Science
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Supplementary Materials for

Arylsulfonylacetamides as bifunctional reagents for alkene aminoarylation

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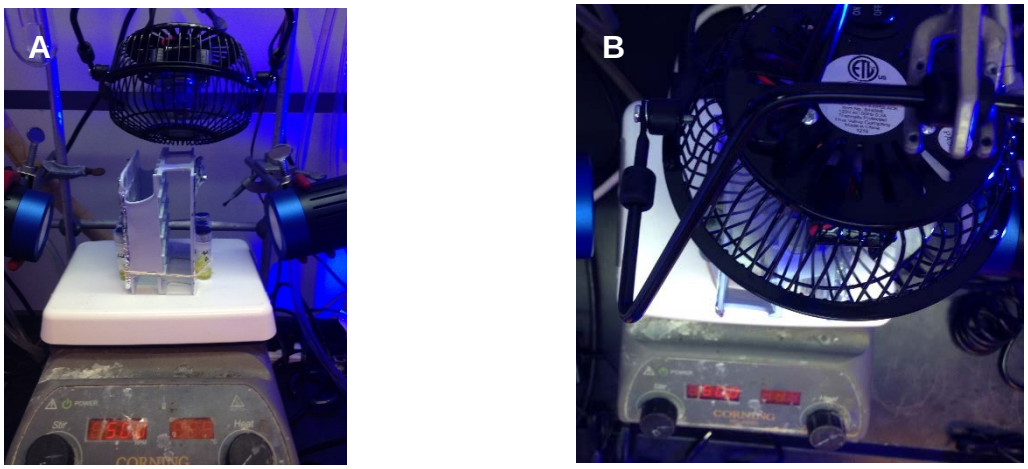
General Information

All chemicals were used as received and stored as recommended by the supplier. Reactions were monitored by thin layer chromatography (TLC) using glass-backed plates pre-coated with 230–400 mesh silica gel (250 mm thickness) with fluorescent indicator F254, available from EMD Millipore (cat. #: 1.05715.0001). Plates were visualized with a dual short wave/long wave UV lamp. Column flash chromatography was performed using 230-400 mesh silica (SiliCycle cat. #: R12030B) gel or via automated column chromatography. NMR spectra were recorded on Varian MR400, Varian Inova 500, Varian Vnmrs 500, or Varian Vnmrs 700 spectrometers. Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CHCl_3$ at 7.26 ppm and for DMSO 2.50. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm and for DMSO 39.52 for center of septet. ^{19}F NMR chemical shifts were reportd as δ, parts per million, relative to $CFCl_3$ at 0.0 ppm. The abbreviations s, br. s, d, dd, br. d, ddd, t, q, br. q, qi, m, and br. m stand for the resonance multiplicity singlet, broad singlet, doublet, doublet of doublets, broad doublet, doublet of doublet of doublets, triplet, quartet, broad quartet, quintet, multiplet and broad multiplet, respectively. IR spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrometer fitted with an ATR accessory. Melting points were obtained using a Mel-Temp 3.0 (model no. 1401). Mass Spectra were recorded at the Mass Spectrometry Facility at the Department of Chemistry of the University of Michigan in Ann Arbor, MI on an Agilent Q-TOF HPCL-MS with ESI high resolution mass spectrometer using electrospray ionization (ESI), positive ion mode, or electron impact ionization (EI). Fluorescence quenching was recorded using a Horiba Scientific Fluoromax 2 using DataMax software. We thank Dr. James Windak and Dr. Paul Lennon at the University of Michigan Department of Chemistry instrumentation facility for conducting these experiments. X-Ray Crystallography work was done by Dr. Jeff. W. Kampf. UV-Vis measurements were obtained on a Shimadzu UV-1601 UV-Vis Spectrometer. Electrochemical data was collected on a CHI600E potentiostat with the accompanying CH Instruments software. H150 Blue grow lights from Kessil were used as the visible light irradiation source.

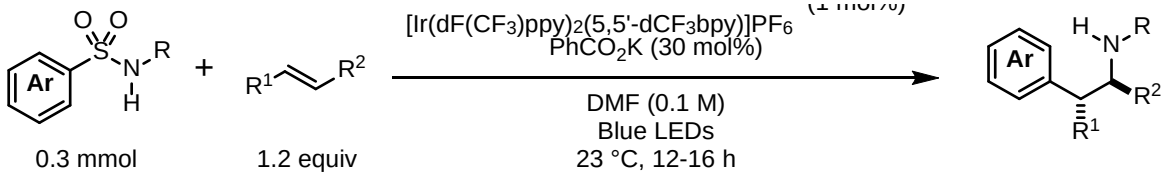
Figure S1: General Reaction Set-up

Unless stated otherwise, all reactions were run on a 0.3 mmol scale in a 2-dram vial equipped with an oval shaped stir bar. 1 x H150 Blue Kessil lamp sufficiently irradiated 1-3 reaction vials at one time, about 5 cm away (Fig. S1A, side view). At this distance, with a fan dissipating the standing atmosphere (Fig. S1B, top view), the air temperature surrounding the reactions did not exceed 25 ˚C.



General reaction set-up for radical aminoarylation

Figure S2: General Procedure A: Radical Aminoarylation of Alkenes (0.3 mmol scale):



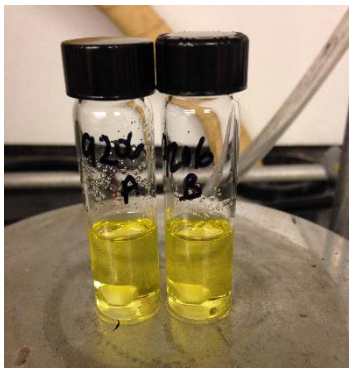
Unless otherwise noted, to a flame dried 2-dram vial, equipped with a teflon coated oval shaped stir bar, was added (aryl-sulfonyl)acetamide (1 equiv, 0.3 mmol), potassium benzoate (14.4 mg, 30 mol%), and $Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$ (3 mg, 1 mol%). The vial contents were then dissolved in anhydrous DMF (3 mL, 0.1 M). Finally, the alkene (1.2 equiv) was added to the reaction vial. The reaction was sparged under argon for 15 min, quickly capped and sealed with parafilm. Reactions were irradiated with 1 x blue H150 Kessil LED light and stirred (500 to 550 rpm) for 12 to 16 h at room temperature.

Reaction workup was performed by diluting the reaction with 15 mL dH_2O and extracting the aqueous layer with EtOAc (3 x 10 mL). The organic layers were combined, washed with 5 wt% LiCl (3 x 10 mL), brine (15 mL), dried over sodium sulfate, filtered and concentrated to provide the crude residue, which was purified by flash column chromatography.

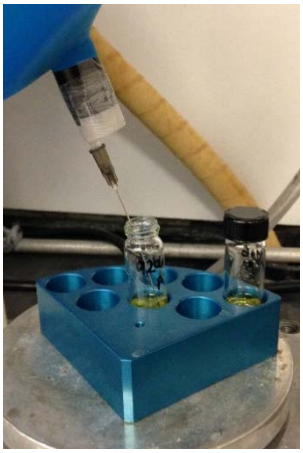
Step-by-step Reaction Set-up Pictures

Step 1: Flame dried 2-dram vial and stir bar

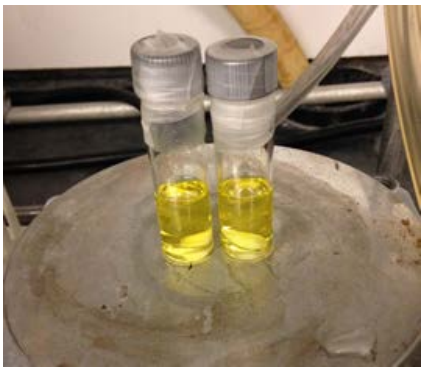
Step 2: Solid reagents loaded



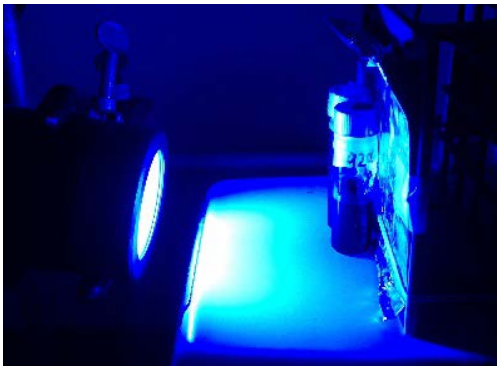
Step 3: Solid reagents diluted in DMF (0.1 M)



Step 4: Sparge degassing technique with argon balloon and 4” hypodermic needle



Step 5: Vial-cap juncture wrapped in parafilm immediately after argon sparging

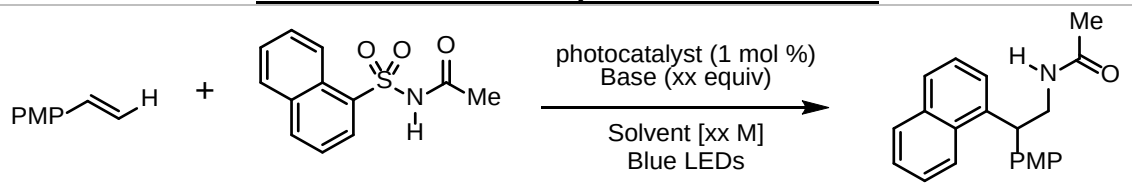


Step 6: Blue light irradiation with 1 x H150 blue Kessil grow lamp, 500 rpm, and fan for cooling

Reaction Optimization Experiments

Optimization reactions were conducted on 0.3 mmol scale according to **General Procedure A**. Yields reported are from isolation.

Table S1: Reaction Optimiziation Results

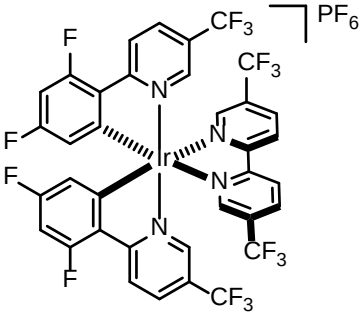


A **B** **"General Procedure A" 0.3 mmol scale** **C**

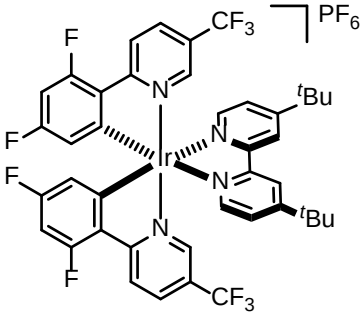
Entry	B equiv	Base	Base equiv.	Catalyst	Solvent [M]	C (% yield)
1	3	KOAc	3	None	DMF [0.1] M	0
2	3	KOAc	3	[Ir-1] (no light)	DMF [0.1] M	0
3	3	KOAc	3	[Ir-1]	DMF [0.1 M]	46
4	3	NaOAc	3	[Ir-1]	DMF [0.1 M]	42
5	3	K_2HPO_4	3	[Ir-1]	DMF [0.1 M]	23
6	3	K_2CO_3	3	[Ir-1]	DMF [0.1 M]	11
7	3	K_3PO_4	3	[Ir-1]	DMF [0.1 M]	41
8	3	Pyridine	3	[Ir-1]	DMF [0.1 M]	9
9	1	KOAc	0.3	[Ir-1]	DMF [0.1 M]	32
10	1	$PhCO_2K$	0.3	[Ir-1]	DMF [0.1 M]	41
11	1	CF_3CO_2K	0.3	[Ir-1]	DMF [0.1 M]	10
12	1	K_3PO_4	0.3	[Ir-1]	DMF [0.1 M]	30
13	1	Pyridine	0.3	[Ir-1]	DMF [0.1 M]	0
14	1	$PhCO_2K$	0.3	[Ir-1]	DMF [0.2 M]	7
15	1	$PhCO_2K$	0.3	[Ir-1]	DMF [0.4 M]	<5
16	1	K_3PO_4	0.3	[Ir-1]	DMSO [0.1 M]	10
17	1	K_3PO_4	0.3	[Ir-1]	MeCN [0.1 M]	11
18	1	K_3PO_4	0.3	[Ir-1]	THF [0.1 M]	0
19	1	$PhCO_2K$	0.3	[Ir-1]	THF:DMF [0.1 M]	30
20	1	K_3PO_4	0.3	[Ir]-2	DMF [0.1 M]	0
21	1	K_3PO_4	0.3	[Ir]-2	DMF [0.1 M]	0
22	1	K_3PO_4	0.3	[Ru]-1	DMF [0.1 M]	0
23	1	K_3PO_4	0.3	[Ru]-2	DMF [0.1 M]	0
24	1	Pyridine	0.3	AcrMe	DMF [0.1 M]	13
25	1	K_3PO_4 + ^iPrOH	0.3 + 10	[Ir-1]	DMF [0.1 M]	34
26	1	DABCO	0.3	[Ir-1]	DMF [0.1 M]	<10
27	1	Et_3N	0.3	[Ir-1]	DMF [0.1 M]	<10
28	1	$PhMe_2SiH$	1	[Ir-1]	DMF [0.1 M]	<10
29	1	$(EtO)_3SiH$	1	[Ir-1]	DMF [0.1 M]	<10
30	1	1,4-cyclohexadiene	0.6	[Ir-1]	DMF [0.1 M]	30

Table S2: Photocatalyst Redox Potentials

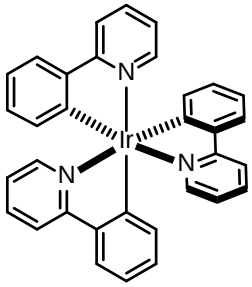
Photocatalysts



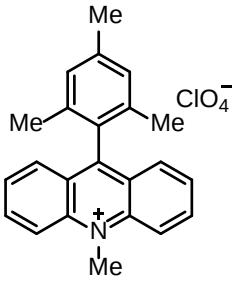
$Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$
[Ir]-1



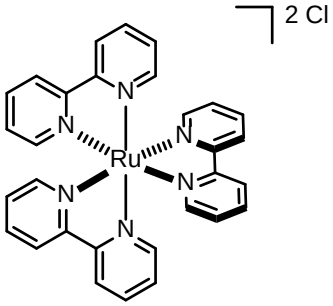
$Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$
[Ir]-2



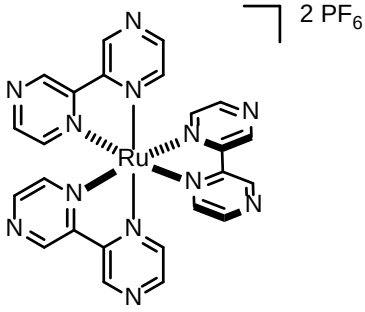
fac-$Ir(ppy)_3$
[Ir]-3



Acr-Me ClO_4^-
AcrMe



$Ru(bpy)_3Cl_2 \bullet 6H_2O$
[Ru]-1

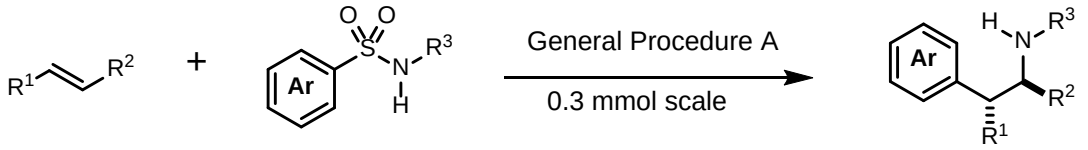


$Ru(bpz)_3(PF_6)_2$
[Ru]-2

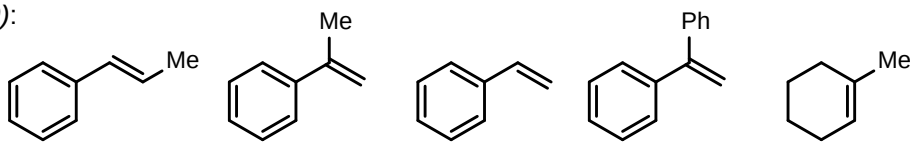
Photocatalyst	Reference	M^+/M^*	M^*/M^-	M^+/M	M/M^-
[Ir]-1	*(40)*	+1.68 V	–0.43 V	+1.94 V	–0.69 V
[Ir]-2	*(44)*	–1.21 V	+0.89 V	+1.69 V	–1.37 V
[Ir]-3	*(41)*	–1.73 V	+0.31 V	+0.77 V	–2.19 V
Acr-Me$^+$ClO$_4^-$	*(45)*	--	+1.88 V	--	–0.49 V
[Ru]-1	*(41)*	–0.81 V	+0.77 V	+1.29 V	–1.33 V
[Ru]-2	*(41)*	–0.26 V	+1.45 V	+1.86 V	–0.80 V

Electrochemical potentials reported vs. SCE reference electrode in MeCN Solvent.

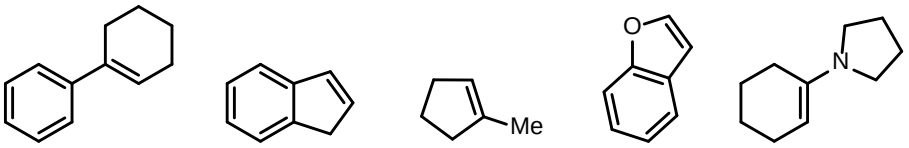
Table S3: Unreactive Substrates for Aminoarylation Reaction



Alkenes Surveyed *(39)*:



$E_{p/2}$ = (vs SCE in MeCN)	1.74	1.91	1.97	1.54	1.94



$E_{p/2}$ (vs SCE) = (vs SCE in MeCN)	1.64	1.66	1.75	1.74	0.32

Attempted Sulfonamides:

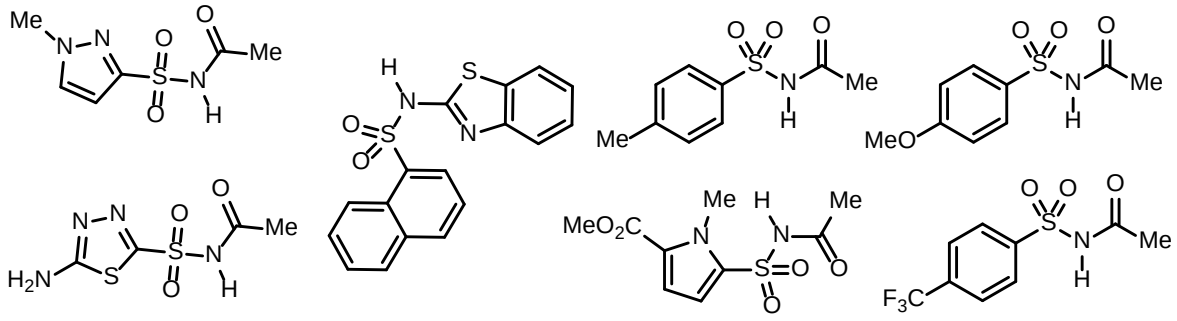


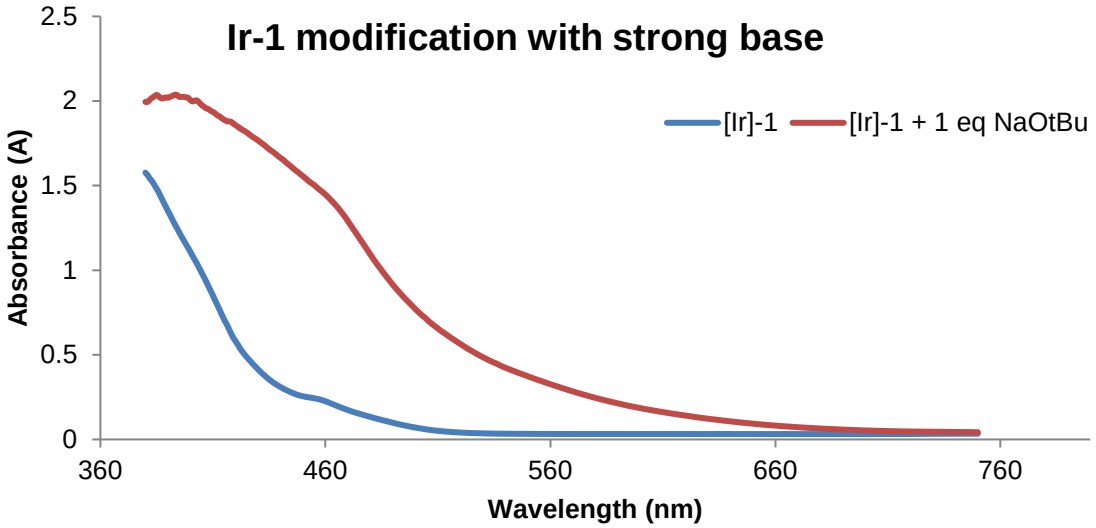
Figure S3: Strong base interaction with $Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$

Experimental Procedure

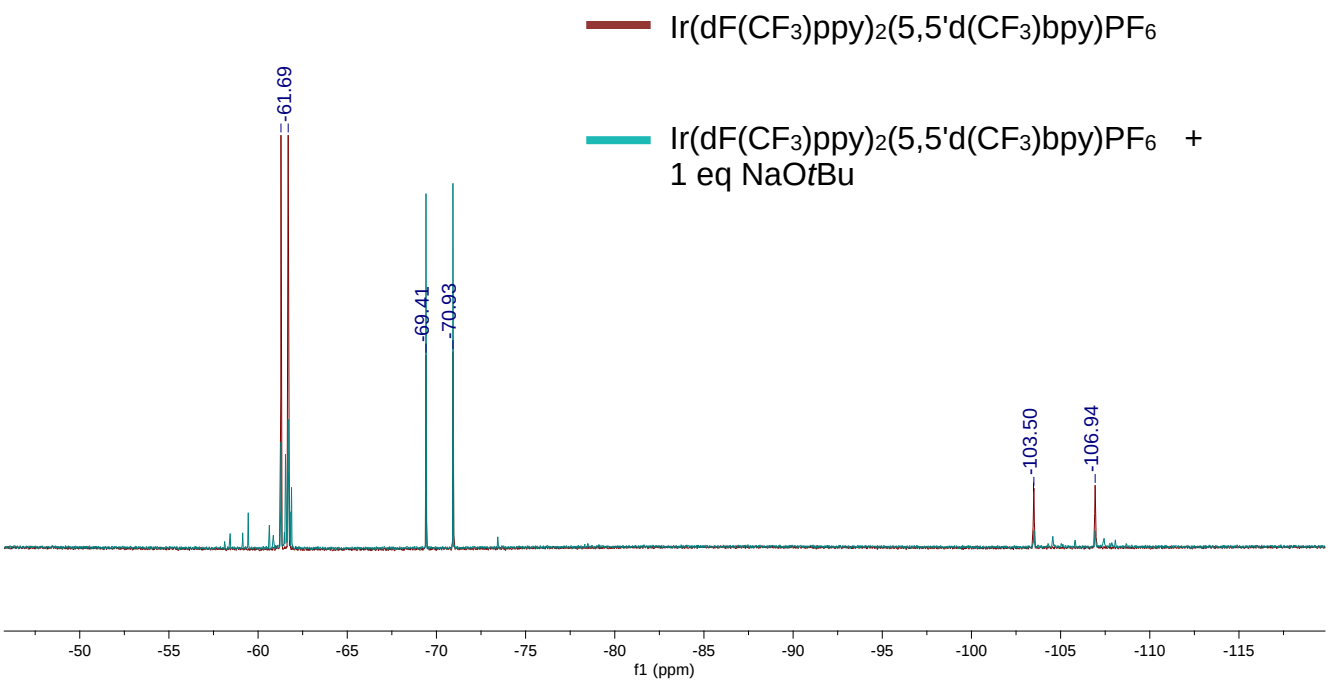
UV-Vis: A 25 μM solution of Ir-1 in 2 mL of DMF was prepared by weighing 1.6 mg of Ir-1 into a volumetric flask and then diluting to 5 mL. The spectra of this solution was recorded. Separately, 1.7 mg of Ir-1 was weighed into a 5 mL volumetric flask followed by 7.7 mg of NaO*t*Bu. The solids were then diluted in 5 mL of DMF and homogenized using a pipette. The spectra of the homogeneous solution was recorded.

NMR titration: To a 1 dram vial 2 mL of DMSO-d6 and 5 mg of photocatalyst were mixed. Separately 3.36 mg of NaO*t*Bu in 1 mL of DMSO-d6 was prepared. Five solutions were prepared in standard NMR tubes by combining the following listed volumes.

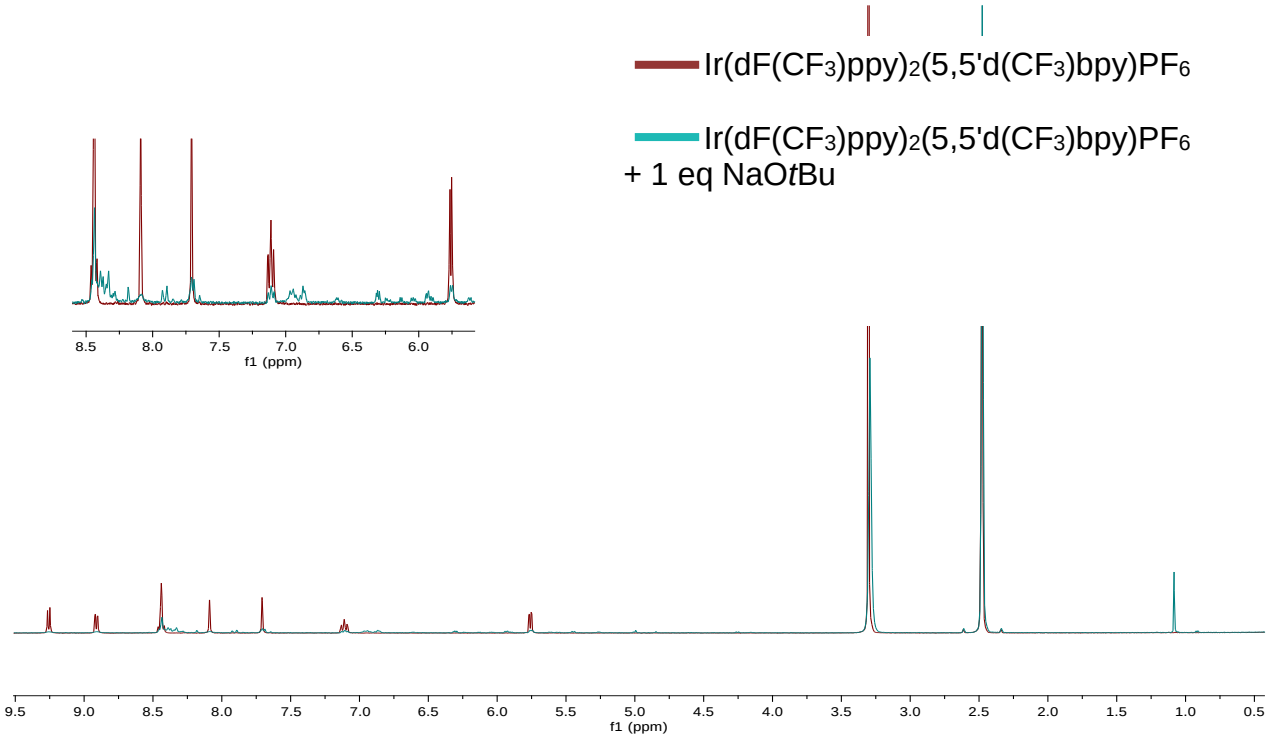
Ir-1 volume (mL)	Base volume (mL)	Void Volume	total volume - 500 μL
0.4	0	0.1	0.5
0.4	0.0125	0.0875	0.5
0.4	0.025	0.075	0.5
0.4	0.045	0.0625	0.5
0.4	0.05	0.05	0.5


Ir-1 modification with strong base
[Ir]-1
[Ir]-1 + 1 eq NaOtBu
Absorbance (A)
2.5
2
1.5
1
0.5
0
360
460
560
660
760
Wavelength (nm)

^{19}F NMR (471 MHz, DMSO-D_6) for Ir(dF(CF_3)ppy)$_2$(5,5'd(CF_3)bpy)PF_6



^{19}F NMR (471 MHz, DMSO-D$_6$) for Ir(dF(CF$_3$)ppy)$_2$(5,5'd(CF$_3$)bpy)PF$_6$



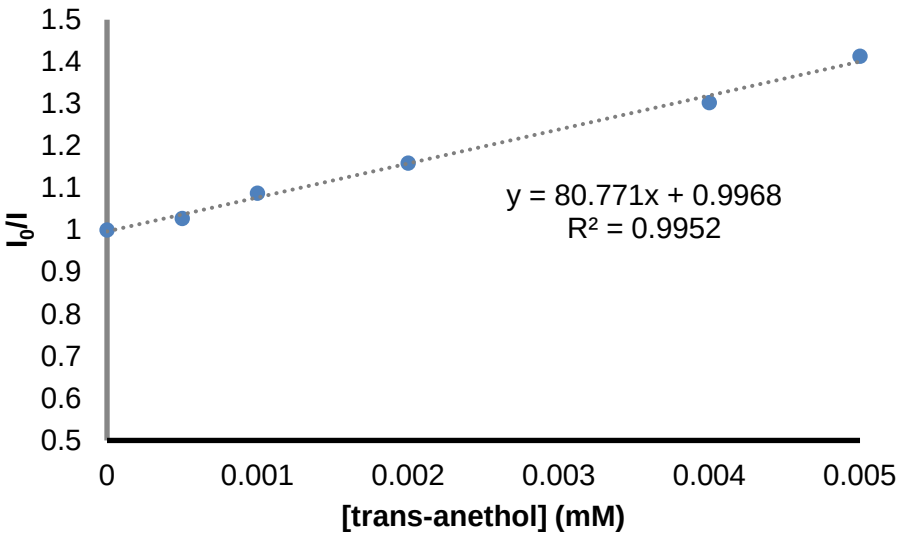
Kinetic Profiling and Mechanism Elucidation Experiments
Figure S4: Stern-Volmer Quenching Experiment

Fluorescence quenching of [Ir]-1 was recorded with a Horiba Scientific Fluoromax 2 using DataMax software. Samples consisting of the noted concentrations were prepared and degassed by sparging with argon for 3 minutes prior to each measurement. The solutions were irradiated at 420 nm and luminescence was measured at 593 nm. I_0/I values were generated from the average of three scans taken per quencher concentration. The quenching studies were repeated three times. Potassium benzoate was not sufficiently soluble in DMF in order to run this analysis.

Conclusion: This quenching study supports the hypothesis of alkene activation over sulfonamide activation as the sulfonamide is not shown to quench the photocatalyst.

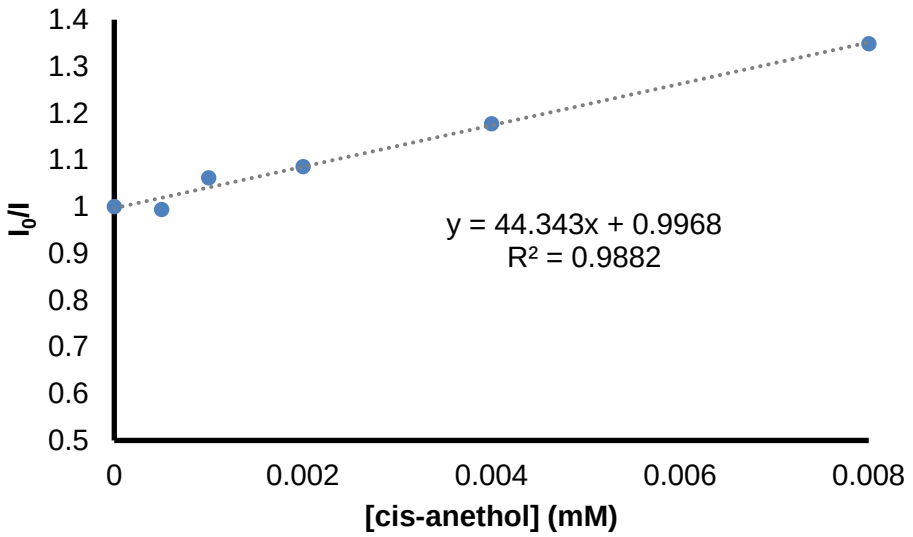
Constant [Ir]-1, variable *E*-anethole

Run #	[Q] (mM)	scan 1	scan 2	scan 3	average	I_0/I
1	0	1279652	1279595	1277671	1278973	1
	0.5	1239028	1240121	1237808	1238986	1.032274
	1	1198883	1201995	1197508	1199462	1.066289
	2	1139567	1136768	1134669	1137001	1.124865
	4	966005	967975	966423	966801	1.322891
	5	915329	913206	913369	913968	1.399363
2	0	1338796	1335993	1333927	1336239	1
	0.5	1299050	1296895	1293265	1296403	1.030728
	1	1189198	1187756	1186116	1187690	1.125074
	2	1112948	1111220	1111004	1111724	1.201952
	4	1035308	1033016	1030568	1032964	1.293597
	5	941187	939153	936440	938926.7	1.423156
3	0	1323583	1322346	1318529	1321486	1
	0.5	1297235	1296530	1291170	1294978	1.02047
	1	1235964	1233167	1231129	1233420	1.0714
	2	1150680	1148221	1146468	1148456	1.150663
	4	1026073	1023204	1019673	1022983	1.291796
	5	936491	932451	930715	933219	1.416051



Constant [Ir]-1, variable *Z*-anethole

Run #	[Q] (mM)	scan 1	scan 2	scan 3	average	I_0/I
1	0	1563299	1568831	1563814	1565315	1
	0.0005	1506480	1502415	1505346	1504747	1.040251
	0.001	1612968	1610825	1609429	1611074	0.971597
	0.002	1277113	1278729	1279468	1278437	1.224398
	0.004	1293512	1292485	1291087	1292361	1.211205
	0.008	1132608	1130304	1125737	1129550	1.385786
2	0	1500716	1503267	1498616	1500866	1
	0.0005	1460206	1460267	1459212	1459895	1.028065
	0.001	1353200	1352411	1350893	1352168	1.10997
	0.002	1362804	1362675	1361090	1362190	1.101804
	0.004	1296812	1295625	1290413	1294283	1.159612
	0.008	1090574	1083777	1082080	1085477	1.382679
3	0	1452602	1453180	1450419	1452067	1
	0.0005	1513751	1509306	1513027	1512028	0.960344
	0.001	1435001	1433724	1429664	1432796	1.01345
	0.002	1361539	1356950	1352472	1356987	1.070067
	0.004	1218421	1214864	1212004	1215096	1.195022
	0.008	1110932	1102370	1099683	1104328	1.314887



Constant [Ir]-1, variable sulfonylacetamide 2

Run #	[Q] (mM)	scan 1	scan 2	scan 3	average	I_0/I
1	0	1379545	1379215	1379257	1379339	1
	0.5	1407231	1408755	1404343	1406776	0.980496
	1	1421023	1419515	1420010	1420183	0.971241
	2	1241674	1242138	1238751	1240854	1.111604
	4	1369068	1368141	1369533	1368914	1.007616
	8	1345129	1344560	1346924	1345538	1.025121
2	0	1315329	1314718	1314642	1314896	1
	0.5	1365594	1362761	1365947	1364767	0.963458
	1	1358677	1357730	1356903	1357770	0.968423
	2	1311015	1312800	1314739	1312851	1.001558
	4	1358471	1359711	1361332	1359838	0.966951
	8	1368996	1366131	1365807	1366978	0.9619
3	0	1285963	1286332	1284033	1285443	1
	0.5	1426932	1427614	1425122	1426556	0.901081
	1	123400	1423014	1422116	989510	1.29907
	2	1349385	1348451	1345525	1347787	0.953743
	4	1370793	1367963	1372327	1370361	0.938032
	5	1363714	1366155	1361547	1363805	0.942541

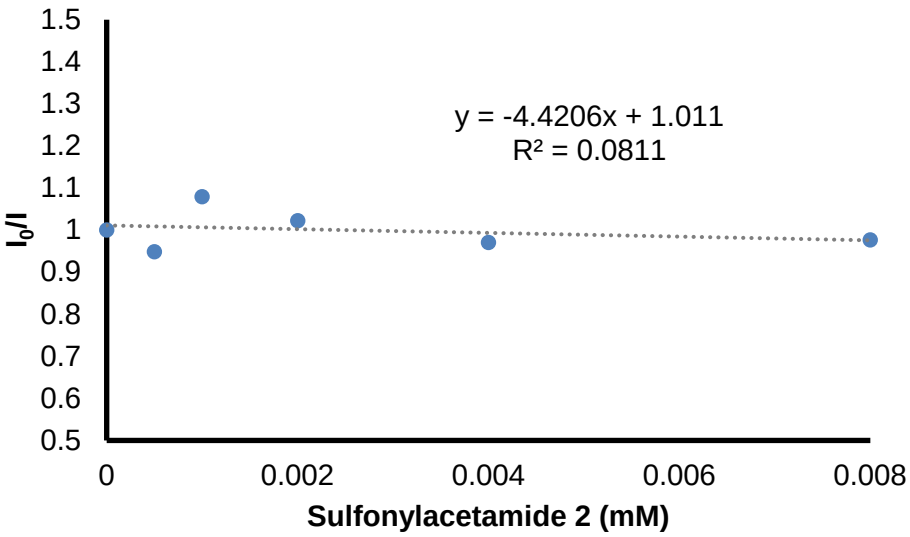
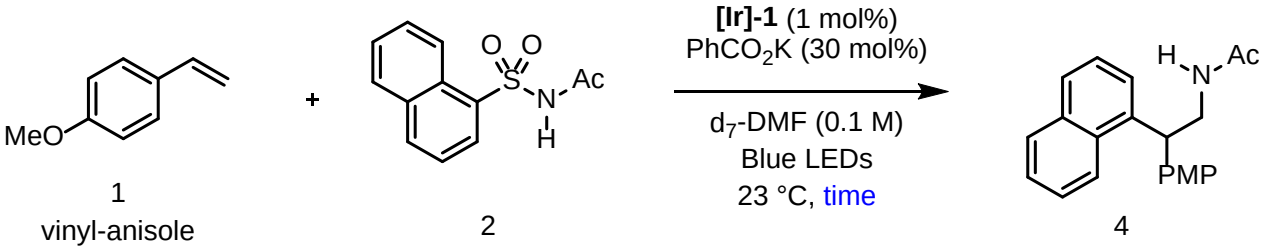

y = -4.4206x + 1.011
R² = 0.0811
I0/I
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0
0.002
0.004
0.006
0.008
Sulfonylacetamide 2 (mM)

Figure S5: Reaction Profile and Initial Rates for Aminoaryation with vinyl-Anisole



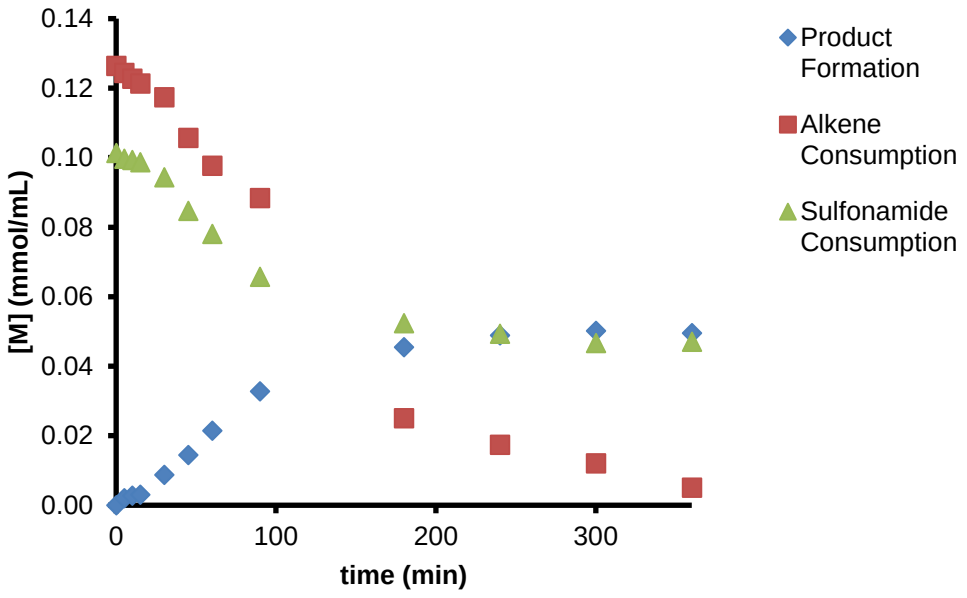
To a flame dried 2-dram vial, equipped with a teflon coated oval shaped stir bar, was added vinyl-anisole (20.1 mg, 0.15 mmol), *N*-(1-naphthylsulfonyl)acetamide (37.4 mg, 0.15 mmol), potassium benzoate (7.21 mg, 30 mol%), and Ir(dF(CF_3)ppy)$_2$(5,5'd(CF_3)bpy)PF_6 (1.5 mg, 1 mol%). The vial contents were then dissolved in anhydrous d_7-DMF (1.5 mL, 0.1 M) followed by addition of trimethyl(phenyl)silane (8.52 µL, 0.05 mmol) as an internal standrad. The reaction was sparged under argon for 15 min before the 1.5 mL solution volume was equally seperated between 3 argon sparged NMR tubes (0.5 mL each). The tubes were quickly capped and sealed with parafilm. Time zero (t_0) ^{1}H-NMR measurements were taken of all three samples prior to irradiation. Then, the 3 NMR tubes were irradiated with 1 x blue H150 Kessil LED light (~2 cm) and cooled by one overhead fan. After the alloted time (i.e. 5, 10, 15, 20... min), the light was turned off and reaction solution analyzed by ^{1}H-NMR.

Analysis: The concentrations and yields for the aminoarylation substrates and product were plotted against time in minutes. The slope through five points for the first ~20% reaction conversion was utilized to calculate the initial rates of reaction. The procedure was repeated in triplicate (3 ^{1}H-NMR measurements) and the average of these three trials was determined. Calculated values are tabulated below.

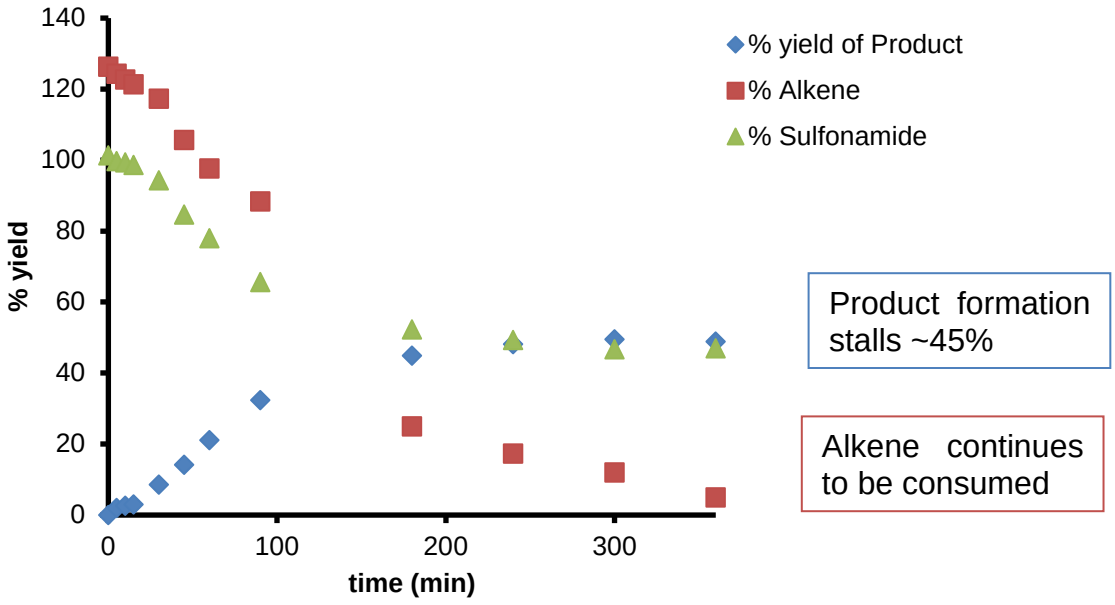
Aminoarylation Reaction Profile with vinyl-anisole
([M] vs. time)

	Avg. 3 trials [M] (mmol/mL)		
min	**Product Formation**	**Alkene Consumption**	**Sulfonamide Consumption**
0	0.0000	0.12633	0.10133
5	0.0020	0.12433	0.09967
10	0.0027	0.12267	0.09933
15	0.0030	0.12133	0.09867
30	0.0087	0.11733	0.09433
45	0.0144	0.10567	0.08467
60	0.0214	0.09767	0.07800
90	0.0328	0.08833	0.06567
180	0.0455	0.02500	0.05233
240	0.0488	0.01733	0.04933
300	0.0501	0.01200	0.04667
360	0.0495	0.00500	0.04700

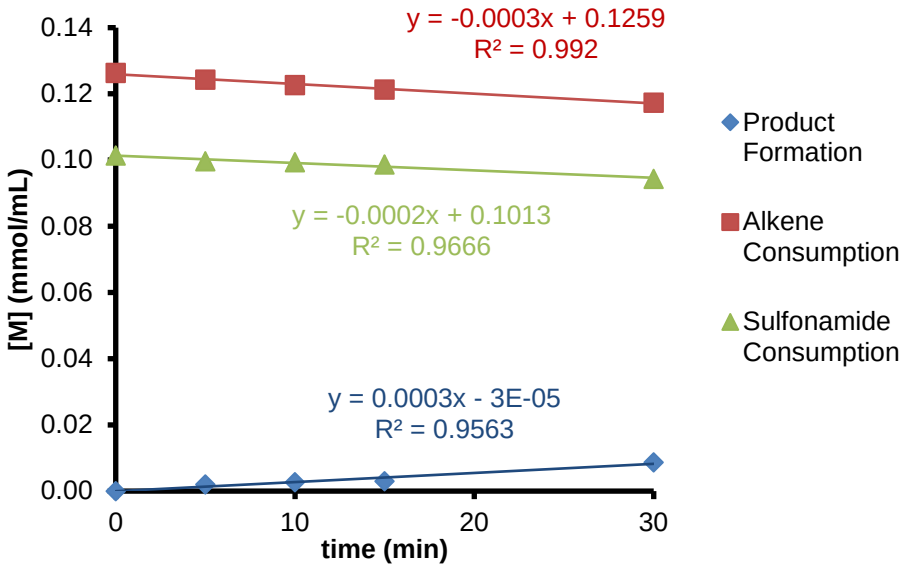
Plotted Aminoarylation Reaction Profile with vinyl-anisole
([M] vs. time)



Plotted Aminoarylation Reaction Profile with vinyl-anisole
(yield vs. time)

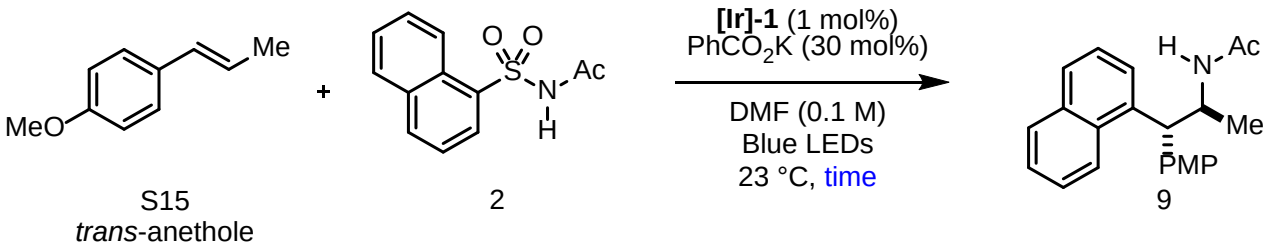


Plotted Initial Rates for Aminoarylation with vinyl-anisole ([M] vs. time)



	Average of 3 trials		
	Product Formation	**Vinyl-Anisole Consumption**	**Sulfonamide Consumption**
Initial rate ([M] • min^{-1})	0.0003	-0.0003	-0.0002
R^2	0.9563	0.9920	0.9666

Figure S6: Reaction Profile and Initial Rates for Aminoaryation with *trans*-Anethole



S15
trans-anethole

2

9

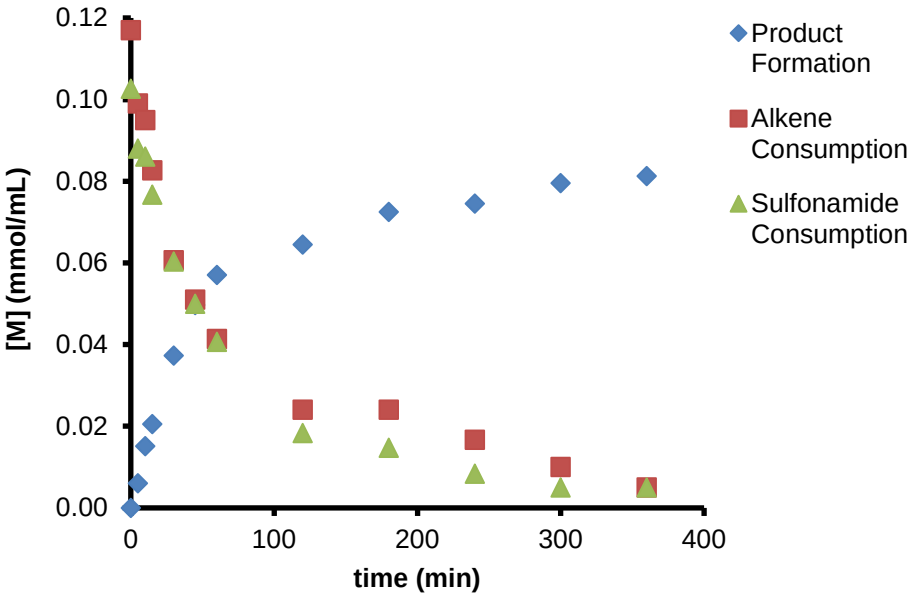
To a flame dried 2-dram vial, equipped with a teflon coated oval shaped stir bar, was added *trans*-anethole (54 µL, 0.36 mmol), *N*-(1-naphthylsulfonyl)acetamide (75 mg, 0.3 mmol), potassium benzoate (14.4 mg, 30 mol%), and $Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$ (3 mg, 1 mol%). The vial contents were then dissolved in anhydrous DMF (3 mL, 0.1 M) followed by addition of trimethyl(phenyl)silane (17 µL, 0.1 mmol) as an internal standrad. The reaction was sparged under argon for 15 min before the 3 mL solution volume was equally seperated between 3 argon sparged NMR tubes (1 mL each). The tubes were quickly capped and sealed with parafilm. Time zero (t_0) ^{1}H-NMR measurements were taken of all three samples prior to irradiation. Then, the 3 NMR tubes were irradiated with 1 x blue H150 Kessil LED light (~2 cm) and cooled by one overhead fan. After the alloted time (i.e. 5, 10, 15, 20... min), the light was turned off and reaction solution analyzed by ^{1}H-NMR.

Analysis: The concentrations and yields for the aminoarylation substrates and product were plotted against time in minutes. The slope through five points for the first ~20% reaction conversion was utilized to calculate the initial rates of reaction. The procedure was repeated in triplicate (3 ^{1}H-NMR measurements) and the average of these three trials was determined. Calculated values are tabulated below.

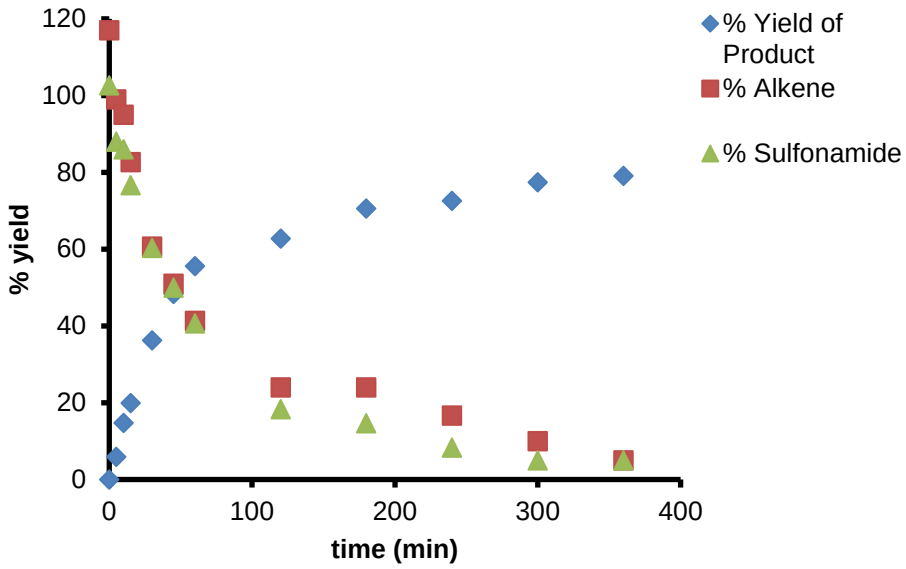
Aminoarylation Reaction Profile with trans-Anethole ([M] vs. time)

	Avg. of 3 trials [M] (mmol/mL)		
min	**Product Formation**	**Alkene Consumption**	**Sulfonamide Consumption**
0	0.0000	0.1170	0.1027
5	0.0060	0.0990	0.0880
10	0.0151	0.0950	0.0860
15	0.0205	0.0827	0.0767
30	0.0373	0.0607	0.0603
45	0.0497	0.0510	0.0500
60	0.0571	0.0413	0.0407
120	0.0644	0.0240	0.0183
180	0.0725	0.0240	0.0147
240	0.0745	0.0167	0.0083
300	0.0795	0.0100	0.0050
360	0.0812	0.0050	0.0050

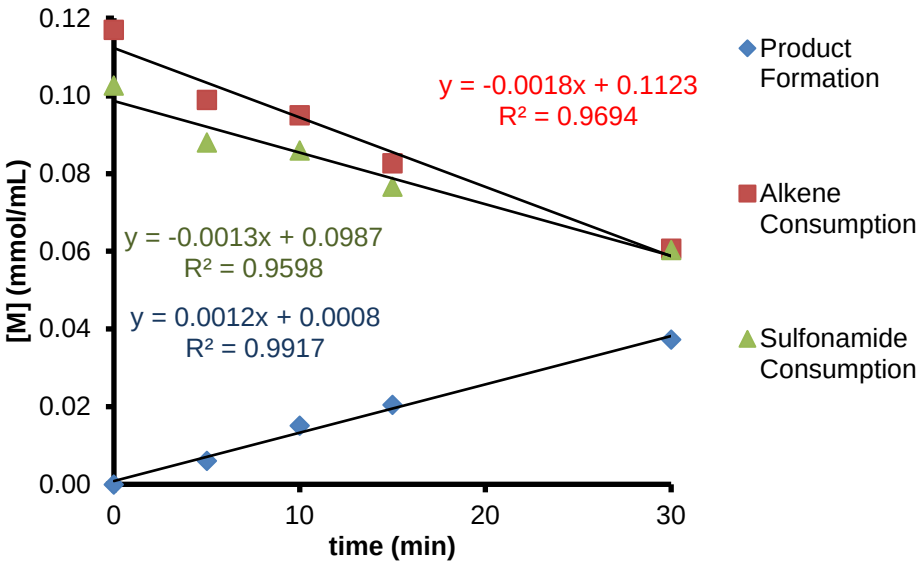
Plotted Aminoarylation Reaction Profile with trans-Anethole ([M] vs. time)



Plotted Aminoarylation Reaction Profile with *trans*-Anethole
(yield vs. time)

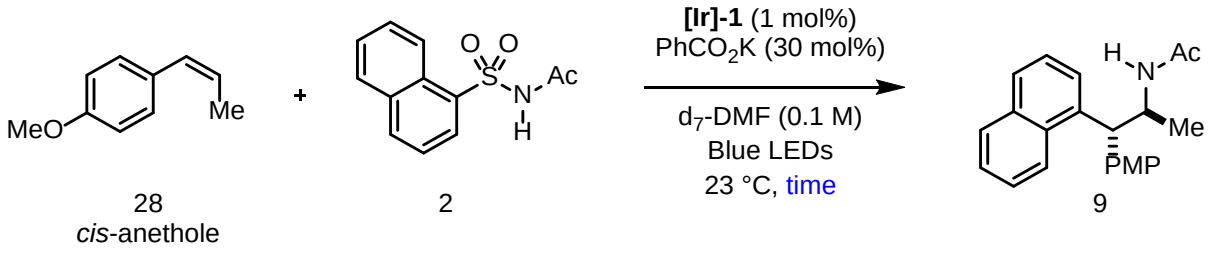


Plotted Initial Rates for Aminoarylation with *trans*-Anethole
([M] vs. time)



	Average of 3 trials		
	Product Formation	***trans*-Anethole Consumption**	**Sulfonamide Consumption**
Initial rate ([M] • min^{-1})	0.0012	-0.0018	-0.0013
R^2	0.9917	0.9694	0.9598

Figure S7: Reaction Profile and Initial Rates for Aminoaryation with *cis*-Anethole



28
cis-anethole

2

9

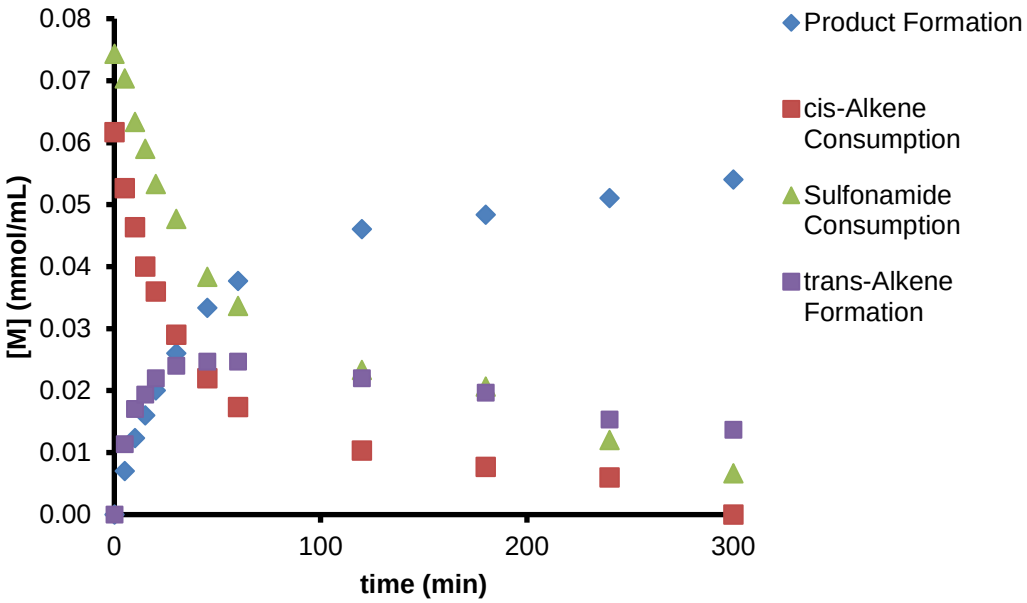
To a flame dried 2-dram vial, equipped with a teflon coated oval shaped stir bar, was added *cis*-anethole (35.6 mg, 0.24 mmol), *N*-(1-naphthylsulfonyl)acetamide (49.9 mg, 0.2 mmol), potassium benzoate (9.61 mg, 30 mol%), and $Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$ (2 mg, 1 mol%). The vial contents were then dissolved in anhydrous d_7-DMF (2 mL, 0.1 M) followed by addition of trimethyl(phenyl)silane (11.4 µL, 0.066 mmol) as an internal standrad. The reaction was sparged under argon for 15 min before the 2 mL solution volume was equally seperated between 3 argon sparged NMR tubes (0.67 mL each). The tubes were quickly capped and sealed with parafilm. Time zero (t_0) ^{1}H-NMR measurements were taken of all three samples prior to irradiation. Then, the 3 NMR tubes were irradiated with 1 x blue H150 Kessil LED light (~2 cm) and cooled by one overhead fan. After the alloted time (i.e. 5, 10, 15, 20... min), the light was turned off and reaction solution analyzed by ^{1}H-NMR.

Analysis: The concentrations and yields for the aminoarylation substrates and product were plotted against time in minutes. The slope through five points for the first ~20% reaction conversion was utilized to calculate the initial rates of reaction. The procedure was repeated in triplicate (3 ^{1}H-NMR measurements) and the average of these three trials was determined. Calculated values are tabulated below.

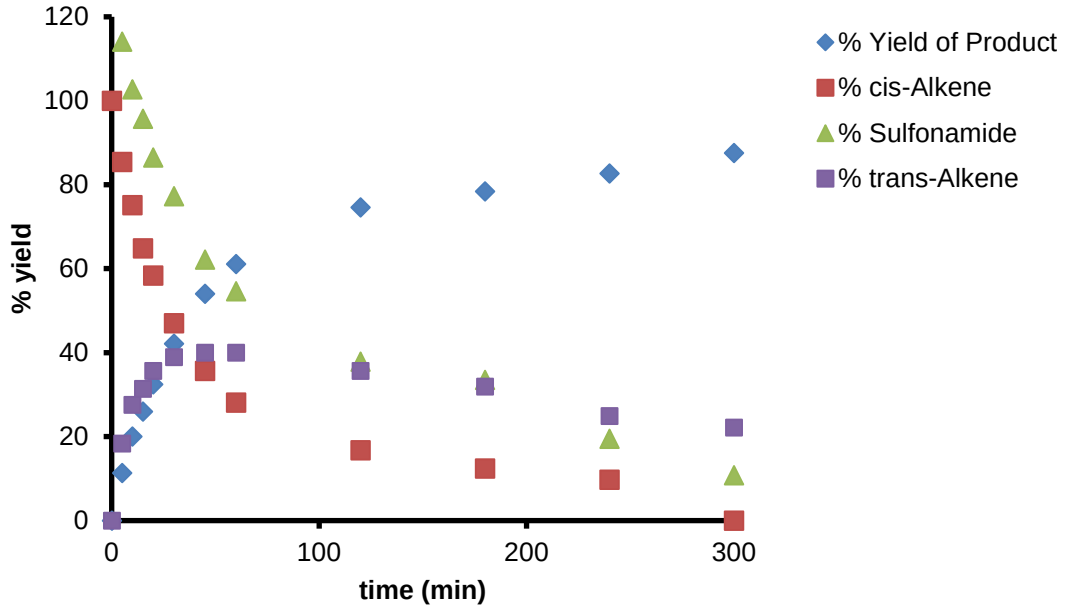
Aminoarylation Reaction Profile with *cis*-Anethole
([M] vs. time)

	Avg. of 3 trials [M] (mmol/mL)			
min	**Product Formation**	***cis*-Anethole Consumption**	**Sulfonamide Consumption**	***trans*-Anethole Formation**
0	0.0000	0.0617	0.0743	0.0000
5	0.0070	0.0527	0.0703	0.0113
10	0.0123	0.0463	0.0633	0.0170
15	0.0160	0.0400	0.0590	0.0193
20	0.0200	0.0360	0.0533	0.0220
30	0.0260	0.0290	0.0477	0.0240
45	0.0333	0.0220	0.0383	0.0247
60	0.0377	0.0173	0.0337	0.0247
120	0.0460	0.0103	0.0233	0.0220
180	0.0484	0.0077	0.0207	0.0197
240	0.0510	0.0060	0.0120	0.0153
300	0.0540	0.0000	0.0067	0.0137

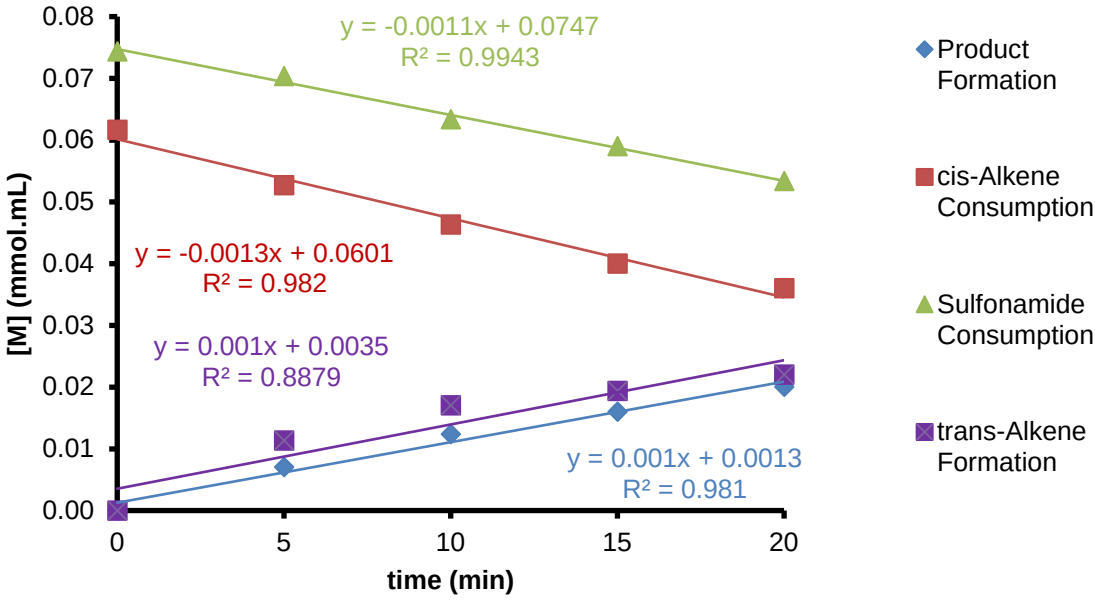
Plotted Aminoarylation Reaction Profile with *cis*-Anethole
([M] vs. time)



Plotted Aminoarylation Reaction Profile with *cis*-Anethole
(yield vs. time)

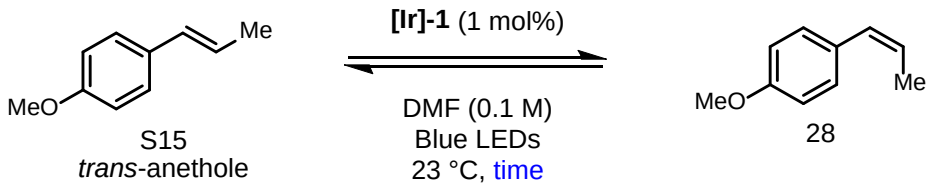


Plotted Initial Rates for Aminoarylation with *cis*-Anethole
([M] vs. time)



	Average of 3 trials			
	Product Formation	***cis*-Anethole Consumption**	**Sulfonamide Consumption**	***trans*-Anethole Formation**
Initial rate ([M] • min^{-1})	0.0010	-0.0013	-0.0011	-0.0010
R^2	0.9810	0.9820	0.9943	0.8879

Figure S8: Reaction Profile and Initial Rates for Alkene Isomerization with *trans*-Anethole

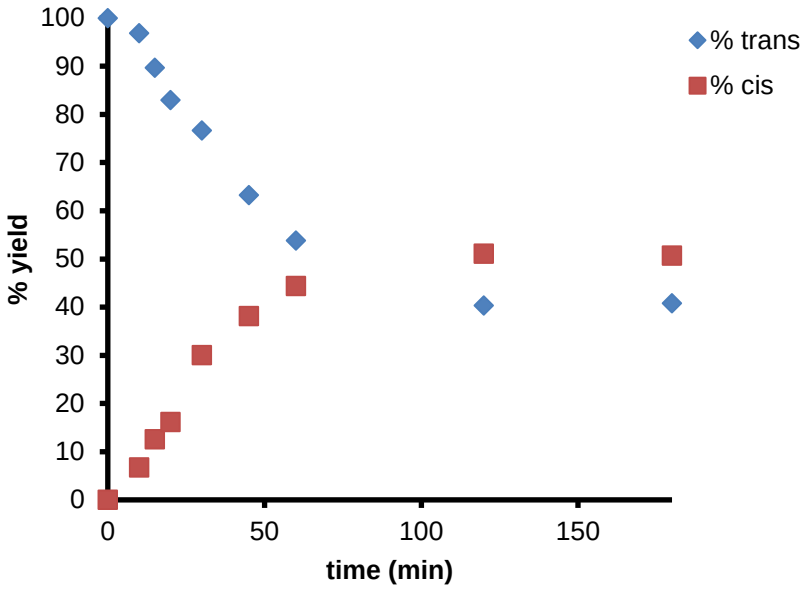


To a flame dried 2-dram vial, equipped with a teflon coated oval shaped stir bar, was added *trans*-anethole (14.8 mg, 0.1 mmol) and $Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$ (1 mg, 1 mol%). The vial contents were then dissolved in anhydrous d_7-DMF (1 mL, 0.1 M) followed by addition of trimethyl(phenyl)silane (5.68 µL, 0.033 mmol) as an internal standrad. The reaction was sparged under argon for 15 min before the 1 mL solution volume was equally seperated between 2 argon sparged NMR tubes (0.5 mL each). The tubes were quickly capped and sealed with parafilm. Time zero (t_0) ^{1}H-NMR measurements were taken of both samples prior to irradiation. Then, the 2 NMR tubes were irradiated with 1 x blue H150 Kessil LED light (~2 cm) and cooled by one overhead fan. After the alloted time (i.e.10, 15, 20... min), the light was turned off and reaction solution analyzed by ^{1}H-NMR.

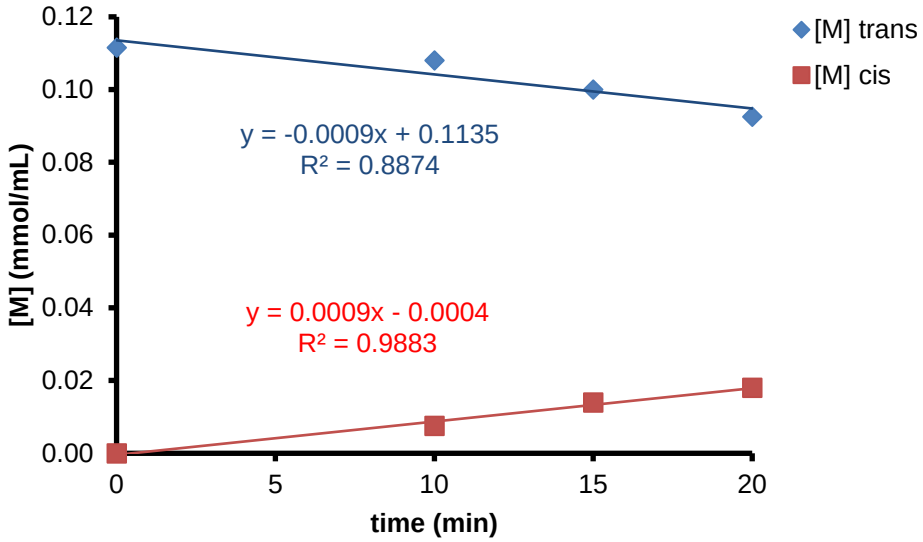
Analysis: The alkene yields for the isomerization were plotted against time in minutes. The slope through five points for the first ~20% reaction conversion was utilized to calculate the initial rate of isomerization. The procedure was repeated and the average of these two trials was determined. Calculated values are tabulated below.

	Average of 2 trials	
min	% trans-anethole	% cis-anethole
0	100.00	0.00
10	96.86	6.73
15	89.69	12.56
20	82.96	16.14
30	76.68	30.04
45	63.23	38.12
60	53.81	44.39
120	40.36	51.12
180	40.81	50.67

Plotted Isomerization Reaction Profile with *cis*-Anethole
(yield vs. time)

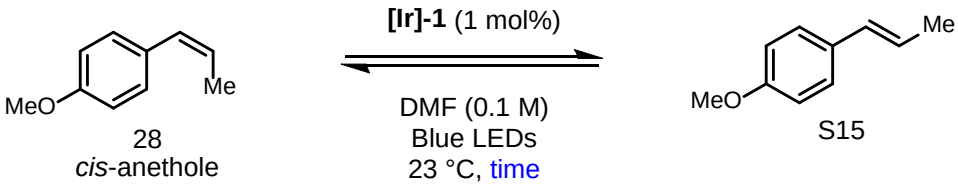


Plotted Initial Rates for Isomerization with *cis*-Anethole
([M] vs. time)



	Avg. of 2 trials	
	cis-Anethole Formation	trans-Anethole Consumption
Initial rate ([M] • min^{-1})	0.0009	-0.0009
R^2	0.9883	0.8874

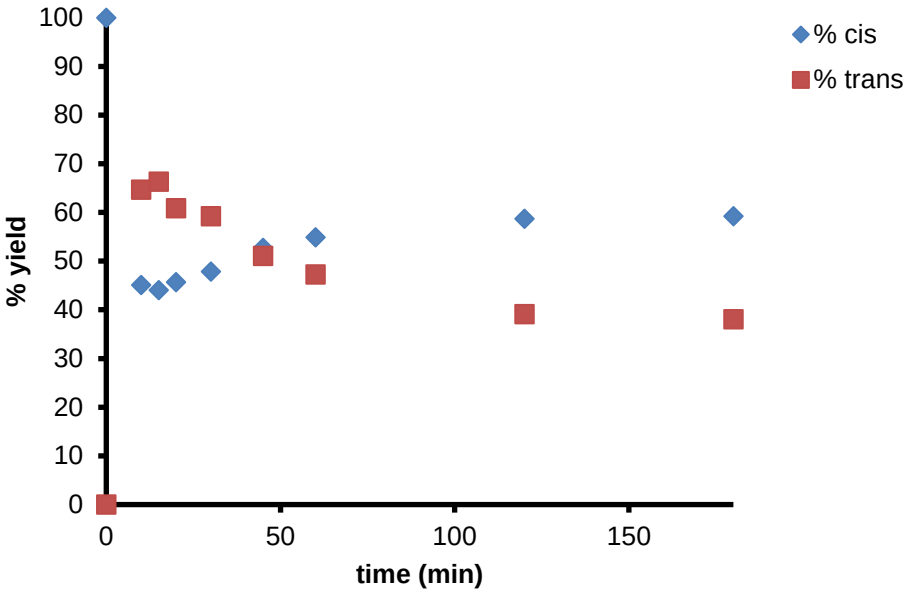
Figure S9: Reaction Profile for Alkene Isomerization with *cis*-Anethole



To a flame dried 2-dram vial, equipped with a teflon coated oval shaped stir bar, was added *cis*-anethole (14.8 mg, 0.1 mmol) and Ir(dF(CF_3)ppy)$_2$(5,5'd(CF_3)bpy)PF_6 (1 mg, 1 mol%). The vial contents were then dissolved in anhydrous d_7-DMF (1 mL, 0.1 M) followed by addition of trimethyl(phenyl)silane (5.68 µL, 0.033 mmol) as an internal standrad. The reaction was sparged under argon for 15 min before the 1 mL solution volume was equally seperated between 2 argon sparged NMR tubes (0.5 mL each). The tubes were quickly capped and sealed with parafilm. Time zero (t_0) ^{1}H-NMR measurements were taken of both samples prior to irradiation. Then, the 2 NMR tubes were irradiated with 1 x blue H150 Kessil LED light (~2 cm) and cooled by one overhead fan. After the alloted time (i.e.10, 15, 20... min), the light was turned off and reaction solution analyzed by ^{1}H-NMR.

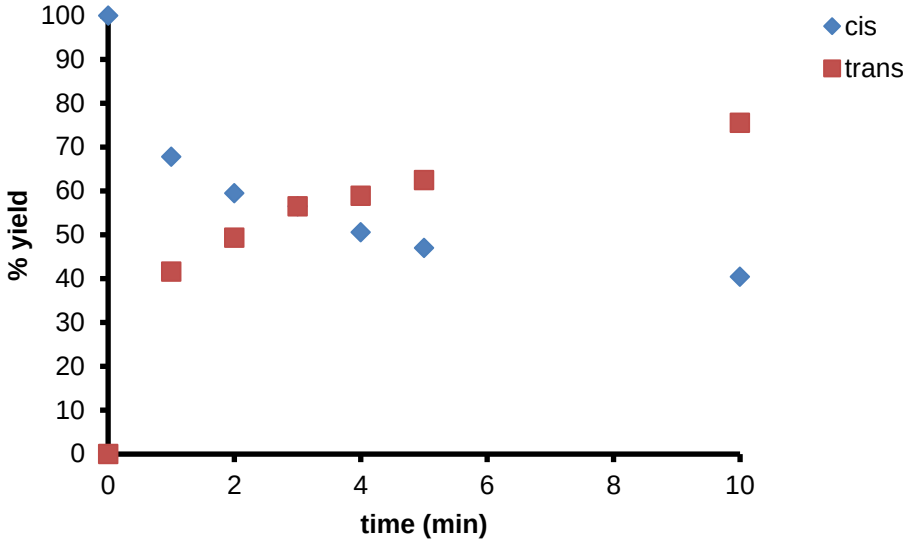
Analysis: The alkene yields for the isomerization were plotted against time in minutes. Because the isomerization of *cis*-trans anethole is so rapid, initial rates could not be determined. Qualitatively, these isomerization studies suggest the following:

Plotted Isomerization Reaction Profile with *trans*-Anethole (yield vs. time)



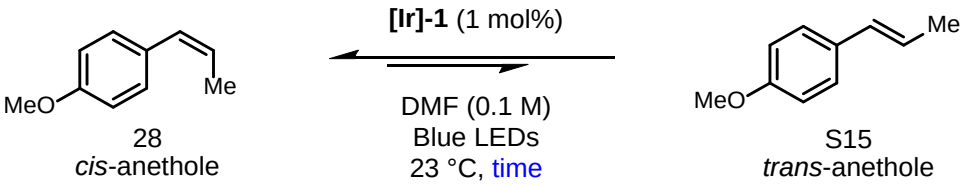
	Average of 2 trials	
min	% cis	% trans
0	100.00	0.00
10	45.11	64.67
15	44.02	66.30
20	45.65	60.87
30	47.83	59.24
45	52.72	51.09
60	54.89	47.28
120	58.70	39.13
180	59.24	38.04

Plotted Isomerization Reaction Profile for 10 min with *trans*-Anethole (yield vs. time)



	Average of 2 trials	
min	% cis	% trans
0	100.00	0.00
1	67.86	41.67
2	59.52	49.40
3	56.55	56.55
4	50.60	58.93
5	47.02	62.50
10	40.48	75.60

Figure S10: Determinaion of Photostationary State Between *cis*-Anethole and *trans*-Anethole



28
cis-anethole

(1.4)

S15
trans-anethole

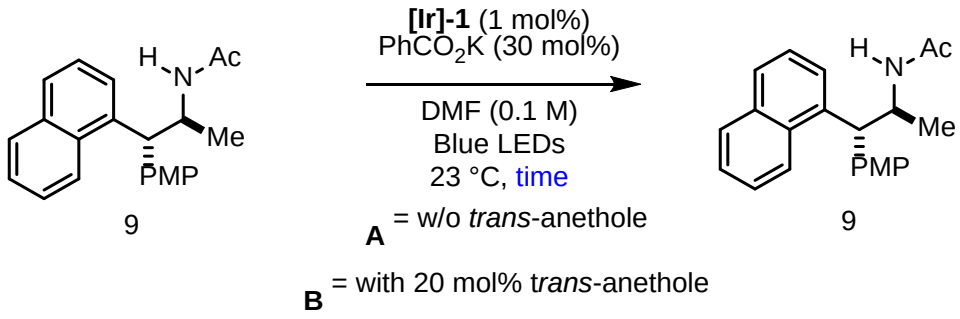
(1)

The following isomeric ratios were extrapolated from the above alkene isomerization experiments. The cis:trans ratios were taken from t_{final} (180 min) once the equilibrium state between the two isomers had been observed.

	From *trans* to *cis*		**From *cis* to *trans***	
Time (minutes)	% cis	% trans	% cis	% trans
180	50.67	40.81	59.24	38.04
Normalized yields	55.39	44.61	60.90	39.10

Photostationary State between cis-Anethole and trans-Anethole		
min	% cis	% trans
180	58.15 (1.4)	41.86 (1)

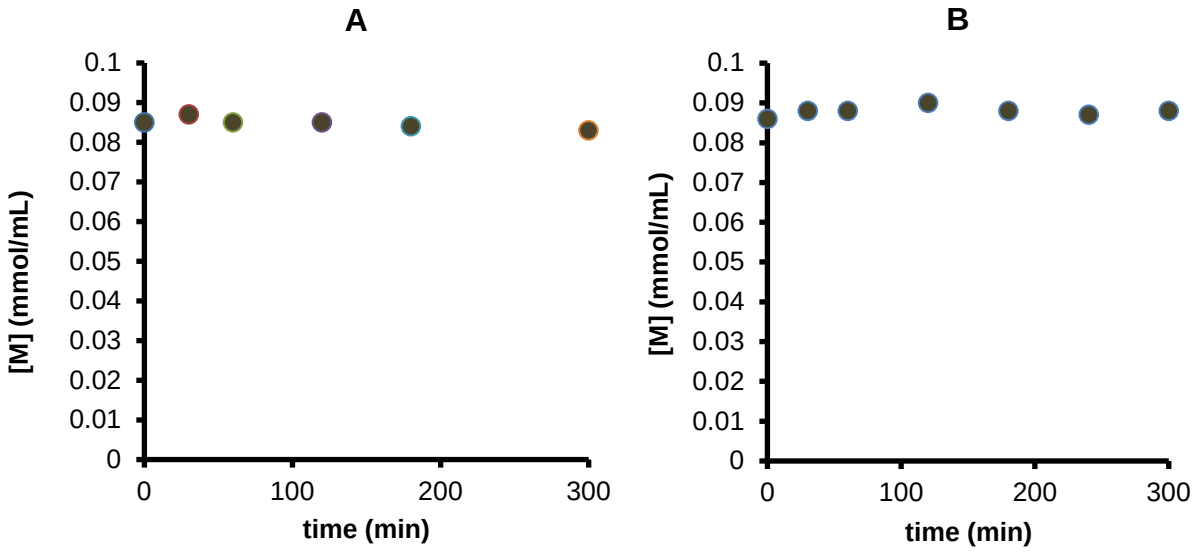
Figure S11: Aminoarylation Product Stability Assay



In order to validate the stability of the aminoarylation product and to be sure that it is not decomposing under the title reaction conditions over time, a stability assay analysis was performed.

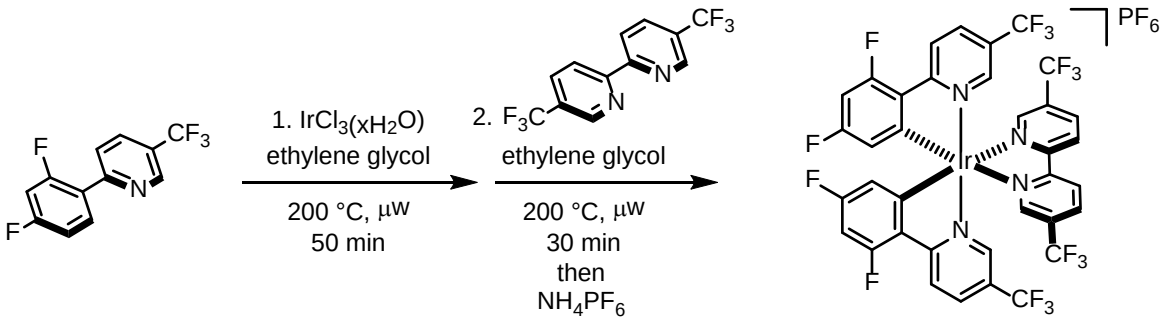
To a flame dried 2-dram vial, equipped with a teflon coated oval shaped stir bar, was added the aminoaryylation product (33.3 mg, 0.1 mmol), potassium benzoate (4.81 mg, 30 mol%), $Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$ (1 mg, 1 mol%), and in the case of trial **B** *trans*-anethole (2.97 µL, 0.02 mmol, 20 mol%). No *trans*-anethole was added for trial **A**. The vial contents were then dissolved in anhydrous DMF (1 mL, 0.1 M) followed by addition of trimethyl(phenyl)silane (5.7 µL, 0.033 mmol) as an internal standrad. The reaction was sparged under argon for 15 min before the 1 mL solution volume was added to an argon sparged NMR tube. The tube were quickly capped and sealed with parafilm. Time zero (t_0) ^{1}H-NMR measurements were taken prior to irradiation. Then, the NMR tubes were irradiated with 1 x blue H150 Kessil LED light (~2 cm) and cooled by one overhead fan. After the alloted time (i.e. 5, 10, 15, 20... min), the light was turned off and reaction solution analyzed by ^{1}H-NMR.

Analysis: The concentration of the aminoarylation product was plotted against time in minutes. As the plots below suggest, no noticable degradation of the aminoarylation product occurs either in the presence or absence of *trans*-anethole. These results suggest the aminoarylation product is stable and does not readily undergo decomposition.


A
B
[M] (mmol/mL)
time (min)
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
100
200
300

Preparation of Reagents:

Preparation of $Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$ (3)/[Ir]-1



$Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)PF_6$
(3)/[Ir]-1

The following procedure has been adopted from a two-step, one-pot literature procedure from our laboratory disclosing the synthesis of heteroleptic-Ir(I) complexes through microwave irradiation (*46*).

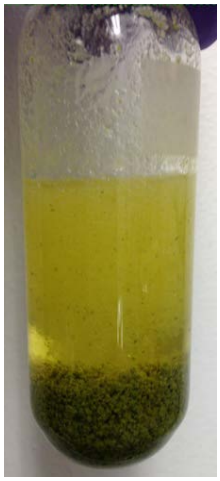
To an oven dried 20 mL microwave vial was charged a magnetic stirring bar, $IrCl_3$-xH_2O (507 mg, 1.6 mmol, 1 equiv), and 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine (1.04 g, 4.0 mmol, 2.5 equiv). The vial contents were dissolved in ethylene glycol (15 mL) and then the microwave vial capped. Then the reaction was sonicated for 3 minutes to increase homogeneity (picture **A**). The reaction was heated in a microwave reactor at 200 °C for 50 min with a 5 min pre-stir period. After the reaction had cooled to room temperature (picture **B**), 5-(trifluoromethyl)-2-[5-(trifluoromethyl)-2-pyridyl]pyridine (617 mg, 2.1 mmol, 2 equiv) was added, the vial re-capped, and the reaction was heated to 200 °C for 30 min with a 5 min pre-stir period.

After the reaction had cooled to room temperature (pictuure **C**), the solution was dissolved in dH_2O (50 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were combined and concentrated down, followed by the addition of NH_4PF_6 (10 g in ~50 mL dH_2O). The whole was placed in the freezer overnight to allow for maximum crystal formation. The yellow/orange crystals were filtered and washed with cold Et_2O. Re-crystallization was performed with pentane and acetone (insoluble in pentane) to provide the title complex as a free-flowing yellow powder (1.08 g, 59%).

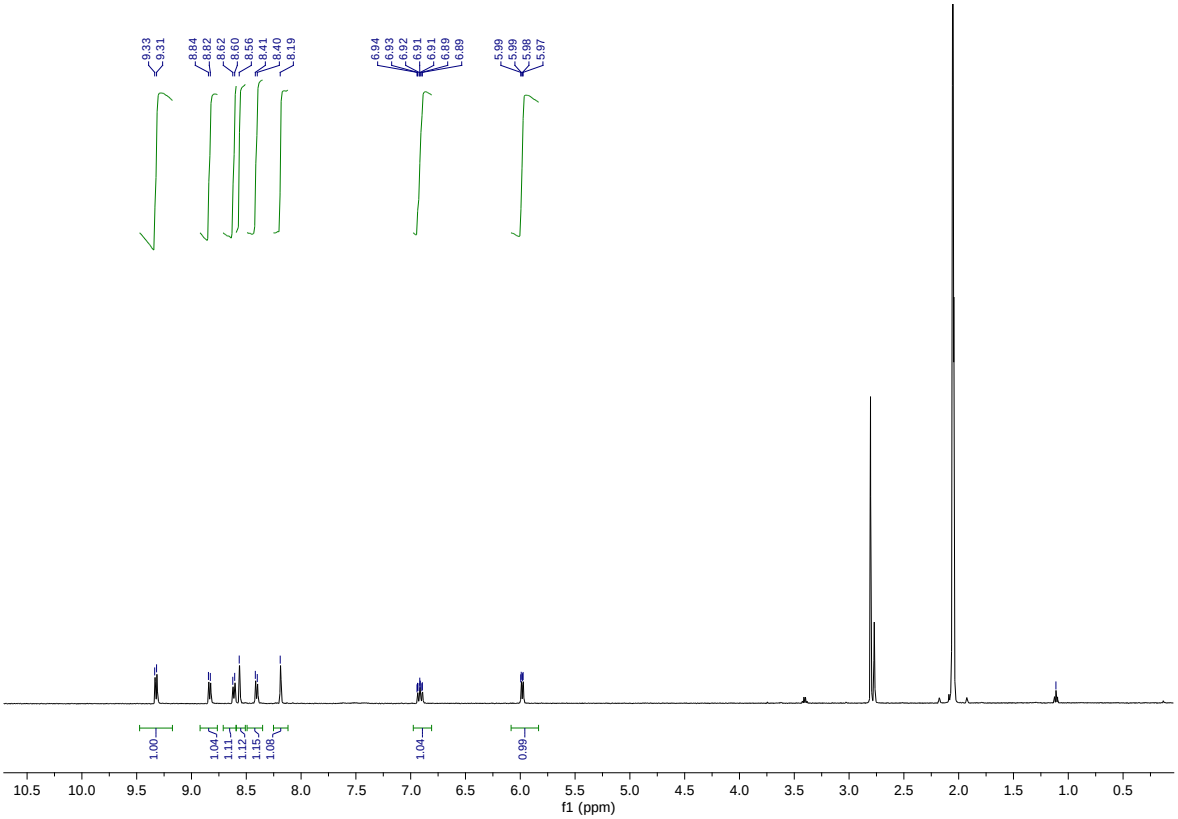
^1H and ^{19}F NMR characterization data is identical to that reported in the literature (*17*).

^1H NMR (500 MHz, d_6-Acetone) δ = 9.32 (d, *J* = 8.6 Hz, 1H), 8.83 (d, *J* = 8.5 Hz, 1H), 8.61 (d, *J* = 8.7 Hz, 1H), 8.56 (s, 1H), 8.40 (d, *J* = 8.9 Hz, 1H), 8.19 (s, 1H), 6.91 (t, *J* = 11.7 Hz, 1H), 5.98 (dd, *J* = 8.4, 2.2 Hz, 1H) ppm

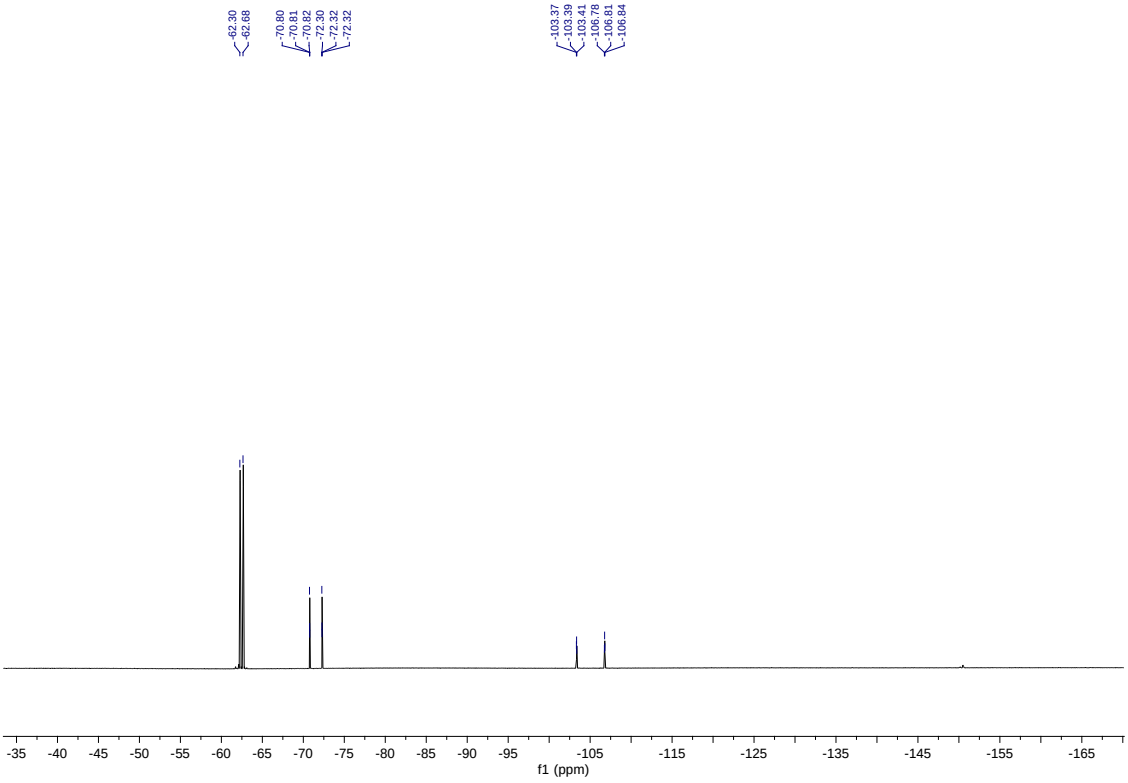
^{19}F NMR (471 MHz, d_6-Acetone) δ = -62.66 (d, *J* = 107.9 Hz), -71.75 (d, J_{P-F} = 707.4 Hz), -103.14 (dd, *J* = 20.1, 9.3 Hz), -106.81 (t, *J* = 12.2 Hz) ppm

A: After sonication	**B:** After step 1	**C**: After step 2
		

^{1}H NMR (500 MHz, d_6-Acetone) for Ir(dF(CF_3)ppy)$_2$(5,5'd(CF_3)bpy)PF_6

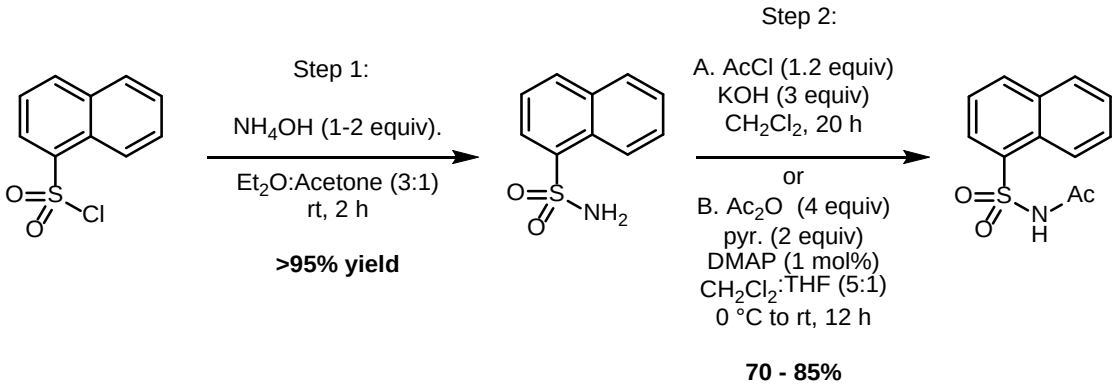


^{19}F NMR (471 MHz, d_6-Acetone) for Ir(dF(CF_3)ppy)$_2$(5,5'd(CF_3)bpy)PF_6



Acyl Sulfonamides:

***N*-(naphthalen-1-ylsulfonyl)acetamide (2)**



(*Step 1):*To a dry 250 mL round bottom flask equipped with a sizable oval shaped stir bar, a 3:1 mixture of Ether:Acetone was prepared (100 mL total). To this the solid naphthalene-1-sulfonyl chloride (10.0 g, 44.1 mmol), added into the flask. The solution is homogeneous at this point. Then by dropwise addition, saturated NH_4OH ((5809 µl) 44.1 mmol, 1 equiv) was added at 0 °C. The reaction was checked by TLC (4:6 EtOAc:Hexanes). If the reaction was not complete in 1 hour, an additional 1 equiv of NH_4OH was added to ensure full conversion.

The reaction was then neutralized to a pH of 6-7. Caution should be taken to not inhale the off gassing excess ammonia from the solution, and this will process faster if the reaction is under a continuous flush of nitrogen gas. Dilute the reaction in an equal volume of water and extract 2x with an equal amount of ethyl acetate. Combine the organic portions and dry over sodium sulfate, with a final concentration *in vacuo* to reveal a white powder.

(Step 2A):To a dry 250 mL round bottom flask equipped with a sizeable oval shaped stir bar, KOH (4426 mg, 78.9 mmol – crushed fine powder) and naphthalene-1-sulfonamide (5.45 g, 26.3 mmol) were added. The flask was evacuated and backfilled with nitrogen 3 times, after which the contents were diluted in dichloromethane solvent (50 mL). After stirring for a few minutes, acetyl chloride (2244 µL, 31.6 mmol) was added dropwise at room temperature. During this addition, the reaction very noticeably goes heterogeneous, then homogeneous and then back to heterogeneous. After 2 hours this reaction is complete, but is stable if left under nitrogen for up to 24 hours. At this point the reaction was diluted with 100 mL of water and acidified past neutrality. These contents were then transferred to a 500 mL separatory funnel and the aqueous layer was extracted 2x times with 75 mL of CH_2Cl_2. The CH_2Cl_2 extracts were combined, and concentrated, and the product was recrystallized in methanol to yield dense white crystals.

Alternatively, the product can be separated from the starting material by first combining the CH_2Cl_2 extraction and concentrating *in vacuo* to take back up in a

minimal amount of EtOAc (60 mL). This was then extracted 5x times with 60 mL of 5 % $NaHCO_3$ aq solution. These combined aqueous extracts were then acidified using 4 M HCl beyond neutrality (product becomes insoluble in solution. Finally, the desired product can be extracted from the acidic aqueous layer using EtOAc or CH_2Cl_2. Combination and drying over Na_2SO_4 and concentration in vacuo yields the desired product. The product can be further purified by recrystallization in MeOH. Non-recystallized material is lighter in density, and more difficult to handle.

*(Step 2B):*To a flame dried 100 mL round bottom flask equipped with a magnetic stir bar was added naphthalene-1-sulfonamide (1 g, 4.83 mmol), DMAP (6 mg, 1 mol%), CH_2Cl_2 (35 mL), and THF (6 mL). The reaction mixture at this point appears mostly heterogeneous. Then the reaction was cooled to 0 °C and via syringe was added pyridine (777 µL, 9.65 mmol, 2 equiv) followed by acetic anhydride (1.82 mL, 19.3 mmol, 4 equiv). The whole slowly became more homogeneous over a few minutes. The reaction was slowly allowed to warm to rt while stirring overnight (12 h). Upon completion of the reaction as judged by TLC analysis (40% EtOAc in Hex), the reaction was diluted in 20 mL dH_2O, layers separated, and the aqueous layer washed with 20 mL CH_2Cl_2. The organic layers were combined and rinsed with 1 N HCl (2 x 20 mL), brine, dried over sodium sulfate, filtered and concentrated *in vacuo* to provide white, compact crystals. The product may be further purified via flash column chromatography (0-40% EtOAc in Hex elution gradient).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.68 (bs, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.51 (d, *J* = 7.2 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.63 (dd, *J* = 12.5, 7.3 Hz, 2H), 2.03 (s, 3H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.1, 135.8, 134.2, 133.0, 132.1, 129.4, 128.9, 128.0, 127.1, 124.2, 123.6, 23.4 ppm

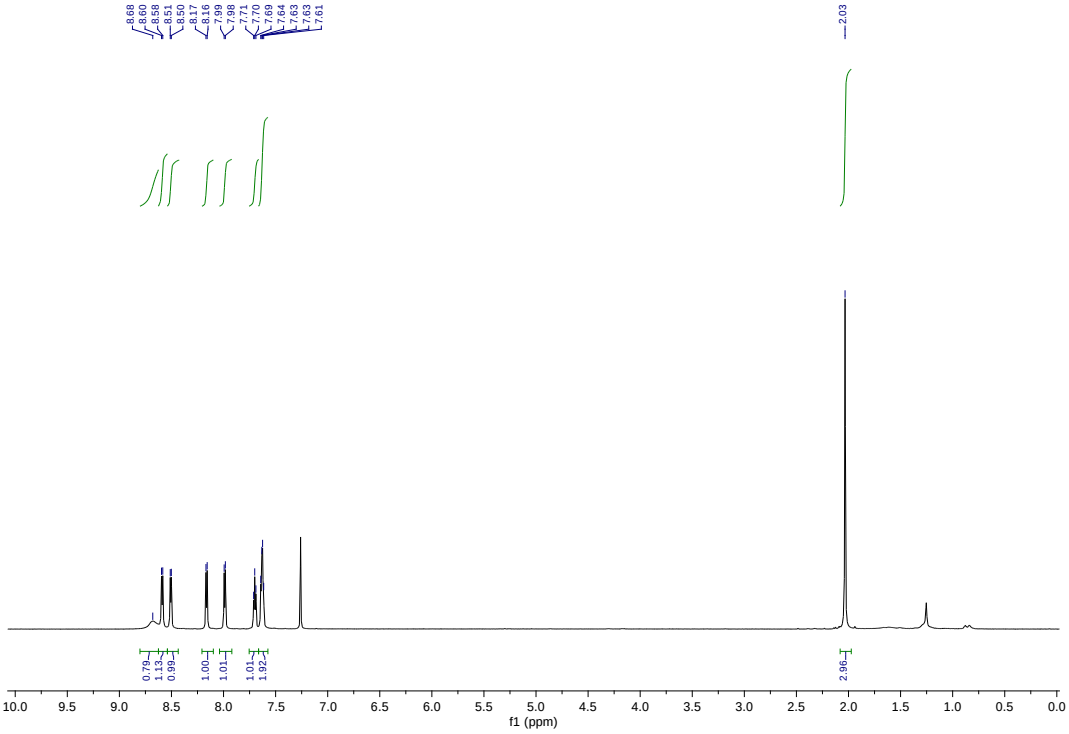
R_f (4:6 – EtOAc:Hex) = 0.3

IR (*neat*): 3246, 1730, 1441, 1410, 1372, 1328, 1215, 1127, 760, 734 cm^{-1}

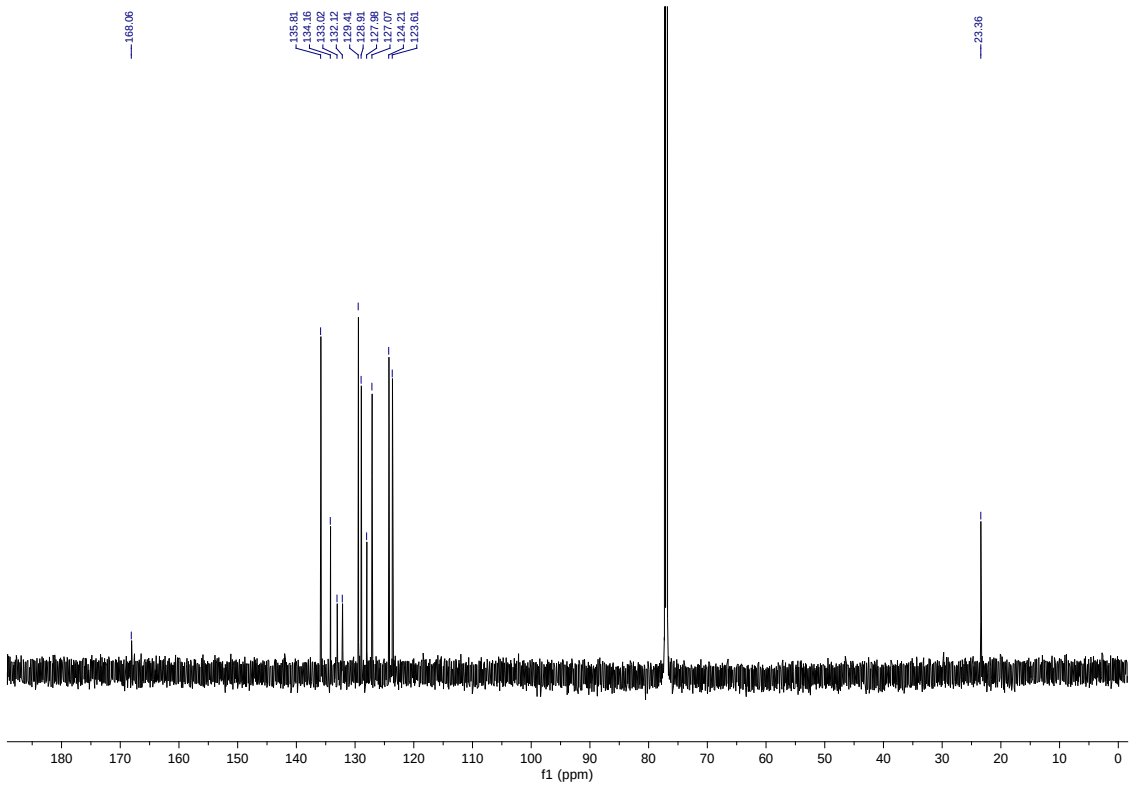
HRMS (ESI+) *m/z* calculated for $C_{12}H_{11}NO_3S$ $[M+H]^+$ 250.0532, found 250.0529

MP: 184–187 °C

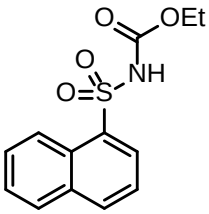
^{1}H NMR (700 MHz, $CDCl_3$) for 2



^{13}C NMR (176 MHz, $CDCl_3$) for 2



ethyl (naphthalen-1-ylsulfonyl)carbamate (S1)



To a 100 mL round bottom flask charged with a magnetic stir bar was added naphthalene-1-sulfonamide (1 g, 4.83 mmol), DMAP (29.5 mg, 0.24 mmol), CH_2Cl_2 (30 mL), and ethyl chloroformate (0.59 mL, 6.27 mmol). The whole was cooled to 0 °C then triethylamine (0.74 mL, 5.31 mmol) was added dropwise via syringe. The reaction slowly went from a white, heterogeneous mixture to a clear colorless, homogenous solution. The reaction was gradually warmed to rt and monitored by TLC (50% EtOAc in Hex). After 2 h, the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with EtOAc (30 mL) then washed 3 x with 1 N HCl (10 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 40% EtOAc in Hex elution gradient) provided the title substrate as a compact white solid (782 mg, 59%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.60 (d, *J* = 8.6 Hz, 1H), 8.49 (d, *J* = 7.4 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.80 (s, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.62 (dt, *J* = 12.1, 7.5 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 150.2, 135.7, 134.1, 132.8, 132.4, 129.3, 128.8, 128.0, 127.0, 124.1, 123.9, 63.1, 13.9 ppm

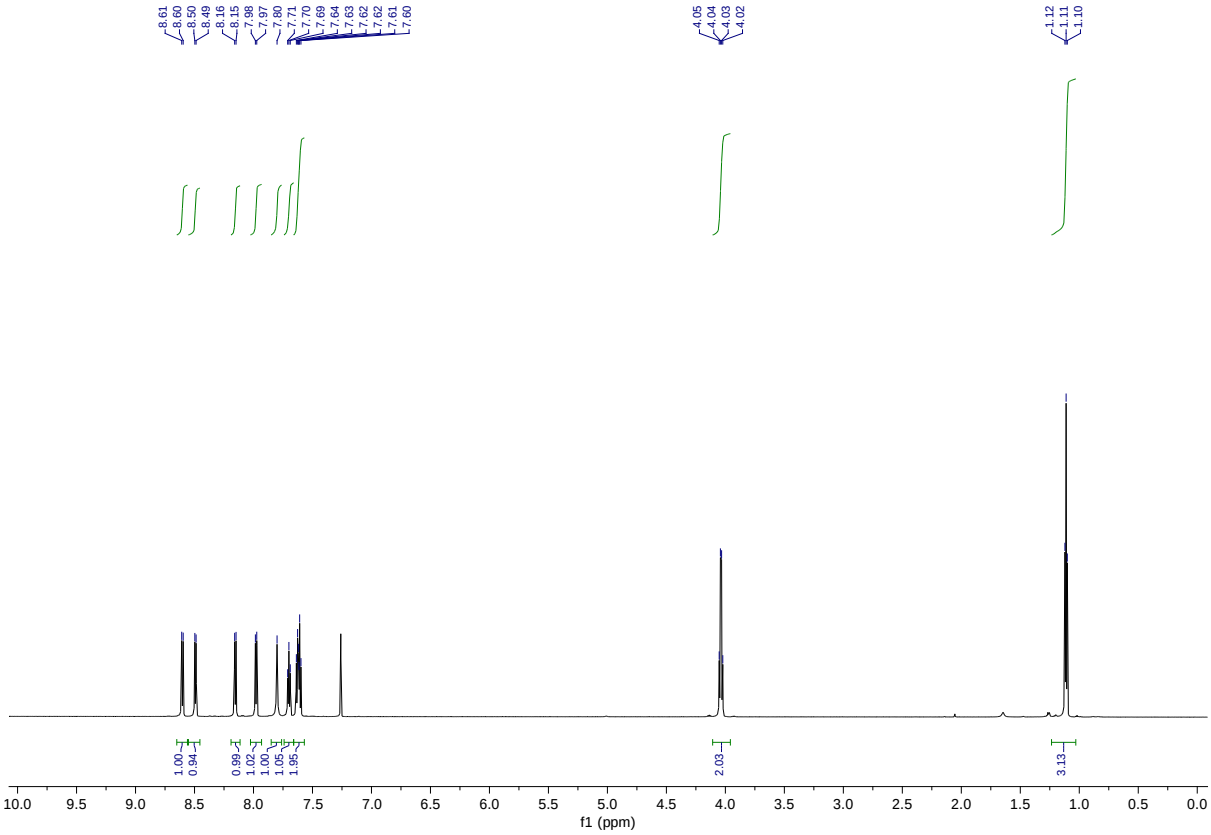
R_f (5:5 – EtOAc:Hex) = 0.5

IR (*neat*): 3081, 1712, 1507, 1476, 1352, 1309, 1167, 1139, 917, 802, 766 cm^{-1}

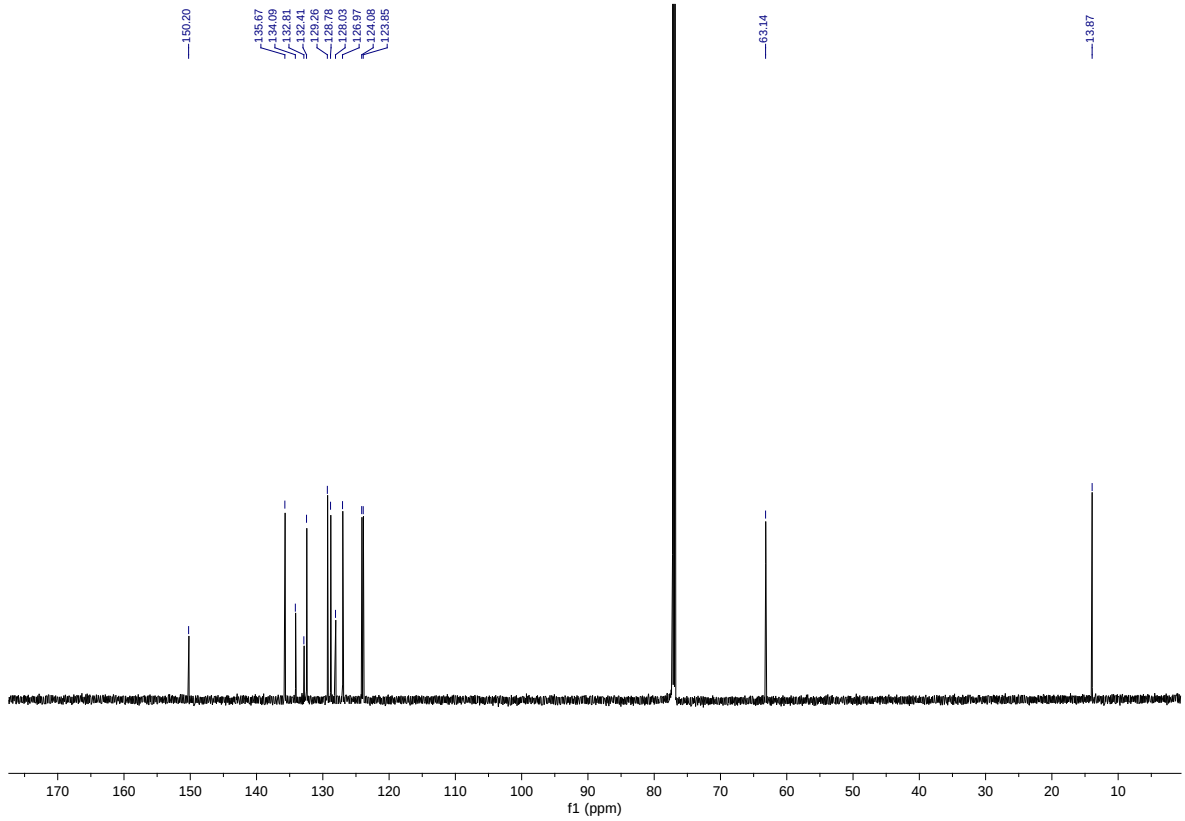
HRMS (ESI+) *m/z* calculated for $C_{13}H_{13}NO_4S$ [M+H]+ 280.00638, found 280.0634.

MP: 137–140 °C

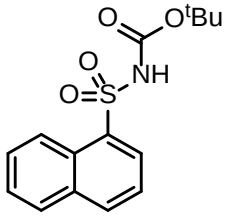
^{1}H NMR (700 MHz, $CDCl_3$) for S1



^{13}C NMR (176 MHz, $CDCl_3$) for S1



tert-butyl (naphthalen-1-ylsulfonyl)carbamate (S2)



To a 50 mL round bottom flask charged with a magnetic stir bar was added naphthalene-1-sulfonamide (1 g, 4.83 mmol), DMAP (58.9 mg, 0.483 mmol), CH_2Cl_2 (30 mL), and BOC anhydride (1.22 mL, 5.31 mmol). The whole was cooled to 0 °C then triethylamine (0.74 mL, 5.31 mmol) was added dropwise via syringe. The reaction slowly went from a cloudy white color to clear. The whole was slowly warmed to rt and monitored by TLC (50% EtOAc in Hex). After 2 h, the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with EtOAc (30 mL) then washed 3 x with 1 N HCl (10 mL). The organiclayer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 40% EtOAc in Hex elution gradient) provided the title substrate as a compact white solid (1.02 g, 69%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 8.6 Hz, 1H), 8.45 (d, *J* = 7.2 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.63 – 7.59 (m, 3H), 1.27 (s, 9H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 149.0, 135.4, 134.1, 133.2, 132.1, 129.2, 128.7, 128.0, 126.9, 124.0, 123.9, 84.3, 27.7 ppm

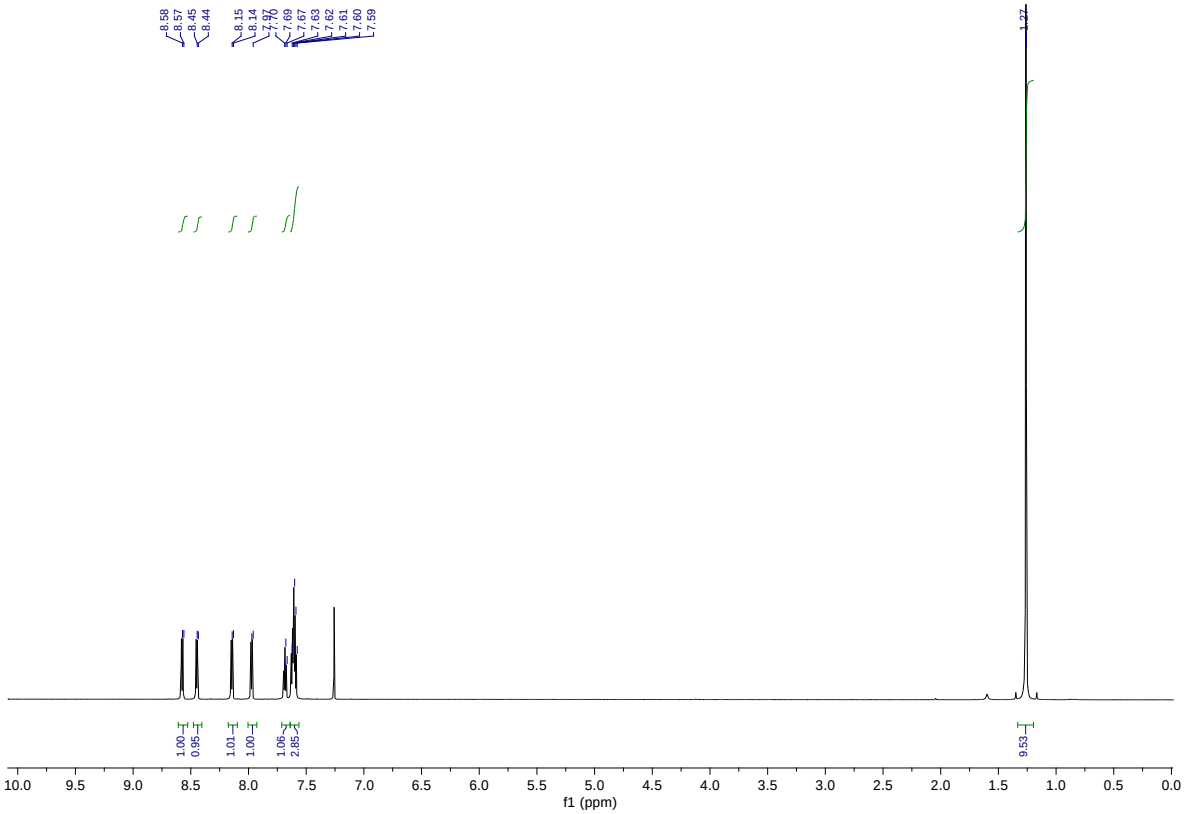
R_f (5:5 – EtOAc:Hex) = 0.5

IR (*neat*): 3073, 2982, 1701, 1354, 1332, 1134, 804, 777 cm^{-1}

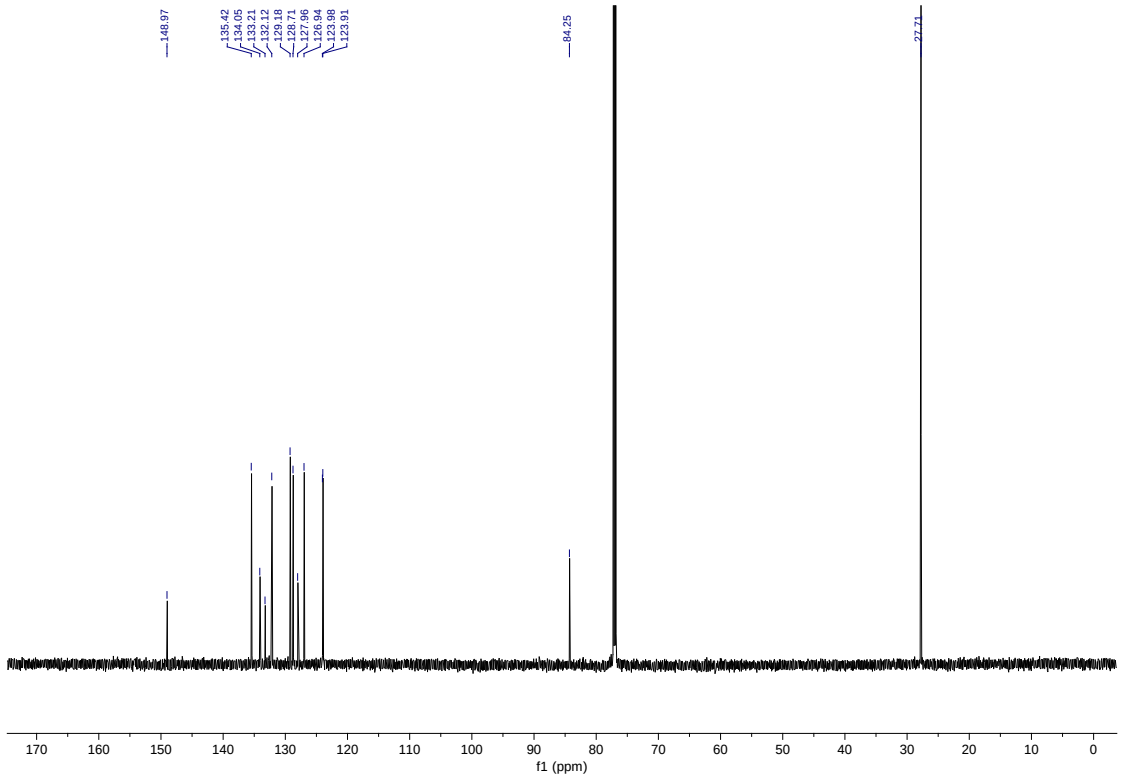
HRMS (ESI+) *m/z* calculated for $C_{15}H_{17}NO_4S$ [M+H]+ 308.0951, found 308.0947.

MP: 134–138 °C

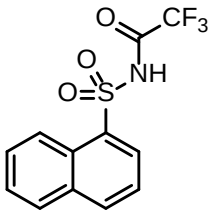
^{1}H NMR (700 MHz, $CDCl_3$) for S2



^{13}C NMR (176 MHz, $CDCl_3$) for S2



2,2,2-trifluoro-N-(naphthalen-1-ylsulfonyl)acetamide (S3)



To a 100 mL round bottom flask charged with a magnetic stir bar was added naphthalene-1-sulfonamide (1 g, 4.83 mmol), DMAP (58.9 mg, 0.483 mmol), CH_2Cl_2 (40 mL), and TFAA (0.783 mL, 5.31 mmol). The whole was cooled to 0 °C then triethylamine (0.74 mL, 5.31 mmol) was added dropwise via syringe. The reaction slowly went from a cloudy white color to clear. The whole was slowly warmed to rt and monitored by TLC (50% EtOAc in Hex). After 4 h, the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with EtOAc (30 mL) then washed 3 x with 1 N HCl (10 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 40% EtOAc in Hex elution gradient) provided the title substrate as a compact white solid (1.28 g, 88%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.06 (bs, 1H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.14 – 8.01 (m, 2H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.72 – 7.40 (m, 3H) ppm

^{13}C NMR (176 MHz, DMSO-d_6): δ = 159.9 (q, *J* = 32.9 Hz), 139.9, 133.6, 131.7, 128.3, 128.3, 127.4, 126.6, 126.1, 124.3, 117.6 (q, *J* = 291.4 Hz)

^{19}F NMR (377 MHz, DMSO-d_6) = δ -74.1 ppm

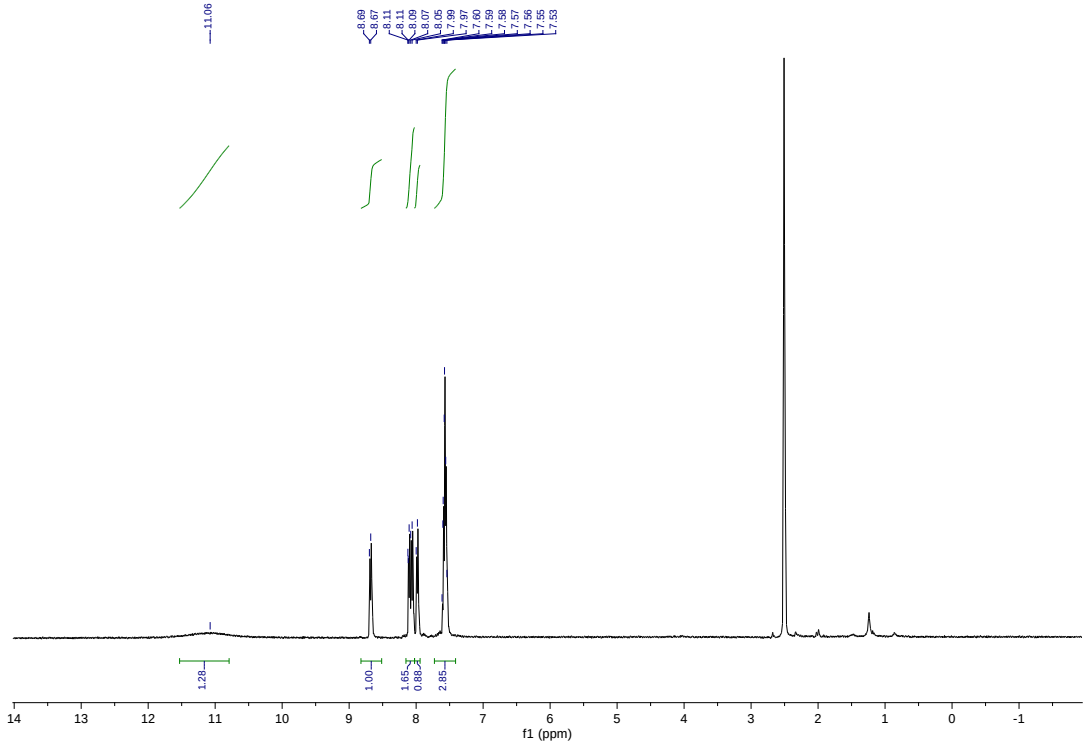
R_f (5:5 – EtOAc:Hex) = 0.3

IR (*neat*): 3209, 1762, 1508, 1452, 1362, 1201, 1108, 988, 765 cm^{-1}

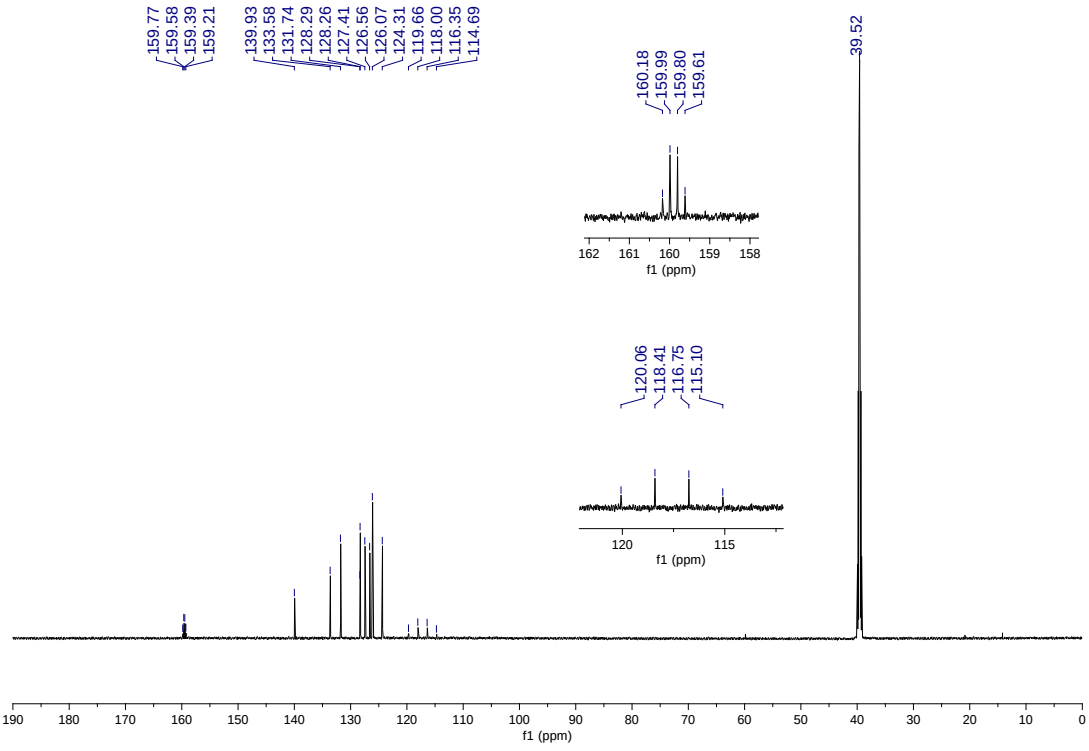
HRMS (ESI+) *m/z* calculated for $C_{12}H_8F_3NO_3S$ [M+H]+ 326.0069, found 326.0066.

MP: 165-168 °C

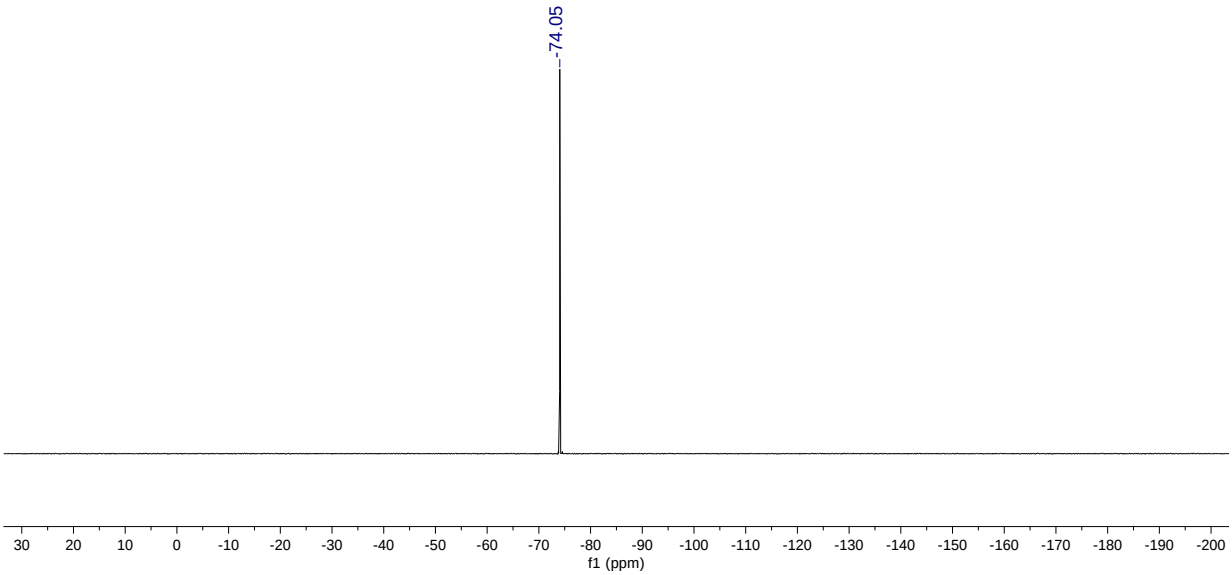
^{1}H NMR (400 MHz, DMSO-d$_6$) for S3



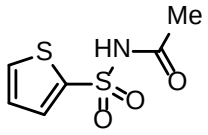
^{13}C NMR (176 MHz, DMSO-d$_6$) for S3



^{19}F NMR (377 MHz, $CDCl_3$) for S3



***N*-(thiophen-2-ylsulfonyl)acetamide (S4)**



To a flame dried 250 mL round bottom flask charged with a magnetic stir bar was added thiophene-2-sulfonamide (3 g, 18.4 mmol), DMAP (22.5 mg, 0.184 mmol), CH_2Cl_2 (50 mL), and THF (10 mL). The reaction appears mostly heterogeneous. Then the reaction was cooled to 0 °C then via syringe was added pyridine (4.44 mL, 55.1 mmol) followed by acetic anhydride (6.95 mL, 73.5 mmol). The reaction was allowed to warm to rt and monitored by TLC (50% EtOAc in Hex). After 3 h, the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with EtOAc (30 mL) then washed 3 x with 1 N HCl (10 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 50% EtOAc in Hex elution gradient) provided the title substrate as a compact white solid (2.57 g, 68%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 7.90 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.71 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.14 (dd, *J* = 4.9, 3.9 Hz, 1H), 2.13 (s, 3H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.1, 138.6, 135.2, 134.2, 127.5, 23.6 ppm

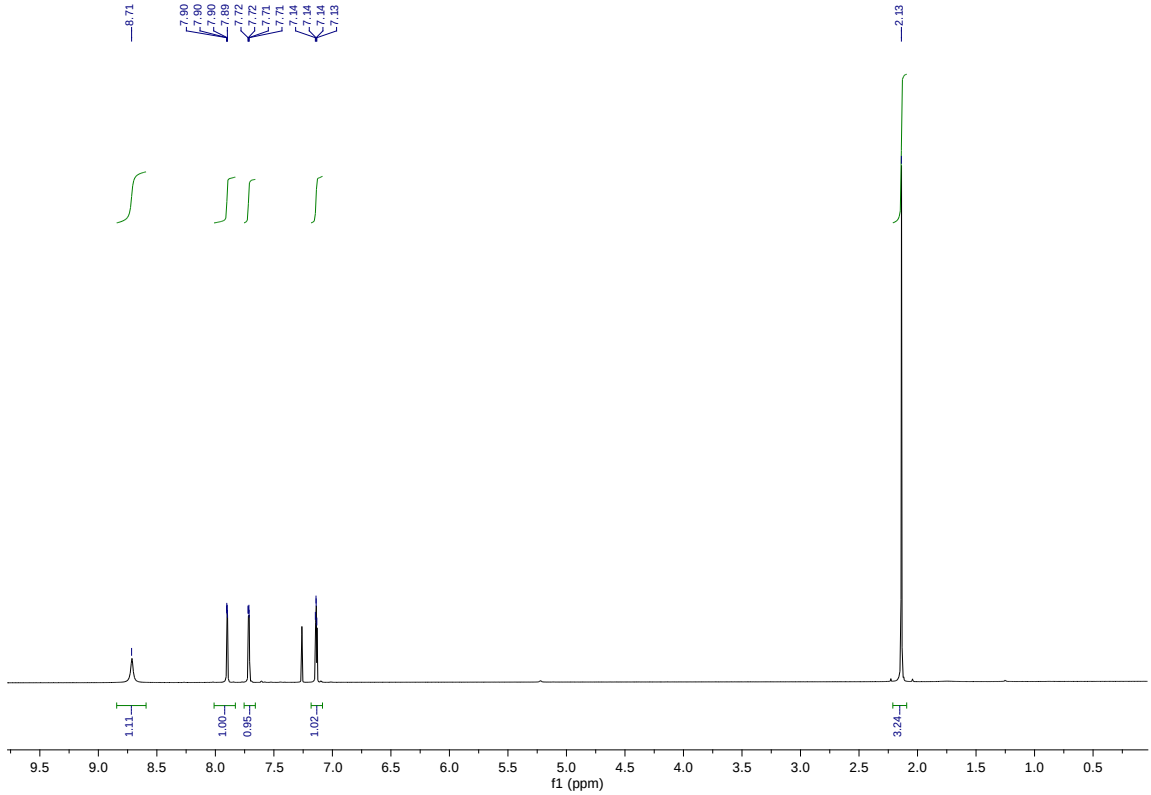
R_f (5:5 – EtOAc:Hex) = 0.4

IR (*neat*): 3105, 1688, 1446, 1421, 1368, 1351, 1017, 999, 728 cm^{-1}

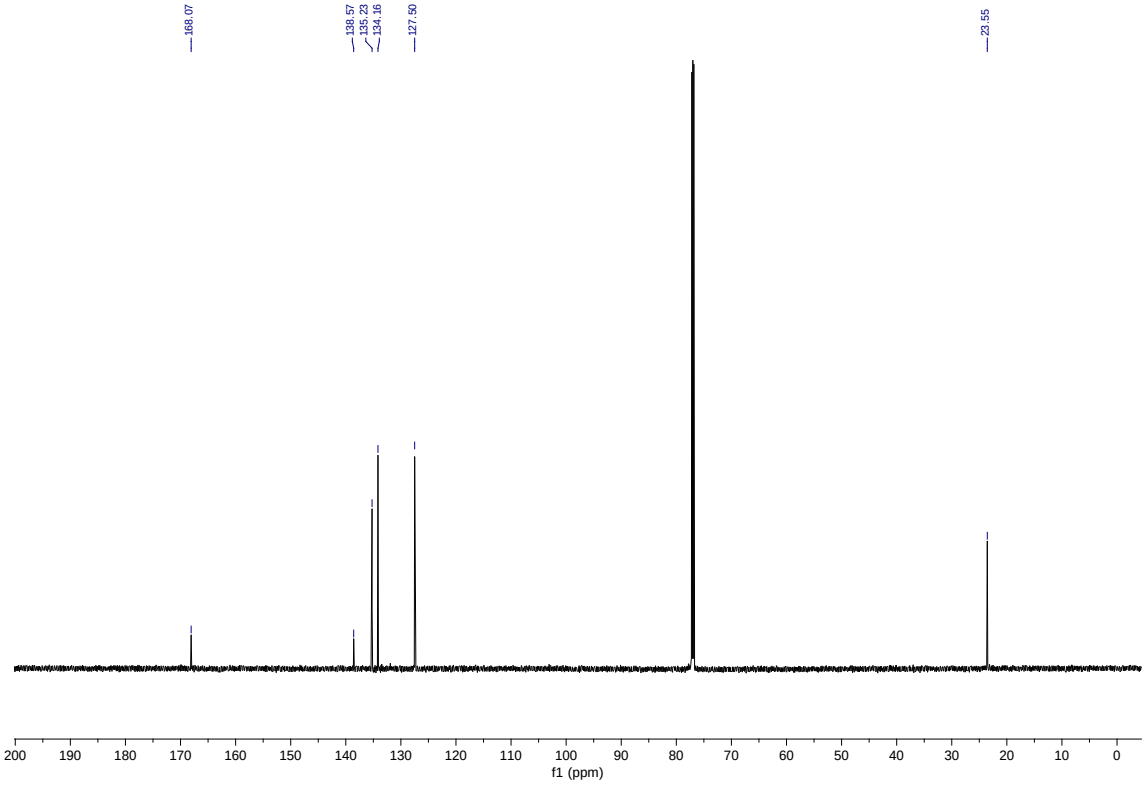
HRMS (EI) *m/z* calculated for $C_6H_7NO_3S_2$ [M^+] 204.9867, found 204.9871.

MP: 84–87 °C

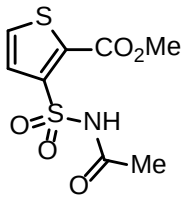
^{1}H NMR (700 MHz, $CDCl_3$) for S4



^{13}C NMR (176 MHz, $CDCl_3$) for S4



methyl 3-(*N*-acetylsulfamoyl)thiophene-2-carboxylate (S5)



To a flame dried 100 mL round bottom flask charged with a magnetic stir bar was added methyl 3-sulfamoylthiophene-2-carboxylate (500 mg, 2.26 mmol), DMAP (2.76 mg, 0.0226 mmol), CH_2Cl_2 (35.0 mL), and THF (5.00 mL). The reaction appears mostly heterogeneous. The whole was cooled to 0 °C then via syringe was added pyridine (0.546 mL, 6.78 mmol) and acetic anhydride (0.854 mL, 9.04 mmol). The reaction was allowed to warm to rt and monitored by TLC (50% EtOAc in Hex). After 12 h, the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with EtOAc (30 mL) then washed 3 x with 1 N HCl (10 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 50% EtOAc in Hex elution gradient) provided the title substrate as a compact white solid (512 mg, 86%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.92 (s, 1H), 7.72 (d, *J* = 5.2 Hz, 1H), 7.58 (d, *J* = 5.2 Hz, 1H), 3.95 (s, 3H), 2.15 (s, 3H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.5, 160.3, 142.9, 132.6, 131.5, 130.4, 53.3, 23.6 ppm

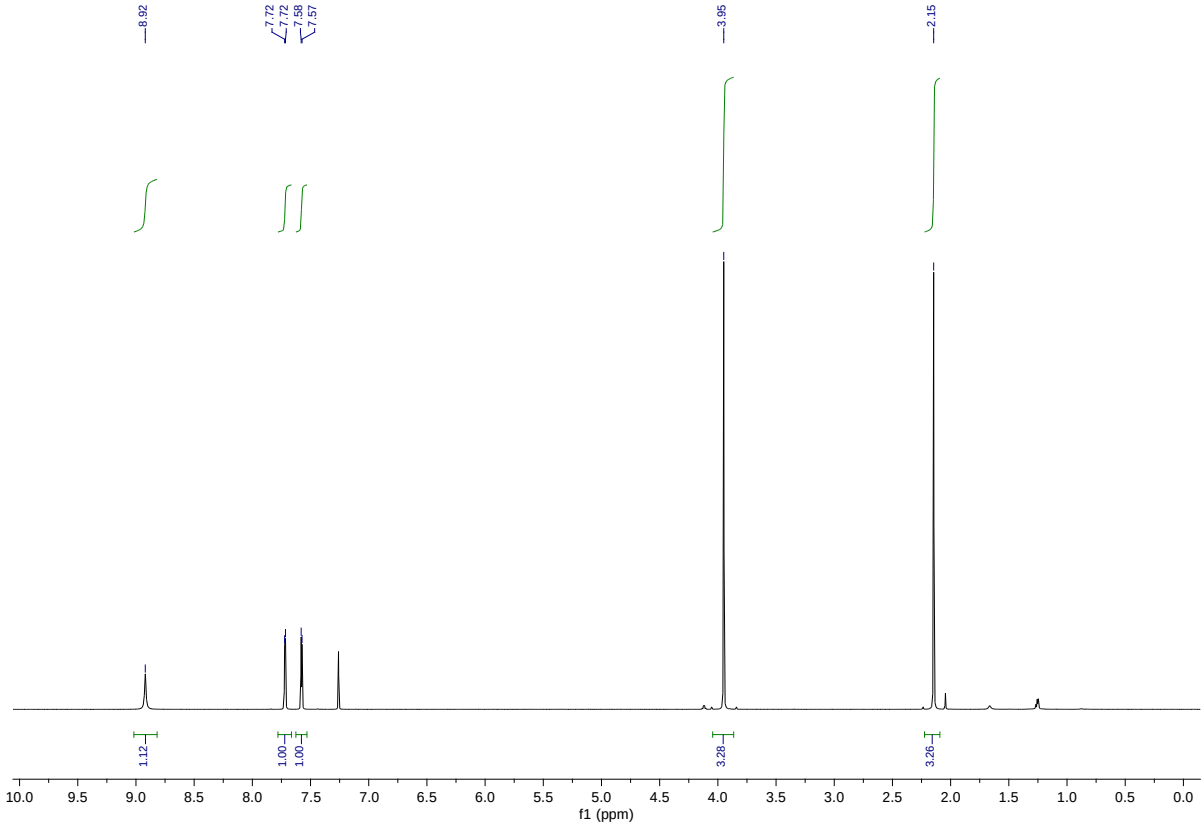
R_f (5:5 – EtOAc:Hex) = 0.2

IR (*neat*): 3131, 1719, 1701, 1435, 1358, 1265, 1173, 1144, 898, 772 cm^{-1}

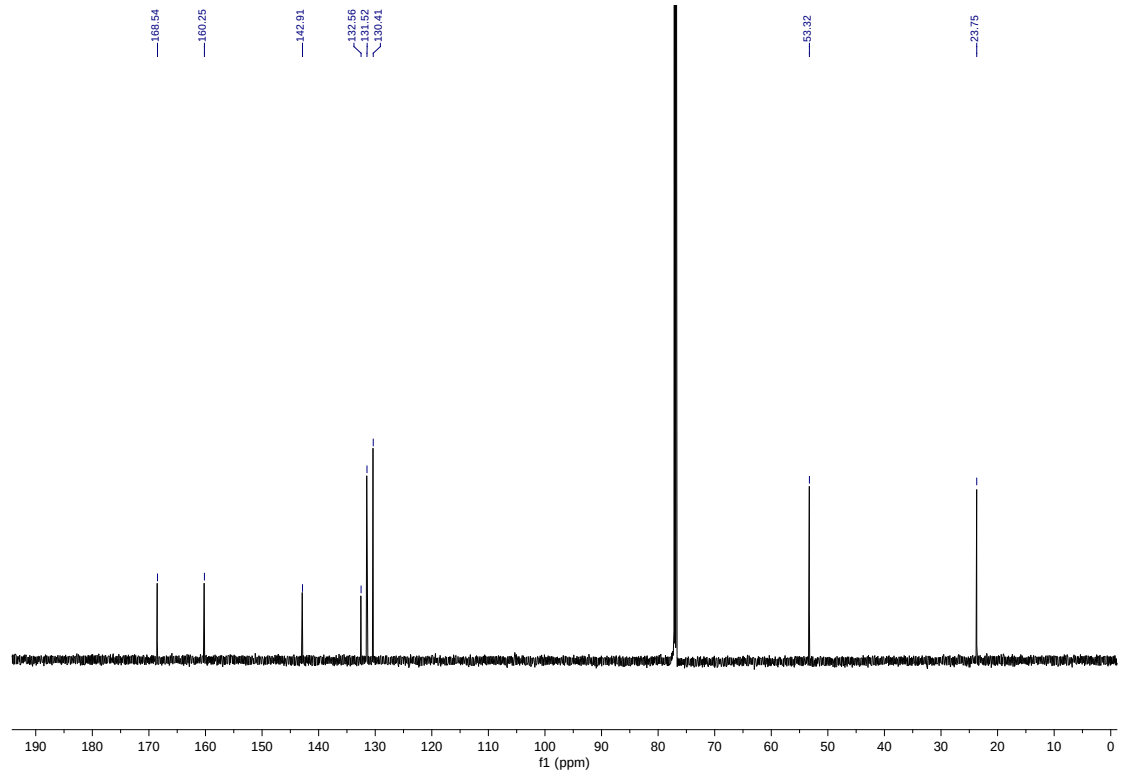
HRMS (ESI+) *m/z* calculated for $C_8H_9NO_5S_2Na$ $[M+Na]^+$ 285.9814, found 285.9818.

MP: 178–181 °C

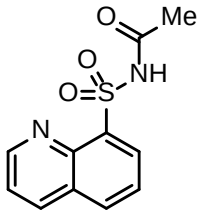
^{1}H NMR (700 MHz, $CDCl_3$) for S5



^{13}C NMR (176 MHz, $CDCl_3$) for S5



***N*-(quinolin-8-ylsulfonyl)acetamide (S6)**



To a flame dried 250 mL round bottom flask charged with a magnetic stir bar was added quinoline-8-sulfonamide (1000 mg, 4.80 mmol), DMAP (5.87 mg, 0.0480 mmol), CH_2Cl_2 (35.0 mL), and THF (5.00 mL). The reaction appears mostly heterogeneous. The whole was cooled to 0 °C then via syringe was added pyridine (0.387 mL, 4.80 mmol) followed by acetic anhydride (1.82 mL, 19.2 mmol). The reaction was allowed to warm to rt and monitored by TLC (50% EtOAc in Hex). After 12 h, the reaction was diluted in 100 mL dH_2O. The white crystalline solid were filtered off and washed with cold acetone to provide the title substrate as a compact white solid (1.03 g, 86%).

^{1}H NMR (700 MHz, DMSO-d_3): δ = 12.32 (s, 1H), 9.10 (m, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.46 (d, *J* = 8.1 Hz, 1H), 8.35 (d, *J* = 8.1 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.72 (dd, *J* = 8.2, 4.1 Hz, 1H), 1.88 (s, 3H) ppm

^{13}C NMR (176 MHz, DMSO-d_3): δ = 169.0, 151.5, 142.8, 137.1, 135.2, 134.7, 133.1, 128.5, 125.6, 122.6, 23.1 ppm

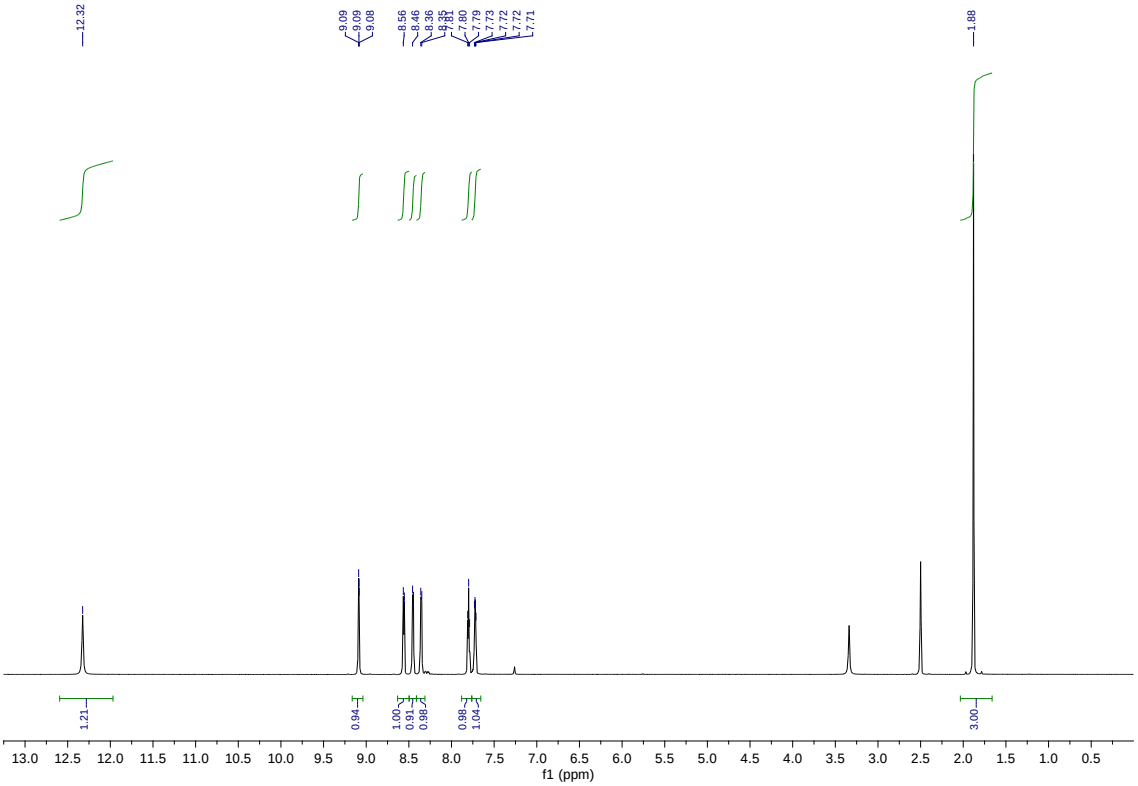
R_f (5:5 – EtOAc:Hex) = 0.3

IR (*neat*): 3003, 2818, 1713, 1499, 1457, 1330, 1166, 1139, 995, 973 cm^{-1}

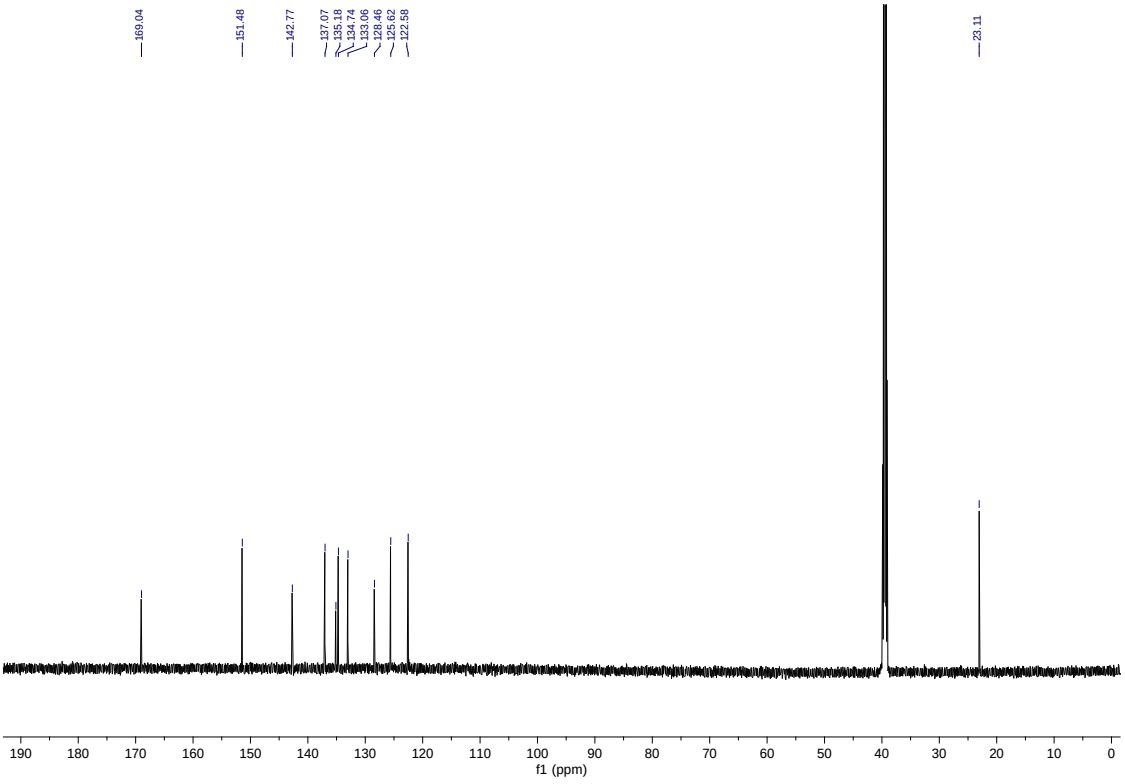
HRMS (ESI+) *m/z* calculated for $C_{11}H_{10}N_2O_3S$ $[M+H]^+$ 251.0485, found 251.0484.

MP: 240–245 °C

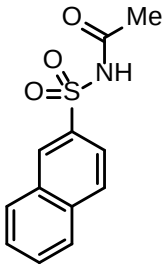
^{1}H NMR (700 MHz, DMSO-d_6) for S6



^{13}C NMR (176 MHz, DMSO-d_3) for S6



***N*-(naphthalen-2-ylsulfonyl)acetamide (S7)**



To a flame dried 100 mL round bottom flask equipped with a magnetic stir bar was added naphthalene-1-sulfonamide (1 g, 4.83 mmol), DMAP (6 mg, 1 mol%), CH_2Cl_2 (35 mL), and THF (6 mL). The reaction mixture at this point appears mostly heterogeneous. Then the reaction was cooled to 0 °C and via syringe was added pyridine (777 uL, 9.65 mmol, 2 equiv) followed by acetic anhydride (1.82 mL, 19.3 mmol, 4 equiv). The whole slowly became more homogeneous over a few minutes. The reaction was slowly allowed to warm to rt while stirring overnight (12 h). Upon completion of the reaction as judged by TLC analysis (40% EtOAc in Hex), the reaction was diluted in 20 mL dH2O, layers separated and the aqueous layer was extracted with 20 mL CH_2Cl_2. The organic layers were combined and rinsed with 1 N HCl (2 x 20 mL), brine, dried over sodium sulfate, filtered and concentrated *in vacuo* to provide a white powder. The material may be further purified via flash column chromatography (0 to 40% EtOAc in Hex elution gradient) to provide the title substrate as a compact white solid (848 mg, 78%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.67 (bm, 2H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.99 (s, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 2.09 (s, 3H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.0, 135.5, 135.1, 131.9, 130.5, 129.6, 129.5, 129.4, 127.9, 127.8, 122.5, 23.5 ppm

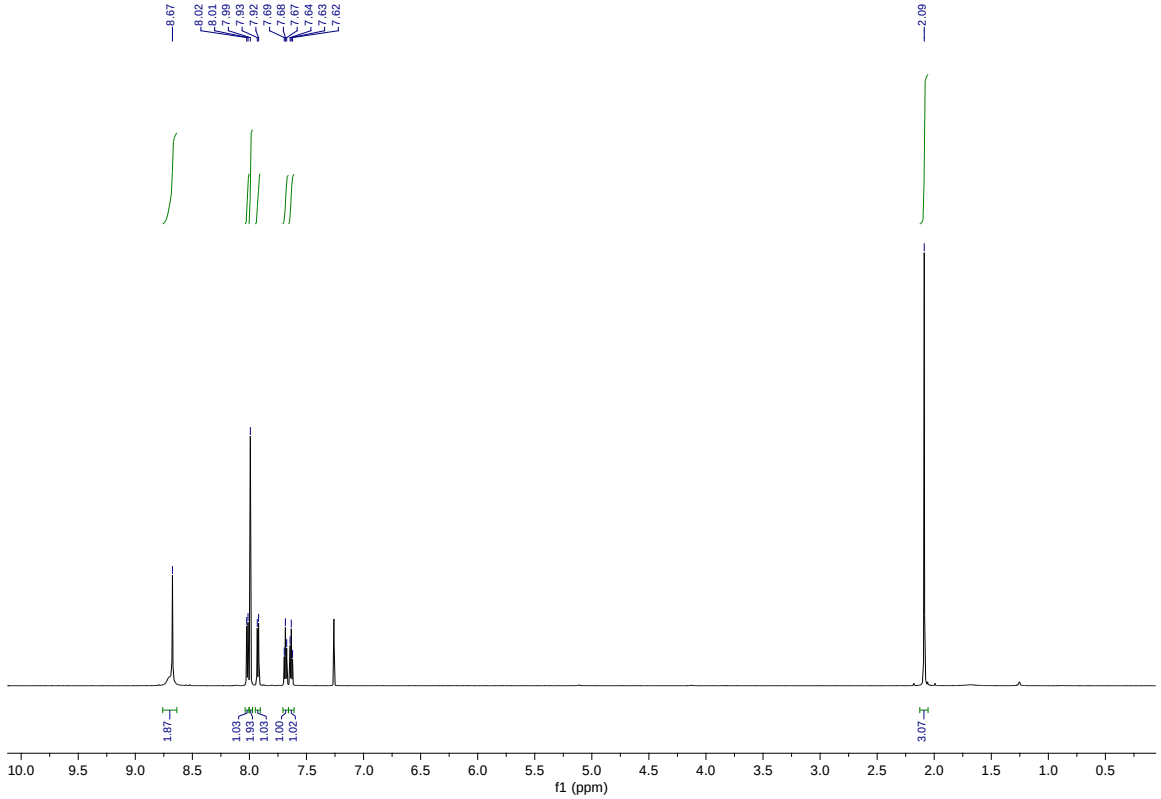
R_f (5:5 – EtOAc:Hex) = 0.3

IR (*neat*): 3274, 1719, 1436, 1412, 1328, 1150, 1126, 994, 877, 747 cm^{-1}

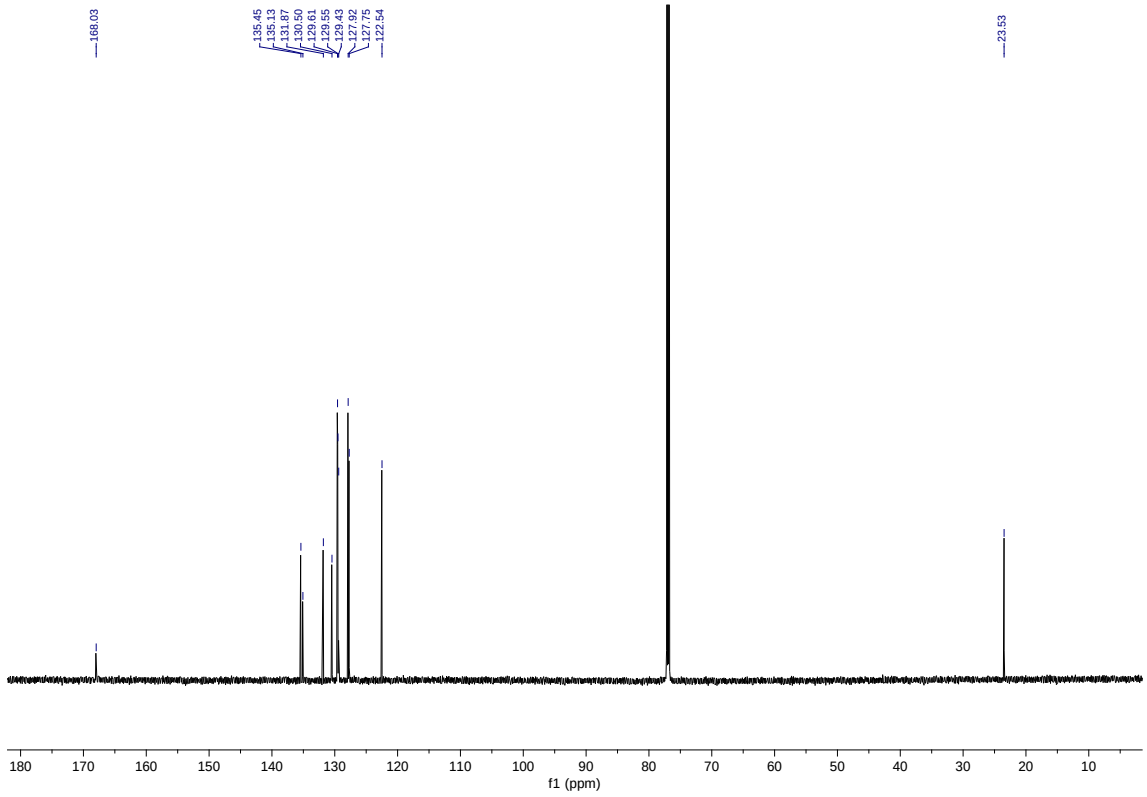
HRMS (ESI+) *m/z* calculated for $C_{12}H_{11}NO_3S$ $[M+H]^+$ 272.0352, found 272.0353.

MP: 137–139 °C

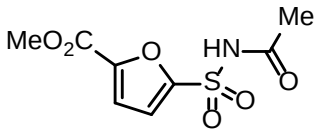
^{1}H NMR (700 MHz, $CDCl_3$) for S7



^{13}C NMR (176 MHz, $CDCl_3$) for S7



methyl 5-(*N*-acetylsulfamoyl)furan-2-carboxylate (S8)



To a flame dried 100 mL round bottom flask equipped with a magnetic stir bar was added methyl 5-sulfamoylfuran-2-carboxylate (184 mg, 0.897 mmol), DMAP (1.10 mg, 0.00897 mmol), CH_2Cl_2 (20.0 mL), and THF (5.00 mL). The reaction mixture at this point appears mostly heterogeneous. Then the reaction was cooled to 0 °C and via syringe was added pyridine (0.217 mL, 2.69 mmol) followed by acetic anhydride (0.339 mL, 3.59 mmol). The whole slowly became more homogeneous over a few minutes. The reaction was slowly allowed to warm to rt while stirring for 3 h. Upon completion of the reaction as judged by TLC analysis (50% EtOAc in Hex), the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with CH_2Cl_2 (15 mL) then washed 3 x with 1 N HCl (10 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 50% EtOAc in Hex elution gradient) provided the title substrate as a compact white solid (172 mg, 78%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.89 (s, 1H), 7.38 (d, *J* = 3.6 Hz, 1H), 7.24 (d, *J* = 3.6 Hz, 1H), 3.93 (s, 3H), 2.17 (s, 3H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.0, 158.0, 148.9, 147.3, 120.3, 118.0, 52.8, 23.6 ppm

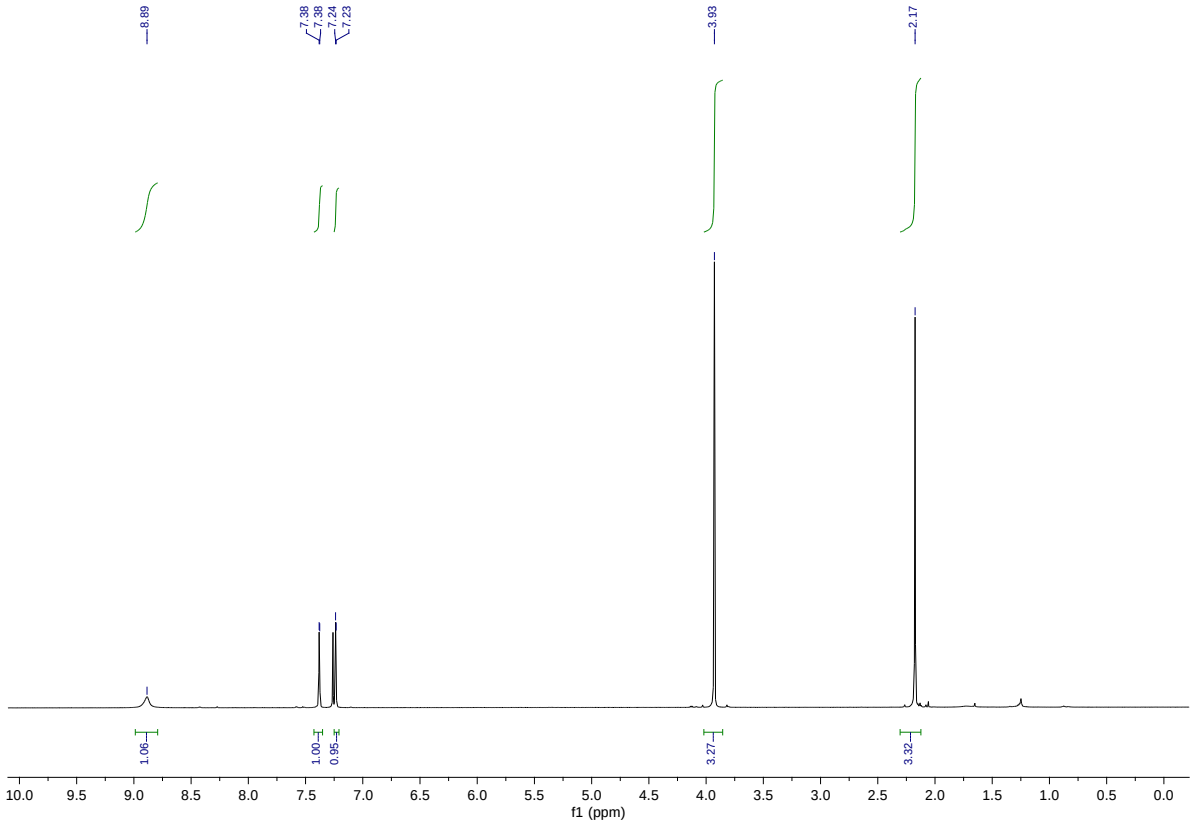
R_f (5:5 – EtOAc:Hex) = 0.2

IR (*neat*): 3303, 3159, 1732, 1574, 1431, 1355, 1040, 917 cm^{-1}

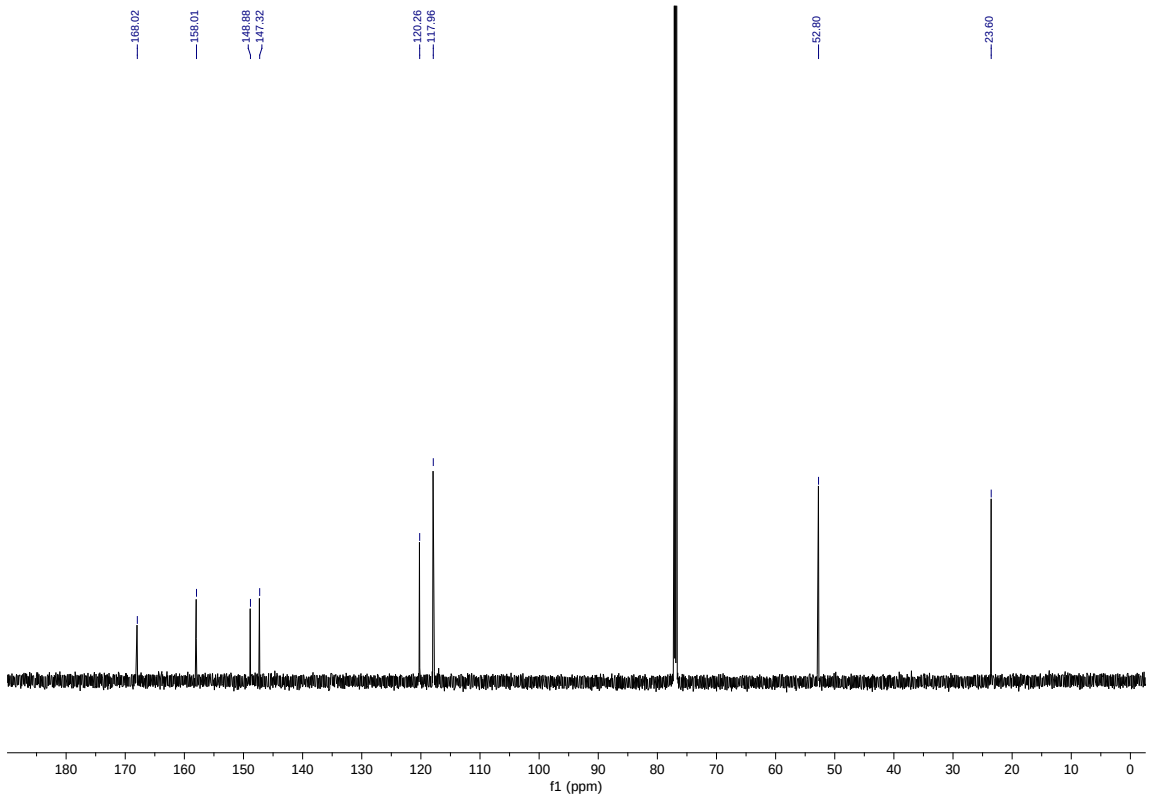
HRMS (ESI+) *m/z* calculated for $C_8H_9NO_6S$ $[M+H]^+$ 265.0489, found 265.0488.

MP: 133–137 °C

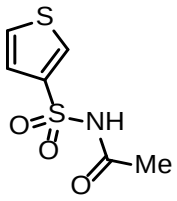
^{1}H NMR (700 MHz, $CDCl_3$) for S8



^{13}C NMR (176 MHz, $CDCl_3$) for S8



***N*-(thiophen-3-ylsulfonyl)acetamide (S9)**



To a flame dried 100 mL round bottom flask equipped with a magnetic stir bar was added thiophene-3-sulfonamide (1000 mg, 6.13 mmol), DMAP (7.48 mg, 0.0613 mmol), CH_2Cl_2 (35.0 mL), and THF (5.0 mL). The reaction mixture at this point appears mostly heterogeneous. Then the reaction was cooled to 0 °C and via syringe was added pyridine (1.48 mL, 18.4 mmol) followed by acetic anhydride (2.32 mL, 24.5 mmol). The whole slowly became more homogeneous over a few minutes. The reaction was slowly allowed to warm to rt while stirring for 12 h. Upon completion of the reaction as judged by TLC analysis (50% EtOAc in Hex), the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with CH_2Cl_2 (25 mL) then washed 3 x with 1 N HCl (20 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 50% EtOAc in Hex elution gradient) provided the title substrate as a compact white solid (1.12 g, 89%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.78 (s, 1H), 8.32 – 8.20 (m, 1H), 7.60 – 7.48 (m, 1H), 7.44 (dd, *J* = 5.1, 3.1 Hz, 1H), 2.11 (s, 3H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.3, 138.0, 133.7, 127.8, 126.1, 23.6 ppm

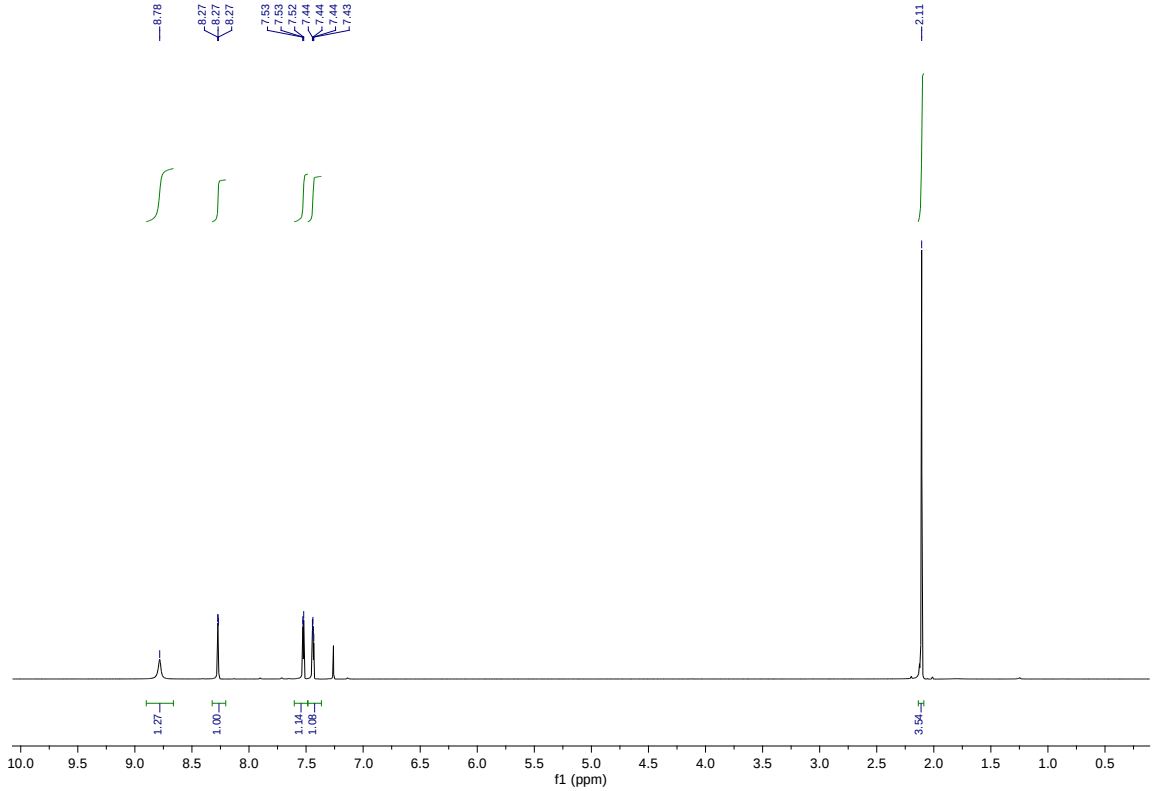
R_f (5:5 – EtOAc:Hex) = 0.3

IR (*neat*): 3070, 2867, 1691, 1460, 1417, 1346, 1235, 1157, 788 cm^{-1}

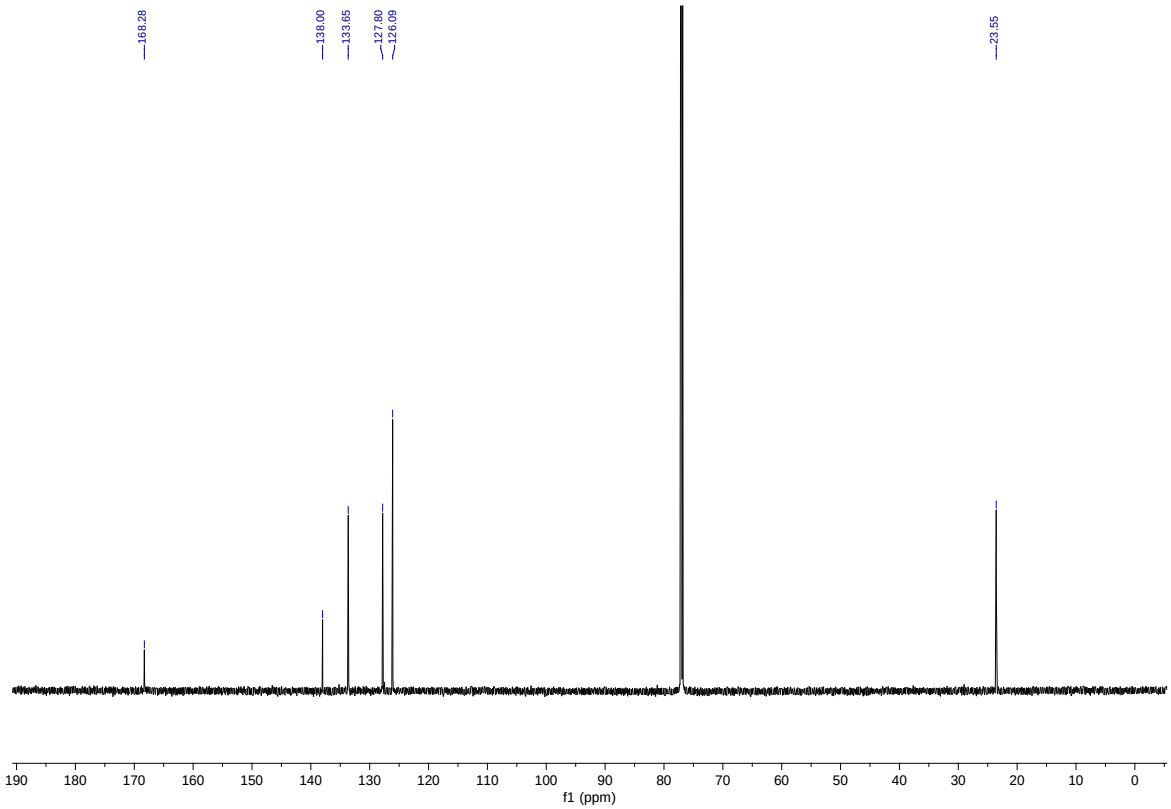
HRMS (ESI+) *m/z* calculated for $C_6H_7NO_3S_2Na$ $[M+Na]^+$ 227.9760, found 227.9757.

MP: 98–101 °C

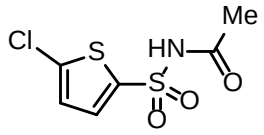
^{1}H NMR (700 MHz, $CDCl_3$) for S9



^{13}C NMR (176 MHz, $CDCl_3$) for S9



***N*-((5-chlorothiophen-2-yl)sulfonyl)acetamide (S10)**



To a flame dried 100 mL round bottom flask equipped with a magnetic stir bar was added 5-chlorothiophene-2-sulfonamide (500 mg, 2.53 mmol), DMAP (3.09 mg, 0.0253 mmol), CH_2Cl_2 (35.0 mL), and THF (5.00 mL). Then the reaction was cooled to 0 °C and via syringe was added pyridine (0.611 mL, 7.59 mmol) followed by acetic anhydride (0.956 mL, 10.1 mmol). The whole slowly became more homogeneous over a few minutes. The reaction was slowly allowed to warm to rt while stirring for 12 h. Upon completion of the reaction as judged by TLC analysis (50% EtOAc in Hex), the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with CH_2Cl_2 (25 mL) then washed 3x with 1 N HCl (20 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 50% EtOAc in Hex elution gradient) provided the title substrate as a compact white powder (486 mg, 77%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.69 (d, *J* = 4.1 Hz, 1H), 6.97 (d, *J* = 4.1 Hz, 1H), 2.14 (s, 3H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.1, 140.0, 136.0, 134.7, 126.8, 23.6 ppm

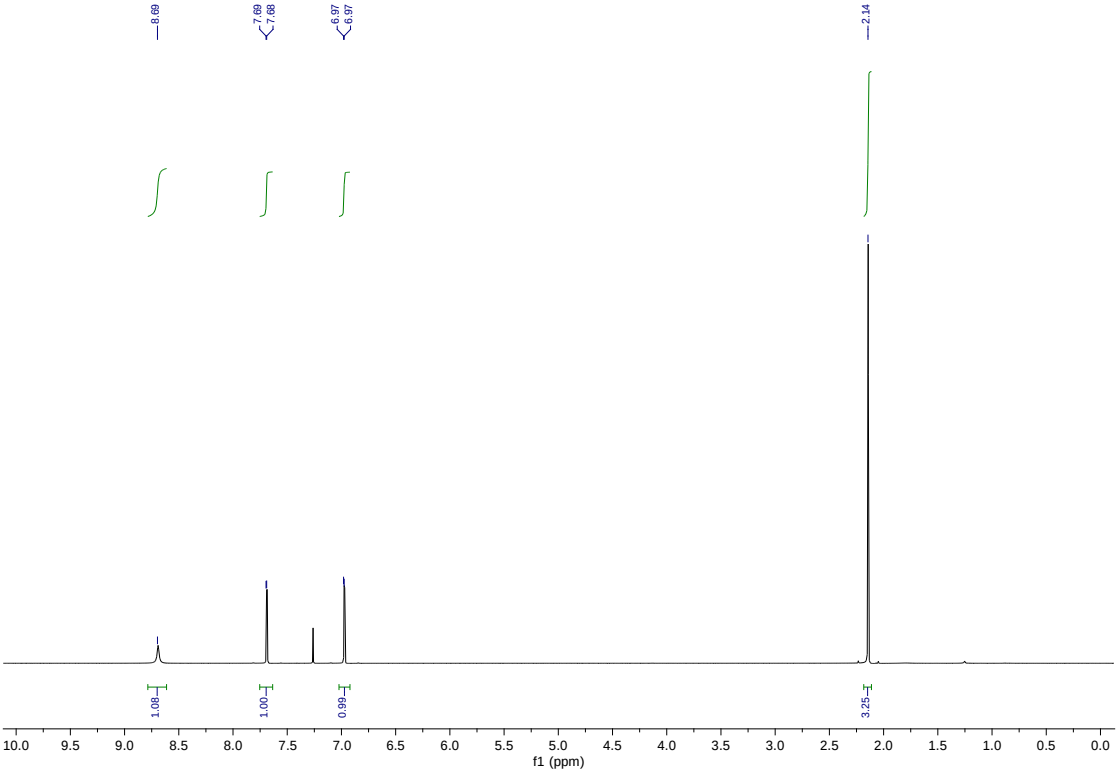
R_f (5:5 – EtOAc:Hex) = 0.4

IR (*neat*): 3076, 2874, 1689, 1463, 1409, 1357, 1235, 1162, 1004, 990 cm^{-1}

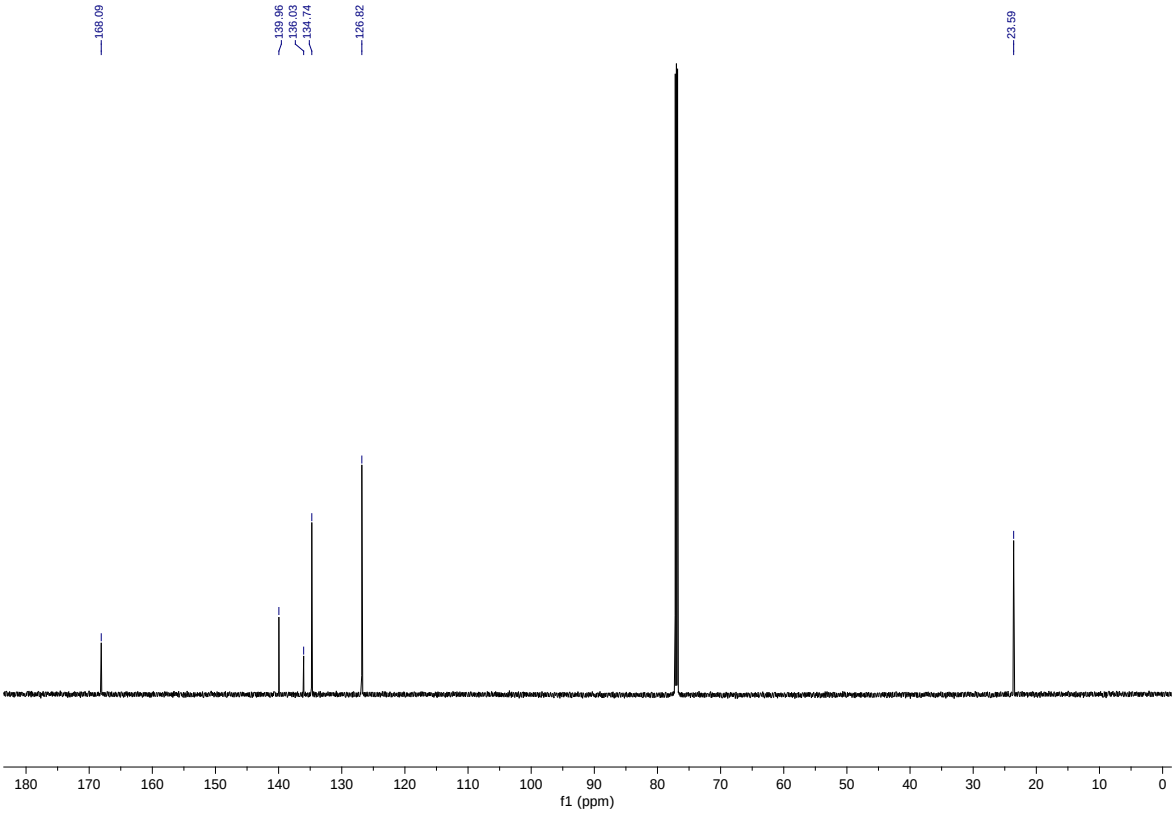
HRMS (ESI+) *m/z* calculated for $C_6H_6ClNO_3S_2$ $[M+H]^+$ 239.9550, found 239.9548.

MP: 106–109 °C

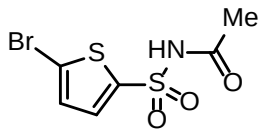
^{1}H NMR (700 MHz, $CDCl_3$) for S10



^{13}C NMR (176 MHz, $CDCl_3$) for S10



***N*-((5-bromothiophen-2-yl)sulfonyl)acetamide (S11)**



To a flame dried 100 mL round bottom flask equipped with a magnetic stir bar was added 5-bromothiophene-2-sulfonamide (1000 mg, 4.13 mmol), DMAP (5.05 mg, 0.0413 mmol), CH_2Cl_2 (35.0 mL), and THF (5.0 mL). Then the reaction was cooled to 0 °C and via syringe was added pyridine (1.0 mL, 12.4 mmol) followed by acetic anhydride (1.56 mL, 16.5 mmol). The whole slowly became more homogeneous over a few minutes. The reaction was slowly allowed to warm to rt while stirring for 12 h. Upon completion of the reaction as judged by TLC analysis (50% EtOAc in Hex), the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with CH_2Cl_2 (25 mL) then washed 3 x with 1 N HCl (20 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 50% EtOAc in Hex elution gradient) provided the title substrate as a compact white powder (1.07 g, 91%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 7.64 (d, *J* = 4.1 Hz, 1H), 7.11 (d, *J* = 4.1 Hz, 1H), 2.13 (s, 3H) ppm

^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.0, 138.9, 135.4, 130.4, 122.7, 23.6 ppm

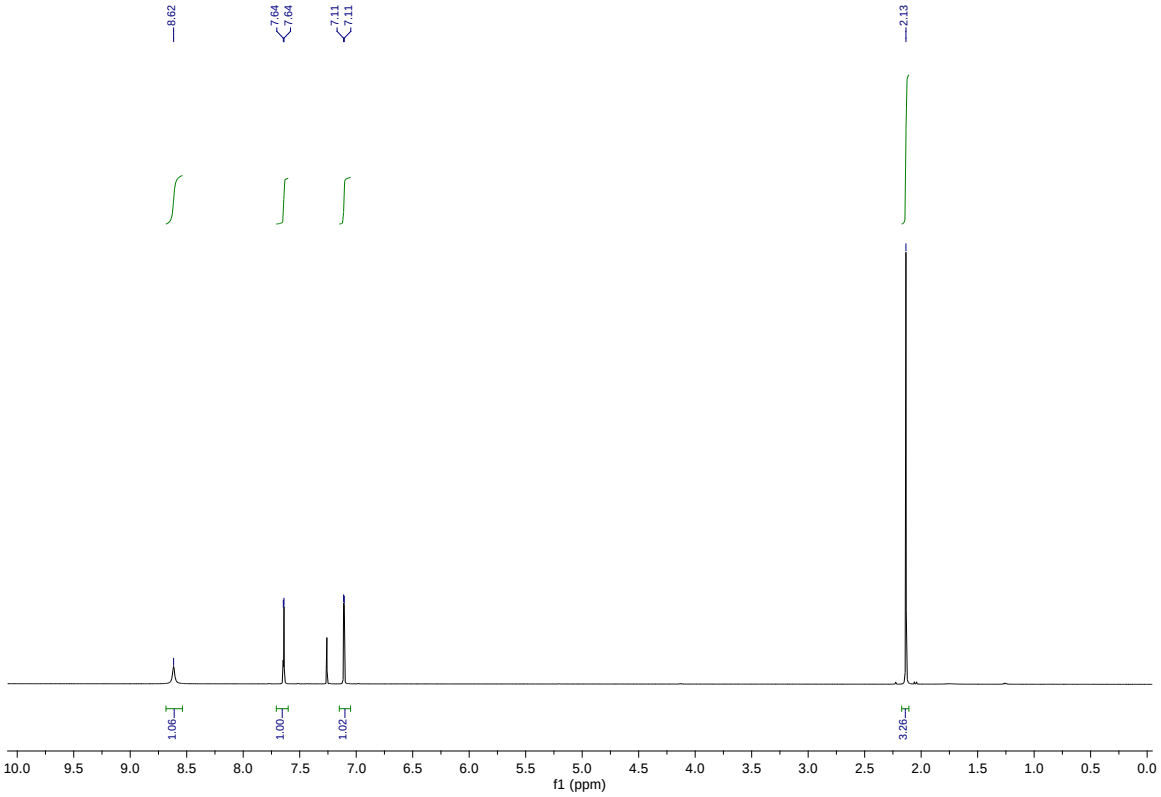
R_f (5:5 – EtOAc:Hex) = 0.3

IR (*neat*): 3301, 1713, 1412, 1395, 1209, 1155, 1025, 799, 678 cm^{-1}

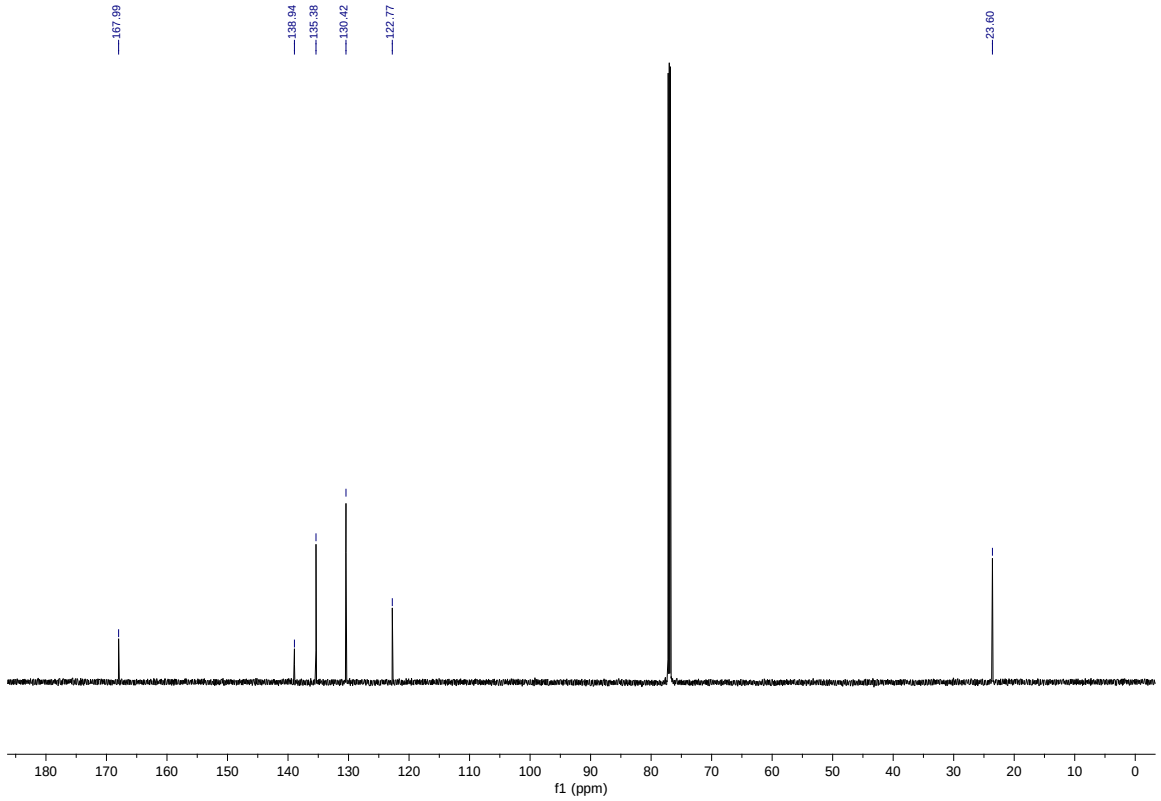
HRMS (ESI+) *m/z* calculated for $C_6H_6BrNO_3S_2$ $[M+Na]^+$ 305.8865, found 305.8869.

MP: 110–113 °C

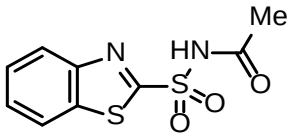
^{1}H NMR (700 MHz, $CDCl_3$) for S11



^{13}C NMR (176 MHz, $CDCl_3$) for S11



***N*-(benzo[d]thiazol-2-ylsulfonyl)acetamide (S12)**



To a flame dried 100 mL round bottom flask equipped with a magnetic stir bar was added 1,3-benzothiazole-2-sulfonamide (294 mg, 1.37 mmol), DMAP (1.68 mg, 0.0137 mmol), CH_2Cl_2 (35.0 mL), and THF (5.0 mL). Then the reaction was cooled to 0 °C and via syringe was added pyridine (0.322 mL, 4.12 mmol) followed by acetic anhydride (0.519 mL, 5.49 mmol). The whole slowly became more homogeneous over a few minutes. The reaction was slowly allowed to warm to rt while stirring for 12 h. Upon completion of the reaction as judged by TLC analysis (50% EtOAc in Hex), the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with CH_2Cl_2 (25 mL) then washed 3 x with 1 N HCl (20 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a white solid. Purification by flash column chromatography (10 to 50% EtOAc in Hex elution gradient) provided the title substrate as a compact white solid (443 mg, 99%).

^{1}H NMR (700 MHz, DMSO-d_6): δ = 13.06 (s, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 7.75 – 7.61 (m, 2H), 2.04 (s, 3H) ppm

^{13}C NMR (176 MHz, DMSO-d_6): δ = 169.7, 165.4, 151.4, 136.3, 128.1, 127.9, 124.7, 123.3, 23.4 ppm

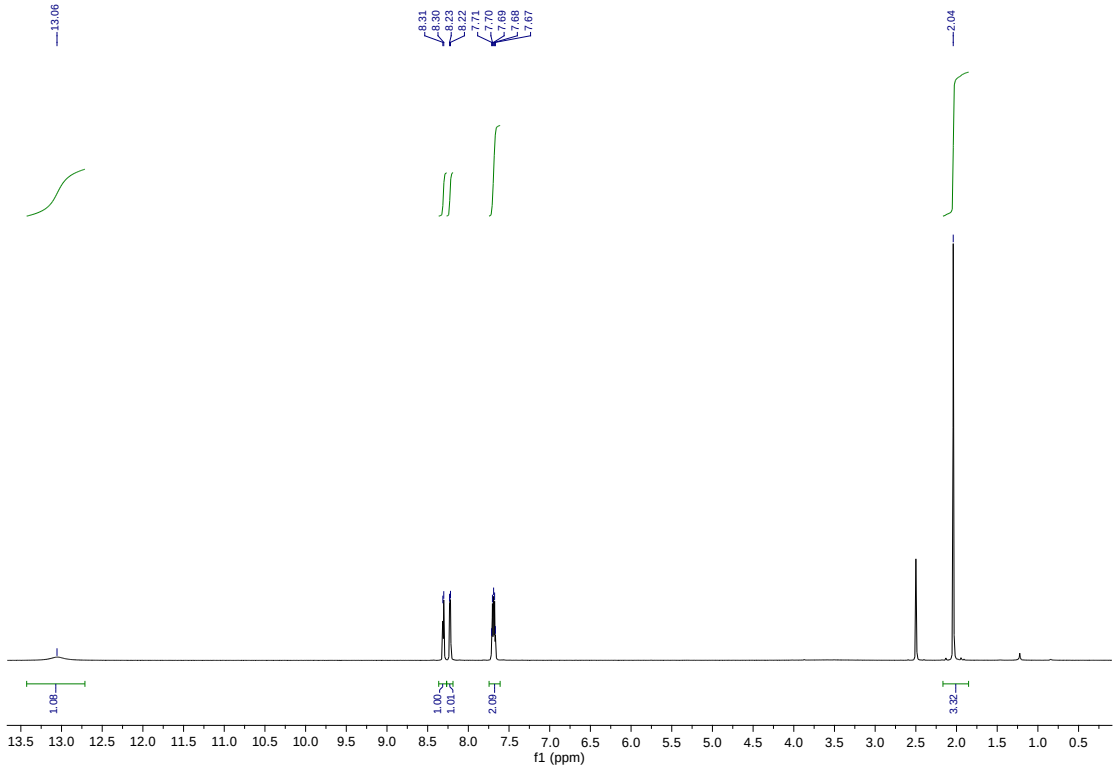
R_f (5:5 – EtOAc:Hex) = 0.1

IR (*neat*): 3022, 2855, 1726, 1484, 1358, 1162, 1132, 1094, 994 cm^{-1}

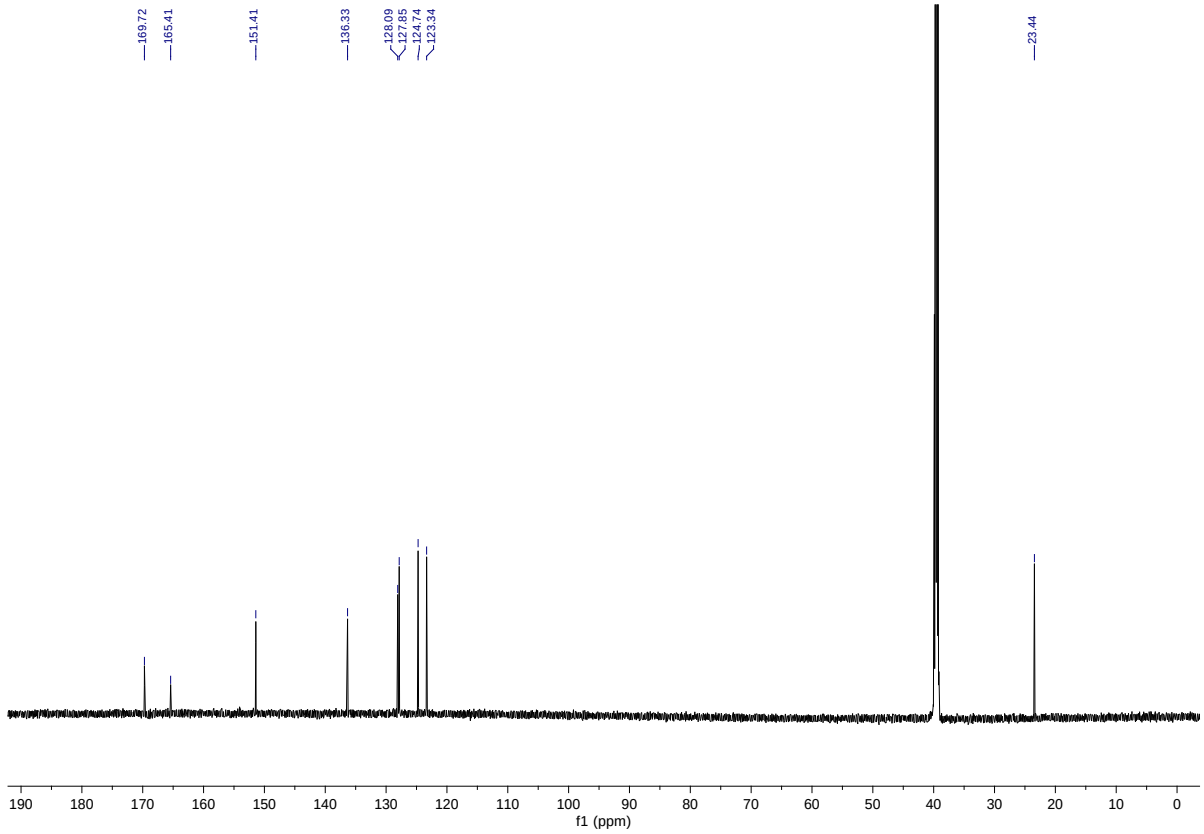
HRMS (ESI+) *m/z* calculated for $C_9H_8N_2O_3S_2$ $[M+H]^+$ 257.0049, found 257.0052.

MP: 194–197 °C

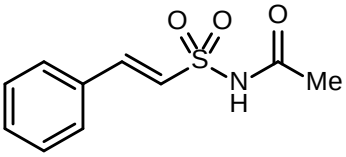
^{1}H NMR (700 MHz, DMSO-d$_6$) for S12



^{13}C NMR (176 MHz, DMSO-d$_6$) for S12



***(E)*-N-(styrylsulfonyl)acetamide (S13)**



A 25 mL flame dried round bottom flask charged with a magnetic stir bar was added KOH (91.9 mg, 1.64 mmol) and (*E*)-2-phenylethenesulfonamide (100 mg, 0.546 mmol). The flask was septa capped and put under nitrogen, before diluting in CH_2Cl_2 [0.2 M]. This reaction was then cooled to 0 °C followed by dropwise addition of AcCl (58.2 µL, 1.5 equiv) to the reaction. Over 2.5 hours, the reaction was allowed to warm to room temperature. The reaction was quenched by adding 4 M HCl at 0 °C to equal the mmol of KOH added. This was then diluted in water and extracted 3x with CH_2Cl_2. The CH_2Cl_2 layers were combined dried over sodium sulfate, filtered and concentrated to provide the crude residue which was purified by column chromatography (4:6 EtOAc to Hexanes) to afford the desired acetamide (52 mg, 42%).

^{1}H NMR (400 MHz, DMSO-d6) δ = 11.84 (s, 1H), 7.75 (d, *J* = 6.3 Hz, 2H), 7.60 – 7.35 (m, 5H), 1.97 (s, 3H) ppm

^{13}C NMR (126 MHz, DMSO-d6) δ = 169.1, 142.6, 132.3, 131.1, 129.1, 128.9, 125.9, 23.4 ppm

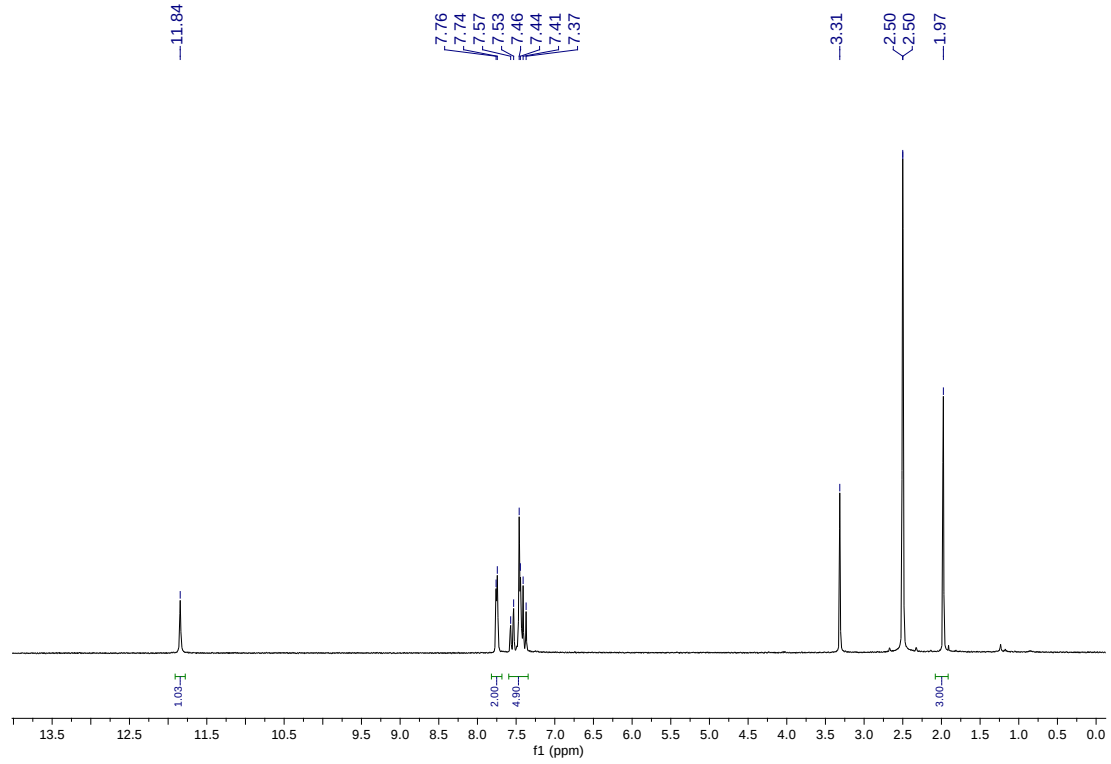
R_f (1:1 – EtOAc:Hex) = 0.4

IR (*neat*): 3243, 3049, 1714, 1615, 1417, 1369, 1326, 1213, 1199, 1142, 1039, 991, 968, 944, 869, 824, 805, 744, 687, 651, 631, 609 cm^{-1}

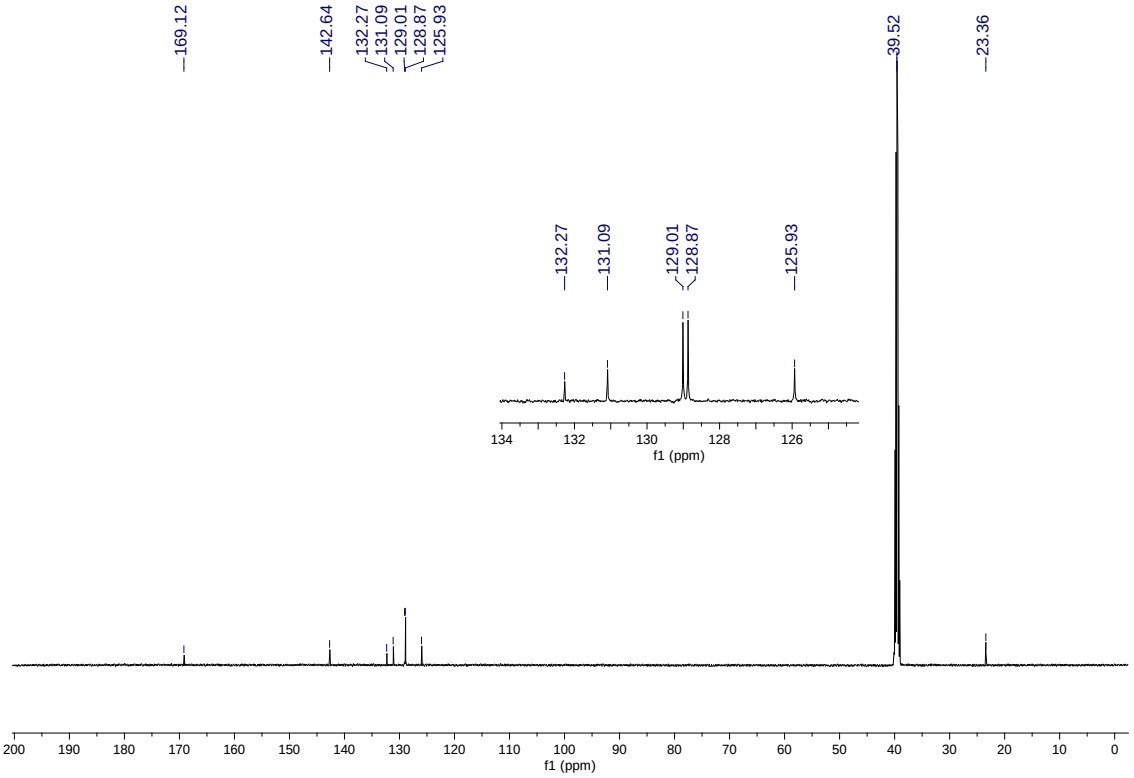
HRMS (ESI+) *m/z* calculated for $[M+H]^+$ 226.0532, found 226.0532.

MP: 108–111 °C

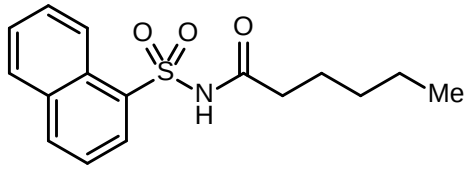
^{1}H NMR (400 MHz, DMSO--d6) for S13



^{13}C NMR (126 MHz, DMSO-d6) for S13



***N*-(naphthalen-1-ylsulfonyl)hexanamide (S14)**



To a dry round bottom flask hexanoic acid (420 mg, 3.62 mmol) was added and diluted into 6 mL of DCM and 100 µL of DMF. This solution was cooled to 0°C and oxyalyl chloride was added neat and dropwise over the course of 3 minutes. The reaction was stirred at 0°C for 30 minutes. Then the reaction was warmed to room temperature and concentrated *in vacuo* to a thick yellow oil. The reaction was then taken back up into a fresh supply of 6 mL of DCM, followed by naphthalene-1-sulfonamide (500 mg, 2.41 mmol) in one portion. Slow addition of pyridine (389 µL, 2 equiv) and DMAP (14.7 mg, 0.05 eq), occurred with considerable exotherm. The reaction was then stirred for 15 hours, and stopped by the addition of 10 mL of water. The whole was transferred to a separatory funnel and extracted three times with 15 mL of ethyl acetate. The combine organic layer was then washed with saturated sodium bicarbonate followed by saturated soidum chloride solutions. Drying over magnesium sulfate and concentration *in vacuo* afforded an orange oil that was purified on column (0-50% EtOAc in Hexanes) to afford N-(1-naphthylsulfonyl)hexanamide (382 mg, 1.25 mmol, yield: 52%)

^{1}H NMR (700 MHz, DMSO-d6) δ 12.40 (s, 1H), 8.61 (d, J = 8.6 Hz, 1H), 8.33 (d, J = 7.4 Hz, 2H), 8.16 (m, 1H), 7.79 (t, J = 7.0 Hz, 1H), 7.76 – 7.69 (m, 2H), 1.36 – 1.28 (m, 2H), 1.04 (m, 2H), 0.90 (m, 2H), 0.66 (dt, J = 7.2, 5.3 Hz, 3H) ppm

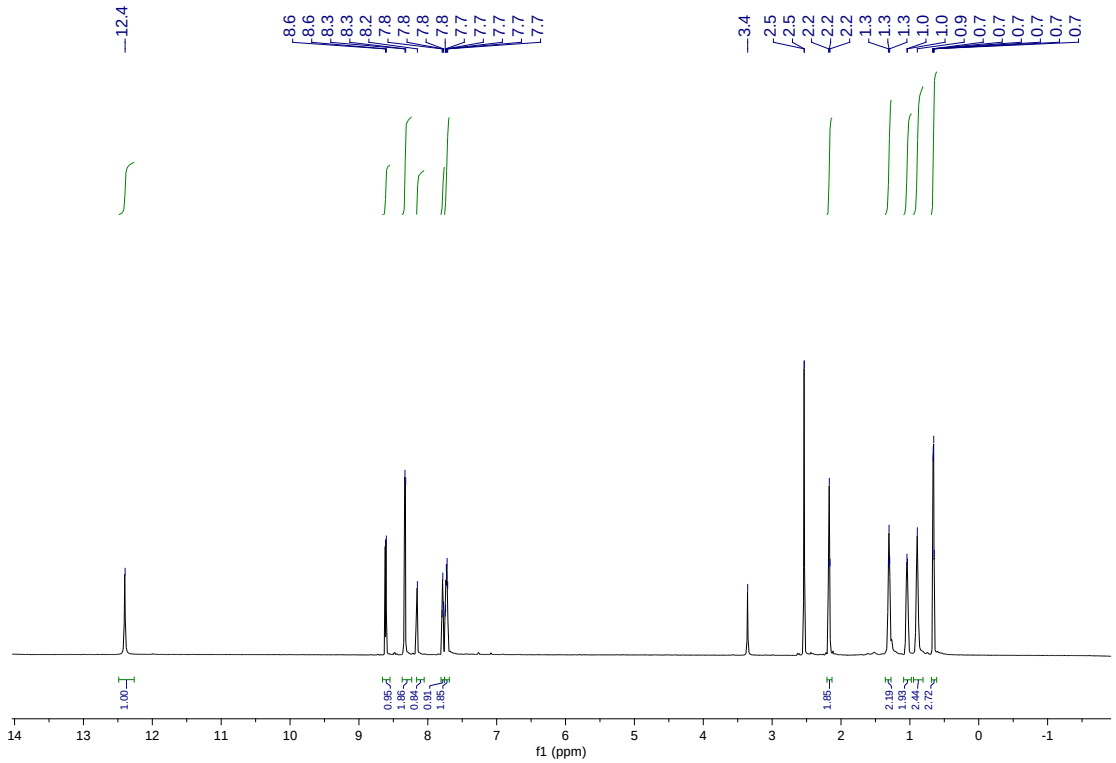
^{13}C NMR (176 MHz, DMSO-d6) δ = 172.4, 135.9, 134.8, 134.5, 132.1, 130.1, 129.2, 128.2, 127.8, 125.3, 124.5, 36.3, 31.1, 24.7, 22.5, 14.5 ppm

R_f = 0.5 in 1:1 Hexanes:EtOAc

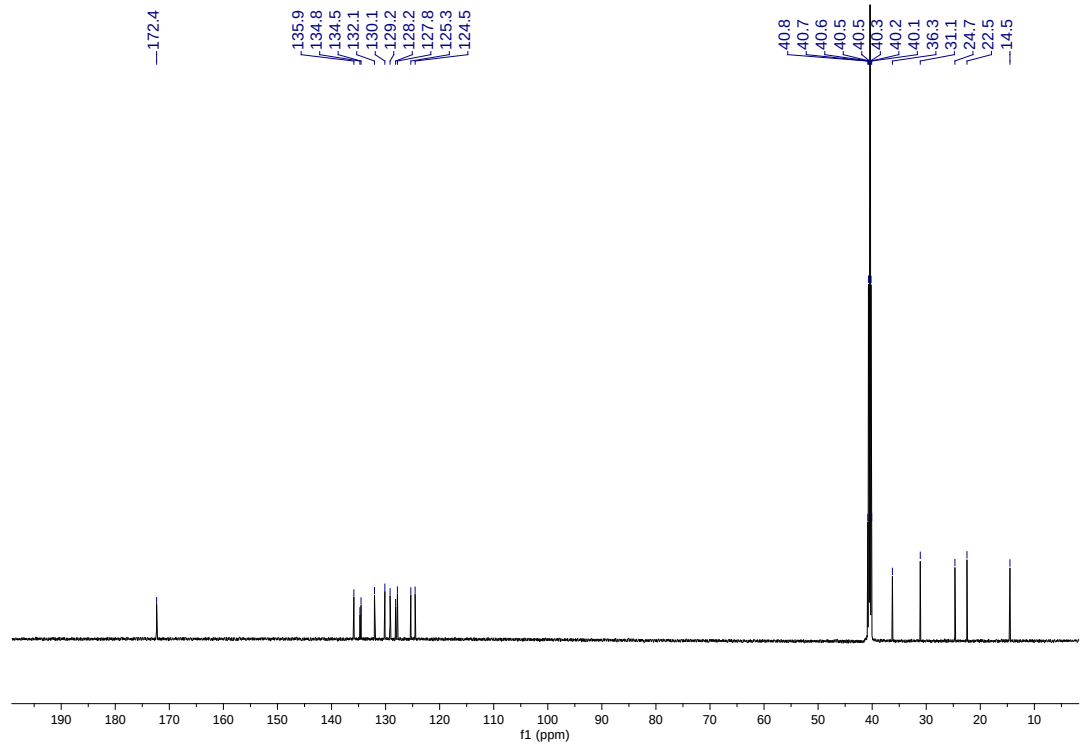
IR (neat)**:** 3301, 2958, 2926, 2869, 1713, 1506, 1472, 1442, 1411, 1364, 1324, 1271, 1221, 1204, 1177, 1160, 1144, 1131, 1085, 1057, 1035, 975, 945, 864, 807.3, 797.5, 776.3, 741, 678, 653, 636 cm^{-1}

HRMS (ESI+) *m/z* calculated for $[M+H]^+$ 306.1164, found 306.1158.

^{1}H NMR (700 MHz, DMSO-d6) for S14

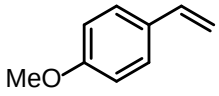


^{13}C NMR (175 MHz, DMSO-d6) for S14



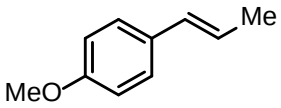
***p*-methoxybenzene alkenes:**

1-methoxy-4-vinylbenzene (1)



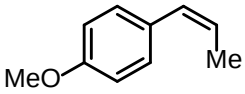
Vinyl-anisole was purchased from Sigma Aldrich (97%, item # 141003) and was distilled under hi-vac (~ 13 mbar), at 60 °C. It was then stored in the dark, under argon in a 4 dram vial for the remainder of the work.

(E)-1-methoxy-4-(prop-1-en-1-yl)benzene (S15)



trans-Anethole was purchased from AK Scientific (98%, item # X8716) and was used as received. The material was stored in the dark and under argon when not in use.

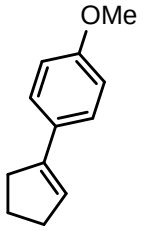
(Z)-1-methoxy-4-(prop-1-en-1-yl)benzene (28)



Z-anethole preparation was repeated based on the procedure detailed by Yoon and co-workers (*47*). (*Step 1)*:To a dry round bottom flask, 1-ethynyl-4-methoxy-benzene (1000 mg, 7.57 mmol) was added as a clear liquid and diluted into solution with 20 mL of THF. The solution was cooled to -78°C for 30 minutes and then the starting material was deprotonated with the dropwise addition of LiHMDS (8.323 µL, 1.1 equiv) over the course of 10 minutes. The solution was allowed to stir and deprotonate for 30 minutes. Following this time, MeI (565 µL, 1.2 equiv) was added dropwise, and the reaction was allowed to stir another 30 minutes before warming to room temperature. The reaction was quenchinged wit 4 mL of saturated aqueous ammonium chloride solution, and diluted in 30 mL of water. The whole was transferred to a separatory funnel where 20 mL of diethyl ether was added and the layers were separated. The aqueous layer was then extracted twice more with 30 mL of diethylether each time. The combined organic layer was then washed with saturated sodium chloride solution and dried over magnesium sulfate. Concentration *in vacuo* produced an orange oil that was then purified by a short column (0-5% EtOAc in Hexanes) to afford 1-methoxy-4-prop-1-ynyl-benzene which was taken directly onto the next step.

(*Step 2)*: To a flame dried flask, a solution of cyclohexene (15.2 mmol, 2.11 equiv, 1601 µL) was diluted in 8 mL of THF. The solution was cooled to 0°C and then a 2.0 M solution of BH_3•DMS complex in toluene was added (749µLm 1.1 equiv). After 10 minutes the reaction becomes heterogeneous, and this was allowed to stir for another twenty minutes. After this time, 1-methoxy-4-prop-1-ynyl-benzene was added as a 1 M solution in THF, to the reaction at 0°C. This was allowed to stir for 45 minutes, followed by quenching with 1 mL of glacial acetic acid. The acid quench was allowed to stir for 45 minutes and warm up to room temperature. The reaction solution was transferred to a separatory funnel and diluted in 30 mL of water. The layers were separated and the aqueous layer was extracted twice more with 30 mL of diethyl ether each time. The combined organic layer was washed with saturated sodium bicarbonate followed by saturated aqueous sodium chloride solution. Drying over magnesium sulfate followed by concentration *in vacuo* afforded an oil that was purified by silica chromatography (0-5% EtOAc in Hexanes). The spectral data of 1-methoxy-4-[(Z)-prop-1-enyl]benzene (512 mg, 49% yield) was consistent with the literature (*48*).

1-(cyclopent-1-en-1-yl)-4-methoxybenzene (S16)



The following procedure was followed according to that reported in the literature for the preparation of the title substrate.

$CeCl_3 \cdot 7H_2O$ (2218 mg, 9.00 mmol) was quickly ground to a fine powder in a mortar, placed in a three-neck 250 mL round bottom flask and dried at 140 °C for 2 h. At rt, nitrogen gas was introduced, and anhydrous THF (25 mL) was added with vigorous stirring. The suspension was stirred for 1.5 h at rt. To a cold (-78 °C) and stirred solution of 4-bromoanisole (0.828 mL, 6.60 mmol) in anhydrous THF (25 mL) was added 1.6 M nBuLi in hexanes (4.50 mL, 7.20 mmol). This solution was stirred at -78 °C for 1.5 h then added to the cold (-78 °C) suspension of $CeCl_3$ in THF. The resulting solution was stirred at -78 °C for 1 h. Cyclopentanone (0.531 mL) 6.00 mmol) dissolved in anhydrous THF (5 mL) was added to the corresponding organocerium reagent. The resulting mixture was stirred at -78 °C for 1h then at rt for 1 h. At -30 °C, after dilution with anhydrous THF (20 mL), DBU (2.32 mL, 10.5 mmol, 3 equiv) then MsCl (1.39 mL, 10.5 mmol, 3 equiv) were added dropwise. The reaction mixture was then allowed to warm to rt and stirred overnight. At 0 °C, aqueous HCl 1 M (15 mL) was added and the solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 30 mL). The resulting organic layers were washed with aqueous NaOH 2 M (10 mL), water (10 mL), brine (10 mL), dried over sodium sulfate and the solvent evaporated to provide a light yellow oil. The residue was purified by flash column chromatography on silica gel using

a 0 to 1% EtOAc in Hex elution gradient to provide the desired olefin as a white fluffy powder (616 mg, 59%).

All analytical data matches that reported in the literature (*49*).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.08 – 5.99 (m, 1H), 3.81 (s, 3H), 2.68 (td, *J* = 7.8, 2.1 Hz, 2H), 2.52 (td, *J* = 7.7, 2.3 Hz, 2H), 2.08 – 1.95 (m, 2H) ppm

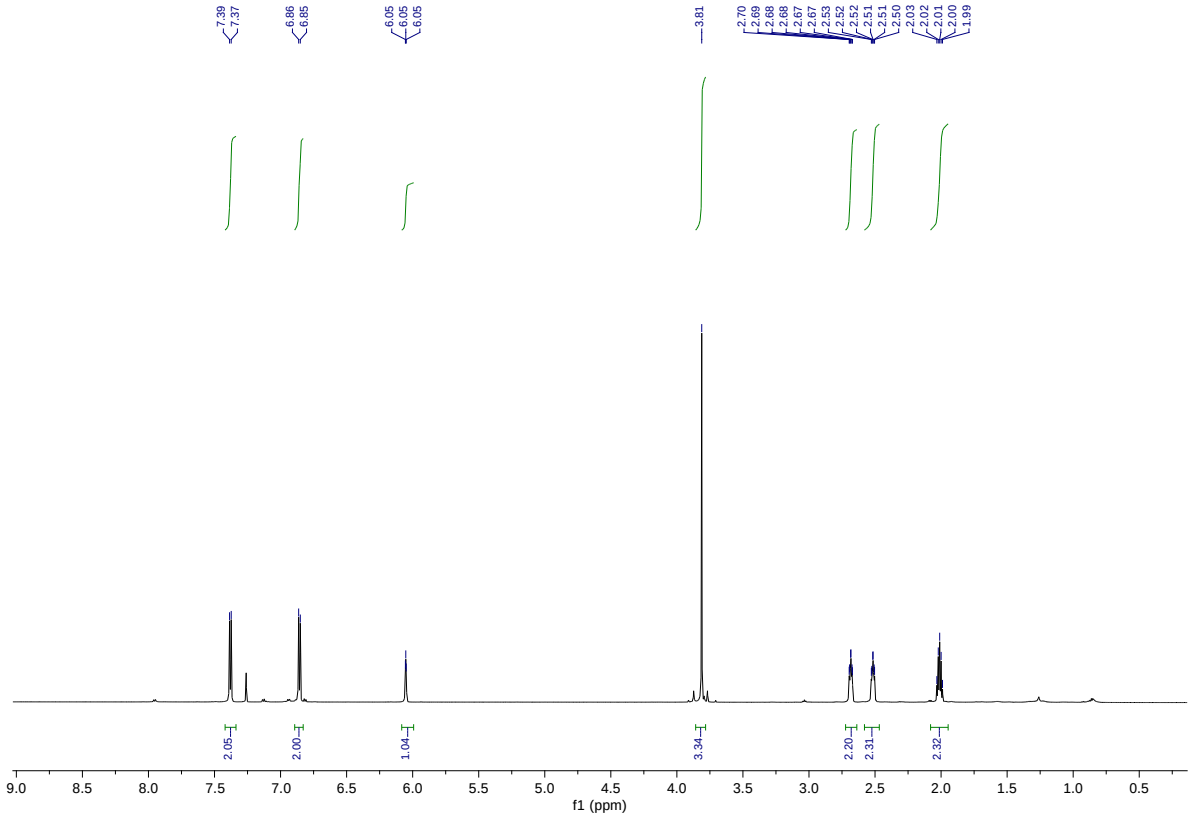
^{13}C NMR (176 MHz, $CDCl_3$): δ = 158.5, 141.8, 129.7, 126.7, 123.9, 113.6, 55.3, 33.3, 33.2, 23.4 ppm

R_f (1:9 – EtOAc:Hex) = 0.6

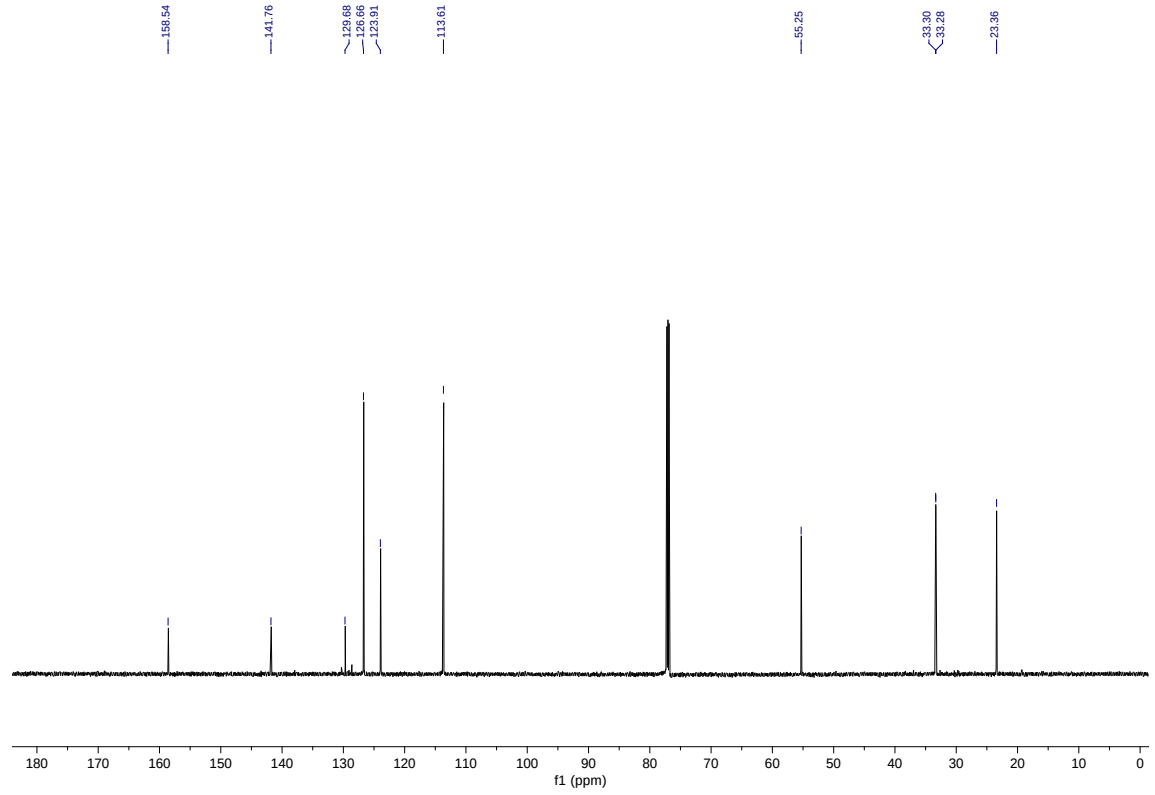
IR (*neat*): 2951, 2894, 2841, 1601, 1510, 1309, 1252, 1180, 1030 cm^{-1}

HRMS (EI) *m/z* calculated for $C_{12}H_{14}O$ [M+] 174.1045, found 174.1042.

^{1}H NMR (700 MHz, $CDCl_3$) for S16

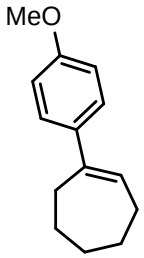


^{13}C NMR (176 MHz, $CDCl_3$) for S16



1-(4-methoxyphenyl)cyclohept-1-ene (S17)

The following procedure was followed according to that reported in the literature for the preparation of the title substrate.



$CeCl_3 \cdot 7H_2O$ (2218 mg, 9.00 mmol) was quickly ground to a fine powder in a mortar, placed in a three-neck 250 mL round bottom flask and dried at 140 °C for 2 h. At rt, nitrogen gas was introduced, and anhydrous THF (25 mL) was added with vigorous stirring. The suspension was stirred for 1.5 h at rt. To a cold (-78 °C) and stirred solution of 4-bromoanisole (0.828 mL, 6.60 mmol) in anhydrous THF (25 mL) was added 1.6 M nBuLi in hexanes (4.50 mL, 7.20 mmol). This solution was stirred at -78 °C for 1.5 h then added to the cold (-78 °C) suspension of $CeCl_3$ in THF. The resulting solution was stirred at -78 °C for 1 h. Cycloheptanone (0.709 mL, 6.00 mmol) dissolved in anhydrous THF (5 mL) was added to the corresponding organocerium reagent. The resulting mixture was stirred at -78 °C for 1 h then at rt for 1 h. At -30 °C, after dilution with anhydrous THF (20 mL), DBU (2.32 mL, 10.5 mmol, 3 equiv) then MsCl (1.39 mL, 10.5 mmol, 3 equiv) were added dropwise. The reaction mixture was then allowed to warm to rt and stirred overnight. At 0 °C, aqueous HCl 1 M (15 mL) was added and the solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 30 mL). The resulting organic layers were washed with aqueous NaOH 2 M (10 mL), water (10 mL), brine (10 mL), dried over sodium sulfate and the solvent evaporated to provide a light yellow oil. The residue was purified by flash column chromatography on silica gel using a 0 to 1% EtOAc in Hex elution gradient to provide the desired olefin as a colorless oil (655 mg, 54%).

All analytical data matches that reported in the literature (*48*).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.03 (t, *J* = 6.7 Hz, 1H), 3.81 (s, 3H), 2.64 – 2.54 (m, 2H), 2.28 (dd, *J* = 11.0, 6.5 Hz, 2H), 1.84 (dt, *J* = 11.8, 6.0 Hz, 2H), 1.64 (dt, *J* = 11.3, 5.8 Hz, 2H), 1.56 (dt, *J* = 11.3, 5.9 Hz, 2H) ppm

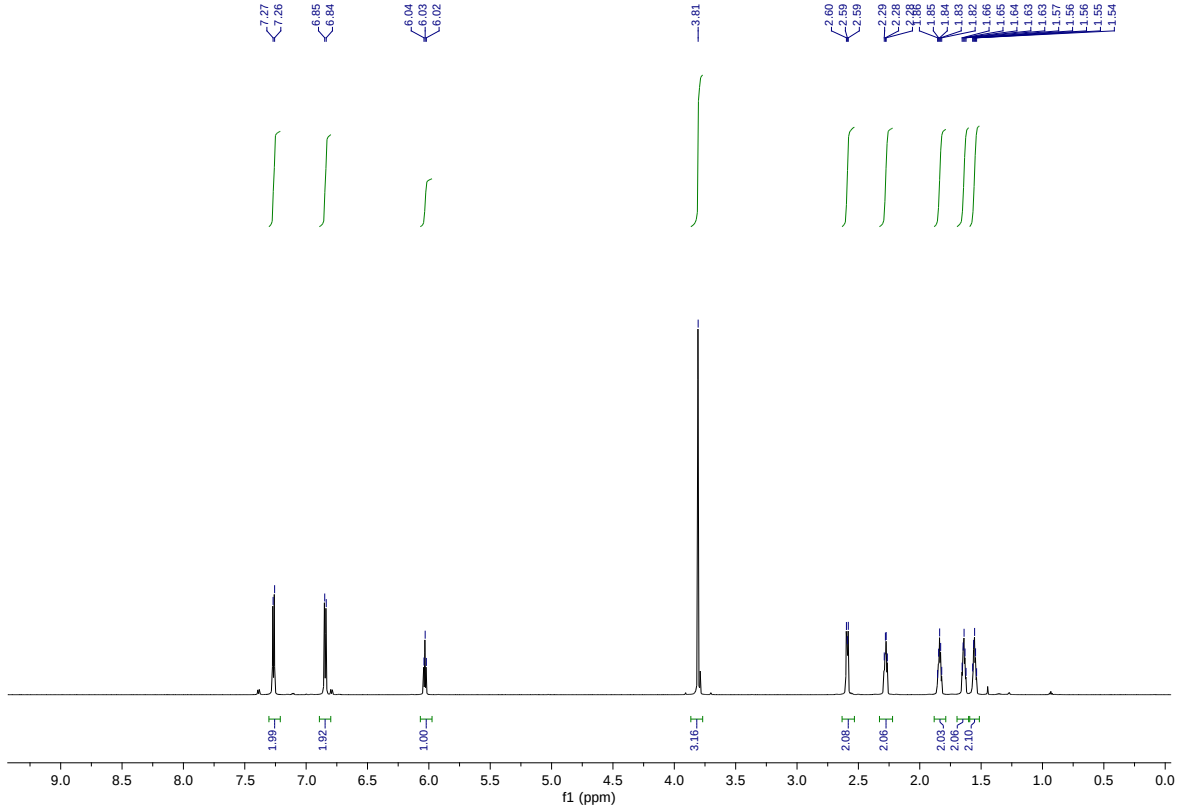
^{13}C NMR (176 MHz, $CDCl_3$): δ = 158.2, 144.3, 137.5, 128.8, 126.7, 113.4, 55.3, 32.8, 32.7, 28.8, 26.9, 26.8 ppm

R_f (1:9 – EtOAc:Hex) = 0.8

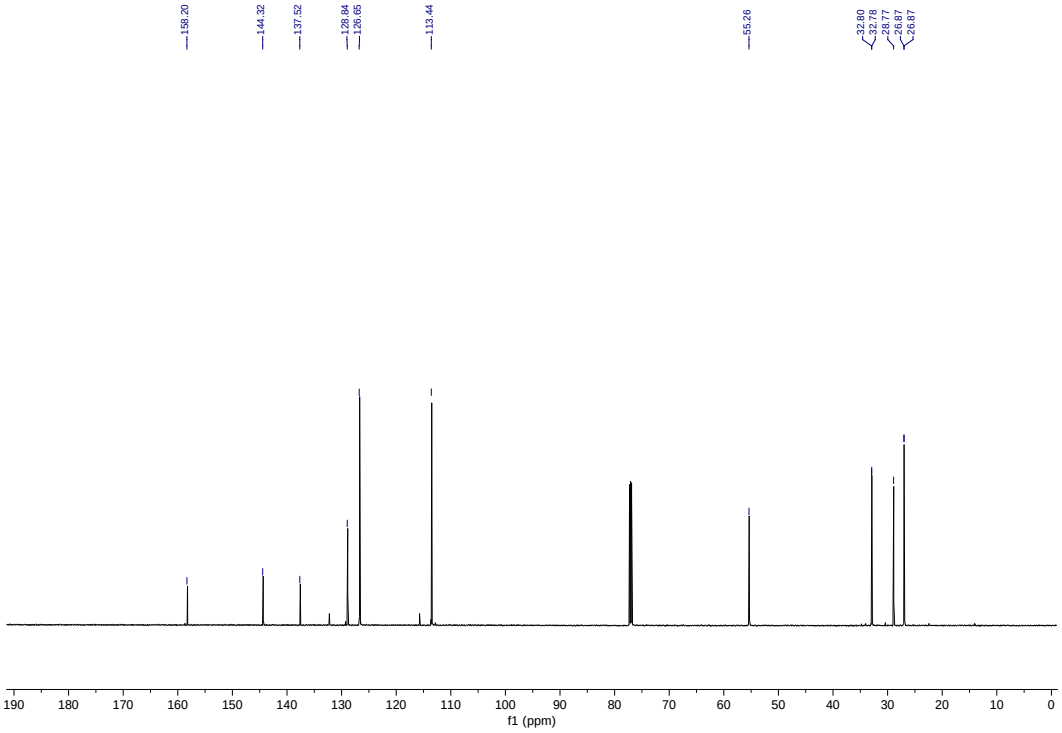
IR (*neat*): 2916, 2834, 1606, 1509, 1489, 1286, 1242, 1177, 1032 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{14}H_{18}O$ [M+H]+ 203.1430, found 203.1424.

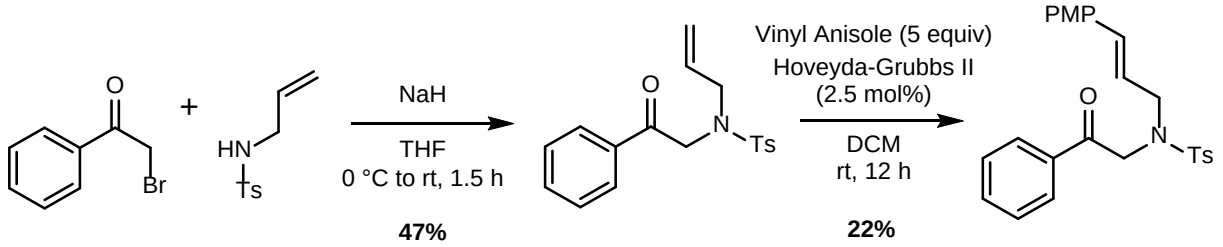
^{1}H NMR (700 MHz, $CDCl_3$) for S17



^{13}C NMR (176 MHz, $CDCl_3$) for S17



***N*-[(E)-3-(4-methoxyphenyl)allyl]-4-methyl-N-phenacyl-benzenesulfonamide (S18)**



To a flame dried 50 mL round bottom flask charged with a magentic stir bar was added *N*-allyl-4-methyl-benzenesulfonamide (637 mg, 3.01 mmol, 1.2 equiv) 5 mL of DMF. To this, NaH (60%, 86.6 mg, 2.26 mmol, 0.9 equiv) was added portion-wise to the flask and the sulfonamide was allowed to react at 0 °C for 30 minutes. After this time, 2-bromo-1-phenyl-ethanone (500 mg, 2.51 mmol, 1 equiv), was diluted separately in 6 mL of DMF and transferred to the reaction via syringe at 0 °C. The reaction was slowly allowed to warm to room temperature over 1 h, and then quenched with 7 mL of aqueous 5% citric acid and 7 mL of 10% sodium thiosulfate at 0 °C. The mixture was then transferred to a separatory funnel and extracted 3 times with 50 mL of diethyl ether. The combined ether extracts were washed with saturated sodium bicarbonate solution, followed by 5% LiCl wash (equal volume). The combined organic fractions were dried over sodium sulfate and then concentrated *in vacuo* to provide a crude dark oil which was purified by silica gel chromatography (30% EtOAc in Hexanes). *N*-allyl-4-methyl-*N*-phenacyl-benzenesulfonamide isolated in 47% yield (396 mg), and corresponded to literature characterization (*50*).

To a flame dried 25 mL round bottom flask charged with a magnetic stir bar was added *N*-allyl-4-methyl-*N*-phenacyl-benzenesulfonamide (100 mg, 0.304 mmol), 6 mL of dry CH_2Cl_2, followed by 1-methoxy-4-vinyl-benzene (202 µL, 1.52 mmol, 5 equiv). The reaction was sparged by an argon line for 5 minutes. Then Hoveyda-Grubbs II (CAS No. 301224-40-8) (4.76 mg, 0.00759 mmol, 2.5 mol %) was added, the flask was flushed with argon and then the reaction was capped and allowed to stir for 12 hours. Following this time, the crude mixture was pushed through a celite plug and concentrated to provide the crude residue. The material was purified by silica gel chromatography (3:7 ethyl acetate/Hexanes), and the stilbene impurity was triturated out with cold ether, after concentrating to yield 29 mg of the title substrate (22% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.1 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 6.33 (d, J = 15.8 Hz, 1H), 6.33 (d, J = 15.8 Hz, 1H), 5.88 (dt, J = 14.6, 7.0 Hz, 1H), 5.88 (dt, J = 14.6, 7.0 Hz, 1H), 4.76 (s, 2H), 4.05 (d, J = 7.0 Hz, 2H), 3.80 (s, 3H), 2.45 (s, 3H) ppm

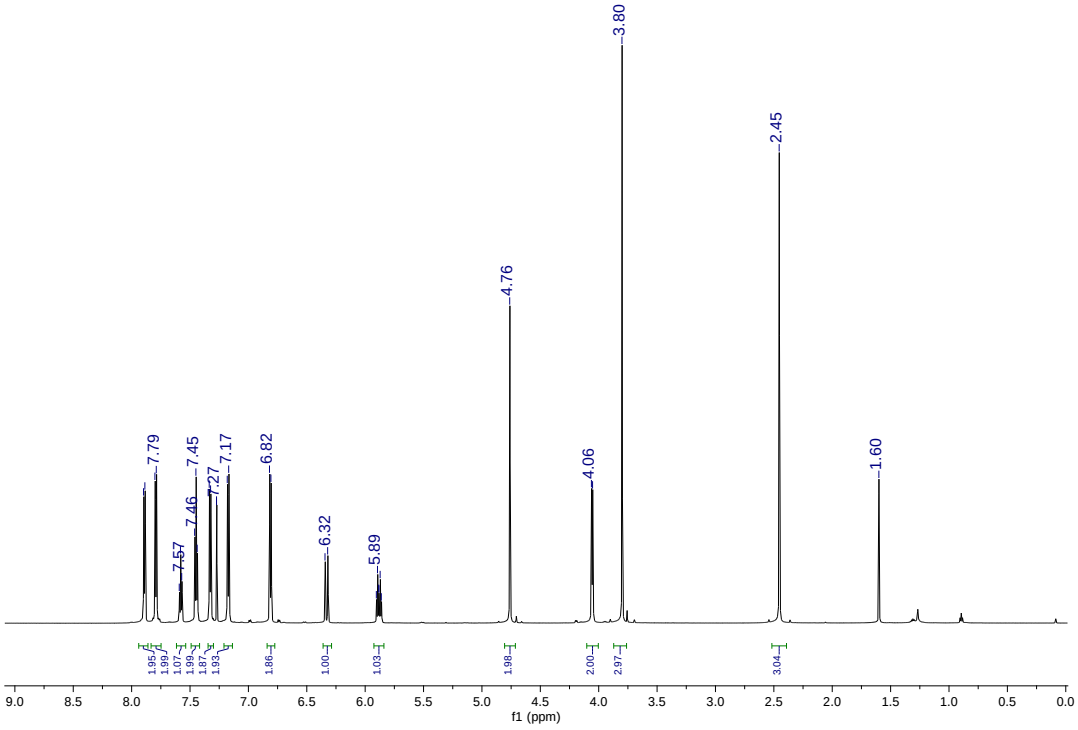
^{13}C NMR (176 MHz, $CDCl_3$) δ = 194.2, 159.5, 143.4, 136.9, 134.9, 134.4, 133.7, 129.6, 128.7, 128.7, 128.0, 127.7, 127.5, 121.0, 113.9, 55.3, 51.9, 50.5, 21.6 ppm

R_f (3:7 – EtOAc:Hex) = 0.3

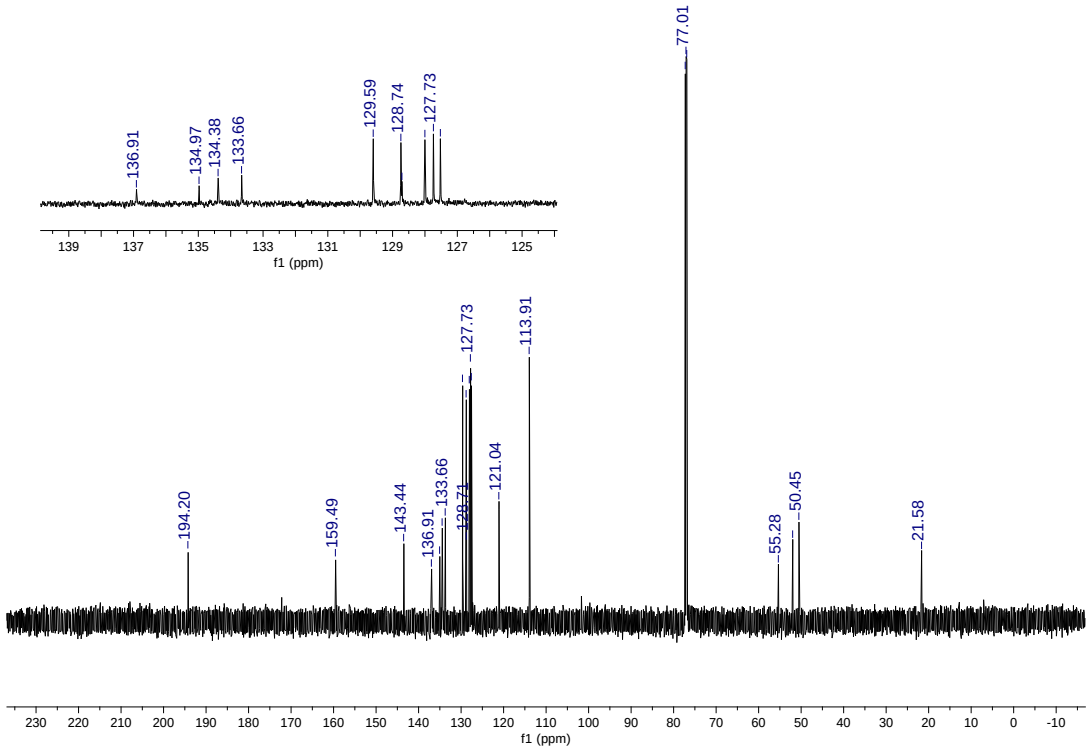
IR (*neat*): 2932, 2836, 2254, 1699, 1606, 1579, 1510, 1448, 1420, 1334, 1304, 1249, 1224, 1174, 1154, 1092, 1059, 1032, 1001, 971, 906, 856, 839, 812, 729, 689, 668, 607 cm^{-1}

HRMS (ESI+): predicted $[M+Na]^+$ 458.1397, observed 458.1389.

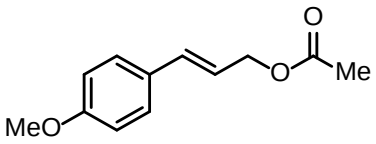
^1H NMR (700 MHz, $CDCl_3$) for S18



^{13}C NMR (700 MHz, $CDCl_3$) for S18



***(E)*-3-(4-methoxyphenyl)allyl acetate (S19)**



To a solution of (E)-3-(4-methoxyphenyl)prop-2-en-1-ol (200 mg, 1.22 mmol) in CH_2Cl_2 (15 mL) and THF (5 mL) was added DMAP (14.9 mg, 0.122 mmol). Then the reaction was cooled to 0 °C and via syringe was added pyridine (0.294 mL, 3.65 mmol) followed by acetic anhydride (0.345 mL, 3.65 mmol). The reaction was slowly allowed to warm to rt while stirring for 12 h. Upon completion of the reaction as judged by TLC analysis (10% EtOAc in Hex), the reaction was concentrated under reduced pressure to give a light yellow oil. This crude mixture was diluted with EtOAc (25 mL) then washed 3 x with 1 N HCl (20 mL). The organic layer was washed with brine, dried over sodium sulfate, and filtered to give a crude, colorless oil. Purification by flash column chromatography (0 to 5% EtOAc in Hex elution gradient) provided the title substrate as a clear, colorless oil (219 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.15 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.70 (d, *J* = 6.6 Hz, 2H), 3.81 (s, 3H), 2.09 (s, 3H) ppm

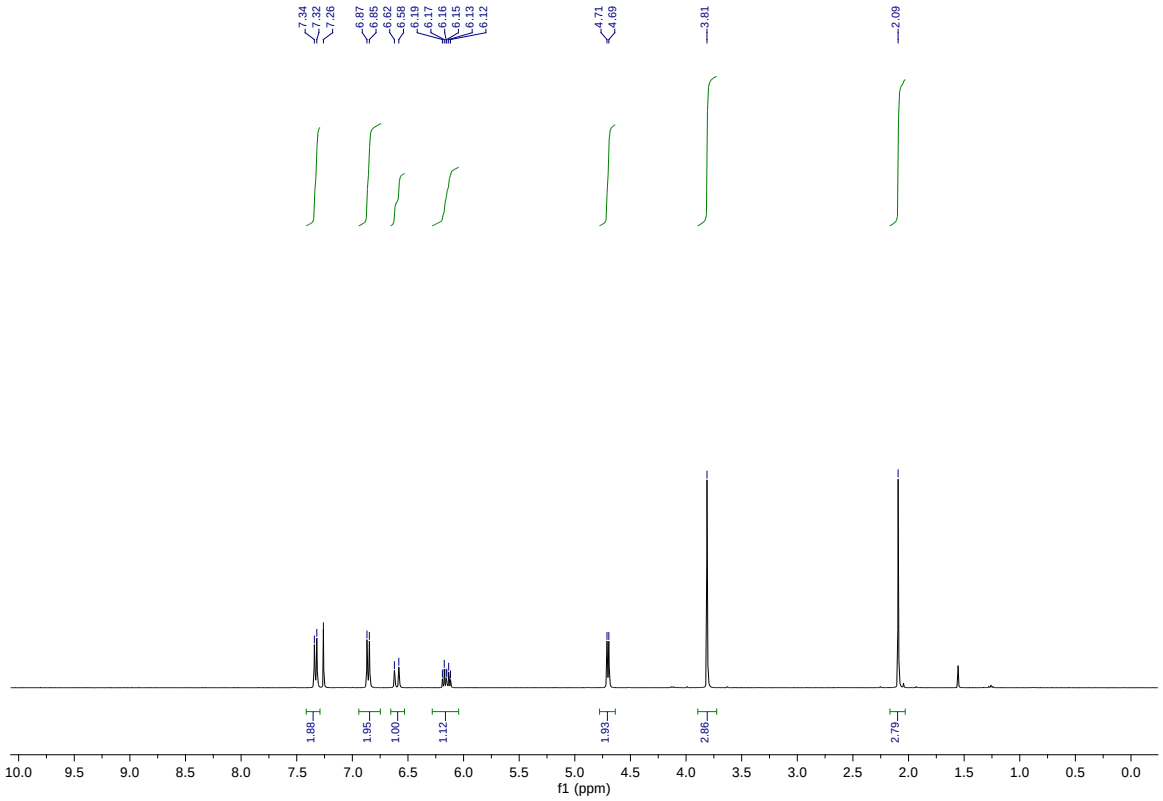
^{13}C NMR (176 MHz, $CDCl_3$) δ = 170.9, 159.5, 134.0, 128.9, 127.8, 120.8, 113.9, 65.3, 55.3, 21.0 ppm

R_f (1:10 – EtOAc:Hex) = 0.7

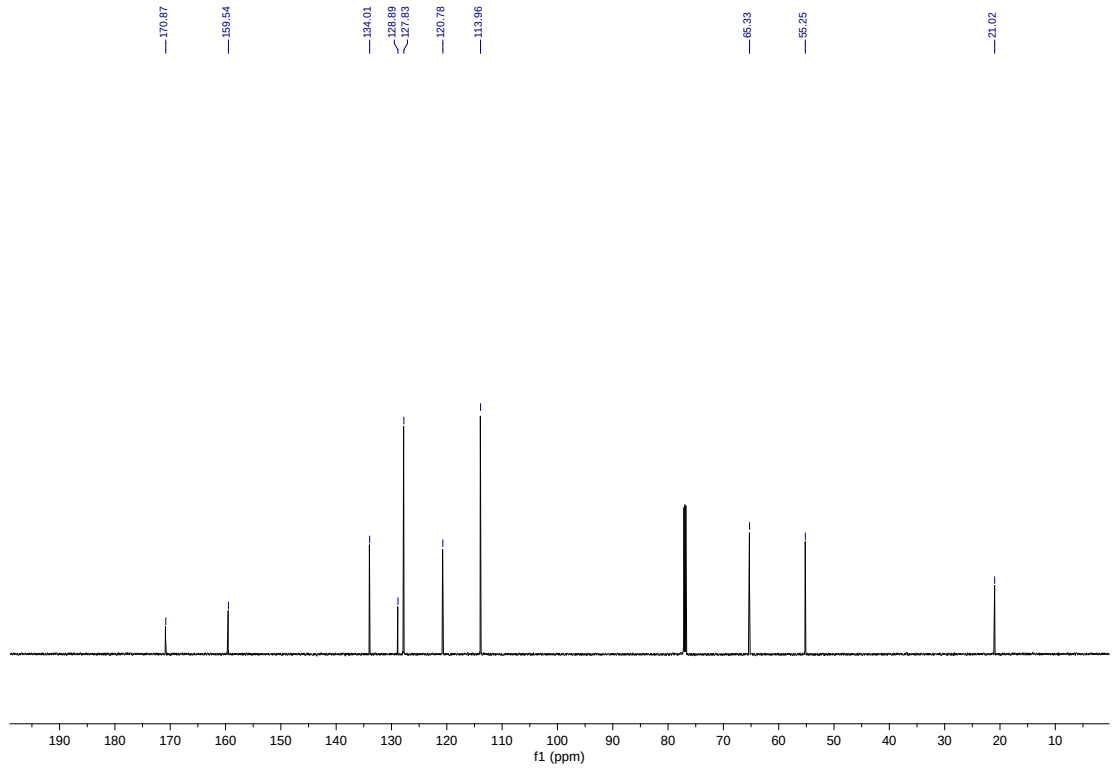
IR (*neat*): 2938, 1733, 1607, 1362, 1222, 1174, 1023, 958, 842 cm^{-1}

HRMS (EI) *m/z* calculated for $C_{12}H_{14}O_3$ $[M]^+$ 206.0943, found 206.0951.

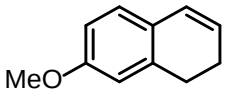
^{1}H NMR (400 MHz, $CDCl_3$) for S19



^{13}C NMR (700 MHz, $CDCl_3$) for S19



7-methoxy-1,2-dihydronaphthalene (S20)

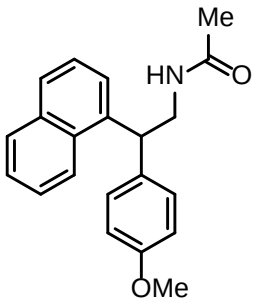


A solution of 6-methoxytetralin-1-one (1000 mg, 5.67 mmol) in diethyl ether (17 mL) was added to a suspension of $LiAlH_4$ (108 mg, 2.84 mmol) in diethyl ether (8.5 mL). The temperature of the reaction as kept below 5 °C during this addition. The addition process took, 30 minutes, and the reaction was allowed to stir for 30 more minutes to reach completion. The reaction was quenched by the addition of 220 µL of a 3M NaOH solution at 0 °C, followed by 600 µL of water. The solution was then gravity filtered to remove the aluminum salts, and then washed with 30 mL of water, followed by 30 mL of saturated sodium chloride solution. Drying over magnesium sulfate and concentration yielded a clear liquid.

The crude alcohol was dissolved in toluene (30 mL, 0.2 M), and 4-methylbenzenesulfonic acid;hydrate (6.75 mg, 0.0355 mmol) was added. The reaction was heated to reflux for no longer than 30 minutes, and then cooled to room temperature. The mixture was washed with 30 mL of water followed by 30 mL of saturated sodium chloride solution, followed by drying over magnesium sulfate. Vacuum filtration with additional washing with ethyl acetate removed the dessicant, while azeotropic distillation of the toluene with ethyl acetate afforded a brown oil free of toluene. The brown oil was distilled to yield under vacuum at 0.2 mbar/80 °C afforded 7-methoxy-1,2-dihydronaphthalene (275 mg, 1.72 mmol, yield: 30%). Spectral data of the product corresponded with previous reports (*51*).

Aminoarylation Products:

***N*-(2-(4-methoxyphenyl)-2-(naphthalen-1-yl)ethyl)acetamide (4)**



The **General Procedure A** was followed performing the reaction with *N*-(1-naphthylsulfonyl)acetamide (75 mg, 0.3 mmol) and 1-methoxy-4-vinyl-benzene (48 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a white foam (39 mg, 41%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.53 (bs, 1H), 4.96 (t, *J* = 7.7 Hz, 2H), 4.03 (ddd, *J* = 13.6, 7.5, 6.0 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.76 (s, 3H), 1.88 (s, 3H) ppm

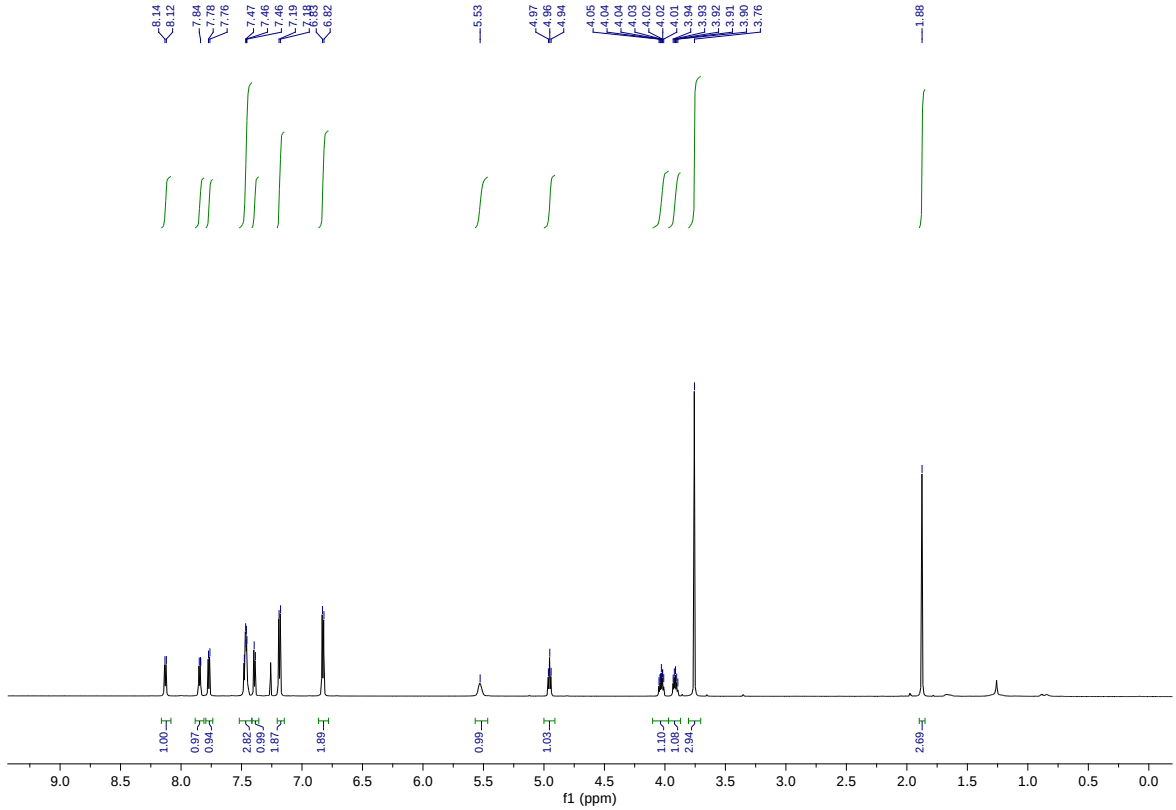
^{13}C NMR (176 MHz, $CDCl_3$): δ = 170.1, 158.3, 137.5, 134.1, 133.9, 131.9, 129.1, 128.8, 127.6, 126.3, 125.7, 125.3, 124.2, 123.7, 114.1, 55.2, 45.1, 44.1, 23.3 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

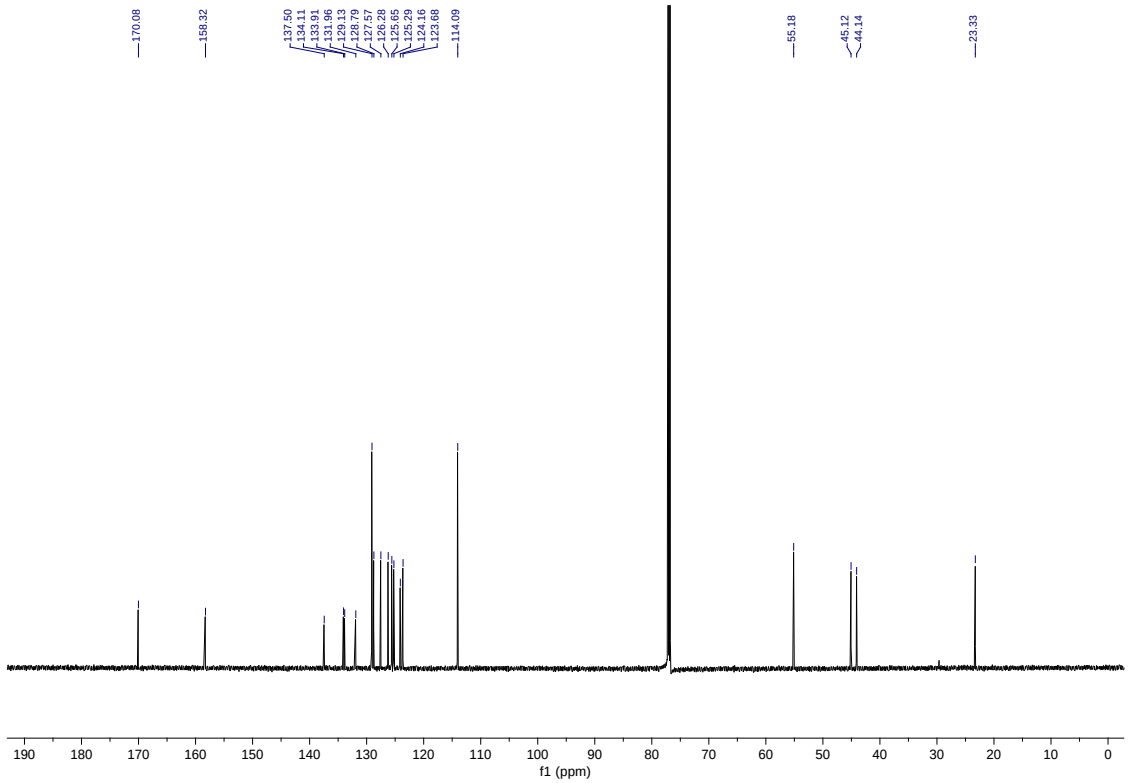
IR (*neat*): 2929, 1648, 1547, 1510, 1260, 1240, 1140, 1025, 781 cm^{-1}

HRMS (ESI) *m/z* calculated for $C_{21}H_{21}NO_2$ $[M+H]^+$ 320.1645, found 320.1645.

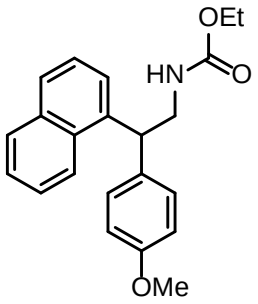
^{1}H NMR (700 MHz, $CDCl_3$) for 4



^{13}C NMR (176 MHz, $CDCl_3$) for 4



ethyl-(2-(4-methoxyphenyl)-2-(naphthalen-1-yl)ethyl)carbamate (5)



The **General Procedure A** was followed performing the reaction with ethyl-*N*-(1-naphthylsulfonyl)carbamate (251 mg, 0.9 mmol) and 1-methoxy-4-vinyl-benzene (40 µL, 0.3 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (38 mg, 36%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 6.9 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.46 (m, 3H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.95 (bs, 1H), 4.73 (bs, 1H), 4.09 (m, 2H), 3.96 (dd, *J* = 13.4, 6.3 Hz, 1H), 3.90 – 3.79 (m, 1H), 1.19 (t, *J* = 6.5 Hz, 3H) ppm

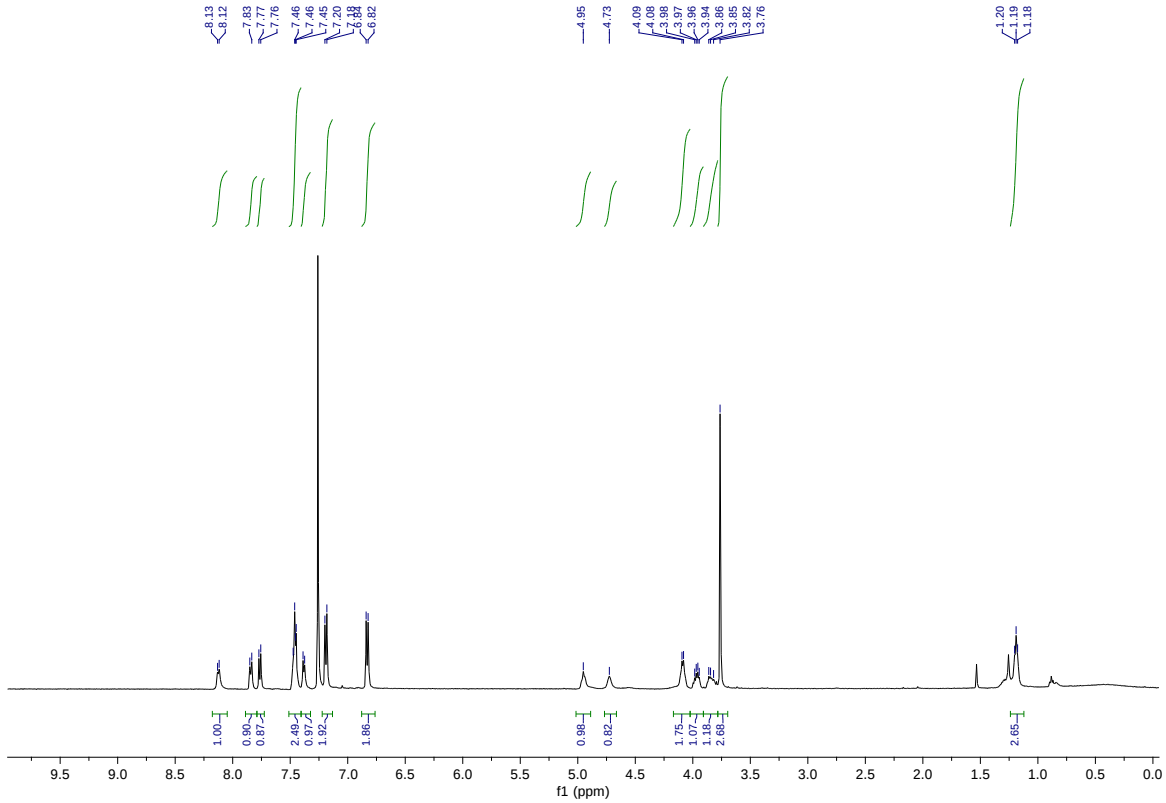
^{13}C NMR (176 MHz, $CDCl_3$): δ = 158.3, 156.5, 137.5, 134.1, 133.9, 131.9, 129.2, 128.8, 127.6, 126.3, 125.6, 125.3, 124.1, 123.7, 114.1, 60.8, 55.2, 45.7, 45.5, 14.6 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

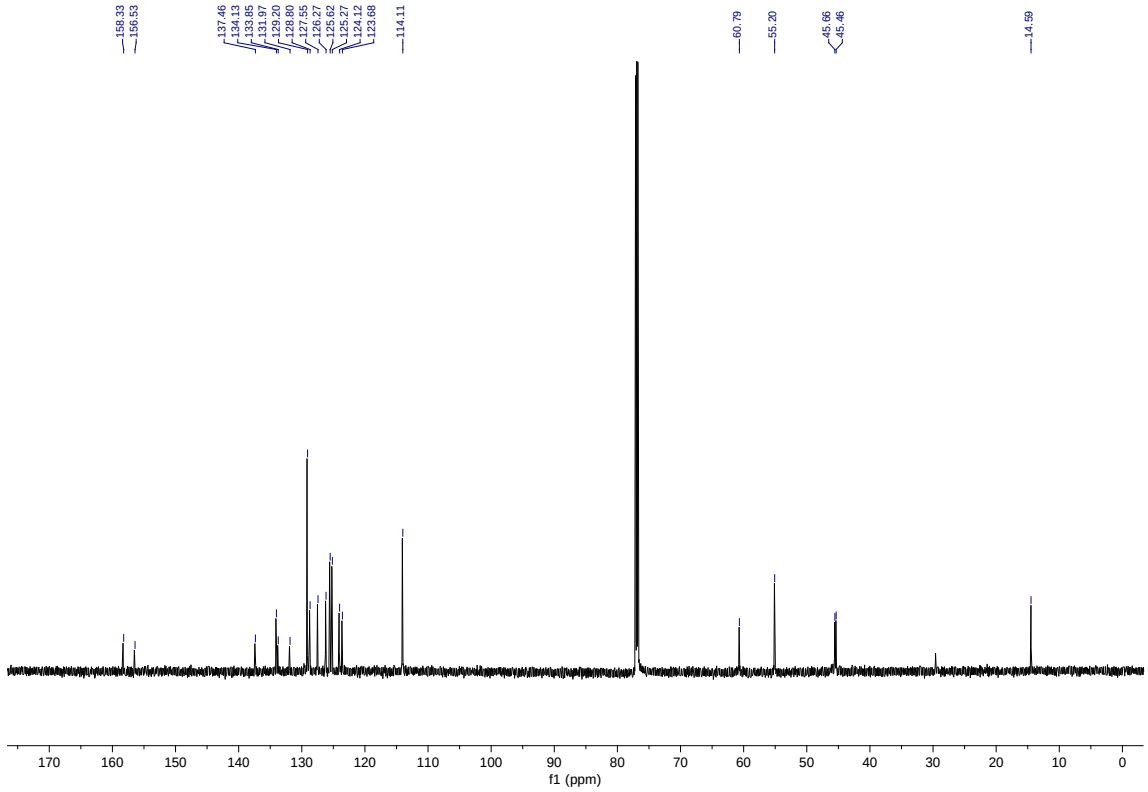
IR (*neat*): 2931, 1693, 1609, 1509, 1244, 1177, 1032, 799, 729 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{22}H_{23}NO_3$ $[M+H]^+$ 350.1751, found 350.1747.

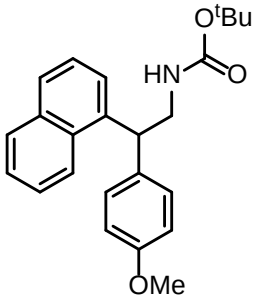
^{1}H NMR (500 MHz, $CDCl_3$) for 5



^{13}C NMR (176 MHz, $CDCl_3$) for 5



***tert*-butyl-(2-(4-methoxyphenyl)-2-(naphthalen-1-yl)ethyl)carbamate (6)**



The **General Procedure A** was followed performing the reaction with *t*-butyl-*N*-(1-naphthylsulfonyl)carbamate (277 mg, 0.9 mmol) and 1-methoxy-4-vinyl-benzene (40 µL, 0.3 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a white foam (30 mg, 27%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.42 (d, *J* = 6.6 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 4.93 (t, *J* = 7.0 Hz, 1H), 4.62 (s, 1H), 3.89 (dd, *J* = 13.3, 6.3 Hz, 1H), 3.84 (dd, *J* = 12.9, 6.2 Hz, 1H), 3.76 (s, 3H), 1.41 (s, 9H) ppm

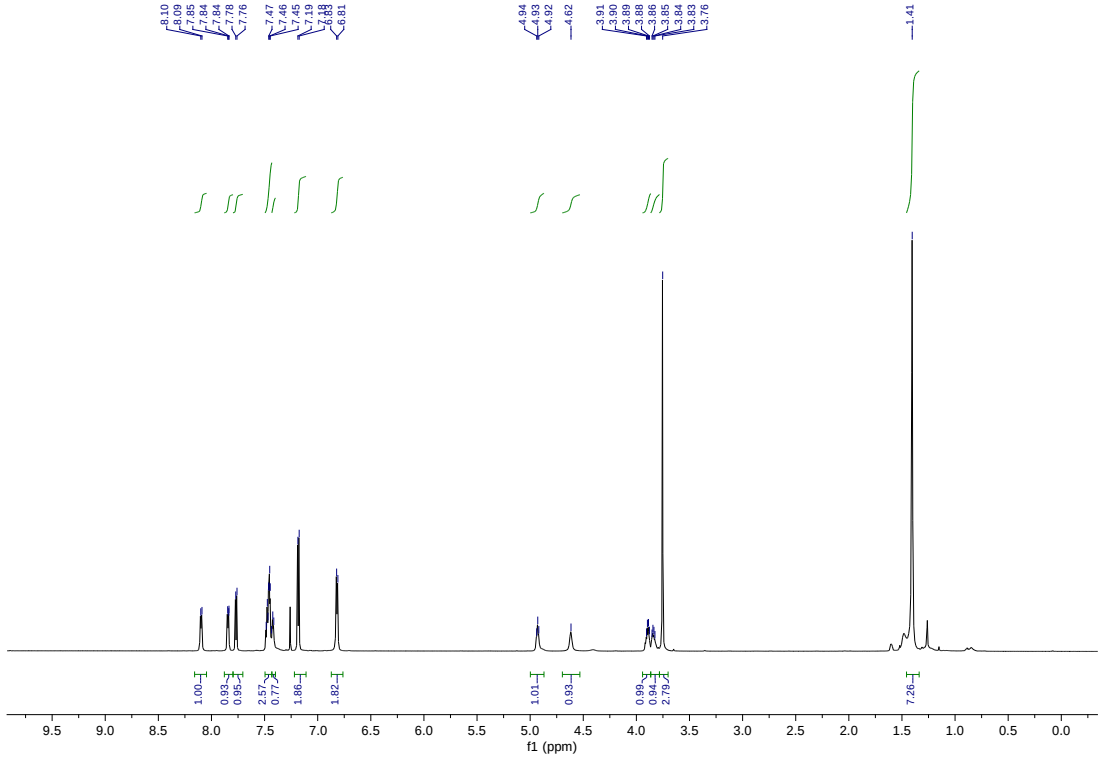
^{13}C NMR (176 MHz, $CDCl_3$): δ = 158.2, 155.8, 137.6, 134.1, 132.1, 129.2, 128.8, 127.5, 126.2, 125.6, 125.3, 124.1, 123.7, 114.0, 79.3, 55.2, 45.7, 45.2, 29.7, 28.4 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

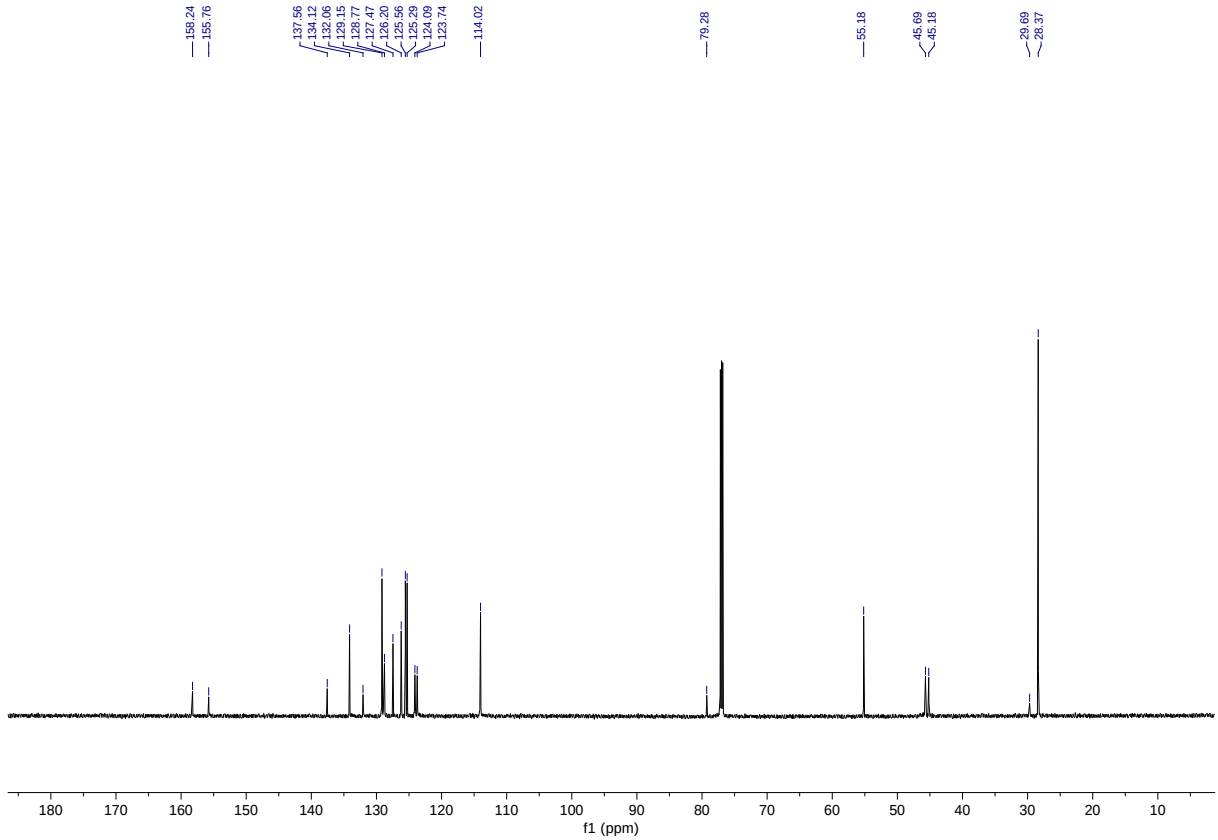
IR (*neat*): 2975, 1696, 1508, 1365, 1245, 1161, 1035, 799, 780 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{24}H_{27}NO_3$ $[M+H]^+$ 378.2064, found 378.2049.

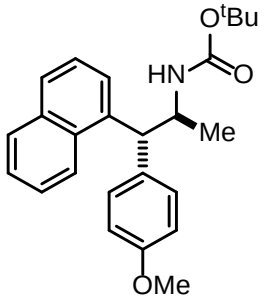
^{1}H NMR (700 MHz, $CDCl_3$) for 6



^{13}C NMR (176 MHz, $CDCl_3$) for 6



***tert*-butyl-1-(4-methoxyphenyl)-1-(naphthalen-1-yl)propan-2-yl)carbamate (8)**



The **General Procedure A** was followed performing the reaction with *t*-butyl- *N*-(1-naphthylsulfonyl)carbamate (277 mg, 0.9 mmol) and *trans*-anethole (45 µL, 0.3 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a white foam (43 mg, 37%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 2H), 4.61 (s, 1H), 4.56 (d, *J* = 9.9 Hz, 1H), 4.33 (s, 1H), 3.72 (s, 3H), 1.33 (s, 9H), 1.18 (d, *J* = 5.7 Hz, 3H) ppm

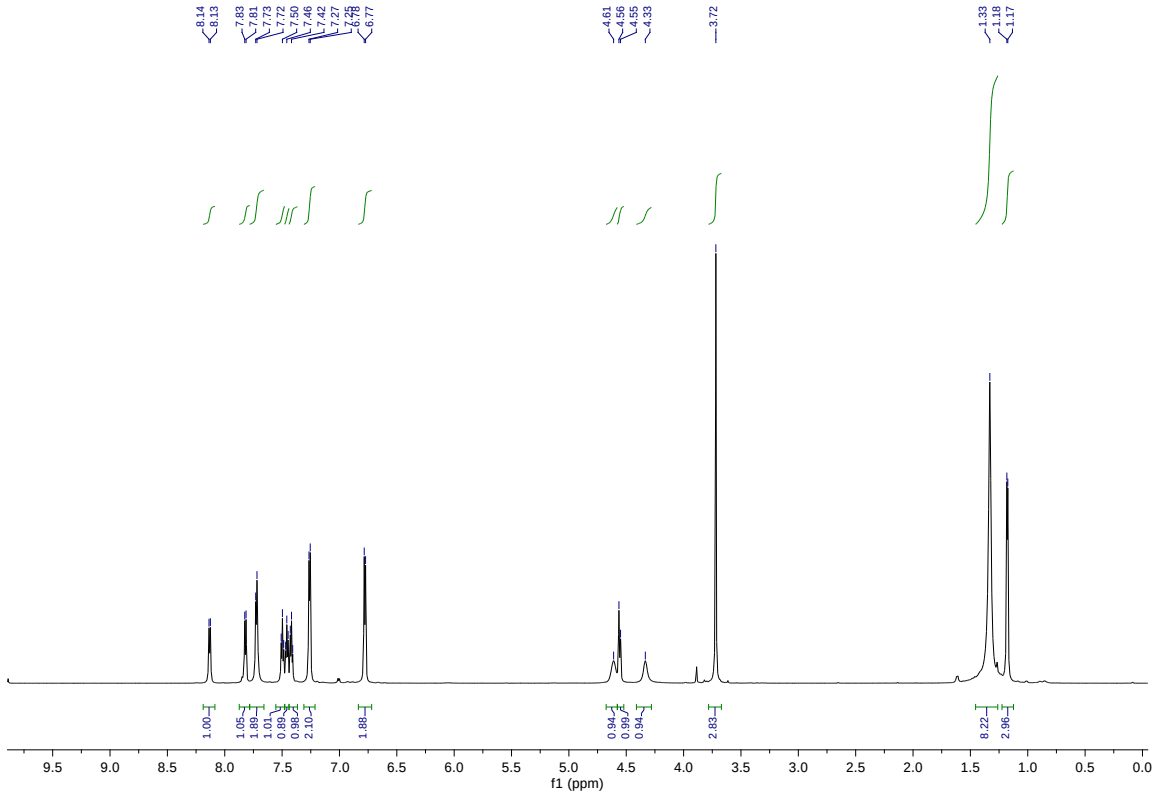
^{13}C NMR (176 MHz, $CDCl_3$): δ = 158.1, 155.3, 137.5, 134.1, 132.0, 129.4, 128.9, 127.1, 125.9, 125.5, 125.2, 124.4, 123.3, 114.3, 113.9, 79.1, 55.1, 52.2, 49.3, 28.3, 21.1 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

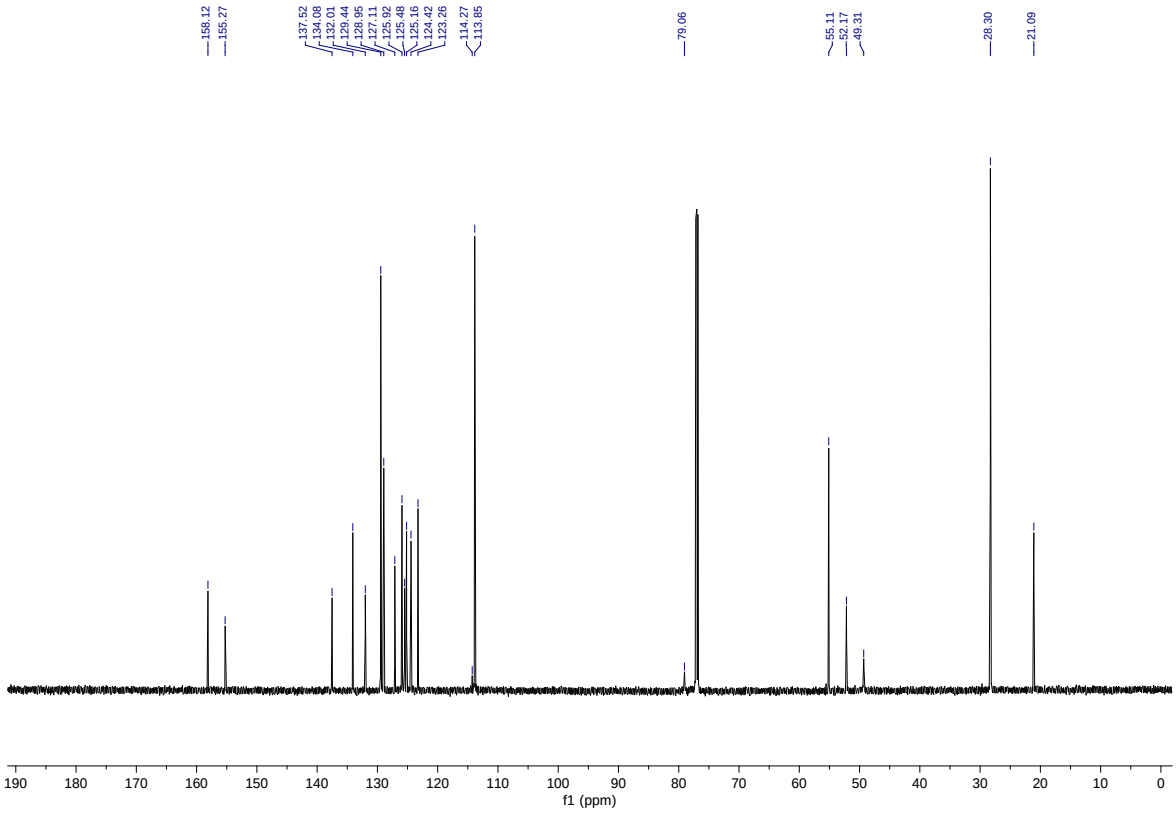
IR (*neat*): 2974, 2831, 1689, 1609 1509, 1452, 1365, 1247, 1162, 929, 782 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{25}H_{29}NO_3$ $[M+H]^+$ 392.2220, found 392.2230.

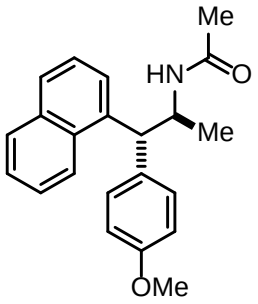
^{1}H NMR (700 MHz, $CDCl_3$) for 8



^{13}C NMR (176 MHz, $CDCl_3$) for 8



***N*-1-(4-methoxyphenyl)-1-(naphthalen-1-yl)propan-2-yl)acetamide (9)**



With *trans*-Anethole: The **General Procedure A** was followed performing the reaction with *N*-(1-naphthylsulfonyl)acetamide (75 mg, 0.3 mmol) and *trans*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (82 mg, 82%).

With *cis*-Anethole: The **General Procedure A** was followed performing the reaction with *N*-(1-naphthylsulfonyl)acetamide (75 mg, 0.3 mmol) and *cis*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (72 mg, 72%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.47 (td, *J* = 8.1, 7.1 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 5.22 (d, *J* = 7.8 Hz, 1H), 5.01 – 4.87 (m, 1H), 4.58 (d, *J* = 10.4 Hz, 1H), 3.72 (s, 3H), 1.74 (s, 3H), 1.17 (d, *J* = 6.3 Hz, 3H) ppm

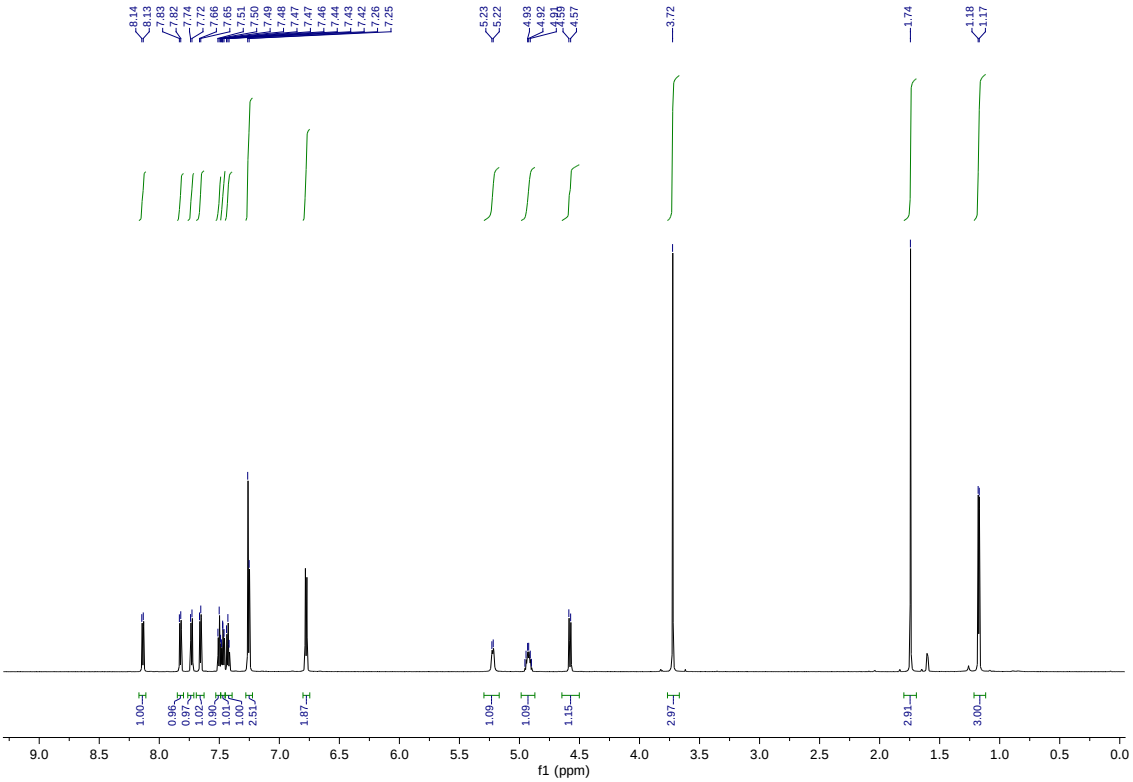
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.4, 158.2, 137.1, 134.1, 133.7, 131.9, 129.5, 129.1, 127.3, 126.0, 125.6, 125.3, 124.2, 123.2, 113.9, 55.1, 51.9, 48.1, 23.4, 20.7 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

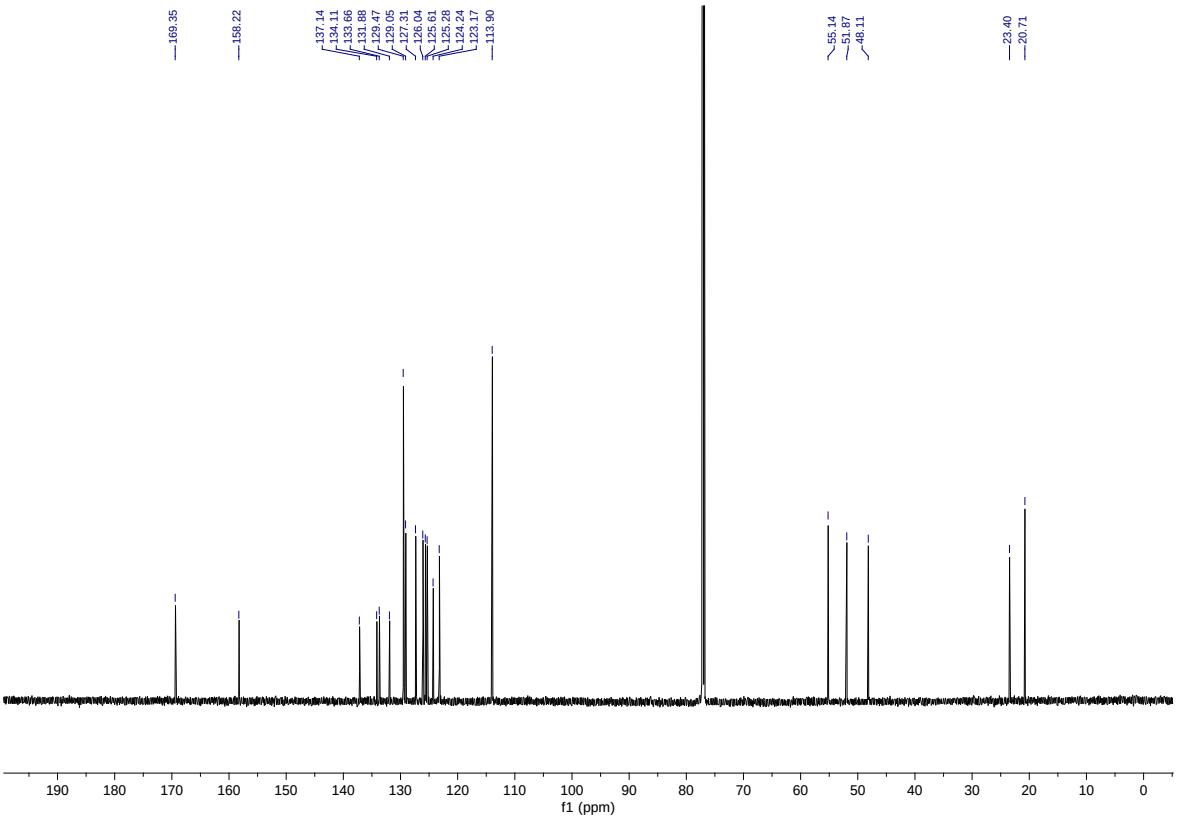
IR (*neat*): 3089, 2929, 1637, 1509, 1370, 1302, 1249, 1177, 1031 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{22}H_{23}NO_2$ $[M+H]^+$ 334.1802, found 334.1802.

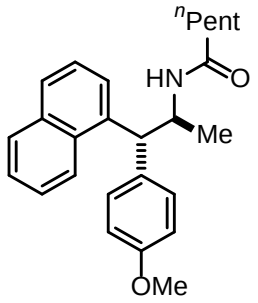
^{1}H NMR (700 MHz, $CDCl_3$) for 9



^{13}C NMR (176 MHz, $CDCl_3$) for 9



***N*-1-(4-methoxyphenyl)-1-(naphthalen-2-yl)propan-2-yl)-*n*-pentamide (10)**



The **General Procedure A** was followed performing the reaction on 0.2 mmol scale with *N*-(1-naphthylsulfonyl)hexanamide and *trans*-anethole (59.3 mg, 0.400 mmol). Purification by flash column chromatography (SiO_2, 90:10 to 60:40 Hex:EtOAc) to furnish the title compound as a light yellow foam (45%). Further removal of residual *N*-(1-naphthylsulfonyl)hexanamide (~10%) was done by washing with 1 N NaOH and extracting into Et_2O. Reconcentration of the purified product provided a light yellow foam (20.7 mg, 25%).

^{1}H NMR (400 mHz, CDCl3) = δ 8.16 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.46 – 7.38 (t, 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 5.20 (d, J = 8.6 Hz, 1H), 4.95 (m, 1H), 4.60 (d, J = 10.5 Hz, 1H), 3.73 (s, 3H), 1.90 (dtd, J = 29.3, 14.5, 7.5 Hz, 2H), 1.47 – 0.86 (m, 9H), 0.78 (t, J = 7.2 Hz, 2H) ppm

^{13}C NMR (100 mHz, CDCl3) = 172.4, 158.2, 137.3, 134.1, 133.8, 131.9, 129.5, 129.1, 127.3, 126.0, 125.6, 125.2, 124.5, 123.1, 113.9, 55.1, 51.9, 48.0, 36.9, 31.2, 25.3, 22.3, 20.8, 13.8 ppm

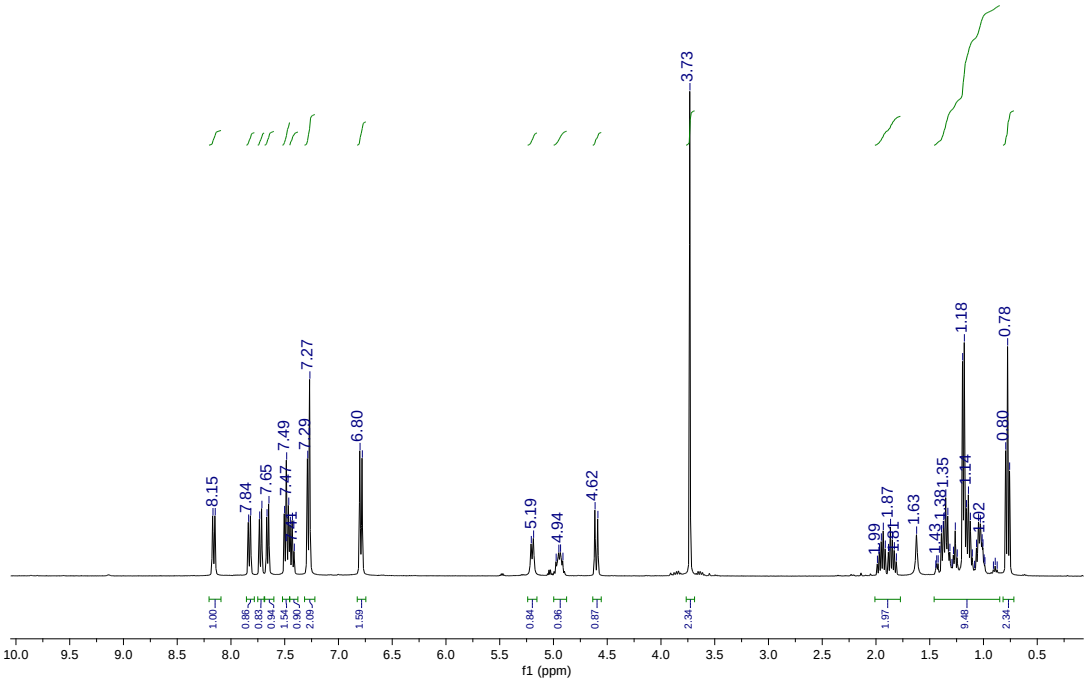
R_f (4:6 – EtOAc:Hex) = 0.5

IR (*neat*) = 2996, 2932, 2253, 1641, 1510, 1252, 905, 784, 729, 649 cm^{-1}

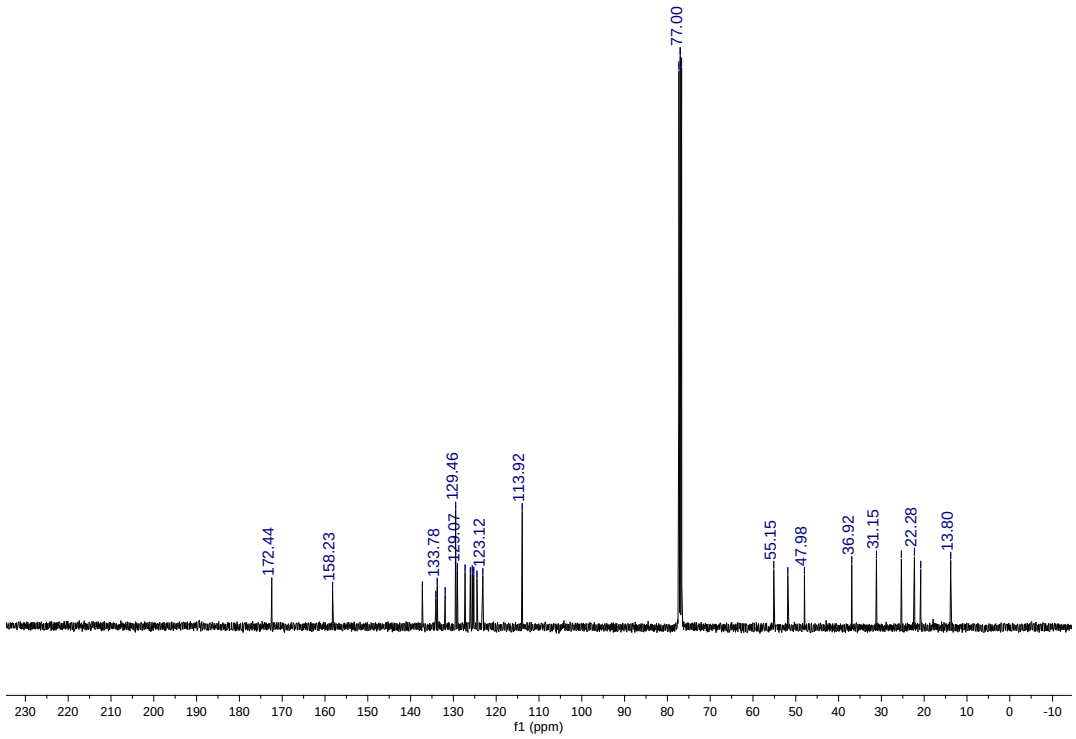
HRMS (ESI+) *m/z* calculated for $C_{26}H_{31}NO_2$ [M=H$^+$] 390.2428, found 390.2431.

,

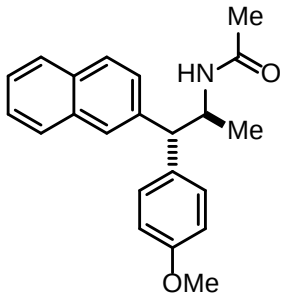
^{1}H NMR (400 MHz, $CDCl_3$) of 10



^{13}C NMR (100 MHz, $CDCl_3$) for 10



***N*-1-(4-methoxyphenyl)-1-(naphthalen-2-yl)propan-2-yl)acetamide (11)**



The **General Procedure A** was followed performing the reaction with *N*-(2-naphthylsulfonyl)acetamide (75 mg, 0.3 mmol) and *trans*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (78 mg, 78%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.73 (m, 1H), 7.45 (td, *J* = 11.0, 3.9 Hz, 1H), 7.42 (t, *J* = 6.9 Hz, 1H), 7.38 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.22 (d, *J* = 8.4 Hz, 1H), 5.01 – 4.87 (m, 1H), 3.97 (d, *J* = 9.7 Hz, 1H), 3.76 (s, 3H), 1.77 (s, 3H), 1.17 (d, *J* = 6.4 Hz, 3H) ppm

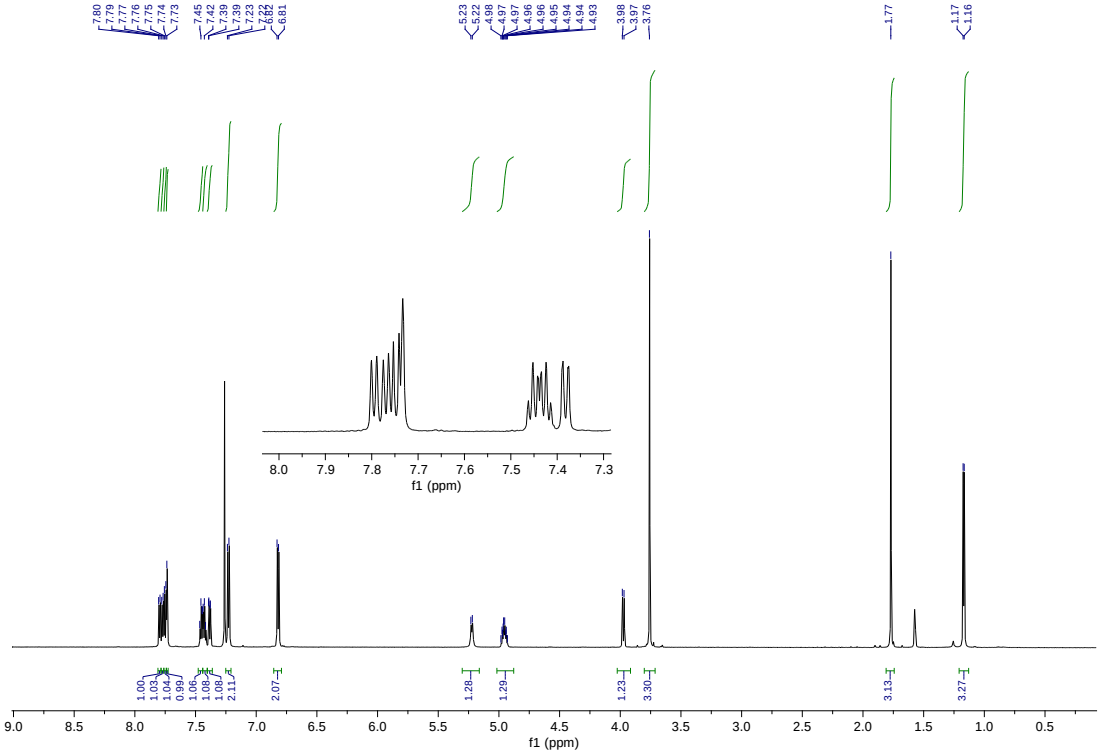
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.3, 158.3, 139.6, 134.2, 133.4, 132.2, 129.3, 128.3, 127.8, 127.5, 126.5, 126.4, 126.1, 125.6, 114.1, 57.2, 55.2, 47.5, 23.5, 20.3 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

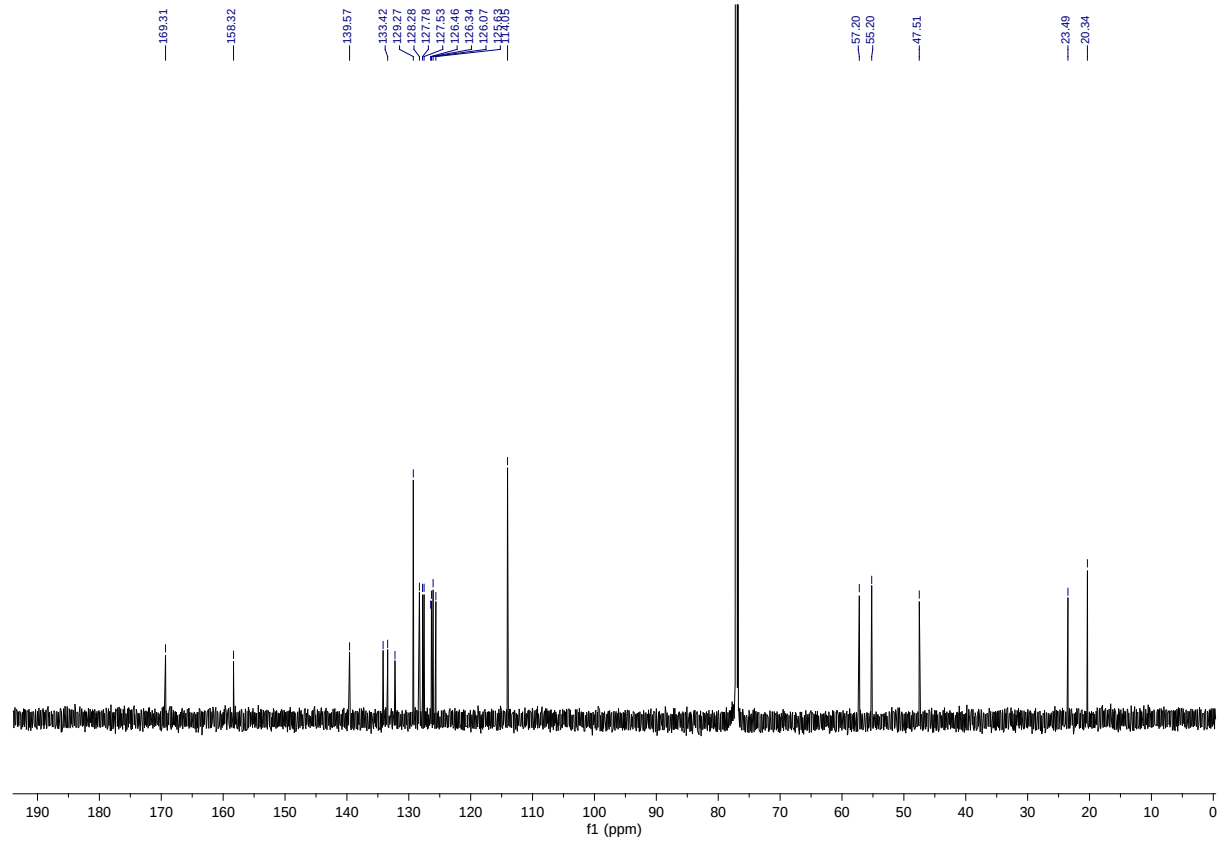
IR (*neat*): 3268, 2971, 1636, 1509, 1371, 1247, 1178, 1032, 915 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{22}H_{23}NO_2$ $[M+H]^+$ 334.1802, found 334.1805.

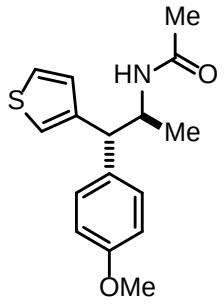
^{1}H NMR (700 MHz, $CDCl_3$) for 11



^{13}C NMR (176 MHz, $CDCl_3$) for 11



***N*-1-(4-methoxyphenyl)-1-(thiophen-3-yl)propan-2-yl)acetamide (12)**



The **General Procedure A** was followed performing the reaction with *N*-(3-thienylsulfonyl)acetamide (62 mg, 0.3 mmol) and *trans*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (26 mg, 30%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.24 – 7.21 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.09 (s, 1H), 6.93 (d, *J* = 4.8 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.20 (d, *J* = 8.1 Hz, 1H), 4.83 – 4.66 (m, 1H), 3.94 (d, *J* = 8.7 Hz, 1H), 3.78 (s, 3H), 1.87 (s, 3H), 1.07 (d, *J* = 6.5 Hz, 3H) ppm

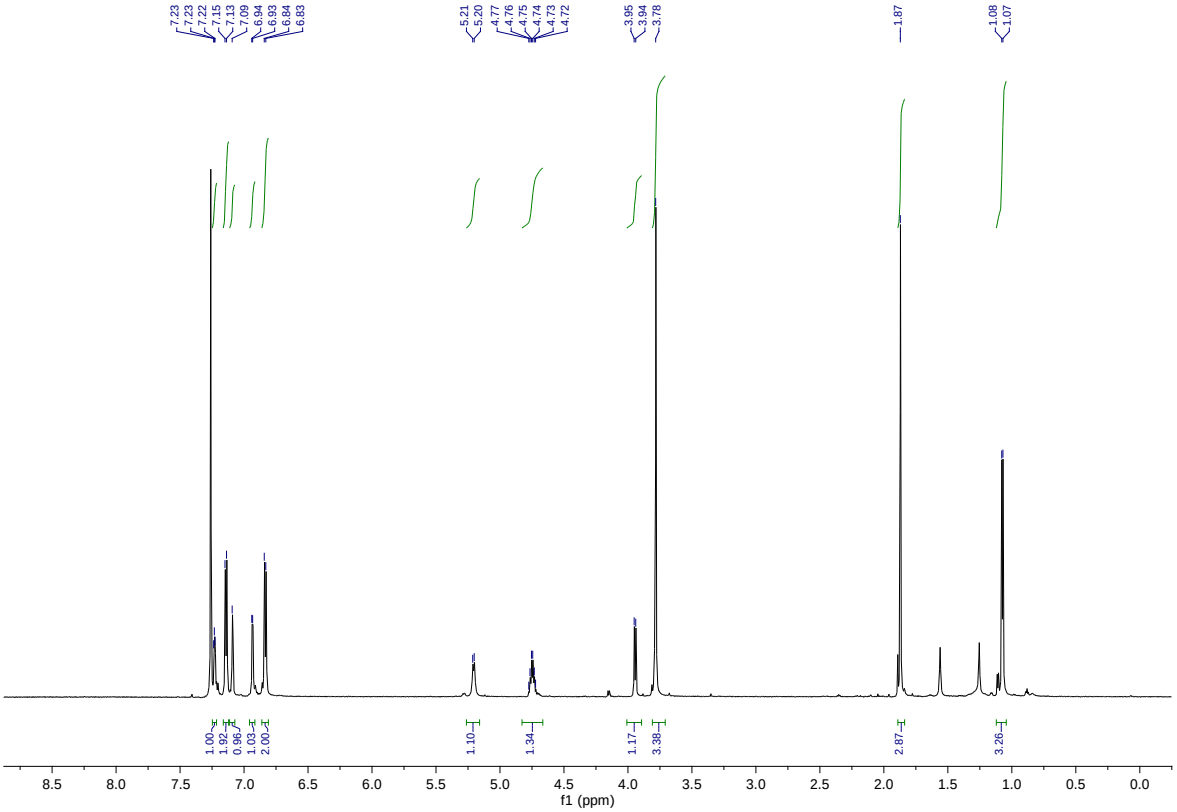
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.2, 158.4, 142.8, 133.4, 129.5, 127.8, 125.6, 120.9, 113.9, 55.2, 52.2, 48.2, 23.6, 19.6 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

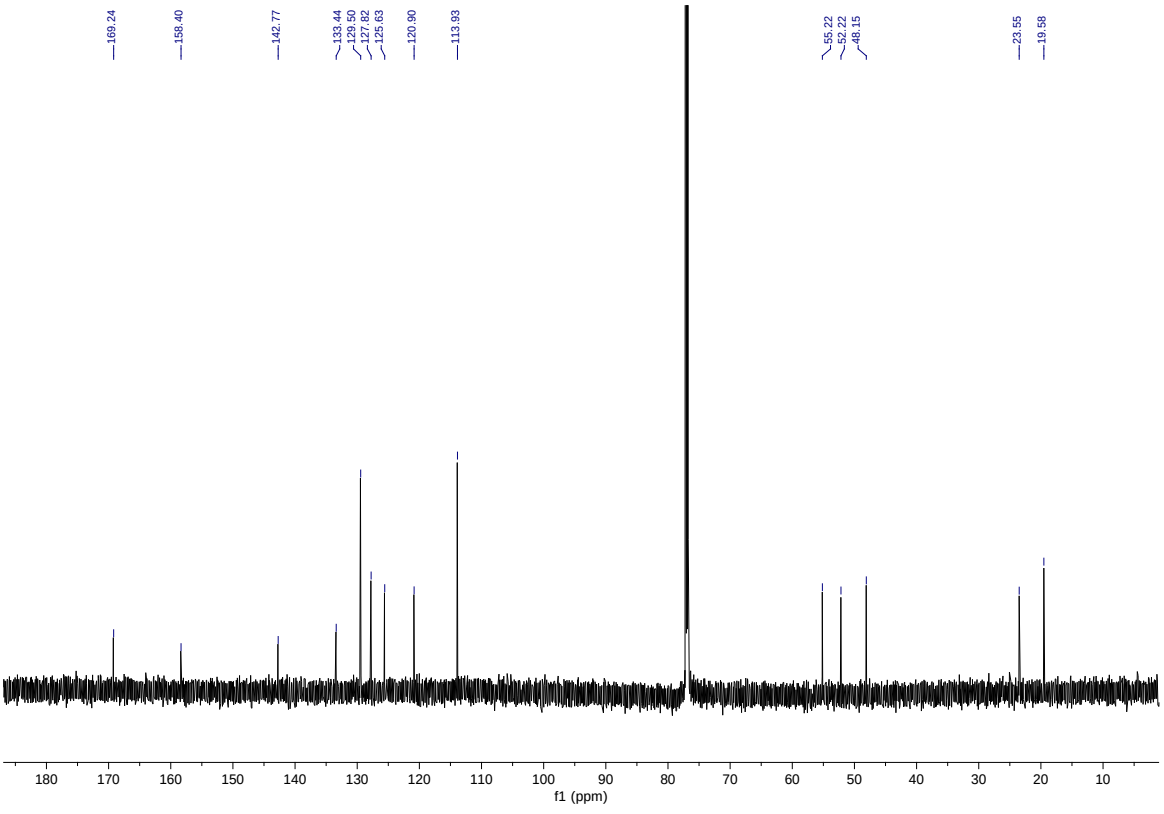
IR (*neat*): 3325, 3000, 1628, 1511, 1373, 1251, 1032, 849, 796, 708 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{16}H_{19}NO_2S$ $[M+H]^+$ 290.1209, found 290.1211.

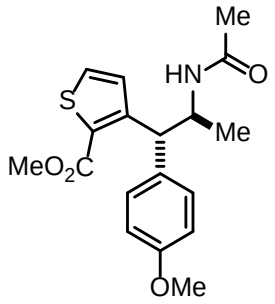
^{1}H NMR (700 MHz, $CDCl_3$) for 12



^{13}C NMR (176 MHz, $CDCl_3$) for 12



methyl-2-acetamido-1-(4-methoxyphenyl)propyl)thiophene-2-carboxylate (13)



The **General Procedure A** was followed performing the reaction with methyl 3-(acetylsulfamoyl)thiophene-2-carboxylate (79 mg, 0.3 mmol) and *trans*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (92 mg, 89%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 5.2 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 5.2 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.86 (d, *J* = 9.0 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.86 – 4.65 (m, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 1.75 (s, 3H), 1.12 (d, *J* = 6.4 Hz, 3H) ppm

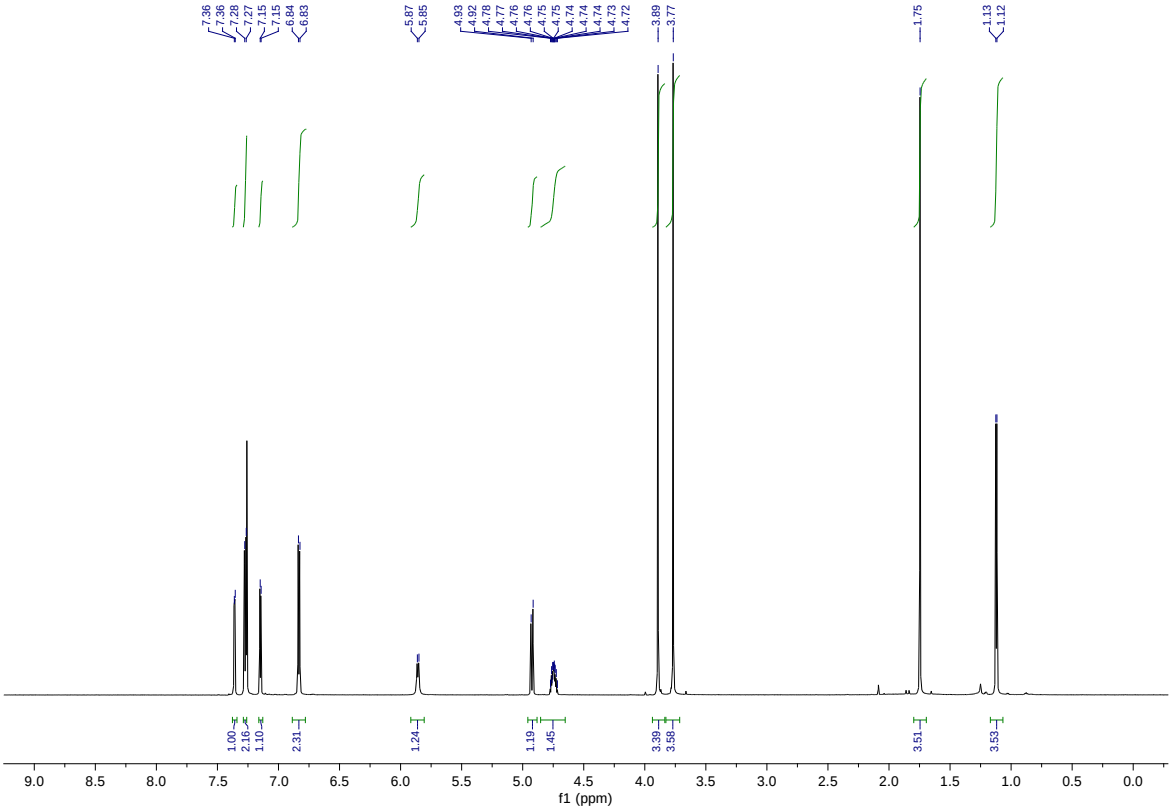
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.1, 163.9, 158.4, 151.8, 133.1, 130.9, 129.5, 129.0, 126.2, 114.0, 55.2, 52.0, 49.6, 49.1, 23.3, 20.7 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

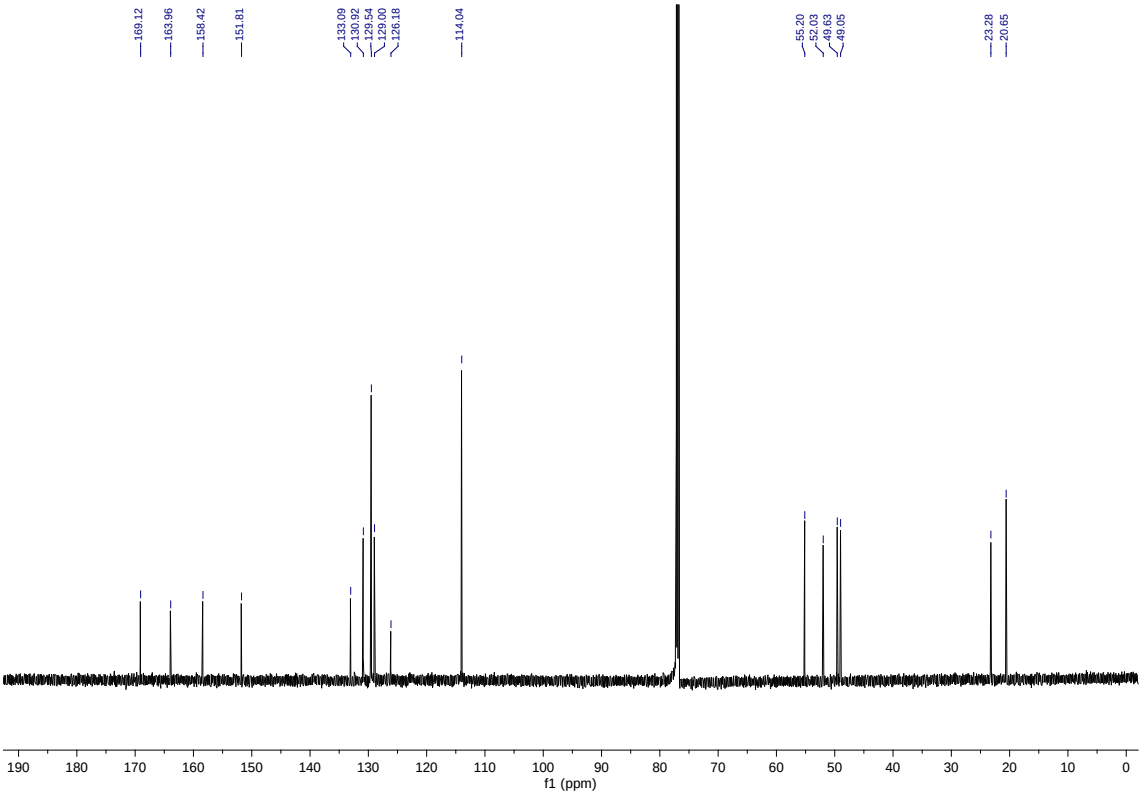
IR (*neat*): 3289, 2941, 1718, 1639, 1585, 1512, 1445, 1226, 1104, 1075, 829 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{18}H_{21}NO_4S$ $[M+H]^+$ 348.1264, found 348.1265.

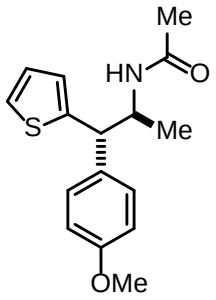
^{1}H NMR (700 MHz, $CDCl_3$) for 13



^{13}C NMR (176 MHz, $CDCl_3$) for 13



***N*-1-(4-methoxyphenyl)-1-(thiophen-2-yl)propan-2-yl)acetamide (14)**



The **General Procedure A** was followed performing the reaction with *N*-(2-thienylsulfonyl)acetamide (62 mg, 0.3 mmol) and *trans*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (69 mg, 69%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 4.9 Hz, 1H), 6.93 – 6.91 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.31 (d, *J* = 8.3 Hz, 1H), 4.73 – 4.67 (m, 1H), 4.15 (d, *J* = 8.1 Hz, 1H), 3.79 (s, 3H), 1.89 (s, 3H), 1.11 (d, *J* = 6.6 Hz, 3H) ppm

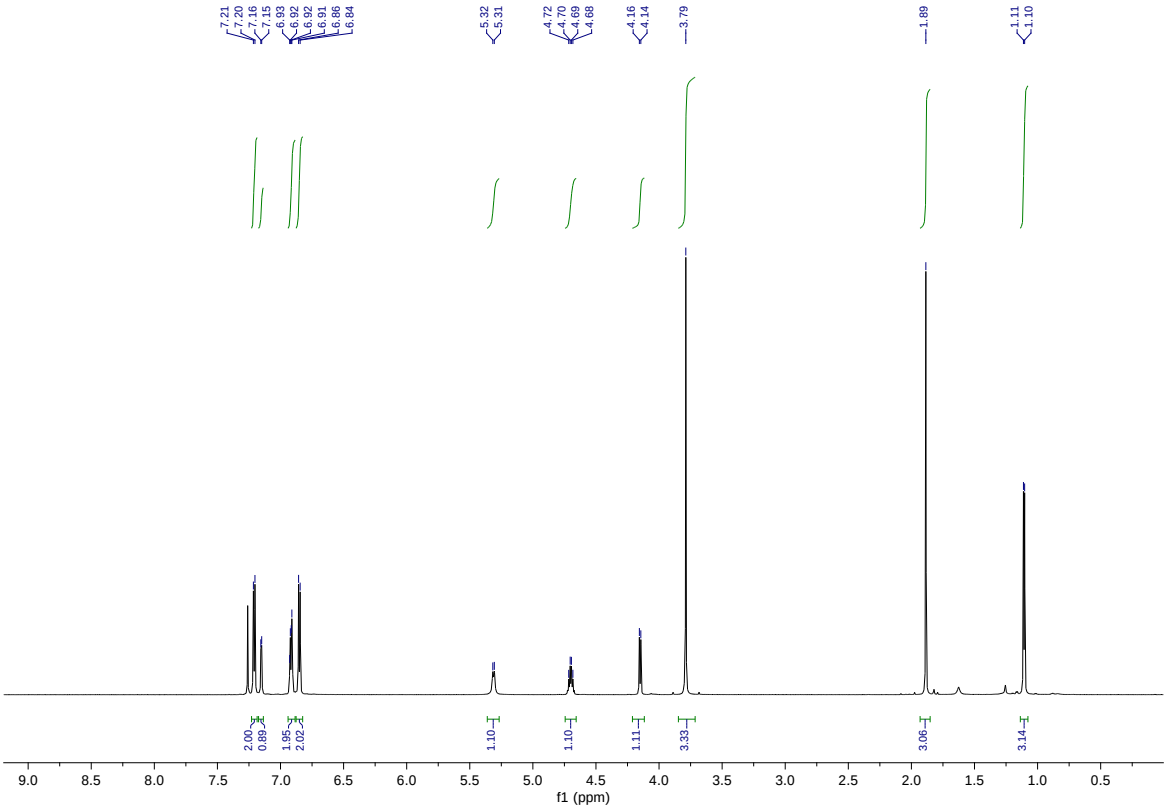
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.3, 158.6, 145.6, 133.2, 129.5, 126.7, 124.9, 124.1, 113.9, 55.2, 51.6, 49.1, 23.5, 19.5 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

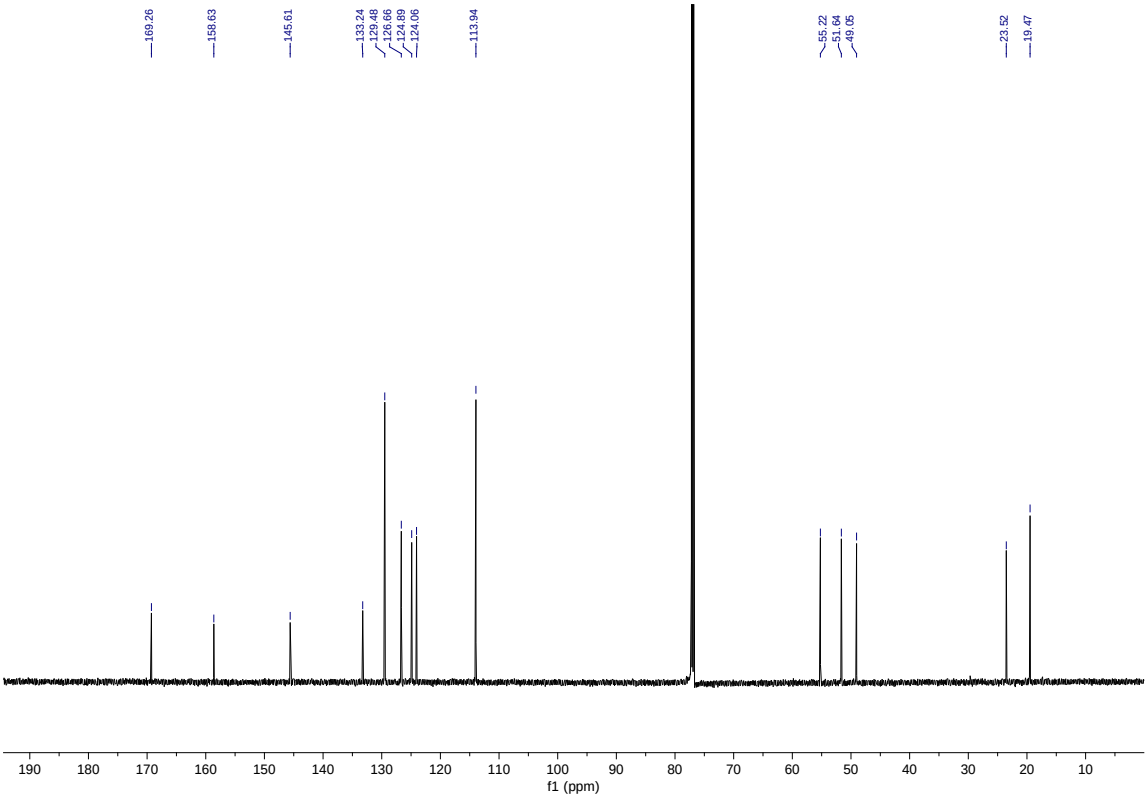
IR (*neat*): 2987, 2983, 1638, 1538, 1512, 1373, 1282, 1030 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{16}H_{19}NO_2S$ $[M+H]^+$ 290.1209, found 290.1209.

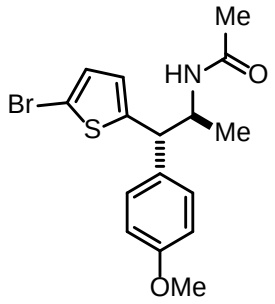
^{1}H NMR (700 MHz, $CDCl_3$) for 14



^{13}C NMR (176 MHz, $CDCl_3$) for 14



***N*-1-(5-bromothiophen-2-yl)-1-(4-methoxyphenyl)propan-2-yl)acetamide (15)**



The **General Procedure A** was followed performing the reaction with *N*-[(5-bromo-2-thienyl)sulfonyl]acetamide (85 mg, 0.3 mmol) and *trans*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (49 mg, 45%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.5 Hz, 2H), 6.86 – 6.85 (m, 3H), 6.67 (d, *J* = 3.6 Hz, 1H), 5.27 (d, *J* = 7.4 Hz, 1H), 4.77 – 4.55 (m, 1H), 4.06 (d, *J* = 8.1 Hz, 1H), 3.79 (s, 3H), 1.92 (s, 3H), 1.09 (d, *J* = 6.6 Hz, 3H) ppm

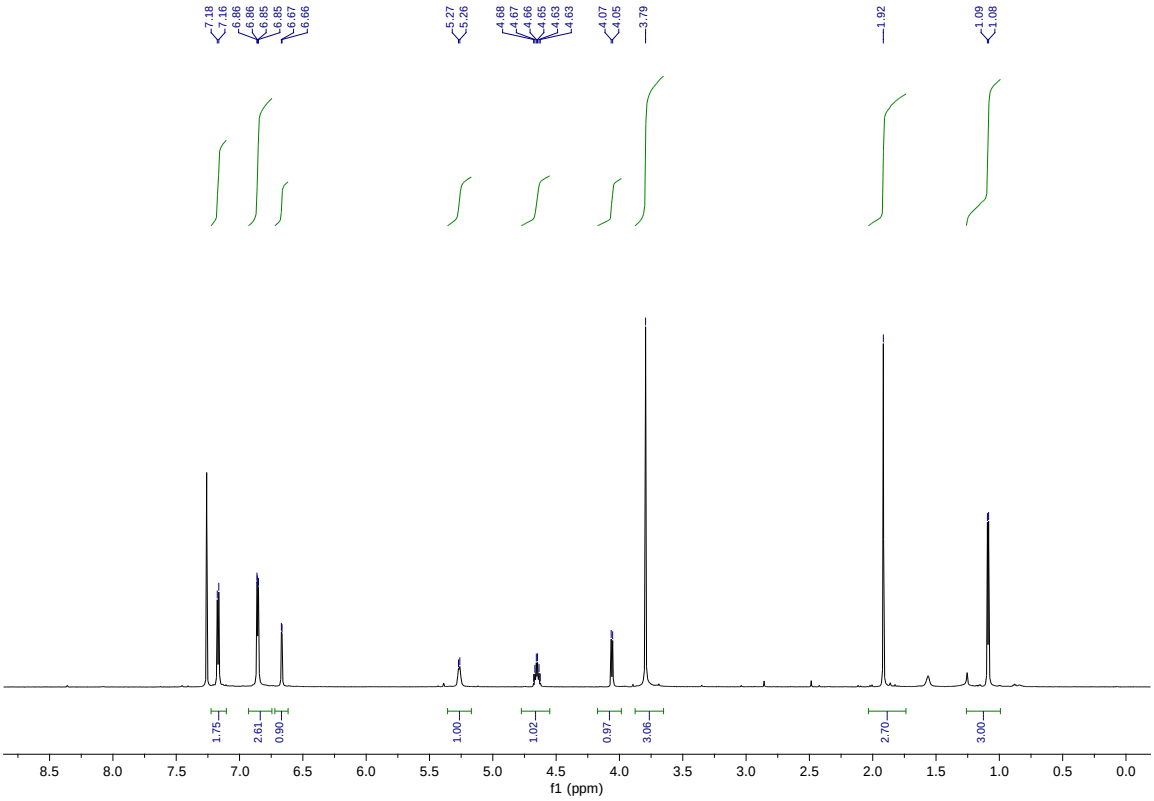
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.3, 158.8, 147.5, 132.4, 129.5, 129.4, 125.2, 114.1, 110.5, 55.3, 51.9, 48.7, 23.6, 19.3 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

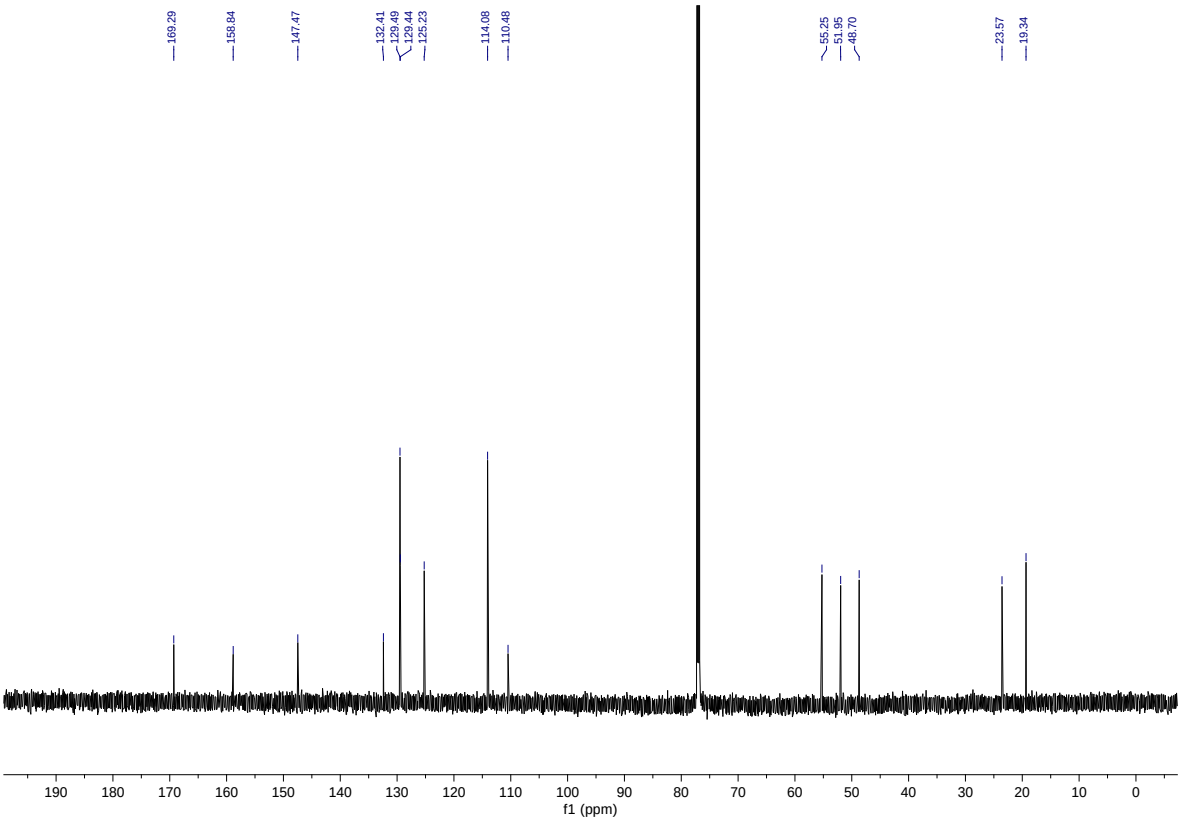
IR (*neat*): 3313, 2930, 1627, 1511, 1446, 1372, 1281, 1222, 1175, 801 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{16}H_{18}BrNO_2S$ $[M+H]^+$ 368.0314, found 368.0315.

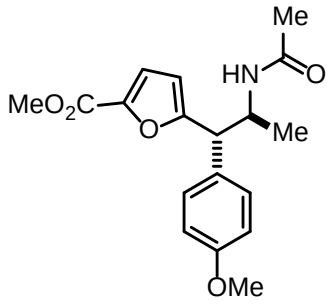
^{1}H NMR (700 MHz, $CDCl_3$) for 15



^{13}C NMR (176 MHz, $CDCl_3$) for 15



Methyl-2-acetamido-1-(4-methoxyphenyl)propyl)furan-2-carboxylate (16)



The **General Procedure A** was followed performing the reaction with methyl 5-(acetylsulfamoyl)furan-2-carboxylate (74 mg, 0.3 mmol) and *trans*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a white foam (79 mg, 80%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 3.5 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.29 (d, *J* = 3.4 Hz, 1H), 5.53 (d, *J* = 9.3 Hz, 1H), 4.77 – 4.60 (m, 1H), 4.05 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 1.89 (s, 3H), 1.07 (d, *J* = 6.7 Hz, 3H) ppm

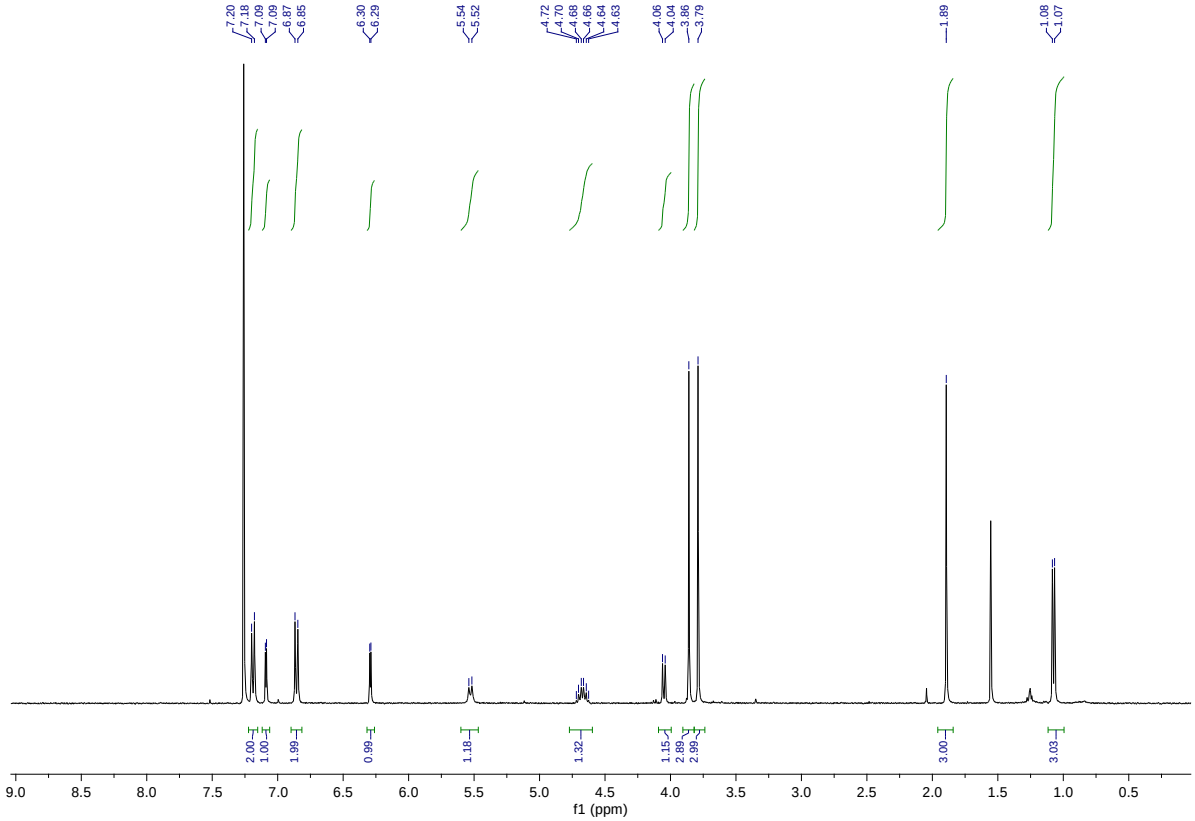
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.3, 160.4, 159.1, 158.9, 143.5, 130.1, 129.5, 119.1, 114.1, 109.3, 55.2, 51.8, 50.4, 48.2, 23.5, 19.5 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

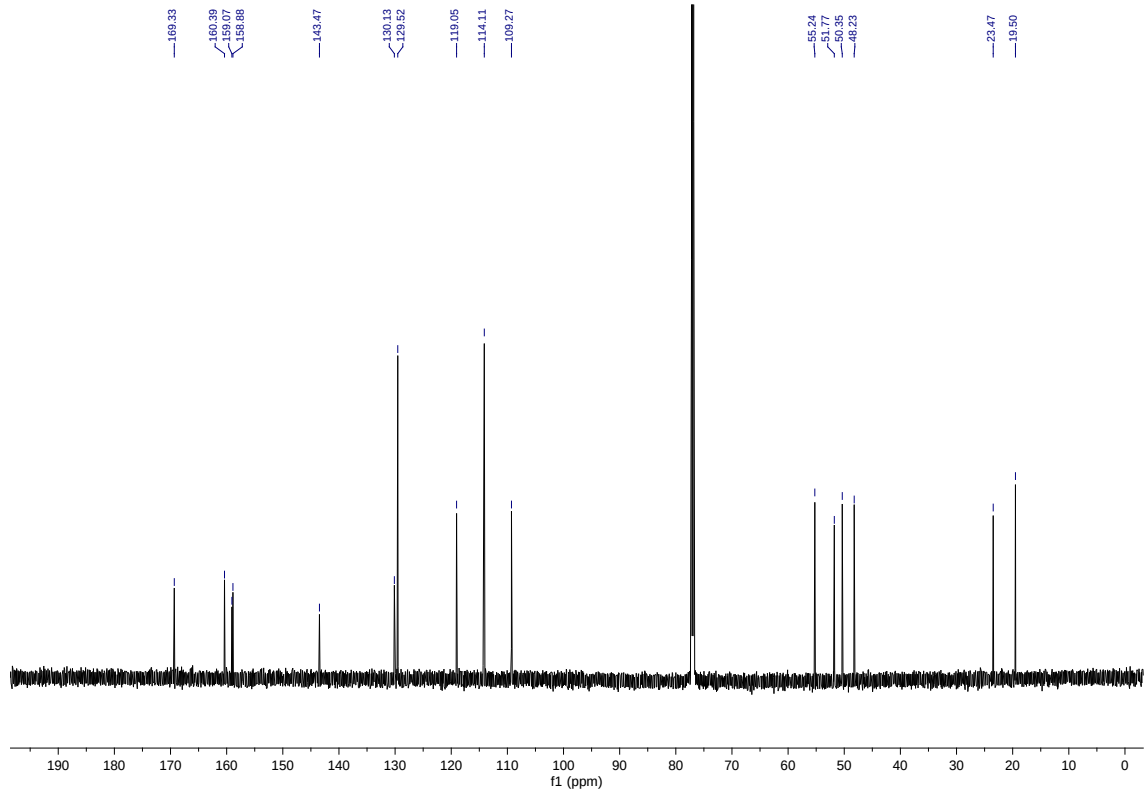
IR (*neat*): 3294, 2989, 1721, 1634, 1628, 1515, 1308, 1251, 1126, 1031, 826 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{18}H_{21}NO_5$ $[M+H]^+$ 332.1492, found 332.1491.

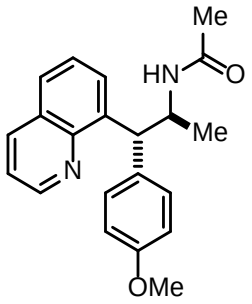
^{1}H NMR (700 MHz, $CDCl_3$) for 16



^{13}C NMR (176 MHz, $CDCl_3$) for 16



***N*-1-(4-methoxyphenyl)-1-(quinolin-8-yl)propan-2-yl)acetamide (17)**



The **General Procedure A** was followed performing the reaction with methyl *N*-(8-quinolylsulfonyl)acetamide (62 mg, 0.25 mmol) and *trans*-anethole (44 µL, 0.3 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (47 mg, 58%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.95 (d, *J* = 2.7 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.42 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.44 (s, 1H), 5.45 (d, *J* = 11.1 Hz, 1H), 4.89 – 4.76 (m, 1H), 3.76 (s, 3H), 1.48 (s, 3H), 1.25 (d, *J* = 6.3 Hz, 3H) ppm

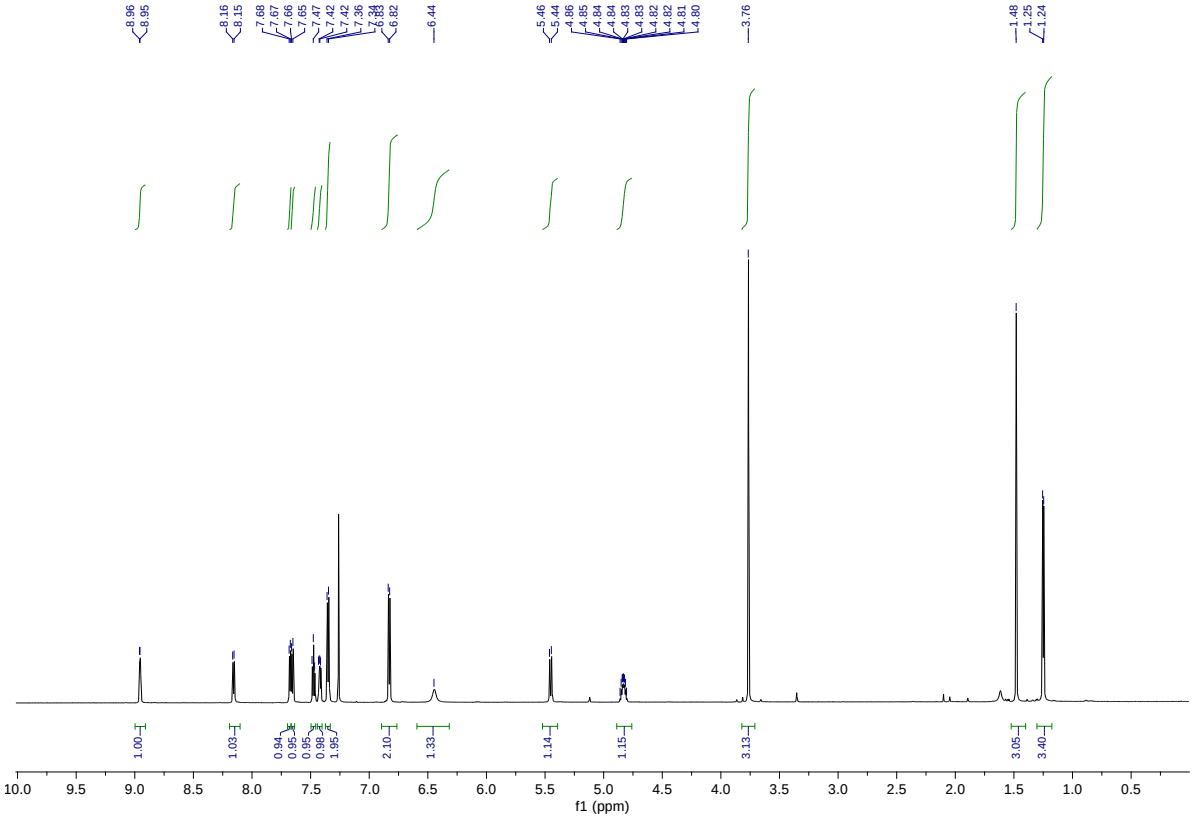
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.1, 158.1, 149.2, 146.6, 141.1, 136.9, 134.2, 129.8, 128.8, 128.4, 126.8, 126.5, 120.8, 113.8, 55.2, 49.6, 48.9, 23.1, 21.0 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

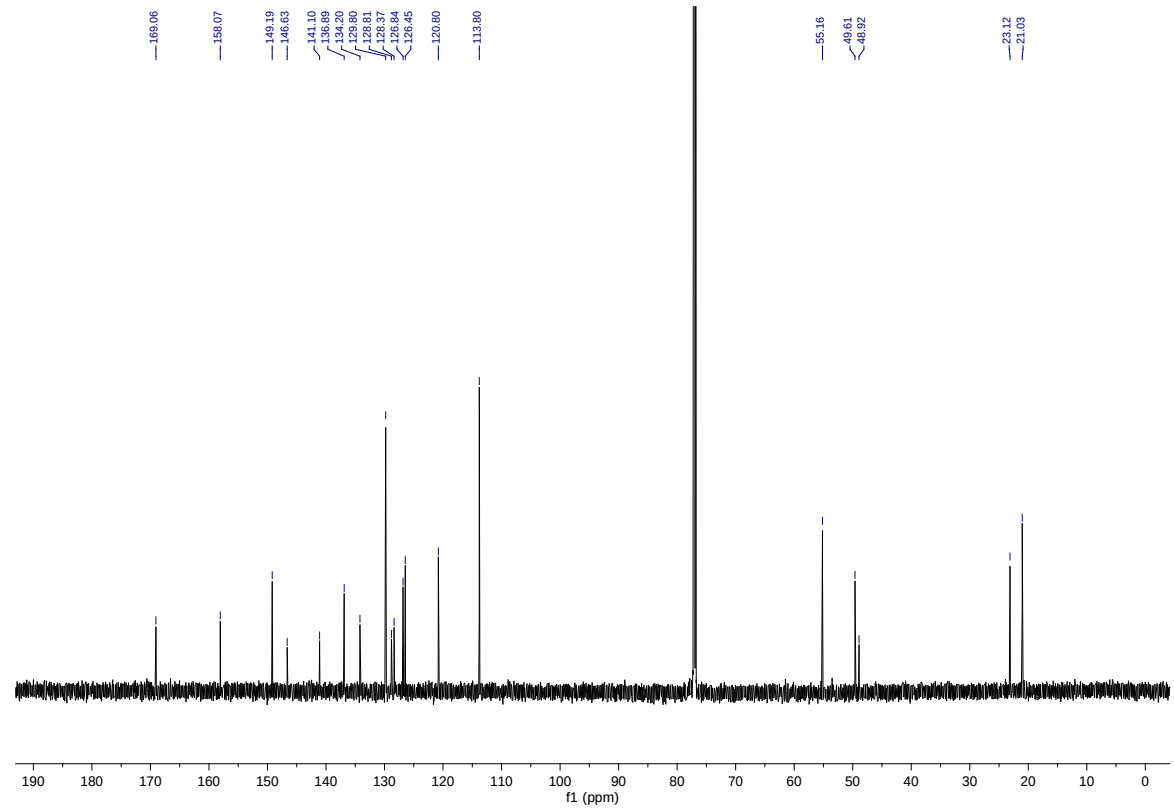
IR (*neat*): 3259, 2965, 1664, 1638, 1495, 1369, 1302, 1230, 1031, 930 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{21}H_{22}N_2O_2$ $[M+H]^+$ 335.1754, found 335.1752.

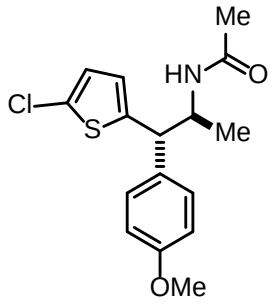
^{1}H NMR (700 MHz, $CDCl_3$) for 17



^{13}C NMR (176 MHz, $CDCl_3$) for 17



***N*-1-(5-chlorothiophen-2-yl)-1-(4-methoxyphenyl)propan-2-yl)acetamide (18)**



The **General Procedure A** was followed performing the reaction with *N*-[(5-chloro-2-thienyl)sulfonyl]acetamide (72 mg, 0.3 mmol) and *trans*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (67 mg, 79%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 3.8 Hz, 1H), 6.68 (d, *J* = 3.6 Hz, 1H), 5.30 (d, *J* = 8.5 Hz, 1H), 4.71 – 4.58 (m, 1H), 4.03 (d, *J* = 8.2 Hz, 1H), 3.79 (s, 3H), 1.92 (s, 3H), 1.09 (d, *J* = 6.6 Hz, 3H) ppm

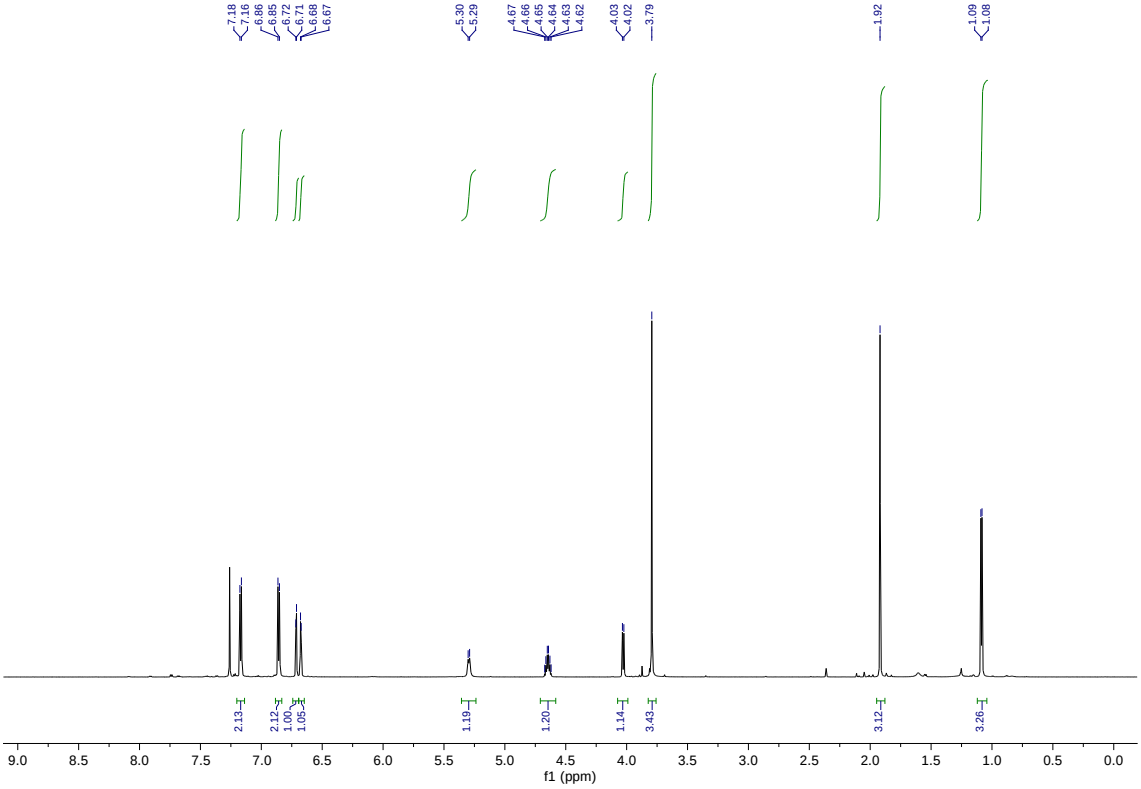
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.3, 158.8, 144.6, 132.4, 129.5, 128.3, 125.6, 124.2, 114.1, 55.2, 51.9, 48.7, 23.6, 19.3 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

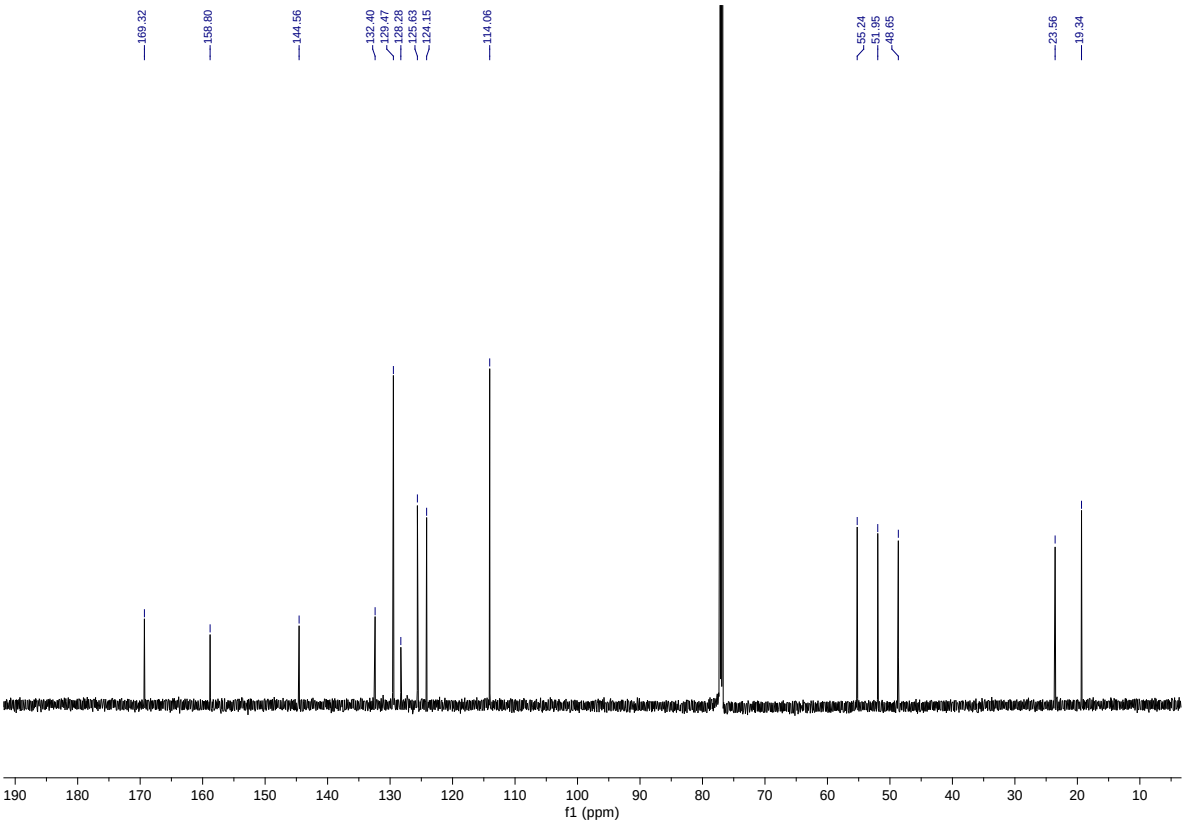
IR (*neat*): 3275, 2985, 1652, 1585, 1511, 1484, 1249, 1034 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{16}H_{18}ClNO_2S$ $[M+H]^+$ 324.0820, found 324.0819.

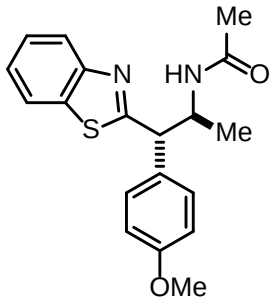
^{1}H NMR (700 MHz, $CDCl_3$) for 18



^{13}C NMR (176 MHz, $CDCl_3$) for 18



***N*-1-(benzothiazol-2-yl)-1-(4-methoxyphenyl)propan-2-yl)acetamide (19)**



The **General Procedure A** was followed performing the reaction with *N*-(1,3-benzothiazol-2-ylsulfonyl)acetamide (77 mg, 0.3 mmol) and *trans*-anethole (54 µL, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (43 mg, 42%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.76 (dq, *J* = 13.0, 6.4 Hz, 1H), 4.48 (d, *J* = 5.9 Hz, 1H), 3.78 (s, 3H), 1.91 (s, 3H), 1.27 (d, *J* = 6.7 Hz, 3H) ppm

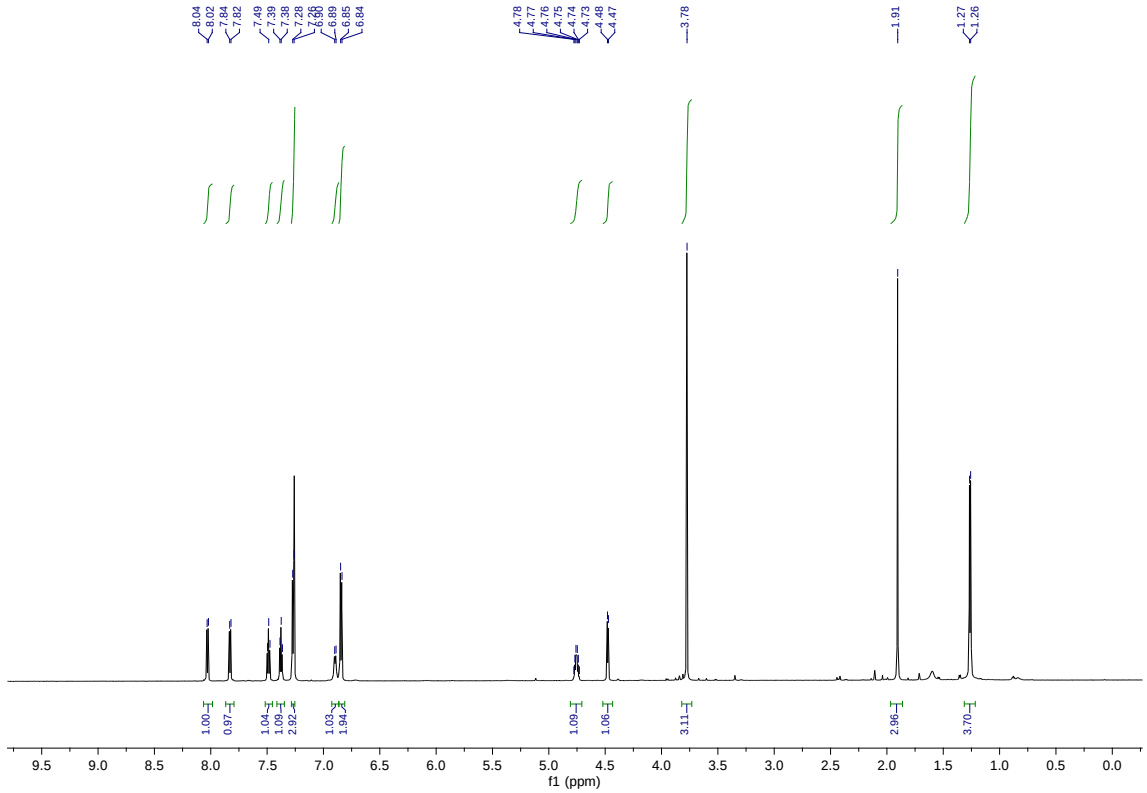
^{13}C NMR (176 MHz, $CDCl_3$): δ = 171.9, 169.4, 159.0, 152.9, 134.9, 130.9, 129.4, 126.1, 125.1, 122.9, 121.6, 114.1, 55.2, 53.8, 49.7, 23.6, 20.1 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

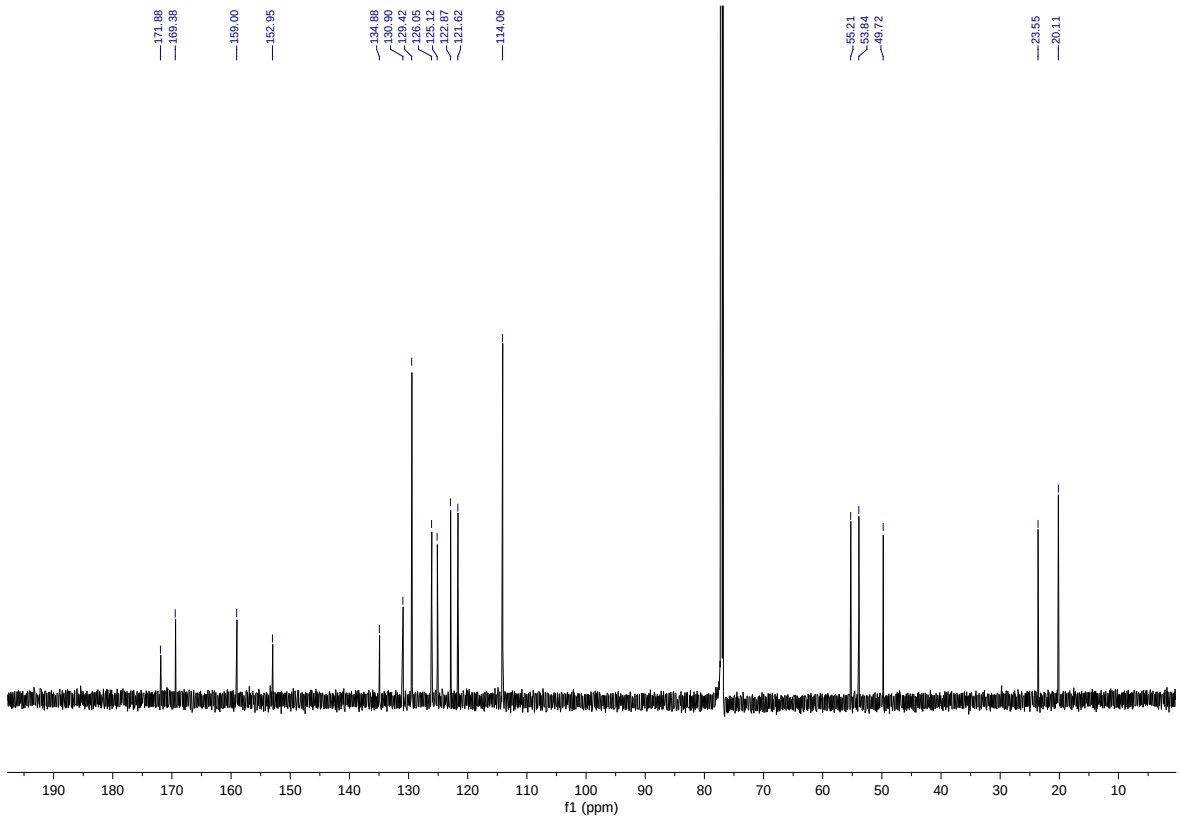
IR (*neat*): 3309, 2924, 1639, 1531, 1515, 1247, 1183, 1038, 832, 757 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{19}H_{20}N_2O_2S$ $[M+H]^+$ 341.1318, found 341.1320.

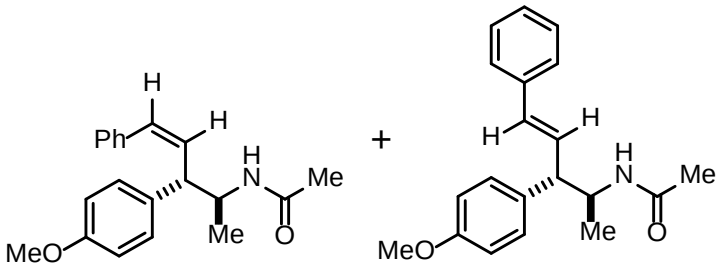
^{1}H NMR (700 MHz, $CDCl_3$) for 19



^{13}C NMR (176 MHz, $CDCl_3$) for 19



***N*-(3-(4-methoxyphenyl)-5-phenylpent-4-en-2-yl)acetamide (20)**



minor ***major***

The **General Procedure A** was followed performing the reaction with N-[(E)-styryl]sulfonylacetamide (20.1 mg, 0.0894 mmol) and *trans*-anethole (13.3 mg, 0.0894 mmol) and purification by flash column chromatography (SiO_2, 30:70 Hex:EtOAc) to furnish the title compound (23 mg, 83%).

Major Diastereomer:

^{1}H NMR (700 MHz, $CDCl_3$) δ 1.94 (s, 3H), 1.06 (d, J=6.6 Hz, 3H), 3.39 (t, J= 8.2 Hz, 3H), 3.80 (s, 3H), 4.43-4.36 (m, 1H), 5.39 (d, J=6.2 Hz, 1H), 6.39 (dd,J = 15.8, 8.1 Hz, 1H), 6.44 (d, J = 15.8 Hz, 1H), 7.18-7.37 (m, 9H) ppm

Minor diastereomer:

^{1}H NMR (700 MHz, $CDCl_3$) δ = 0.94 (d, J = 6.6 Hz, 3H), 1.92 (s, 3H), 3.66 (t, J = 9.83, 1H), 3.80 (s, 3H), 4.27 (m, 1H), 5.16 (d, J=8.45, 1H), 5.99 (t, J=11.2 Hz, 1H), 6.59 (d, J=11.6 Hz, 1H), 7.18-7.37 (m, 9H) ppm

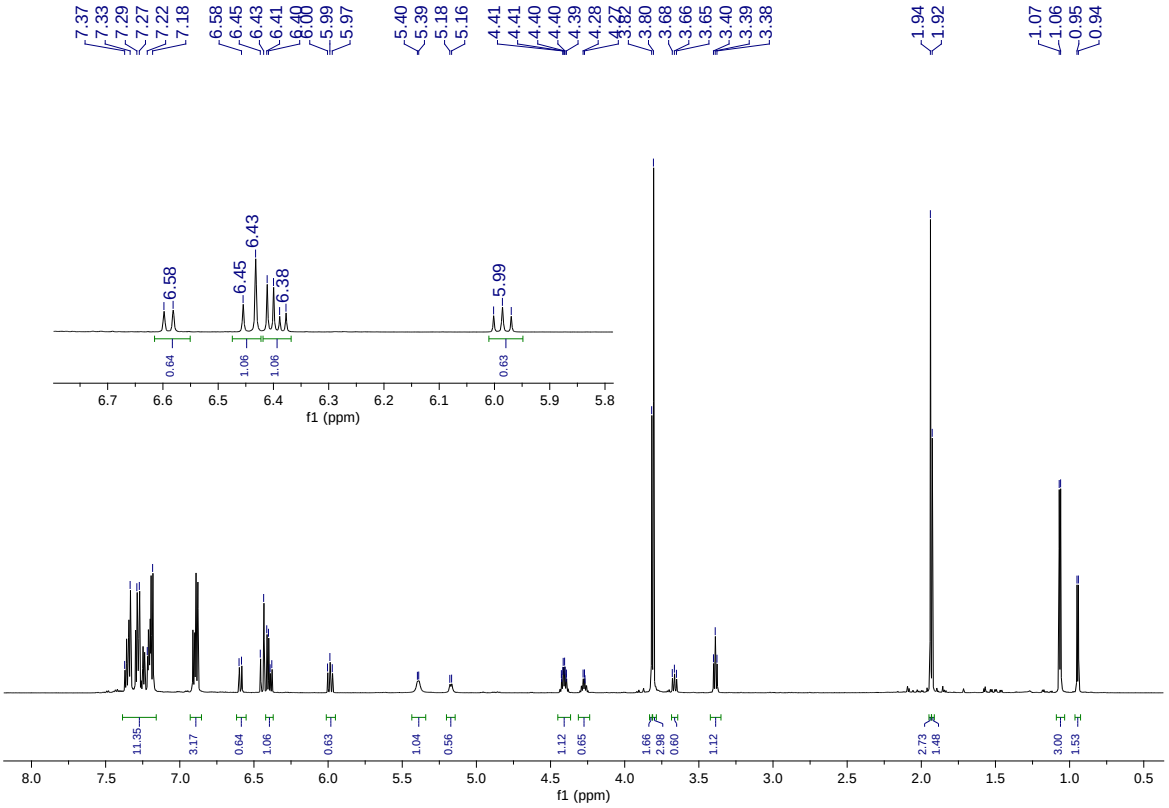
^{13}C NMR (mixture): (176 mHz, $CDCl_3$) δ = 169.4, 158.5, 158.4, 137.1, 137.0, 133.5, 133.0, 133.0, 131.3, 131.0, 130.1, 129.6, 129.1, 128.7, 128.5, 128.3, 127.3, 127.0, 126.2, 114.2, 114.1, 55.3, 54.9, 50.0, 49.5, 49.1, 23.6, 23.5, 18.8, 18.6 ppm

R_f (7:3 – EtOAc:Hex) = 0.5

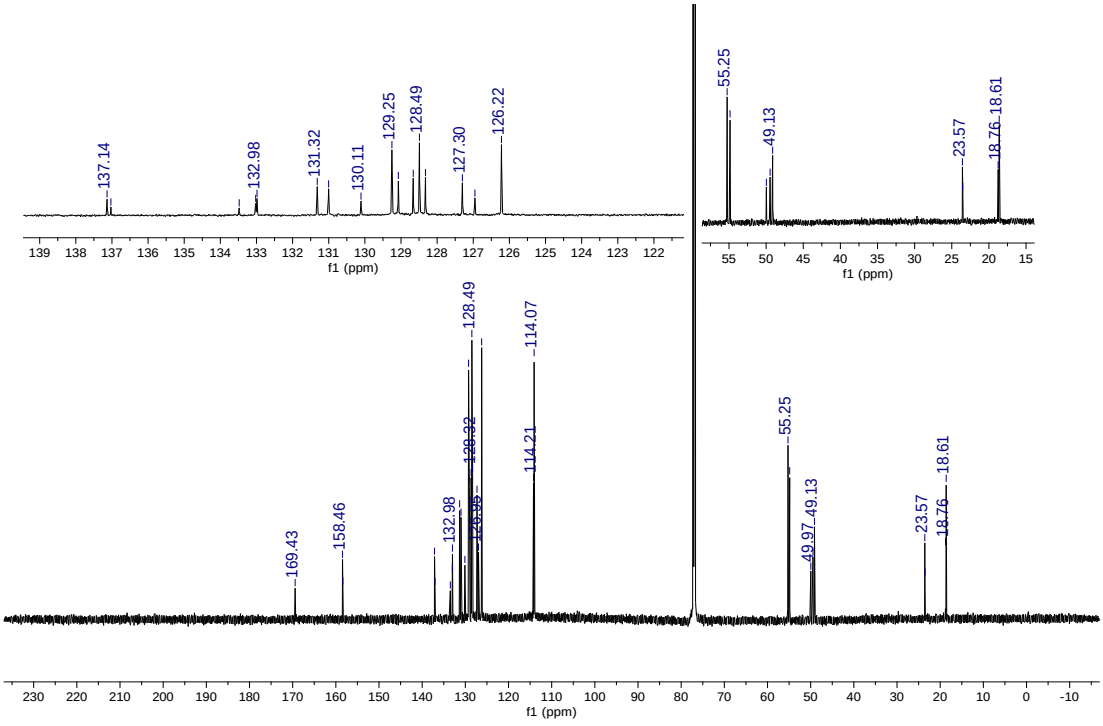
IR (*neat*): 3283.5, 2969.8, 2836.8 2244.7, 1651.1, 1610.5, 1550.3, 1511.6, 1449.9, 1372.4, 1301.8, 1250.8, 1178.4, 1147.5, 1034.9, 964.9, 908.9, 829.3, 732.1, 696.7, 650.4, 624.6, 607.5 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{20}H_{23}NO_2$ $[M+H]^+$ 310.1807, found 310.1805.

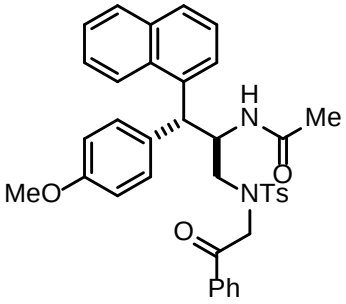
^{1}H NMR (700 MHz, $CDCl_3$) for 20



^{13}C NMR (176 MHz, $CDCl_3$) for 20



***N*-(1-(4-methoxyphenyl)-3-((4-methyl-N-(2-oxo-2-phenylethyl)phenyl)sulfonamido)-1-(naphthalen-1-yl)propan-2-yl)acetamide (21)**



The **General Procedure A** was followed performing the reaction with N-(1-naphthylsulfonyl)acetamide (18.9 mg, 0.0758 mmol) and *N*-[(*E*)-3-(4-methoxyphenyl)allyl]-4-methyl-*N*-phenacyl-benzenesulfonamide (33.0 mg, 0.0758 mmol) and purification by flash column chromatography (SiO_2, 30:70 Hex:EtOAc) to furnish the title compound (10 mg, 28%).

^{1}H NMR (700 MHz, $CDCl_3$) δ = 8.16 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.62 – 7.55 (m, 4H), 7.45 (m, 5H), 7.22 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 5.71 (d, J = 9.2 Hz, 1H, N-H), 5.13 (ddd, J = 20.1, 9.8, 3.8 Hz, 1H), 4.96, 4.81 (ABq, 2H, J_{AB} = 18.9) 4.87 (d, J = 9.9 Hz, 1H), 3.64 (dd, J = 15.1, 10.1 Hz, 1H), 3.31 (dd, J = 15.1, 3.7 Hz, 1H) ppm

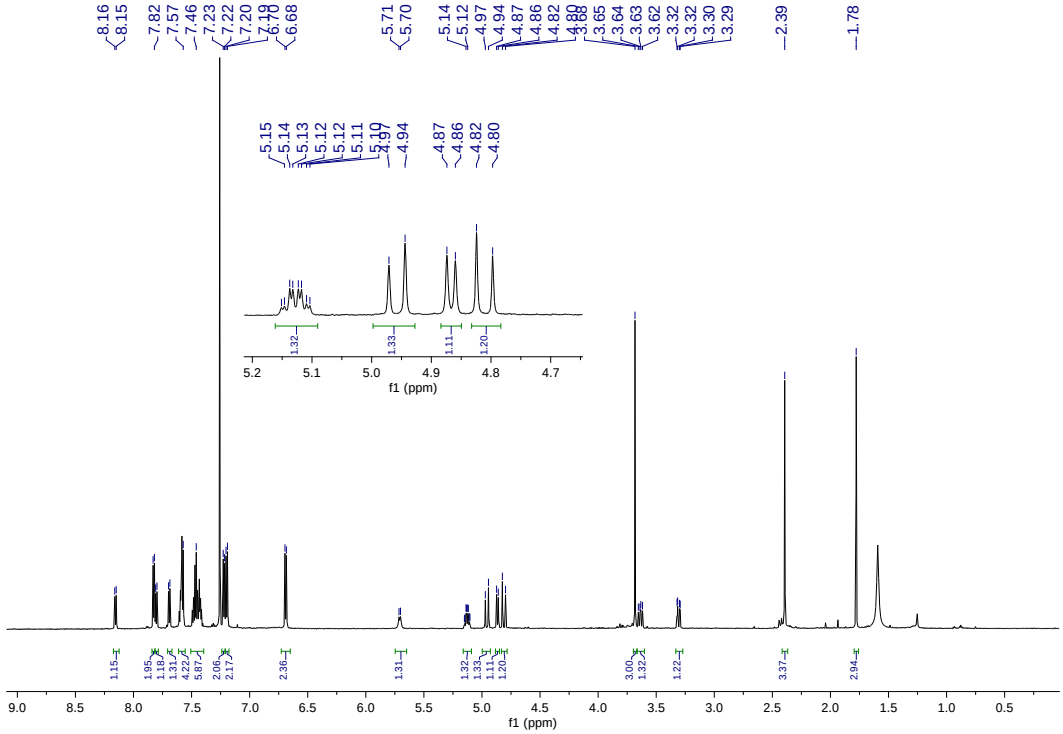
^{13}C NMR (mixture): (176 MHz, $CDCl_3$) δ = 193.7, 171.1, 158.3, 143.4, 137.2, 137.0, 134.8, 134.1, 133.9, 132.8, 131.7, 129.5, 129.1, 128.8, 127.9, 127.4, 127.3, 126.2, 125.5, 125.3, 124.6, 123.1, 114.2, 55.1, 52.4, 50.7, 49.3, 48.2, 23.3, 21.5 ppm

R_f (7:3 – EtOAc:Hex) = 0.5

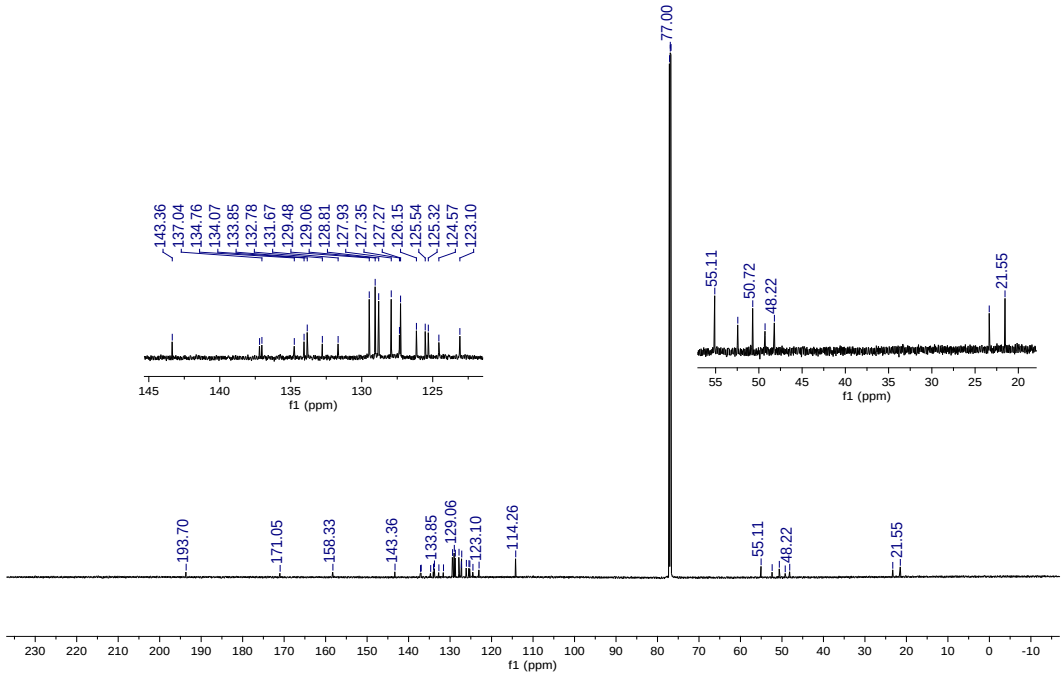
IR (*neat*): 2833, 2790, 2752, 2730, 2709, 1699, 1658, 1597, 1511, 1449, 1333, 1304, 1253, 1226, 1157, 1033, 980, 812, 785 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{37}H_{36}N_2O_5S$ $[M+H]^+$ 621.2423, found 621.2418.

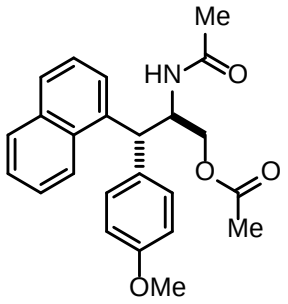
^{1}H NMR (700 MHz, $CDCl_3$) for 21



^{13}C NMR (176 MHz, $CDCl_3$) for 21



2-acetamido-3-(4-methoxyphenyl)-3-(naphthalen-1-yl)propyl acetate (22)



The **General Procedure A** was followed performing the reaction with *N*-(1-naphthylsulfonyl)acetamide (74.8 mg, 0.300 mmol) and [(E)-3-(4-methoxyphenyl)allyl] acetate (74.2 mg, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→50:50 Hex:EtOAc) to furnish the title compound as a white foam (70 mg, 60%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 9.8 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.40 (d, *J* = 9.1 Hz, 1H), 5.21 – 5.08 (m, 1H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.18 (dd, *J* = 11.3, 2.9 Hz, 1H), 3.96 (dd, *J* = 11.3, 4.0 Hz, 1H), 3.71 (s, 3H), 2.15 (s, 3H), 1.76 (s, 3H). ppm

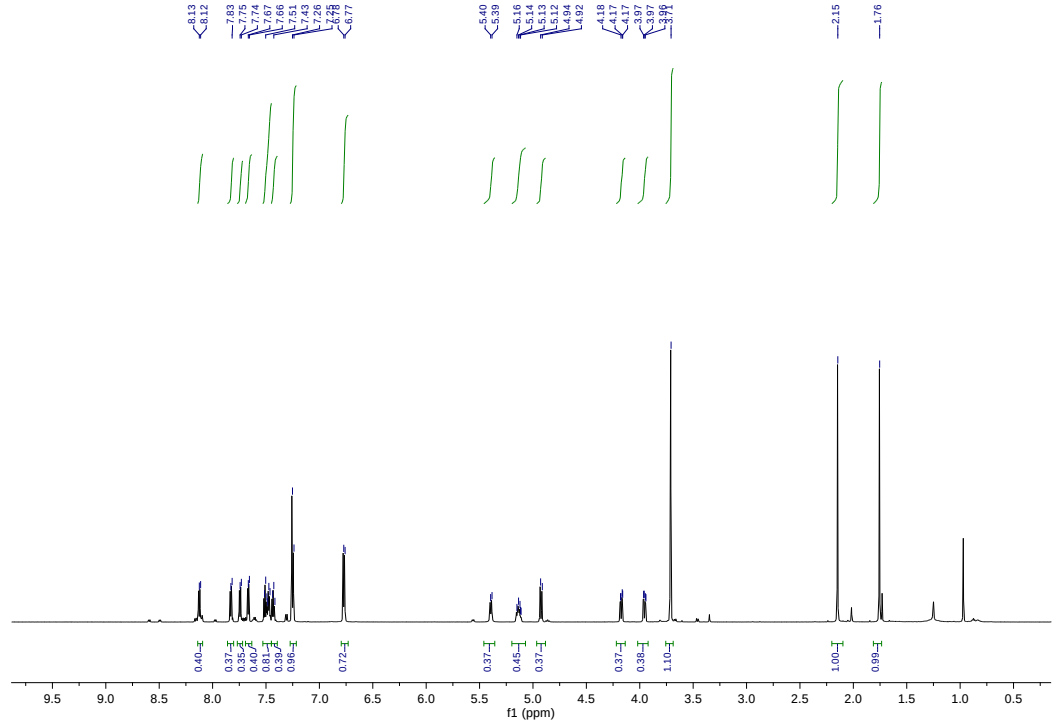
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.8, 158.5, 136.2, 134.2, 132.4, 131.8, 129.3, 129.1, 127.5, 126.1, 125.6, 125.4, 124.1, 123.0, 114.2, 65.1, 55.2, 50.8, 46.5, 23.2, 20.9.ppm

R_f (5:5 – EtOAc:Hex) = 0.1

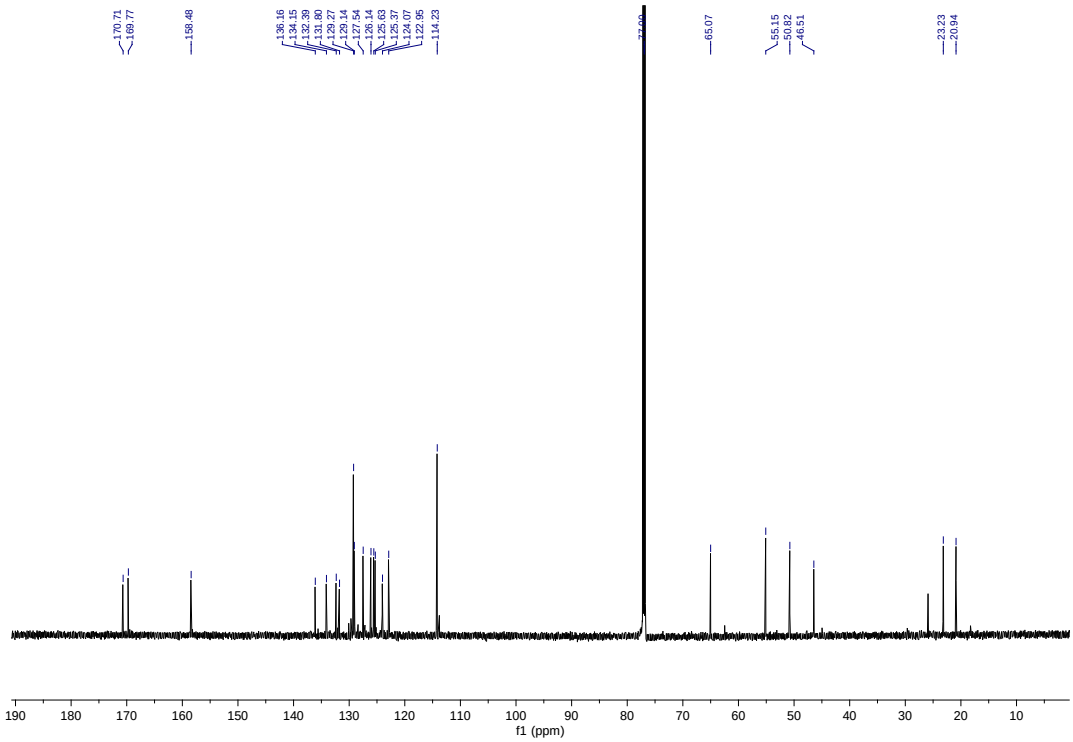
IR (*neat*): 2929, 2752,1737, 1648, 1510, 1369, 1243, 1177, 1032, 783, 728 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{24}H_{25}NO_4$ $[M+H]^+$ 392.1856, found 392.1856.

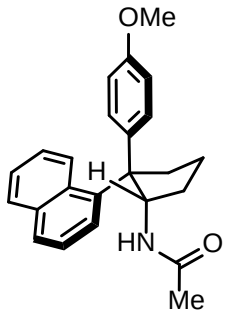
^{1}H NMR (700 MHz, $CDCl_3$) for 22



^{13}C NMR (176 MHz, $CDCl_3$) for 22



***N*-(2-(4-methoxyphenyl)-2-(naphthalen-1-yl)cyclopentyl)acetamide (23)**



The **General Procedure A** was followed performing the reaction with *N*-(1-naphthylsulfonyl)acetamide (75 mg, 0.3 mmol) and 1-(cyclopenten-1-yl)-4-methoxy-benzene (63 mg, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (40 mg, 37%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.47 (dd, *J* = 13.3, 7.3 Hz, 1H), 4.88 (d, *J* = 7.4 Hz, 1H), 3.73 (s, 3H), 2.67 – 2.59 (m, 1H), 2.59 – 2.50 (m, 1H), 2.17 (s, 1H), 1.84 (dd, *J* = 19.9, 10.0 Hz, 1H), 1.78 – 1.66 (m, 1H), 1.60 (dd, *J* = 20.6, 9.5 Hz, 1H), 1.40 (s, 3H) ppm

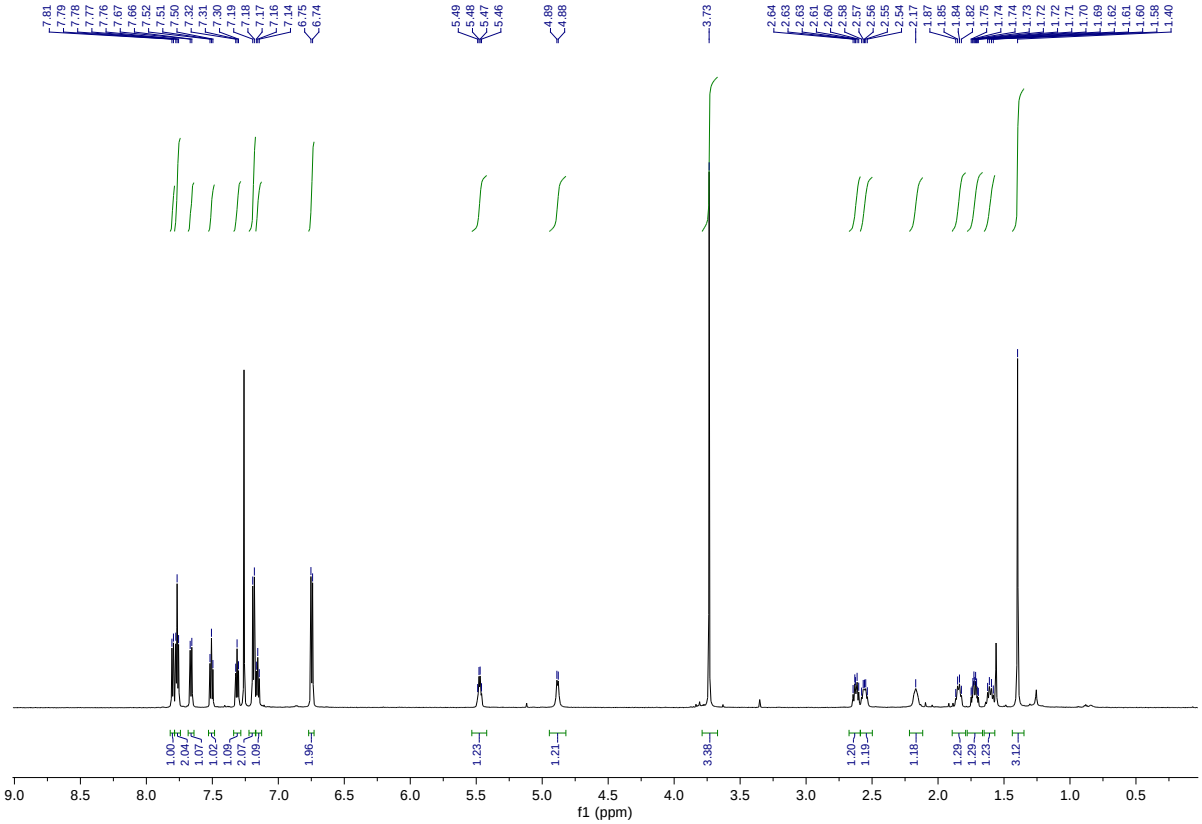
^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.8, 157.6, 139.9, 139.1, 134.7, 131.9, 128.7, 128.6, 127.4, 126.8, 126.0, 125.4, 125.3, 124.7, 113.7, 58.9, 55.1, 54.9, 41.6, 34.0, 23.1, 20.7 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

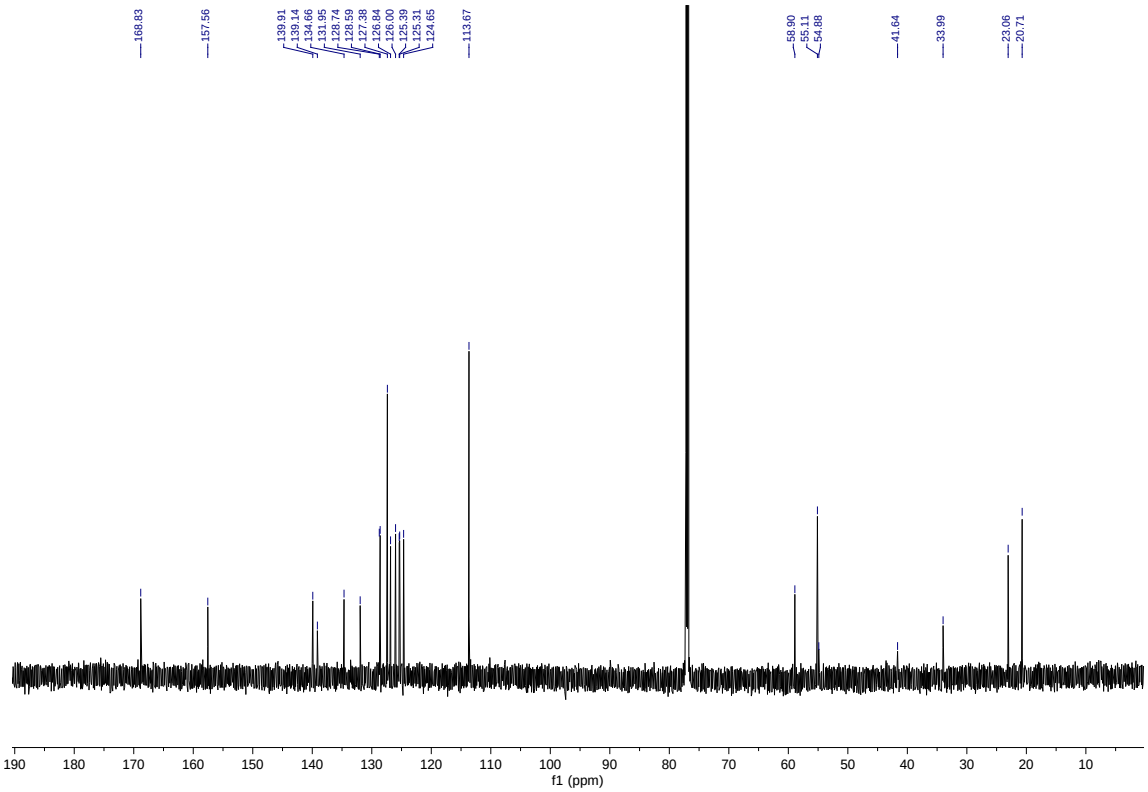
IR (*neat*): 2954, 1642, 1609, 1508, 1372, 1249, 1183, 1034, 827, 776 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{24}H_{25}NO_2$ $[M+H]^+$ 360.1958, found 360.1962.

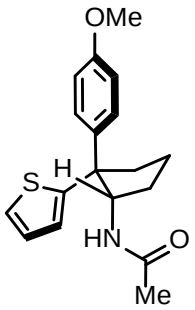
^{1}H NMR (700 MHz, $CDCl_3$) for 23



^{13}C NMR (176 MHz, $CDCl_3$) for 23



***N*-(2-(4-methoxyphenyl)-2-(thiophen-2-yl)cyclopentyl)acetamide (24)**



The **General Procedure A** was followed performing the reaction with *N*-(2-thienylsulfonyl)acetamide (62 mg, 0.3 mmol) and 1-(cyclopenten-1-yl)-4-methoxy-benzene (63 mg, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foamy oil (55 mg, 58%).

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.25 – 7.17 (m, 3H), 6.98 (dd, *J* = 4.8, 3.7 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 3.0 Hz, 1H), 5.36 (d, *J* = 9.4 Hz, 1H), 5.01 (dd, *J* = 17.3, 9.9 Hz, 1H), 3.78 (s, 3H), 2.63 (ddd, *J* = 13.9, 9.5, 4.4 Hz, 1H), 2.25 – 2.13 (m, 2H), 2.03 – 1.94 (m, 1H), 1.92 (s, 3H), 1.81 (ddd, *J* = 17.8, 11.3, 4.5 Hz, 1H), 1.60 – 1.51 (m, 1H) ppm

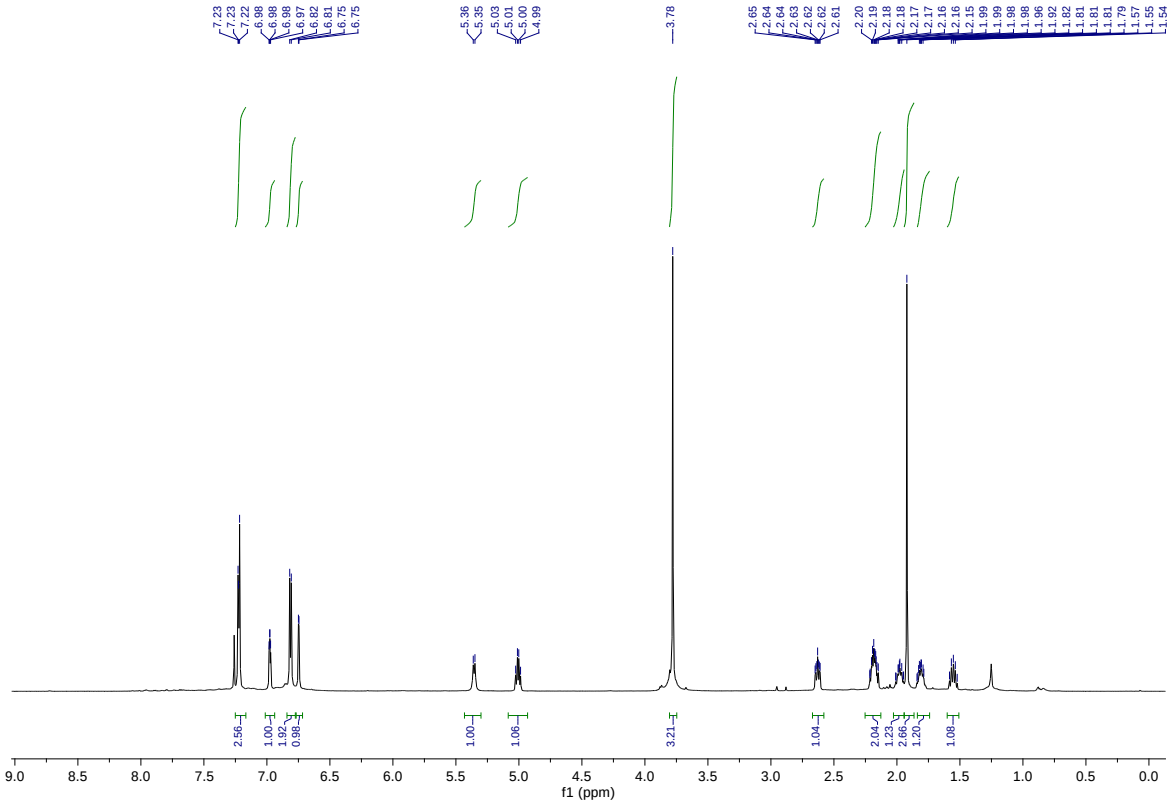
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.3, 158.0, 149.8, 139.4, 128.0, 126.7, 126.1, 124.7, 113.5, 55.1, 54.7, 54.6, 41.3, 30.4, 23.7, 19.5 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

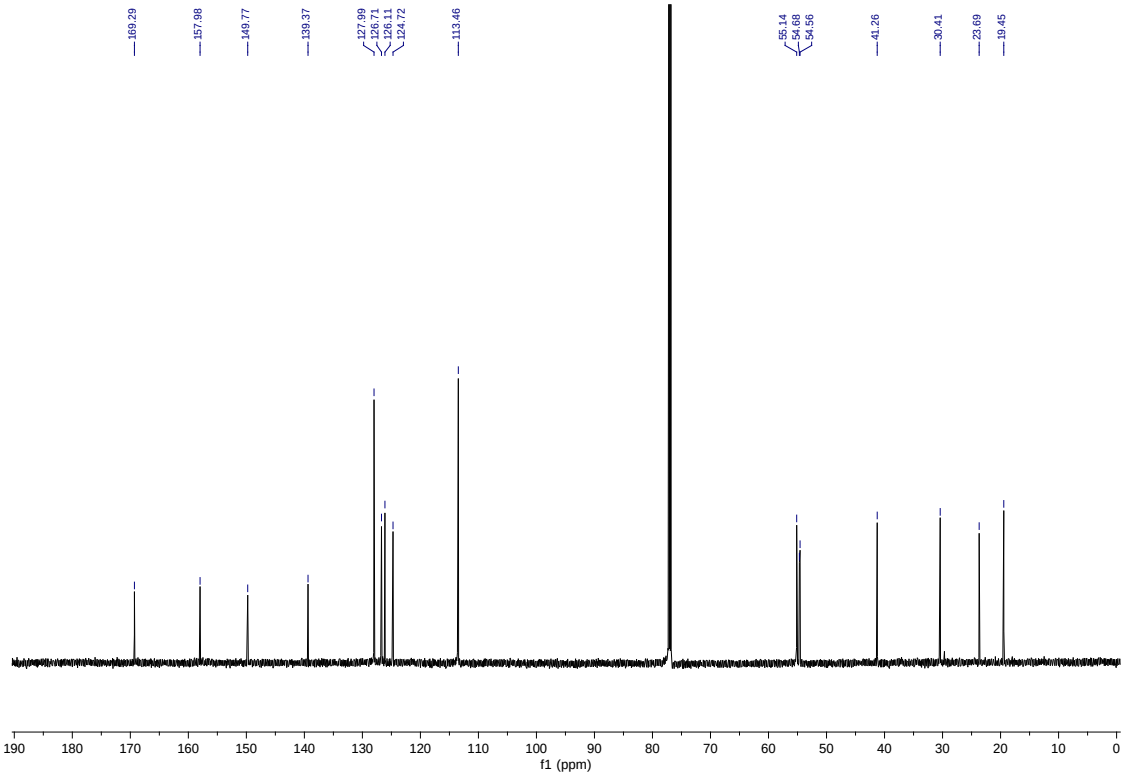
IR (*neat*): 3292, 2927, 1651, 1607, 1510, 1372, 1248, 1181, 1032, 827 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{18}H_{21}NO_2S$ $[M+H]^+$ 316.1366, found 316.1364.

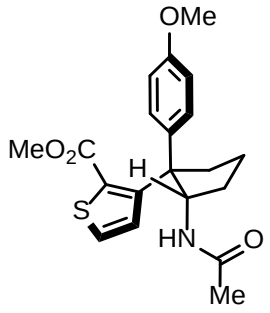
^{1}H NMR (700 MHz, $CDCl_3$) for 24



^{13}C NMR (176 MHz, $CDCl_3$) for 24



Methyl-2-acetamido-1-(4-methoxyphenyl)cyclopentyl)thiophene-2-carboxylate (25)



The **General Procedure A** was followed performing the reaction with methyl 3-(acetylsulfamoyl)thiophene-2-carboxylate (79 mg, 0.3 mmol) and 1-(cyclopenten-1-yl)-4-methoxy-benzene (63 mg, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as an off white foam (62 mg, 55%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 5.2 Hz, 1H), 7.21 (d, *J* = 5.2 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.39 (d, *J* = 6.3 Hz, 1H), 5.03 (q, *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H), 2.44 – 2.40 (bm, 1H), 2.39 – 2.33 (bm, 2H), 1.89 – 1.80 (bm, 4H), 1.77 – 1.67 (bm, 1H), 1.67 – 1.55 (bm, 2H) ppm

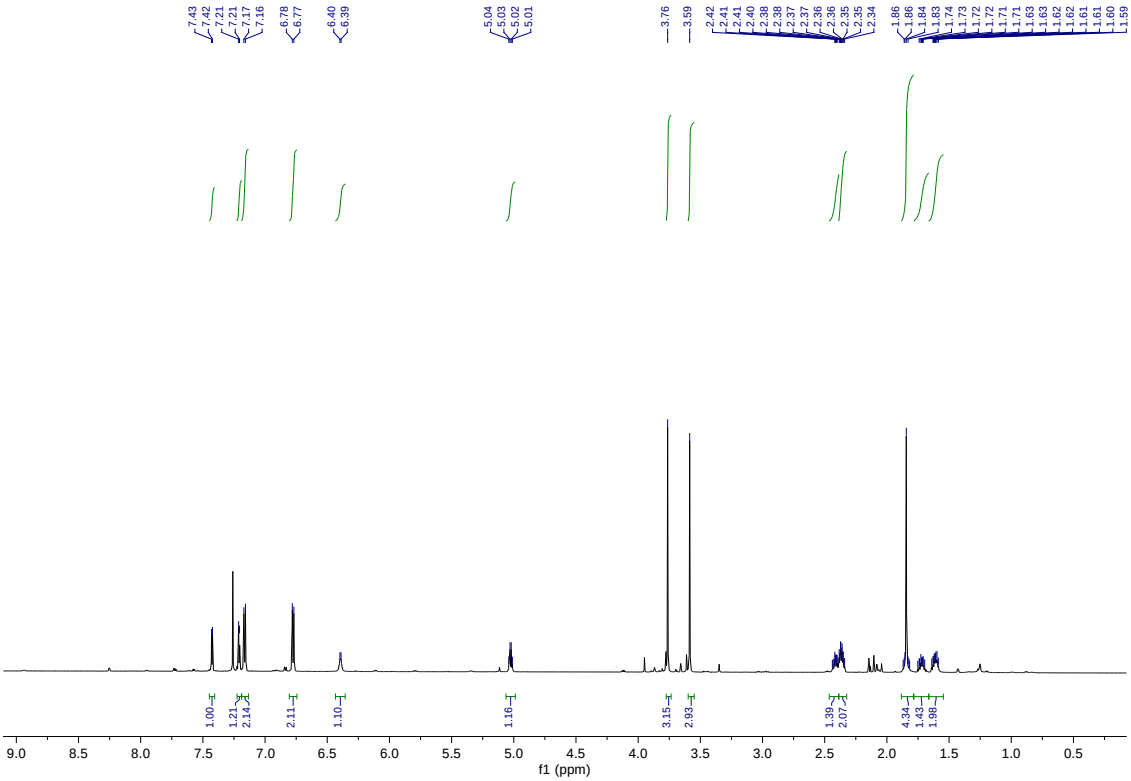
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.8, 163.3, 157.6, 150.4, 137.5, 131.2, 129.0, 128.4, 127.8, 113.2, 56.5, 56.3, 55.2, 52.4, 39.9, 31.0, 23.4, 20.6 ppm

R_f (5:5 – EtOAc:Hex) = 0.2

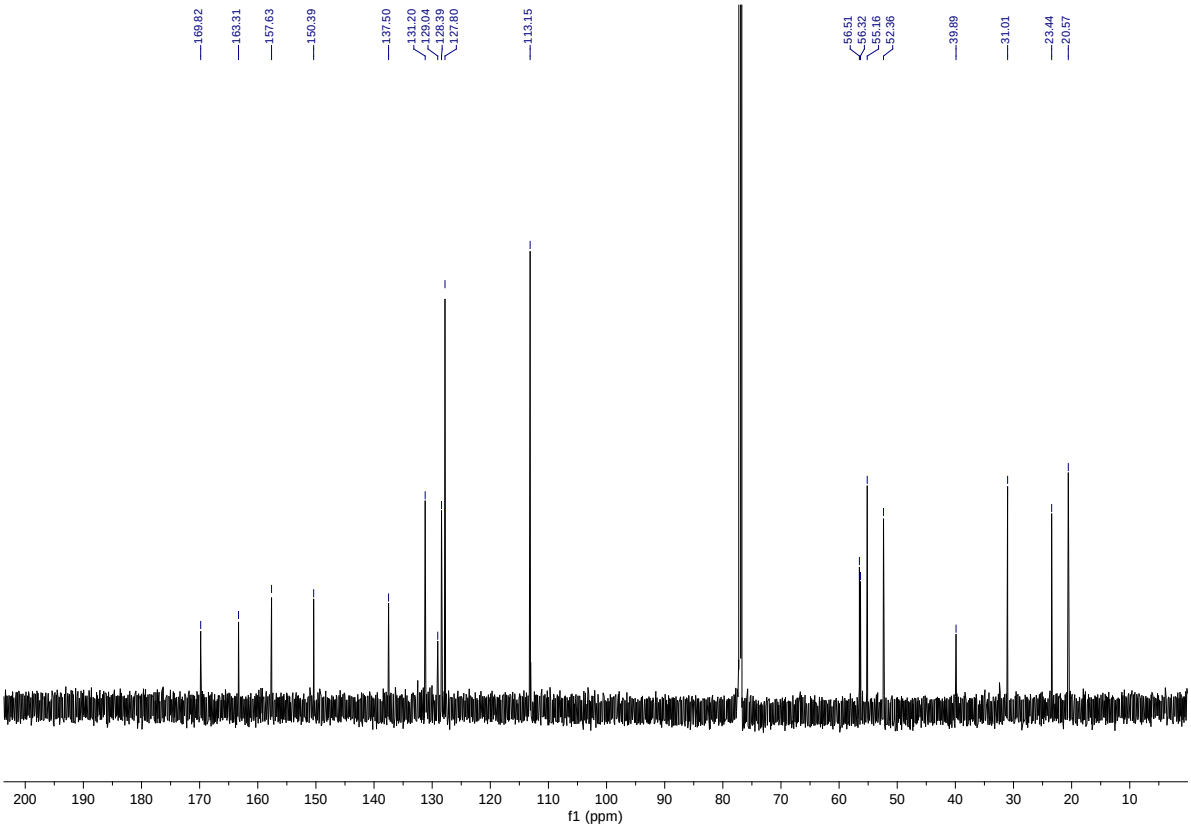
IR (*neat*): 3290, 2949, 1719, 1649, 1510, 1434, 1371, 1246, 1182, 1031, 780 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{20}H_{23}NO_4S$ $[M+H]^+$ 374.1421, found 374.1428.

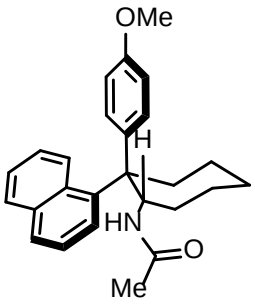
^{1}H NMR (700 MHz, $CDCl_3$) for 25



^{13}C NMR (176 MHz, $CDCl_3$) for 25



***N*-(4-methoxyphenyl)-2-(naphthalen-1-yl)cycloheptyl)acetamide (26)**



The **General Procedure A** was followed performing the reaction with *N*-(1-naphthylsulfonyl)acetamide (75 mg, 0.3 mmol) and 1-(4-methoxyphenyl)cycloheptene (73 mg, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (36 mg, 31%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.80 – 7.72 (m, 2H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.04 (m, 3H), 6.73 (d, *J* = 8.4 Hz, 2H), 5.22 (bs, 1H), 5.15 (bs, 1H), 3.74 (s, 3H), 2.61 (dd, *J* = 15.0, 9.2 Hz, 1H), 2.51 – 2.40 (m, 1H), 2.36 (d, *J* = 22.7 Hz, 1H), 2.21 – 2.12 (m, 1H), 1.90 (s, 1H), 1.75 (dd, *J* = 14.2, 6.6 Hz, 1H), 1.71 – 1.61 (m, 1H), 1.56 (bs, 2H), 1.49 (dd, *J* = 12.7, 8.6 Hz, 1H), 1.35 (s, 3H) ppm

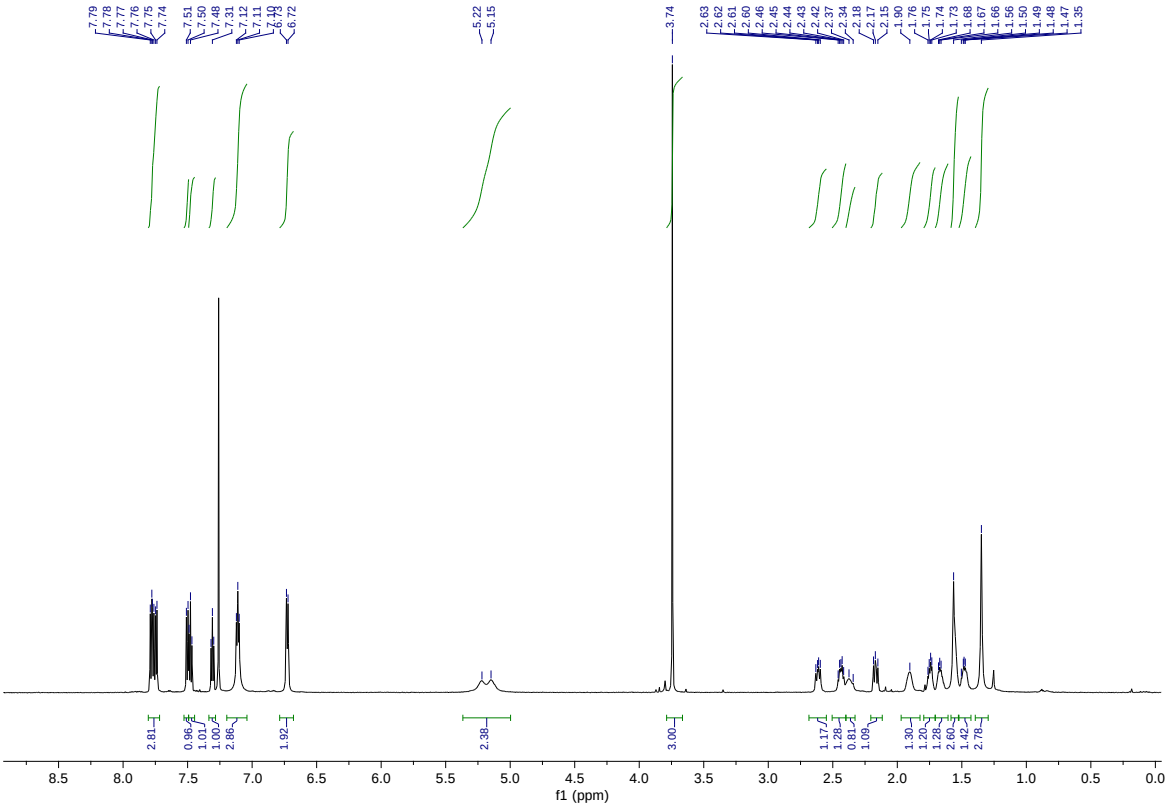
^{13}C NMR (176 MHz, $CDCl_3$): δ = 168.5, 157.4, 142.1, 140.9, 135.0, 132.3, 128.8, 128.5, 127.4, 125.6, 125.2, 125.1, 124.2, 113.6, 56.9, 55.1, 55.0, 42.1, 32.0, 29.7, 24.8, 24.6, 22.8 ppm

R_f (5:5 – EtOAc:Hex) = 0.1

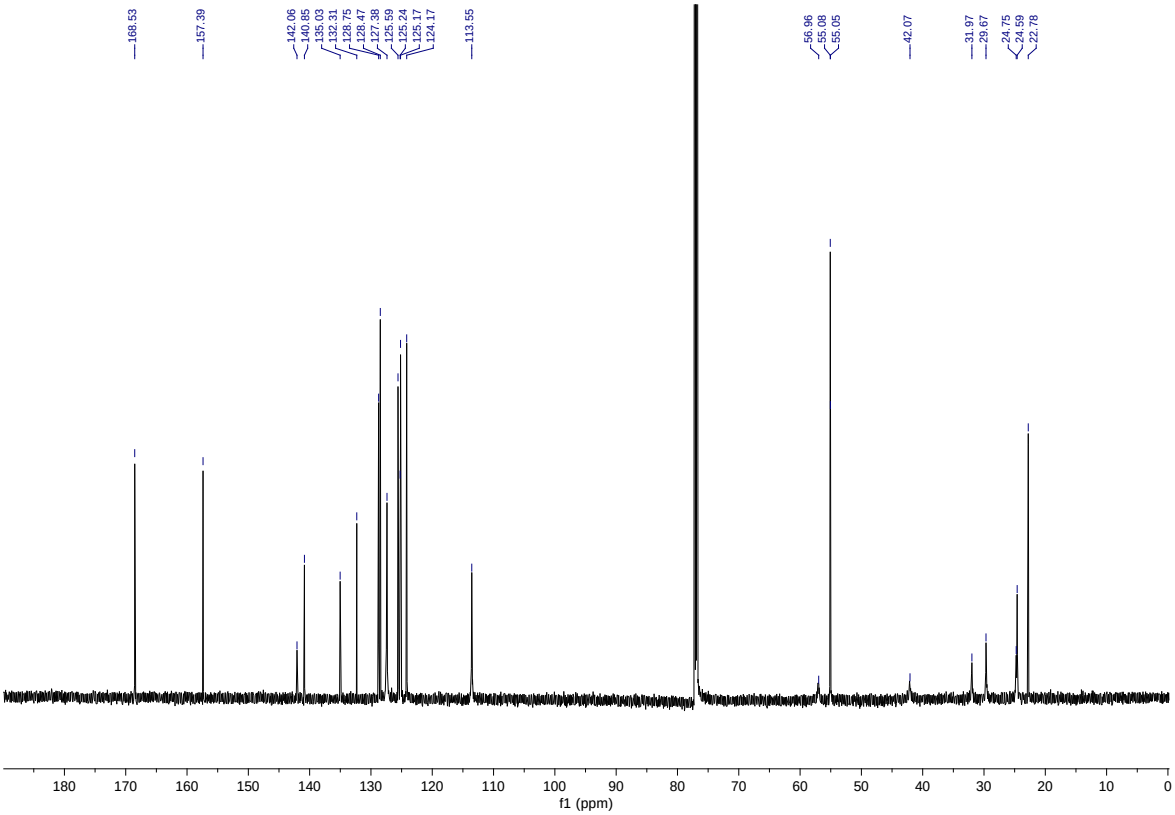
IR (*neat*): 2928, 2859, 1650, 1608, 1508, 1462, 1247, 1183, 726 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{26}H_{29}NO_2$ $[M+H]^+$ 388.2271, found 388.2268.

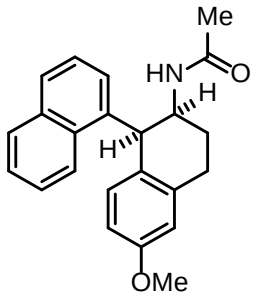
^{1}H NMR (700 MHz, $CDCl_3$) for 26



^{13}C NMR (176 MHz, $CDCl_3$) for 26



_N_-6-methoxy-1,2,3,4-tetrahydro-[1,1'-binaphthalen]-2-yl)acetamide (27)



The **General Procedure A** was followed performing the reaction with *N*-(1-naphthylsulfonyl)acetamide (75 mg, 0.3 mmol) and 7-methoxy-1,2-dihydronaphthalene (57.7 mg, 0.36 mmol) and purification by flash column chromatography (SiO_2, 90:10→30:70 Hex:EtOAc) to furnish the title compound as a light yellow foam (29 mg, 28%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 6.9 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.73 (d, *J* = 1.8 Hz, 1H), 6.63 (dd, *J* = 8.5, 2.2 Hz, 1H), 5.38 (d, *J* = 2.5 Hz, 1H), 4.77 (bs, 2H), 3.80 (s, 3H), 3.17 – 2.98 (m, 2H), 1.99 (ddd, *J* = 24.0, 12.0, 5.9 Hz, 1H), 1.74 (dd, *J* = 12.3, 5.9 Hz, 1H), 1.54 (s, 3H) ppm

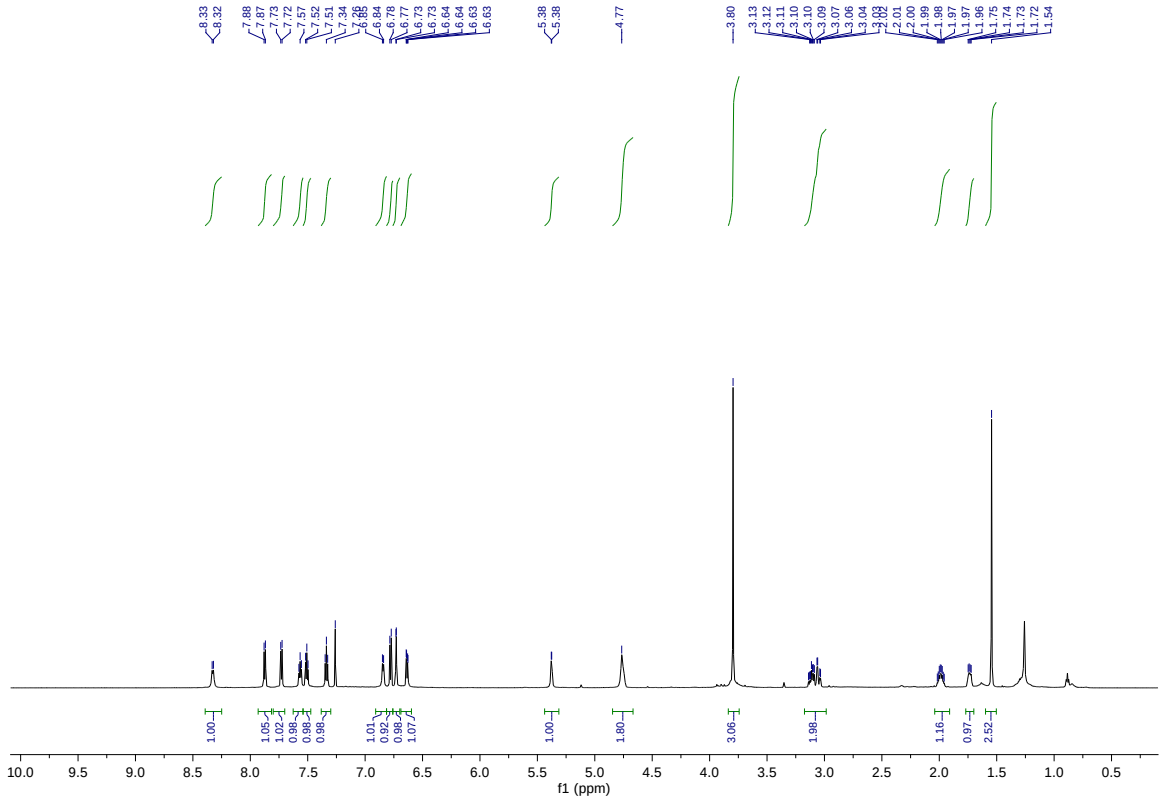
^{13}C NMR (176 MHz, $CDCl_3$): δ = 169.5 (s), 158.1 (s), 138.6 (s), 137.1 (s), 133.5 (s), 133.3 (s), 131.9 (s), 130.6 (s), 129.7 (s), 128.7 (s), 127.2 (s), 126.1 (s), 125.6 (s), 125.1 (s), 123.7 (s), 113.1 (s), 112.6 (s), 55.2 (s), 48.4 (s), 29.7 (s), 28.8 (s), 24.0 (s), 23.4 (s) ppm

R_f (5:5 – EtOAc:Hex) = 0.1

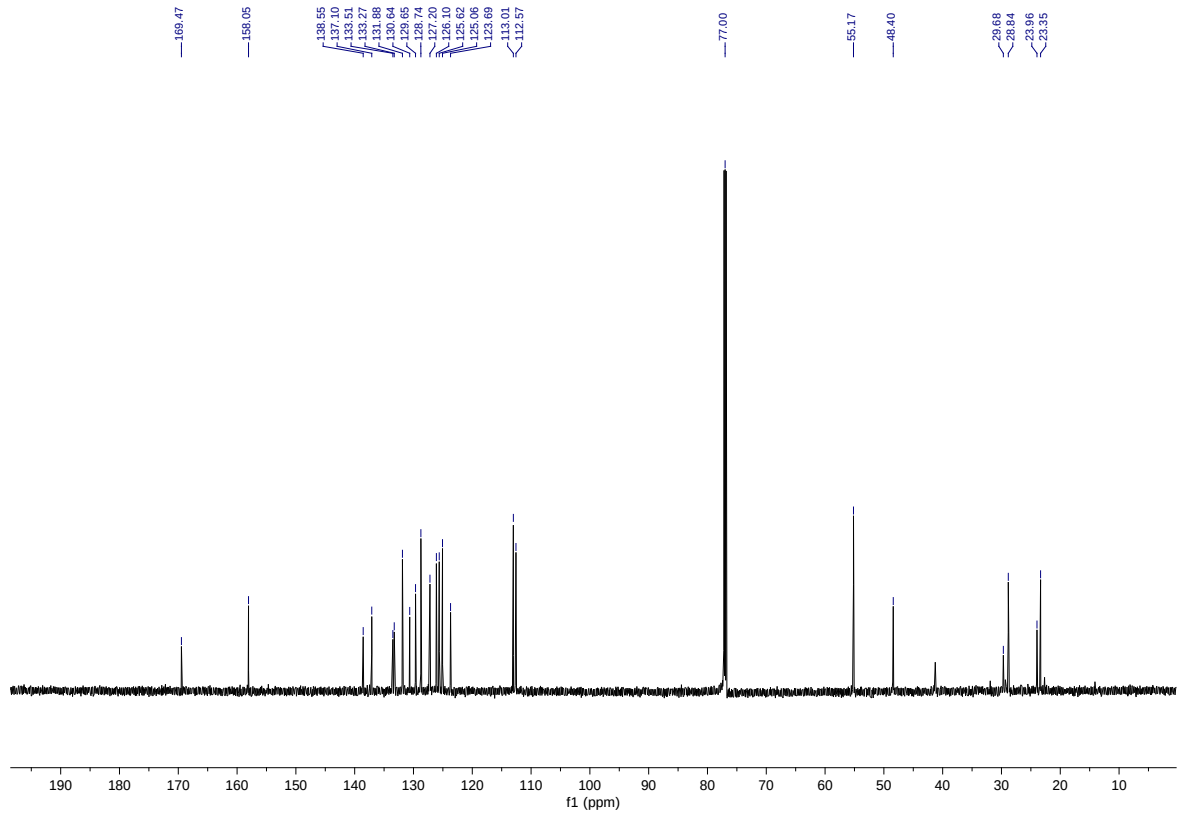
IR (*neat*): 2923, 2851, 1651, 1609, 1499, 1268, 1229, 1038, 907, 726, 647 cm^{-1}

HRMS (ESI+) *m/z* calculated for $C_{23}H_{23}NO_2$ $[M+H]^+$ 346.1802, found 346.1803.

^{1}H NMR (700 MHz, $CDCl_3$) for 27



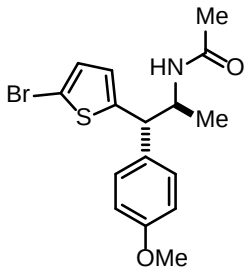
^{13}C NMR (176 MHz, $CDCl_3$) for 27

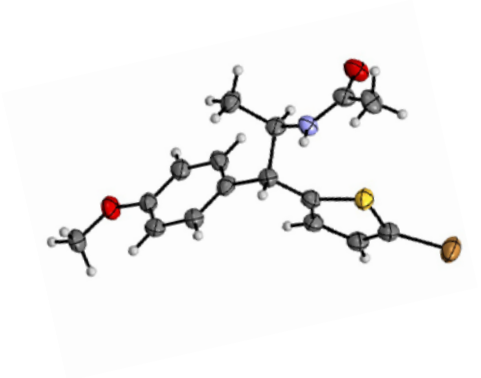


X-Ray Crystallography Data

Crystallographic data for:

***N*-1-(5-bromothiophen-2-yl)-1-(4-methoxyphenyl)propan-2-yl)acetamide (15)**





Structural figure of compound **15**, with 50% probability ellipsoids.

Accession Number

The structure of **15** has been deposited in the Cambridge Crystallographic Data Center under accession number CCDC: 1572215.

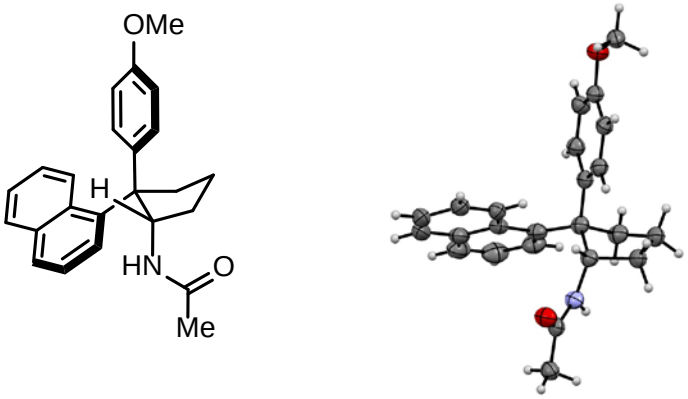
Structure Determination

Colorless plates of **15** were grown from by diethyl ether/pentane vapor diffusion at 22 °C. A crystal of dimensions 0.04 x 0.02 x 0.01 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω The exposure times were 15 sec. for the low angle images, 80 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 24869 reflections to a maximum 2θ value of 138.84° of which 3075 were independent and 2171 were greater than 2σ(I). The final cell constants (Table S4) were based on the xyz centroids of 3709 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package (*52*), using the space group P2(1)/c with Z = 4 for the formula $C_{16}H_{18}NO_2SBr$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of refined and idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0599 and wR2 = 0.1512 [based on I > 2sigma(I)], R1 = 0.0894 and wR2 = 0.1732 for all data (*53, 54*). Additional details are presented in Table S4. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table S4. Crystal data and structure refinement.

Empirical formula	C16 H18 Br N O2 S
Formula weight	368.28
Temperature	85(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 16.2401(10) A alpha = 90 deg. b = 10.9158(5) A beta = 101.798(7) deg. c = 9.5079(6) A gamma = 90 deg.
Volume	1649.89(17) A^3
Z, Calculated density	4, 1.483 Mg/m^3
Absorption coefficient	4.607 mm^-1
F(000)	752
Crystal size	0.040 x 0.020 x 0.010 mm
Theta range for data collection	2.780 to 69.421 deg.
Limiting indices	-19<=h<=19, -13<=k<=13, -11<=l<=11
Reflections collected / unique	24869 / 3075 [R(int) = 0.1138]
Completeness to theta	= 67.684 99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.81698
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3075 / 0 / 197
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0599, wR2 = 0.1512
R indices (all data)	R1 = 0.0894, wR2 = 0.1732
Extinction coefficient	n/a
Largest diff. peak and hole	1.452 and -0.856 e.A^-3

***N*-(2-(4-methoxyphenyl)-2-(naphthalen-1 yl)cyclopentyl)acetamide (23)**



Structural figure of compound **23**, with 50% probability ellipsoids

Accession Number

The structure of **23** has been deposited in the Cambridge Crystallographic Data Center under accession number CCDC: 1572214.

Structure Determination

Colorless blocks of **23** were grown by vapor diffusion of diethyl ether into a pentane solution of the compound at 22 ° C. A crystal of dimensions 0.10 x 0.10 x 0.09 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω The exposure times were 1 sec. for the low angle images, 4 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 28115 reflections to a maximum 2θ value of 138.62° of which 6933 were independent and 5766 were greater than 2σ(I). The final cell constants (Table S5) were based on the xyz centroids of 8542 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package (*52*), using the space group P1bar with Z = 4 for the formula $C_{24}H_{25}NO_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of refined and idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0537 and wR2 = 0.1504 [based on I > 2sigma(I)], R1 = 0.0634 and wR2 = 0.1646 for all data (*53, 54*). Additional details are presented in Table S5. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table S5. Crystal data and structure refinement for **23**.

Empirical formula	C24 H25 N O2
Formula weight	359.45
Temperature	85(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.3165(6) A alpha = 88.002(3) deg. b = 12.6453(6) A beta = 76.578(4) deg. c = 16.9508(5) A gamma = 83.003(5) deg.
Volume	1927.92(17) A^3
Z, Calculated density	4, 1.238 Mg/m^3
Absorption coefficient	0.613 mm^-1
F(000)	768
Crystal size	0.100 x 0.100 x 0.090 mm
Theta range for data collection	2.680 to 69.309 deg.
Limiting indices	-11<=h<=11, -15<=k<=15, -20<=l<=20
Reflections collected / unique	28115 / 6933 [R(int) = 0.0461]
Completeness to theta	= 67.684 97.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.76174
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6933 / 0 / 500
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.1504
R indices (all data)	R1 = 0.0634, wR2 = 0.1646
Extinction coefficient	0.0040(5)
Largest diff. peak and hole	0.273 and -0.248 e.A^-3

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