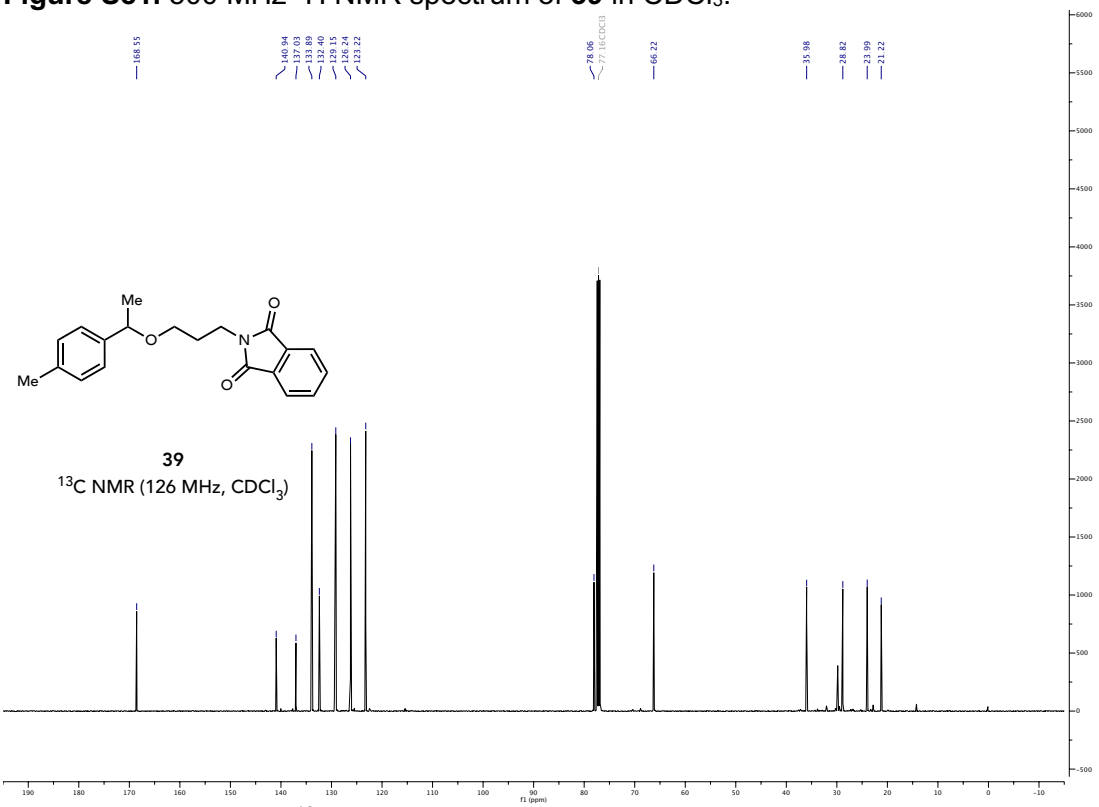


Figure S82. 126 MHz ^{13}C NMR spectrum of **39** in $CDCl_3$.

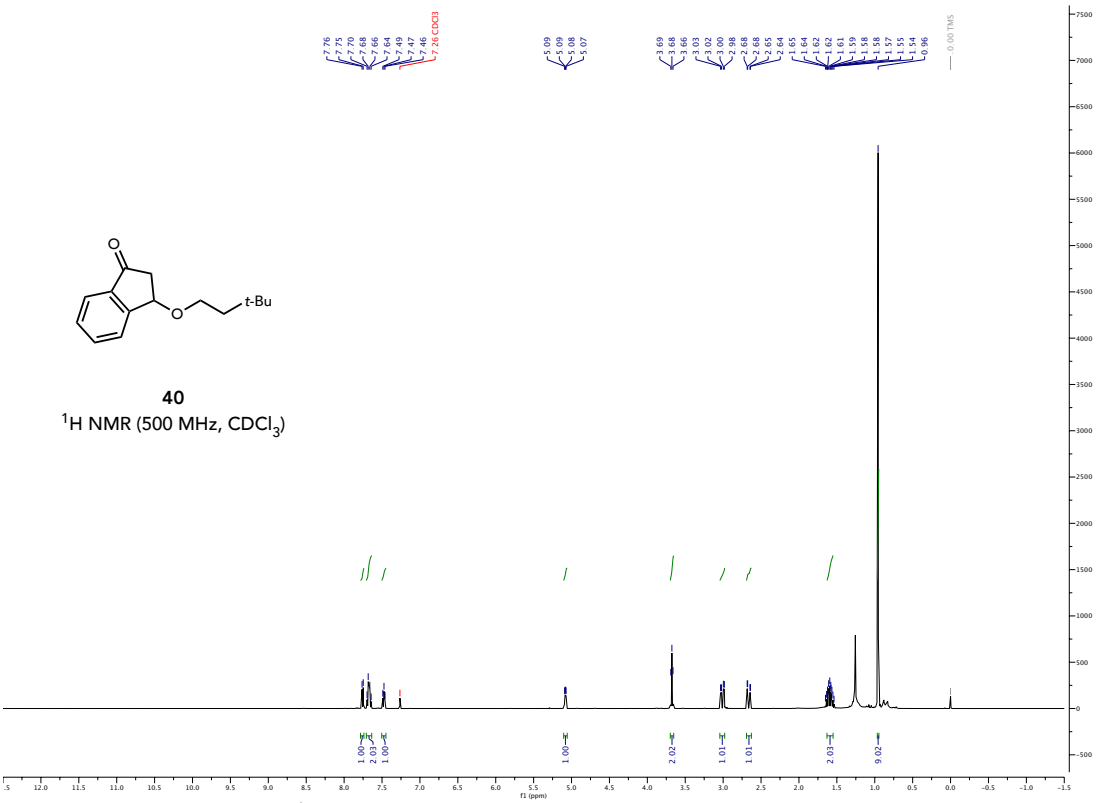


Figure S83. 500 MHz ^{1}H NMR spectrum of **40** in $CDCl_3$.

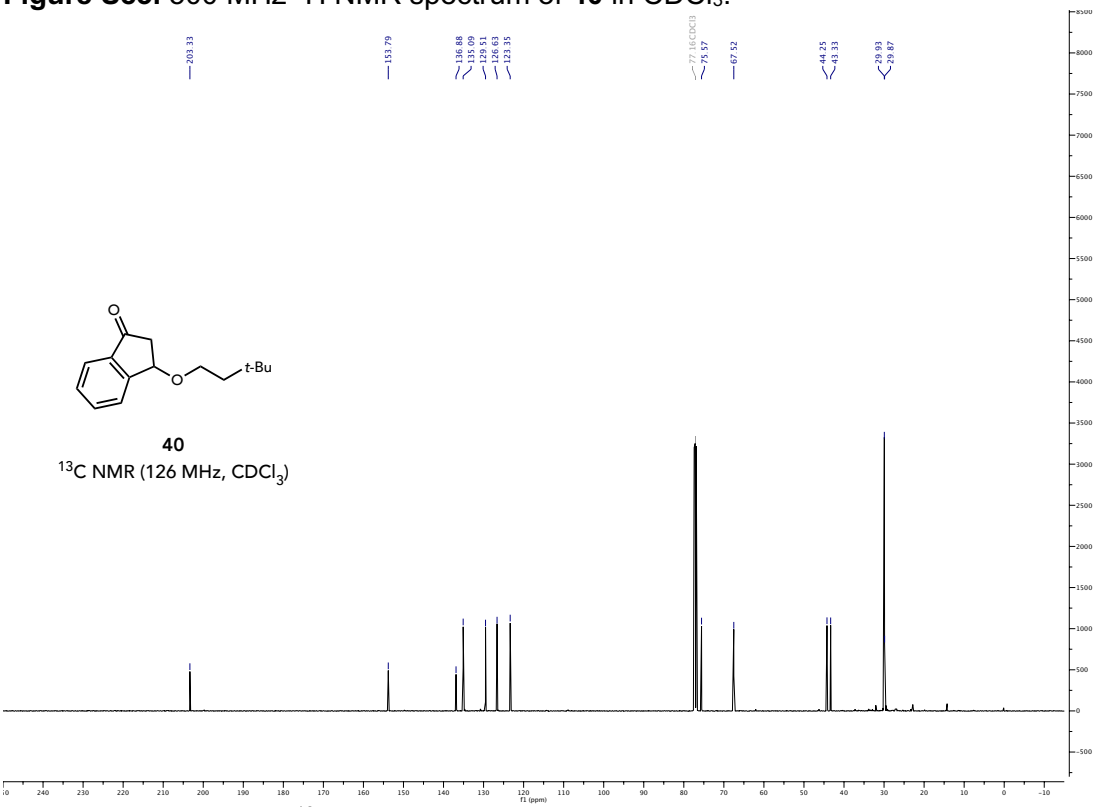


Figure S84. 126 MHz ^{13}C NMR spectrum of **40** in $CDCl_3$.

Figure S85. 500 MHz ^{1}H NMR spectrum of **41** in $CDCl_3$.

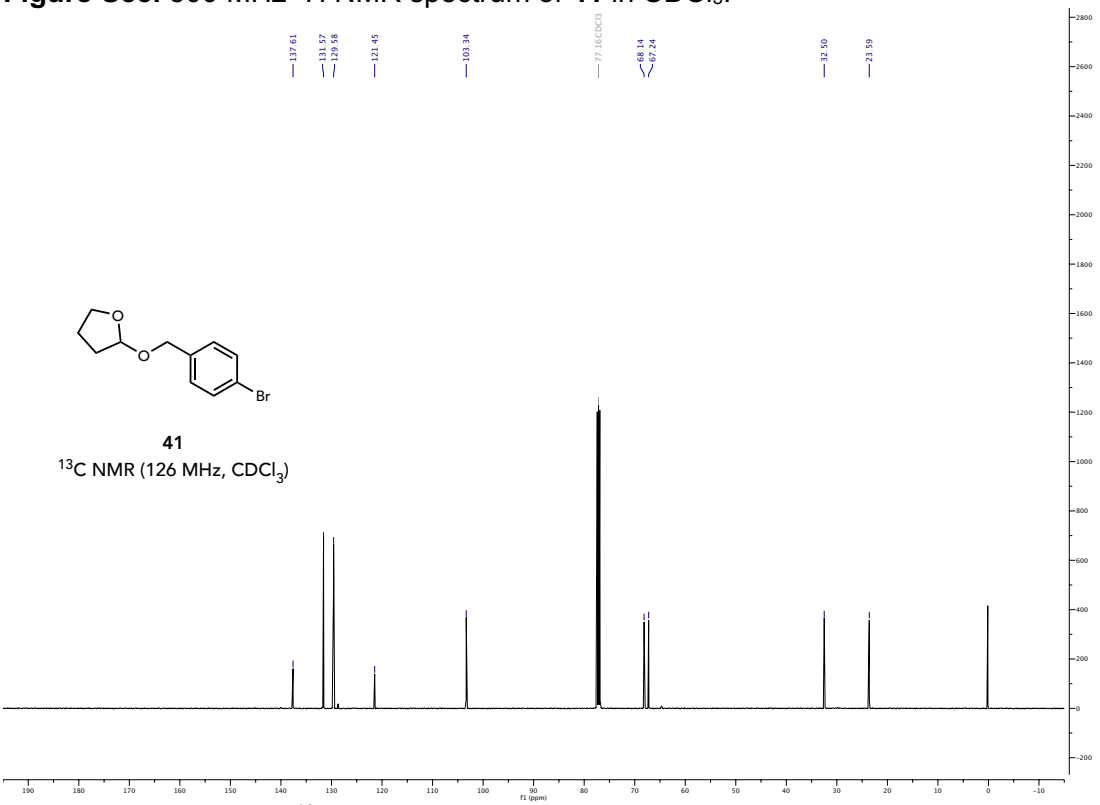


Figure S86. 126 MHz ^{13}C NMR spectrum of **41** in $CDCl_3$.

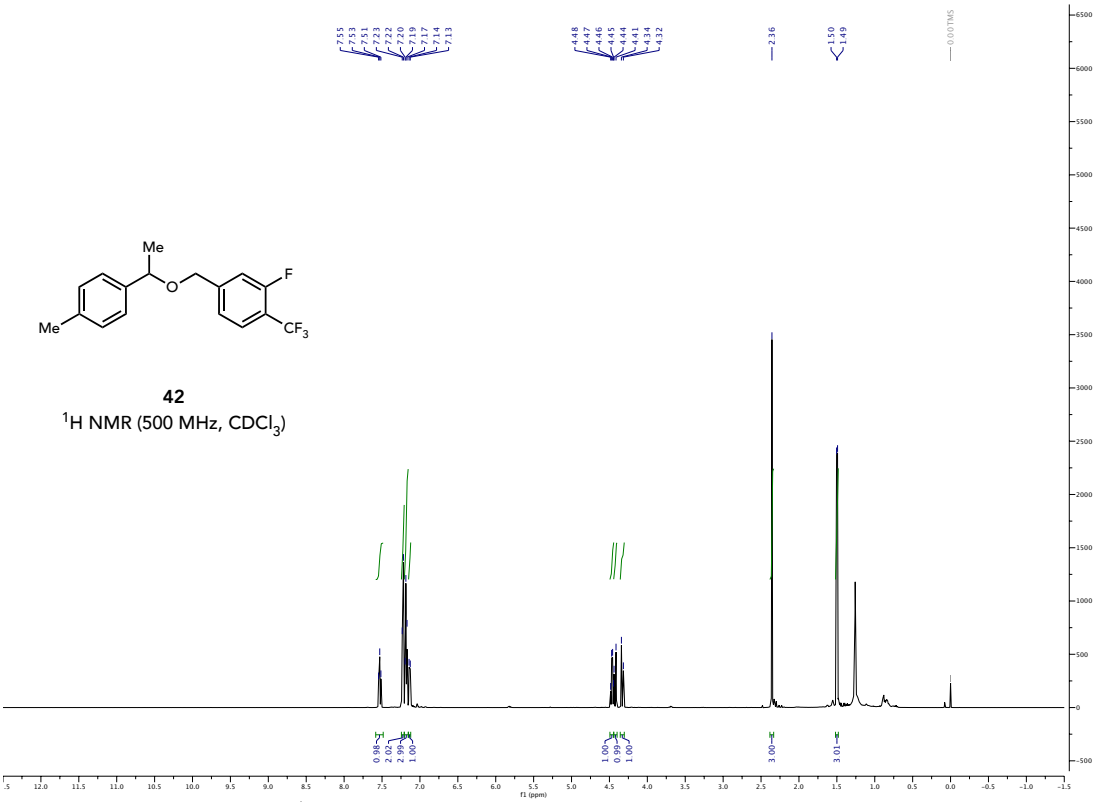


Figure S87. 500 MHz ^{1}H NMR spectrum of **42** in $CDCl_3$.

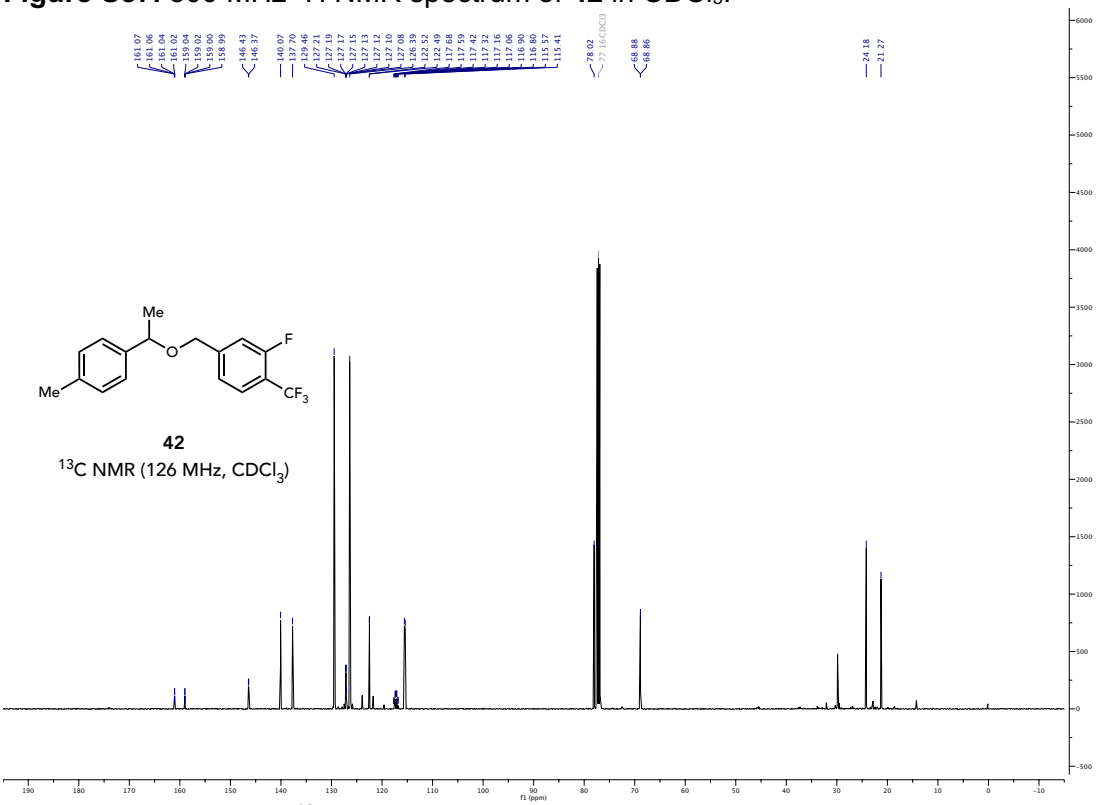


Figure S88. 126 MHz ^{13}C NMR spectrum of **42** in $CDCl_3$.

Figure S89. 377 MHz ^{19}F NMR spectrum of **42** in $CDCl_3$.

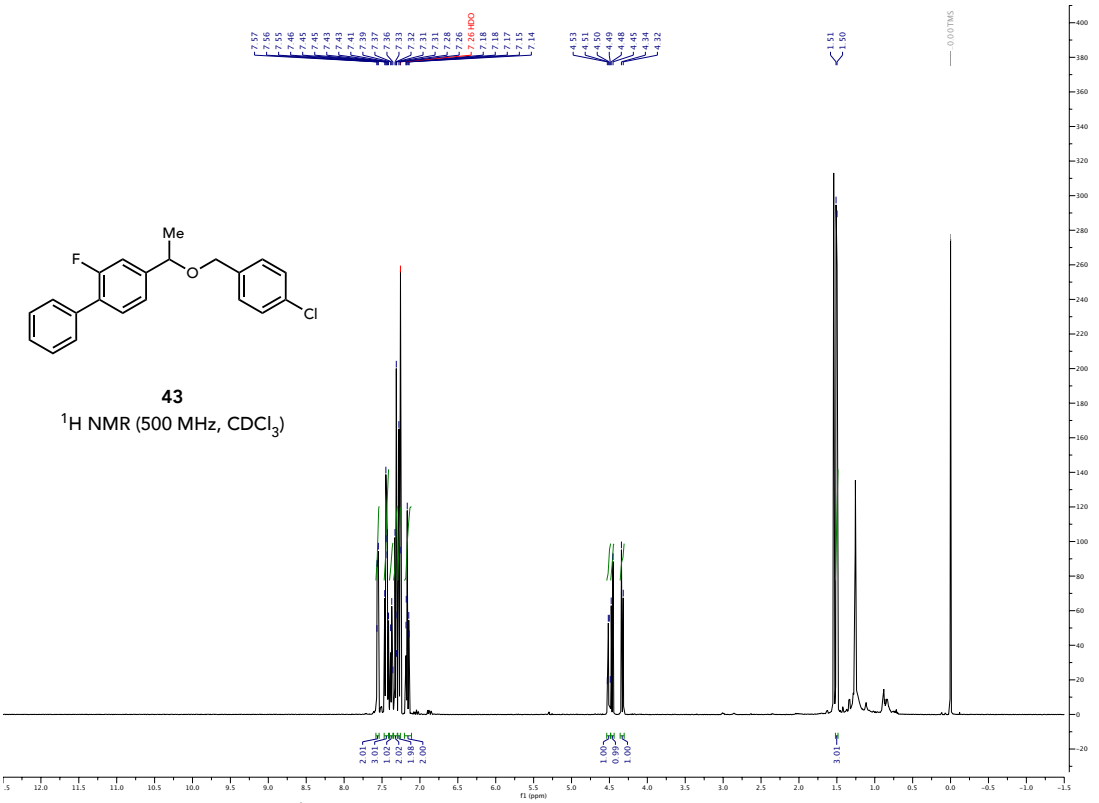


Figure S90. 500 MHz ^{1}H NMR spectrum of **43** in $CDCl_3$.

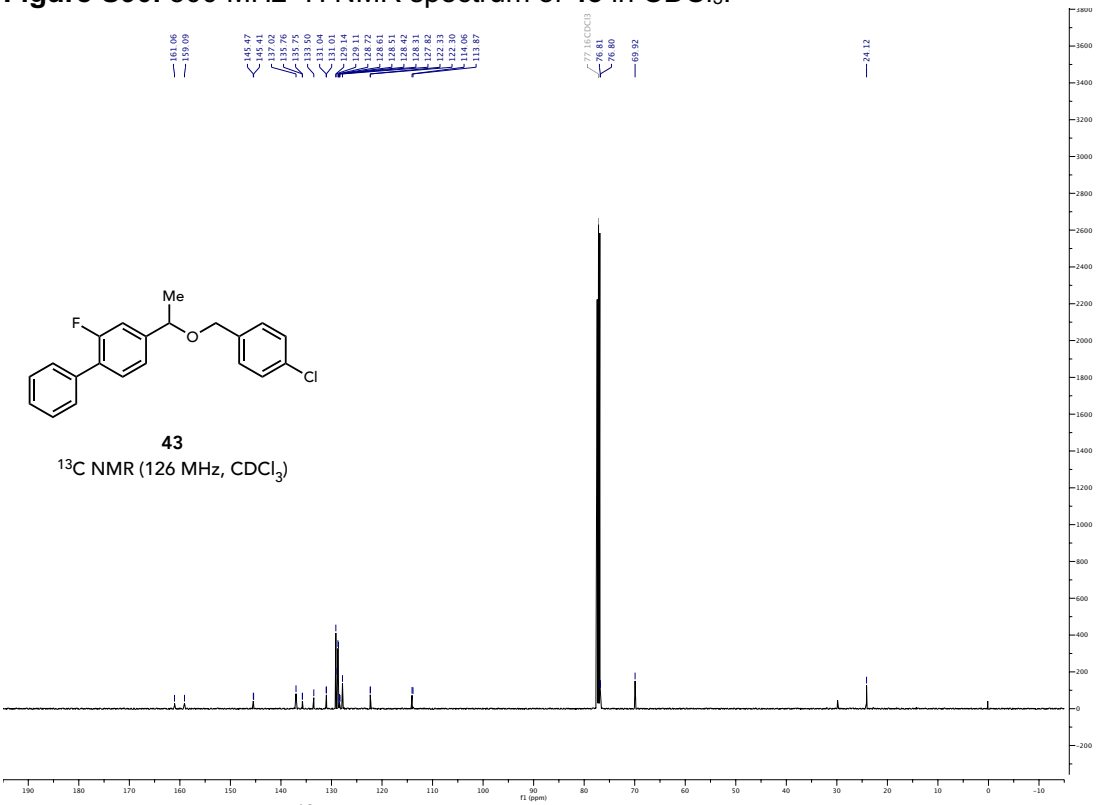


Figure S91. 126 MHz ^{13}C NMR spectrum of **43** in $CDCl_3$.

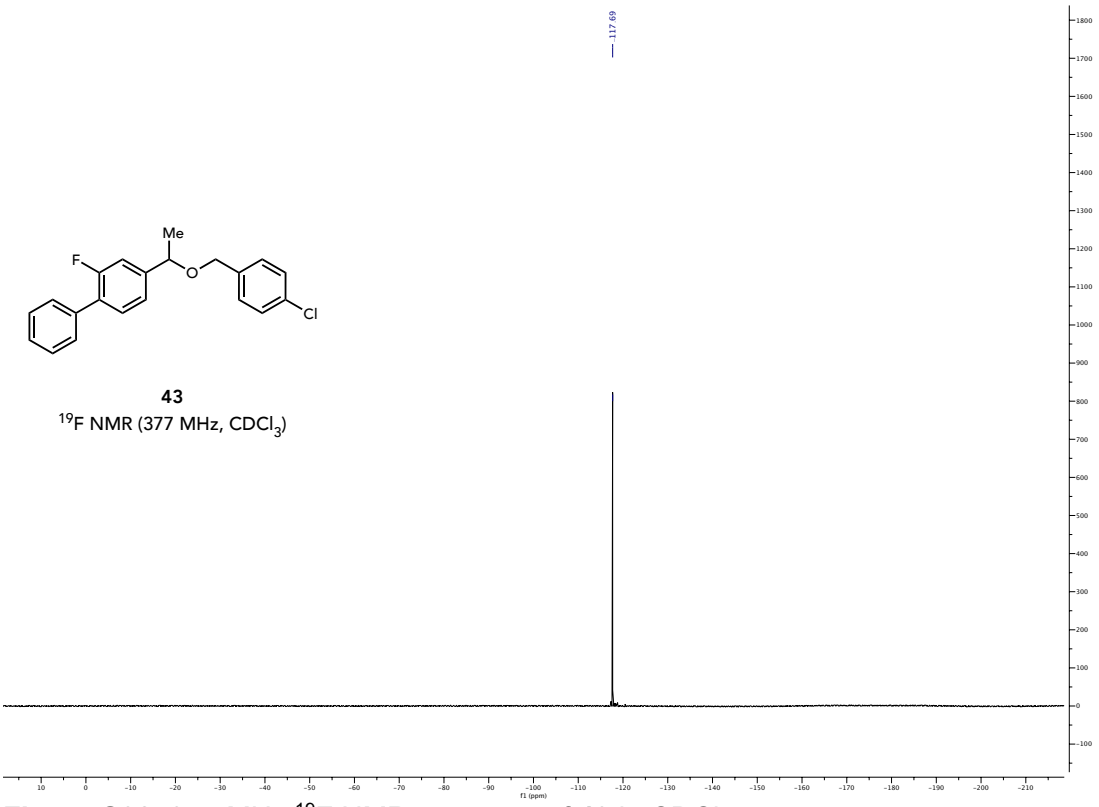


Figure S92. 377 MHz ^{19}F NMR spectrum of **43** in $CDCl_3$.

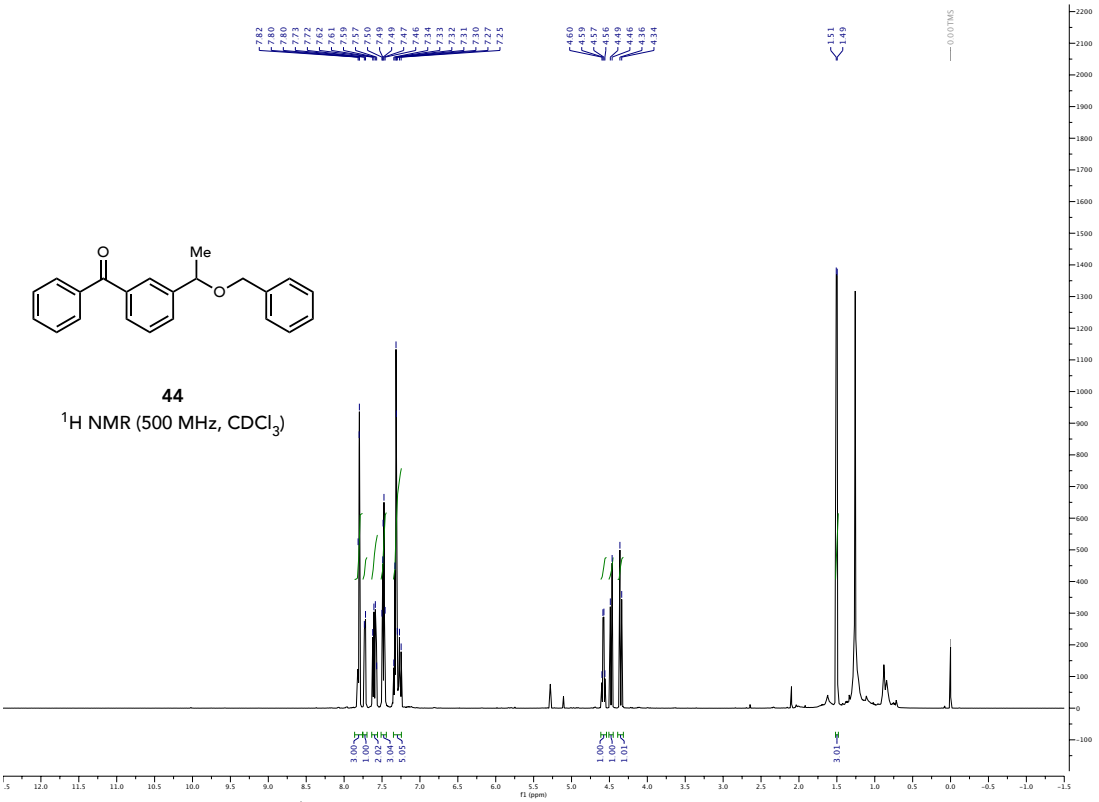


Figure S93. 500 MHz ^{1}H NMR spectrum of **44** in $CDCl_3$.

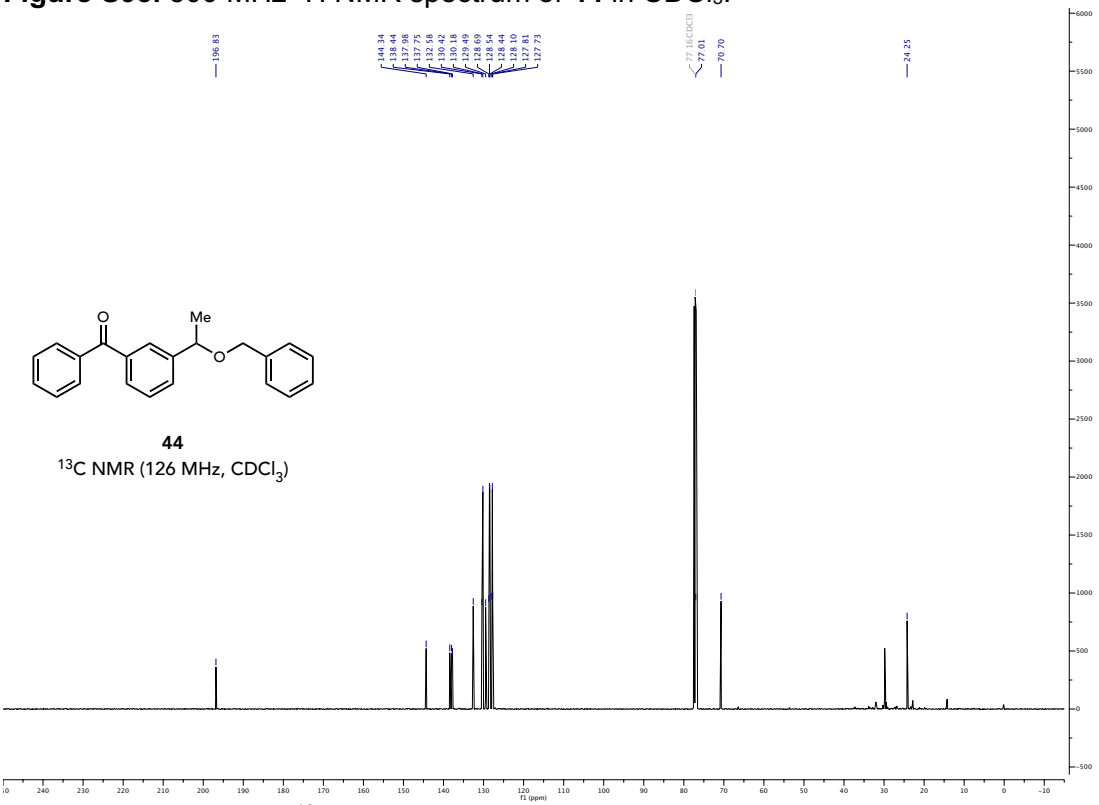


Figure S94. 126 MHz ^{13}C NMR spectrum of **44** in $CDCl_3$.

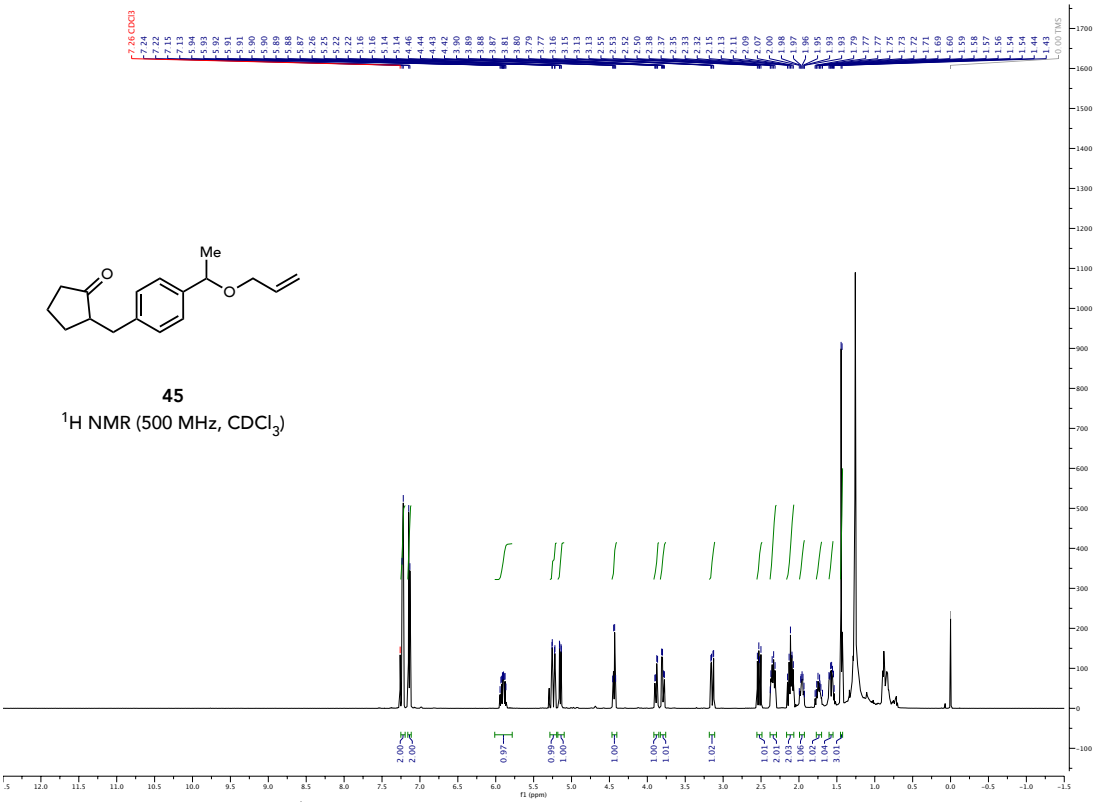


Figure S95. 500 MHz ^{1}H NMR spectrum of **45** in $CDCl_3$.

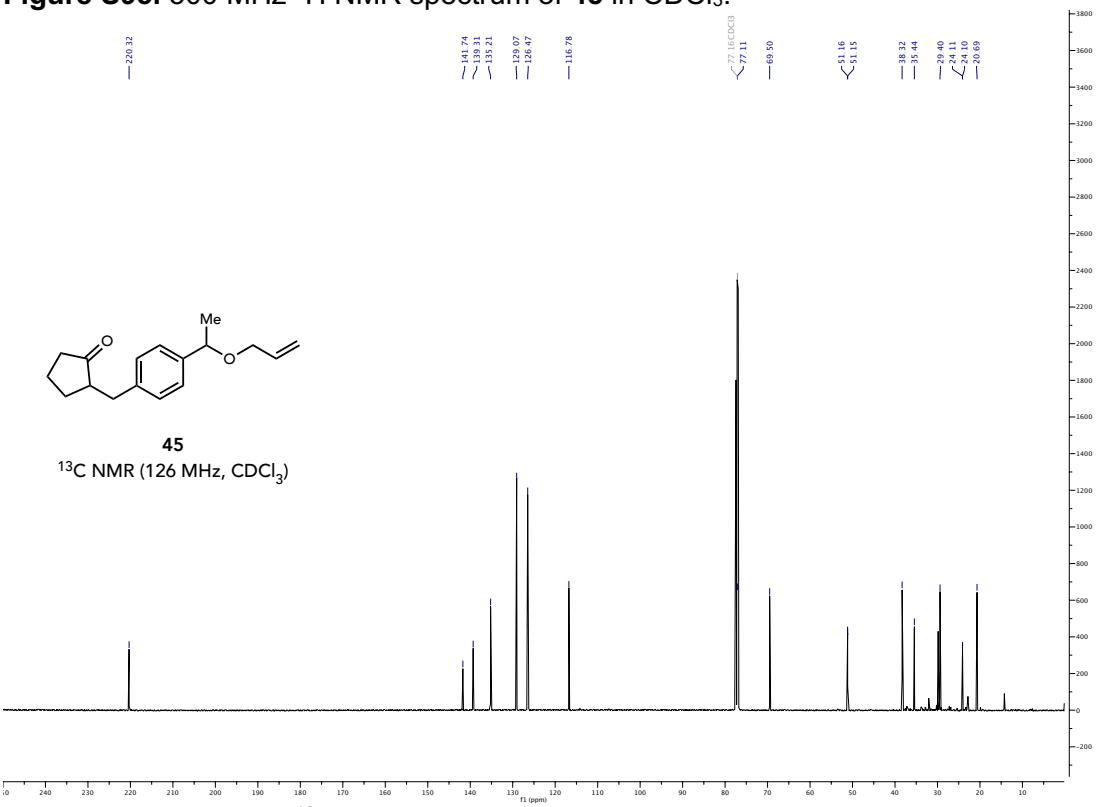


Figure S96. 126 MHz ^{13}C NMR spectrum of **45** in $CDCl_3$.

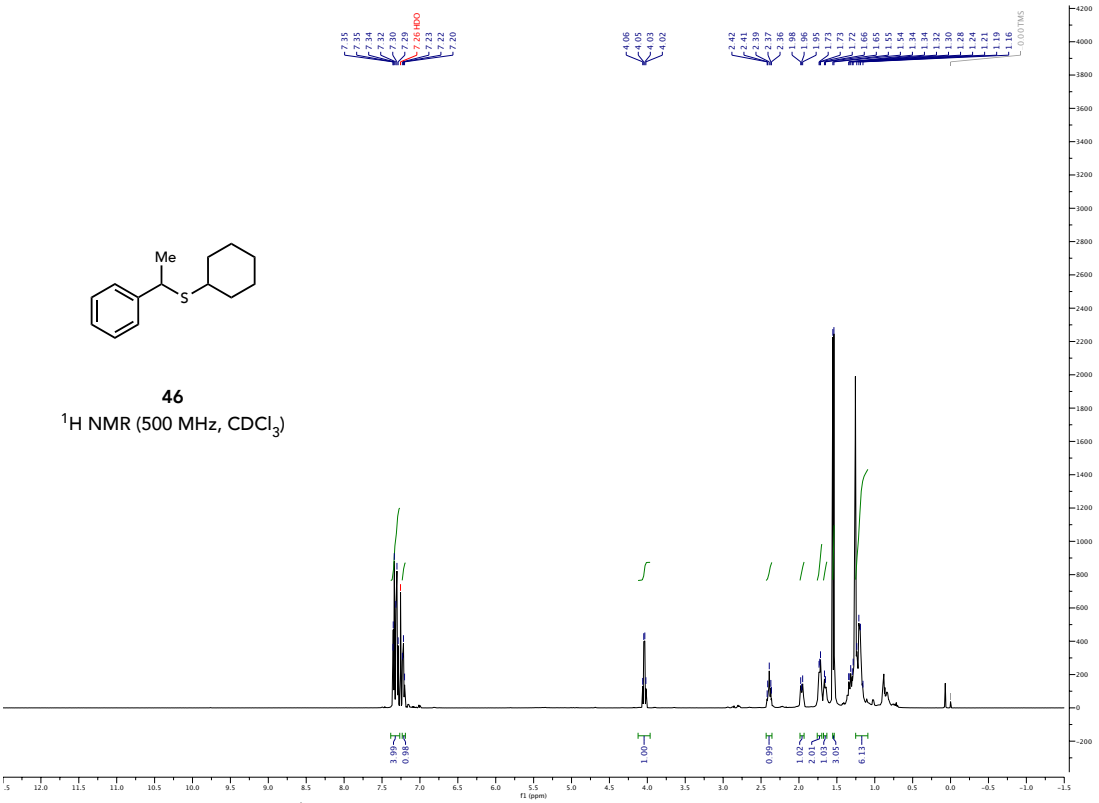


Figure S97. 500 MHz ^{1}H NMR spectrum of **46** in $CDCl_3$.

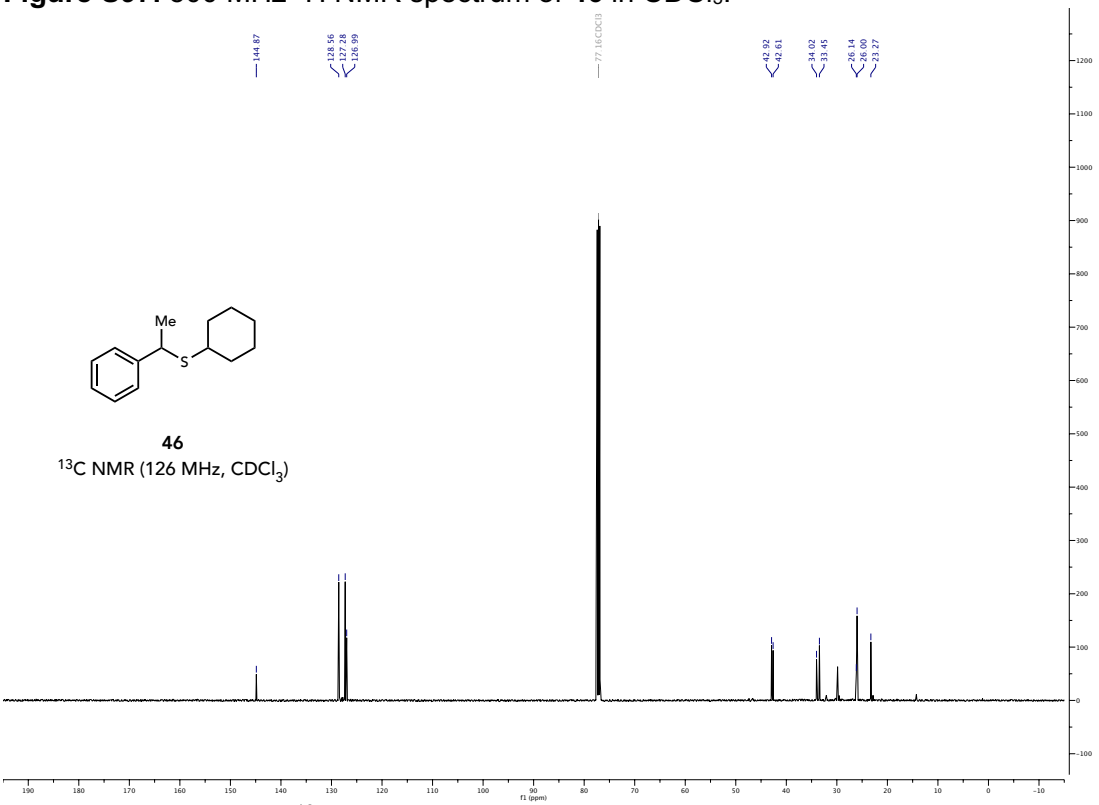


Figure S98. 126 MHz ^{13}C NMR spectrum of **46** in $CDCl_3$.

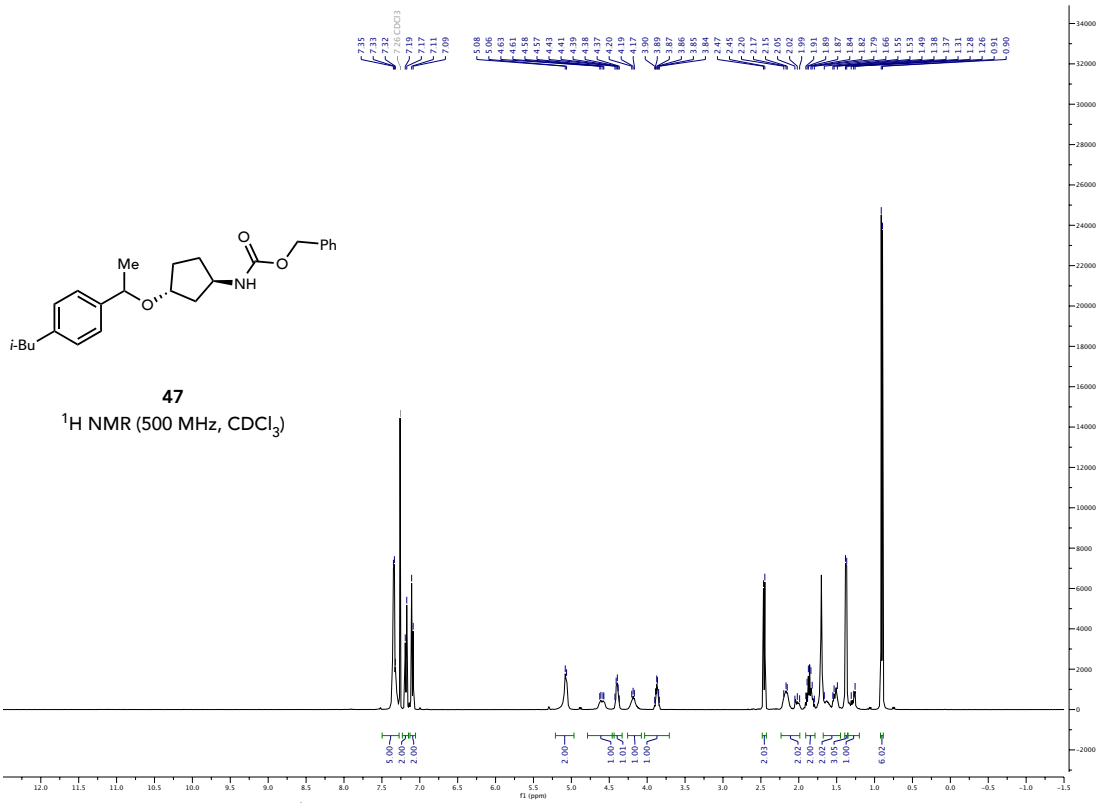


Figure S99. 500 MHz ^{1}H NMR spectrum of **47** in $CDCl_3$.

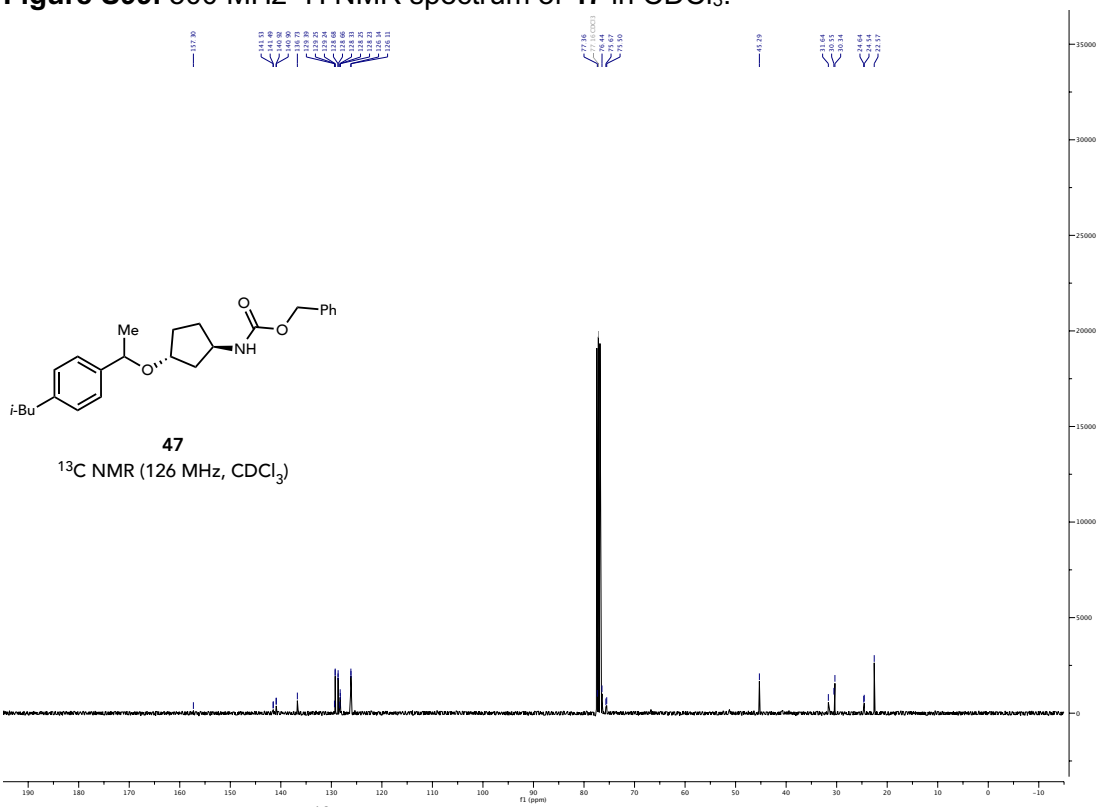


Figure S100. 126 MHz ^{13}C NMR spectrum of **47** in $CDCl_3$.

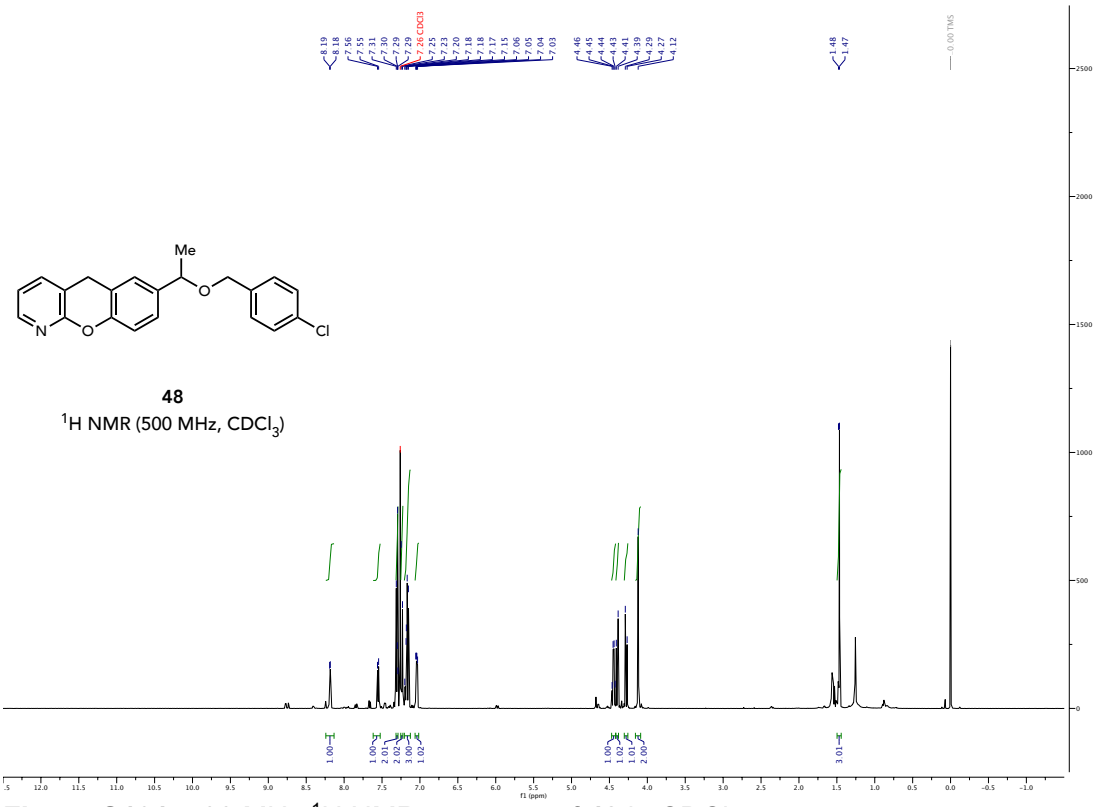


Figure S101. 500 MHz ^{1}H NMR spectrum of **48** in $CDCl_3$.

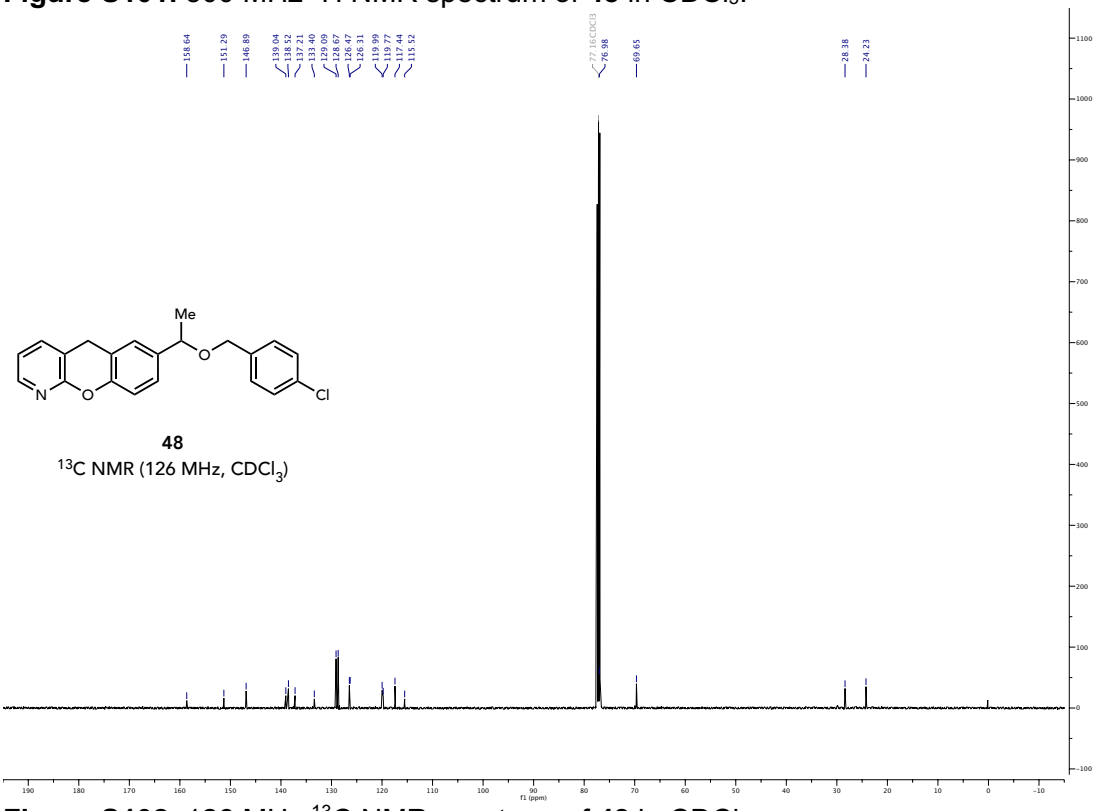


Figure S102. 126 MHz ^{13}C NMR spectrum of **48** in $CDCl_3$.

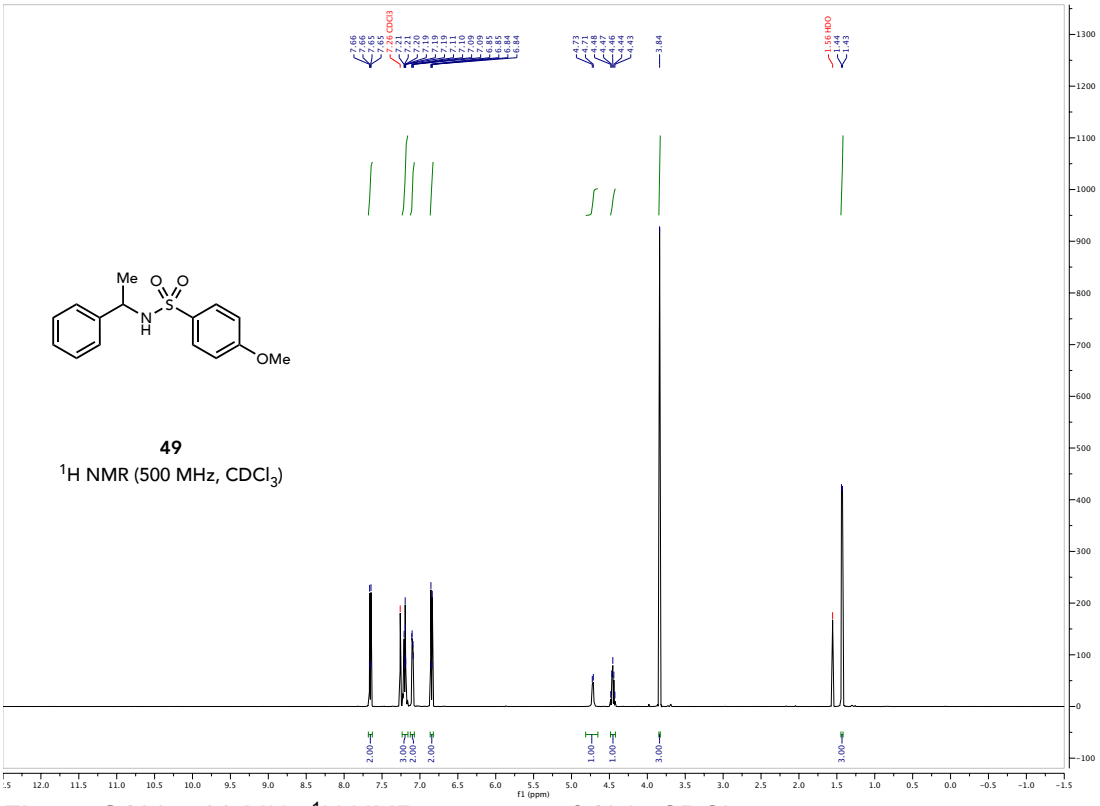


Figure S103. 500 MHz ^{1}H NMR spectrum of **49** in $CDCl_3$.

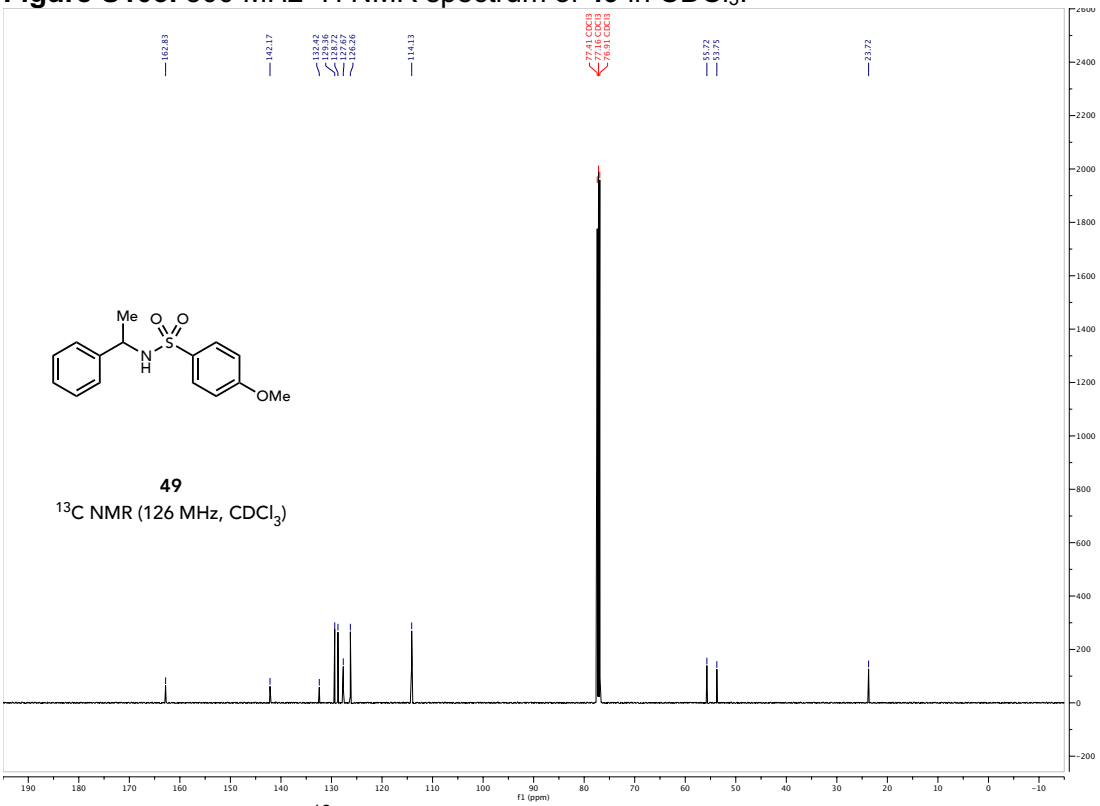


Figure S104. 126 MHz ^{13}C NMR spectrum of **49** in $CDCl_3$.

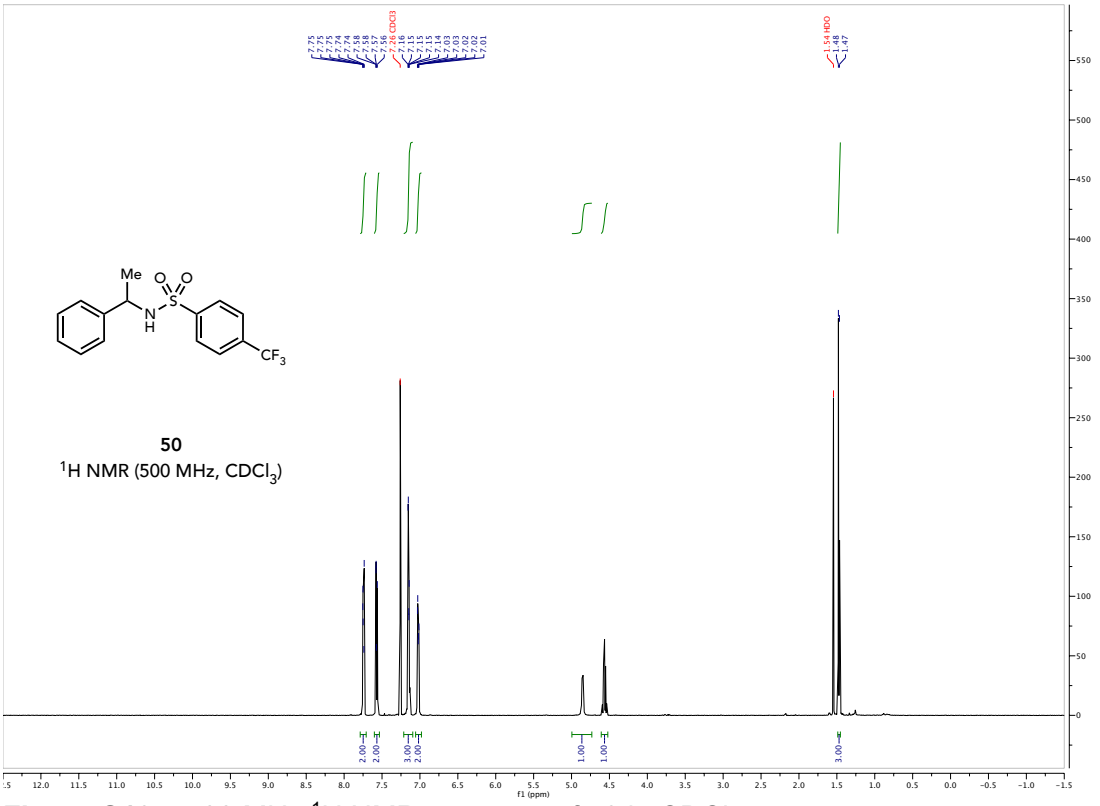


Figure S105. 500 MHz ^{1}H NMR spectrum of **50** in $CDCl_3$.

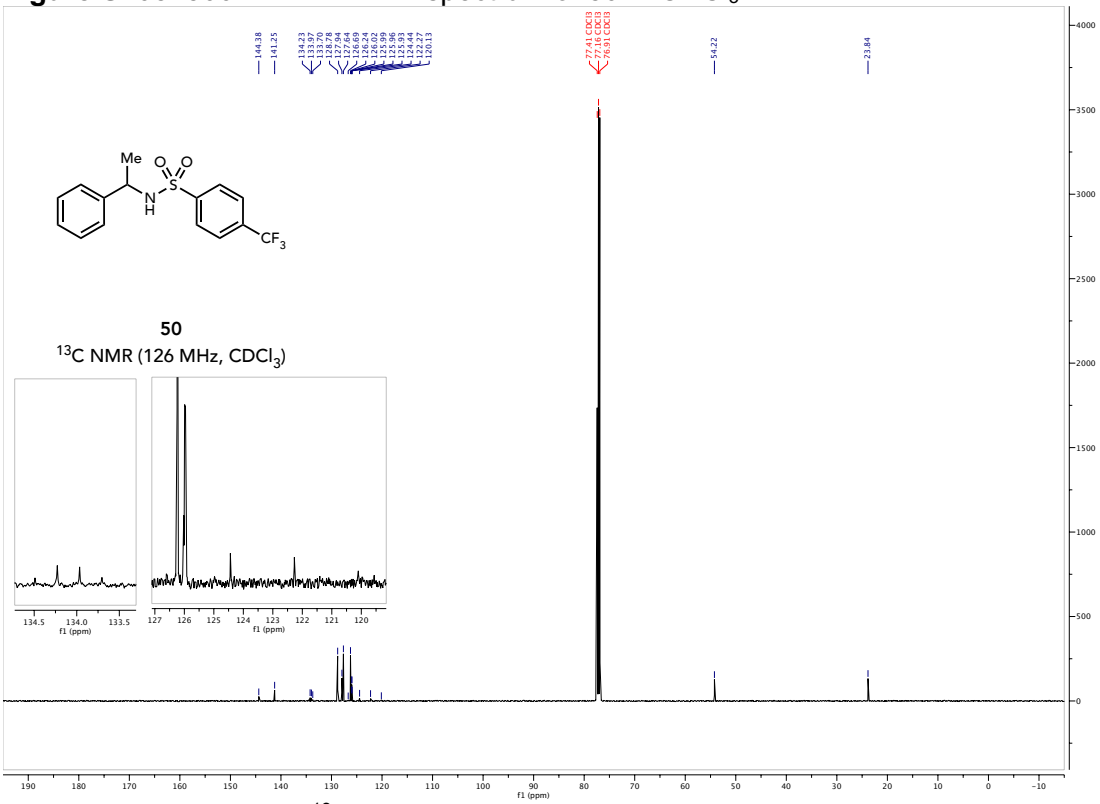


Figure S106. 126 MHz ^{13}C NMR spectrum of **50** in $CDCl_3$.

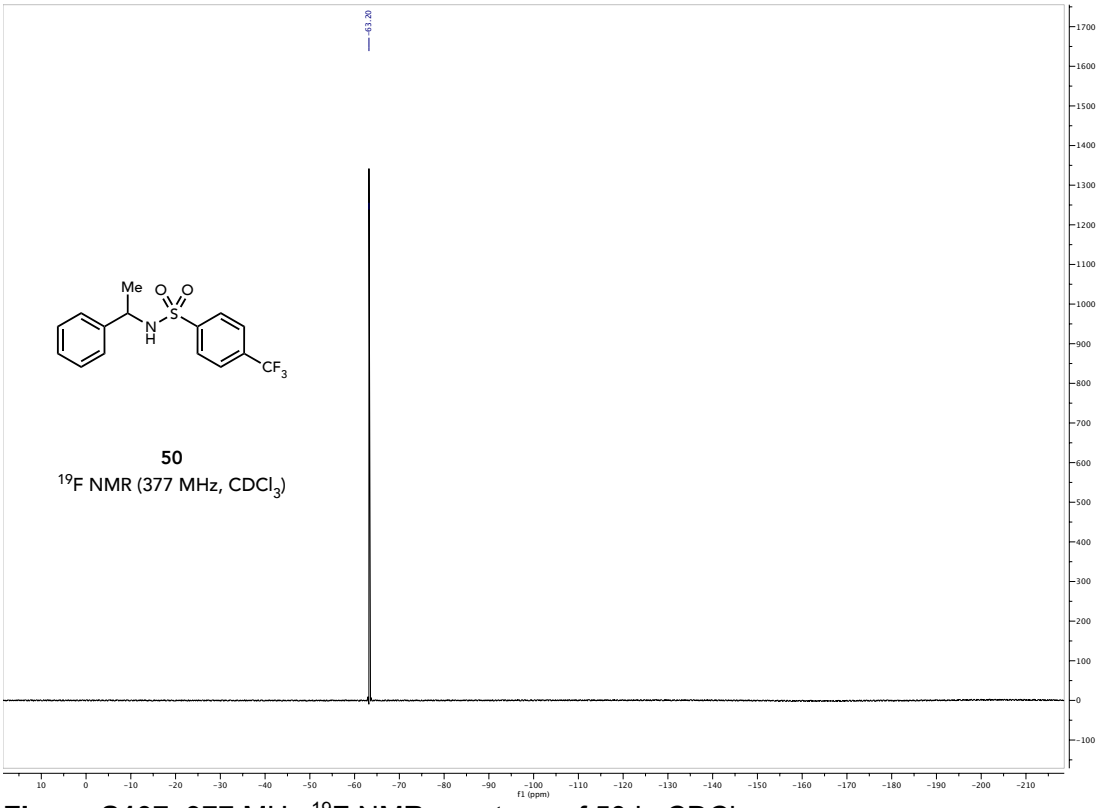


Figure S107. 377 MHz ^{19}F NMR spectrum of **50** in $CDCl_3$.

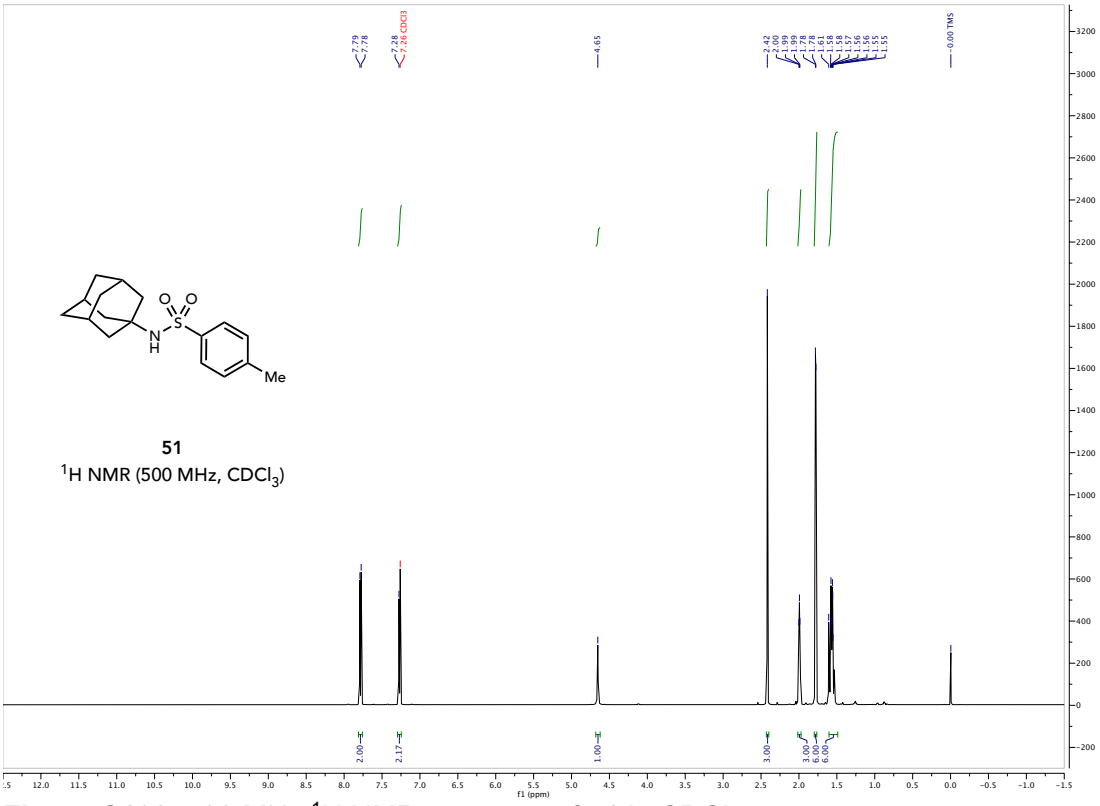


Figure S108. 500 MHz ^{1}H NMR spectrum of **51** in $CDCl_3$.

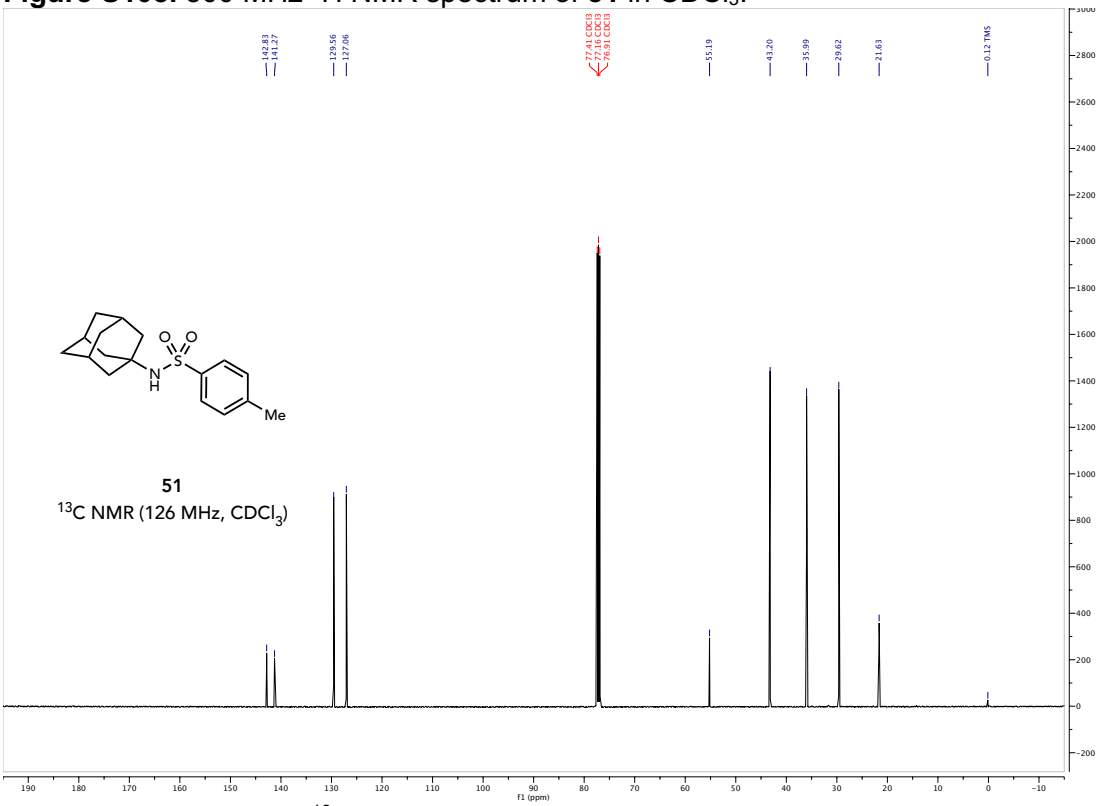


Figure S109. 126 MHz ^{13}C NMR spectrum of **51** in $CDCl_3$.

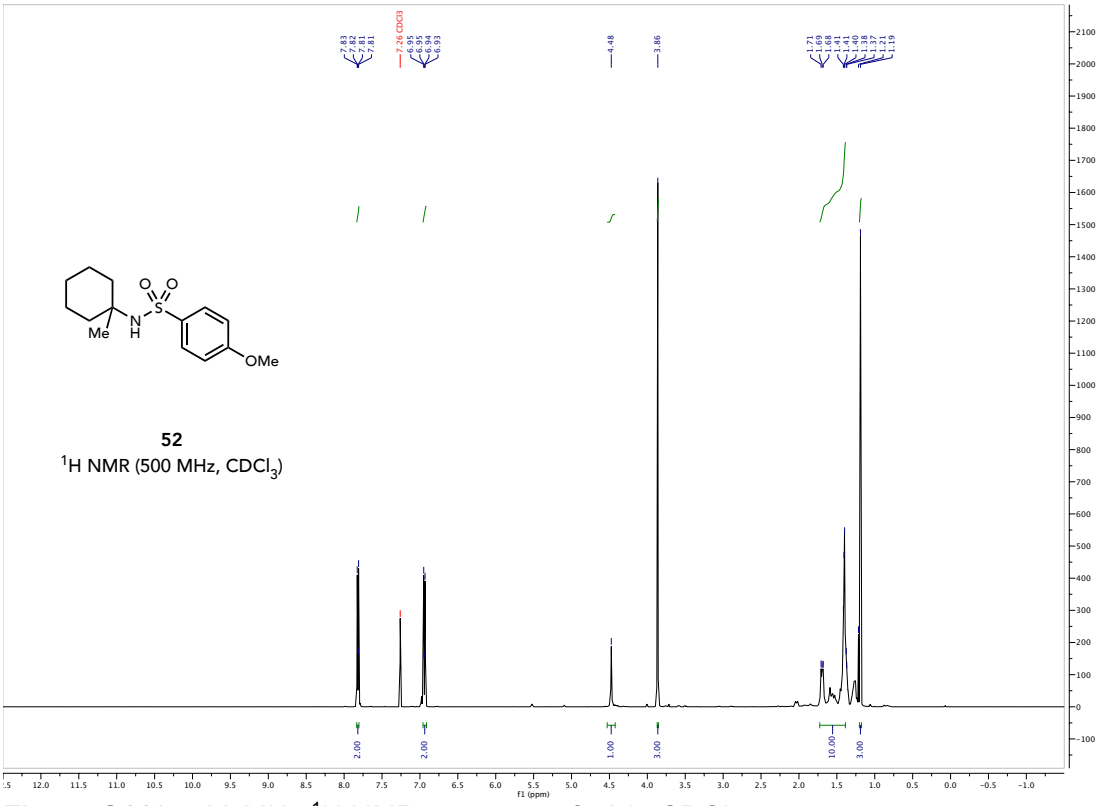


Figure S110. 500 MHz ^{1}H NMR spectrum of **52** in $CDCl_3$.

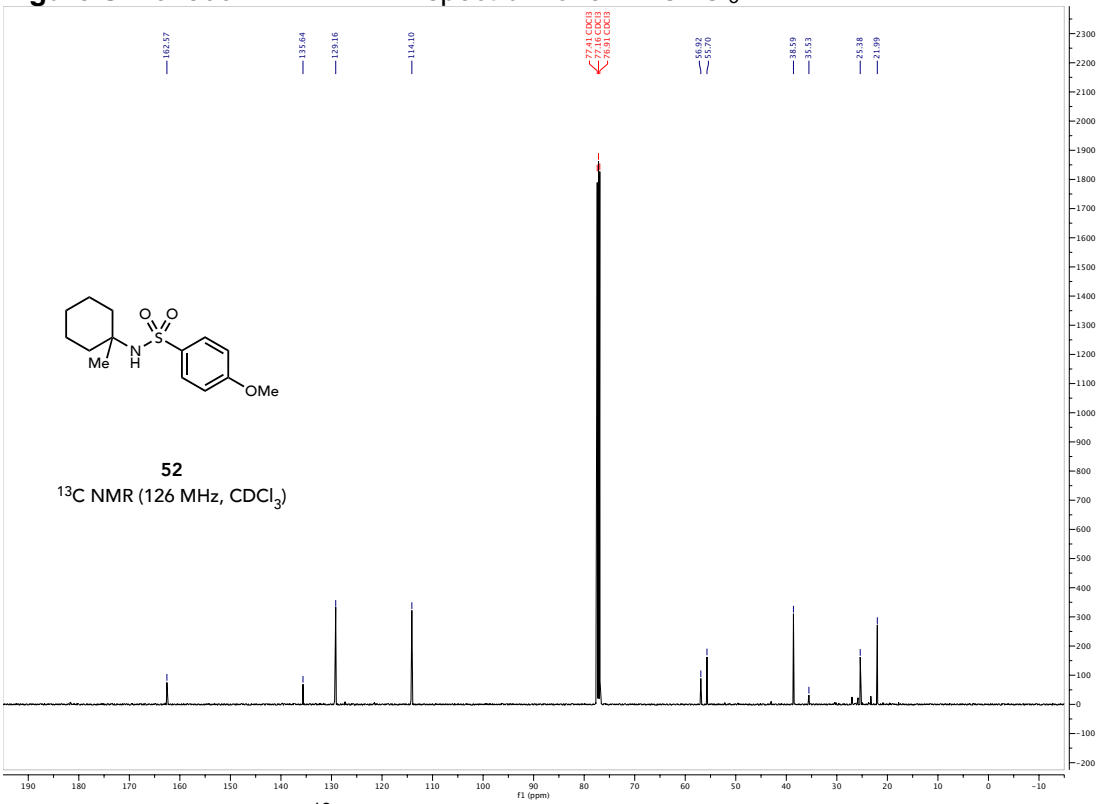


Figure S111. 126 MHz ^{13}C NMR spectrum of **52** in $CDCl_3$.

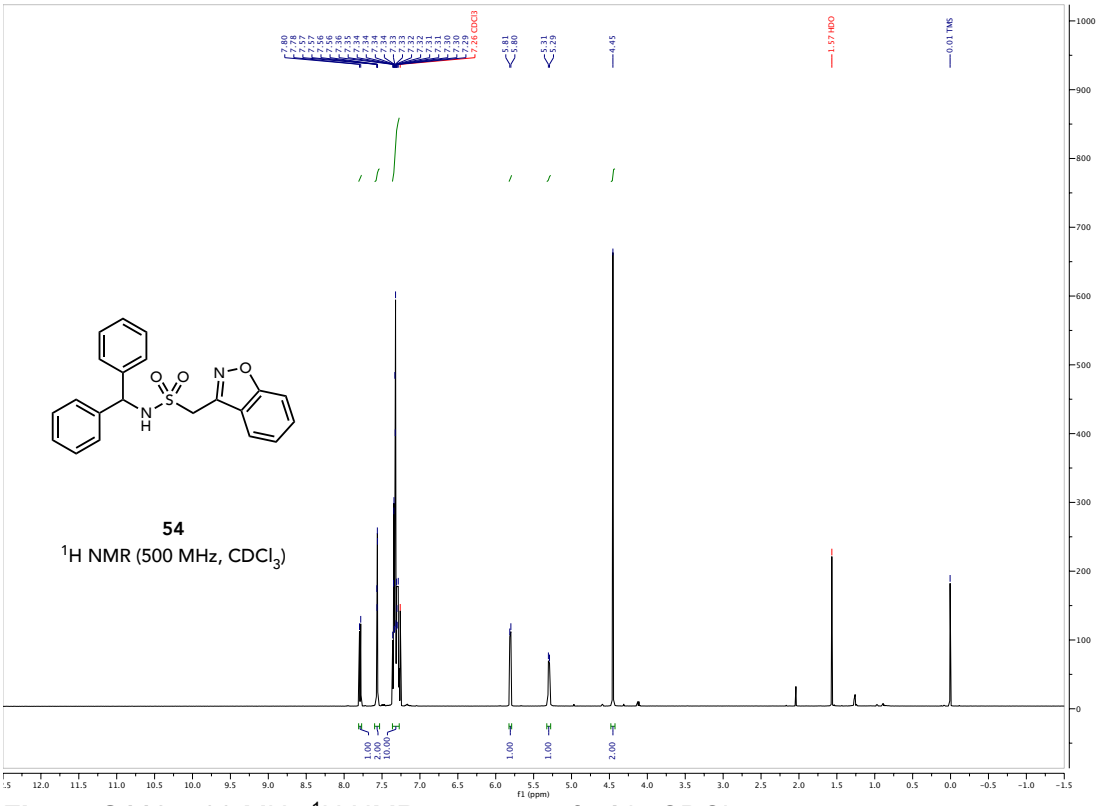


Figure S112. 500 MHz ^{1}H NMR spectrum of **54** in $CDCl_3$.

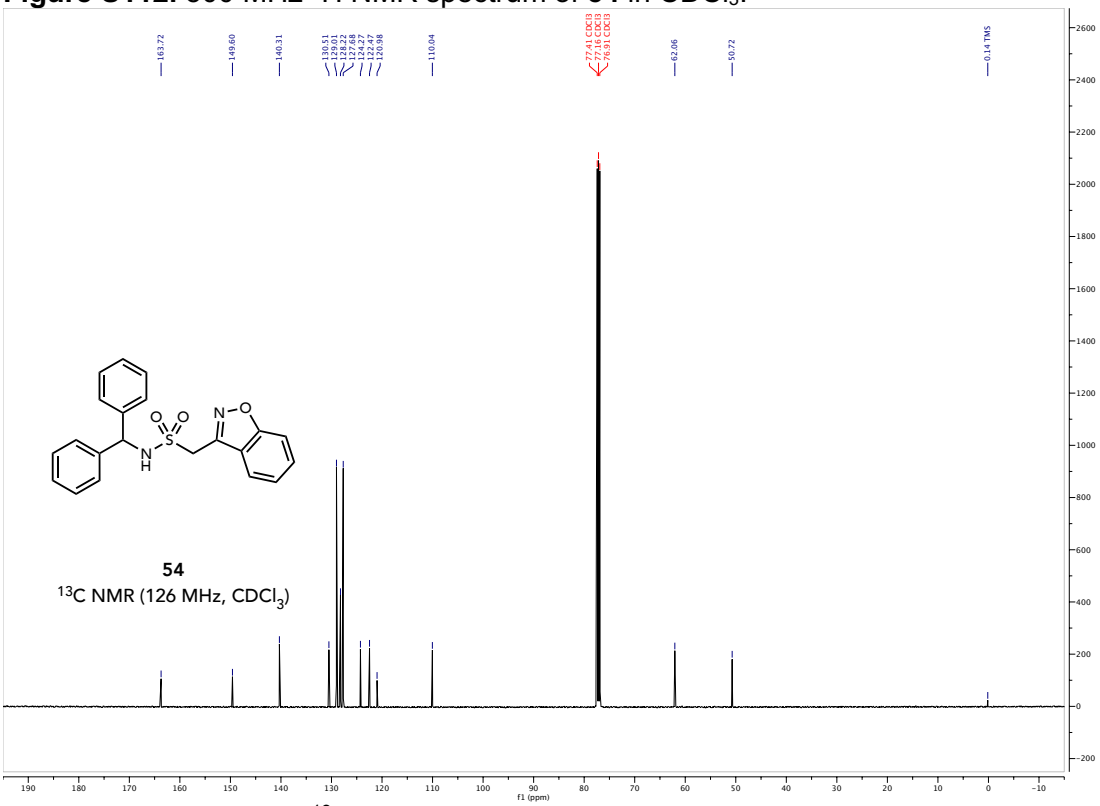


Figure S113. 126 MHz ^{13}C NMR spectrum of **54** in $CDCl_3$.

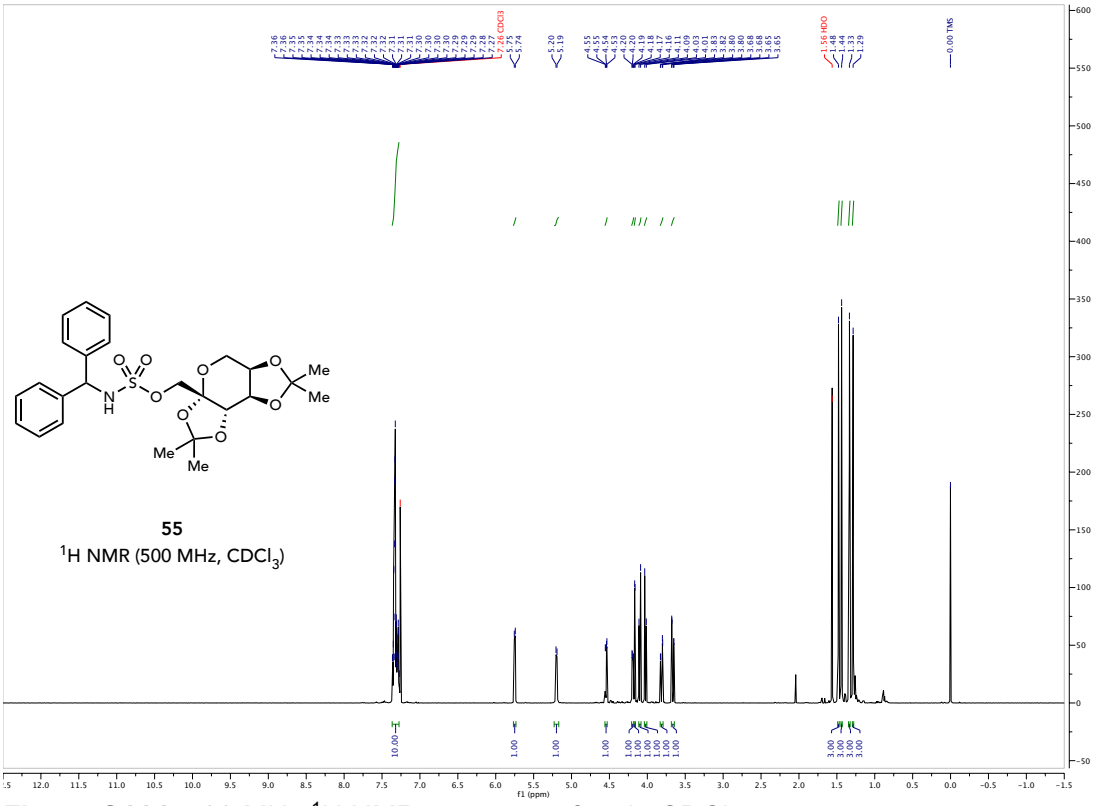


Figure S114. 500 MHz ^{1}H NMR spectrum of **55** in $CDCl_3$.

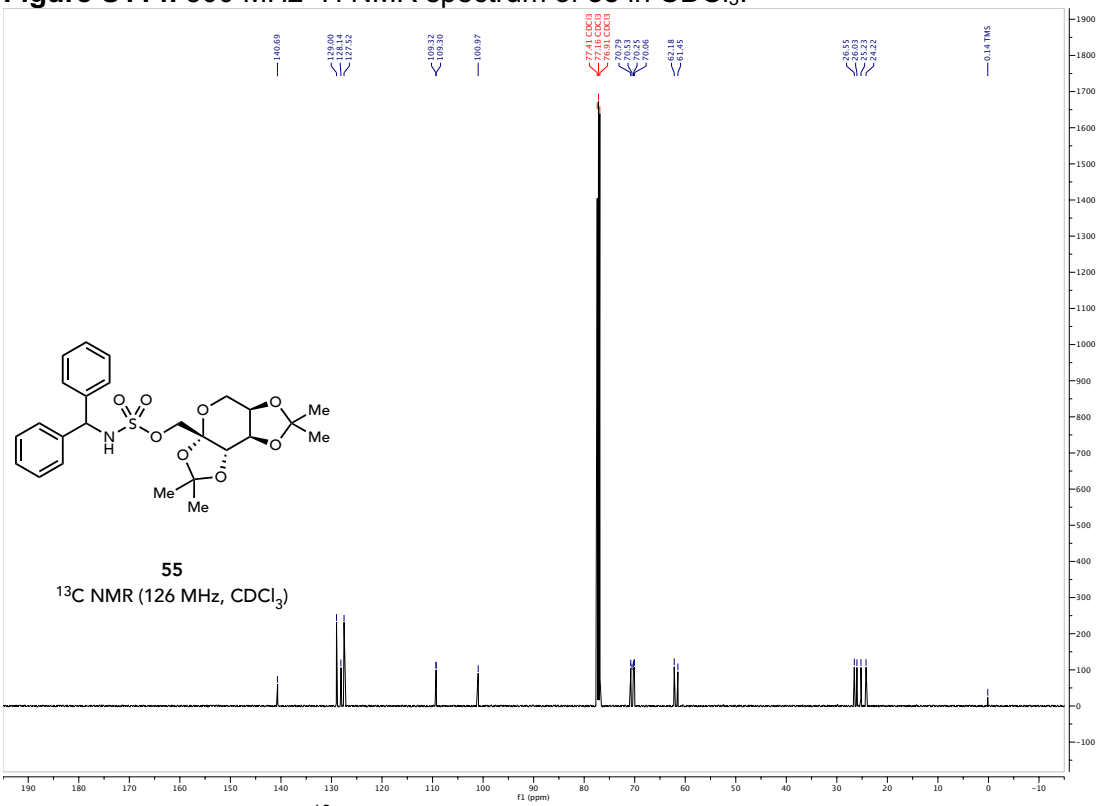


Figure S115. 126 MHz ^{13}C NMR spectrum of **55** in $CDCl_3$.

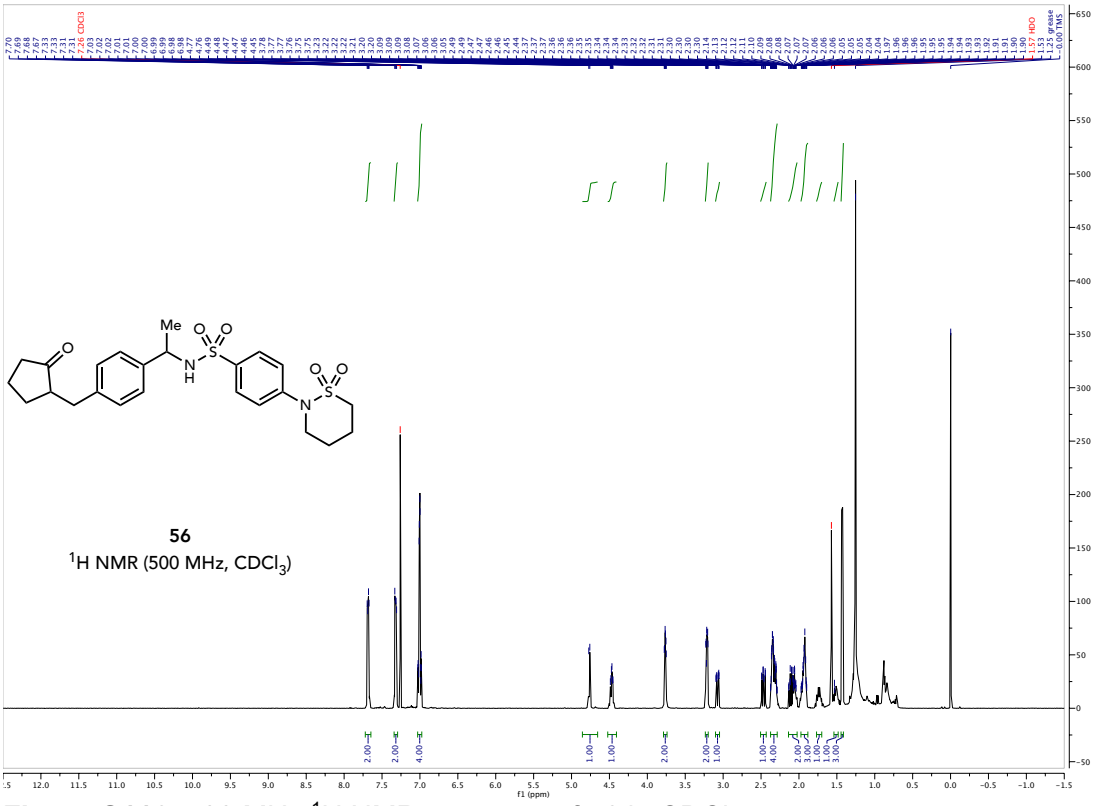


Figure S116. 500 MHz ^{1}H NMR spectrum of **56** in $CDCl_3$.

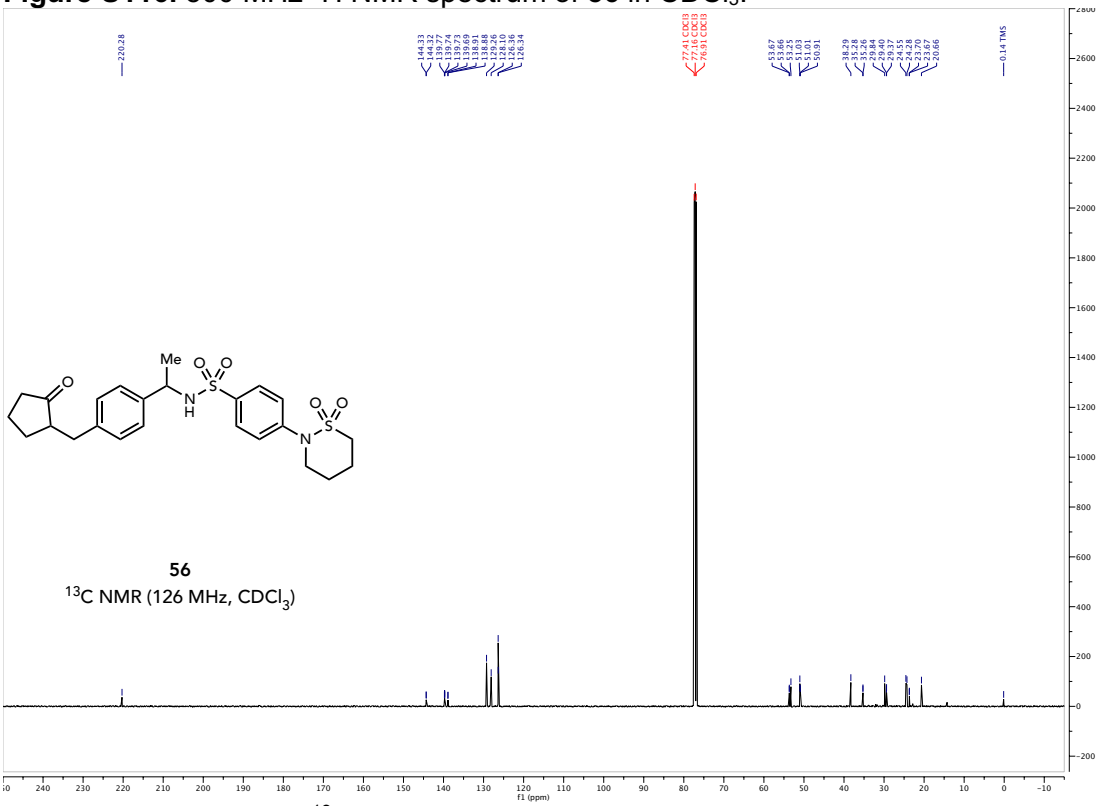


Figure S117. 126 MHz ^{13}C NMR spectrum of **56** in $CDCl_3$.

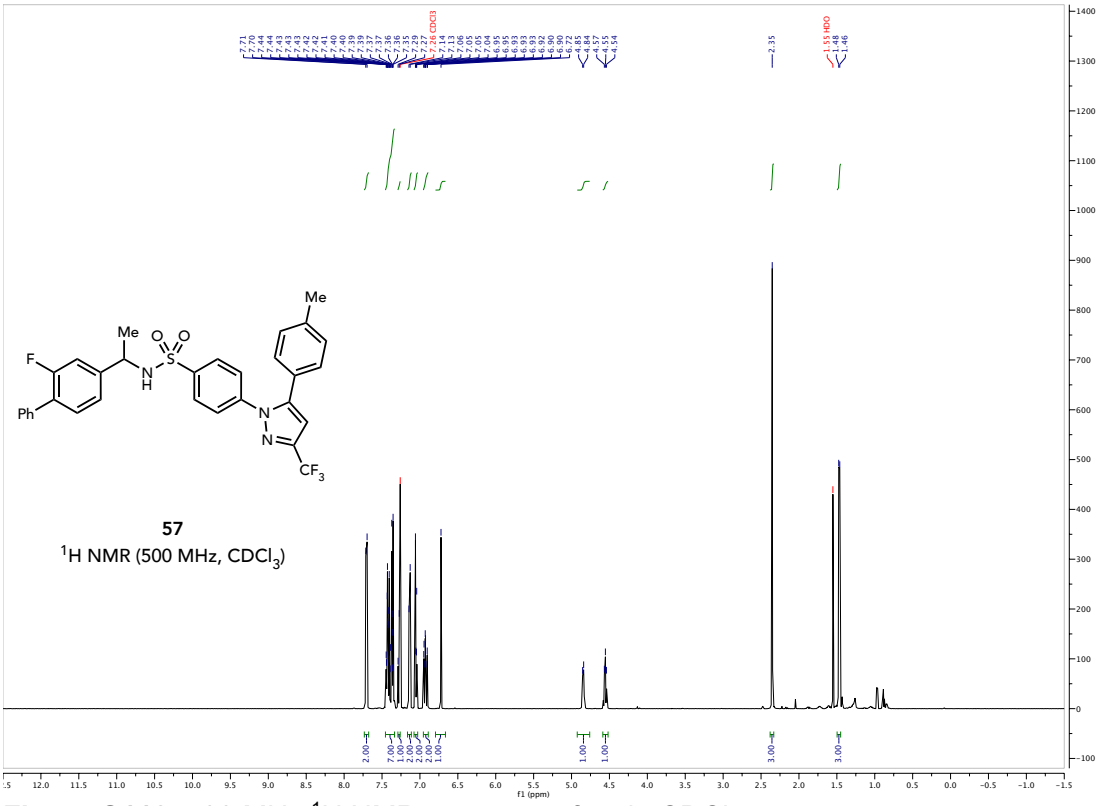


Figure S118. 500 MHz ^{1}H NMR spectrum of **57** in $CDCl_3$.

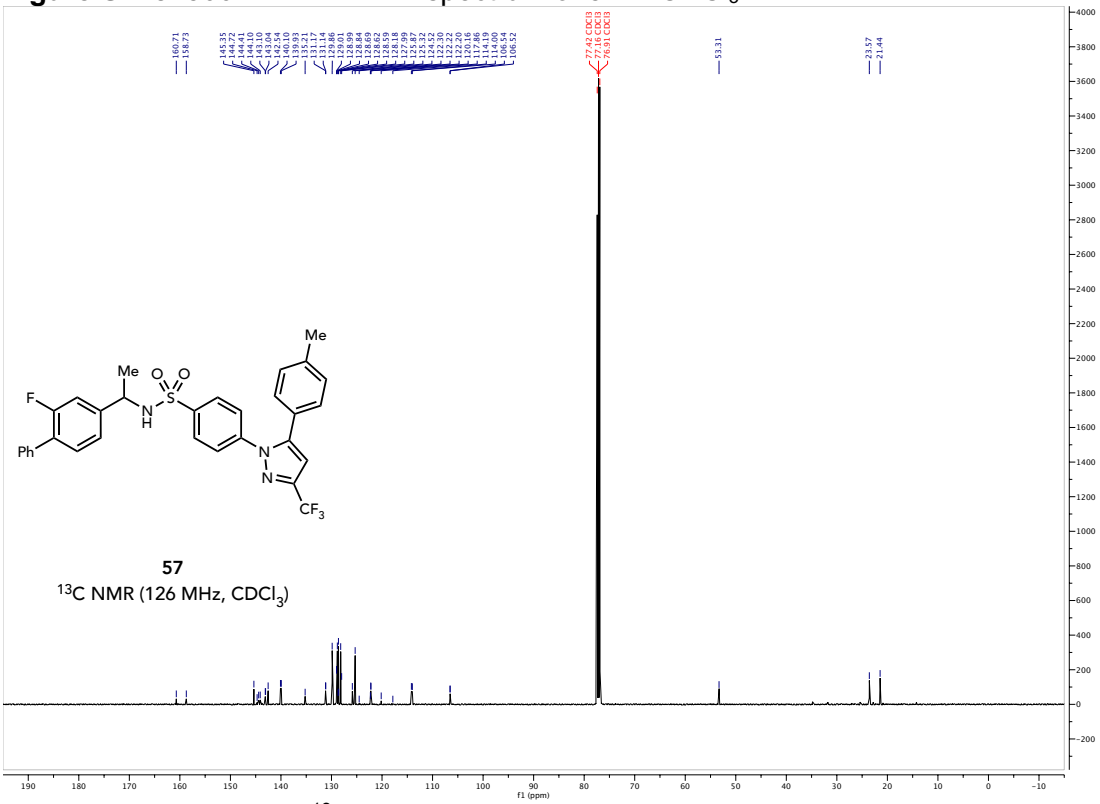


Figure S119. 126 MHz ^{13}C NMR spectrum of **57** in $CDCl_3$.

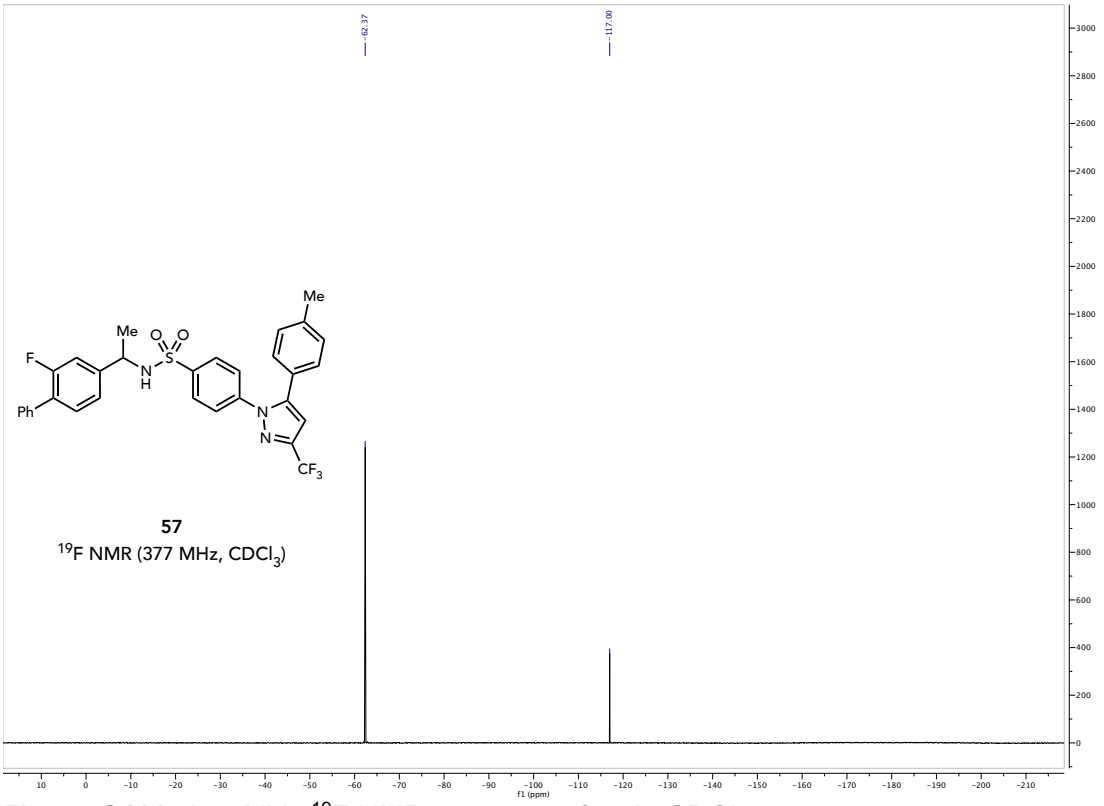


Figure S120. 377 MHz ^{19}F NMR spectrum of **57** in $CDCl_3$.

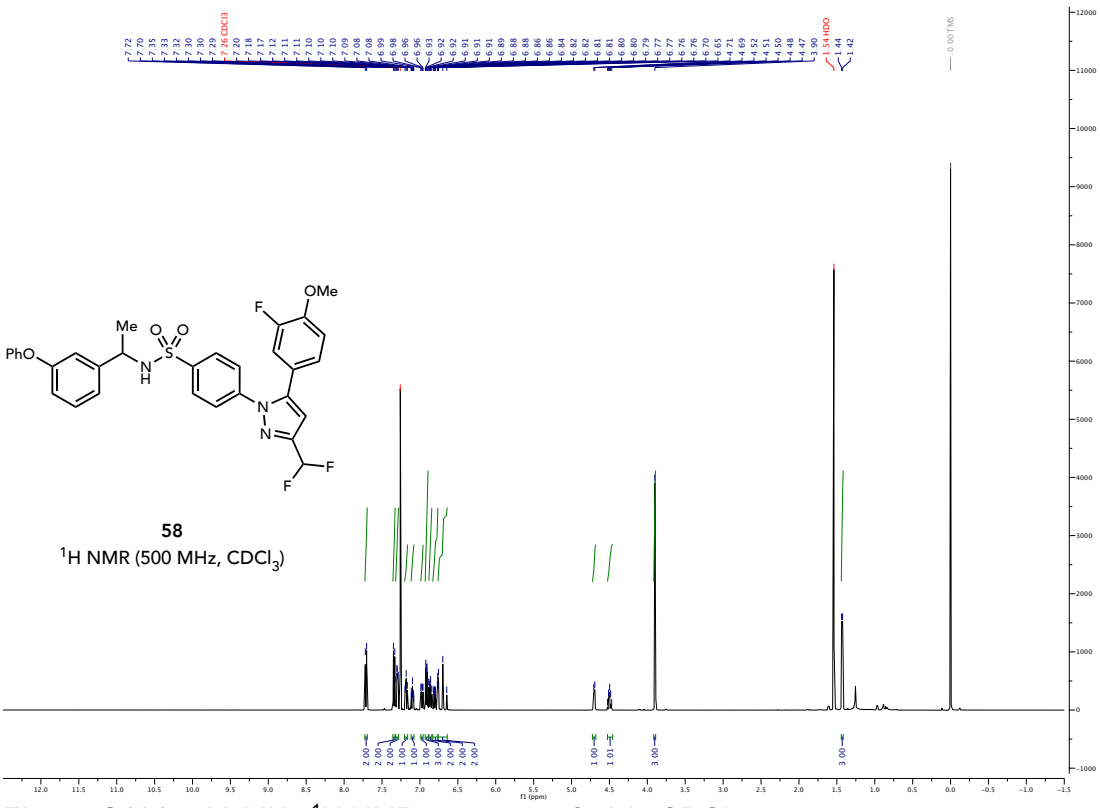


Figure S121. 500 MHz ^{1}H NMR spectrum of **58** in $CDCl_3$.

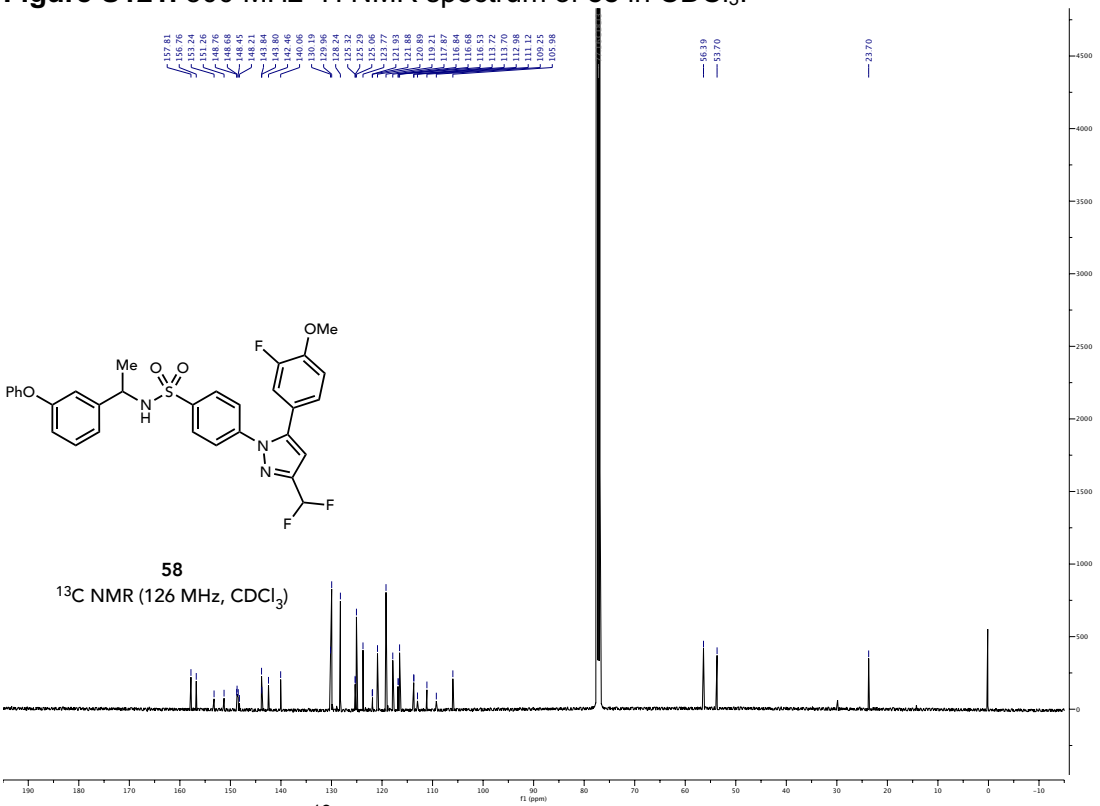


Figure S122. 126 MHz ^{13}C NMR spectrum of **58** in $CDCl_3$.

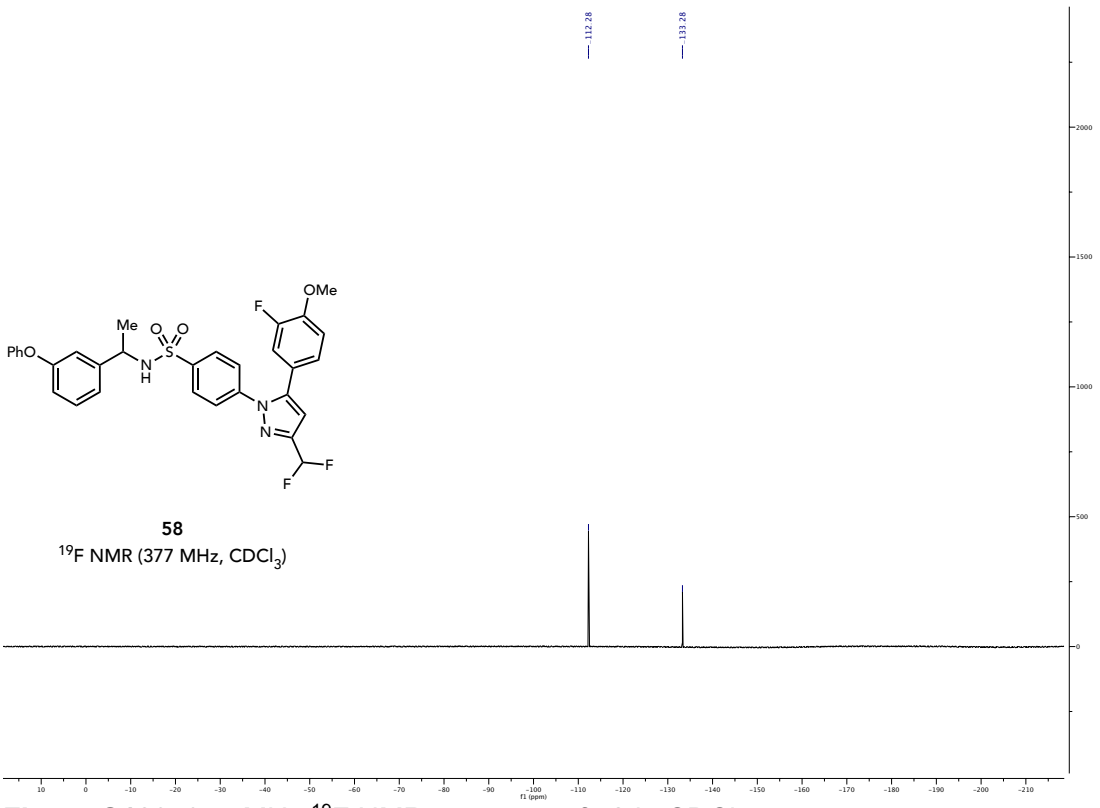


Figure S123. 377 MHz ^{19}F NMR spectrum of **58** in $CDCl_3$.

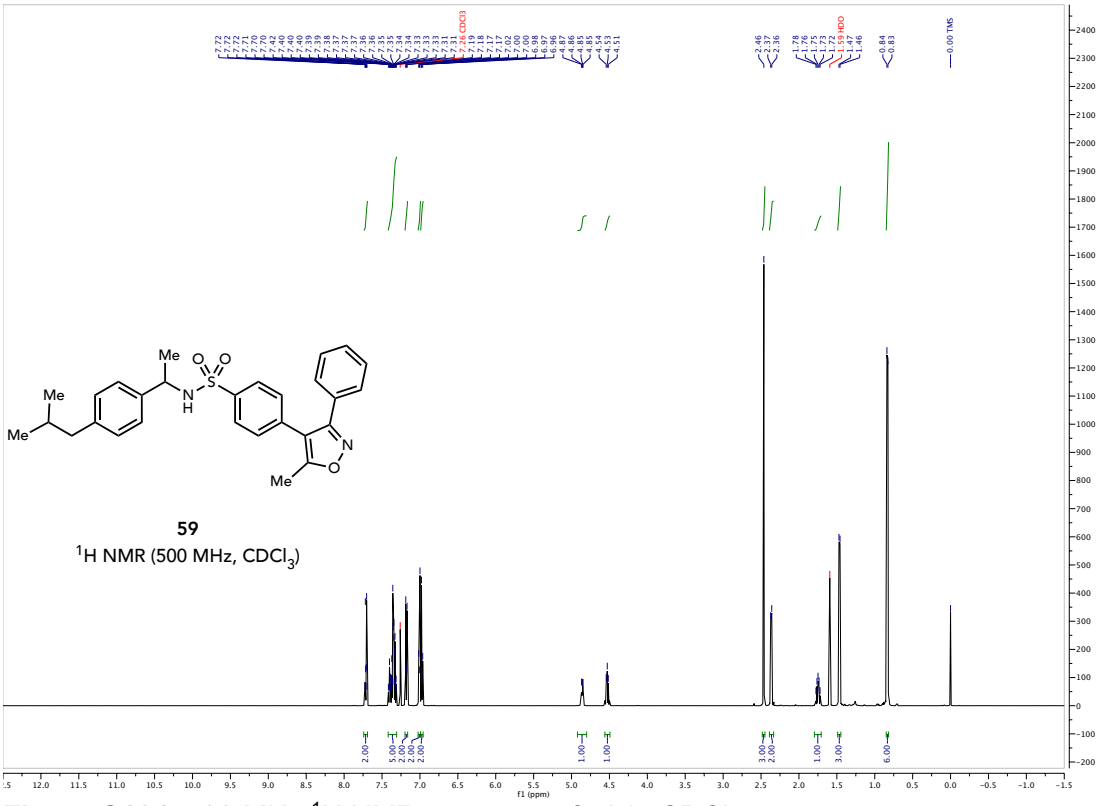


Figure S124. 500 MHz ^{1}H NMR spectrum of **59** in $CDCl_3$.

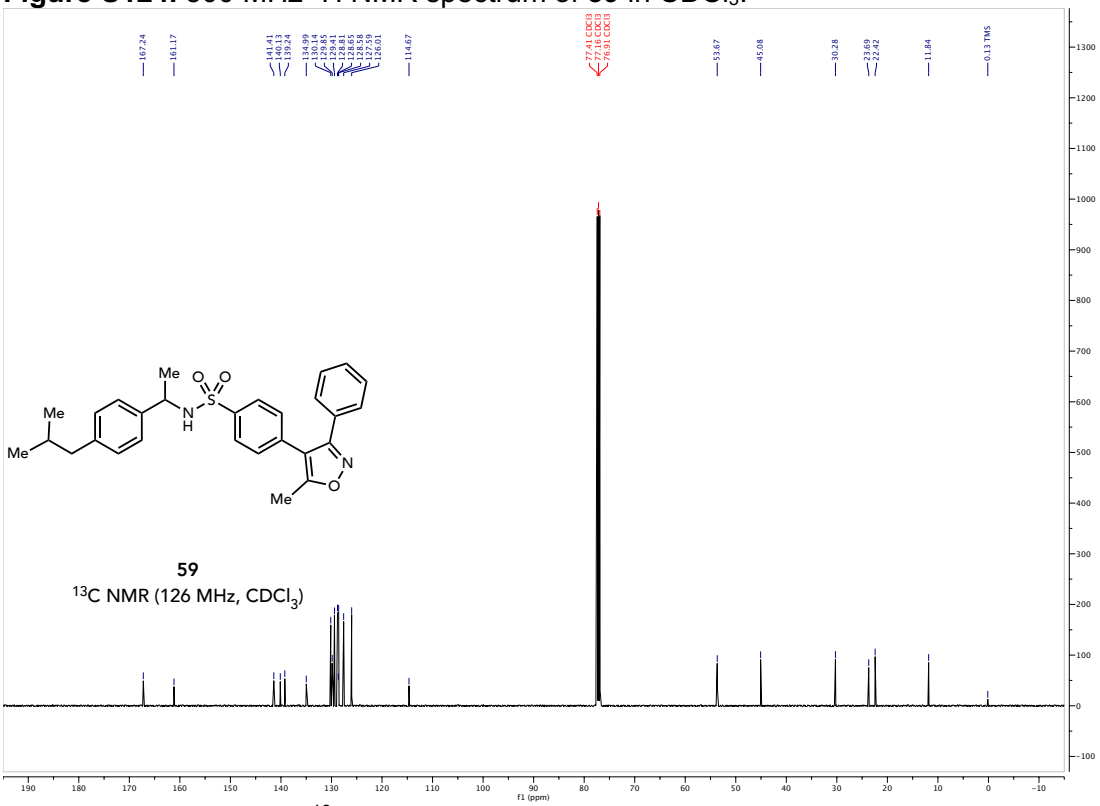


Figure S125. 126 MHz ^{13}C NMR spectrum of **59** in $CDCl_3$.

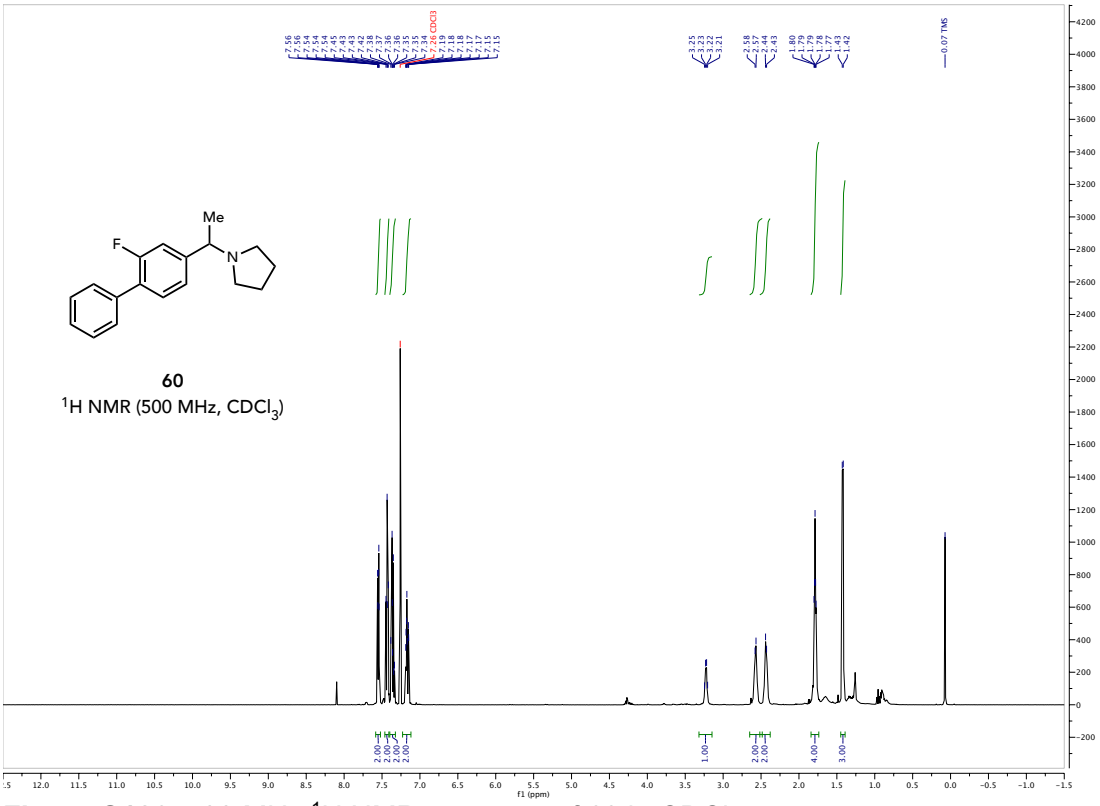


Figure S126. 500 MHz ^{1}H NMR spectrum of **60** in $CDCl_3$.

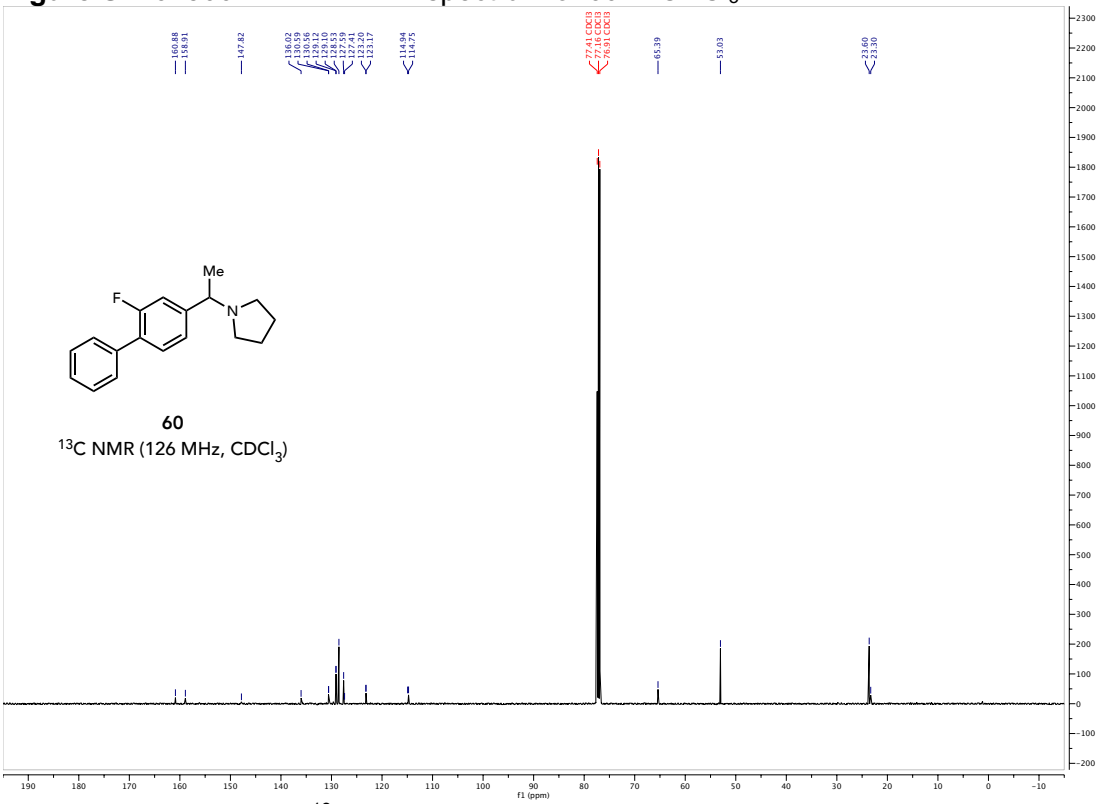


Figure S127. 126 MHz ^{13}C NMR spectrum of **60** in $CDCl_3$.

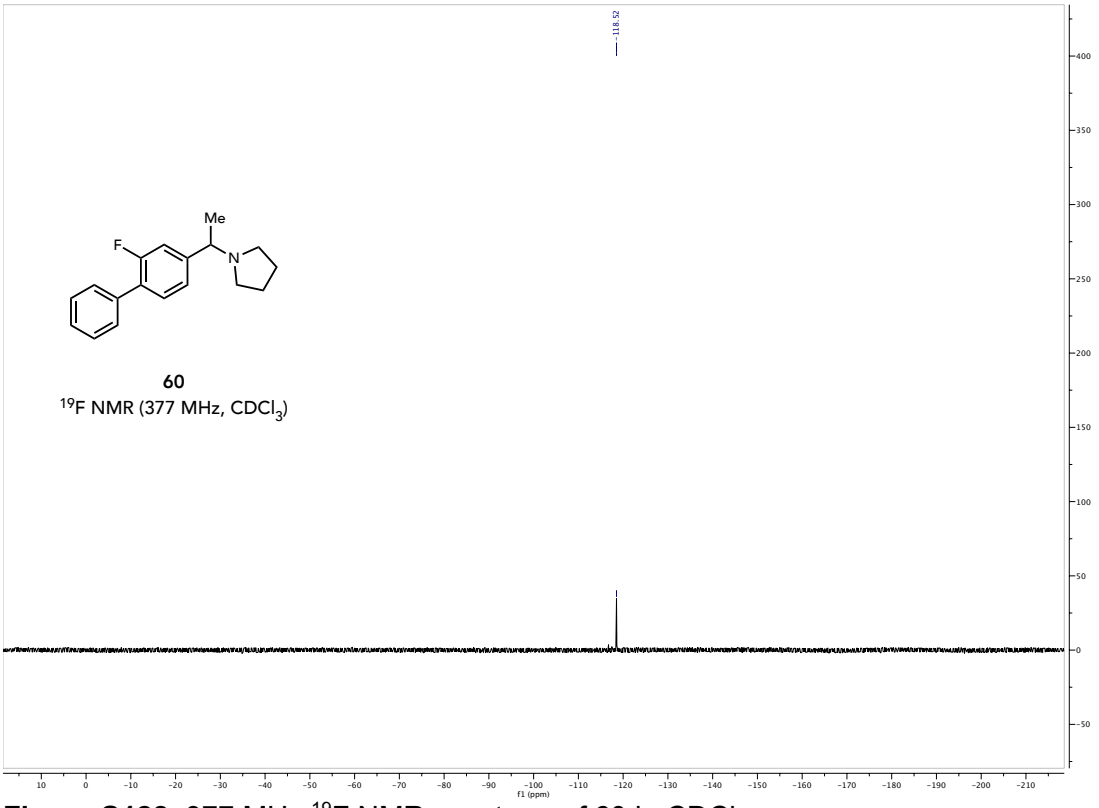


Figure S128. 377 MHz ^{19}F NMR spectrum of **60** in $CDCl_3$.

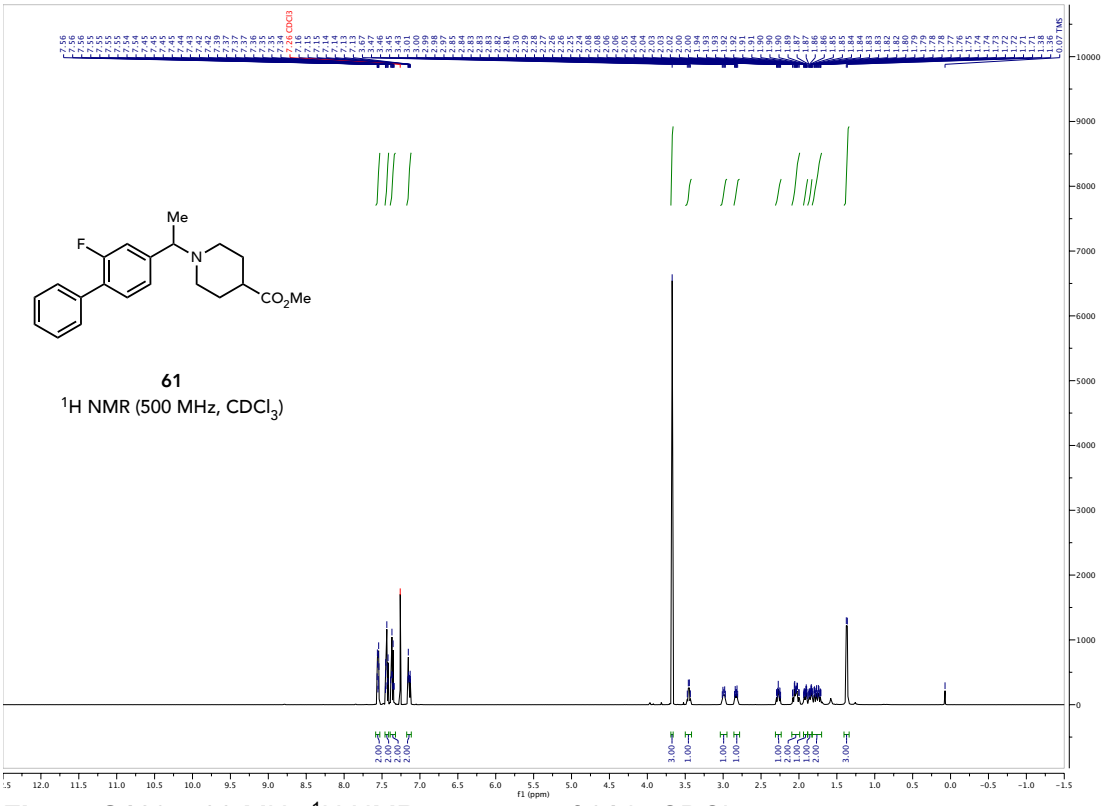


Figure S129. 500 MHz ^{1}H NMR spectrum of **61** in $CDCl_3$.

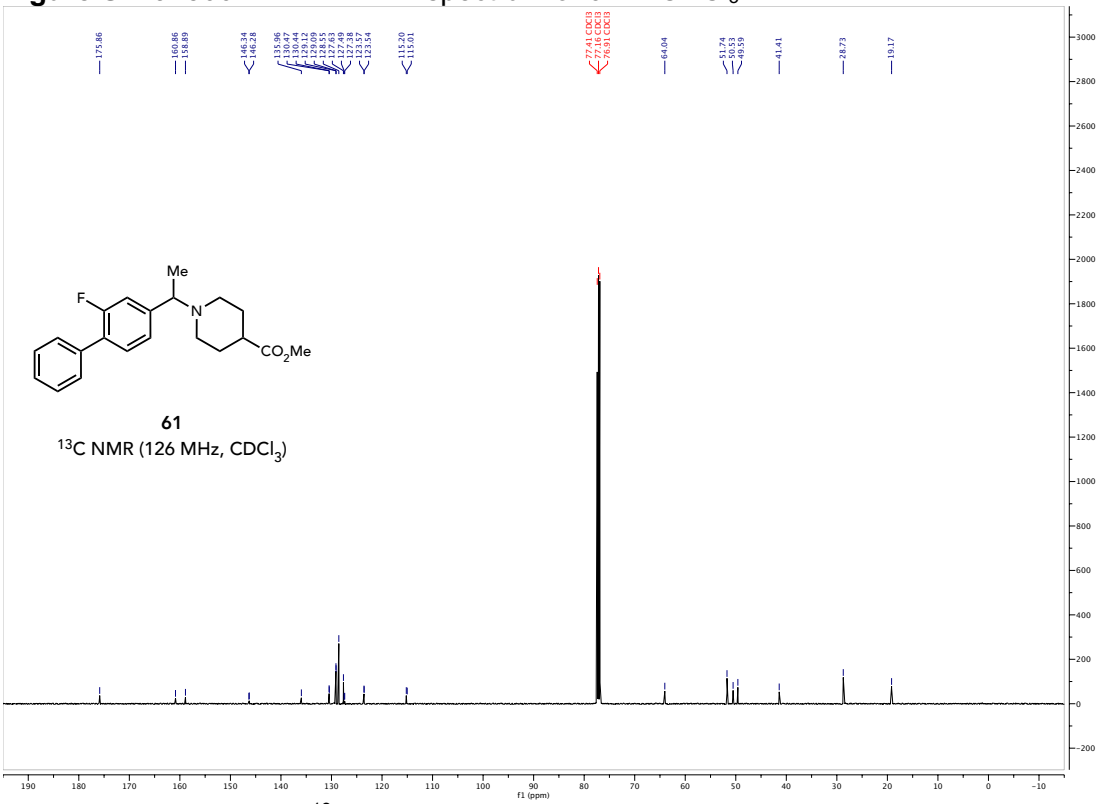


Figure S130. 126 MHz ^{13}C NMR spectrum of **61** in $CDCl_3$.

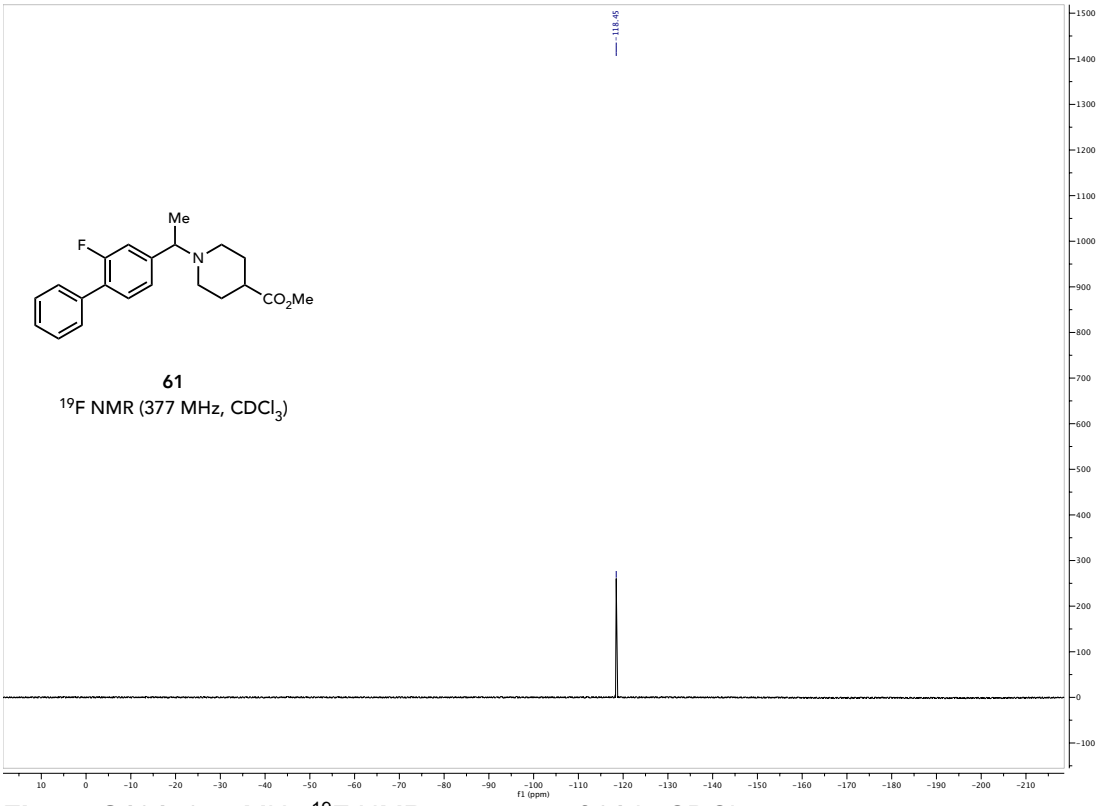


Figure S131. 377 MHz ^{19}F NMR spectrum of **61** in $CDCl_3$.

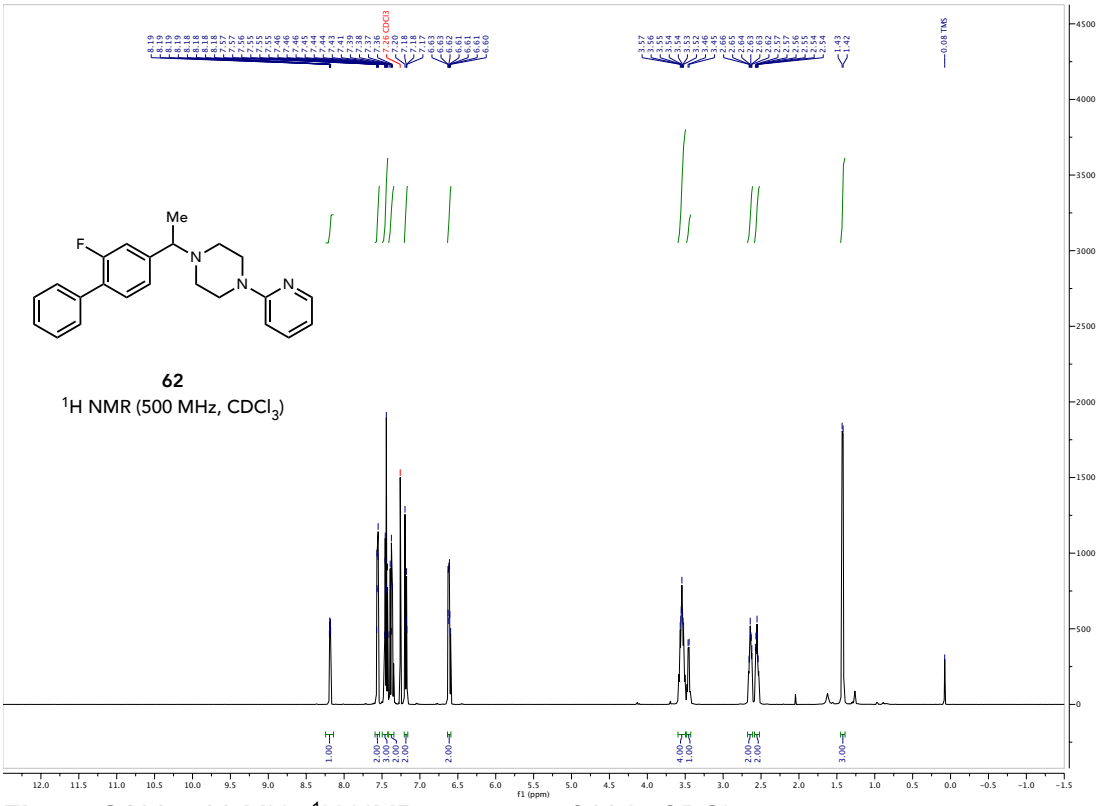


Figure S132. 500 MHz ^{1}H NMR spectrum of **62** in $CDCl_3$.

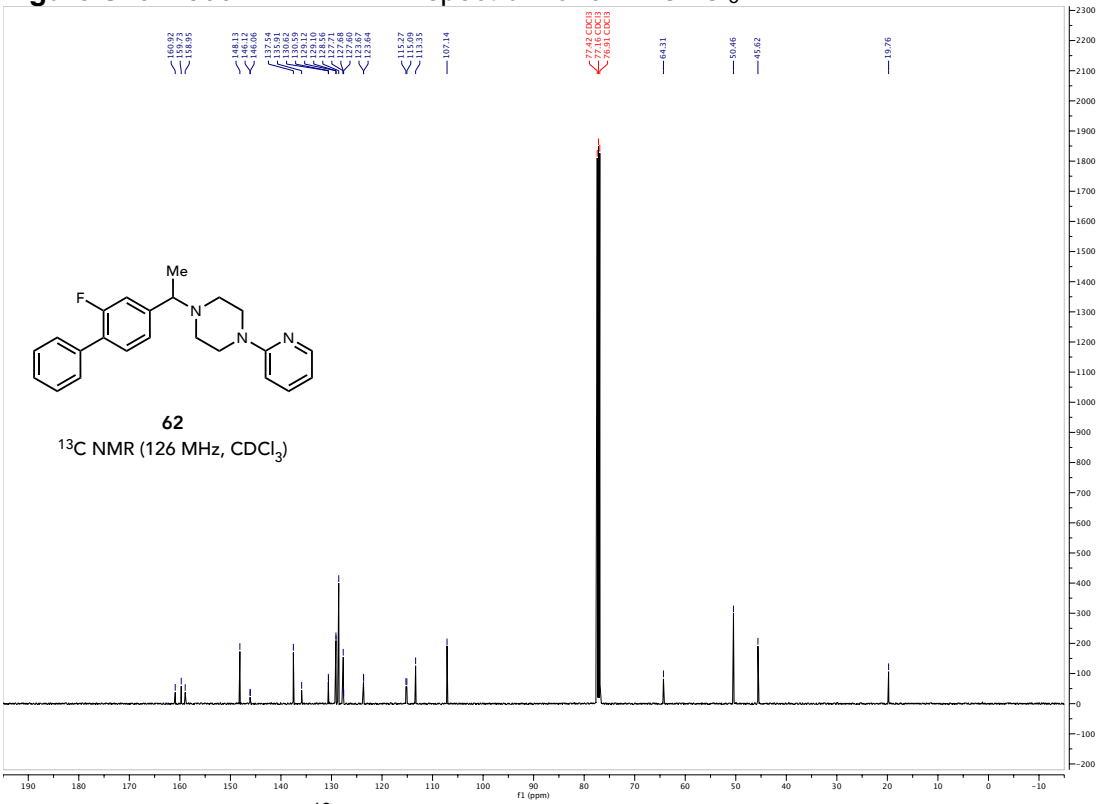


Figure S133. 126 MHz ^{13}C NMR spectrum of **62** in $CDCl_3$.

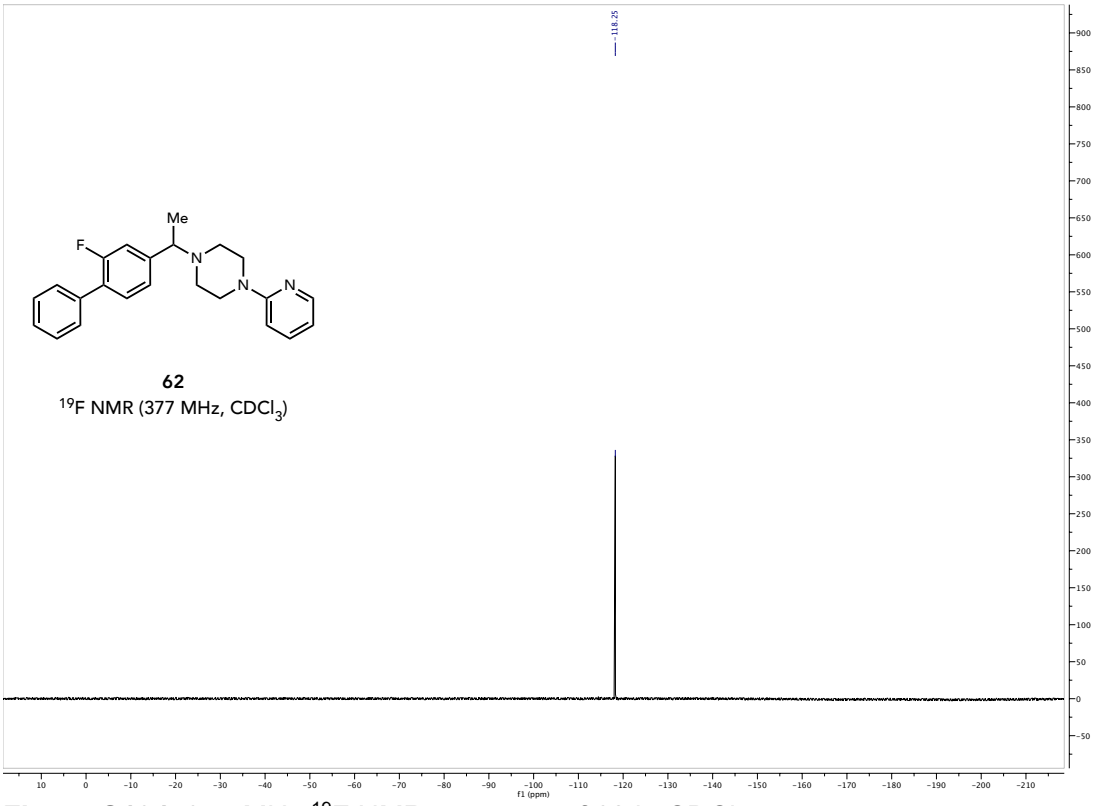


Figure S134. 377 MHz ^{19}F NMR spectrum of **62** in $CDCl_3$.

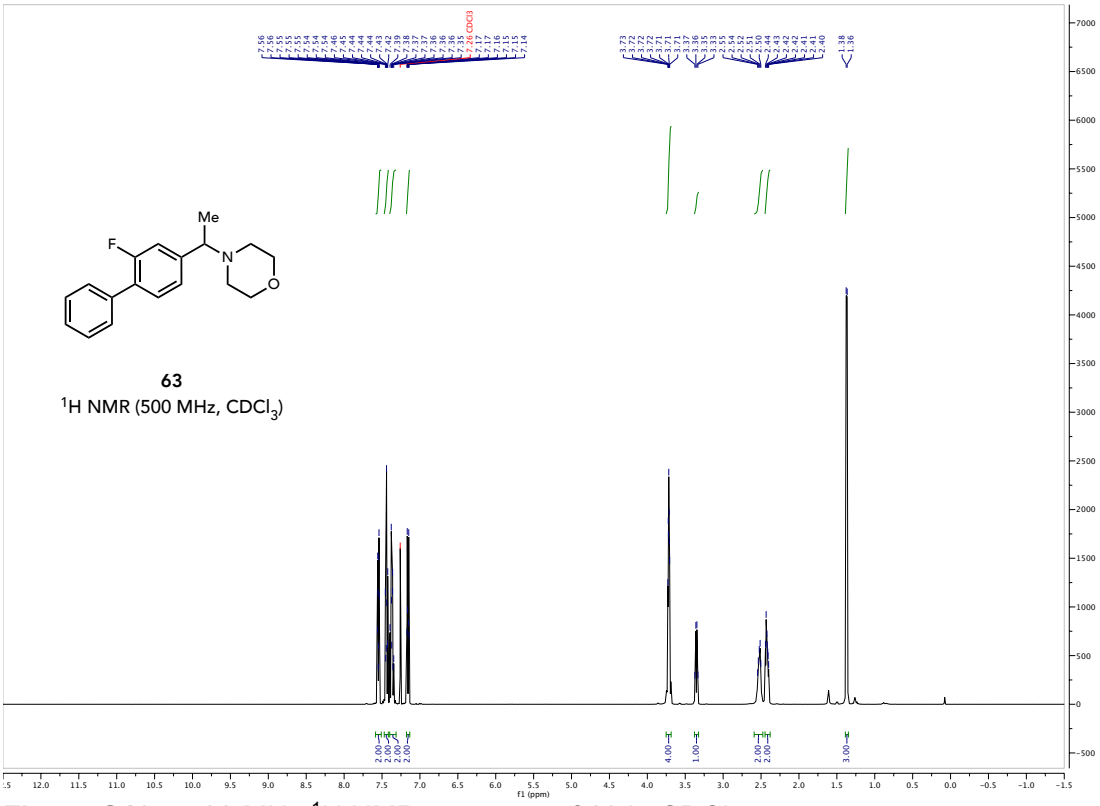


Figure S135. 500 MHz ^{1}H NMR spectrum of **63** in $CDCl_3$.

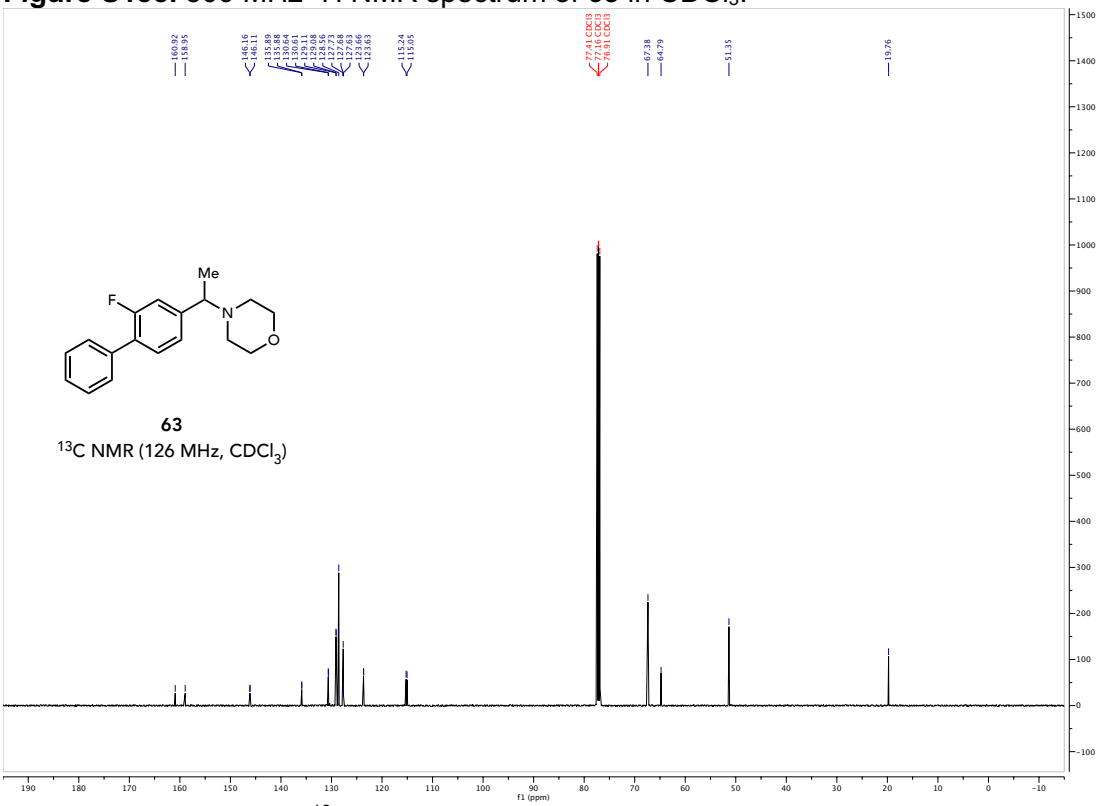


Figure S136. 126 MHz ^{13}C NMR spectrum of **63** in $CDCl_3$.

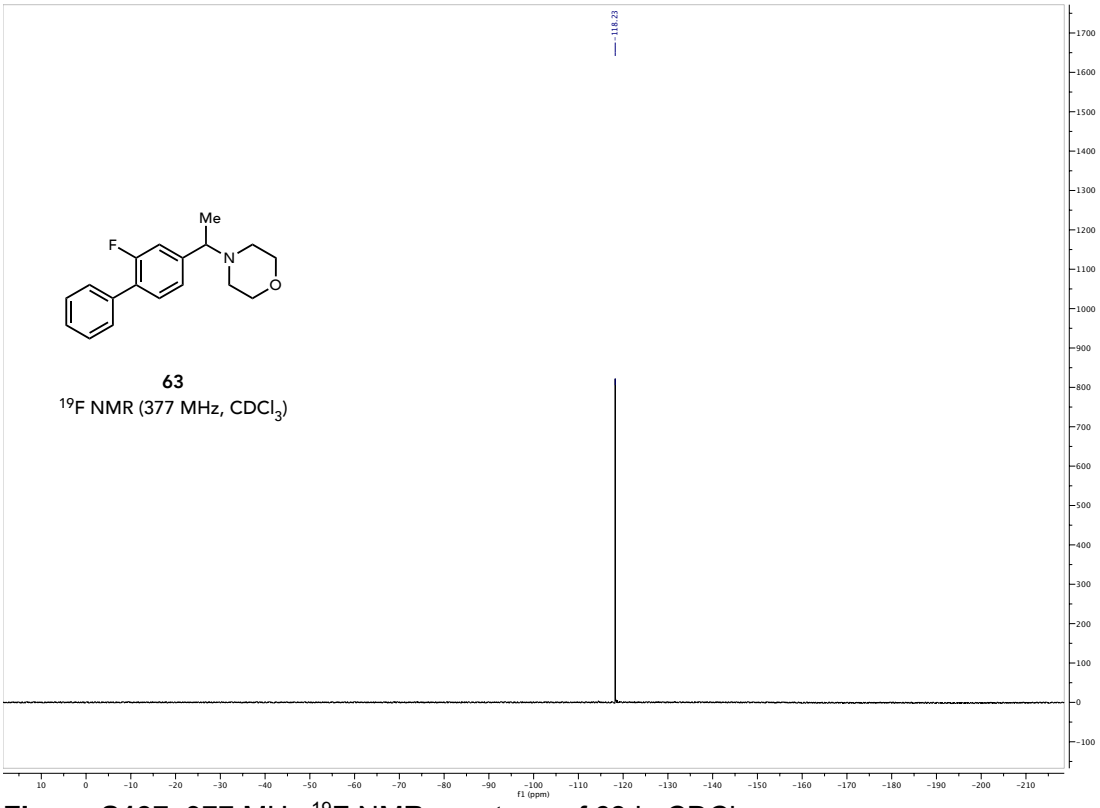


Figure S137. 377 MHz ^{19}F NMR spectrum of **63** in $CDCl_3$.

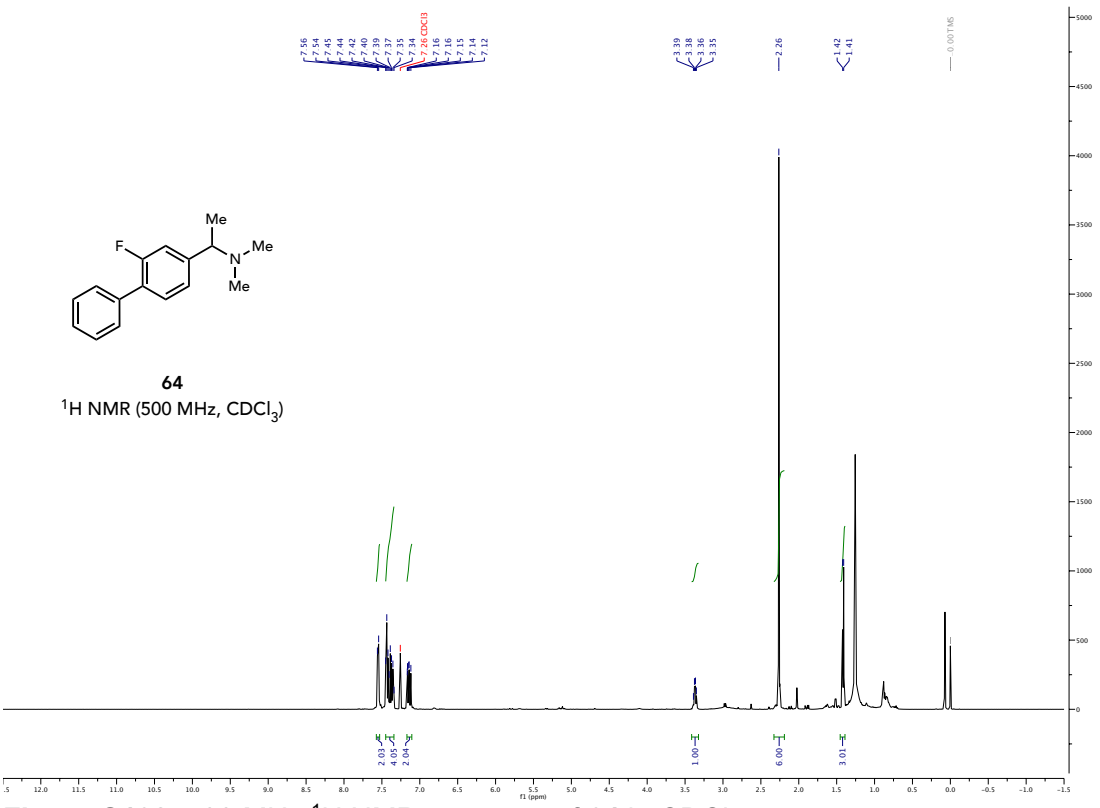


Figure S138. 500 MHz ^{1}H NMR spectrum of **64** in $CDCl_3$.

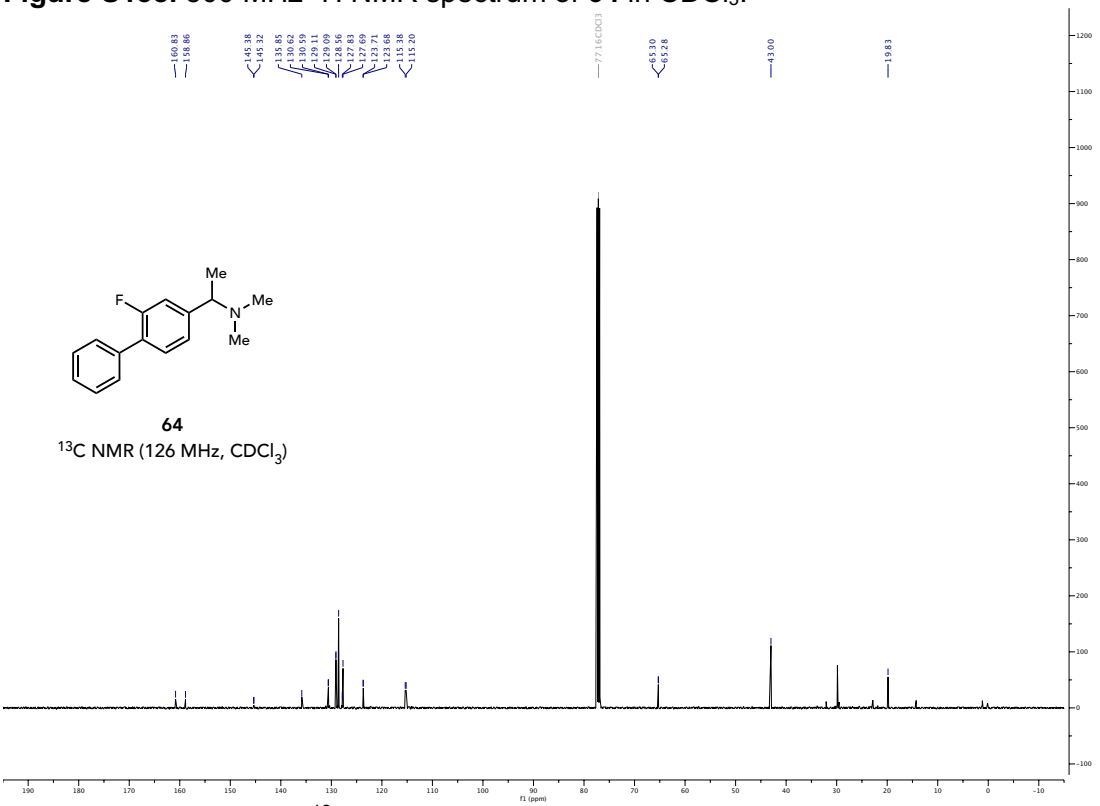


Figure S139. 126 MHz ^{13}C NMR spectrum of **64** in $CDCl_3$.

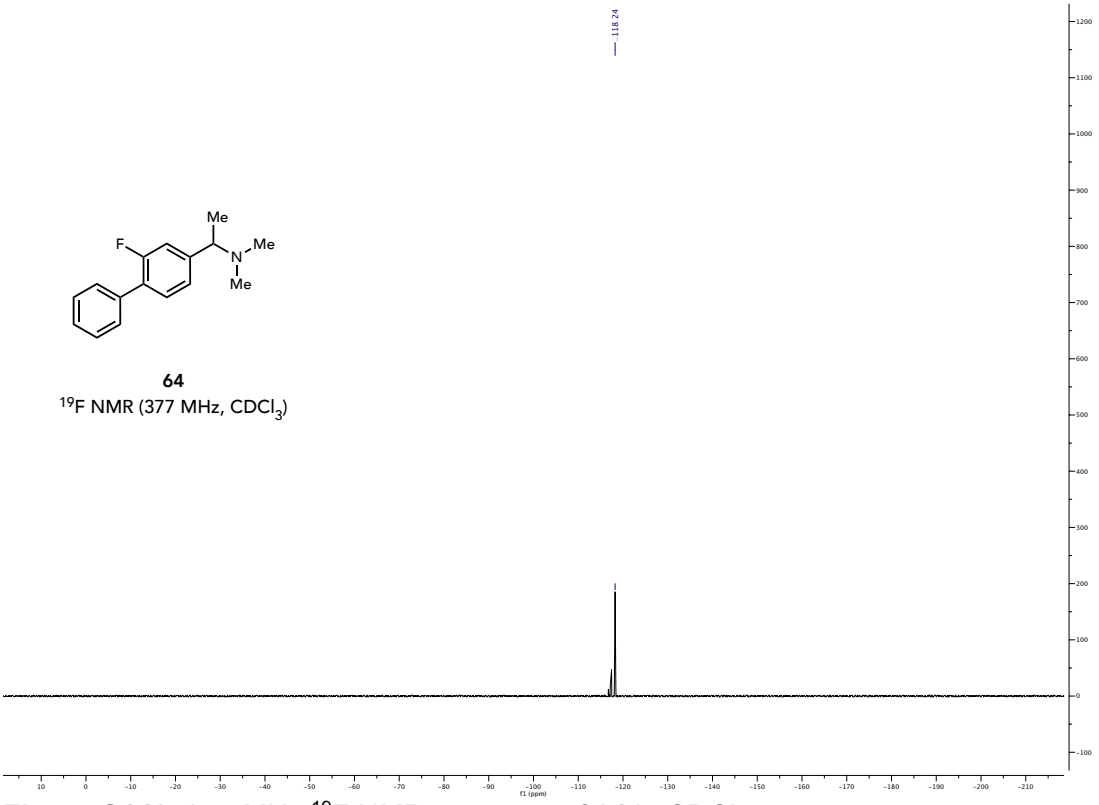


Figure S140. 377 MHz ^{19}F NMR spectrum of **64** in $CDCl_3$.

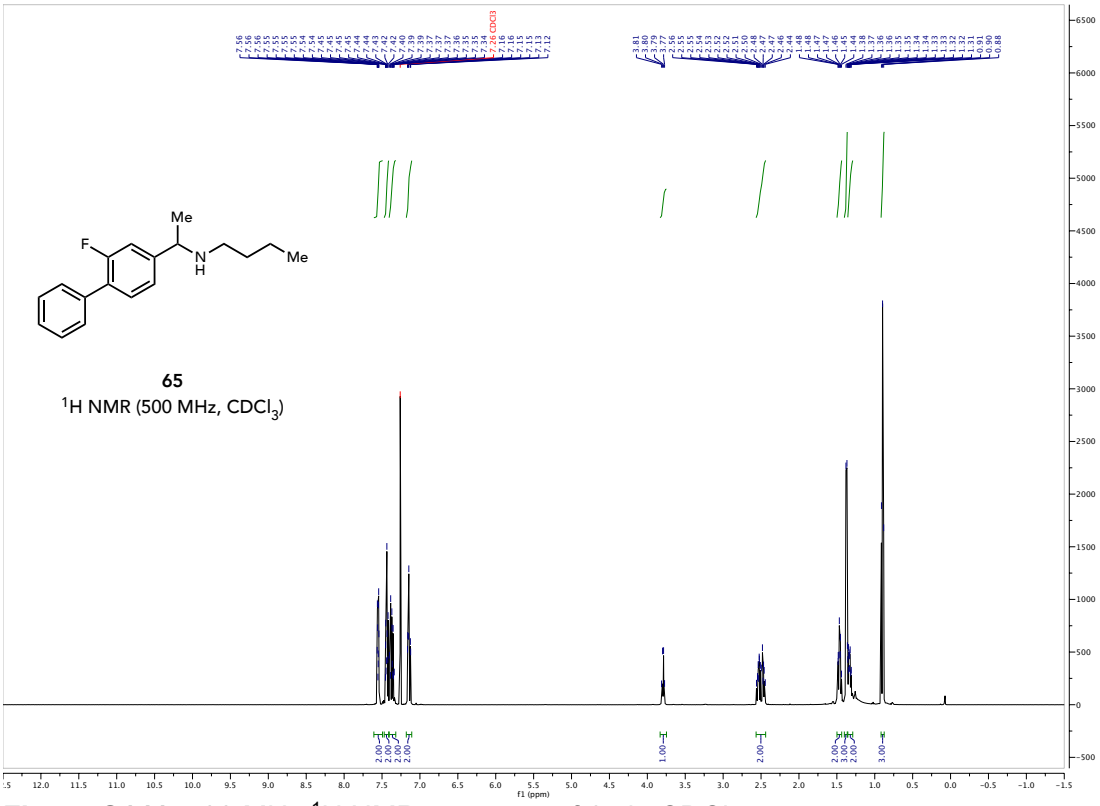


Figure S141. 500 MHz ^{1}H NMR spectrum of **65** in $CDCl_3$.

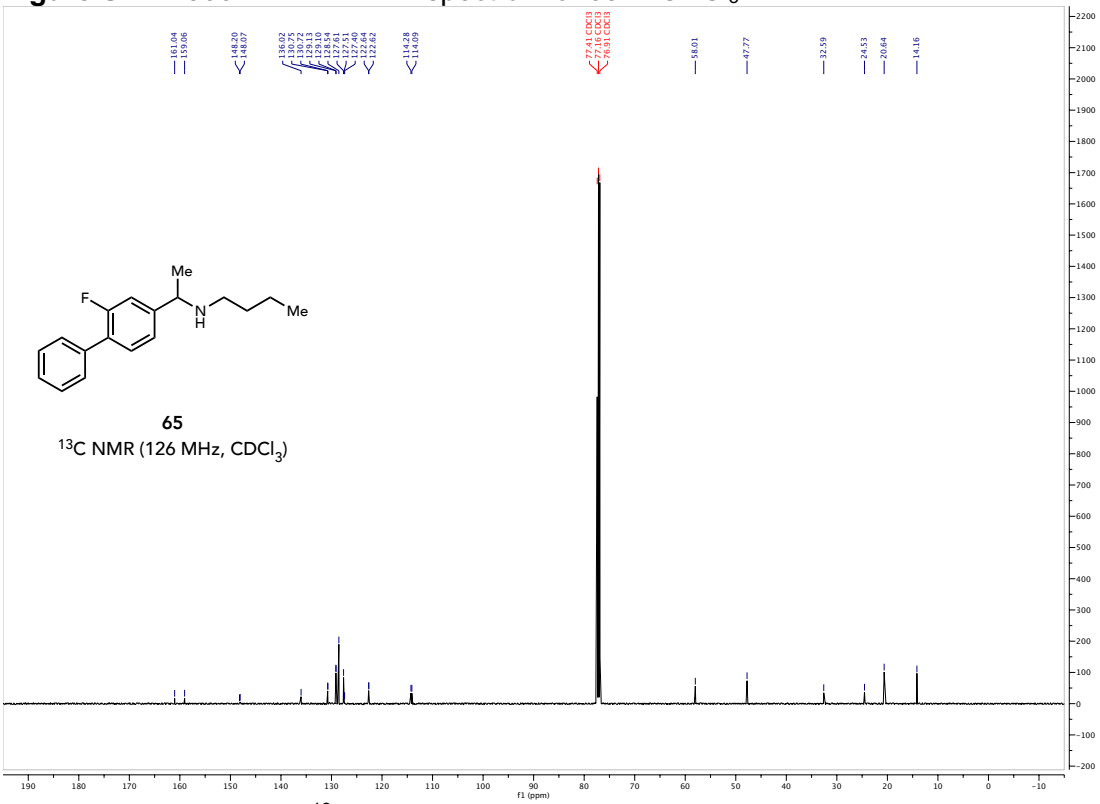


Figure S142. 126 MHz ^{13}C NMR spectrum of **65** in $CDCl_3$.

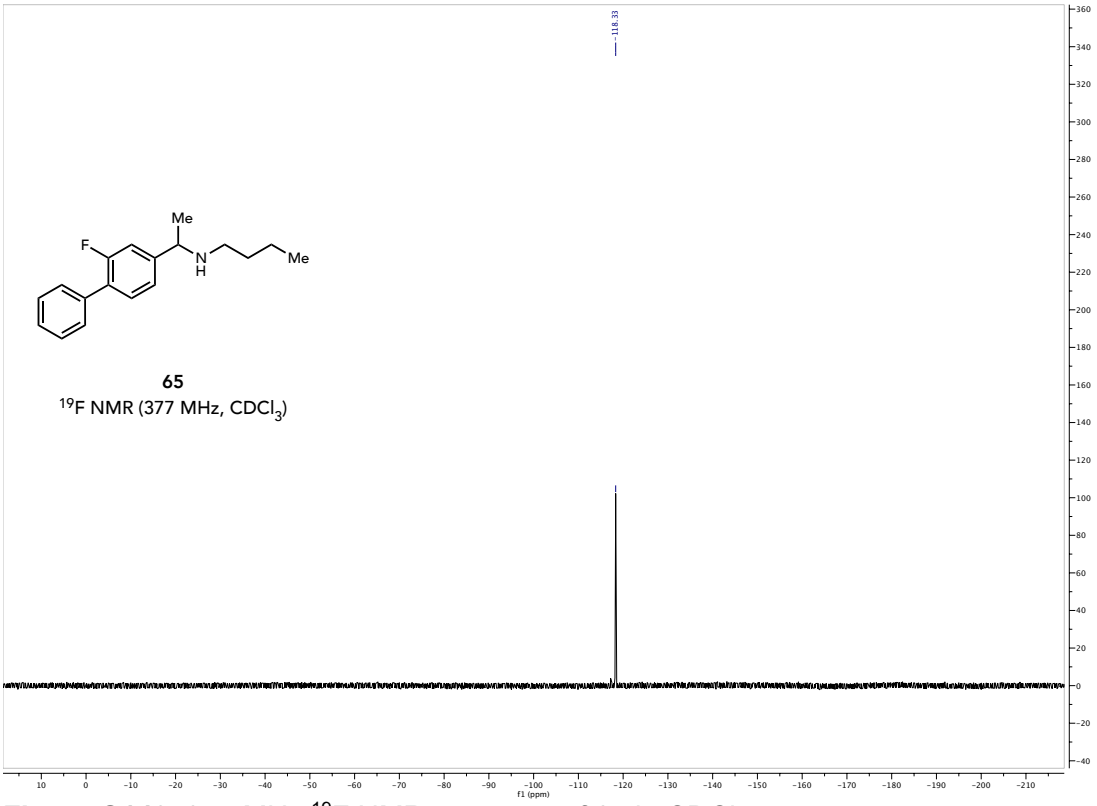


Figure S143. 377 MHz ^{19}F NMR spectrum of **65** in $CDCl_3$.

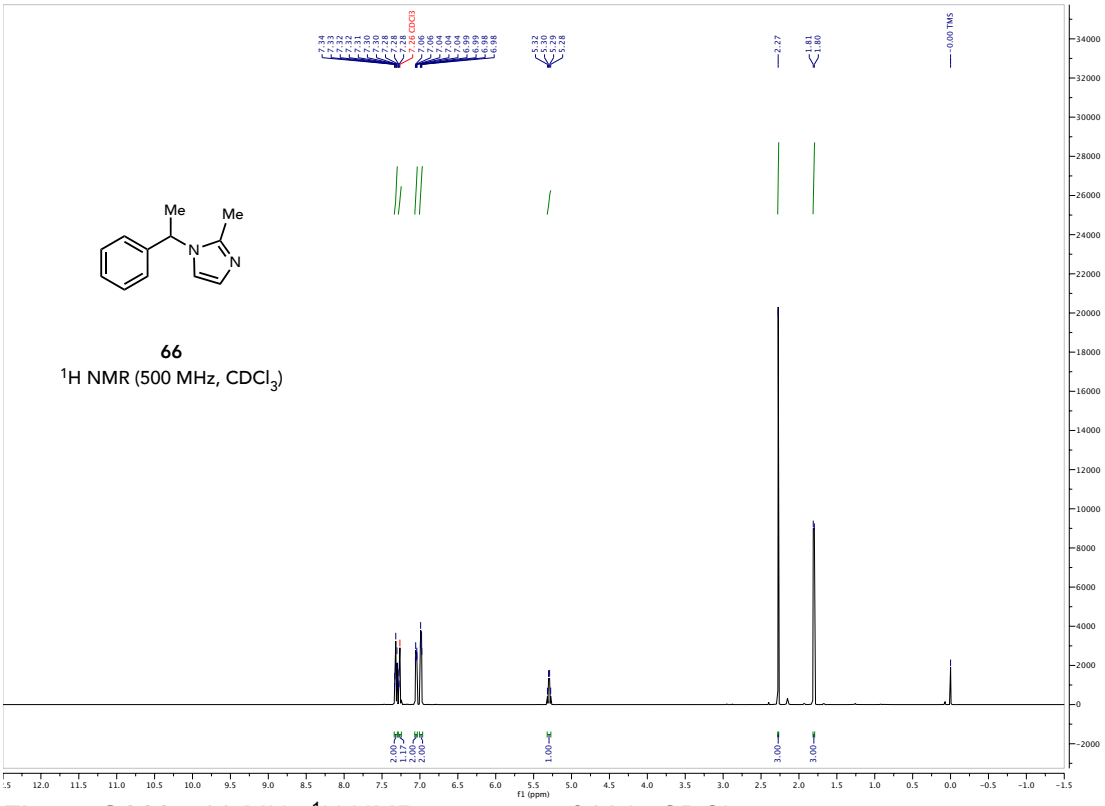


Figure S144. 500 MHz ^{1}H NMR spectrum of **66** in $CDCl_3$.

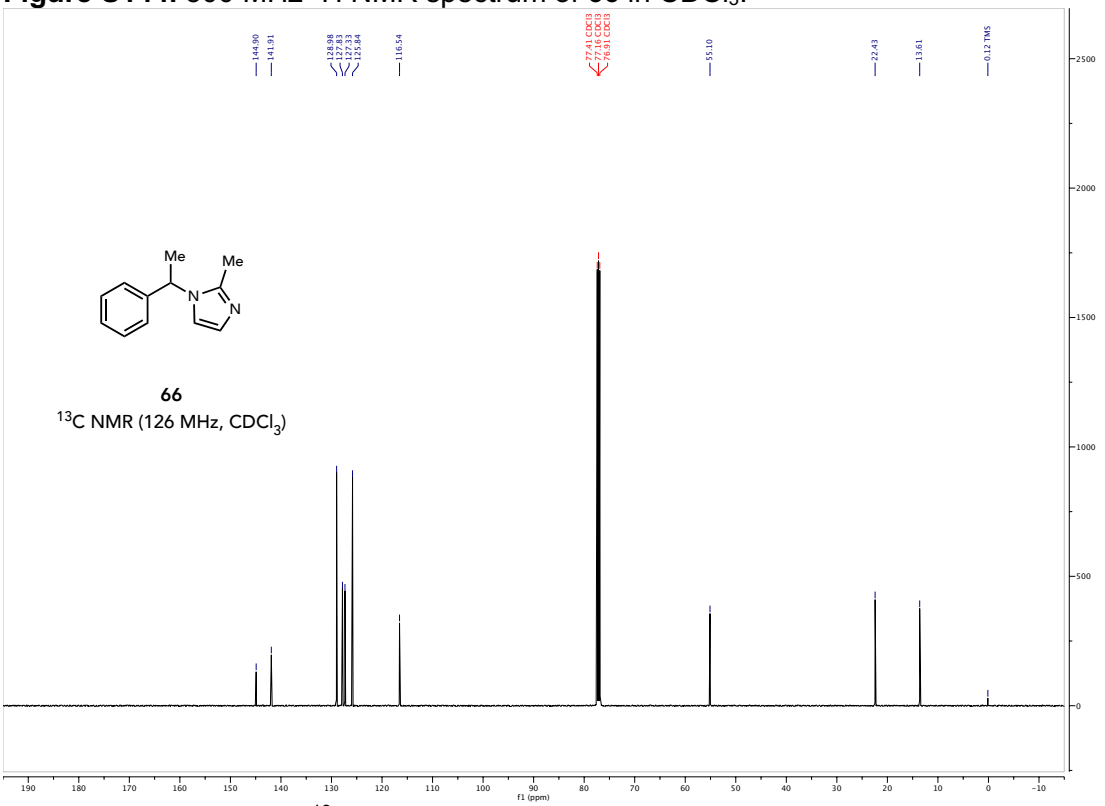


Figure S145. 126 MHz ^{13}C NMR spectrum of **66** in $CDCl_3$.

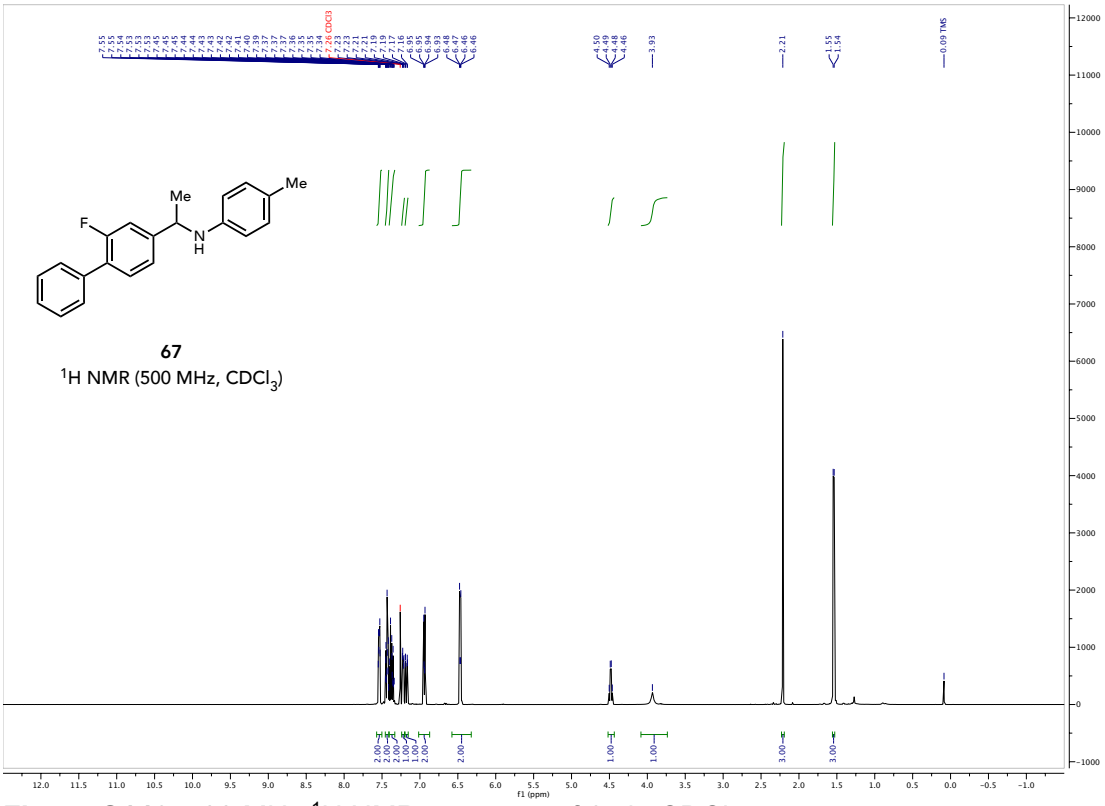


Figure S146. 500 MHz ^{1}H NMR spectrum of **67** in $CDCl_3$.

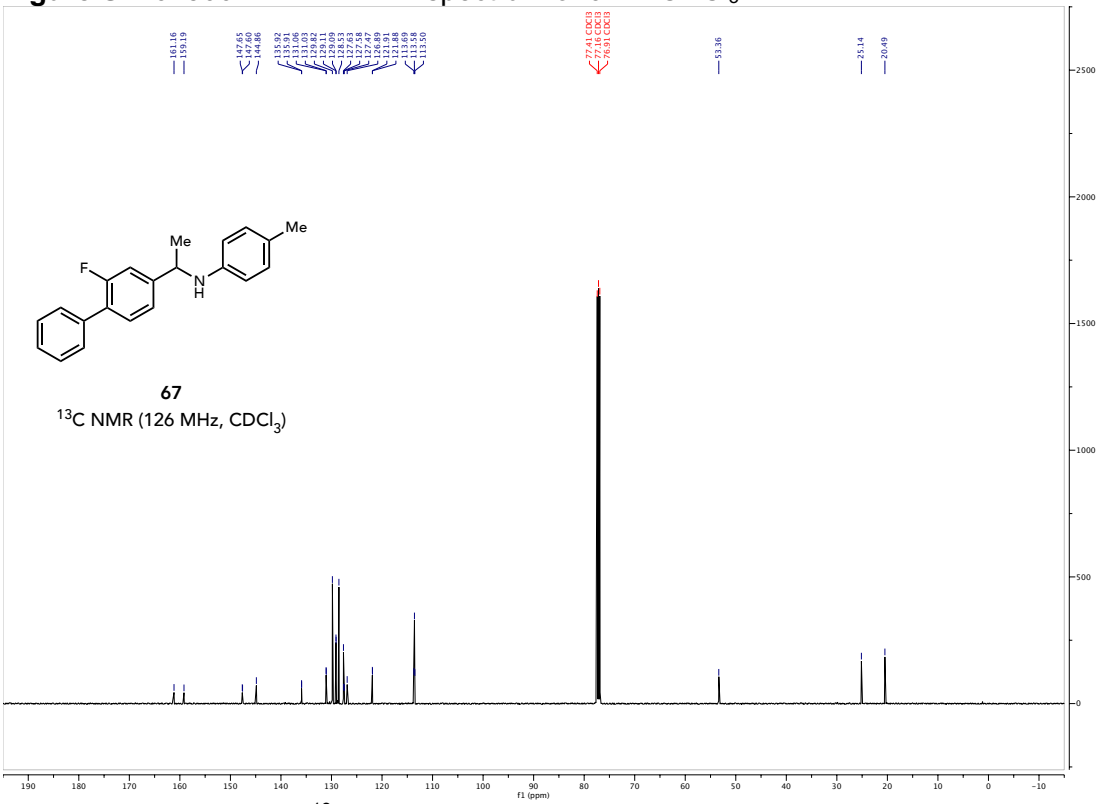


Figure S147. 126 MHz ^{13}C NMR spectrum of **67** in $CDCl_3$.

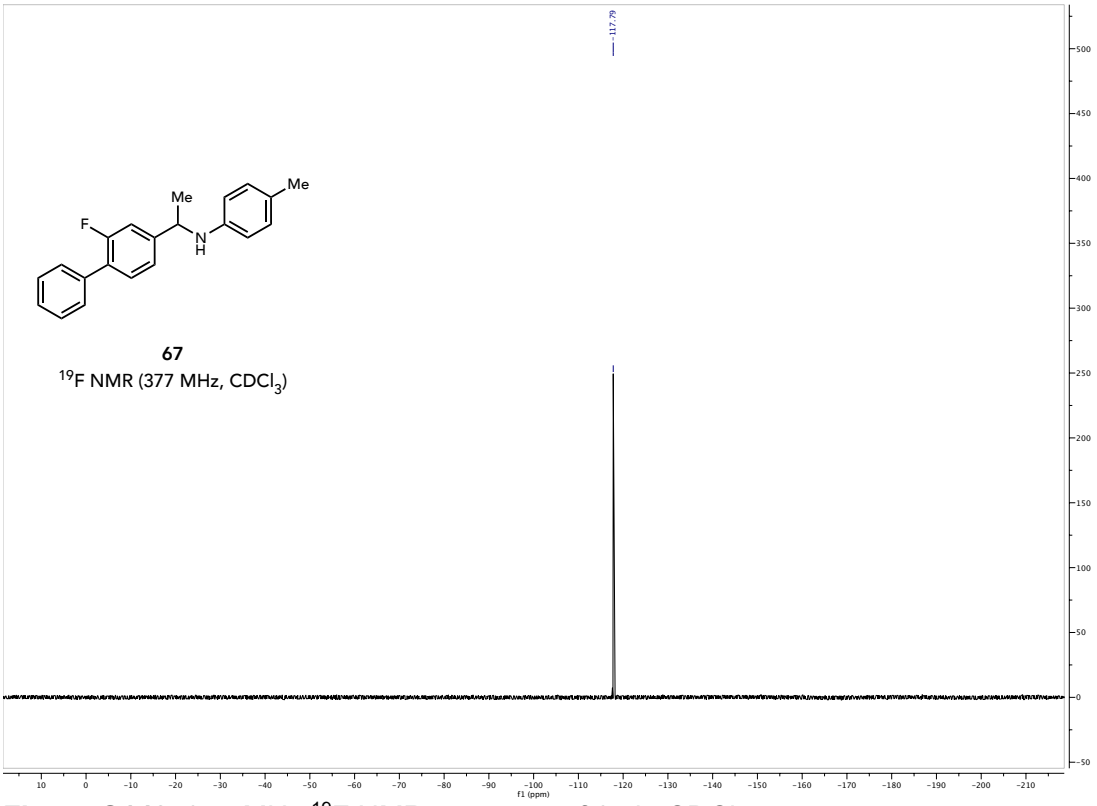


Figure S148. 377 MHz ^{19}F NMR spectrum of **67** in $CDCl_3$.

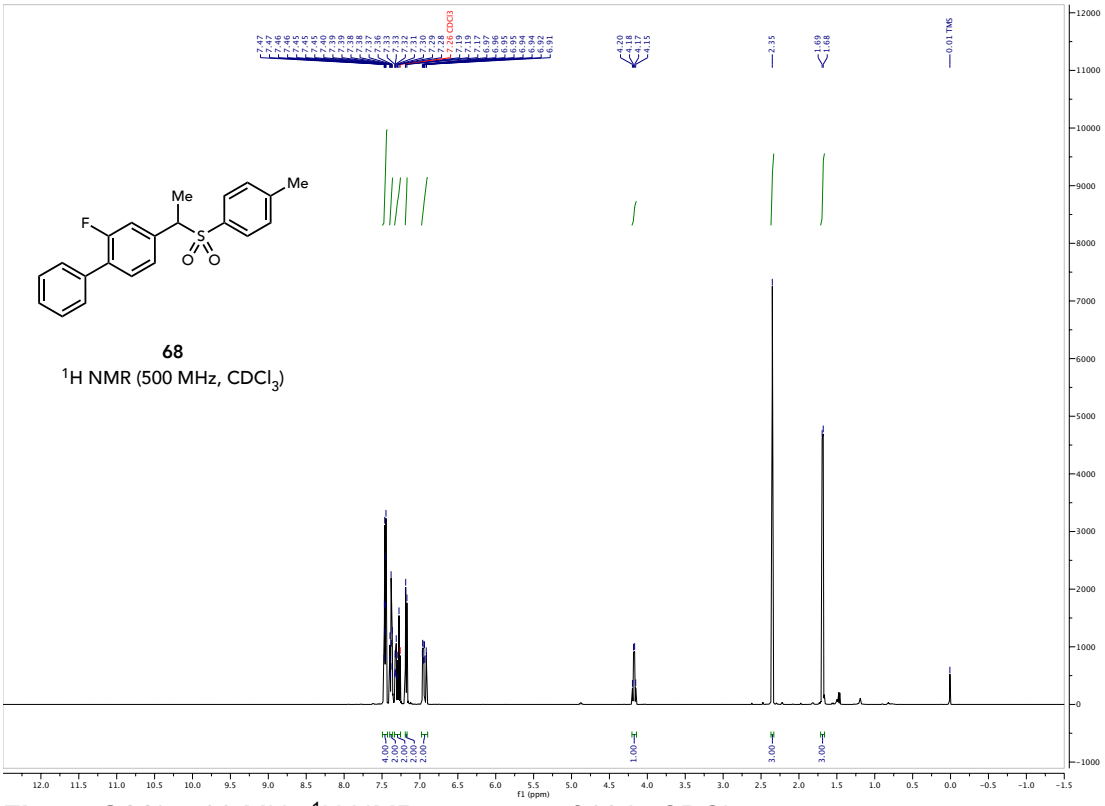


Figure S149. 500 MHz ^{1}H NMR spectrum of **68** in $CDCl_3$.

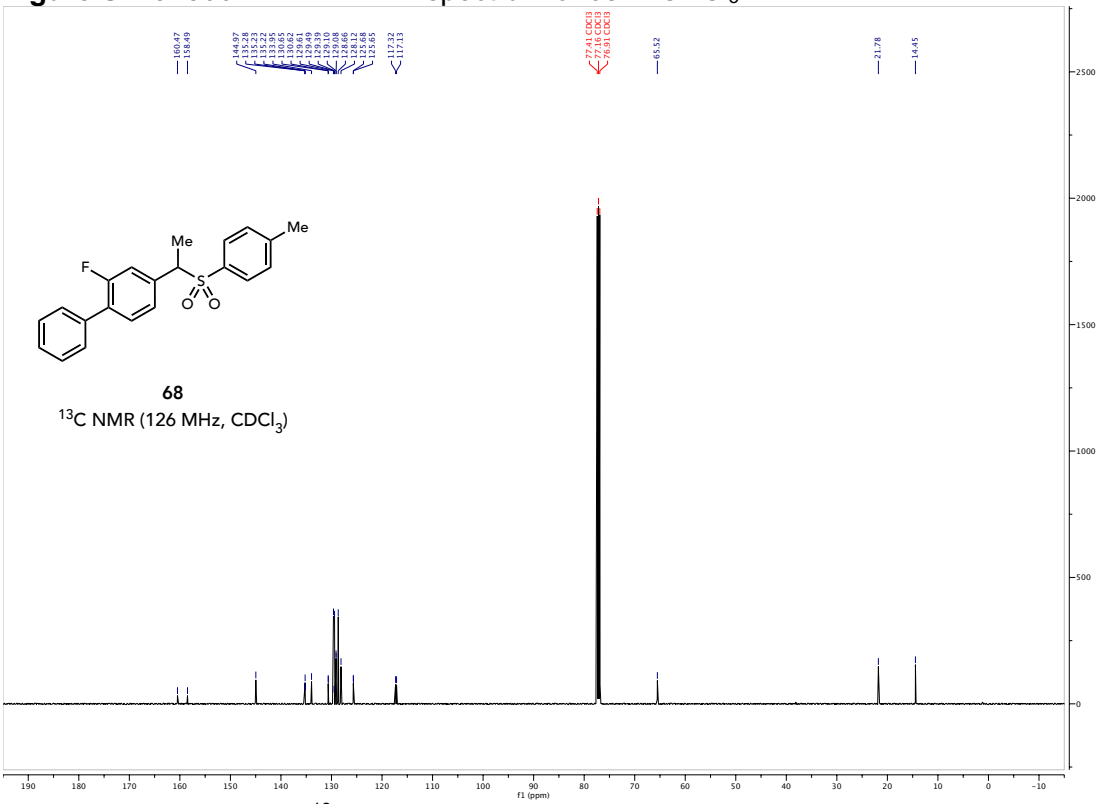


Figure S150. 126 MHz ^{13}C NMR spectrum of **68** in $CDCl_3$.

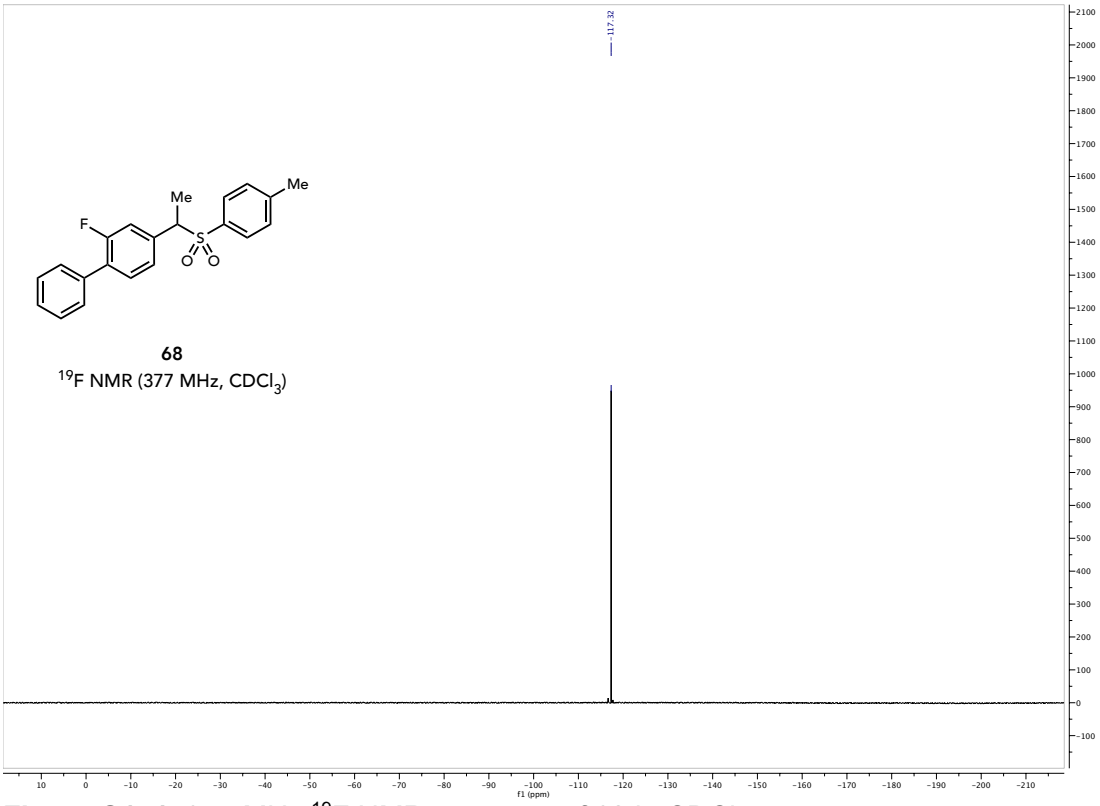


Figure S151. 377 MHz ^{19}F NMR spectrum of **68** in $CDCl_3$.

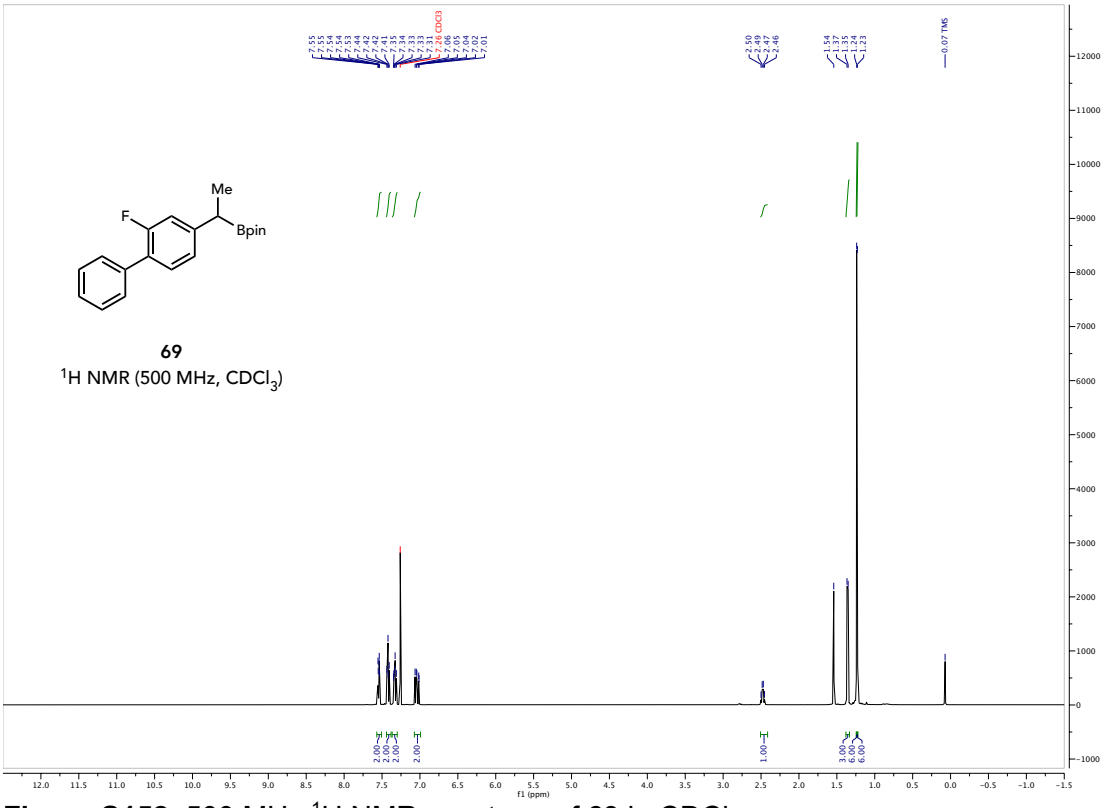


Figure S152. 500 MHz ^{1}H NMR spectrum of **69** in $CDCl_3$.

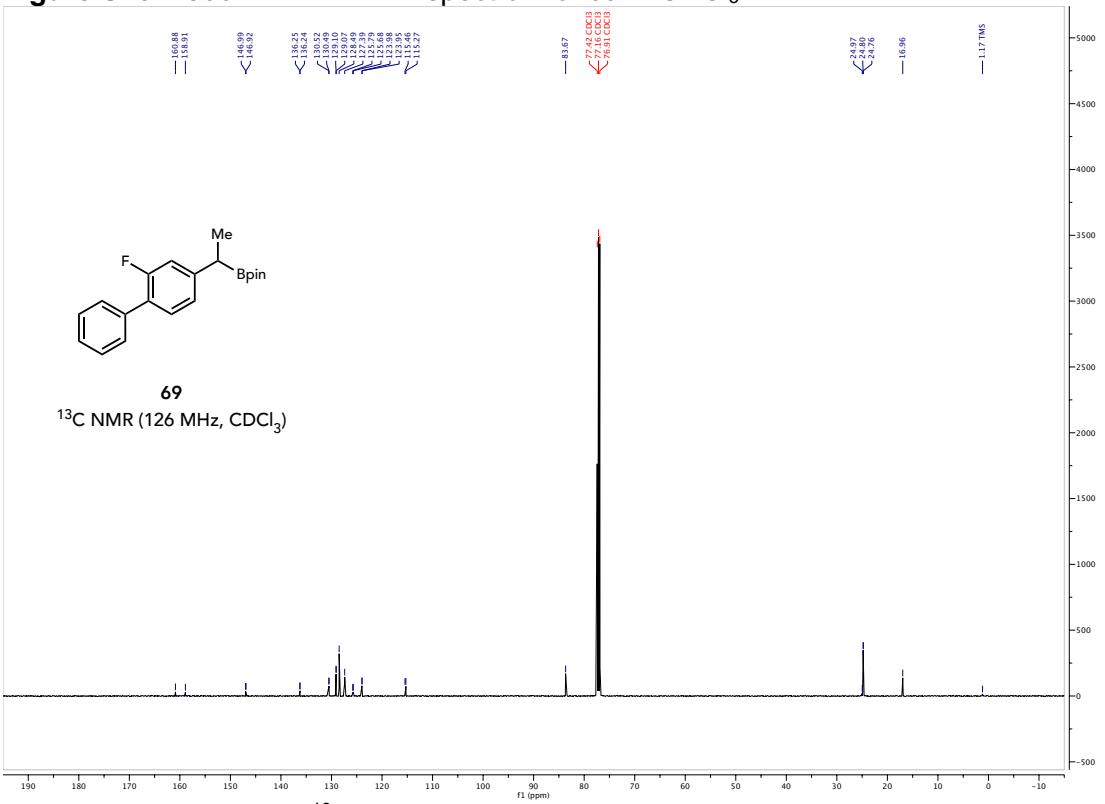


Figure S153. 126 MHz ^{13}C NMR spectrum of **69** in $CDCl_3$.

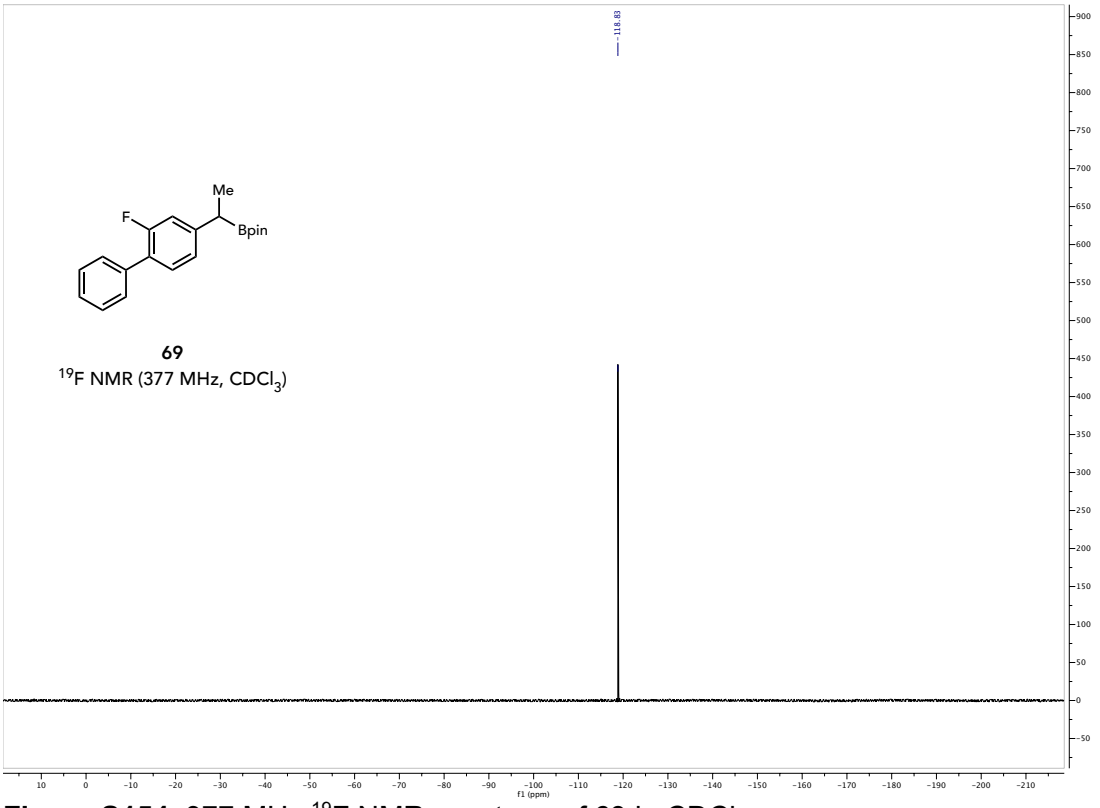


Figure S154. 377 MHz ^{19}F NMR spectrum of **69** in $CDCl_3$.

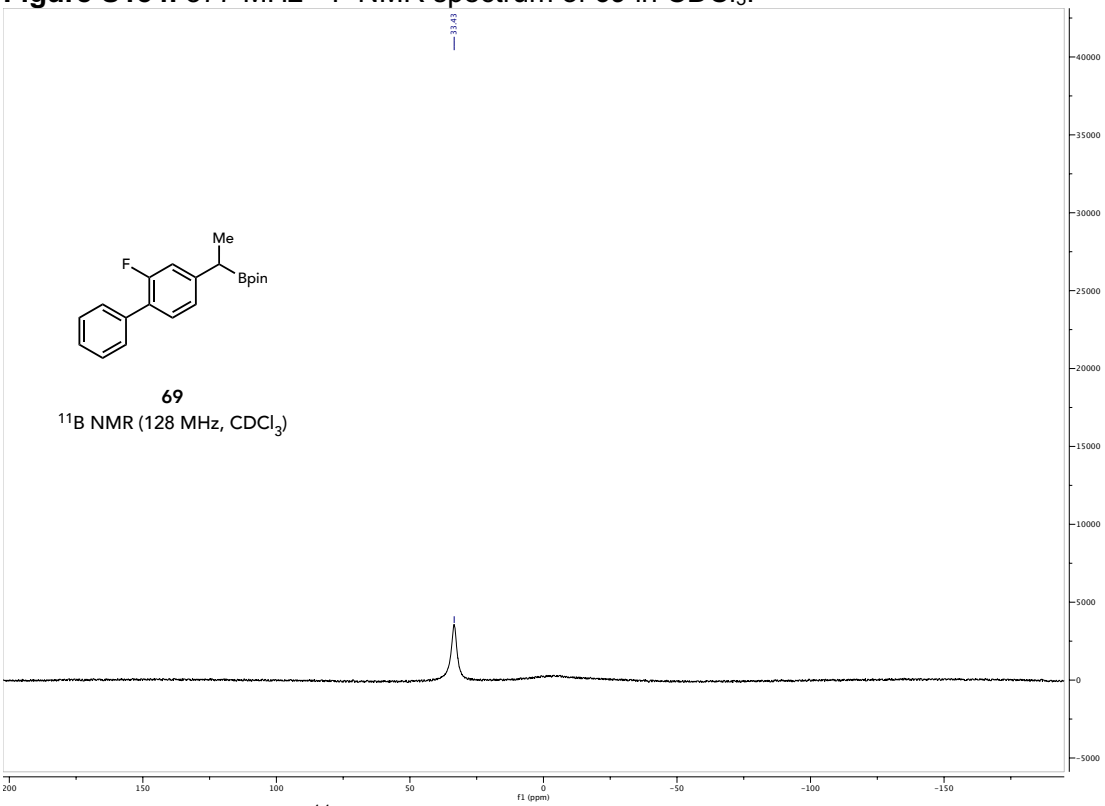


Figure S155. 128 MHz ^{11}B NMR spectrum of **69** in $CDCl_3$.

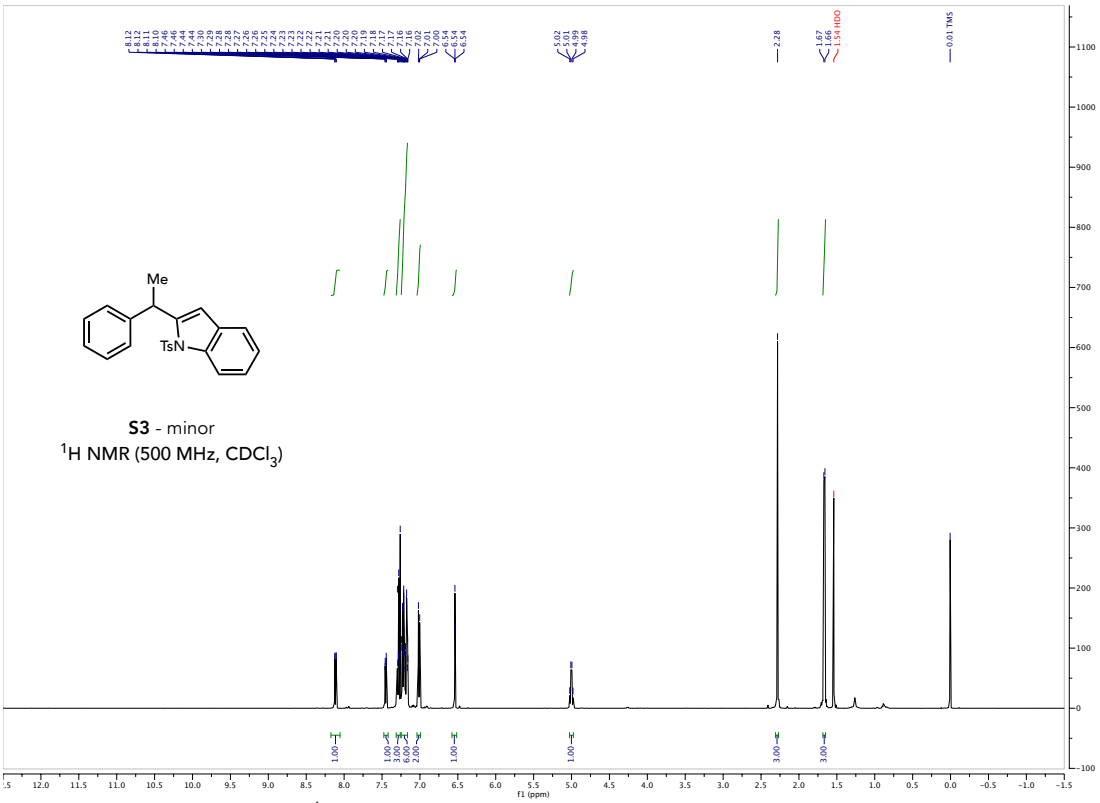


Figure S156. 500 MHz ^{1}H NMR spectrum of **S3** - minor in $CDCl_3$.

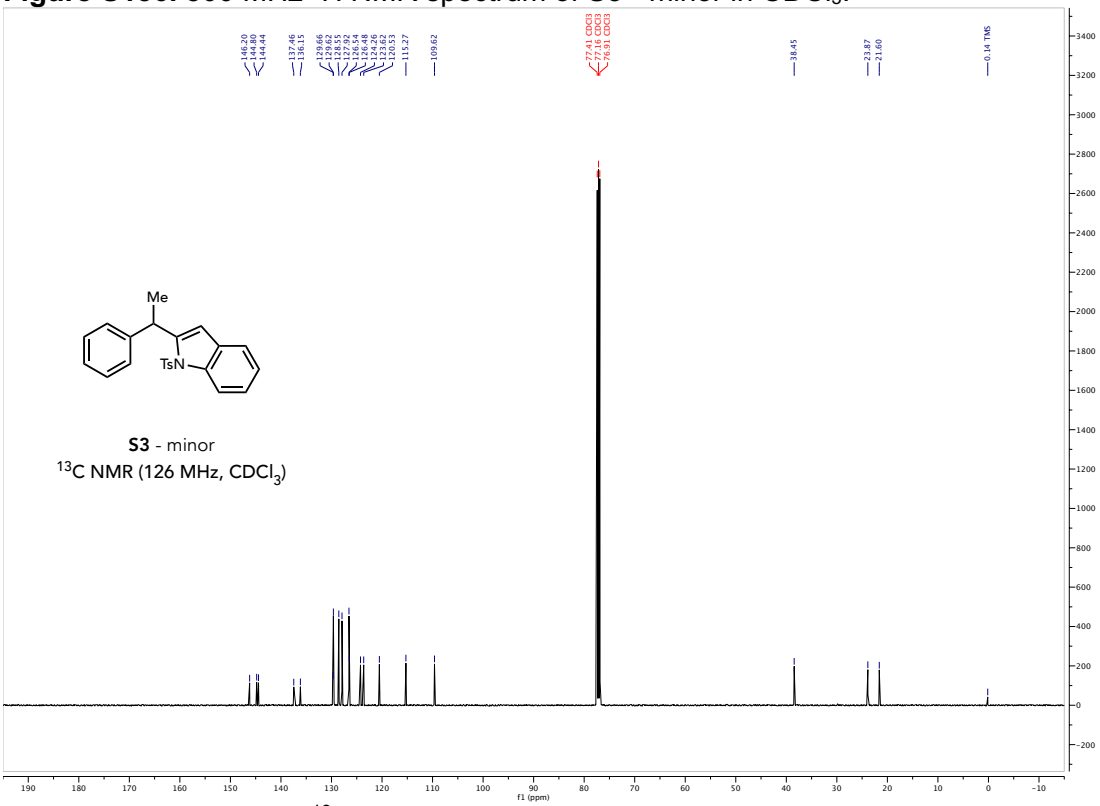


Figure S157. 126 MHz ^{13}C NMR spectrum of **S3** - minor in $CDCl_3$.

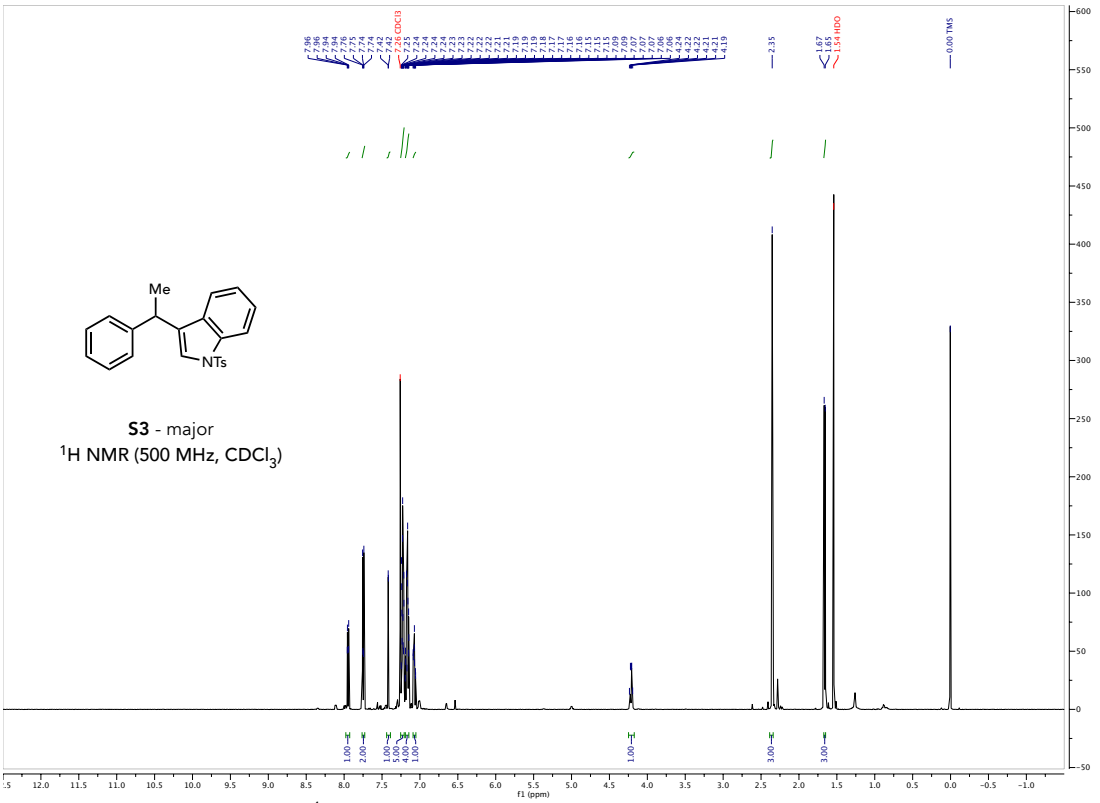


Figure S158. 500 MHz ^{1}H NMR spectrum of **S3** – major in $CDCl_3$.

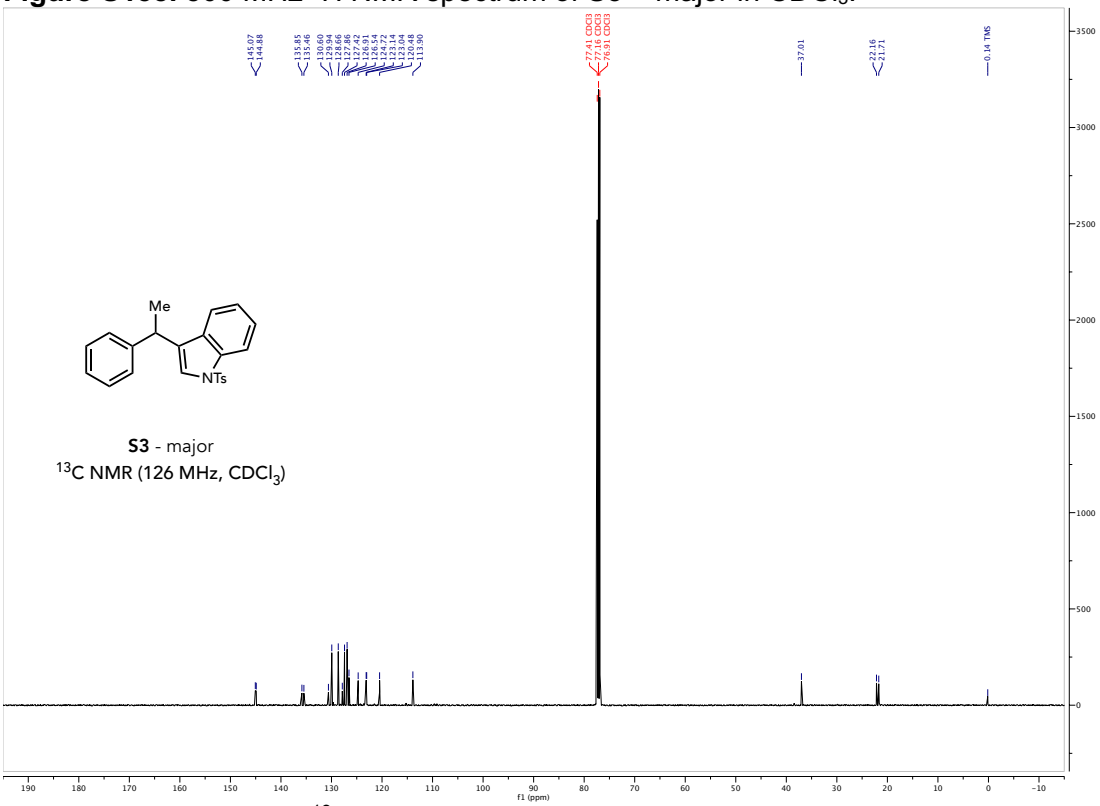


Figure S159. 126 MHz ^{13}C NMR spectrum of **S3** – major in $CDCl_3$.

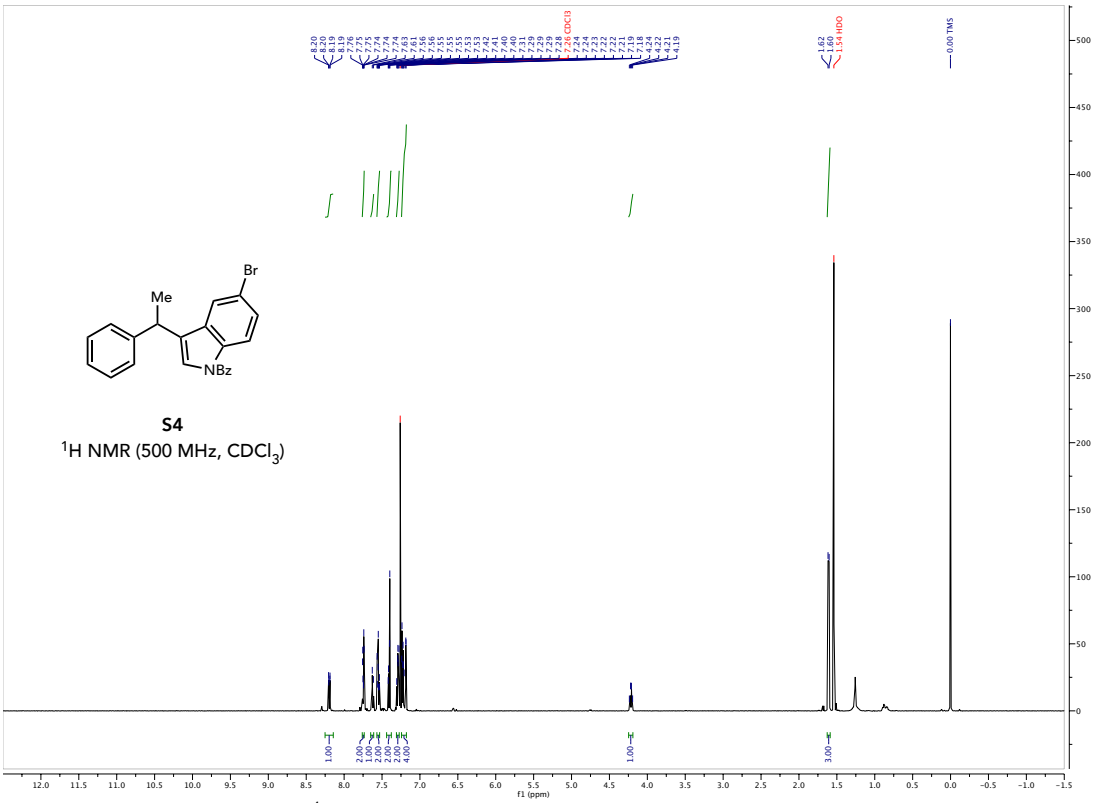


Figure S160. 500 MHz ^{1}H NMR spectrum of **S4** in $CDCl_3$.

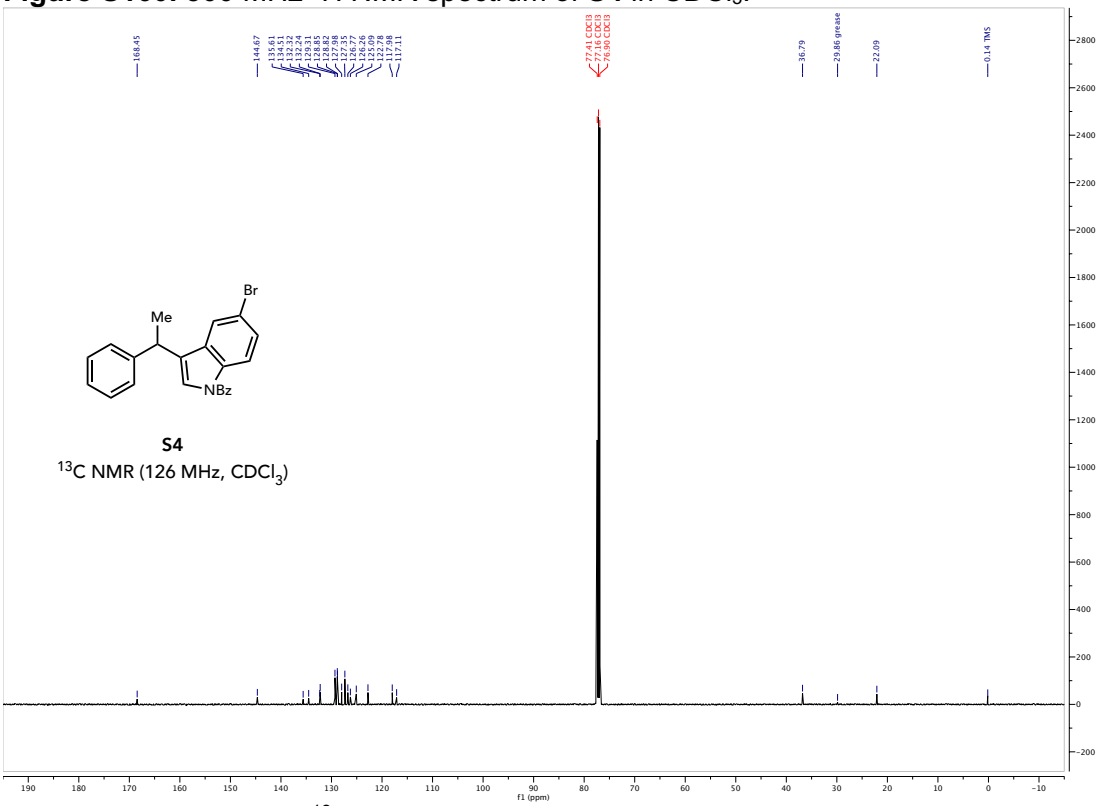


Figure S161. 126 MHz ^{13}C NMR spectrum of **S4** in $CDCl_3$.

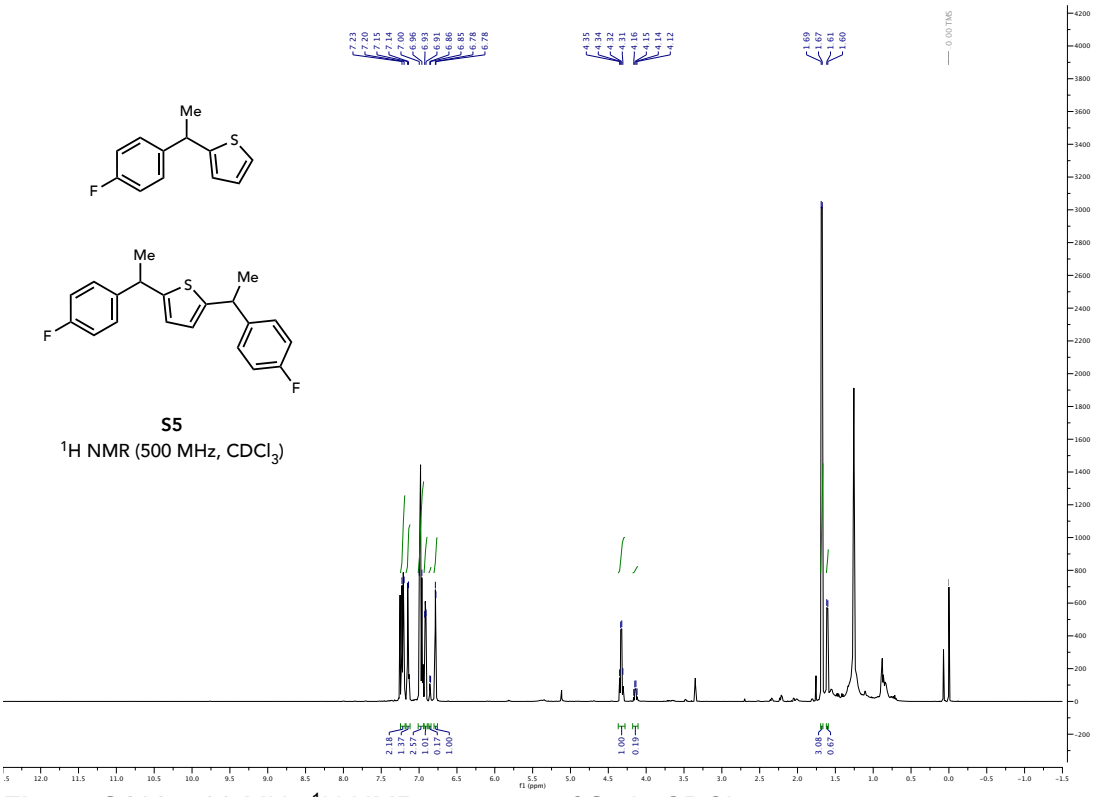


Figure S162. 500 MHz ^{1}H NMR spectrum of **S5** in $CDCl_3$.

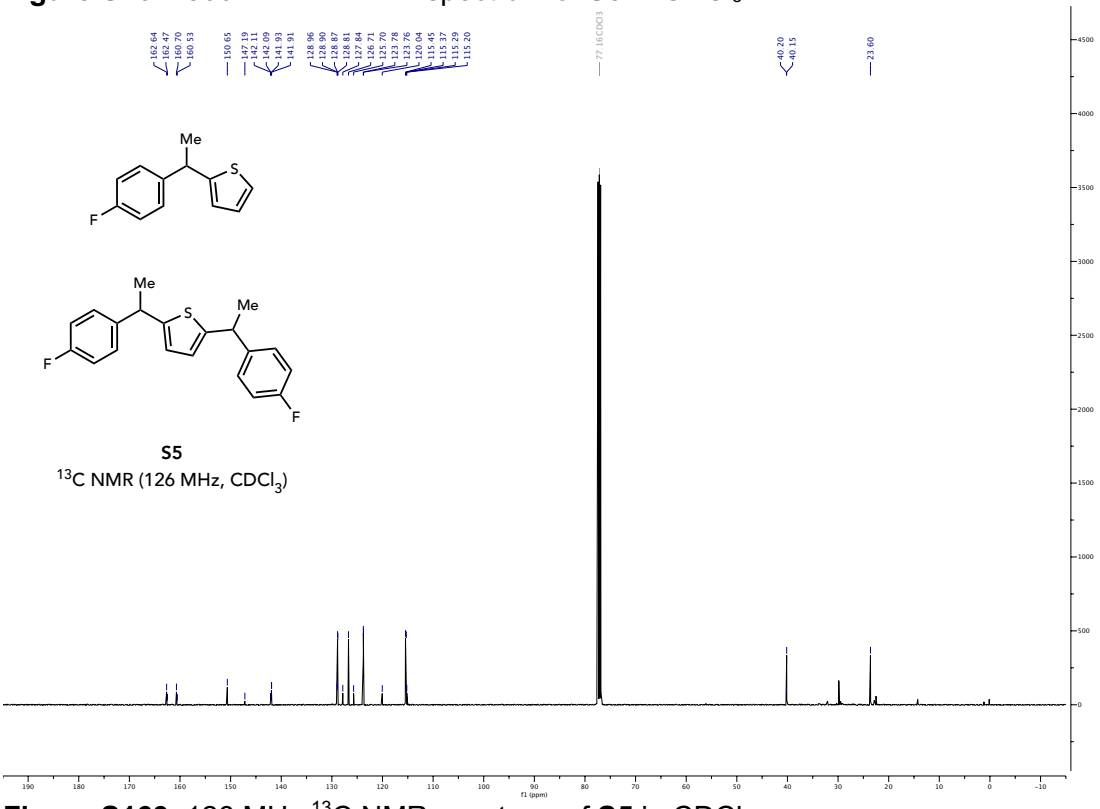


Figure S163. 126 MHz ^{13}C NMR spectrum of **S5** in $CDCl_3$.

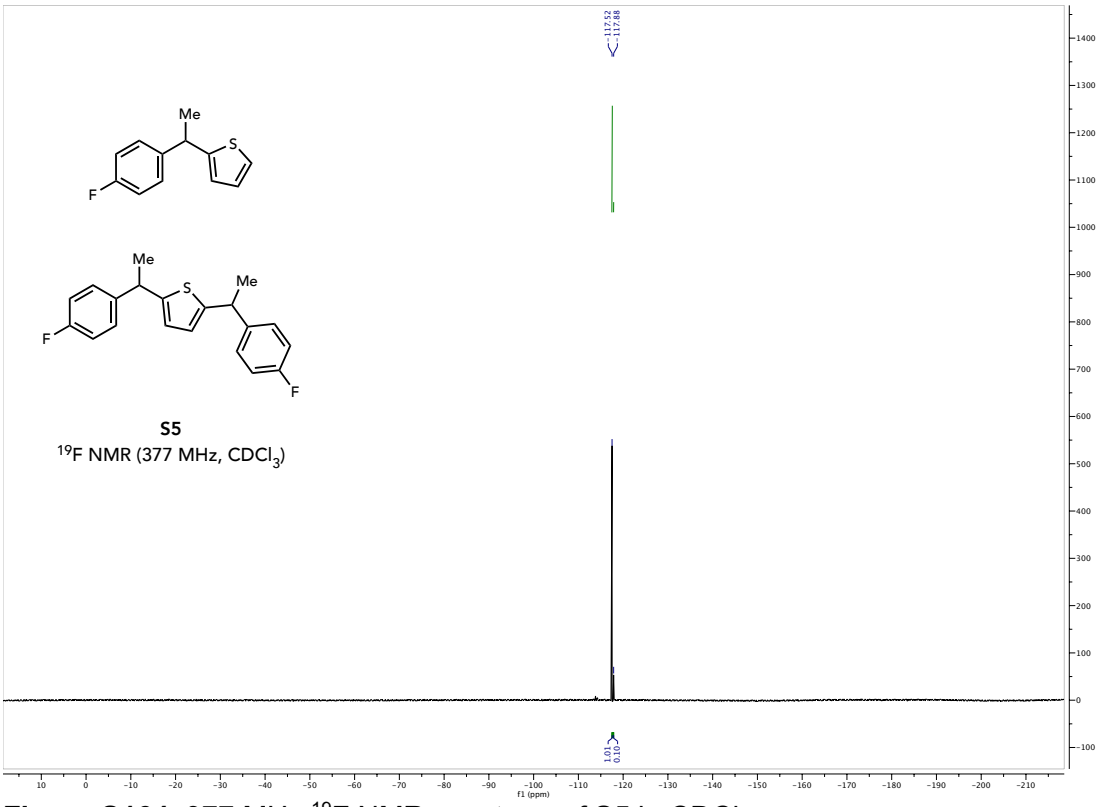


Figure S164. 377 MHz ^{19}F NMR spectrum of **S5** in $CDCl_3$.

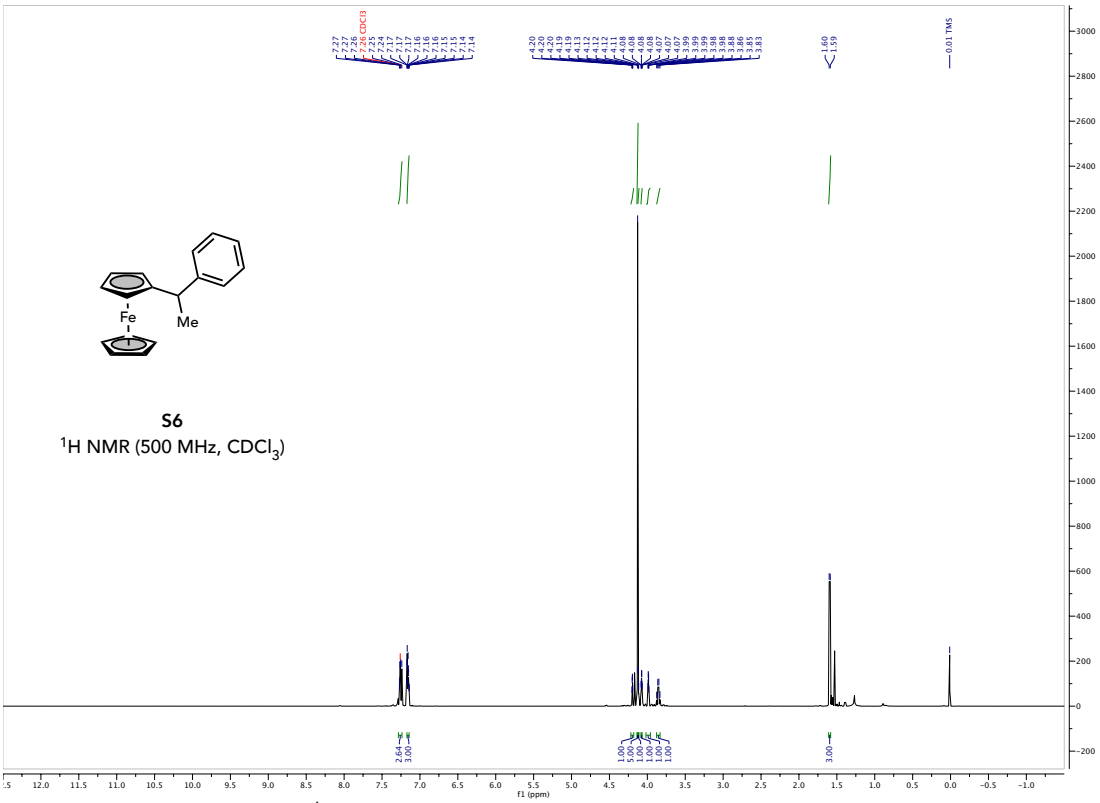


Figure S165. 500 MHz ^{1}H NMR spectrum of **S6** in $CDCl_3$.

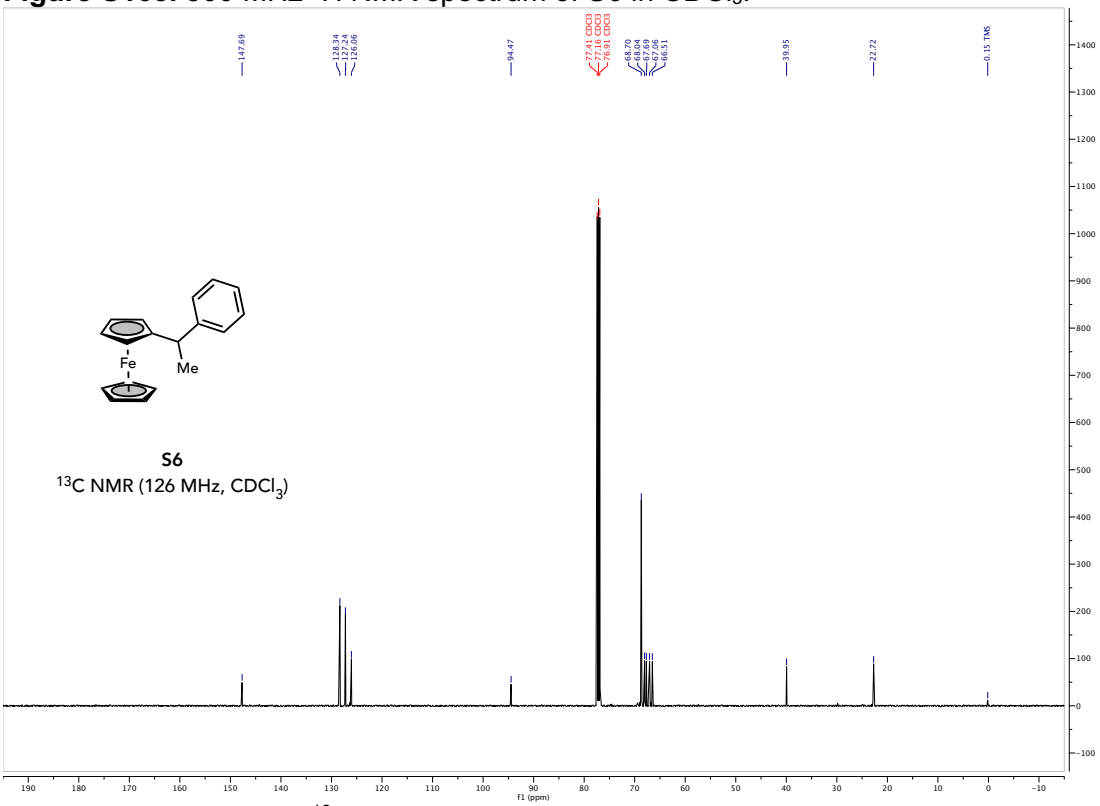


Figure S166. 126 MHz ^{13}C NMR spectrum of **S6** in $CDCl_3$.

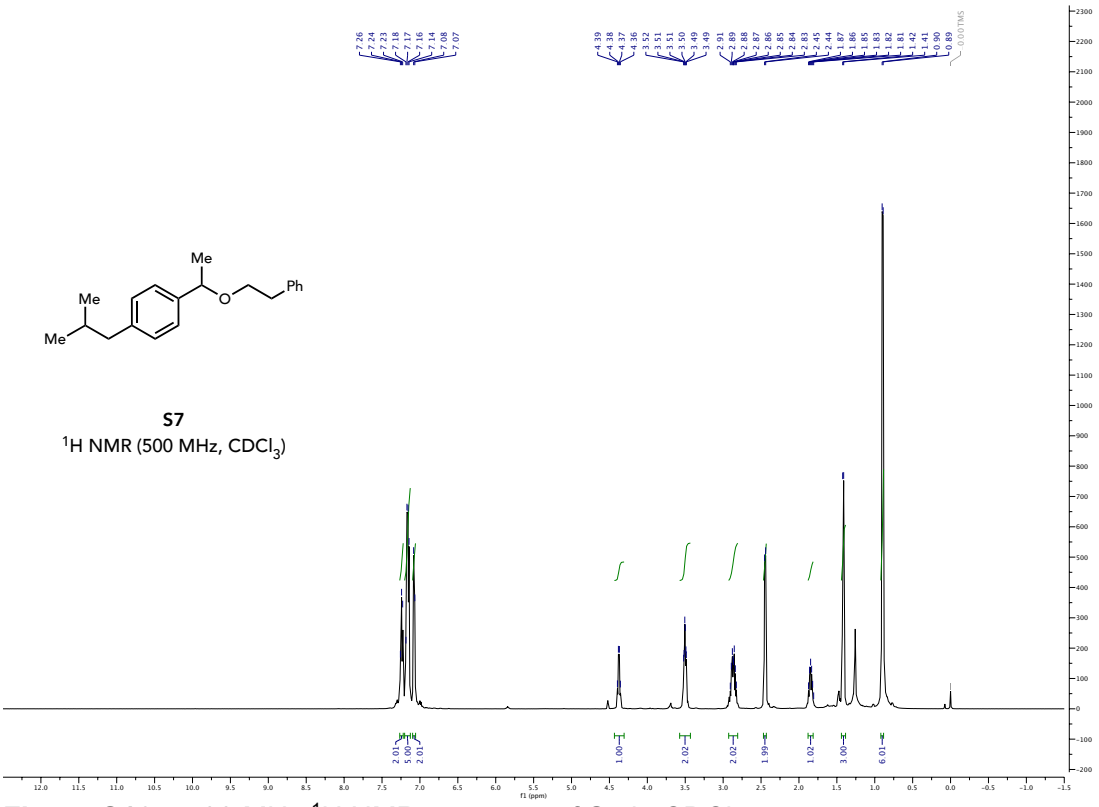


Figure S167. 500 MHz ^{1}H NMR spectrum of **S7** in $CDCl_3$.

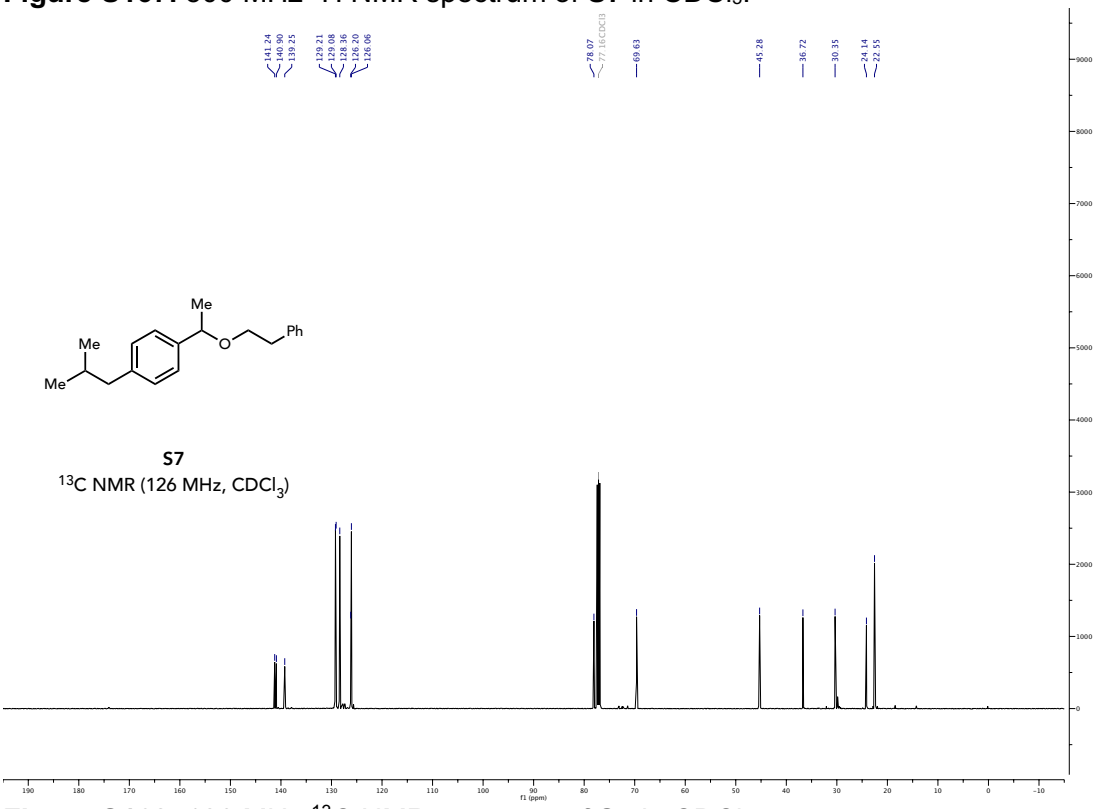


Figure S168. 126 MHz ^{13}C NMR spectrum of **S7** in $CDCl_3$.

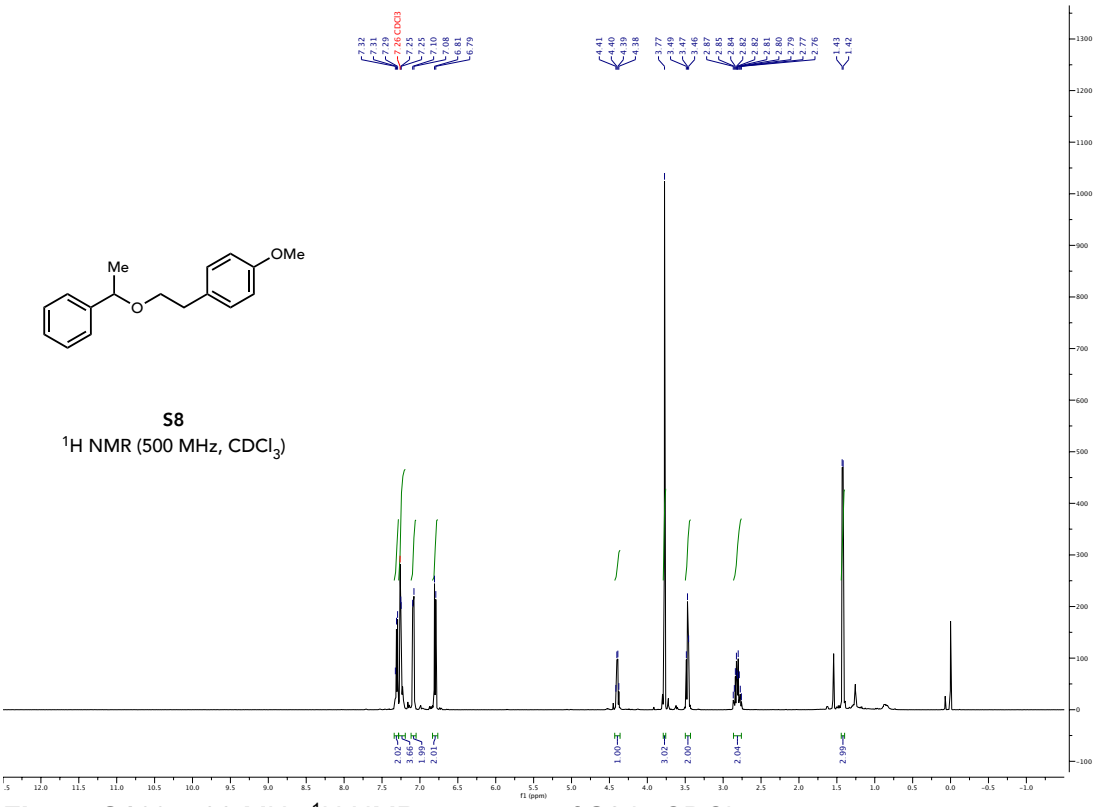


Figure S169. 500 MHz ^{1}H NMR spectrum of **S8** in $CDCl_3$.

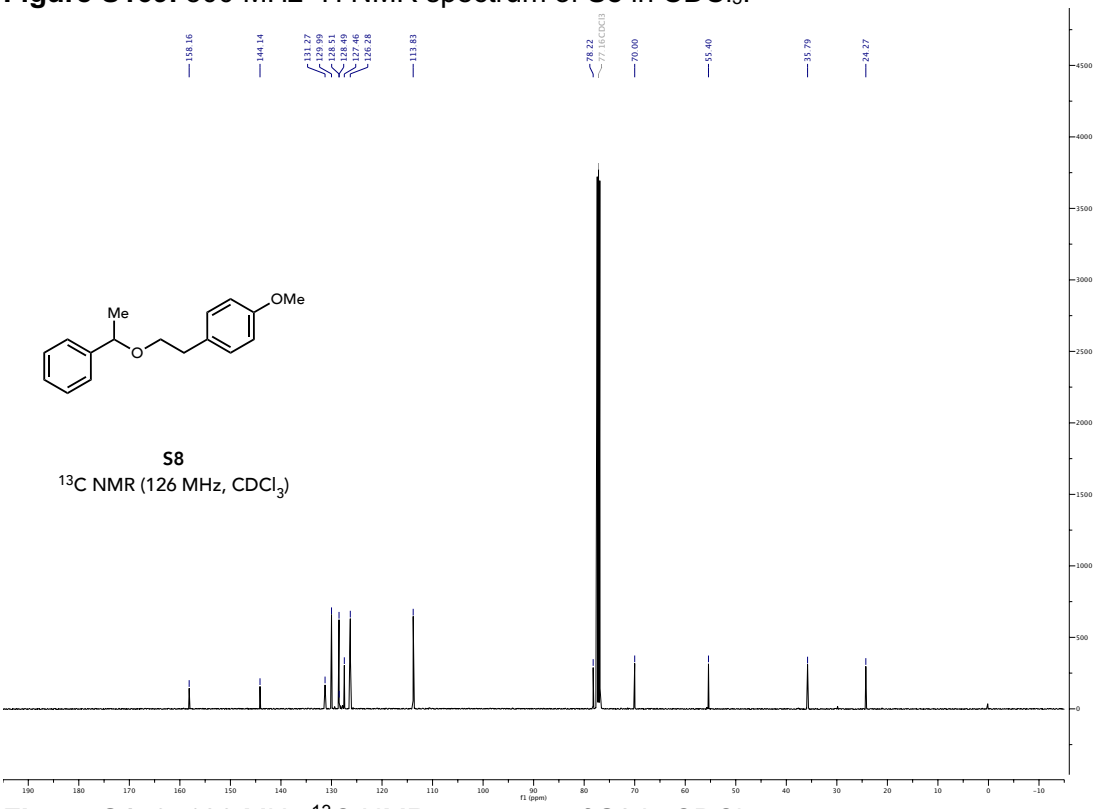


Figure S170. 126 MHz ^{13}C NMR spectrum of **S8** in $CDCl_3$.

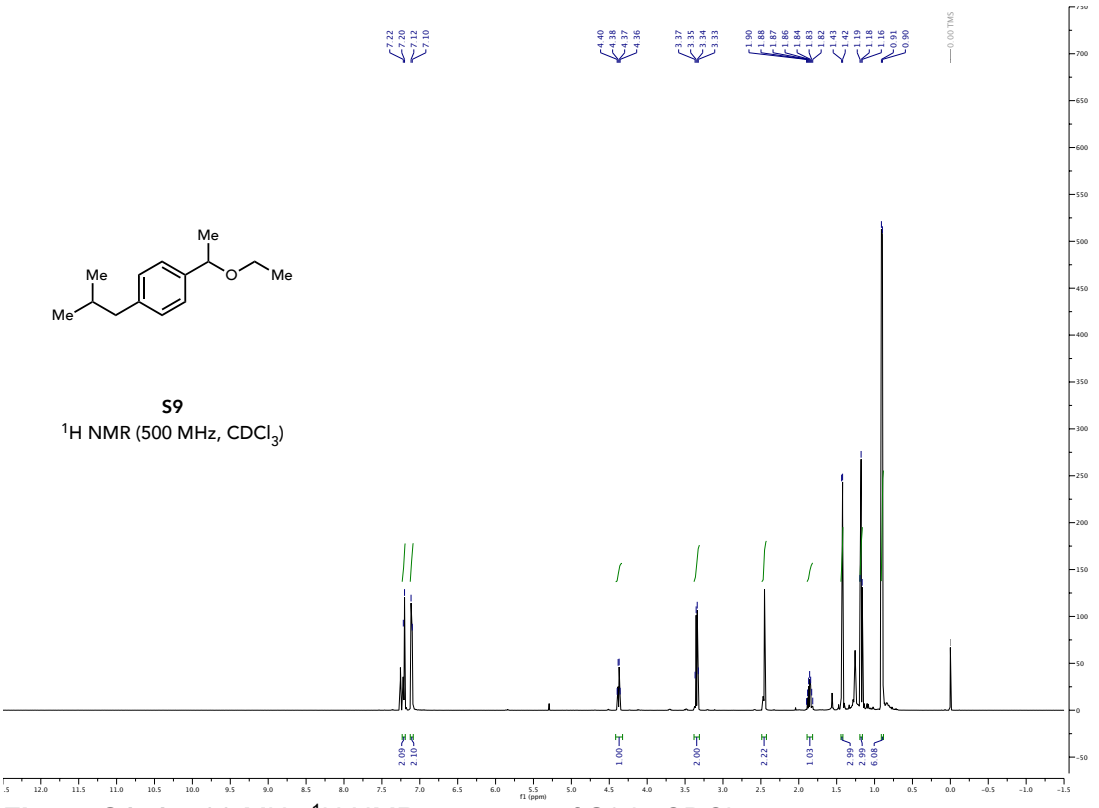


Figure S171. 500 MHz ^{1}H NMR spectrum of **S9** in $CDCl_3$.

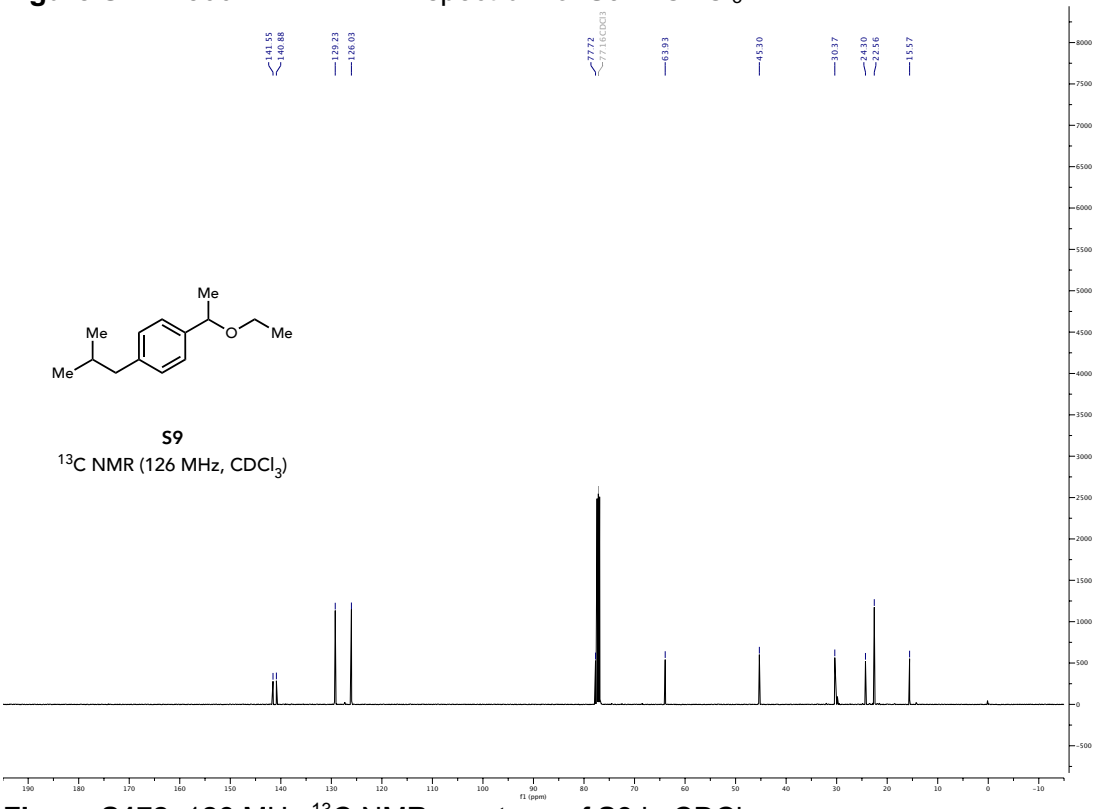


Figure S172. 126 MHz ^{13}C NMR spectrum of **S9** in $CDCl_3$.

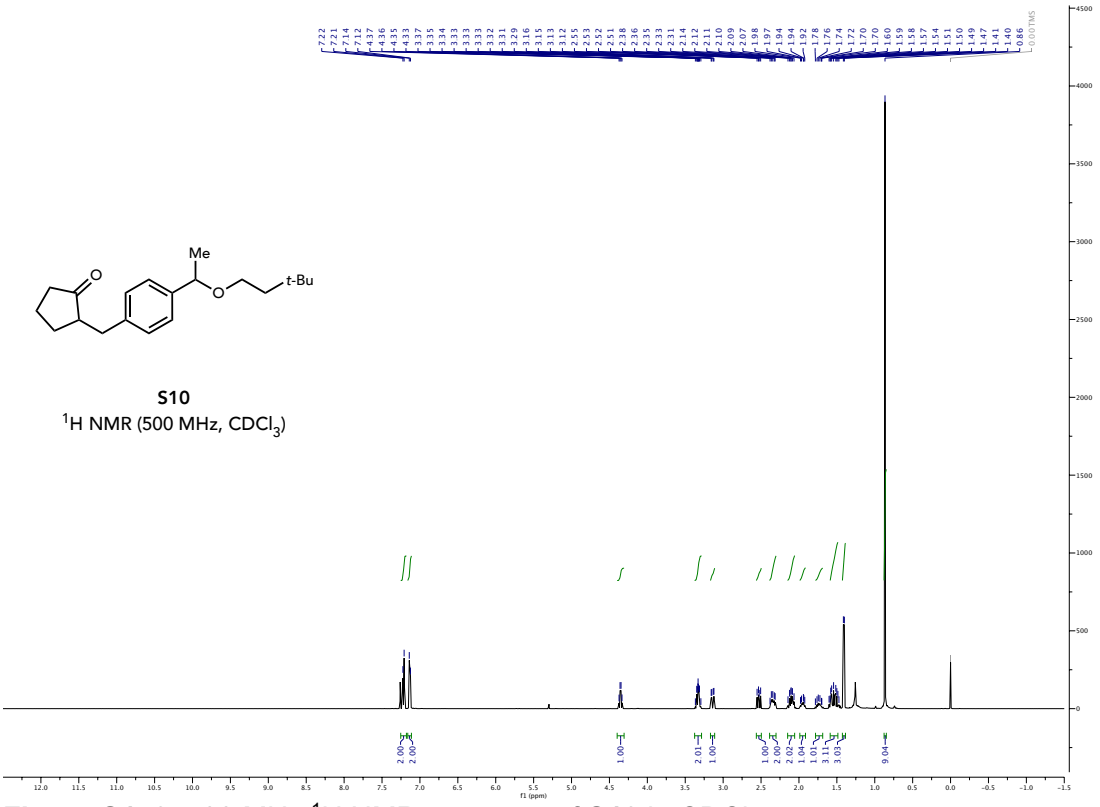


Figure S173. 500 MHz ^{1}H NMR spectrum of **S10** in $CDCl_3$.

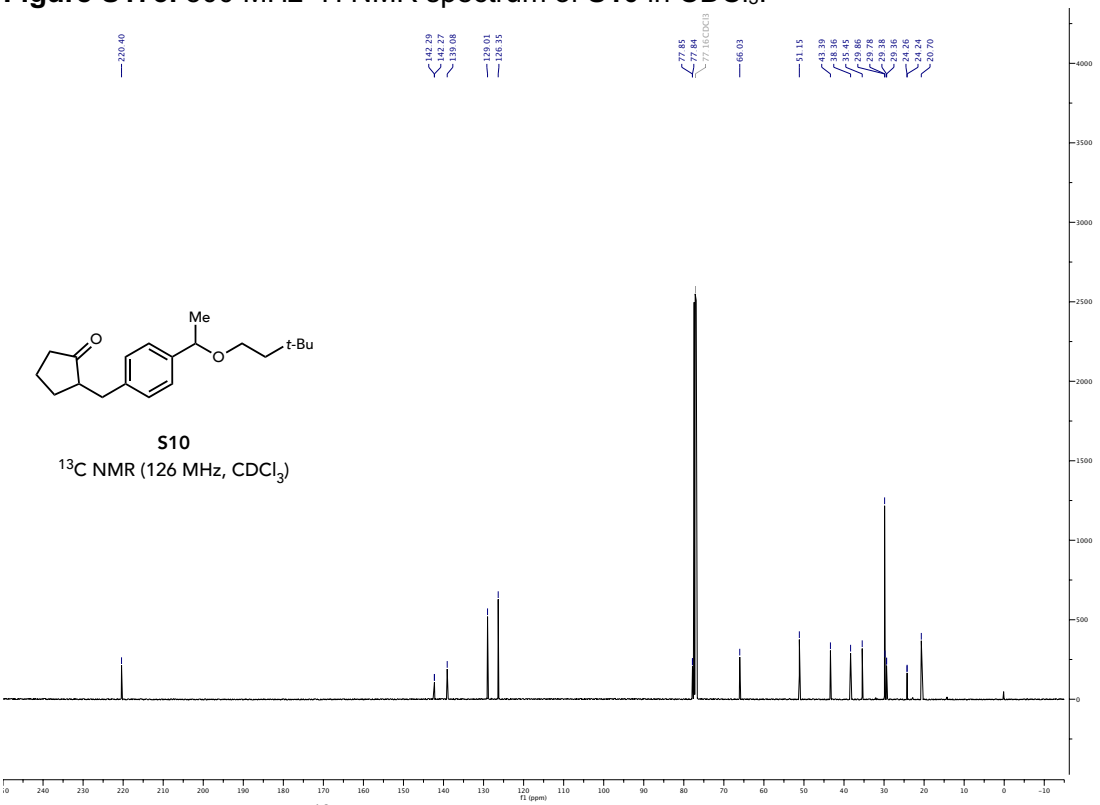


Figure S174. 126 MHz ^{13}C NMR spectrum of **S10** in $CDCl_3$.

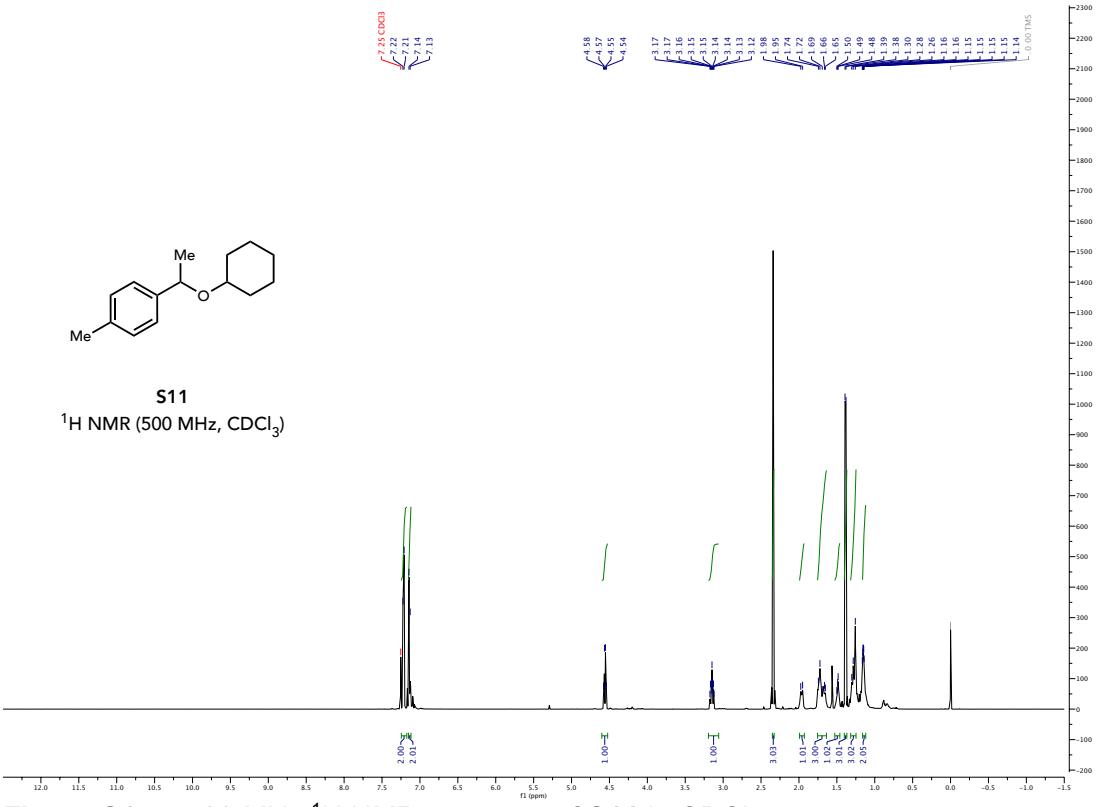


Figure S175. 500 MHz ^{1}H NMR spectrum of **S11** in $CDCl_3$.

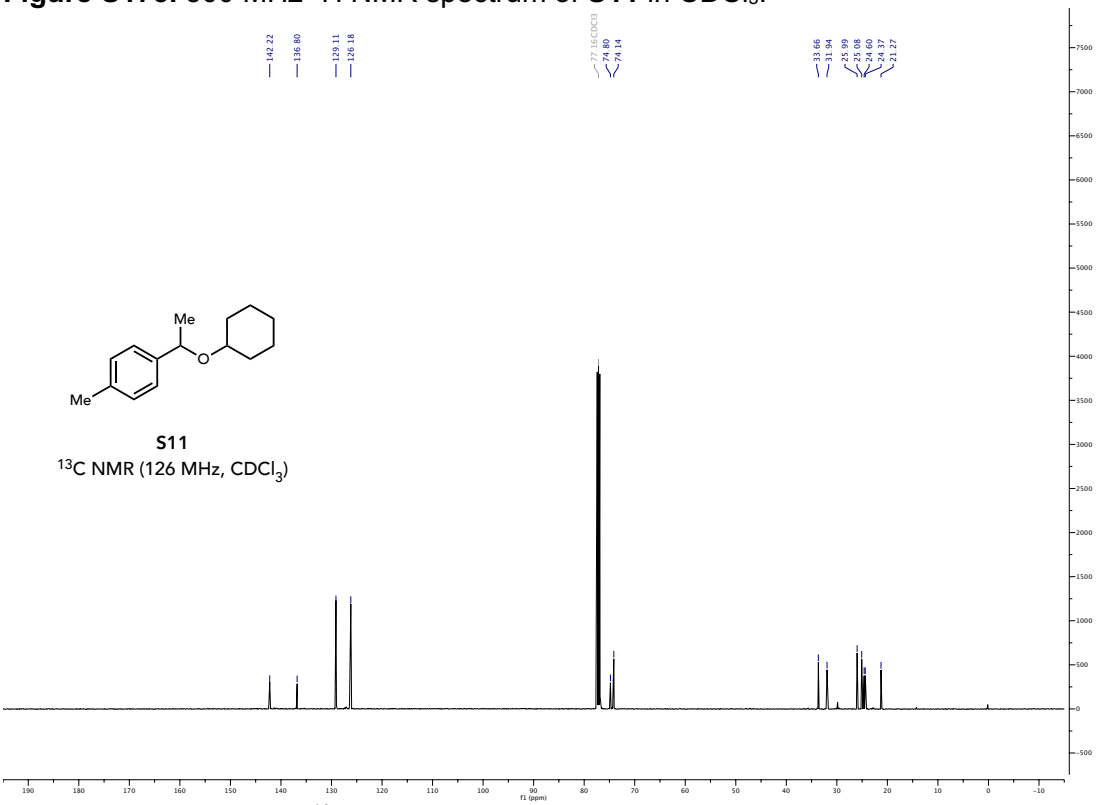


Figure S176. 126 MHz ^{13}C NMR spectrum of **S11** in $CDCl_3$.

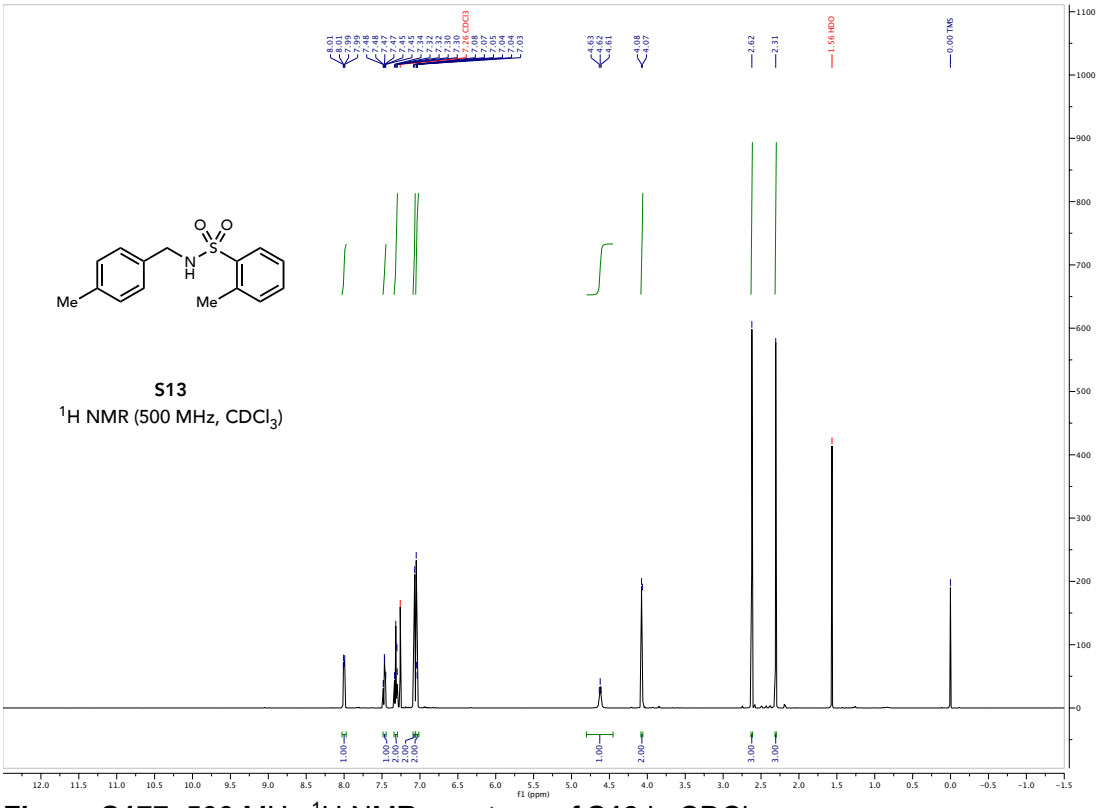


Figure S177. 500 MHz ^{1}H NMR spectrum of **S13** in $CDCl_3$.

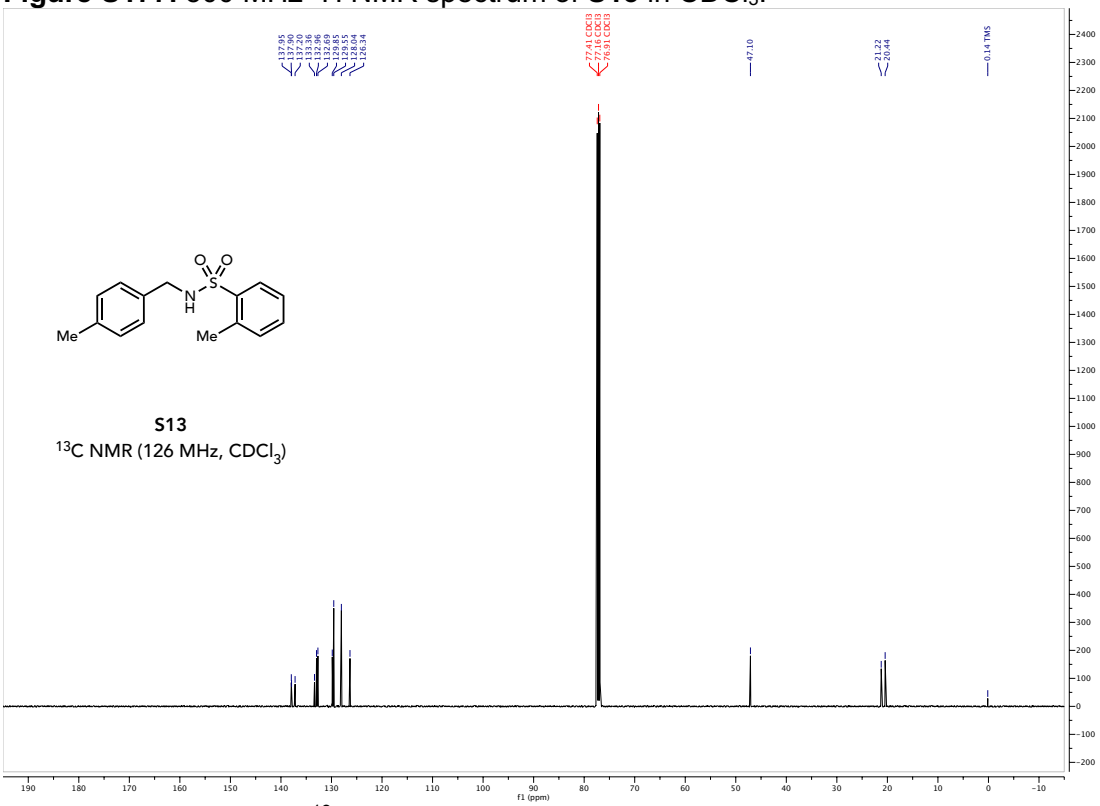


Figure S178. 126 MHz ^{13}C NMR spectrum of **S13** in $CDCl_3$.

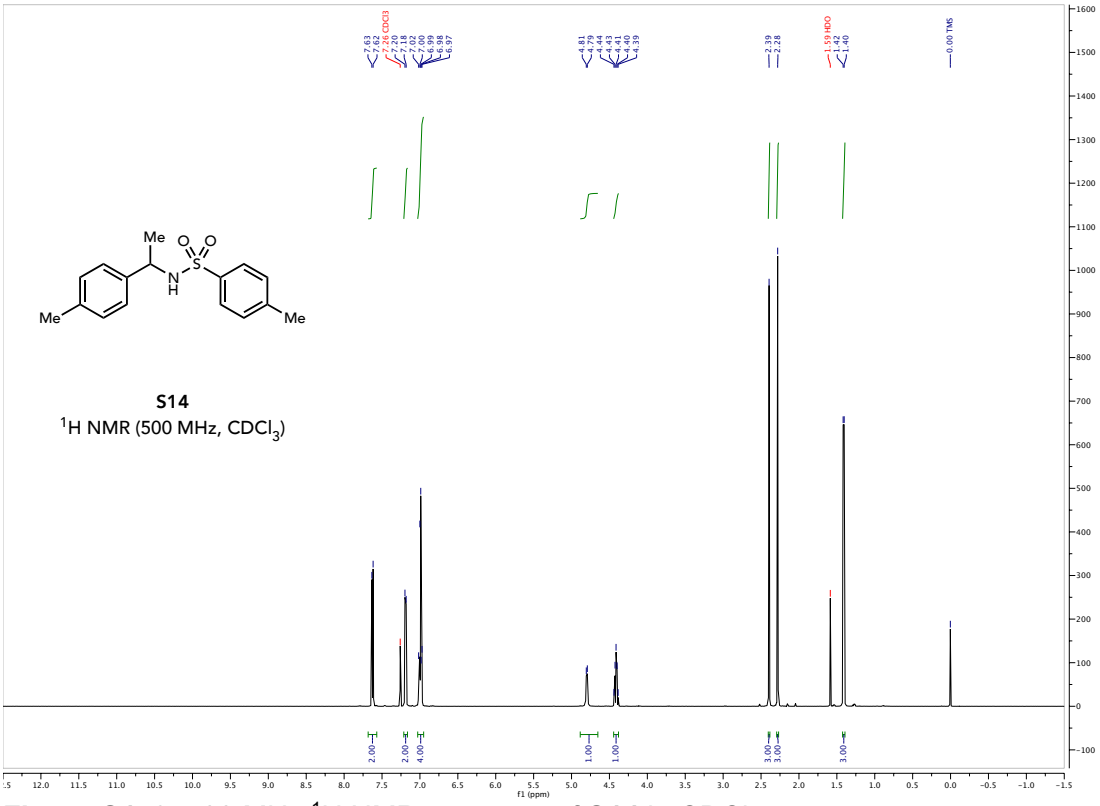


Figure S179. 500 MHz ^{1}H NMR spectrum of **S14** in $CDCl_3$.

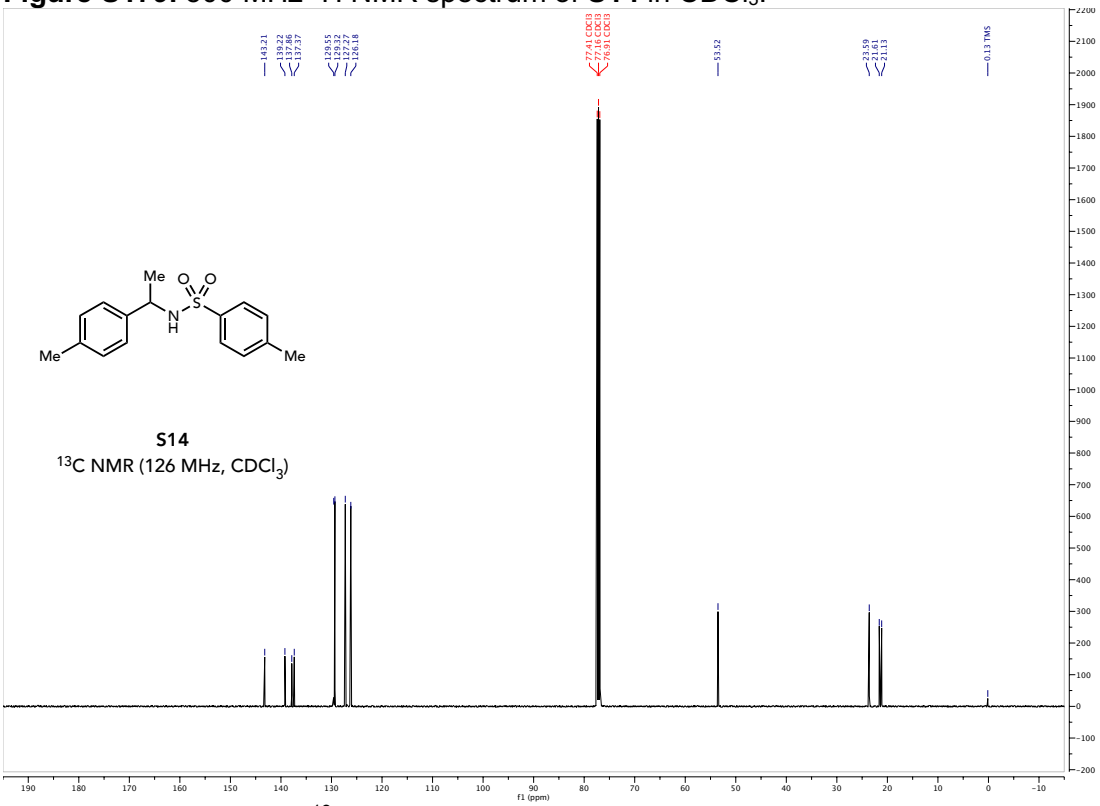


Figure S180. 126 MHz ^{13}C NMR spectrum of **S14** in $CDCl_3$.

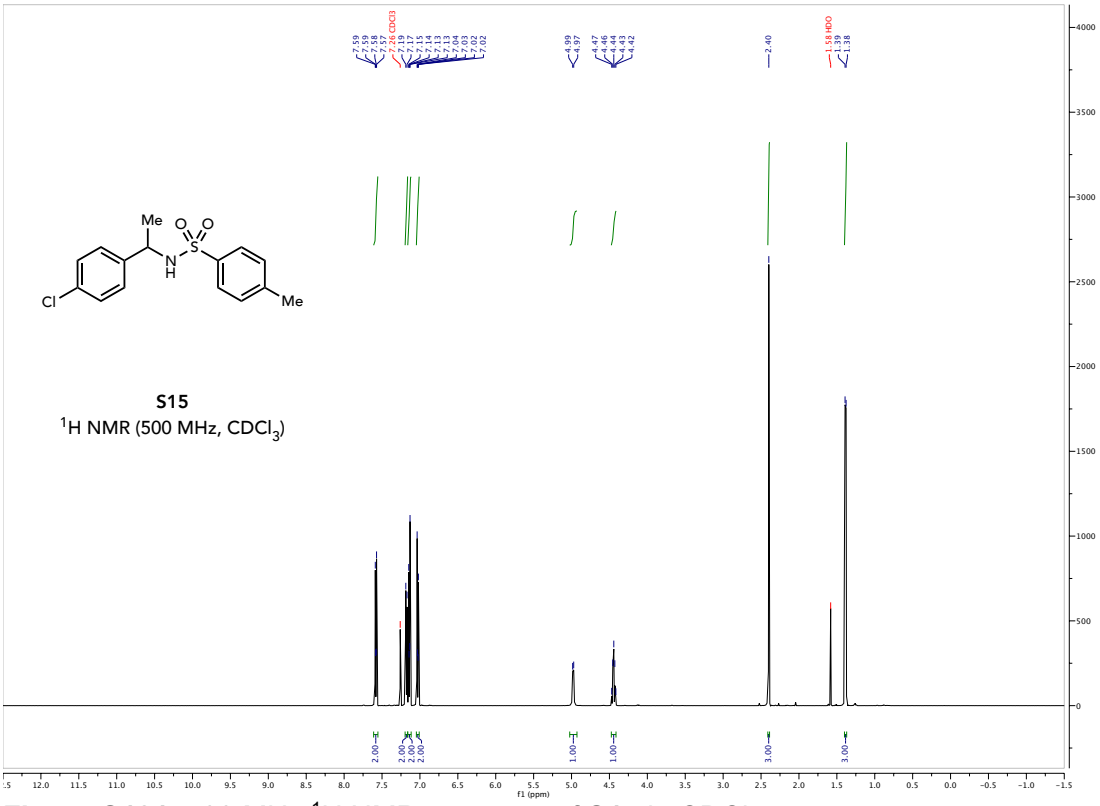


Figure S181. 500 MHz ^{1}H NMR spectrum of **S15** in $CDCl_3$.

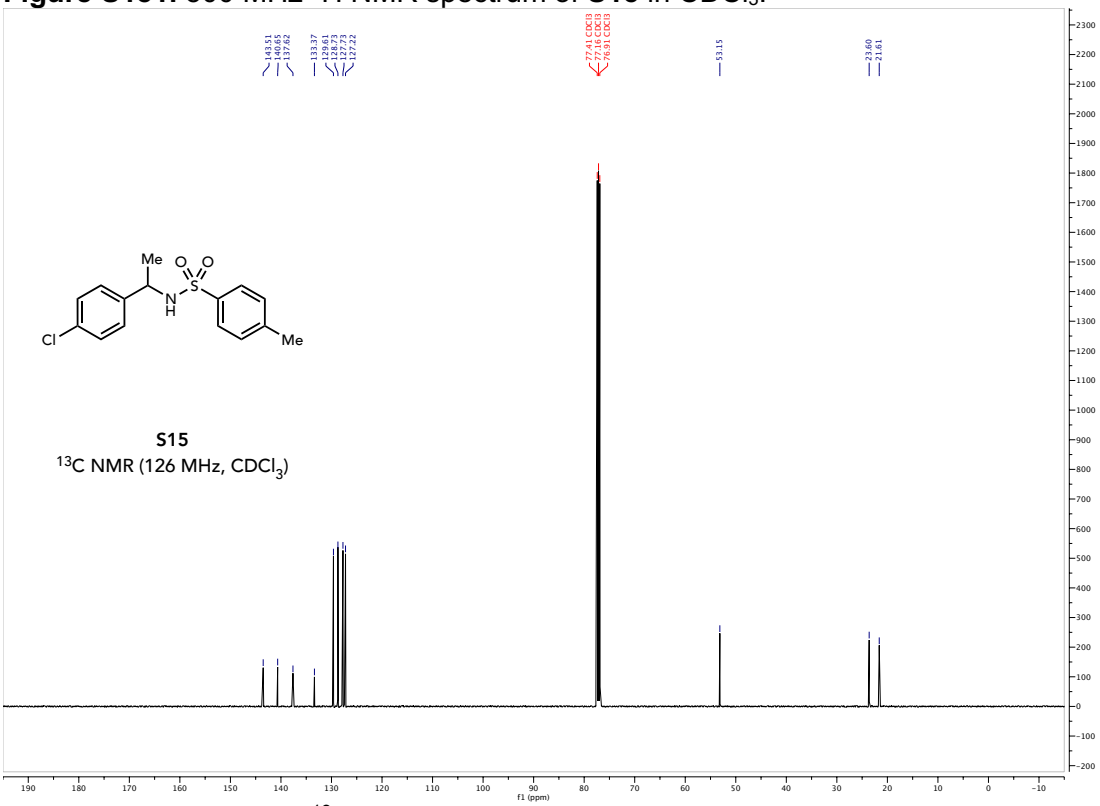


Figure S182. 126 MHz ^{13}C NMR spectrum of **S15** in $CDCl_3$.

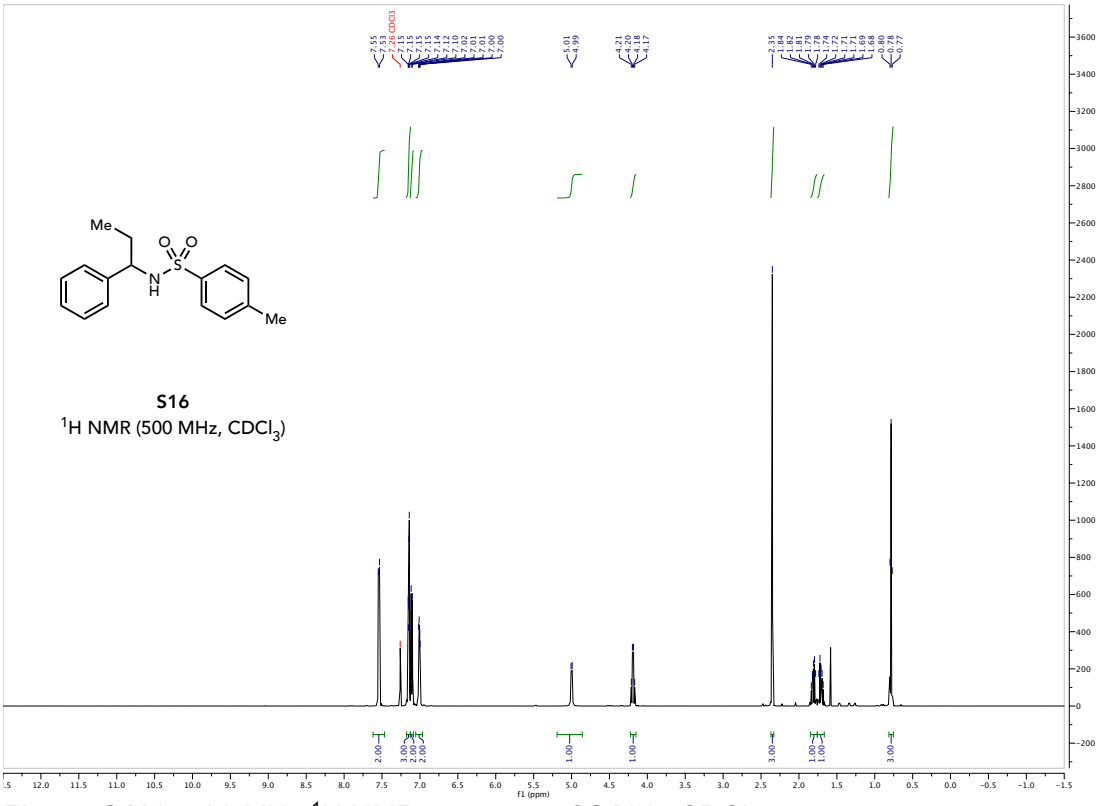


Figure S183. 500 MHz ^{1}H NMR spectrum of **S16** in $CDCl_3$.

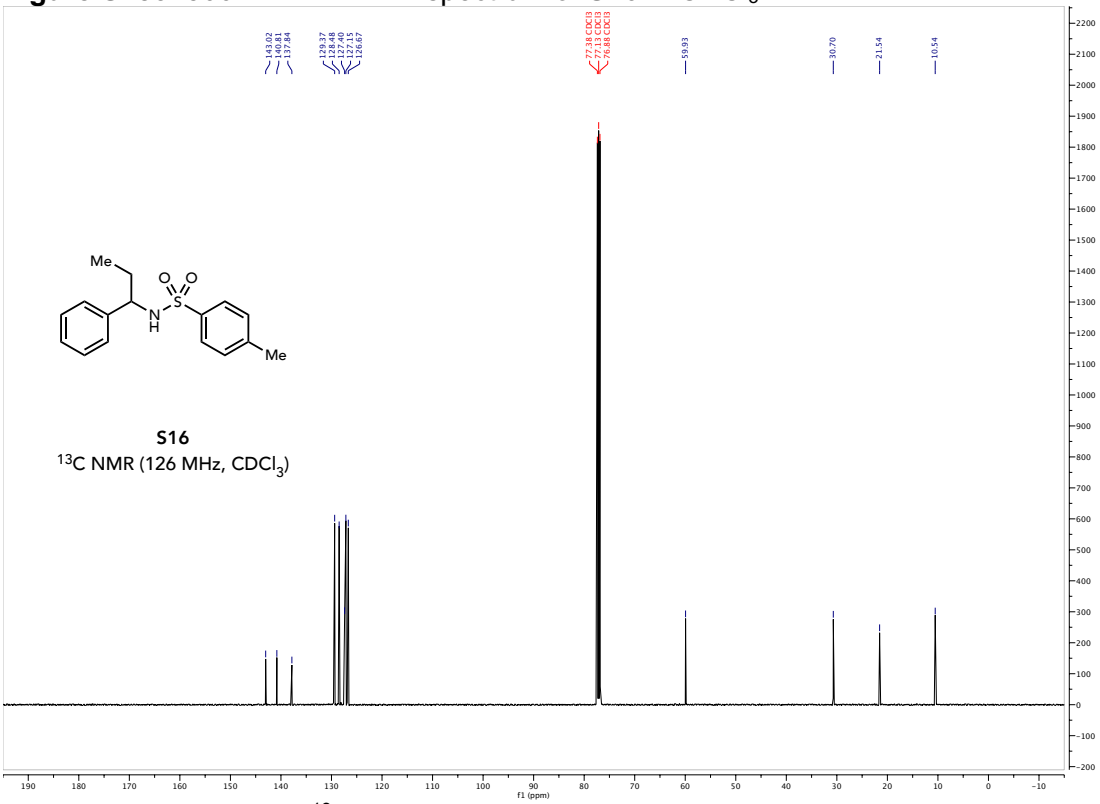


Figure S184. 126 MHz ^{13}C NMR spectrum of **S16** in $CDCl_3$.

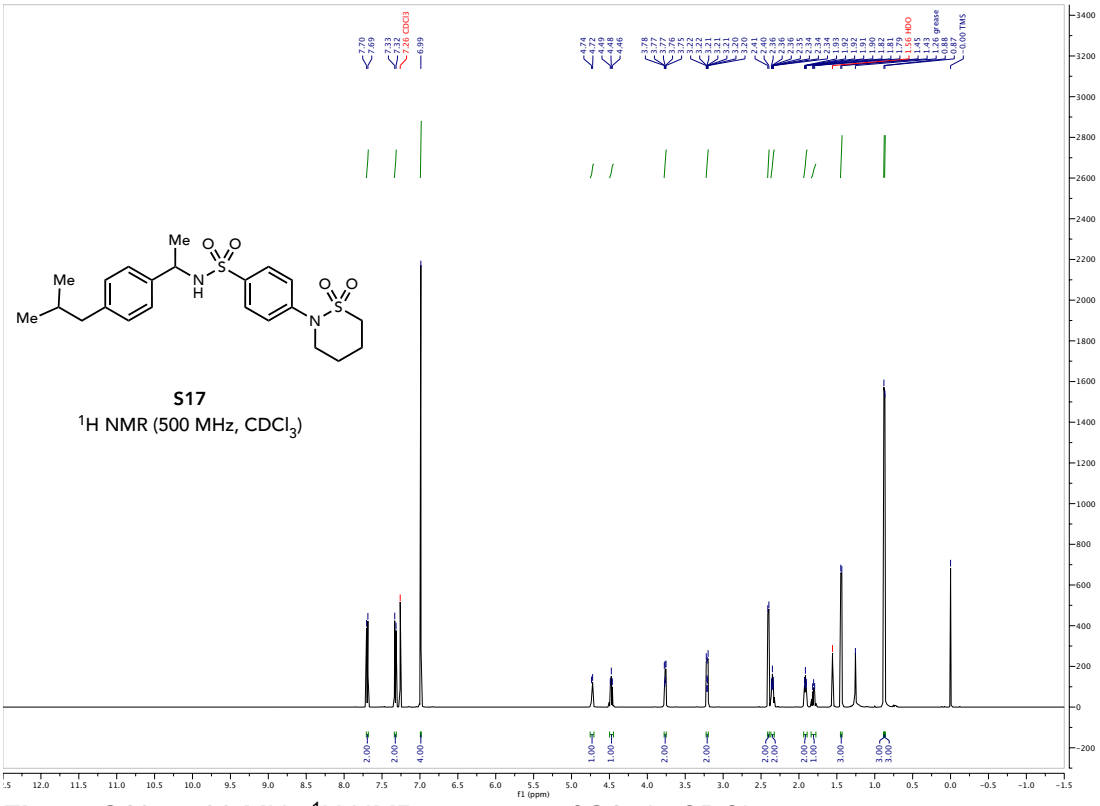


Figure S185. 500 MHz ^{1}H NMR spectrum of **S17** in $CDCl_3$.

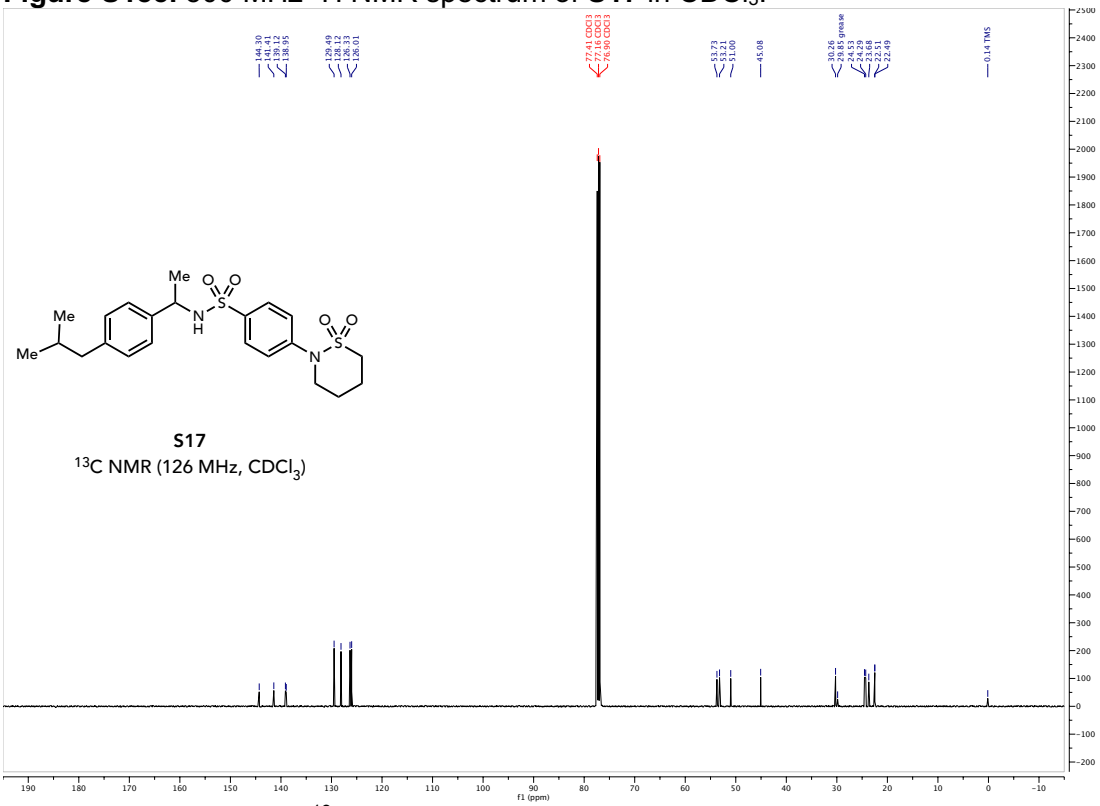


Figure S186. 126 MHz ^{13}C NMR spectrum of **S17** in $CDCl_3$.

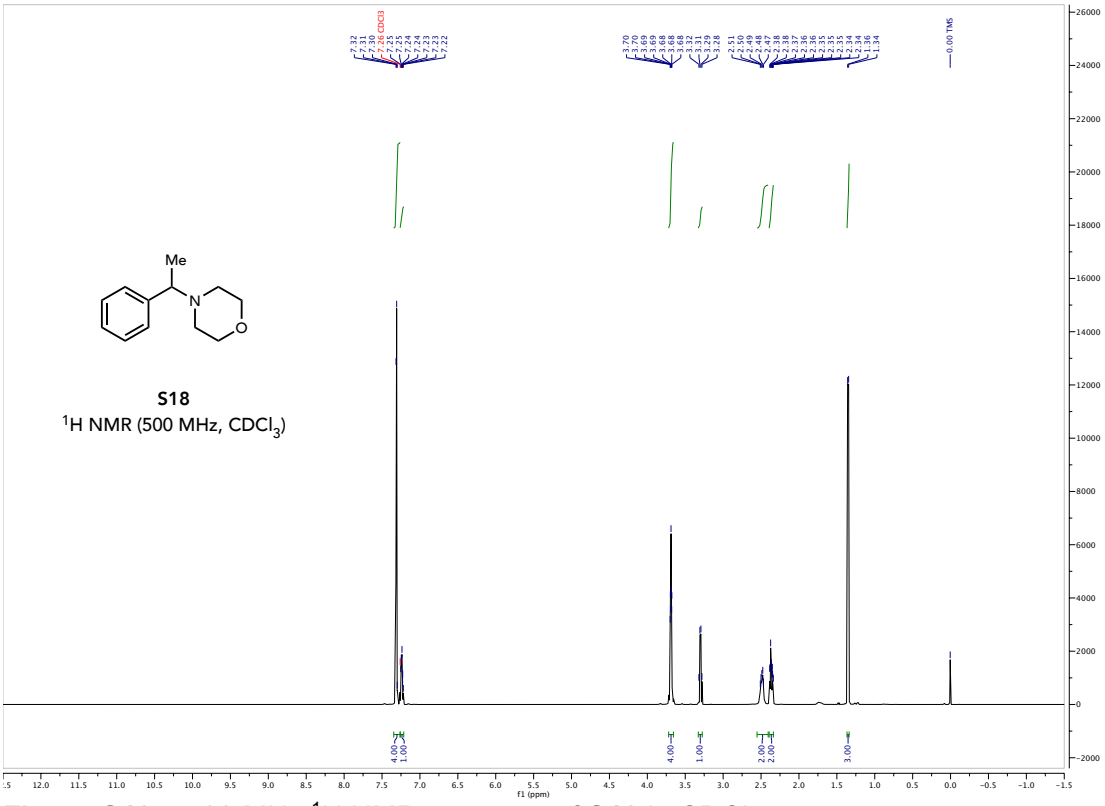


Figure S187. 500 MHz ^{1}H NMR spectrum of **S18** in $CDCl_3$.

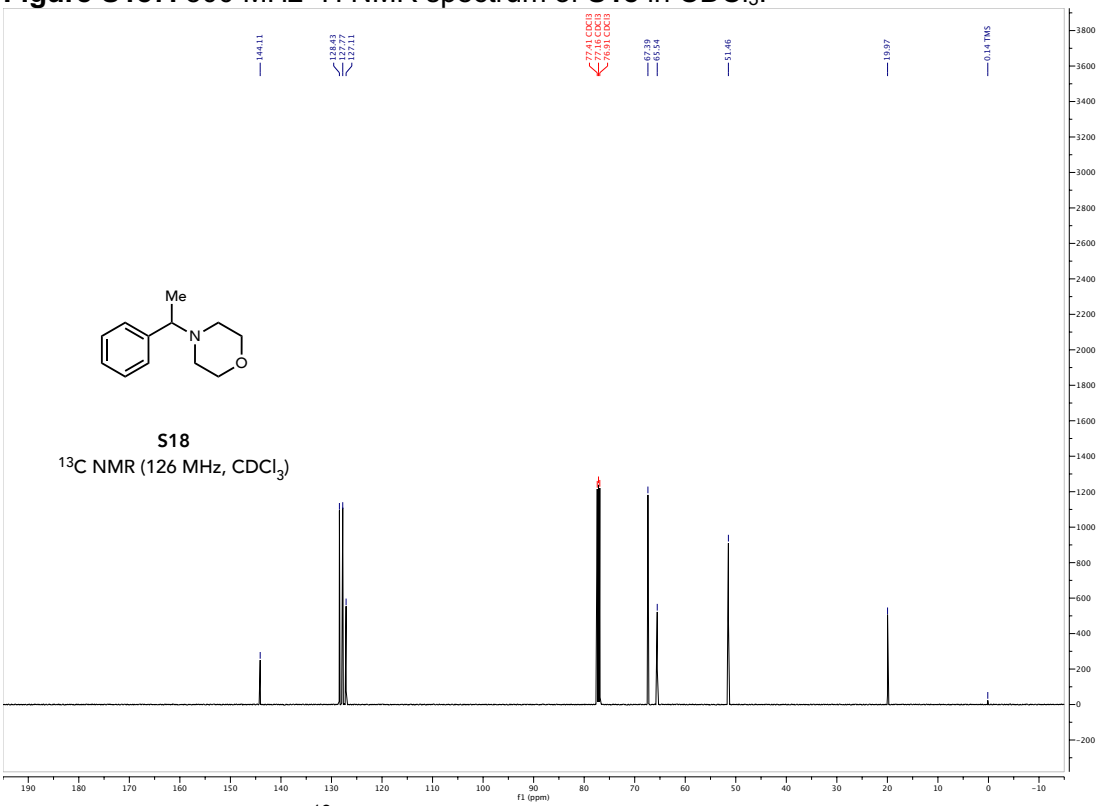


Figure S188. 126 MHz ^{13}C NMR spectrum of **S18** in $CDCl_3$.

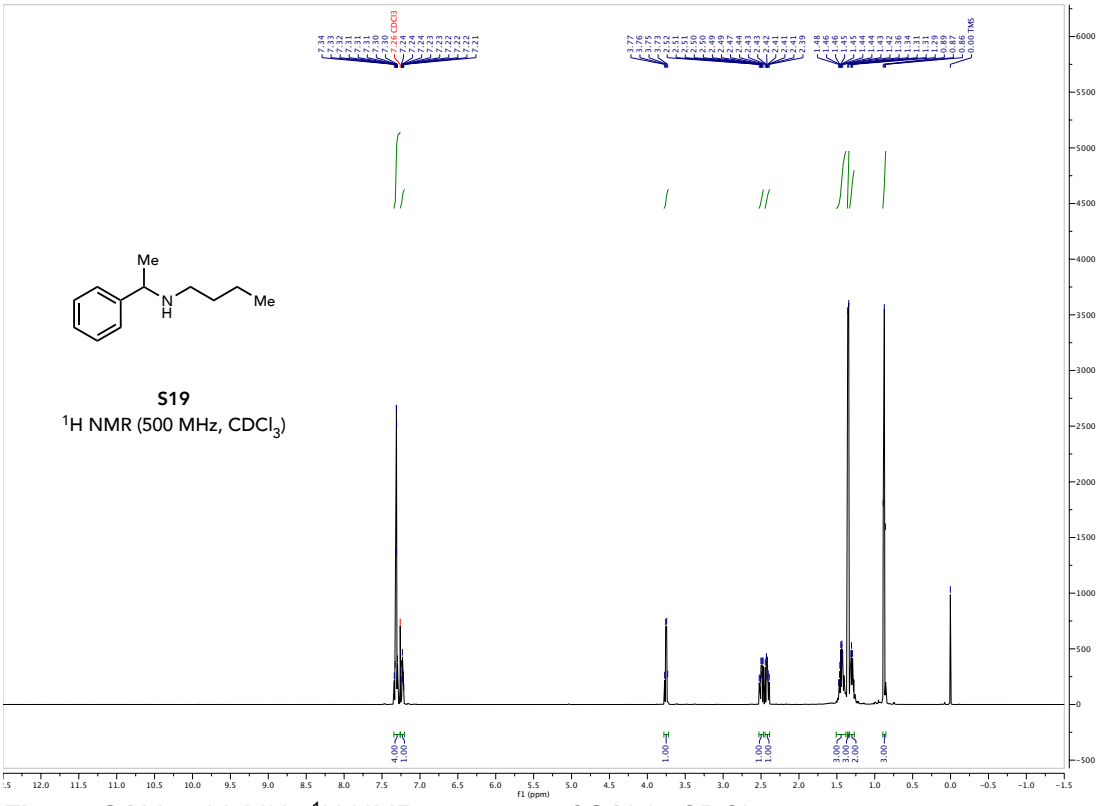


Figure S189. 500 MHz ^{1}H NMR spectrum of **S19** in $CDCl_3$.

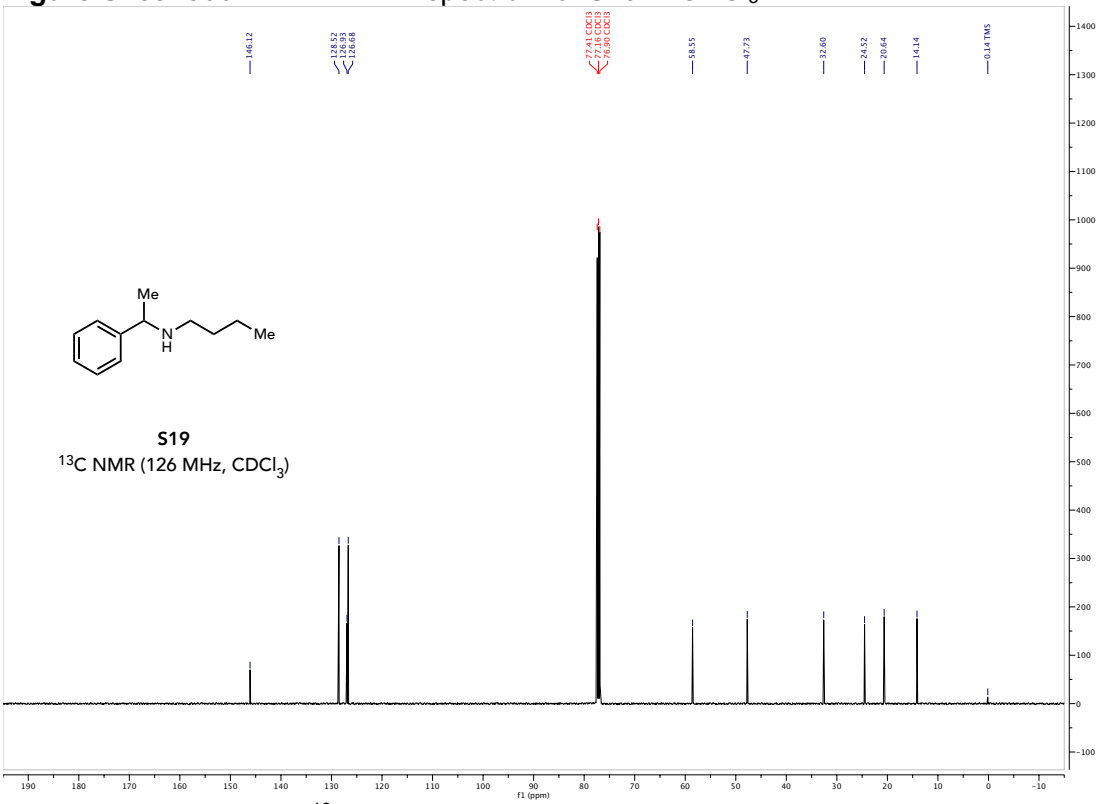


Figure S190. 126 MHz ^{13}C NMR spectrum of **S19** in $CDCl_3$.

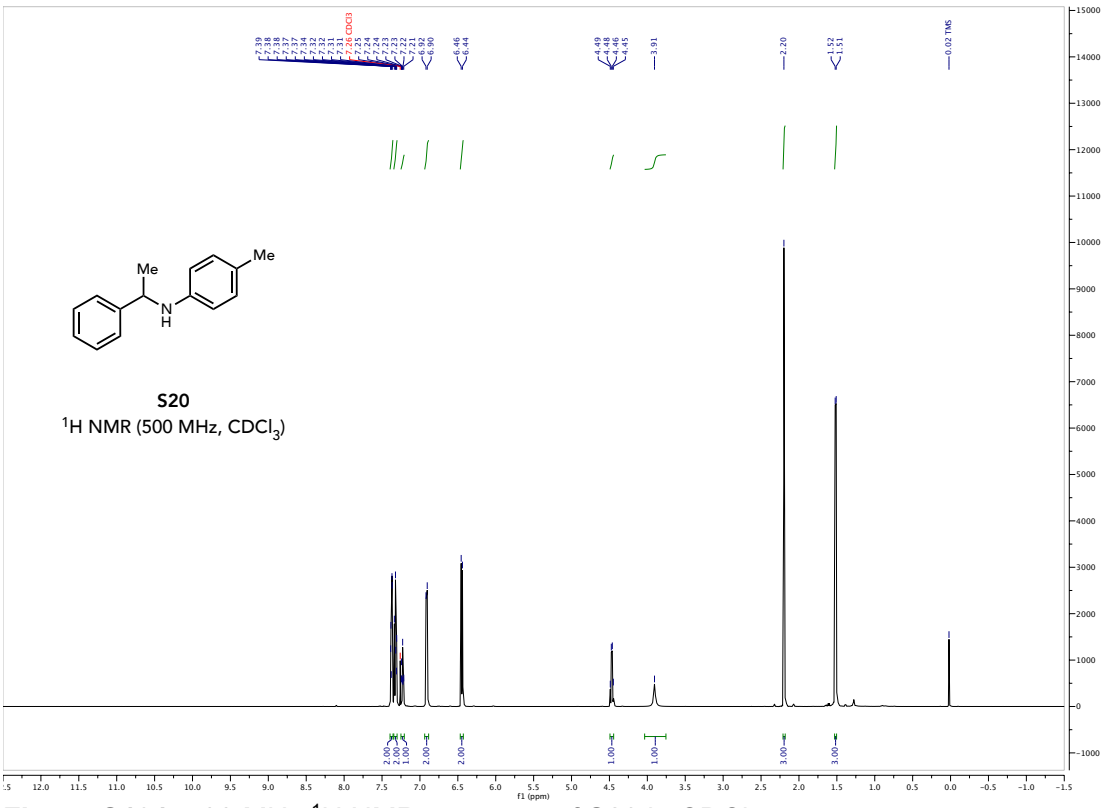


Figure S191. 500 MHz ^{1}H NMR spectrum of **S20** in $CDCl_3$.

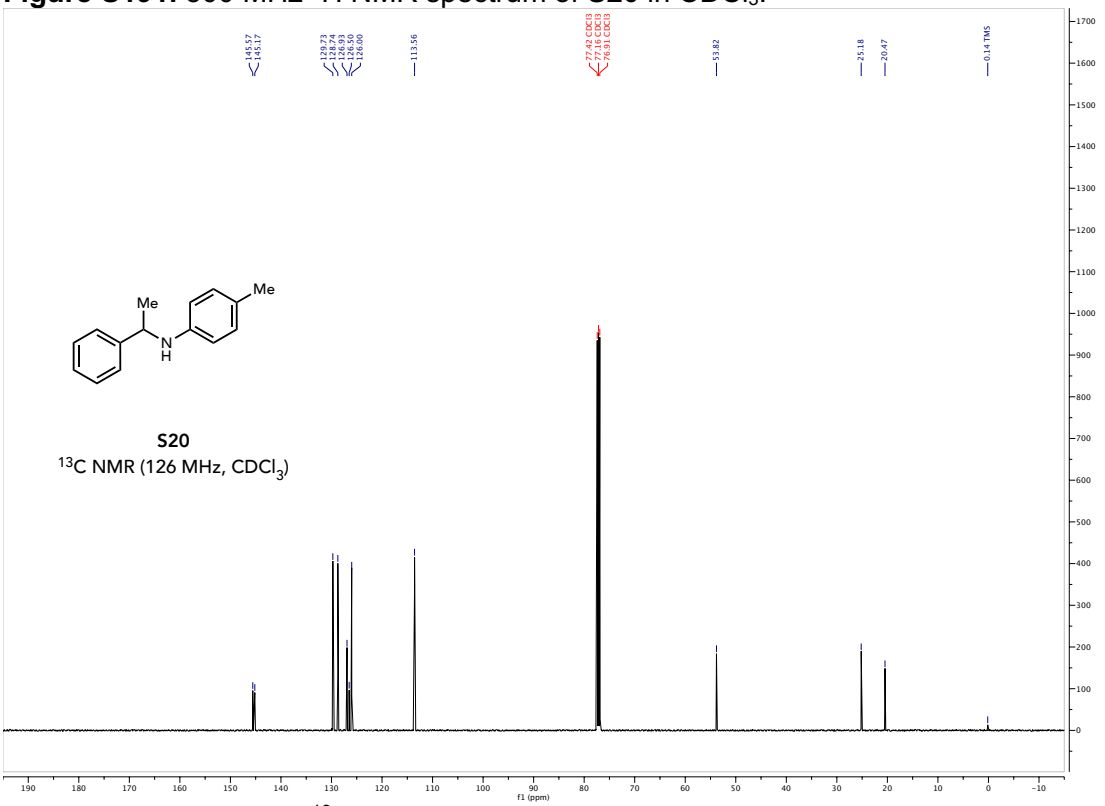


Figure S192. 126 MHz ^{13}C NMR spectrum of **S20** in $CDCl_3$.