Supplementary Information

Decarboxylative cross-nucleophile coupling via ligand-to-metal charge transfer photoexcitation of Cu(II) carboxylates

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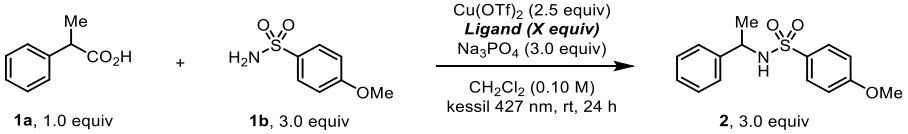
A. General Information

Dichloromethane, tetrahydrofuran, diethyl ether, toluene, and acetonitrile were dried by elution through alumina as described by Grubbs.[44] $Cu(OTf)_2$ was purchased from Oakwood Chemical and stored in glovebox. Methanol, ethanol, isopropanol, allyl alcohol, 2-(allyloxy)ethan-1-ol and 3-methylbut-3-en-ol were 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 source. 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 $KMnO_4$. 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

Sulfonamidation reactions:

Supplementary Table 1. Ligands.

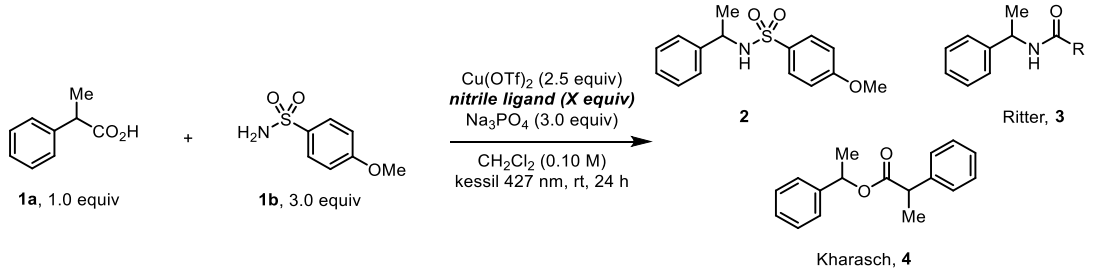


1a, 1.0 equiv **1b**, 3.0 equiv **2**, 3.0 equiv

Entry	Ligand	% **2**	% recovered **1b**	% recovered **1a**
1	none	1	74	63
2	1,10-phen (0.10 equiv.)	3	74	49
3	(*t*-Bu)$_3$terpy (0.20 equiv.)	2	76	73
4	bpy (0.20 equiv.)	3	77	70
5	DABCO (0.20 equiv.)	4	73	51
6	KTp (0.10 equiv.)	3	84	62
7	PPh_3 (0.10 equiv.)	6	72	54
8	dtbbpy (0.05 equiv.)	3	80	51
9	dtbbpy (0.10 equiv.)	5	70	48
10	dtbbpy (0.20 equiv.)	5	87	60
11	dtbbpy (2.0 equiv.)	6	83	78
12	MeCN (2.7 equiv.)	15	60	53

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), the ligand (if solid), **1b** (56.2 mg, 3.0 equiv., 0.30 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), and the ligand (if liquid). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 μL) is as an internal standard.

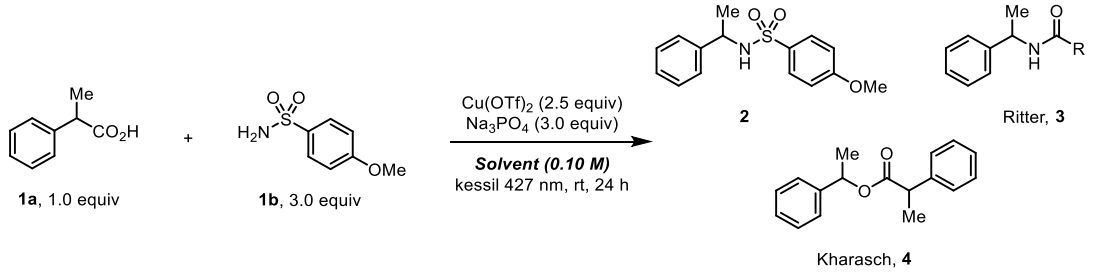
Supplementary Table 2. Nitrile Ligands.



Entry	nitrile	nitrile loading	% **2**	% **3**	% **4**	% recovered **1b**	% recovered **1a**
1	MeCN	2.0	18	4	2	81	24
2	MeCN	2.5	21	3	6	67	22
3	MeCN	5.0	25	5	8	69	22
4	MeCN	10	40	43	7	54	2
5	MeCN	20	44	42	2	50	0
6	MeCN	30	43	43	4	51	1
7	EtCN	2.0	19	0	5	64	20
8	EtCN	2.5	27	0	7	64	19
9	EtCN	5.0	26	0	6	65	14
10	EtCN	10	51	29	8	40	0
11	EtCN	20	42	51	2	41	0
12	CyCN	2.0	38	0	5	44	0
13	CyCN	2.5	44	0	7	29	0
14	CyCN	5.0	58	0	9	24	0
15	CyCN	10	46	17	11	26	0
16	CyCN	15	32	18	13	38	0
17	*i*-PrCN	2.0	34	0	5	62	7
18	*i*-PrCN	2.5	46	0	5	51	3
19	*i*-PrCN	5.0	59	2	4	32	0
20	*i*-PrCN	10	49	7	5	35	0
21	*i*-PrCN	15	37	20	13	41	0
22	*i*-PrCN	20	39	21	5	42	0
23	PhCN	2.0	13	0	2	71	20
24	PhCN	2.5	18	0	3	65	11
25	PhCN	5.0	34	0	4	46	13
26	PhCN	10	32	7	4	42	2
27	PhCN	20	42	16	5	41	0

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), and **1b** (56.2 mg, 3.0 equiv., 0.30 mmol). **1a** is delivered *via* a stock solution in CH_2Cl_2 (15 mg/mL, 1.0 mL, 0.10 M), and the nitrile (x equiv.) is added. The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

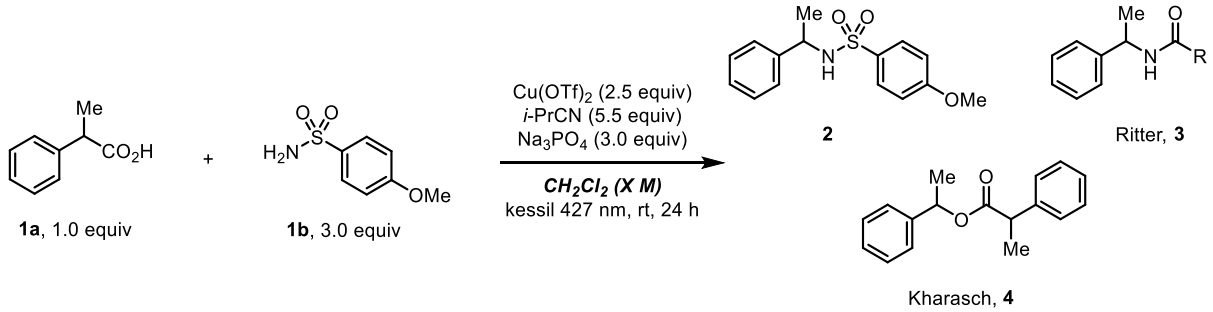
Supplementary Table 3. Solvent.



Entry	Solvent	% **2**	% **3**	% **4**	% recovered **1b**	% recovered **1a**
1	THF	0	–	0	89	54
2	Et_2O	0	–	0	87	72
3	EtOAc	0	–	0	90	62
4	DMF	0	–	0	52	58
5	DMA	0	–	0	44	31
6	DMSO	0	–	0	48	53
7	PhOMe	0	–	0	77	67
8	PhMe	0	–	0	75	64
9	$PhCF_3$	0	–	0	78	68
10	MeCN	0	75	5	85	6
11	PhCN	25	42	6	76	4
12	DCE	1	–	0	76	61
13	DCM	2	–	0	74	63
14	PhMe (+ 5.5 equiv. *i*-PrCN)	15	1	4	77	41
15	$PhCF_3$ (+ 5.5 equiv. *i*-PrCN)	23	6	15	74	21
16	DCE (+ 5.5 equiv. *i*-PrCN)	48	4	10	69	4
17	DCM (+ 5.5 equiv. *i*-PrCN)	66	0	15	61	2

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), **1b** (56.2 mg, 3.0 equiv., 0.30 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), solvent (1.0 mL, 0.10 M), and *i*-PrCN (0 or 50 µL, 0 or 5.5 equiv., 0 or 0.55 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

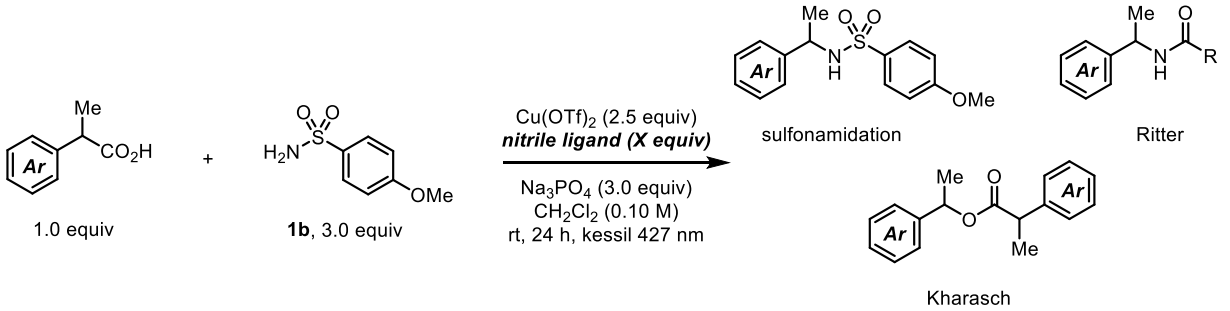
Supplementary Table 4. Concentration.



entry	concentration (M)	% **2**	% **3**	% **4**	% recovered **1a**
1	0.05	53	1	15	2
2	0.075	45	1	20	19
3	0.10	66	0	15	3
4	0.16	42	2	22	13
5	0.20	31	3	17	35
6	0.30	22	5	14	49
7	0.40	34	7	14	13
8	0.50	26	7	13	32

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), **1b** (56.2 mg, 3.0 equiv., 0.30 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (X M), and *i*-PrCN (50 µL, 5.5 equiv., 0.55 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

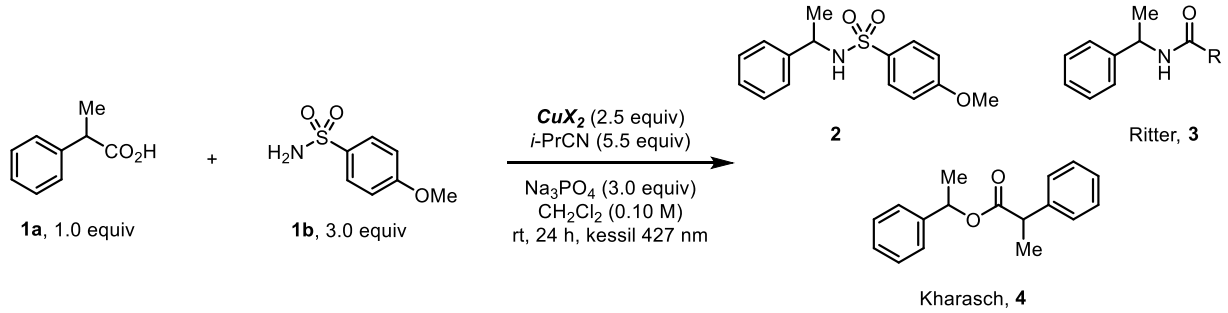
Supplementary Table 5. *i*-PrCN vs. MeCN.



Entry	Ar	nitrile ligand	% sulfonamidation	% Ritter	% Kharasch
1	4-Me-Ph	MeCN (10 equiv.)	91	0	5
2	4-Me-Ph	*i*-PrCN (5.5 equiv.)	95	0	2
3	4-*i*-Bu-Ph	MeCN (10 equiv.)	80	0	12
4	4-*i*-Bu-Ph	*i*-PrCN (5.5 equiv.)	99	0	<1
5	4-Cl-Ph	MeCN (10 equiv.)	16	42	4
6	4-Cl-Ph	*i*-PrCN (5.5 equiv.)	48	0	8
7	Ph	MeCN (10 equiv.)	40	43	7
8	Ph	*i*-PrCN (5.5 equiv.)	66	0	15

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), **1b** (56.2 mg, 3.0 equiv., 0.30 mmol), the carboxylic acid (1.0 equiv., 0.10 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), and either MeCN (52 µL, 10 equiv., 1.0 mmol) or *i*-PrCN (50 µL, 5.5 equiv., 0.55 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

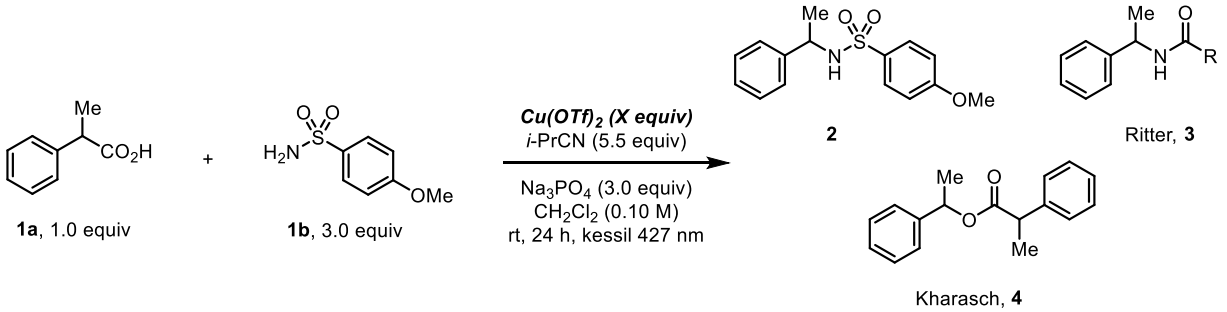
Supplementary Table 6. Cu(II) salts.



Entry	Cu salt	% **2**	% **3**	% **4**	% recovered **1b**	% recovered **1a**
1	$Cu(OTf)_2$	66	0	15	53	3
2	$Cu(NTf_2)_2$	24	0	3	78	1
3	$CuBr_2$	0	0	0	71	45
4	$Cu(OAc)_2$	0	0	0	66	42
5	$Cu(OPiv)_2$	0	0	0	69	49
6	$Cu(isobutyrate)_2$	0	0	0	70	49
7	$Cu(TFA)_2$•MeCN	0	0	0	68	41
8	$Cu(eh)_2$	0	0	0	71	45
9	$Cu(acac)_2$	0	0	0	70	49
10	CuF_2	0	0	0	74	45
11	$Cu(OMe)_2$	0	0	0	67	42
12	$CuCl_2$	0	0	0	71	43
13	$CuSO_4$	0	0	0	63	39

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with the Cu(II) salt (2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), **1b** (56.2 mg, 3.0 equiv., 0.30 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), and *i*-PrCN (50 µL, 5.5 equiv., 0.55 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

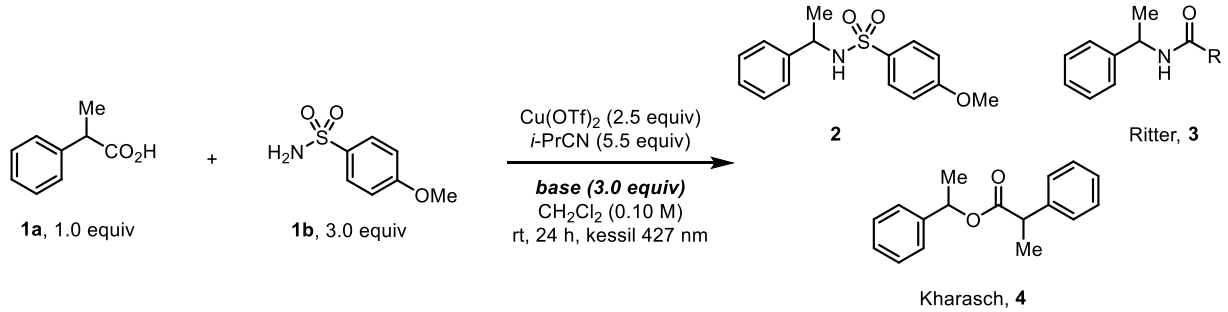
Supplementary Table 7. Cu(II) equivalencies.



Entry	equiv. $Cu(OTf)_2$	% **2**	% **3**	% **4**	% recovered **1a**
1	1.0	15	2	8	21
2	1.5	35	3	18	18
3	2.0	53	4	19	12
4	2.5	66	0	15	0
5	3.0	65	3	18	1

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (X equiv.), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), **1b** (56.2 mg, 3.0 equiv., 0.30 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), and *i*-PrCN (50 µL, 5.5 equiv., 0.55 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

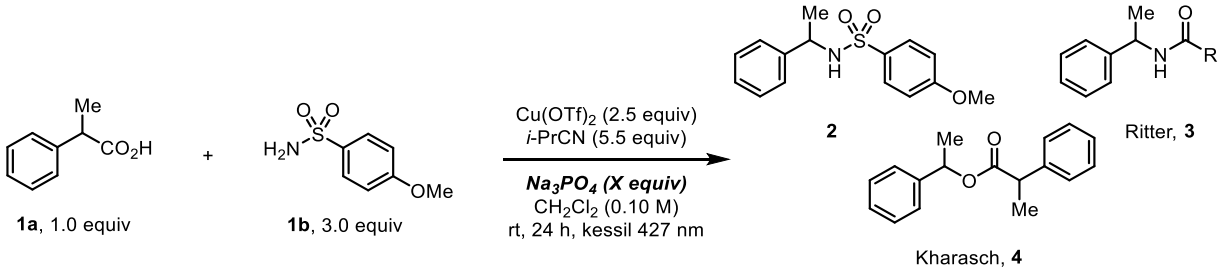
Supplementary Table 8. Bases.



Entry	base	% **2**	% **3**	% **4**	% recovered **1b**	% recovered **1a**
1	Na_2CO_3	58	4	6	31	0
2	K_2CO_3	66	3	7	34	0
3	Cs_2CO_3	2	0	0	95	32
4	Na_3PO_4	66	3	15	31	0
5	K_3PO_4	10	1	2	34	28
6	NaOAc	25	1	2	18	23
7	CsF	45	2	12	48	5
8	K_2HPO_4	42	2	5	40	10
9	Na_2HPO_4	54	2	13	36	6
10	pyridine	63	2	2	34	4
11	KH_2PO_4	18	1	2	16	25

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), the base (3.0 equiv., 0.30 mmol), **1b** (56.2 mg, 3.0 equiv., 0.30 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), and *i*-PrCN (50 µL, 5.5 equiv., 0.55 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

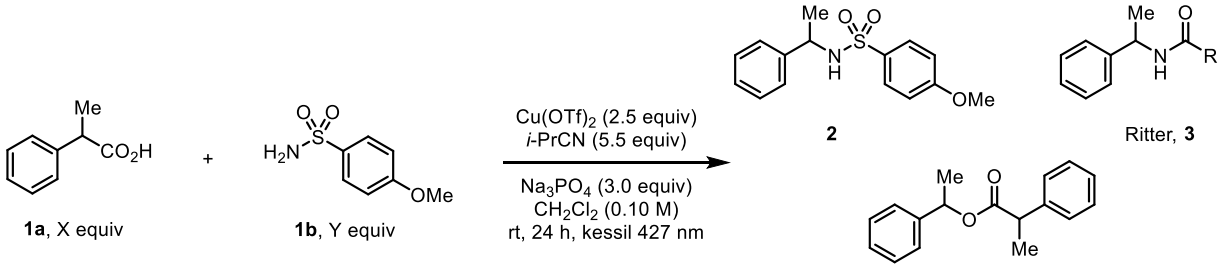
Supplementary Table 9. Base loading.



Entry	equiv. Na_3PO_4	% **2**	% **3**	% **4**	% recovered **1a**
1	1.0	38	1	9	0.27
2	1.5	38	1	14	0.27
3	2.0	41	1	14	0.20
4	3.0	61	0	15	0.41

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (X equiv.), **2a** (56.2 mg, 3.0 equiv., 0.30 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), and *i*-PrCN (50 µL, 5.5 equiv., 0.55 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

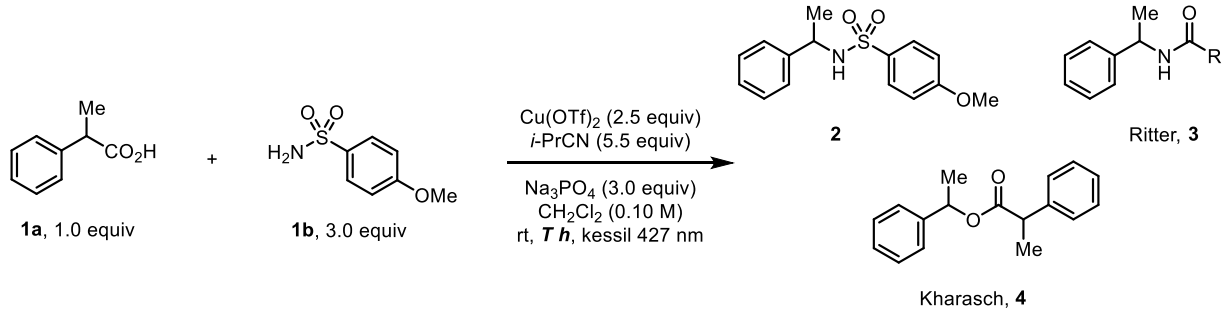
Supplementary Table 10. Substrate loadings.



Entry	equiv. **1a**	equiv. **1b**	% **2**	% **3**	% **4**	% recovered **1a**
1	1.0	1.0	19	1	39	5
2	1.0	1.2	23	1	37	7
3	1.0	1.5	30	0	31	3
4	1.0	3.0	61	0	15	0
5	1.0	5.0	28	0	8	43
6	1.5	1.0	9	1	27	58
7	2.0	1.0	7	1	28	53
8	3.0	1.0	4	0	18	65

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), **2a** (X equiv.), **1a** (Y equiv.), CH_2Cl_2 (1.0 mL, 0.10 M), and *i*-PrCN (50 µL, 5.5 equiv., 0.55 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

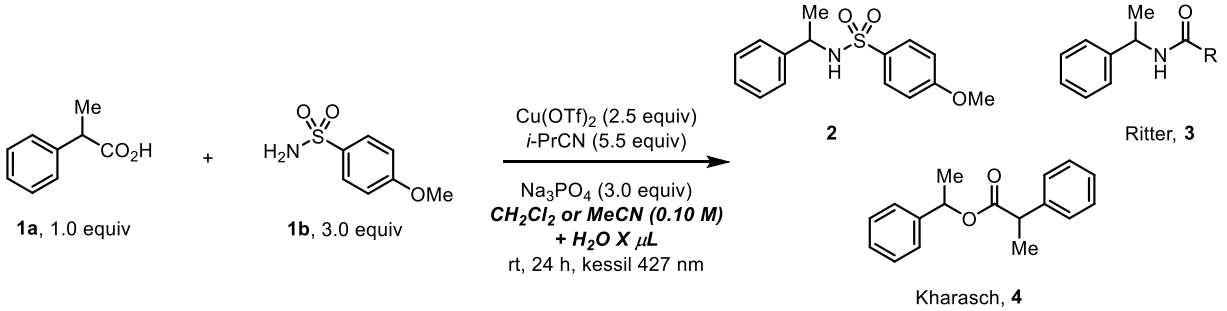
Supplementary Table 11. Time course.



Entry	Time (h)	% **2**	% **3**	% **4**	% recovered **1a**
1	1	5	0	2	55
2	2	15	1	4	36
3	4	20	1	6	28
4	6	22	1	7	40
5	7	21	2	6	41
6	16	39	3	8	18
7	18	45	3	15	11
8	20	56	3	11	5
9	24	61	0	15	0

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), **1b** (56.2 mg, 3.0 equiv., 0.30 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), and *i*-PrCN (50 µL, 5.5 equiv., 0.55 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W Kessil PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After the given time, the crude reaction mixture is diluted with EtOAc and 2.0 M aqueous HCl. Yields are determined by GC analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

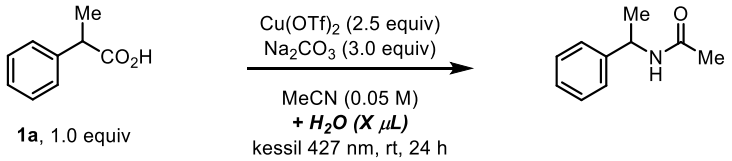
Supplementary Table 12. Water addition under sulfonamidation conditions.



Entry	H_2O (μL)	Solvent	% **2**	% **3**	% **4**	% recovered **1b**	% recovered **1a**
1[a]	0	CH_2Cl_2	2	–	0	74	63
2[a]	1	CH_2Cl_2	2	–	0	91	96
3[a]	10	CH_2Cl_2	2	–	0	95	94
4[a]	25	CH_2Cl_2	0	–	0	93	99
5[a]	50	CH_2Cl_2	0	–	0	95	97
6	0	CH_2Cl_2	66	0	15	61	2
7	1	CH_2Cl_2	33	19	0	78	64
8	10	CH_2Cl_2	16	9	0	87	70
9	25	CH_2Cl_2	1	4	0	89	91
10	50	CH_2Cl_2	1	3	0	92	94
11[a]	0	MeCN	0	75	0	85	6
12[a]	1	MeCN	4	69	0	82	19
13[a]	10	MeCN	1	15	0	83	64
14[a]	25	MeCN	1	12	0	76	69
15[a]	50	MeCN	5	14	0	73	71

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), **2a** (56.2 mg, 3.0 equiv., 0.30 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (1.0 mL, 0.10 M), *i*-PrCN (50 μL, 5.5 equiv., 0.55 mmol), and H_2O (X μL). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^{1}H NMR analysis using 1-methylnaphthalene (10 μL) is as an internal standard. [a.] Reaction conducted without *i*-PrCN ligand.

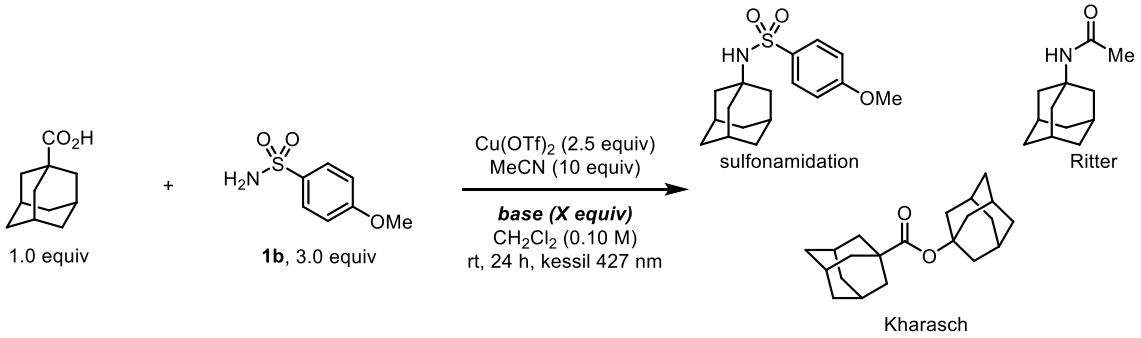
Supplementary Table 13. Water addition under Ritter conditions.



Entry	H_2O (μL)	% product	% recovered **1a**
1	0	73	6
2	0.2	70	5
3	0.5	60	4
4	1.0	54	10
5	2.0	50	14
6	3.0	44	18
7	4.0	33	25
8	5.0	0	29
9	10	0	21
10	25	0	27
11	50	0	21
12	100	0	23

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_2CO_3 (10.6 mg, 1.0 equiv., 0.10 mmol), **1a** (15.0 mg, 1.0 equiv., 0.10 mmol), MeCN (2.0 mL, 0.10 M), and H_2O (X μL). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W 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 2.0 M aqueous HCl. Yields are determined by GC or ^1H NMR analysis using 1-methylnaphthalene (10 μL) is as an internal standard.

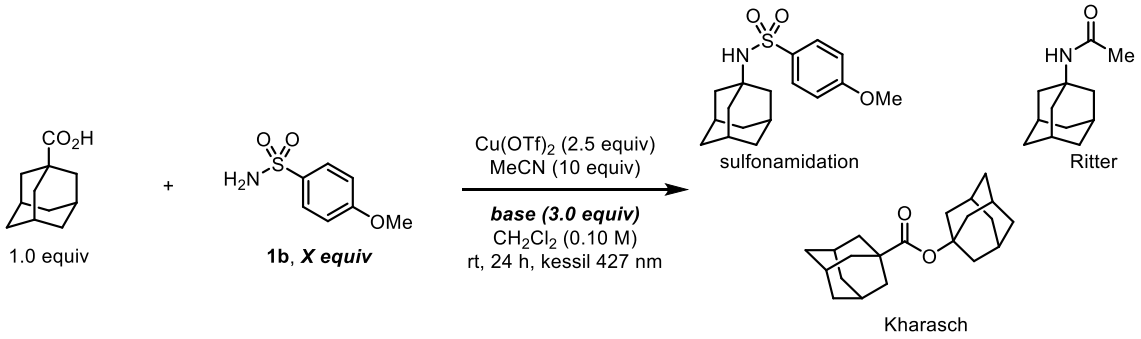
Supplementary Table 14. Miscellaneous Optimization with Adamantyl Acid: bases and loadings.



Entry	base (equiv.)	equiv. **1b**	sulfonamidation/IS	Ritter/IS	Kharasch/IS	acid/IS
1	Na_3CO_3 (3)	3	0.95	0.41	0.65	0
2	K_2CO_3 (1)	3	0.65	0.27	0.45	0.41
3	K_2CO_3 (1.5)	3	0.69	0.27	0.47	0.30
4	K_2CO_3 (3)	3	1.11	0.37	0.68	0
5	K_2CO_3 (5)	3	0.30	0.19	0.26	0.64
6	Na_3PO_4 (1)	3	1.16	0.40	0.65	0
7	Na_3PO_4 (1.5)	3	1.47	0.48	0.79	0.00
8	Na_3PO_4 (3)	3	0.96	0.45	0.72	0
9	Na_3PO_4 (2)	3	0.57	0.32	0.41	0.30
10	Na_3PO_4 (5)	3	0.74	0.41	0.59	0.13

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 (49.2 mg, 3.0 equiv., 0.30 mmol), **1b** (56.2 mg, 3.0 equiv., 0.30 mmol), 1-adamantane carboxylic acid (18.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (0.50 mL, 0.20 M), and MeCN (52 µL, 10 equiv., 1.0 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W Kessil PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After the given time, the crude reaction mixture is diluted with EtOAc and 2.0 M aqueous HCl. Analyte/internal standard ratios (IS) are determined by GC analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

Supplementary Table 15. Sulfonamide loading with promising bases.

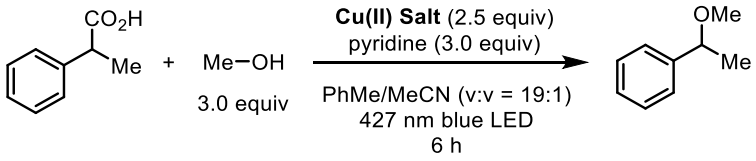


Entry	base	equiv. **1b**	sulfonamidation/IS	Ritter/IS	Kharasch/IS	acid/IS
1	Na_3PO_4	1.0	0.73	0.54	0.85	0.00
2	Na_3PO_4	1.5	0.89	0.44	0.78	0.00
3	Na_3PO_4	3.0	1.04	0.34	0.68	0.00
4	Na_3PO_4	5.0	1.10	0.40	0.66	0.00
5	K_2CO_3	1.0	0.16	0.20	0.31	0.54
6	K_2CO_3	1.5	0.30	0.17	0.27	0.64
7	K_2CO_3	3.0	0.32	0.16	0.27	0.65
8	K_2CO_3	5.0	0.31	0.17	0.26	0.59

General procedure: In a nitrogen-filled glovebox, an oven-dried 4-mL vial equipped with a stir bar is charged with $Cu(OTf)_2$ (90.3 mg, 2.5 equiv., 0.25 mmol), Na_3PO_4 or K_2CO_3 (3.0 equiv., 0.30 mmol), **2a** (X equiv.), 1-adamantane carboxylic acid (18.0 mg, 1.0 equiv., 0.10 mmol), CH_2Cl_2 (0.50 mL, 0.20 M), and MeCN (52 µL, 10 equiv., 1.0 mmol). The vial is sealed, removed from the glovebox, and irradiated, with stirring, at 427 nm with a 40W Kessil PR160 lamp in a PhotoRedox Box. A fan is used to maintain the vial at room temperature. After the given time, the crude reaction mixture is diluted with EtOAc and 2.0 M aqueous HCl. Analyte/internal standard (IS) ratios are determined by GC analysis using 1-methylnaphthalene (10 µL) is as an internal standard.

Optimization for Etherification:

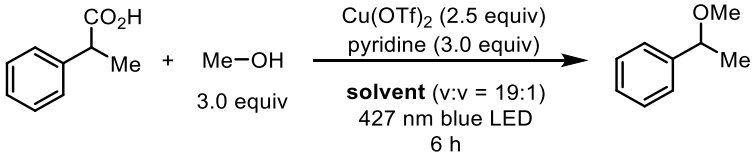
Supplementary Table 16. Cu(II) Salt.



Entry	Cu(II) Salt	Product Yield
1	$Cu(OTf)_2$	78%
2	$Cu(TFA)_2 \cdot MeCN$	10%
3	$Cu(OAc)_2 \cdot H_2O$	12%
4	$Cu(BF_4)_2 \cdot 4H_2O$	8%
5	$Cu(ClO_4)_2 \cdot 6H_2O$	12%
6	$CuCl_2$	14%
7	$CuBr_2$	16%

General procedure: to an oven-dried 1 dram vial, add 2-phenylpropionic acid (15.0 mg, 0.1 mmol) and dry MeOH (9.6 mg, 0.3 mmol, 3 equiv.). To an oven-dried 15 mL Schlenk tube, add $Cu(OTf)_2$ (90.4 mg, 0.25 mmol, 2.5 equiv.), freshly distilled pyridine (24 µL) and acetonitrile (50 µL). The 1 dram vial was rinsed with 0.95 mL dry PhMe, and the content was added to the Schlenk tube. The mixture was degassed by freeze-pump-thaw (3 x 3 min cycles) and refilled with nitrogen, and then was irradiated with one 40 W blue LED for 6 h. The reaction was diluted with 2 mL diethyl ether and washed with deionized water (4 mL). The organic layer was passed through a pad of Na_2SO_4 and analyzed by 1H NMR with 1-methylnaphthalene as internal standard.

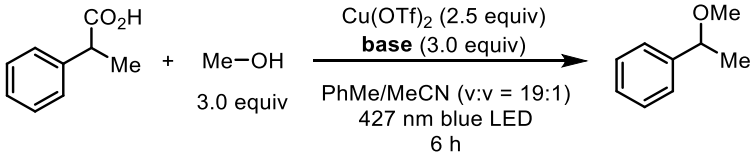
Supplementary Table 17. Solvents.



Entry	Solvent	Product Yield
1	MeCN	24%
2	DCM	20%
3	1,2-DCE	62%
4	1,2-DCE:MeCN = 19:1	67%
5	1,2-DCE:MeCN = 9:1	55%
6	1,2-DCE:MeCN = 6:1	48%
7	DMF	7%
8	DMA	9%
9	PhMe	57%
10	PhMe:MeCN = 19:1	78%
11	PhMe:MeCN = 9:1	73%
12	PhMe:MeCN = 6:1	71%

General procedure: to an oven-dried 1 dram vial, add 2-phenylpropionic acid (15.0 mg, 0.1 mmol) and dry MeOH (9.6 mg, 0.3 mmol, 3 equiv.). To an oven-dried 15 mL Schlenk tube, add $Cu(OTf)_2$ (90.4 mg, 0.25 mmol, 2.5 equiv.) and freshly distilled pyridine (24 μL). The 1 dram vial was rinsed with dry solvents, and the content was added to the Schlenk tube. The mixture was degassed by freeze-pump-thaw (3 x 3 min cycles) and refilled with nitrogen, and then was irradiated with one 40 W blue LED for 6 h. The reaction was diluted with 2 mL diethyl ether and washed with deionized water (4 mL). The organic layer was passed through a pad of Na_2SO_4 and analyzed by 1H NMR with 1-methylnaphthalene as internal standard.

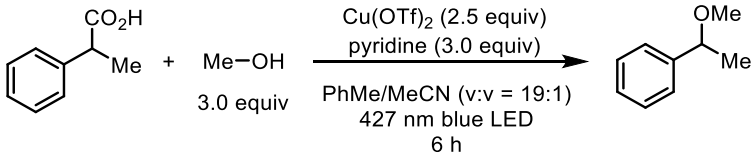
Supplementary Table 18. Bases.



Entry	Base	Product Yield
1	pyridine	78%
2	quinoline	66%
3	mTBD	14%
4	KH_2PO_4	8%
5	K_2HPO_4	5%
6	Na_3PO_4	20%
7	Cs_2CO_3	22%

General procedure: to an oven-dried 1 dram vial, add 2-phenylpropionic acid (15.0 mg, 0.1 mmol) and dry MeOH (9.6 mg, 0.3 mmol, 3 equiv.). To an oven-dried 15 mL Schlenk tube, add $Cu(OTf)_2$ (90.4 mg, 0.25 mmol, 2.5 equiv.) and base (0.3 mmol, 3 equiv.). The 1 dram vial was rinsed with dry solvents, and the content was added to the Schlenk tube. The mixture was degassed by freeze-pump-thaw (3 x 3 min cycles) and refilled with nitrogen, and then was irradiated with one 40 W blue LED for 6 h. The reaction was diluted with 2 mL diethyl ether and washed with deionized water (4 mL). The organic layer was passed through a pad of Na_2SO_4 and analyzed by 1H NMR with 1-methylnaphthalene as internal standard.

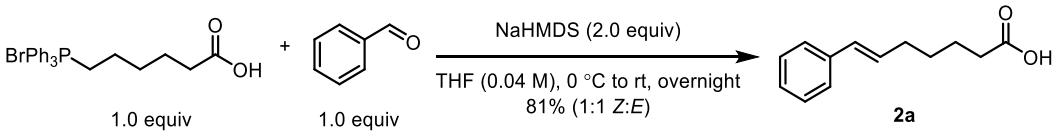
Supplementary Table 19. Control Experiments.



Entry	Deviation from optimal conditions	Product Yield
1	No light	78%
2	No pyridine	0%
3	No $Cu(OTf)_2$	0%

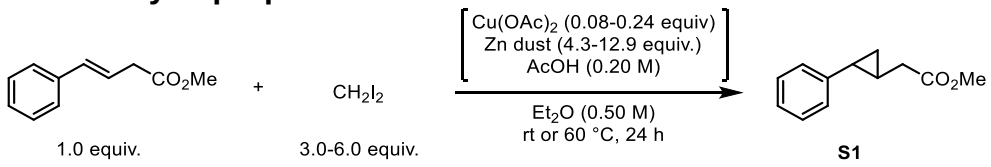
C. Substrate Preparation

Mechanistic probe substrate 2a:



A flame-dried round-bottomed flask equipped with a stir bar was charged with the phosphonium salt (4.59 g, 10 mmol, 1.0 equiv.) and anhydrous THF (20 mL, 0.50 M). The flask was sealed and stirred under a nitrogen atmosphere. To a separate flame-dried flask was added NaHMDS (3.78 g, 20.6 mmol, 2.06 equiv.) and anhydrous THF (200 mL, 0.10 M). The solution of NaHMDS was slowly transferred to the suspension of the phosphonium salt at rt *via* cannula. Addition time is approximately 30 minutes. After the addition, the mixture was allowed to stir at rt for 1 h. Next, a solution of benzaldehyde (1.20 mL, 10.9 mmol, 1.09 equiv.) in anhydrous THF (3.0 mL, 3.6 M) was added in a dropwise fashion. The mixture was allowed to stir at rt overnight. The reaction was quenched by addition of 1 M aqueous HCl and extracted with ethyl acetate (3x40 mL). The combined organic layers were dried with $MgSO_4$, filtered, and the solvent removed by rotary evaporation to obtain the crude product, which was purified by column chromatography on silica gel, eluting with 20-30% ethyl acetate in hexanes. The product **2a** was obtained as a clear oil (1.65 g, 1:1 *Z*:*E*, 81%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.13 (br s, 1H), 7.40 – 7.30 (m, 4H), 7.27 – 7.18 (m, 1H), 6.51 – 6.45 (m, 0.5H), 6.45 – 6.39 (m, 0.5H), 6.23 (dt, *J* = 15.8, 6.9 Hz, 0.5H), 5.67 (dt, *J* = 11.6, 7.2 Hz, 0.5H), 2.42 (t, *J* = 7.4 Hz, 1H), 2.38 (t, *J* = 7.4 Hz, 2H), 2.27 (q, *J* = 7.3 Hz, 1H), 1.81 – 1.65 (m, 2H), 1.63 – 1.49 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.71, 178.59, 137.56, 136.58, 131.52, 129.69, 128.86, 128.81, 128.28, 127.52, 126.62, 126.39, 123.04, 121.26, 34.00, 33.90, 33.42, 32.49, 28.79, 28.21, 28.16, 27.72. The spectral data matched those previously reported.[45]

Simmons-Smith Cyclopropanation to access S1:



Part I: Preparation of Zn/Cu couple[46]

A 24-mL glass vial equipped with a stir bar was charged with $Cu(OAc)_2$ (352 mg, 1.8 mmol, 0.08 equiv.) and AcOH (10 mL, 0.18 M in Cu). The solution was heated to 60 °C with vigorous stirring. To the vial was added Zn dust (6.18 g, 9.5 mmol, 4.3 equiv.) in one portion. The blue mixture immediately turned dark black/purple. The mixture was stirred at 60 °C for 15 min, after which point stirring was disengaged and the solids were allowed to settle. A 9” pipette was used to remove AcOH. Next, the purple solid was washed with diethyl ether (5x10 mL) until the rinsings no longer carried the AcOH odor. The Zn/Cu was thus used without further purification or drying.

Part II: Formation of carbenoid[47]

A flame-dried pear-shaped flask equipped with a stir bar was charged with freshly prepared Zn/Cu (all of the material made in Part I was added, and a quantitative yield was assumed). Anhydrous diethyl ether (20 mL) was added, and the mixture was sealed under a nitrogen atmosphere and allowed to stir at rt. An addition funnel is installed, and a solution of CH_2I_2 (4.85 mL, 60 mmol, 3 equiv.) in diethyl ether (15 mL) was added. **CAUTION: the CH_2I_2 solution must be added extremely slowly, as significant bubble and heat generation were observed. As more of the solution is added, the addition rate can be increased.** After all the CH_2I_2 solution had been added, the mixture was allowed to stir at 60 °C for 1 h. The carbenoid was used without purification in the next step. A quantitative yield was assumed.

Part III: Cyclopropanation[47]

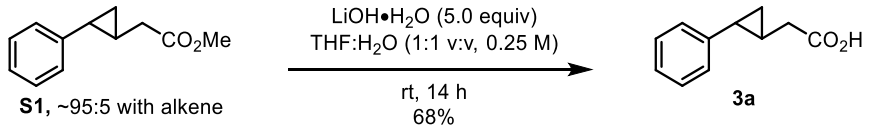
To the flask of the freshly prepared carbenoid (see Part II) was added the alkene (2.1 mL, 11.3 mmol, 1.0 equiv.) at 60 °C. GC-FID analysis was used to monitor the reaction every 12-24 h. To push the reaction to completion required two additional iterations of Part I and Part II, with the carbenoid being added directly to the alkene-containing flask. The reaction did not reach completion until 96 h. Upon completion, the reaction was cooled to rt and filtered over silica to remove solids. The organic filtrate was quenched with 1 M HCl and extracted with diethyl ether (3x50 mL). The combined organic layers were dried with $MgSO_4$, filtered, and the solvent removed by rotary evaporation. The crude product was purified by filtration through a silica plug (20% EtOAc in hexanes) to remove a maroon-colored impurity. The material thus obtained (1.50 g) was used in the next step without further purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.18 – 7.12 (m, 1H), 7.12 – 7.06 (m, 2H), 3.70 (s, 3H), 2.47 (dd, *J* = 15.9, 7.0 Hz, 1H), 2.36 (dd, *J* = 15.9, 7.0 Hz, 1H), 1.82 – 1.72 (m, 1H), 1.45 – 1.33 (m, 1H), 1.01 (dt, *J* = 8.7, 5.3 Hz, 1H), 0.87 (dt, *J* = 8.7, 5.3 Hz, 1H). The spectral data matched those previous reported.[48]

Note: Reaction times changed drastically based on the scale. Significant screening and optimization of conditions was required. The raw data obtained during this process is provided below (**Table S20**). The cyclopropane:alkene ratios given were determined by GC-FID analysis of reaction aliquots.

Supplementary Table 20. Optimization of Simmons-Smith reaction.

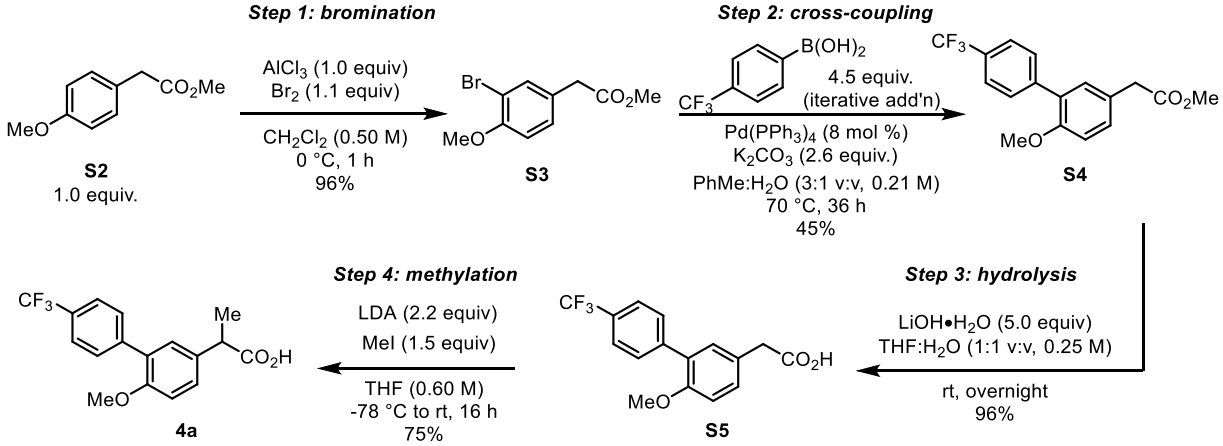
Entry	scale	equiv. Cu/Zn	equiv. CH_2I_2	T (°C)	t (h)	cyclopropane:alkene	Yield	Notes
1	1 mmol	0.08/4.3	3.0	rt	24	19:81	not isolated	
2	1 mmol	0.08/4.3	3.0	60	24	93:7	0.125 g, 66%	
3	20 mmol	0.08/4.3	3.0	60	24 48	58:42 61:39	not isolated	
4	4 mmol	0.08/4.3	3.0	60	24	96:4	0.517 g, 68%	4x 1.0 mmol reactions
5	12 mmol	0.24/12.9	9.0	60	24 48 72 96	29:71 56:44 74:26 >99:1	1.50 g, 66%	3x iterative add'n of Cu/Zn/CH_2I_2

Ester Hydrolysis to access 3a:[49]



A 24-mL glass vial equipped with a stir bar was charged with the crude cyclopropyl ester **S1** (0.760 g, 4.0 mmol), THF (8 mL, 0.5 M), H_2O (8 mL, 0.5 M), and $LiOH•H_2O$ (0.839 g, 20 mmol, 5 equiv.). The mixture was stirred at rt for 14 h, after which point it was quenched with 6 M aqueous HCl until the pH reached ~2. The layers were separated, and the organic extract was dried with $MgSO_4$, filtered, and the solvent removed by rotary evaporation. Crude ^{1}H NMR of the residue indicated 5% of the parent alkene was present as an impurity. Column chromatography on silica, eluting with 40% EtOAc in hexanes, afforded the pure cyclopropyl acid **3a** as a pale yellow, low-melting solid (0.470 g, 68%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.37 (br s, 1H), 7.33 – 7.25 (m, 2H), 7.24 – 7.16 (m, 1H), 7.16 – 7.07 (m, 2H), 2.53 (dd, *J* = 16.2, 6.9 Hz, 1H), 2.44 (dd, *J* = 16.2, 7.2 Hz, 1H), 1.82 (dt, *J* = 9.3, 4.9 Hz, 1H), 1.52 – 1.36 (m, 1H), 1.06 (dt, *J* = 8.5, 5.3 Hz, 1H), 0.92 (dt, *J* = 8.8, 5.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.74, 142.33, 128.33, 126.05, 125.73, 38.70, 22.91, 18.04, 15.29. The spectral data matched those previously reported.[50]

Synthesis of Acid 4a:



Step 1: Bromination of S2:[51]

To a round-bottomed flask equipped with a stir bar was added $AlCl_3$ (2.67 g, 20 mmol, 1.0 equiv.), methylene chloride (40 mL, 0.50 M), and methyl 2-(4-methoxyphenyl)acetate **S2** (3.18 mL, 20 mmol, 1.0 equiv.). The mixture was cooled to 0 °C and bromine (1.13 mL, 22 mmol, 1.1 equiv.) was added in a slow, dropwise fashion. After stirring at 0 °C for 1 h, the mixture was carefully poured over 50 mL of an ice-H_2O slurry. The mixture was washed with methylene chloride (2x30 mL) and the combined organic layers were then washed with sodium thiosulphate (2x10 mL) to quench excess bromine. The combined organic extracts were dried with magnesium sulfate, filtered, and concentrated *via* rotary evaporation. Although spectroscopically pure, the product was further purified by flash chromatography on silica, eluting with 20% EtOAc in hexanes. The bromide **S3** was thus obtained as a pale yellow oil (4.95 g, 96%). **^{1}H NMR**

(500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 2.2 Hz, 1H), 7.21 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 3.57 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.83, 155.06, 134.07, 129.36, 127.47, 111.91, 111.62, 56.28, 52.17, 39.82. The spectral data matched that previously reported.[52]

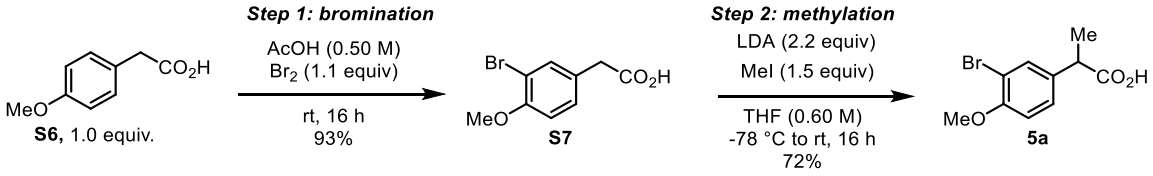
Step 2: Suzuki coupling of S3:[53]
A round-bottomed flask equipped with a stir bar and reflux condenser was charged with $Pd(PPh_3)_4$ (463 mg, 0.41 mmol, 4.1 mol %), the bromide **S3** (2.63 g, 10 mmol, 1.0 equiv.), and 4-(trifluoromethyl)phenylboronic acid (3.87 g, 20 mmol, 2.0 equiv.). Toluene (33 mL, 0.30 M) and 2.0 M aqueous K_2CO_3 (12.75 mL, 2.6 equiv. K_2CO_3) were next added, and the mixture was sparged with nitrogen for 20 min. The mixture was then warmed to 70 °C and stirred for 18 h, after which point conversion was assessed by thin layer chromatography (0.45:0.5:5 CH_2Cl_2:Et_2O:hexane). Due to significant remaining bromide **S3**, a second addition of $Pd(PPh_3)_4$ (0.423 mg) and 4-(trifluoromethyl)phenylboronic acid (1.85 g) was performed, and the mixture was once again sparged and heated at 70 °C for an additional 18 h. After cooling to room temperature, the crude mixture was filtered through a thick pad of silica on a fritted glass funnel to remove solids. The filtrate was transferred to a separatory funnel, and the layers were separated. The aqueous layer was washed with EtOAc (2x20 mL). The combined organic extracts were dried with magnesium sulfate, filtered, and the solvent was removed by rotary evaporation. Product **S4** was used directly in the next step.

Step 3: Hydrolysis of S4:[49]
A round-bottomed flask equipped with a stir bar was charged with ester **S4** (1.45 g, 4.5 mmol), THF (9 mL, 0.5 M), H_2O (9 mL, 0.5 M), and $LiOH•H_2O$ (0.937 g, 22 mmol, 5 equiv.). The mixture was stirred at rt overnight, after which point it was quenched with 6 M aqueous HCl until the pH reached ~2. The layers were separated, and the organic layer was dried with sodium sulfate, filtered, and the solvent removed by rotary evaporation. The crude product thus obtained was analytically pure and used in the next step without further purification (1.33 g, 93%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.21 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 3.74 (s, 3H), 3.58 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.11, 155.75, 141.76, 131.80, 130.29, 129.83, 129.41, 129.08 (q, *J* = 32.5 Hz), 125.65, 124.92 (q, *J* = 3.9 Hz), 124.24 (q, *J* = 272.2 Hz), 111.51, 55.68, 39.95.

Step 4: Methylation of S5:[54] Under nitrogen, a flame-dried round-bottomed flask equipped with a stir bar was charged with diisopropylamine (1.91 mL, 13.6 mmol, 2.2 equiv.) and anhydrous THF (23 mL, 0.60 M). Next, the mixture was cooled to –78 °C, and *n*-BuLi (5.41 mL, 2.5 M in hexane, 13.5 mmol, 2.2 equiv.) was added in a dropwise

fashion. After stirring at –78 °C for 30 min, the carboxylic acid **S5** was added as a solution in THF in a dropwise fashion (1.91 g, 6.1 mmol, 1.0 equiv., 11 mL THF). The mixture was allowed to warm to 0 °C and was stirred for 1 h. The mixture was then cooled back to –78 °C, and methyl iodide (0.58 mL, 9.3 mmol, 1.5 equiv.) was added in a dropwise fashion. The mixture was stirred at rt for 16 h after which point it was quenched by the addition of 1.0 M HCl. The layers were separated, and the aqueous layer was washed with diethyl ether (3x30 mL). The combined organic extracts were dried with sodium sulfate, filtered, and the solvent removed by rotary evaporation. Flash column chromatography on silica gel, eluting with 10% EtOAc in hexanes afforded the product **4a** as a white solid (1.57 g, 79%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.06 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.34 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.30 – 7.27 (m, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 3.83 (s, 3H), 3.77 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.86, 155.77, 141.90, 141.88, 132.18, 129.84 (q, *J* = 32.3 Hz), 129.43, 129.10, 128.46, 124.91 (q, *J* = 3.8 Hz), 124.29 (q, *J* = 271.9 Hz), 111.51, 55.69, 44.36, 18.19.

Synthesis of acid 5a:

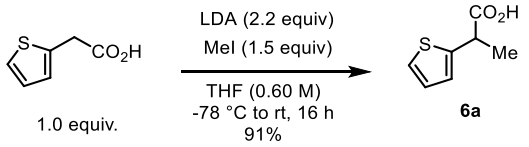


Step 1: Bromination of S6:[55] A round-bottomed flask equipped with a stir bar was charged with 4-methoxyphenylacetic acid **S6** (4.98 g, 30 mmol, 1.0 equiv.), AcOH (60 mL, 0.50 M), and bromine (1.70 mL, 33 mmol, 1.1 equiv.). The mixture was stirred at rt for 16 h, after which point AcOH was removed *in vacuo*. The crude product was taken up in ethyl acetate and washed with sodium thiosulfate (15 mL) and water (2x20 mL). The organic layer was dried with magnesium sulfate, filtered, and the solvent removed *in vacuo*. The product **S7** is purified by flash chromatography on silica, eluting with 40-50% EtOAc in hexanes (6.86 g, 93%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.76 (br s, 1H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 3.57 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.58, 155.24, 134.18, 129.49, 126.66, 111.93, 111.71, 56.28, 39.66. The spectral data matched those previously reported.[55]

Step 2: Methylation of S7:[54] Under nitrogen, a flame-dried round-bottomed flask equipped with a stir bar was charged with diisopropylamine (3.80 mL, 27.0 mmol, 2.2 equiv.) and anhydrous THF (44 mL, 0.60 M). Next, the mixture was cooled to –78 °C, and *n*-BuLi (10.75 mL, 2.5 M in hexane, 26.9 mmol, 2.2 equiv.) was added in a dropwise fashion. After stirring at –78 °C for 30 min, the carboxylic acid **S7** was added as a solution in THF in a dropwise fashion (2.94 g, 12.0 mmol, 1.0 equiv., 20 mL THF). The mixture was allowed to warm to 0 °C and was stirred for 1 h. The mixture was then cooled back to –78 °C, and methyl iodide (1.12 mL, 18.0 mmol, 1.5 equiv.) was added in a dropwise fashion. The mixture was stirred at rt for 16 h after which point it was quenched by the addition of 1.0 M HCl. The layers were separated, and the aqueous layer was washed with diethyl ether (3x30 mL). The combined organic extracts were dried with sodium sulfate, filtered, and the solvent removed by rotary evaporation. Flash

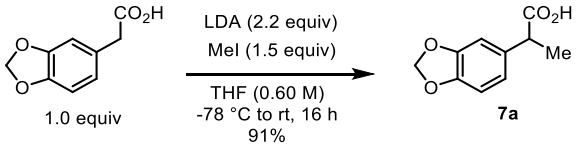
column chromatography on silica gel, eluting with 20% EtOAc in hexanes afforded the product **5a** as a white solid (2.23 g, 72%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.00 (br s, 1H), 7.53 (d, *J* = 2.2 Hz, 1H), 7.25 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 3.69 (q, *J* = 7.2 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.66, 155.22, 133.22, 132.47, 127.70, 111.95, 111.78, 56.30, 44.06, 18.11.

Synthesis of acid 6a:[54]



Under nitrogen, a flame-dried round-bottomed flask equipped with a stir bar was charged with diisopropylamine (3.80 mL, 26.8 mmol, 2.2 equiv.) and anhydrous THF (45 mL, 0.60 M). Next, the mixture was cooled to –78 °C, and *n*-BuLi (10.75 mL, 2.5 M in hexane, 26.9 mmol, 2.2 equiv.) was added in a dropwise fashion. After stirring at –78 °C for 30 min, the carboxylic acid was added as a solution in THF in a dropwise fashion (1.74 g, 12.2 mmol, 1.0 equiv., 20 mL THF). The mixture was allowed to warm to 0 °C and was stirred for 1 h. The mixture was then cooled back to –78 °C, and methyl iodide (1.15 mL, 18.3 mmol, 1.5 equiv.) was added in a dropwise fashion. The mixture was stirred at rt for 16 h after which point it was quenched by the addition of 1.0 M HCl. The layers were separated, and the aqueous layer was washed with diethyl ether (3x30 mL). The combined organic extracts were dried with sodium sulfate, filtered, and the solvent removed by rotary evaporation. Flash column chromatography on silica gel, eluting with 20% EtOAc in hexanes afforded the product as a pale yellow oil (1.73 g, 91%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.36 (s, 1H), 7.25 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.02 (dt, *J* = 3.5, 1.2 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.51, 141.97, 126.76, 125.21, 124.61, 40.63, 19.06. The spectral data matched those previously reported.[56]

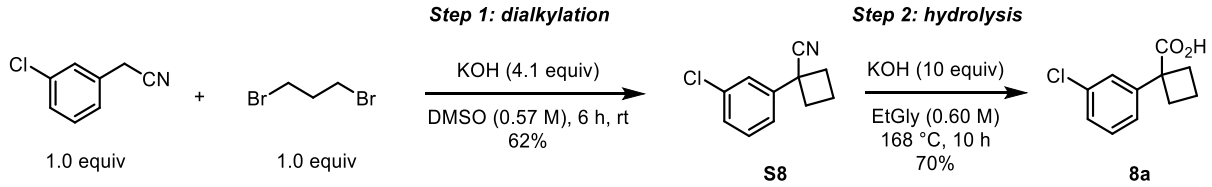
Synthesis of acid 7a:[54]



Under nitrogen, a flame-dried round-bottomed flask equipped with a stir bar was charged with diisopropylamine (5.32 mL, 37.9 mmol, 2.2 equiv.) and anhydrous THF (63 mL, 0.60 M). Next, the mixture was cooled to –78 °C, and *n*-BuLi (15.08 mL, 2.5 M in hexane, 37.7 mmol, 2.2 equiv.) was added in a dropwise fashion. After stirring at –78 °C for 30 min, the carboxylic acid was added as a solution in THF in a dropwise fashion (3.09 g, 17.14 mmol, 1.0 equiv., 30 mL THF). The mixture was allowed to warm to 0 °C and was stirred for 1 h. The mixture was then cooled back to –78 °C, and methyl iodide (1.60 mL, 25.6 mmol, 1.5 equiv.) was added in a dropwise fashion. The mixture was stirred at rt for 16 h after which point it was quenched by the addition of 1.0 M HCl. The layers were separated, and the aqueous layer was washed with diethyl ether (3x30 mL). The combined organic extracts were dried with sodium sulfate, filtered, and the solvent removed by rotary evaporation. Flash column chromatography on silica gel, eluting with

30% EtOAc in hexanes afforded the product as a white solid (3.03 g, 91%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.37 (s, 1H), 6.89 – 6.83 (m, 1H), 6.82 – 6.76 (m, 2H), 5.96 (s, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.13, 147.87, 146.89, 133.52, 120.90, 108.34, 107.99, 101.10, 44.89, 18.26. The spectral data matched those previously reported.[56]

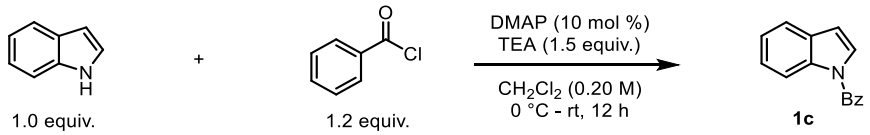
Synthesis of acid 8a:



Step 1: Dialkylation:[57] A solution of 3-chlorobenzonitrile (2.36 mL, 20 mmol) and 1,3-dibromopropane (2.03 mL, 20 mmol) in DMSO (4 mL, 5.7 M) was added in a slow, dropwise fashion to a stirring suspension of KOH (4.56 g, 4.1 equiv.) in DMSO (35 mL, 0.57 M) at room temperature under air. The mixture was allowed to stir at rt for 6 h, after which point it was quenched by the addition of water. The mixture was washed with ethyl acetate (3x20 mL), and the combined organic extracts were dried with magnesium sulfate, filtered, and the solvent was removed by rotary evaporation. Flash chromatography on silica gel, eluting with 10% EtOAc in hexanes, afforded the nitrile **S8** as a clear oil (2.39 g, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 1H), 7.40 – 7.30 (m, 3H), 2.95 – 2.78 (m, 2H), 2.69 – 2.57 (m, 2H), 2.47 (dp, *J* = 11.7, 8.9 Hz, 1H), 2.11 (dtt, *J* = 11.7, 9.0, 4.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.75, 134.97, 130.26, 128.15, 125.98, 123.88, 123.80, 39.90, 34.60, 17.05. The spectral data matched those previously reported.[58]

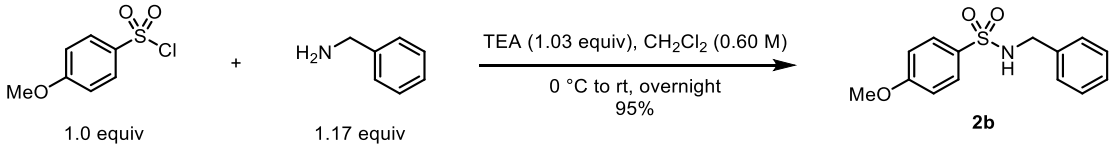
Step 2: Hydrolysis of S8:[57] A mixture of the nitrile **S8** (2.39 g, 12.45 mmol) and KOH (6.99 g, 124.5 mmol) was dissolved in ethylene glycol (21 mL, 0.60 M) in a round-bottomed flask equipped with a stir bar and condenser. The mixture was heated to 168 °C for 10 h, after which point it was allowed to cool to rt. Water and ethyl acetate were added, and the organic layer was separated. The aqueous layer was further washed with ethyl acetate (2x20 mL). The combined organic layers were dried with sodium sulfate, filtered, and the solvent removed by rotary evaporation. Flash chromatography on silica, eluting with 30% EtOAc in hexanes, afforded purified acid **8a**, which was further purified by recrystallization with CH2Cl2 and pentane (1.82 g, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.12 (s, 1H), 7.37 – 7.18 (m, 4H), 2.95 – 2.80 (m, 2H), 2.69 – 2.42 (m, 2H), 2.13 (dp, *J* = 11.3, 8.6 Hz, 1H), 1.91 (dtt, *J* = 11.3, 9.4, 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.79, 145.09, 134.28, 129.60, 127.11, 126.82, 124.66, 51.91, 32.24, 16.62. The spectral data matched those previously reported.

Synthesis of nucleophile 1c:[59]



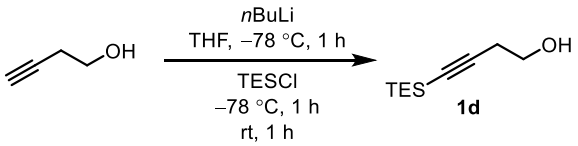
A round-bottomed flask equipped with a stir bar was charged with indole (1.22 g, 10.4 mmol, 1.0 equiv.), DMAP (14.2 mg, 0.10 equiv.), methylene chloride (52 mL, 0.20 M), and triethylamine (2.2 mL, 15.9 mmol, 1.5 equiv.). Benzoyl chloride (1.45 mL, 12.4 mmol, 1.2 equiv.) was added in a dropwise fashion at 0 °C and the mixture was then allowed to stir at rt for 12 h. The reaction was quenched by the addition of 1 M HCl and extracted with methylene chloride (3x20 mL). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The product was purified by flash chromatography on silica gel, eluting with 20% EtOAc in hexane (2.1 g, 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.71 (m, 2H), 7.71 – 7.62 (m, 2H), 7.60 – 7.52 (m, 2H), 7.42 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.38 – 7.32 (m, 2H), 6.65 (d, *J* = 3.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.84, 136.00, 134.55, 131.98, 130.78, 129.24, 128.65, 127.69, 124.99, 124.01, 120.94, 116.44, 108.64. The spectral data matched those previously reported.[60]

Synthesis of nucleophile 2b:[61]



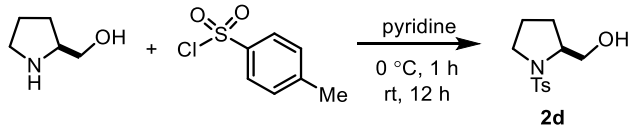
A round-bottomed flask equipped with a stir bar was charged with 4-methoxybenzenesulfonyl chloride (3.1 g, 15 mmol, 1.0 equiv.), methylene chloride (25 mL, 0.60 M), and benzylamine (1.92 mL, 17.6 mmol, 1.17 equiv.). The mixture was cooled to 0 °C, and triethylamine (2.15 mL, 15.4 mmol, 1.03 equiv.) was added in a slow, dropwise fashion. The mixture was allowed to stir at rt overnight, after which point it was quenched by addition of 1.0 M HCl. The layers were separated, and the aqueous layer was washed with methylene chloride (2x20 mL). The combined organic extracts were dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by precipitation from methylene chloride with pentane as the antisolvent (3.95 g, 95%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.14 – 7.10 (m, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.52 (t, *J* = 6.3 Hz, 1H), 4.05 (d, *J* = 6.0 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.98, 136.29, 131.46, 129.34, 128.73, 127.96, 127.89, 114.30, 55.65, 47.29. The spectral data matched those previously reported.[62]

Synthesis of nucleophile 1d:



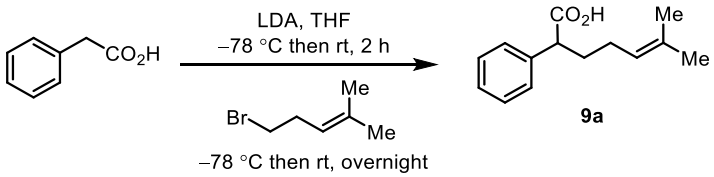
Prepared according to literature procedure.[63] To a stirred solution of 3-butyn-1-ol (0.23 mL, 3.0 mmol) in THF (0.7 M, 4.3 mL), a solution of *n*BuLi in hexanes (2.5 equiv., 3.8 mL, 2.1 M) was added slowly at –78 °C. After stirring at that temperature for 1 h, TESCl (2.5 equiv., 1mL, 7.5 mmol) was added. The reaction was continued at –78 °C for 1 h and was warmed to rt. It was quenched with saturated aqueous NH_4Cl solution after 1 h. The aqueous layer was extracted with EtOAc for three times and the combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressured. The crude was purified by flash column chromatography in 0 – 20 % EtOAc in hexanes to afford faint yellow oil (0.218 g, 39%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 3.72 (dt, 2H, J = 6.22, 6.22 Hz), 2.53 (t, 2H, J = 6.23 Hz), 1.78 (t, 1H, J = 6.55 Hz), 0.98 (t, 9 H, J = 7.91 Hz), 0.59 (q, 6H, J = 7.88 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 104.46, 84.44, 61.17, 24.46, 7.59, 4.55.

Synthesis of nucleophile 2d:



Prepared according to literature procedure.[64] To a solution of L-prolinol (0.202 g, 2 mmol) in distilled pyridine (2 mL), tosyl chloride (0.46 g, 2.46 mmol) was added at 0 °C. The mixture was stirred for 1 h at that temperature, and then allowed to warm to room temp and stir for 12 h. The crude mixture was poured into aqueous 1 M HCl solution and extracted with DCM. The combined organic layers was dried over Na_2SO_4 and purified by flash column chromatography in 1:1 hexanes/EtOAc to yield **2d** as a white solid (0.25 g, 0.98 mmol, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.74 (d, 2H, J = 8.27 Hz), 7.33 (d, 2H, J = 8.03 Hz), 3.65 (m, 3 H), 3.46 (dt, 1H, J = 10.46, 6.31 Hz), 3.27 (dt, 2H, J = 10.49, 6.92 Hz), 2.75 (m, 1H), 2.44 (s, 3H), 1.79 (ddt, 1H, J = 12.79, 8.23, 6.68 Hz), 1.69 (m, 2H), 1.45 (dp, 1H, J = 12.72, 6.46 Hz).

Synthesis of acid 9a:

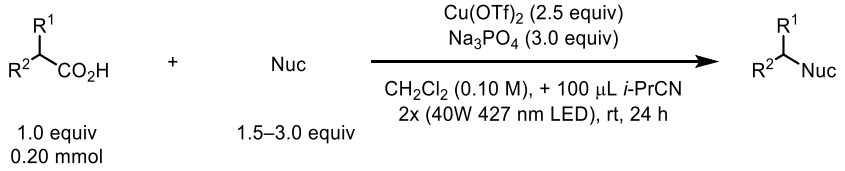


Freshly made LDA solution in THF (5 mmol, 5.7 mL) was cooled to – 78 °C, to which a THF solution of phenylacetic acid (0.34 g, 2.5 mmol, 1.5 mL) was added slowly. The reaction was warmed to rt and stirred for 2 h. It was cooled to – 78 °C again when 5-bromo-2-methylpent-2-ene (0.5 mL, 3.8 mmol) was added slowly. The reaction was warmed to rt and stirred overnight, before 3 M aqueous HCl solution was added until pH < 3. The aqueous layer was extracted with Et_2O and the combined organic layers were

washed with brine and dried over Na_2SO_4. The crude mixture was concentrated and purified by flash chromatography in 3:1 petanes/Et_2O to yield **8a** as a yellow oil (0.41 g, 1.87 mmol, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 11.57 (br s, 1H), 7.28 (m, 5H), 5.07 (tdd, 1H, J = 5.72, 2.90, 1.42 Hz), 3.55 (t, 1H, J =7.61 Hz), 2.11 (m, 1H), 1.95 (q, 2H, J =7.32 Hz), 1.82 (m, 1H), 1.66 (d, 3H, J = 1.41 Hz), 1.50 (d, 3H, J = 1.33 Hz). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) = 180.6, 138.4, 132.7, 128.6, 127.4, 123.1, 50.9, 33.0, 25.8, 25.6, 17.7, 17.6. **HRMS** (FTMS + p ESI) calculated for $C_{14}H_{17}O_2$ $[M - H]^-$ 217.1234, found 217.1234.

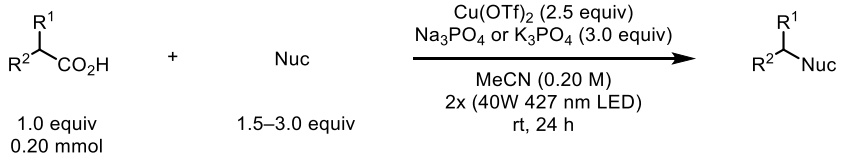
D. Experimental Procedure, Characterization, and Isolation

General Procedure A:



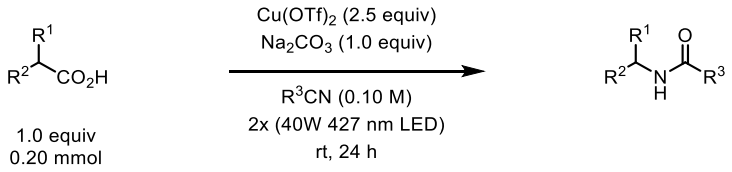
An oven-dried 6-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with $Cu(OTf)_2$ (180.8 mg, 2.5 equiv., 0.50 mmol), Na_3PO_4 (98.2 mg, 3.0 equiv., 0.60 mmol), the sulfonamide nucleophile (1.5–3.0 equiv.), the carboxylic acid (1.0 equiv., 0.20 mmol), methylene chloride (2.0 mL, 0.10 M), and isobutyronitrile (100 μL, 5.5 equiv., 1.1 mmol). 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 adsorbed directly on diatomaceous earth (Celite®). The product is purified by flash chromatography on silica gel, eluting with mixtures of ethyl acetate and hexanes.

General Procedure B:



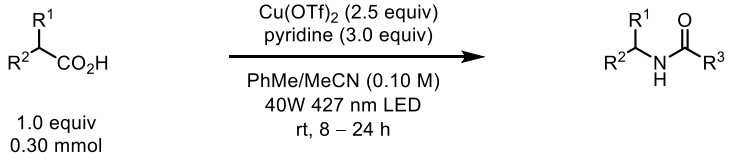
An oven-dried 6-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with $Cu(OTf)_2$ (180.8 mg, 2.5 equiv., 0.50 mmol), Na_3PO_4 (98.2 mg, 3.0 equiv., 0.60 mmol) or K_3PO_4 (127.4 mg, 3.0 equiv., 0.60 mmol), the nitrogen nucleophile (1.5–3.0 equiv.), the carboxylic acid (1.0 equiv., 0.20 mmol), and acetonitrile (2.0 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 adsorbed directly on diatomaceous earth (Celite®). The product is purified by flash chromatography on silica gel, eluting with mixtures of ethyl acetate and hexanes.

General Procedure C:



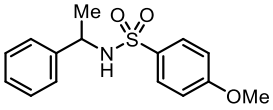
An oven-dried 6-mL vial equipped with a stir bar is brought into a nitrogen-filled glovebox and charged with $Cu(OTf)_2$ (180.8 mg, 2.5 equiv., 0.50 mmol), Na_2CO_3 (21.2 mg, 1.0 equiv., 0.20 mmol), the carboxylic acid (1.0 equiv., 0.20 mmol), and the nitrile (2.0 mL, 0.10 M). The vial is sealed with 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 adsorbed directly on diatomaceous earth (Celite®). The product is purified by flash chromatography on silica gel, eluting with mixtures of ethyl acetate and hexanes.

General Procedure D:



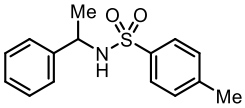
To an oven-dried Schlenk tube of 15 cm diameter, carboxylic acid (0.3 mmol) and alcohol (0.3 mmol – 1.5 mmol, 1 – 5 equiv.) and copper(II) trifluoromethanesulfonate (0.75 mmol, 271.25 mg) were added, followed by freshly distilled pyridine (0.9 mmol, 73 µL) and acetonitrile (0.15 mL). The reaction mixture was degassed by freeze-pump-thaw for four 4-min cycles and refilled with nitrogen. It was irradiated for variable periods of time in front of a 40 W blue LED lamp. The reaction mixture was diluted with ethyl acetate or diethyl ether (2 mL) and then washed with deionized water (2 x 5 mL). The aqueous layer was extracted with ethyl acetate or diethyl ether (5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated and purified by flash column chromatography.

4-methoxy-*N*-(1-phenylethyl)benzenesulfonamide (2)



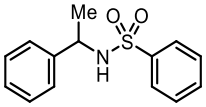
Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and 2-phenylpropanoic acid (30.0 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a clear oil (42.5 mg, 73% yield). **^{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: $[M+Na]^+$ calculated for $C_{15}H_{17}NO_3SNa$, 314.0821; found, 314.0816.

4-methyl-*N*-(1-phenylethyl)benzenesulfonamide (5)



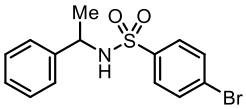
Prepared according to **General Procedure A** with 4-methylbenzenesulfonamide (102.7 mg, 3.0 equiv., 0.60 mmol) and 2-phenylpropanoic acid (30.0 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a clear oil (37.4 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.15 (m, 5H), 7.13 – 7.04 (m, 2H), 4.86 (d, *J* = 6.9 Hz, 1H, N–H), 4.45 (p, *J* = 6.9 Hz, 1H), 2.38 (s, 3H), 1.42 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.30, 142.09, 137.62, 129.59, 128.68, 127.62, 127.21, 126.23, 53.73, 23.69, 21.65. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{15}H_{17}NO_2SNa$, 298.0872; found, 298.0866.

***N*-(1-phenylethyl)benzenesulfonamide (6)**



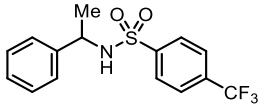
Prepared according to **General Procedure A** with benzenesulfonamide (94.3 mg, 3.0 equiv., 0.60 mmol) and 2-phenylpropanoic acid (30.0 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 15% ethyl acetate in hexanes, afforded the product as a white solid (31.6 mg, 60% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.15 (m, 3H), 7.15 – 7.03 (m, 2H), 4.85 (d, *J* = 6.9 Hz, 1H, N–H), 4.50 (p, *J* = 6.9 Hz, 1H), 1.44 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.95, 140.79, 132.51, 128.98, 128.73, 127.73, 127.18, 126.24, 53.86, 23.71. **mp:** 99.7 – 101.3 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{15}NO_2SNa$, 284.0716; found, 284.0710.

4-bromo-*N*-(1-phenylethyl)benzenesulfonamide (7)



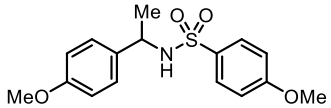
Prepared according to **General Procedure A** with 4-bromobenzenesulfonamide (141.6 mg, 3.0 equiv., 0.60 mmol) and 2-phenylpropanoic acid (30.0 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 15% ethyl acetate in hexanes, afforded the product as a white crystalline solid (32.4 mg, 48% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.22 – 7.15 (m, 3H), 7.13 – 6.97 (m, 2H), 4.92 (d, *J* = 6.9 Hz, 1H, N–H), 4.50 (p, *J* = 6.9 Hz, 1H), 1.45 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.52, 139.74, 132.13, 128.77, 128.69, 127.82, 127.39, 126.24, 54.02, 23.79. **mp:** 113.5 – 115.9 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{14}BrNO_2SNa$, 361.9821; found, 361.9814.

_N_-(1-phenylethyl)-4-(trifluoromethyl)benzenesulfonamide (8)



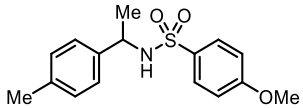
Prepared according to **General Procedure A** with 4-(trifluoromethyl)benzenesulfonamide (135.1 mg, 3.0 equiv., 0.60 mmol) and 2-phenylpropanoic acid (30.0 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a white solid (29.3 mg, 45% yield). **^{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 -63.21 (s, 3F). **mp:** 118.7 – 120.1 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{15}H_{14}F_3NO_2SNa$, 352.0590; found, 352.0583.

4-methoxy-_N_-(1-(4-methoxyphenyl)ethyl)benzenesulfonamide (9)



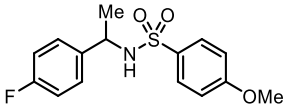
Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and 2-(4-methoxyphenyl)propanoic acid (36.0 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as an off-white solid (63.9 mg, 99% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 4.75 (d, *J* = 6.6 Hz, 1H, N–H), 4.40 (m, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.79, 159.08, 134.32, 132.51, 129.37, 127.50, 114.11, 114.04, 55.71, 55.41, 53.23, 23.59. **mp:** 119.8 – 120.9 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{19}NO_4SNa$, 344.0927; found, 344.0922.

4-methoxy-_N_-(1-(p-tolyl)ethyl)benzenesulfonamide (10)



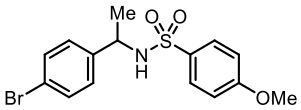
Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and 2-(*p*-tolyl)propanoic acid (32.8 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20-30% ethyl acetate in hexanes, afforded the product as a white solid (59.3 mg, 97% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 4.82 (d, *J* = 6.7 Hz, 1H, N–H), 4.40 (m, 1H), 3.84 (s, 3H), 2.28 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.80, 139.27, 137.32, 132.48, 129.37, 129.33, 126.20, 114.09, 55.71, 53.51, 23.65, 21.13. **mp:** 98.5 – 98.9 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{19}NO_3SNa$, 328.0978; found, 328.0973.

***N*-(1-(4-fluorophenyl)ethyl)-4-methoxybenzenesulfonamide (11)**



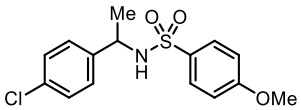
Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and 2-(4-fluorophenyl)propanoic acid (33.6 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (47.5 mg, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.9 Hz, 2H), 7.07 (dd, *J* = 8.5, 5.3 Hz, 2H), 6.92 – 6.79 (m, 4H), 4.97 (d, *J* = 6.6 Hz, 1H, N–H), 4.45 (m, 1H), 3.84 (s, 3H), 1.39 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.11, 162.90, 161.16, 138.03, 138.01, 132.30, 129.33, 128.04, 127.97, 115.52, 115.35, 114.14, 23.58. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -114.97 (s, 1F). **mp:** 105.9 – 106.9 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{15}H_{16}FNO_3SNa$, 332.0727; found, 332.0721.

***N*-(1-(4-bromophenyl)ethyl)-4-methoxybenzenesulfonamide (12)**



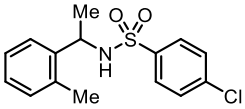
Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and 2-(4-bromophenyl)propanoic acid (45.8 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a white crystalline solid (47.3 mg, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 4.88 (d, *J* = 6.8 Hz, 1H, N–H), 4.43 (p, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.95, 141.20, 132.16, 131.69, 129.33, 128.14, 121.41, 114.14, 55.79, 53.22, 23.62. **mp:** 143.6 – 145.7 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{15}H_{16}BrNO_3SNa$, 391.9927; found, 391.9921.

***N*-(1-(4-chlorophenyl)ethyl)-4-methoxybenzenesulfonamide (13)**



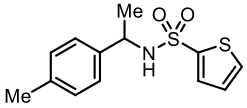
Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and 2-(4-chlorophenyl)propanoic acid (36.9 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (42.4 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 4.77 – 4.62 (m, 1H, N–H), 4.45 (p, *J* = 6.9 Hz, 1H), 3.85 (s, 3H), 1.40 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.96, 140.65, 133.38, 132.19, 129.35, 128.77, 127.78, 114.15, 55.77, 53.15, 23.68. **mp:** 121.1 – 122.3 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{15}H_{16}ClNO_3SNa$, 348.0432; found, 348.0427.

4-chloro-*N*-(1-(o-tolyl)ethyl)benzenesulfonamide (14)



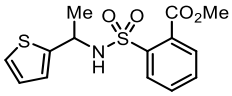
Prepared according to **General Procedure A** with 4-chlorobenzenesulfonamide (115.0 mg, 3.0 equiv., 0.60 mmol) and 2-(*o*-tolyl)propanoic acid (32.8 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 15% ethyl acetate in hexanes, afforded the product as a white solid (44.2 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.09 – 7.04 (m, 1H), 7.04 – 6.97 (m, 3H), 5.05 (d, *J* = 6.8 Hz, 1H, N–H), 4.79 (p, *J* = 6.8 Hz, 1H), 2.23 (s, 3H), 1.40 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.70, 139.19, 138.83, 134.64, 130.63, 129.04, 128.44, 127.51, 126.56, 125.34, 49.97, 23.27, 19.18. **mp:** 110.8 – 112.0 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{15}H_{16}ClNO_2SNa$, 332.0483; found, 332.0476.

***N*-(1-(p-tolyl)ethyl)thiophene-2-sulfonamide (15)**



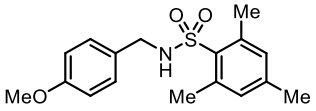
Prepared according to **General Procedure A** with thiophene-2-sulfonamide (97.9 mg, 3.0 equiv., 0.60 mmol) and 2-(*p*-tolyl)propanoic acid (32.8 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a clear oil (55.9 mg, 99% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.44 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.97 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.94 (d, *J* = 7.0 Hz, 1H, N–H), 4.51 (m, 1H), 2.29 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.72, 138.90, 137.54, 132.42, 131.87, 129.42, 127.27, 126.08, 53.89, 23.59, 21.19. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{13}H_{15}NO_2S_2Na$, 304.0436; found, 304.0431.

Methyl 2-(*N*-(1-(thiophen-2-yl)ethyl)sulfamoyl)benzoate (16)



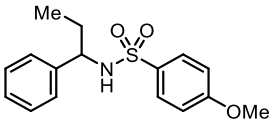
Prepared according to **General Procedure A** with methyl 2-sulfamoylbenzoate (129.1 mg, 3.0 equiv., 0.60 mmol) and 2-(thiophen-2-yl)propanoic acid (31.2 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a clear oil (36.4 mg, 56% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.75 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.54 (td, *J* = 7.6, 1.6 Hz, 1H), 7.50 (td, *J* = 7.6, 1.6 Hz, 1H), 7.00 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.76 (dt, *J* = 3.5, 1.1 Hz, 1H), 6.72 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 1H, N–H), 4.89 (m, 1H), 3.96 (s, 3H), 1.55 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.15, 145.94, 140.41, 132.05, 131.70, 130.67, 129.96, 129.49, 126.53, 124.61, 124.55, 53.48, 50.13, 24.27. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{15}NO_4S_2Na$, 348.0335; found, 348.0329.

N-(4-methoxybenzyl)-2,4,6-trimethylbenzenesulfonamide (17)



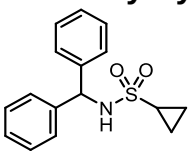
Prepared according to **General Procedure A** with 2,4,6-trimethylbenzenesulfonamide (119.6 mg, 3.0 equiv., 0.60 mmol) and 2-(4-methoxyphenyl)acetic acid (33.2 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20-30% ethyl acetate in hexanes, afforded the product as a white solid (48.5 mg, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.96 (s, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.58 (br t, *J* = 6.0 Hz, 1H, N–H), 4.01 (d, *J* = 6.0 Hz, 2H), 3.77 (s, 3H), 2.64 (s, 7H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.49, 142.42, 139.33, 133.71, 132.13, 129.45, 128.53, 114.22, 55.45, 46.50, 25.11, 21.09. **mp:** 100.6 – 101.3 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{21}NO_3SNa$, 342.1134; found, 342.1128.

4-methoxy-*N*-(1-phenylpropyl)benzenesulfonamide (18)



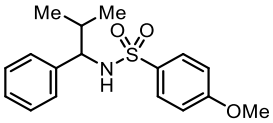
Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and 2-phenylbutanoic acid (32.8 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as an off-white solid (28.5 mg, 47% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.9 Hz, 2H), 7.18 – 7.12 (m, 3H), 7.06 – 6.97 (m, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 4.91 (d, *J* = 7.2 Hz, 1H, N–H), 4.18 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 1.81 (dp, *J* = 13.8, 7.3 Hz, 1H), 1.71 (dp, *J* = 13.8, 7.3 Hz, 1H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.69, 140.86, 132.52, 129.29, 128.56, 127.49, 126.72, 113.97, 59.96, 55.69, 30.77, 10.59. **mp:** 86.4 – 87.4 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{19}NO_3SNa$, 328.0978; found, 328.0971.

N-benzhydrylcyclopropanesulfonamide (19)



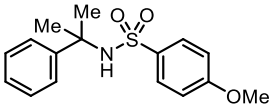
Prepared according to **General Procedure A** with cyclopropanesulfonamide (72.7 mg, 3.0 equiv., 0.60 mmol) and 2,2-diphenylacetic acid (42.5 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a white crystalline solid (54.0 mg, 94% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 8H), 7.31 – 7.22 (m, 2H), 5.75 (d, *J* = 7.5 Hz, 1H, N–H), 5.06 (d, *J* = 7.5 Hz, 1H), 2.07 (tt, *J* = 8.1, 4.9 Hz, 1H), 1.02 (dt, *J* = 4.9, 2.5 Hz, 2H), 0.73 – 0.65 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.32, 128.92, 128.00, 127.63, 61.44, 31.68, 6.04. **mp:** 141.0 – 142.0 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{17}NO_2SNa$, 310.0872; found, 310.0867.

4-methoxy-*N*-(2-methyl-1-phenylpropyl)benzenesulfonamide (20)



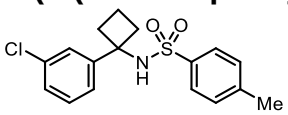
Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and 3-methyl-2-phenylbutanoic acid (35.6 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20-30% ethyl acetate in hexanes, afforded the product as an off-white solid (25.5 mg, 40% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.9 Hz, 2H), 7.15 – 7.08 (m, 3H), 6.96 – 6.84 (m, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 5.05 (d, *J* = 8.3 Hz, 1H, N–H), 4.01 (m, 1H), 3.79 (s, 3H), 1.92 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.73 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.57, 140.09, 132.40, 129.25, 128.25, 127.18, 127.07, 113.84, 64.25, 55.66, 34.54, 19.50, 18.99. **mp:** 91.5 – 92.6 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{21}NO_3SNa$, 342.1134; found, 342.1128.

4-methoxy-*N*-(2-phenylpropan-2-yl)benzenesulfonamide (21)



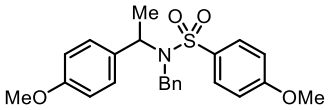
Prepared according to **General Procedure B** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol), 2-methyl-2-phenylpropanoic acid (32.8 mg, 1.0 equiv., 0.20 mmol), and Na_3PO_4 (98.2 mg, 3.0 equiv., 0.60 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a white solid (35.8 mg, 59% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.9 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.10 (m, 3H), 6.82 (d, *J* = 8.9 Hz, 2H), 4.91 (s, 1H, N–H), 3.84 (s, 3H), 1.63 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.51, 145.24, 134.60, 129.18, 128.34, 127.22, 125.68, 113.98, 58.73, 55.71, 29.96. **mp:** 127.5 – 129.3 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{19}NO_3SNa$, 328.0978; found, 328.0972.

***N*-(1-(3-chlorophenyl)cyclobutyl)-4-methylbenzenesulfonamide (22)**



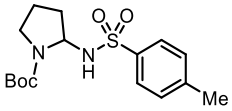
Prepared according to **General Procedure A** with 4-methylbenzenesulfonamide (51.4 mg, 1.5 equiv., 0.30 mmol) and 1-(3-chlorophenyl)cyclobutane-1-carboxylic acid (42.1 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 15-20% ethyl acetate in hexanes, afforded the product as a white crystalline solid (27.9 mg, 42% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.11 (m, 1H), 7.10 – 6.96 (m, 5H), 5.21 (s, 1H, N–H), 2.71 – 2.46 (m, 4H), 2.34 (s, 3H), 2.17 – 1.98 (m, 1H), 1.77 – 1.66 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.23, 142.94, 138.60, 134.20, 129.38, 129.18, 127.48, 127.21, 126.87, 124.93, 61.41, 35.61, 21.55, 15.32. **mp:** 131.6 – 132.7 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{18}ClNO_2SNa$, 358.0639; found, 358.0632.

***N*-benzyl-4-methoxy-N-(1-(4-methoxyphenyl)ethyl)benzenesulfonamide (23)**



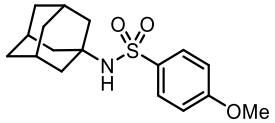
Prepared according to **General Procedure B** with *N*-benzyl-4-methoxybenzenesulfonamide (166.4 mg, 3.0 equiv., 0.60 mmol), 2-(4-methoxyphenyl)propanoic acid (36.0 mg, 1.0 equiv., 0.20 mmol) , and Na_3PO_4 (98.2 mg, 3.0 equiv., 0.60 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a clear oil (49.8 mg, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 2H), 7.22 – 7.14 (m, 3H), 7.14 – 7.05 (m, 2H), 6.97 – 6.89 (m, 4H), 6.72 (d, *J* = 8.8 Hz, 2H), 5.15 (q, *J* = 7.1 Hz, 1H), 4.42 (d, *J* = 15.7 Hz, 1H), 3.98 (d, *J* = 15.7 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 1.35 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.73, 159.15, 138.26, 133.41, 131.53, 129.34, 129.33, 128.43, 128.22, 127.24, 114.22, 113.71, 55.96, 55.76, 55.41, 47.87, 18.71. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{25}NO_4SNa$, 434.1397; found, 434.1390.

***tert*-butyl 2-((4-methylphenyl)sulfonamido)pyrrolidine-1-carboxylate (24)**



Prepared according to **General Procedure B** with 4-methylbenzenesulfonamide (51.4 mg, 1.5 equiv., 0.30 mmol), (*tert*-butoxycarbonyl)proline (43.0 mg, 1.0 equiv., 0.20 mmol), and K_3PO_4 (127.8 mg, 3.0 equiv., 0.60 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (53.4 mg, 79% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (br d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 5.48 – 4.62 (m, 2H), 3.51 – 3.03 (m, 2H), 2.42 (s, 3H), 2.32 – 1.69 (m, 4H), 1.36 (br s, 9H). (mixture of rotamers). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.22, 153.37, 143.57, 138.54, 137.45, 129.83, 126.94, 81.02, 80.49, 68.55, 46.39, 45.99, 33.35, 31.25, 28.42, 22.92, 21.81, 21.66. (mixture of rotamers). **mp:** 118.8 – 119.7 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{24}N_2O_4SNa$, 363.1349; found, 363.1344.

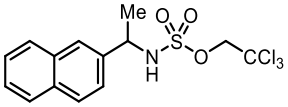
***N*-adamantan-1-yl-4-methoxybenzenesulfonamide (25)**



Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and adamantane-1-carboxylic acid (36.1 mg, 1.0 equiv., 0.20 mmol). Only 1.0 equivalent (49.2 mg) of Na_3PO_4 was required for this substrate. Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (44.2 mg, 69% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.60 (s, 1H, N–H), 3.86 (s, 3H), 2.09 – 1.96 (m, 4H), 1.72 – 1.69 (m, 2H), 1.66 – 1.48 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.53, 135.92, 129.15, 114.08, 68.36, 55.69, 55.12, 45.50, 43.22,

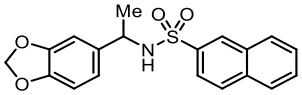
36.22, 36.00, 30.87, 29.62. **mp:** 132.4 – 134.2 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{23}NO_3SNa$, 344.1291; found, 344.1286.

2,2,2-trichloroethyl (1-(naphthalen-2-yl)ethyl)sulfamate (26)



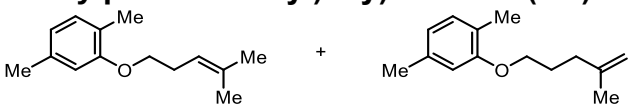
Prepared according to **General Procedure A** with 2,2,2-trichloroethyl sulfamate (137.1 mg, 3.0 equiv., 0.60 mmol) and 2-(naphthalen-2-yl)propanoic acid (40.0 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as an off-white solid (44.9 mg, 59% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.63 – 7.51 (m, 3H), 7.49 (dd, *J* = 8.2, 7.2 Hz, 1H), 5.57 (p, *J* = 6.8 Hz, 1H), 5.07 (d, *J* = 6.8 Hz, 1H, N–H), 4.49 (d, *J* = 10.9 Hz, 1H), 4.47 (d, *J* = 10.9 Hz, 1H), 1.82 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.88, 134.18, 130.42, 129.26, 129.23, 127.09, 126.24, 125.47, 123.40, 122.77, 93.45, 78.28, 51.12, 22.47. **mp:** 101.1 – 101.9 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{14}Cl_3NO_3SNa$, 403.9652; found, 403.9651.

***N*-(1-(benzo[d][1,3]dioxol-5-yl)ethyl)naphthalene-2-sulfonamide (27)**



Prepared according to **General Procedure A** with naphthalene-2-sulfonamide (124.4 mg, 3.0 equiv., 0.60 mmol) and 2-(benzo[d][1,3]dioxol-5-yl)propanoic acid (38.8 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as an off-white solid (58.6 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.9 Hz, 1H), 8.01 – 7.81 (m, 3H), 7.70 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.67 – 7.50 (m, 2H), 6.56 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 6.43 (d, *J* = 1.9 Hz, 1H), 5.80 – 5.64 (m, 1H), 5.50 (m, 1H), 4.87 (d, *J* = 6.4 Hz, 1H, N–H), 4.48 (m, 1H), 1.40 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.69, 146.92, 137.48, 135.50, 134.72, 132.05, 129.35, 129.28, 128.79, 128.73, 127.91, 127.44, 122.44, 120.02, 107.96, 106.57, 101.05, 53.91, 23.68. **mp:** 124.7 – 126.1 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{17}NO_4SNa$, 378.0771; found, 378.0766.

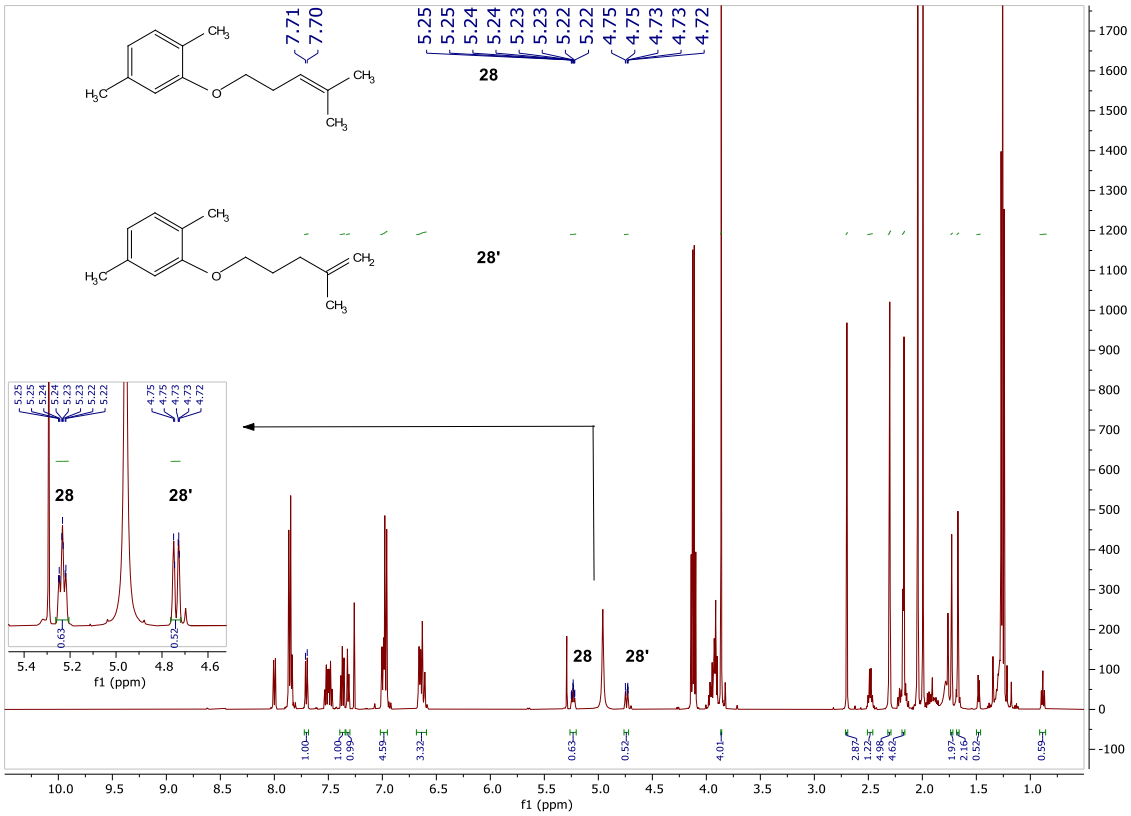
1,4-dimethyl-2-((4-methylpent-3-en-1-yl)oxy)benzene (28) and 1,4-dimethyl-2-((4-methylpent-4-en-1-yl)oxy)benzene (28')



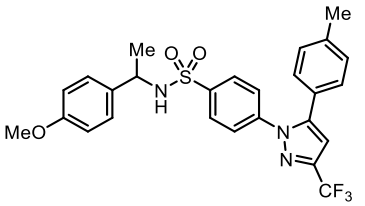
28 **28'**

Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and gemfibrozil (50.0 mg, 1.0 equiv., 0.20 mmol). ^{1}H NMR analysis of the crude reaction mixture indicated a **28:28'** ratio of 1.2:1 with a combined yield of 81%. The products were not isolated. The spectral data used to assign the ratios match that previous reported.[65] The ^{1}H NMR spectrum of the crude

reaction mixture is provided below. The integrations have been referenced to 1-methylnaphthalene (20 µL) as an internal standard (peaks at 7.70 and 7.71 ppm).

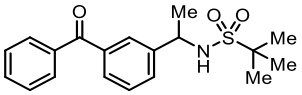


***N*-(1-(4-methoxyphenyl)ethyl)-4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (29)**



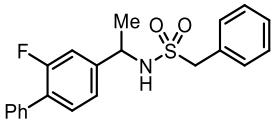
Prepared according to **General Procedure A** with 4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (114.4 mg, 3.0 equiv., 0.30 mmol) and 2-(4-methoxyphenyl)propanoic acid (18.0 mg, 1.0 equiv., 0.10 mmol). Purification by flash chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, afforded the product as a white crystalline solid (49.5 mg, 96% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.75 – 6.71 (m, 3H), 4.65 (d, *J* = 6.6 Hz, 1H, N–H), 4.47 (m, 1H), 3.74 (s, 3H), 2.37 (s, 3H), 1.43 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.31, 145.34, 144.18 (q, *J* = 38.5 Hz), 142.33, 140.45, 139.90, 133.61, 129.86, 128.84, 128.19, 127.48, 125.87, 125.40, 121.26 (q, *J* = 269.4 Hz), 114.14, 106.39 (q, *J* = 3.4 Hz), 55.42, 53.54, 23.64, 21.47. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.41 (s, 3F). **mp:** 153.0 – 156.0 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}F_3N_3O_3SNa$, 538.1383; found, 538.1437.

***N*-(1-(3-benzoylphenyl)ethyl)-2-methylpropane-2-sulfonamide (30)**



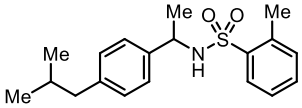
Prepared according to **General Procedure A** with 2-methylpropane-2-sulfonamide (82.3 mg, 3.0 equiv., 0.60 mmol) and 2-(3-benzoylphenyl)propanoic acid (50.9 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in pentane, afforded the product as a white crystalline solid (39.0 mg, 57% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 3H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 6.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.46 (m, 3H), 4.76 (m, 1H), 4.19 (d, *J* = 8.9 Hz, 1H, N–H), 1.60 (d, *J* = 6.9 Hz, 3H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.57, 144.21, 138.26, 137.56, 132.76, 130.25, 130.22, 129.49, 128.95, 128.53, 127.37, 60.07, 54.36, 25.48, 24.37. **mp:** 97.8 – 98.7 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{23}NO_3SNa$, 368.1291; found, 368.1285.

***N*-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)-1-phenylmethanesulfonamide (31)**



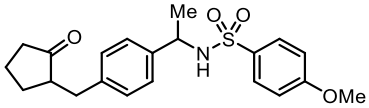
Prepared according to **General Procedure A** with phenylmethanesulfonamide (102.7 mg, 3.0 equiv., 0.60 mmol) and 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (48.9 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 20-30% ethyl acetate in hexanes, afforded the product as a white crystalline solid (38.8 mg, 53% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.41 – 7.27 (m, 4H), 7.28 – 7.20 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 13.2 Hz, 1H), 4.58 (m, 1H), 4.38 (d, *J* = 7.3 Hz, 1H, N–H), 4.16 (d, *J* = 14.0 Hz, 1H), 4.08 (d, *J* = 14.0 Hz, 1H), 1.50 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.95, 158.97, 144.36, 144.31, 135.37, 131.33, 131.30, 130.84, 129.11, 129.09, 128.92, 128.86, 128.03, 122.36, 122.34, 114.25, 114.07, 60.28, 53.52, 24.16. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.76 (s, 1F). **mp:** 157.3 – 159.0 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{20}FNO_2SNa$, 392.1091; found, 392.1084.

***N*-(1-(4-isobutylphenyl)ethyl)-2-methylbenzenesulfonamide (32)**



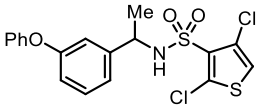
Prepared according to **General Procedure A** with 2-methylbenzenesulfonamide (102.7 mg, 3.0 equiv., 0.60 mmol) and 2-(4-isobutylphenyl)propanoic acid (41.3 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 15% ethyl acetate in hexanes, afforded the product as a clear oil (64.1 mg, 97% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 8.2 Hz, 1H), 7.19 (m, 2H), 6.94 (s, 4H), 4.74 (d, *J* = 7.0 Hz, 1H, N–H), 4.42 (m, 1H), 2.50 (s, 3H), 2.38 (d, *J* = 7.1 Hz, 2H), 1.85 – 1.71 (m, 1H), 1.44 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.30, 139.14, 138.61, 137.00, 132.66, 132.38, 129.73, 129.37, 126.11, 125.90, 53.58, 45.08, 30.28, 23.38, 22.47, 22.45, 20.30. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{25}NO_2SNa$, 354.1498; found, 354.1493.

4-methoxy-*N*-(1-(4-((2-oxocyclopentyl)methyl)phenyl)ethyl)benzenesulfonamide (33)



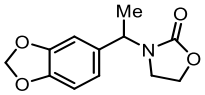
Prepared according to **General Procedure A** with 4-methoxybenzenesulfonamide (112.3 mg, 3.0 equiv., 0.60 mmol) and 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoic acid (49.3 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 40-50% ethyl acetate in hexanes, afforded the product as a white solid (61.7 mg, 80% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 4.92 (d, *J* = 6.9 Hz, 1H, N–H), 4.42 (p, *J* = 6.9 Hz, 1H), 3.83 (s, 3H), 3.06 (ddd, *J* = 13.9, 4.3, 2.0 Hz, 1H), 2.45 (ddd, *J* = 13.9, 9.5, 2.7 Hz, 1H), 2.40 – 2.23 (m, 2H), 2.14 – 2.05 (m, 1H), 2.05 – 2.00 (m, 1H), 1.99 – 1.90 (m, 1H), 1.82 – 1.68 (m, 1H), 1.55 – 1.44 (m, 1H), 1.40 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 220.29, 162.76, 140.13, 140.12, 139.43, 132.43, 129.35, 129.14, 126.36, 114.05, 55.70, 53.40, 51.06, 38.29, 35.23, 29.29, 23.63, 23.62, 20.65. **mp:** 104.8 – 105.4 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{25}NO_4SNa$, 410.1397; found, 410.1390.

2,4-dichloro-*N*-(1-(3-phenoxyphenyl)ethyl)thiophene-3-sulfonamide (34)



Prepared according to **General Procedure A** with 2,4-dichlorothiophene-3-sulfonamide (139.3 mg, 3.0 equiv., 0.60 mmol) and 2-(3-phenoxyphenyl)propanoic acid (48.5 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 15% ethyl acetate in hexanes, afforded the product as a pale yellow oil (37.3 mg, 44% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.0 Hz, 2H), 6.91 – 6.80 (m, 3H), 6.82 – 6.76 (m, 1H), 5.12 (d, *J* = 7.6 Hz, 1H, N–H), 4.52 (m, 1H), 1.49 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.92, 156.68, 143.16, 137.08, 130.10, 130.03, 129.52, 127.06, 126.77, 123.88, 120.64, 119.39, 117.85, 116.18, 54.06, 23.52. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{15}Cl_2NO_3S_2Na$, 449.9763; found, 449.9756.

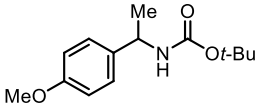
3-(1-(benzo[d][1,3]dioxol-5-yl)ethyl)oxazolidin-2-one (35)



Prepared according to **General Procedure B** with oxazolidin-2-one (26.1 mg, 1.5 equiv., 0.30 mmol), 2-(benzo[d][1,3]dioxol-5-yl)propanoic acid (38.8 mg, 1.0 equiv., 0.20 mmol), and Na_3PO_4 (98.2 mg, 3.0 equiv., 0.60 mmol). Purification by flash chromatography on silica gel, eluting with 50% ethyl acetate in hexanes, afforded the product as a white solid (40.3 mg, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.87 – 6.73 (m, 3H), 5.96 (s, 2H), 5.13 (q, *J* = 7.1 Hz, 1H), 4.29 (td, *J* = 8.9, 6.9 Hz, 1H), 4.23 (td, *J* = 8.9, 6.7 Hz, 1H), 3.47 (td, *J* = 8.8, 6.7 Hz, 1H), 3.17 (td, *J* = 8.8, 6.9 Hz, 1H), 1.53 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.05, 148.14, 147.34, 133.63, 120.42,

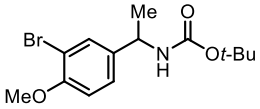
108.35, 107.82, 101.32, 62.05, 51.43, 40.13, 16.74. **mp:** 99.8 – 101.2 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{12}H_{13}NO_4Na$, 258.0737; found, 258.0734.

tert-butyl (1-(4-methoxyphenyl)ethyl)carbamate (36)



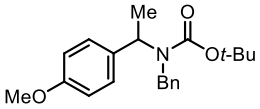
Prepared according to **General Procedure B** with *tert*-butyl carbamate (35.1 mg, 1.5 equiv., 0.30 mmol), 2-(4-methoxyphenyl)propanoic acid (36.0 mg, 1.0 equiv., 0.20 mmol), and Na_3PO_4 (98.2 mg, 3.0 equiv., 0.60 mmol). Purification by flash chromatography on silica gel, eluting with 10% ethyl acetate in hexanes, afforded the product as a white solid (42.3 mg, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.84 – 4.67 (m, 2H), 3.79 (s, 3H), 1.50 – 1.33 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.82, 155.24, 136.34, 128.15, 114.06, 79.47, 57.31, 50.32, 28.55, 24.01.**mp:** 85.1 – 85.8 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{21}NO_3Na$, 274.1414; found, 274.1409.

tert-butyl (1-(3-bromo-4-methoxyphenyl)ethyl)carbamate (37)



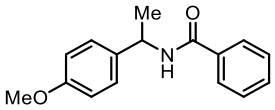
Prepared according to **General Procedure B** with *tert*-butyl carbamate (35.1 mg, 1.5 equiv., 0.30 mmol), 2-(3-bromo-4-methoxyphenyl)propanoic acid (51.8 mg, 1.0 equiv., 0.20 mmol), and Na_3PO_4 (98.2 mg, 3.0 equiv., 0.60 mmol). Purification by flash chromatography on silica gel, eluting with 10-20% ethyl acetate in hexanes, afforded the product as a white solid (34.0 mg, 52% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.3 Hz, 1H), 7.21 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.85 – 4.63 (m, 2H), 3.88 (s, 3H), 1.49 – 1.34 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.15, 155.07, 138.06, 130.96, 126.31, 112.07, 111.88, 79.76, 56.46, 49.38, 28.53, 22.76. **mp:** 67.6 – 68.6 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{20}BrNO_3Na$, 352.0519; found, 352.0515.

tert-butyl benzyl(1-(4-methoxyphenyl)ethyl)carbamate (38)



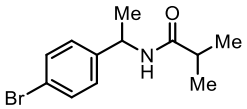
Prepared according to **General Procedure B** with *tert*-butyl benzylcarbamate (62.2 mg, 1.5 equiv., 0.30 mmol), 2-(4-methoxyphenyl)propanoic acid (36.0 mg, 1.0 equiv., 0.20 mmol), and Na_3PO_4 (98.2 mg, 3.0 equiv., 0.60 mmol). Purification by flash chromatography on silica gel, eluting with 10% ethyl acetate in hexanes, afforded the product as a clear oil (47.7 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.07 (m, 7H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.87 – 5.17 (m, 1H), 4.67 – 4.28 (m, 1H), 4.16 – 3.89 (m, 1H), 3.80 (s, 3H), 1.48 – 1.33 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.84, 156.28, 140.03, 134.02, 128.56, 128.24, 127.00, 126.60, 113.79, 79.99, 55.43, 52.55, 47.10, 28.54, 18.59. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{27}NO_3Na$, 364.1883; found, 364.1878.

***N*-(1-(4-methoxyphenyl)ethyl)benzamide (39)**



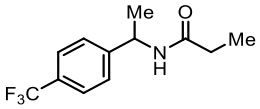
Prepared according to **General Procedure B** with benzamide (36.3 mg, 1.5 equiv., 0.30 mmol), 2-(4-methoxyphenyl)propanoic acid (36.0 mg, 1.0 equiv., 0.20 mmol), and Na_3PO_4 (98.2 mg, 3.0 equiv., 0.60 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (27.4 mg, 54% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.27 (d, *J* = 7.4 Hz, 1H, N–H), 5.30 (m, 1H), 3.80 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.62, 159.09, 135.38, 134.83, 131.57, 128.69, 127.64, 127.04, 114.25, 55.47, 48.80, 21.74. **mp:** 122.2 – 122.9 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{17}NO_2Na$, 278.1152; found, 278.1148.

***N*-(1-(4-bromophenyl)ethyl)isobutyramide (40)**



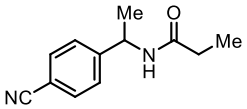
Prepared according to **General Procedure C** with 2-(4-bromophenyl)propanoic acid (45.8 mg, 1.0 equiv., 0.20 mmol) and isobutyronitrile (2.0 mL, 0.10 M). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white crystalline solid (43.0 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 5.64 (d, *J* = 7.6 Hz, 1H, N–H), 5.06 (m, 1H), 2.34 (hept, *J* = 6.9 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.13 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.19, 142.63, 131.83, 127.97, 121.16, 48.02, 35.74, 21.83, 19.75, 19.65. **mp:** 148.3 – 149.0 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{12}H_{16}BrNONa$, 292.0308; found, 292.0304.

***N*-(1-(4-(trifluoromethyl)phenyl)ethyl)propionamide (41)**



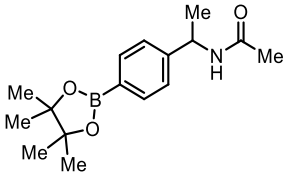
Prepared according to **General Procedure C** with 2-(4-(trifluoromethyl)phenyl)propanoic acid (43.6 mg, 1.0 equiv., 0.20 mmol) and propionitrile (2.0 mL, 0.10 M). Purification by flash chromatography on silica gel, eluting with 50% ethyl acetate in hexanes, afforded the product as a white crystalline solid (46.1 mg, 94% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 5.73 – 5.63 (m, 1H, N–H), 5.17 (m, 1H), 2.23 (m, 2H), 1.49 (d, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.04, 147.67, 147.66, 129.80 (q, *J* = 32.2 Hz), 127.49, 126.57, 125.79 (q, *J* = 3.8 Hz), 124.25 (q, *J* = 271.9 Hz), 48.53, 29.83, 22.00, 9.86. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.51 (s, 3F). **mp:** 115.1 – 115.9 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{12}H_{14}F_3NONa$, 268.0920; found, 268.0916.

N-(1-(4-cyanophenyl)ethyl)propionamide (42)



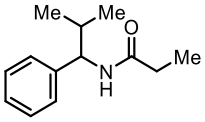
Prepared according to **General Procedure C** with 2-(4-cyanophenyl)propanoic acid (35.0 mg, 1.0 equiv., 0.20 mmol) and propionitrile (2.0 mL, 0.10 M). Purification by flash chromatography on silica gel, eluting with 70% ethyl acetate in hexanes, afforded the product as a clear oil (31.9 mg, 79% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 5.64 (m, 1H, N–H), 5.14 (m, 1H), 2.24 (qd, *J* = 7.6, 1.9 Hz, 1H), 1.48 (d, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.11, 149.10, 132.68, 126.98, 118.89, 111.30, 48.67, 29.78, 21.92, 9.83. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{12}H_{14}N_2ONa$, 225.0998; found, 225.0995.

N-(1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)acetamide (43)



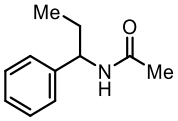
Prepared according to **General Procedure C** with 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoic acid (27.6 mg, 1.0 equiv., 0.10 mmol) and acetonitrile (1.0 mL, 0.10 M). Purification by flash chromatography on silica gel, eluting with 70% ethyl acetate in hexanes, afforded the product as a white solid (31.8 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.69 (d, *J* = 8.1 Hz, 1H), 5.14 (m, 1H), 1.98 (s, 3H), 1.48 (d, *J* = 6.9 Hz, 3H), 1.33 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.16, 146.41, 135.39, 125.68, 83.95, 49.01, 24.99, 23.63, 21.83. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.78 (s). **mp:** 121.7 – 123.1 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{24}BNO_3Na$, 312.1742; found, 312.1736.

N-(2-methyl-1-phenylpropyl)propionamide (44)



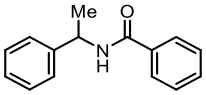
Prepared according to **General Procedure C** with 3-methyl-2-phenylbutanoic acid (35.6 mg, 1.0 equiv., 0.20 mmol) and propionitrile (2.0 mL, 0.10 M). Purification by flash chromatography on silica gel, eluting with 50% ethyl acetate in hexanes, afforded the product as a white solid (32.0 mg, 78% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 3H), 5.70 (d, *J* = 8.2 Hz, 1H, N–H), 4.77 (dd, *J* = 8.2, 7.8 Hz, 1H), 2.23 (m, 2H), 2.03 (dh, *J* = 7.8, 6.7 Hz, 1H), 1.15 (t, *J* = 7.6 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.07, 141.85, 128.62, 127.26, 127.07, 59.00, 33.57, 30.08, 19.93, 18.96, 10.07. **mp:** 84.9 – 85.6 °C. **HRMS** (FTMS + p ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{20}NO$, 206.1539; found, 206.1538.

***N*-(1-phenylpropyl)acetamide (45)**



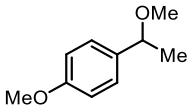
Prepared according to **General Procedure C** with 2-phenylbutanoic acid (32.8 mg, 1.0 equiv., 0.20 mmol) and acetonitrile (2.0 mL, 0.10 M). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (25.7 mg, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.23 (m, 3H), 5.72 (m, 1H, N–H), 4.88 (m, 1H), 1.98 (s, 3H), 1.86 – 1.78 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.36, 142.21, 128.80, 127.51, 126.80, 55.08, 29.19, 23.65, 10.88. **mp:** 75.3 – 77.2 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{11}H_{15}NONa$, 200.1046; found, 200.1044.

***N*-(1-phenylethyl)benzamide (46)**



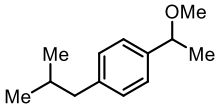
Prepared according to **General Procedure C** with 2-phenylpropanoic acid (30.0 mg, 1.0 equiv., 0.20 mmol) and benzonitrile (2.0 mL, 0.10 M). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white solid (28.0 mg, 62% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.45 – 7.34 (m, 6H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1H, N–H), 5.35 (m, 1H), 1.61 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.70, 143.24, 134.73, 131.63, 128.91, 128.71, 127.63, 127.06, 126.41, 49.36, 21.86. **mp:** 121.8 – 122.3 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{15}H_{15}NONa$, 248.1046; found, 248.1043.

1-Methoxy-4-(1-methoxyethyl)benzene (47)



Prepared according to **General Procedure D** with 2-(4-methoxyphenyl)propionic acid (54.1 mg, 1.0 equiv., 0.3 mmol) and methanol (9.6 mg, 1.0 equiv., 0.3 mmol). Irradiation time is 5 h. Column condition is 30:1 pentanes/Et_2O. Isolated 40.7 mg clear oil (82% yield). NMR data matched literature values.[66] **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.24 (d, 2H, J = 8.64 Hz), 6.89 (d, 2H, J = 8.64 Hz), 4.25 (q, 1H, J = 6.43 Hz), 3.81 (s, 3H), 3.20 (s, 3H), 1.42 (d, 3H, J = 6.43 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 159.05, 135.53, 127.55, 113.85, 79.22, 56.37, 55.38, 24.00.

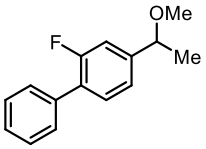
1-Isobutyl-4-(1-methoxyethyl)benzene (48)



Prepared according to **General Procedure D** with 2-(4-isobutylphenyl)propanoic acid (61.9 mg, 1.0 equiv., 0.3 mmol) and methanol (9.6 mg, 1.0 equiv., 0.3 mmol).Irradiation time is 16 h. Column condition is 125:1 DCM/acetone. Isolated 44.9 mg pale yellow oil (78% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) = 7.20 (d, 2H, J = 8.03 Hz), 7.12 (d,

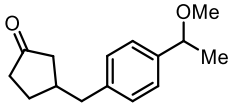
2H, J = 8.03 Hz), 4.27 (q, 1H, J = 6.45 Hz), 3.22 (s, 3H), 2.46 (d, 2H, J = 7.20 Hz), 1.86 (dp, 1H, J = 13.55, 6.74 Hz), 1.43 (d, 3H, J = 6.46 Hz), 0.90 (d, 6H, J = 6.64 Hz).**^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) = 141.06, 140.78, 129.27, 126.12, 79.61, 56.50, 45.28, 30.38, 23.89, 22.55. **HRMS** (FTMS + p ESI) calculated for $C_{13}H_{19}O$ $[M–H]^+$ 191.1430, found 191.1430.

2-Fluoro-4-(1-methoxyethyl)-1,1'-biphenyl (49)



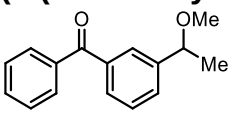
Prepared according to **General Procedure D** with 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (73.3 mg, 1.0 equiv., 0.3 mmol) and methanol (9.6 mg, 1.0 equiv., 0.3 mmol). Irradiation time is 24 h. Column condition is 35:1 pentanes/Et_2O. Isolated 45.2 mg white solid (65% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) = 7.55 (dd, 2H, J = 6.85, 1.47 Hz), 7.43 (dt, 3H, J = 16.75, 7.60 Hz), 7.37 (tt, 1H, J = 7.43, 1.47 Hz), 7.14 (m, 1H), 4.33 (q, 1H, J = 6.46 Hz), 3.29 (s, 3H), 1.46 (d, 3H, J = 6.42 Hz).**^{13}C NMR** (150 MHz, $CDCl_3$) δ (ppm) = 160.83, 159.19, 145.56, 145.51, 135.82, 130.90, 130.87, 129.12, 129.10, 128.57, 128.20, 128.11, 127.75, 122.22, 122.20, 113.91, 113.76, 79.03, 79.02, 56.81, 23.90. **^{19}F NMR** (377 MHz, $CDCl_3$) δ (ppm) = -117.95. **mp** 35.5 – 36.4 °C. **HRMS** (FTMS + p ESI) calculated for $C_{15}H_{15}FO$ $[M]^+$ 230.1101, found 230.1102.

3-(4-(1-Methoxyethyl)benzyl)cyclopentan-1-one (50)



Prepared according to **General Procedure D** with 2-(4-((3-oxocyclopentyl)methyl)phenyl)propanoic acid (73.9 mg, 1.0 equiv., 0.3 mmol) and methanol (9.6 mg, 1.0 equiv., 0.3 mmol). Irradiation time is 6 h. Column condition is 10:1 to 5:1 pentanes/Et_2O. Isolated 32.4 mg clear oil (46% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) =7.22 (d, 2H, J = 8.08 Hz), 7.15 (d, 2H, J = 8.05 Hz), 4.27 (q, 1H, J = 6.45 Hz), 3.22 (s, 3H), 3.14 (dd, 1H, J = 13.87, 4.11 Hz), 2.53 (dd, 1H, J = 13.89, 9.50 Hz), 2.34 (m, 2H), 2.10 (m, 2H), 1.96 (m, 1H), 1.74 (dtdd, J = 12.88, 10.60, 8.39, 6.35 Hz), 1.56 (dtd, 1H, J = 12.74, 10.82, 6.57 Hz), 1.42 (d, 3H, J = 6.44 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 220.35, 141.46, 139.32, 129.06, 126.43, 79.49, 56.53, 51.16, 38.33, 35.42, 29.36, 23.85, 23.83, 20.68. **HRMS** (FTMS + p ESI) calculated for $C_{14}H_{17}O$ $[M – OMe]^+$ 201.1274, found 201.1274.

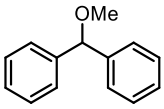
(3-(1-Methoxyethyl)phenyl)(phenyl)methanone (51)



Prepared according to **General Procedure D** with 2-(3-benzoylphenyl)propanoic acid (76.3 mg, 1.0 equiv., 0.3 mmol) and methanol (28.8 mg, 3.0 equiv., 0.9 mmol). Irradiation time is 16 h, with 3 equiv. MeOH. Column condition is 10:1 pentanes/Et_2O. Isolated 32.7 mg clear oil(49% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.81 (dd,

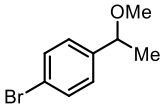
2H, J = 8.28, 1.34 Hz), 7.75 (t, 1H, J = 1.79 Hz), 7.70 (dt, 1H, J = 7.55, 1.47 Hz), 7.58 (m, 2H), 7.48 (m, 3H), 4.37 (q, 1H, J = 6.46 Hz), 3.26 (s, 3H), 1.46 (d, 3H, J = 6.42 Hz).**^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 196.85, 144.19, 137.94, 137.78, 132.58, 130.25, 130.18, 129.49, 128.60, 128.47, 128.44, 127.94, 79.41, 56.75, 23.96. **HRMS** (FTMS + p ESI) calculated for $C_{16}H_{17}O_2$ $[M+H]^+$ 241.1223, found 241.1220.

(Methoxymethylene)dibenzene (52)



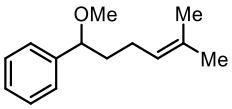
Prepared according to **General Procedure D** with diphenylacetic acid (63.7 mg, 1.0 equiv., 0.3 mmol) and methanol (9.6 mg, 1.0 equiv., 0.3 mmol).Irradiation time is 18 h. Column condition is 50:1 pentanes/Et_2O. Isolated 43.6 mg clear oil (73% yield). NMR data matched literature values.[67] **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) = 7.32 (m, 10H), 5.25 (s, 1H), 3.40 (s, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) = 142.21, 128.53, 127.59, 127.05, 85.57, 57.17.

1-Bromo-4-(1-methoxyethyl)benzene (53)



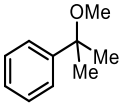
Prepared according to **General Procedure D** with 2-(4-bromophenyl)propanoic acid (68.7 mg, 1.0 equiv., 0.3 mmol) and methanol (9.6 mg, 1.0 equiv., 0.3 mmol). Irradiation time is 16 h. Column condition is 32:1 pentanes/Et_2O. Isolated 29.8 mg clear oil (46% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) =7.47 (d, 2H, J = 8.45 Hz), 7.19 (d, 2H, J = 8.31 Hz), 4.26 (q, 1H, J = 6.50 Hz), 3.21 (s, 3H), 1.40 (d, 3H, J = 6.47 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 142.76, 131.71, 128.06, 121.32, 79.17, 56.65, 23.95. **HRMS** (FTMS + p ESI) calculated for $C_9H_{12}Br$ $[M - OMe + H]^+$ 196.9960, found 196.9958.

(1-Methoxy-5-methylhex-4-en-1-yl)benzene (54)



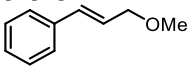
Prepared according to **General Procedure D** with **8a** (65.5 mg, 1.0 equiv., 0.3 mmol) and methanol (48.0 mg, 5.0 equiv., 1.5 mmol). Irradiation time is 16 h. Column condition is 80:1 pentanes/Et_2O. Isolated 28 mg clear oil (50% yield). NMR data matched literature.[68] **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.34 (dd, 2H, J = 8.05, 6.68 Hz), 7.27 (m, 2H), 5.10 (m, 1H), 4.07 (dd, 1H, J = 7.67, 5.73 Hz), 3.20 (s, 3H), 2.01 (q, 2H, J = 7.48 Hz), 1.84 (dtd, 1H, J = 14.31, 7.80, 6.42 Hz), 1.68 (d, 3H, J = 1.37 Hz), 1.63 (dtd, 1H, J = 13.53, 7.76, 5.71 Hz), 1.57 (d, 3H, J = 1.23 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 142.57, 132.08, 128.45, 127.56, 126.88, 124.07, 83.53, 56.76, 38.33, 25.87, 24.47, 17.82. **HRMS** (FTMS + p ESI) calculated for $C_{14}H_{20}O$ $[M]^+$ 241.1223, found 241.1220.

(2-Methoxypropan-2-yl)benzene (55)



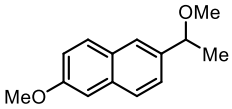
Prepared according to **General Procedure D** with 2-methyl-2-phenylpropanoic acid (49.3 mg, 1.0 equiv., 0.3 mmol) and methanol (28.8 mg, 3.0 equiv., 0.9 mmol). Irradiation time is 17 h. Column condition is 30:1 pentanes/Et_2O. Isolated 29.0 mg clear oil (64% yield). NMR data matched literature values.[69] **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.41 (m, 2H), 7.34 (dd, 2H, J = 8.49, 6.88 Hz), 7.25 (tt, 1H, J = 6.69, 1.36 Hz), 3.08 (s, 3H), 1.54 (s, 6H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 146.06, 128.33, 126.96, 125.94, 50.80, 28.10.

(*E*)-(3-Methoxyprop-1-en-1-yl)benzene (56)



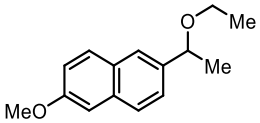
Prepared according to **General Procedure D** with (*E*)-4-phenylbut-3-enoic acid (48.7 mg, 1.0 equiv., 0.3 mmol) and methanol (28.8 mg, 3.0 equiv., 0.9 mmol). Irradiation time is 16 h. Column condition is 20:1 pentanes/Et_2O. Isolated 17.7 mg clear oil (40% yield). NMR data matched literature values.[70] **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.39 (dd, 2H, J = 7.39, 1.43 Hz), 7.31 (t, 2H, J = 7.67 Hz), 7.25 (m, 1H), 6.61 (dd, 1H, J = 15.82, 1.45 Hz), 6.28 (dd, 1H, J = 15.87, 6.00 Hz), 4.10 (dd, 2H, J = 6.04, 1.46 Hz), 3.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 136.87, 132.59, 128.69, 127.80, 126.62, 126.12, 73.25, 58.14.

2-Methoxy-6-(1-methoxyethyl)naphthalene (57)



Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and methanol (9.6 mg, 1.0 equiv., 0.3 mmol). Irradiation time is 24 h. Column condition is 5:1 pentanes/Et_2O. Isolated 52.5 mg white solid (81% yield). NMR data matched literature values.[71] **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.74 (t, 2H, J = 9.16 Hz), 7.66 (m, 1H), 7.43 (dd, 1H, J = 8.43, 1.75 Hz), 7.15 (m, 2H), 4.43 (q, 1H, J = 6.44 Hz), 3.93 (s, 3H), 3.25 (s, 3H), 1.51 (d, 3H, J = 6.48 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 157.66, 138.62, 134.22, 129.41, 128.75, 127.33, 125.23, 124.79, 119.01, 105.71, 79.81, 56.60, 55.44, 24.03. **mp** 53.3 – 54.7 °C.

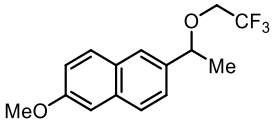
2-(1-Ethoxyethyl)-6-methoxynaphthalene (58)



Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and ethanol (41.5 mg, 3.0 equiv., 0.9 mmol). Irradiation time is 24 h. Column condition is 15:1 hexanes/EtOAc. Isolated 55.0 mg white solid (80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.72 (m, 2H), 7.65

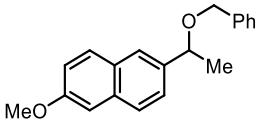
(m, 1H), 7.44 (dd, 1H, J = 8.47, 1.78 Hz), 7.14 (m, 2H), 4.53 (q, 1H, J = 6.48 Hz), 3.92 (s, 3H), 3.38 (qd, 2H, J = 7.05, 1.01 Hz), 1.55 z(d, 3H, J = 6.46 Hz), 1.19 (t, 3H, J = 6.99 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 157.72, 139.48, 134.23, 129.43, 128.87, 127.27, 125.02, 124.92, 118.96, 105.90, 77.97, 64.04, 55.48, 24.31, 15.58. **mp** 50.2 – 51.0 °C. **HRMS** (FTMS + p ESI) calculated for $C_{15}H_{18}O_2$ $[M]^+$ 230.1301, found 130.1299.

2-Methoxy-6-(1-(2,2,2-trifluoroethoxy)ethyl)naphthalene (59)



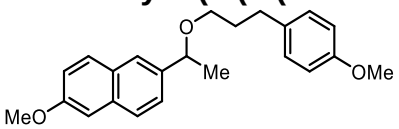
Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and 2,2,2-trifluoroethan-1-ol (90.0 mg, 3.0 equiv., 0.9 mmol). Column condition is 10:1 hexanes/EtOAc. Isolated 45.7 mg clear oil (54% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.74 (dd, 2H, J = 16.39, 8.67 Hz), 7.66 (d, 1H, J = 1.61 Hz), 7.43 (dd, 1H, J = 8.50, 1.77 Hz), 7.16 (m, 2H), 4.70 (q, 1H, J = 6.46 Hz), 3.93 (s, 3H), 3.67 (m, 2H), 1.57 (d, 3H, J = 6.41 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 158.09, 136.90, 134.61, 129.50, 128.75, 127.78, 125.64, 124.52, 119.34, 105.91, 79.79, 66.25, 65.98, 65.71, 65.44, 55.50, 23.85. **^{19}F NMR** (377 MHz, $CDCl_3$) δ (ppm) = –74.07 (q, $J_{C–F}$ = 34 Hz). **mp** 45.3 – 45.9 °C. **HRMS** (FTMS + p ESI) calculated for $C_{15}H_{15}F_3O_2$ $[M]^+$ 284.1019, found 284.1015.

2-(1-(Benzyloxy)ethyl)-6-methoxynaphthalene (60)



Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and benzyl alcohol (32.4 mg, 1.0 equiv., 0.3 mmol). Irradiation time is 7 h. Column condition is 15:1 pentanes/Et_2O. Isolated 59.1 mg clear oil (67% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) = 7.76 (d, 1H, J = 8.57 Hz), 7.73 (d, 1H, J = 8.20 Hz), 7.69 (s, 1H), 7.50 (m, 1H), 7.32 (m, 5H), 7.16 (dd, 2H, J = 7.92, 1.86 Hz), 4.63 (q, 1H, J = 6.47 Hz), 4.47 (dd, 1H, J = 11.88, 1.56 Hz), 4.47 (dd, 1H, J = 11.91, 1.58 Hz), 3.94 (s, 3H), 1.57 (dd, 3H, J = 6.45, 1.71 Hz). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) = 157.81, 138.93, 138.84, 134.34, 129.47, 128.88, 128.50, 127.87, 127.60, 127.43, 125.38, 125.01, 119.04, 105.93, 70.43, 55.49, 24.28. **HRMS** (FTMS + p ESI) calculated for $C_{20}H_{20}O_2$ $[M]^+$ 292.1458, found 292.1452.

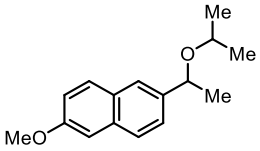
2-Methoxy-6-(1-(3-(4-methoxyphenyl)propoxy)ethyl)naphthalene (61)



Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and 3-(4-methoxyphenyl)propan-1-ol (149.5 mg, 3.0 equiv., 0.9 mmol). Irradiation time is 16 h. Column condition is 20:1 hexanes/EtOAc. Isolated 63.1 mg clear oil (60% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ

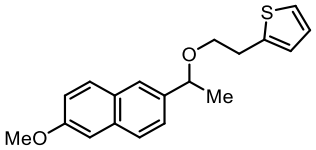
(ppm) = 7.72 (m, 2H), 7.64 (m, 1H), 7.44 (dd, 1H, J = 8.40, 1.70 Hz), 7.14 (d, 2H, J = 7.86 Hz), 7.04 (m, 2H), 6.77 (m, 2H), 4.50 (q, 1H, J = 6.47 Hz), 3.92 (s, 3H), 3.33 (t, 2H, J = 6.39 Hz), 2.65 (m, 1H), 2.56 (dt, 1H, J = 13.98, 7.67 Hz), 1.85 (dddd, 2H, J = 13.34, 8.87, 6.58, 2.32 Hz), 1.51 (d, 3H, J = 6.47 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 157.80, 157.73, 139.41, 134.29, 134.24, 129.45, 128.85, 127.27, 125.11, 124.99, 118.96, 113.81, 105.90, 78.19, 67.94, 55.48, 55.38, 31.89, 31.61, 24.17. **HRMS** (FTMS + p ESI) calculated for $C_{23}H_{26}O_3Na$ $[M + Na]^+$ 373.1774, found 373.1772.

2-(1-Isopropoxyethyl)-6-methoxynaphthalene (62)



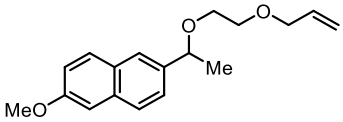
Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and isopropanol (90.2 mg, 5.0 equiv., 1.5 mmol). Irradiation time is 24 h. Column condition is 8:1 hexanes/EtOAc. Isolated 55.3 mg clear oil (75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.72 (m, 2H), 7.66 (m, 1H), 7.46 (dd, 1H, J = 8.49, 1.29 Hz), 7.14 (m, 2H), 4.66 (q, 1H, J = 6.45 Hz), 3.91 (s, 3H), 3.52 (heptd, 1H, J = 6.11, 0.91 Hz), 1.47 (dd, 3H, J = 6.46, 0.66 Hz), 1.18 (dd, 3H, J = 5.95, 0.92 Hz), 1.10 (dd, 3H, J = 6.22, 1.01 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 157.68, 140.10, 134.16, 129.40, 128.85, 127.19, 125.04, 124.93, 118.92, 105.90, 74.88, 68.59, 55.47, 24.83, 23.52, 21.54. **HRMS** (FTMS + p ESI) calculated for $C_{16}H_{20}O_2$ $[M]^+$ 244.1458, found 244.1456.

2-(2-(1-(6-Methoxynaphthalen-2-yl)ethoxy)ethyl)thiophene (63)



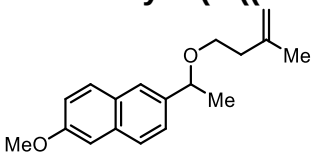
Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and 2-(thiophen-2-yl)ethan-1-ol (115.4 mg, 3.0 equiv., 0.9 mmol). Irradiation time is 15 h. Column condition is 15:1 hexanes/EtOAc. Isolated 60.9 mg opaque gel (65% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) = 7.70 (dd, 2H, J = 14.02, 8.54 Hz), 7.61 (d, 1H, J = 1.69 Hz), 7.41 (dd, 1H, J = 8.43, 1.74 Hz), 7.13 (m, 3H), 6.91 (dd, 1H, J = 5.14, 3.42 Hz), 6.81 (m, 1H), 4.56 (q, 1H, J = 6.45 Hz), 3.92 (s, 3H), 3.56 (td, 2H, J = 6.81, 3.66 Hz), 3.09 (td, 3H, J = 6.83, 2.68 Hz), 1.52 (d, 3H, J = 6.49 Hz). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) = 157.73, 141.61, 138.99, 134.24, 129.46, 128.82, 127.29, 126.72, 125.23, 125.10, 124.92, 123.69, 118.98, 105.84, 78.51, 69.39, 55.47, 30.84, 24.18. **HRMS** (FTMS + p ESI) calculated for $C_{19}H_{20}O_2S$ $[M]^+$ 312.1179, found 312.1172.

2-(1-(2-(Allyloxy)ethoxy)ethyl)-6-methoxynaphthalene (64)



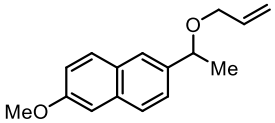
Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and 2-(allyloxy)ethan-1-ol (91.9 mg, 3.0 equiv., 0.9 mmol). Irradiation time is 16 h. Column condition is 10:1 hexanes/EtOAc. Isolated 56.1 mg yellow oil (70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.72 (dd, 2H, J = 8.44, 7.13 Hz), 7.67 (d, 1H, J = 1.56 Hz), 7.45 (dd, 1H, J = 8.48, 1.69 Hz), 7.14 (m, 2H), 5.91 (ddt, 1H, J = 17.34, 10.42, 5.61 Hz), 5.27 (dd, 1H, J = 17.21, 1.72 Hz), 5.17 (dd, 1H, J = 10.40, 1.56 Hz), 4.59 (q, 1H, J = 6.45 Hz), 4.01 (m, 2H), 3.92 (s, 3H), 3.58 (dd, 2H, J = 5.01, 3.99 Hz), 1.53 (d, 3H, J = 6.51 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 157.75, 139.04, 135.02, 134.27, 129.45, 128.86, 127.31, 125.21, 124.97, 118.97, 117.04, 105.89, 78.62, 72.30, 69.74, 68.02, 55.47, 24.23. **HRMS** (FTMS + p ESI) calculated for $C_{18}H_{22}O_3Na$ $[M + Na]^+$ 309.1461, found 309.1454.

2-methoxy-6-(1-((3-methylbut-3-en-1-yl)oxy)ethyl)naphthalene (65)



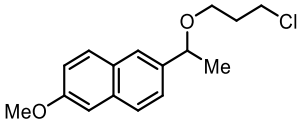
Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and 3-methylbut-3-en-1-ol (77.5 mg, 3.0 equiv., 0.9 mmol). Irradiation time is 16 h. Column condition is 15:1 hexanes/EtOAc. Isolated 56.5 mg clear oil (70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.72 (dd, 2H, J = 8.43, 6.34 Hz), 7.66 (m, 1H), 7.44 (dd, 1H, J = 8.50, 1.69 Hz), 7.14 (d, 2H, J = 8.35 Hz), 4.71 (m, 2H), 4.53 (q, 1H, J = 6.45 Hz), 3.92 (s, 3H), 3.44 (m, 2H), 2.31 (t, 2H, J = 7.02 Hz), 1.70 (t, 3H, J = 1.08 Hz), 1.50 (d, 3H, J = 6.46 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 157.73, 143.17, 139.34, 134.24, 129.44, 128.86, 127.27, 125.08, 124.95, 118.96, 111.41, 105.90, 78.24, 67.32, 55.48, 38.17, 24.23, 22.97. **HRMS** (FTMS + p ESI) calculated for $C_{18}H_{22}O_2Na$ $[M + Na]^+$ 293.1512, found 293.1505.

2-(1-(Allyloxy)ethyl)-6-methoxynaphthalene (66)



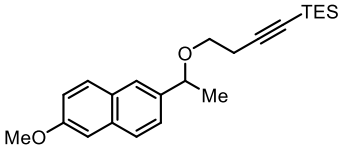
Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and allyl alcohol (87.2 mg, 5.0 equiv., 1.5 mmol). Irradiation time is 16 h. Column condition is 18:1 hexanes/EtOAc. Isolated 60.5 mg white solid (83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.73 (t, 2H, J = 8.34 Hz), 7.66 (d, 1H, J = 1.66 Hz), 7.45 (dd, 1H, J = 8.40, 1.73 Hz), 7.15 (d, 2H, J = 8.32 Hz), 5.92 (ddt, 1H, J = 16.29, 10.78, 5.60 Hz), 5.24 (dd, 1H, J = 17.19, 1.76 Hz), 5.16 (dd, 1H, J = 10.38, 1.62 Hz), 4.60 (q, 1H, J = 6.48 Hz), 3.92 (s, 3H), 3.92 (m, 1H), 3.83 (m, 1H), 1.52 (d, 3H, J = 6.48 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 157.78, 138.99, 135.23, 134.29, 129.45, 128.87, 127.35, 125.21, 124.96, 119.01, 116.86, 105.90, 69.55, 55.49, 24.18. **mp** 47.9 – 48.7 °C. **HRMS** (FTMS + p ESI) calculated for $C_{16}H_{18}O_2$ $[M]^+$ 242.1301, found 242.1299.

2-(1-(3-Chloropropoxy)ethyl)-6-methoxynaphthalene (67)



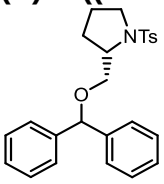
Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and 3-chloropropan-1-ol (28.4 mg, 1.0 equiv., 0.3 mmol). Irradiation time is 16 h. Column condition is 20:1 hexanes/EtOAc. Isolated 60.6 mg clear oil (70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.72 (m, 2H), 7.64 (m, 1H), 7.42 (dt, 1H, J = 8.46, 1.60 Hz), 7.15 (dt, 2H, J = 11.73, 2.29 Hz), 4.53 (q, 1H, J = 6.46 Hz), 3.93 (s, 3H), 3.65 (m, 2H), 3.46 (m, 2H), 2.03 (dqd, 2H, J = 12.94, 5.78, 2.57 Hz), 1.50 (dd, 3H, J = 6.57, 1.49 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 157.77, 139.00, 134.28, 129.43, 128.83, 127.35, 125.06, 124.77, 119.02, 105.89, 78.45, 65.12, 55.45, 42.23, 33.13, 24.06. **mp** 38.3 – 38.9 °C. **HRMS** (FTMS + p ESI) calculated for $C_{16}H_{19}ClO_2Na$ $[M + Na]^+$ 301.0966, found 301.0960.

Triethyl(4-(1-(6-methoxynaphthalen-2-yl)ethoxy)but-1-yn-1-yl)silane (68)



Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and **1e** (276.5 mg, 5.0 equiv., 1.5 mmol). Irradiation time is 8 h. Column condition is 30:1 hexanes/EtOAc. Isolated 77.9 mg clear oil (70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.72 (dd, 2H, J = 8.55, 5.45 Hz), 7.65 (d, 1H, J = 1.60 Hz), 7.45 (dd, 1H, J = 8.47, 1.74 Hz), 7.15 (d, 2H, J = 8.66 Hz), 4.59 (q, 1H, J = 6.46 Hz), 3.92 (s, 3H), 3.46 (m, 2H), 2.52 (m, 2H), 1.50 (d, 2H, J = 6.43 Hz), 0.96 (t, 9H, J = 7.89 Hz), 0.56 (q, 6H, J = 7.91 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 157.78, 139.02, 134.29, 129.44, 128.85, 127.35, 125.06, 124.86, 119.01, 105.90, 105.07, 82.85, 78.40, 67.12, 55.48, 29.86, 24.20, 21.70, 7.60, 4.61. **HRMS** (FTMS + p ESI) calculated for $C_{23}H_{32}Si\ O_2Na$ $[M + Na]^+$ 391.2064, found 391.2062.

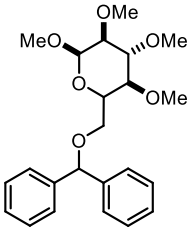
(*S*)-2-((Benzhydryloxy)methyl)-1-tosylpyrrolidine (69)



Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and **2e** (229.8 mg, 3.0 equiv., 0.9 mmol). Irradiation time is 24 h. Column condition is 5:1 hexanes/EtOAc. Isolated 110.0 mg opaque gel (87% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.67 (d, 2H, J = 8.30 Hz), 7.32 (m, 7H), 7.26 (m, 5H), 5.39 (s, 1H), 3.81 (tt, 1H, J = 8.05, 3.32 Hz), 3.71 (dd, 1H, J = 9.46, 3.66 Hz), 3.45 (dd, 1H, J = 9.44, 8.01 Hz), 3.39 (ddd, 1H, J = 9,89, 7.26, 3.94 Hz), 2.41 (s, 3H), 3.11 (ddd, 1H, J = 9.82, 8.26, 6.74 Hz), 1.96 (m, 1H), 1.82 (dqd, 1H, J = 9.06, 7.69, 6.11 Hz), 1. 56 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) =

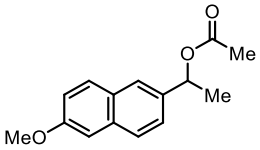
143.44, 142.41, 142.28, 134.74, 129.75, 128.53, 128.50, 127.68, 127.61, 127.59, 127.09, 84.37, 71.80, 59.35, 49.36, 29.10, 24.18, 21.67. **mp** 55.8 – 59.1 °C. **HRMS** (FTMS + p ESI) calculated for $C_{25}H_{27}NO_3SNa$ $[M + Na]^+$ 444.1603, found 444.1597.

(3*S*,4*R*,5*S*,6*R*)-2-((Benzhydryloxy)methyl)-3,4,5,6-tetramethoxytetrahydro-2H-pyran (70)



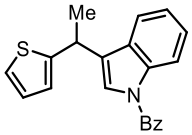
Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and ((3*S*,4*R*,5*S*,6*R*)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-yl)methanol (70.9 mg, 1.0 equiv., 0.3 mmol). Irradiation time is 24 h. Column condition is 3:1 hexanes/EtOAc. Isolated 63.0 mg clear oil (52% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.36 (m, 4H), 7.31 (m, 4H), 7.24 (m, 2H), 5.44 (s, 1H), 4.83 (d, 1H, J = 3.59 Hz), 3.64 (td, J = 4.07, 3.48, 2.25 Hz), 3.52 (m, 4H), 3.49 (m, 4H), 3.38 (s, 3H), 3.28 (m, 1H), 3.22 (dd, 1H, J = 9.60, 3.57 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 142.42, 142.34, 128.45, 127.58, 127.47, 127.28, 127.02, 97.52, 84.27, 83.87, 82.00, 79.81, 70.42, 67.92, 61.03, 60.62, 59.14, 55.19. **HRMS** (FTMS + p ESI) calculated for $C_{23}H_{30}O_6Na$ $[M + Na]^+$ 425.1935, found 425.1930.

1-(6-methoxynaphthalen-2-yl)ethyl acetate (71)



Prepared according to **General Procedure D** with (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (69.1 mg, 1.0 equiv., 0.3 mmol) and acetic acid (6.1 mg, 1.0 equiv., 0.3 mmol). Irradiation time is 16 h. Column condition is 20:1 hexanes/EtOAc. Isolated 19.0 mg clear oil (30% yield). NMR data matched literature values.[72] **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.73 (m, 3H), 7.45 (dd, J = 8.56, 1.61 Hz, 1H), 7.14 (m, 2H), 3.92 (s, 3H), 2.09 (s, 3H), 1.61 (d, J = 6.59 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 170.52, 157.99, 136.84, 134.36, 129.65, 128.76, 127.30, 125.14, 124.87, 119.20, 105.80, 72.61, 55.46, 22.24, 21.57.

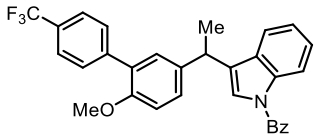
phenyl(3-(1-(thiophen-2-yl)ethyl)-1H-indol-1-yl)methanone (72)



Prepared according to **General Procedure A** with (1H-indol-1-yl)(phenyl)methanone (66.4 mg, 1.5 equiv., 0.30 mmol) and 2-(thiophen-2-yl)propanoic acid (31.2 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 2.5% diethyl ether in pentane, afforded the product as a clear oil (26.5 mg, 40% yield). **^{1}H**

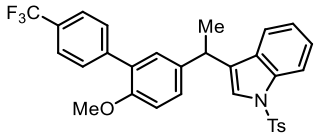
NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.70 (m, 2H), 7.60 (tt, *J* = 7.6, 1.4 Hz, 1H), 7.53 (tt, *J* = 6.6, 1.4 Hz, 2H), 7.46 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.18 (d, *J* = 1.0 Hz, 1H), 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.87 (dt, *J* = 3.5, 1.1 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 1H), 1.74 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.66, 149.36, 136.86, 134.89, 132.02, 130.11, 129.33, 128.77, 126.81, 126.75, 125.22, 123.97, 123.85, 123.67, 119.88, 116.68, 32.35, 22.88. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{17}NOSNa$, 354.0923; found, 354.0918.

(3-(1-(6-methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)ethyl)-1H-indol-1-yl)(phenyl)methanone (73)



Prepared according to **General Procedure A** with (1H-indol-1-yl)(phenyl)methanone (66.4 mg, 1.5 equiv., 0.30 mmol) and 2-(6-methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)propanoic acid (64.9 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 2.5% diethyl ether in pentane, afforded the product as a white solid (94.9 mg, 95% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.68 – 7.60 (m, 3H), 7.60 – 7.50 (m, 4H), 7.39 – 7.30 (m, 2H), 7.24 – 7.18 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 1.65 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.44, 154.93, 142.22, 137.56, 136.78, 134.84, 131.82, 130.35, 129.81, 129.69, 129.12, 128.91 (q, *J* = 32.4 Hz), 128.60, 128.08, 126.82, 124.98, 124.84 (q, *J* = 3.8 Hz), 124.33 (q, *J* = 271.9 Hz), 123.81, 123.61, 119.91, 116.43, 111.38, 55.62, 36.01, 22.12. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.40 (s, 3F). mp: 82.2 – 87.2 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{31}H_{24}F_3NO_2Na$, 522.1651; found, 522.1649.

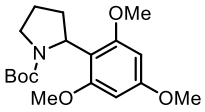
3-(1-(6-methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)ethyl)-1-tosyl-1H-indole (74)



Prepared according to **General Procedure A** with 1-tosyl-1H-indole (81.4 mg, 1.5 equiv., 0.30 mmol) and 2-(6-methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)propanoic acid (64.9 mg, 1.0 equiv., 0.20 mmol). Purification by flash chromatography on silica gel, eluting with 2.5% diethyl ether in pentane, afforded the product as a white solid (83.5 mg, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 1.2 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.17 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.11 (d, *J* = 6.7 Hz, 4H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 2.30 (s, 3H), 1.68 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.61, 155.10, 142.39, 142.38, 137.73, 136.95, 135.01, 131.99, 130.52, 129.98, 129.86, f129.33, 129.29, 129.20, 129.07 (q, J = 33.4 Hz), 128.77, 128.69, 126.99, 125.58 (q, J = 271.9 Hz), 125.15, 125.00 (q, J = 3.74 Hz) , 123.98, 123.78, 120.08, 116.60, 111.55, 55.79, 36.18, 22.29, 14.21. **^{19}F NMR** (377

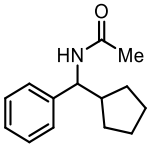
MHz, $CDCl_3$) δ -62.38 (s, 3F). **mp:** 92.7 – 95.0 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{31}H_{26}F_3NO_3SNa$, 572.1478; found, 572.1475.

***tert*-butyl 2-(2,4,6-trimethoxyphenyl)pyrrolidine-1-carboxylate (75)**



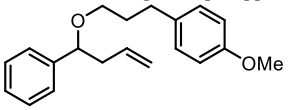
Prepared according to **General Procedure C** with 1,3,5-trimethoxybenzene (50.4 mg, 1.5 equiv., 0.30 mmol), (*tert*-butoxycarbonyl)proline (43.0 mg, 1.0 equiv., 0.20 mmol), and K_3PO_4 (127.8 mg, 3.0 equiv., 0.60 mmol). Purification by flash chromatography on silica gel, eluting with 30% ethyl acetate in hexanes, afforded the product as a white crystalline solid (62.8 mg, 93% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ [6.23 (s, 0.33H)], 6.11 (s, 1.77H), [5.25 (t, *J* = 7.5 Hz, 0.17H)], 5.18 (t, *J* = 8.2 Hz, 0.83H), [3.83 (s, 0.5H)], 3.80 (s, 2.5H), 3.76 (s, 5H), [3.70 (s, 1H)], 3.68 – 3.57 (m, 0.84H), 3.56 – 3.36 (m, 1.16H), 2.20 – 2.07 (m, 0.9H), 2.07 – 1.86 (m, 1.62H), 1.83 – 1.73 (m, 0.95H), 1.72 – 1.65 (m, 0.53H), [1.39 (s, 1.5H)], 1.12 (s, 7.5H). (mixture of rotamers, signals for the minor are given in brackets where identifiable). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.69, 159.85, 159.64, 159.28, 158.78, 158.62, 154.47, 113.04, 112.49, 105.08, 91.52, 90.78, 78.24, 56.27, 56.13, 55.86, 55.46, 55.34, 52.51, 52.05, 47.44, 46.95, 32.96, 32.67, 28.78, 28.29, 25.32, 25.19 (mixture of rotamers). **mp:** 77.9 – 80.7 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{27}NO_5Na$, 360.1781; found, 360.1777.

***N*-(cyclopentyl(phenyl)methyl)acetamide (76)**



Prepared according to **General Procedure C** with 7-phenylhept-6-enoic acid (40.9 mg, 1.0 equiv., 0.20 mmol) and acetonitrile (2.0 mL, 0.10 M). Purification by flash chromatography on silica gel, eluting with 30-40% ethyl acetate in hexanes, afforded the product as a white solid (22.6 mg, 52% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 6H), 5.75 (d, *J* = 8.6 Hz, 1H, N–H), 4.79 (m, 2H), 2.31 – 2.19 (m, 1H), 1.96 (s, 3H), 1.85 – 1.75 (m, 1H), 1.71 – 1.64 (m, 1H), 1.61 – 1.40 (m, 5H), 1.21 – 1.12 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.15, 142.72, 128.66, 127.34, 127.17, 58.01, 45.66, 30.43, 30.11, 25.46, 25.44, 23.70. **mp:** 111.7 – 112.4 °C. **HRMS** (FTMS + p ESI) m/z: $[M+Na]^+$ calculated for $C_{14}H_{19}NONa$, 240.1359; found, 240.1356.

1-methoxy-4-(3-((1-phenylbut-3-en-1-yl)oxy)propyl)benzene (77)

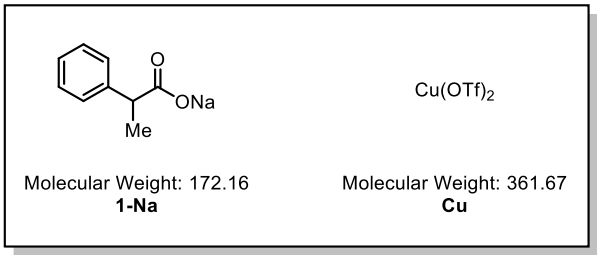


Prepared according to **General Procedure D** with 2-(2-phenylcyclopropyl)acetic acid (52.9 mg, 1.0 equiv., 0.3 mmol) and 3-(4-methoxyphenyl)propan-1-ol (149.6mg, 3.0 equiv., 0.9 mmol). Irradiation time is 24 h. Column condition is 20:1 pentanes/Et_2O. Isolated 6 mg clear oil (7% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 7.31 (m, 5H), 7.06 (d, 2H, J = 8.49 Hz), 6.80 (d, 2H, J = 8.57 Hz), 5.81 (ddt, 1H, J = 17.15, 10.22, 6.93

Hz), 5.03 (m, 2H), 4.23 (dd, 1H, J = 7.67, 5.76 Hz), 3.78 (s, 3H), 3.34 (dt, 1H, J = 9.40, 6.28 Hz), 3.26 (dt, 1H, J = 9.35, 6.31 Hz), 2.60 (m, 3H), 2.40 (dddt, 1H, J = 14.25, 7.09, 5.76, 1.33 Hz), 1.83 (ddd, 2H, J = 14.04, 7.69, 6.31 Hz). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) = 157.83, 142.57, 135.25, 134.34, 129.47, 128.43, 127.60, 126.83, 116.87, 113.83, 82.20, 68.11, 55.40, 42.83, 31.86, 31.61. **HRMS** (FTMS + p ESI) calculated for $C_{20}H_{25}O_2$ $[M + H]^+$ 297.1849, found 297.1844.

E. UV-Vis studies of Cu(II) with carboxylate 1-Na.

Objective: To gain insight into Cu speciation in solution and the photochemical properties of the resulting complexes.



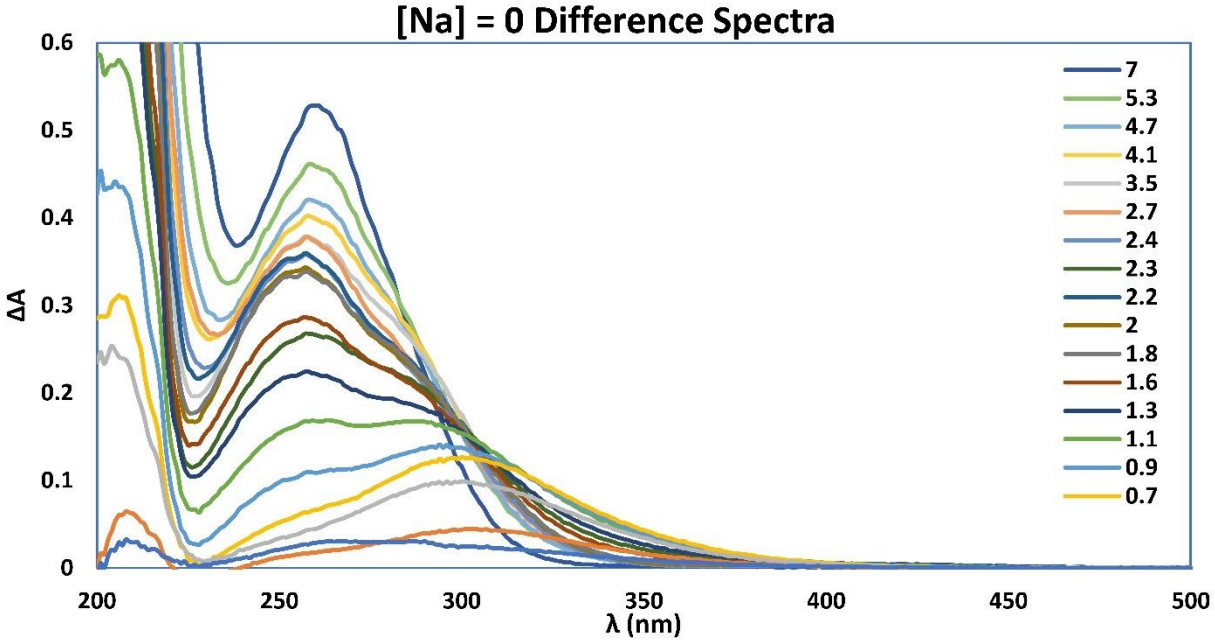
Operational notes: Three stock solutions of $Cu(OTf)_2$ (**Cu**) and the sodium carboxylate derived from **1** (hereafter referred to as **1-Na**) were prepared in anhydrous MeCN. These solutions were then used to produce mixtures of **1-Na** and **Cu** at the desired ratios in separate cuvettes for UV-Vis analysis. An important operational note: **1-Na** is insoluble in MeCN and required added $Cu(OTf)_2$ to promote dissolution. This was done by preparing **1-Na** solution C with the parent **Cu** solution A to maintain a constant [Cu] across all runs. Volumetric glassware and syringes were employed for all solutions and manipulations. Details are given below (**Supplementary Table 21**).

Solution A:	**Solution B:**	**Solution C:**
3.0 mg $Cu(OTf)_2$	1.9 mg **1-Na**	1.0 mg **1-Na**
100 mL MeCN	50.0 mL Solution A	10.0 mL solution A
0.083 mM Cu	**0.221 mM 1-Na, 0.083 mM Cu**	**0.581 mM 1-Na, 0.083 mM Cu**

Supplementary Table 21. Solutions prepared for UV-Vis titration of **Cu** with **1-Na.**

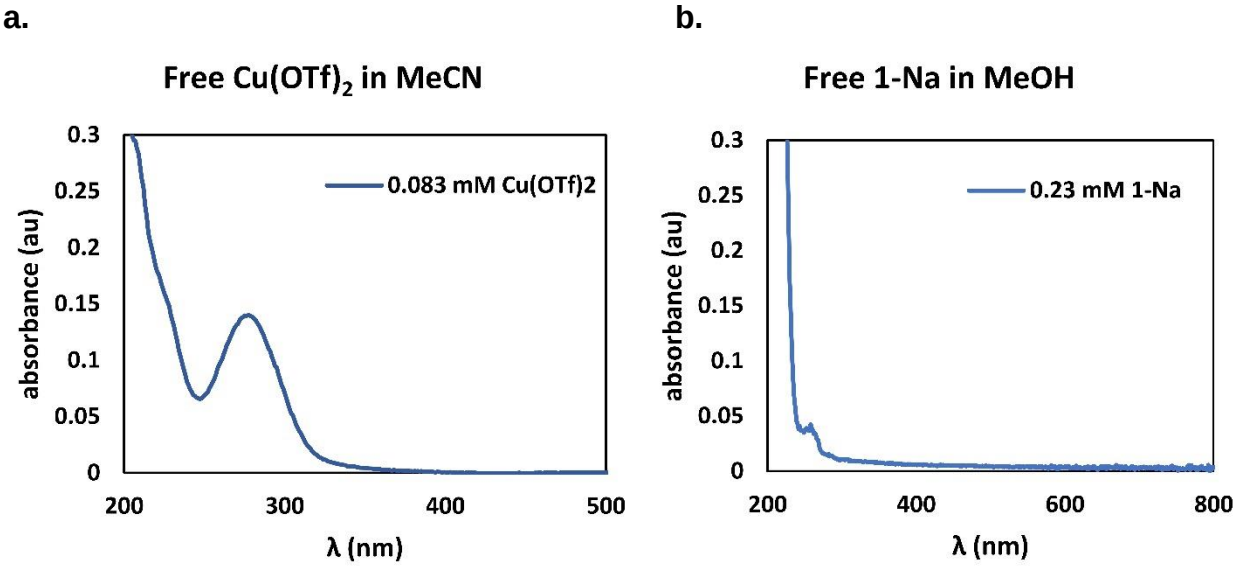
Cuvette	[Na carboxylate] (mM)	[$Cu(Otf)_2$] (mM)	1-Na:Cu
1	0.000	0.083	0.0
2	0.007	0.083	0.1
3	0.018	0.083	0.2
4	0.037	0.083	0.4
5	0.055	0.083	0.7
6	0.074	0.083	0.9
7	0.092	0.083	1.1
8	0.110	0.083	1.3
9	0.129	0.083	1.6
10	0.147	0.083	1.8
11	0.166	0.083	2.0
12	0.184	0.083	2.2
13	0.194	0.083	2.3
14	0.202	0.083	2.4
15	0.221	0.083	2.7
16	0.290	0.083	3.5
17	0.339	0.083	4.1
18	0.387	0.083	4.7
19	0.436	0.083	5.3
20	0.581	0.083	7.0

UV-Vis measurements for each mixture were obtained in triplicate and, after blank subtraction, the data was averaged. Next, the background UV-vis spectrum of free $Cu(OTf)_2$ (with no added **1-Na**) was subtracted out to look at differences in absorbance properties relative to free $Cu(OTf)_2$. Finally, the data was normalized by assuming A = 0 at 500 nm to account for imperfections in the cuvettes. The results are summarized in **Supplementary Figure 1** below.

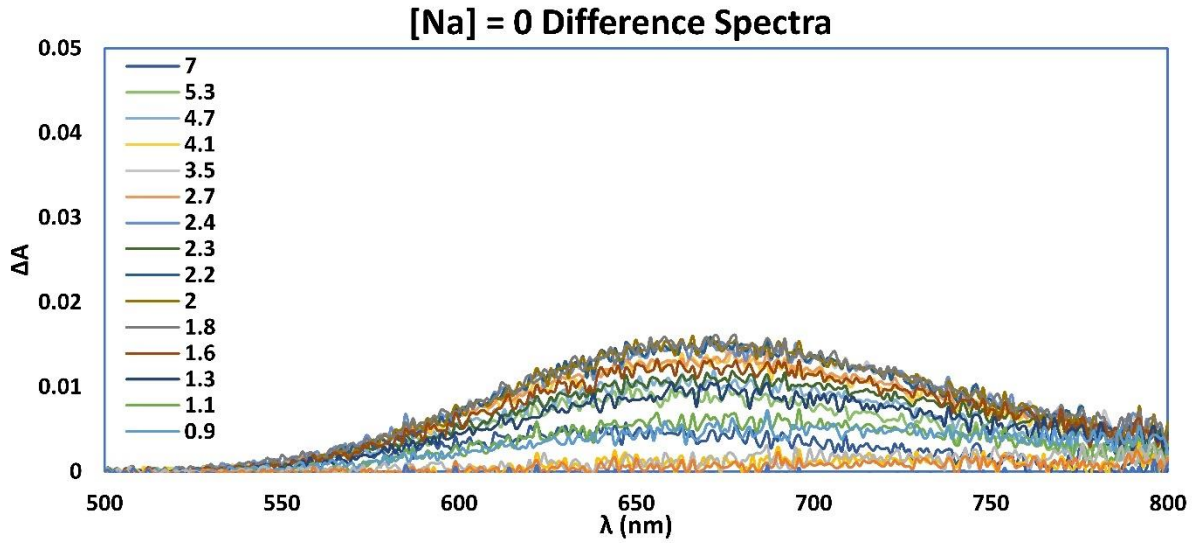


Supplementary Figure 1. UV-Vis titration study of $Cu(OTf)_2$ + **1-Na** (200-500 nm range). The legend refers to the **1-Na:Cu** ratio.

UV-Vis traces for free $Cu(OTf)_2$ and **1-Na** are also provided (**Supplementary Figure 2**). Importantly, **1-Na** proves to be only weakly absorbing in the relevant (250-800 nm) range. This suggests that the observed changes in absorbance are largely due to changes in the Cu speciation, and not a result of increased [**1-Na**]. This is further supported by the distinct changes in the d-d bands between 500-800 nm, suggesting a change in the metal complex is occurring (**Supplementary Figure 3**).

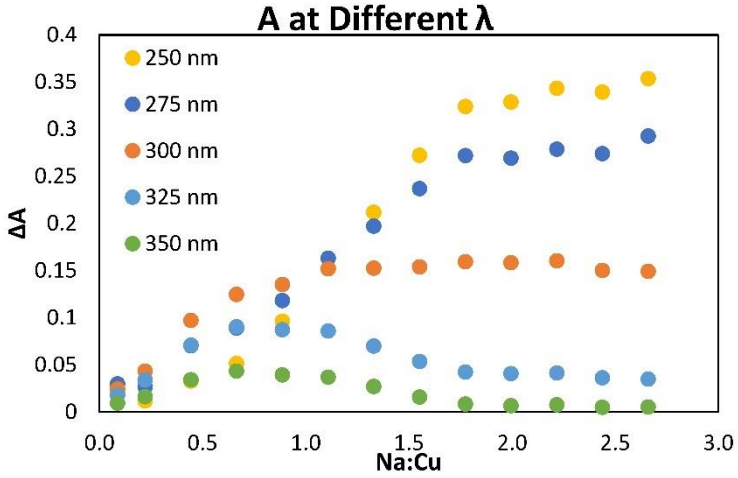


Supplementary Figure 2. a, $Cu(OTf)_2$ UV-Vis absorbance. **b**, **1-Na** UV-Vis absorbance**.**



Supplementary Figure 3. UV-Vis titration study of $Cu(OTf)_2$ + **1-Na** (500-800 nm range). The legend refers to the **1-Na:Cu** ratio.

As indicated by the data above, a considerable change in absorbance properties results as $Cu(OTf)_2$ is titrated with **1-Na**. To understand the dynamic of the interaction between these two species, absorbances were monitored at several fixed wavelengths (**Supplementary Figure 4**). At 250 nm, a change in absorbance was observed from 0:1 **1-Na:Cu** up to just below 2:1 **1-Na:Cu**, supporting the binding of ~2 carboxylates to a single Cu(II) center.

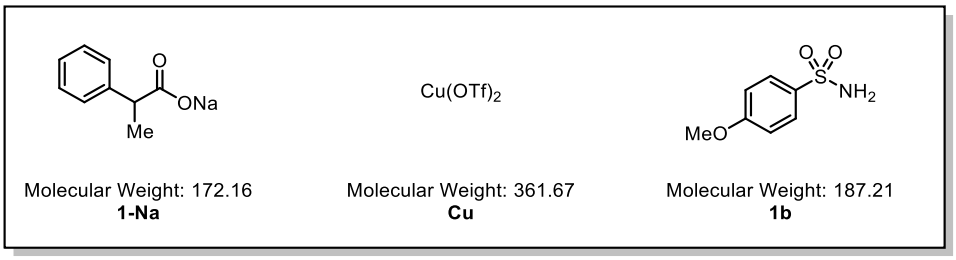


Supplementary Figure 4. Monitoring absorbance at fixed wavelengths to understand binding dynamics.

Studying changes in absorbance at 350 nm reveals a sequential binding mechanism may be operative, as different growth and decay regimes are observed from 0:1 to 1:1 **1-Na:Cu** and again from 1:1 to 2:1 **1-Na:Cu**. At all wavelengths, no meaningful changes in absorbance are observed going beyond 2:1 **1-Na:Cu** indicating a saturation effect.

F. UV-Vis studies of Cu(II) with sulfonamide 1b.

Objective: To study the interaction between $Cu(OTf)_2$ and the sulfonamide (**1b**), such as a soft deprotonation or a simple Lewis acid-Lewis base binding, both in the presence and absence of **1-Na** as an internal base.



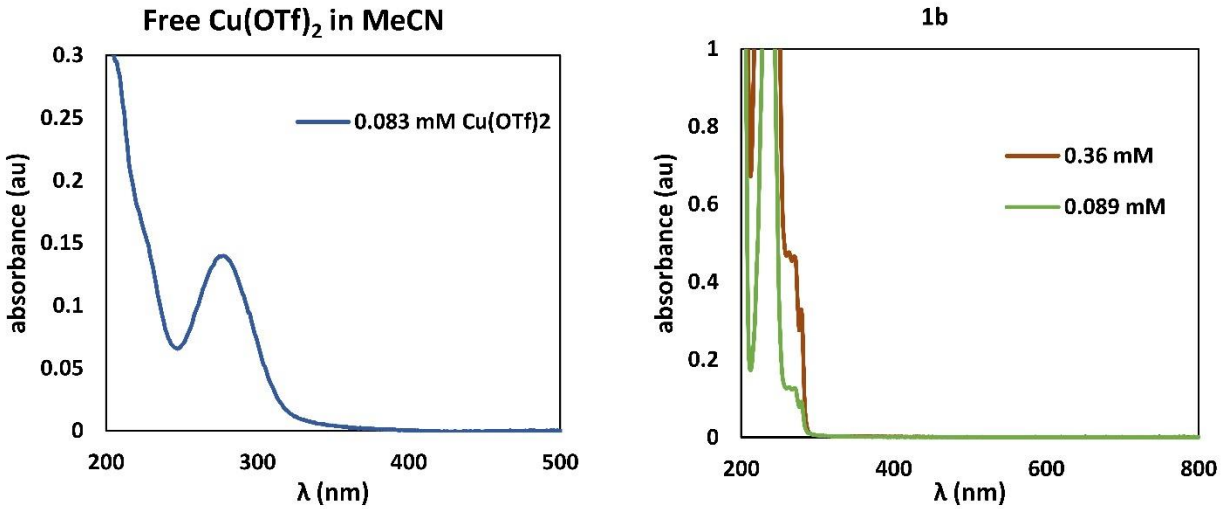
Molecular Weight: 172.16	Molecular Weight: 361.67	Molecular Weight: 187.21
1-Na	**Cu**	**1b**

Operational notes: Two stock solutions of $Cu(OTf)_2$ were prepared in anhydrous MeCN. Solution A contained only $Cu(OTf)_2$, and Solution C contained added **1-Na** (2.3:1 **1-Na:Cu ratio**). A third stock solution of the sulfonamide in anhydrous MeCN was also prepared (Solution B). These solutions were then used to produce mixtures of **1-Na**, **Cu**, and the sulfonamide at the desired ratios in separate cuvettes for UV-Vis analysis. A constant [Cu] was maintained across all runs. Volumetric glassware and syringes were employed for all solutions and manipulations.

Solution A:	**Solution B:**	**Solution C:**
9.7 mg $Cu(OTf)_2$	5.0 mg **1b**	5.2 mg **1-Na**
100 mL MeCN	50.0 mL MeCN	50.0 mL solution A
0.269 mM $Cu(OTf)_2$	**0.534 mM 1b**	**0.604 mM 1-Na, 0.268 mM Cu**

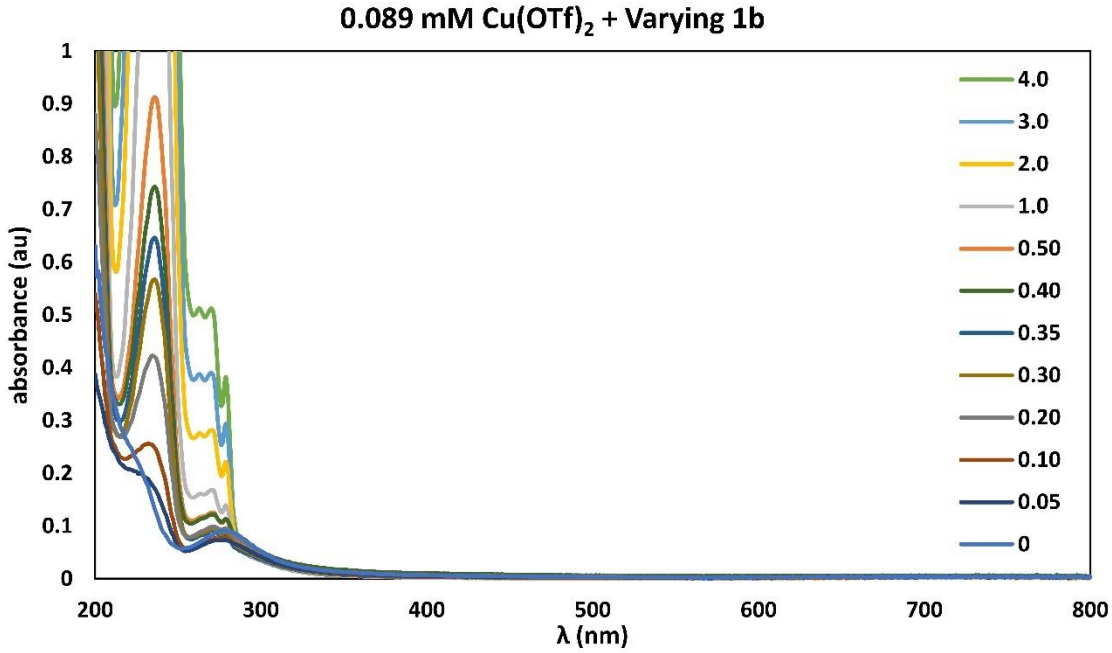
First, UV-Vis absorbance traces of free $Cu(OTf)_2$ and the free sulfonamide **1b** were obtained (**Supplementary Figure 5**). Sulfonamide **1b** was found to be more absorbent than $Cu(OTf)_2$ in the 200-400 nm range. The results of the titration are provided below (**Supplementary Figure 6**).

a. **b.**

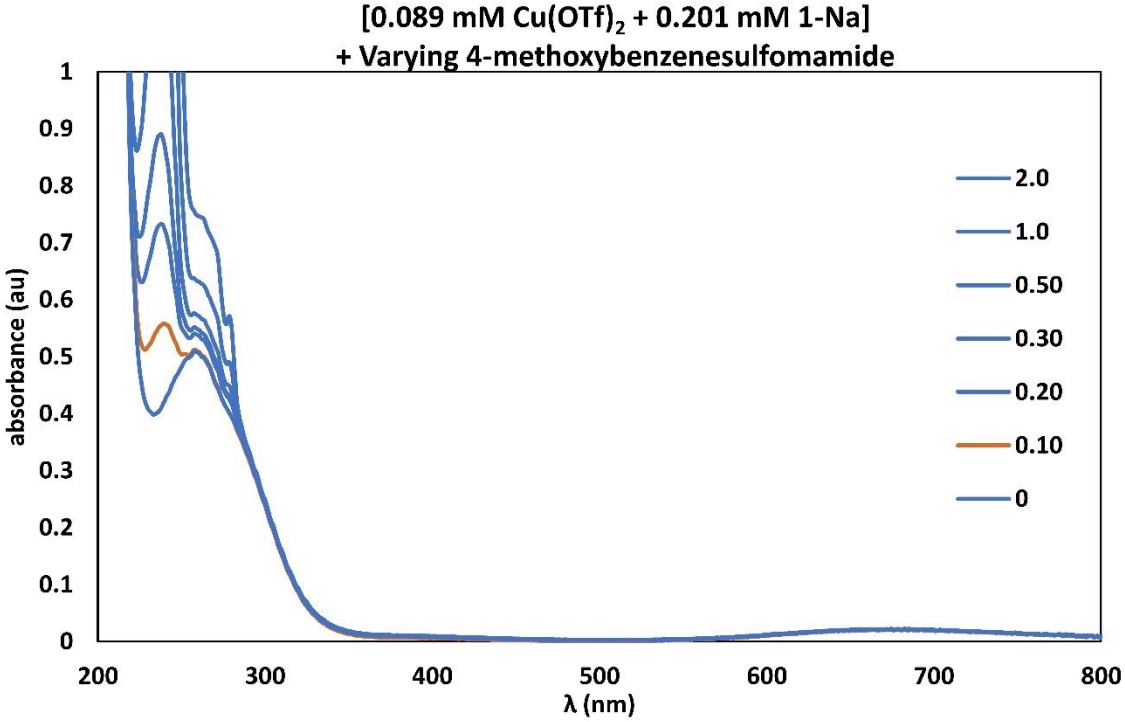


Supplementary Figure 5. a, $Cu(OTf)_2$ UV-Vis absorbance. **b**, **1b** UV-Vis absorbance**.**

a.



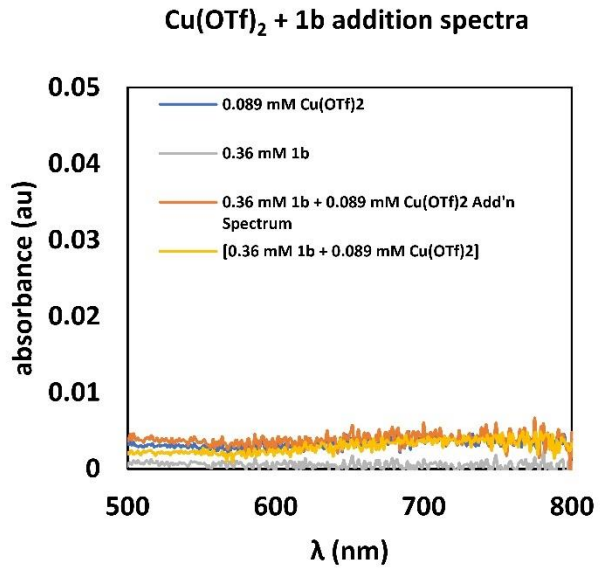
b.



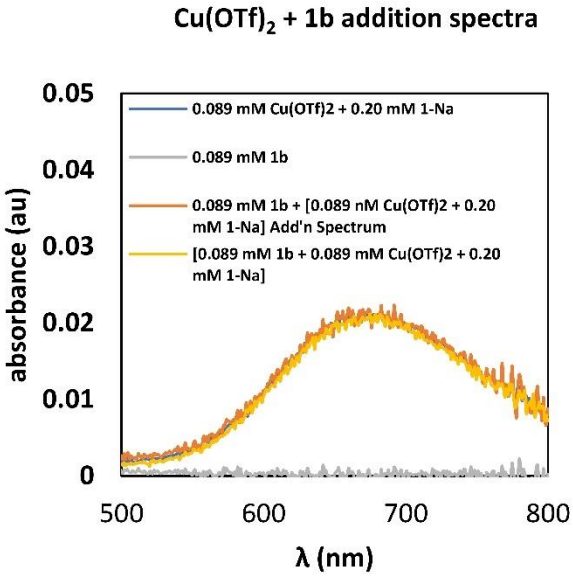
Supplementary Figure 6. **a**, UV-Vis titration study of $Cu(OTf)_2$ + **1b** (200-800 nm range). The legend refers to the **1b:Cu** ratio. **b**, UV-Vis titration study of $Cu(OTf)_2$ + **1-Na** + **1b** (200-800 nm range). The legend refers to the **1b:Cu** ratio.

The overall traces indicate little meaningful interaction between sulfonamide **1b** and $Cu(OTf)_2$. Given the high absorbance of **1b** compared to $Cu(OTf)_2$, the individual and addition spectra in the 500-800 nm d-d transition range (where $Cu(OTf)_2$ absorbs more strongly) were also scrutinized (**Supplementary Figure 7**). The excellent overlap further supports the lack of an interaction.

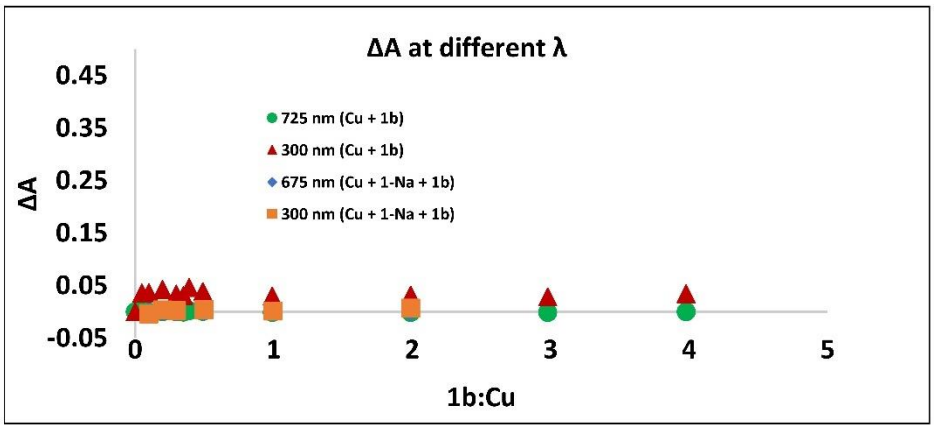
a.



b.



c.



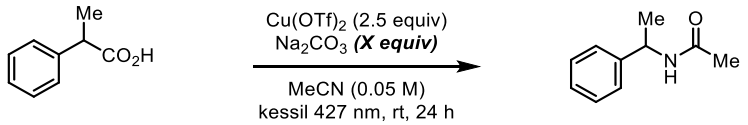
Supplementary Figure 7. a, UV-Vis addition spectra of $Cu(OTf)_2$ + **1b** (200-800 nm). [**Cu**] = 0.089 mM and [**1b**] = 0.36 mM. **b**, UV-Vis addition spectra of $Cu(OTf)_2$ + **1-Na** + **1b** (200-800 nm). [**Cu**] = 0.089 mM, [**1-Na**] = 0.20 mM, and [**1b**] = 0.089 mM. **c**, Monitoring absorbance at fixed wavelengths to understand binding dynamics.

To further confirm the lack of a meaningful interaction between $Cu(OTf)_2$ and the sulfonamide **1b**, changes in absorbance at fixed wavelengths were monitored, which further reveals no significant changes, regardless of the presence of **1-Na** as an internal base (**Supplementary Figure 7c**).

G. Study of reaction performance as a function of 1a loading at 427 nm.

Objective: As outlined above in the UV-Vis titration studies of carboxylate **1-Na** and **Cu(OTf)$_2$**, the speciation and absorbance properties of the Cu(II) complex(es) in solution can be influenced by the equivalencies of the carboxylate (i.e., the **1-Na:Cu** ratio). To study whether this dynamic behavior has an impact on preparative decarboxylative cross-coupling reactions, we elected to study the performance of the Ritter amidation and sulfonamidation reactions as a function of acid equivalencies. We hypothesized that at high acid loadings, the yield of the decarboxylative cross-coupled products would diminish due to the blue-shift in the absorbance of the Cu(II) species out of the visible range and into the UV.

Ritter Conditions:

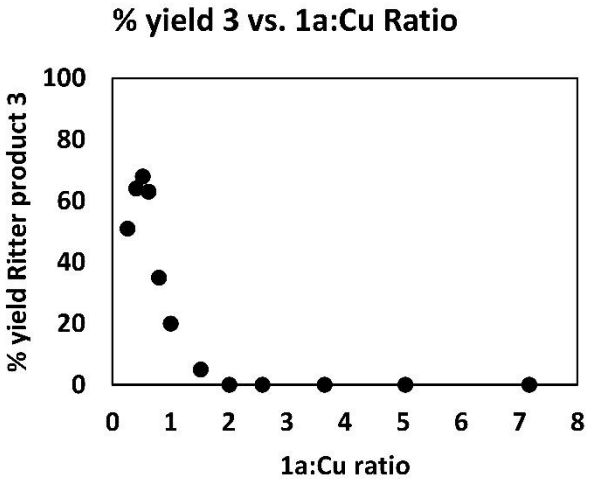


1a, X equiv **3**

Experimental: Oven-dried 4-mL vials were brought into a nitrogen-filled glovebox and charged with Cu(OTf)$_2$ (72.6 mg, 0.20 mmol), Na_2CO_3 (5.3 – 148.4 mg, 0.05 – 1.4 mmol), 1-phenylpropionic acid (7.5 – 210 mg, 0.05 – 1.4 mmol), stir bar, and acetonitrile (2.0 mL). The vials were sealed with screwcaps bearing teflon septa, removed from the glovebox, and placed in a Hepatochem PhotoRedOx Box on a stir plate. The vials were irradiated at 427 nm with a 40 W Kessil PR160 lamp with stirring at 800 rpm. A fan was used to maintain the vials at room temperature. After 24 h, the vials were removed from the photoreactor and diluted with 1.0 mL EtOAc and 1.0 mL 2 M aqueous HCl. 1-Methylnaphthalene (10 µL) was added as an internal standard, and 15 drops were removed for GC analysis. Yields were calculated based on either the acid or Cu(OTf)$_2$ as the limiting reagent (depending on acid loading) and assuming complete reduction to Cu(0) is operative.

Supplementary Table 22. Decarboxylative Ritter reaction performance as a function of **1a** equivalencies.

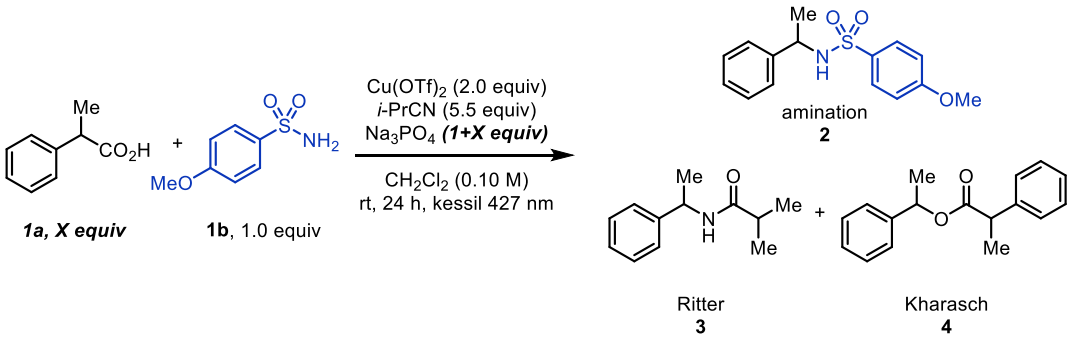
Entry	X	**1a**:Cu	% **3**	% rsm **1a**	mass balance (%)
1	0.53	0.26	51	0	62
2	0.82	0.41	64	0	74
3	1.03	0.52	68	5	92
4	1.23	0.62	63	4	86
5	1.59	0.80	35	33	82
6	2.00	1.00	20	57	80
7	3.04	1.52	5	95	100
8	4.02	2.01	0	100	100
9	5.15	2.58	0	100	100
10	7.30	3.65	0	100	100
11	10.09	5.04	0	100	100
12	14.33	7.17	0	100	100



Supplementary Figure 8. Yield of the decarboxylative Ritter product **3** as a function of **1a:Cu** ratio.

In line with the UV-Vis titration studies and our hypothesis, the yield of the decarboxylative Ritter product **3** drops precipitously as the **1a:Cu** ratio is increased beyond 0.6:1 (**Supplementary Table 22**, **Supplementary Figure 8**). Importantly, **1a** is recovered unreacted at higher ratios, supporting that other pathways are not occurring that consume this substrate. These results suggest that the species formed at high **1a:Cu** ratios are photochemically inactive at 427 nm and that the species formed at low **1a:Cu** ratios is responsible for the observed reactivity. An important implication of these observations: modulation of the **1a:Cu** ratio is critical for enabling the photochemical decarboxylation with visible light with high chemoselectivity.

Sulfonamide Conditions:

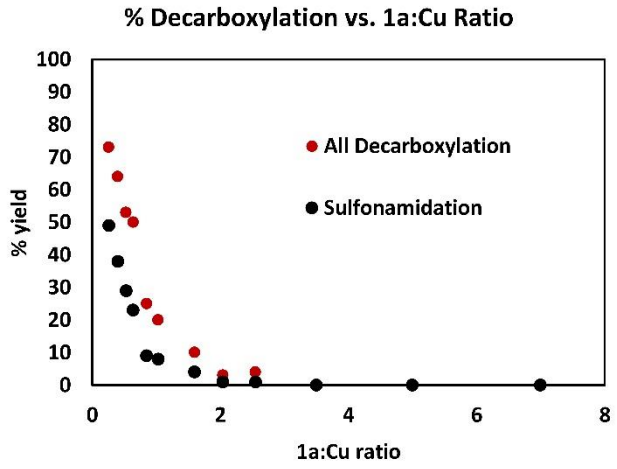


Experimental: Oven-dried 4-mL vials equipped with stir bars were brought into a nitrogen-filled glovebox and charged with $Cu(OTf)_2$ (72.6 mg, 0.20 mmol), Na_3PO_4 (24.1 – 246 mg, 0.05 – 1.4 mmol), 1-phenylpropanoic acid **1a** (7.5 – 210 mg, 0.05 – 1.4 mmol), 4-methoxybenzenesulfonamide **1b** (18.7 mg, 0.10 mmol), methylene chloride (1.0 mL, 0.10 M), and isobutyronitrile (50 µL, 0.55 mmol). The vials were sealed with screwcaps bearing teflon septa, removed from the glovebox, and placed in a Hepatochem PhotoRedOx Box on a stir plate. The vials were irradiated at 427 nm with a 40 W Kessil PR160 lamp with stirring at 800 rpm. A fan was used to maintain the vials at room temperature. After 24 h, the vials were removed from the photoreactor and

diluted with 1.0 mL EtOAc and 1.0 mL 2 M aqueous HCl. 1-Methylnaphthalene (10 µL) was added as an internal standard, and 15 drops were removed for GC analysis. Yields were calculated based on either the acid or the sulfonamide as the limiting reagent (depending on acid loading).

Supplementary Table 23. Decarboxylative sulfonamidation reaction performance as a function of **1a** equivalencies.

Entry	X	**1a:Cu**	% **2**	% **3**	% **4**	% rsm **1a**	% rsm **1b**	mass balance (%)
1	0.5	0.26	49	4	20	0	52	73
2	0.8	0.40	38	4	22	0	48	64
3	1.1	0.53	29	4	20	32	54	97
4	1.3	0.64	23	7	20	1	49	51
5	1.7	0.85	9	6	10	45	58	70
6	2.1	1.03	8	4	8	54	57	74
7	3.2	1.60	4	2	4	85	63	95
8	4.1	2.04	1	0	2	92	59	95
9	5.1	2.55	1	1	2	91	58	95
10	7.0	3.50	0	0	0	89	55	89
11	10	5.00	0	0	0	87	65	87
12	14	7.00	0	0	0	87	67	87



Supplementary Figure 9. Yield of the decarboxylative products as a function of **1a:Cu** ratio. All decarboxylation also includes the Ritter (**3**) and Kharasch (**4**) products.

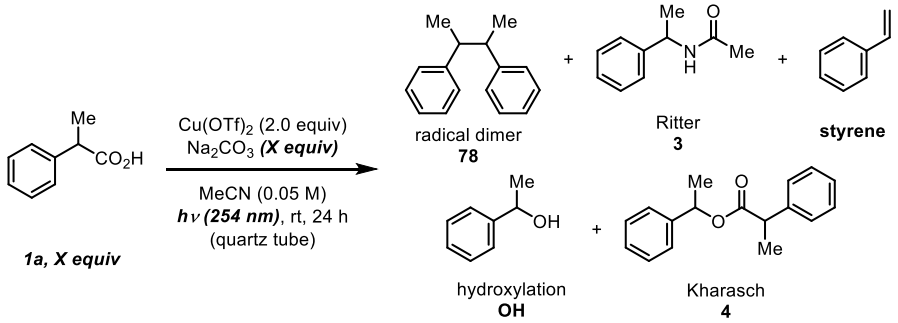
As with the study of the Ritter conditions and also in line with our hypothesis, the yield of the decarboxylative sulfonamidation product **2** drops precipitously as the **1a:Cu** ratio is increased (**Supplementary Table 23**, **Supplementary Figure 9**). The same trend is observed when considering all decarboxylation products observed under these conditions, which includes those resulting from Kharasch (**4**) and Ritter (**3**) reactions. Importantly, the acid **1a** is recovered unreacted at higher ratios, supporting that other pathways are not occurring that would consume this substrate. These results support

that the species formed at high **1a:Cu** ratios are photochemically inactive at 427 nm and that the species formed at low acid:Cu ratios is responsible for the observed reactivity. An important implication of these observations: modulation of the **1a:Cu** ratio is critical for enabling chemoselective photochemical decarboxylation with visible light.

H. Study of reaction performance as a function of 1a loading at 254 nm.

Objective: Given that productive photochemical decarboxylation is diminished at high **1a:Cu** ratios under visible light conditions, we hypothesized that shifting the wavelength of irradiation might restore reactivity. In the UV-Vis titration studies of the carboxylate **1-Na** and $Cu(OTf)_2$ outlined above, a significant blue-shift into the UV is observed at higher **1a:Cu**. We thus elected to study reaction performance under UV irradiation conditions.

Ritter Conditions:



Experimental: Oven-dried quartz tubes equipped with stir bars were brought into a nitrogen-filled glovebox and charged with $Cu(OTf)_2$ (72.6 mg, 0.20 mmol), Na_2CO_3 (5.3-148.4 mg, 0.05-1.4 mmol), 1-phenylpropionic acid **1a** (7.5-210 mg, 0.05-1.4 mmol), and acetonitrile (2.0 mL). The tubes were sealed with rubber septa and electrical tape, removed from the glovebox, and placed in a Rayonet RPR-200 photoreactor fitted with 254 nm bulbs. The tubes were irradiated with stirring at 600 rpm. A fan was used to maintain the tubes at room temperature. After 24 h, the tubes were removed from the photoreactor and diluted with 1.0 mL EtOAc and 1.0 mL 2 M aqueous HCl. 1-Methylnaphthalene (10 µL) was added as an internal standard, and aliquots were removed for GC and ^{1}H NMR analyses. Yields were calculated based on either the acid or $Cu(OTf)_2$ as the limiting reagent (depending on loading) and assuming complete reduction to Cu(0) is operative.

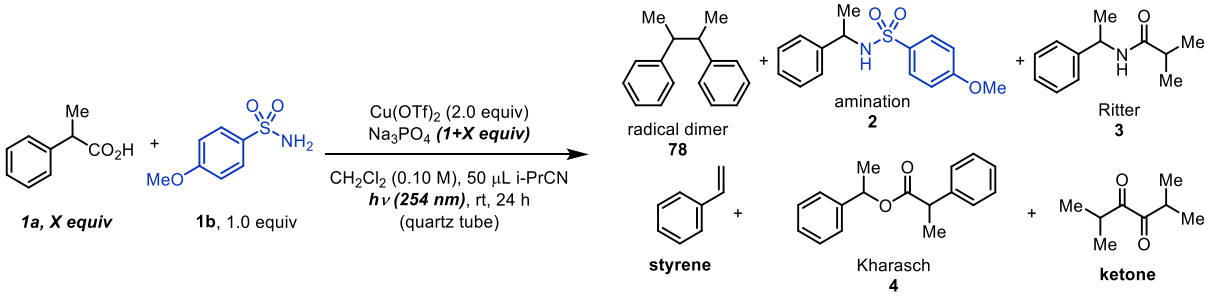
Supplementary Table 24. Decarboxylative Ritter reaction under UV irradiation.

Entry	mmol **1a**	**1a:Cu**	% **78**	% **3**	% **styrene**	% **OH**	% **4**	% rsm **1a**
1	1.41	7.07	64	0	2	0	0	85
2	0.50	2.52	35	1	3	0	0	74
3	0.21	1.04	21	21	1	6	7	24
4	0.11	0.55	0	73	0	7	5	5
5[a]	1.40	–	1	0	0	0	0	98

[a.] Control reaction in the absence of $Cu(OTf)_2$.

Comments: Upon irradiation at 254 nm, significant decarboxylative reactivity is observed at all **1a:Cu** ratios (**Supplementary Table 24**). Importantly, this includes the 7:1 **1a:Cu** ratio that was photochemically inactive at 427 nm. This supports the overall hypothesis that restoration of decarboxylation can be achieved by shifting the wavelength of irradiation. Of note, the chemoselectivity of the process does not favor the Ritter product **3** at high **1a:Cu** ratios, but instead the radical dimer **78**. However, at low **1a:Cu**, chemoselectiviy is reversed, favoring the Ritter product **3**. We attribute this to an increased rate of radical production at high **1a:Cu** where the λ_{max} (260 nm) of the species more closely matches the 254 nm wavelength of irradiation as compared to that which is formed at low **1a:Cu**.

Sulfonamide Conditions:



Experimental: Oven-dried quartz tubes equipped with stir bars were brought into a nitrogen-filled glovebox and charged with $Cu(OTf)_2$ (72.6 mg, 0.20 mmol), Na_3PO_4 (24.1-246 mg, 0.05-1.4 mmol), 1-phenylpropanoic acid **1a** (7.5-210 mg, 0.05-1.4 mmol), 4-methoxybenzenesulfonamide **1b** (18.7 mg, 0.10 mmol), methylene chloride (1.0 mL, 0.10 M), and isobutyronitrile (50 µL, 0.55 mmol). The tubes were sealed with rubber septa and electrical tape, removed from the glovebox, and placed in a Rayonet RPR-200 photoreactor fitted with 254 nm bulbs. The tubes were irradiated with stirring at 600 rpm. A fan was used to maintain the tubes at room temperature. After 24 h, the tubes were removed from the photoreactor and diluted with 1.0 mL EtOAc and 1.0 mL 2 M aqueous HCl. 1-Methylnaphthalene (10 µL) was added as an internal standard, and aliquots were removed for GC and ^{1}H NMR analyses. Yields were calculated based on either the acid or sulfonamide as the limiting reagent (depending on acid loading).

Supplementary Table 25. Decarboxylative sulfonamidation under UV irradiation.

Entry	X	**1a:Cu**	% **78**	% **2**	% **3**	% **styrene**	% **4**	% **ketone**	% rsm **1a**
1	14.1	7.03	62	1	0	4	4	2	24
2	5.0	2.52	21	2	6	4	11	6	30
3	2.1	1.03	0	3	6	0	18	22	26
4	1.0	0.52	0	15	6	0	12	28	2
5[a]	14.3	–	<1	0	0	0	0	0	98

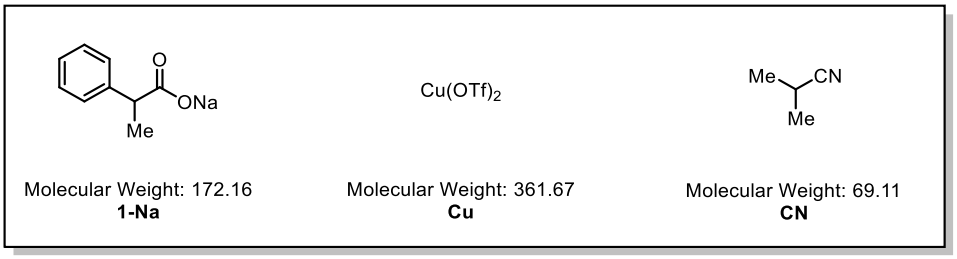
[a.] Control reaction in the absence of $Cu(OTf)_2$.

Comments: Irradiation at 254 nm results in significant decarboxylative reactivity at the 7:1 **1a:Cu** ratio that was photochemically inactive at 427 nm (**Supplementary Table**

25). In this case, the chemoselectivity of the process does not favor the sulfonamidation product **2**, but instead the radical dimer **78**. This is likely due to an increased rate of radical production relative to a slower rate of processing by Cu(II). At lower **1a:Cu** ratios, the yield of the sulfonamidation product **2** is only modest compared to when the standard irradiation at 427 nm is applied. We attribute this to the degradation of the *i*-PrCN ligand in a reductive coupling process to produce a diketone byproduct. Not only is the enabling ligand destroyed, but the carboxylic acid also appears to be consumed by this process.

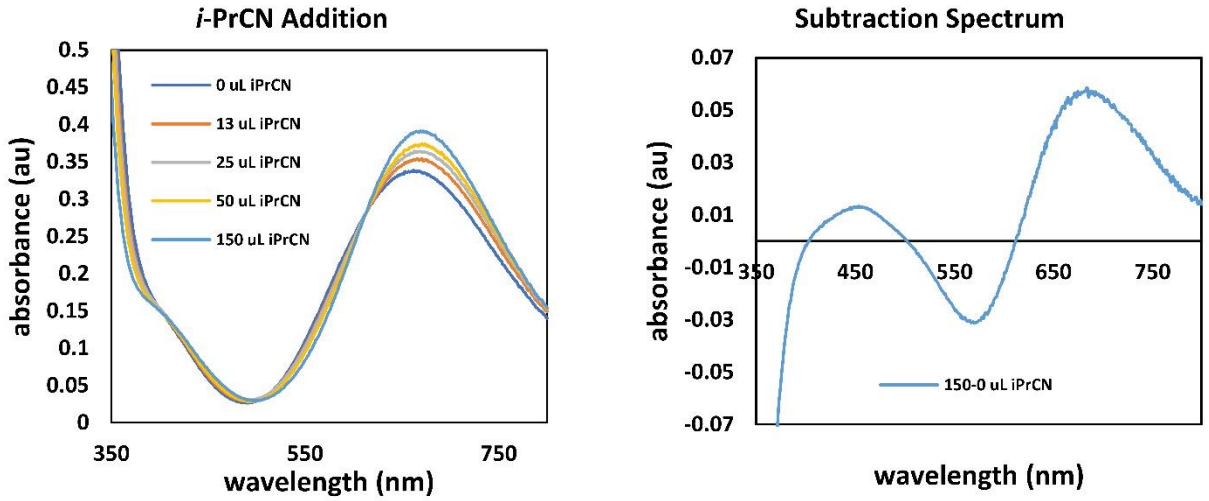
I. UV-Vis studies of Cu(II) with *i*-PrCN

Objective: To determine the role of the nitrile ligand by studying the interaction between a preformed Cu(II) carboxylate and *i*-PrCN in CH_2Cl_2.



Operational Notes: An authentic reaction mixture was prepared by adding 90.7 mg $Cu(OTf)_2$ (0.25 mmol), 16.3 mg **1a** (0.10 mmol), 16.9 mg Na_3PO_4 (0.10 mmol), and 1.0 mL CH_2Cl_2 (0.10 M) to a vial. The sulfonamide was omitted to simplify analysis. Following thorough mixing, the solids were allowed to settle, and the mixture was filtered to remove insoluble material. A 500 µL aliquot was removed and diluted to 3.0 mL in a cuvette (~41.8 mM Cu). UV-Vis spectra were obtained (averages of ten measurements) after 0, 13, 25, 50, and 150 µL of *i*-PrCN had been added directly to the cuvette. The results are summarized in **Supplementary Figure 10** below.

a. **b.**



Supplementary Figure 10. a, UV-Vis titration study with the *i*-PrCN ligand. **b**, Subtraction spectrum of the solution containing 150 and 0 µL *i*-PrCN.

As outlined in the UV-Vis trace above, a significant modulation of the d-d transition band between 550-800 nm is observed, suggesting that the nitrile binds directly to the Cu(II) center. Three isosbestic points are observed at 404, 506, and 612 nm. Between 506-612 nm, a decrease in absorbance is observed. However, this is likely inconsequential to reaction performance, as the spectral output of the blue LEDs utilized in the preparative coupling reactions is centered between 400-460 nm. By contrast, between 404-505 nm, an increase in absorbance is observed. This could be more clearly visualized by studying the subtraction spectrum (**Supplementary Figure 10b**).

Albeit modest, the increase in absorbance upon addition of a nitrile ligand could explain the crucial role it plays in enabling the photodecarboxylative mechanism. Another explanation could be due to increased solubility of the reagents. We favor the former, as reaction performance is poor in other media where solubility is high (**Supplementary Table 3**). However, based on the evidence gathered at this point, either role cannot be strictly supported or refuted.

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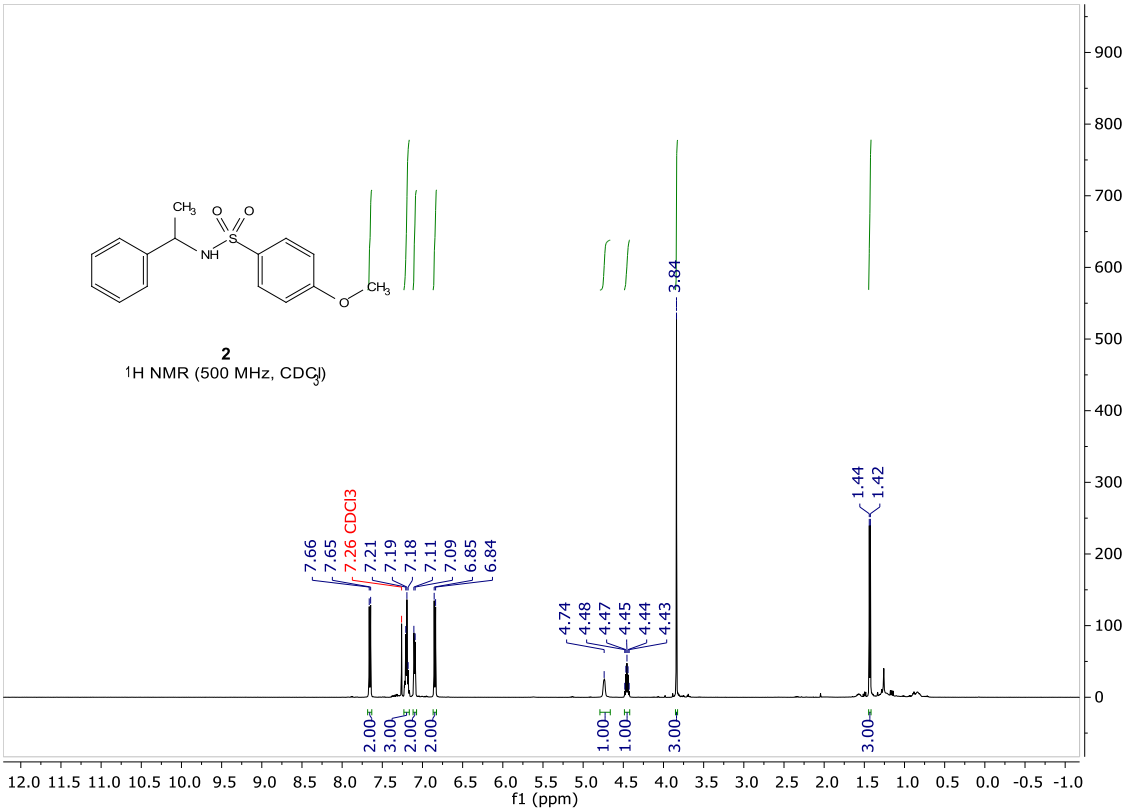
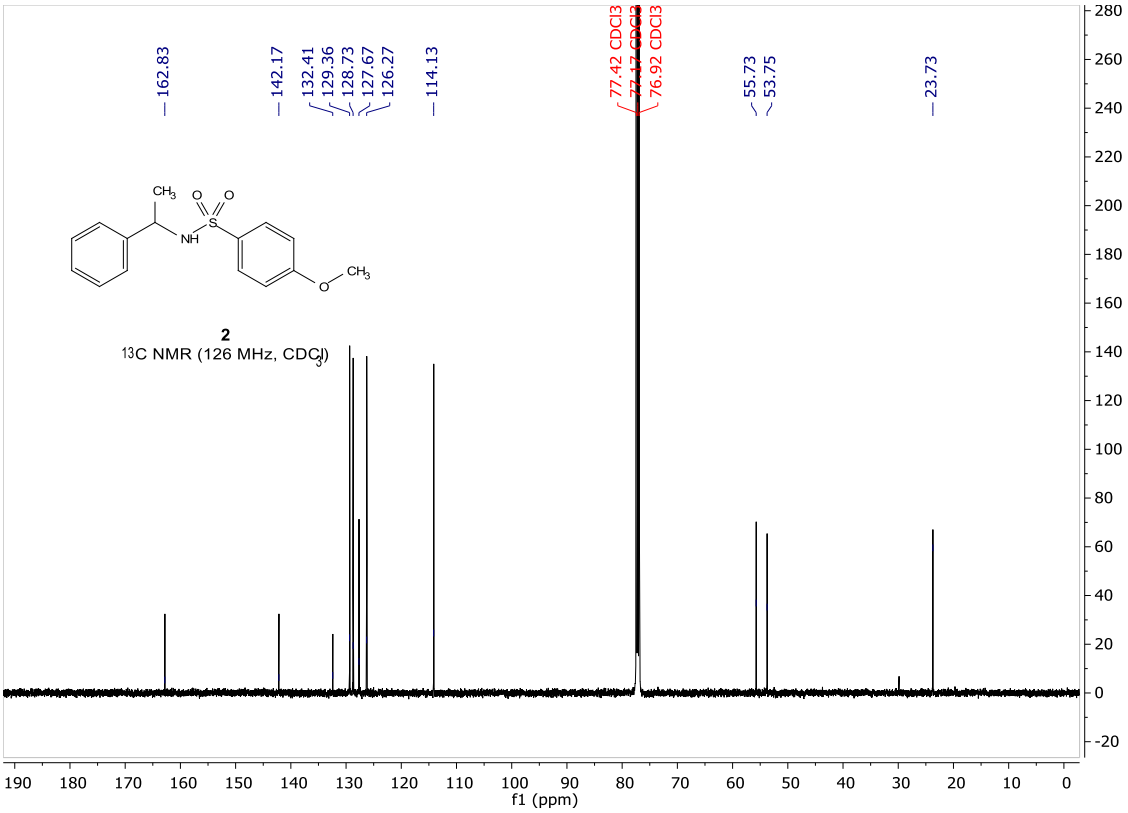
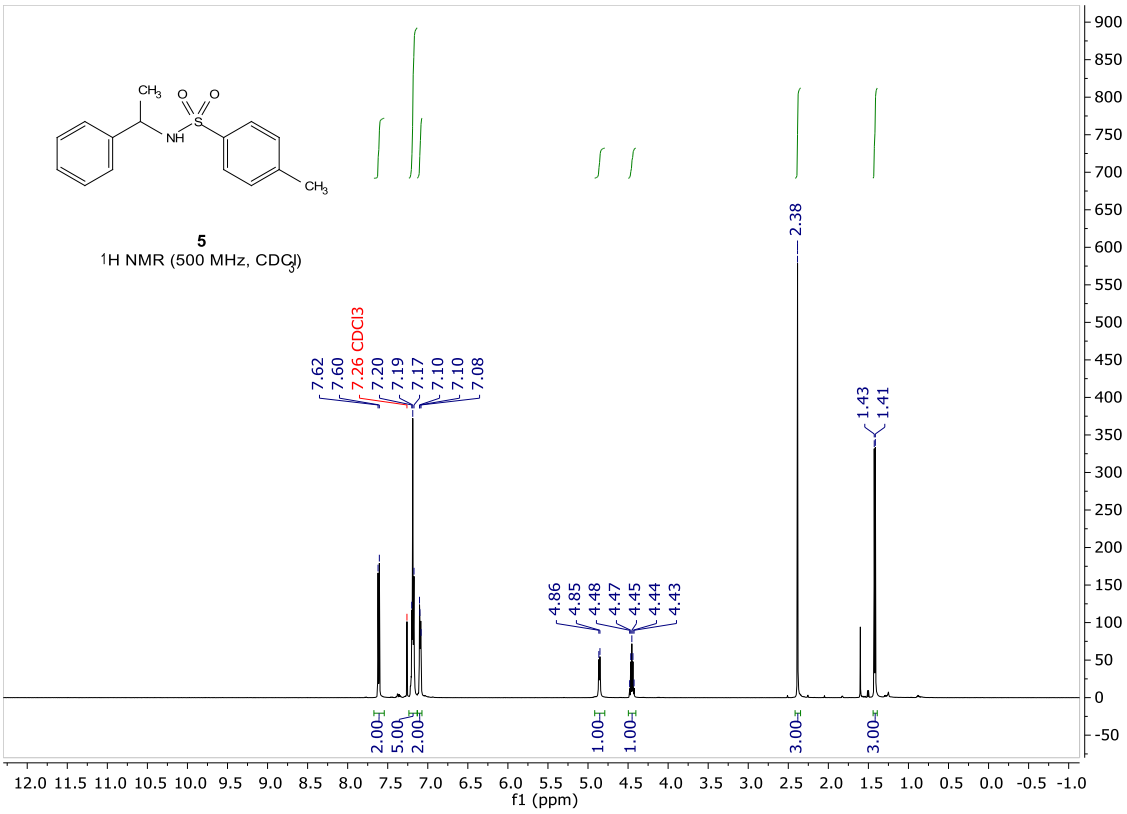
K. NMR Spectra



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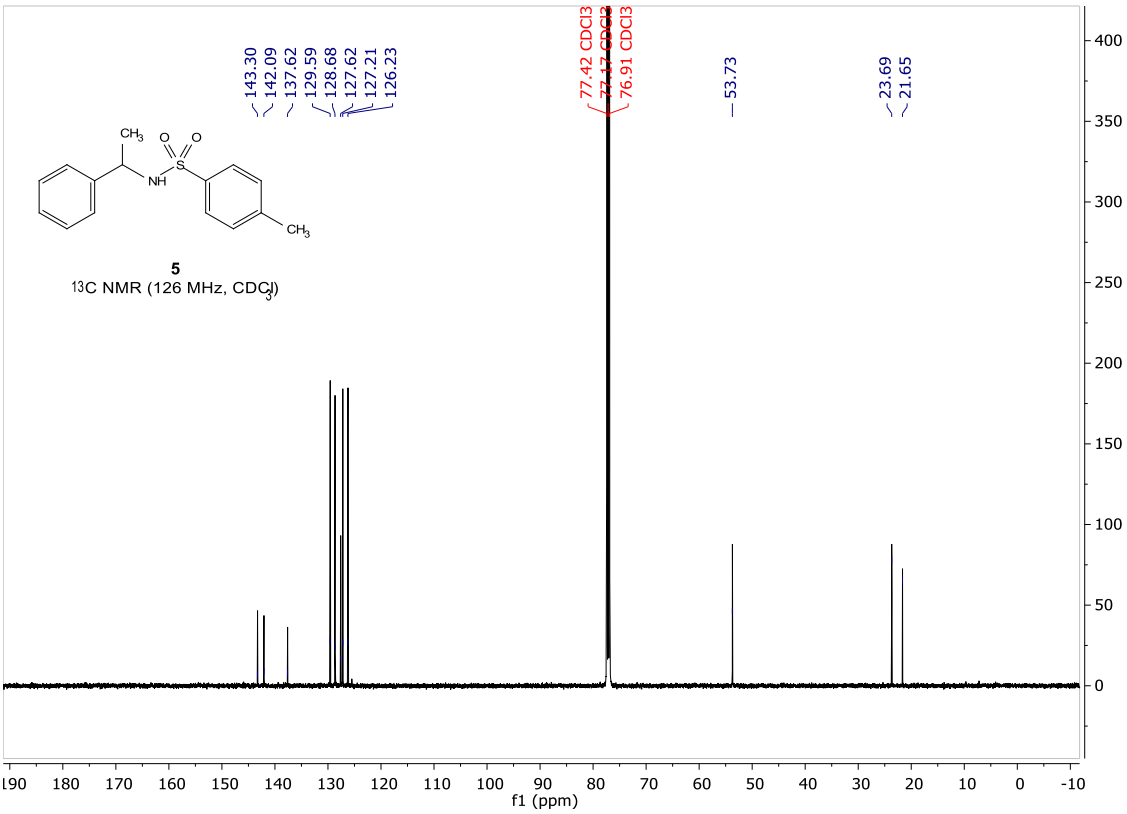
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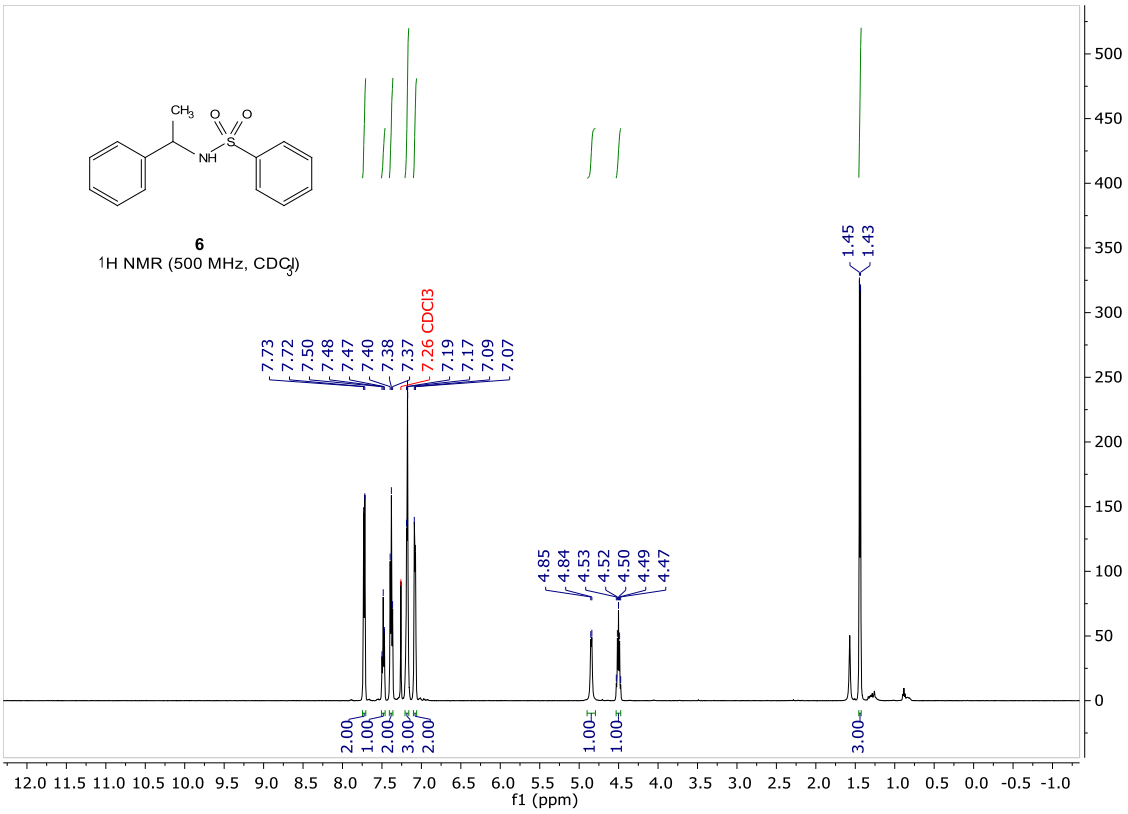
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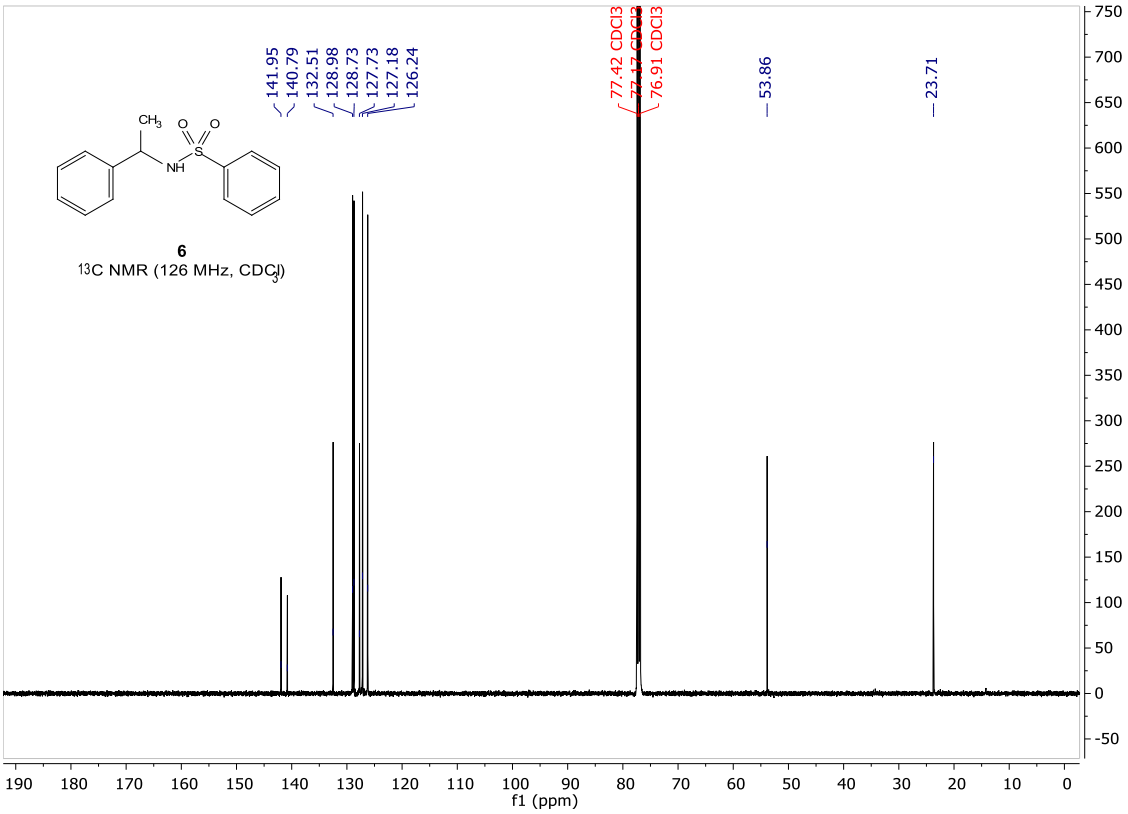
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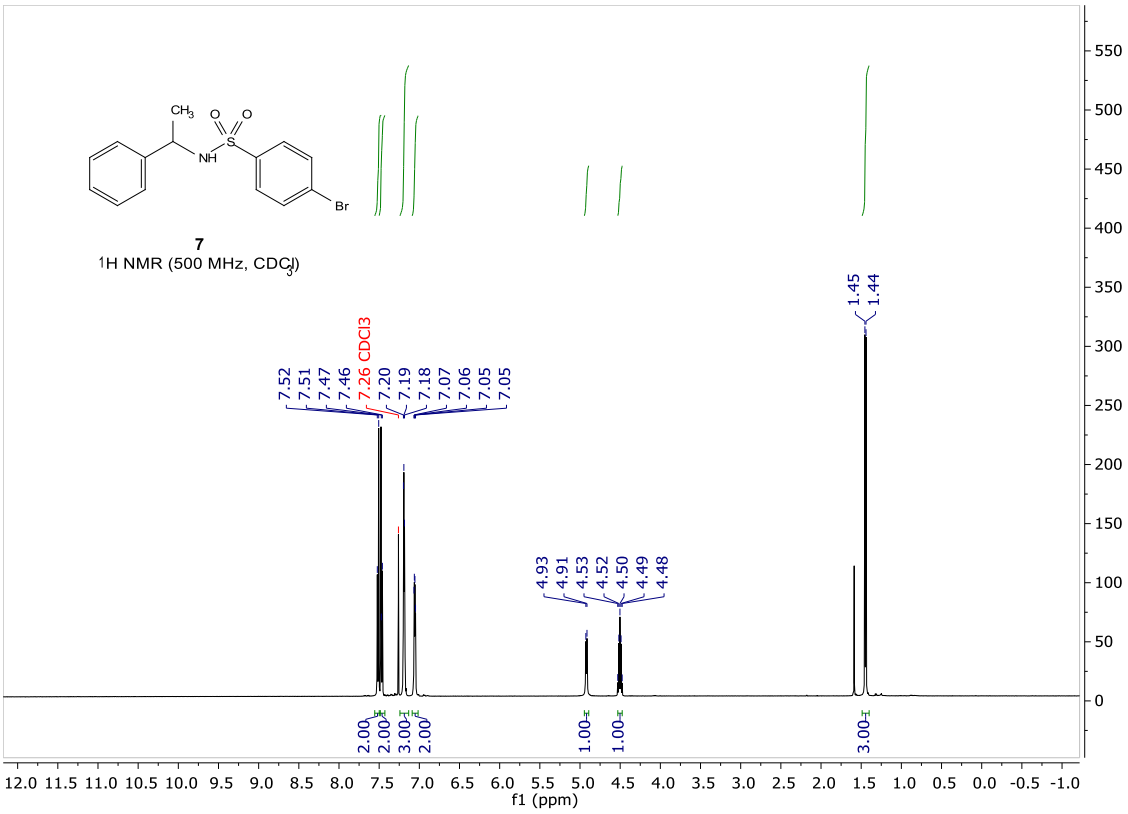
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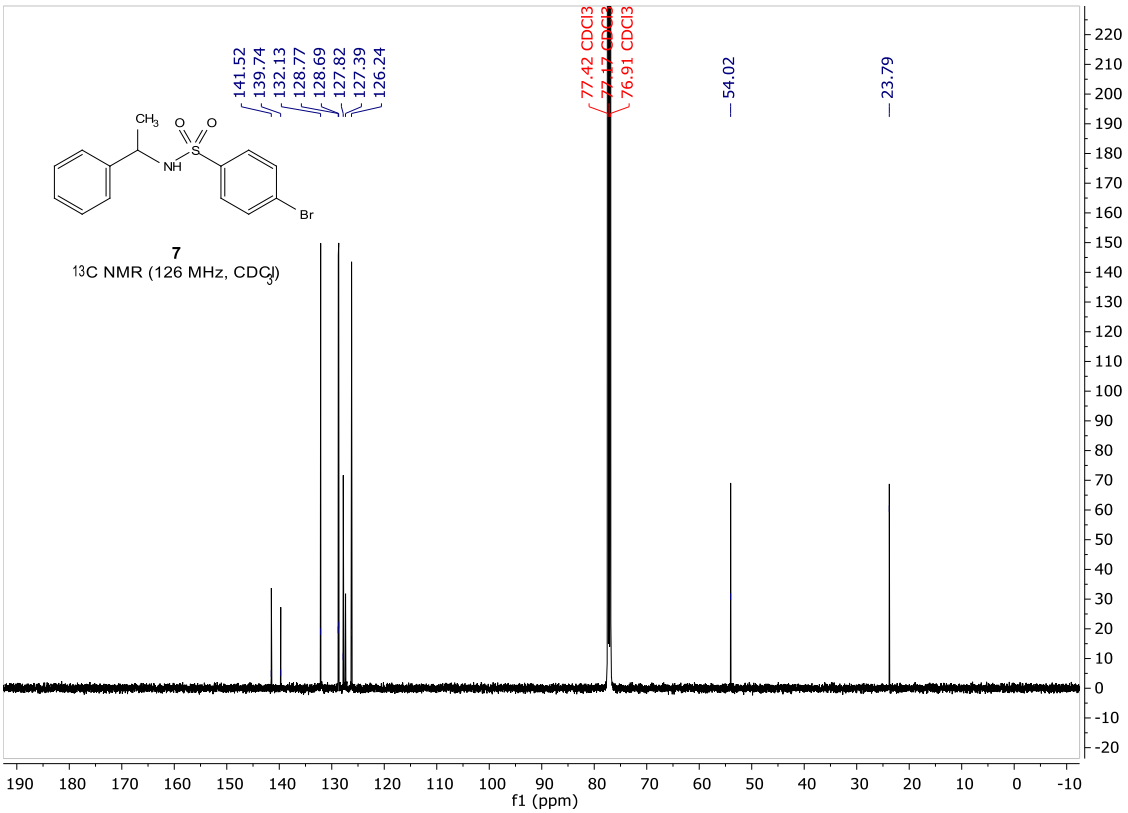
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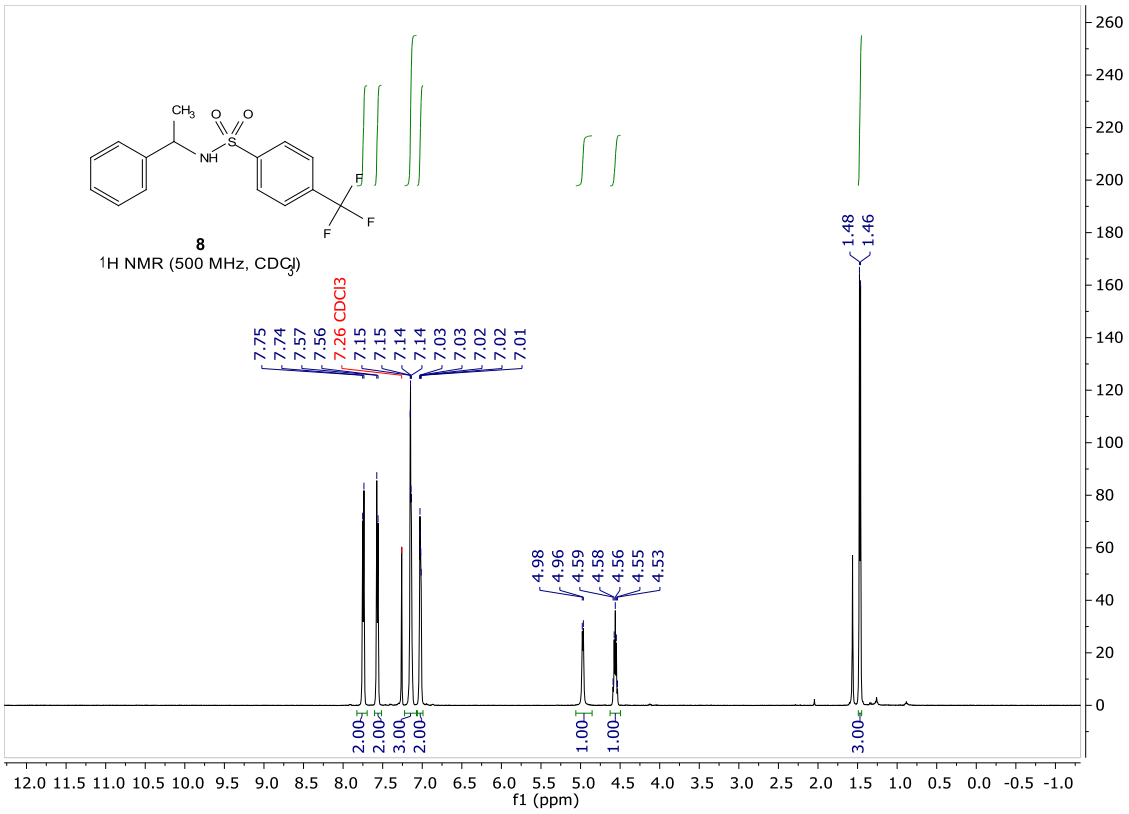
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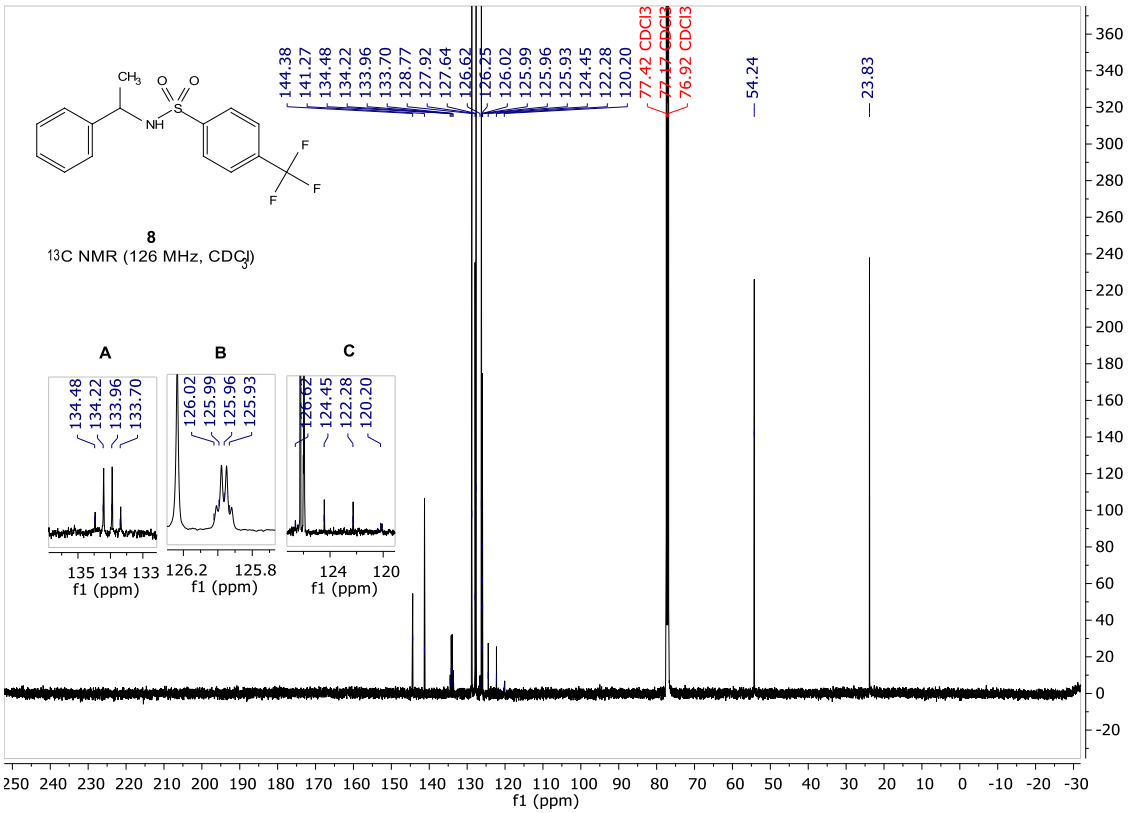
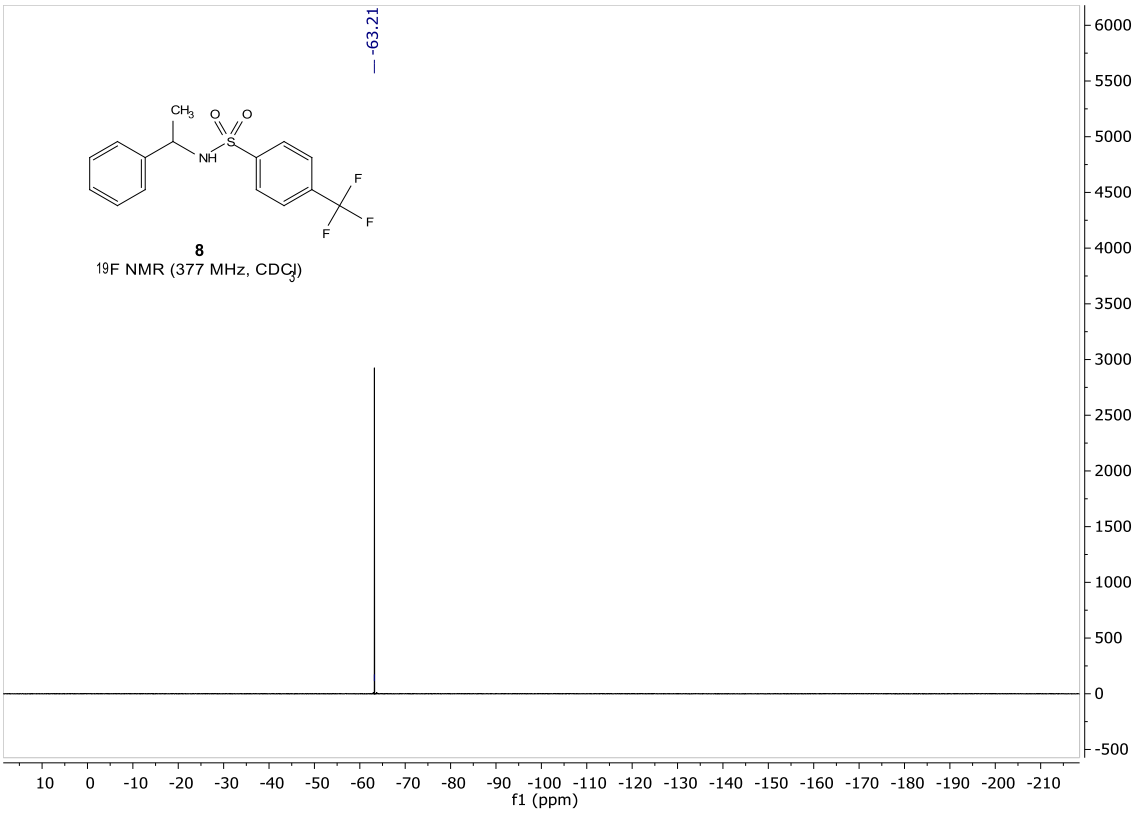
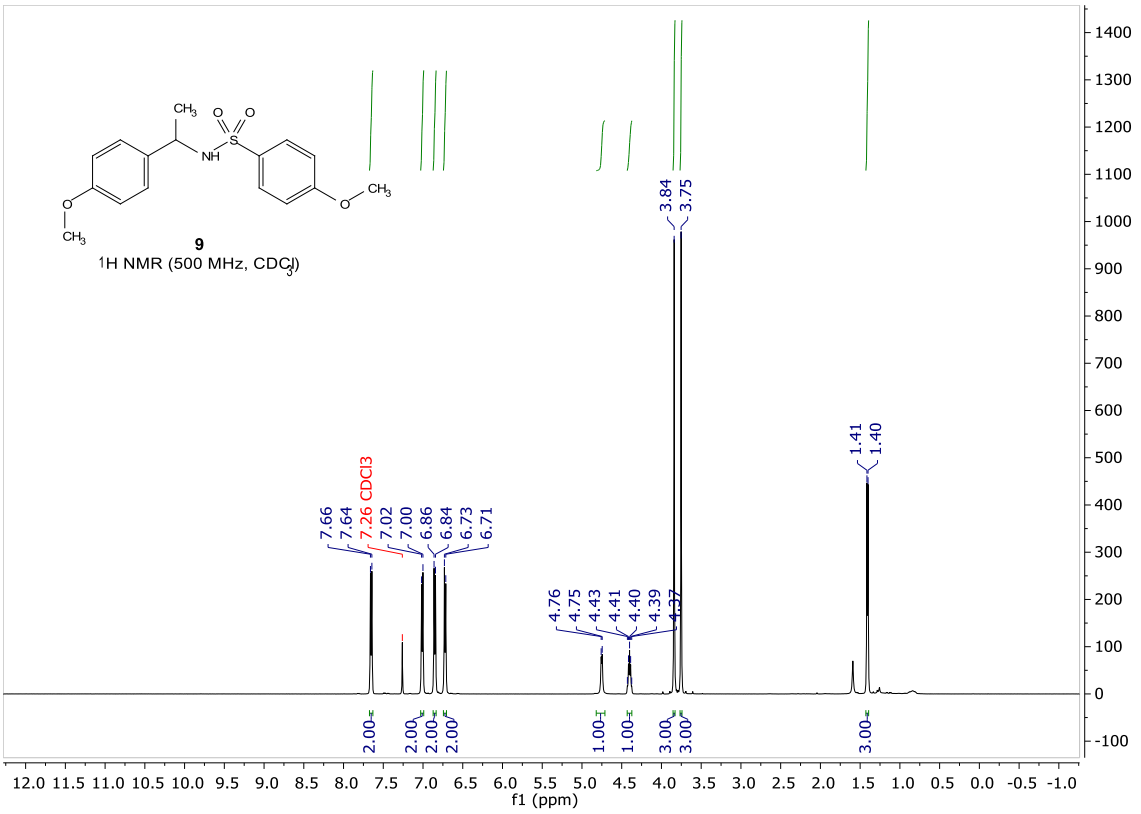
1.00
1.00
3.00
f1 (ppm)

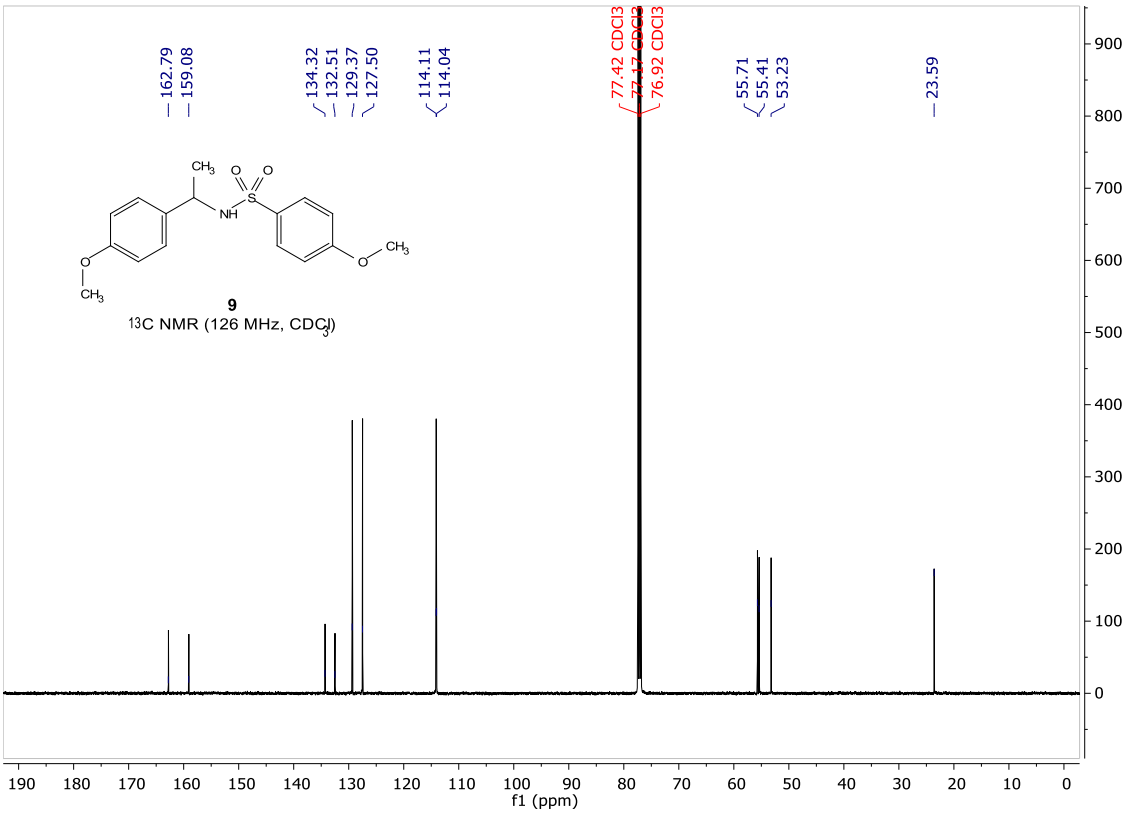

8
13C NMR (126 MHz, CDCl3)
144.38
141.27
134.48
134.22
133.96
133.70
128.77
127.92
127.64
126.62
126.25
126.02
125.99
125.96
125.93
124.45
122.28
120.20
77.42 CDCl3
77.17 CDCl3
76.92 CDCl3
54.24
23.83
A
B
C
f1 (ppm)

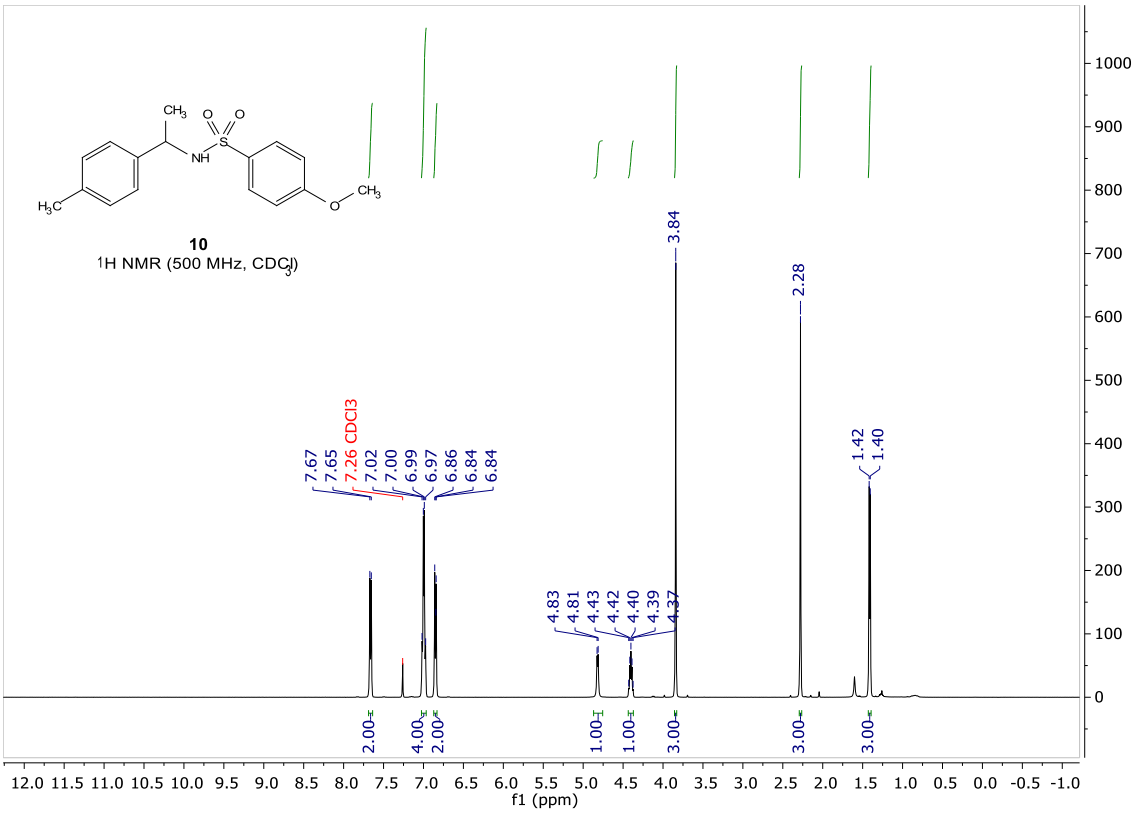


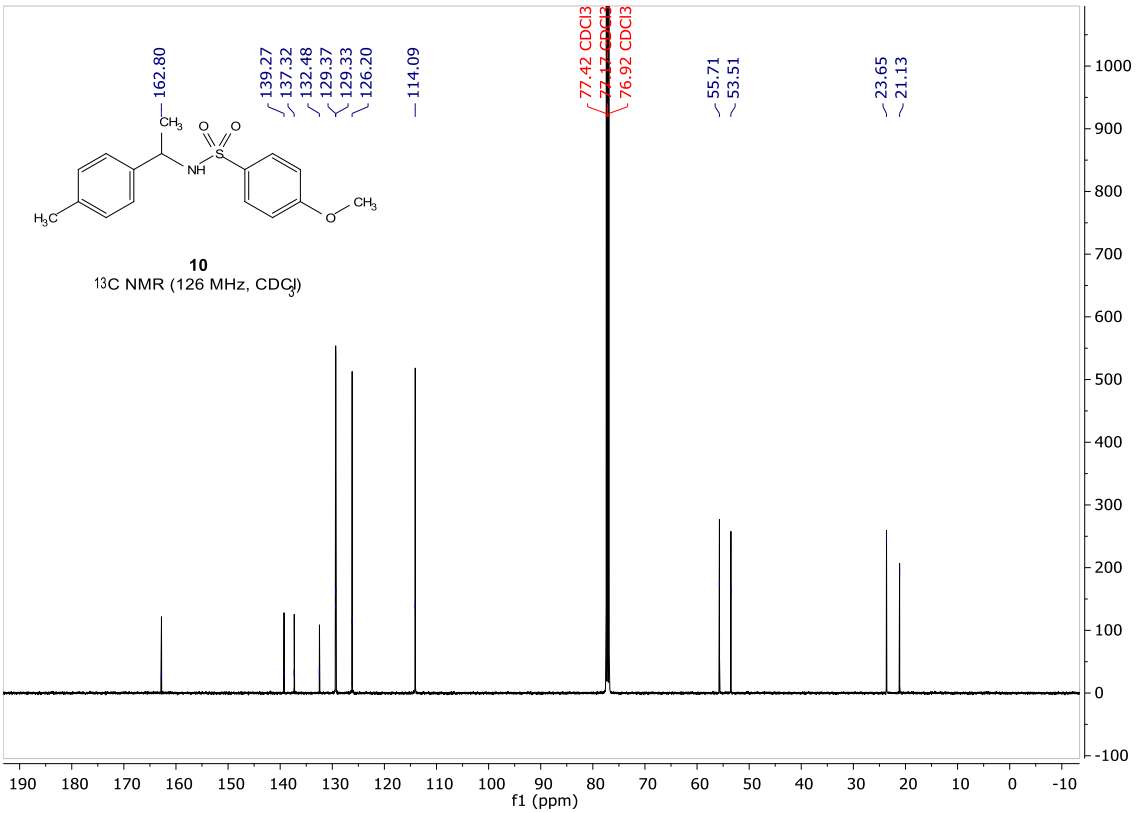
8

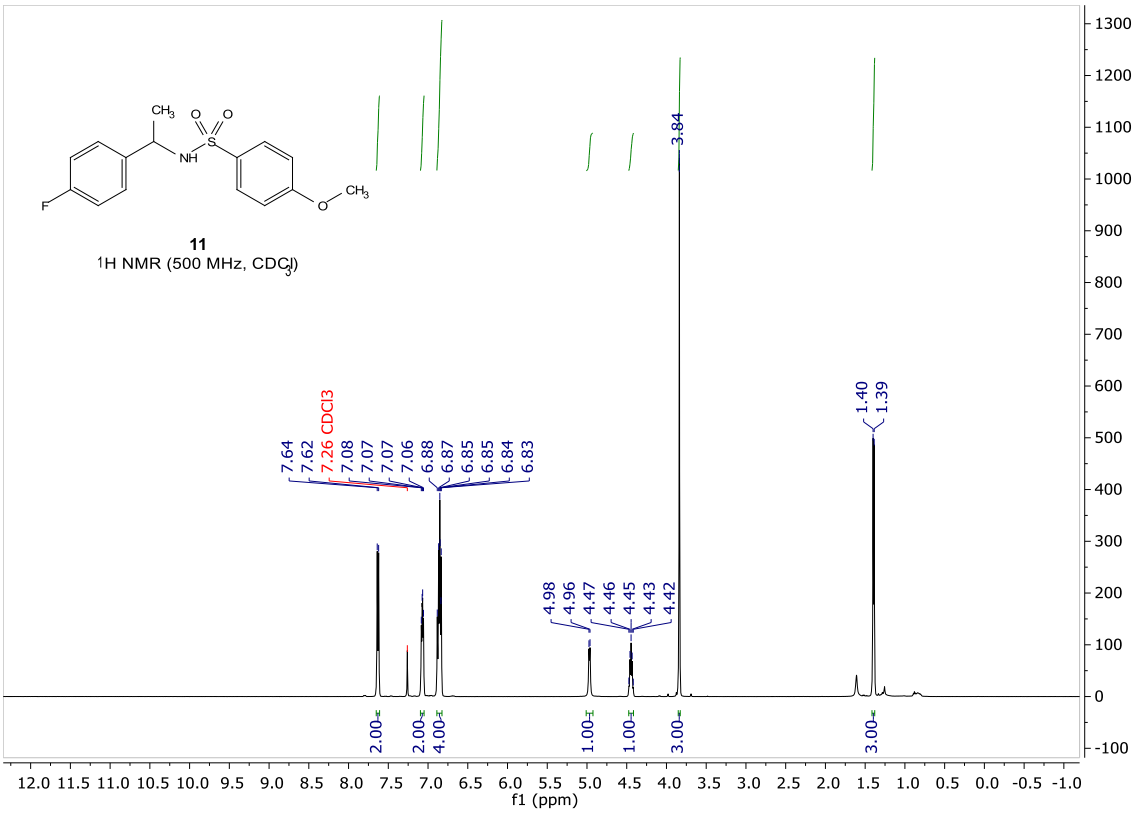
^{19}F NMR (377 MHz, $CDCl_3$)

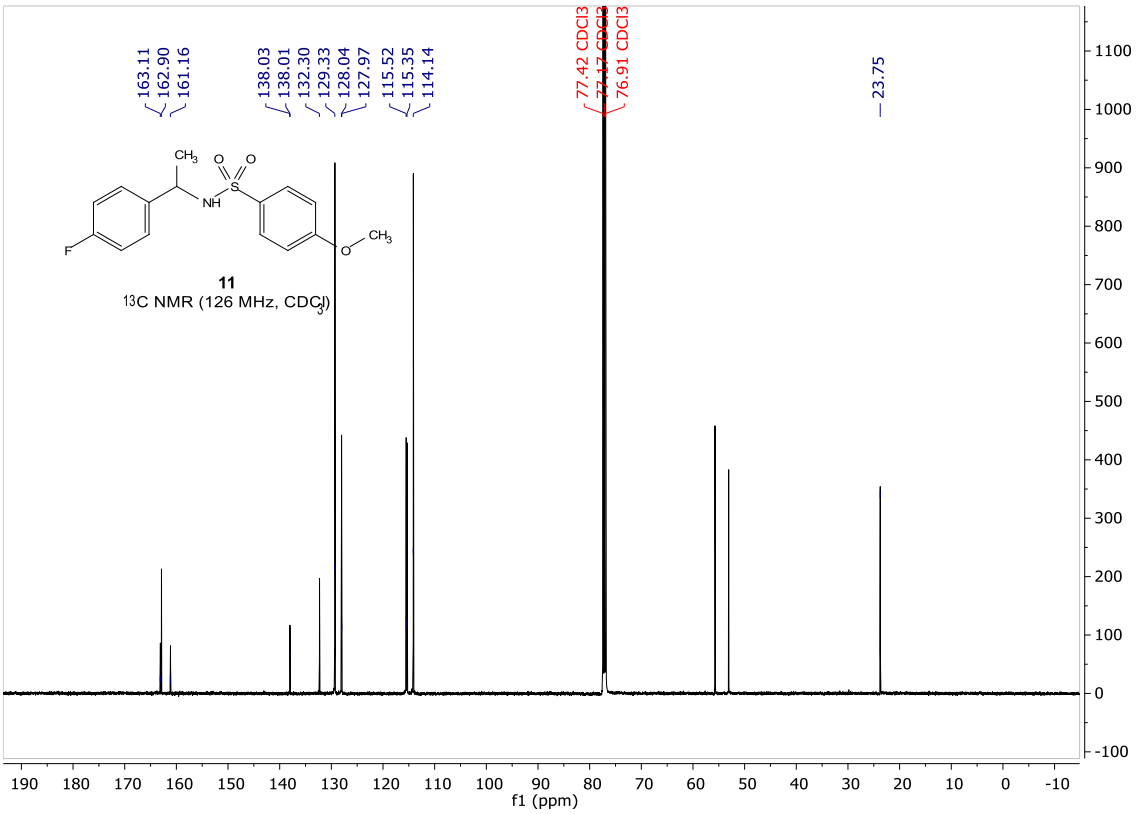

9
1H NMR (500 MHz, CDCl3)
7.66
7.64
7.26 CDCl3
7.02
7.00
6.86
6.84
6.73
6.71
4.76
4.75
4.43
4.41
4.40
4.39
4.37
3.84
3.75
1.41
1.40
2.00
2.00
2.00
2.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

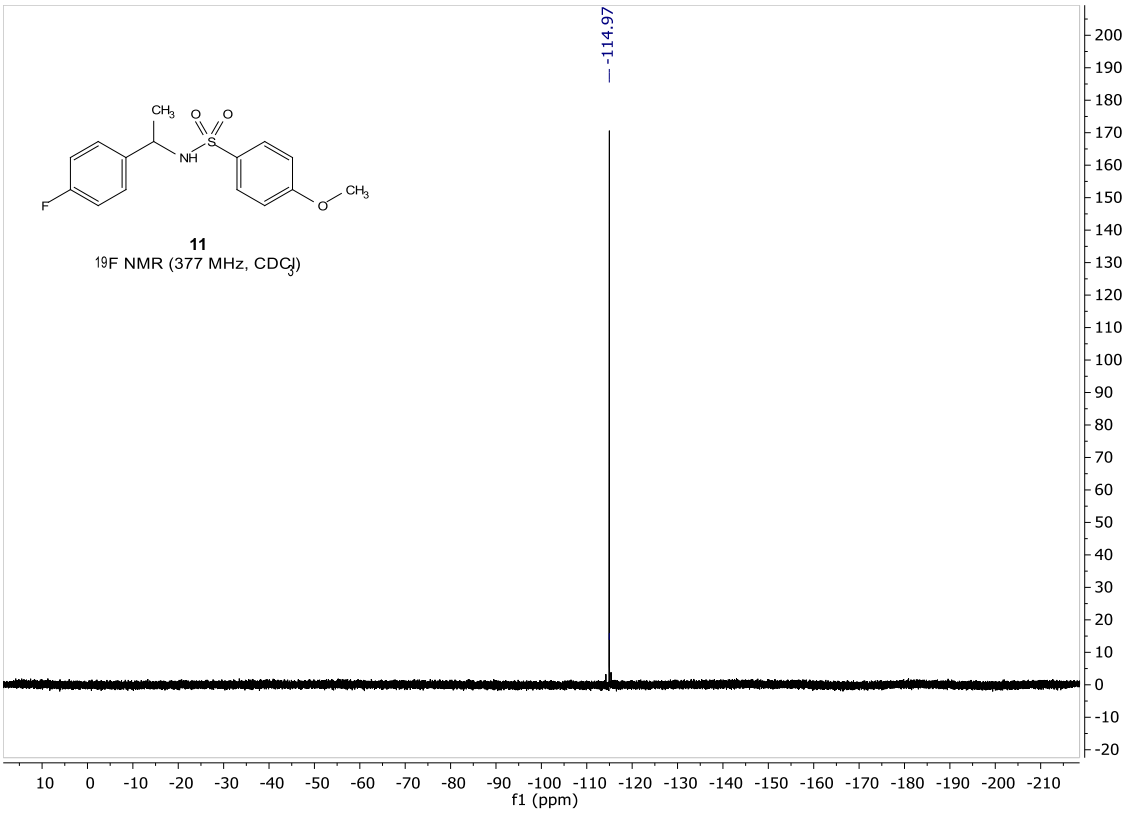

9
13C NMR (126 MHz, CDCl3)
162.79
159.08
134.32
132.51
129.37
127.50
114.11
114.04
77.42 CDCl3
77.17 CDCl3
76.92 CDCl3
55.71
55.41
53.23
23.59
f1 (ppm)


10
1H NMR (500 MHz, CDCl3)
7.67
7.65
7.26 CDCl3
7.02
7.00
6.99
6.97
6.86
6.84
6.84
4.83
4.81
4.43
4.42
4.40
4.39
4.37
3.84
2.28
1.42
1.40
2.00
4.00
2.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)


10
13C NMR (126 MHz, CDCl3)
162.80
139.27
137.32
132.48
129.37
129.33
126.20
114.09
77.42 CDCl3
76.92 CDCl3
55.71
53.51
23.65
21.13
f1 (ppm)

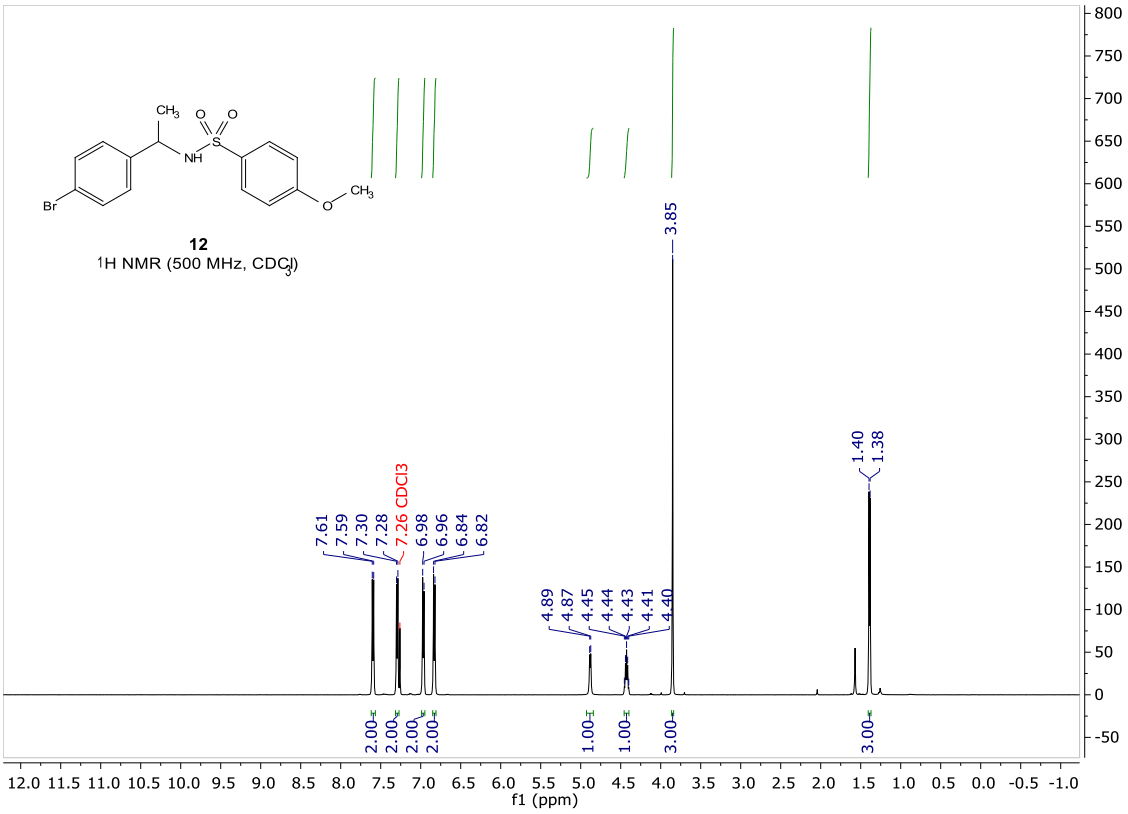

11
1H NMR (500 MHz, CDCl3)
7.64
7.62
7.26 CDCl3
7.08
7.07
7.07
7.06
6.88
6.87
6.85
6.85
6.84
6.83
4.98
4.96
4.47
4.46
4.45
4.43
4.42
3.84
1.40
1.39
2.00
2.00
4.00
1.00
1.00
3.00
3.00
f1 (ppm)


11
13C NMR (126 MHz, CDCl3)
163.11
162.90
161.16
138.03
138.01
132.30
129.33
128.04
127.97
115.52
115.35
114.14
77.42 CDCl3
76.91 CDCl3
23.75
f1 (ppm)



11

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


12
1H NMR (500 MHz, CDCl3)
7.61
7.59
7.30
7.28
7.26 CDCl3
6.98
6.96
6.84
6.82
4.89
4.87
4.45
4.44
4.43
4.41
4.40
3.85
1.40
1.38
2.00
2.00
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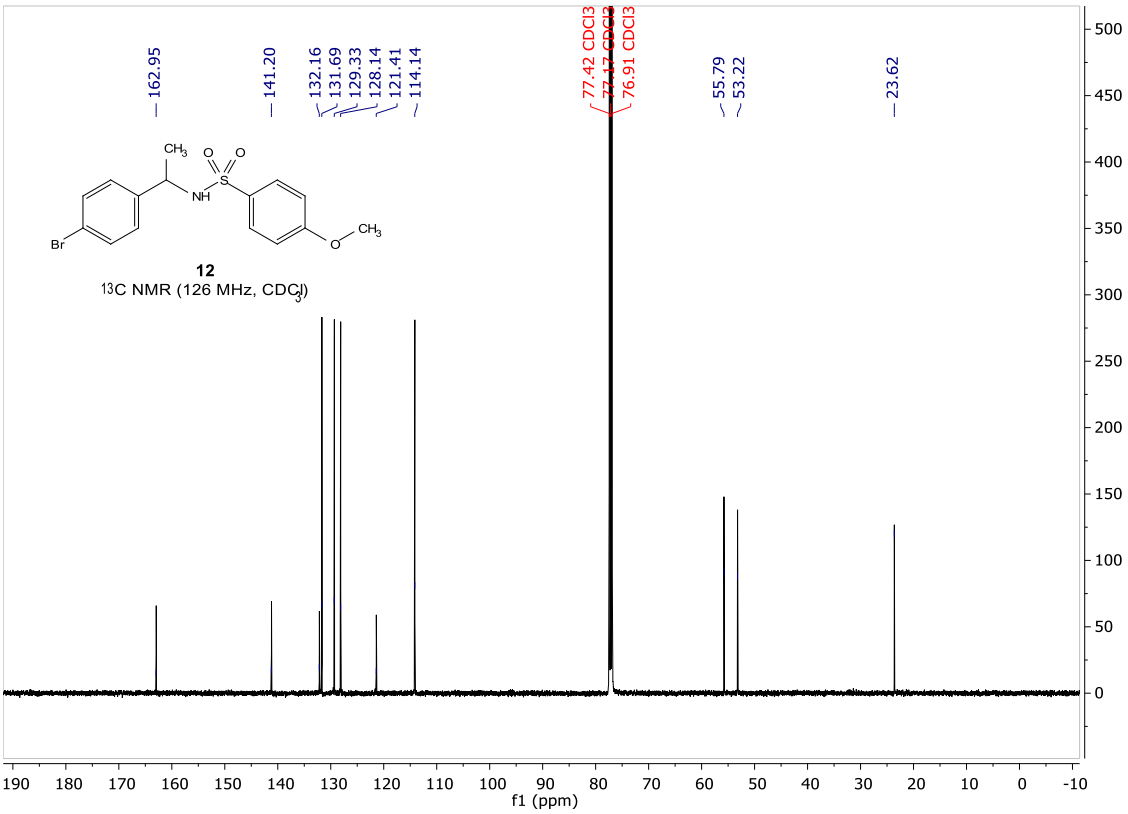
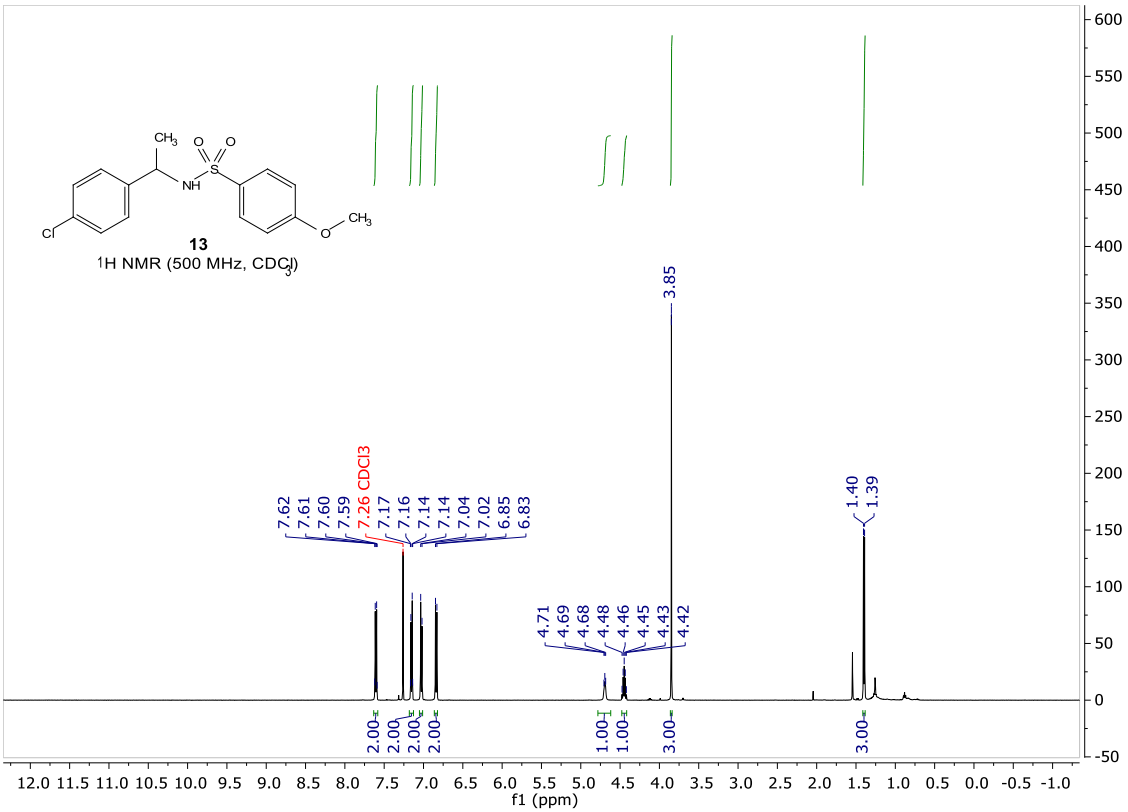
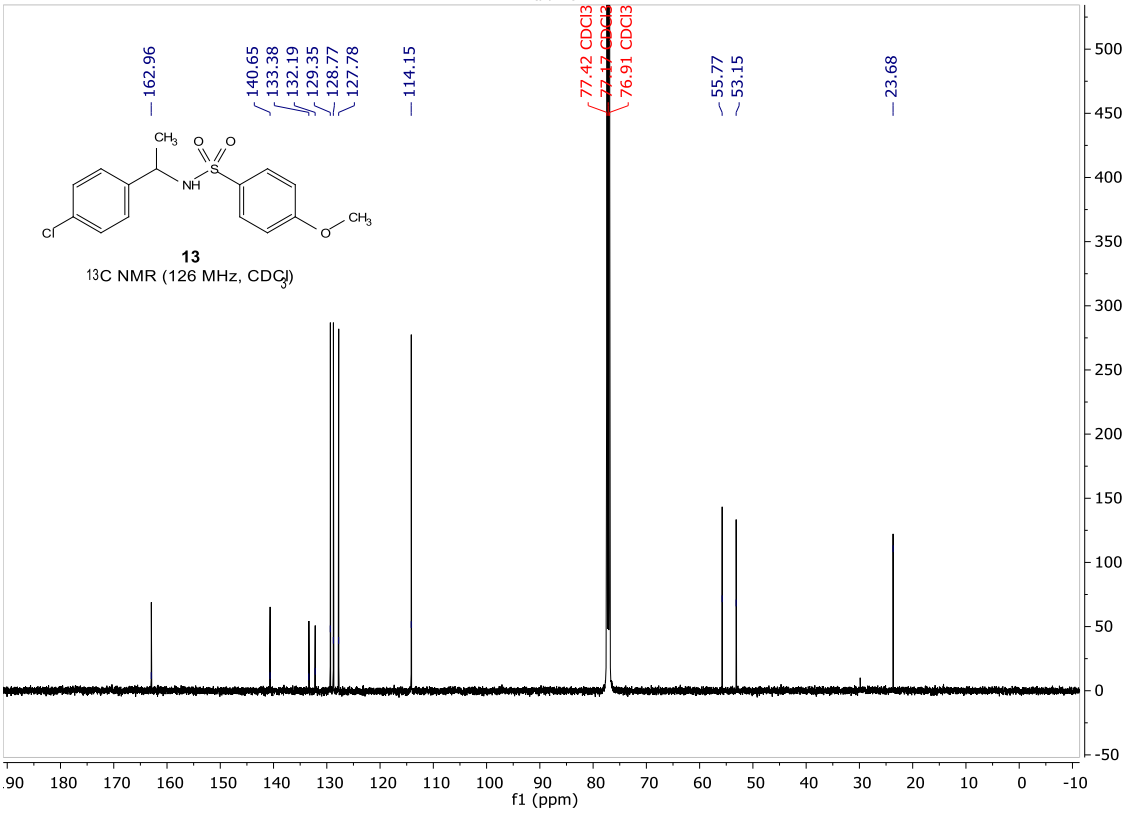
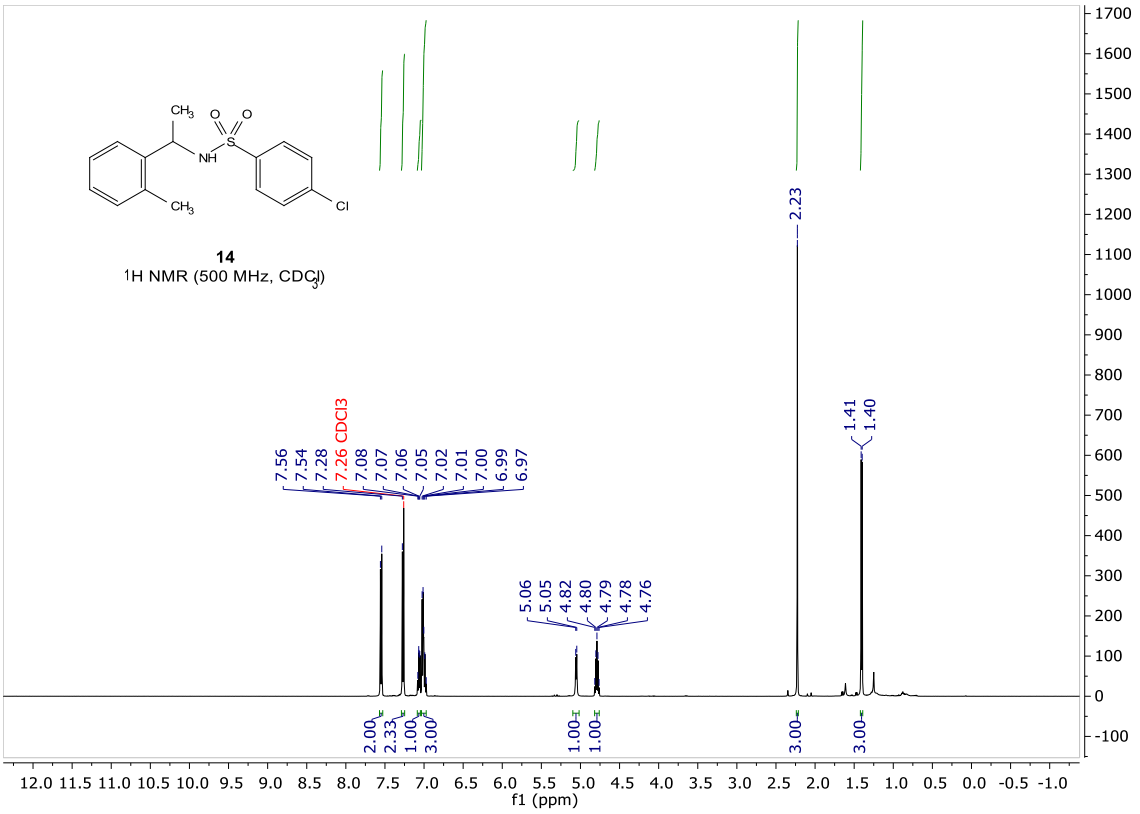
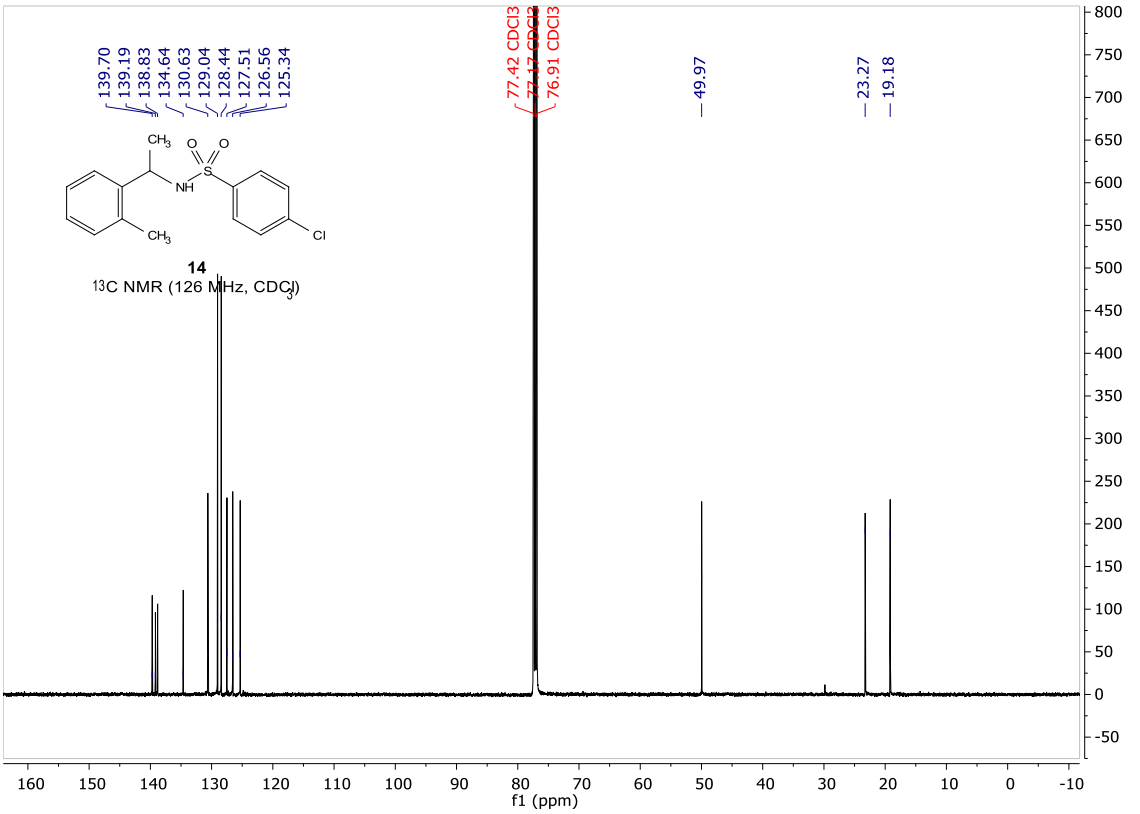
2.00
1.00
1.00
3.00
3.00
f1 (ppm)

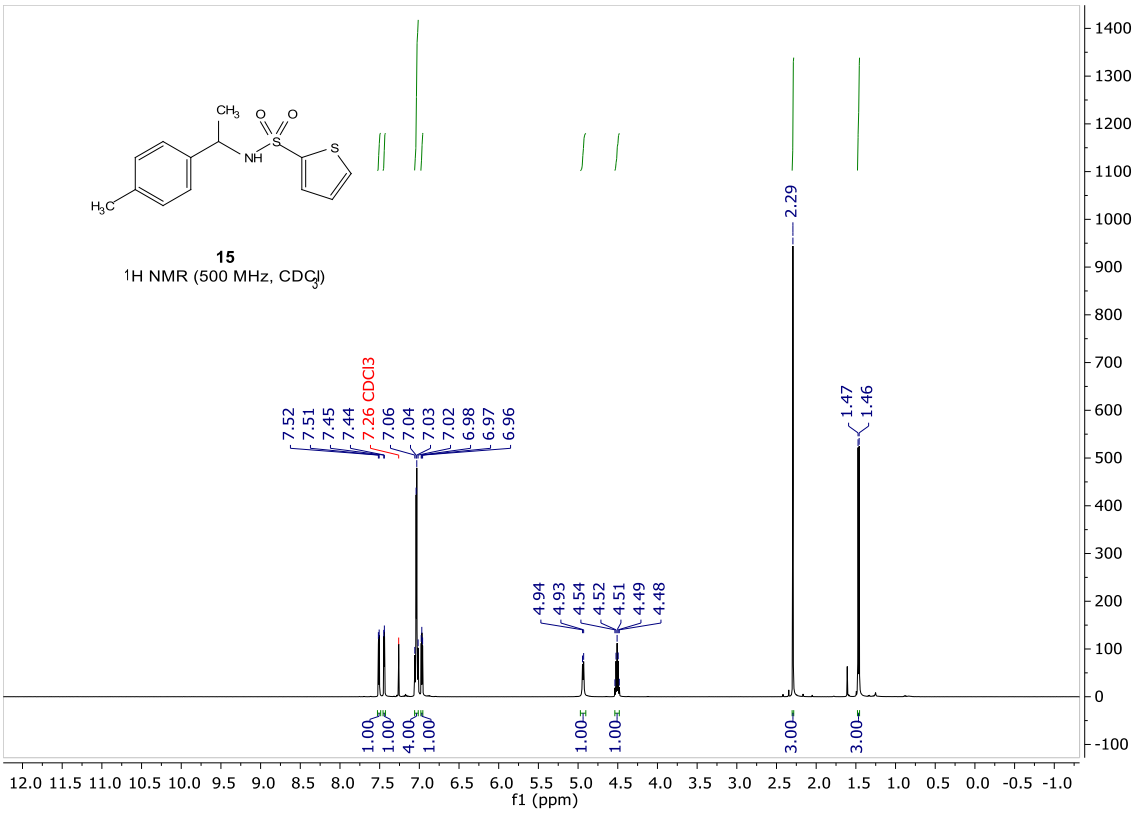

12
13C NMR (126 MHz, CDCl3)
162.95
141.20
132.16
131.69
129.33
128.14
121.41
114.14
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
55.79
53.22
23.62
f1 (ppm)

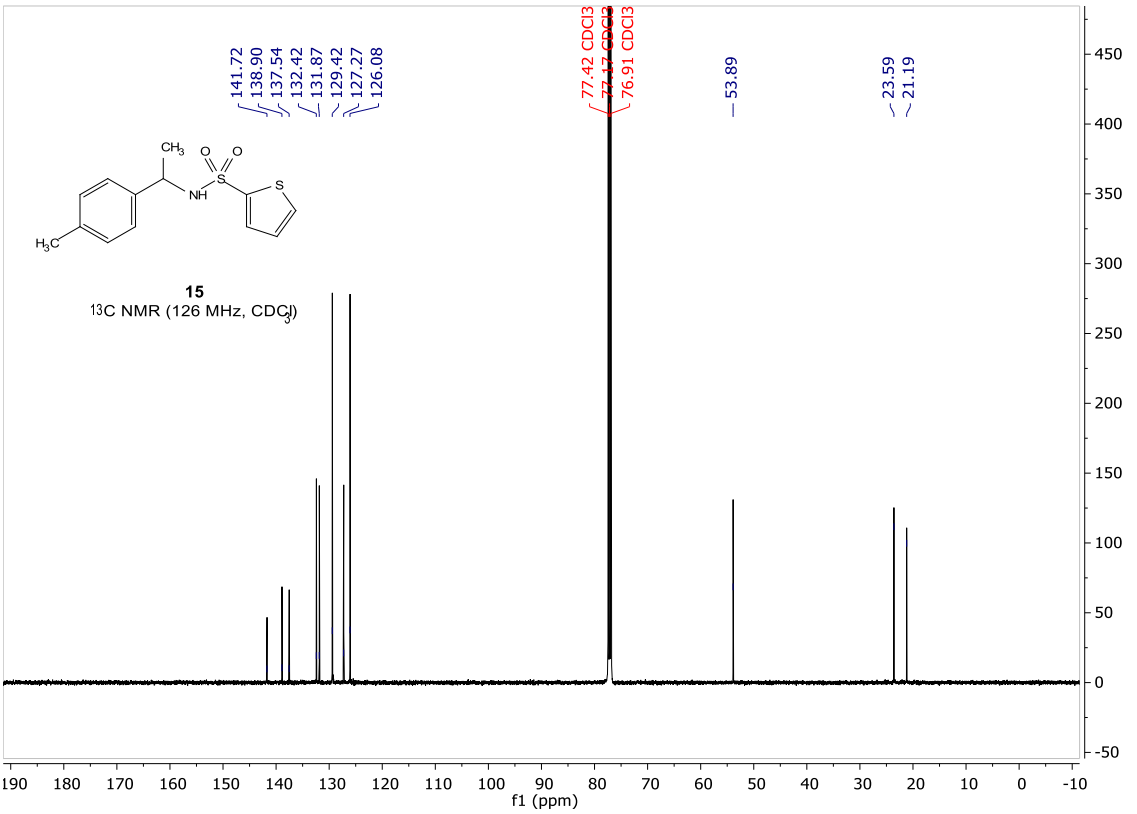

13
1H NMR (500 MHz, CDCl3)
7.62
7.61
7.60
7.59
7.26 CDCl3
7.17
7.16
7.14
7.14
7.04
7.02
6.85
6.83
4.71
4.69
4.68
4.48
4.46
4.45
4.43
4.42
3.85
1.40
1.39
2.00
2.00
2.00
2.00
1.00
1.00
3.00
3.00
f1 (ppm)

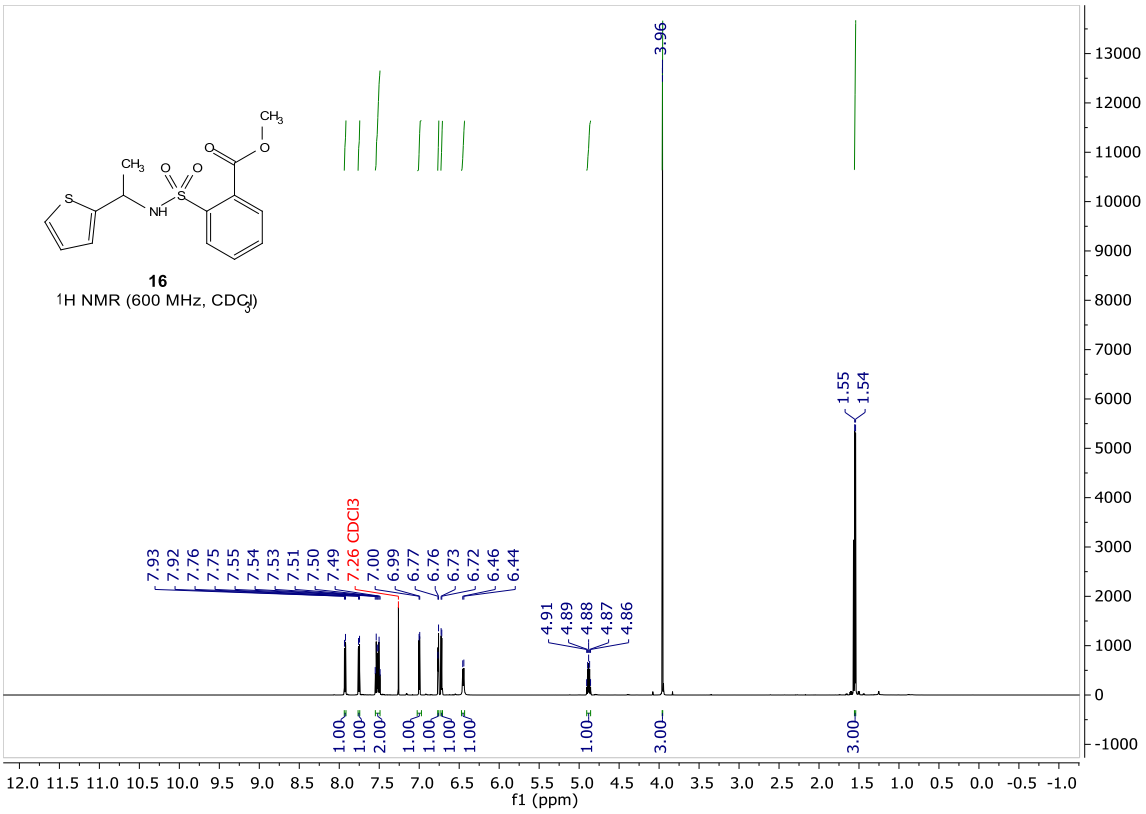

13
13C NMR (126 MHz, CDCl3)
162.96
140.65
133.38
132.19
129.35
128.77
127.78
114.15
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
55.77
53.15
23.68
f1 (ppm)


14
1H NMR (500 MHz, CDCl3)
7.56
7.54
7.28
7.26 CDCl3
7.08
7.07
7.06
7.05
7.02
7.01
7.00
6.99
6.97
5.06
5.05
4.82
4.80
4.79
4.78
4.76
2.23
1.41
1.40
2.00
2.33
1.00
3.00
1.00
1.00
3.00
3.00
f1 (ppm)


14
13C NMR (126 MHz, CDCl3)
139.70
139.19
138.83
134.64
130.63
129.04
128.44
127.51
126.56
125.34
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
49.97
23.27
19.18
f1 (ppm)


15
1H NMR (500 MHz, CDCl3)
7.52
7.51
7.45
7.44
7.26 CDCl3
7.06
7.04
7.03
7.02
6.98
6.97
6.96
4.94
4.93
4.54
4.52
4.51
4.49
4.48
2.29
1.47
1.46
1.00
1.00
4.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)


15
13C NMR (126 MHz, CDCl3)
141.72
138.90
137.54
132.42
131.87
129.42
127.27
126.08
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
53.89
23.59
21.19
f1 (ppm)


16
1H NMR (600 MHz, CDCl3)
7.93
7.92
7.76
7.75
7.55
7.54
7.53
7.51
7.50
7.49
7.26 CDCl3
7.00
6.99
6.77
6.76
6.73
6.72
6.46
6.44
4.91
4.89
4.88
4.87
4.86
3.96
1.55
1.54
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2.00
1.00
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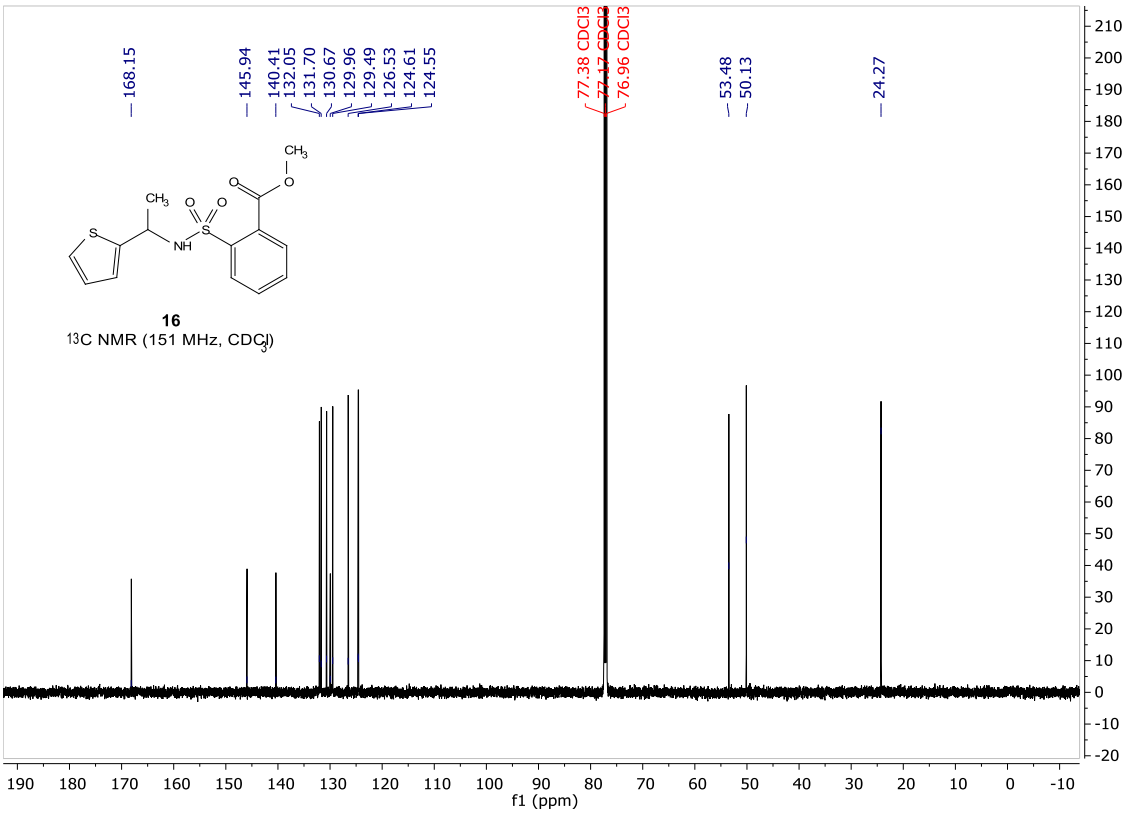
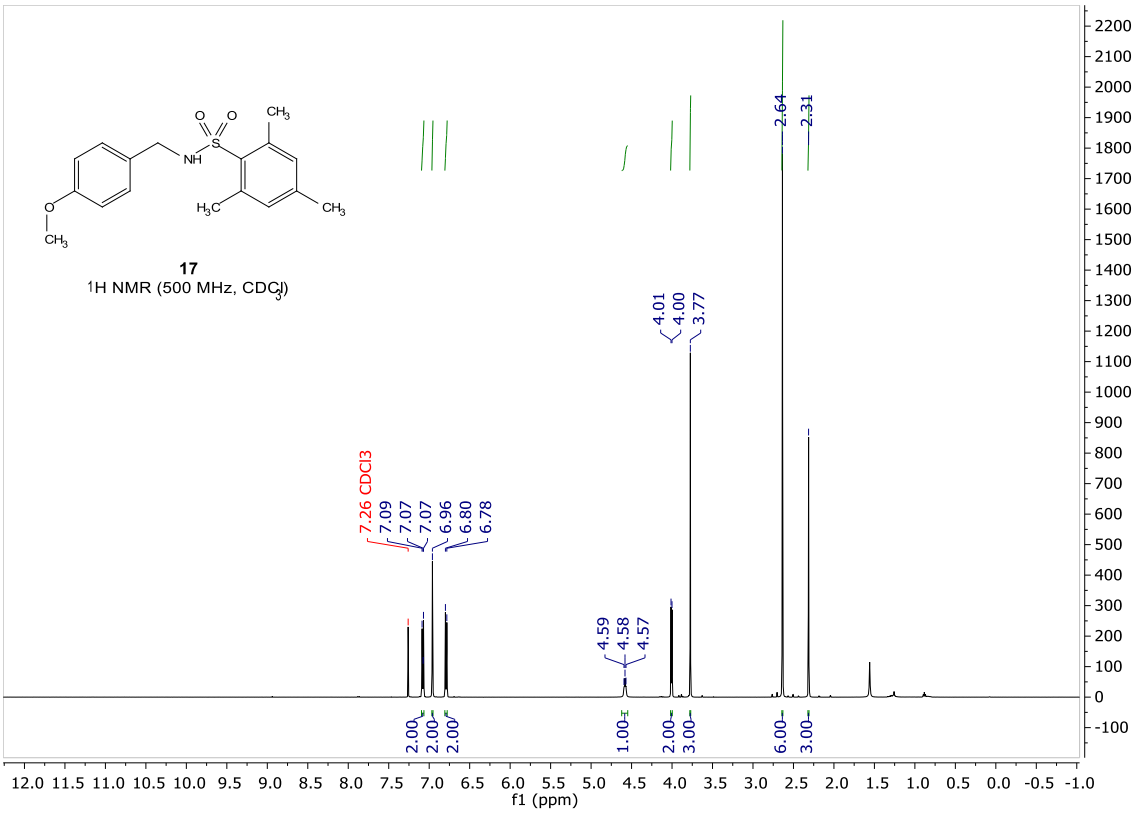
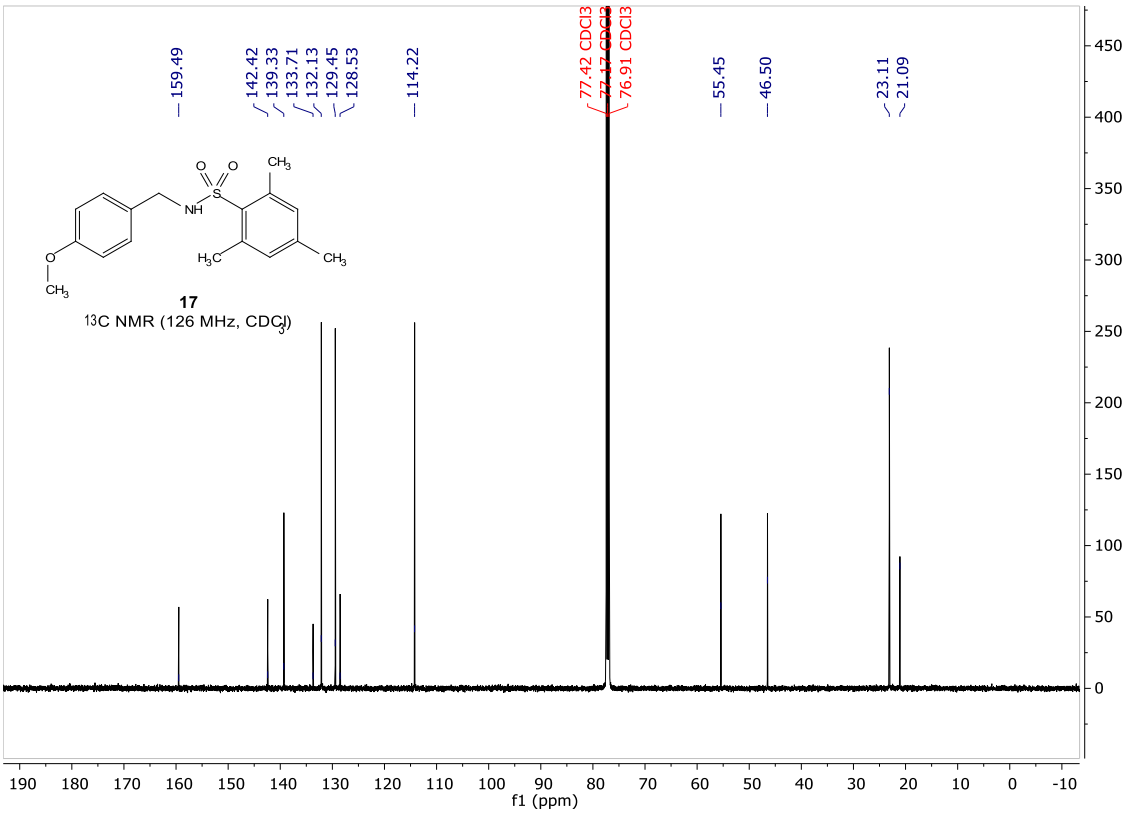
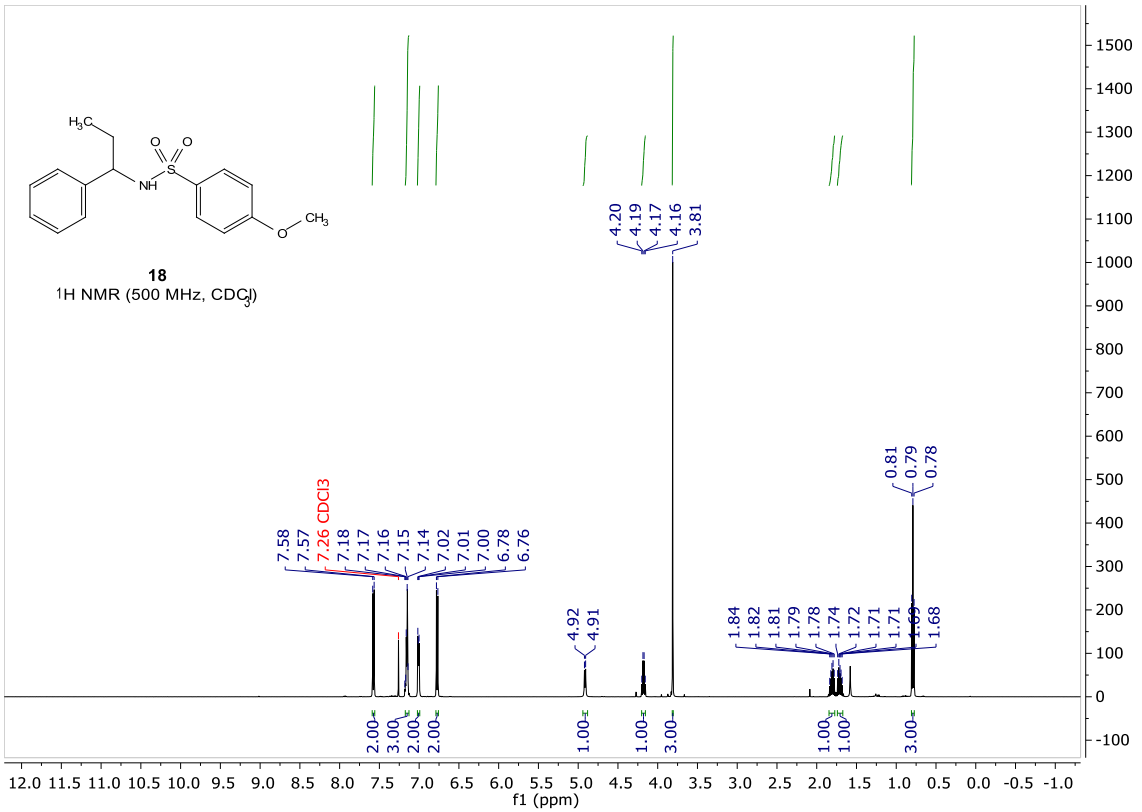
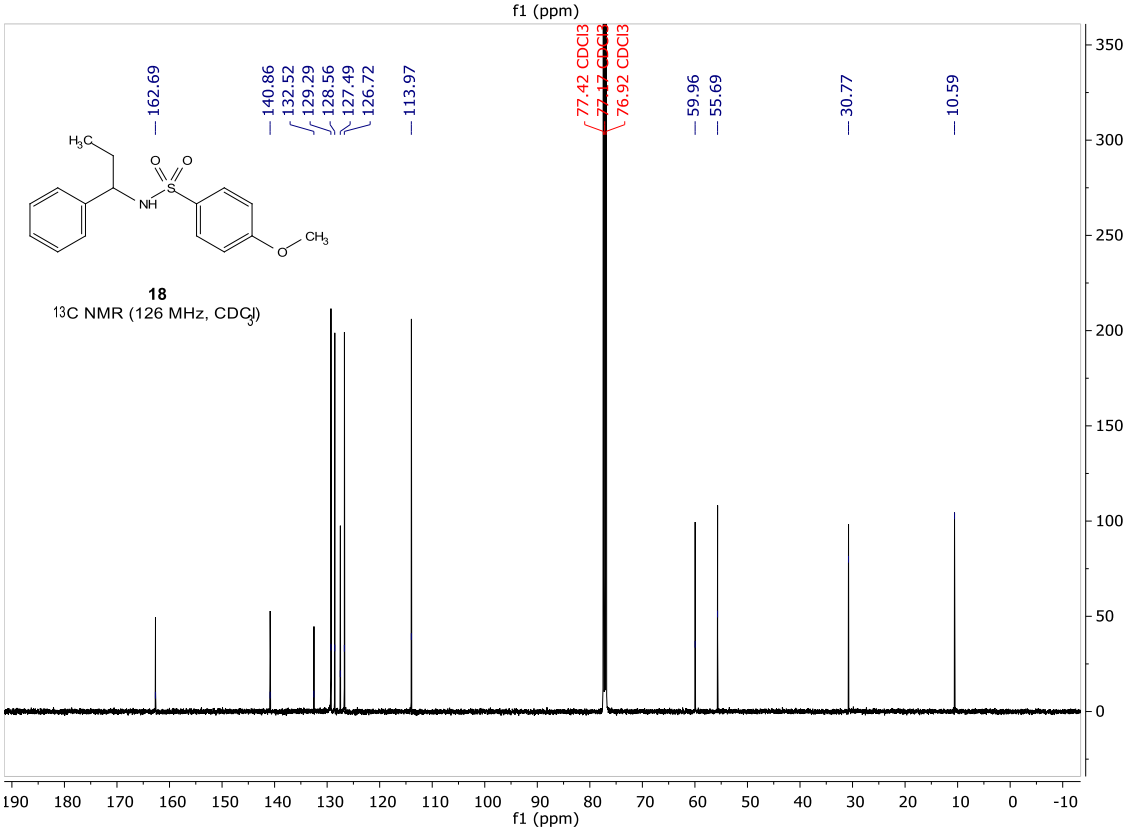
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

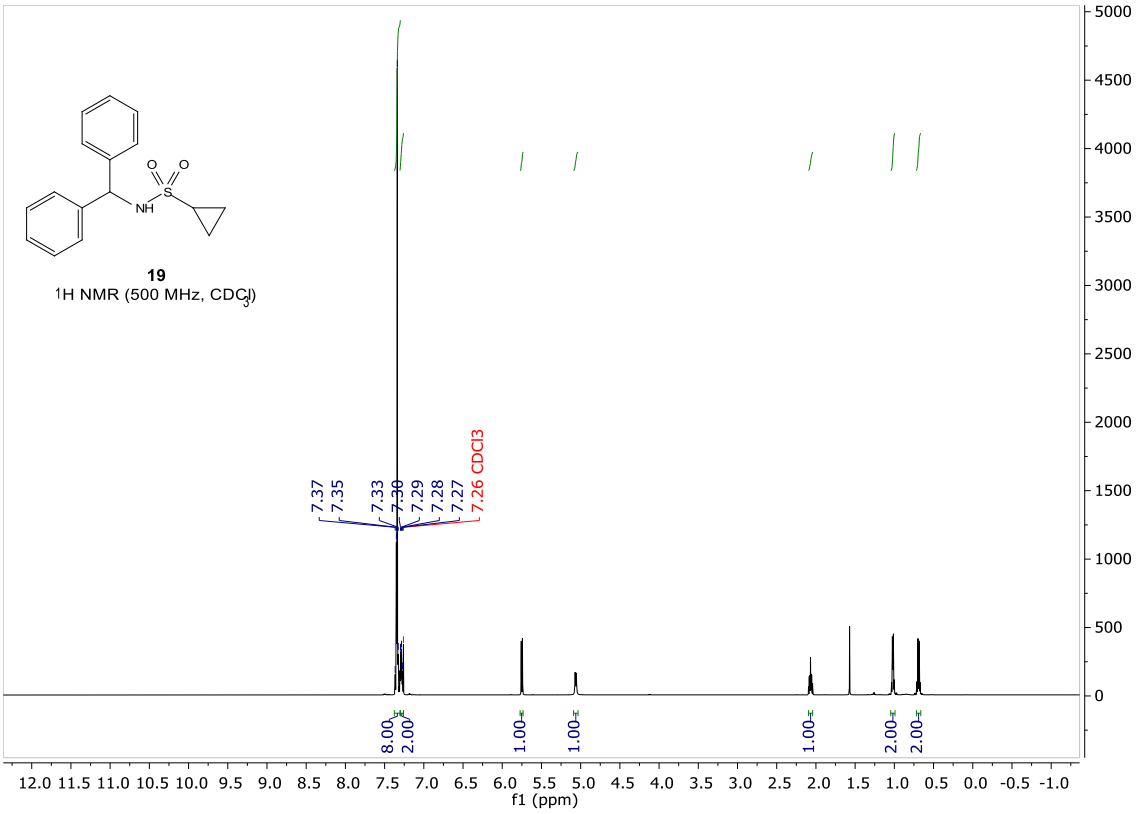

16
13C NMR (151 MHz, CDCl3)
168.15
145.94
140.41
132.05
131.70
130.67
129.96
129.49
126.53
124.61
124.55
77.38 CDCl3
77.17 CDCl3
76.96 CDCl3
53.48
50.13
24.27
f1 (ppm)

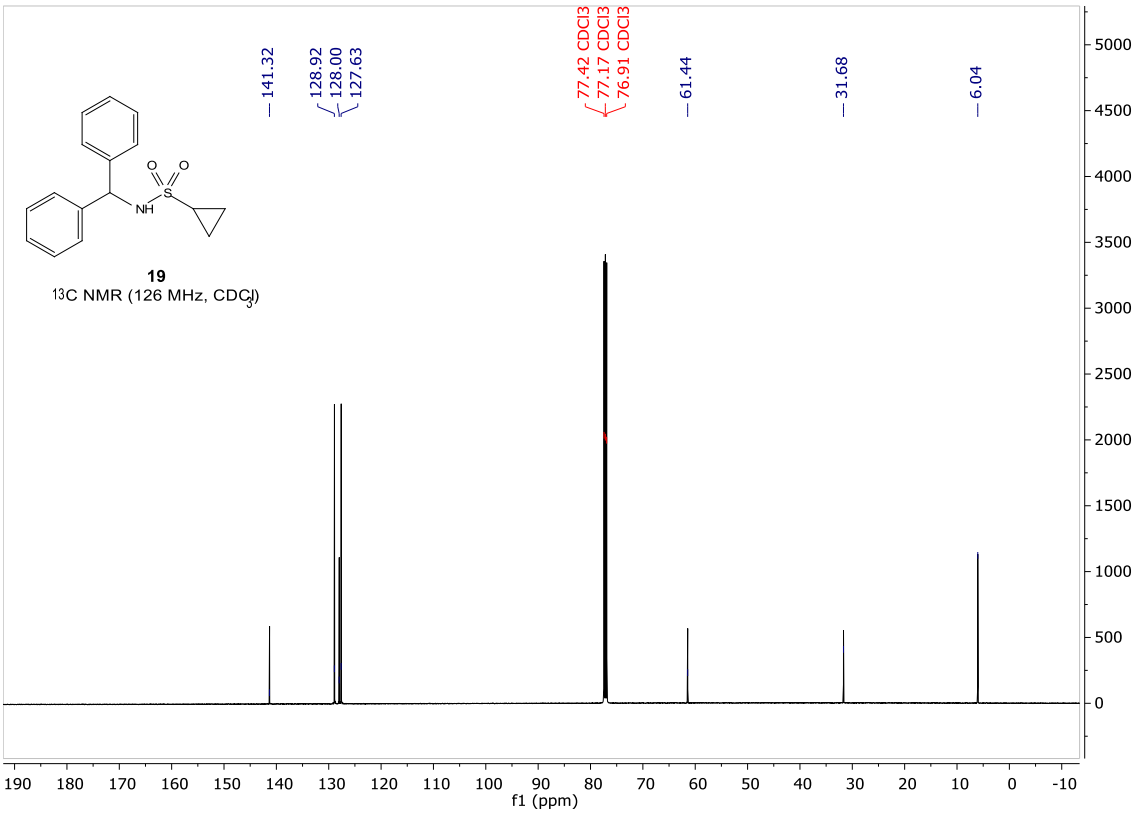

17
1H NMR (500 MHz, CDCl3)
7.26 CDCl3
7.09
7.07
7.07
6.96
6.80
6.78
4.59
4.58
4.57
4.01
4.00
3.77
2.64
2.31
2.00
2.00
2.00
1.00
2.00
3.00
6.00
3.00
f1 (ppm)

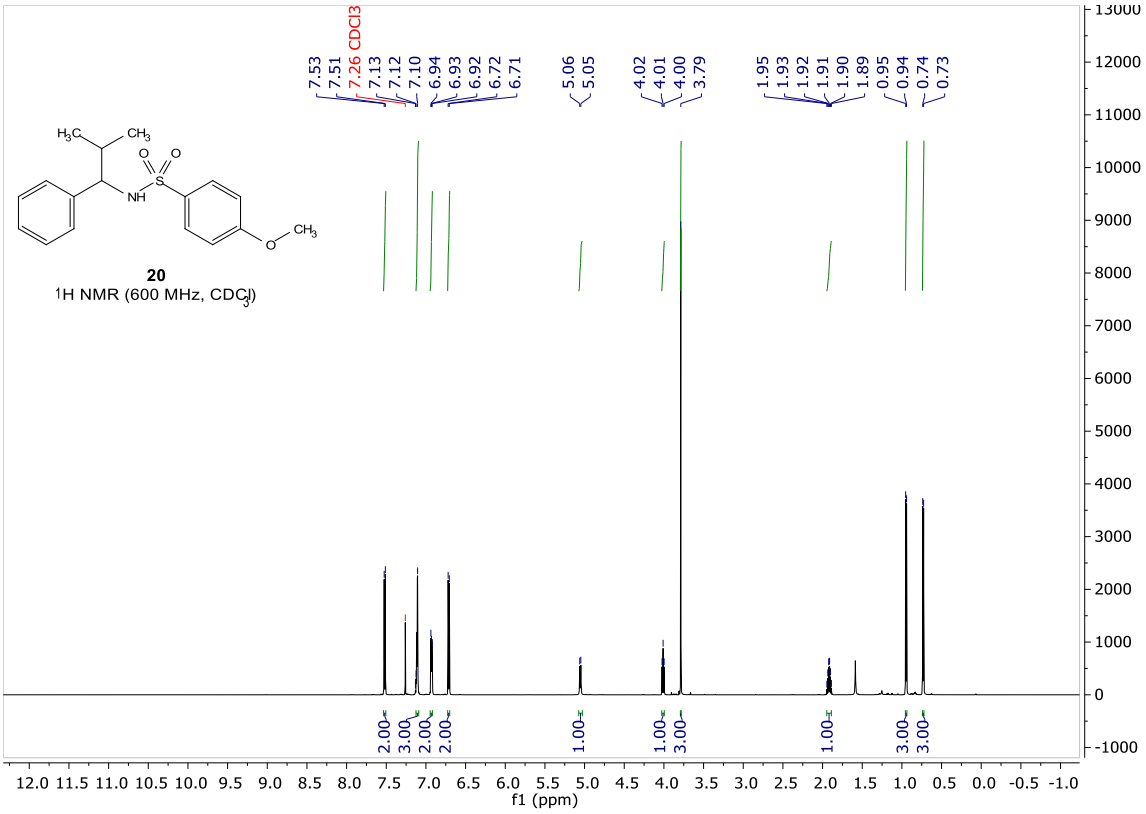

17
13C NMR (126 MHz, CDCl3)
159.49
142.42
139.33
133.71
132.13
129.45
128.53
114.22
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
55.45
46.50
23.11
21.09
f1 (ppm)


18
1H NMR (500 MHz, CDCl3)
7.58
7.57
7.26 CDCl3
7.18
7.17
7.16
7.15
7.14
7.02
7.01
7.00
6.78
6.76
4.92
4.91
4.20
4.19
4.17
4.16
3.81
1.84
1.82
1.81
1.79
1.78
1.74
1.72
1.71
1.71
1.69
1.68
0.81
0.79
0.78
2.00
3.00
2.00
2.00
1.00
1.00
3.00
1.00
1.00
3.00
f1 (ppm)


18
13C NMR (126 MHz, CDCl3)
162.69
140.86
132.52
129.29
128.56
127.49
126.72
113.97
77.42 CDCl3
77.17 CDCl3
76.92 CDCl3
59.96
55.69
30.77
10.59
f1 (ppm)

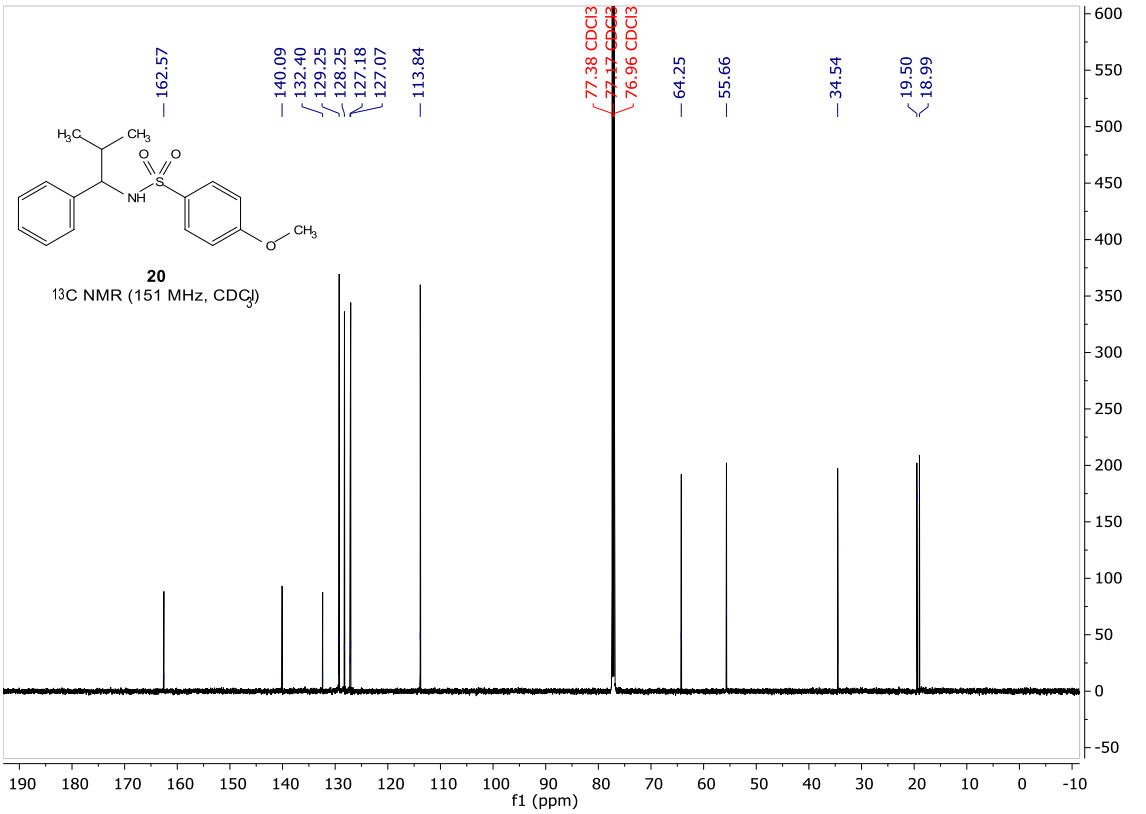

19
1H NMR (500 MHz, CDCl3)
7.37
7.35
7.33
7.30
7.29
7.28
7.27
7.26 CDCl3
8.00
2.00
1.00
1.00
1.00
2.00
2.00
f1 (ppm)


19
13C NMR (126 MHz, CDCl3)
141.32
128.92
128.00
127.63
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
61.44
31.68
6.04
f1 (ppm)



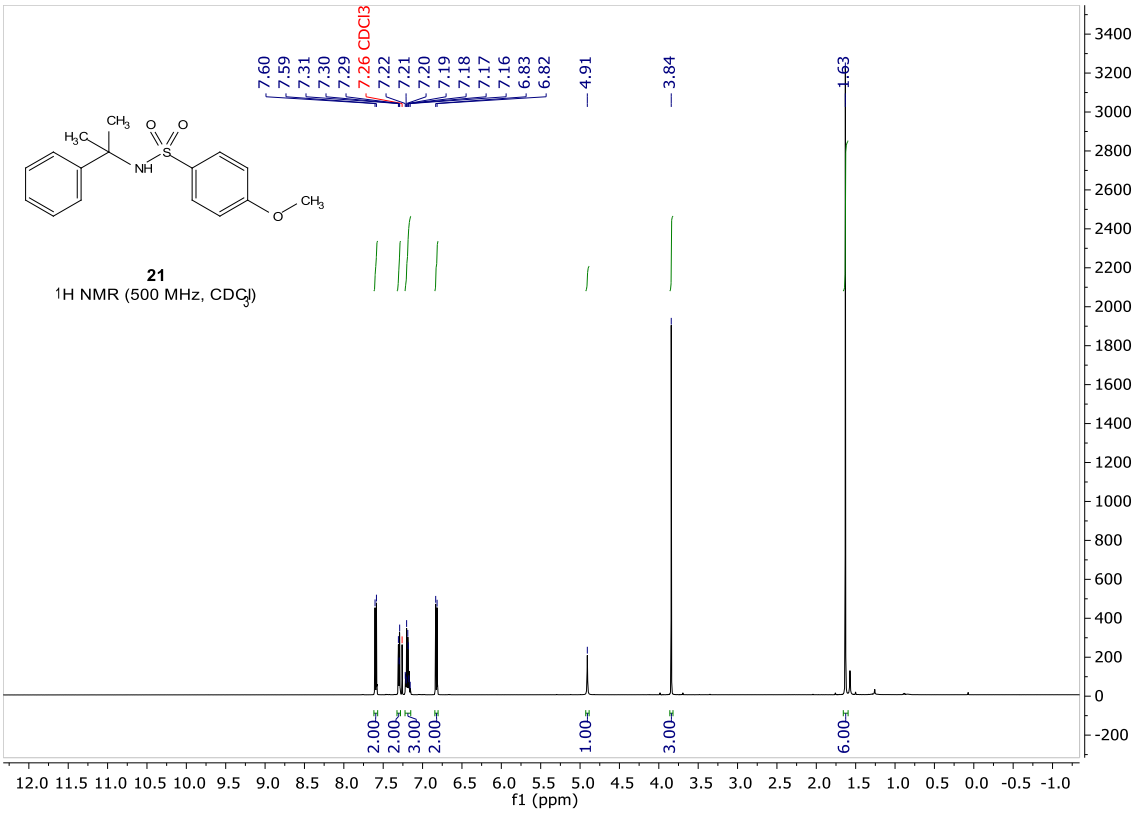
20

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

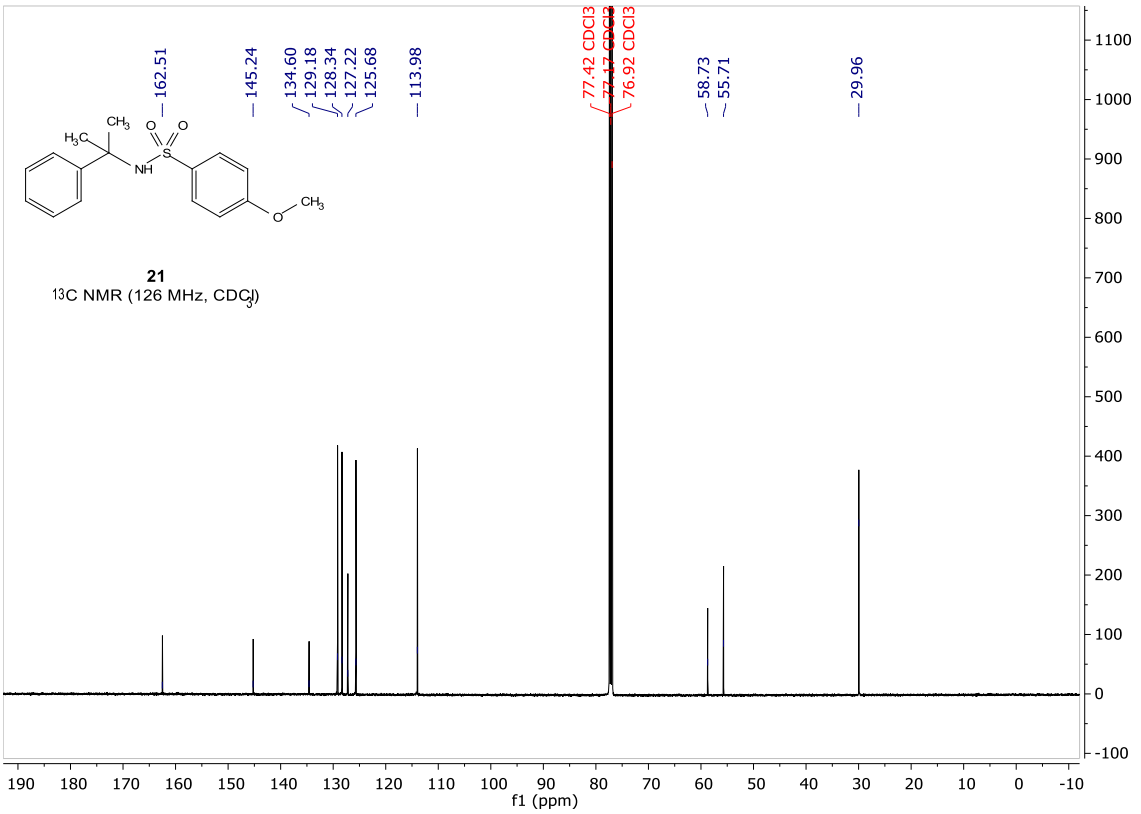


20

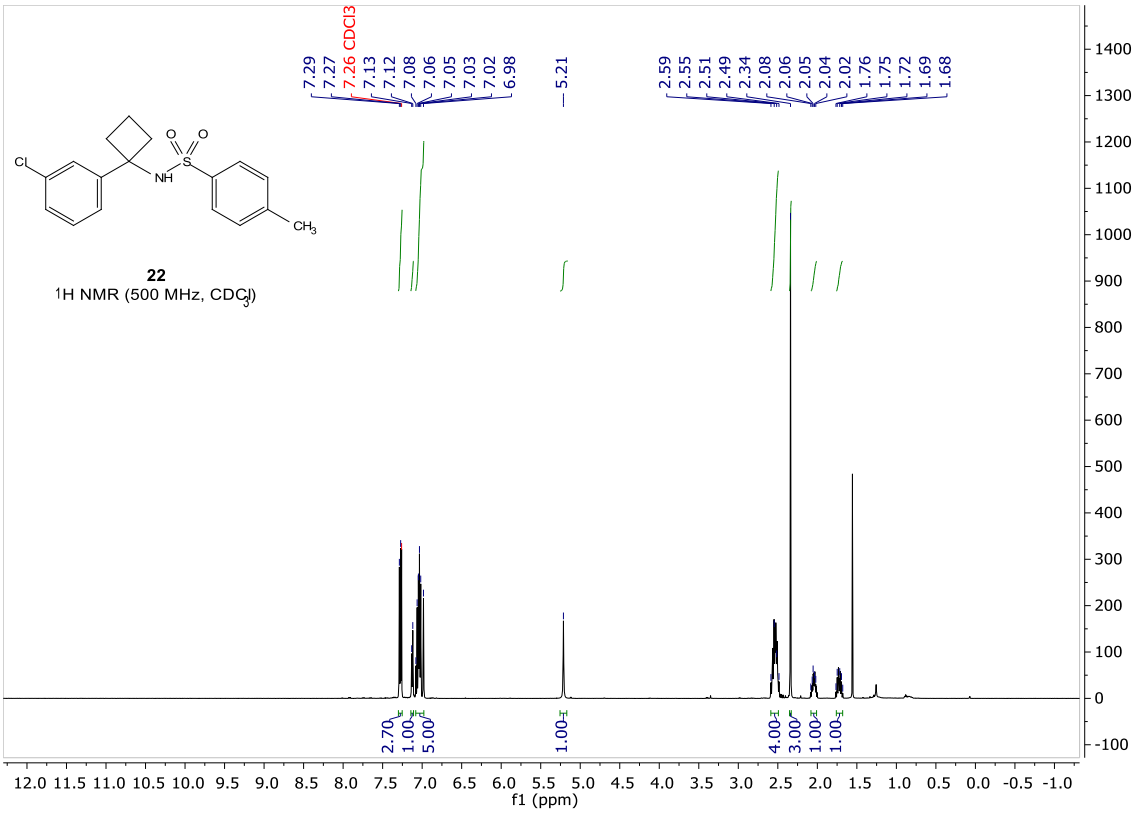
^{13}C NMR (151 MHz, $CDCl_3$)

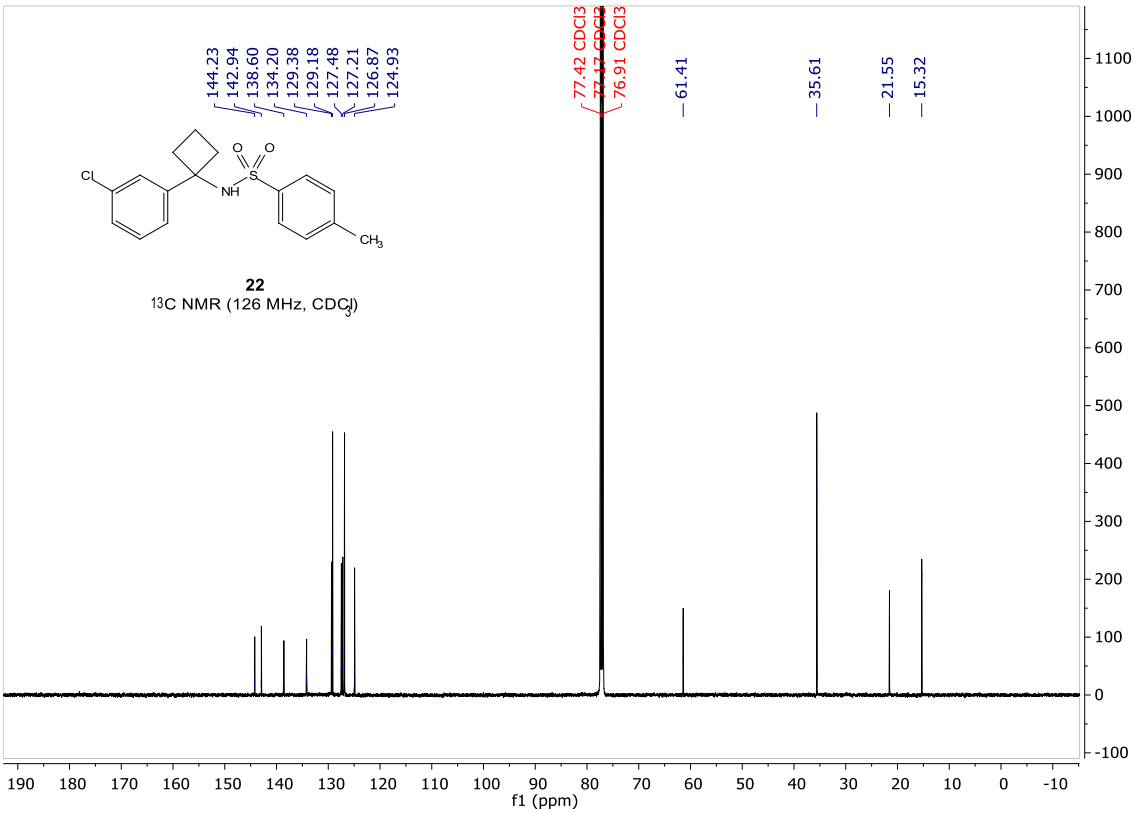


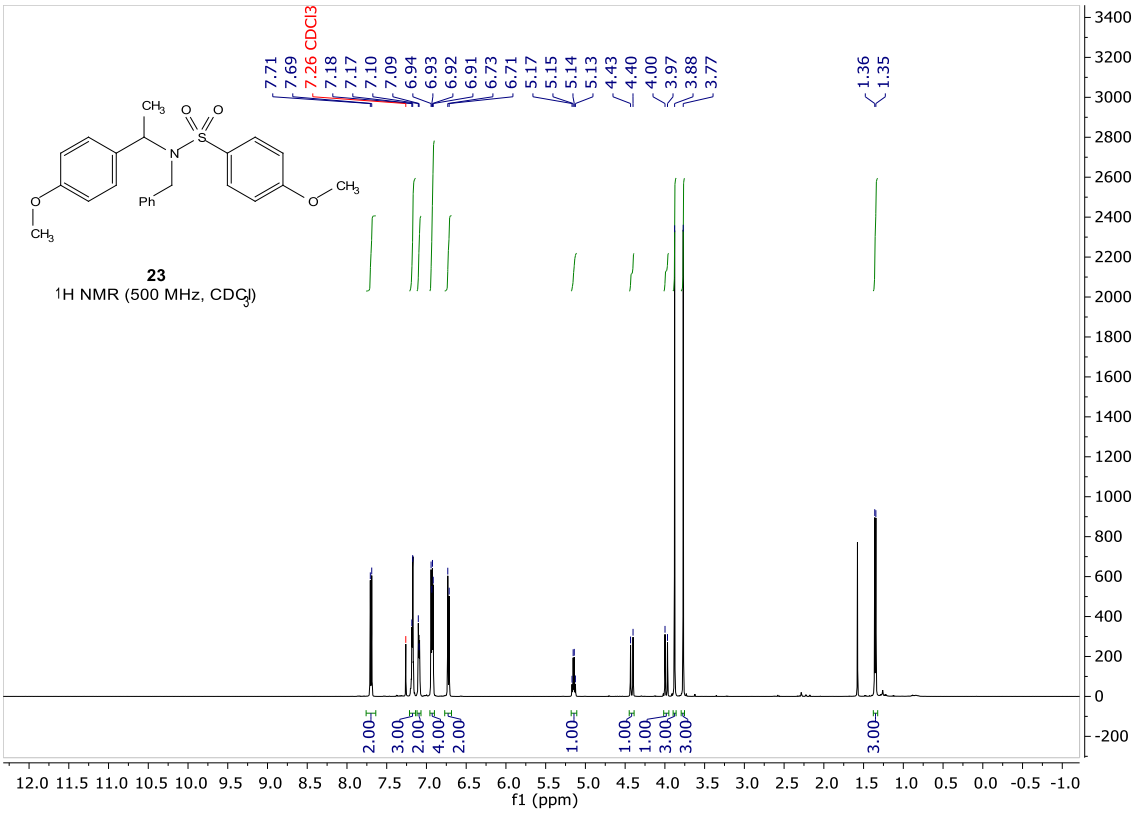
21
^{1}H NMR (500 MHz, $CDCl_3$)

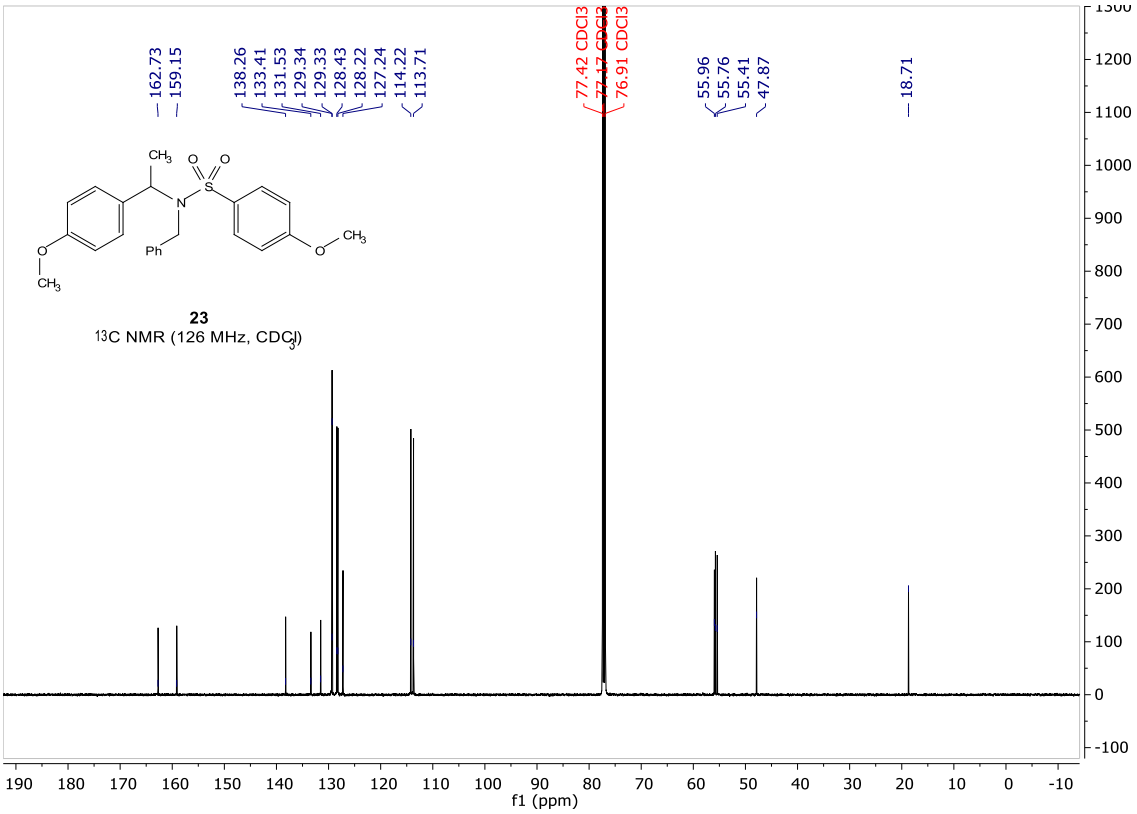


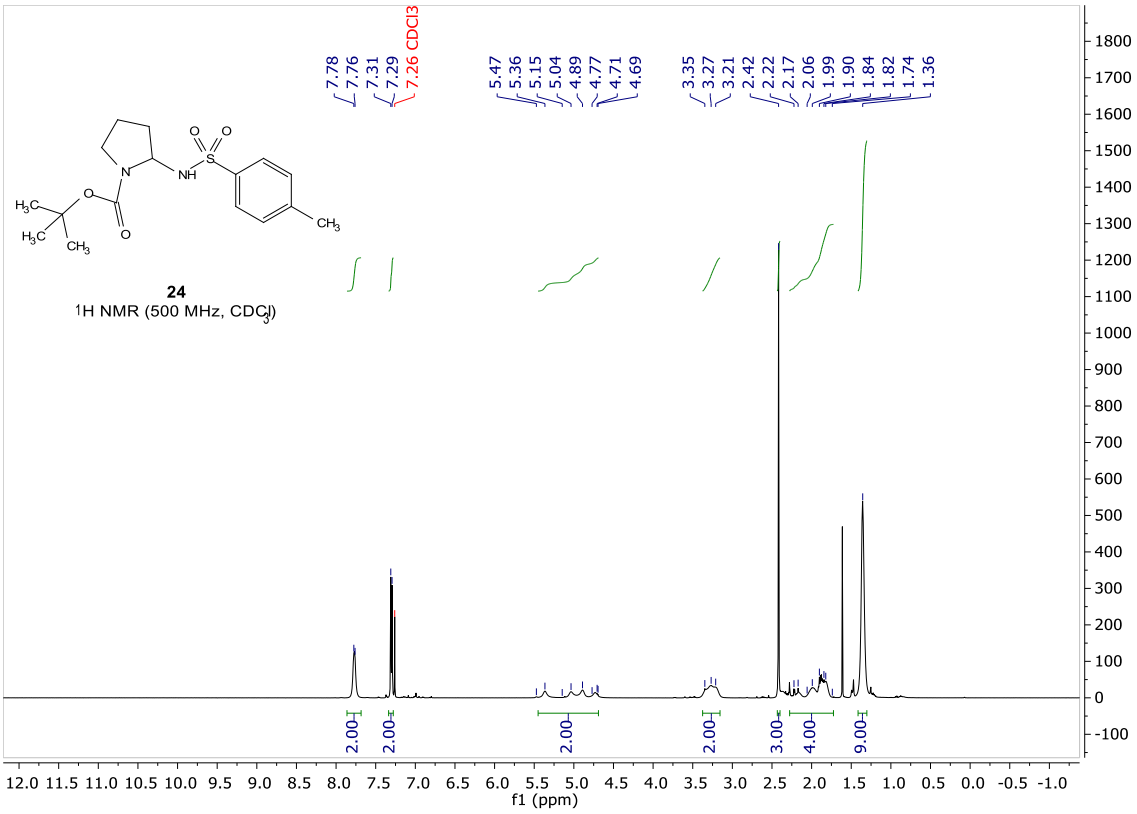
21
^{13}C NMR (126 MHz, $CDCl_3$)


7.29
7.27
7.26 CDCl3
7.13
7.12
7.08
7.06
7.05
7.03
7.02
6.98
5.21
2.59
2.55
2.51
2.49
2.34
2.08
2.06
2.05
2.04
2.02
1.76
1.75
1.72
1.69
1.68
Cl
O
O
S
NH
CH3
22
1H NMR (500 MHz, CDCl3)
2.70
1.00
5.00
1.00
4.00
3.00
1.00
1.00
f1 (ppm)


144.23
142.94
138.60
134.20
129.38
129.18
127.48
127.21
126.87
124.93
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
61.41
35.61
21.55
15.32
Cl
O
O
S
NH
CH3
22
13C NMR (126 MHz, CDCl3)
f1 (ppm)

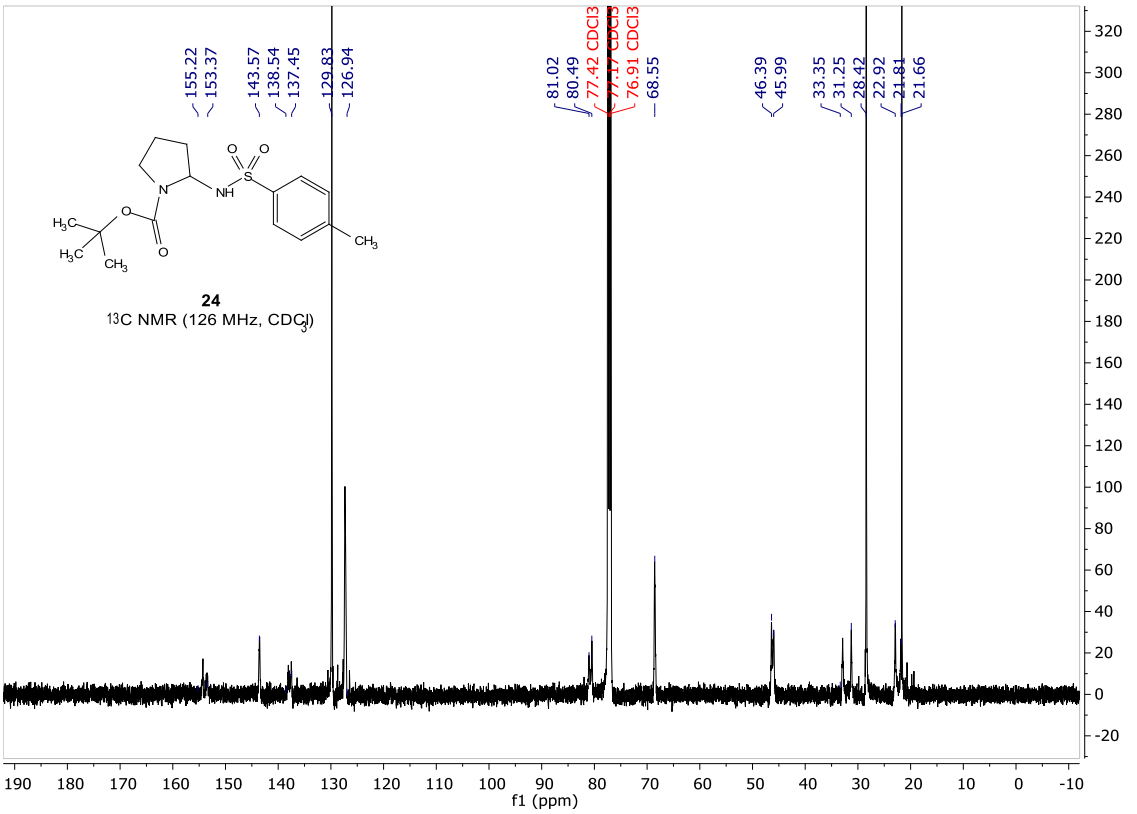

7.71
7.69
7.26 CDCl3
7.18
7.17
7.10
7.09
6.94
6.93
6.92
6.91
6.73
6.71
5.17
5.15
5.14
5.13
4.43
4.40
4.00
3.97
3.88
3.77
1.36
1.35
CH3
O
O
S
N
Ph
O
CH3
O
CH3
23
1H NMR (500 MHz, CDCl3)
2.00
3.00
2.00
4.00
2.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)


162.73
159.15
138.26
133.41
131.53
129.34
129.33
128.43
128.22
127.24
114.22
113.71
77.42 CDCl3
76.91 CDCl3
55.96
55.76
55.41
47.87
18.71
CH3
O
O
S
N
Ph
O
CH3
O
CH3
23
13C NMR (126 MHz, CDCl3)
f1 (ppm)



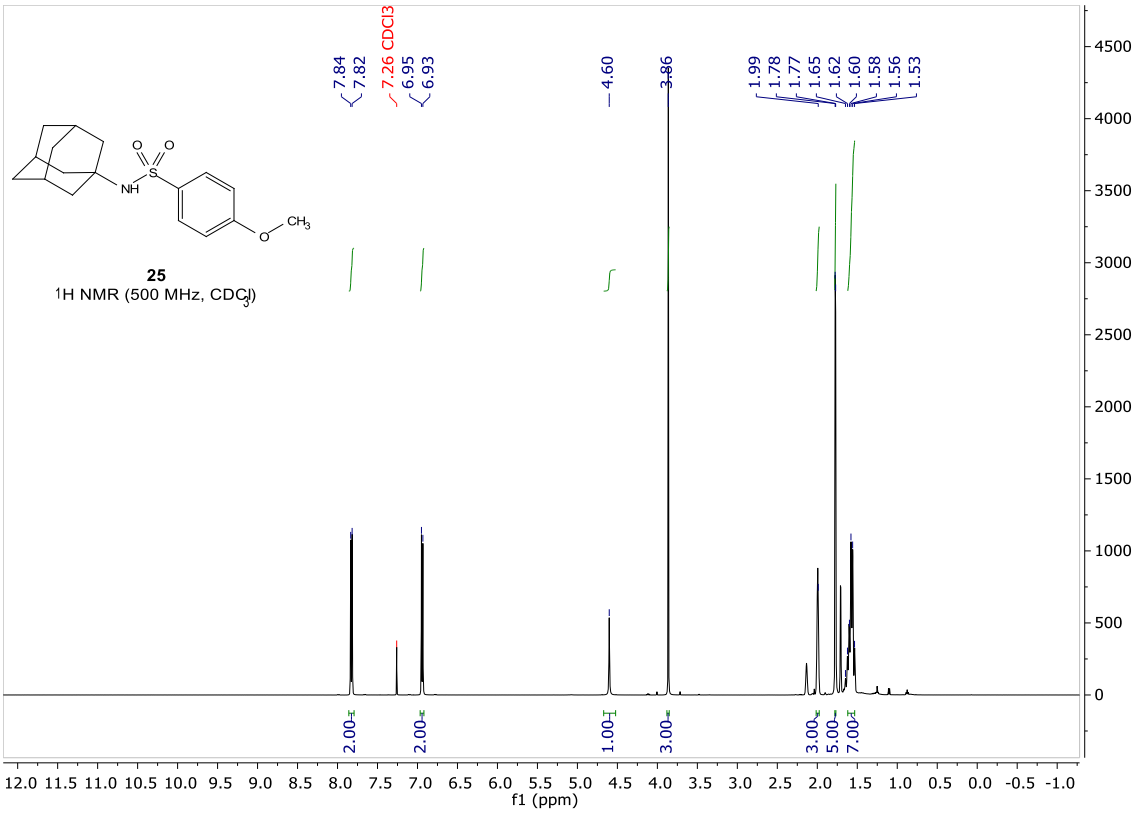
24

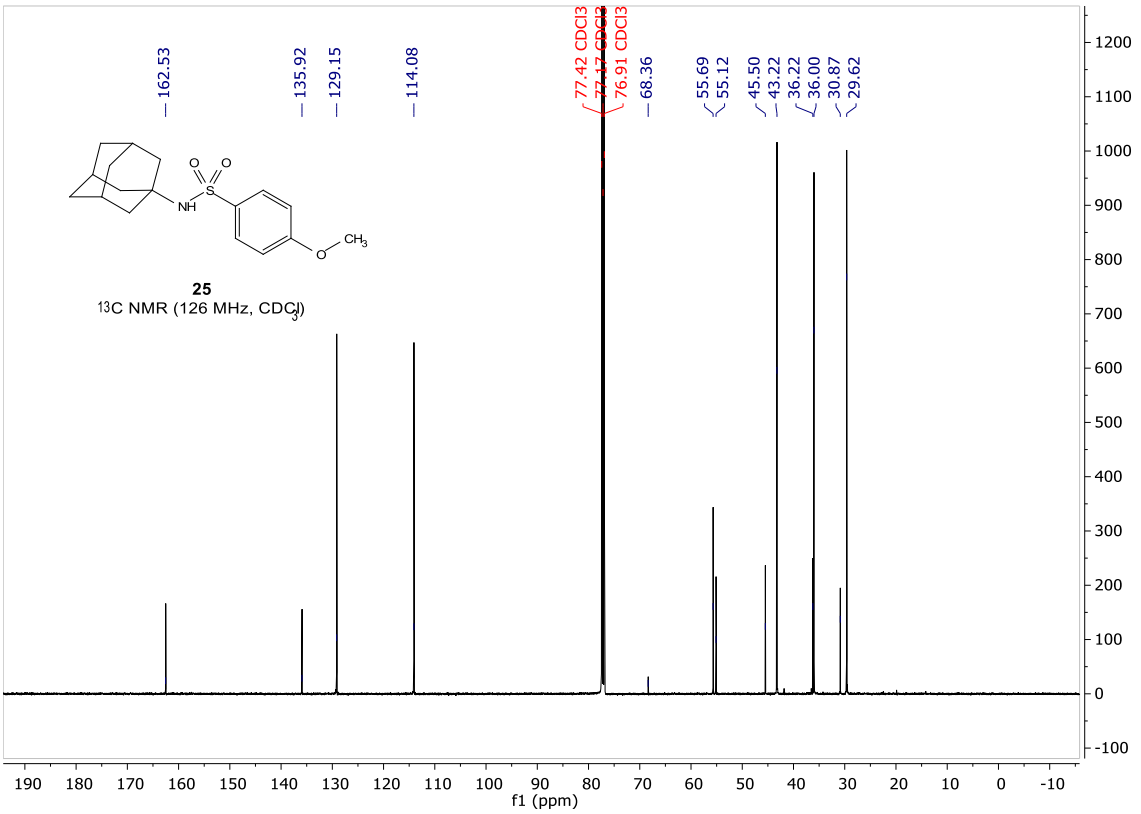
^{1}H NMR (500 MHz, $CDCl_3$)

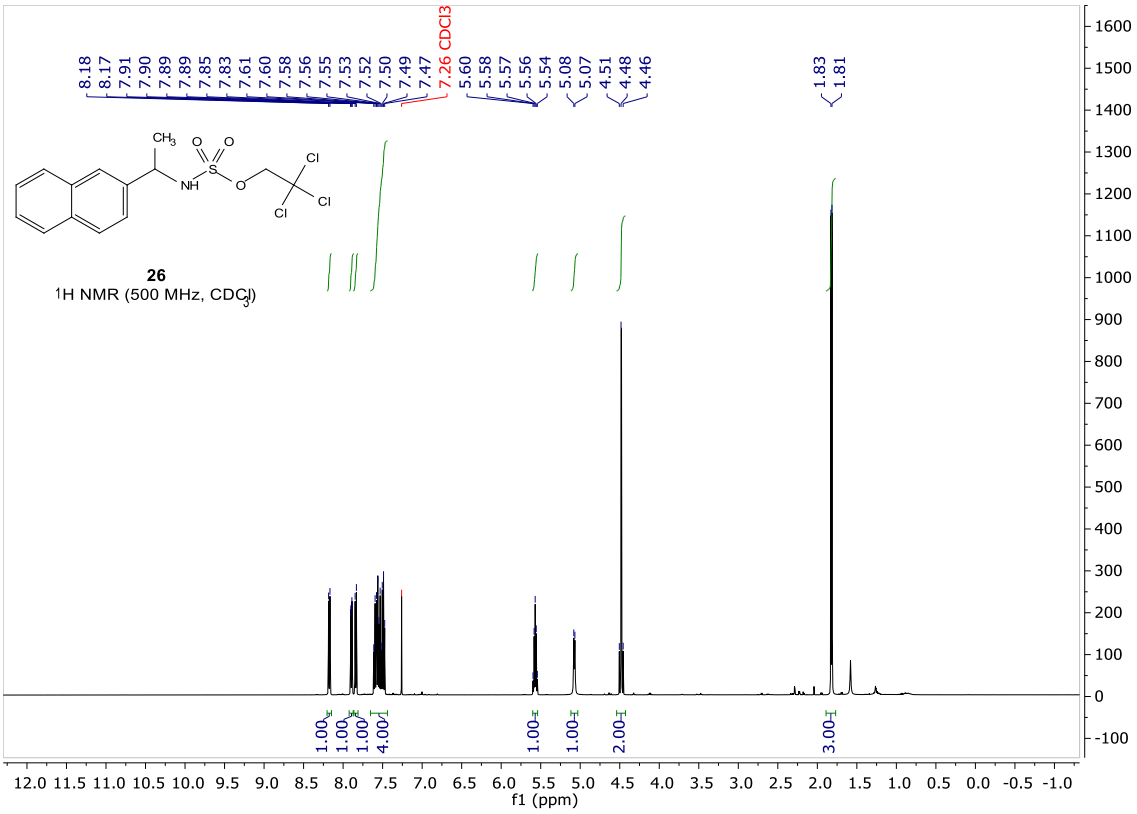


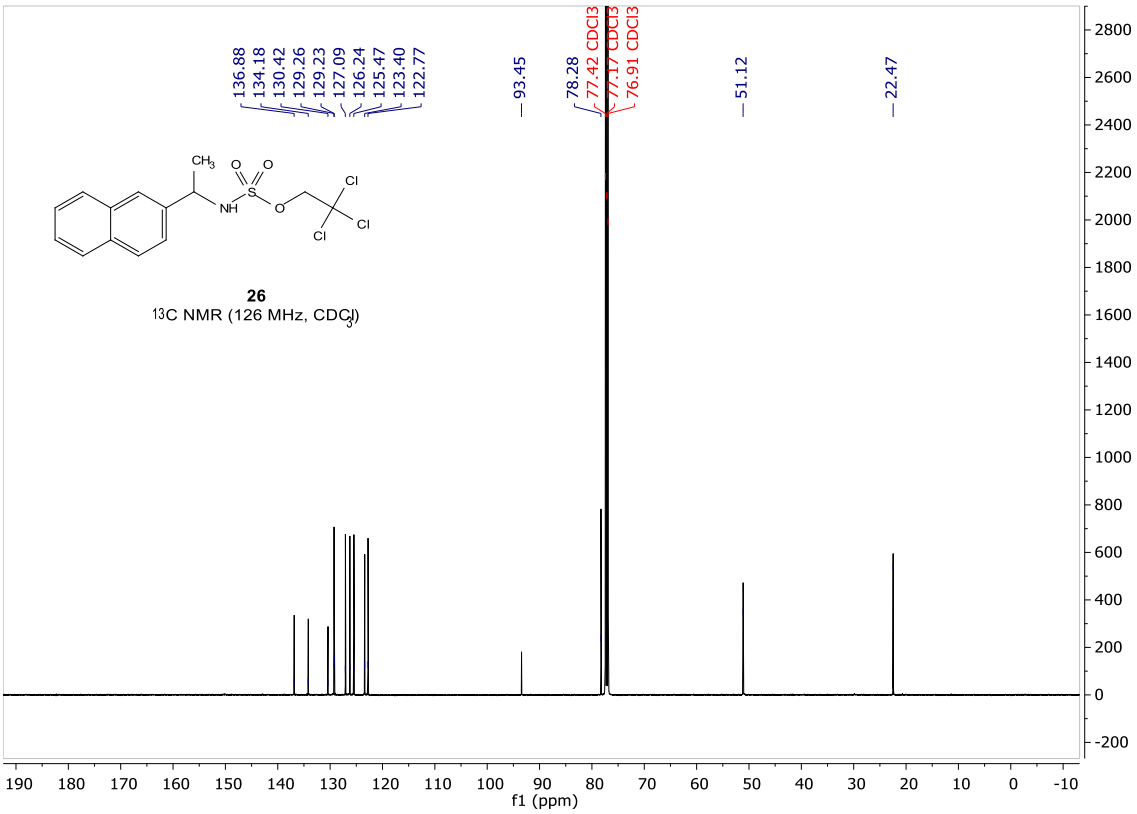
24

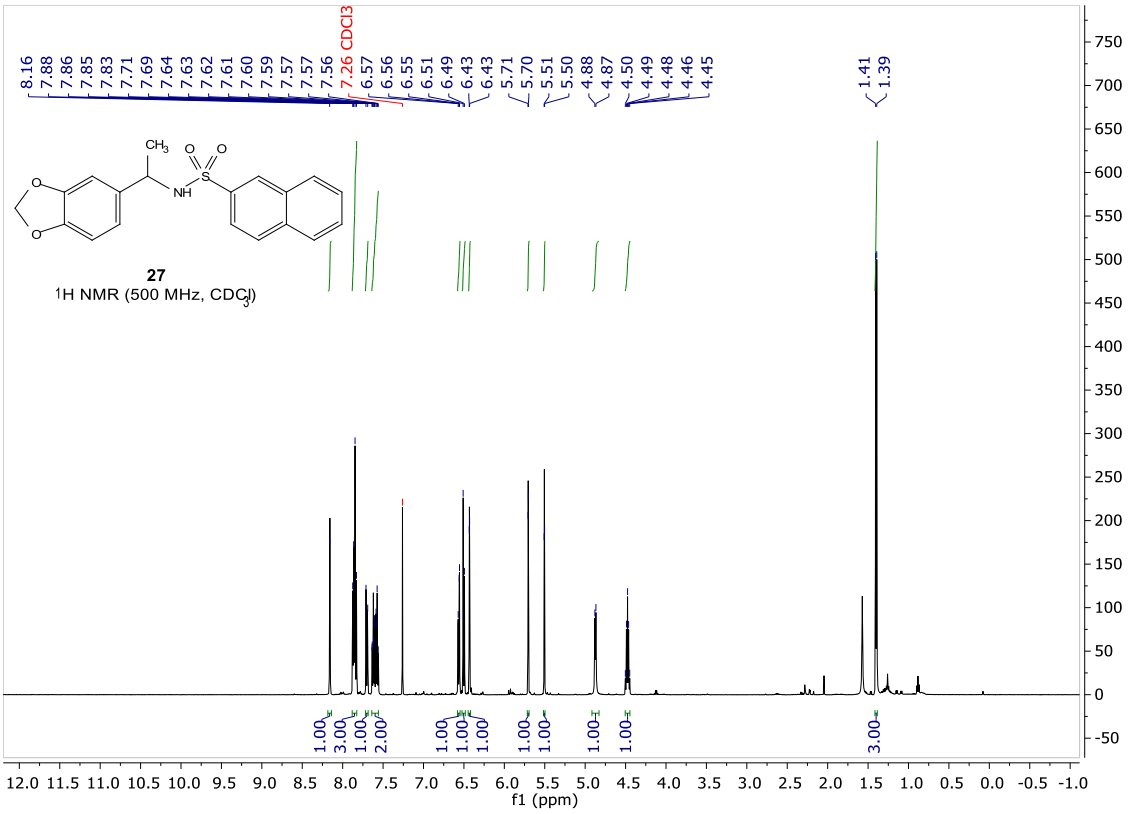
^{13}C NMR (126 MHz, $CDCl_3$)

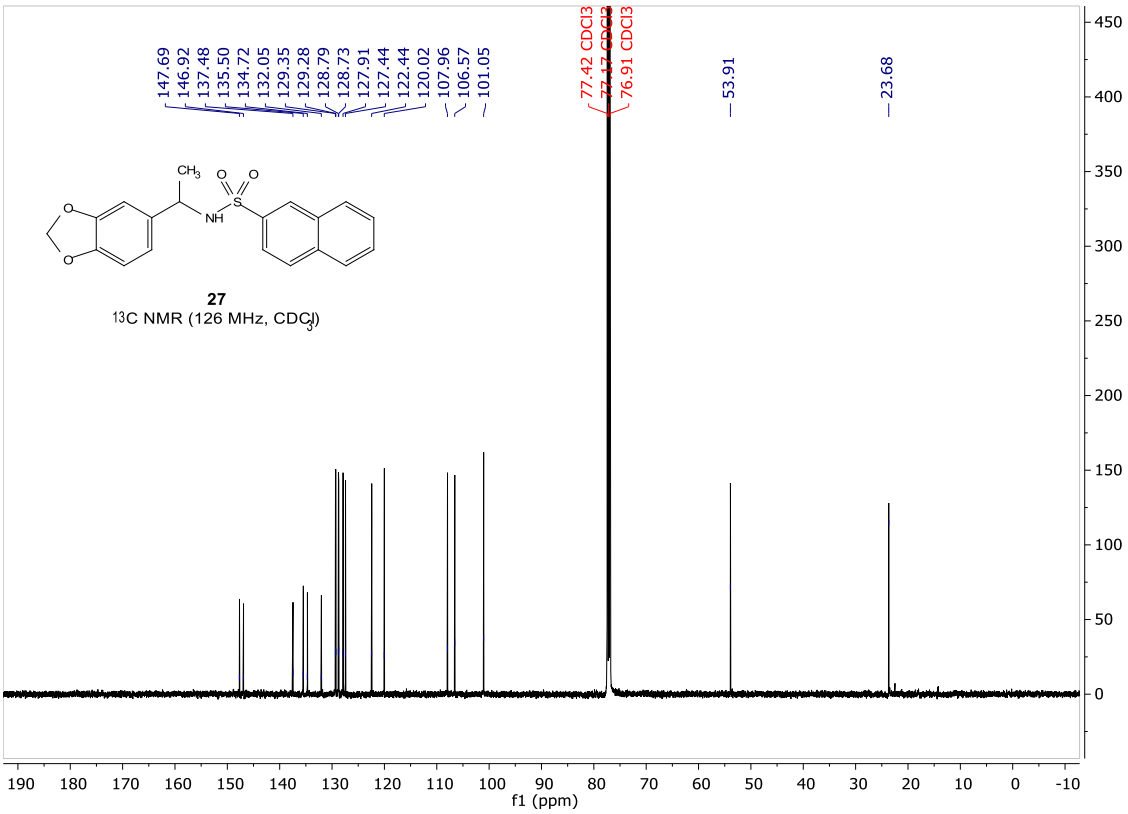

7.84
7.82
7.26 CDCl3
6.95
6.93
4.60
3.86
1.99
1.78
1.77
1.65
1.62
1.60
1.58
1.56
1.53
NH
O
S
O
CH3
O
25
1H NMR (500 MHz, CDCl3)
2.00
2.00
1.00
3.00
3.00
5.00
7.00
f1 (ppm)

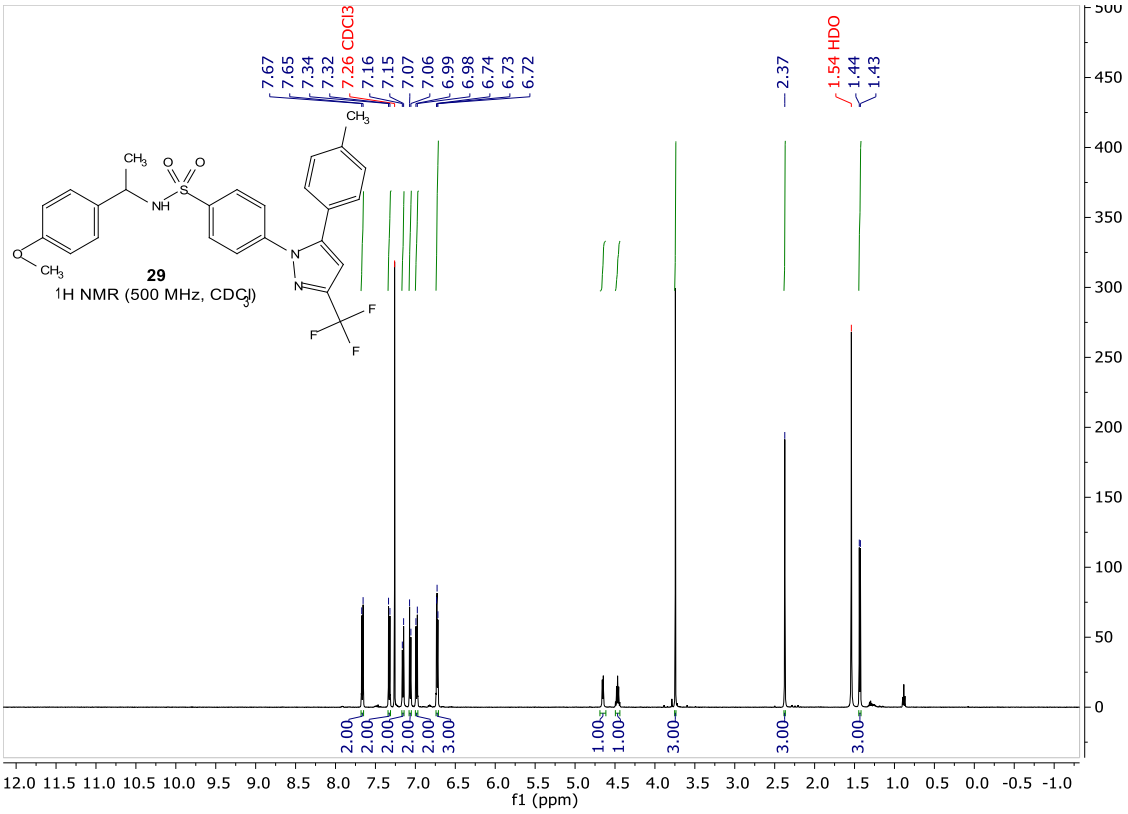

162.53
135.92
129.15
114.08
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
68.36
55.69
55.12
45.50
43.22
36.22
36.00
30.87
29.62
NH
O
S
O
CH3
O
25
13C NMR (126 MHz, CDCl3)
f1 (ppm)

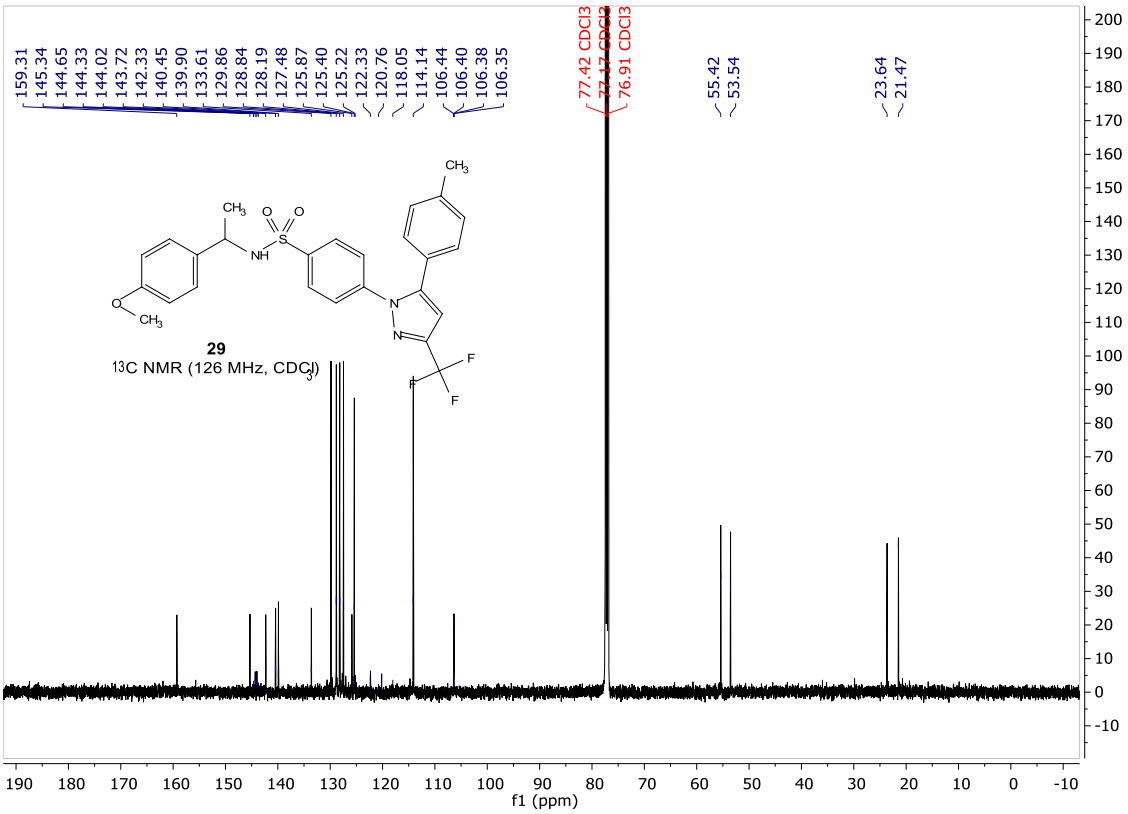

8.18
8.17
7.91
7.90
7.89
7.89
7.85
7.83
7.61
7.60
7.58
7.56
7.55
7.53
7.52
7.50
7.49
7.47
7.26 CDCl3
5.60
5.58
5.57
5.56
5.54
5.08
5.07
4.51
4.48
4.46
1.83
1.81
CH3
O
O
S
NH
O
Cl
Cl
Cl
26
1H NMR (500 MHz, CDCl3)
1.00
1.00
1.00
4.00
1.00
1.00
2.00
3.00
f1 (ppm)

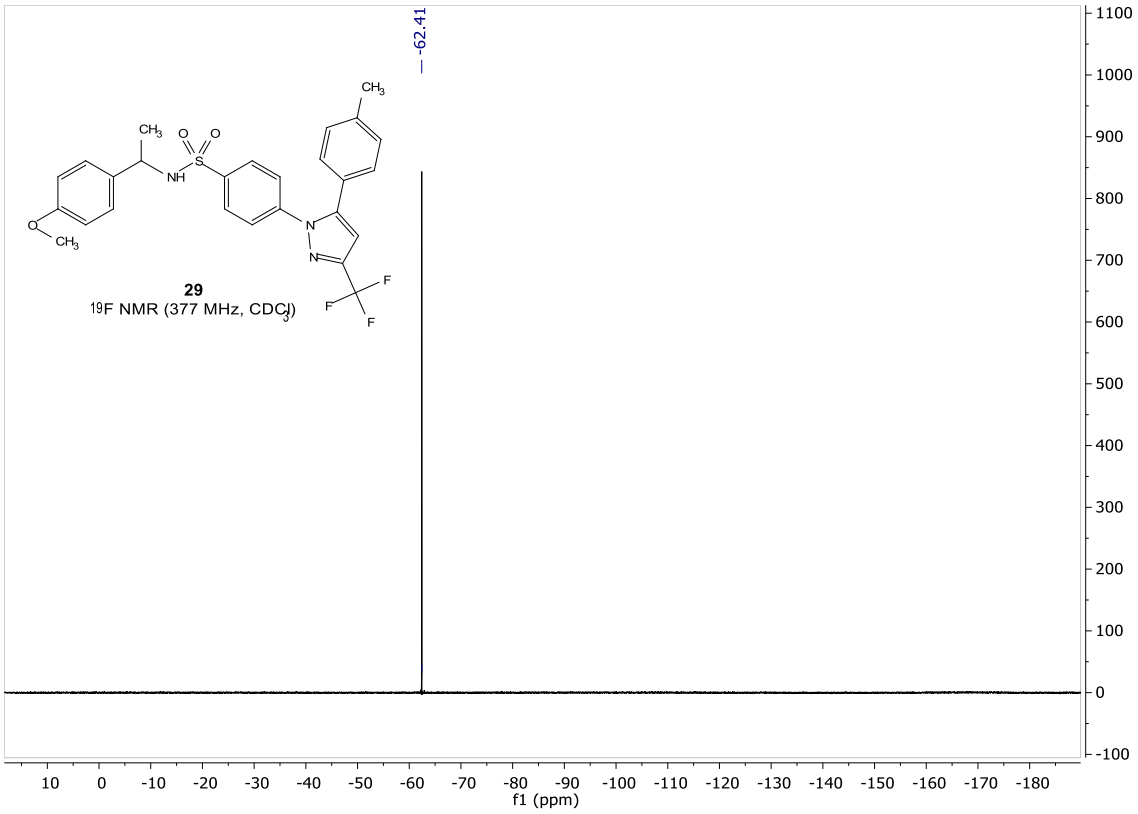

136.88
134.18
130.42
129.26
129.23
127.09
126.24
125.47
123.40
122.77
93.45
78.28
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
51.12
22.47
CH3
O
O
S
NH
O
Cl
Cl
Cl
26
13C NMR (126 MHz, CDCl3)
f1 (ppm)

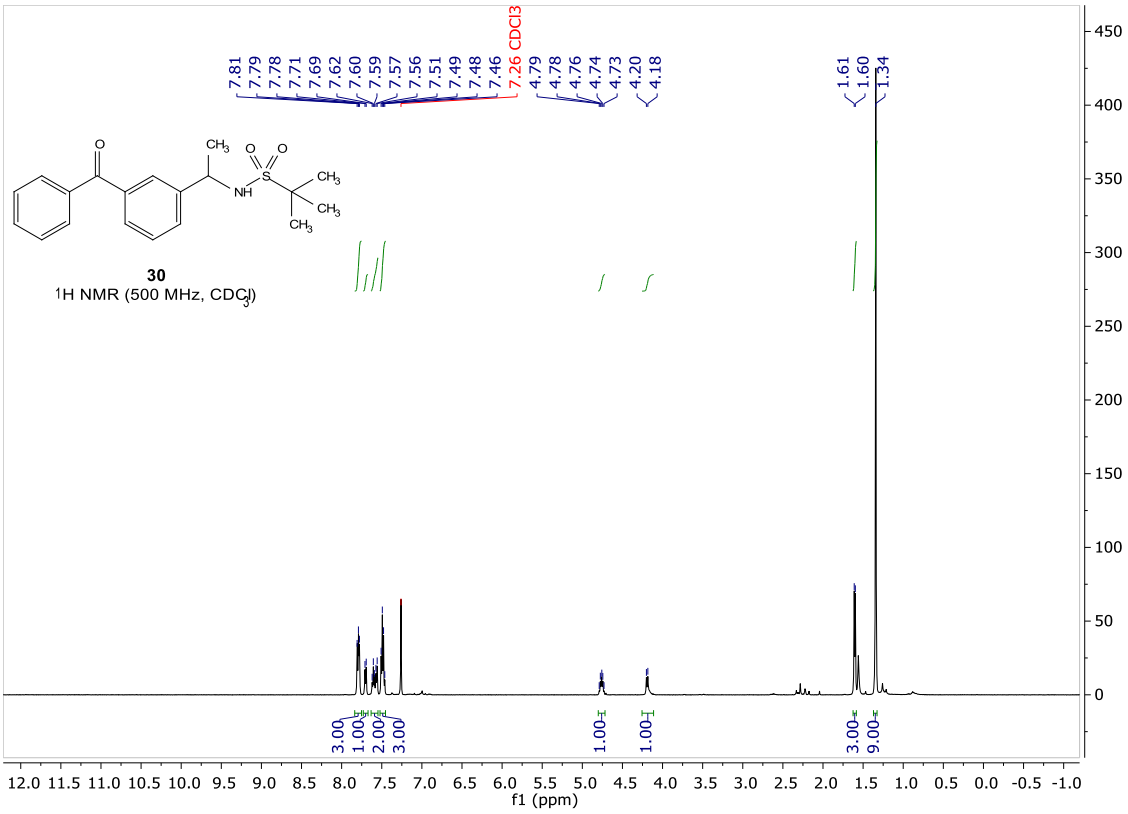

8.16
7.88
7.86
7.85
7.83
7.71
7.69
7.64
7.63
7.62
7.61
7.60
7.59
7.57
7.57
7.56
7.26 CDCl3
6.57
6.56
6.55
6.51
6.49
6.43
6.43
5.71
5.70
5.51
5.50
4.88
4.87
4.50
4.49
4.48
4.46
4.45
1.41
1.39
CH3
O
O
S
NH
O
O
27
1H NMR (500 MHz, CDCl3)
1.00
3.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)


147.69
146.92
137.48
135.50
134.72
132.05
129.35
129.28
128.79
128.73
127.91
127.44
122.44
120.02
107.96
106.57
101.05
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
53.91
23.68
CH3
O
O
S
NH
O
O
27
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.67
7.65
7.34
7.32
7.26 CDCl3
7.16
7.15
7.07
7.06
6.99
6.98
6.74
6.73
6.72
2.37
1.54 HDO
1.44
1.43
29
1H NMR (500 MHz, CDCl3)
2.00
2.00
2.00
2.00
2.00
3.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

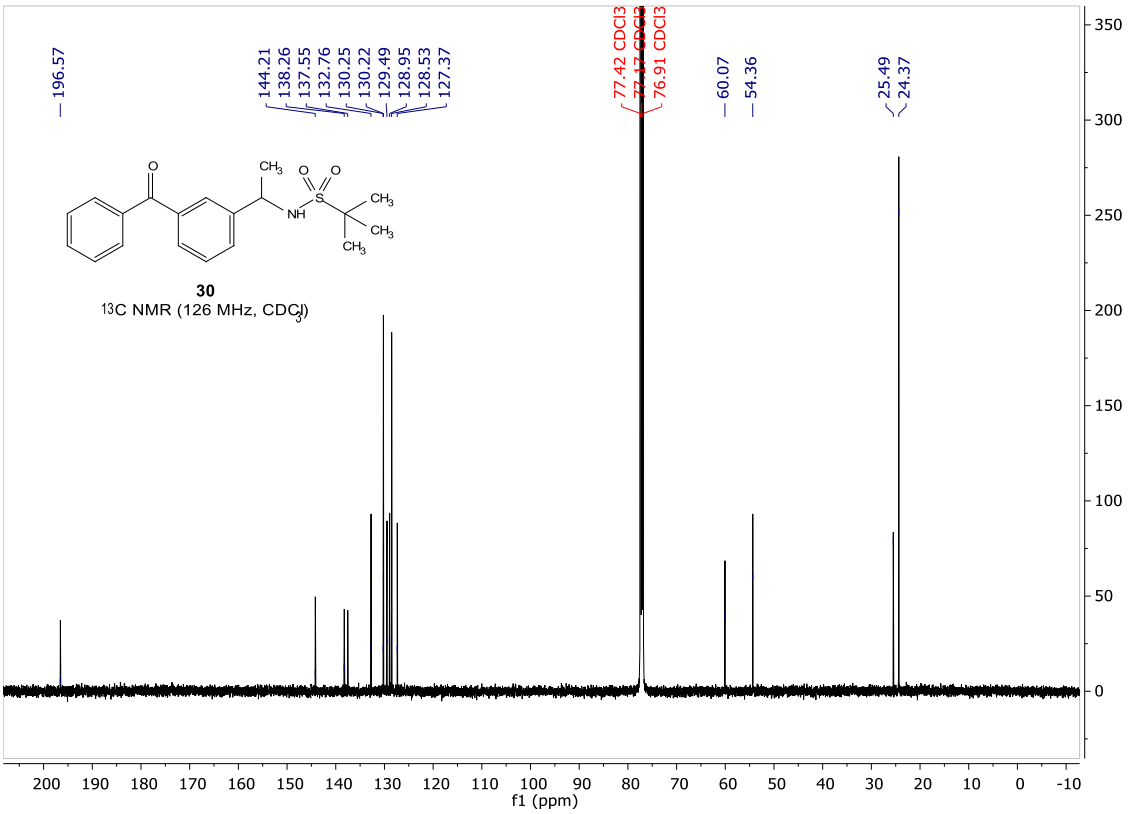

159.31
145.34
144.65
144.33
144.02
143.72
142.33
140.45
139.90
133.61
129.86
128.84
128.19
127.48
125.87
125.40
125.22
122.33
120.76
118.05
114.14
106.44
106.40
106.38
106.35
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
55.42
53.54
23.64
21.47
29
13C NMR (126 MHz, CDCl3)
f1 (ppm)


-62.41
CH3
O
O
S
NH
CH3
O
CH3
N
N
F
F
F
29
19F NMR (377 MHz, CDCl3)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)



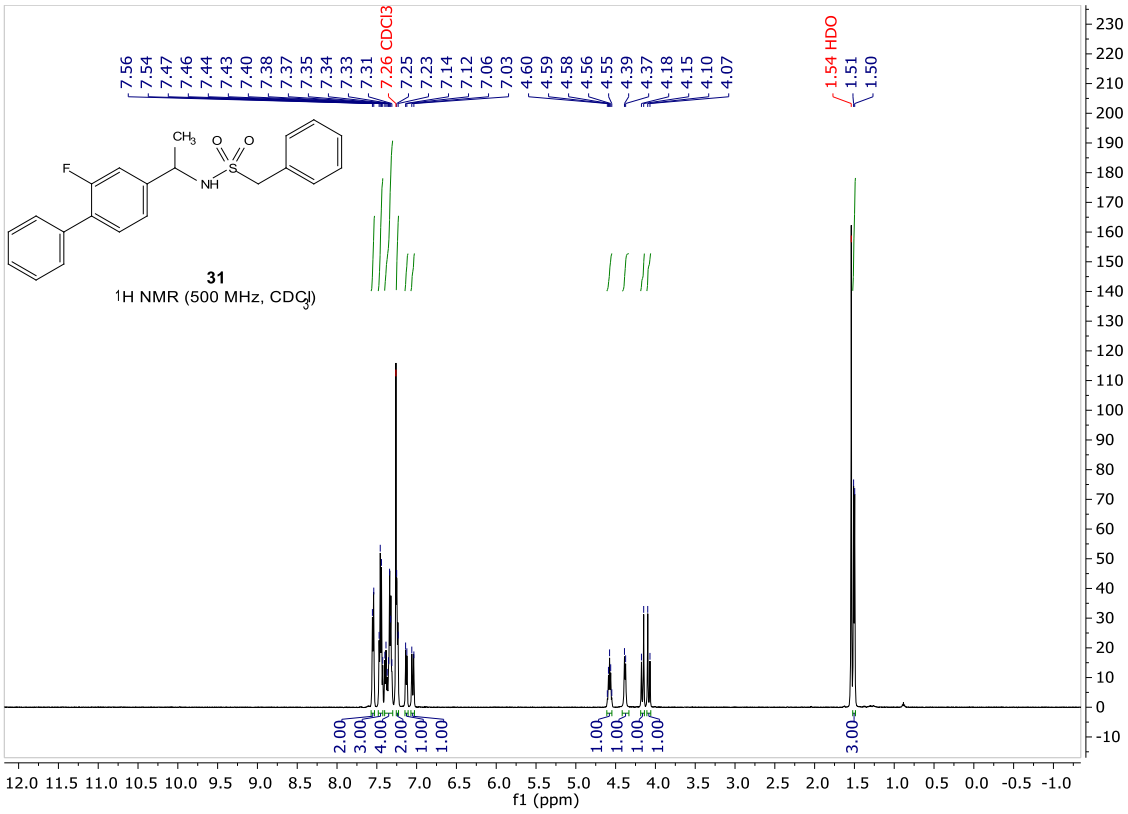
30

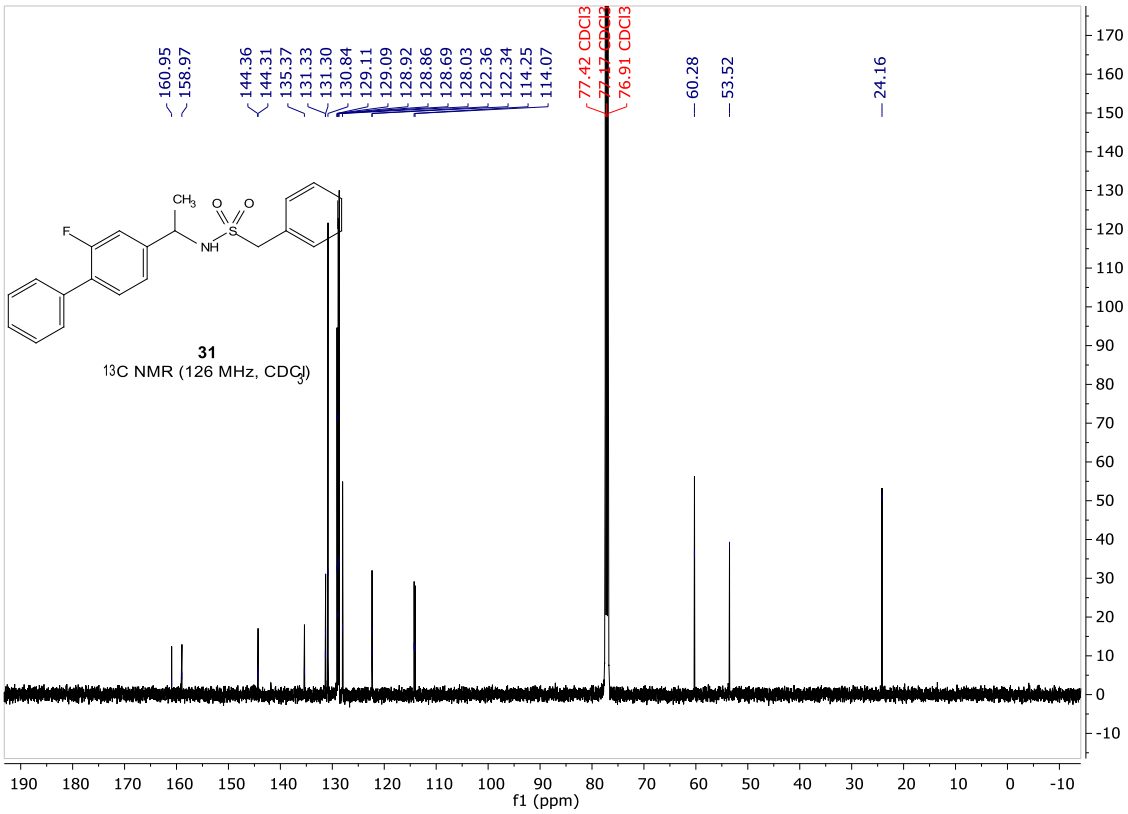
^{1}H NMR (500 MHz, $CDCl_3$)

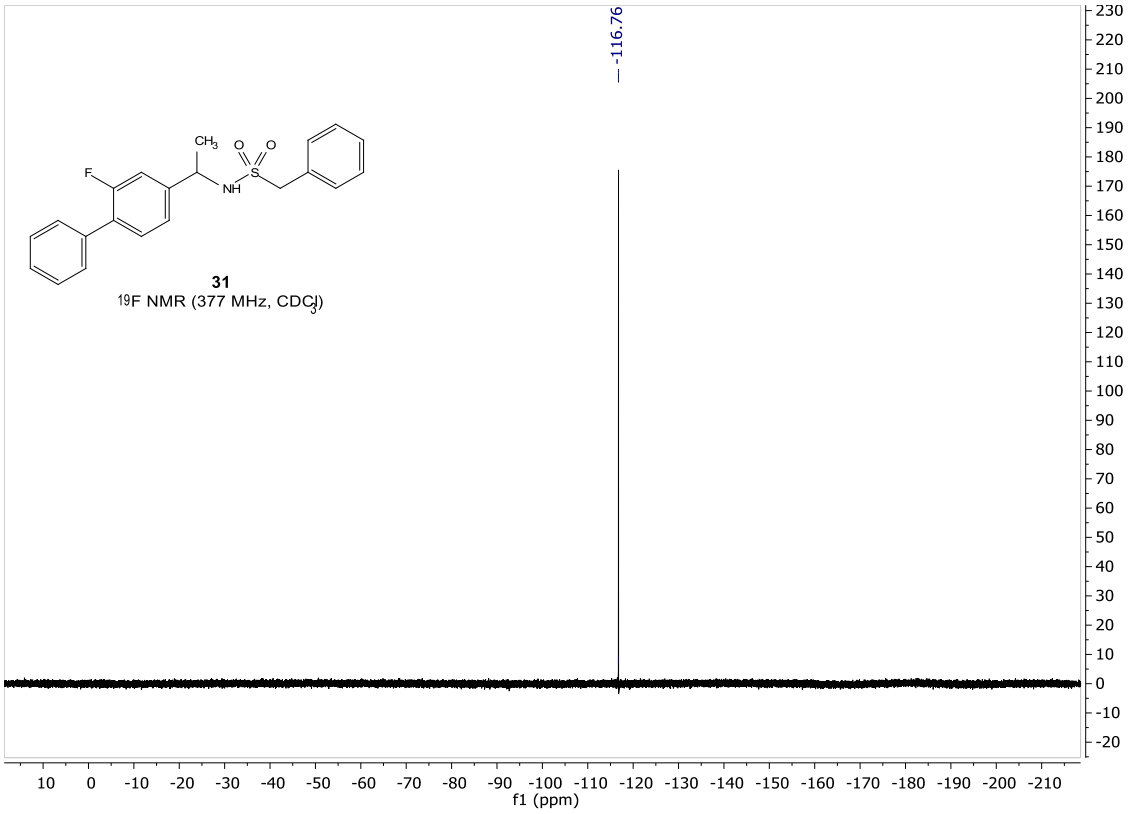


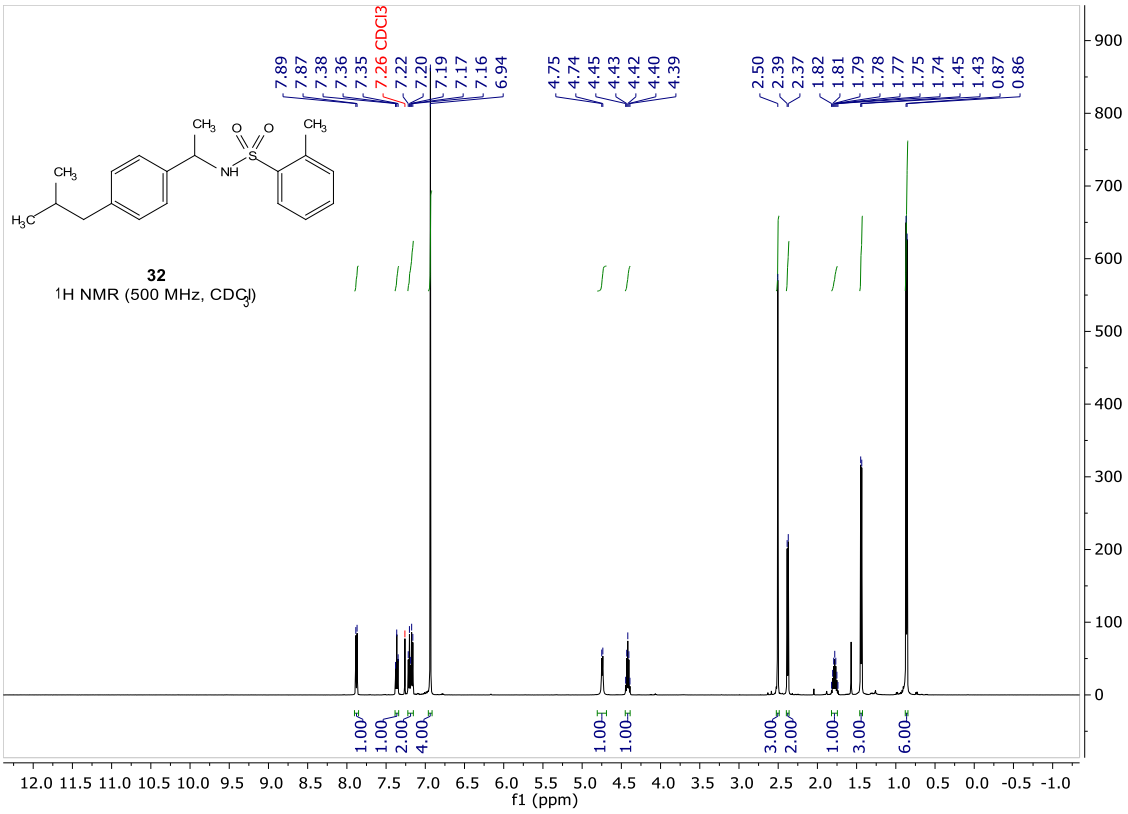
30

^{13}C NMR (126 MHz, $CDCl_3$)

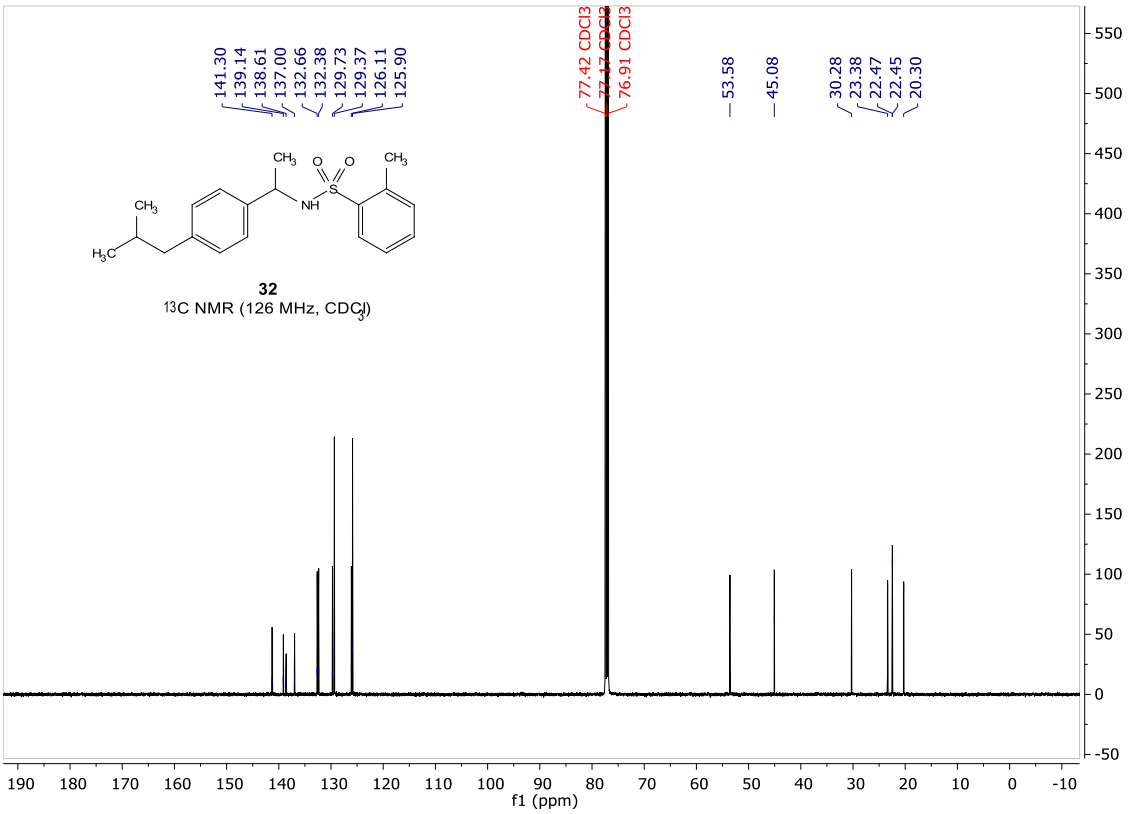

7.56
7.54
7.47
7.46
7.44
7.43
7.40
7.38
7.37
7.35
7.34
7.33
7.31
7.26 CDCl3
7.25
7.23
7.14
7.12
7.06
7.03
4.60
4.59
4.58
4.56
4.55
4.39
4.37
4.18
4.15
4.10
4.07
1.54 HDO
1.51
1.50
CH3
O
O
S
NH
F
31
1H NMR (500 MHz, CDCl3)
2.00
3.00
4.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)


160.95
158.97
144.36
144.31
135.37
131.33
131.30
130.84
129.11
129.09
128.92
128.86
128.69
128.03
122.36
122.34
114.25
114.07
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
60.28
53.52
24.16
CH3
O
O
S
NH
F
31
13C NMR (126 MHz, CDCl3)
f1 (ppm)

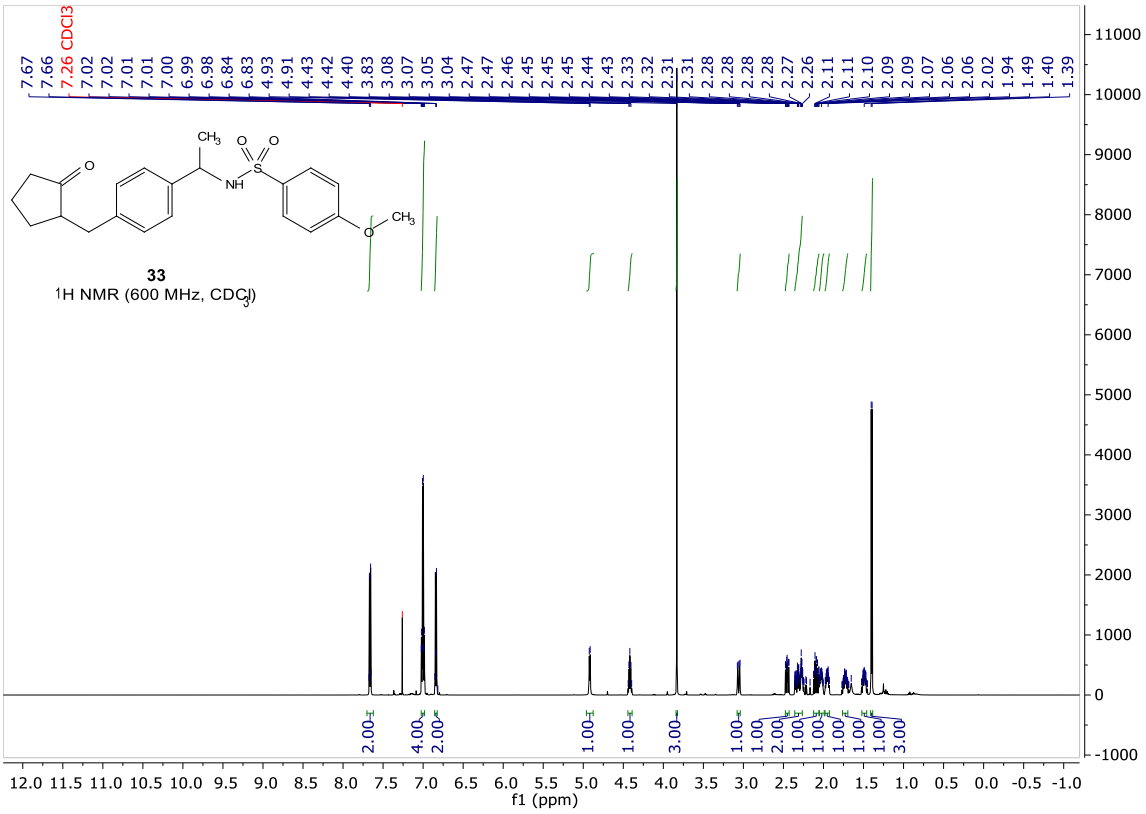

-116.76
CH3
O
O
F
S
NH
31
19F NMR (377 MHz, CDCl3)
f1 (ppm)

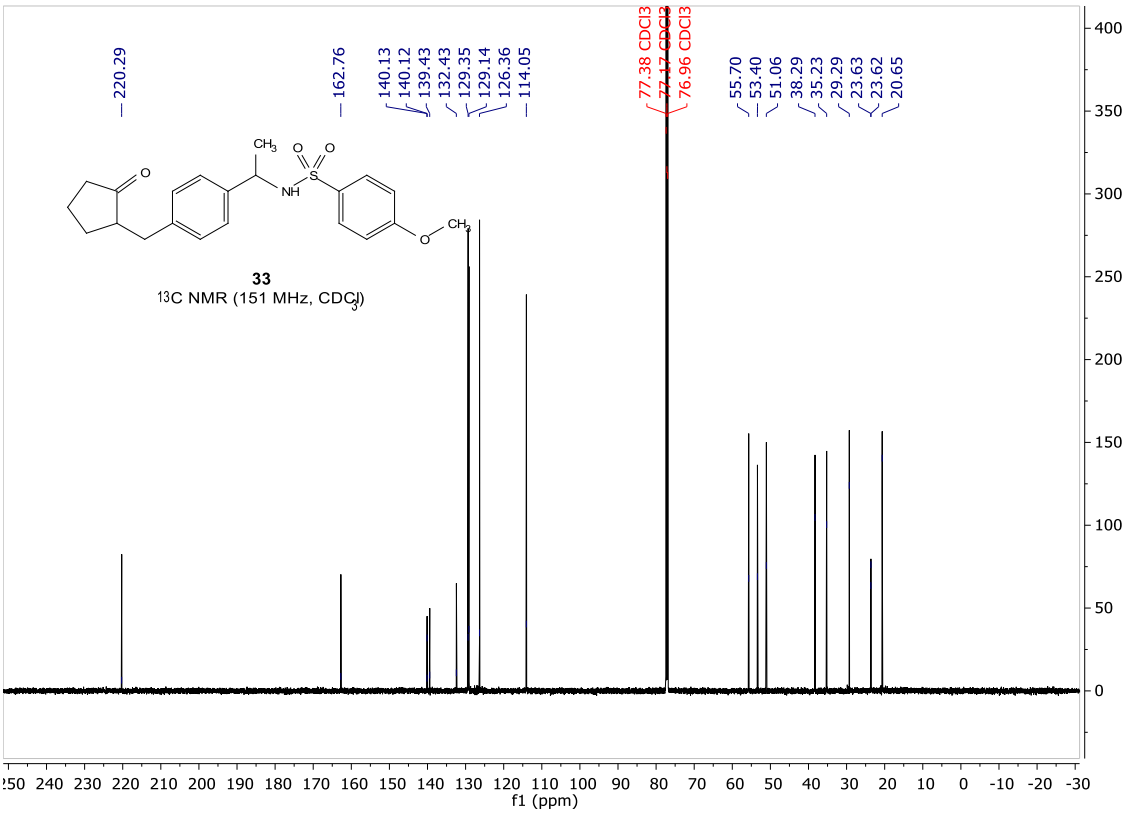


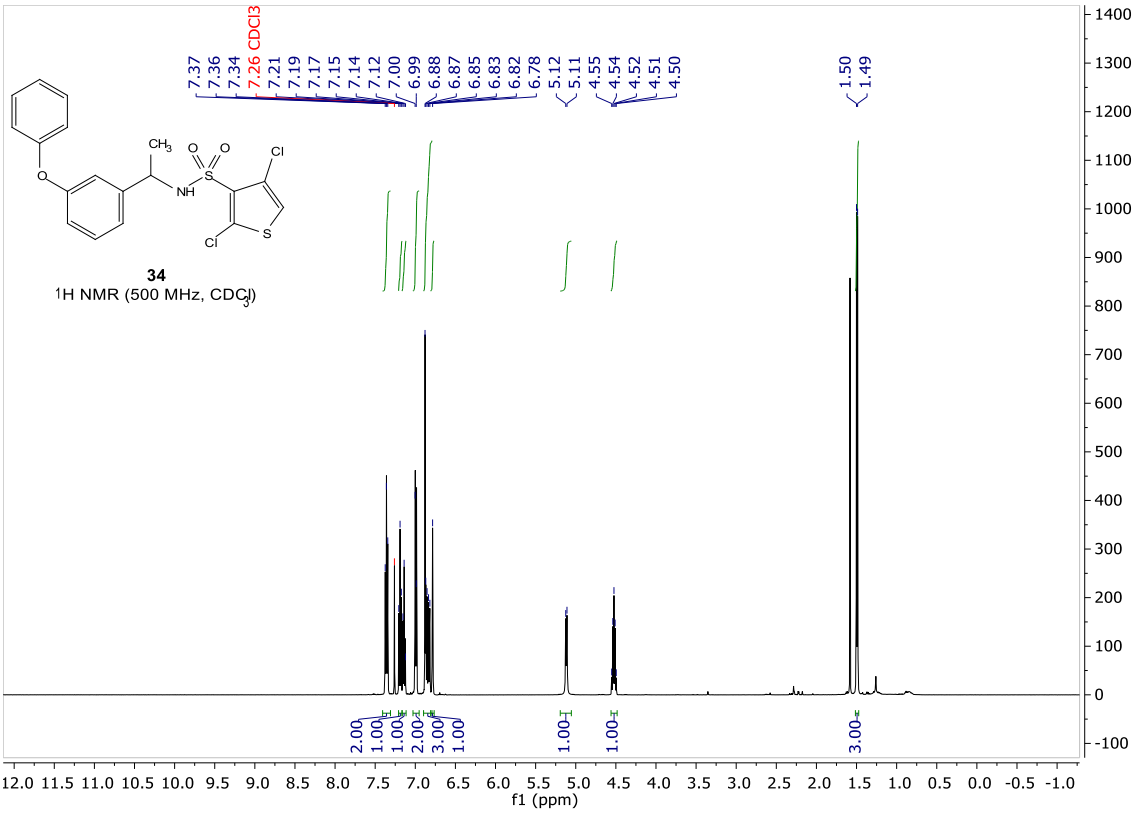
32
^{1}H NMR (500 MHz, $CDCl_3$)

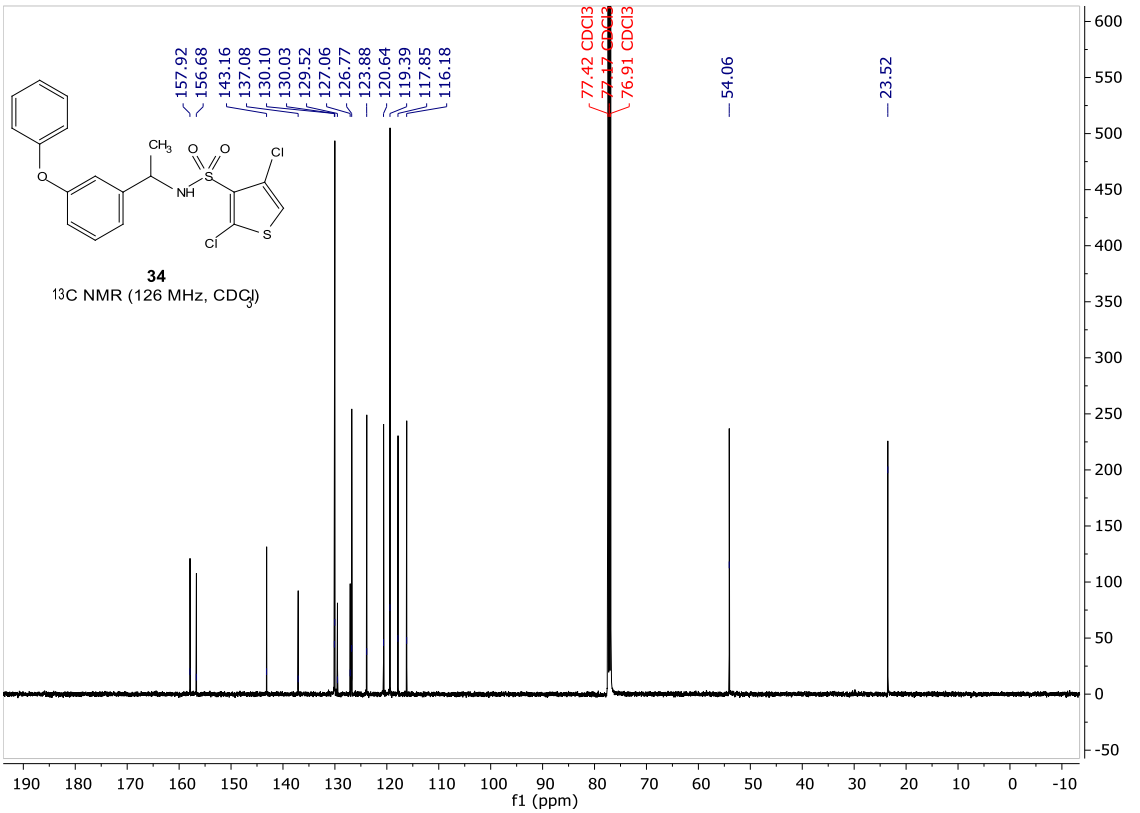


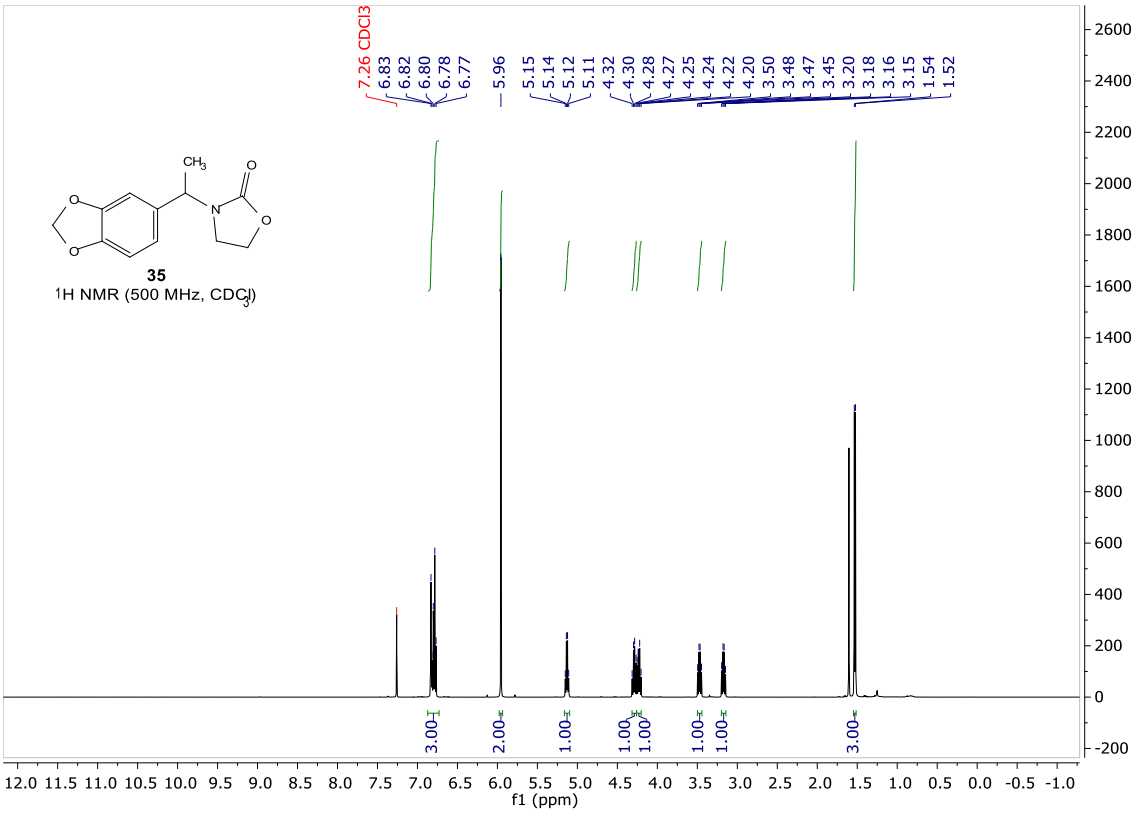
32
^{13}C NMR (126 MHz, $CDCl_3$)

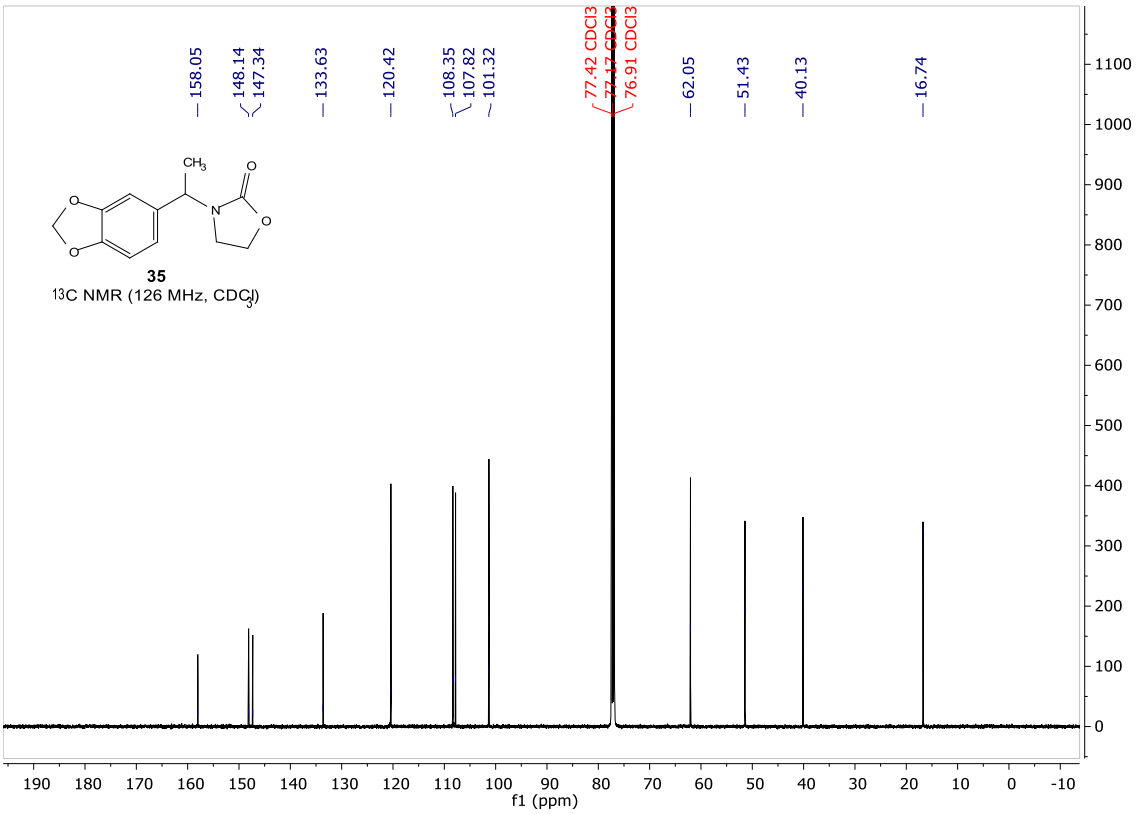

7.67 7.66 7.26 CDCl3 7.02 7.02 7.01 7.01 7.00 6.99 6.98 6.84 6.83 4.93 4.91 4.43 4.42 4.40 3.83 3.08 3.07 3.05 3.04 2.47 2.46 2.45 2.45 2.45 2.44 2.43 2.33 2.32 2.31 2.31 2.28 2.28 2.28 2.28 2.27 2.26 2.11 2.11 2.10 2.09 2.09 2.07 2.06 2.06 2.02 1.94 1.49 1.40 1.39
33
1H NMR (600 MHz, CDCl3)
2.00 4.00 2.00 1.00 1.00 3.00 1.00 1.00 2.00 1.00 1.00 1.00 1.00 3.00
f1 (ppm)

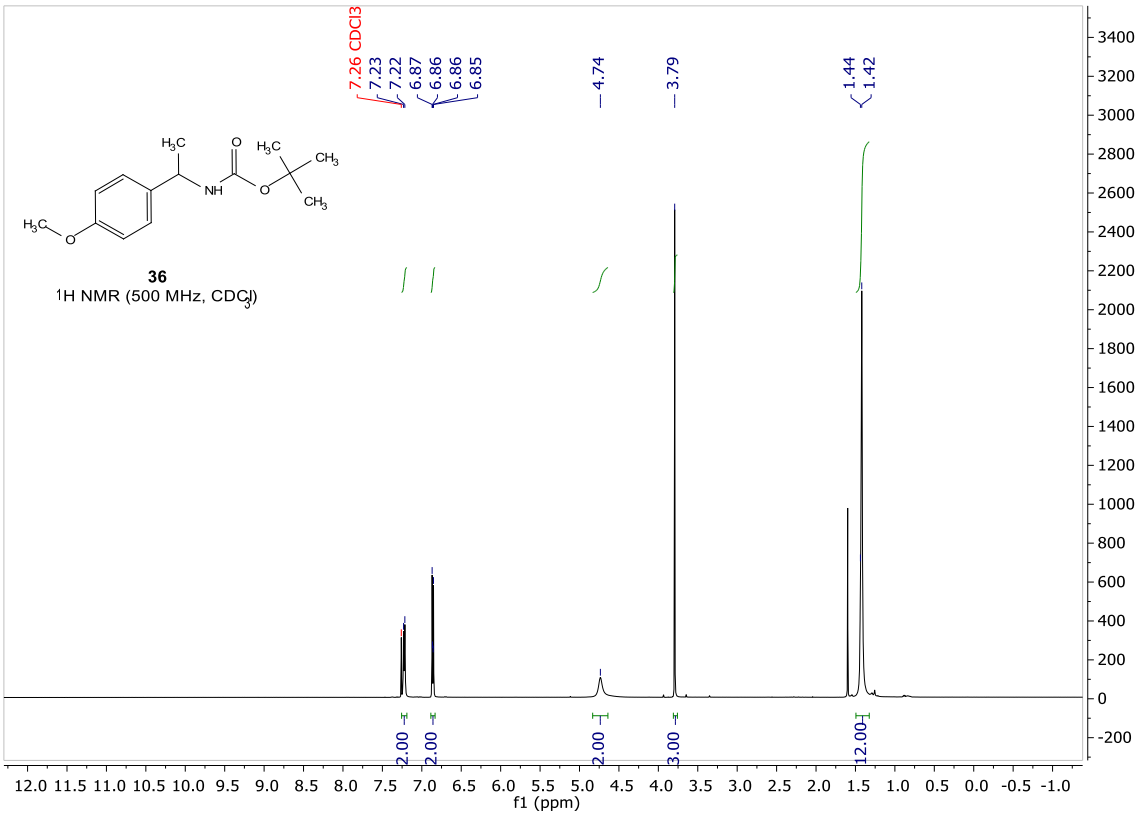

220.29 162.76 140.13 140.12 139.43 132.43 129.35 129.14 126.36 114.05 77.38 CDCl3 77.17 CDCl3 76.96 CDCl3 55.70 53.40 51.06 38.29 35.23 29.29 23.63 23.62 20.65
33
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.37
7.36
7.34
7.26 CDCl3
7.21
7.19
7.17
7.15
7.14
7.12
7.00
6.99
6.88
6.87
6.85
6.83
6.82
6.78
5.12
5.11
4.55
4.54
4.52
4.51
4.50
1.50
1.49
CH3
O
O
S
NH
Cl
Cl
S
O
34
1H NMR (500 MHz, CDCl3)
2.00
1.00
1.00
2.00
3.00
1.00
1.00
1.00
3.00
f1 (ppm)


157.92
156.68
143.16
137.08
130.10
130.03
129.52
127.06
126.77
123.88
120.64
119.39
117.85
116.18
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
54.06
23.52
CH3
O
O
S
NH
Cl
Cl
S
O
34
13C NMR (126 MHz, CDCl3)
f1 (ppm)

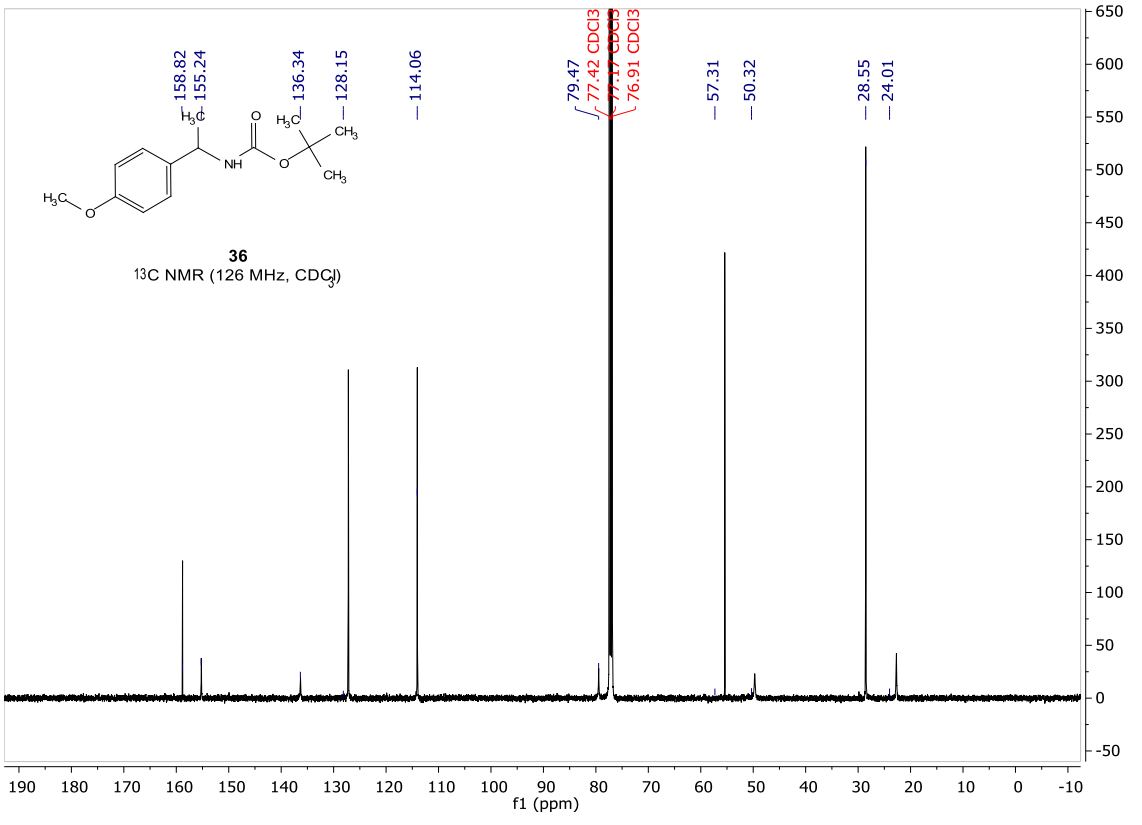

7.26 CDCl3
6.83
6.82
6.80
6.78
6.77
5.96
5.15
5.14
5.12
5.11
4.32
4.30
4.28
4.27
4.25
4.24
4.22
4.20
3.50
3.48
3.47
3.45
3.20
3.18
3.16
3.15
1.54
1.52
CH3
O
N
O
O
O
35
1H NMR (500 MHz, CDCl3)
3.00
2.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)


158.05
148.14
147.34
133.63
120.42
108.35
107.82
101.32
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
62.05
51.43
40.13
16.74
CH3
O
N
O
O
O
35
13C NMR (126 MHz, CDCl3)
f1 (ppm)



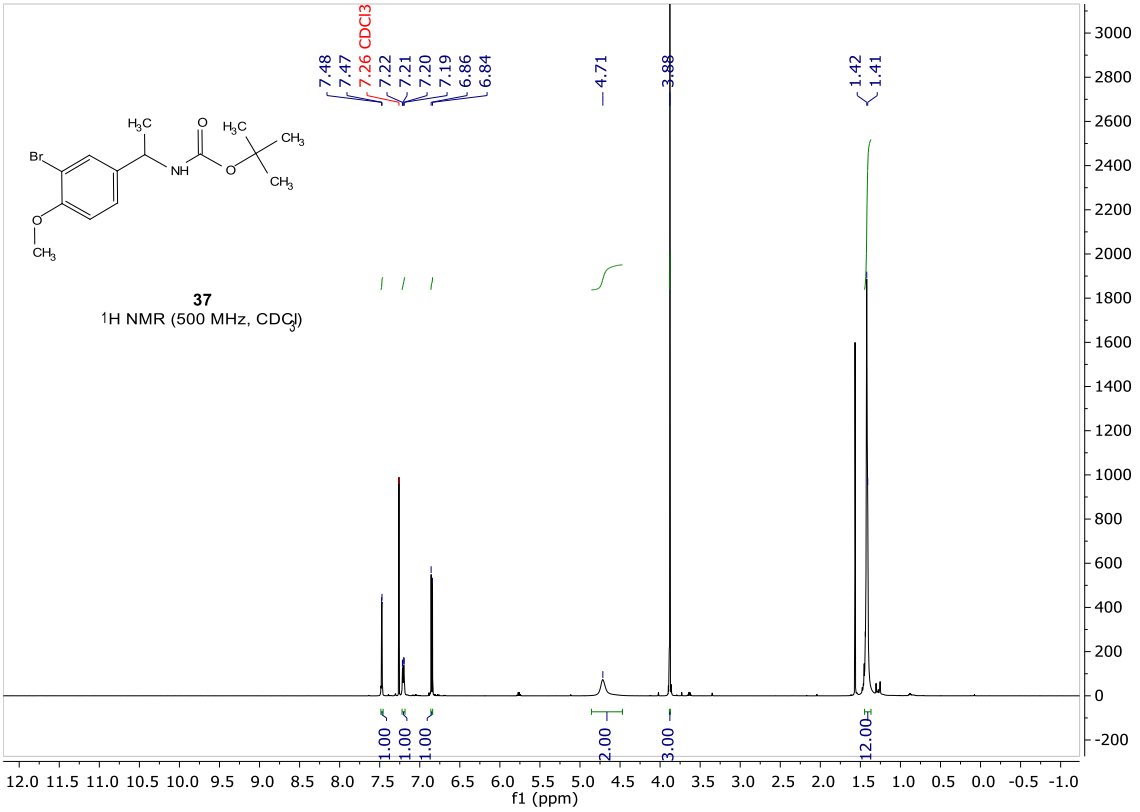
36

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



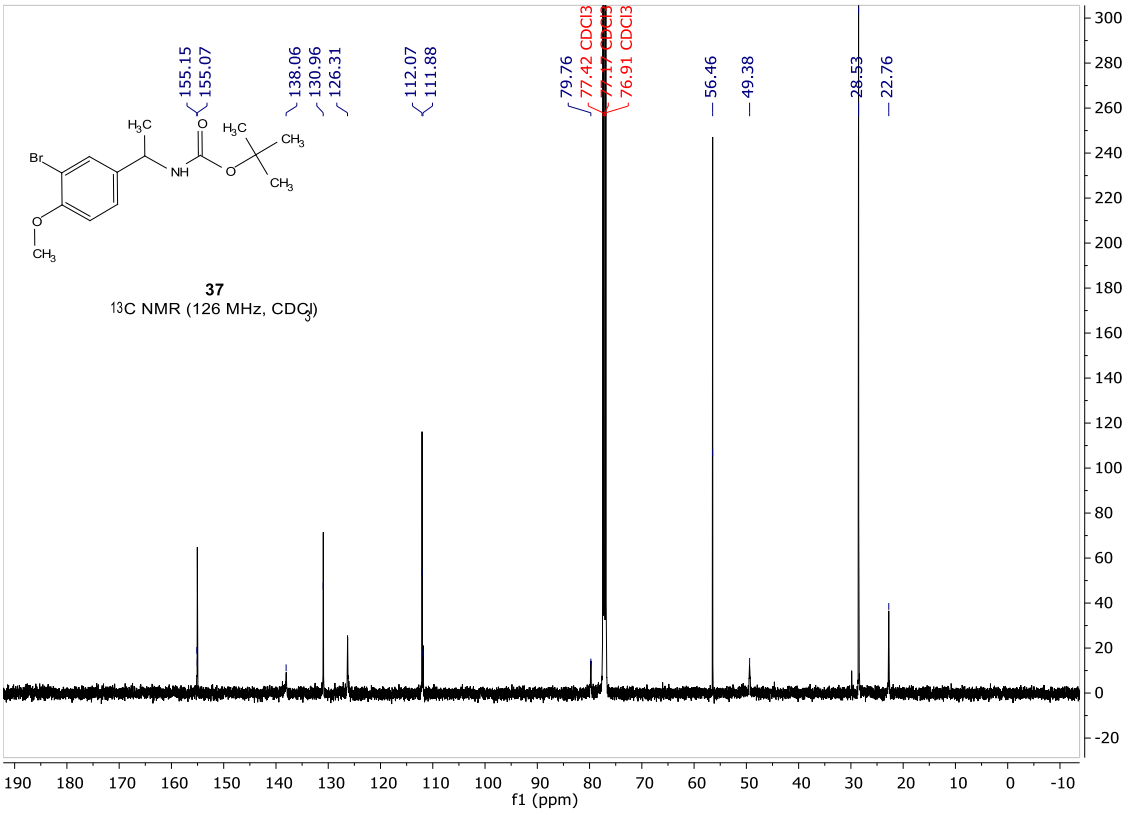
36

^{13}C NMR (126 MHz, $CDCl_3$)



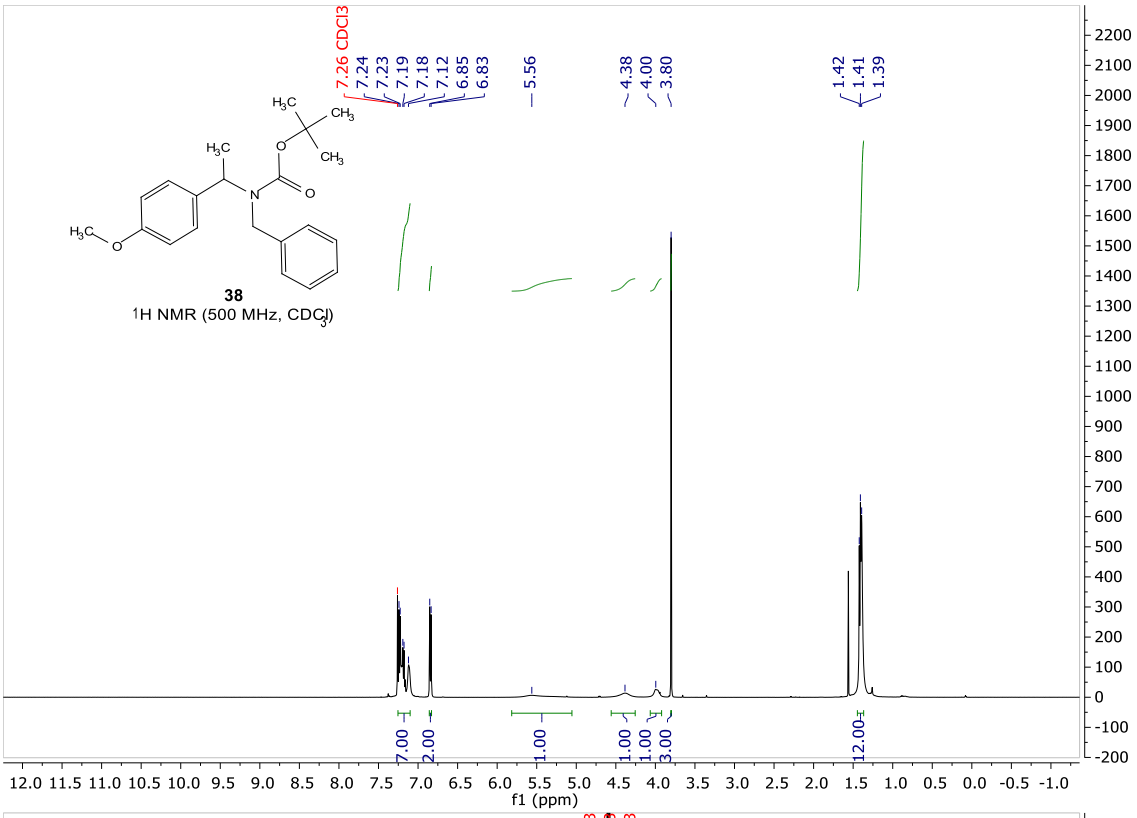
37

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



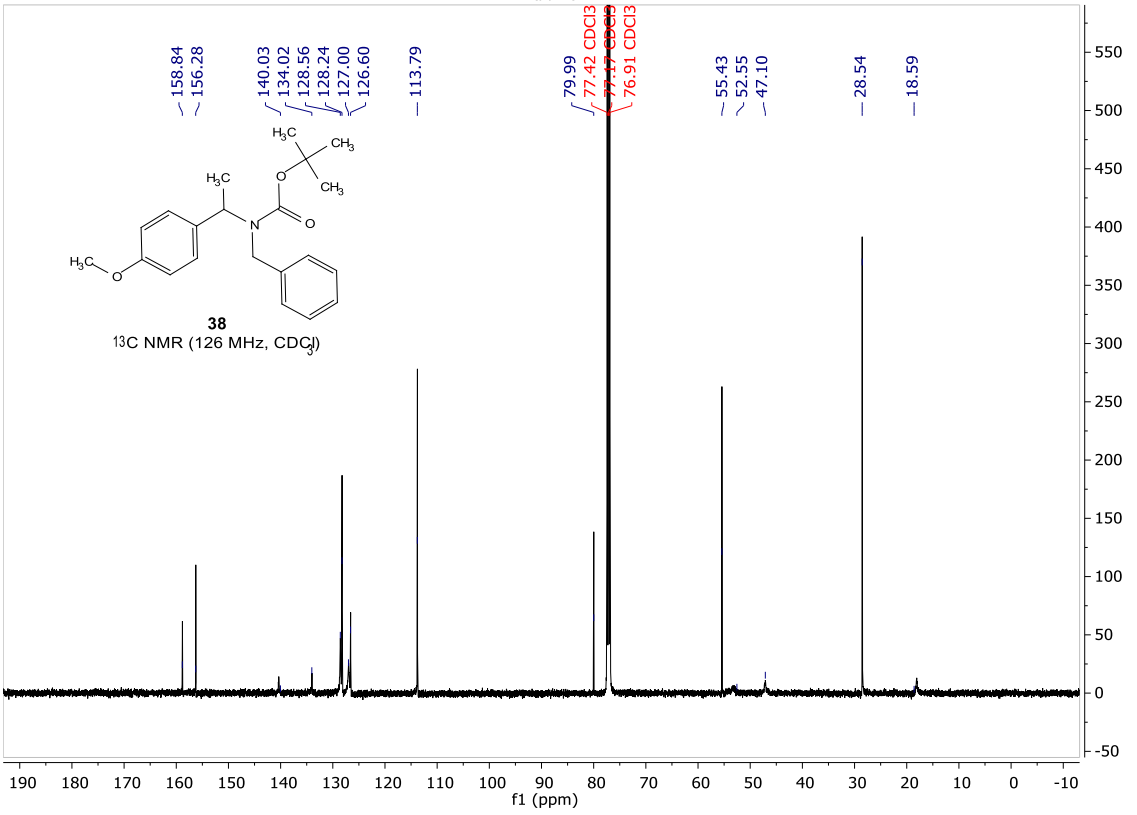
37

^{13}C NMR (126 MHz, $CDCl_3$)



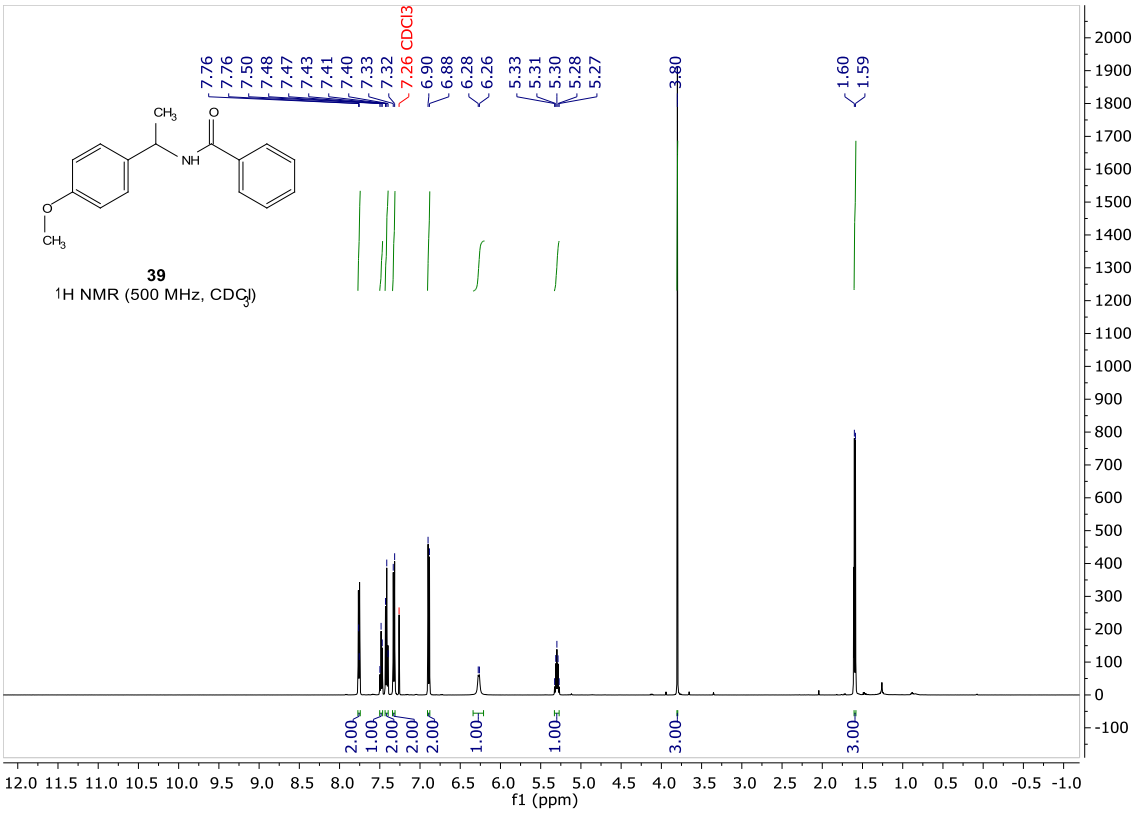
38

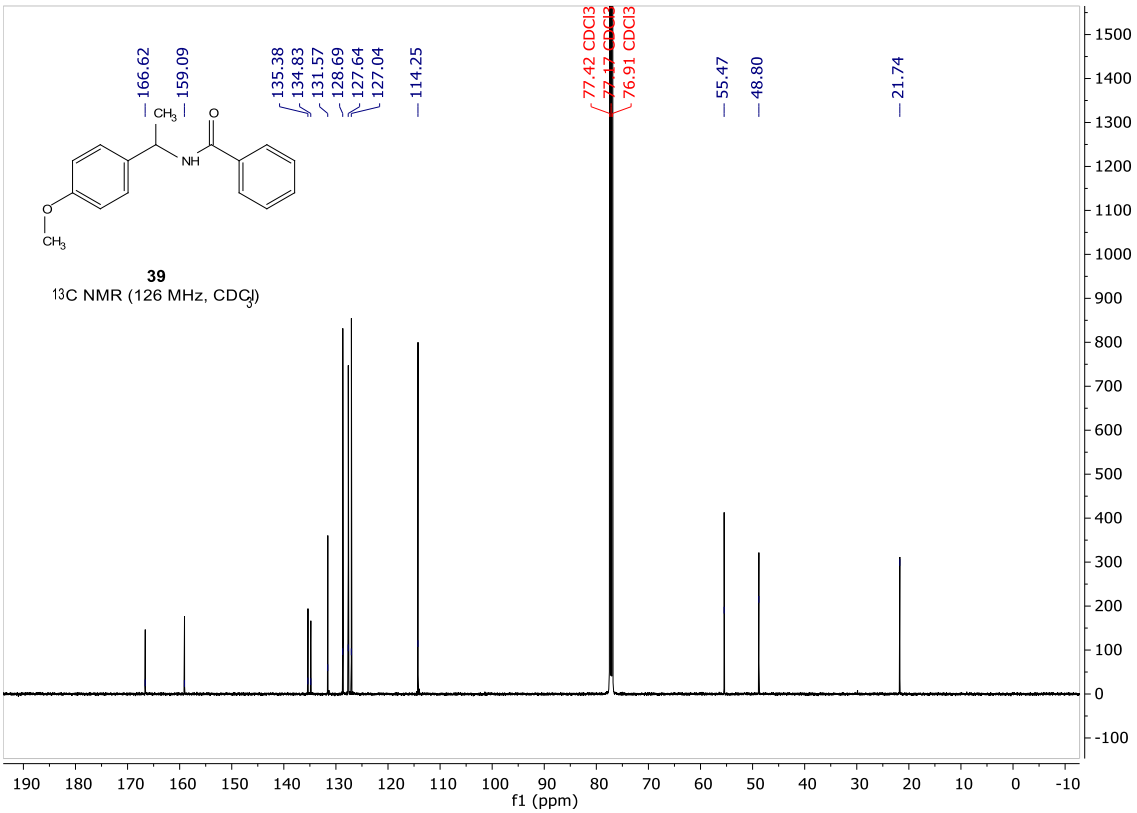
^{1}H NMR (500 MHz, $CDCl_3$)

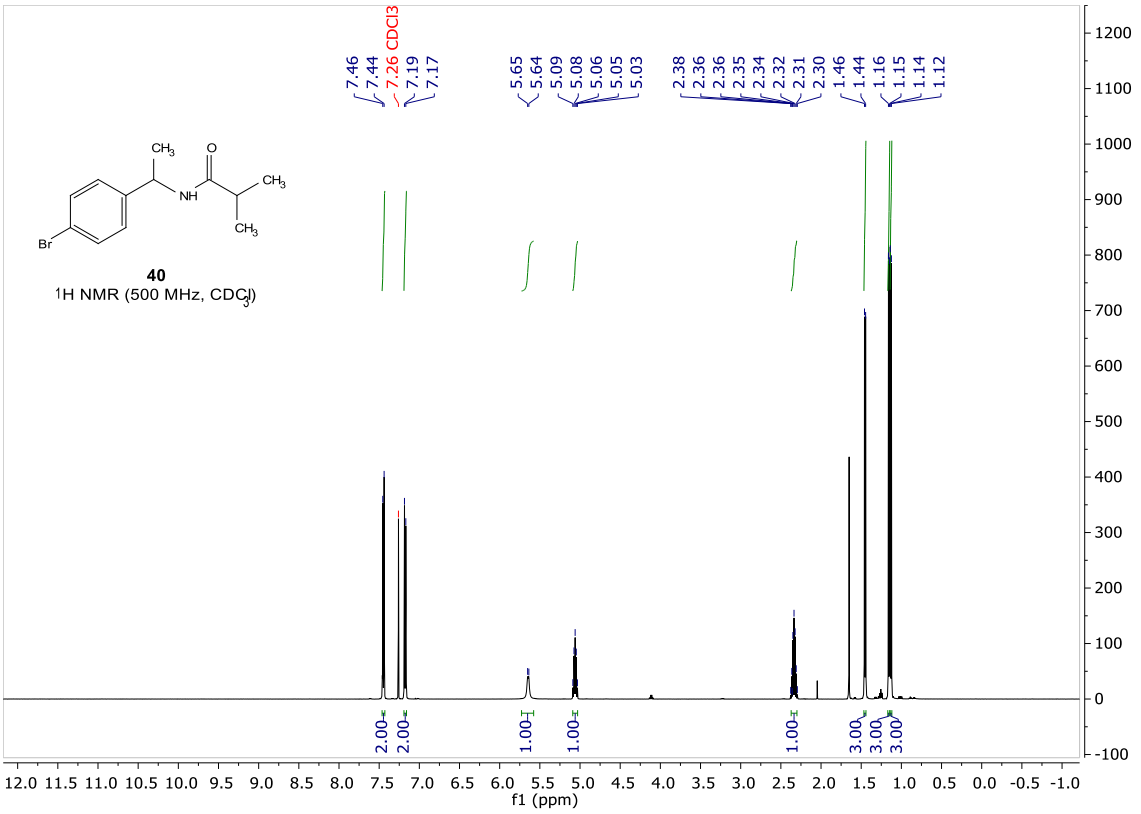


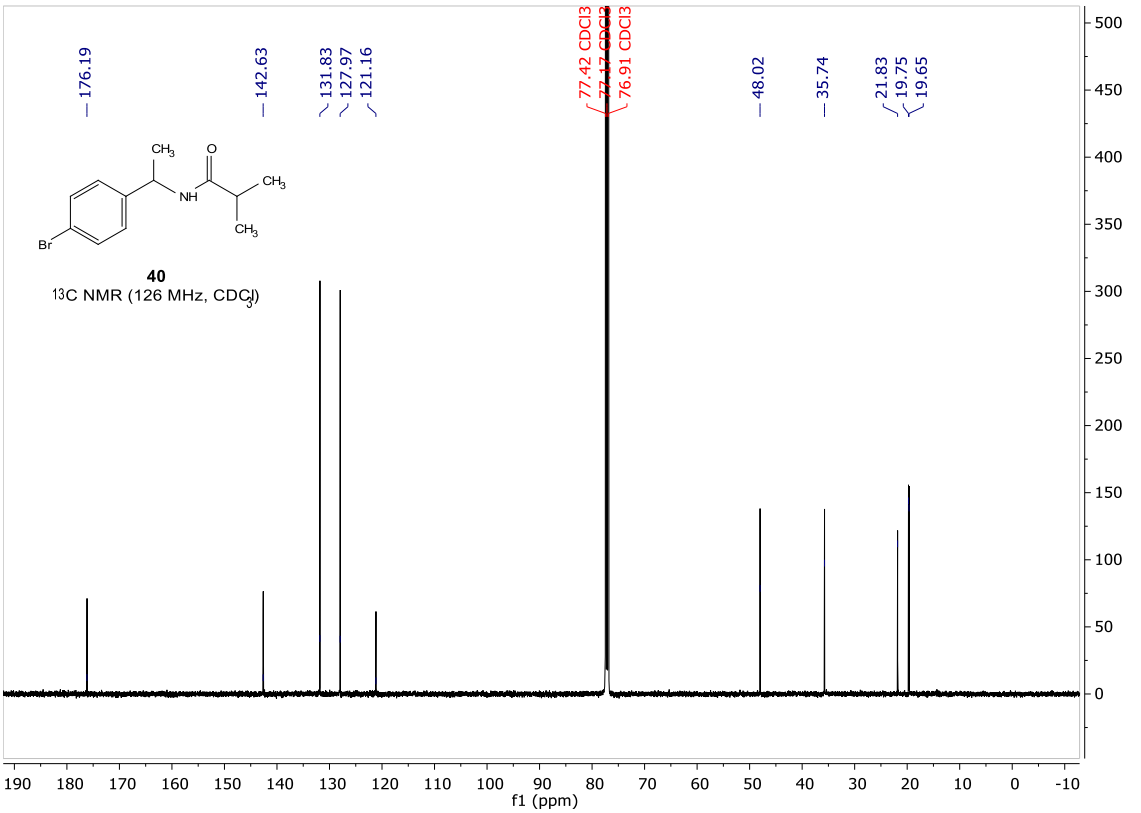
38

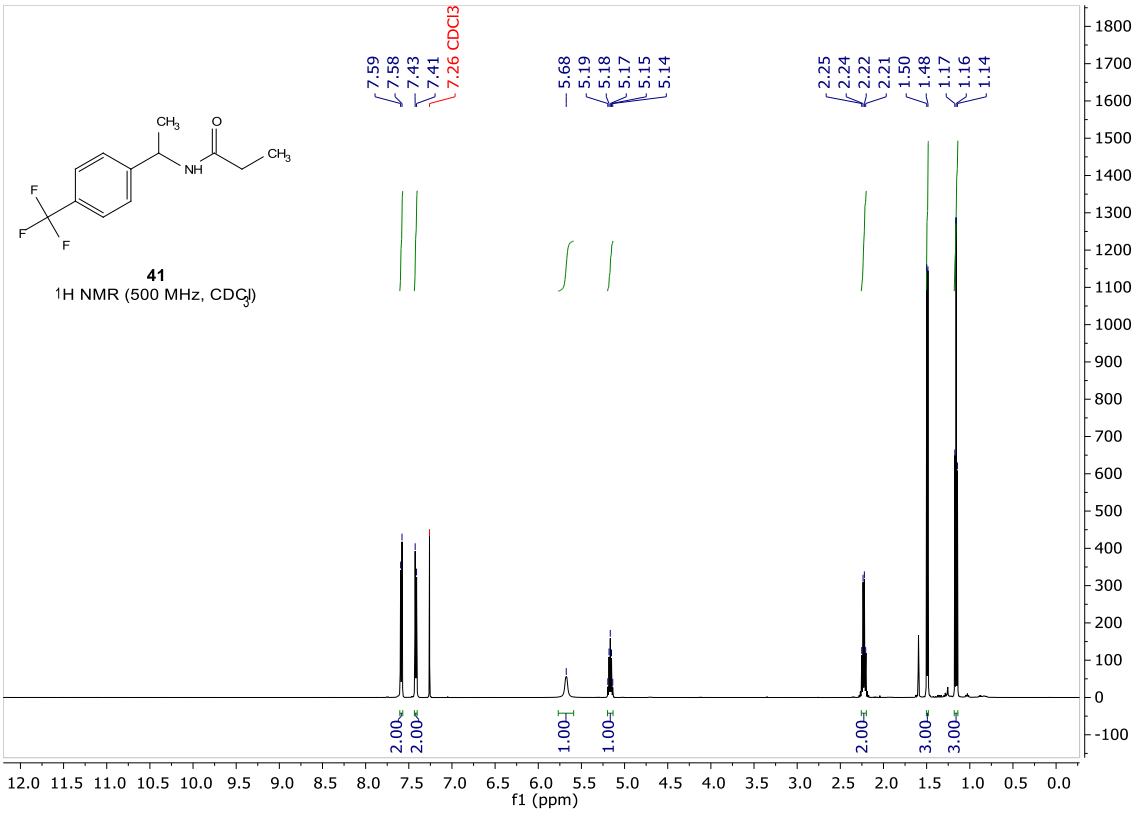
^{13}C NMR (126 MHz, $CDCl_3$)

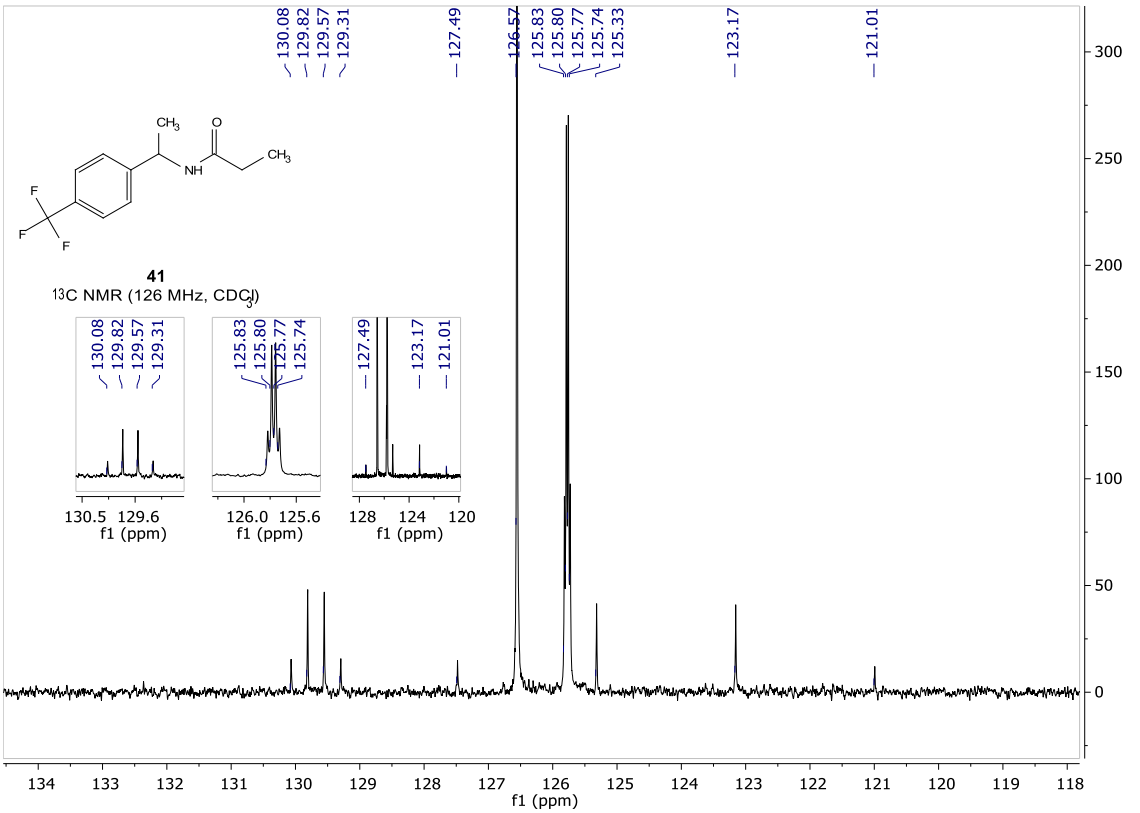

7.76
7.76
7.50
7.48
7.47
7.43
7.41
7.40
7.33
7.32
7.26 CDCl3
6.90
6.88
6.28
6.26
5.33
5.31
5.30
5.28
5.27
3.80
1.60
1.59
CH3
O
NH
O
CH3
39
1H NMR (500 MHz, CDCl3)
2.00
1.00
2.00
2.00
2.00
1.00
1.00
3.00
3.00
f1 (ppm)

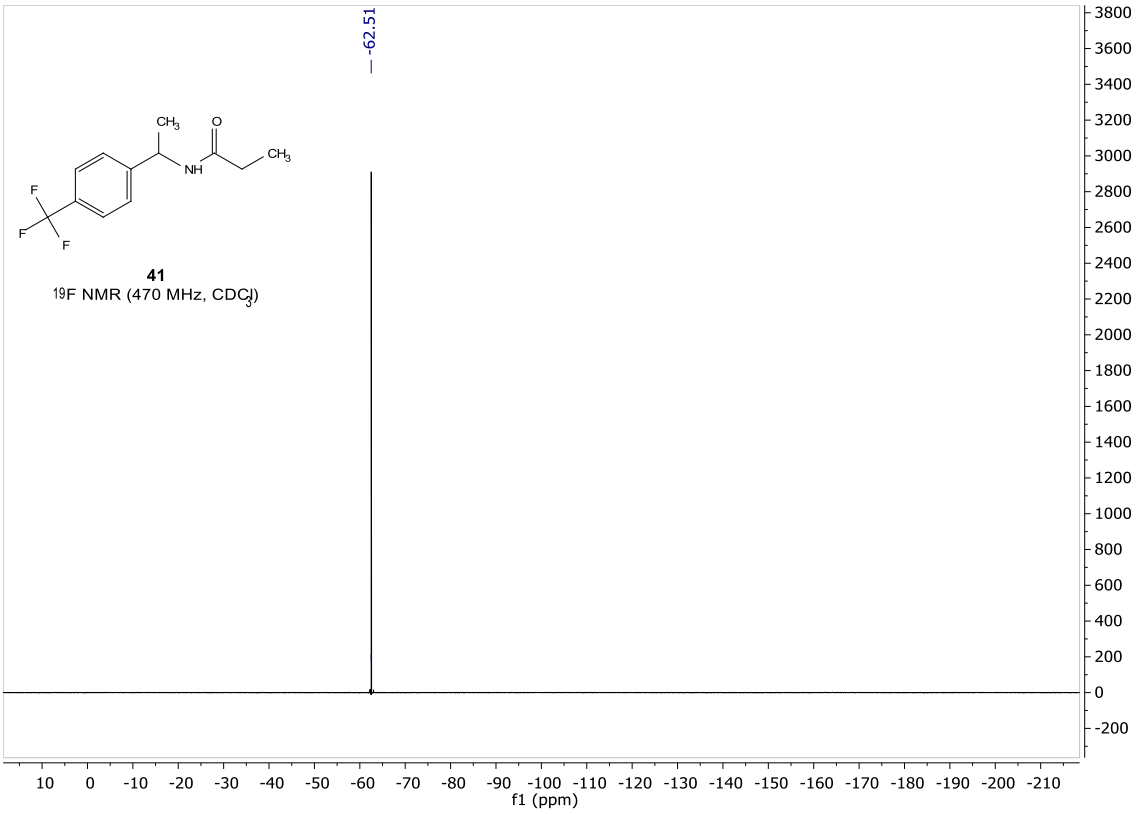

166.62
159.09
135.38
134.83
131.57
128.69
127.64
127.04
114.25
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
55.47
48.80
21.74
CH3
O
NH
O
CH3
39
13C NMR (126 MHz, CDCl3)
f1 (ppm)

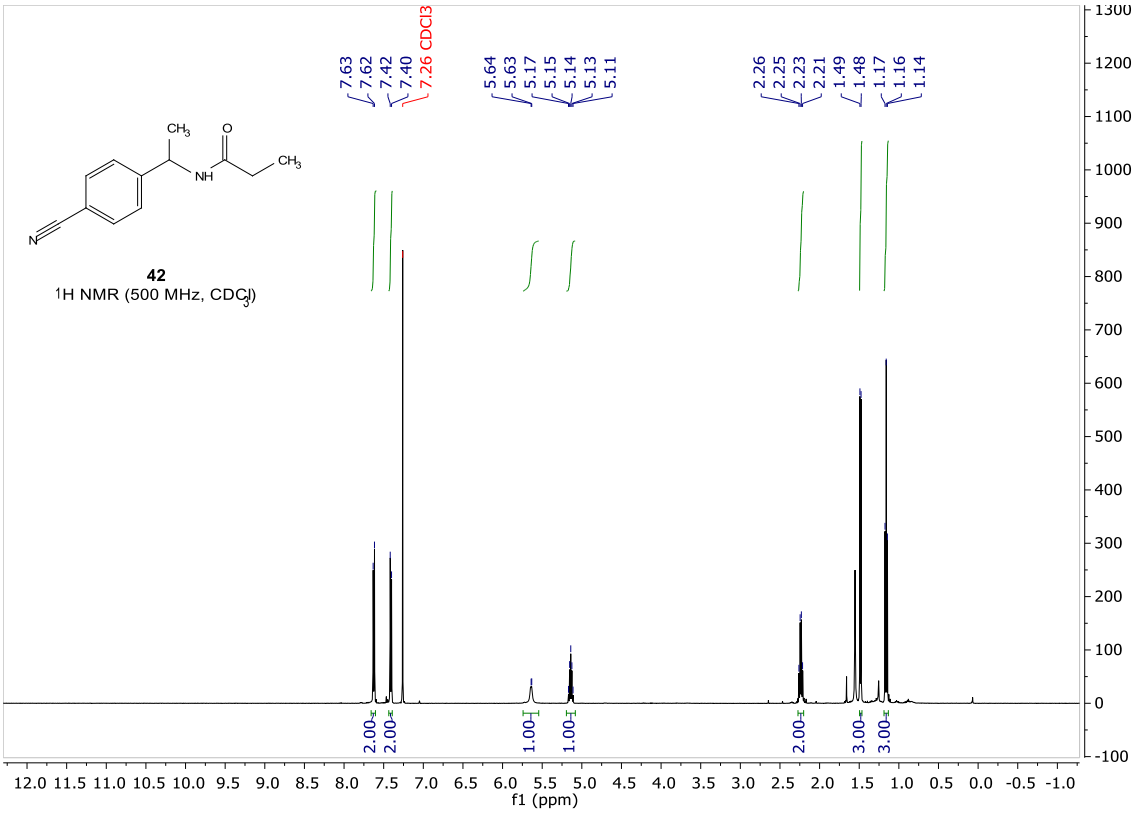

7.46
7.44
7.26 CDCl3
7.19
7.17
5.65
5.64
5.09
5.08
5.06
5.05
5.03
2.38
2.36
2.36
2.35
2.34
2.32
2.31
2.30
1.46
1.44
1.16
1.15
1.14
1.12
CH3
O
NH
CH3
CH3
Br
40
1H NMR (500 MHz, CDCl3)
2.00
2.00
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

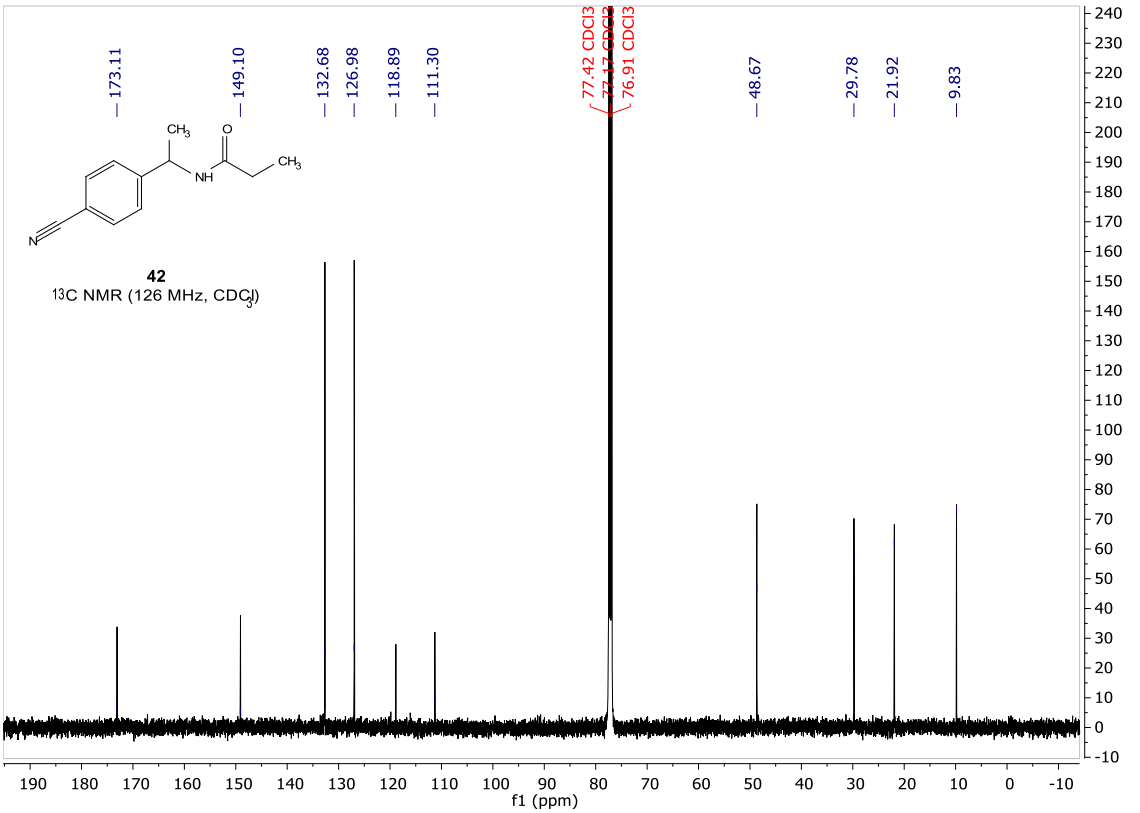

176.19
142.63
131.83
127.97
121.16
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
48.02
35.74
21.83
19.75
19.65
CH3
O
NH
CH3
CH3
Br
40
13C NMR (126 MHz, CDCl3)
f1 (ppm)

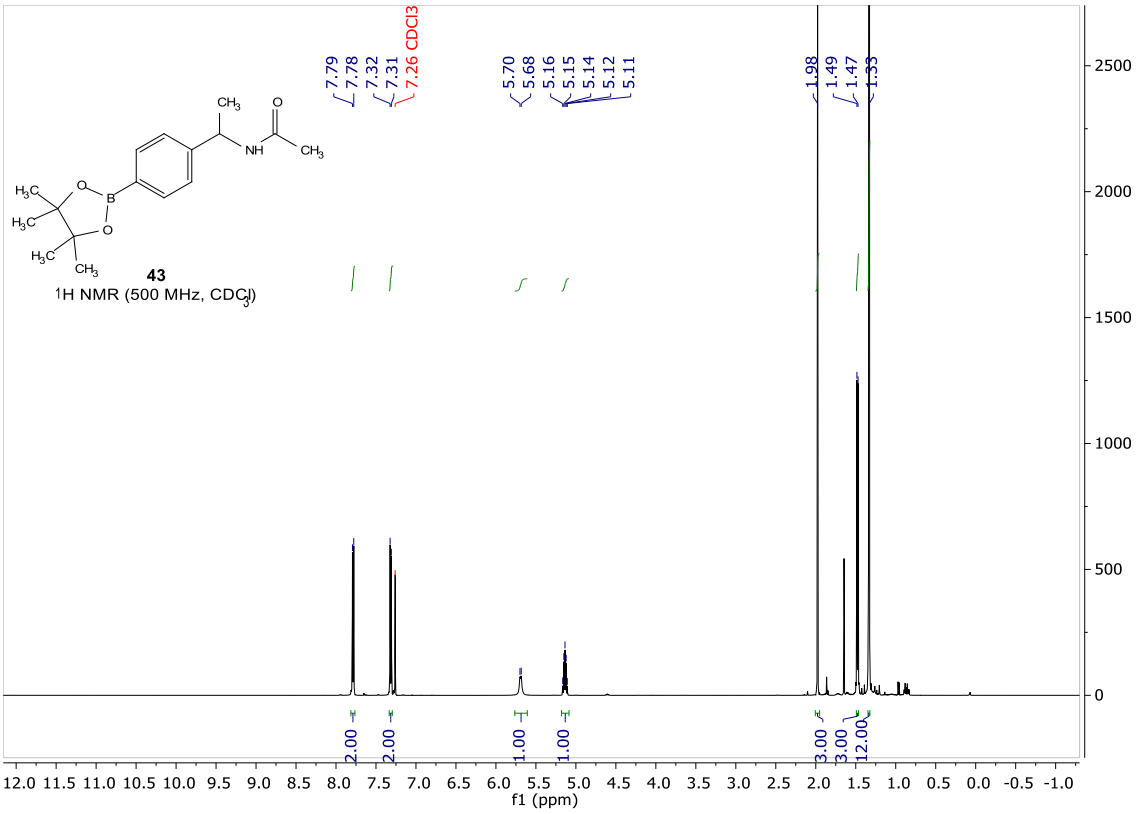

7.59
7.58
7.43
7.41
7.26 CDCl3
5.68
5.19
5.18
5.17
5.15
5.14
2.25
2.24
2.22
2.21
1.50
1.48
1.17
1.16
1.14
41
1H NMR (500 MHz, CDCl3)
2.00
2.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

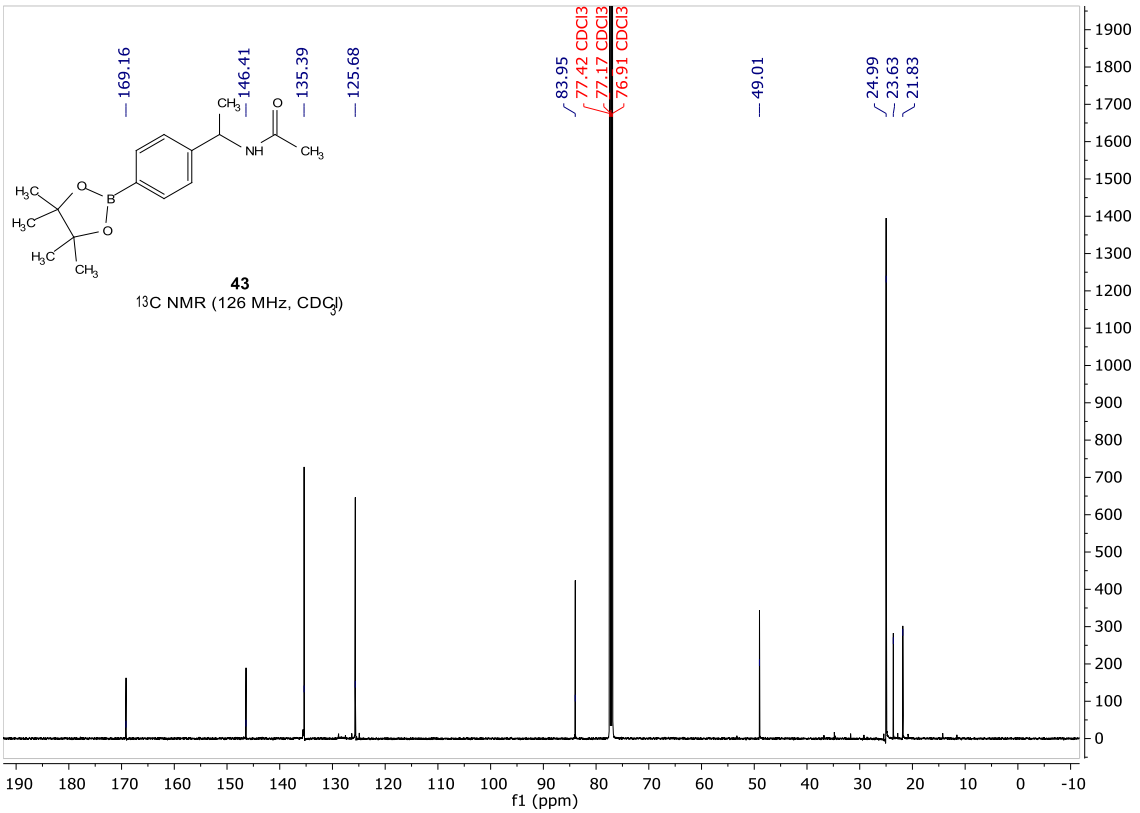

130.08
129.82
129.57
129.31
127.49
126.57
125.83
125.80
125.77
125.74
125.33
123.17
121.01
41
13C NMR (126 MHz, CDCl3)
f1 (ppm)

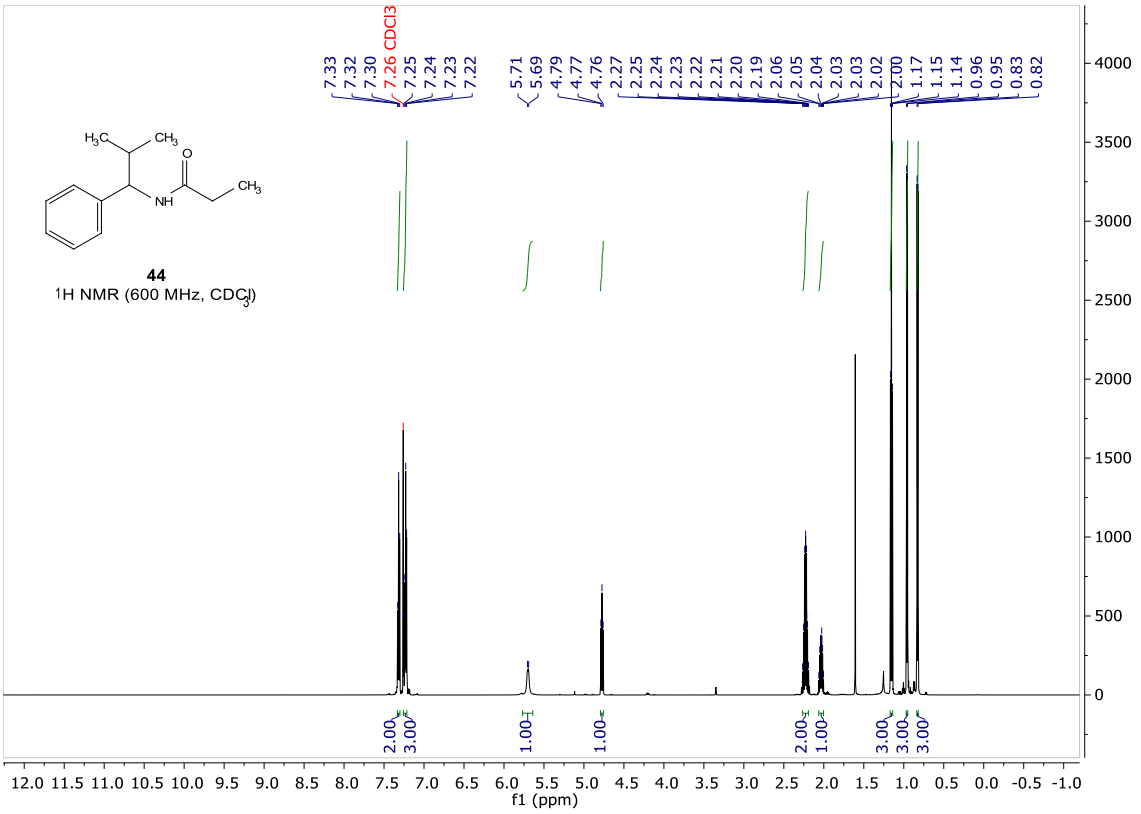

-62.51
CH3
O
NH
CH3
F
F
F
41
19F NMR (470 MHz, CDCl3)
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

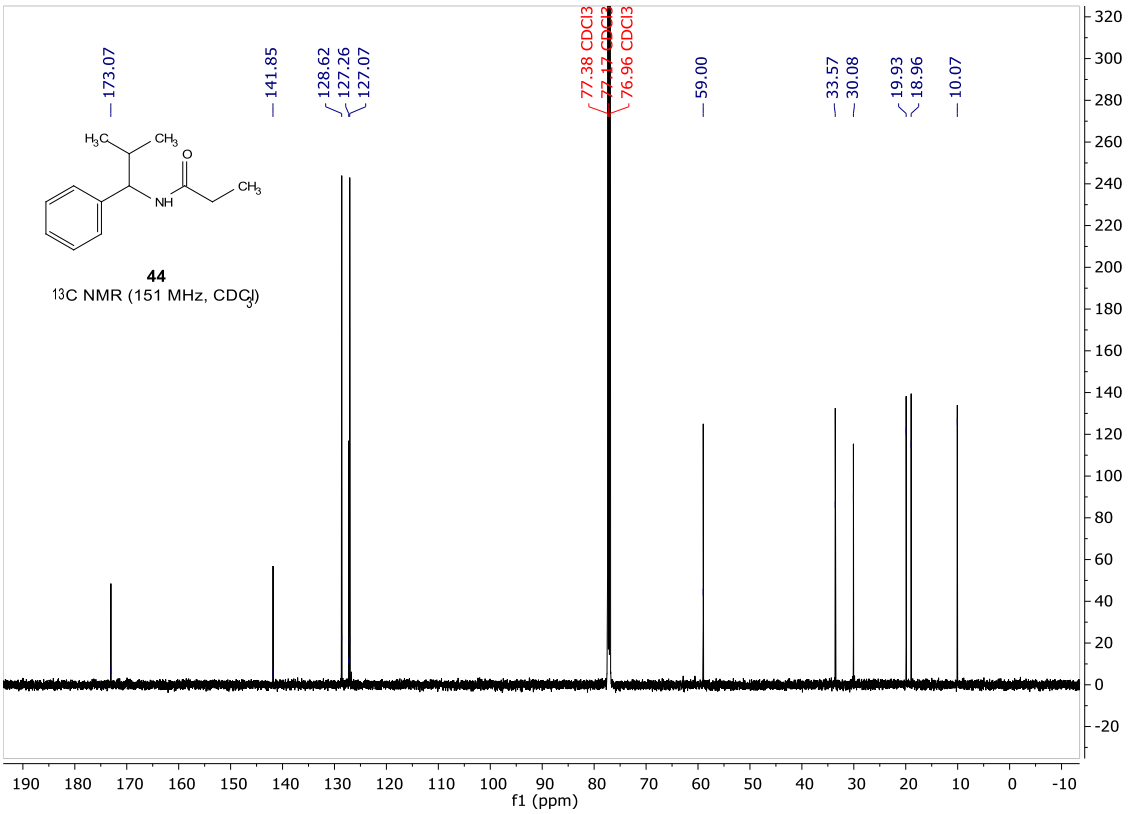

7.63
7.62
7.42
7.40
7.26 CDCl3
5.64
5.63
5.17
5.15
5.14
5.13
5.11
2.26
2.25
2.23
2.21
1.49
1.48
1.17
1.16
1.14
CH3
O
NH
CH3
N
42
1H NMR (500 MHz, CDCl3)
2.00
2.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

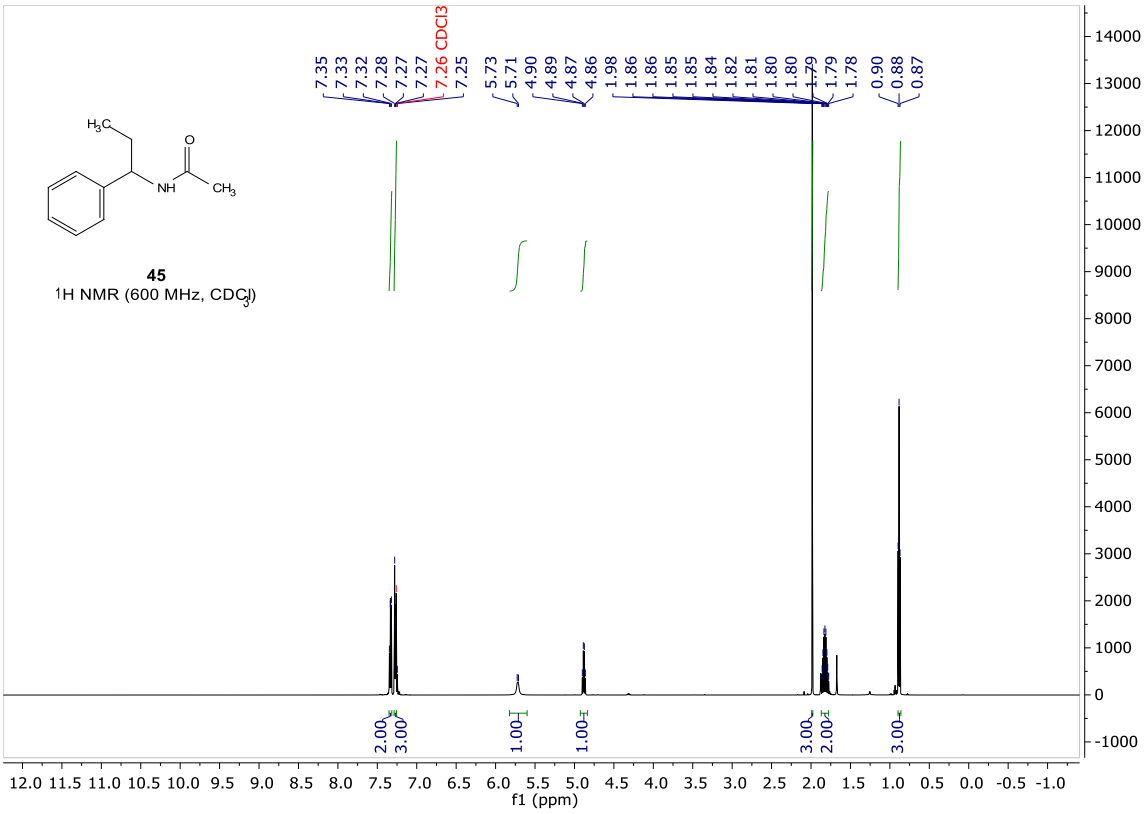

173.11
149.10
132.68
126.98
118.89
111.30
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
48.67
29.78
21.92
9.83
CH3
O
NH
CH3
N
42
13C NMR (126 MHz, CDCl3)
f1 (ppm)

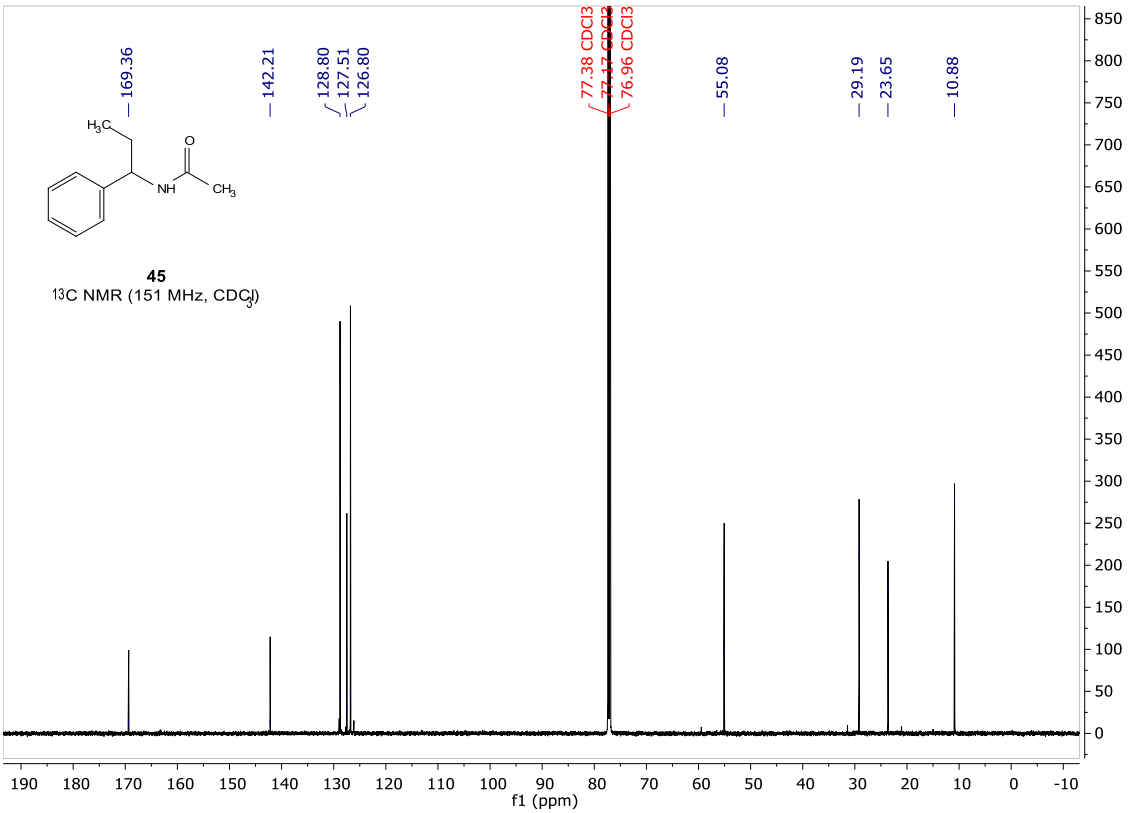

7.79
7.78
7.32
7.31
7.26 CDCl3
5.70
5.68
5.16
5.15
5.14
5.12
5.11
1.98
1.49
1.47
1.33
2.00
2.00
1.00
1.00
3.00
3.00
12.00
f1 (ppm)
43
1H NMR (500 MHz, CDCl3)

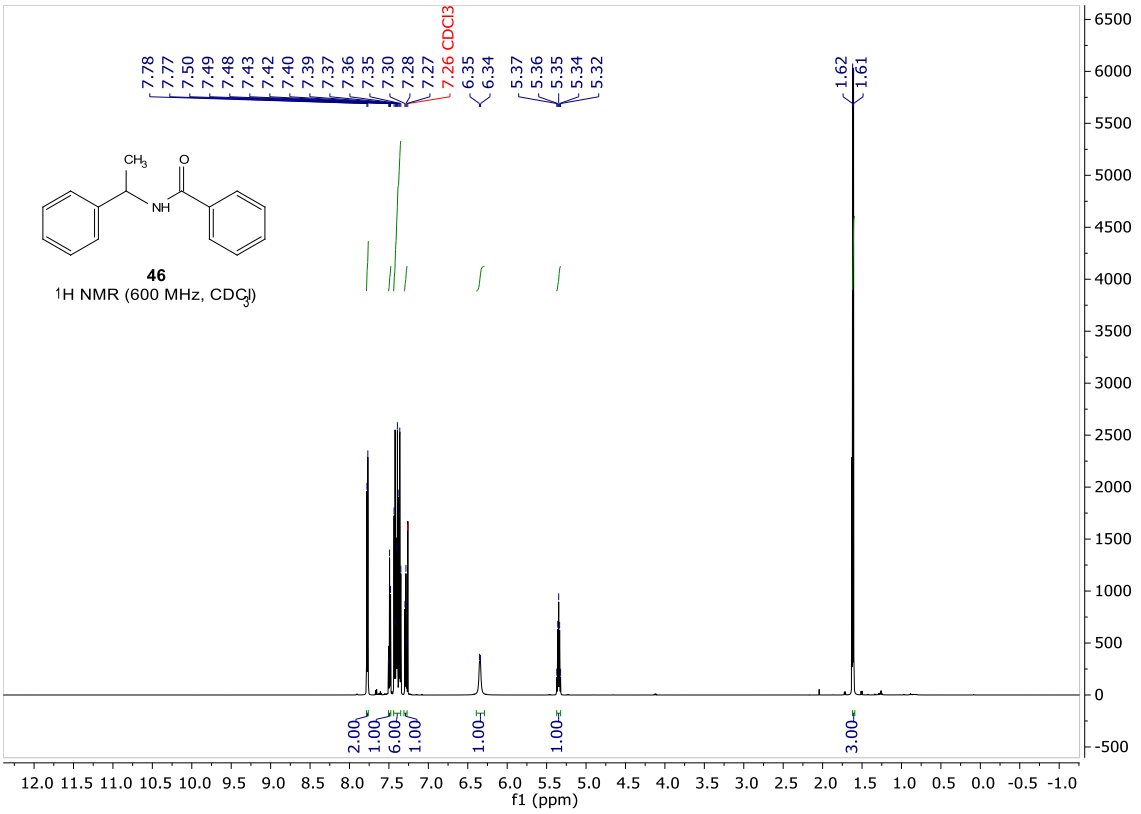

169.16
146.41
135.39
125.68
83.95
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
49.01
24.99
23.63
21.83
f1 (ppm)
43
13C NMR (126 MHz, CDCl3)

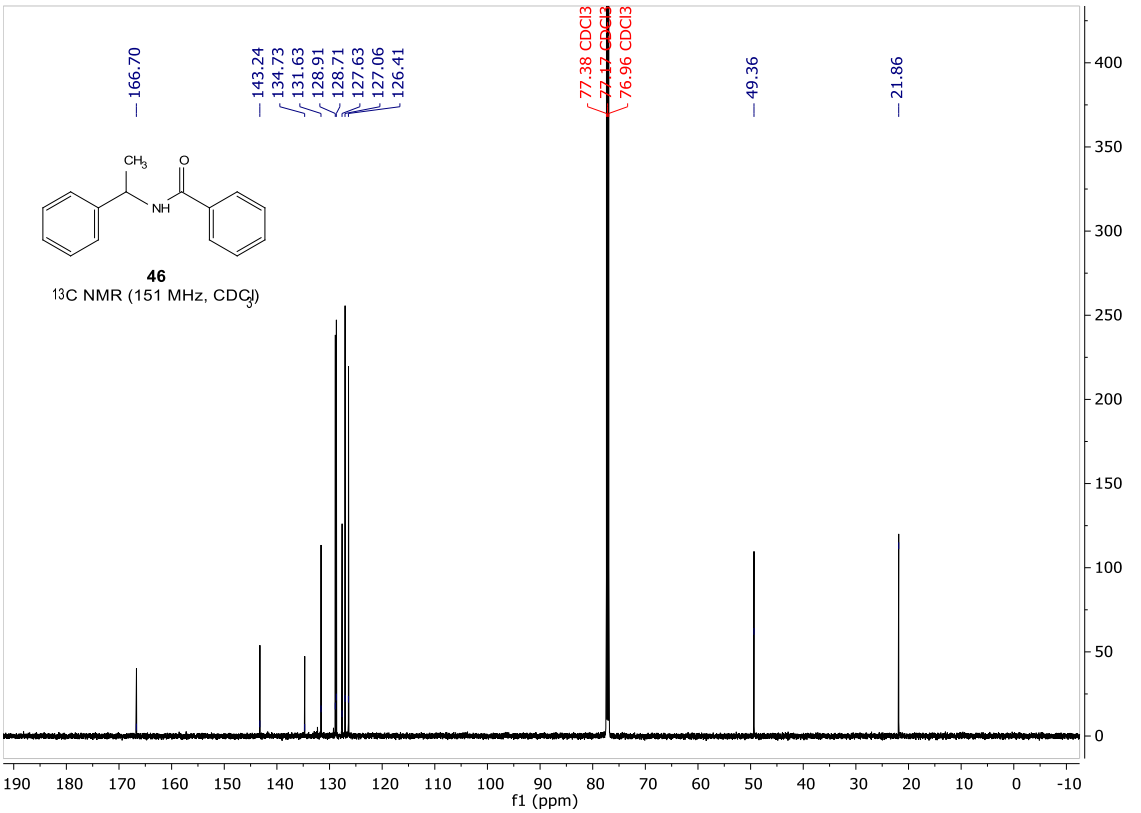

7.33
7.32
7.30
7.26 CDCl3
7.25
7.24
7.23
7.22
5.71
5.69
4.79
4.77
4.76
2.27
2.25
2.24
2.23
2.22
2.21
2.20
2.19
2.06
2.05
2.04
2.03
2.03
2.02
2.00
1.17
1.15
1.14
0.96
0.95
0.83
0.82
H3C
CH3
O
NH
CH3
44
1H NMR (600 MHz, CDCl3)
2.00
3.00
1.00
1.00
2.00
1.00
3.00
3.00
3.00
f1 (ppm)

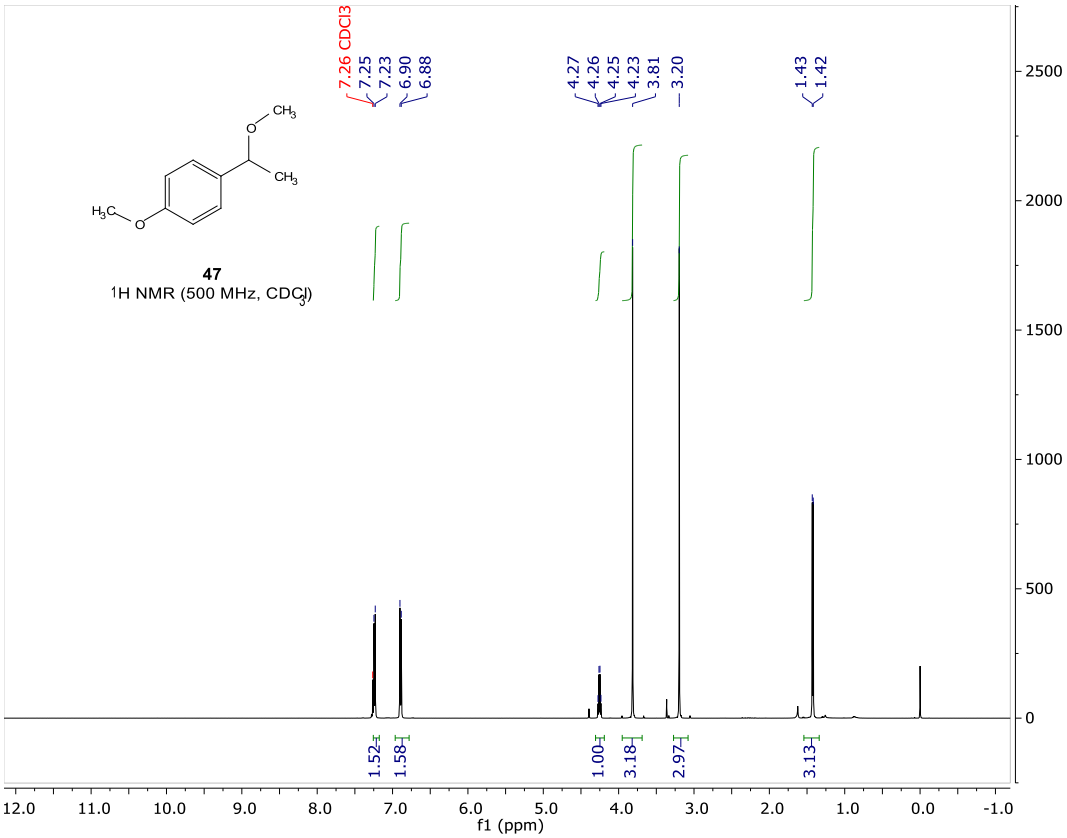

173.07
141.85
128.62
127.26
127.07
77.38 CDCl3
77.17 CDCl3
76.96 CDCl3
59.00
33.57
30.08
19.93
18.96
10.07
H3C
CH3
O
NH
CH3
44
13C NMR (151 MHz, CDCl3)
f1 (ppm)

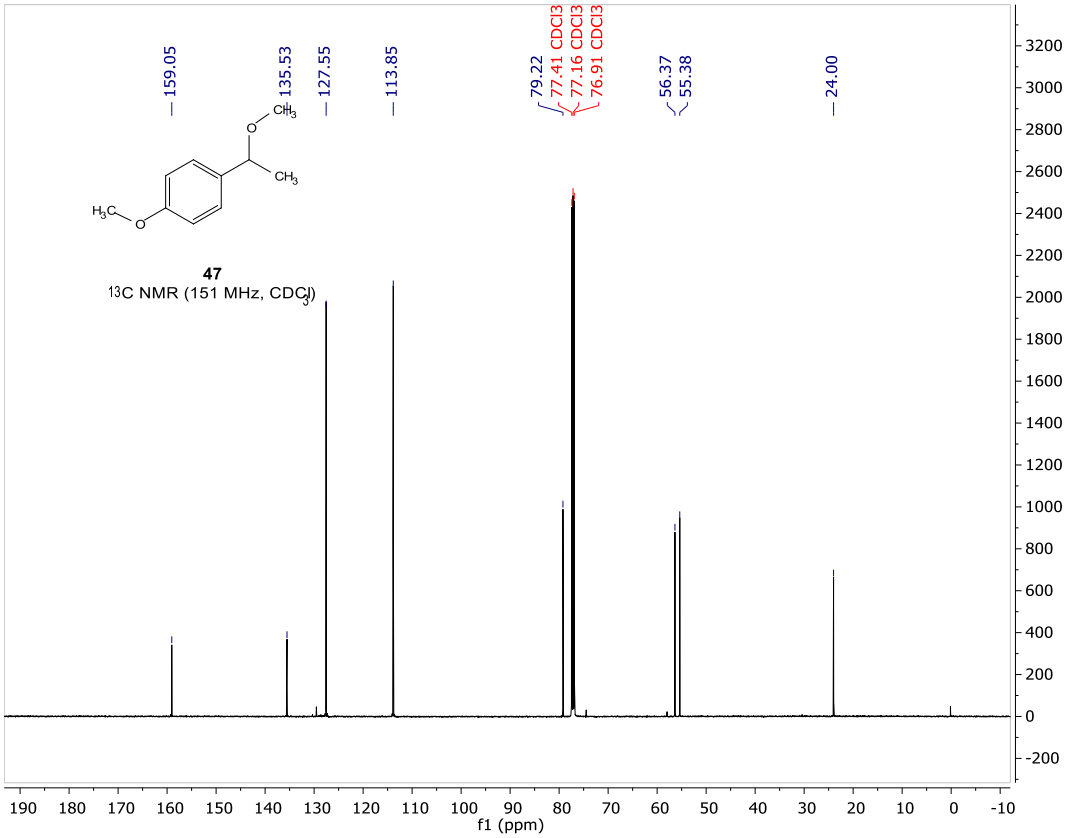

7.35
7.33
7.32
7.28
7.27
7.27
7.26 CDCl3
7.25
5.73
5.71
4.90
4.89
4.87
4.86
1.98
1.86
1.86
1.85
1.85
1.84
1.82
1.81
1.80
1.80
1.79
1.79
1.78
0.90
0.88
0.87
H3C
O
NH
CH3
45
1H NMR (600 MHz, CDCl3)
2.00
3.00
1.00
1.00
3.00
2.00
3.00
f1 (ppm)

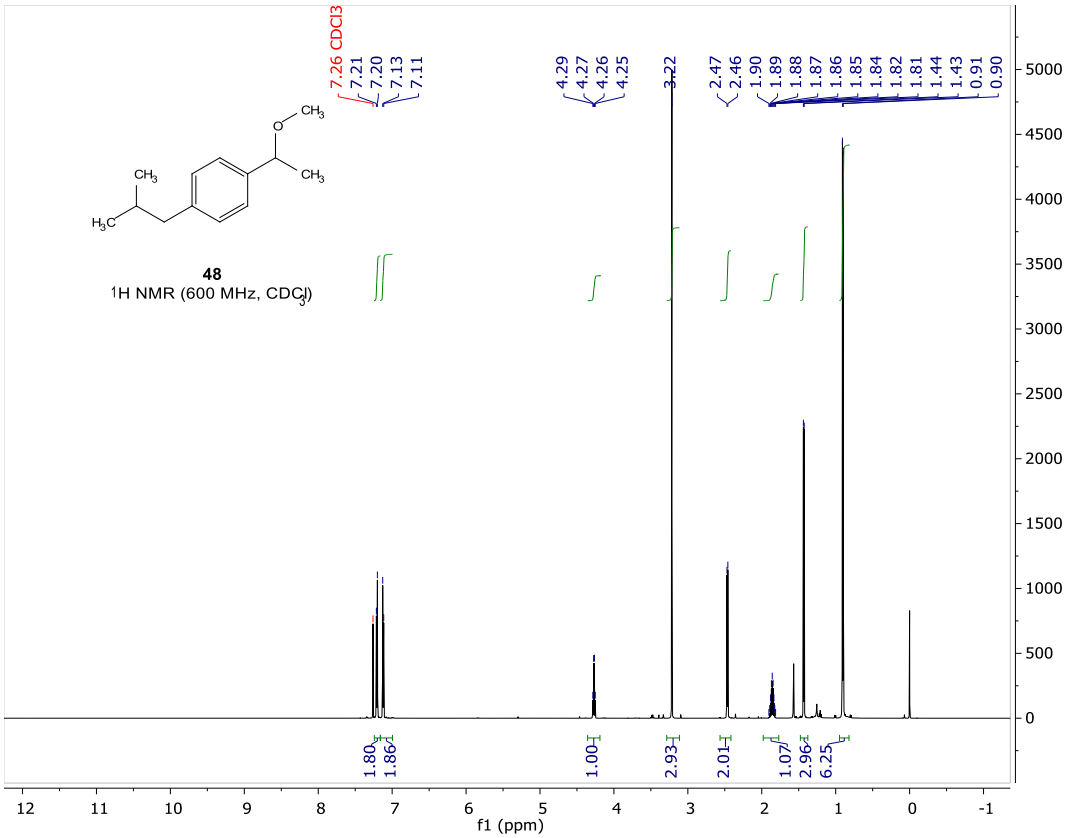

169.36
142.21
128.80
127.51
126.80
77.38 CDCl3
77.17 CDCl3
76.96 CDCl3
55.08
29.19
23.65
10.88
H3C
O
NH
CH3
45
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.78
7.77
7.50
7.49
7.48
7.43
7.42
7.40
7.39
7.37
7.36
7.35
7.30
7.28
7.27
7.26 CDCl3
6.35
6.34
5.37
5.36
5.35
5.34
5.32
1.62
1.61
CH3
O
NH
46
1H NMR (600 MHz, CDCl3)
2.00
1.00
6.00
1.00
1.00
1.00
3.00
f1 (ppm)


166.70
143.24
134.73
131.63
128.91
128.71
127.63
127.06
126.41
77.38 CDCl3
77.17 CDCl3
76.96 CDCl3
49.36
21.86
CH3
O
NH
46
13C NMR (151 MHz, CDCl3)
f1 (ppm)

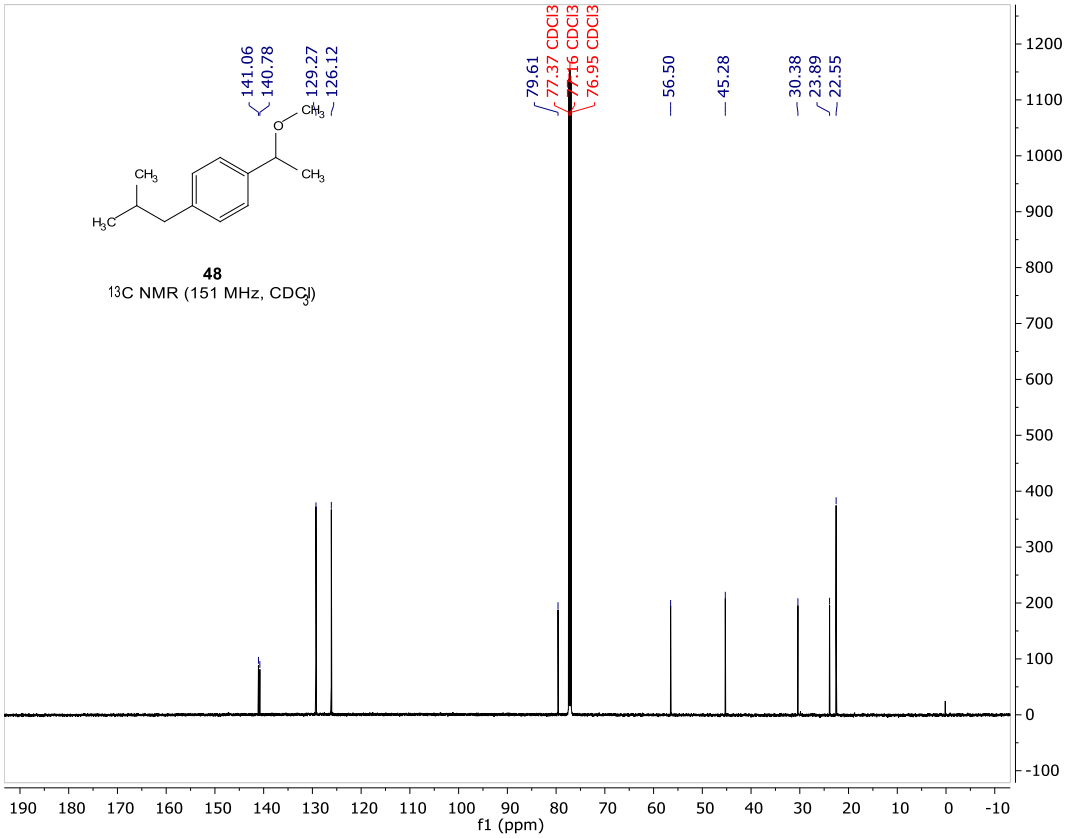

7.26 CDCl3
7.25
7.23
6.90
6.88
4.27
4.26
4.25
4.23
3.81
3.20
1.43
1.42
CH3
O
CH3
H3C
O
47
1H NMR (500 MHz, CDCl3)
1.52
1.58
1.00
3.18
2.97
3.13
2500
2000
1500
1000
500
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


159.05
135.53
127.55
113.85
79.22
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.37
55.38
24.00
CH3
O
CH3
H3C
O
47
13C NMR (151 MHz, CDCl3)
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



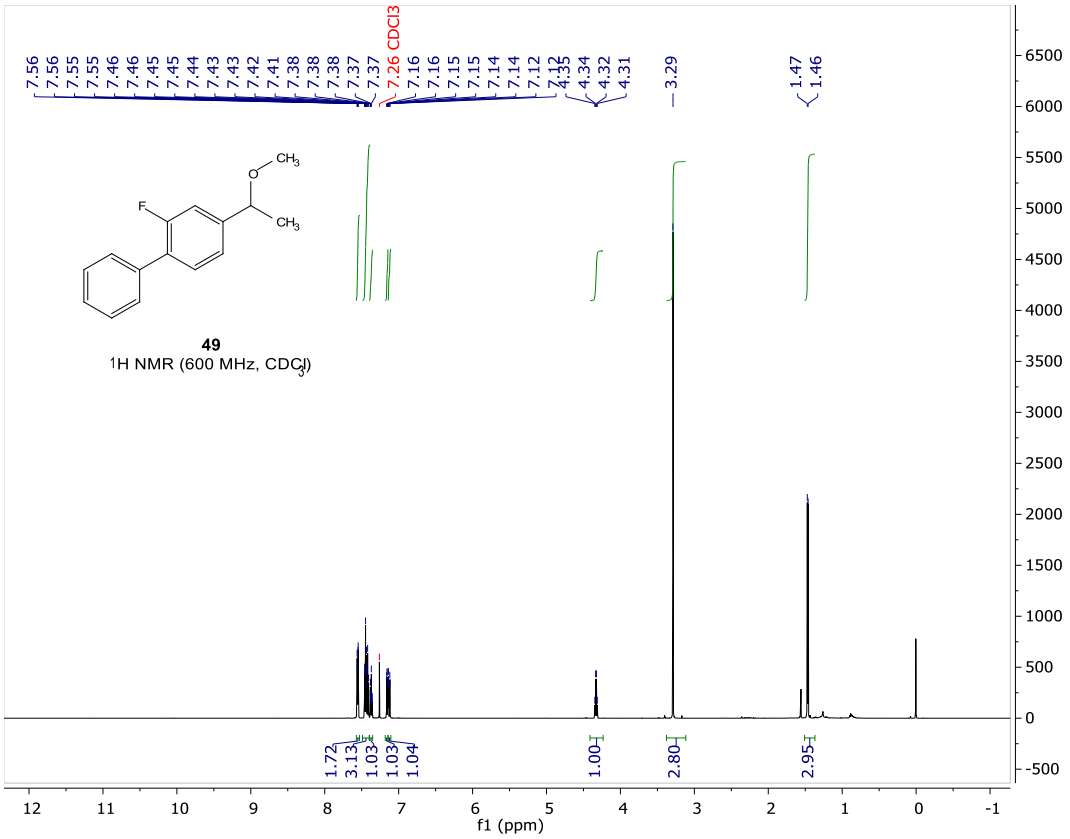
48

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



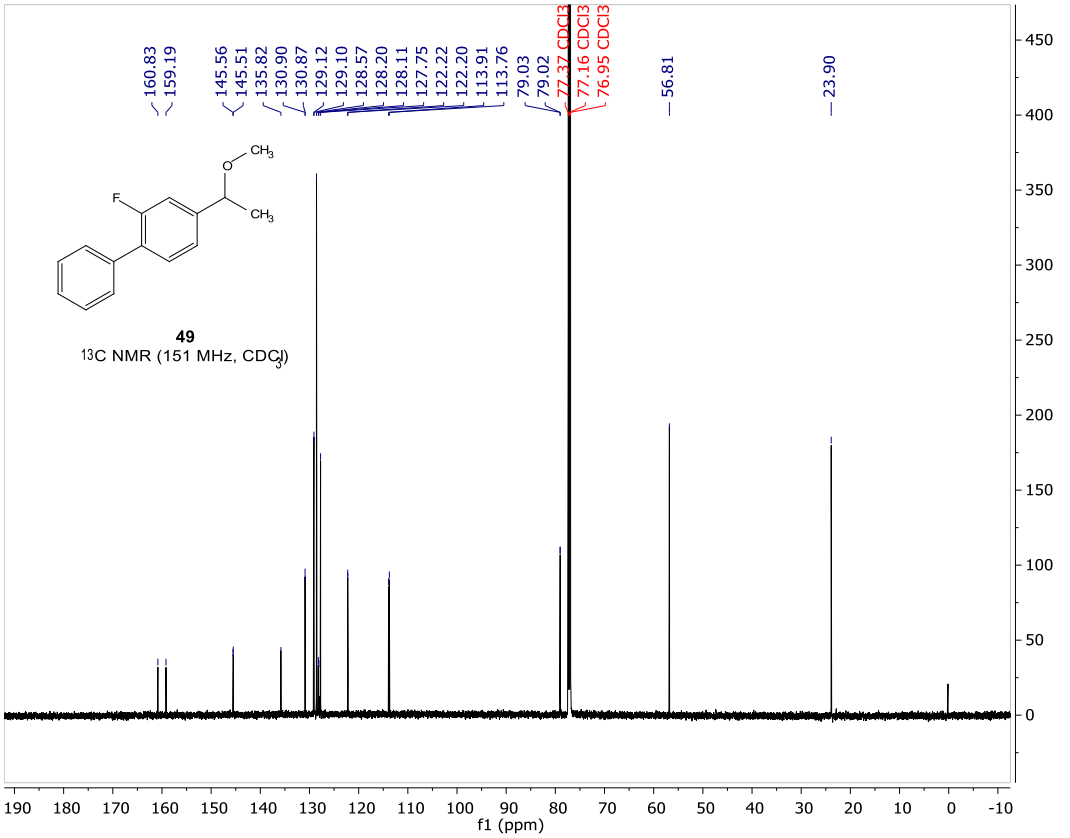
48

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



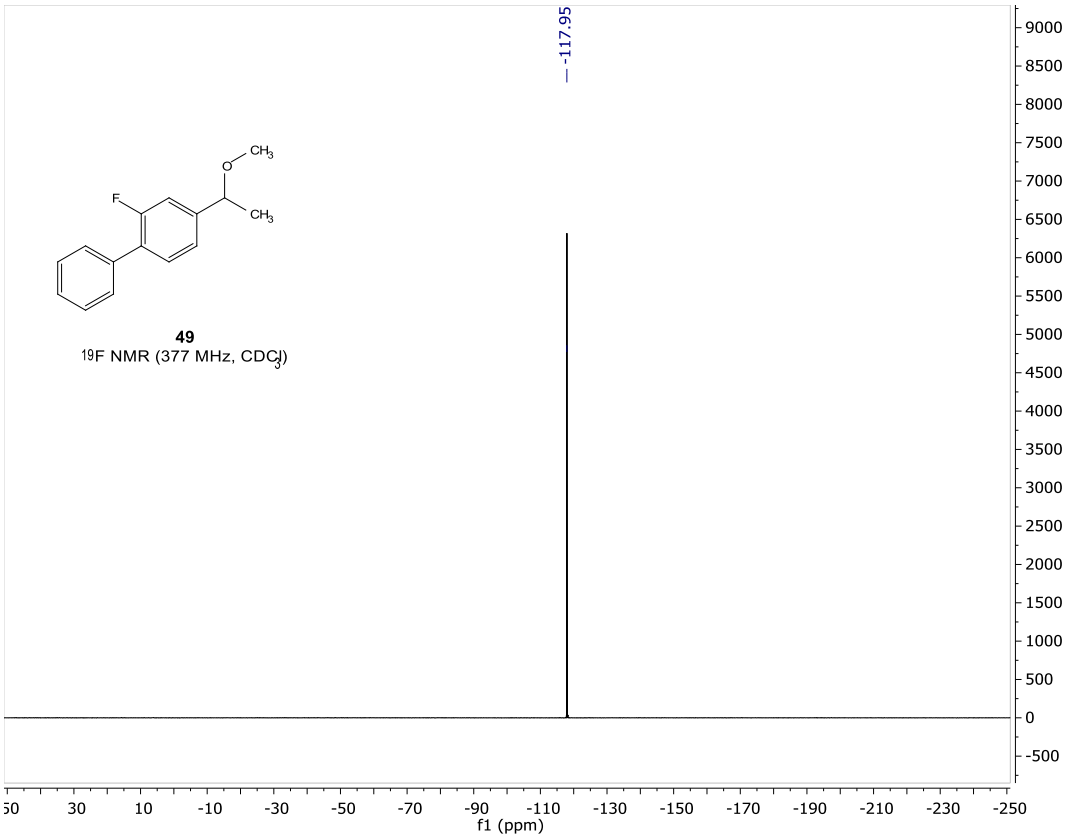
49

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



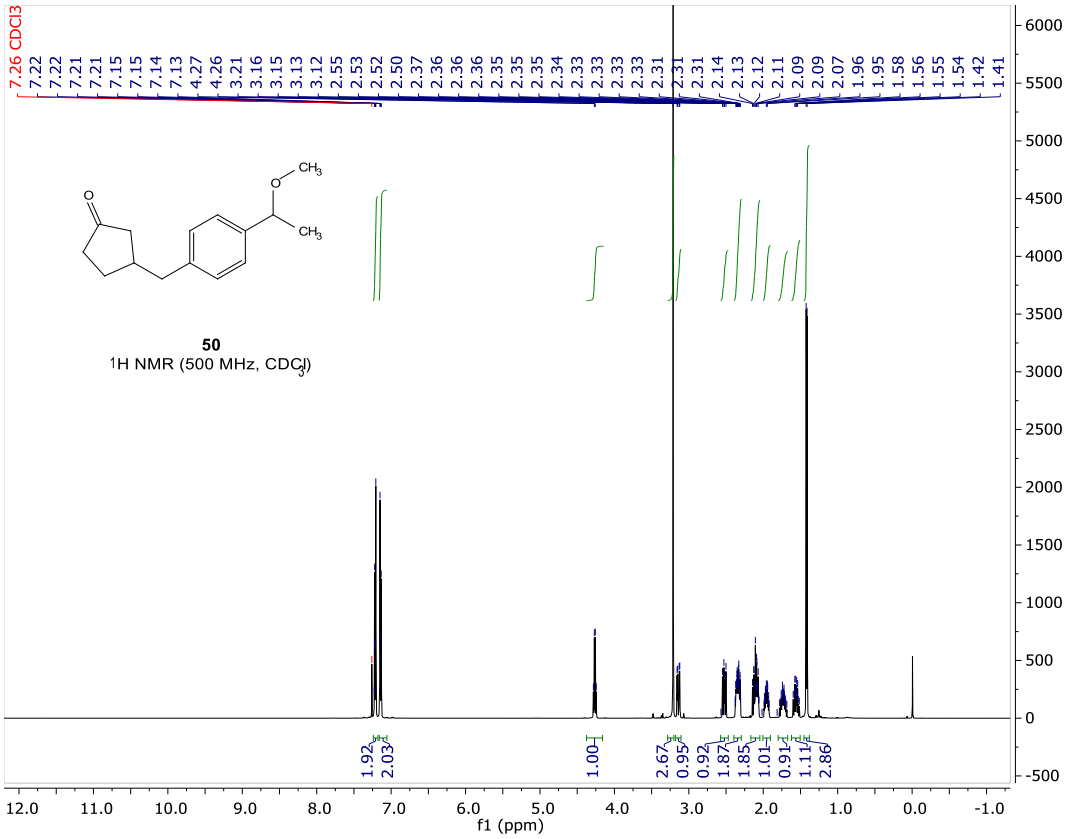
49

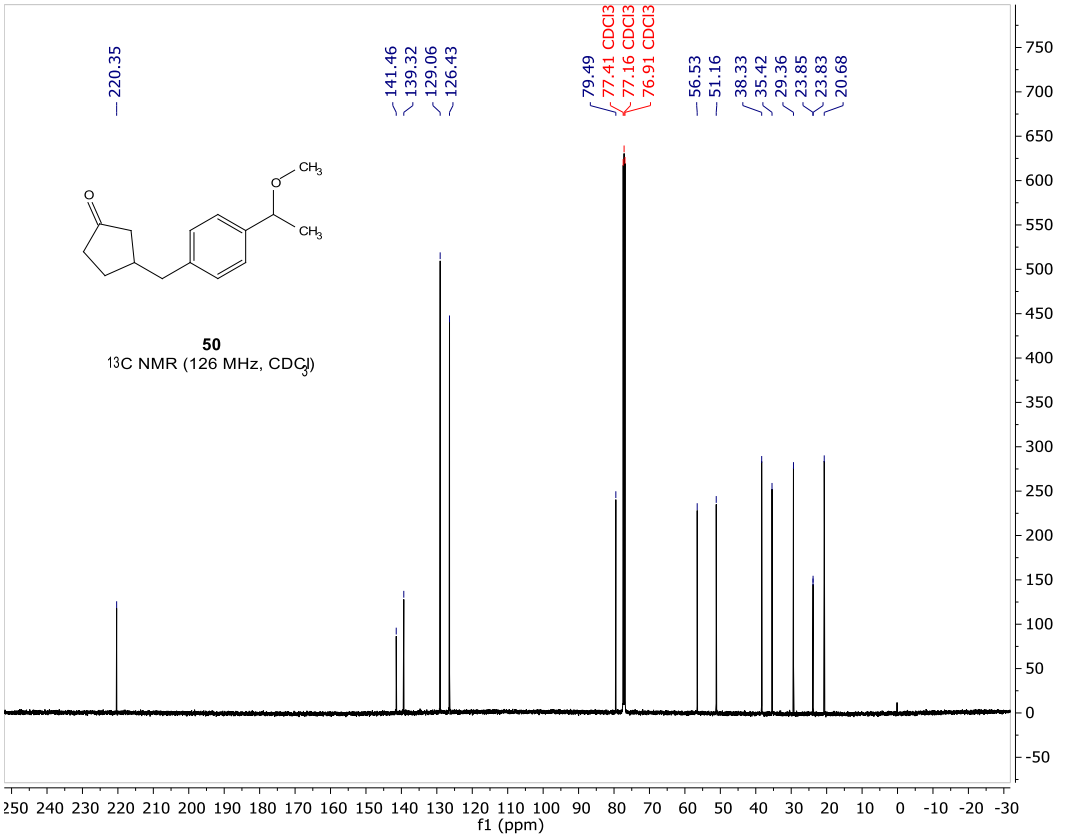
^{13}C NMR (151 MHz, $CDCl_3$)

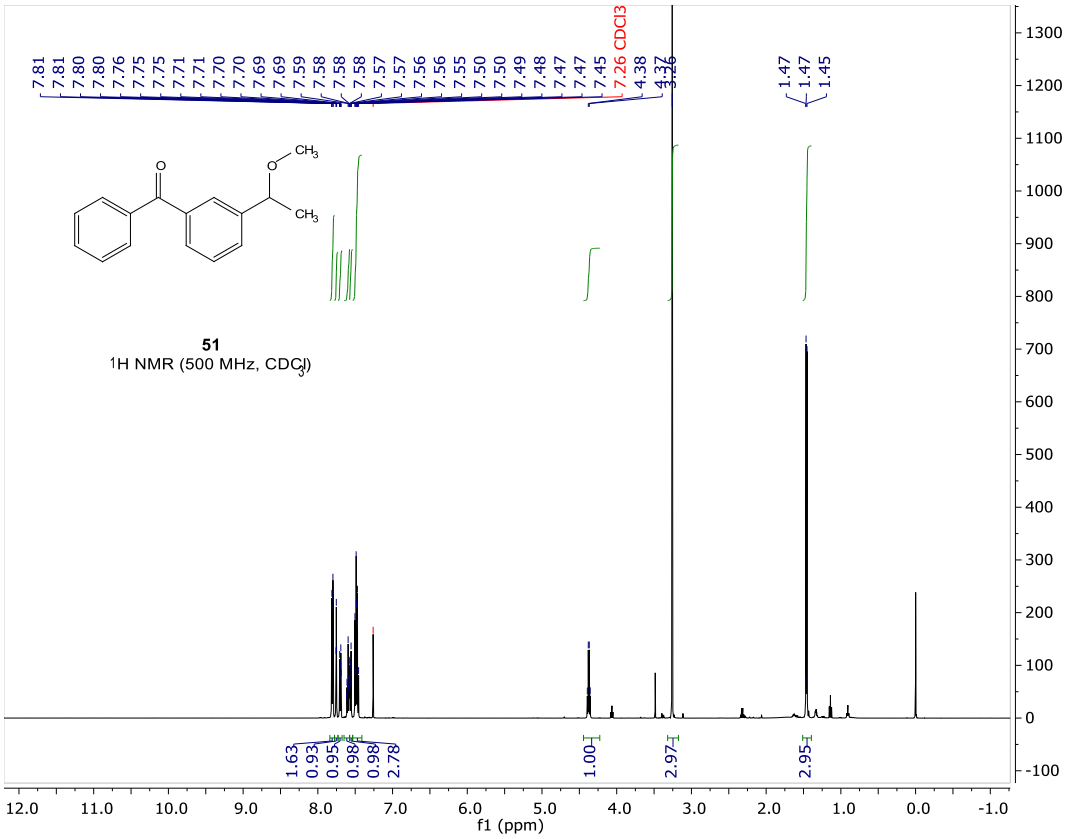


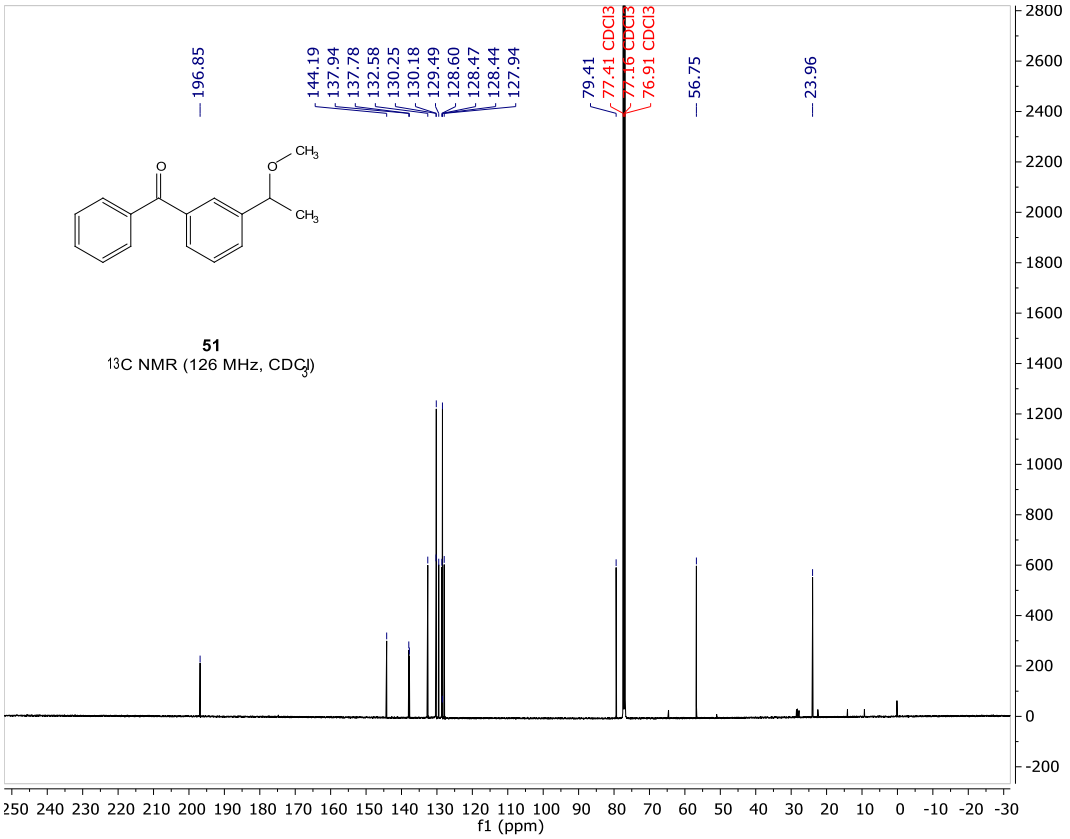
49

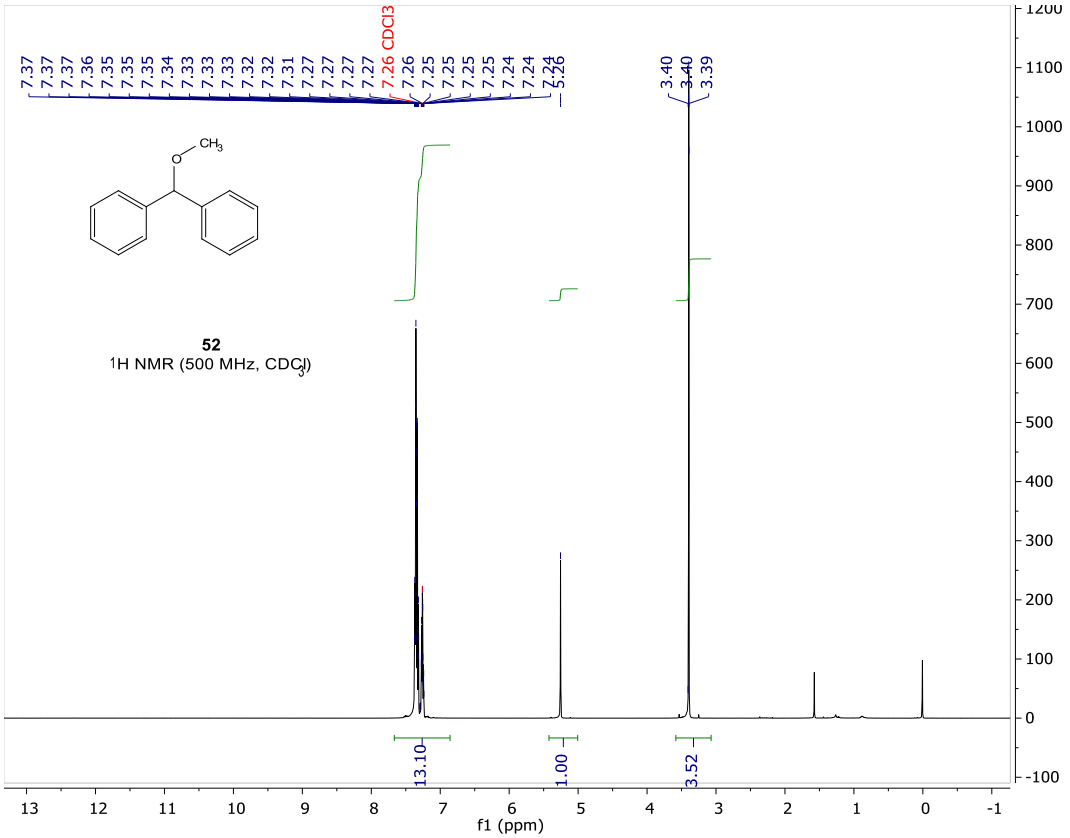
^{19}F NMR (377 MHz, $CDCl_3$)

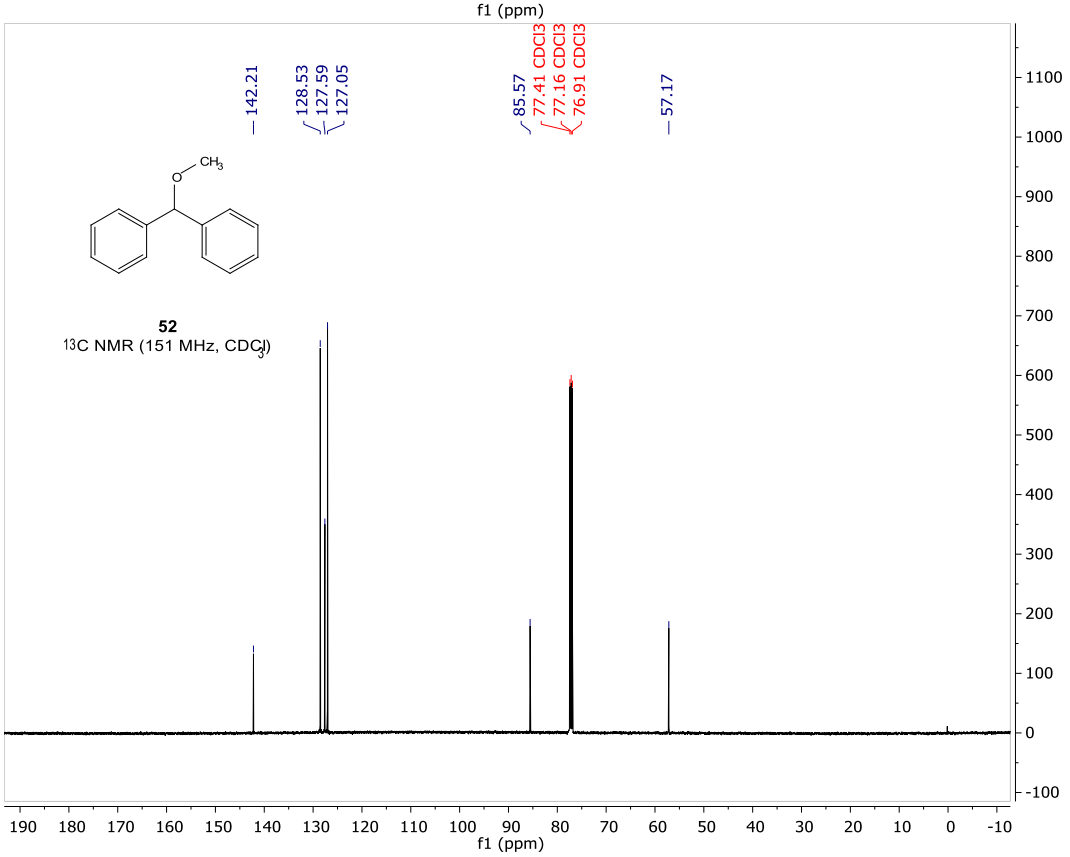

7.26 CDCl3
7.22
7.22
7.21
7.21
7.15
7.15
7.14
7.13
4.27
4.26
3.21
3.16
3.15
3.13
3.12
2.55
2.53
2.52
2.50
2.37
2.36
2.36
2.36
2.35
2.35
2.35
2.34
2.33
2.33
2.33
2.33
2.31
2.31
2.31
2.14
2.13
2.12
2.11
2.09
2.09
2.07
1.96
1.95
1.58
1.56
1.55
1.54
1.42
1.41
O
O
CH3
CH3
50
1H NMR (500 MHz, CDCl3)
1.92
2.03
1.00
2.67
0.95
0.92
1.87
1.85
1.01
0.91
1.11
2.86
f1 (ppm)

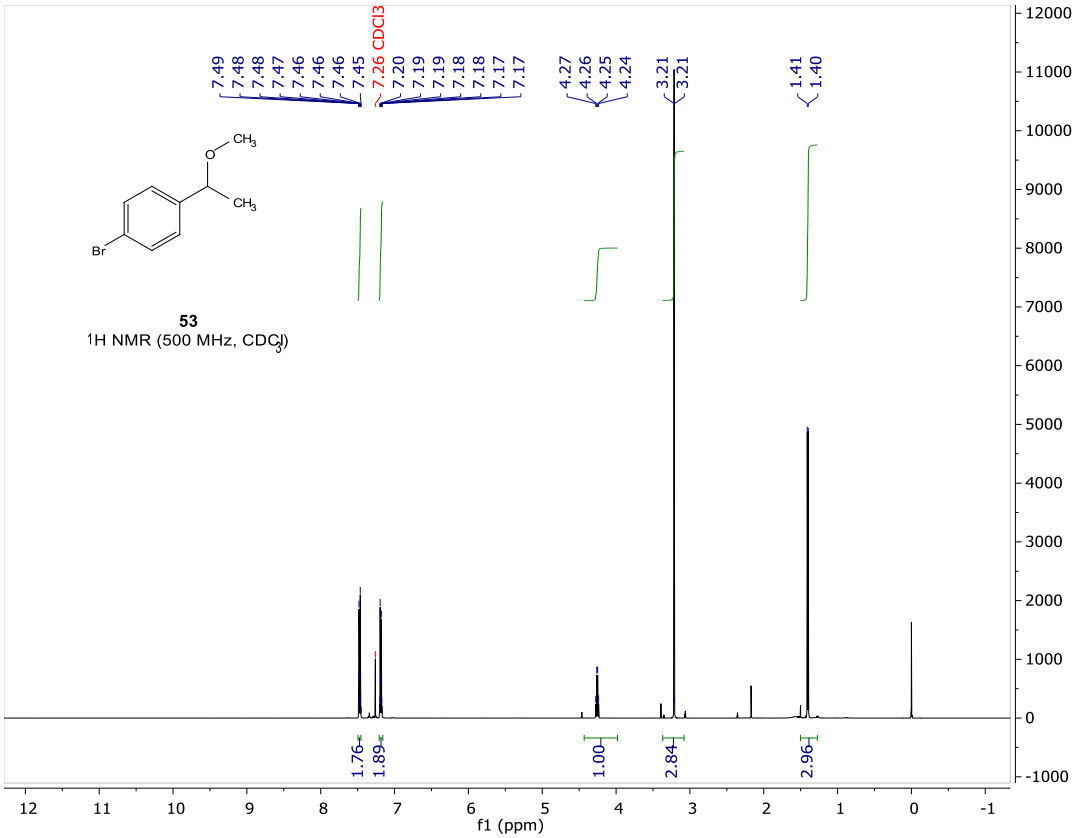

220.35
141.46
139.32
129.06
126.43
79.49
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.53
51.16
38.33
35.42
29.36
23.85
23.83
20.68
O
O
CH3
CH3
50
13C NMR (126 MHz, CDCl3)
f1 (ppm)

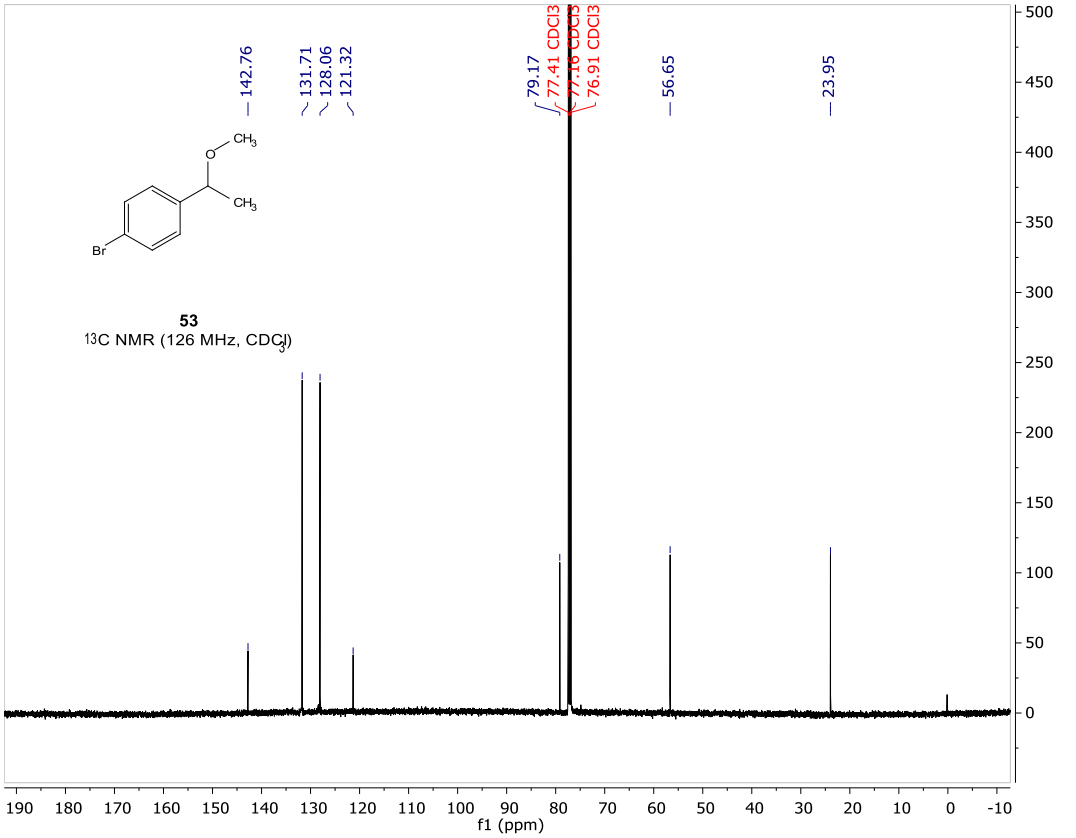

7.81 7.81 7.80 7.80 7.76 7.75 7.75 7.71 7.71 7.70 7.70 7.69 7.69 7.59 7.58 7.58 7.58 7.57 7.57 7.56 7.56 7.55 7.50 7.50 7.49 7.48 7.47 7.47 7.45 7.26 CDCl3 4.38 4.37 3.26 1.47 1.47 1.45
O
O
CH3
CH3
51
1H NMR (500 MHz, CDCl3)
1.63 0.93 0.95 0.98 0.98 2.78 1.00 2.97 2.95
f1 (ppm)

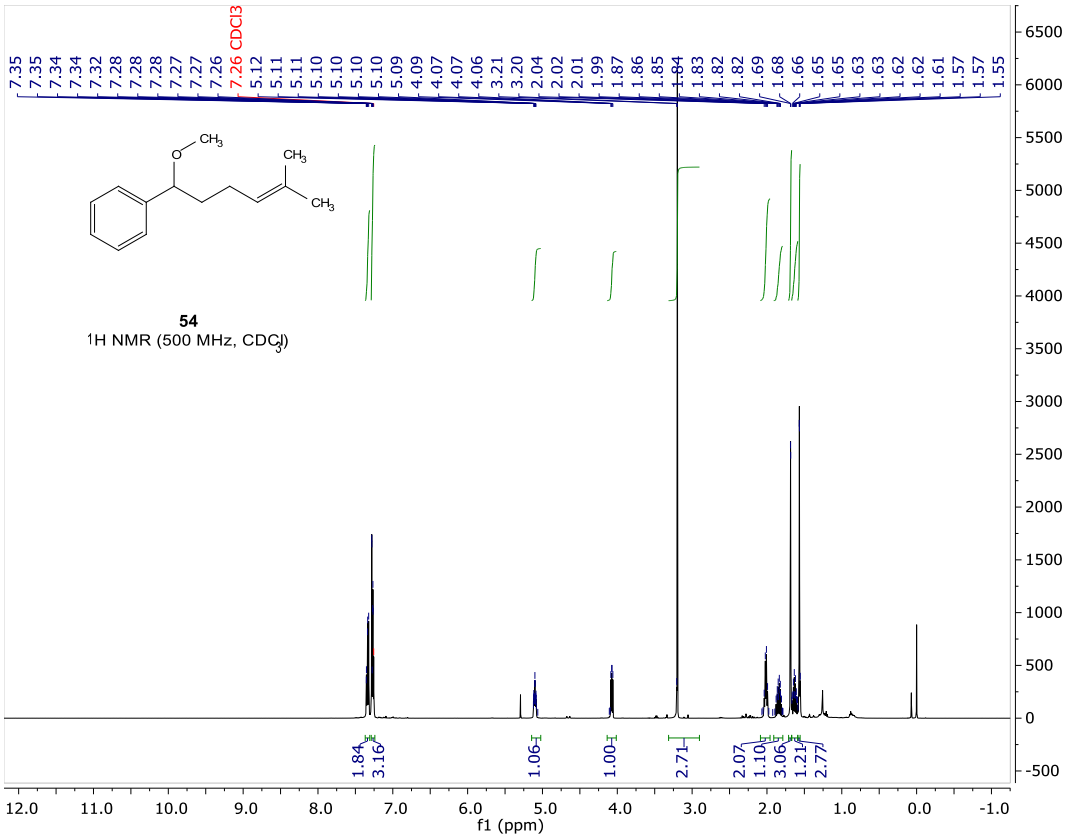

196.85 144.19 137.94 137.78 132.58 130.25 130.18 129.49 128.60 128.47 128.44 127.94 79.41 77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 56.75 23.96
O
O
CH3
CH3
51
13C NMR (126 MHz, CDCl3)
f1 (ppm)

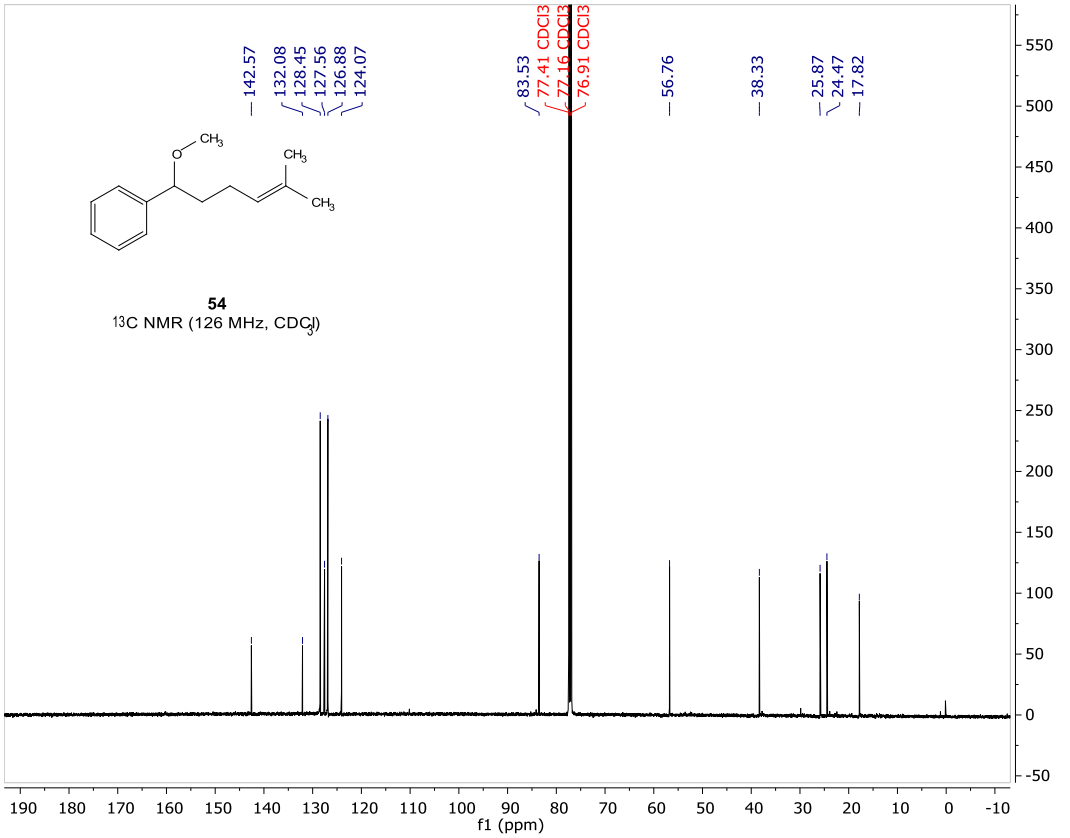

7.37
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.27
7.27
7.27
7.27
7.26 CDCl3
7.26
7.25
7.25
7.25
7.25
7.24
7.24
7.24
5.26
3.40
3.40
3.39
CH3
O
52
1H NMR (500 MHz, CDCl3)
13.10
1.00
3.52
f1 (ppm)

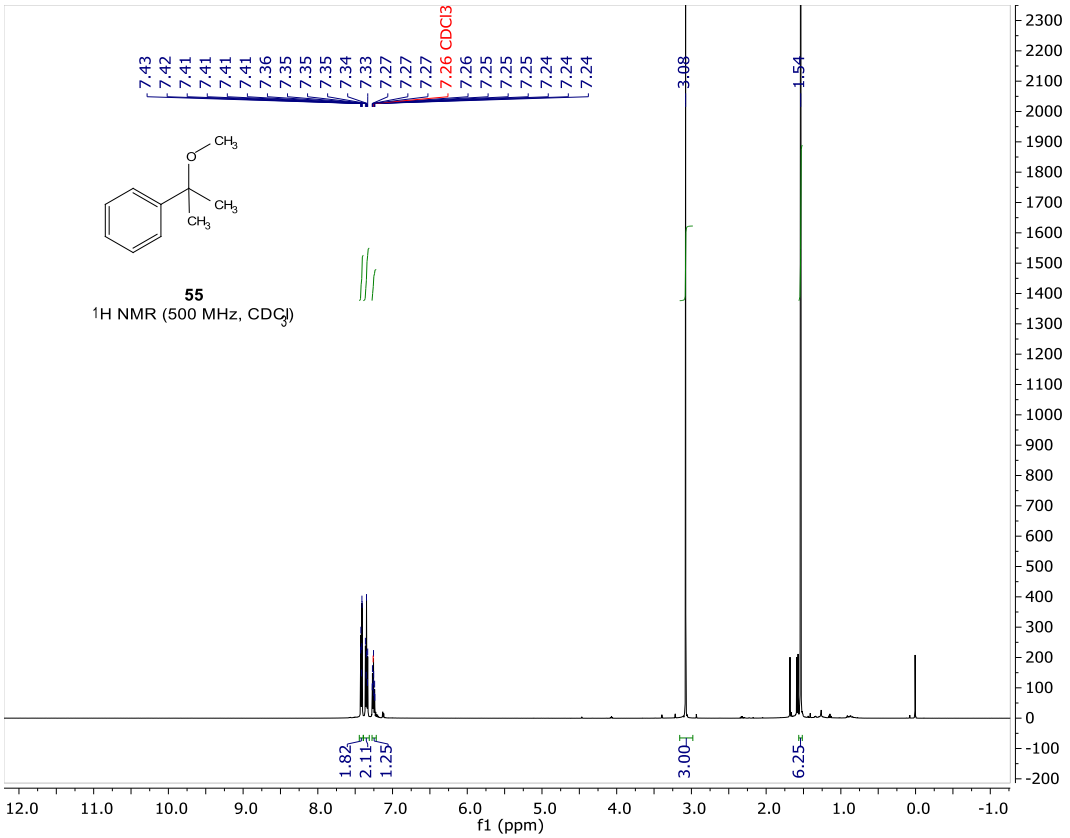

142.21
128.53
127.59
127.05
85.57
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
57.17
CH3
O
52
13C NMR (151 MHz, CDCl3)
f1 (ppm)

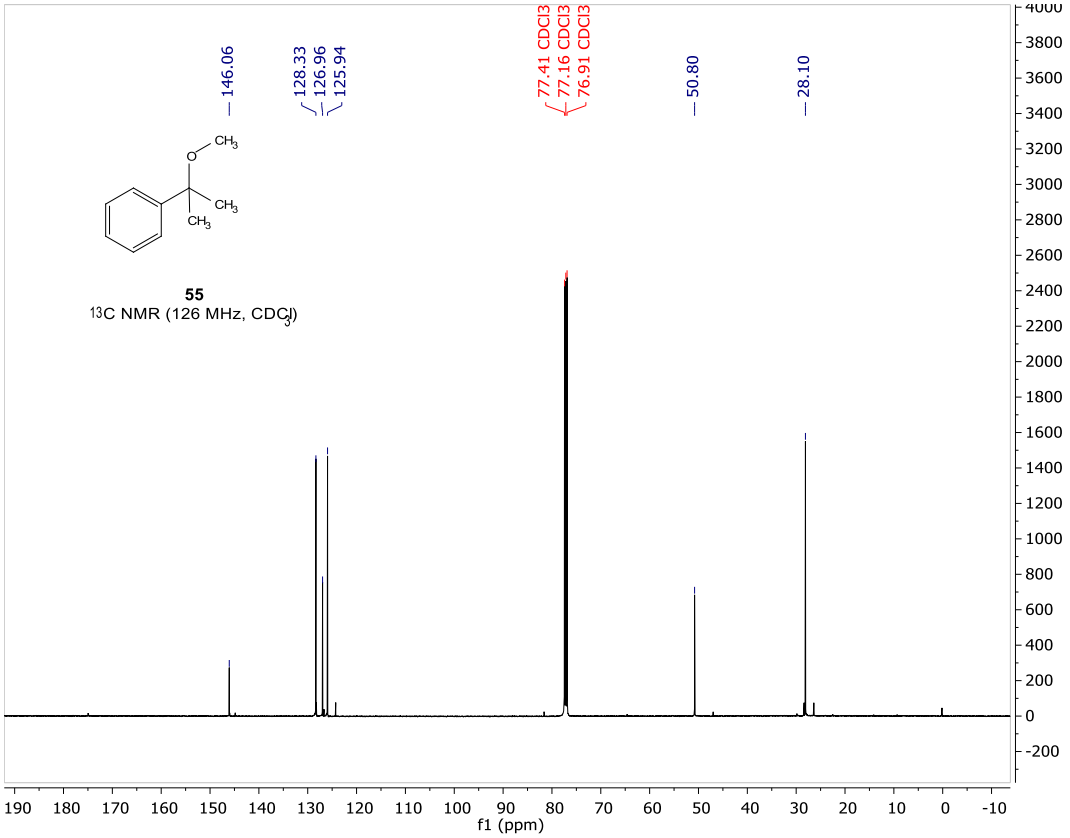

7.49
7.48
7.48
7.47
7.46
7.46
7.46
7.45
7.26 CDCl3
7.20
7.19
7.19
7.18
7.18
7.17
7.17
4.27
4.26
4.25
4.24
3.21
3.21
1.41
1.40
CH3
O
CH3
Br
53
1H NMR (500 MHz, CDCl3)
1.76
1.89
1.00
2.84
2.96
f1 (ppm)

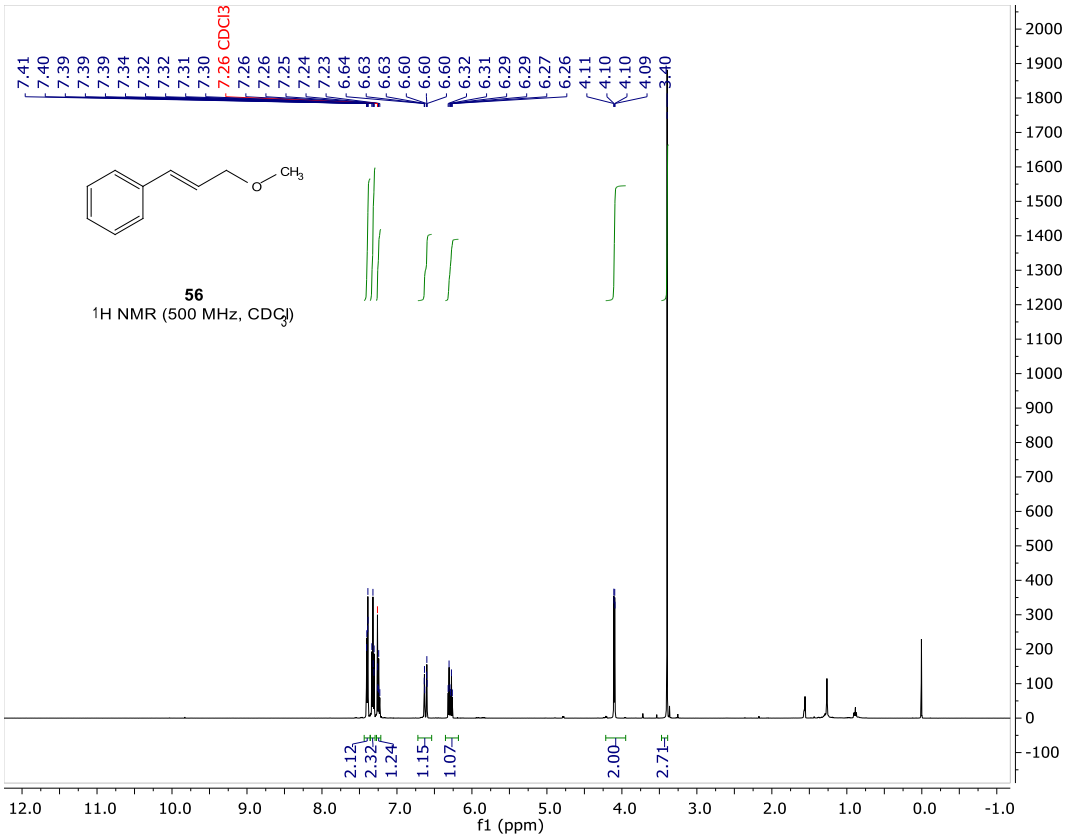

142.76
131.71
128.06
121.32
79.17
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.65
23.95
CH3
O
CH3
Br
53
13C NMR (126 MHz, CDCl3)
f1 (ppm)

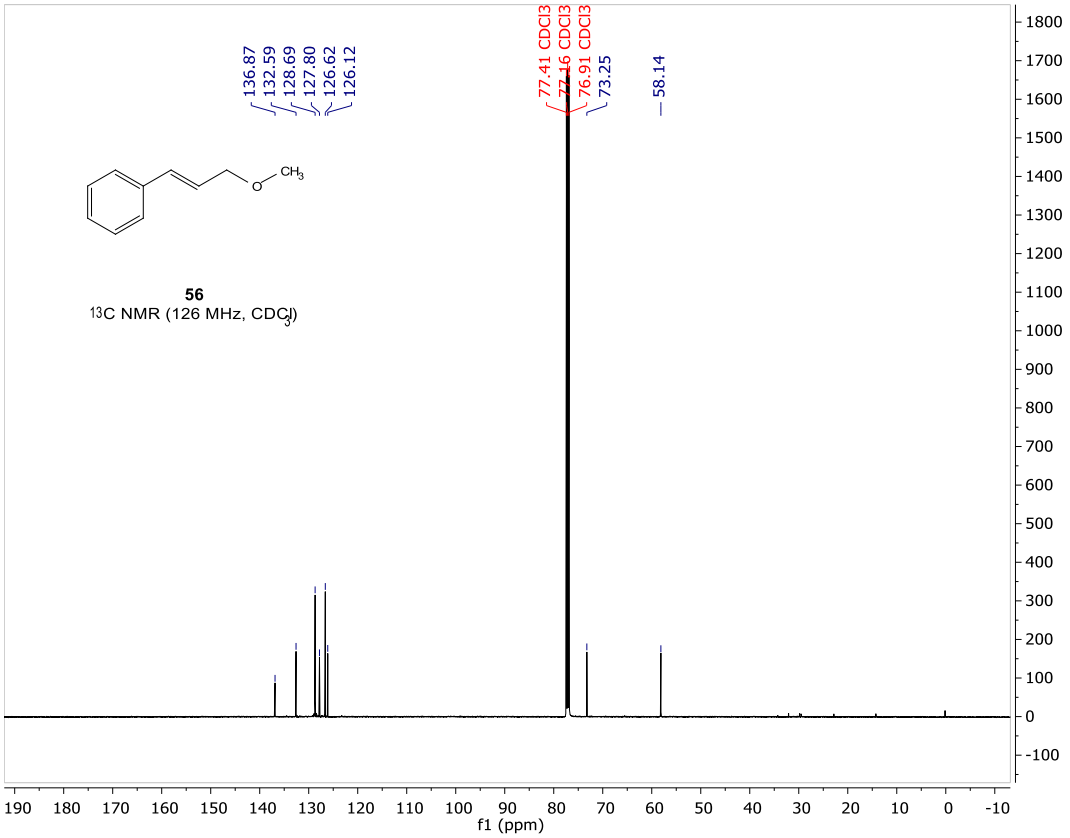

7.35 7.35 7.34 7.34 7.32 7.28 7.28 7.28 7.27 7.27 7.26 7.26 CDCl3 5.12 5.11 5.11 5.10 5.10 5.10 5.10 5.09 4.09 4.07 4.07 4.06 3.21 3.20 2.04 2.02 2.01 1.99 1.87 1.86 1.85 1.84 1.83 1.82 1.82 1.69 1.68 1.66 1.65 1.65 1.63 1.63 1.62 1.62 1.61 1.57 1.57 1.55
CH3
O
CH3
CH3
54
1H NMR (500 MHz, CDCl3)
1.84
3.16
1.06
1.00
2.71
2.07
1.10
3.06
1.21
2.77
f1 (ppm)

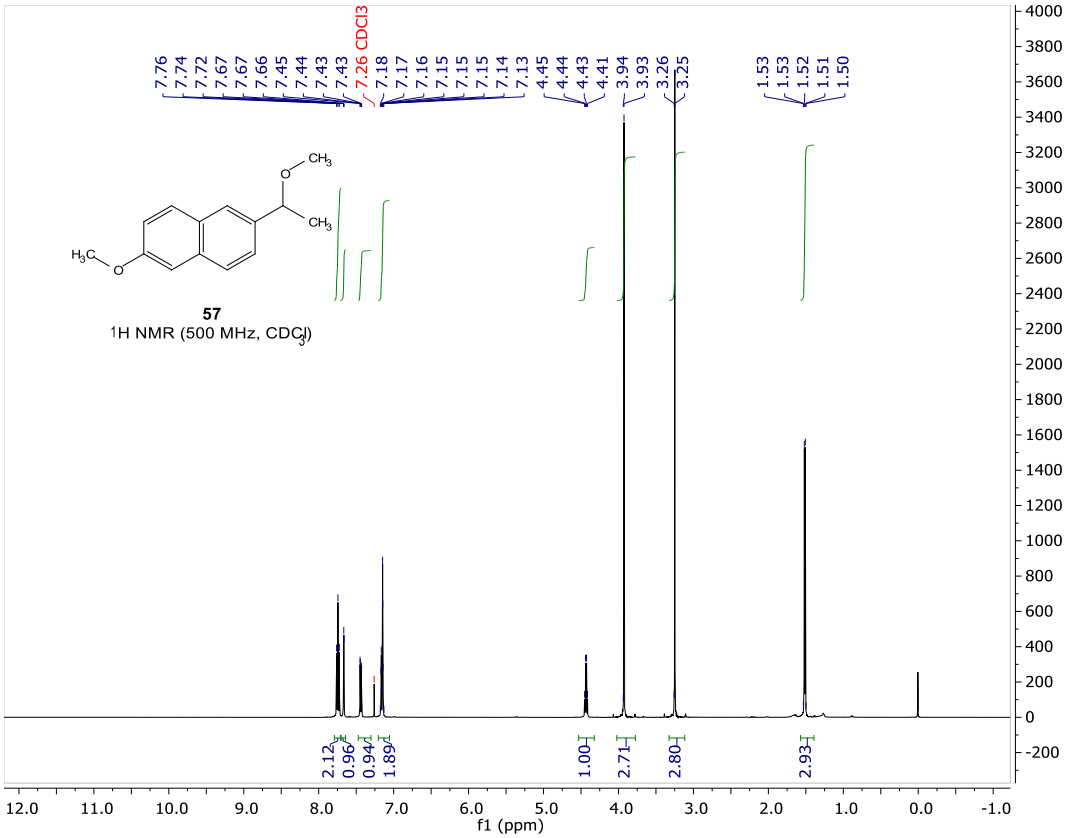

142.57
132.08
128.45
127.56
126.88
124.07
83.53
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.76
38.33
25.87
24.47
17.82
CH3
O
CH3
CH3
54
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.43
7.42
7.41
7.41
7.41
7.41
7.36
7.35
7.35
7.35
7.34
7.33
7.27
7.27
7.27
7.26 CDCl3
7.26
7.25
7.25
7.25
7.24
7.24
7.24
3.08
1.54
55
1H NMR (500 MHz, CDCl3)
1.82
2.11
1.25
3.00
6.25
f1 (ppm)


146.06
128.33
126.96
125.94
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
50.80
28.10
55
13C NMR (126 MHz, CDCl3)
f1 (ppm)

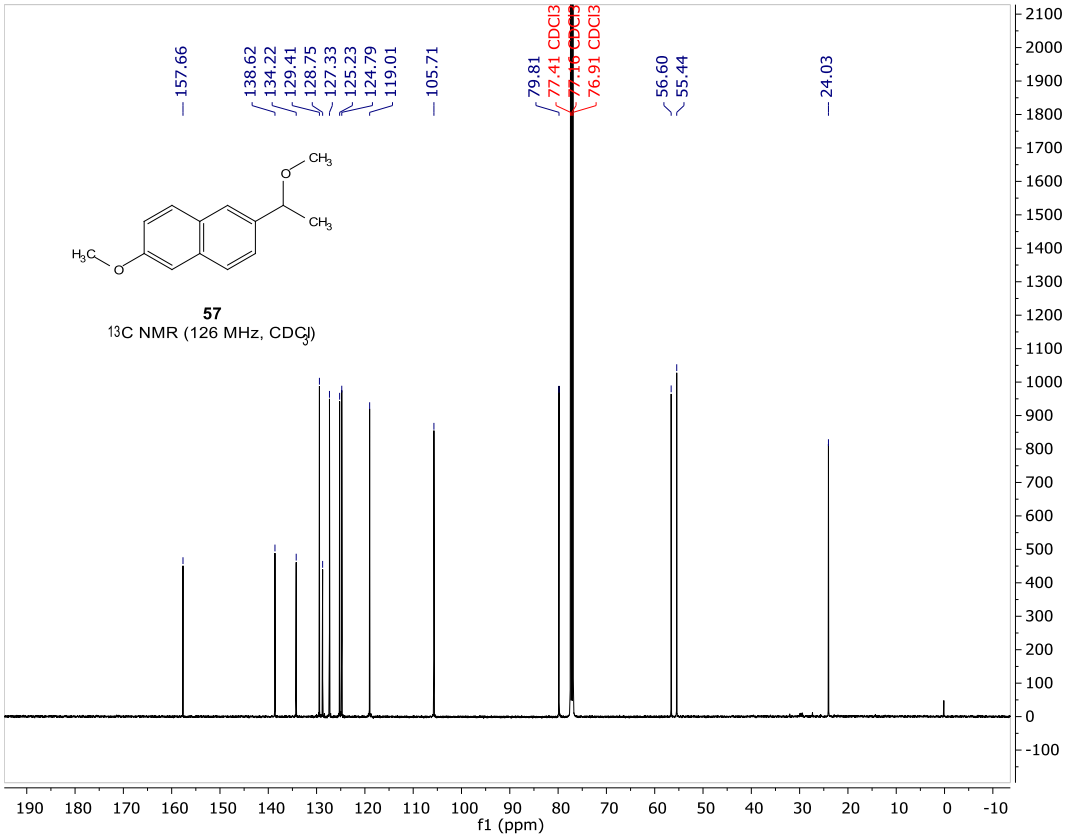

7.41
7.40
7.39
7.39
7.39
7.34
7.32
7.32
7.31
7.30
7.26 CDCl3
7.26
7.26
7.25
7.24
7.23
6.64
6.63
6.63
6.60
6.60
6.60
6.32
6.31
6.29
6.29
6.27
6.26
4.11
4.10
4.10
4.09
3.40
CH3
O
56
1H NMR (500 MHz, CDCl3)
2.12
2.32
1.24
1.15
1.07
2.00
2.71
f1 (ppm)


136.87
132.59
128.69
127.80
126.62
126.12
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
73.25
58.14
CH3
O
56
13C NMR (126 MHz, CDCl3)
f1 (ppm)



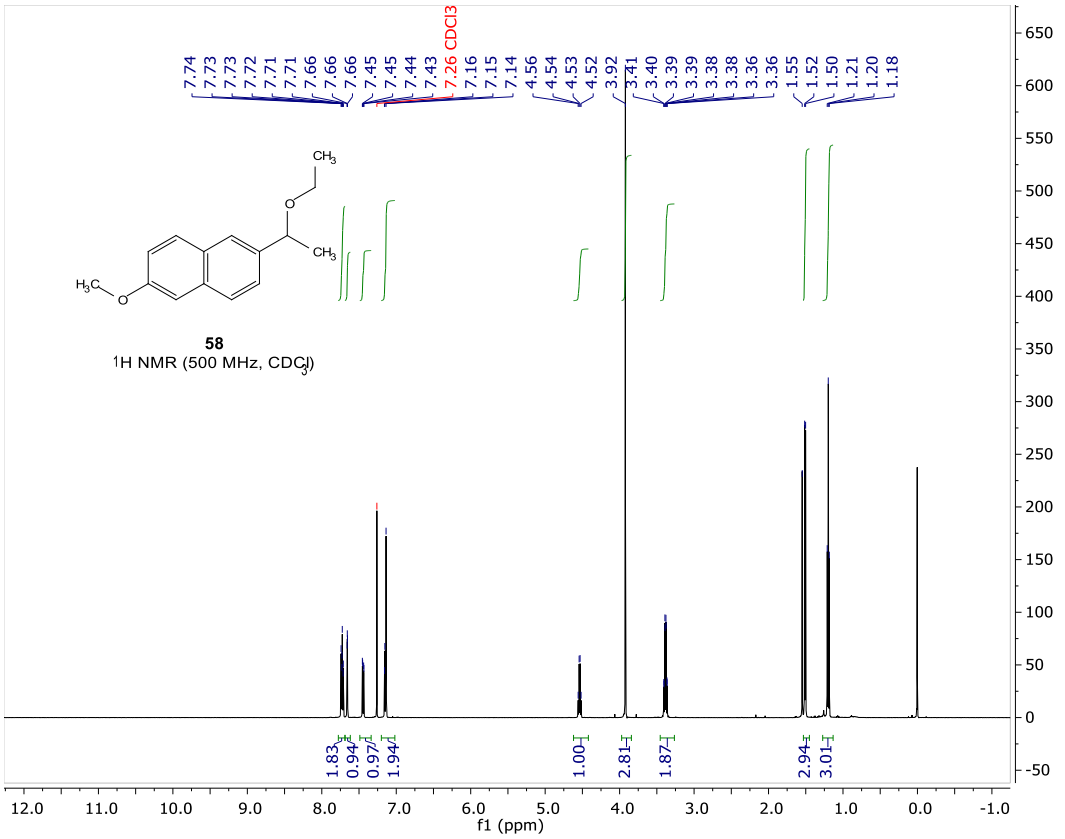
57

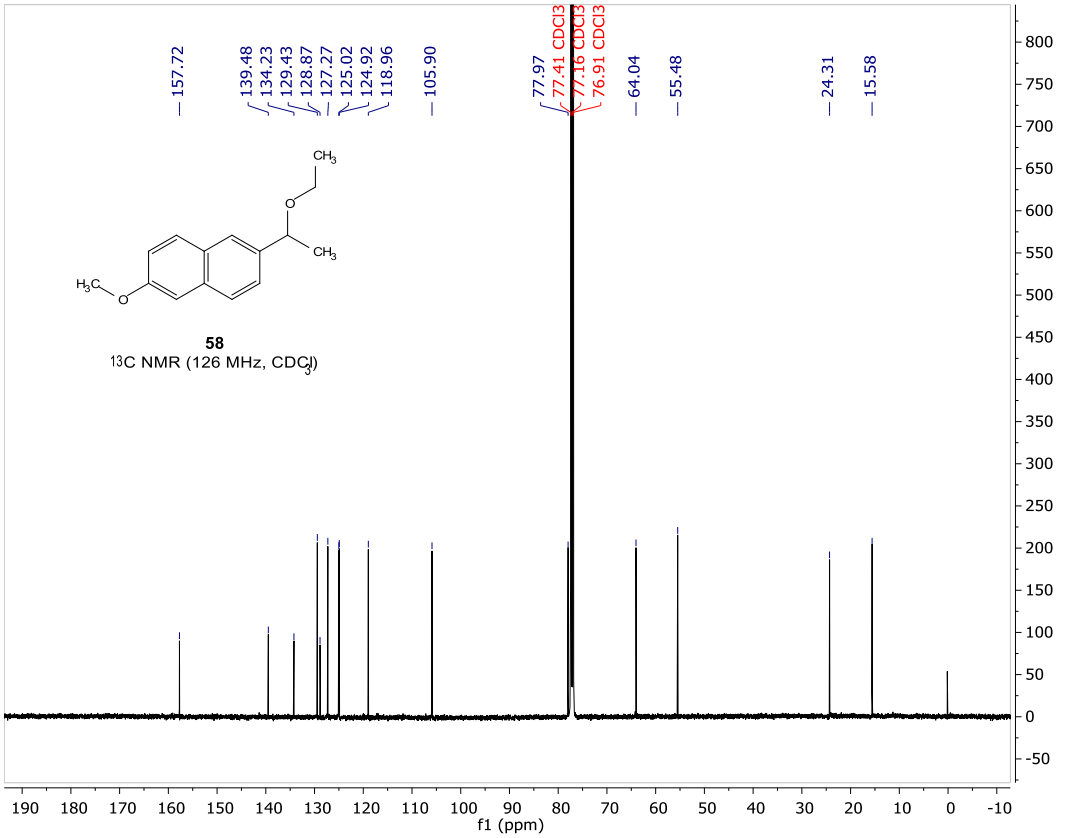
^{1}H NMR (500 MHz, $CDCl_3$)

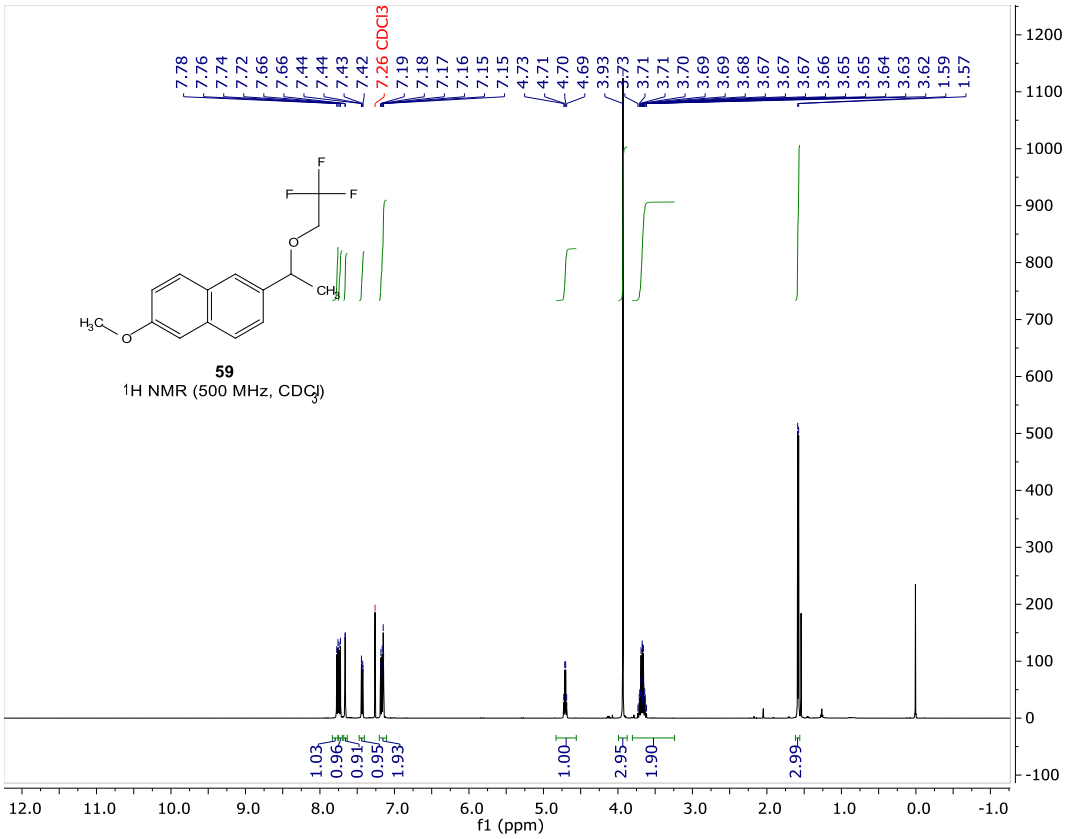


57

^{13}C NMR (126 MHz, $CDCl_3$)

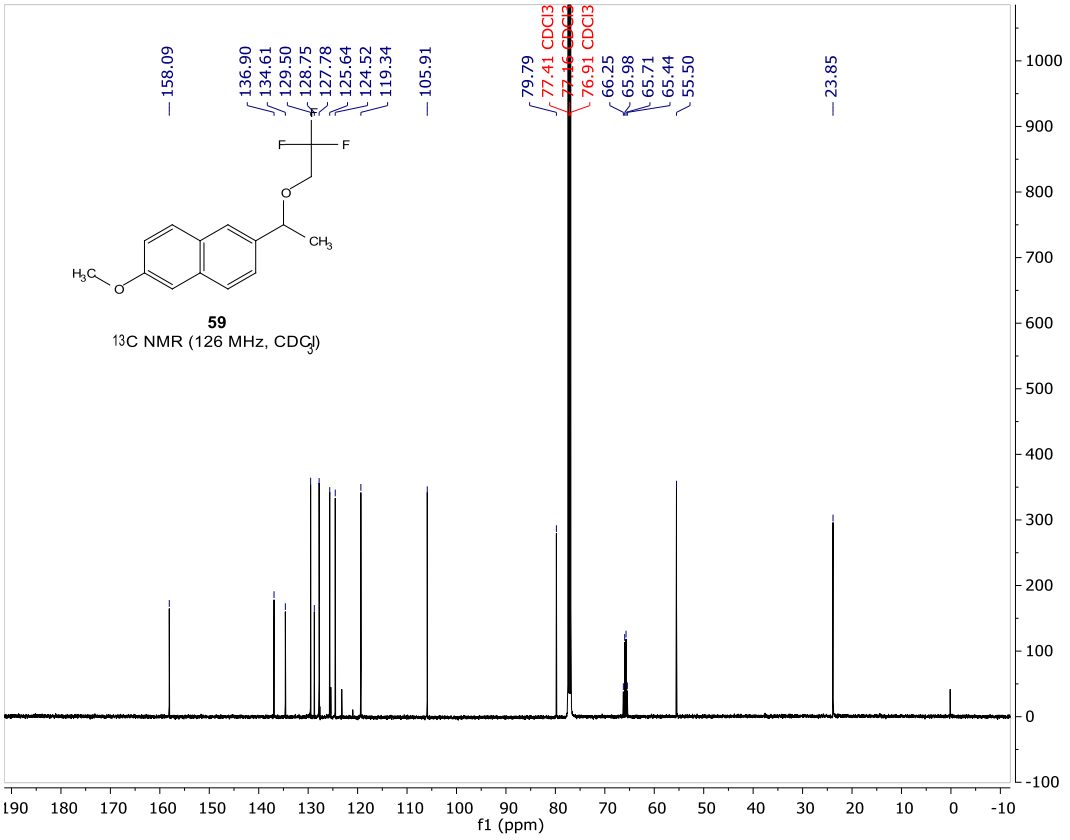

7.74
7.73
7.73
7.72
7.71
7.71
7.66
7.66
7.66
7.45
7.45
7.44
7.43
7.26 CDCl3
7.16
7.15
7.14
4.56
4.54
4.53
4.52
3.92
3.41
3.40
3.39
3.39
3.38
3.38
3.36
3.36
1.55
1.52
1.50
1.21
1.20
1.18
CH3
O
CH3
H3C
O
58
1H NMR (500 MHz, CDCl3)
1.83
0.94
0.97
1.94
1.00
2.81
1.87
2.94
3.01
f1 (ppm)


157.72
139.48
134.23
129.43
128.87
127.27
125.02
124.92
118.96
105.90
77.97
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
64.04
55.48
24.31
15.58
CH3
O
CH3
H3C
O
58
13C NMR (126 MHz, CDCl3)
f1 (ppm)



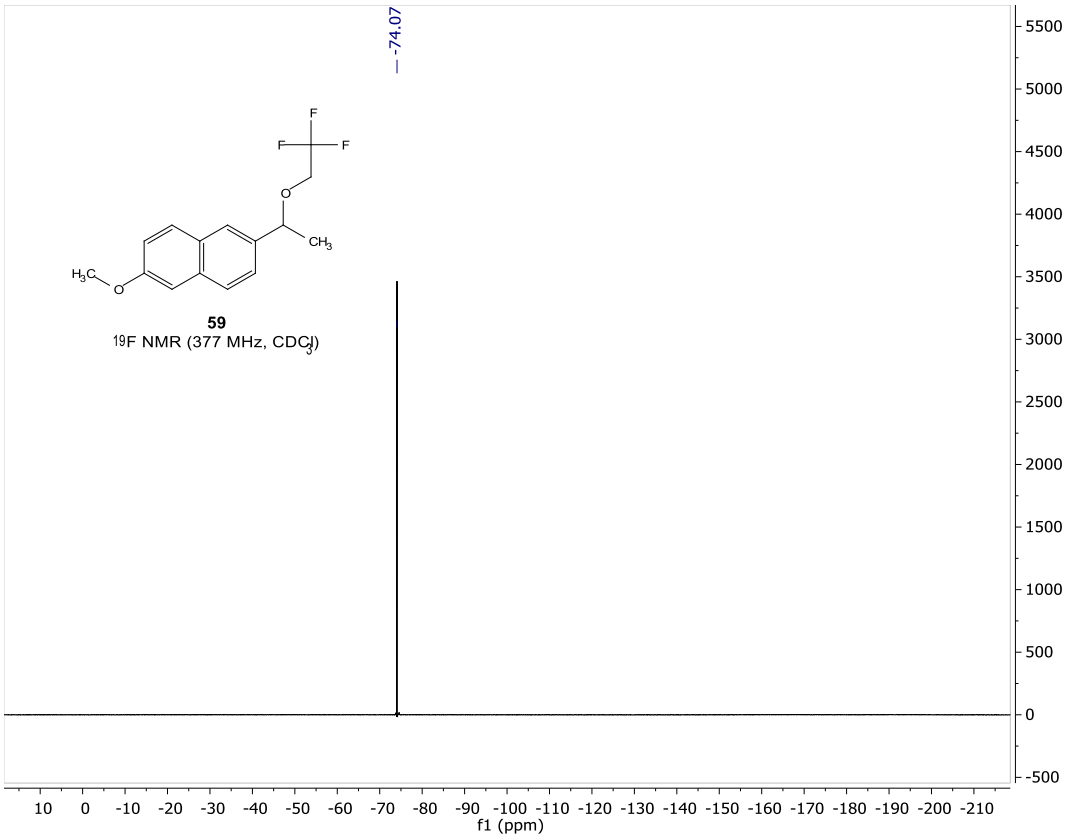
59

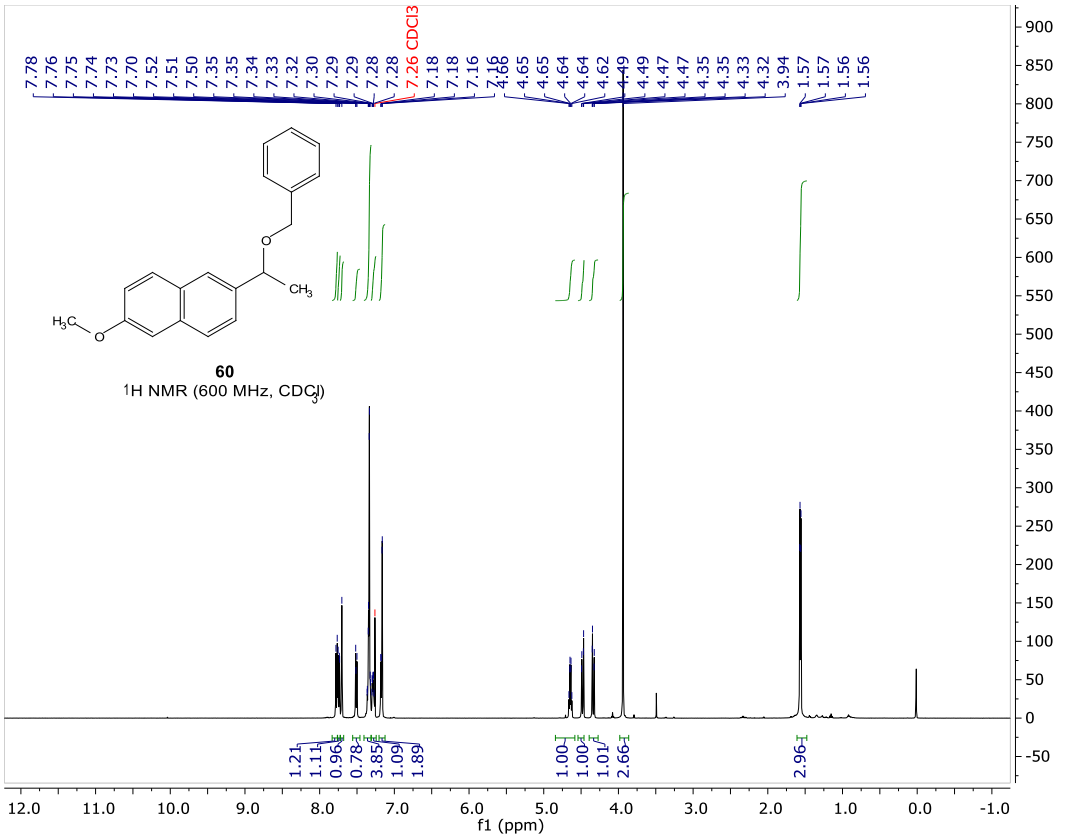
^{1}H NMR (500 MHz, $CDCl_3$)

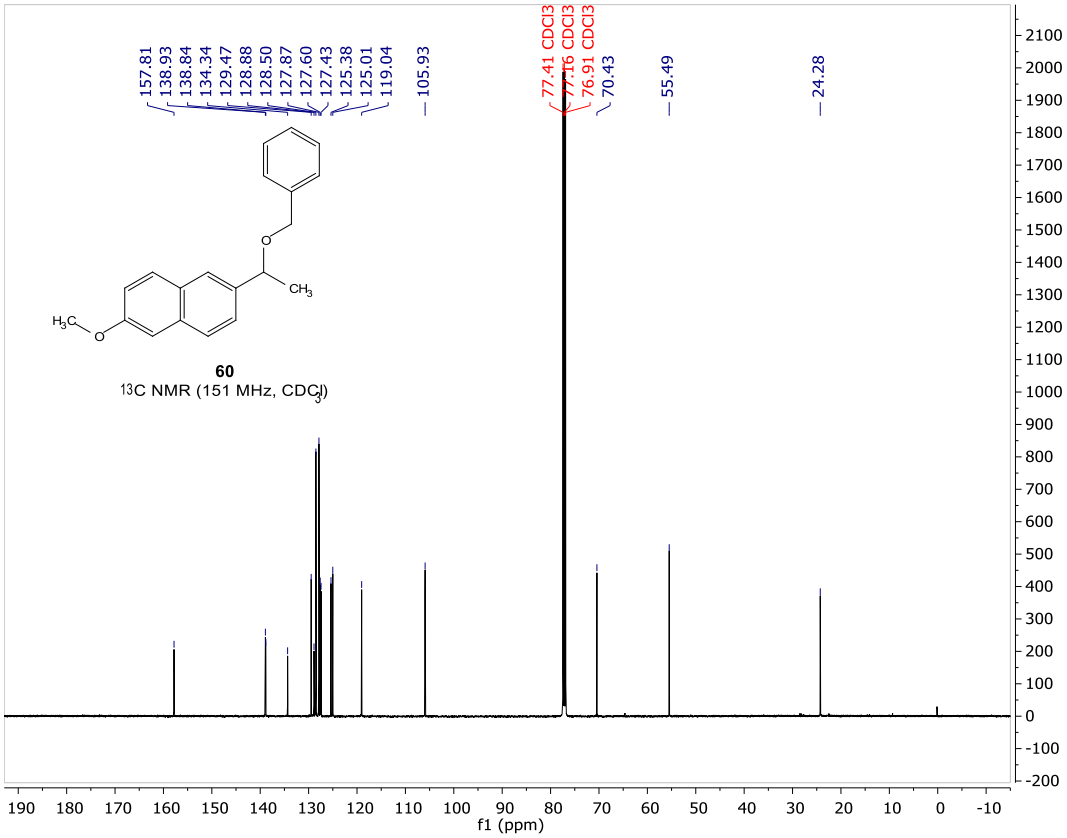


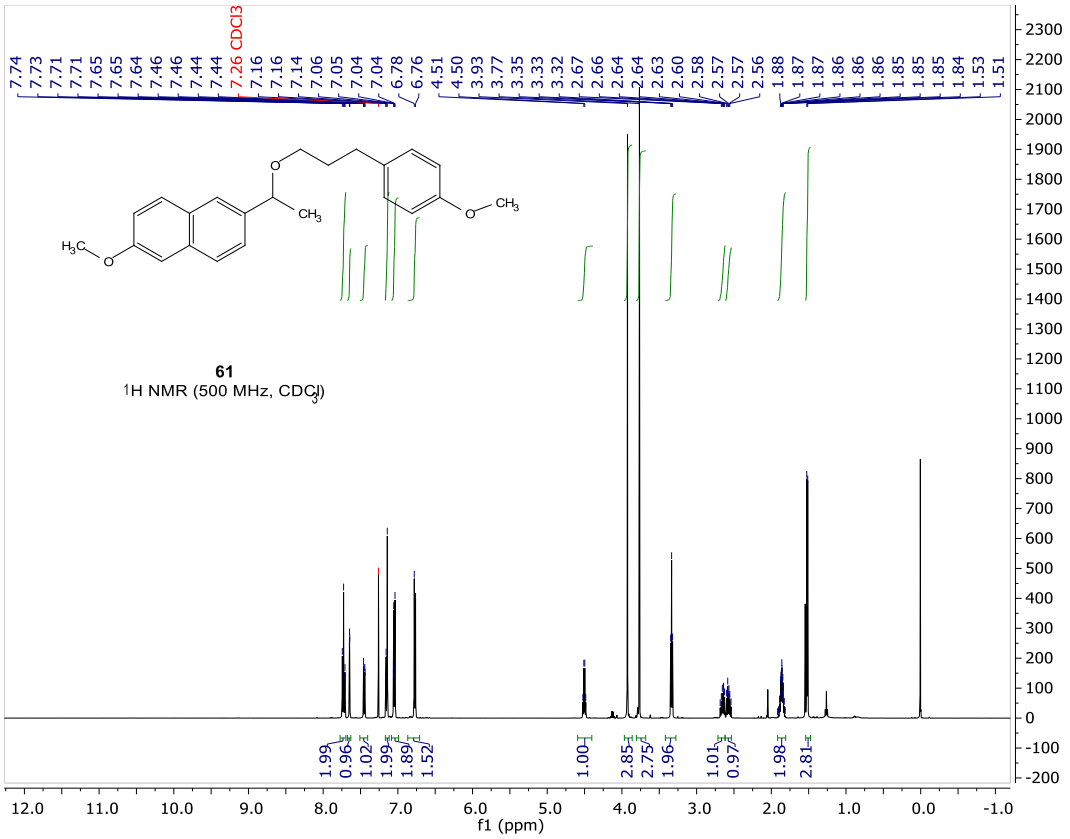
59

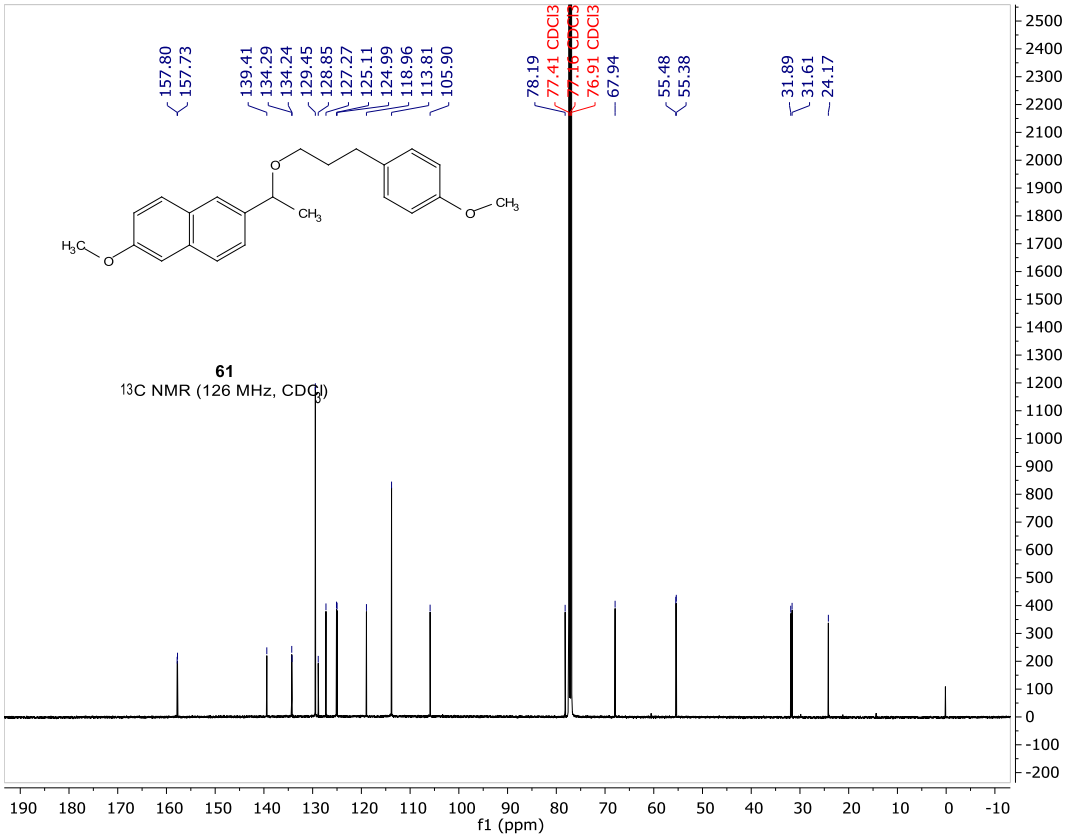
^{13}C NMR (126 MHz, $CDCl_3$)

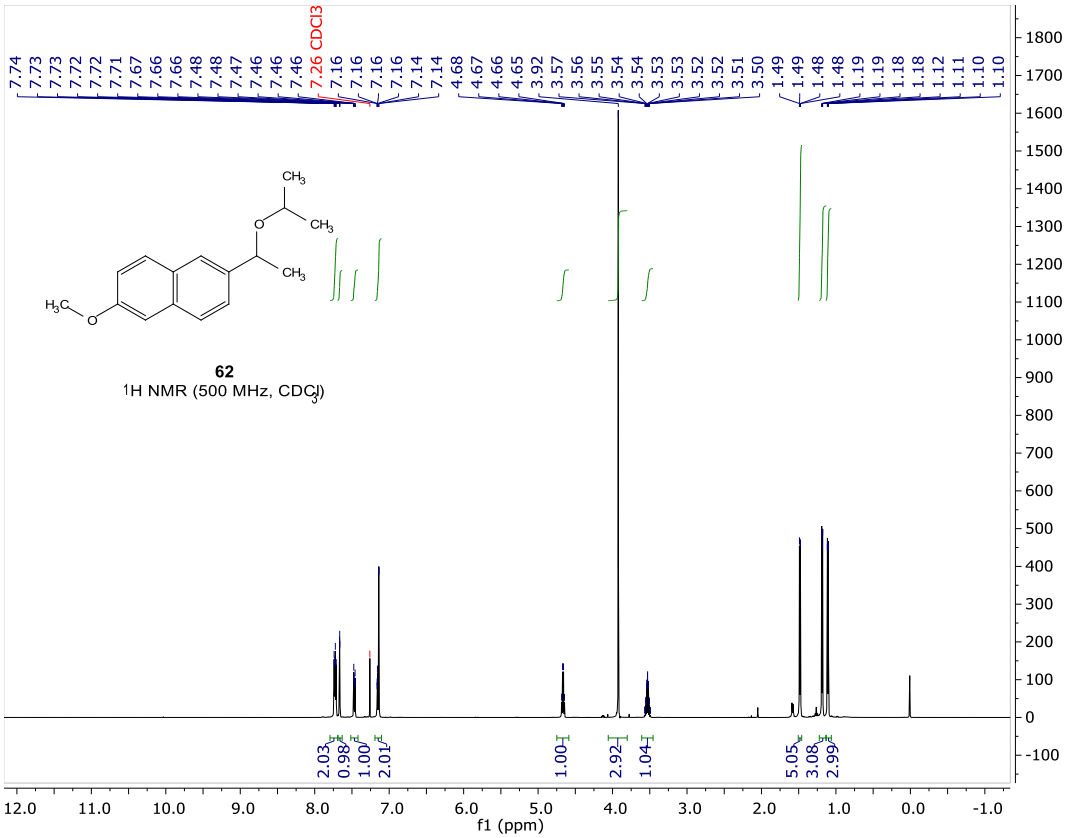

-74.07
F
F
F
O
CH3
H3C
O
59
19F NMR (377 MHz, CDCl3)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

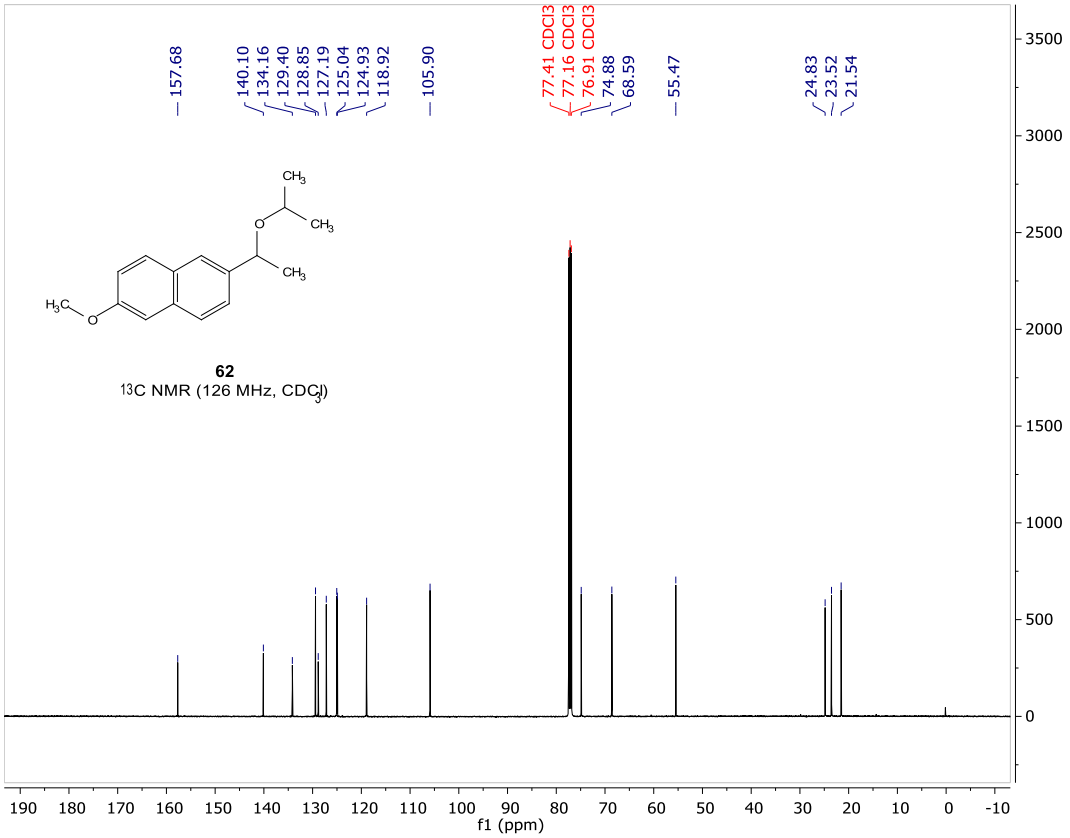

7.78 7.76 7.75 7.74 7.73 7.70 7.52 7.51 7.50 7.35 7.35 7.34 7.33 7.32 7.30 7.29 7.29 7.28 7.28 7.26 CDCl3 7.18 7.18 7.16 4.65 4.65 4.64 4.64 4.62 4.49 4.49 4.47 4.47 4.35 4.35 4.33 4.32 3.94 1.57 1.57 1.56 1.56
CH3
H3C
O
60
1H NMR (600 MHz, CDCl3)
1.21 1.11 0.96 0.78 3.85 1.09 1.89 1.00 1.00 1.01 2.66 2.96
f1 (ppm)

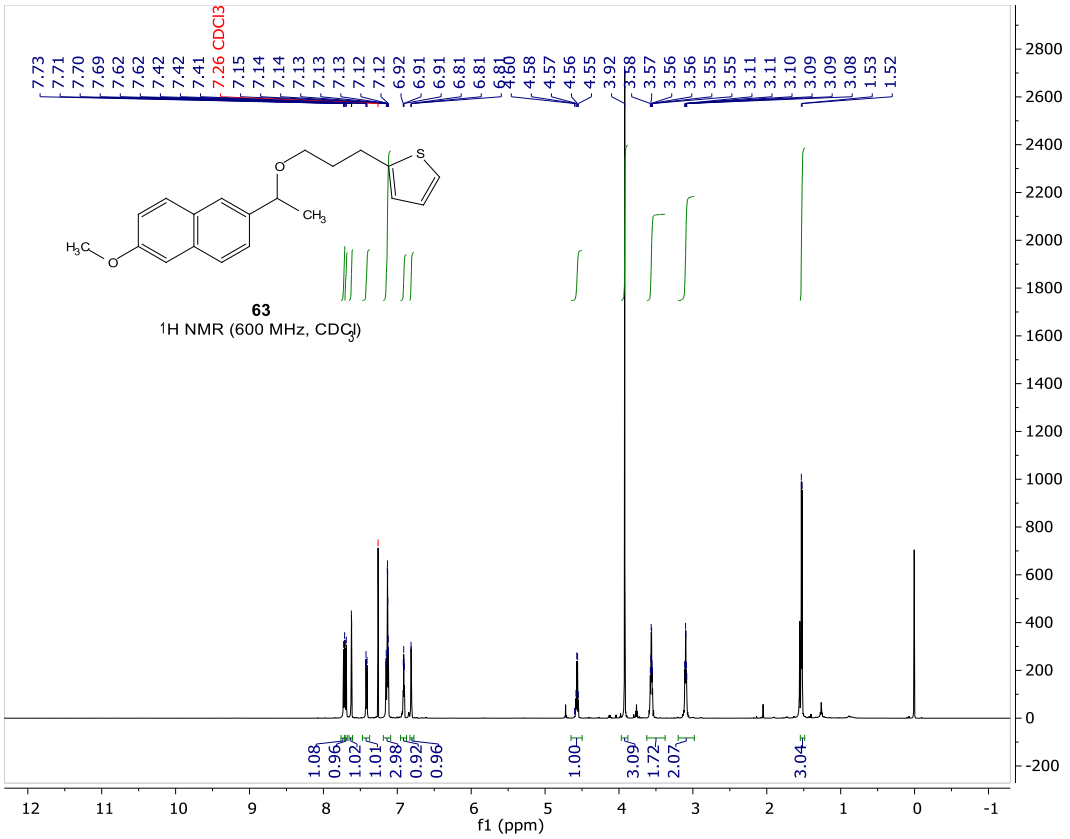

157.81 138.93 138.84 134.34 129.47 128.88 128.50 127.87 127.60 127.43 125.38 125.01 119.04 105.93 77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 70.43 55.49 24.28
CH3
H3C
O
60
13C NMR (151 MHz, CDCl3)
f1 (ppm)

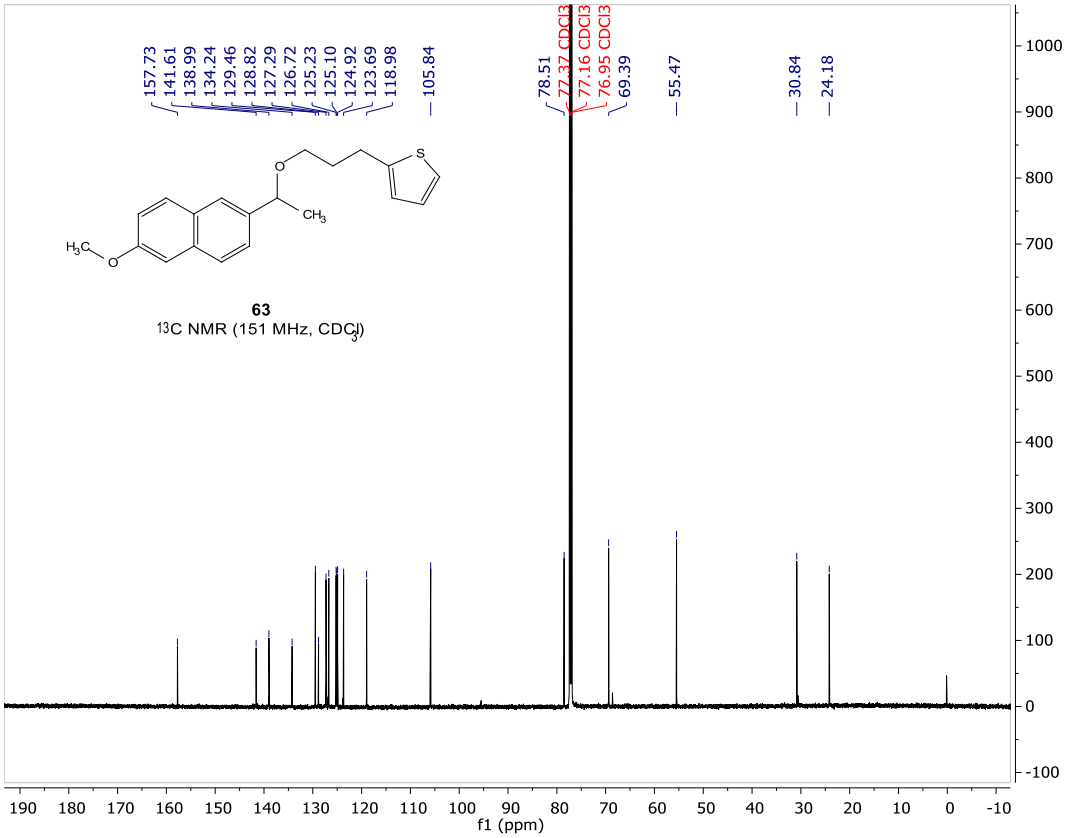

7.74 7.73 7.71 7.71 7.65 7.65 7.64 7.46 7.46 7.44 7.44 7.26 CDCl3 7.16 7.16 7.14 7.06 7.05 7.04 7.04 6.78 6.76 4.51 4.50 3.93 3.77 3.35 3.33 3.32 2.67 2.66 2.64 2.64 2.63 2.60 2.58 2.57 2.57 2.56 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.85 1.84 1.53 1.51
61
1H NMR (500 MHz, CDCl3)
1.99 0.96 1.02 1.99 1.89 1.52 1.00 2.85 2.75 1.96 1.01 0.97 1.98 2.81
f1 (ppm)

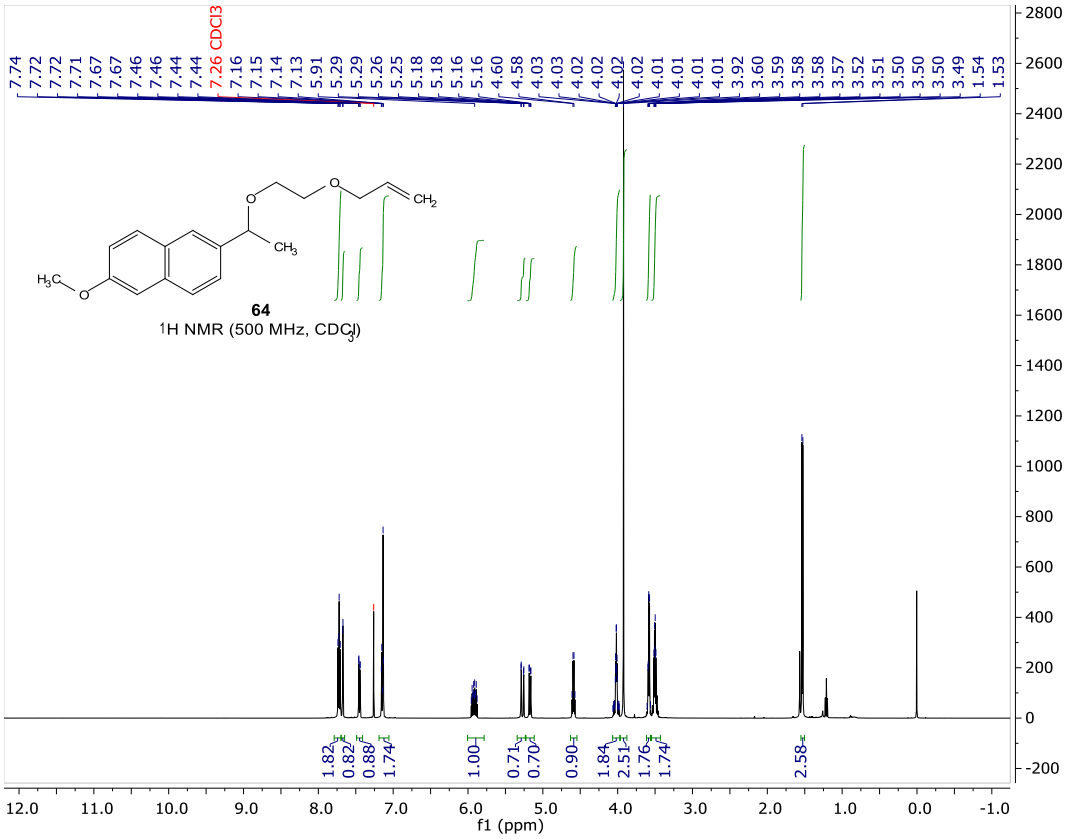

157.80 157.73 139.41 134.29 134.24 129.45 128.85 127.27 125.11 124.99 118.96 113.81 105.90 78.19 77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 67.94 55.48 55.38 31.89 31.61 24.17
61
13C NMR (126 MHz, CDCl3)
f1 (ppm)

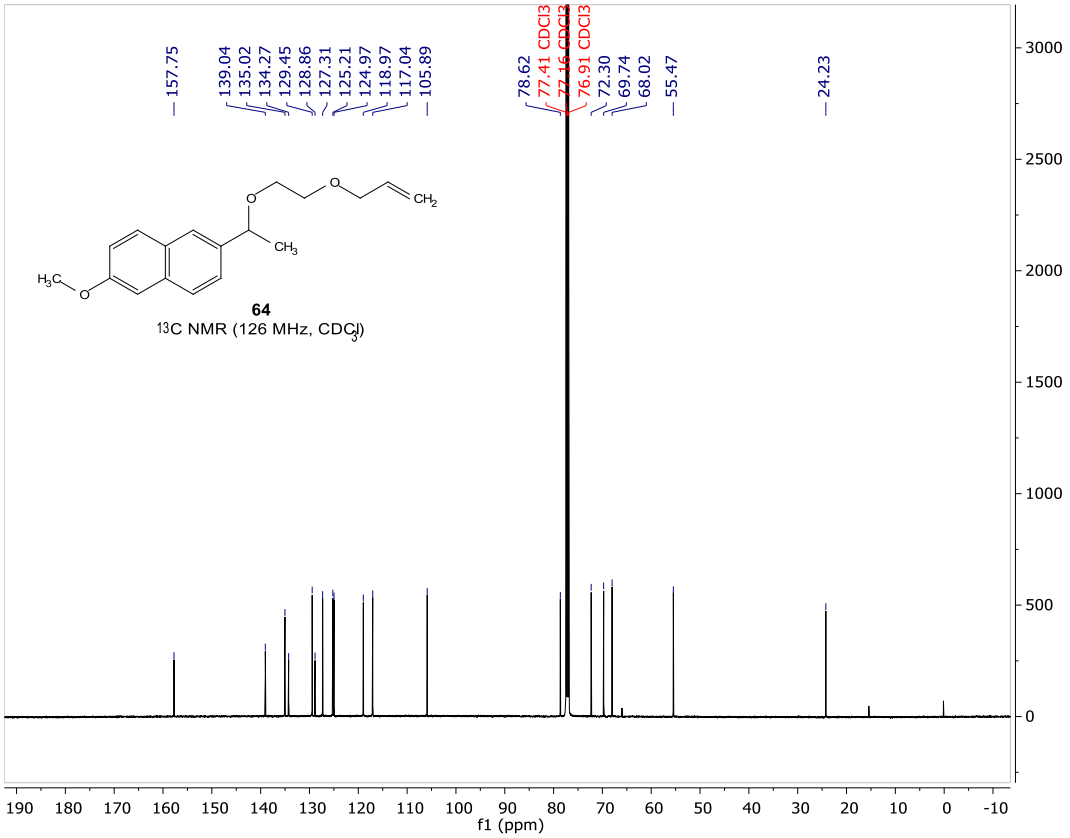

7.74 7.73 7.73 7.72 7.72 7.71 7.67 7.66 7.66 7.48 7.48 7.47 7.46 7.46 7.46 7.26 CDCl3 7.16 7.16 7.16 7.16 7.14 4.68 4.67 4.66 4.65 3.92 3.57 3.56 3.55 3.54 3.54 3.53 3.53 3.52 3.52 3.51 3.50 1.49 1.49 1.48 1.48 1.19 1.19 1.18 1.18 1.12 1.11 1.10 1.10
62
1H NMR (500 MHz, CDCl3)
2.03 0.98 1.00 2.01 1.00 2.92 1.04 5.05 3.08 2.99
f1 (ppm)

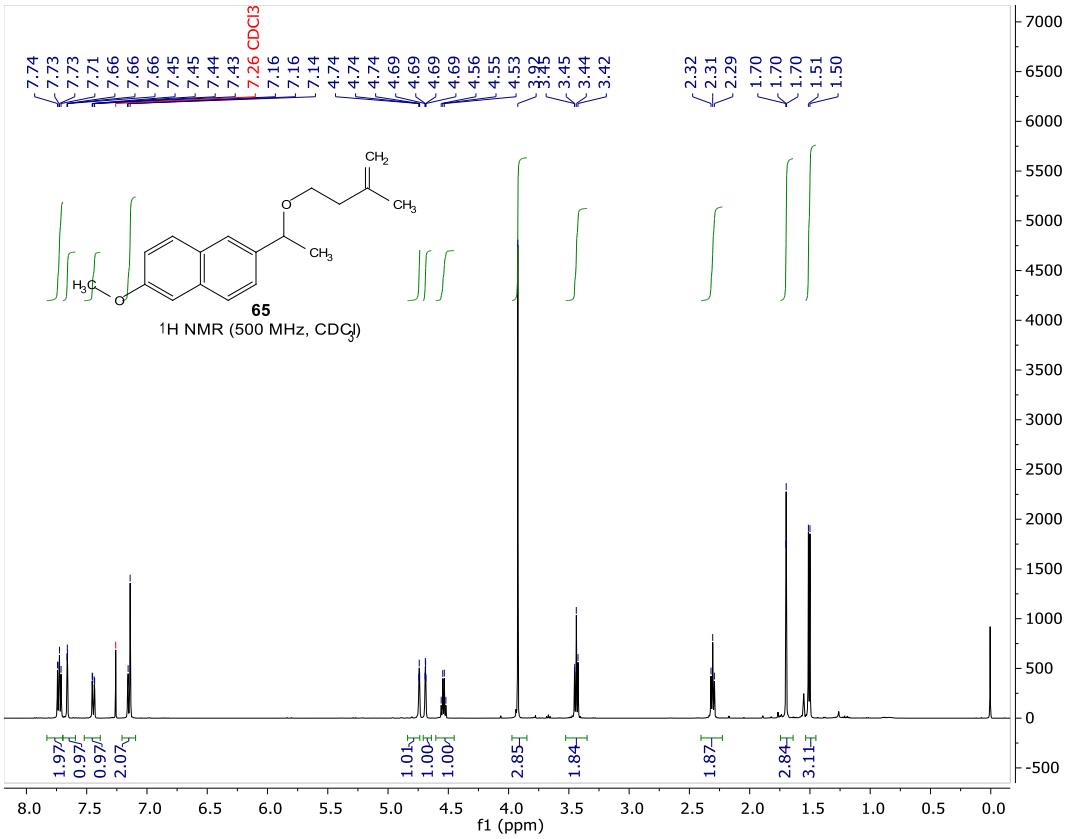

157.68 140.10 134.16 129.40 128.85 127.19 125.04 124.93 118.92 105.90 77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 74.88 68.59 55.47 24.83 23.52 21.54
62
13C NMR (126 MHz, CDCl3)
f1 (ppm)

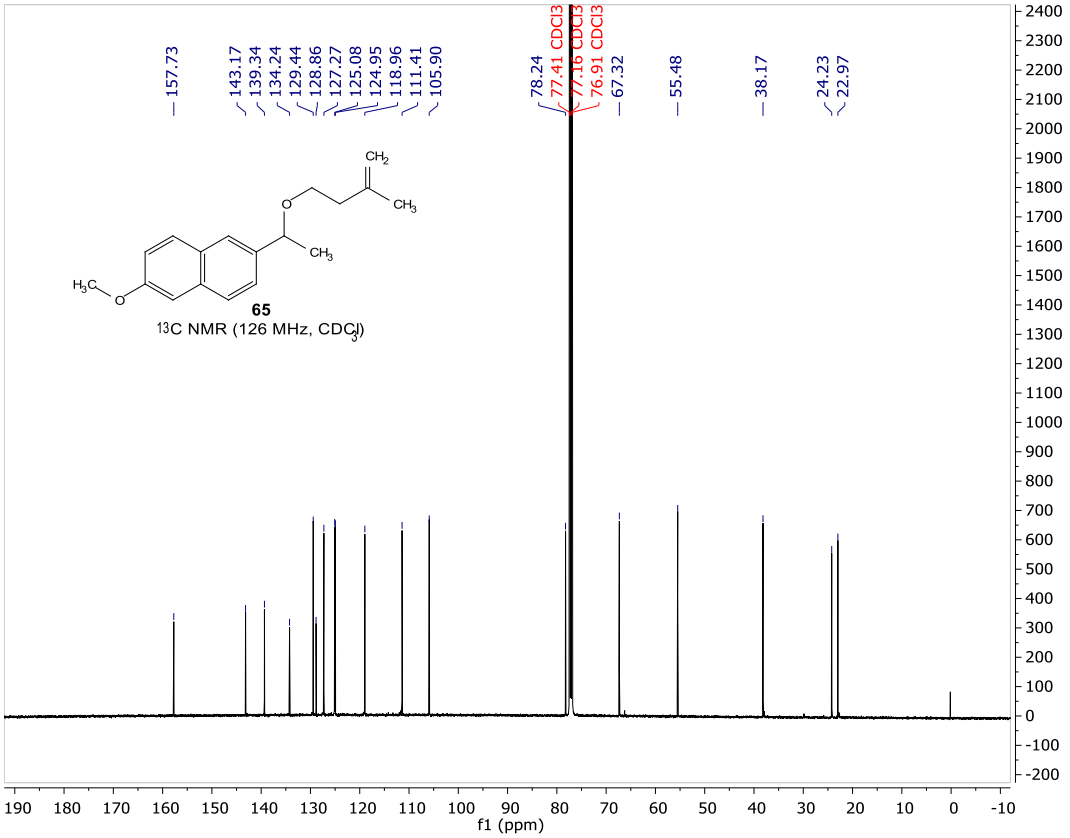

7.73 7.71 7.70 7.69 7.62 7.62 7.42 7.42 7.41 7.26 CDCl3 7.15 7.14 7.14 7.13 7.13 7.13 7.12 7.12 6.92 6.91 6.91 6.81 6.81 6.81 4.60 4.58 4.57 4.56 4.55 3.92 3.58 3.57 3.56 3.56 3.55 3.55 3.11 3.11 3.10 3.09 3.09 3.08 1.53 1.52
O
S
CH3
H3C
O
63
1H NMR (600 MHz, CDCl3)
1.08 0.96 1.02 1.01 2.98 0.92 0.96 1.00 3.09 1.72 2.07 3.04
f1 (ppm)

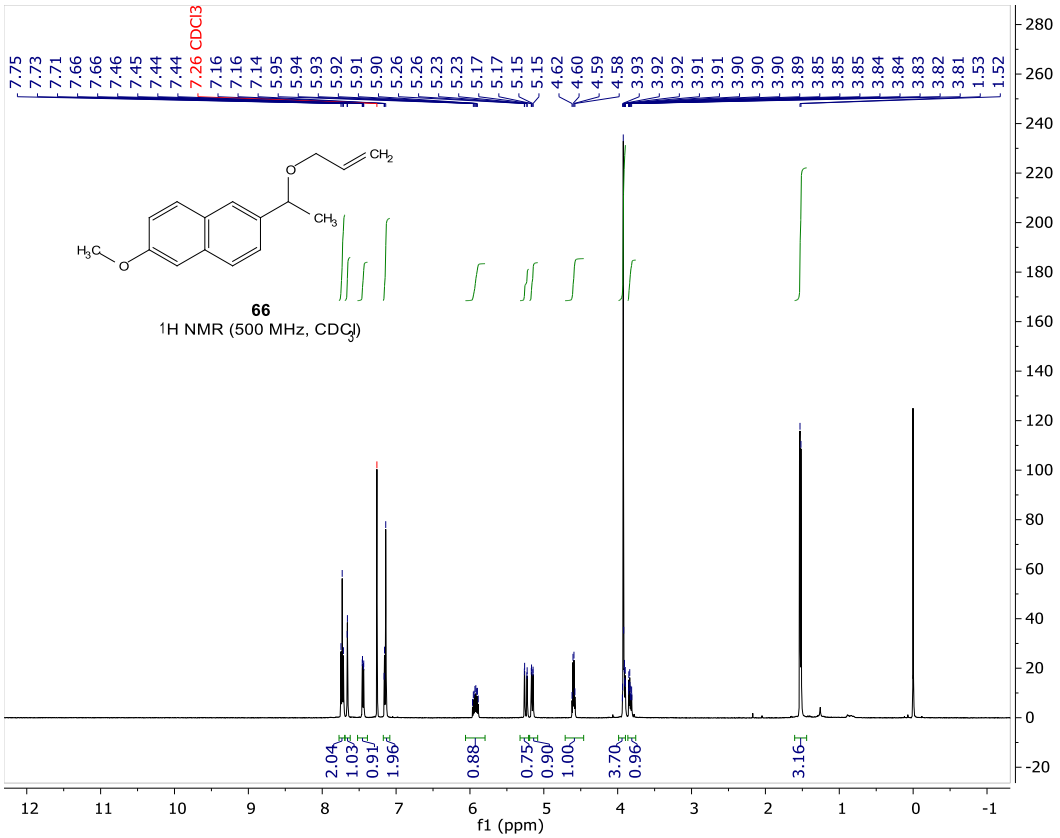

157.73 141.61 138.99 134.24 129.46 128.82 127.29 126.72 125.23 125.10 124.92 123.69 118.98 105.84
78.51 77.37 CDCl3 77.16 CDCl3 76.95 CDCl3 69.39 55.47 30.84 24.18
O
S
CH3
H3C
O
63
13C NMR (151 MHz, CDCl3)
f1 (ppm)

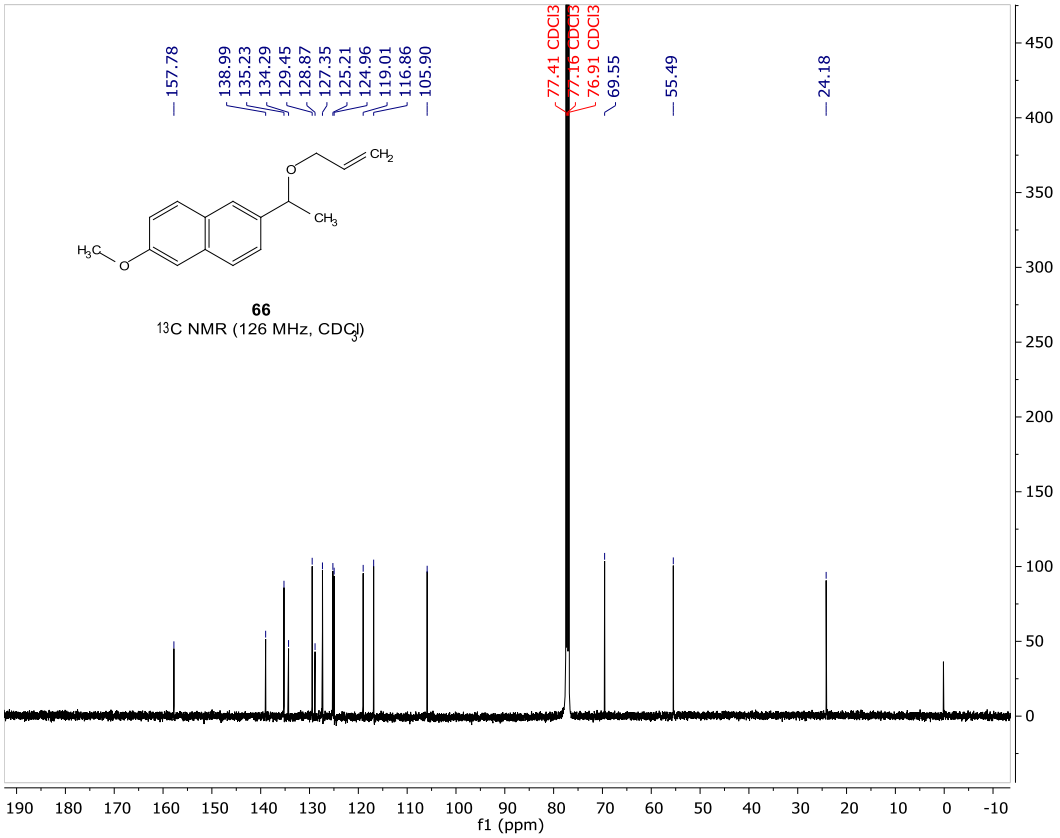

7.74 7.72 7.72 7.71 7.67 7.67 7.46 7.46 7.44 7.44 7.26 CDCl3 7.16 7.15 7.14 7.13 5.91 5.29 5.29 5.26 5.25 5.18 5.18 5.16 5.16 4.60 4.58 4.03 4.03 4.02 4.02 4.02 4.02 4.01 4.01 4.01 4.01 3.92 3.60 3.59 3.58 3.58 3.57 3.52 3.51 3.50 3.50 3.50 3.49 1.54 1.53
64
1H NMR (500 MHz, CDCl3)
1.82 0.82 0.88 1.74 1.00 0.71 0.70 0.90 1.84 2.51 1.76 1.74 2.58
f1 (ppm)

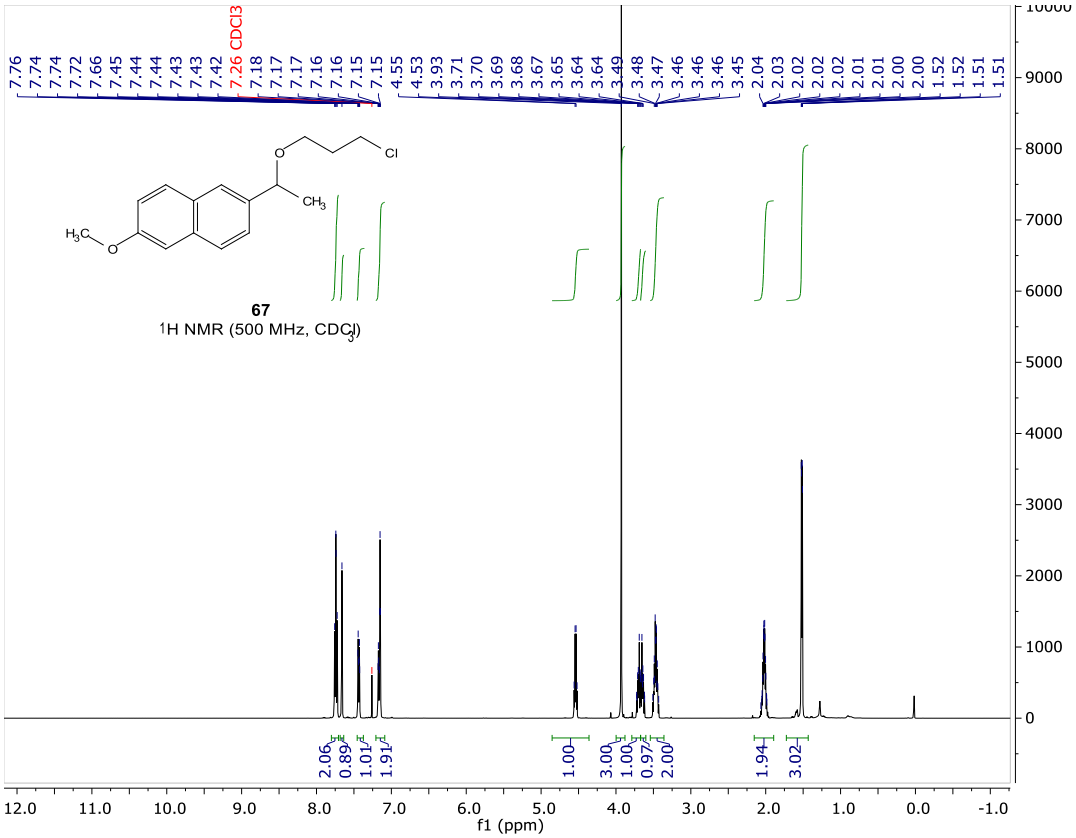

157.75 139.04 135.02 134.27 129.45 128.86 127.31 125.21 124.97 118.97 117.04 105.89 78.62 77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 72.30 69.74 68.02 55.47 24.23
64
13C NMR (126 MHz, CDCl3)
f1 (ppm)

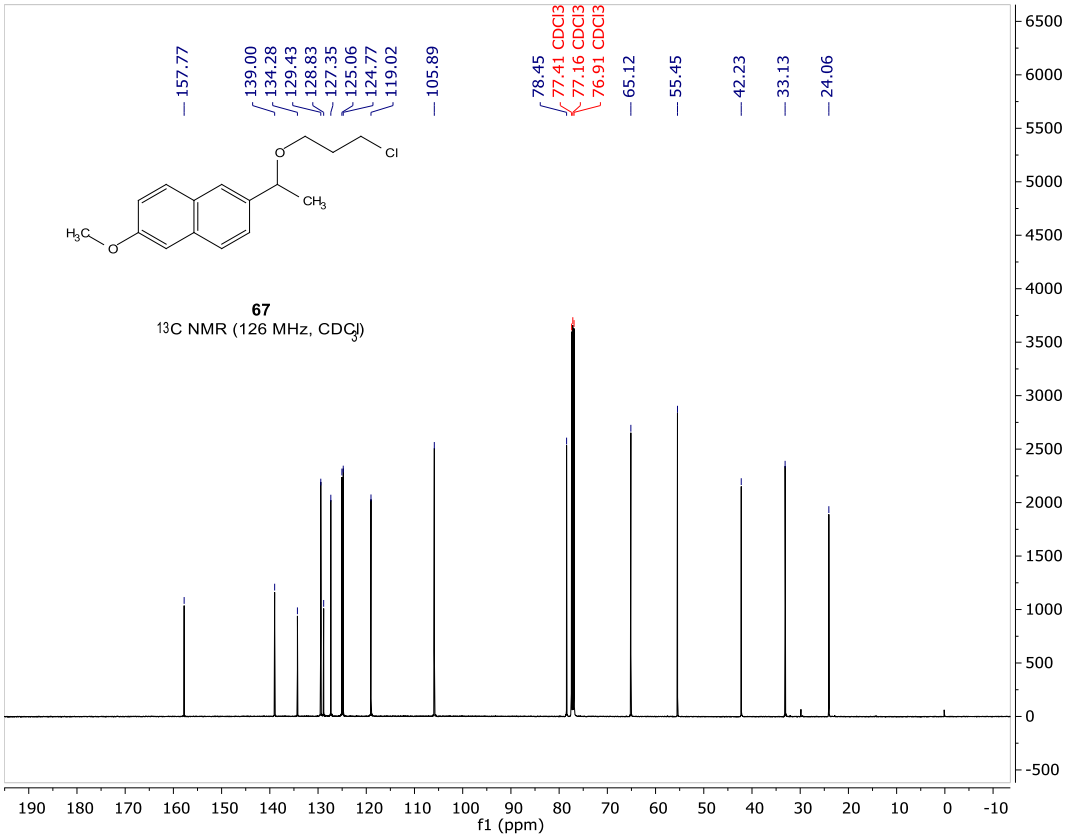

7.74
7.73
7.73
7.71
7.66
7.66
7.66
7.45
7.45
7.44
7.43
7.26 CDCl3
7.16
7.16
7.14
4.74
4.74
4.74
4.69
4.69
4.69
4.69
4.56
4.55
4.53
3.92
3.45
3.45
3.44
3.42
2.32
2.31
2.29
1.70
1.70
1.70
1.51
1.50
CH2
CH3
O
CH3
H3C
O
65
1H NMR (500 MHz, CDCl3)
1.97
0.97
0.97
2.07
1.01
1.00
1.00
2.85
1.84
1.87
2.84
3.11
f1 (ppm)

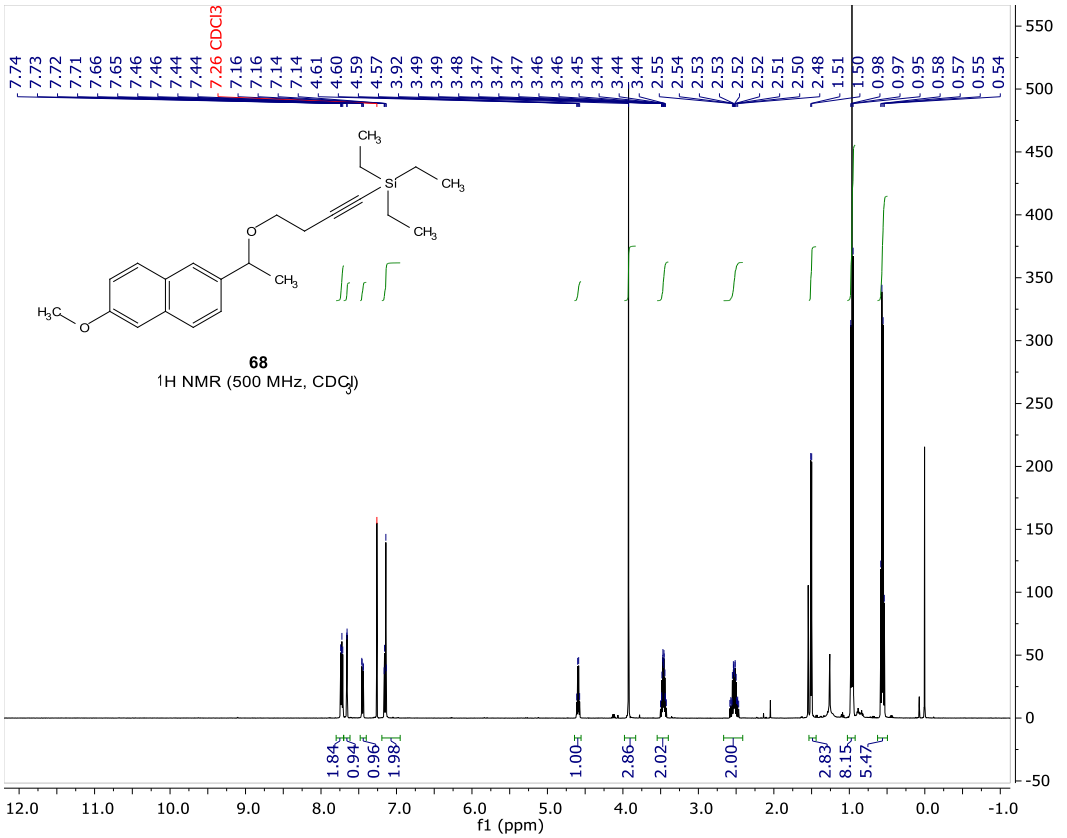

157.73
143.17
139.34
134.24
129.44
128.86
127.27
125.08
124.95
118.96
111.41
105.90
78.24
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.32
55.48
38.17
24.23
22.97
CH2
CH3
O
CH3
H3C
O
65
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.75 7.73 7.71 7.66 7.66 7.46 7.45 7.44 7.44 7.26 CDCl3 7.16 7.16 7.14 5.95 5.94 5.93 5.92 5.91 5.90 5.26 5.26 5.23 5.23 5.17 5.17 5.15 5.15 4.62 4.60 4.59 4.58 3.93 3.92 3.92 3.91 3.91 3.90 3.90 3.90 3.89 3.85 3.85 3.85 3.84 3.84 3.83 3.82 3.81 1.53 1.52
CH2
O
CH3
H3C
O
66
1H NMR (500 MHz, CDCl3)
2.04 1.03 0.91 1.96 0.88 0.75 0.90 1.00 3.70 0.96 3.16
f1 (ppm)


157.78 138.99 135.23 134.29 129.45 128.87 127.35 125.21 124.96 119.01 116.86 105.90
77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 69.55 55.49 24.18
CH2
O
CH3
H3C
O
66
13C NMR (126 MHz, CDCl3)
f1 (ppm)

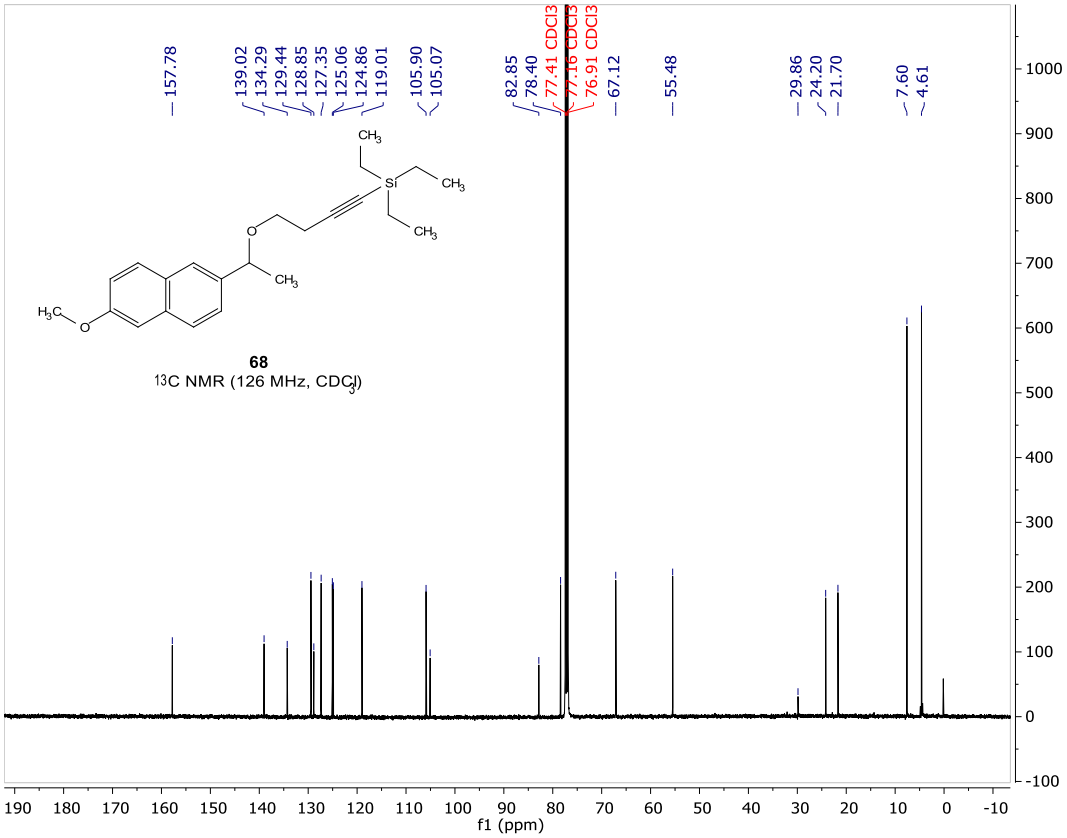

7.76 7.74 7.74 7.72 7.66 7.45 7.44 7.44 7.43 7.43 7.42 7.26 CDCl3 7.18 7.17 7.17 7.16 7.16 7.15 7.15 4.55 4.53 3.93 3.71 3.70 3.69 3.68 3.67 3.65 3.64 3.64 3.49 3.48 3.47 3.46 3.46 3.46 3.45 2.04 2.03 2.02 2.02 2.02 2.01 2.01 2.00 2.00 1.52 1.52 1.51 1.51
Cl
O
CH3
H3C
O
67
1H NMR (500 MHz, CDCl3)
2.06 0.89 1.01 1.91 1.00 3.00 1.00 0.97 2.00 1.94 3.02
f1 (ppm)


157.77 139.00 134.28 129.43 128.83 127.35 125.06 124.77 119.02 105.89 78.45 77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 65.12 55.45 42.23 33.13 24.06
Cl
O
CH3
H3C
O
67
13C NMR (126 MHz, CDCl3)
f1 (ppm)



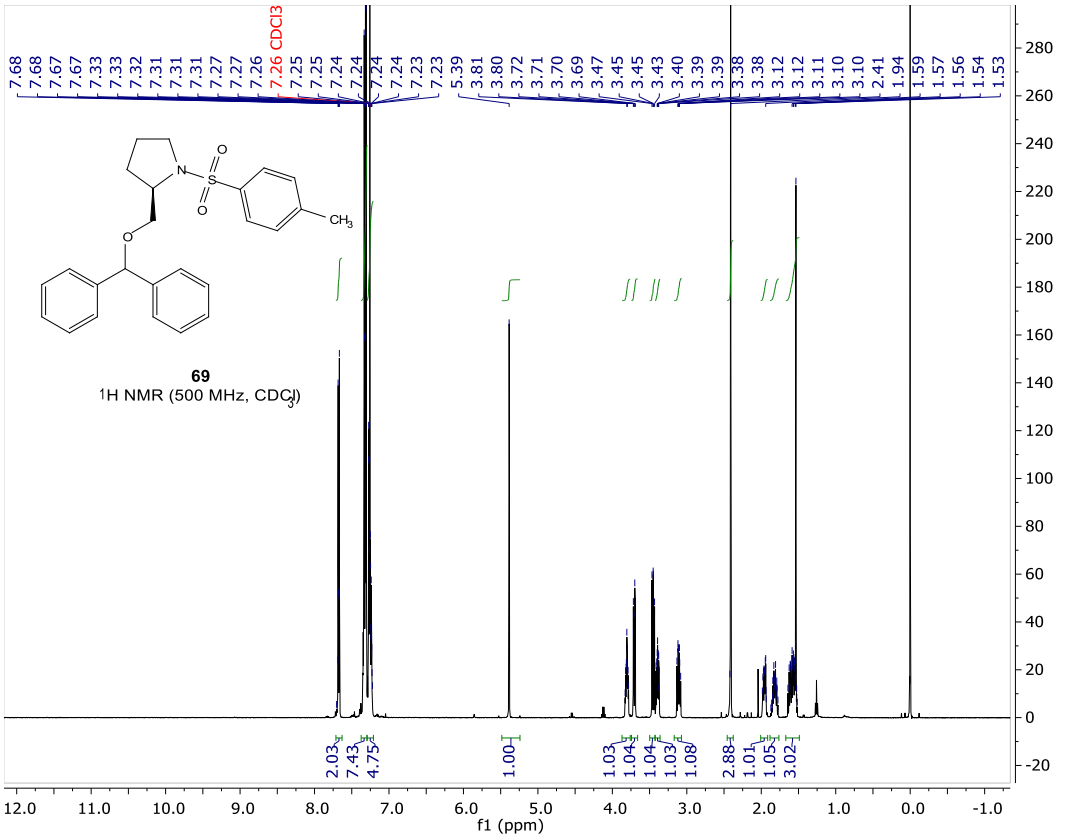
68

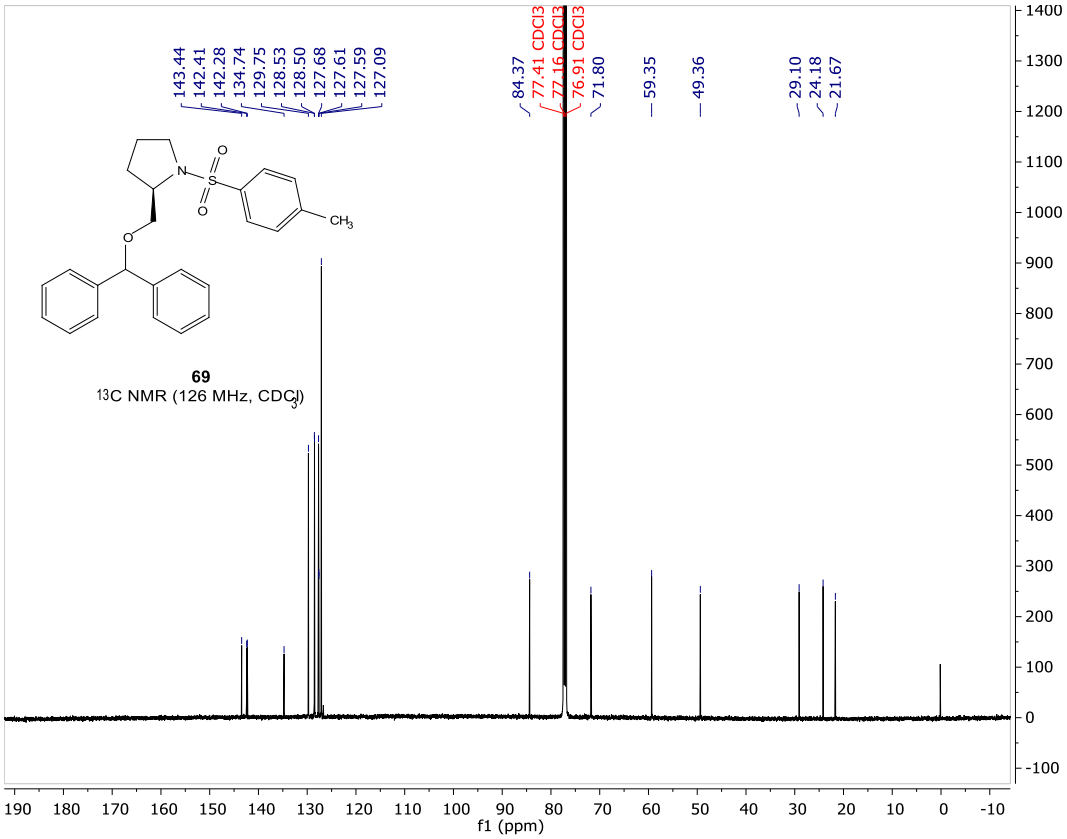
^{1}H NMR (500 MHz, $CDCl_3$)

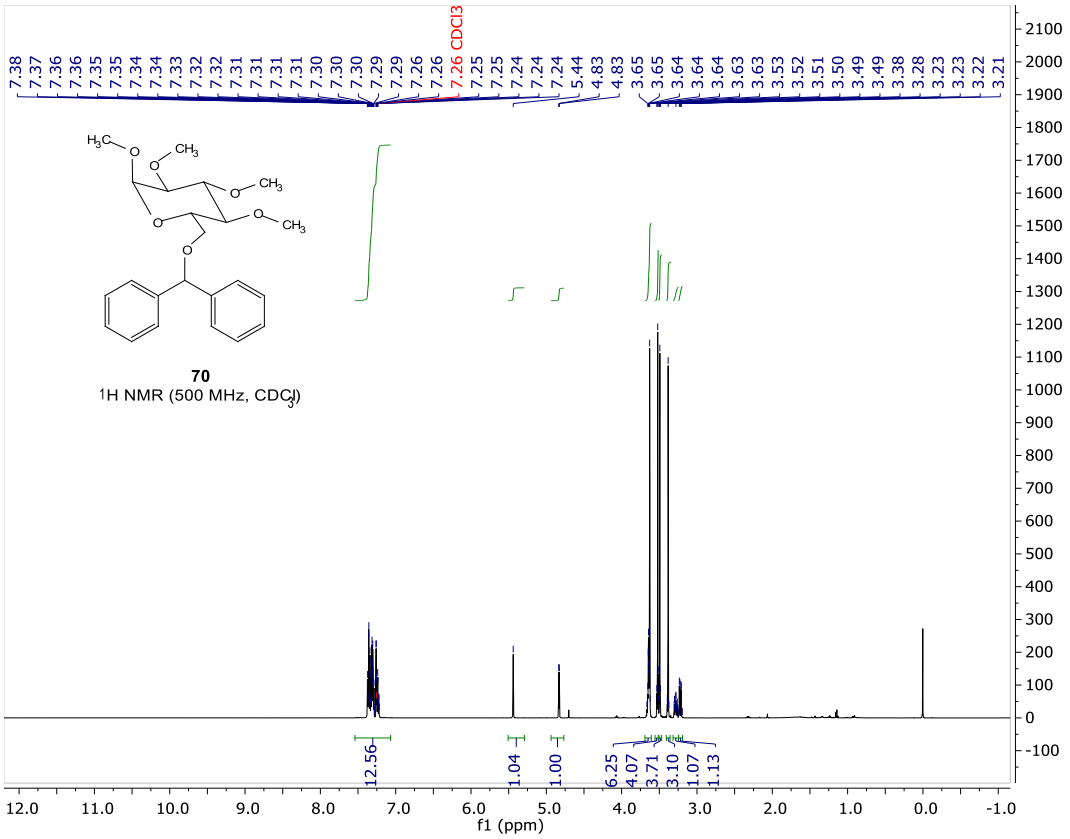


68

^{13}C NMR (126 MHz, $CDCl_3$)

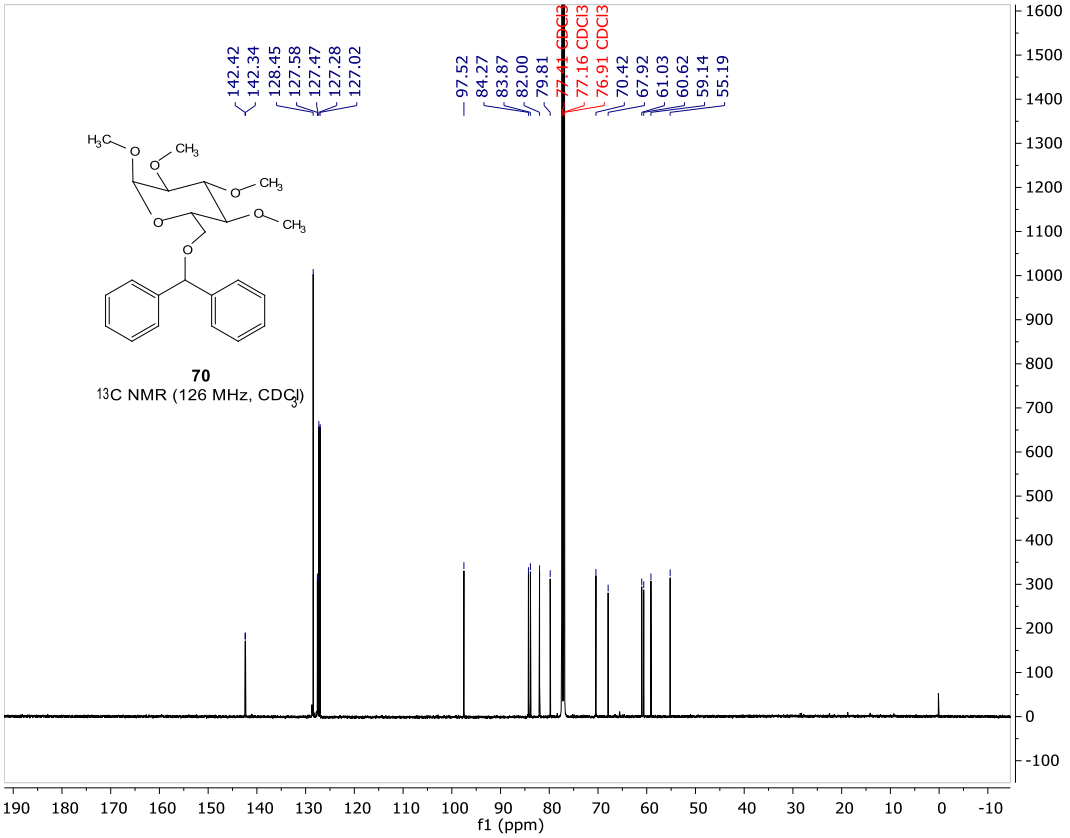

7.68 7.68 7.67 7.67 7.33 7.33 7.32 7.31 7.31 7.31 7.27 7.27 7.26 7.26 CDCl3 7.25 7.25 7.24 7.24 7.24 7.24 7.23 5.39 3.81 3.80 3.72 3.71 3.70 3.69 3.47 3.45 3.45 3.43 3.40 3.39 3.39 3.38 3.38 3.12 3.11 3.10 2.41 1.94 1.59 1.57 1.56 1.54 1.53
69
1H NMR (500 MHz, CDCl3)
2.03 7.43 4.75 1.00 1.03 1.04 1.04 1.03 1.08 2.88 1.01 1.05 3.02
f1 (ppm)


143.44 142.41 142.28 134.74 129.75 128.53 128.50 127.68 127.61 127.59 127.09 84.37 77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 71.80 59.35 49.36 29.10 24.18 21.67
69
13C NMR (126 MHz, CDCl3)
f1 (ppm)



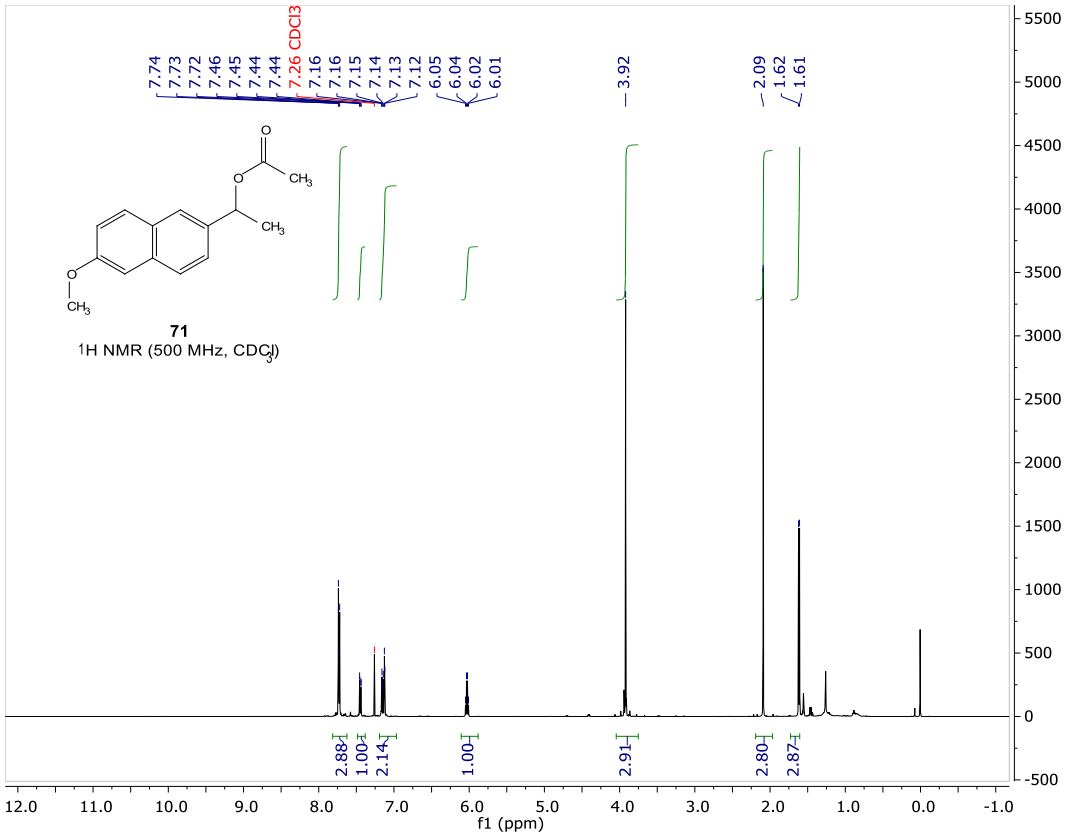
70

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



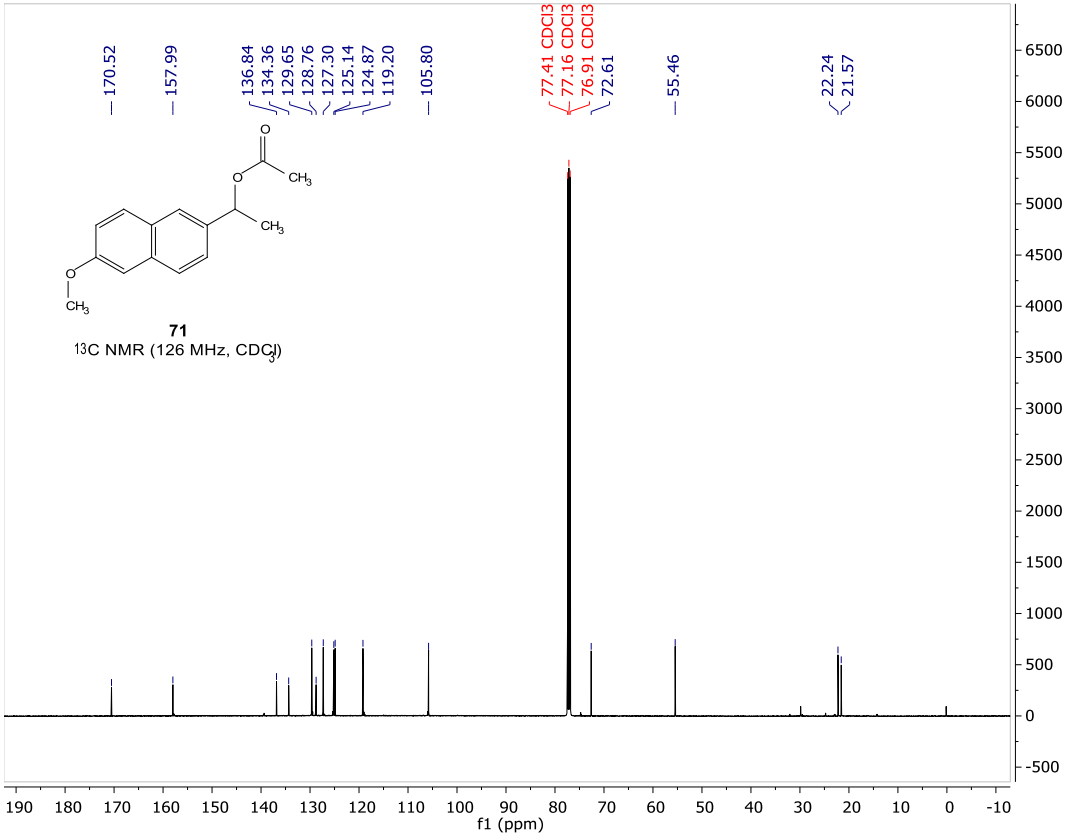
70

^{13}C NMR (126 MHz, $CDCl_3$)



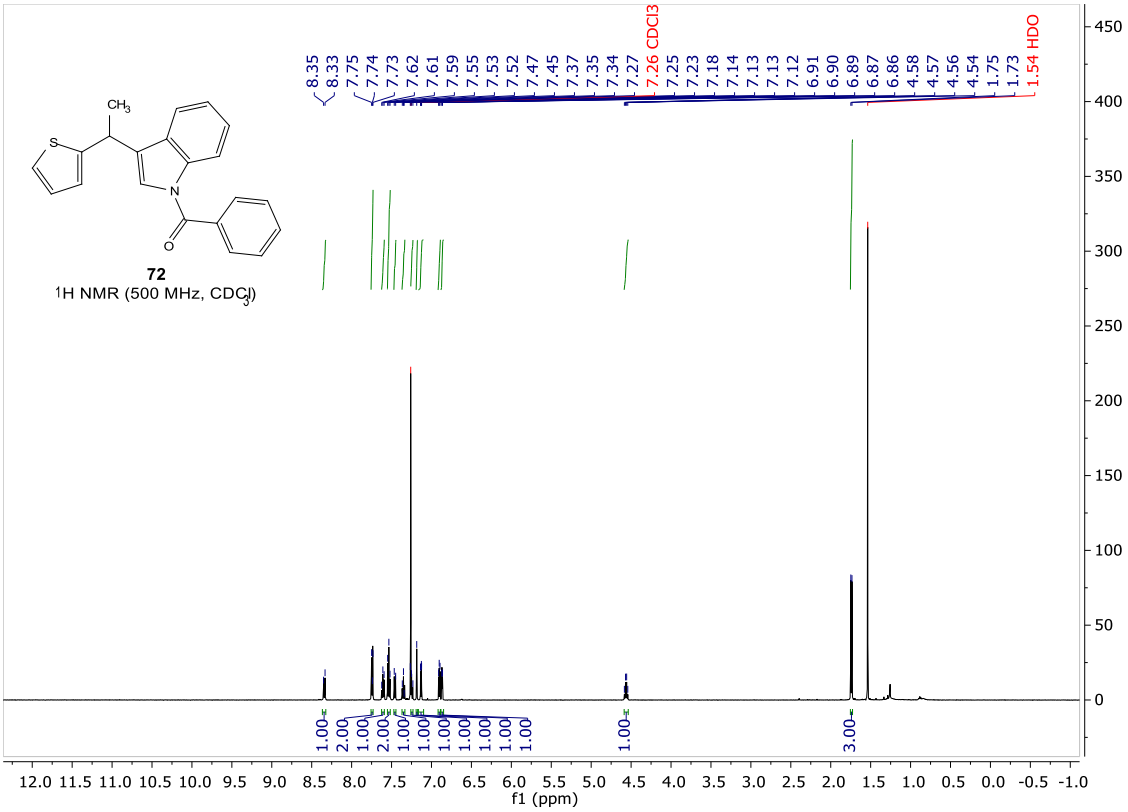
71

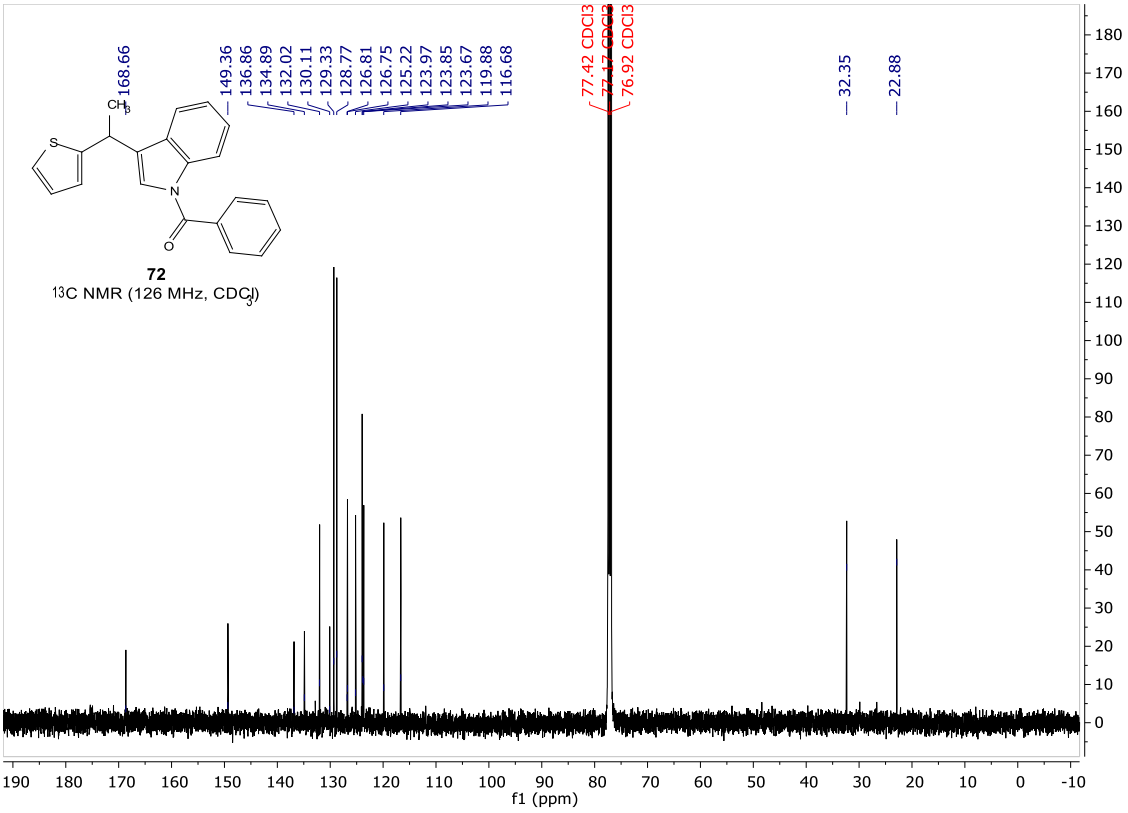
^{1}H NMR (500 MHz, $CDCl_3$)

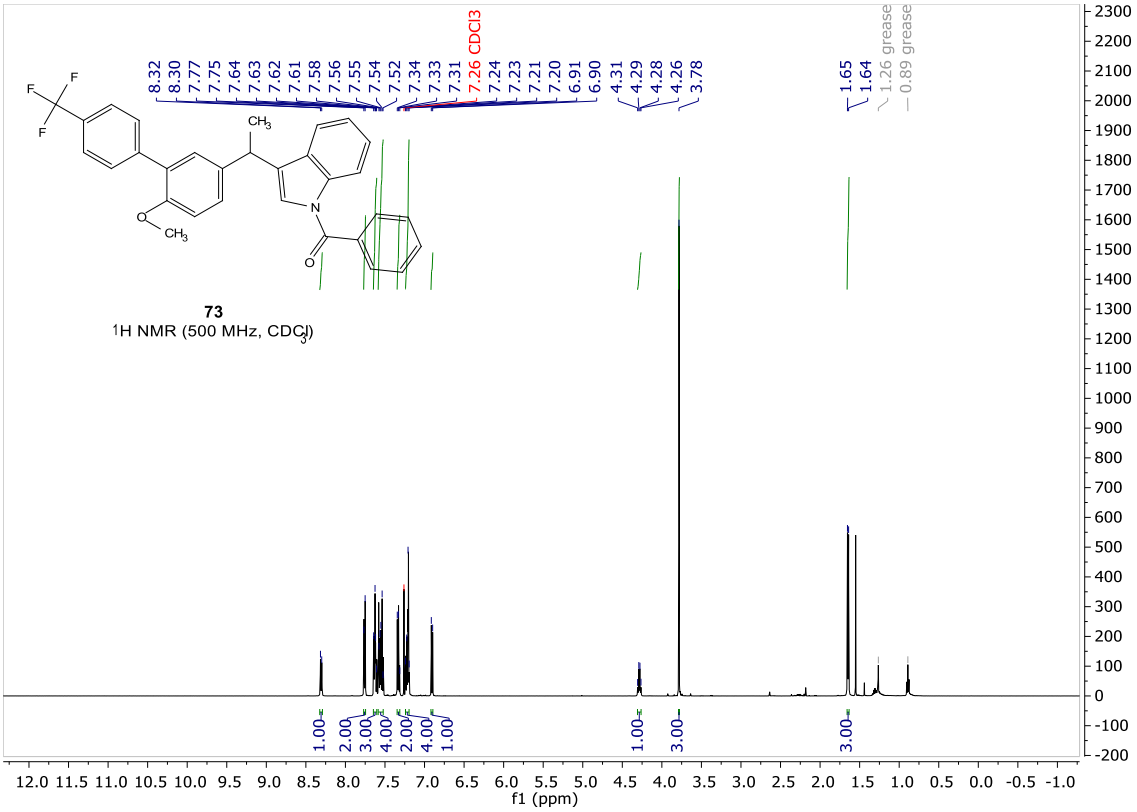


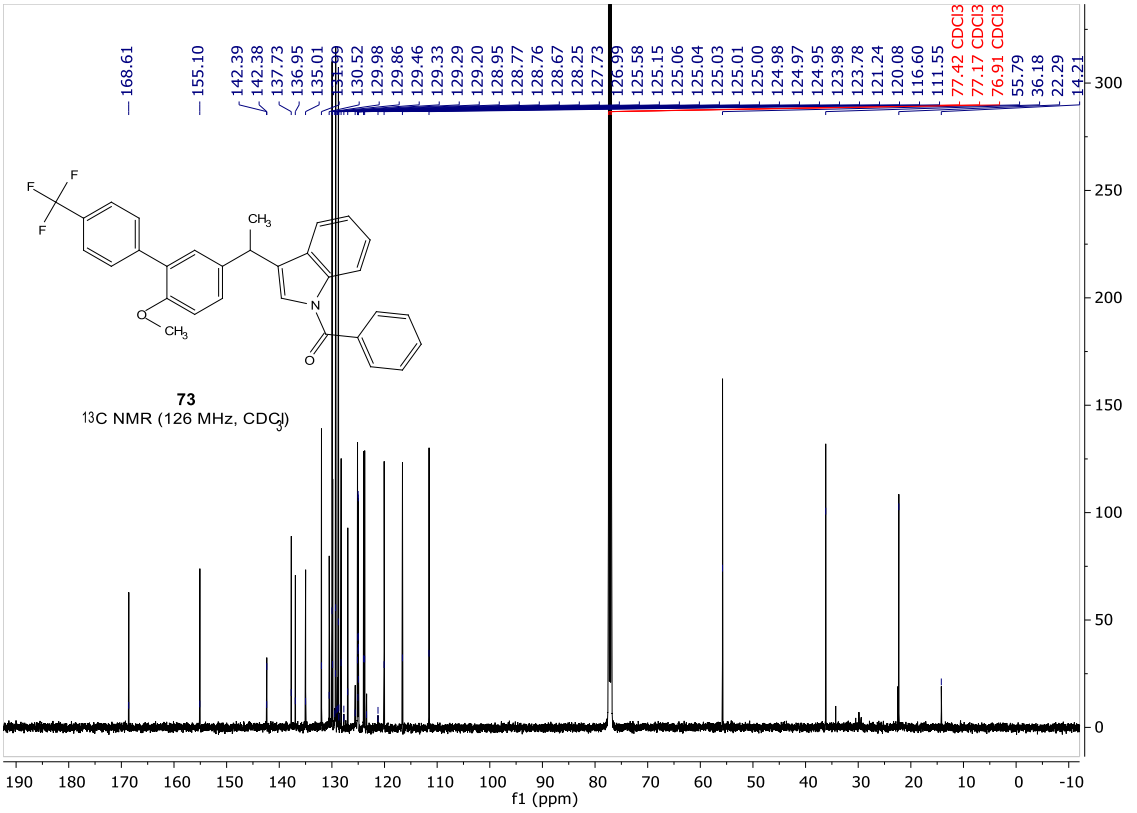
71

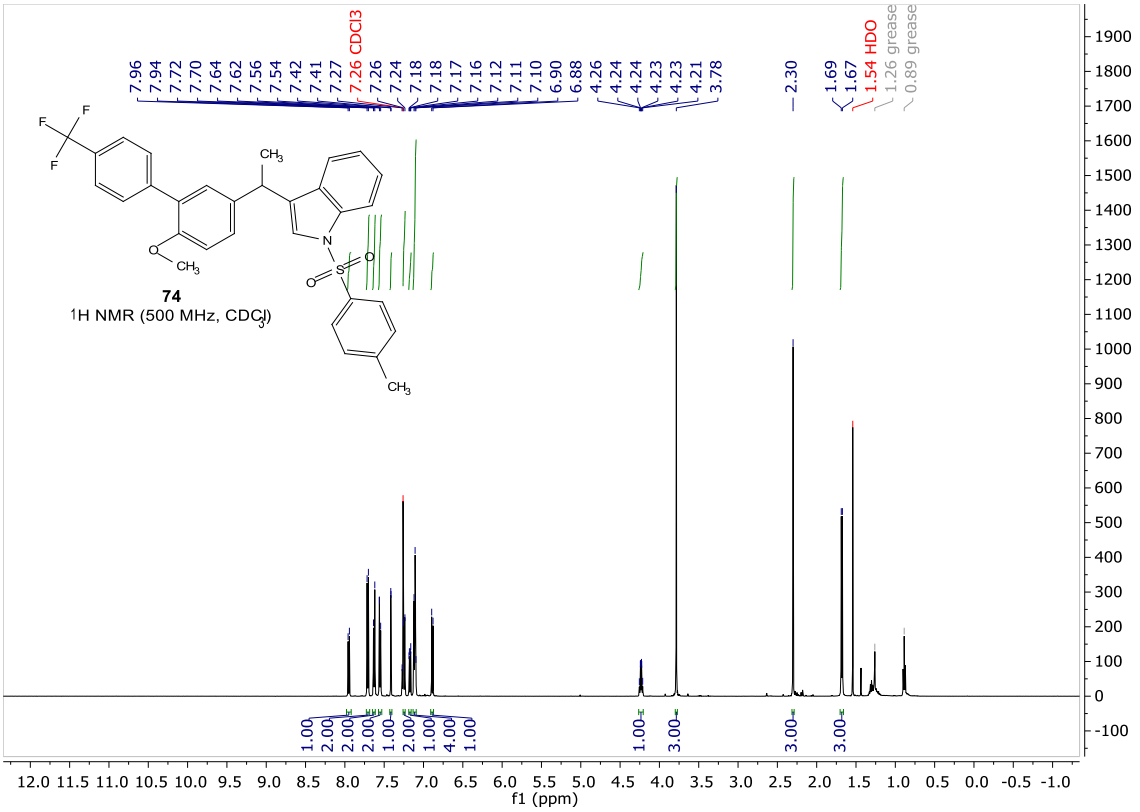
^{13}C NMR (126 MHz, $CDCl_3$)

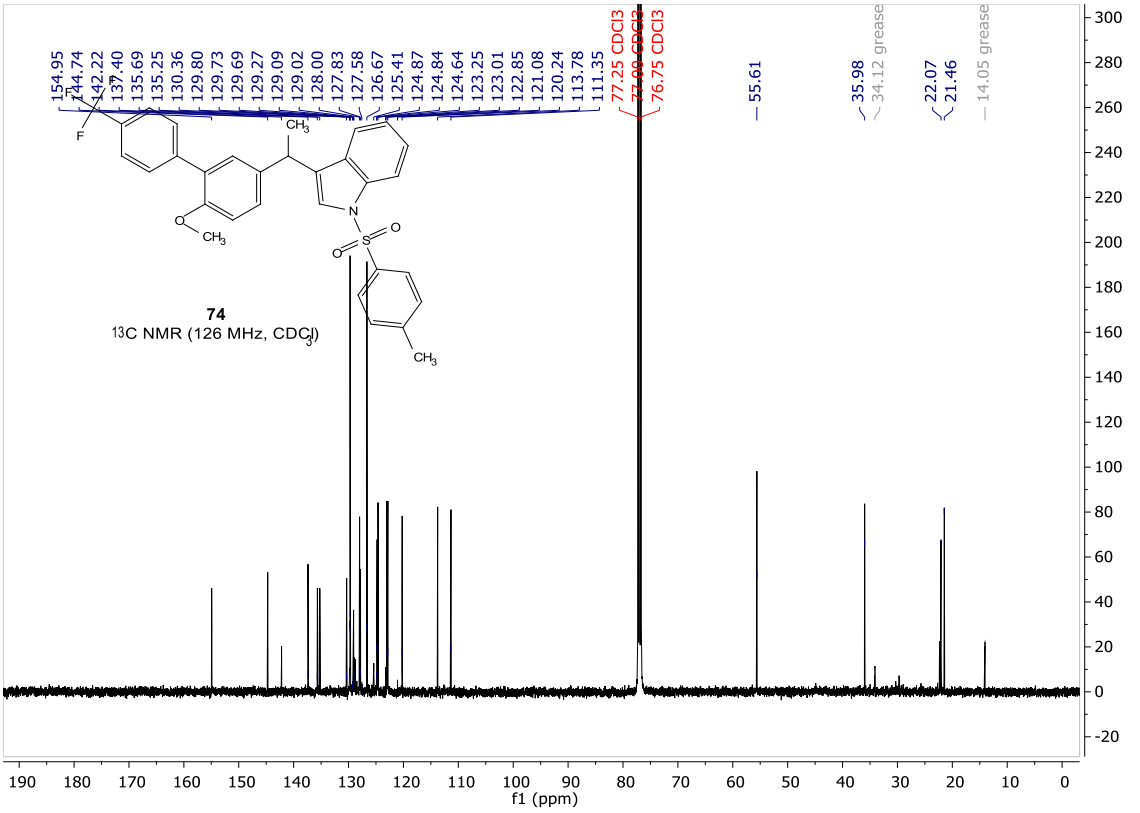

72
1H NMR (500 MHz, CDCl3)
8.35
8.33
7.75
7.74
7.73
7.62
7.61
7.59
7.55
7.53
7.52
7.47
7.45
7.37
7.35
7.34
7.27
7.26 CDCl3
7.25
7.23
7.18
7.14
7.13
7.13
7.12
6.91
6.90
6.89
6.87
6.86
4.58
4.57
4.56
4.54
1.75
1.73
1.54 HDO
1.00
2.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

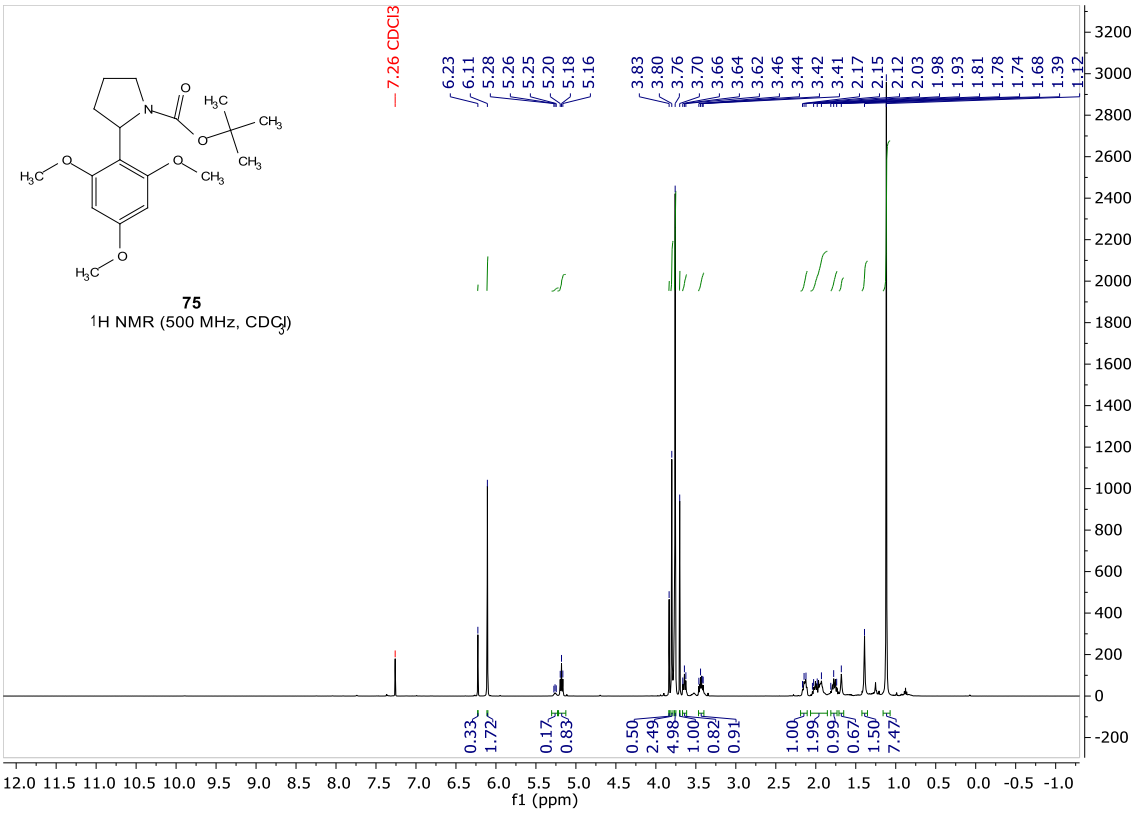

72
13C NMR (126 MHz, CDCl3)
168.66
149.36
136.86
134.89
132.02
130.11
129.33
128.77
126.81
126.75
125.22
123.97
123.85
123.67
119.88
116.68
77.42 CDCl3
77.17 CDCl3
76.92 CDCl3
32.35
22.88
f1 (ppm)


8.32
8.30
7.77
7.75
7.64
7.63
7.62
7.61
7.58
7.56
7.55
7.54
7.52
7.34
7.33
7.31
7.26 CDCl3
7.24
7.23
7.21
7.20
6.91
6.90
4.31
4.29
4.28
4.26
3.78
1.65
1.64
1.26 grease
0.89 grease
73
1H NMR (500 MHz, CDCl3)
1.00
2.00
3.00
4.00
2.00
4.00
1.00
1.00
3.00
3.00
f1 (ppm)


168.61
155.10
142.39
142.38
137.73
136.95
135.01
131.99
130.52
129.98
129.86
129.46
129.33
129.29
129.20
128.95
128.77
128.76
128.67
128.25
127.73
126.99
125.58
125.15
125.06
125.04
125.03
125.01
125.00
124.98
124.97
124.95
123.98
123.78
121.24
120.08
116.60
111.55
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
55.79
36.18
22.29
14.21
73
13C NMR (126 MHz, CDCl3)
f1 (ppm)

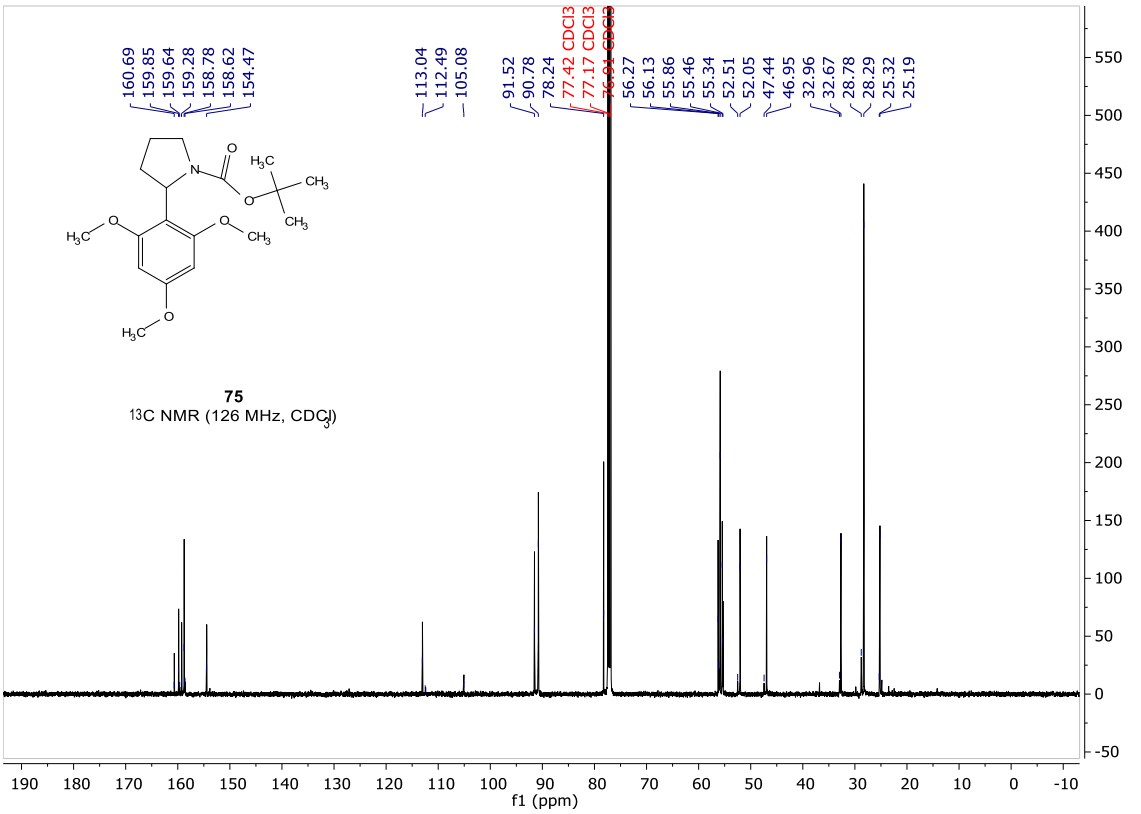

74
1H NMR (500 MHz, CDCl3)
7.96
7.94
7.72
7.70
7.64
7.62
7.56
7.54
7.42
7.41
7.27
7.26 CDCl3
7.26
7.24
7.18
7.18
7.17
7.16
7.12
7.11
7.10
6.90
6.88
4.26
4.24
4.24
4.23
4.23
4.21
3.78
2.30
1.69
1.67
1.54 HDO
1.26 grease
0.89 grease
1.00
2.00
2.00
2.00
1.00
2.00
1.00
4.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)


74
13C NMR (126 MHz, CDCl3)
154.95
144.74
142.22
137.40
135.69
135.25
130.36
129.80
129.73
129.69
129.27
129.09
129.02
128.00
127.83
127.58
126.67
125.41
124.87
124.84
124.64
123.25
123.01
122.85
121.08
120.24
113.78
111.35
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
55.61
35.98
34.12 grease
22.07
21.46
14.05 grease
f1 (ppm)



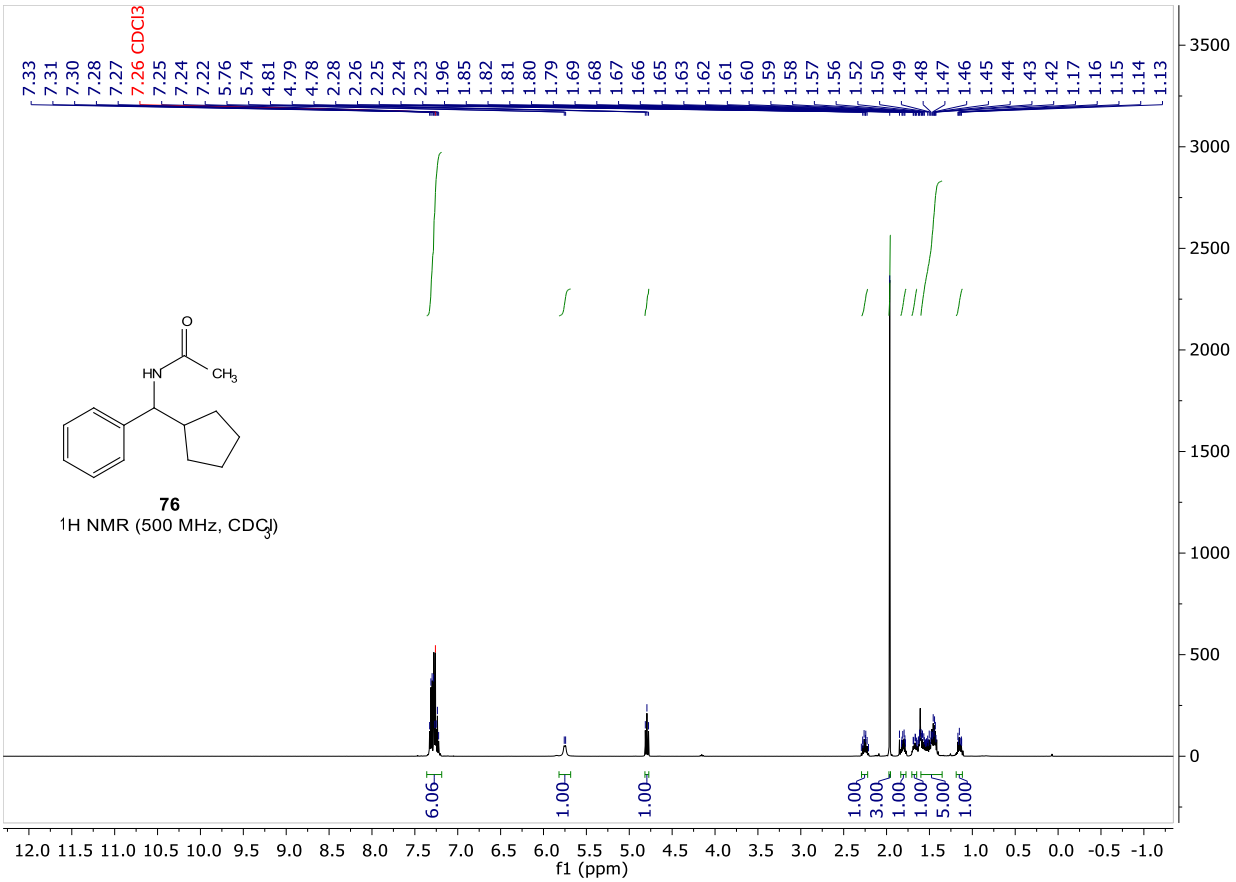
75

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



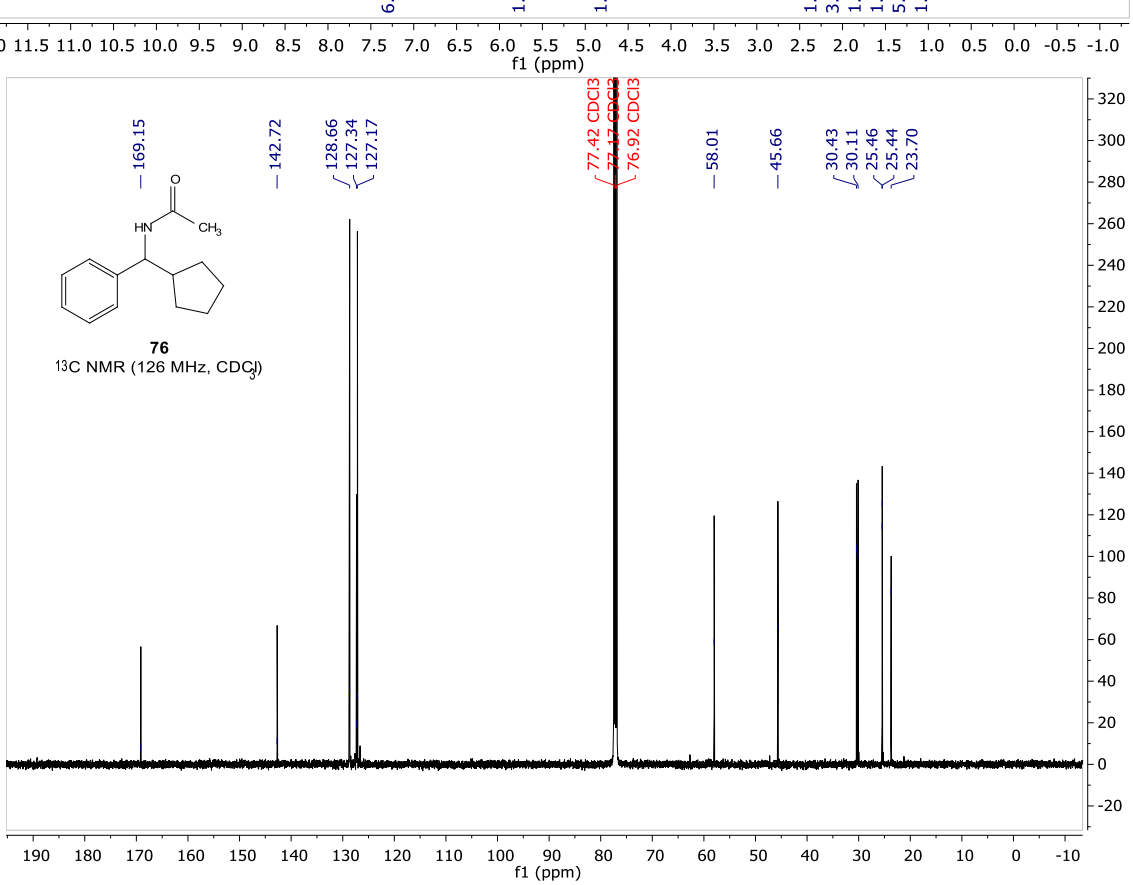
75

^{13}C NMR (126 MHz, $CDCl_3$)



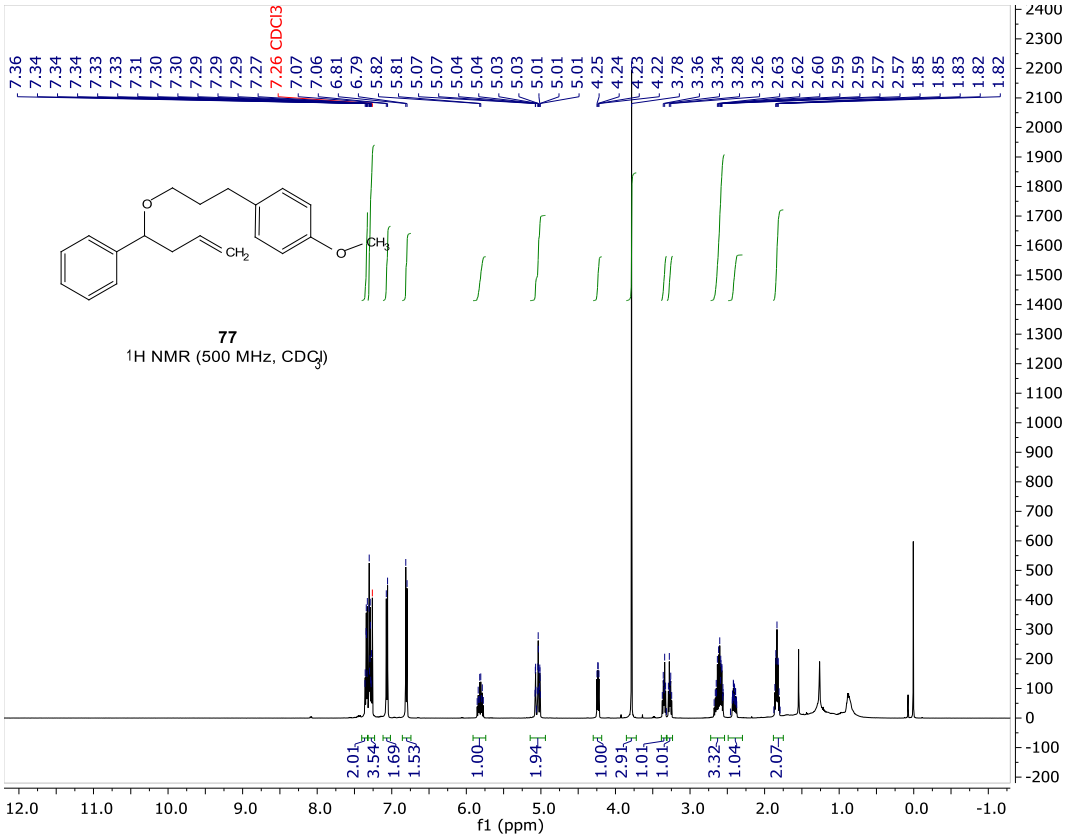
76

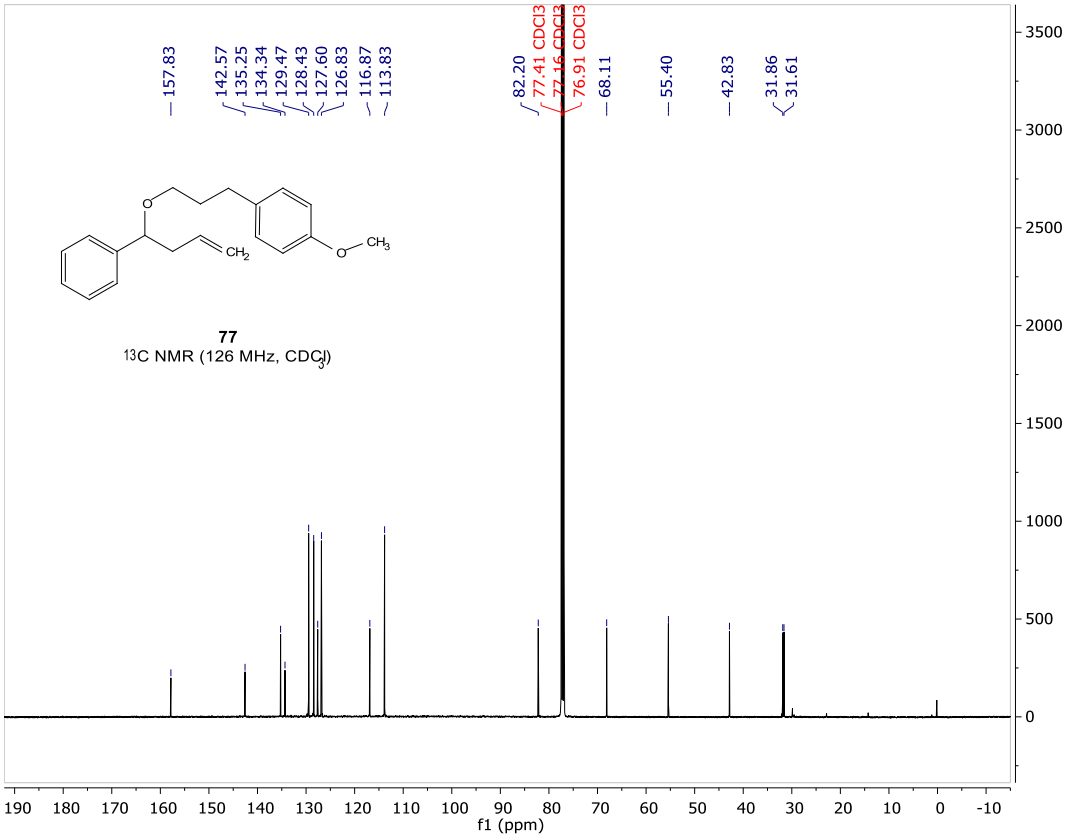
^{1}H NMR (500 MHz, $CDCl_3$)



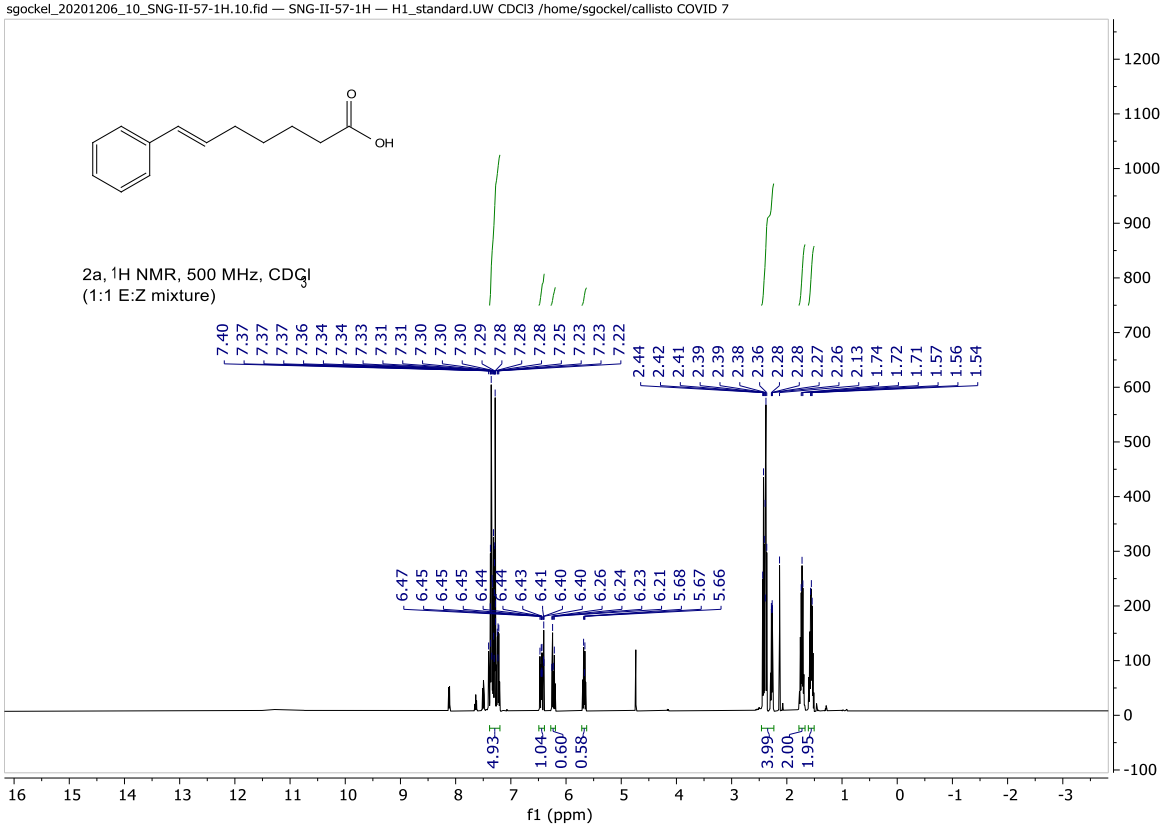
76

^{13}C NMR (126 MHz, $CDCl_3$)

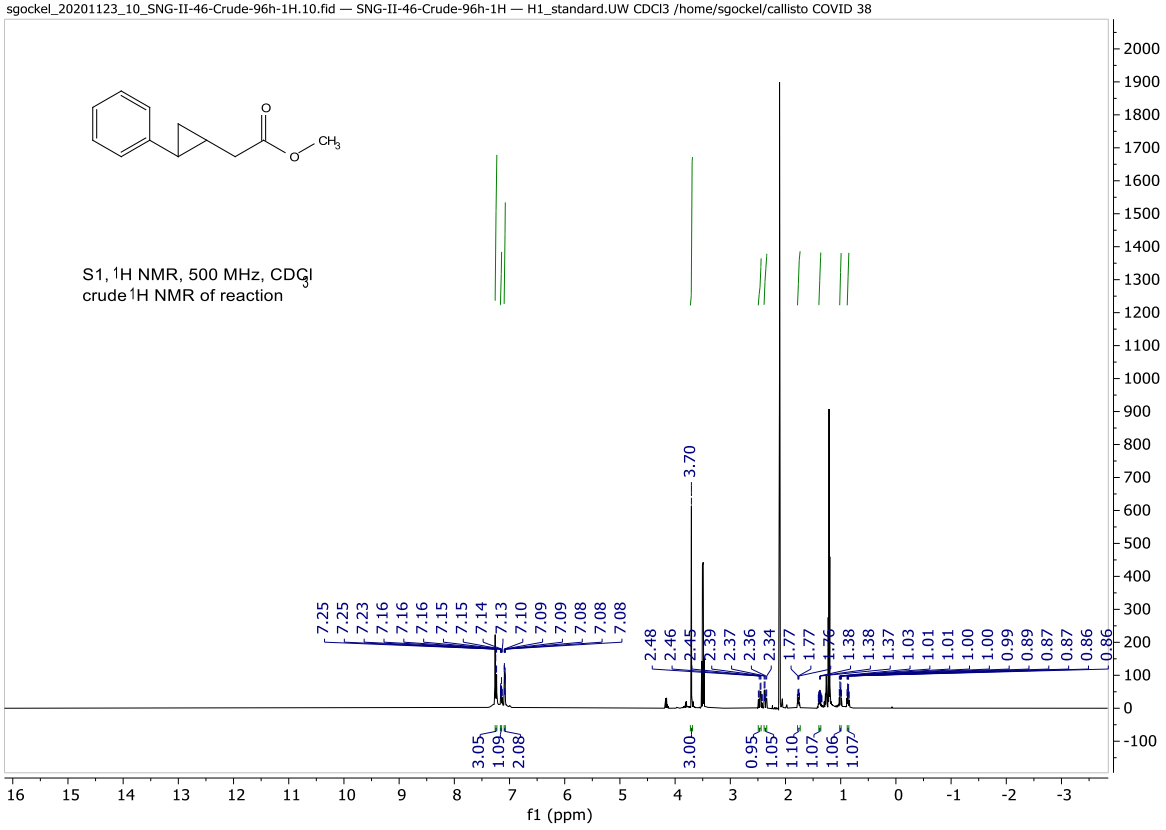

7.36 7.34 7.34 7.34 7.33 7.33 7.31 7.30 7.30 7.29 7.29 7.29 7.27 7.26 CDCl3 7.07 7.06 6.81 6.79 5.82 5.81 5.07 5.07 5.04 5.04 5.03 5.03 5.01 5.01 5.01 4.25 4.24 4.23 4.22 3.78 3.36 3.34 3.28 3.26 2.63 2.62 2.60 2.59 2.59 2.57 2.57 1.85 1.85 1.83 1.82 1.82
O
CH2
O
CH3
77
1H NMR (500 MHz, CDCl3)
2.01 3.54 1.69 1.53 1.00 1.94 1.00 2.91 1.01 1.01 3.32 1.04 2.07
f1 (ppm)

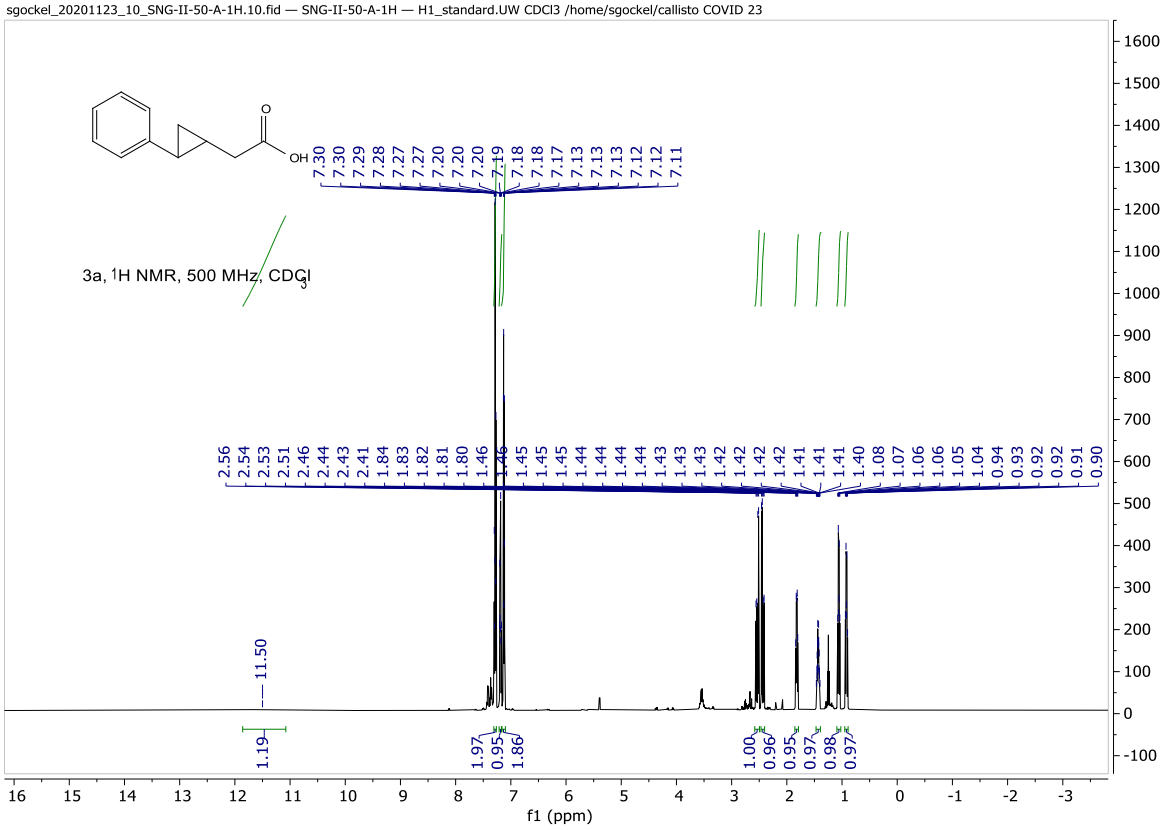

157.83 142.57 135.25 134.34 129.47 128.43 127.60 126.83 116.87 113.83
82.20 77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 68.11 55.40 42.83 31.86 31.61
O
CH2
O
CH3
77
13C NMR (126 MHz, CDCl3)
f1 (ppm)

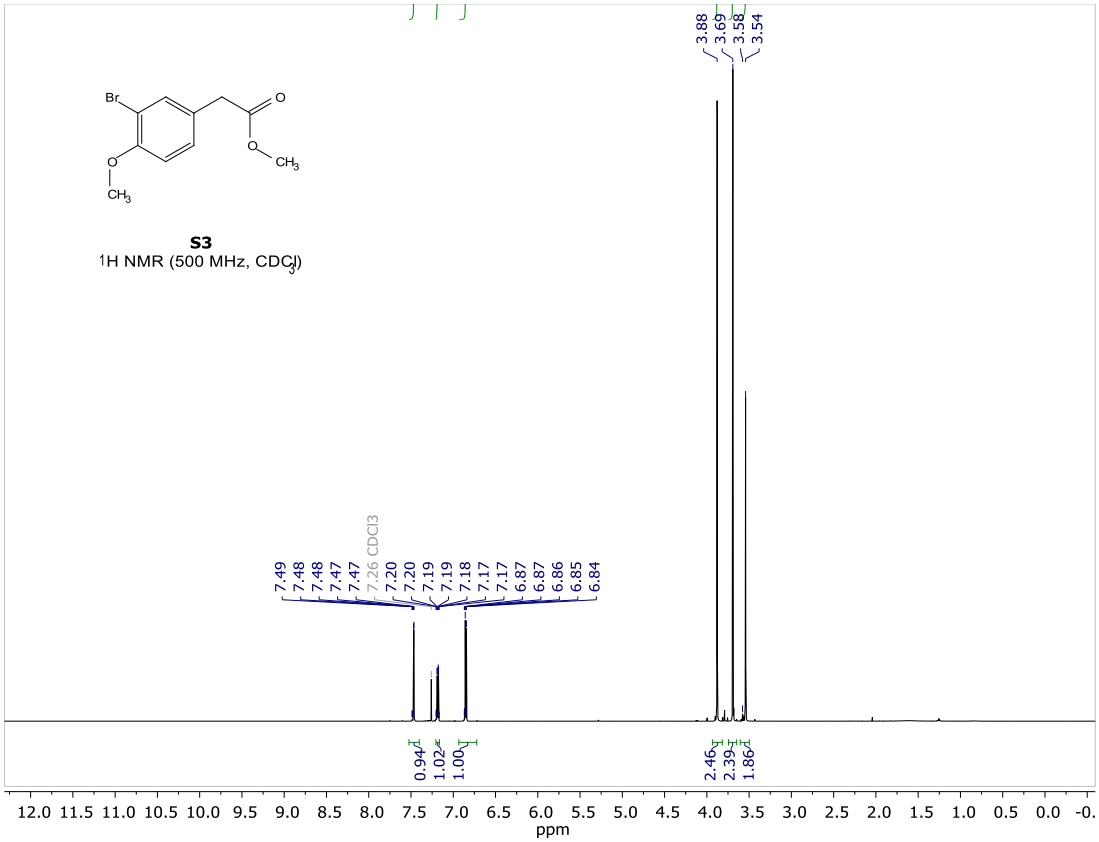
sgockel_20201206_10_SNG-II-57-1H.10.fid — SNG-II-57-1H — H1_standard.UW CDCl3 /home/sgockel/callisto COVID 7

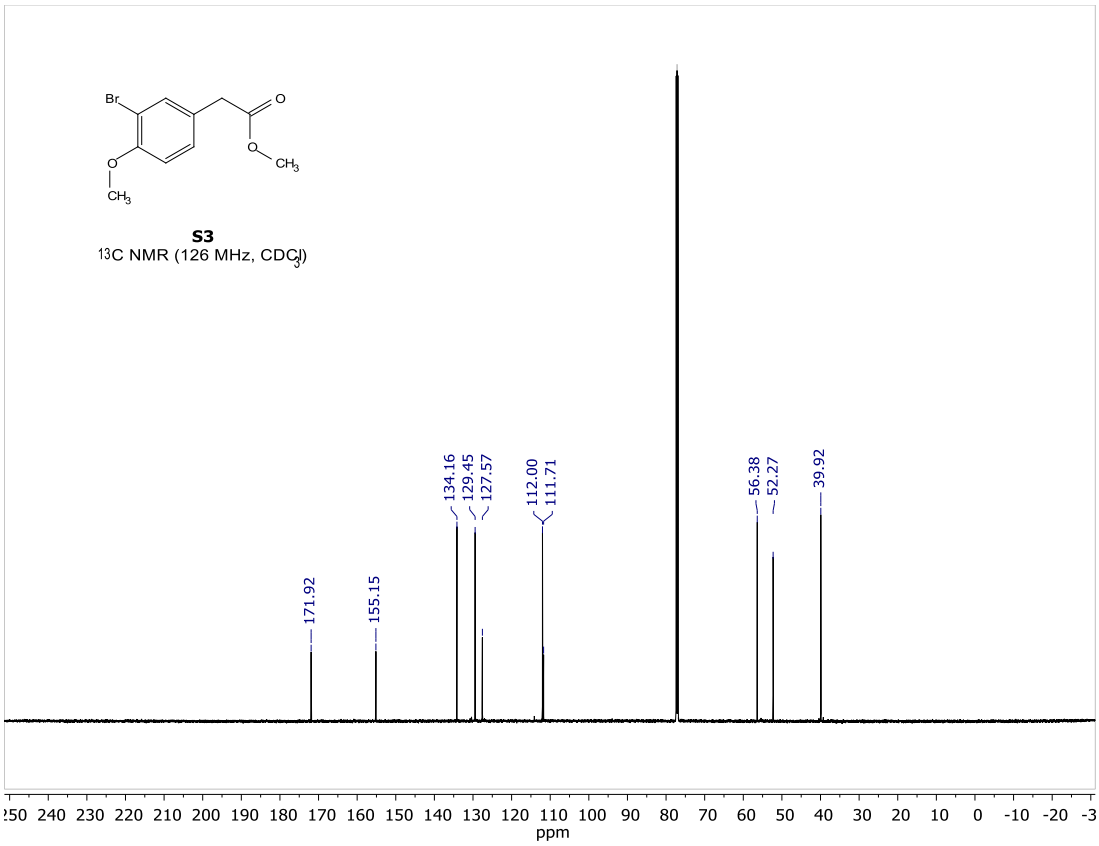


sgockel_20201123_10_SNG-II-46-Crude-96h-1H.10.fid — SNG-II-46-Crude-96h-1H — H1_standard.UW CDCl3 /home/sgockel/callisto COVID 38

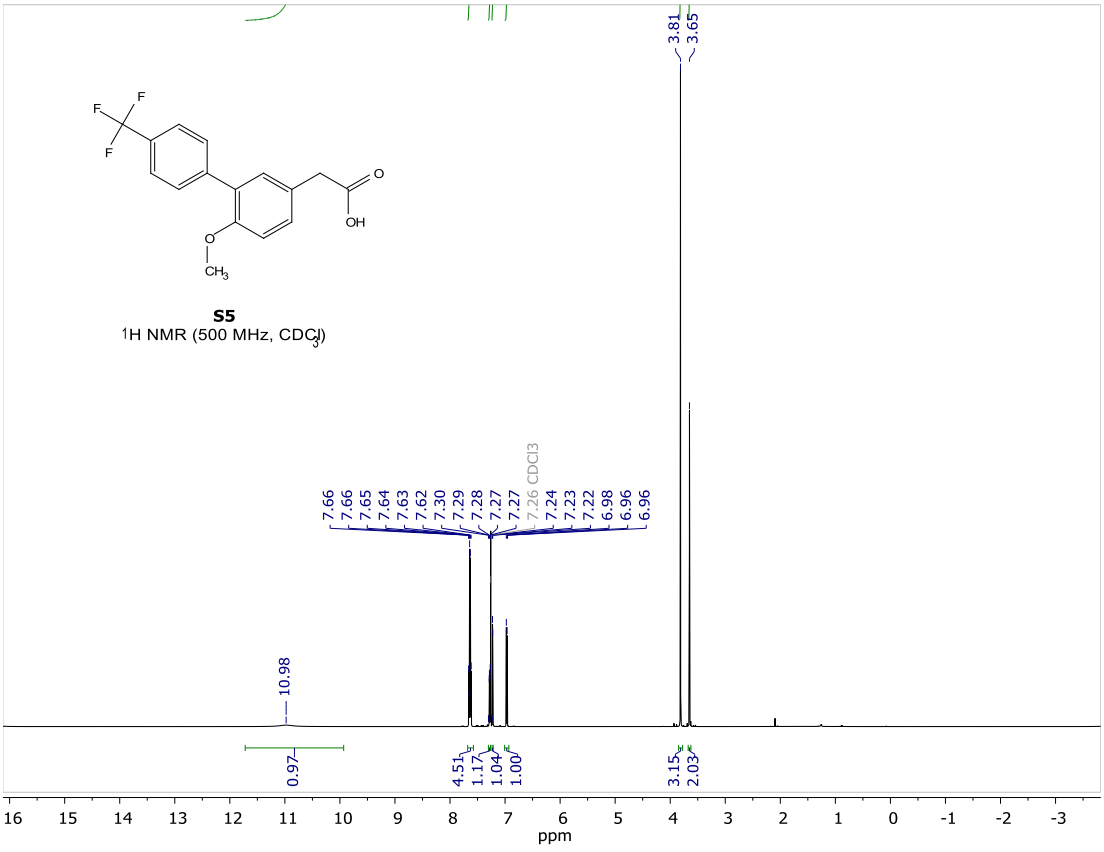



sgockel_20201123_10_SNG-II-50-A-1H.10.fid — SNG-II-50-A-1H — H1_standard.UW CDCl3 /home/sgockel/callisto COVID 23
3a, 1H NMR, 500 MHz, CDCl3
f1 (ppm)

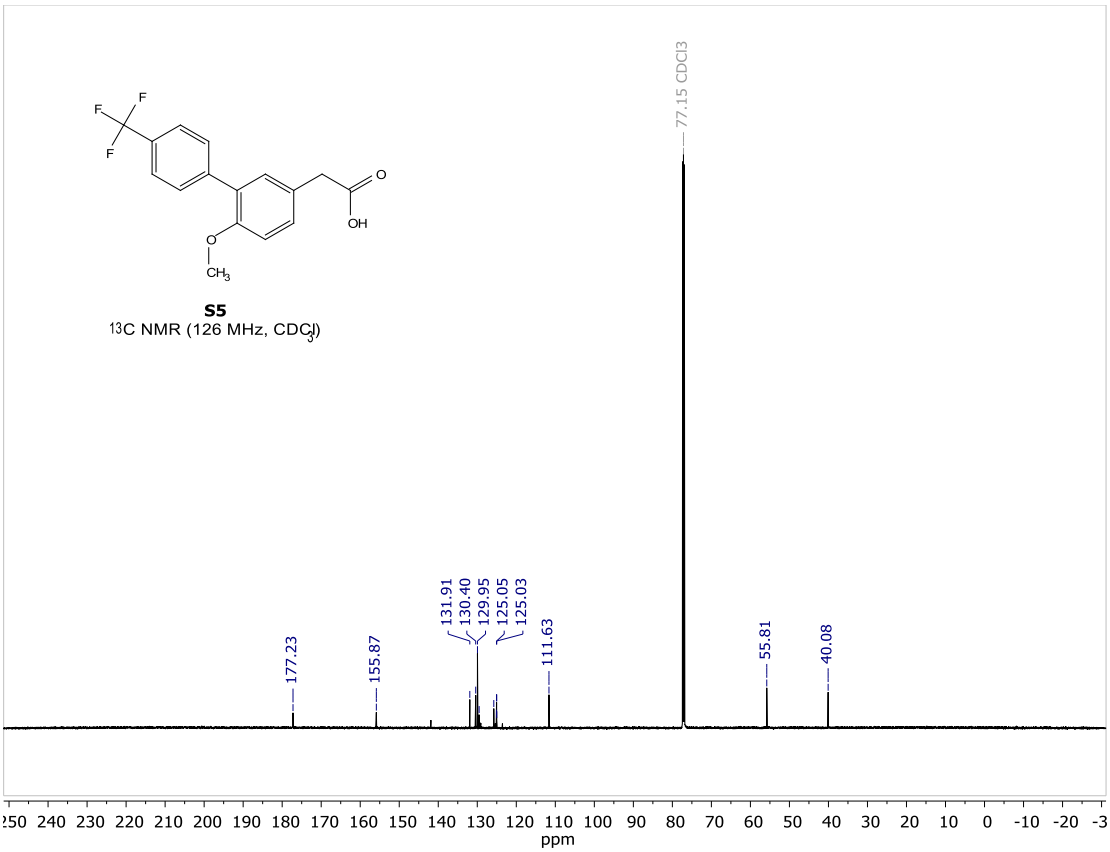

S3
1H NMR (500 MHz, CDCl3)
ppm



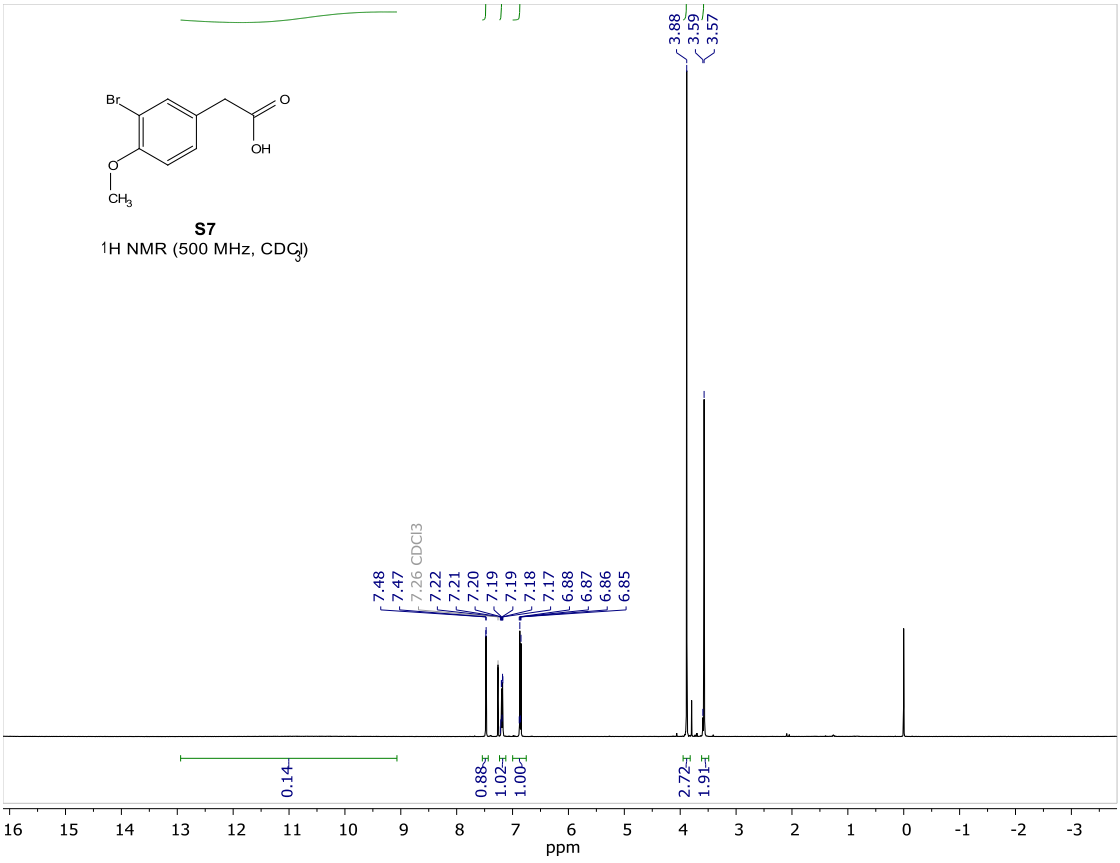
S3
^{13}C NMR (126 MHz, $CDCl_3$)



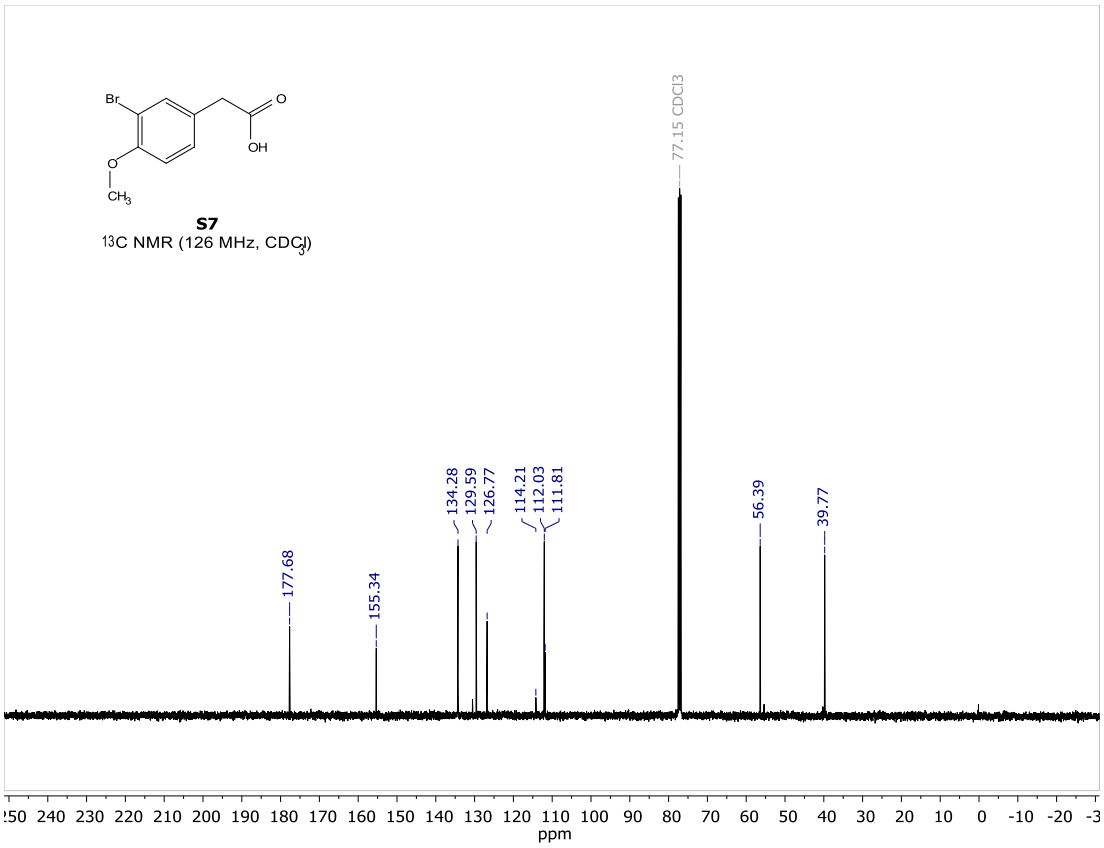
S5
^{1}H NMR (500 MHz, $CDCl_3$)



S5
^{13}C NMR (126 MHz, $CDCl_3$)

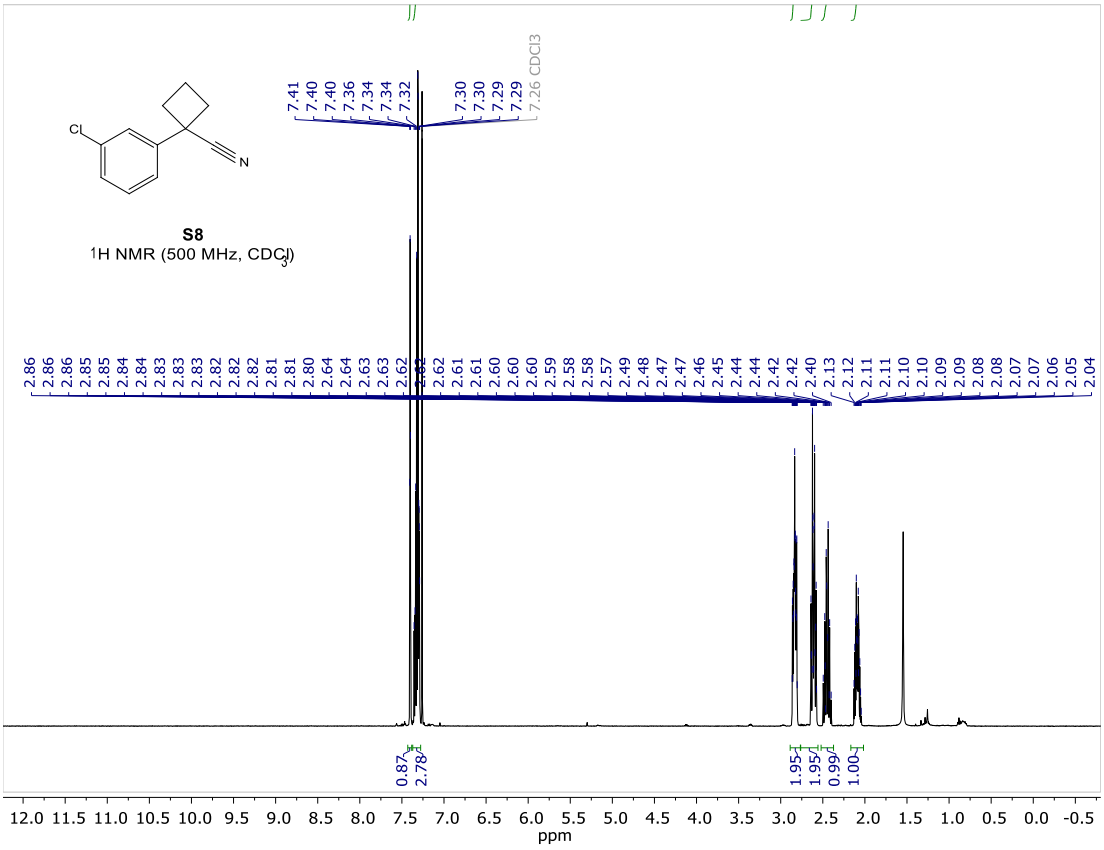


S7
^{1}H NMR (500 MHz, $CDCl_3$)



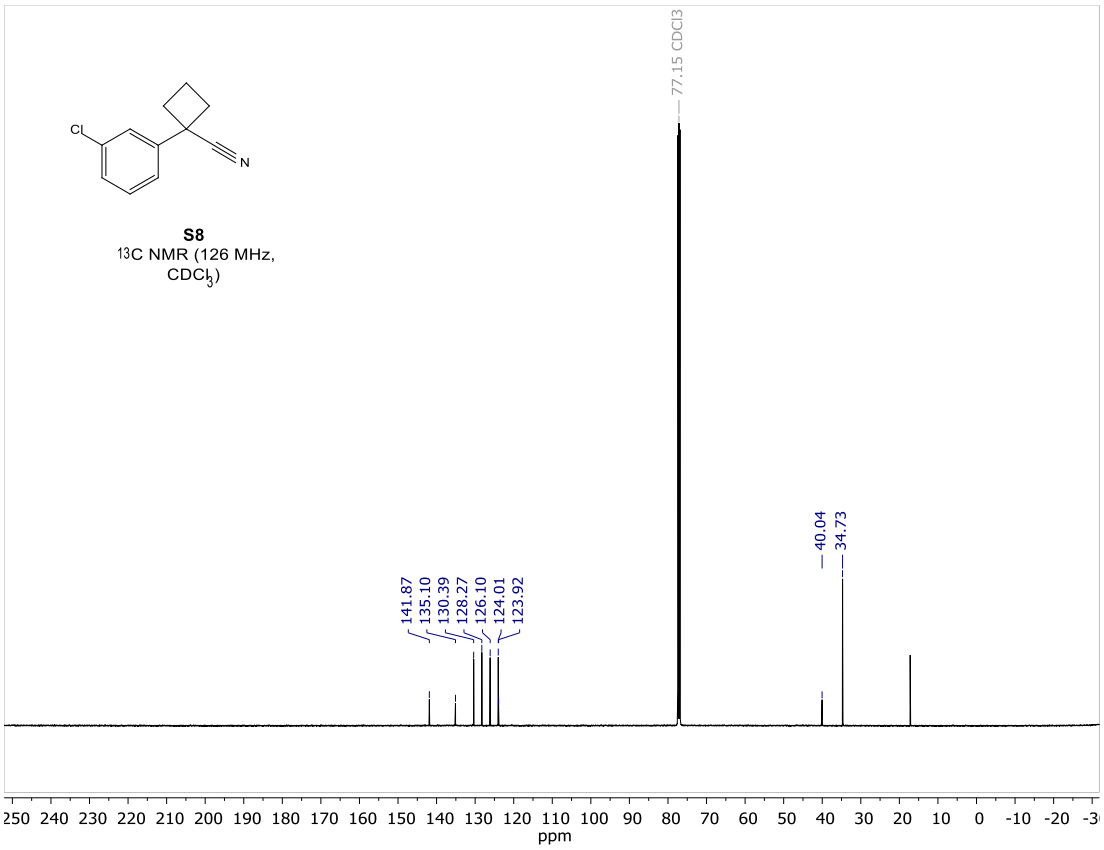
S7

^{13}C NMR (126 MHz, $CDCl_3$)

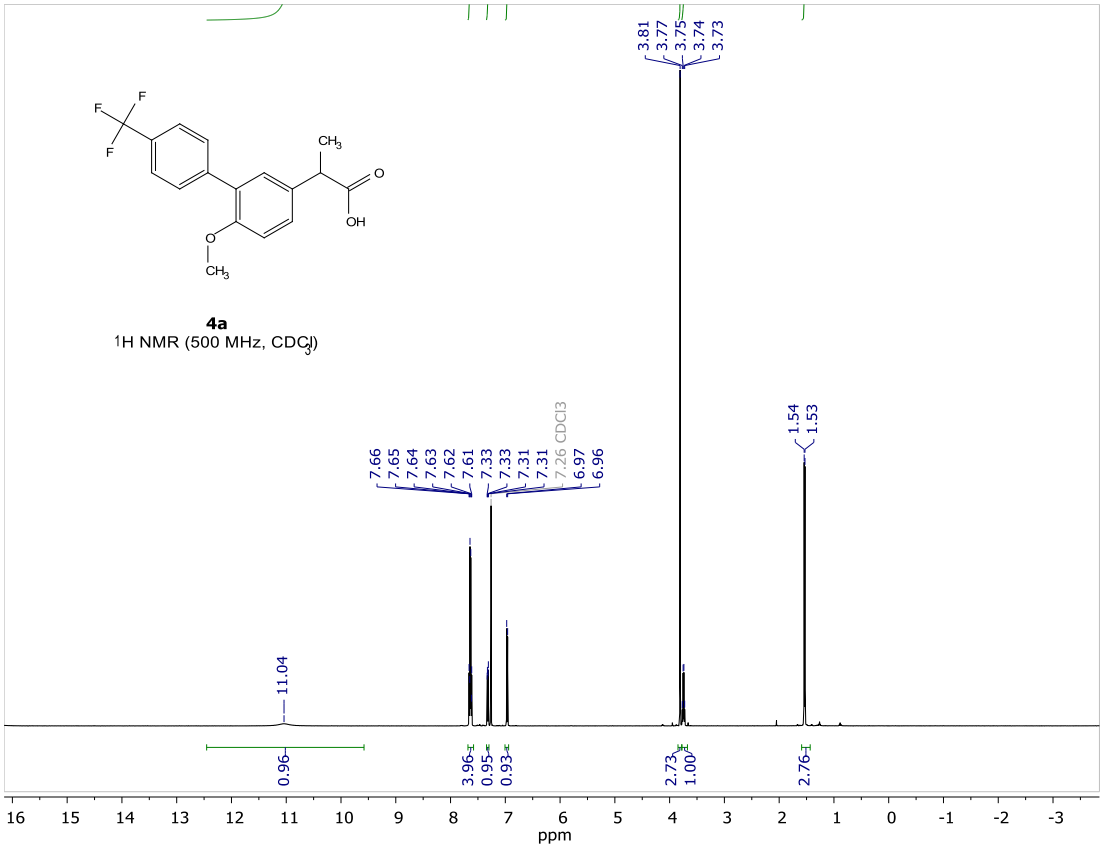


S8

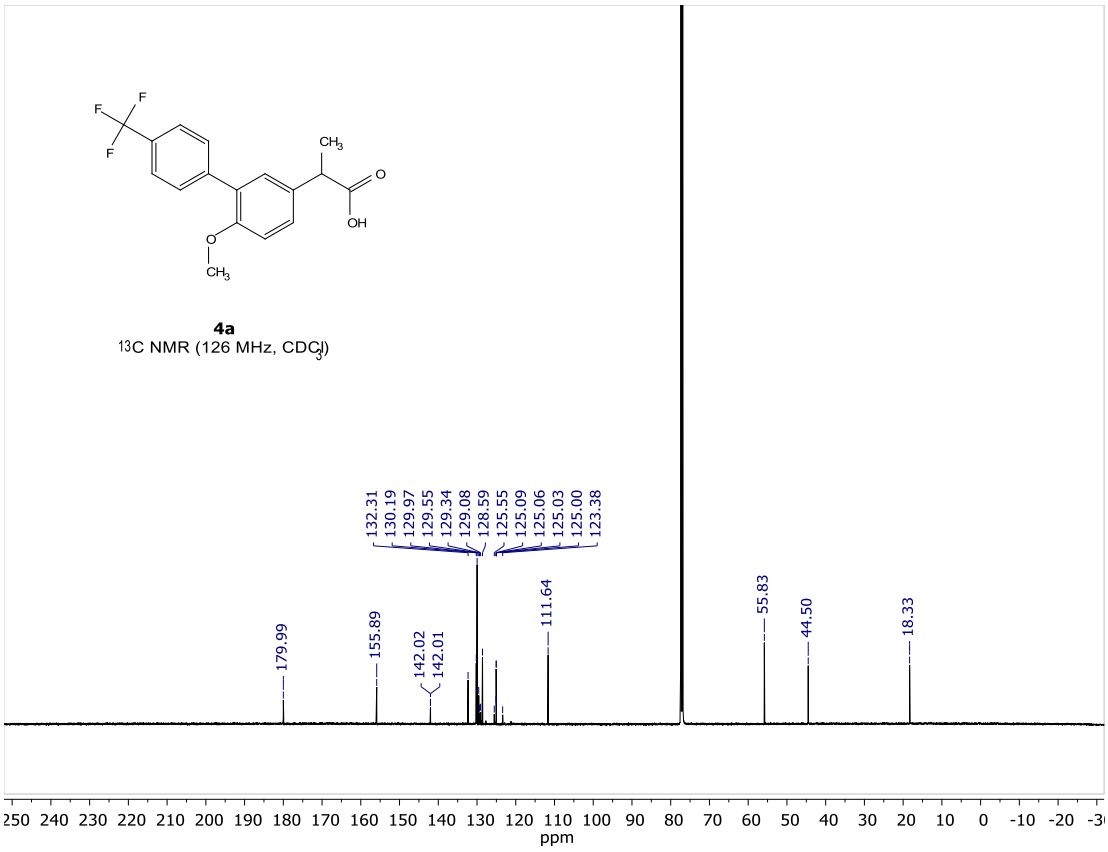
^{1}H NMR (500 MHz, $CDCl_3$)

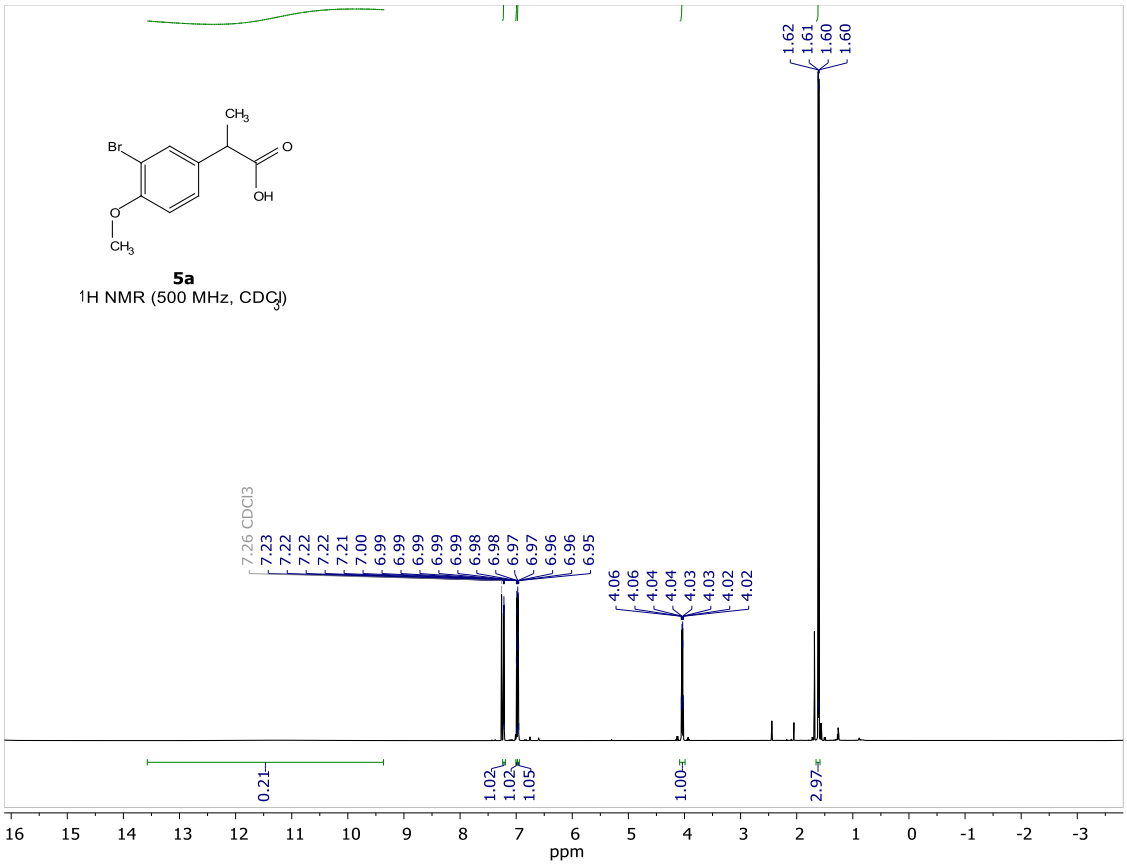


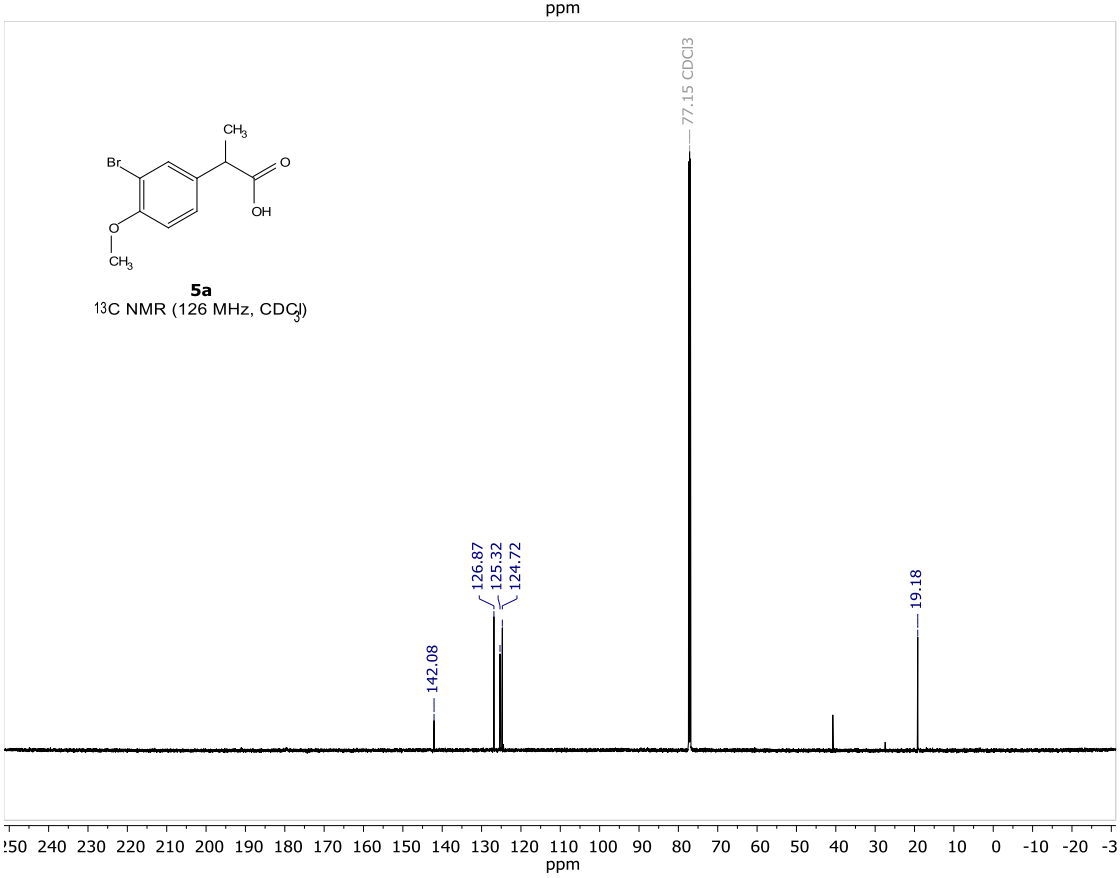
S8
^{13}C NMR (126 MHz, $CDCl_3$)

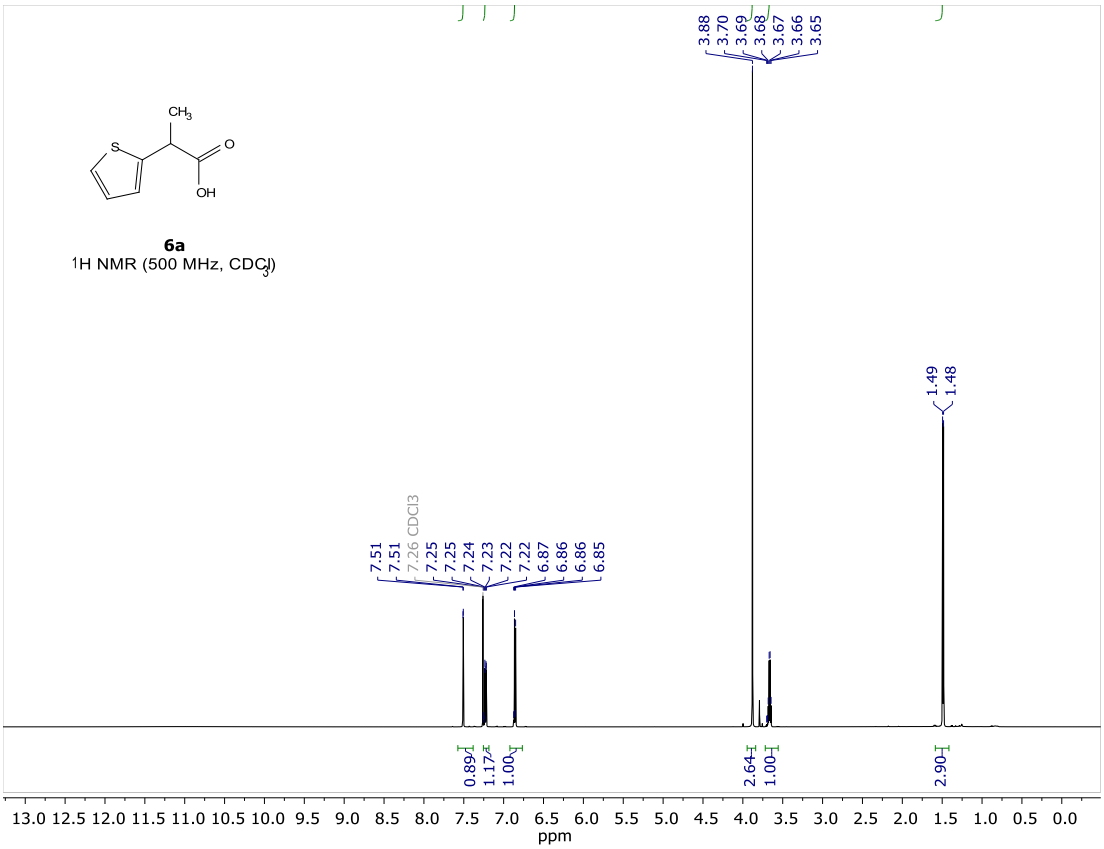


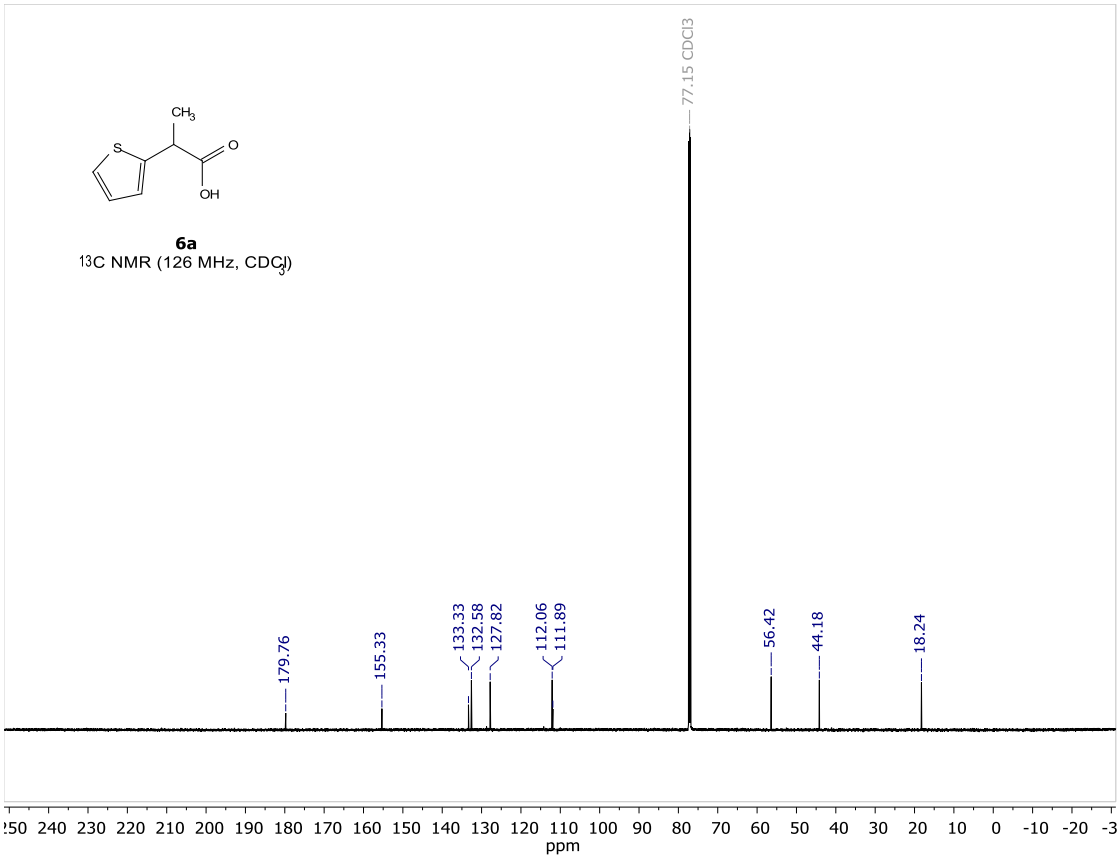
4a
^{1}H NMR (500 MHz, $CDCl_3$)

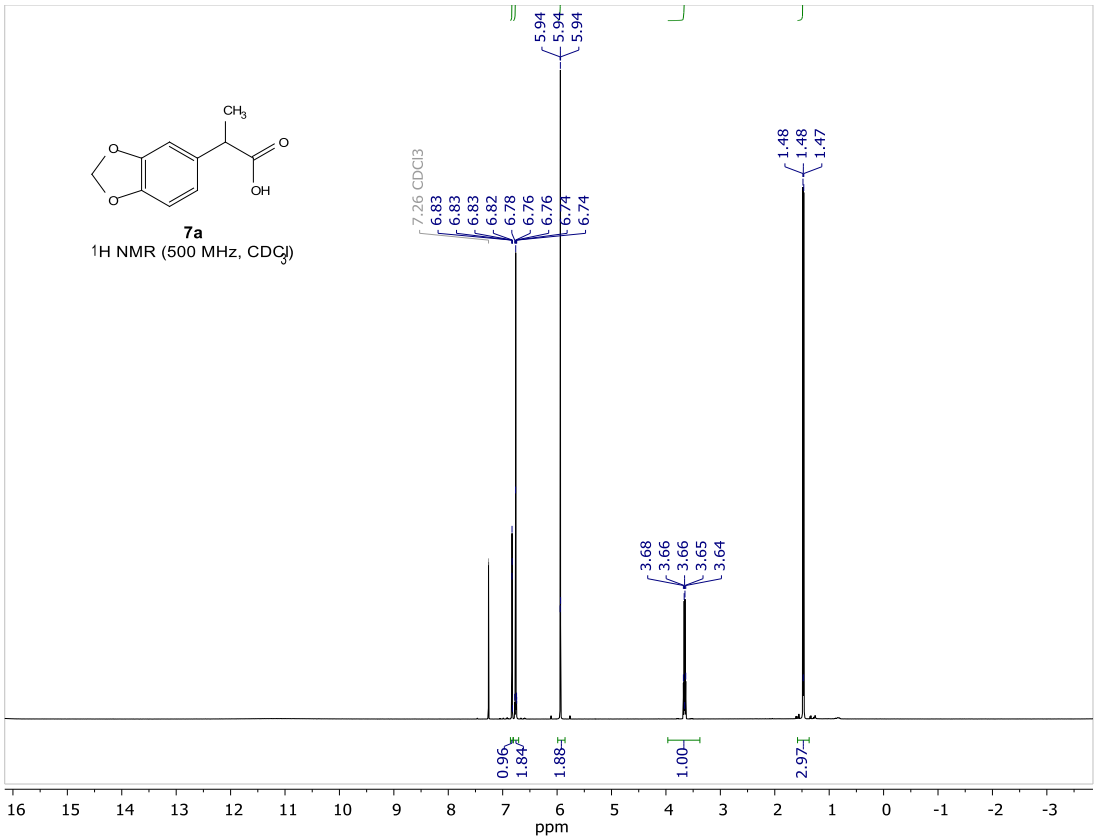

F
F
F
CH3
O
OH
O
CH3
4a
13C NMR (126 MHz, CDCl3)
132.31
130.19
129.97
129.55
129.34
129.08
128.59
125.55
125.09
125.06
125.03
125.00
123.38
179.99
155.89
142.02
142.01
111.64
55.83
44.50
18.33
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm

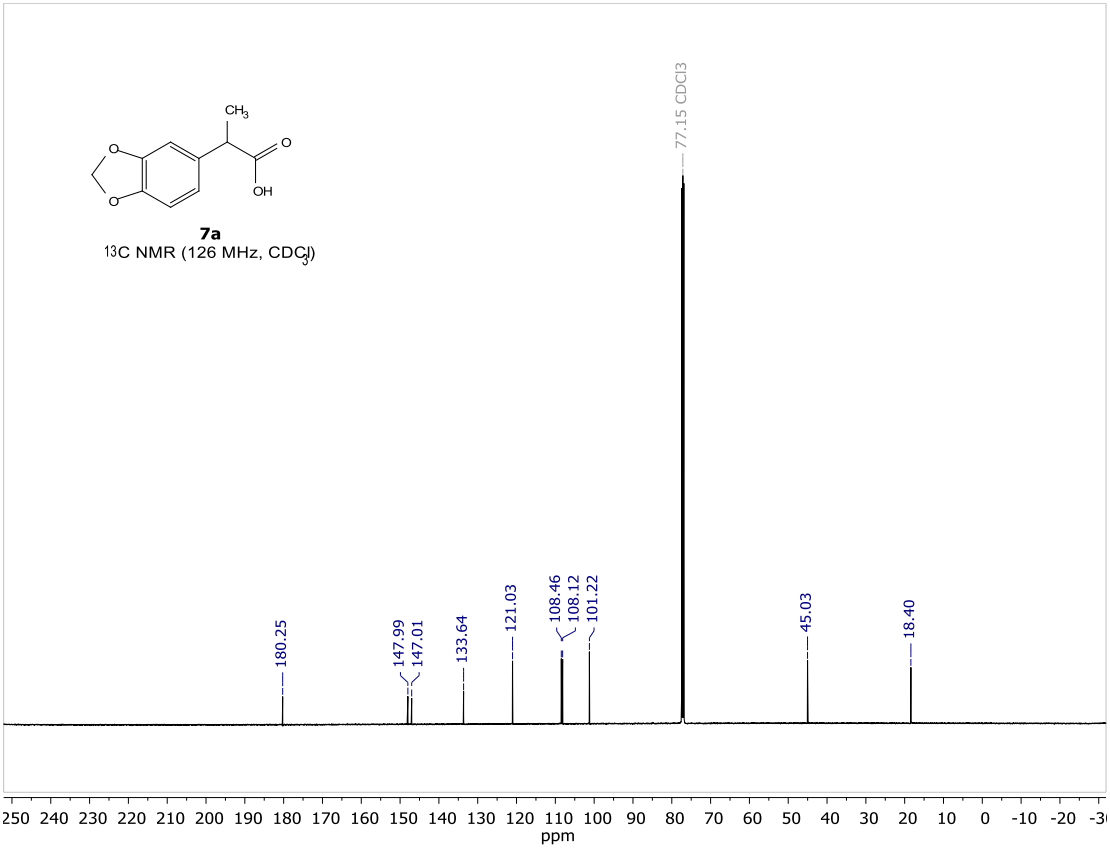

Br
CH3
O
OH
O
CH3
5a
1H NMR (500 MHz, CDCl3)
1.62
1.61
1.60
1.60
7.26 CDCl3
7.23
7.22
7.22
7.22
7.21
7.00
6.99
6.99
6.99
6.99
6.99
6.98
6.98
6.97
6.97
6.96
6.96
6.95
4.06
4.06
4.04
4.04
4.03
4.03
4.02
4.02
0.21
1.02
1.02
1.05
1.00
2.97
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

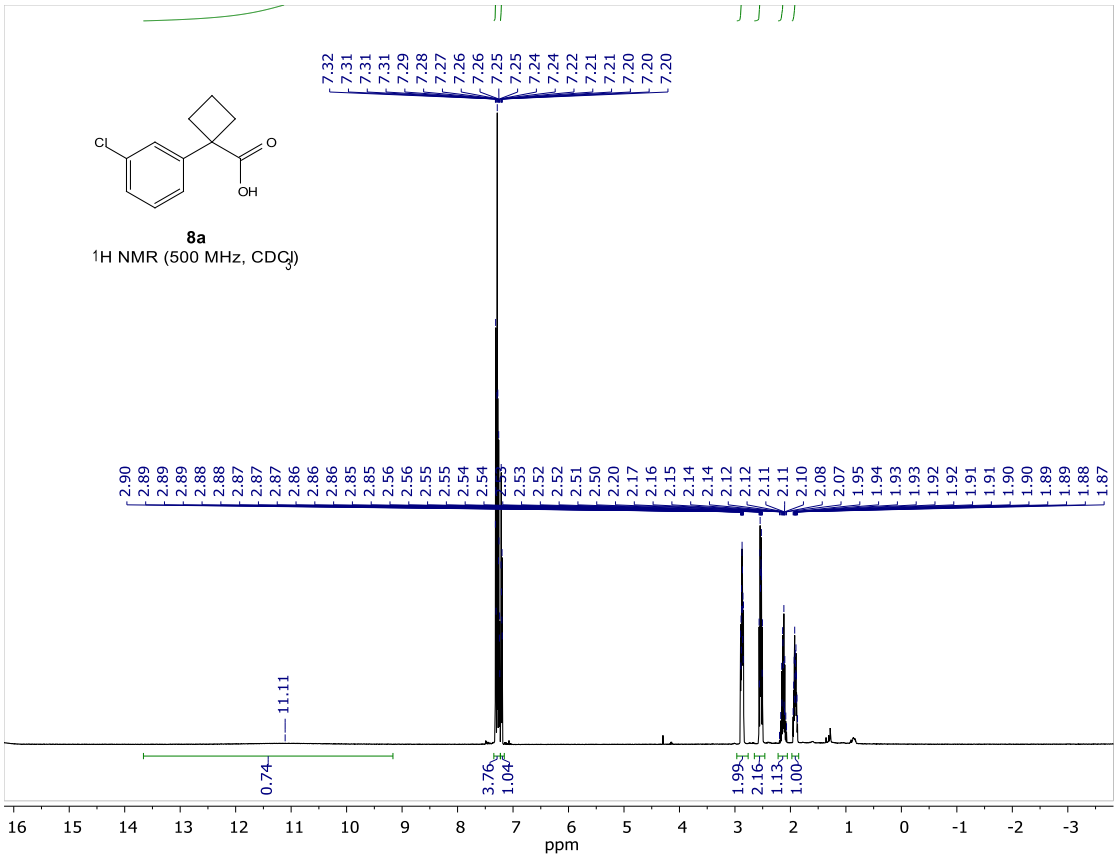

Br
CH3
O
OH
O
CH3
5a
13C NMR (126 MHz, CDCl3)
77.15 CDCl3
126.87
125.32
124.72
142.08
19.18
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -3
ppm

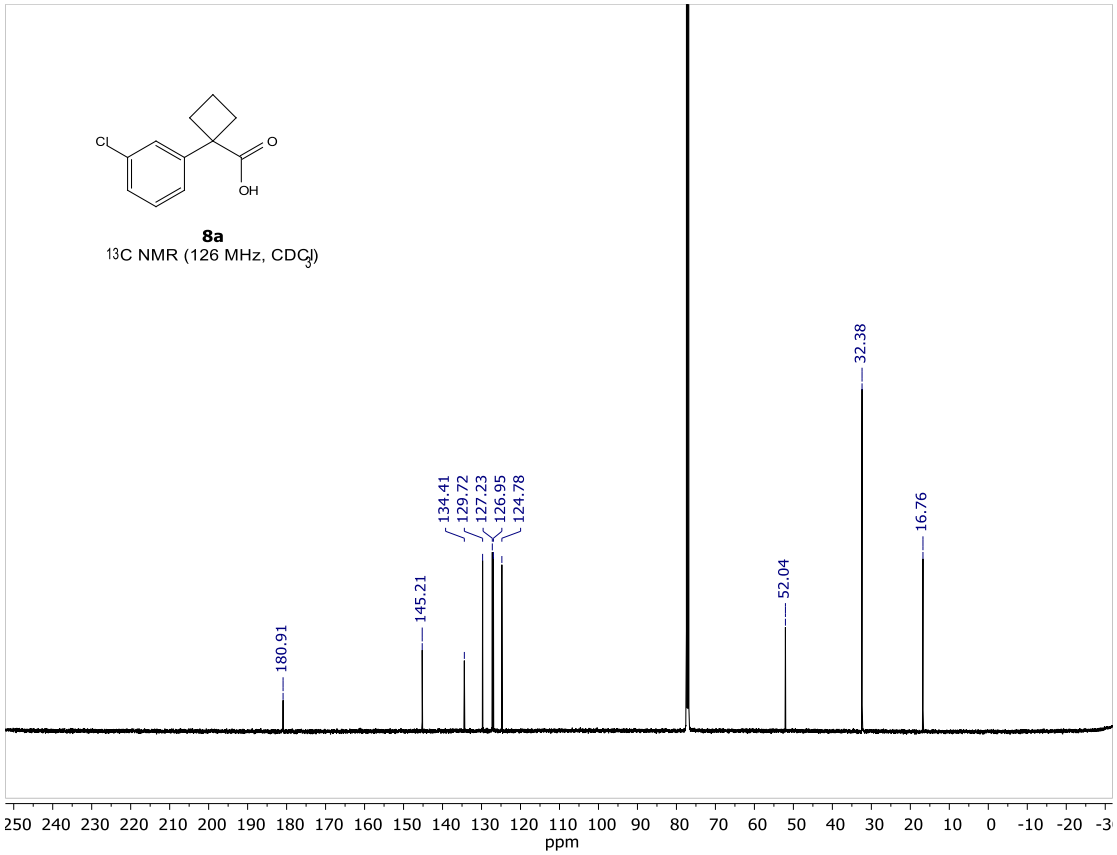

CH3
S
O
OH
6a
1H NMR (500 MHz, CDCl3)
3.88
3.70
3.69
3.68
3.67
3.66
3.65
1.49
1.48
7.51
7.51
7.26 CDCl3
7.25
7.25
7.24
7.23
7.22
7.22
6.87
6.86
6.86
6.85
0.89
1.17
1.00
2.64
1.00
2.90
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

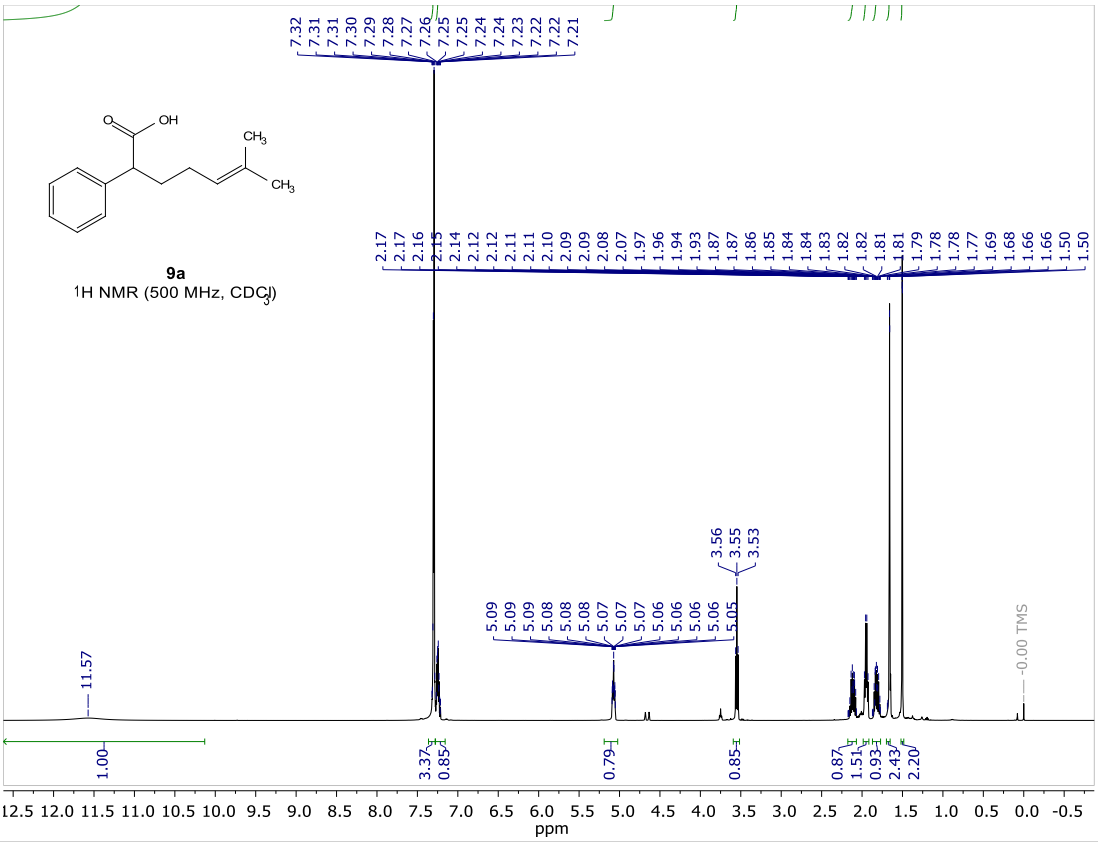

CH3
S
O
OH
6a
13C NMR (126 MHz, CDCl3)
77.15 CDCl3
179.76
155.33
133.33
132.58
127.82
112.06
111.89
56.42
44.18
18.24
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -3
ppm

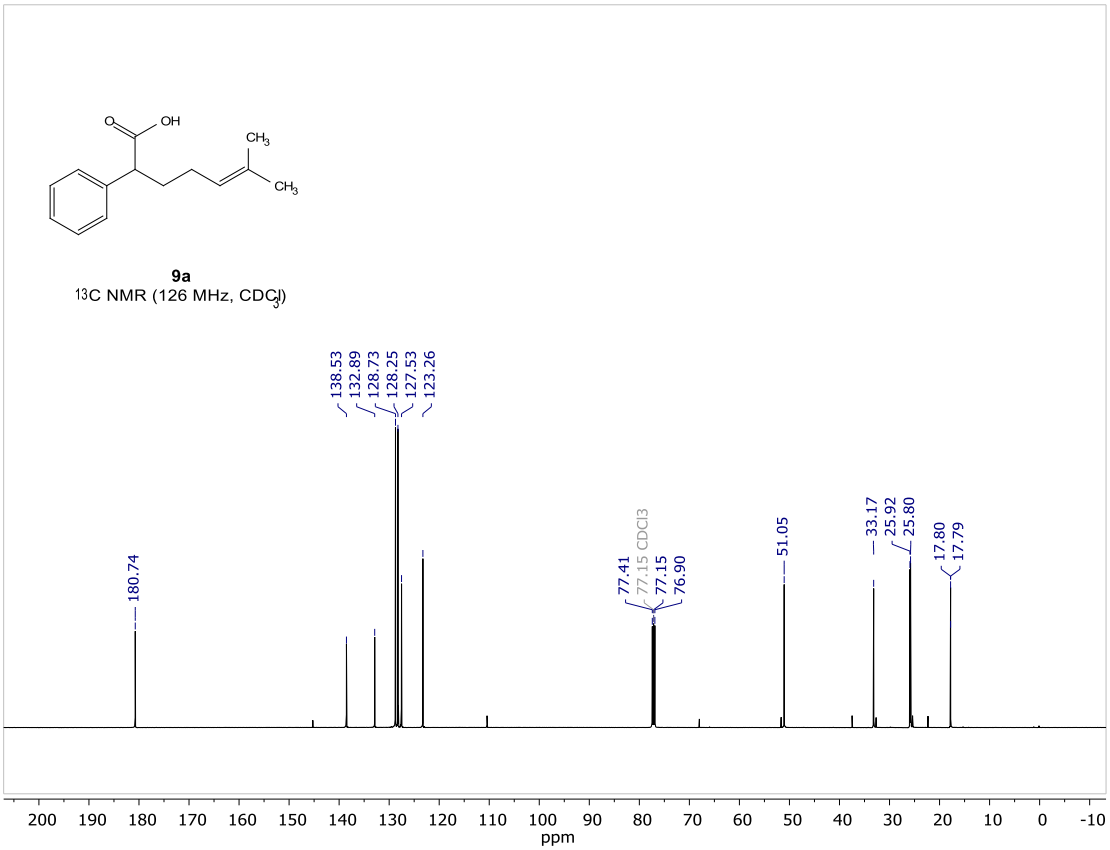

CH3
O
O
O
OH
7a
1H NMR (500 MHz, CDCl3)
7.26 CDCl3
6.83
6.83
6.83
6.82
6.78
6.76
6.76
6.74
6.74
5.94
5.94
5.94
3.68
3.66
3.66
3.65
3.64
1.48
1.48
1.47
0.96
1.84
1.88
1.00
2.97
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

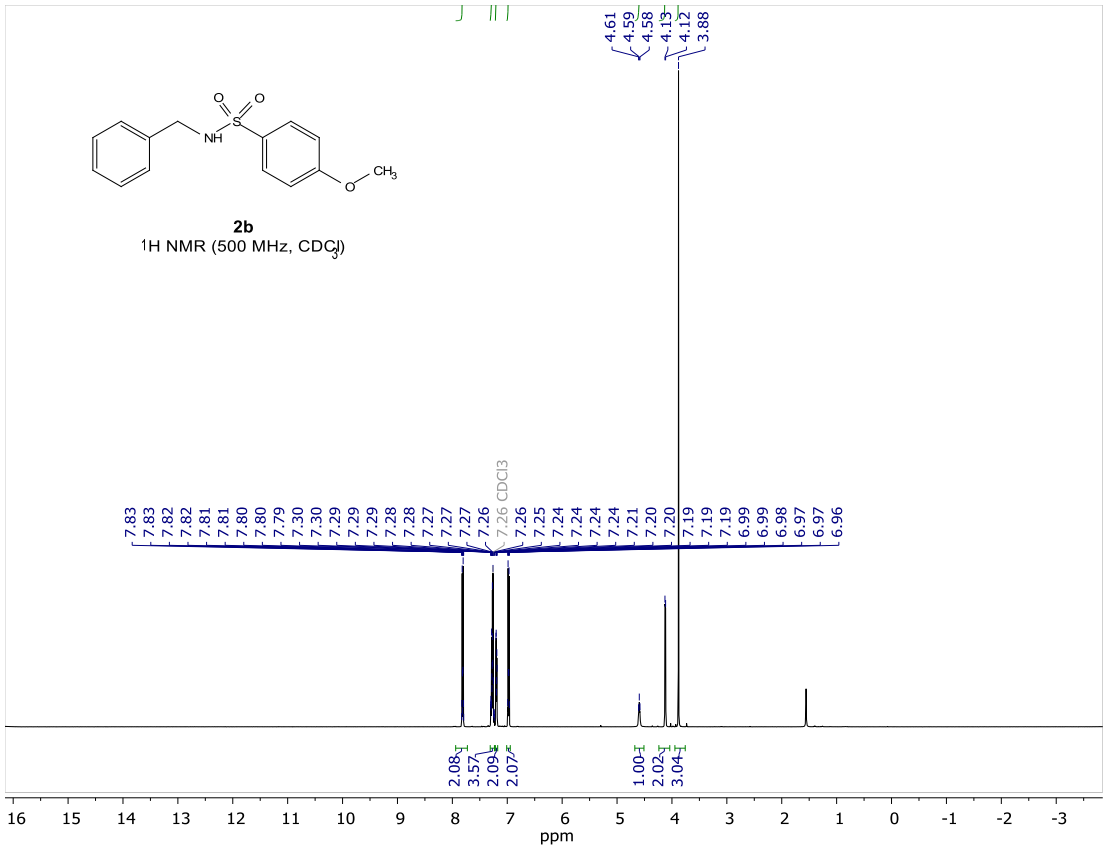

CH3
O
O
O
OH
7a
13C NMR (126 MHz, CDCl3)
77.15 CDCl3
180.25
147.99
147.01
133.64
121.03
108.46
108.12
101.22
45.03
18.40
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm

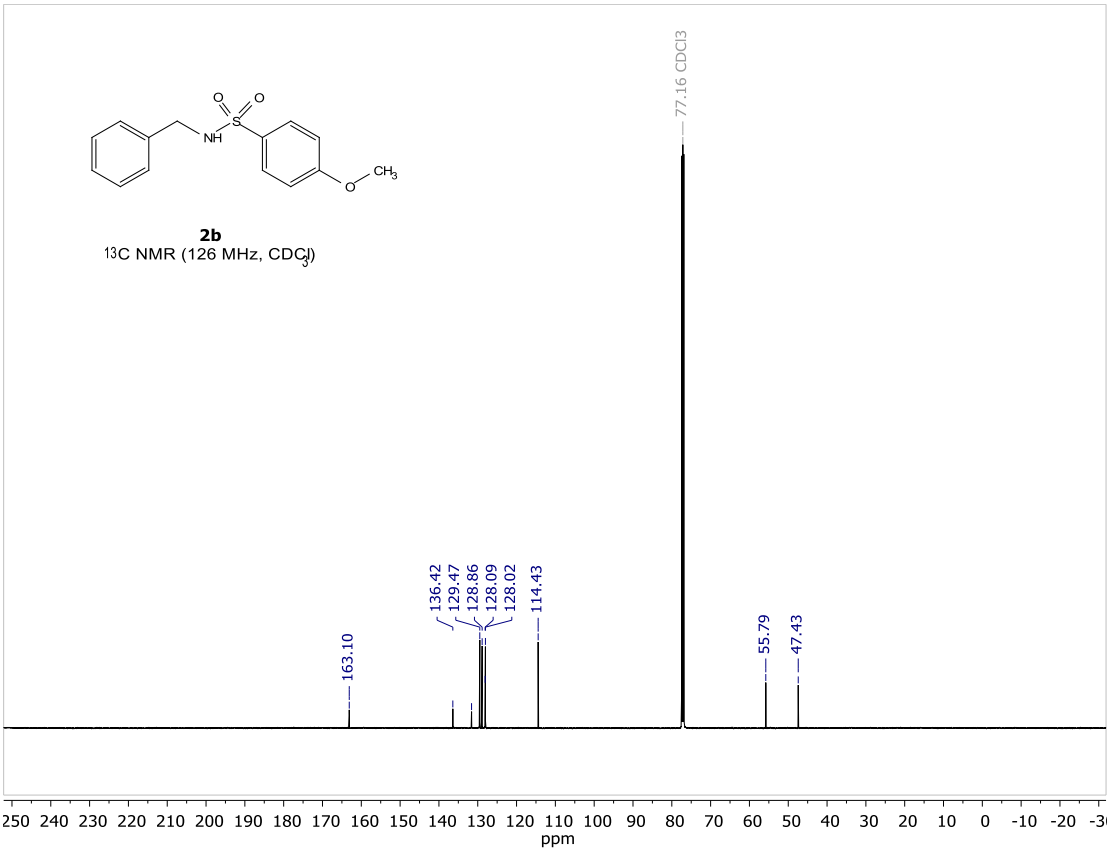

Cl
O
OH
8a
1H NMR (500 MHz, CDCl3)
7.32 7.31 7.31 7.31 7.29 7.28 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.22 7.21 7.21 7.20 7.20 7.20
2.90 2.89 2.89 2.89 2.88 2.88 2.87 2.87 2.87 2.86 2.86 2.86 2.85 2.85 2.56 2.56 2.55 2.55 2.54 2.54 2.53 2.53 2.52 2.52 2.51 2.50 2.20 2.17 2.16 2.15 2.14 2.14 2.12 2.12 2.11 2.11 2.10 2.08 2.07 1.95 1.94 1.93 1.93 1.92 1.92 1.91 1.91 1.90 1.90 1.89 1.89 1.88 1.87
11.11
0.74
3.76
1.04
1.99
2.16
1.13
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

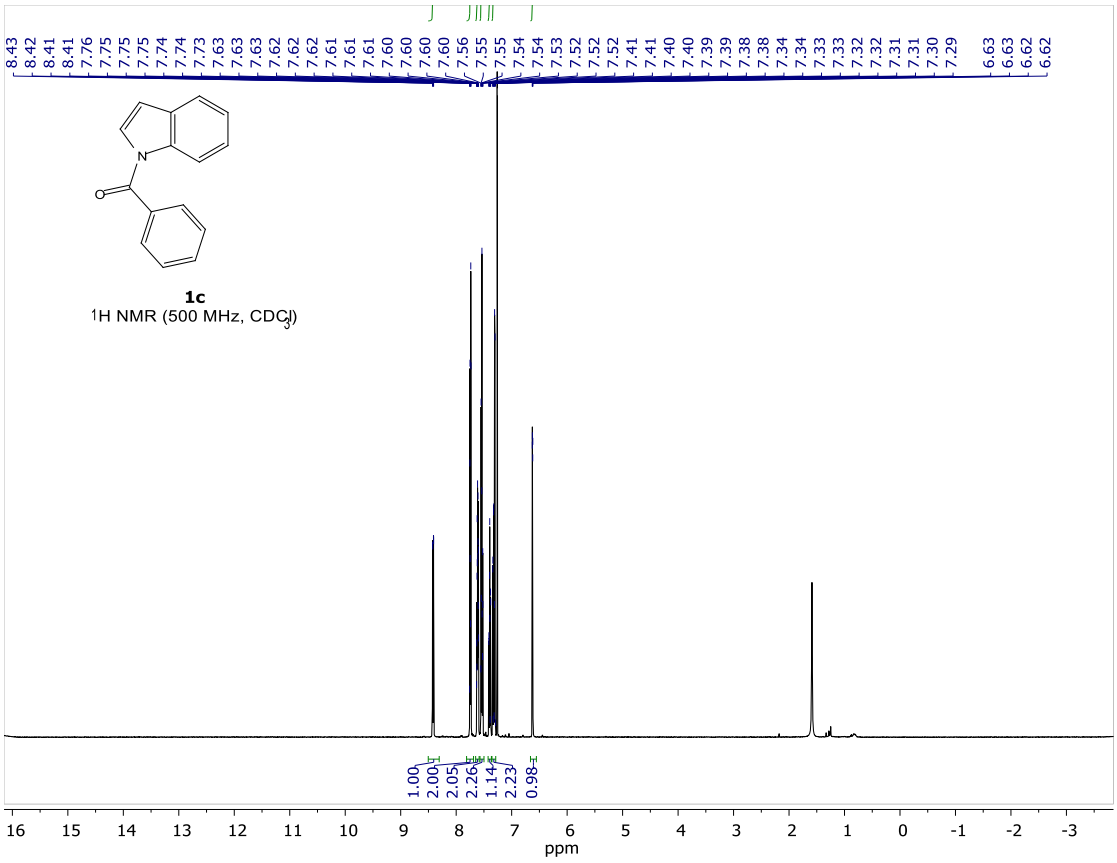

Cl
O
OH
8a
13C NMR (126 MHz, CDCl3)
180.91
145.21
134.41
129.72
127.23
126.95
124.78
52.04
32.38
16.76
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -3
ppm

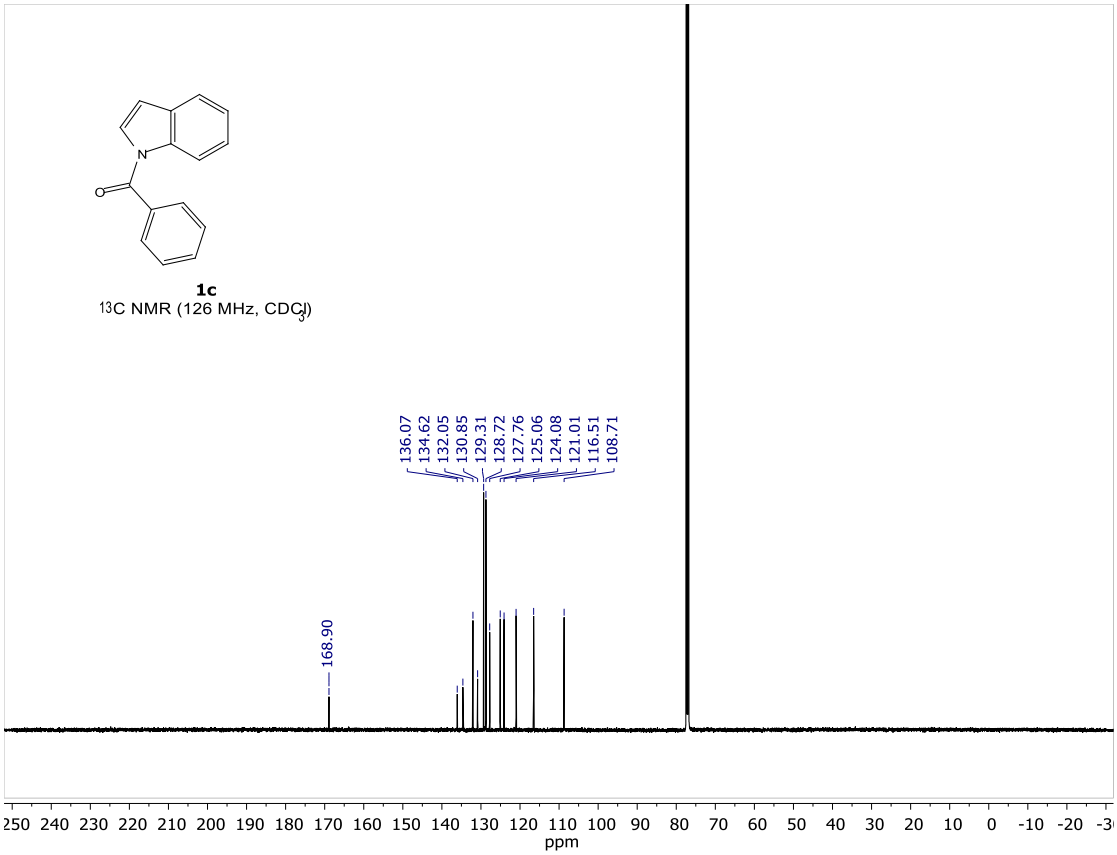

9a
1H NMR (500 MHz, CDCl3)
11.57
7.32 7.31 7.31 7.30 7.29 7.28 7.27 7.26 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.21
2.17 2.17 2.16 2.15 2.14 2.12 2.12 2.11 2.11 2.10 2.09 2.09 2.08 2.07 1.97 1.96 1.94 1.93 1.87 1.87 1.86 1.85 1.84 1.84 1.83 1.82 1.82 1.81 1.81 1.79 1.78 1.78 1.77 1.69 1.68 1.66 1.66 1.50 1.50
5.09 5.09 5.09 5.08 5.08 5.08 5.07 5.07 5.07 5.06 5.06 5.06 5.06 5.05
3.56 3.55 3.53
-0.00 TMS
1.00 3.37 0.85 0.79 0.85 0.87 1.51 0.93 2.43 2.20
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

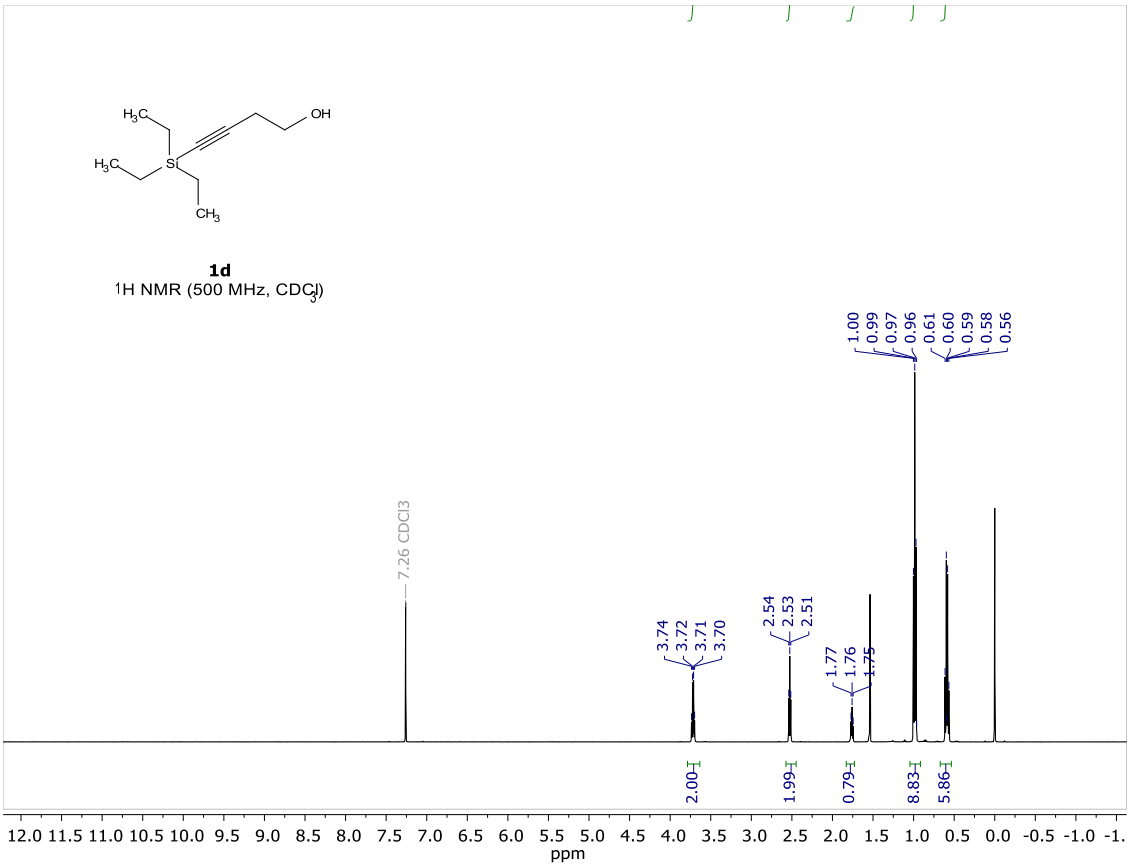

9a
13C NMR (126 MHz, CDCl3)
180.74
138.53 132.89 128.73 128.25 127.53 123.26
77.41 77.15 CDCl3 77.15 76.90
51.05
33.17 25.92 25.80
17.80 17.79
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

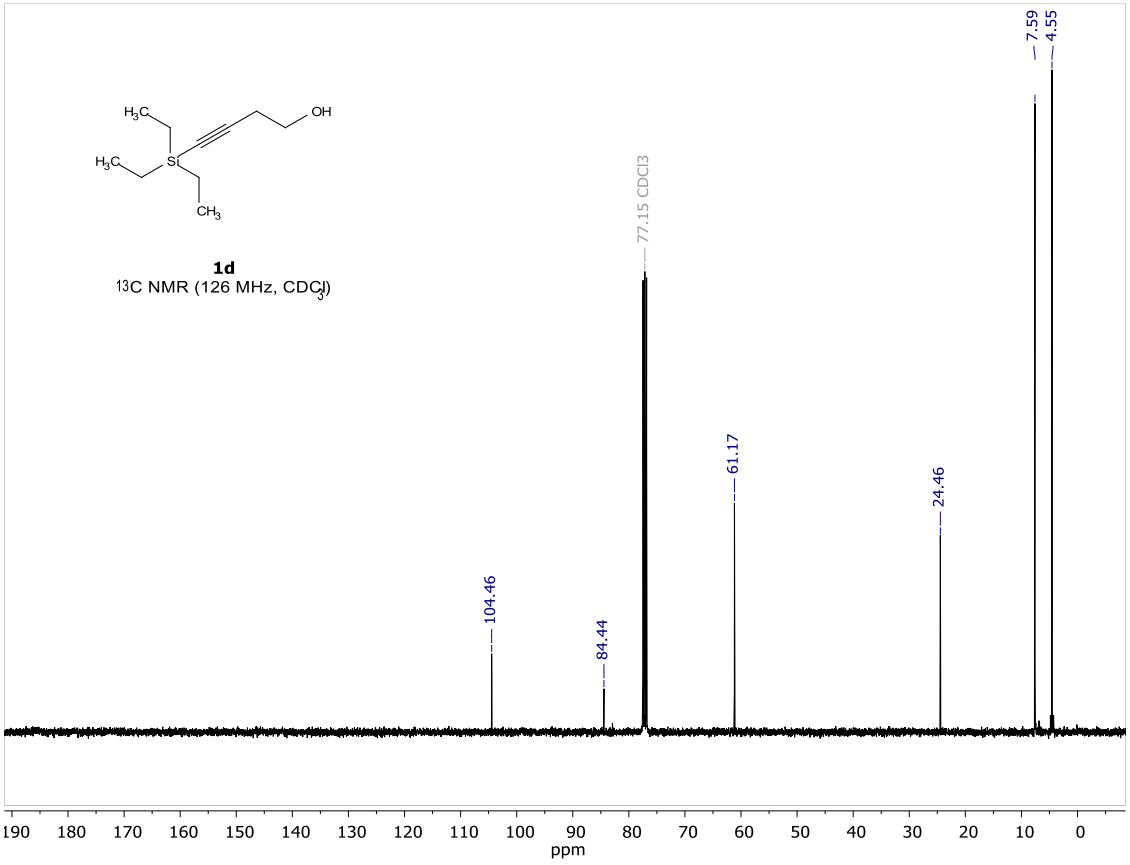

4.61
4.59
4.58
4.13
4.12
3.88
7.83
7.83
7.82
7.82
7.81
7.81
7.80
7.80
7.79
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26 CDCl3
7.25
7.24
7.24
7.24
7.24
7.21
7.20
7.20
7.19
7.19
7.19
6.99
6.99
6.98
6.97
6.97
6.96
2.08
3.57
2.09
2.07
1.00
2.02
3.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

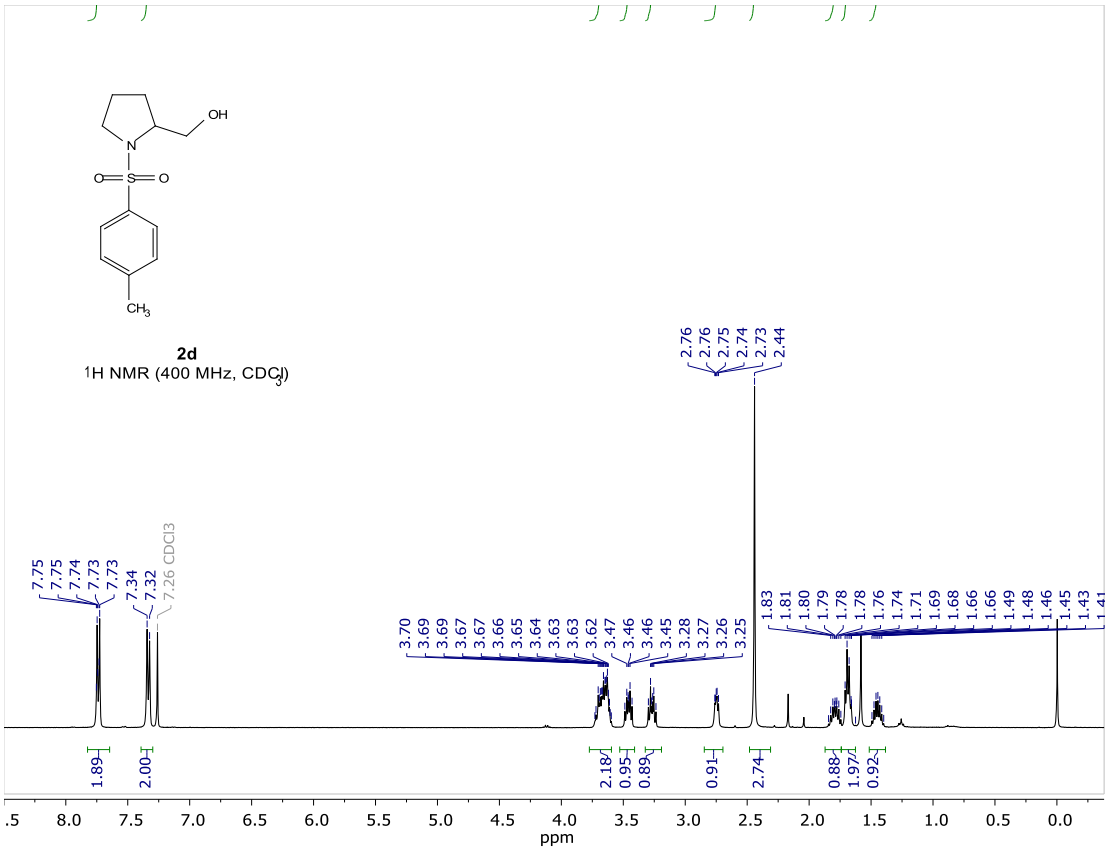

77.16 CDCl3
136.42
129.47
128.86
128.09
128.02
114.43
163.10
55.79
47.43
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm


8.43 8.42 8.41 8.41 7.76 7.75 7.75 7.75 7.74 7.74 7.73 7.63 7.63 7.62 7.62 7.62 7.61 7.61 7.61 7.60 7.60 7.60 7.60 7.56 7.55 7.55 7.54 7.54 7.53 7.52 7.52 7.52 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 6.63 6.63 6.62 6.62 6.62
1c
1H NMR (500 MHz, CDCl3)
1.00 2.00 2.05 2.26 1.14 2.23 0.98
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm


1c
13C NMR (126 MHz, CDCl3)
136.07 134.62 132.05 130.85 129.31 128.72 127.76 125.06 124.08 121.01 116.51 108.71
168.90
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm


H3C
OH
H3C
Si
CH3
1d
1H NMR (500 MHz, CDCl3)
7.26 CDCl3
3.74
3.72
3.71
3.70
2.54
2.53
2.51
1.77
1.76
1.75
1.00
0.99
0.97
0.96
0.61
0.60
0.59
0.58
0.56
2.00
1.99
0.79
8.83
5.86
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
ppm


H3C
OH
H3C
Si
CH3
1d
13C NMR (126 MHz, CDCl3)
77.15 CDCl3
7.59
4.55
104.46
84.44
61.17
24.46
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


OH
N
O
S
O
CH3
2d
1H NMR (400 MHz, CDCl3)
7.75
7.75
7.74
7.73
7.73
7.34
7.32
7.26 CDCl3
3.70
3.69
3.69
3.67
3.67
3.66
3.65
3.64
3.63
3.63
3.62
3.47
3.46
3.46
3.45
3.28
3.27
3.26
3.25
2.76
2.76
2.75
2.74
2.73
2.44
1.83
1.81
1.80
1.79
1.78
1.78
1.76
1.74
1.71
1.69
1.68
1.66
1.66
1.49
1.48
1.46
1.45
1.43
1.41
1.89
2.00
2.18
0.95
0.89
0.91
2.74
0.88
1.97
0.92
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm