Reductive Asymmetric Aza-Mislow-Evans Rearrangement by 1,3,2-Diazaphospholene Catalysis

Guoting Zhang,[a] and Nicolai Cramer*[a]

[a] Dr. G. Zhang, Prof. Dr. N. Cramer
Institute of Chemical Sciences and Engineering (ISIC),
EPFL SB ISIC LCSA, BCH 4305
1015 Lausanne (Swizerland)
E-mail: nicolai.cramer@epfl.ch
Homepage: https://www.epfl.ch/labs/lcsa

Abstract: 1,3,2-diazaphospholene hydrides (DAP-H) emerged as a nucleophilic main-group hydride able to promote smooth conjugate reduction of polarized double bonds. The transiently formed phosphorus-bound enolate provides a potential platform for reductive α-functionalizations. In this respect, asymmetric C-heteroatom bond forming processes are synthetically appealing but remain so far elusive. We report a 1,3,2-diazaphospholene-catalyzed three-step cascade transformation of α,β-unsaturated *N*-sulfinyl acrylamides comprised of a conjugate reduction, [2,3]-sigmatropic aza-Mislow-Evans rearrangement and subsequent S-O bond reductive cleavage. The obtained enantio-enriched α-hydroxyl amides are synthetically highly valuable and formed in good yields and excellent enantiospecificity. The stereo-defined P-bound *N,O*-ketene aminal ensures an excellent transfer of chirality from the sulfur stereocenter to α-carbon atom. The transformation operates under mild conditions at ambient temperature. Moreover, DAP hydrides are found to be competent reductants for the cleavage of the formed sulfenate ester, thus eliminating the required additional step like in traditional Mislow-Evans processes.

Emerging as an alternative to transition-metals, main-group catalysis underwent great progress over the past decades.[1] In this respect, *P*-hydrido-1,3,2-diazaphospholenes (DAP-H) have received considerable attention since their initial discovery[2] linked to their unique hydridicity[3] – an umpolung of the P-H polarity, a feature attributable to the 6π delocalization effect of their heterocyclic core.[4] Synthetic applications of DAP-H are dominated by stoichiometric or catalytic hydride transfer processes across a broad range of polarized unsaturated compounds,[5] including carbonyls,[6] imines,[7] N=N bonds,[8] CO_2,[9] and pyridines,[10] as well as Michael acceptors[11]. Particularly, DAP-catalyzed conjugate reduction of enoates leads to a versatile phosphorus enol intermediate, providing an attractive platform for consecutive α-functionalizations (Scheme 1a). Very few of synthetic applications involving reductive α-functionalization strategy have been reported. Kinjo disclosed a C-C bond formation of the phosphorus enols with nitriles after phosphor-boron exchange.[11] We recently reported a highly selective 1,4-reduction of allyl acrylates triggering Ireland-Claisen rearrangement to form α-allyl carboxylic acids in a diastereoselective manner.[12] While DAP-catalysis emerged as a promising tool for some enantioselective hydride-transfer reactions recently,[13] asymmetric reductive α-functionalization strategy, especially to create chiral carbon-heteroatom bonds remains elusive and challenging.

Enantiopure α-hydroxyl amides are prominent motifs displayed in natural products and biologically active compounds e.g. vitamin B_5,[14] aeruginopeptin 228A,[15] and fulvanine A[16] (Figure 1). There is significant interest in the development of efficient synthetic methods to access such chiral α-hydroxyamides.[17] In this respect, the creation of the oxygen stereocenter can be built by an enantiospecific rearrangement process. The Mislow-Evans reaction is a reversible [2,3]-sigmatropic rearrangement of allylic sulfoxide to sulfenate ester, typically shifted toward the more thermodynamically stable sulfoxide (Scheme 1b).[18] In the presence of an additional external reductant, such as thiophiles or phosphites, reductive cleavage of the sulfenate esters provides allylic alcohols. The concerted rearrangement generally proceeds with good diastereo control. The stereogenic center of the sulfur atom is transmitted to the carbon atom through a five-membered transition state. Lu reported an aza-Mislow-Evans rearrangement of *O*-silyl *N*-sulfinyl *N,O*-ketene acetals generated from chiral *tert*-butyl sulfinamides yielding α-sulfenyloxylamides.[19] The pivotal silylation step requires stoichiometric amounts of a strong base and cryogenic temperature in order to mitigate the degradation of sensitive sulfinamides under basic conditions.[20]

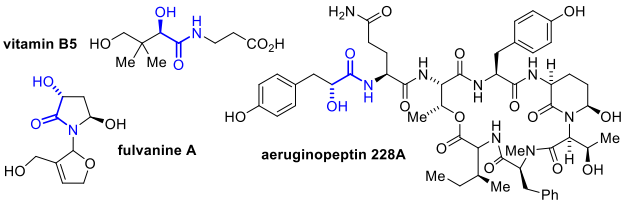
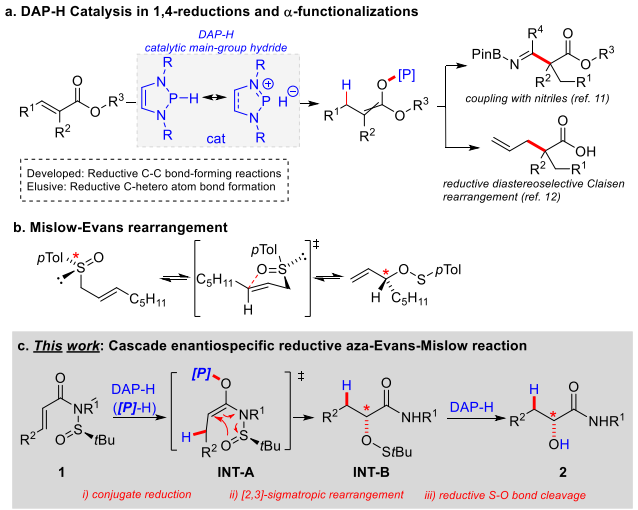


Figure 1. Natural products containing chiral α-hydroxy amides.

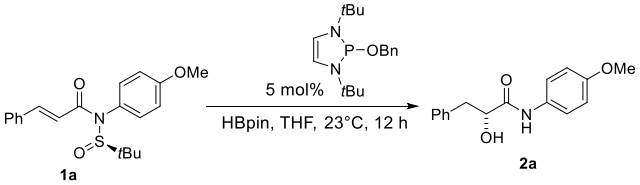
We envisioned an all-in-one three-step cascade reductive *aza*-Mislow-Evans protocol exploiting 1,3,2-diazaphospholenes catalysis operating under mild, base-free conditions at ambient temperature (Scheme 1c). The sequence is triggered by an initial 1,4-hydride transfer from the catalytically generated DAP-H, which would result in phosphorus enol species **INT-A**. The high polarization of **INT-A** would readily trigger the [2,3]-sigmatropic rearrangement at low temperature. In turn, product **INT-B** will be a suitable substrate for DAP-H inducing directly reductive cleavage of S-O bond to release target α-hydroxyl amide **2**. Therefore, *without any* extra operational step for the reduction, the targeted enantioenriched α-hydroxyl amides **2** are obtained. We believed that such cascade process would provide a facile and convenient approach to access chiral α-hydroxy amides.



Scheme 1. DAP-catalyzed reductive cascade aza-Mislow-Evans reaction for the synthesis of chiral α-hydroxyamides.

We investigated the feasibility of the enantiospecific DAP-catalyzed reductive aza-Mislow-Evans rearrangement using (*R*)-*N*-(*tert*-butylsulfinyl)-*N*-(4-methoxyphenyl) cinnamamide (**1a**) as the model substrate (Table 1). After optimization of different variables and conditions, exposure of **1a** to 5 mol% DAP-OBn pre-catalyst and 2.1 equivalents of pinacolborane in THF at ambient temperature smoothly induced the reductive [2,3]-rearrangement (Entry 1). The corresponding α-hydroxy amide **2a** was formed in 79% yield and an enantiomeric ratio of 94:6. Conveniently, the employed reaction conditions directly cleaved the S-O bond of the sulfenate intermediate. The use of one equivalent of pinacolborane drastically reduces the yield of **2a** and is accompanied by substantial amounts α-sulfenyloxy carboxamide (Table 1, Entry 2). This observation is an evidence of the hypothesized dual role of the DAP-H and indicates that 2 equivalents of reductants is the theoretically required amount. A lower reaction temperature (0 ºC) only slightly increased the enantiospecificity at the expense a significantly reduced yield (Entry 3). An increase of the reaction temperature decreased the enantiospecificity (Entry 4). The evaluation of additional terminal reductant revealed that both catecholborane and phenylsilane boost the enantiomeric ratio of **1a** to 99:1 (Entries 5-6). However, this advantage was accompanied by lower yields. Diphenylsilane was not a competent terminal reductant for this reaction (Entry 7). Control experiments clearly confirmed that necessity of both DAP catalyst and reductant for process (Entries 8 and 9).

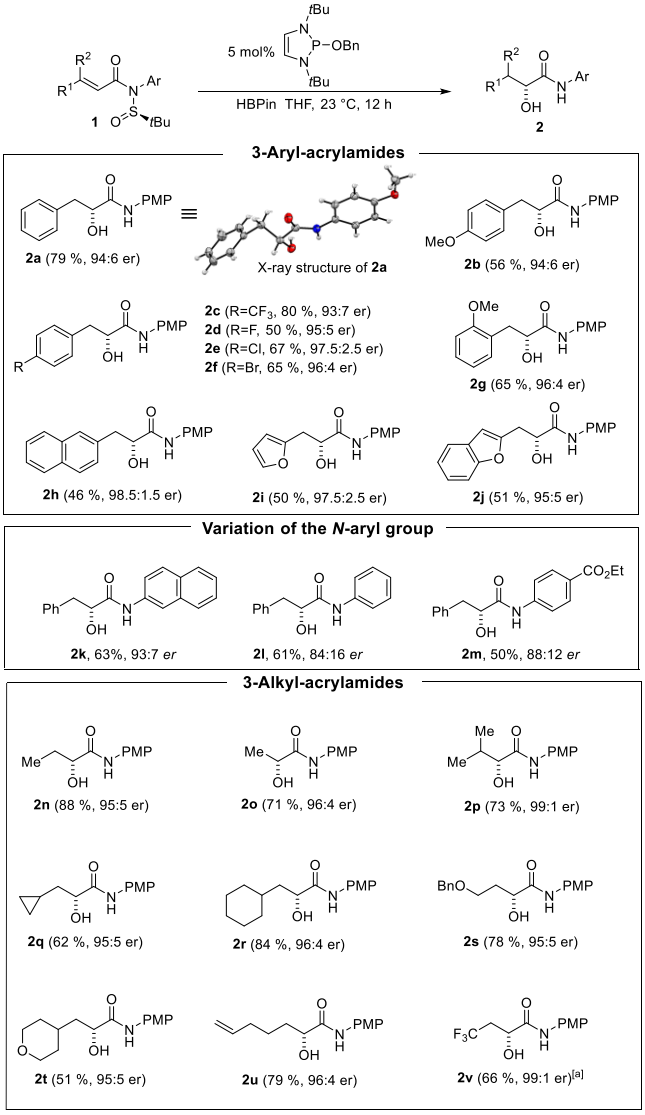
Table 1. Optimization of the reductive Aza-Mislow-Evans process[a]



Entry	Variation from optimal conditions	Yield of **2a** (%)[b]	er[c]
1	none	79	94:6
2	with 1.0 equiv. of HBPin	23	94:6
3	at 0 ˚C	30	95:5
4	at 40 ˚C	54	91:9
5	HBcat instead of HBpin	23	99:1
6	$PhSiH_3$ instead of HBPin	51	99:1
7	Ph_2SiH_2 instead of HBPin	0	n.d.
8	Without HBPin	0	n.d.
9	Without DAP-OBn	0	n.d.

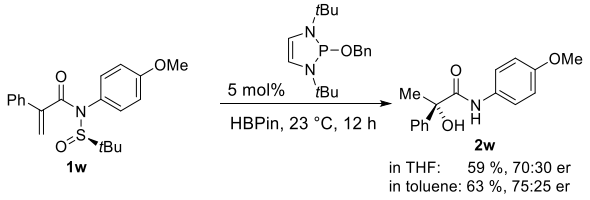
[a]Conditions: 0.1 mmol **1a**, 5 µmol DAP-OBn, and 0.21 mmol HBPin, in THF (0.5 M) at 23 °C for 12 h; [b]Determined by ^{1}H-NMR with internal standard; [c]Determined by chiral HPLC.

With the optimized reaction conditions, we investigated the scope of the reductive asymmetric aza-Mislow-Evans rearrangement (Scheme 2). A range of aryl-substituents on 3-position of acrylic sulfinamide derivatives **1** are well accommodated under standard conditions, giving the corresponding α-hydroxy amides (**2a**-**2j**) in good yields and enantioselectivity. Single crystal X-ray crystallographic analysis of **2a** revealed the absolute configuration of the obtained product to be (*R*).[21] Good reactivities and selectivities were obtained regardless of whether the 3-aryl group was electron-rich (*para*-methoxy phenyl, **2b**, 56%, 94:6 er*;* **2g**, 65% 96:4 er) or electron-deficient (*para*-trifluoromethyl phenyl **2c**, 80%, 93:7 *er*). Substrates with aryl halides (**1d**-**1f**) amenable for subsequent transformations were reacted without degradation of halide group (**2d** (50%, 95:5 *er*), **2e** (67%, 97.5:2.5 *er*), and **2f** (65%, 96:4 *er*). 3-(Naphthalen-2-yl)acryl sulfinamide reacted to product **2d** with an enantiomeric ratio of 98.5:1.5. Heteroaryl groups such as 2-furyl (**2i**, 50%, 97.5:2.5 er) or benzofuryl (**2j**, 51%, 95:5 *er*) are well tolerated in the transformation. The nitrogen substituent of the sulfinamide displays an influence on the stereoselectivity. In particular, electron-rich aryl groups ensure a very good enantiospecificity. For example, exchange of the PMP group by 2-naphthyl (**2k**, 63%, 93:7 *er*), phenyl (**2l**, 61%, 84:16 *er*) or 4-CO_2Mephenyl (**2m**, 50%, 88:12 *er*) slightly reduced selectivities. We next investigated the influence of the substitution order of the double bond on the reactivity and selectivity. Irrespective of number of substituents, e.g. simple acrylamides (**1o**, R^1=R^2=H), crotonamides (**1n**, R^1=Me, R^2=H), di-methyl crotonamides (**1p**, R^1=R^2=Me), the reductive rearrangement proceeded well and with high enantio-fidelity. Notably, the stereoselectivity of the rearrangement increased to 99:1 er (**2p**) with increased of the substitution order of double bond. Moreover, several 3-alkyl-substituted acrylic sulfinamides are suitable substrates for this transformation. These involve cyclopropyl (**2q**, 62%, 95:5 *er*), cyclohexyl (**2r**, 84%, 96:4 *er*), ethers (**2q**, 78%, 95:5 *er* and **2r**, 51%, 95:5 *er*) and non-conjugated alkenyl chains (**2s**, 79%, 96:4 *er*). A electron-withdrawing trifluoromethyl group reacted under longer reaction times, yielding product **2v** with 99:1 *er*.



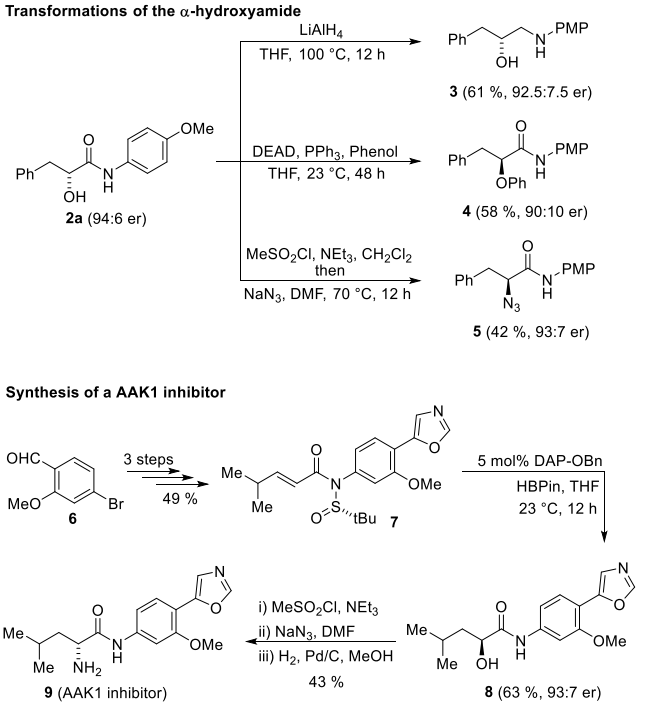
Scheme 2. Scope of reductive asymmetric Mislow-Evans rearrangement. [a]10 mol% DAP-OBn for 48 h.

α-Substituted *N*-*tert*-butylsulfinyl acrylamide **1w** delivered tertiary α-hydroxy amide **2w** in 59% yield under standard conditions albeit somewhat reduced enantioselectivity (Scheme 3). Switching the solvent to toluene slightly improved stereoselectivity to 75:25 er.



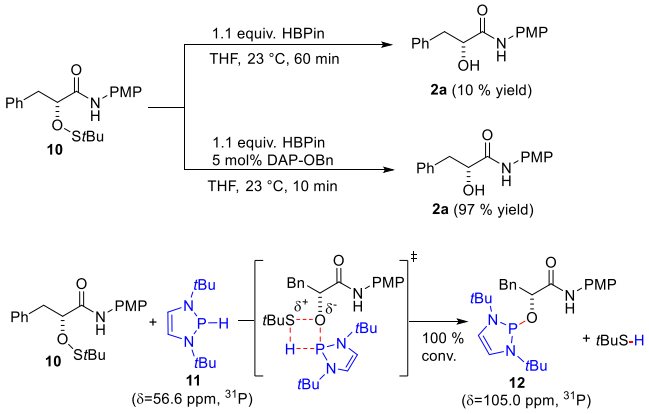
Scheme 3. Reductive aza-Mislow-Evans rearrangement for the synthesis of chiral tertiary α-hydroxy amide **2w**.

To further illustrate the utility of the enantioenriched α-hydroxy amides **2**, follow-up transformations were investigated (Scheme 4). For instance, reduction of the amide functionality of **2a** with $LiAlH_4$ to the corresponding β-amino alcohol **3** occurred without racemization. An inversion of the hydroxyl stereogenic center achieved by a Mitsunobu reaction with phenol as the nucleophile (**4**). A two-step procedure involving mesylation and azidation converted the hydroxyl group of **2a** into the corresponding azide **5** with inversion of configuration. Moreover, the present method was used for the synthesis of potent brain penetrant adaptor protein 2-associated kinase 1 (AAK1) inhibitor **9** (IC_{50}=12 nM), which is of potential use for the treatment of neuropathic pain.[22] The required (*S*)-*N*-sulfinyl acrylamide **7** was synthesized from aryl bromide **6** in 3 steps with 49% overall yield. Subjecting **7** to our standard asymmetric Mislow-Evans rearrangement conditions smoothly provided α-hydroxy amide **8** in 63% yield and, 93:7 *er.* A subsequent mesylation/azidation/hydrogenation sequence provided AAK1 inhibitor **9**.



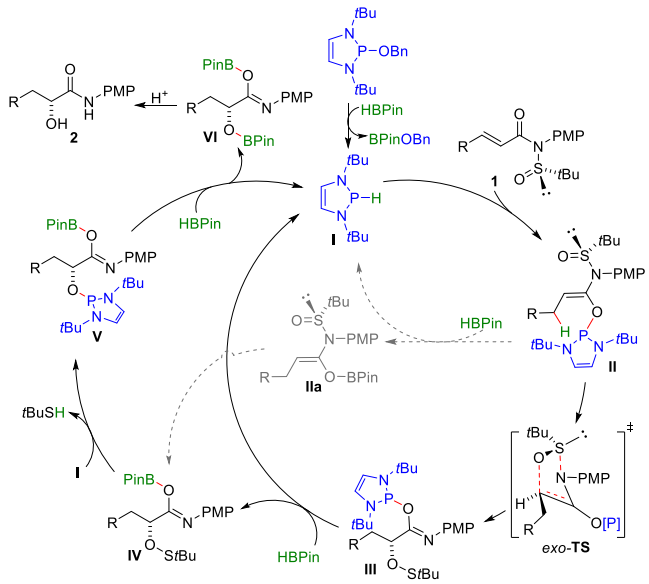
Scheme 4. Transformations and synthetic application of the α-hydroxamides.

To gain insights on the mechanism of the S-O bond cleavage by DAP-H, α-sulfenyloxy carboxamide **10** was subjected to different reaction conditions (Scheme 5). In the absence of DAP catalyst, HBPin reduces **10** only very sluggishly with 10% of **2a** formed in 60 min. In contrast, 5 mol% of DAP-OBn dramatically accelerates the reduction of the S-O bond, yielding 97% of **2a** in just 10 minutes of reaction time under otherwise identical conditions. With the crucial role of DAP-H on S-O bond reduction, a σ-bond metathesis between DAP-H and sulfenate was proposed, but the site of the split was unclear. Exposing **10** to stoichiometric amounts of DAP-H (^{31}P-NMR shift of 56.6 ppm in d_6-THF) immediately generated a new peak at 105.0 ppm. The same signal was reproduced by reacting DAP-Br with **2a** (See SI for details) and was therefore assigned to alkoxy-DAP **12**. In this scenario, *t*BuSH is the second product formed in the σ-bond metathesis step.



Scheme 5. DAP-Catalyzed reductive cleavage of the S-O bond.

Taken together with data on DAP catalysis, these findings contribute to the proposition of the following mechanism and catalytic cycle (Scheme 6). First, DAP-OBn pre-catalyst is converted to the active DAP-H species **I** by σ-bond metathesis with pinacolborane. In turn, hydride **I** engages in a conjugate addition across acryl amide **1** leading to phosphinyl enol ether **II**. Likely, a *cis*-P-enolate geometry for **II** is thermodynamically favoured due to a pronounced sterical hindrance on nitrogen atom. In contrast to the classical Mislow–Evans rearrangement operating by an *endo*-transition state, the pronounced steric interaction between *tert*-butyl sulfinyl group and substituent R destabilize the *endo*-transition state and favour an *exo*-transition state (*exo*-**TS**).[19] This pathway yields *R*-configured α-sulfenyloxy intermediate **III** as confirmed by X-ray crystallographic analysis of product **2a**. Subsequently, σ-bond metathesis of **III** with pinacolborane results in intermediate **IV** and release of DAP-H. In turn, the formed DAP-H promotes reductive cleavage of the sulfenate ester generating **V** and *t*BuSH. A second P-B exchange with pinacolborane yields compound **VI** and closes the catalytic cycle. Hydrolytic work-up and tautomerization delivers product **2**. Alternatively, a pathway involving an early phosphor-boron exchange of **II** to **IIa** is also possible.



Scheme 6. Proposed mechanism for the DAP-catalyzed reductive asymmetric aza Mislow-Evans Rearrangement.

In summary, we developed a DAP-catalyzed conjugate reduction which triggers a cascade process enabling the facile conversion of chiral α,β-unsaturated *N*-sulfinyl acrylamides into various enantio-enriched α-hydroxyl amides. The reductive aza-Mislow-Evans reaction operates under very mild conditions, at ambient temperature without use of strong bases. The transiently generated P-bound *N,O*-ketene aminal collapses with excellent enantiospecificity *via* a [2,3]-sigmatropic rearrangement. Notably, we found that the DAP hydride is a highly competent reductant for the cleavage of the formed sulfenate ester, thus eliminating the required additional step for this operation in the traditional Mislow-Evans process.

Acknowledgements

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Keywords: Asymmetric Synthesis • Phosphorous • Main Group Catalysis • Diazaphospholenes • Sigmatropic Rearrangement

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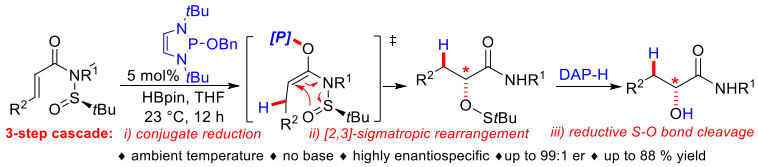

A 1,3,2-diazaphospholene-catalyzed three-step cascade transformation of chiral *N*-sulfinyl acrylamides comprised of a conjugate reduction, enantiospecific [2,3]-sigmatropic aza-Mislow-Evans rearrangement, and subsequent S-O bond reductive cleavage provides access to synthetically valuable enantio-enriched α-hydroxyl amides. Various α-hydroxyl amides are obtained in good yields and high enantioselectivities under very mild conditions.

Supporting Information

Reductive Asymmetric Aza-Mislow-Evans Rearrangement by 1,3,2-Diazaphospholene Catalysis

Guoting Zhang and Nicolai Cramer*

Laboratory of Asymmetric Catalysis and Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland.

*e-mail: nicolai.cramer@epfl.ch

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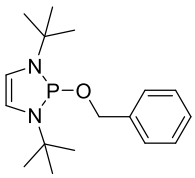
General Methods:

Unless otherwise indicated, all reactions were carried out under nitrogen atmosphere by using standard Schlenk or glovebox techniques in oven-dried glassware with magnetic stirring. Reagents were purchased and used as obtained from the suppliers. Solvents were obtained using a solvent purification system with an aluminum oxide column (Innovative Technologies). Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade). Analytical thin layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualized under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. NMR spectra were recorded on a Bruker Avance 400 spectrometer with a BBFOz ATMA probe. The peaks were internally referenced to residual non-deuterated chloroform in $CDCl_3$ (7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR) or DMSO in DMSO-d_6 (2.50 ppm for ^1H NMR, 39.53 ppm for ^{13}C NMR). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; brs, broad singlet. Electrospray–ionisation HRMS data were acquired on a Q–Tof Ultima mass spectrometer (Waters) or an Agilent LC-MS TOF. High resolution mass are given in m/z. Data from the Lock–Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). The enantiomeric ratio value was determined on an Agilent or Shimadzu HPLC using CHIRALPAK column with hexane and 2-propanol as eluent. Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter. X-ray analysis was performed by Dr. R. Scopelliti and Dr. F.Fadaei Tirani at the EPF Lausanne. Data were collected using a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer operating at T= 140.00(10)K.

Experiment details and characterization data

Preparation of DAP catalyst.

2-(Benzyloxy)-1,3-di-tert-butyl-2,3-dihydro-1H-1,3,2-diazaphosphole



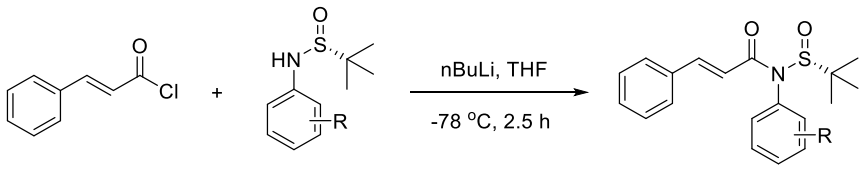
The DAP-OBn was synthesized according to the procedure reported by our group.[1]

In a flame-dried Schlenk flask in the glovebox, a solution of phenylmethanol (167 µL, 1.61 mmol, 1.5 equiv.) and trimethylamine (268 µL, 1.93 mmol, 1.8 equiv.) in THF (1.08 mL) was added dropwise at room temperature to a suspension of 2-halo-1,3,2-diazaphospholene (0.30 g, 1.075 mmol, 1.0 equiv.) in THF (4.3 mL). The mixture was stirred at room temperature for 1h before being evaporated to dryness. The resulting solid was then suspended in toluene and filtered through celite before being dried under vacuum again. Finally, recrystallization of the obtained solid from acetonitrile to obtain white crystal compound.

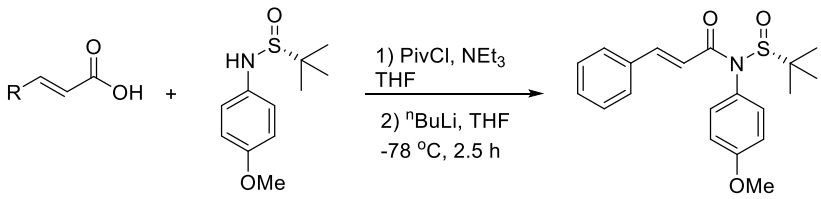
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.26 (d, *J* = 7.1 Hz, 2 H), 7.21 (dd, *J* = 7.1, 7.1 Hz, 1 H), 6.08 (d, *J* = 1.7 Hz, 2 H), 4.22 (d, *J* = 4.7 Hz, 2 H), 1.40 (s, 18 H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 94.2 ppm.

Preparation of *N*-aryl-tert-butansulfinyl acrylic amides.



General Procedure A: To a solution of *N*-aryl-*tert*-butansulfinamide (1.0 equiv.) in THF (0.25 M) was added ^{n}BuLi (1.6 M in hexane, 1.2 equiv.) at -78 °C under N_2. After stirring at this temperature for 30 min, a solution of cinnamyl chloride (1.6 equiv.) in THF (1.6 M). After 2 hours, the reaction was quenched with saturated aqueous ammonium chloride solution (5 mL). The reaction mixture was extracted with ethyl acetate (3 × 15 mL). The combine organic layers were washed with 1 M $NaHCO_3$ (3 × 15 mL) and brine (3 × 15 mL). Then, the collected organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The obtained residue was purified by flash column chromatography on silica gel (3:1 to 1:1 pentane/ethyl acetate) to yield the desired product.



General Procedure B: Freshly distilled Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv) and pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv) were added sequentially to a pre-cooled (-78 °C), stirred solution of the corresponding acrylic acid (1.6 mmol, 1.6 equiv) in THF (10.0 mL) under argon. The resulted mixture was stirred for 5 mins at -78 °C, 40 mins at room temperature, and then cooled again to -78 °C. To another flask containing *N*-PMP-tert-butansulfinamide (1.0 mmol, 1.0 equiv) in 5.0 mL of THF at -78 °C was added ^{n}BuLi (0.72 mL, 1.16 mmol, 1.16 equiv, 1.6 M in hexanes), and the mixture was stirred for 30 min at -78 °C under argon. The latter solution was then transferred to the mixed anhydrides solution via cannula, and the resulting mixture was stirred for 2.5 h at -78 °C under argon. Then solution was quenched with saturated aqueous ammonium chloride. The reaction mixture was extracted with ethyl acetate. The combined organic layers were washed with 1 M NaOH (3 × 15 mL) and brine (3 × 15 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The residue

was purified by flash column chromatography on silica gel (3:1 to 1:1 pentane/ethyl acetate) to yield the desired product.

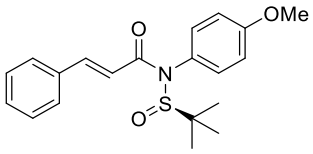
Asymmetric reductive Mislow-Evans reactions of *N*-sulfinyl acrylic amides.

General Procedure C: To a solution of *N*-sulfinyl acrylic amide (1.0 equiv.) in THF (0.5 M) was added 2-(benzyloxy)-1,3-di-tert-butyl-2,3-dihydro-1H-1,3,2-diazaphosphole (DAP catalyst, 5 mol%), and pinacolborane (2.1 equiv.) in the glovebox. Then the mixture was stirred at room temperature overnight. The reaction was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with sodium bicarbonate and brine. The collected organic layers were dried over anhydrous $MgSO_4$. After filtration and concentration, the crude residue was purified by flash column chromatography on silica gel (5:1 to 1:1 pentane/ethyl acetate) to yield the desired α-hydroxyl amide products.

Characterization data

Characterization data of substrates

(R)-*N*-(tert-butylsulfinyl)-*N*-(4-methoxyphenyl)cinnamamide (1a)



General procedure A was followed with *N*-PMP-*tert*-butansulfinamide (454.6 mg, 2.0 mmol, 1.0 equiv.), ^{n}BuLi (1.6 M in hexane, 1.5 mL, 2.4 mmol, 1.2 equiv.), and cinnamyl chloride (533.1 mg, 3.2 mmol, 1.6 equiv.). After purification by flash column chromatography, 632 mg (88%) of **1a** was afforded as a white solid.

Analytical data for **1a**:

M.P. 126-127 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 15.5 Hz, 1H), 7.27-7.20 (m, 5H), 7.19-7.15 (m, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.21 (d, *J* = 15.5 Hz, 1H), 3.77 (s, 3H), 1.12 (s, 9H).

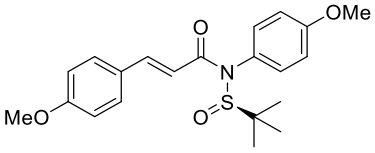
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 160.1, 144.9, 134.6, 132.4, 130.4, 128.9, 128.3, 126.6, 117.8, 114.5, 60.9, 55.6, 23.4.

HRMS (ESI): (m/z): calculated for $C_{20}H_{24}NO_3S^+$ $[M+H]^+$: 358.1471; found 358.1470.

FTIR (cm^{-1}): 1709, 1658, 1505, 1332, 1244, 1164, 1094, 762, 563.

$[\alpha]_D^{20}$ = +175.00 (c = 1.04, $CHCl_3$).

(R, E)-*N*-(tert-butylsulfinyl)-*N*, 3-bis(4-methoxyphenyl)acrylamide (1b)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv.), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv.), (*E*)-3-(4-methoxyphenyl)acrylic acid (285.1 mg, 1.6 mmol, 1.6 equiv.), ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv., 1.7 M in hexanes). After purification by flash column chromatography, 248.6 mg (64%) of **1b** was afforded as a white solid.

Analytical data for **1b**:

M.P.: 112-115 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 15.4 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.20 (m, 2H), 6.98 – 6.93 (m, 2H), 6.85 – 6.79 (m, 2H), 6.15 (d, *J* = 15.5 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 1.20 (s, 9H).

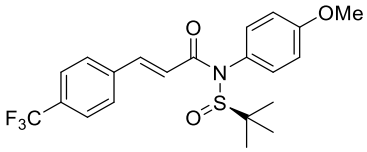
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 161.5, 160.0, 144.6, 132.5, 130.0, 127.4, 126.8, 115.2, 114.4, 77.4, 60.8, 55.6, 55.5, 23.4.

HRMS (ESI): (m/z): calculated for $C_{21}H_{25}NO_4SNa^+$ $[M+Na]^+$: 410.1397; found 410.1396.

FTIR (cm^{-1}): 1656, 1600, 1462, 1248, 1163, 1095, 1030, 1095, 753, 521.

$[\alpha]_D^{20}$ = +213.3 (c = 1.04, $CHCl_3$).

(*R,E*)-*N*-(tert-butylsulfinyl)-*N*-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)acrylamide (1c)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv.), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.172 mL, 1.4 mmol, 1.4 equiv.), (*E*)-3-(4-(trifluoromethyl)phenyl)acrylic acid (345.9 mg, 1.6 mmol, 1.6 equiv.), and ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv., 1.7 M in hexanes). After purification by flash column chromatography, 248.6 mg (64%) of **1c** was afforded as a white solid.

Analytical data for **1c**:

M.P.: 67-78 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 15.6 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.24 (s, 2H), 7.01 – 6.94 (m, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 3.86 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 160.2, 142.8, 138.0, 132.4, 131.8 (q, J_{C-F} = 32.3 Hz), 128.4, 126.4, 125.9 (q, J_{C-F} = 3.8 Hz), 123.9 (q, J_{C-F} = 273.7 Hz), 120.3, 114.6, 61.0, 55.6, 23.4.

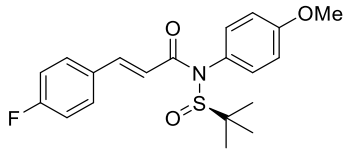
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.91.

HRMS (ESI): (m/z): calculated for $C_{21}H_{23}F_3NO_3S^+$ $[M+H]^+$: 426.1345; found 426.1342.

FTIR (cm^{-1}): 1662, 1619, 1579, 1320, 1247, 1166, 1125, 829, 509.

$[\alpha]_D^{20}$ = +190.17 (c = 1.00, $CHCl_3$).

(R,E)-*N*-(*tert*-butylsulfinyl)-3-(4-fluorophenyl)-*N*-(4-methoxyphenyl)acrylamide (**1d**)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv.), (*E*)-3-(4-fluorophenyl)acrylic acid (190.0 mg, 1.2 mmol, 1.2 equiv.), and ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv., 1.6 M in hexanes). After purification by flash column chromatography, 313.8 mg (84%) of **1d** was afforded as a white solid.

Analytical data for **1d**:

M.P.: 112-117 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 15.5 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.89 (m, 4H), 6.17 (d, *J* = 15.5 Hz, 1H), 3.81 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 163.9 (d, J_{C-F} = 252.5 Hz), 160.0, 143.5, 132.4, 130.8 (d, J_{C-F} = 3.3 Hz), 130.2 (d, J_{C-F} = 8.5 Hz), 126.5, 117.4, 116.0 (d, J_{C-F} = 22.2 Hz), 114.4, 60.8, 55.6, 23.3.

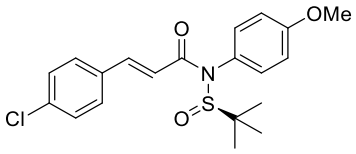
^{19}F NMR (376 MHz, $CDCl_3$) δ -109.37.

HRMS (ESI): (m/z): calculated for $C_{20}H_{23}FNO_3S^+$ $[M+H]^+$: 376.1377; found 376.1381.

FTIR (cm^{-1}): 1659, 1619, 1600, 1508, 1333, 1247, 1160, 1095, 829, 754, 509.

$[\alpha]_D^{20}$ = +186.54 (c = 1.04, $CHCl_3$).

(*R*,*E*)-*N*-(*tert*-butylsulfinyl)-3-(4-chlorophenyl)-*N*-(4-methoxyphenyl)acrylamide (1e)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv.), (*E*)-3-(4-chlorophenyl)acrylic acid (292.2 mg, 1.6 mmol, 1.6 equiv.), ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv., 1.7 M in hexanes). After purification by flash column chromatography, 286.4 mg (73%) of **1e** was afforded as a white solid.

Analytical data for **1e**:

M.P.: 114-116 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 15.5 Hz, 1H), 7.30 – 7.16 (m, 6H), 6.98 – 6.92 (m, 2H), 6.24 (d, *J* = 15.5 Hz, 1H), 3.85 (s, 3H), 1.19 (s, 9H).

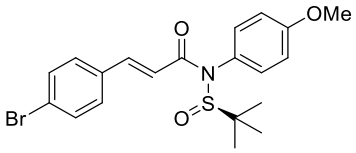
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 160.1, 143.4, 136.3, 133.1, 132.4, 129.5, 129.2, 126.5, 118.3, 114.5, 60.9, 55.6, 23.4.

HRMS (ESI): (m/z): calculated for $C_{20}H_{23}ClNO_3S^+$ $[M+H]^+$: 392.1082; found 392.1076.

FTIR (cm^{-1}): 1659, 1617, 1592, 1506, 1365, 1331, 1246, 1165, 1091, 1032, 1013, 859, 791, 515.

$[\alpha]_D^{20}$ = +186.17 (c = 1.00, $CHCl_3$).

(R,E)-*N*-(*tert*-butylsulfinyl)-3-(4-fluorophenyl)-*N*-(4-methoxyphenyl)acrylamide (1f)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv.), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv.), (*E*)-3-(4-bromophenyl)acrylic acid (363.3 mg, 1.6 mmol, 1.6 equiv.), ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes). After purification by flash column chromatography, 301.5 mg (69%) of **1f** was afforded as a white solid.

Analytical data for **1f**:

M.P.: 125-127 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 15.6 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.01 – 6.93 (m, 2H), 6.27 (d, *J* = 15.6 Hz, 1H), 3.86 (s, 3H), 1.20 (s, 9H).

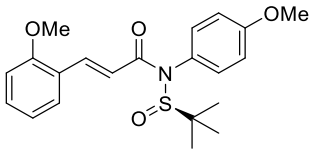
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 160.2, 143.4, 133.6, 132.4, 132.2, 129.7, 126.5, 124.7, 118.4, 114.5, 60.9, 55.6, 23.4.

HRMS (ESI): (m/z): calculated for $C_{20}H_{23}BrNO_3S^+$ $[M+H]^+$: 436.0577; found 436.0574.

FTIR (cm^{-1}): 1661, 1617, 1507, 1487, 1331, 1247, 1167, 1072, 791, 512.

$[\alpha]_D^{20}$ = +190.33 (c = 1.00, $CHCl_3$).

(*R*,*E*)-*N*-(*tert*-butylsulfinyl)-3-(2-methoxyphenyl)-*N*-(4-methoxyphenyl)acrylamide (1g)



General procedure B was followed with *N*-PMP-tert-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv.), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv.), (*E*)-3-(2-methoxyphenyl)acrylic acid (267.2mg, 1.6 mmol, 1.6 equiv.), and ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv., 1.7 M in hexanes). After purification by flash column chromatography, 268.7 mg (69%) of **1g** was afforded as a white solid.

Analytical data for **1g**:

M.P.: 139-142 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 15.7 Hz, 1H), 7.28 – 7.14 (m, 4H), 6.93 – 6.87 (m, 2H), 6.86 – 6.75 (m, 2H), 6.38 (d, *J* = 15.7 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 1.16 (s, 9H).

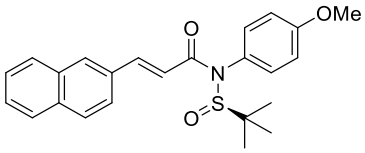
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 159.9, 158.5, 140.2, 132.4, 131.5, 129.4, 126.8, 123.6, 120.6, 118.5, 114.2, 111.1, 60.6, 55.5, 55.3, 23.3.

HRMS (ESI): (m/z): calculated for $C_{21}H_{25}NO_4SNa^+$ $[M+Na]^+$: 410.1397; found 410.1396.

FTIR (cm^{-1}): 1657, 1610, 1506, 1365, 1245, 1162, 1094, 1027, 752, 571.

$[\alpha]_D^{20}$ = +216.83 (c = 1.00, $CHCl_3$).

(*R*,*E*)-*N*-(*tert*-butylsulfinyl)-*N*-(4-methoxyphenyl)-3-(naphthalen-2-yl)acrylamide (1h)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv), (*E*)-3-(naphthalen-2-yl)acrylic acid (317.1 mg, 1.6 mmol, 1.6 equiv), ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes). After purification by flash column chromatography, 301.6 mg (74%) of **1h** was afforded as a white solid.

Analytical data for **1h**:

M.P.: 121-132 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 15.5 Hz, 1H), 7.84 – 7.77 (m, 3H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.38 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.04 – 6.92 (m, 2H), 6.41 (d, *J* = 15.5 Hz, 1H), 3.88 (s, 3H), 1.22 (s, 9H).

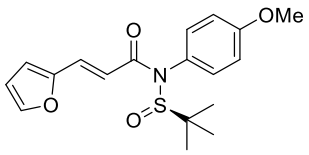
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 160.1, 145.0, 134.3, 133.4, 132.5, 132.2, 130.4, 128.7, 127.9, 127.4, 126.8, 126.7, 123.6, 117.9, 114.5, 60.9, 55.7, 23.4.

HRMS (ESI): (m/z): calculated for $C_{24}H_{25}NNaO_3S^+$ $[M+Na]^+$: 430.1447; found 430.1448.

FTIR (cm^{-1}): 1659, 1612, 1507, 1361, 1323, 1294, 1250, 1165, 1125, 1096, 1032, 751, 505.

$[\alpha]_D^{20}$ = +227.17 (c = 1.00, $CHCl_3$).

(*R*,*E*)-N-(*tert*-butylsulfinyl)-3-(furan-2-yl)-*N*-(4-methoxyphenyl)acrylamide (1i)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv.), (*E*)-3-(furan-2-yl)acrylic acid (221.0 mg, 1.6 mmol, 1.6 equiv.), ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv., 1.7 M in hexanes). After purification by flash column chromatography, 182.4 mg (52%) of **1i** was afforded as a white solid.

Analytical data for **1i**:

M.P.: 115-121 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 15.2 Hz, 1H), 7.37 (d, *J* = 1.8 Hz, 1H), 7.26 – 7.20 (m, 2H), 6.99 – 6.92 (m, 2H), 6.56 (d, *J* = 3.4 Hz, 1H), 6.41 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.18 (d, *J* = 15.2 Hz, 1H), 3.86 (s, 3H), 1.19 (s, 9H).

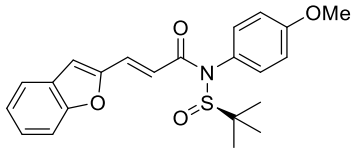
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 160.1, 151.3, 144.8, 132.4, 131.1, 126.6, 115.6, 115.2, 114.5, 112.5, 60.8, 55.6, 23.4.

HRMS (ESI): (m/z): calculated for $C_{20}H_{23}BrNO_3S^+$ $[M+H]^+$: 348.1264; found 348.1264.

FTIR (cm^{-1}): 3120, 2963, 2929, 1657, 1613, 1476, 1160, 1030, 722.

$[\alpha]_D^{20}$ = +188.50 (c = 1.00, $CHCl_3$).

(*R*,*E*)-3-(benzofuran-2-yl)-*N*-(tert-butylsulfinyl)-*N*-(4-methoxyphenyl)acrylamide (1j)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv.), (*E*)-3-(benzofuran-2-yl)acrylic acid (304.3 mg, 1.6 mmol, 1.6 equiv.), ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv., 1.7 M in hexanes). After purification by flash column chromatography, 278.3 mg (70%) of **1j** was afforded as a white solid.

Analytical data for **1j**:

M.P.: 140-142 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 15.1 Hz, 1H), 7.57 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.36 – 7.30 (m, 3H), 7.23 (td, *J* = 7.5, 1.1 Hz, 1H), 7.04 – 7.00 (m, 2H), 6.93 (s, 1H), 6.48 (d, *J* = 15.2 Hz, 1H), 3.90 (s, 3H), 1.24 (s, 9H).

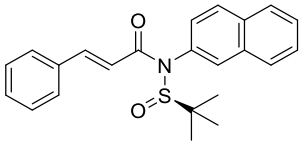
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 160.0, 155.5, 152.6, 132.3, 131.3, 128.4, 126.6, 126.4, 123.4, 121.8, 117.9, 114.5, 111.8, 111.4, 60.8, 55.6, 23.3.

HRMS (ESI): (m/z): calculated for $C_{22}H_{24}NO_4S^+$ $[M+H]^+$: 398.1421; found 398.1424.

FTIR (cm^{-1}): 2246, 1657, 1613, 1506, 1321, 1245, 1206, 1160, 1092, 1015, 722, 541.

$[\alpha]_D^{20}$ = +188.67 (c = 1.00, $CHCl_3$).

(R)-*N*-(tert-butylsulfinyl)-*N*-(naphthalen-2-yl)cinnamamide (1k)



General procedure A was followed with N- naphthalen-*tert*-butansulfinamide (247.3 mg, 1.0 mmol, 1.0 equiv.), ^{n}BuLi (1.6 M in hexane, 0.75 mL, 1.2 mmol, 1.2 equiv.), and cinnamyl chloride (266.6 mg, 1.6 equiv. 1.6 mmol). Column chromatography afforded 229.2 mg (61%) of **1k** as a white solid.

M.P.: 152-153 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dq, *J* = 6.5, 3.3 Hz, 4H), 7.79 (d, *J* = 15.5 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.42 – 7.38 (m, 1H), 7.35 – 7.21 (m, 5H), 6.33 (d, *J* = 15.5 Hz, 1H), 1.21 (s, 9H).

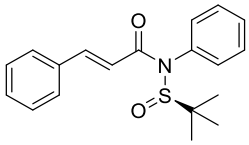
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.01, 145.21, 134.51, 133.29, 133.07, 131.64, 130.48, 130.18, 129.06, 128.90, 128.79, 128.42, 128.36, 127.85, 127.37, 126.97, 117.74, 61.10, 23.48.

HRMS (ESI): (m/z): calculated for $C_{23}H_{24}NO_2S^+$ $[M+H]^+$: 378.1522; found 378.1522.

FTIR (cm^{-1}): 1659, 1618, 1329, 1197, 1163, 1095, 754, 735, 481.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +169.83 (c = 2.16, $CHCl_3$).

(R)-*N*-(tert-butylsulfinyl)-*N*-phenylcinnamamide (1l)



General procedure A was followed with N-phenyl-*tert*-butansulfinamide (197.3 mg, 1.0 mmol, 1.0 equiv.), ^{n}BuLi (1.6 M in hexane, 0.75 mL, 1.2 mmol, 1.2 equiv.), and cinnamyl chloride (266.6 mg, 1.6 equiv. 1.6 mmol). Column chromatography afforded 272.7 mg (83%) of **1l** as a white solid.

M.P. 119.3-121.9 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 15.5 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.36 (s, 2H), 7.34 – 7.29 (m, 5H), 6.28 (d, *J* = 15.5 Hz, 1H), 1.20 (s, 9H).

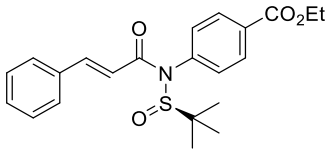
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 145.0, 134.6, 131.2, 130.5, 129.3, 129.3, 129.0, 128.5, 128.3, 117.8, 61.0, 23.4.

HRMS (ESI): (m/z): calculated for $C_{19}H_{22}NO_2S^+$ $[M+H]^+$: 328.1366; found 328.1361.

FTIR (cm-1): 1661, 1617, 1489, 1332, 1168, 1098, 762, 564, 503.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +164.56 (c = 1.26, $CHCl_3$).

Ethyl (R)-4-(*N*-(tert-butylsulfinyl)cinnamamido)benzoate (1m)



General procedure A was followed with *N*-phenyl-*tert*-butansulfinamide (269.4 mg, 1.0 mmol, 1.0 equiv.), ^{n}BuLi (1.6 M in hexane, 0.75 mL, 1.2 mmol, 1.2 equiv.), and cinnamyl chloride (266.6 mg, 1.6 equiv. 1.6 mmol). Column chromatography afforded 250 mg (63%) of **1m** as a white solid.

M.P. 152-158 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.10 (m, 2H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.27 (m, 5H), 6.30 (d, *J* = 15.5 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.19 (s, 9H).

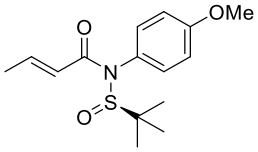
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 165.9, 145.7, 139.0, 134.4, 131.0, 130.9, 130.7, 130.5, 129.0, 128.4, 117.3, 61.6, 61.4, 23.4, 14.5.

HRMS (ESI): (m/z): calculated for $C_{22}H_{26}NO_4S^+$ $[M+H]^+$: 400.1577; found 400.1577.

FTIR (cm^{-1}): 1714, 1664, 1618, 1600, 1332, 1274, 1253, 1167, 1100, 1021, 762, 563.

$[\alpha]_D^{20}$ = +132.08 (c = 0.40, $CHCl_3$).

(*R,E*)-*N*-(tert-butylsulfinyl)-*N*-(4-methoxyphenyl)but-2-enamide (1n)



General procedure A was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv.), ^{n}BuLi (1.6 M in hexane, 0.75 mL, 1.2 mmol, 1.2 equiv.), and (*E*)-but-2-enoyl chloride (0.15 mL, 1.6 equiv. 3.2 equiv.). After purification by flash column chromatography, 206.2 mg (70%) of **1n** was afforded as a colorless oil.

Analytical data for **1n**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 9.0 Hz, 2H), 6.95 (dq, *J* = 15.1, 6.9 Hz, 1H), 6.91 – 6.83 (m, 2H), 5.67 (dd, *J* = 15.1, 2.2 Hz, 1H), 3.77 (s, 3H), 1.71 (dd, *J* = 7.0, 1.7 Hz, 3H), 1.11 (s, 9H).

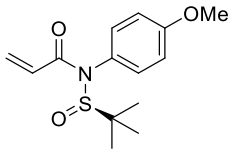
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 159.8, 144.9, 132.2, 126.5, 122.2, 114.2, 60.4, 55.4, 23.2, 18.2.

HRMS (ESI): (m/z): calculated for $C_{15}H_{22}NO_3S^+$ $[M+H]^+$: 296.1315; found 296.1315.

FTIR (cm^{-1}): 1670, 1634, 1508, 1508, 1329, 1293, 1248, 1170, 1097, 1032, 833, 505.

$[\alpha]_D^{20}$ = +148.21 (c = 1.12, $CHCl_3$).

(R)-*N*-(*tert*-butylsulfinyl)-*N*-(4-methoxyphenyl)acrylamide (1o)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv), acrylic acid (0.11 mL, 1.6 mmol, 1.6 equiv), ^{n}BuLi (0.72 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes). After purification by flash column chromatography, 97.7 mg (35%) of **1o** was afforded as a white solid.

Analytical data for **1o**:

M.P. 81-82 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.14 (m, 2H), 6.99 – 6.78 (m, 2H), 6.43 (dd, *J* = 16.8, 1.8 Hz, 1H), 6.04 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.65 (dd, *J* = 10.3, 1.8 Hz, 1H), 3.83 (s, 3H), 1.18 (s, 9H).

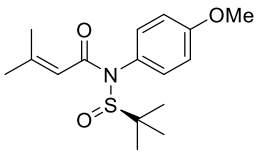
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 160.1, 132.4, 130.5, 128.2, 126.4, 114.5, 60.8, 55.6, 23.4.

HRMS (ESI): (m/z): calculated for $C_{14}H_{20}NO_3S+$ $[M+H]^+$: 282.1158; found 282.1152.

FTIR (cm^{-1}): 1666, 1505, 1398, 1298, 1244, 1193, 1168, 1094, 1028, 727, 541.

$[\alpha]_D^{20}$ = +203 (c = 1.00, $CHCl_3$).

(R)-*N*-(tert-butylsulfinyl)-*N*-(4-methoxyphenyl)-3-methylbut-2-enamide (1p)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv), 3-methylbut-2-enoic acid (160.2 mg, 1.6 mmol, 1.6 equiv), ^{n}BuLi (0.72 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes). After purification by flash column chromatography, 170.0 mg (55%) of **1p** was afforded as a white solid.

Analytical data for **1p**:

M.P.: 104-107 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.15 (m, 2H), 6.93 – 6.90 (m, 2H), 5.53 (s, 1H), 3.84 (s, 3H), 2.14 (d, *J* = 1.3 Hz, 3H), 1.76 (d, *J* = 1.3 Hz, 3H), 1.16 (s, 9H).

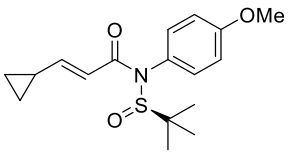
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 159.8, 156.1, 132.2, 127.3, 116.6, 114.3, 60.3, 55.6, 27.8, 23.5, 20.8.

HRMS (ESI): (m/z): calculated for $C_{16}H_{24}NO_3S^+$ $[M+H]^+$: 310.1471; found 310.1472.

FTIR (cm^{-1}): 1656, 1633, 1507, 1444, 1246, 1150, 1094, 895, 749, 575.

$[\alpha]_D^{20}$ = +187.37 (c = 1.06, $CHCl_3$).

(R,E)-*N*-(*tert*-butylsulfinyl)-3-cyclopropyl-*N*-(4-methoxyphenyl)acrylamide (1q)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv), (E)-3-cyclopropylprop-2-enoic acid (179.4 mg, 1.6 mmol, 1.6 equiv), ^{n}BuLi (0.72 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes). After purification by flash column chromatography, 195.3 mg (61%) of **1q** was afforded as a white solid.

M.P. 107.4-109.2 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H), 6.98 – 6.87 (m, 2H), 6.43 (dd, *J* = 14.9, 10.4 Hz, 1H), 5.77 (d, *J* = 15.0 Hz, 1H), 3.84 (s, 3H), 1.49 – 1.35 (m, 1H), 1.17 (s, 9H), 0.94 – 0.82 (m, 2H), 0.60 (dt, *J* = 6.5, 3.2 Hz, 2H).

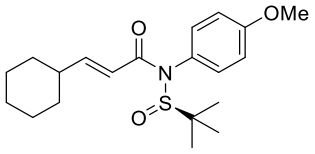
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 159.9, 155.0, 132.5, 126.8, 117.8, 114.3, 60.6, 55.6, 23.4, 15.1, 9.05, 9.03.

HRMS (ESI): (m/z): calculated for $C_{17}H_{24}NO_3S^+$ $[M+H]^+$: 322.1471; found 322.1473.

FTIR (cm^{-1}): 1661, 1622, 1506, 1377, 1275, 1180, 1147, 1094, 978, 946, 543.

$[\alpha]_D^{20}$ = +194.26 (c = 1.19, $CHCl_3$).

(R,E)-*N*-(*tert*-butylsulfinyl)-3-cyclohexyl-*N*-(4-methoxyphenyl)acrylamide (1r)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv), (*E*)-3-cyclohexylprop-2-enoic acid (246.7 mg, 1.6 mmol, 1.6 equiv), and ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv, 1.6 M in hexanes). After purification by flash column chromatography, 287.2 mg (79%) of **1r** was afforded as a white solid.

M.P.: 97-100℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.09 (m, 2H), 6.97 – 6.84 (m, 3H), 5.63 (d, *J* = 15.3 Hz, 1H), 3.82 (s, 3H), 2.06 – 1.94 (m, 1H), 1.71 – 1.51 (m, 6H), 1.20 – 1.16 (m, 2H), 1.15 (s, 9H), 1.09 – 0.89 (m, 2H).

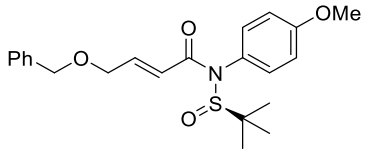
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 159.9, 154.8, 132.3, 126.7, 118.5, 114.3, 60.6, 55.5, 40.9, 31.8, 25.9, 25.7, 23.4.

HRMS (ESI): (m/z): calculated for $C_{18}H_{26}NO_3S^+$ $[M+H]^+$: 364.1941; found 364.1935.

FTIR (cm^{-1}): 1664, 1629, 1506, 1366, 1246, 1167, 1096, 1032, 573.

$[\alpha]_D^{20}$ = +172.22 (c = 1.00, $CHCl_3$).

(R,E)-4-(benzyloxy)-*N*-(*tert*-butylsulfinyl)-*N*-(4-methoxyphenyl)but-2-enamide (1s)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv), (E)-4-phenylmethoxybut-2-enoic acid (307.5 mg, 1.6 mmol, 1.6 equiv), and ^{n}BuLi (0.72 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes). After purification by flash column chromatography, 230.7 mg (57%) of **1s** was afforded as a white solid.

M.P. 96-108 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.19 – 7.09 (m, 4H), 6.99 (dt, *J* = 15.3, 4.2 Hz, 1H), 6.90 (dd, *J* = 9.1, 1.5 Hz, 3H), 6.03 (d, *J* = 15.3 Hz, 1H), 4.40 (s, 2H), 4.07 (dd, *J* = 4.2, 2.0 Hz, 2H), 3.80 (s, 3H), 1.15 (s, 9H).

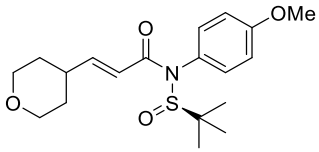
^{13}C NMR (101 MHz, CDCl3) δ 167.7, 160.1, 144.6, 137.7, 132.4, 128.5, 127.9, 127.6, 126.6, 120.9, 114.4, 72.7, 68.9, 60.7, 55.6, 23.4, 23.3.

HRMS (ESI): (m/z): calculated for $C_{22}H_{28}NO_4S^+$ $[M+H]^+$: 402.1734; found 402.1733.

FTIR (cm^{-1}): 1670, 1638, 1507, 1319, 1298, 1280, 1248, 1168, 1096, 1030, 570.

$[\alpha]_D^{20}$ = +131.33 (c = 1.00, $CHCl_3$).

(R,E)-N-(tert-butylsulfinyl)-N-(4-methoxyphenyl)-3-(tetrahydro-2H-pyran-4-yl)acrylamide (1t)



General procedure B was followed with N-PMP-tert-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.279 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.172 mL, 1.4 mmol, 1.4 equiv), (E)-3-(oxan-4-yl)prop-2-enoic acid (249.9 mg, 1.6 mmol, 1.6 equiv), ^{n}BuLi (0.73 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes), column chromatography afforded 281.9 mg (77%) of **1t** as a white solid.

M.P. :136-138 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.87 (m, 3H), 5.67 (d, *J* = 15.3 Hz, 1H), 3.91 (ddd, *J* = 11.5, 4.5, 2.1 Hz, 2H), 3.84 (s, 3H), 3.34 (td, *J* = 11.7, 2.3 Hz, 2H), 2.35 – 2.20 (m, 1H), 1.55 – 1.49 (m, 2H), 1.45 – 1.33 (m, 2H), 1.17 (s, 9H).

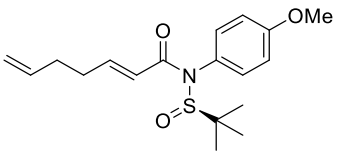
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 160.0, 152.2, 132.3, 126.6, 119.5, 114.4, 67.4, 67.4, 60.7, 55.6, 38.0, 31.5, 31.4, 23.4.

HRMS (ESI): (m/z): calculated for $C_{19}H_{28}NO_4S^+$ $[M+H]^+$: 366.1734; found 366.1736.

FTIR (cm^{-1}): 1665, 1631, 1507, 1247, 1171, 1138, 1095, 544.

$[\alpha]_D^{20}$ = +165.06 (c = 1.04, $CHCl_3$).

(R,E)-*N*-(*tert*-butylsulfinyl)-*N*-(4-methoxyphenyl)hepta-2,6-dienamide (1u)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv), (2*E*)-hepta-2,6-dienoic acid (201 mg, 1.6 mmol, 1.6 equiv), ^{n}BuLi (0.72 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes). After purification by flash column chromatography, 246.0 mg (73%) of **1u** was afforded as a white solid.

M.P.: 52-53 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 2H), 6.98 (dt, *J* = 15.2, 6.7 Hz, 1H), 6.93 – 6.90 (m, 2H), 5.69 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 2H), 4.99 – 4.90 (m, 2H), 3.83 (s, 3H), 2.23 – 2.14 (m, 2H), 2.15 – 2.04 (m, 2H), 1.16 (s, 9H).

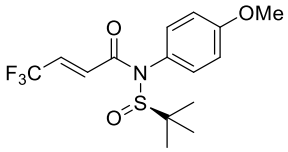
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 160.0, 148.7, 137.1, 132.3, 126.6, 121.4, 115.6, 114.3, 60.6, 55.6, 32.1, 31.7, 23.4.

HRMS (ESI): (m/z): calculated for $C_{18}H_{26}NO_3S^+$ $[M+H]^+$: 336.1628; found 336.1630.

FTIR (cm^{-1}): 1666, 1632, 1506, 1294, 1247, 1167, 1095, 1031, 574.

$[\alpha]_D^{20}$ = +172.76 (c = 1.23, $CHCl_3$).

(R,E)-*N*-(tert-butylsulfinyl)-4,4,4-trifluoro-*N*-(4-methoxyphenyl)but-2-enamide (1v)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv), (*E*)-4,4,4-trifluorobut-2-enoic acid (224 mg, 1.6 mmol, 1.6 equiv), ^{n}BuLi (0.72 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes). After purification by flash column chromatography, 272.6 mg (78%) of **1v** was afforded as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 2H), 6.97 – 6.90 (m, 2H), 6.77 (dq, *J* = 15.5, 6.7 Hz, 1H), 6.35 (d, *J* = 15.4 Hz, 1H), 3.82 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 160.5, 132.0, 130.86 (q, *J* = 35.4 Hz), 128.19 (q, *J* = 5.9 Hz), 125.3, 120.8, 114.7, 61.3, 55.6, 23.2.

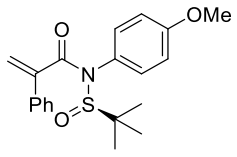
^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2.

HRMS (ESI): (m/z): calculated for $C_{15}H_{19}F_3NO_3S^+$ $[M+H]^+$: 350.1032; found 350.1032.

FTIR (cm^{-1}): 1682, 1653, 1507, 1302, 1275, 1127, 1104, 1031, 539.

$[\alpha]_D^{20}$ = +177.73 (c = 1.10, $CHCl_3$).

(R)-N-(tert-butylsulfinyl)-N-(4-methoxyphenyl)-2-phenylacrylamide (1w)



General procedure B was followed with *N*-PMP-*tert*-butansulfinamide (227.3 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), pivaloyl chloride (0.17 mL, 1.4 mmol, 1.4 equiv), 2-phenylacrylic acid (237.1

mg, 1.6 mmol, 1.6 equiv), ^{n}BuLi (0.72 mL, 1.16 mmol, 1.16 equiv, 1.7 M in hexanes). After purification by flash column chromatography, 193.4 mg (78%) of **1w** was afforded as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 3H), 7.20 (dd, *J* = 6.9, 2.9 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 5.59 (s, 1H), 5.54 (s, 1H), 3.76 (s, 3H), 1.07 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 159.6, 145.6, 136.2, 131.9, 128.7, 128.6, 127.0, 126.2, 118.9, 113.8, 60.7, 55.5, 23.4.

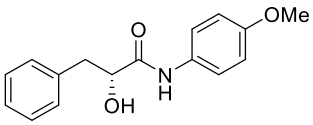
HRMS (ESI): (m/z): calculated for $C_{20}H_{24}NO_3S^+$ $[M+H]^+$: 358.1471; found 358.1470.

FTIR (cm^{-1}): 1668, 1605, 1507, 1461, 1445, 1328, 1300, 1283, 1247, 1169, 1154, 1096, 1030, 559, 544.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +122.14 (c = 0.42, $CHCl_3$).

Characterization data of products

(R)-2-hydroxy-N-(4-methoxyphenyl)-3-phenylpropanamide (2a)



Following the general procedure C with **1a** (35.75 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2a** was obtained (21.3 mg, 79% yield) as a white solid.

Analytical data for **2a**:

M.P.: 127-128 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.27 (dqd, *J* = 6.0, 3.7, 2.8, 1.3 Hz, 3H), 6.87 – 6.81 (m, 2H), 4.38 (dd, *J* = 8.1, 3.8 Hz, 1H), 3.78 (s, 3H), 3.29 (dd, *J* = 13.9, 3.9 Hz, 1H), 3.00 (d, *J* = 4.4 Hz, 1H), 2.95 (dd, *J* = 14.0, 8.5 Hz, 1H).

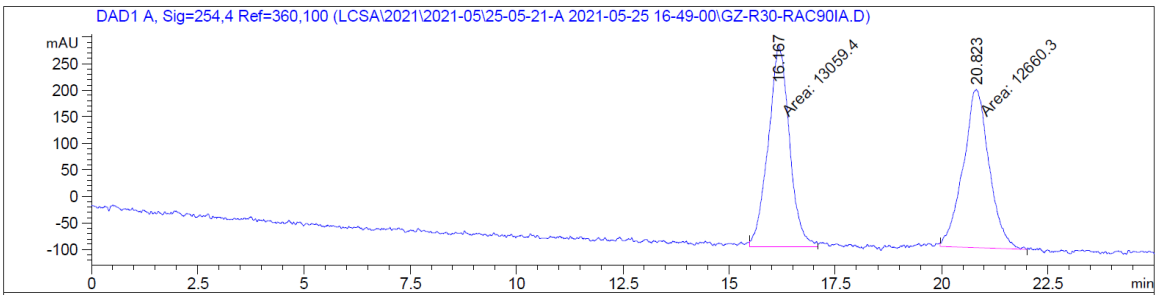
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 156.7, 136.9, 130.3, 129.7, 128.9, 127.2, 121.8, 114.3, 73.2, 55.6, 41.0.

HRMS (ESI): (m/z): calculated for $C_{16}H_{18}NO_3^+$ $[M+H]^+$: 272.1281; found 272.1279.

FTIR (cm^{-1}): 3317, 1648, 1600, 1555, 1511, 1248, 1097, 1039, 832, 728, 697.

$[\alpha]_D^{20}$ = +94.55 (c = 1.04, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 16.3 min, tR (mionr) 21.5 min, 93.5:6.5 *er*.

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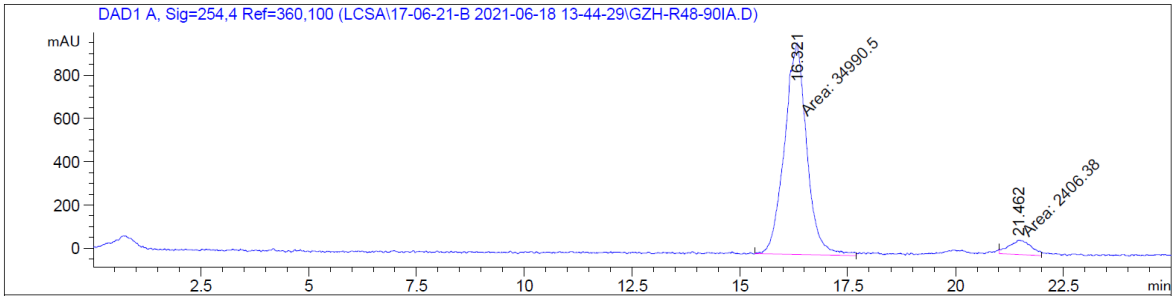
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

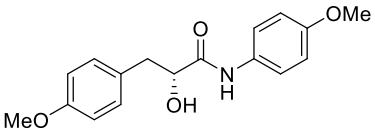
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.167 MM    0.5736 1.30594e4   379.48175  50.7760
   2  20.823 MM    0.7085 1.26602e4   297.83096  49.2240
```



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.321	MM	0.5969	3.49905e4	976.93317	93.5653
2	21.462	MM	0.6042	2406.37866	66.37941	6.4347
Totals :				3.73969e4	1043.31258	

(R)-2-hydroxy-N,3-bis(4-methoxyphenyl)propanamide (2b)



Following the general procedure C with **1b** (38.7 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2b** was obtained (16.83 mg, 56% yield) as a white solid.

Analytical data for **2b**:

M.P. 168-169 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.51 (s, 1H), 7.62 – 7.48 (m, 2H), 7.21 – 7.07 (m, 2H), 6.93 – 6.76 (m, 4H), 5.72 (d, *J* = 5.9 Hz, 1H), 4.15 (ddd, *J* = 8.1, 5.9, 4.2 Hz, 1H), 3.714 (s, 3H), 3.706 (s, 3H), 2.97 (dd, *J* = 13.8, 4.2 Hz, 1H), 2.76 (dd, *J* = 13.8, 8.2 Hz, 1H).

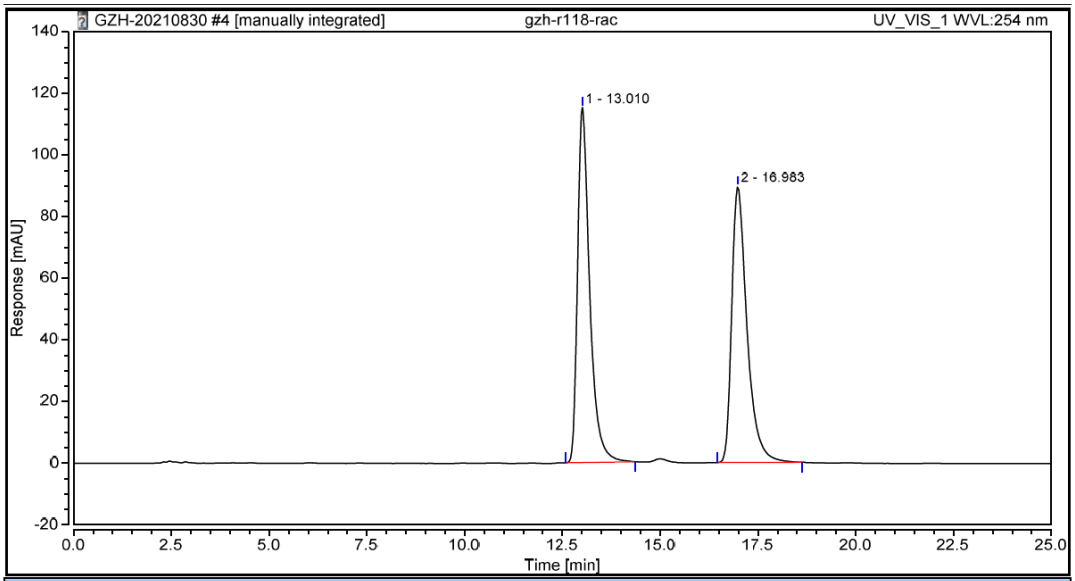
^{13}C NMR (101 MHz, DMSO-d_6) δ 171.85, 157.71, 155.33, 131.70, 130.40, 130.22, 121.19, 113.70, 113.42, 72.91, 55.14, 54.96, 40.20.

HRMS (ESI): (m/z): calculated for $C_{17}H_{20}NO_4^+$ $[M+H]^+$: 302.1387; found 302.1389.

FTIR (cm^{-1}): 3358, 2363, 2342, 1643, 1545, 1514, 1300, 1110, 1079, 1030, 822.

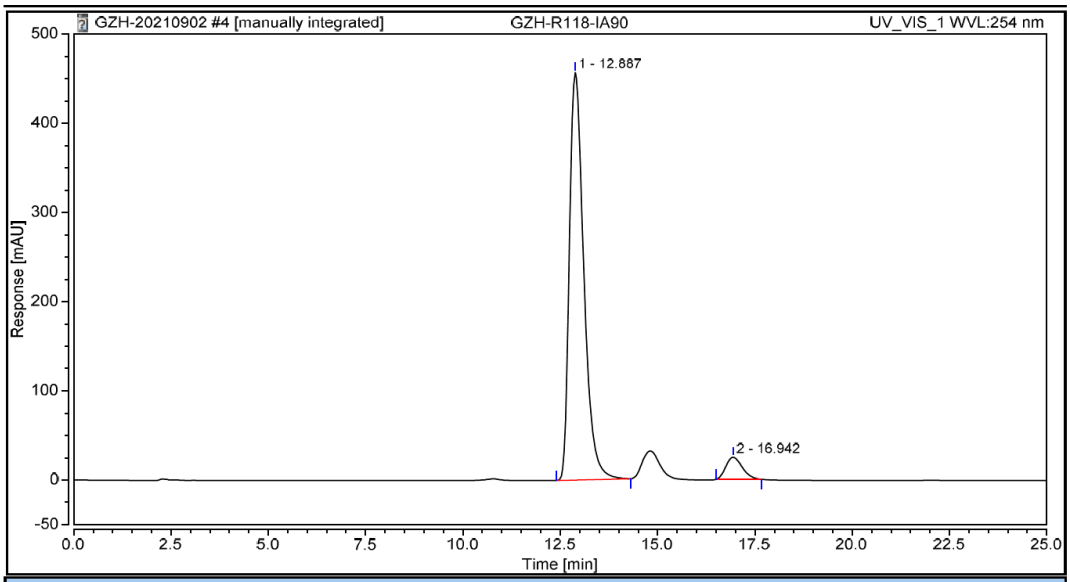
$[\alpha]_D^{20}$ = +60.32 (c = 0.28, $CHCl_3$)

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 12.9 min, tR (minor) 16.9 min, 95:5 *er*.



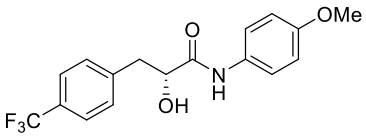
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.010	41.319	115.199	50.57	56.27	n.a.
2		16.983	40.384	89.533	49.43	43.73	n.a.
Total:			**81.703**	**204.731**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.887	195.946	456.911	94.18	94.86	n.a.
2		16.942	12.114	24.764	5.82	5.14	n.a.
Total:			**208.060**	**481.675**	**100.00**	**100.00**	

(R)-2-hydroxy-*N*-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)propanamide (2c)



Following the general procedure C with **1c** (42.6 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2c** was obtained (27.08 mg, 80% yield) as a white solid.

Analytical data for **2c:**

M.P. 172-173 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 (s, 1H), 7.67 – 7.60 (m, 2H), 7.60 – 7.52 (m, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 6.91 – 6.83 (m, 2H), 5.87 (d, *J* = 6.0 Hz, 1H), 4.26 (ddd, *J* = 8.3, 6.0, 4.1 Hz, 1H), 3.72 (s, 3H), 3.14 (dd, *J* = 13.7, 4.0 Hz, 1H), 2.93 (dd, *J* = 13.7, 8.4 Hz, 1H).

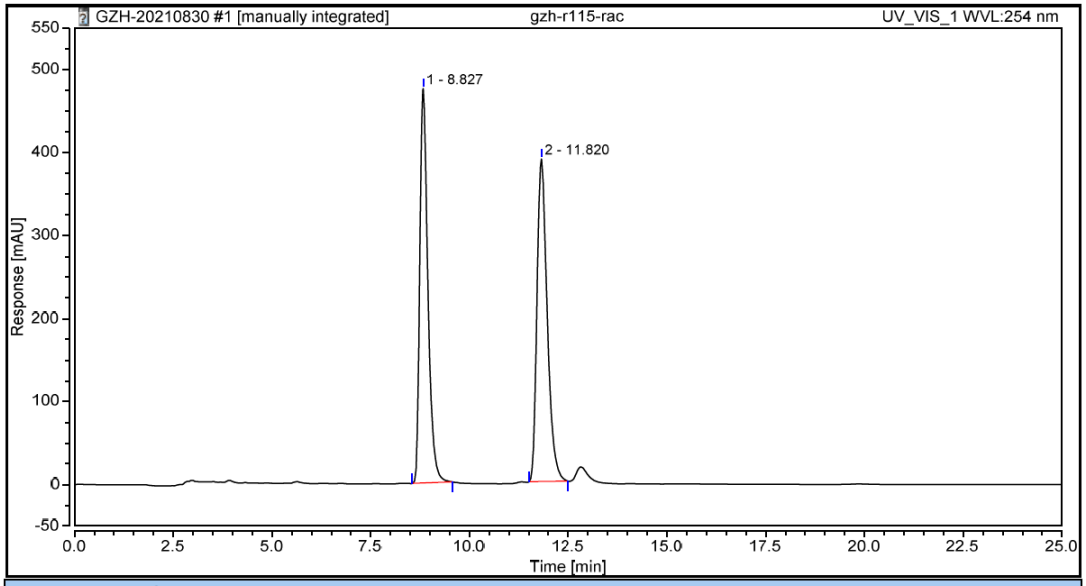
^{13}C NMR (101 MHz, DMSO-d_6) δ 171.9, 155.9, 143.9, 132.0, 130.8, 127.4 (q, $J_{C\text{-}F}$ = 31.7 Hz) 125.2 (q, *J* = 3.7 Hz), 125.0 (q, $J_{C\text{-}F}$ = 272.7 Hz), 121.8, 114.2, 72.7, 55.6, 40.5.

HRMS (ESI): (m/z): calculated for $C_{17}H_{17}F_3NO_3^+$ $[M+H]^+$: 340.1155; found 340.1158.

FTIR (cm^{-1}): 2361, 2340, 1638, 1415, 1329, 1162, 1125, 1110, 1070, 1031, 828.

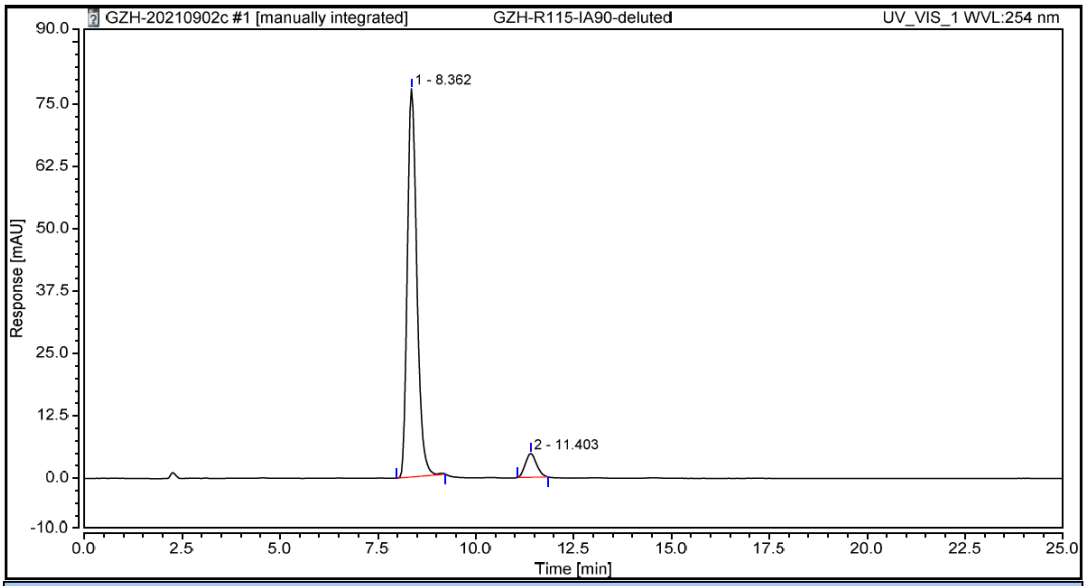
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +82.22 (c = 0.6, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 8.4 min, tR (minor) 11.4 min, 93:7 *er*.



Integration Results

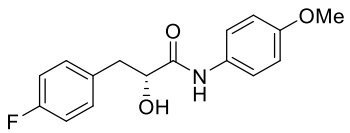
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.827	112.854	475.442	49.26	55.02	n.a.
2		11.820	116.261	388.713	50.74	44.98	n.a.
Total:			**229.114**	**864.155**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.362	21.920	77.813	93.22	94.24	n.a.
2		11.403	1.595	4.754	6.78	5.76	n.a.
Total:			**23.515**	**82.567**	**100.00**	**100.00**	

(R)-3-(4-fluorophenyl)-2-hydroxy-N-(4-methoxyphenyl)propanamide (2d)



Following the general procedure C with **1d** (37.5 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2d** was obtained (14.6 mg, 50% yield) as a white solid.

Analytical data for **2d:**

M.P. 140-141 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.47 – 7.37 (m, 2H), 7.32 – 7.20 (m, 2H), 7.08 – 6.96 (m, 2H), 6.92 – 6.81 (m, 2H), 4.44 – 4.36 (m, 1H), 3.80 (s, 3H), 3.28 (dd, *J* = 14.1, 3.9 Hz, 1H), 2.98 (dd, *J* = 14.1, 8.2 Hz, 1H), 2.81 (s, 1H).

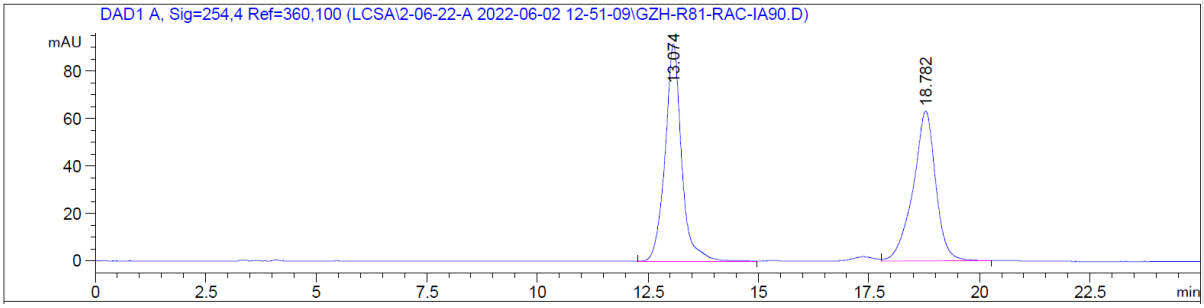
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.43, 162.16 (d, *J* = 245.4 Hz), 156.78, 132.47 (d, *J* = 3.3 Hz), 131.22 (d, *J* = 7.9 Hz), 130.21, 121.77, 115.72 (d, *J* = 21.2 Hz), 114.33, 73.21, 55.61, 40.10.

HRMS (ESI): (m/z): calculated for $C_{16}H_{17}FNO_3^+$ $[M+H]^+$: 290.1187; found 290.1187.

FTIR (cm^{-1}): 3333, 2923, 2359, 2341, 1645, 1598, 1557, 1512, 1231, 1103, 1094, 1033, 834, 815, 806, 506.

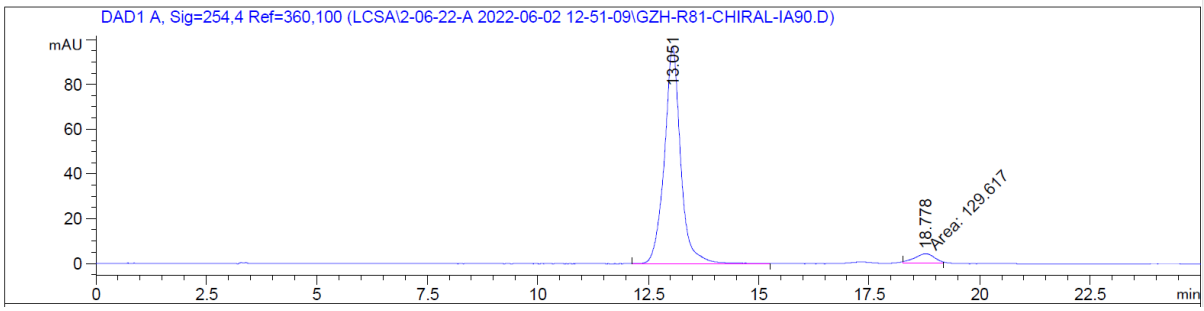
$[\alpha]_D^{20}$ = +87.76 (c = 0.60, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 13.0 min, tR (minor) 18.8 min, 95:5 *er*.



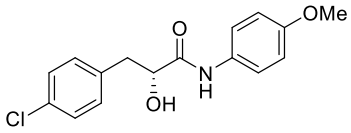
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.074	BB	0.3781	2373.91846	91.66406	51.2672
2	18.782	VB	0.5163	2256.56470	63.23890	48.7328
Totals :				4630.48315	154.90297	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.051	BB	0.3745	2479.88062	96.93379	95.0329
2	18.778	MM	0.5139	129.61665	4.20368	4.9671
Totals :				2609.49727	101.13747	

(R)-3-(4-chlorophenyl)-2-hydroxy-N-(4-methoxyphenyl)propanamide (2e)



Following the general procedure C with **1e** (39.2 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2e** was obtained (20.5 mg, 67% yield) as a white solid.

Analytical data for **2e:**

M.P. 157-159 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.54 (s, 1H), 7.60 – 7.52 (m, 2H), 7.37 – 7.23 (m, 4H), 6.91 – 6.82 (m, 2H), 5.81 (s, 1H), 4.20 (dd, *J* = 8.1, 4.1 Hz, 1H), 3.72 (s, 3H), 3.03 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.84 (dd, *J* = 13.8, 8.2 Hz, 1H).

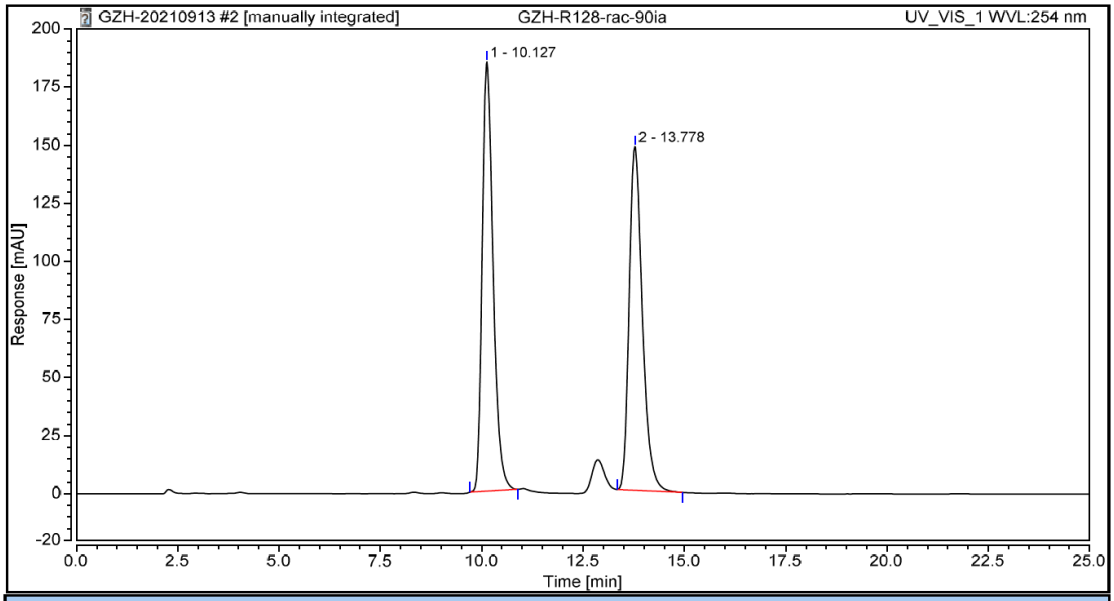
^{13}C NMR (101 MHz, DMSO-d_6) δ 172.0, 155.8, 137.9, 132.1, 131.8, 131.3, 128.4, 121.7, 114.2, 72.9, 55.6, 40.0.

HRMS (ESI): (m/z): calculated for $C_{16}H_{17}ClNO_3^+$ $[M+H]^+$: 306.0891; found 306.0896.

FTIR (cm^{-1}): 3325, 2358, 2342, 1648, 1553, 1510, 1440, 1364, 1341, 964, 833.

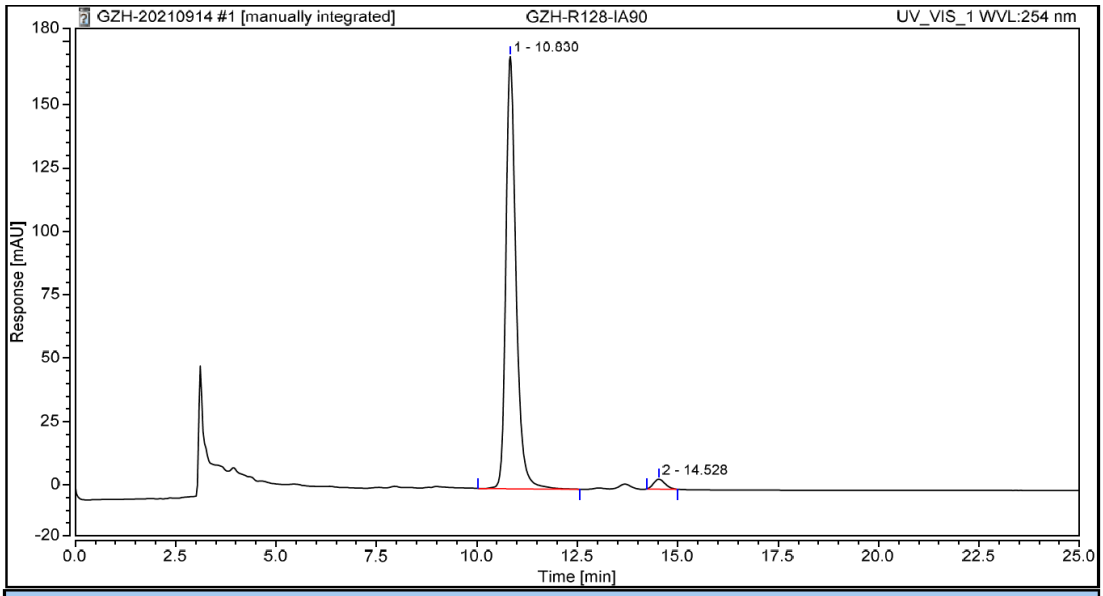
$[\alpha]_D^{20}$ = +62.81 (c = 1.00, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 10.8 min, tR (minor) 14.5 min, 97.5:2.5 *er*.



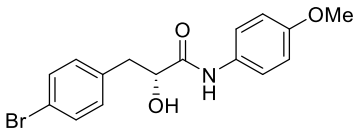
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.127	57.685	184.779	50.83	55.53	n.a.
2		13.778	55.808	148.003	49.17	44.47	n.a.
Total:			**113.494**	**332.781**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.830	50.011	170.538	97.49	97.76	n.a.
2		14.528	1.288	3.912	2.51	2.24	n.a.
Total:			**51.299**	**174.450**	**100.00**	**100.00**	

(R)-3-(4-bromophenyl)-2-hydroxy-N-(4-methoxyphenyl)propanamide (2f)



Following the general procedure C with **1f** (43.64 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2f** was obtained (22.7 mg, 65% yield) as a white solid.

Analytical data for **2f:**

M.P. 168-170 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.54 (s, 1H), 7.60 – 7.52 (m, 2H), 7.50 – 7.42 (m, 2H), 7.26 – 7.17 (m, 2H), 6.91 – 6.82 (m, 2H), 5.81 (d, *J* = 6.0 Hz, 1H), 4.20 (ddd, *J* = 8.2, 5.9, 4.1 Hz, 1H), 3.72 (s, 3H), 3.01 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.82 (dd, *J* = 13.8, 8.2 Hz, 1H).

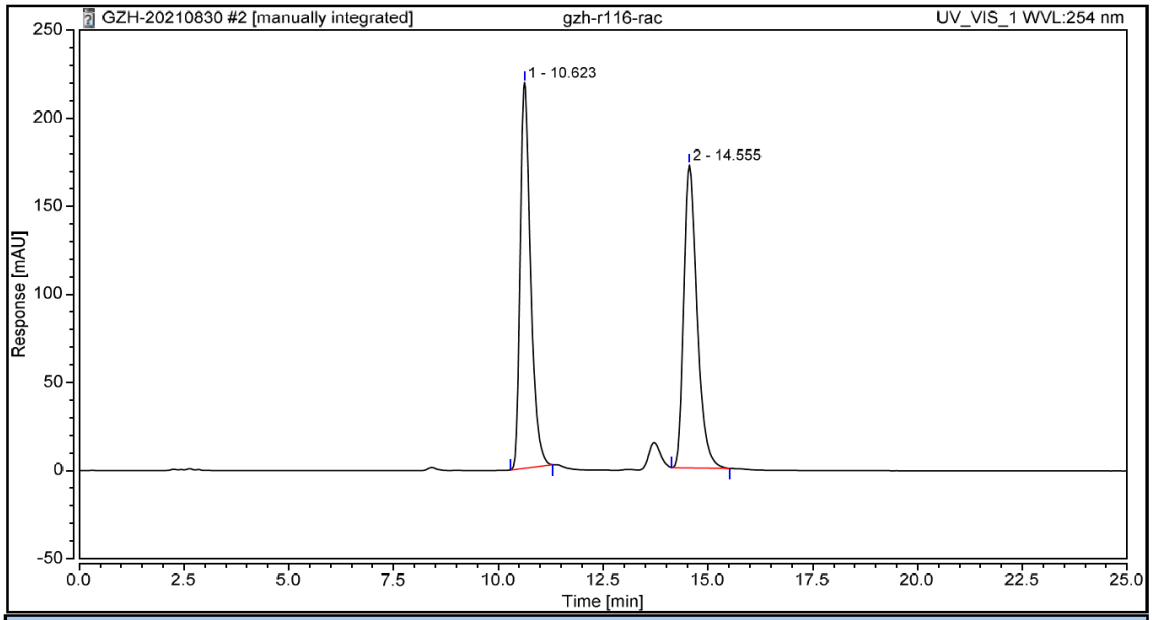
^{13}C NMR (101 MHz, DMSO-d_6) δ 171.5, 155.4, 137.8, 131.7, 131.6, 130.8, 121.2, 119.3, 113.7, 72.4, 55.1, 39.6.

HRMS (ESI): (m/z): calculated for $C_{16}H_{17}BrNO_3^+$ $[M+H]^+$: 350.0386; found 350.0389.

FTIR (cm^{-1}): 3328, 2959, 2923, 2361, 1643, 1546, 1508, 1246, 1100, 1071, 831.

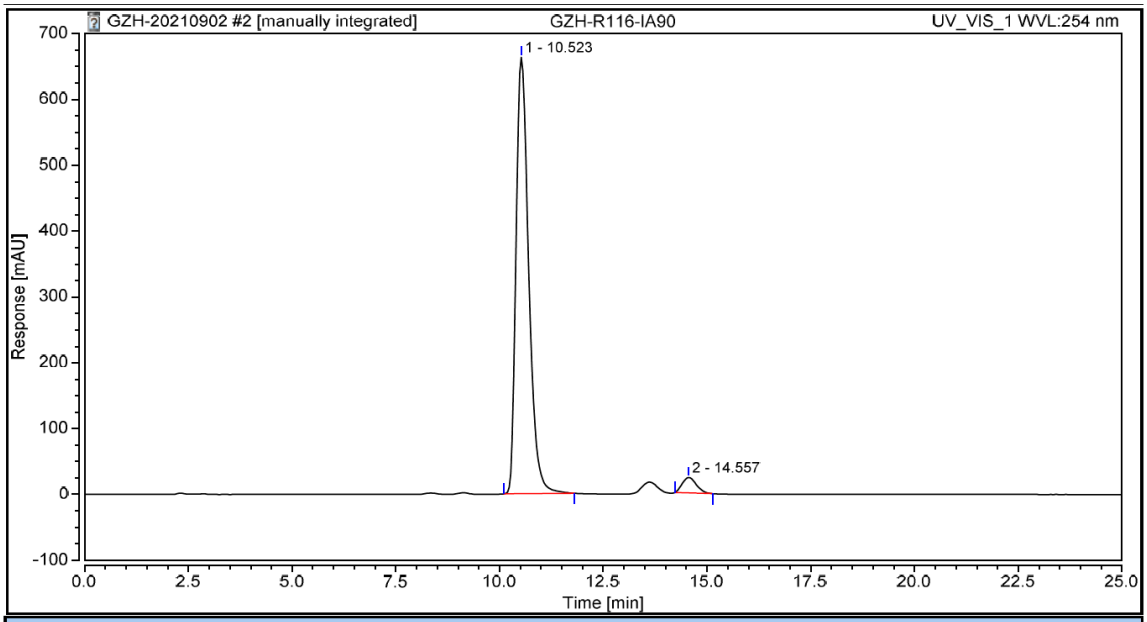
$[\alpha]_D^{20}$ = +88.33 (c = 1.00, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 10.5 min, tR (minor) 14.6 min, 96.5:3.5 *er*.



Integration Results

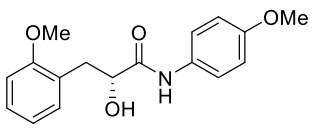
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.623	62.968	219.093	49.86	56.00	n.a.
2		14.555	63.327	172.133	50.14	44.00	n.a.
Total:			**126.295**	**391.226**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.523	234.547	663.188	96.21	96.58	n.a.
2		14.557	9.241	23.492	3.79	3.42	n.a.
Total:			**243.788**	**686.679**	**100.00**	**100.00**	

(R)-2-hydroxy-3-(2-methoxyphenyl)-N-(4-methoxyphenyl)propanamide (2g)



Following the general procedure C with **1g** (38.8 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2g** was obtained (19.6 mg, 65% yield) as a white solid.

Analytical data for **2g:**

M.P. 90 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.37 – 7.29 (m, 2H), 7.23 – 7.15 (m, 3H), 6.92 – 6.81 (m, 2H), 6.81 – 6.73 (m, 2H), 4.37 (dd, *J* = 7.5, 3.7 Hz, 1H), 3.88 (d, *J* = 3.5 Hz, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.34 (dd, *J* = 14.1, 3.8 Hz, 1H), 3.04 (dd, *J* = 14.1, 7.6 Hz, 1H).

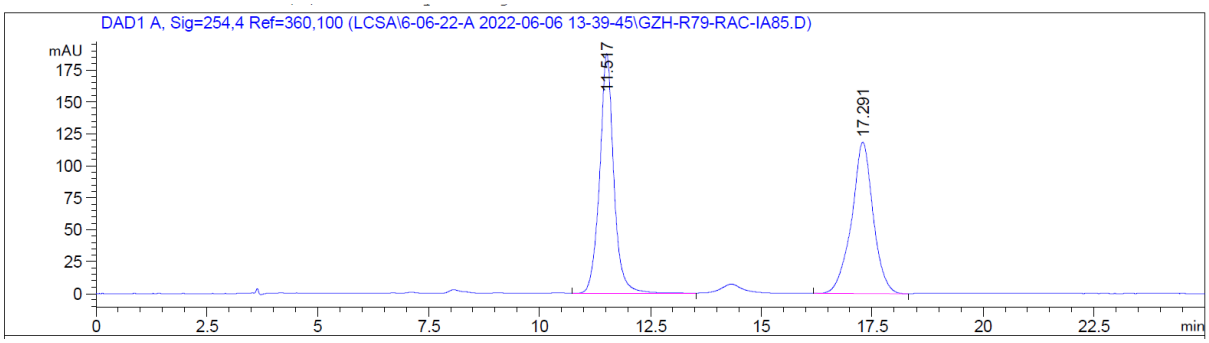
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 157.3, 156.6, 132.1, 130.6, 128.7, 125.5, 121.8, 121.7, 114.2, 110.8, 73.9, 55.8, 55.6, 35.7.

HRMS (ESI): (m/z): calculated for $C_{17}H_{20}NO_4^+$ $[M+H]^+$: 302.1387; found 302.1387.

FTIR (cm^{-1}): 3359, 2924, 2836, 1658, 1599, 1511, 1494, 1243, 1115, 1051, 829, 796.

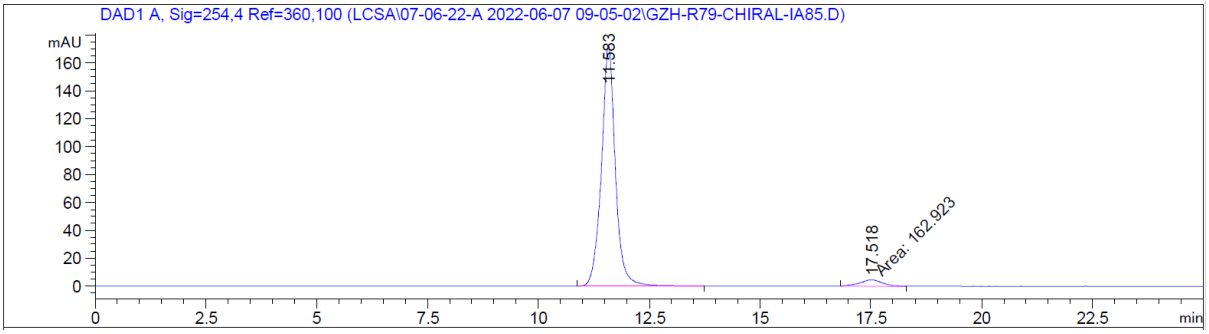
$[\alpha]_D^{20}$ = +111.98 (c = 1.00, $CHCl_3$)

Chiral HPLC (Chiralpak IA, 15 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 11.6 min, tR (minor) 17.5 min, 96:4 *er*.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

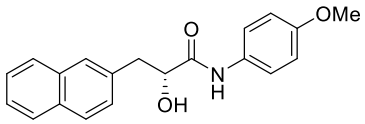
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.517	BB	0.3239	4146.62549	187.57584	50.8468
2	17.291	BB	0.4908	4008.50659	118.44830	49.1532



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.583	BB	0.3205	3762.58838	172.50304	95.8496
2	17.518	MM	0.5841	162.92258	4.64906	4.1504

(R)-2-hydroxy-N-(4-methoxyphenyl)-3-(naphthalen-2-yl)propanamide (2h)



Following the general procedure C with **1h** (40.8 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2h** was obtained (14.8 mg, 46% yield) as a white solid.

Analytical data for **2h:**

M.P. 180 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 (s, 1H), 7.90 – 7.80 (m, 3H), 7.76 (d, *J* = 1.7 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.51 – 7.41 (m, 3H), 6.90 – 6.82 (m, 2H), 5.83 (d, *J* = 5.9 Hz, 1H), 4.32 (ddd, *J* = 8.2, 5.9, 4.1 Hz, 1H), 3.71 (s, 3H), 3.22 (dd, *J* = 13.7, 4.1 Hz, 1H), 3.01 (dd, *J* = 13.7, 8.2 Hz, 1H).

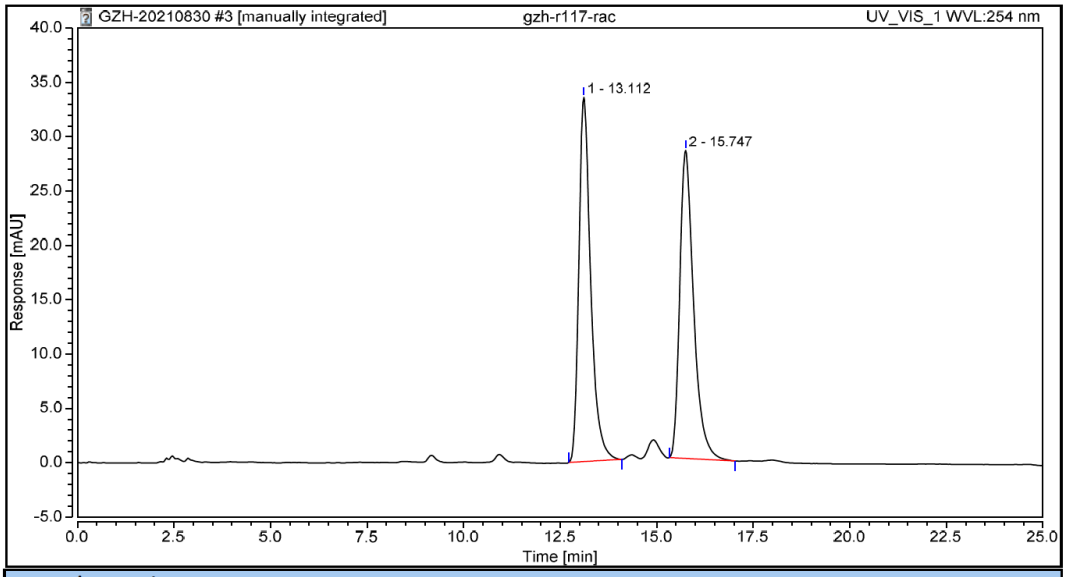
^{13}C NMR (101 MHz, DMSO-d_6) δ 171.8, 155.4, 136.1, 133.0, 131.8, 131.6, 128.2, 127.7, 127.4, 127.3, 127.3, 125.9, 125.3, 121.2, 113.7, 72.7, 55.1, 40.6.

HRMS (ESI): (m/z): calculated for $C_{17}H_{20}NO_4^+$ $[M+H]^+$: 322.1438; found 322.1439.

FTIR (cm^{-1}): 3314, 2955, 1647, 1550, 1508, 1246, 1109, 1034, 830, 740.

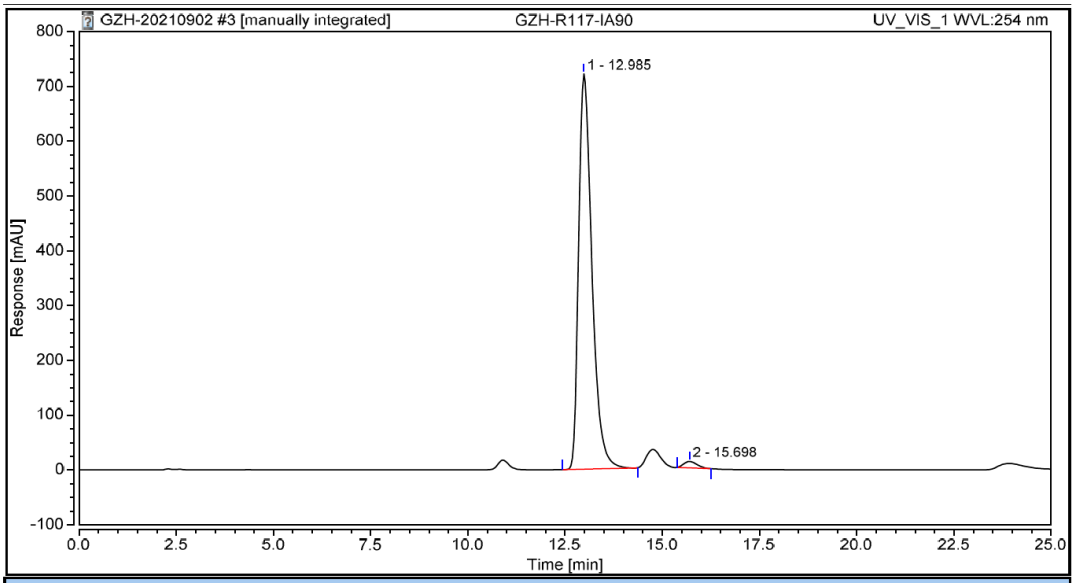
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +56.79 (c = 1.21, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 13.0 min, tR (minor) 15.7 min, 98.5:1.5 *er*.



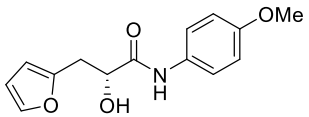
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.112	11.941	33.533	50.29	54.19	n.a.
2		15.747	11.802	28.344	49.71	45.81	n.a.
Total:			**23.743**	**61.877**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.985	284.797	721.634	98.43	98.42	n.a.
2		15.698	4.537	11.596	1.57	1.58	n.a.
Total:			**289.333**	**733.230**	**100.00**	**100.00**	

(R)-3-(furan-2-yl)-2-hydroxy-N-(4-methoxyphenyl)propanamide (2i)



Following the general procedure C with **1i** (34.7 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2i** was obtained (13.0 mg, 46% yield) as a white solid.

Analytical data for **2i:**

M.P. 114-115 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.46 – 7.41 (m, 2H), 7.37 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.96 – 6.79 (m, 2H), 6.34 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.22 – 6.16 (m, 1H), 4.47 (dt, *J* = 7.5, 3.2 Hz, 1H), 3.79 (s, 3H), 3.35 (ddd, *J* = 15.2, 3.8, 0.8 Hz, 1H), 3.12 – 3.01 (m, 2H).

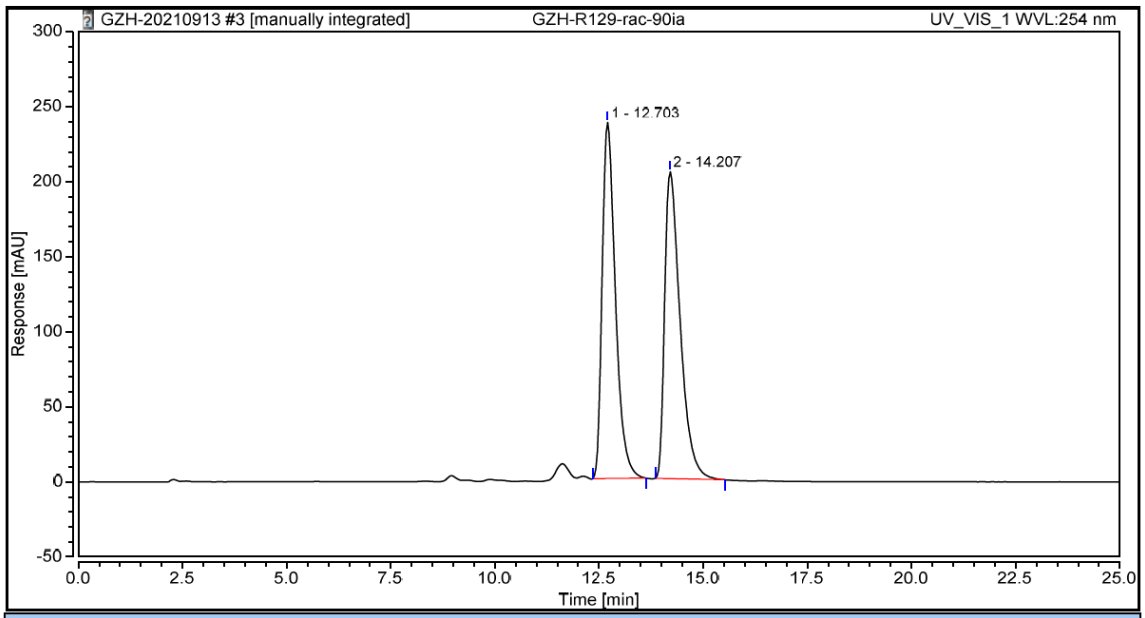
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 156.7, 151.3, 142.4, 130.4, 121.8, 114.3, 110.8, 108.2, 71.5, 55.6, 33.5.

HRMS (ESI): (m/z): calculated for $C_{14}H_{16}NO_4^+$ $[M+H]^+$: 262.1074; found 262.1076.

FTIR (cm^{-1}): 3320, 2924, 1652, 1553, 1509, 1346, 1075, 1014, 834, 731.

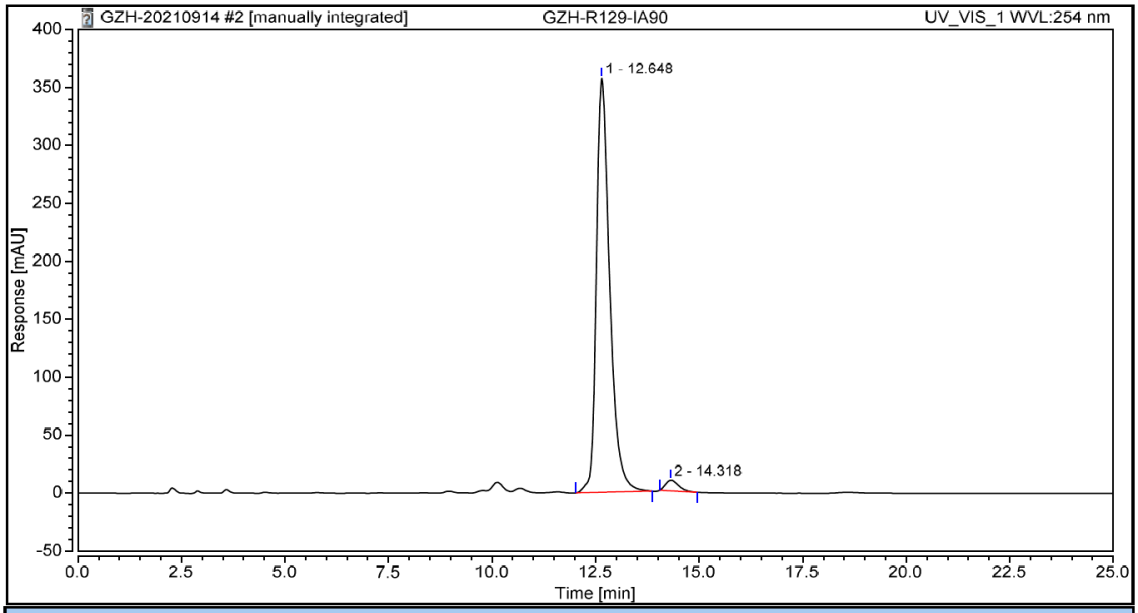
$[\alpha]_D^{20}$ = +76.09 (c = 1.18, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 12.6 min, tR (minor) 14.3 min, 97.5:2.5 *er*.



Integration Results

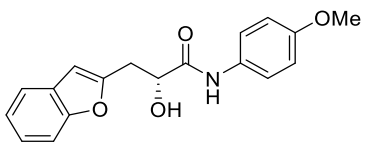
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.703	87.443	237.338	49.80	53.71	n.a.
2		14.207	88.142	204.551	50.20	46.29	n.a.
Total:			**175.585**	**441.890**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.648	133.606	357.429	97.54	97.49	n.a.
2		14.318	3.366	9.185	2.46	2.51	n.a.
Total:			**136.972**	**366.613**	**100.00**	**100.00**	

(R)-3-(benzofuran-2-yl)-2-hydroxy-N-(4-methoxyphenyl)propanamide (2j)



Following the general procedure C with **1j** (39.8 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2j** was obtained (16.0 mg, 51% yield) as a white solid.

Analytical data for **2j:**

M.P. 160-161 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.56 – 7.49 (m, 1H), 7.47 – 7.39 (m, 3H), 7.32 – 7.16 (m, 2H), 6.98 – 6.79 (m, 2H), 6.58 (d, *J* = 0.9 Hz, 1H), 4.57 (dd, *J* = 8.5, 3.6 Hz, 1H), 3.79 (s, 3H), 3.50 (ddd, *J* = 15.3, 3.6, 0.9 Hz, 1H), 3.25 – 3.10 (m, 2H).

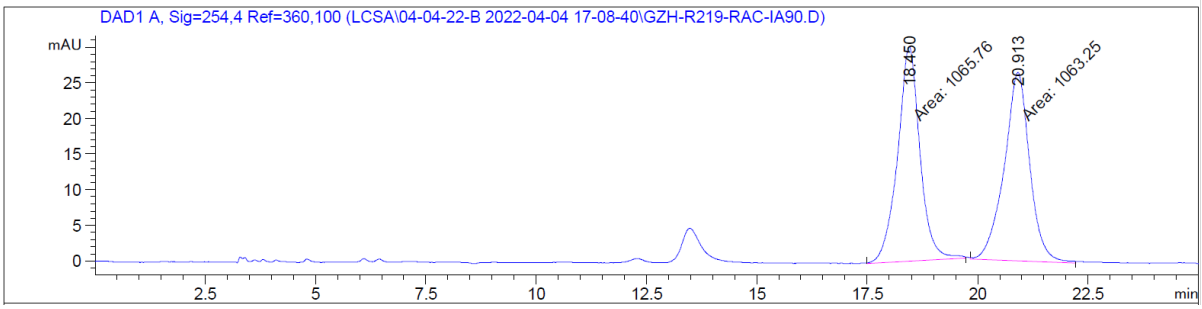
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 156.8, 155.1, 154.4, 130.3, 128.6, 124.1, 123.1, 121.8, 120.9, 114.3, 111.1, 105.2, 71.3, 55.6, 34.0.

HRMS (ESI): (m/z): calculated for $C_{18}H_{18}NO_4^+$ $[M+H]^+$: 312.1230; found 312.1235.

FTIR (cm^{-1}): 3289, 1641, 1597, 1555, 1510, 1454, 1303, 1099, 1008, 797, 751.

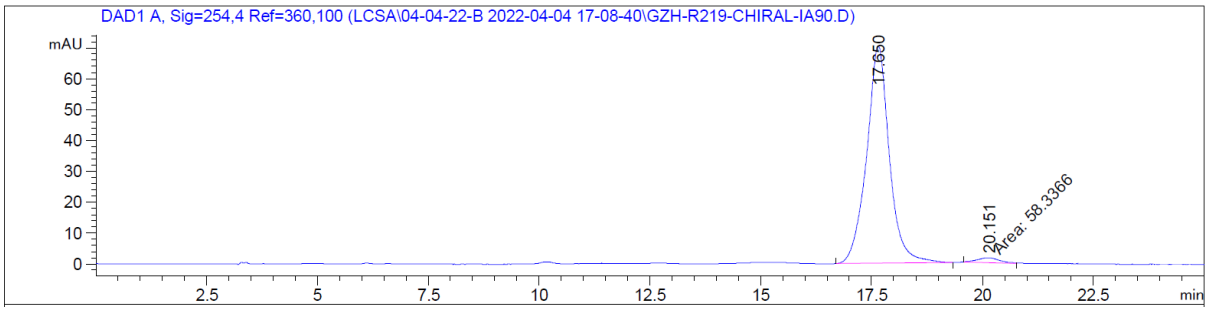
$[\alpha]_D^{20}$ = +100.92 (c = 0.98, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 17.6 min, tR (minor) 20.2 min, 98:2 *er*.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

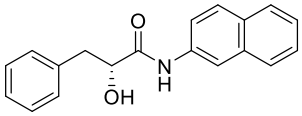
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.450	MM	0.5892	1065.76404	30.14794	50.0589
2	20.913	MM	0.6705	1063.25476	26.42827	49.9411
Totals :				2129.01880	56.57621	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.650	BB	0.5227	2514.77002	70.40264	97.7328
2	20.151	MM	0.5945	58.33656	1.63551	2.2672
Totals :				2573.10658	72.03815	

(R)-2-hydroxy-N-(naphthalen-2-yl)-3-phenylpropanamide (2k)



Following the general procedure C with **1k** (37.8 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2k** was obtained (18.2 mg, 63% yield) as a white solid.

Analytical data for **2k:**

M.P. 153-154 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.25 (d, *J* = 2.1 Hz, 1H), 7.84 – 7.75 (m, 3H), 7.51 – 7.25 (m, 8H), 4.49 (dd, *J* = 8.7, 4.0 Hz, 1H), 3.40 (dd, *J* = 14.0, 4.0 Hz, 1H), 3.04 (dd, *J* = 14.0, 8.7 Hz, 1H), 2.54 (s, 1H).

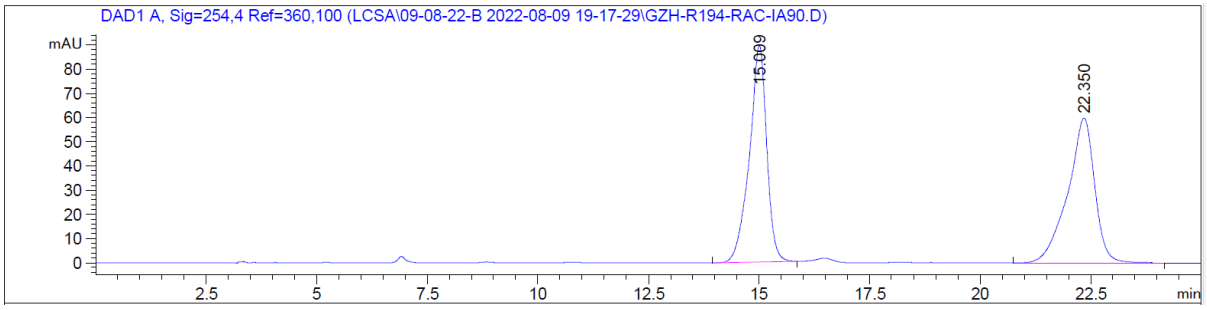
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 136.6, 134.7, 134.0, 130.9, 129.7, 129.2, 129.0, 127.9, 127.7, 127.4, 126.7, 125.3, 119.9, 116.8, 73.4, 41.0.

HRMS (ESI): (m/z): calculated for $C_{19}H_{18}NO_2^+$ $[M+H]^+$: 292.1332; found 292.1332.

FTIR (cm^{-1}): 3308, 2338, 1658, 1631, 1604, 1581, 1170, 1124, 1096, 730, 698.

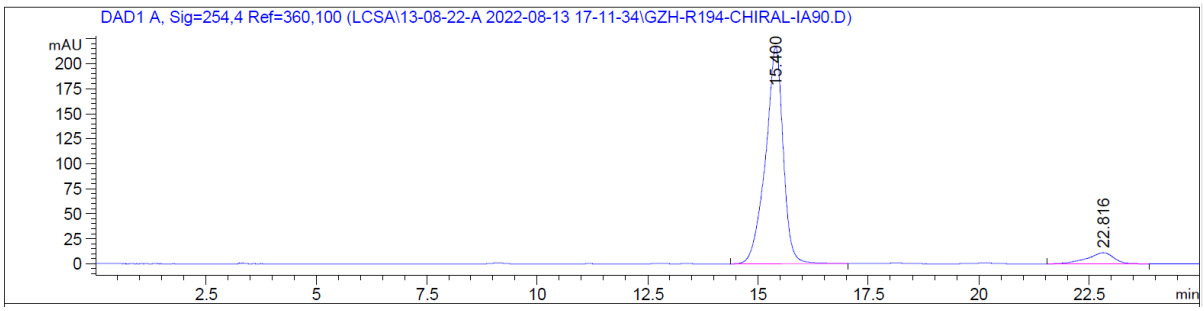
$[\alpha]_D^{20}$ = +105.16 (c = 0.756, $CHCl_3$)

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 15.1 min, tR (minor) 22.3 min, 93:7 *er*.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

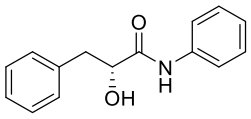
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.009	BB	0.3985	2442.06079	89.44251	49.0080
2	22.350	BB	0.6058	2540.92285	59.78949	50.9920



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.400	BB	0.4040	6022.05908	216.85141	92.7502
2	22.816	BB	0.5857	470.71448	11.21432	7.2498

(R)-2-hydroxy-N,3-diphenylpropanamide (2l)



Following the general procedure C with **1l** (32.8 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2l** was obtained (14.8 mg, 63% yield) as a white solid.

Analytical data for **2l:**

M.P. 120-122 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.43 – 7.39 (m, 2H), 7.25 – 7.15 (m, 7H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.31 (dd, *J* = 8.7, 3.9 Hz, 1H), 3.23 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.87 (dd, *J* = 13.9, 8.6 Hz, 1H), 2.67 – 2.45 (m, 1H).

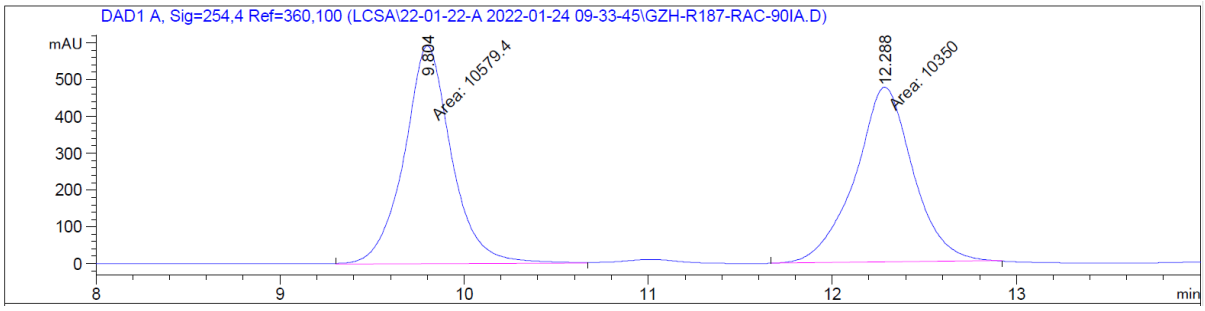
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 137.2, 136.7, 129.7, 129.2, 129.0, 127.3, 124.8, 120.0, 73.3, 41.0.

HRMS (ESI): (m/z): calculated for $C_{15}H_{16}NO_2^+$ $[M+H]^+$: 242.1176; found 242.1181.

FTIR (cm^{-1}): 3307, 1653, 1601, 1540, 1496, 1445, 754, 692.

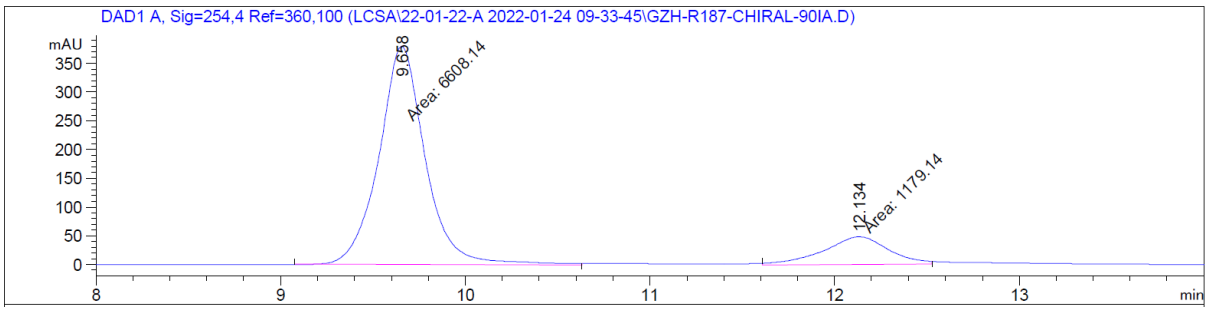
$[\alpha]_D^{20}$ = +68.30 (c = 1.22, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 9.6 min, tR (minor) 12.1 min, 85:15 *er*.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

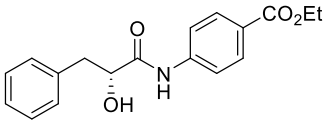
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.804	MM	0.2977	1.05794e4	592.22101	50.5480
2	12.288	MM	0.3635	1.03500e4	474.55698	49.4520
Totals :				2.09294e4	1066.77798	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.658	MM	0.2904	6608.14063	379.21899	84.8582
2	12.134	MM	0.4094	1179.13623	48.00247	15.1418
Totals :				7787.27686	427.22146	

Ethyl (R)-4-(2-hydroxy-3-phenylpropanamido)benzoate (2m)



Following the general procedure C with **1m** (39.9 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2m** was obtained (13.4 mg, 43% yield) as a white solid.

Analytical data for **2m:**

M.P. 134-137 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.07 – 7.98 (m, 2H), 7.64 – 7.56 (m, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 3H), 4.45 (dd, *J* = 8.8, 3.8 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.36 (dd, *J* = 13.9, 3.9 Hz, 1H), 2.98 (dd, *J* = 13.9, 8.8 Hz, 1H), 2.62 (s, 1H), 1.39 (t, *J* = 7.1 Hz, 3H).

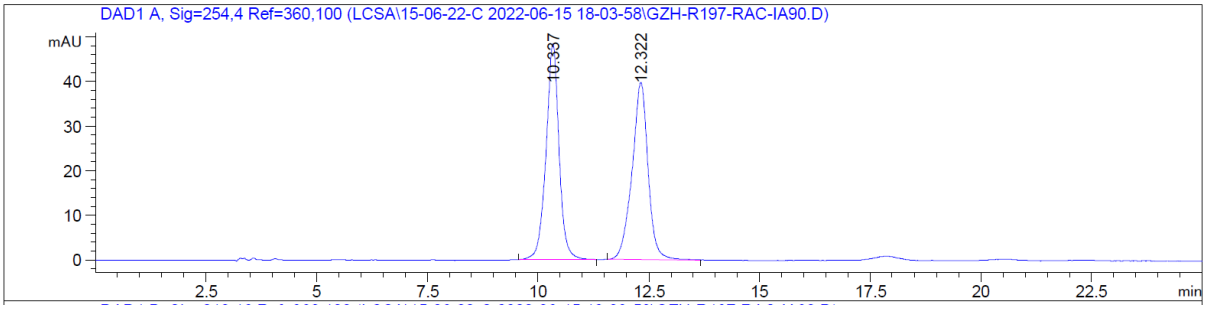
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 166.3, 141.3, 136.5, 130.9, 129.6, 129.2, 127.5, 126.4, 119.0, 73.4, 61.1, 40.9, 14.5.

HRMS (ESI): (m/z): calculated for $C_{18}H_{20}NO_4^+$ $[M+H]^+$: 314.1387; found 314.1389.

FTIR (cm^{-1}): 3341, 2364, 1693, 1526, 1454, 1409, 1368, 1310, 1280, 1176, 1108, 742, 727.

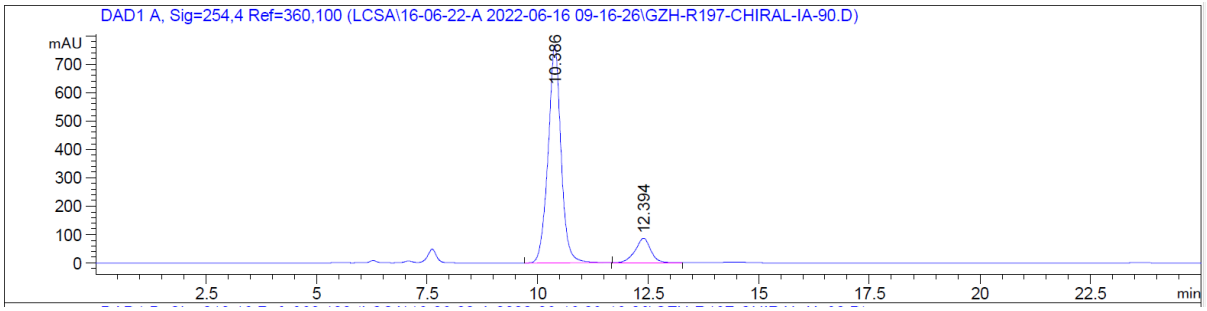
$[\alpha]_D^{20}$ = +89.86 (c = 0.56, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 10.4 min, tR (minor) 12.4 min, 88:12 *er*.




```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

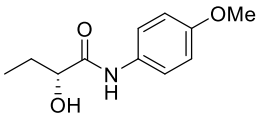
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.337 BB    0.3002  987.83057   48.38101  49.7751
   2  12.322 BB    0.3687  996.75616   39.72305  50.2249
```




```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.386 BB    0.2993 1.55970e4   766.76447  88.2068
   2  12.394 BB    0.3540 2085.31201   86.26049  11.7932
```

(R)-2-hydroxy-N-(4-methoxyphenyl)butanamide (2n)



Following the general procedure C with **1n** (29.5 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2n** was obtained (18.3 mg, 88% yield) as a white solid.

Analytical data for **2n:**

M.P. 70 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.57 – 7.37 (m, 2H), 7.05 – 6.65 (m, 2H), 4.19 (dd, *J* = 7.3, 3.9 Hz, 1H), 3.79 (s, 3H), 2.81 (s, 1H), 1.96 (ddt, *J* = 15.0, 7.5, 3.7 Hz, 1H), 1.78 (dp, *J* = 14.6, 7.3 Hz, 1H), 1.02 (t, *J* = 7.4 Hz, 3H).

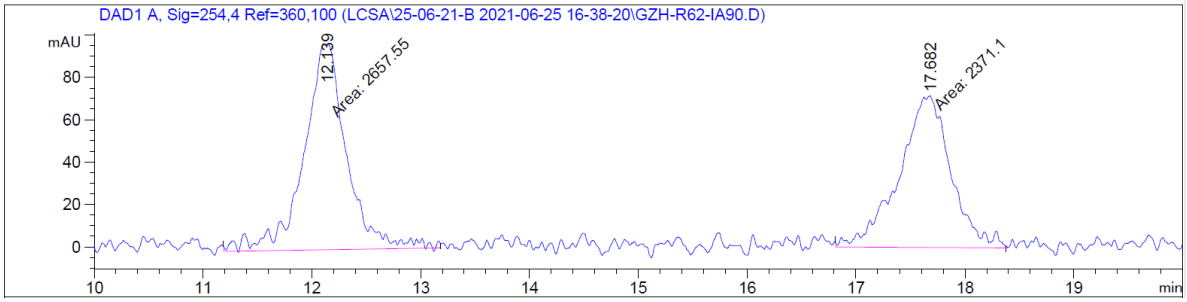
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 156.7, 130.5, 121.6, 114.3, 73.6, 55.6, 28.0, 9.3.

HRMS (ESI): (m/z): calculated for $C_{11}H_{16}NO_3^+$ $[M+H]^+$: 210.1125; found 210.1124.

FTIR (cm^{-1}): 3341, 2924, 2365, 1656, 1513, 1300, 829.

$[\alpha]_D^{20}$ = +3.05 (c = 0.38, $CHCl_3$).

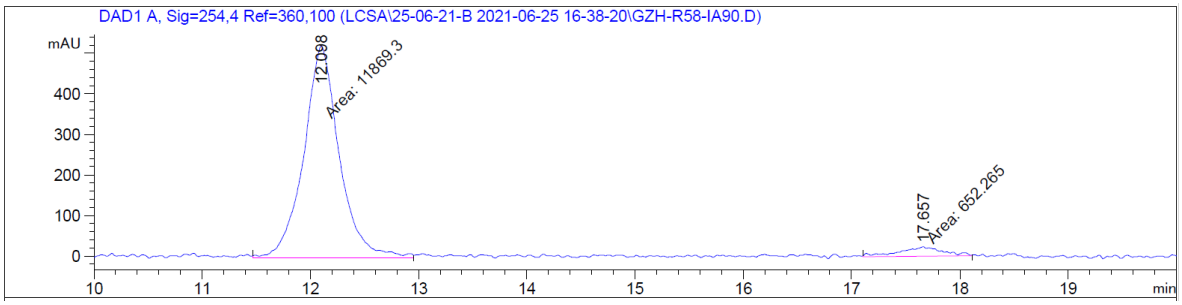
Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 12.1 min, tR (minor) 17.7 min, 95:5 *er*.




```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.139 MM    0.4561 2657.55493   97.12177  52.8482
   2  17.682 MM    0.5521 2371.10278   71.57703  47.1518

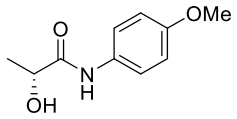
Totals :                  5028.65771  168.69881
```



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.098	MM	0.3778	1.18693e4	523.61414	94.7909
2	17.657	MM	0.4626	652.26520	23.49767	5.2091
Totals :				1.25216e4	547.11181	

(R)-2-hydroxy-N-(4-methoxyphenyl)propanamide (2o)



Following the general procedure C with **1o** (28.1 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2o** was obtained (13.8 mg, 71% yield) as a white solid.

Analytical data for **2o:**

M.P. 79-80 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.49 – 7.40 (m, 2H), 6.89 – 6.81 (m, 2H), 4.33 (q, *J* = 6.8 Hz, 1H), 3.78 (s, 3H), 1.50 (d, *J* = 6.9 Hz, 3H).

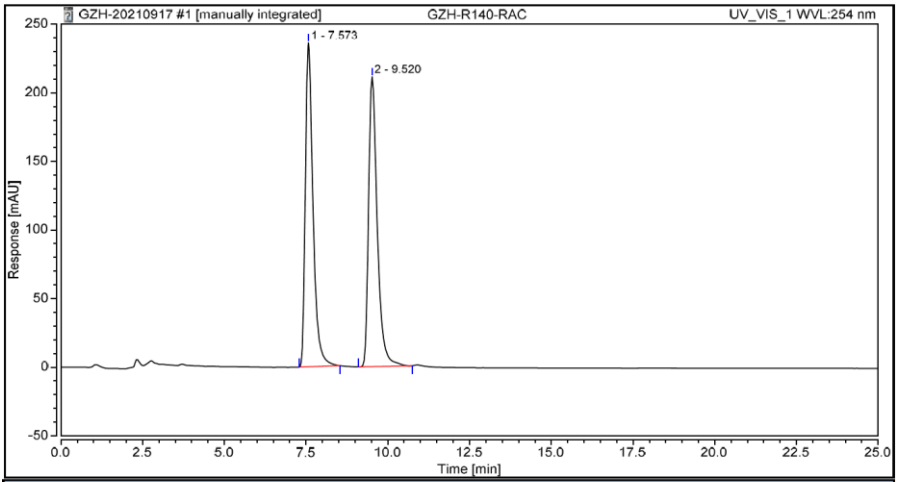
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 156.7, 130.5, 121.7, 114.3, 68.9, 55.6, 21.3.

HRMS (ESI): (m/z): calculated for $C_{10}H_{14}NO_3^+$ $[M+H]^+$: 196.0968; found 196.0973.

FTIR (cm^{-1}): 3315, 2931, 2837, 1655, 1510, 1300, 1245, 1179, 1121, 1079, 1033, 828.

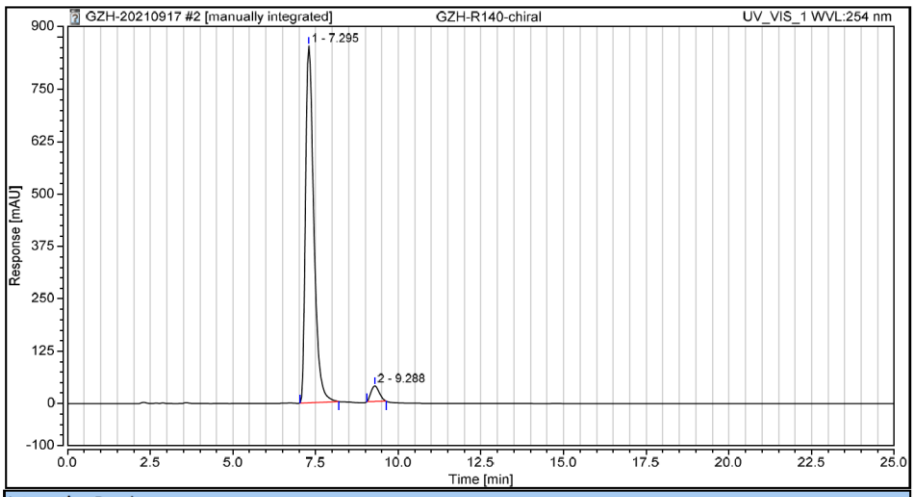
$[\alpha]_D^{20}$ = +9.01 (c = 0.87, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 7.3 min, tR (minor) 9.3 min, 96:4 *er*.



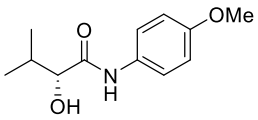
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.573	64.399	236.200	49.79	52.78	n.a.
2		9.520	64.937	211.293	50.21	47.22	n.a.
Total:			**129.336**	**447.493**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.295	249.221	852.341	95.86	95.80	n.a.
2		9.288	10.753	37.400	4.14	4.20	n.a.
Total:			**259.975**	**889.741**	**100.00**	**100.00**	

(R)-2-hydroxy-N-(4-methoxyphenyl)-3-methylbutanamide (2p)



Following the general procedure C with **1p** (30.9 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2p** was obtained (16.3 mg, 73% yield) as a white solid.

Analytical data for **2p:**

M.P. 70-71 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.50 – 7.42 (m, 2H), 6.90 – 6.82 (m, 2H), 4.10 (dd, *J* = 5.1, 3.2 Hz, 1H), 3.79 (s, 3H), 2.71 (d, *J* = 5.0 Hz, 1H), 2.29 (td, *J* = 6.9, 3.1 Hz, 1H), 1.07 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H).

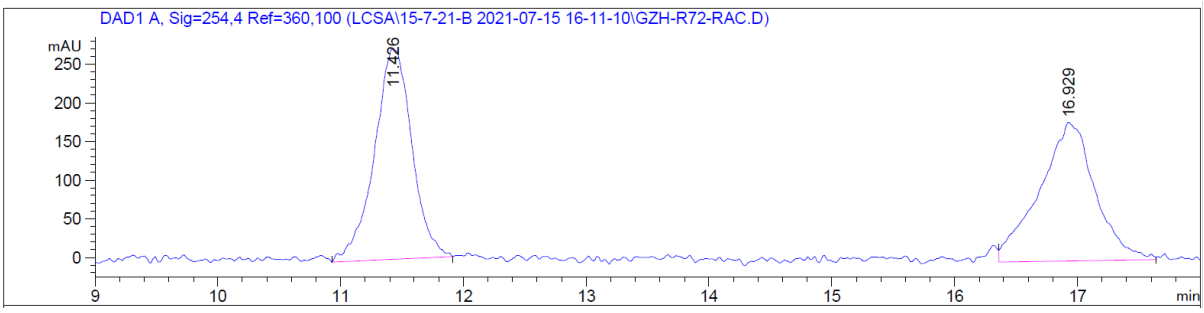
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 156.7, 130.5, 121.7, 114.3, 55.6, 32.0, 19.3, 15.6.

HRMS (ESI): (m/z): calculated for $C_{12}H_{18}NO_3^+$ $[M+H]^+$: 224.1281; found 224.1282.

FTIR (cm^{-1}): 1656, 1512, 1465, 1414, 1300, 1246, 1178, 1031, 828.

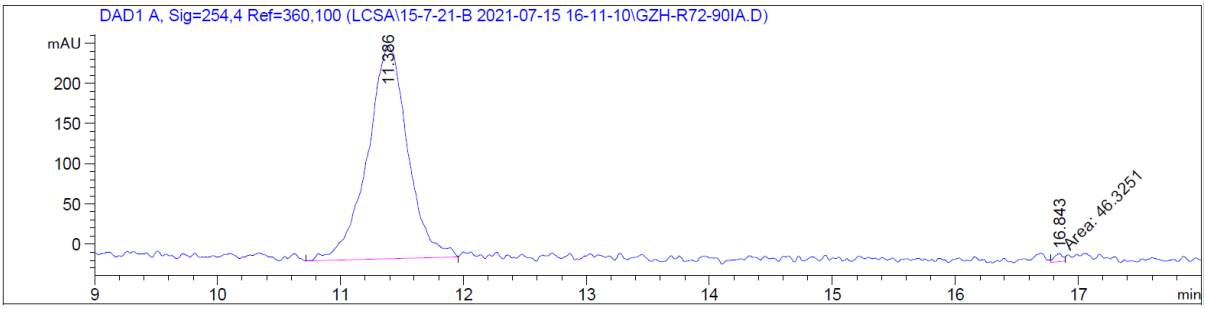
$[\alpha]_D^{20}$ = +52.40 (c = 0.51, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 11.4 min, tR (minor) 16.9 min, 99:1 *er*.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

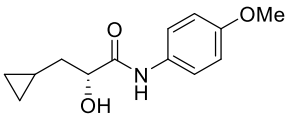
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.426	BB	0.2591	5785.61230	273.12701	50.5837
2	16.929	VV	0.3790	5652.08545	179.67058	49.4163
Totals :				1.14377e4	452.79759	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.386	BV	0.2811	6034.61182	265.55673	99.2382
2	16.843	MM	0.0780	46.32515	9.89232	0.7618
Totals :				6080.93696	275.44905	

(R)-3-cyclopropyl-2-hydroxy-N-(4-methoxyphenyl)propanamide (2q)



Following the general procedure C with **1q** (32.1 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2q** was obtained (14.5 mg, 62% yield) as a white solid.

Analytical data for **2q:**

M.P. 71 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.46 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 4.31 (dd, *J* = 7.8, 3.9 Hz, 1H), 2.95 (s, 1H), 1.85 (ddd, *J* = 14.4, 7.1, 3.9 Hz, 1H), 1.70 (ddd, *J* = 14.6, 7.8, 7.0 Hz, 1H), 0.92 – 0.78 (m, 1H), 0.59 – 0.45 (m, 2H), 0.25 – 0.12 (m, 2H).

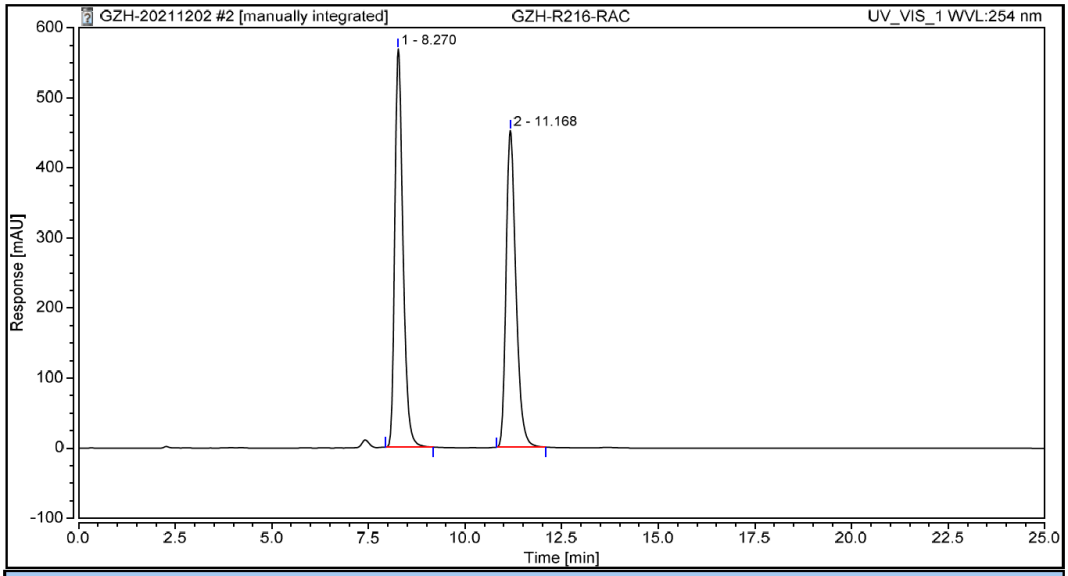
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.34, 156.62, 130.57, 121.60, 114.32, 73.28, 55.62, 39.36, 7.05, 4.60, 3.69.

HRMS (ESI): (m/z): calculated for $C_{13}H_{18}NO_3^+$ $[M+H]^+$: 236.1281; found 236.1285.

FTIR (cm^{-1}): 1651, 1599, 1527, 1510, 1463, 1246, 1077, 824.

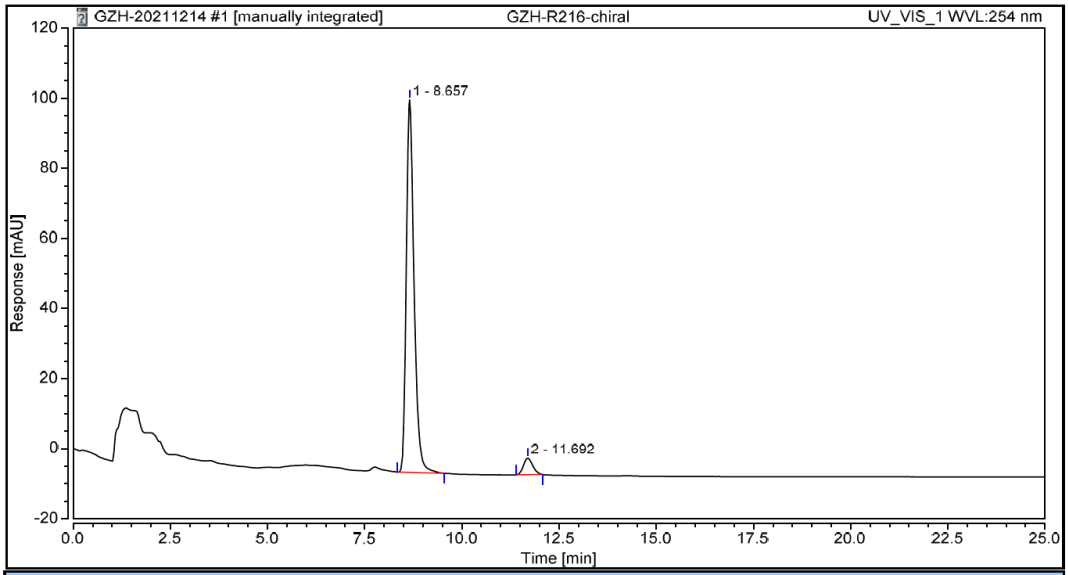
$[\alpha]_D^{20}$ = +36.05 (c = 0.64, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 8.6 min, tR (minor) 11.7 min, 99:1 *er*.



Integration Results

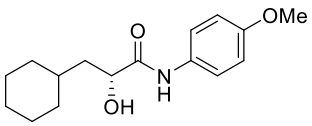
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.270	140.249	568.820	51.16	55.69	n.a.
2		11.168	133.886	452.505	48.84	44.31	n.a.
Total:			**274.134**	**1021.325**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.657	24.463	106.384	94.89	95.71	n.a.
2		11.692	1.317	4.764	5.11	4.29	n.a.
Total:			**25.781**	**111.149**	**100.00**	**100.00**	

(R)-3-cyclohexyl-2-hydroxy-N-(4-methoxyphenyl)propanamide (2r)



Following the general procedure C with **1r** (36.4 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2r** was obtained (23.3 mg, 84% yield) as a white solid.

Analytical data for **2r:**

M.P. 123-124 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.49 – 7.40 (m, 2H), 6.89 – 6.80 (m, 2H), 4.27 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.78 (s, 3H), 1.89 – 1.49 (m, 8H), 1.22 (ddddd, *J* = 24.5, 15.1, 12.1, 8.3, 6.2 Hz, 3H), 1.05 – 0.88 (m, 2H).

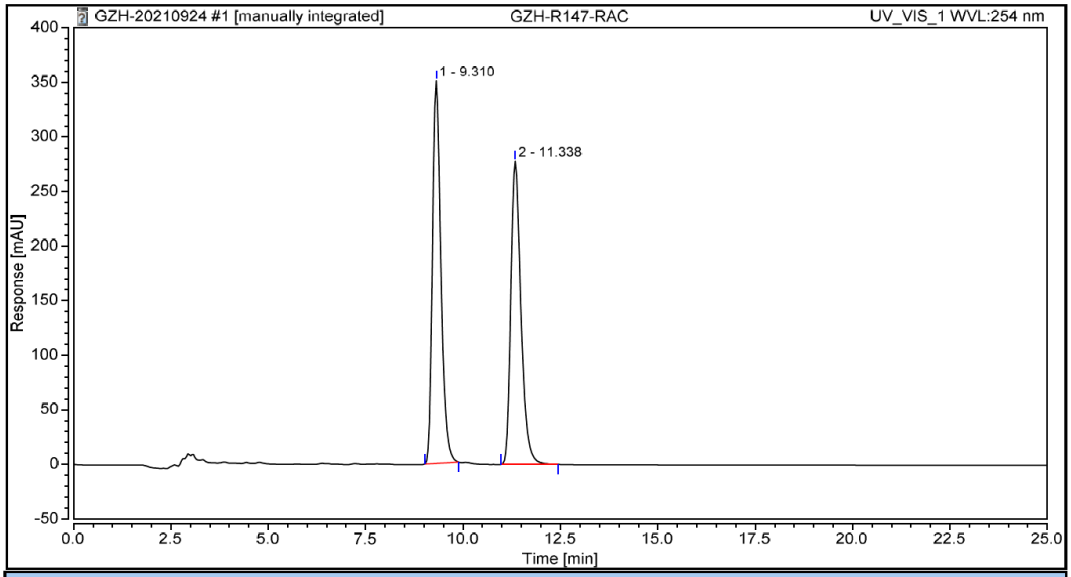
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.43, 156.61, 130.58, 121.58, 114.30, 70.75, 55.61, 42.52, 34.26, 34.10, 32.30, 26.56, 26.44, 26.21.

HRMS (ESI): (m/z): calculated for $C_{16}H_{24}NO_3^+$ $[M+H]^+$: 278.1751; found 278.1753.

FTIR (cm^{-1}): 3320, 2920, 1638, 1551, 1513, 1443, 1414, 1250, 1036, 827.

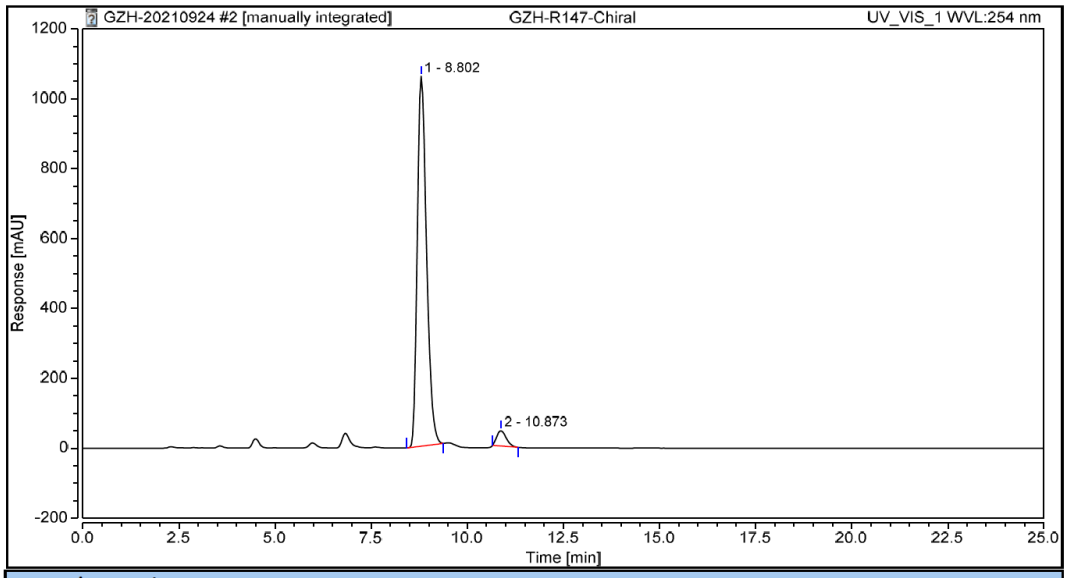
$[\alpha]_D^{20}$ = +39.96 (c = 0.96, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 8.8 min, tR (minor) 10.8 min, 96:4 *er*.



Integration Results

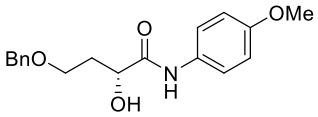
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.310	88.058	350.693	51.28	55.79	n.a.
2		11.338	83.655	277.877	48.72	44.21	n.a.
Total:			**171.713**	**628.570**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.802	296.693	1058.771	95.91	96.02	n.a.
2		10.873	12.644	43.911	4.09	3.98	n.a.
Total:			**309.337**	**1102.682**	**100.00**	**100.00**	

(R)-4-(benzyloxy)-2-hydroxy-N-(4-methoxyphenyl)butanamide (2s)



Following the general procedure C with **1s** (40.2 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2s** was obtained (19.1 mg, 61% yield) as a white solid.

Analytical data for **2s:**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.47 – 7.41 (m, 2H), 7.38 – 7.28 (m, 5H), 6.89 – 6.82 (m, 2H), 4.63 – 4.49 (m, 2H), 4.48 (s, 1H), 4.38 (dd, *J* = 7.8, 3.3 Hz, 1H), 3.91 – 3.71 (m, 5H), 2.30 (ddt, *J* = 15.0, 6.6, 3.3 Hz, 1H), 2.11 (dtd, *J* = 15.3, 7.8, 3.5 Hz, 1H).

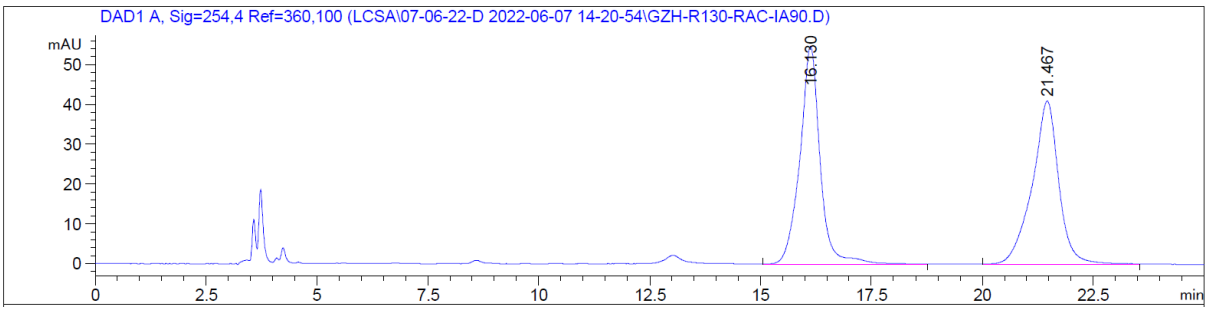
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.04, 156.51, 137.25, 130.73, 128.78, 128.28, 128.02, 121.39, 114.25, 73.89, 73.48, 69.90, 55.61, 33.36.

HRMS (ESI): (m/z): calculated for $C_{18}H_{22}NO_4^+$ $[M+H]^+$: 316.1543; found 316.1546.

FTIR (cm^{-1}): 3352, 2931, 2863, 1656, 1510, 1245, 1178, 1110, 1031, 829, 740, 698, 610.

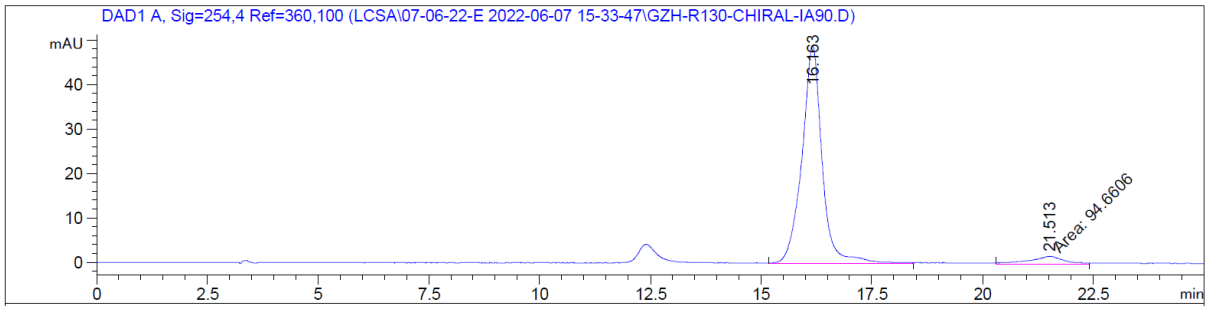
$[\alpha]_D^{20}$ = +39.28 (c = 1.32, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 8.6 min, tR (minor) 11.7 min, 94:6 *er*.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

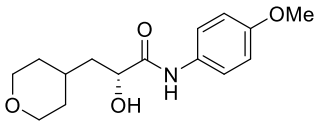
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.130	BB	0.4582	1735.43750	54.68866	50.4783
2	21.467	BB	0.5953	1702.55042	40.93324	49.5217
Totals :				3437.98792	95.62190	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.163	BB	0.4557	1531.42883	48.85885	94.1786
2	21.513	MM	0.9365	94.66064	1.68471	5.8214
Totals :				1626.08947	50.54356	

(R)-2-hydroxy-N-(4-methoxyphenyl)-3-(tetrahydro-2H-pyran-4-yl)propanamide (2t)



Following the general procedure C with **1t** (46.7 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2t** was obtained (15.7 mg, 41% yield) as a white solid.

Analytical data for **2t:**

M.P. 126 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.47 – 7.38 (m, 2H), 6.89 – 6.80 (m, 2H), 4.24 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.98 – 3.89 (m, 2H), 3.78 (s, 3H), 3.38 (tdd, *J* = 11.8, 5.1, 2.3 Hz, 2H), 1.81 (dtd, *J* = 11.9, 8.6, 7.3, 3.7 Hz, 2H), 1.72 – 1.55 (m, 2H), 1.43 – 1.26 (m, 2H).

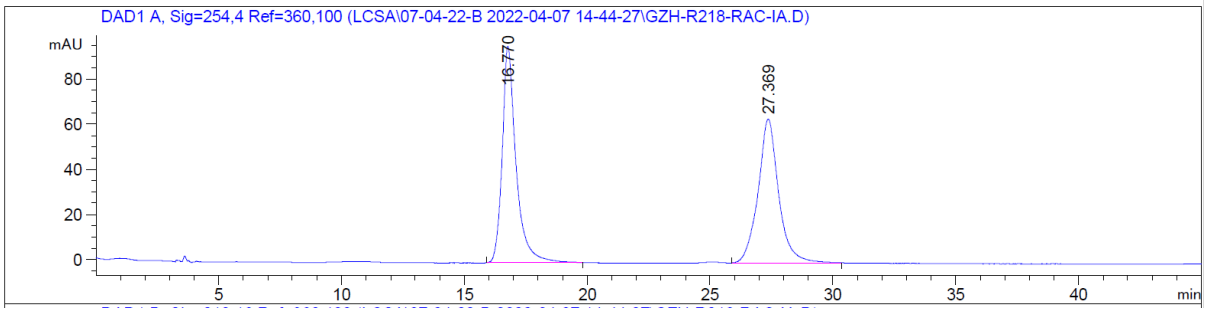
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 156.7, 130.4, 121.6, 114.3, 70.2, 68.1, 68.0, 55.6, 41.8, 33.7, 32.4, 31.6.

HRMS (ESI): (m/z): calculated for $C_{15}H_{22}NO_4$+ $[M+H]^+$: 280.1543; found 316.1546.

FTIR (cm^{-1}): 3309, 2931, 2839, 1655, 1511, 1442, 1414, 1245, 1089, 1034, 830.

$[\alpha]_D^{20}$ = +37.27 (c = 1.28, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 15.9 min, tR (minor) 26.5 min, 94:6 *er*.

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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.770 BB    0.5593 3761.80396   95.97965  50.3459
   2  27.369 BB    0.8289 3710.11157   63.75684  49.6541
```
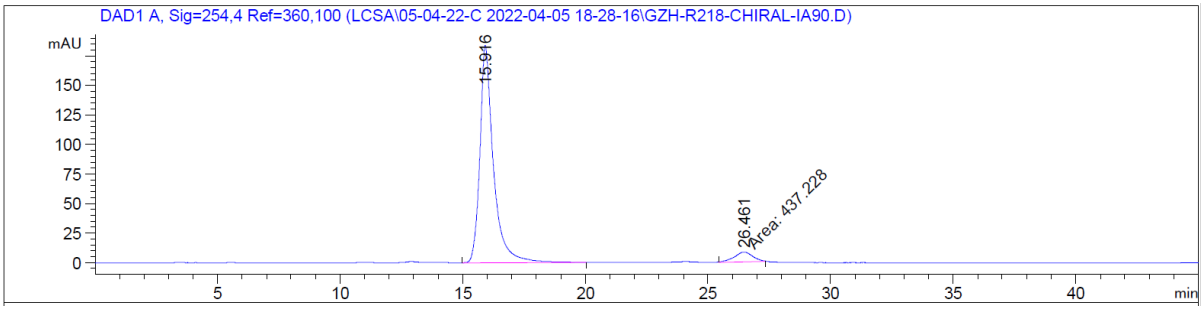
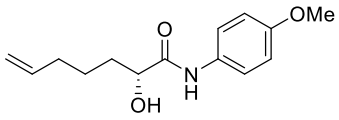



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.916	BB	0.5465	7064.33252	183.77859	94.1715
2	26.461	MM	0.8792	437.22812	8.28794	5.8285

(R)-2-hydroxy-N-(4-methoxyphenyl)hept-6-enamide (2u)



Following the general procedure C with **1u** (33.5 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2u** was obtained (XX mg, XX% yield) as a white solid.

Analytical data for **2u:**

M.P.: 89-90 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.42 – 7.33 (m, 2H), 6.82 – 6.74 (m, 2H), 5.72 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.08 – 4.77 (m, 2H), 4.14 (dd, *J* = 7.9, 3.7 Hz, 1H), 3.71 (s, 3H), 2.77 (s, 1H), 2.16 – 1.96 (m, 2H), 1.84 (ddd, *J* = 12.1, 7.4, 3.6 Hz, 1H), 1.75 – 1.60 (m, 1H), 1.58 – 1.42 (m, 2H).

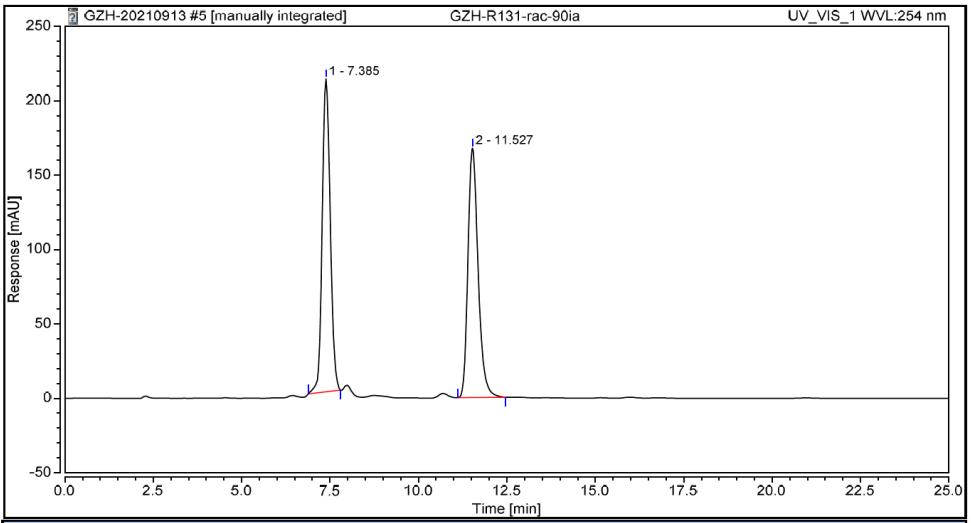
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 156.7, 138.3, 130.4, 121.6, 115.2, 114.3, 72.6, 55.6, 34.4, 33.5, 24.4.

HRMS (ESI): (m/z): calculated for $C_{14}H_{20}NO_3^+$ $[M+H]^+$: 250.1438; found 250.1436.

FTIR (cm^{-1}): 3285, 1641, 1597, 1547, 1510, 1460, 1443, 1322, 1034, 831.

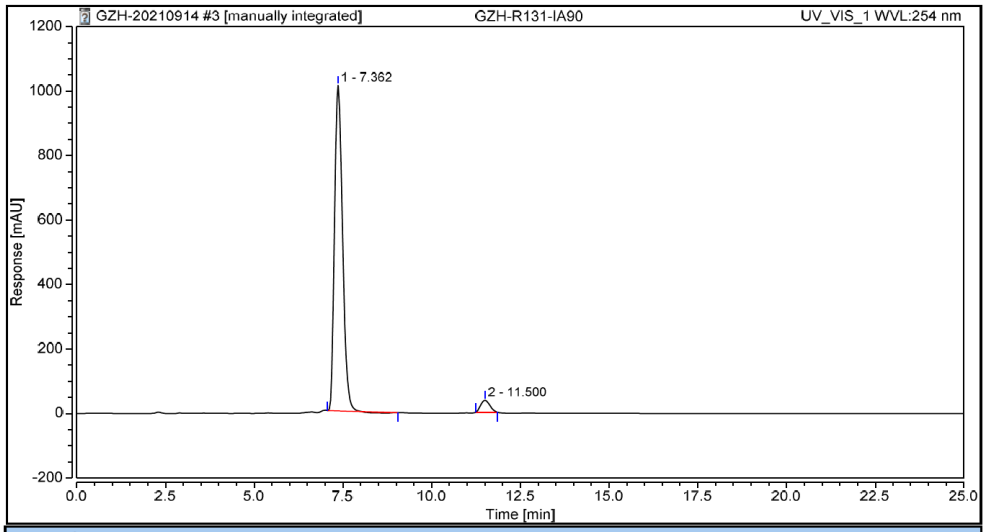
$[\alpha]_D^{20}$ = +36.28 (c = 1.06, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 7.4 min, tR (minor) 11.5 min, 96.5:3.5 *er*.



Integration Results

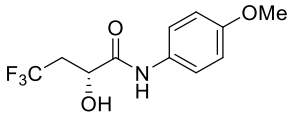
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.385	55.728	210.386	49.93	55.66	n.a.
2		11.527	55.879	167.603	50.07	44.34	n.a.
Total:			**111.607**	**377.989**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.362	263.154	1009.889	95.99	96.44	n.a.
2		11.500	10.993	37.264	4.01	3.56	n.a.
Total:			**274.147**	**1047.153**	**100.00**	**100.00**	

(R)-4,4,4-trifluoro-2-hydroxy-N-(4-methoxyphenyl)butanamide (2v)



Following the general procedure C with **1v** (34.9 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol), the corresponding product **2v** was obtained (17.3 mg, 66% yield) as a white solid.

Analytical data for **2v:**

M.P.: 144-145 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.46 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.60 (d, *J* = 9.8 Hz, 1H), 3.80 (s, 3H), 3.13 – 2.89 (m, 2H), 2.47 (dp, *J* = 15.4, 10.0 Hz, 1H).

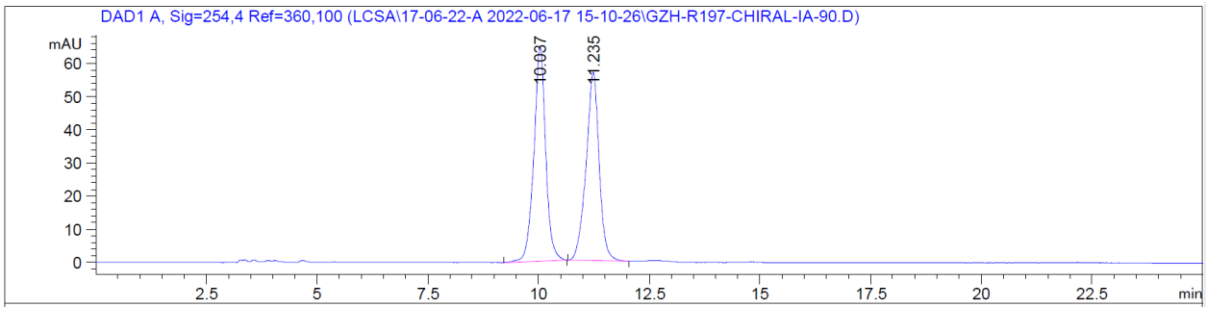
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 157.0, 130.0, 126.0 (q, $J_{C\text{-}F}$ = 188.57 Hz), 121.8, 114.4, 67.6 (q, $J_{C\text{-}F}$ = 3.1 Hz), 55.6, 38.7 (q, $J_{C\text{-}F}$ = 27.9 Hz).

HRMS (ESI): (m/z): calculated for $C_{11}H_{13}F_3NO_3^+$ $[M+H]^+$: 264.0842; found 264.0841.

FTIR (cm^{-1}): 3326, 1658, 1597, 1559, 1517, 1251, 1128, 793, 749.

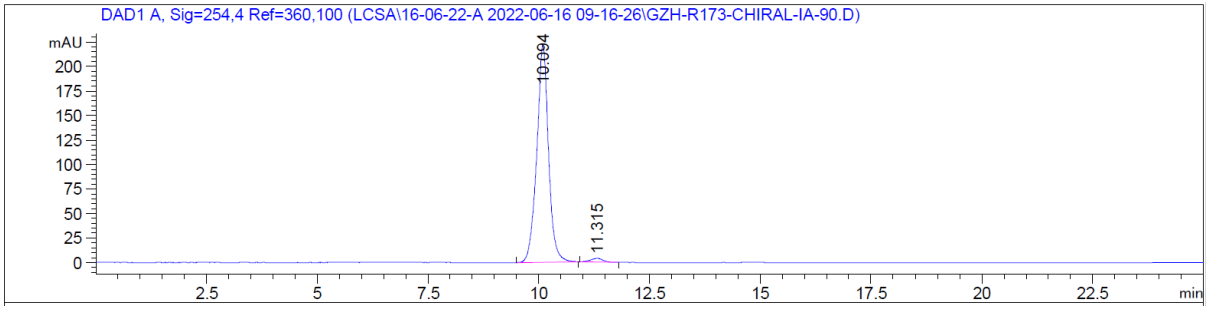
$[\alpha]_D^{20}$ = +15.41 (c = 0.47, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 10.0 min, tR (minor) 11.3 min, 98:2 *er*.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

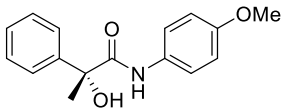
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.037	BB	0.2721	1202.75110	64.94524	50.6708
2	11.235	BB	0.3022	1170.90381	56.87564	49.3292
Totals :				2373.65491	121.82088	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.094	BB	0.2710	4090.57861	222.01001	98.2949
2	11.315	BB	0.2693	70.95937	3.77550	1.7051
Totals :				4161.53799	225.78551	

(R)-2-hydroxy-*N*-(4-methoxyphenyl)-2-phenylpropanamide (2w)



Following the general procedure C with **1w** (35.8 mg, 1.0 equiv., 0.1 mmol), DAP catalyst (1.5 mg, 5 mol%, 0.005 mmol), HBPin (30.5 uL, 2.1 equiv., 0.21 mmol) in toluene (0.2 mL), the corresponding product **2w** was obtained (17.1 mg, 63% yield) as a white solid.

Analytical data for **2w:**

M.P.: 147-149 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.65 – 7.60 (m, 2H), 7.45 – 7.41 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 6.86 – 6.80 (m, 2H), 3.77 (s, 3H), 3.05 (s, 1H, -OH), 1.91 (s, 3H).

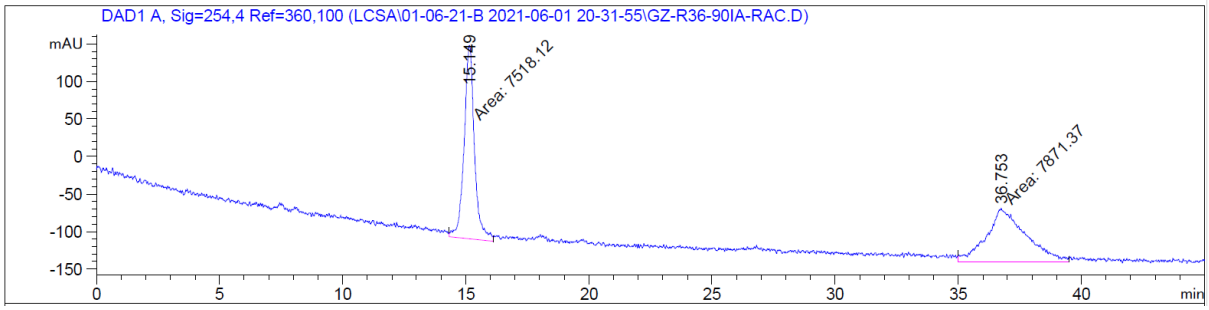
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 156.6, 143.1, 130.7, 128.7, 128.2, 125.4, 121.5, 114.3, 55.6, 27.5.

HRMS (ESI): (m/z): calculated for $C_{16}H_{18}NO_3^+$ $[M+H]^+$: 272.1281; found 272.1279.

FTIR (cm^{-1}): 1661, 1513, 1463, 1446, 1413, 1301, 1246, 1179, 1031, 828.

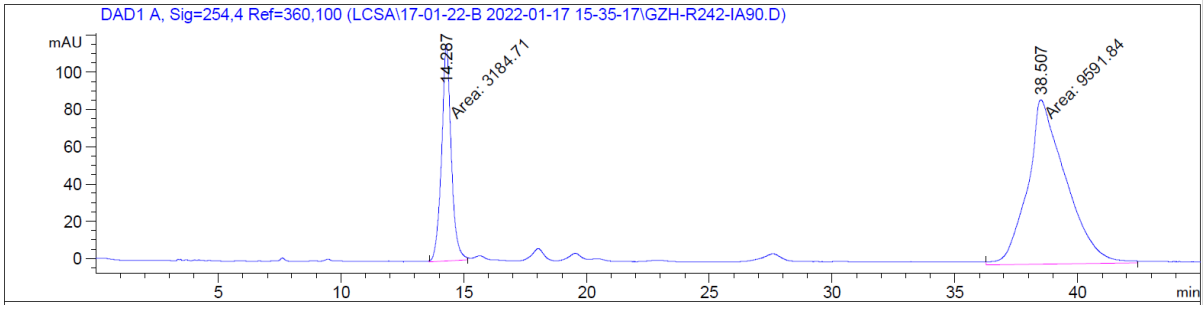
$[\alpha]_D^{20}$ = -6.33 (c = 1.0, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (minor) 14.3 min, tR (major) 38.5 min, 75:25 *er*.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

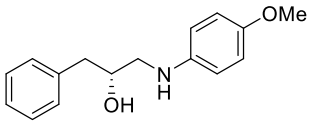
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.149	MM	0.4866	7518.11572	257.51077	48.8523
2	36.753	MM	1.8470	7871.36719	71.02966	51.1477



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.287	MM	0.4558	3184.71167	116.45961	24.9262
2	38.507	MM	1.8110	9591.83789	88.27329	75.0738

(R)-1-((4-methoxyphenyl)amino)-3-phenylpropan-2-ol (3)



In an oven-dried 5 mL pressure tube equipped with a magnetic stirring bar, **2a** (27.13 mg, 0.1 mmol, 1.0 equiv.) was dissolved in THF (0.5 mL, 0.15 M) under a nitrogen atmosphere. The solution was cooled to 0 °C and $LiAlH_4$ (7.6 mg, 0.2 mmol, 2.0 equiv., in 0.5 mL THF) was added dropwise over 10 min. The mixture was then heated at 100 °C for 12 h. The reaction was quenched with brine and filtered. The organic phase was extracted with EtOAc (3 x 5 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography to afford (R)-**3** (15.8 mg, 61% yield) as a brown solid.

Analytical data for **3:**

M.P. : 68-70 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.28 – 7.26 (m, 1H), 7.26 – 7.23 (m, 2H), 6.84 – 6.72 (m, 2H), 6.66 – 6.57 (m, 2H), 4.07 (tdd, *J* = 8.2, 5.4, 3.3 Hz, 1H), 3.75 (s, 3H), 3.26 (dd, *J* = 12.7, 3.3 Hz, 1H), 3.04 (dd, *J* = 12.7, 8.2 Hz, 1H), 2.93 – 2.77 (m, 3H).

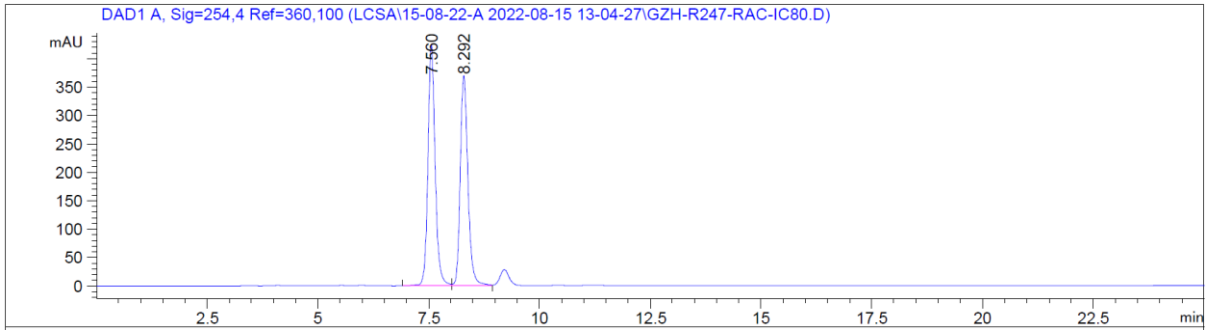
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 142.4, 137.9, 129.5, 128.8, 126.8, 115.0, 71.3, 55.9, 50.8, 41.8.

HRMS (ESI): (m/z): calculated for $C_{16}H_{20}NO_2^+$ $[M+H]^+$: 258.1489; found 258.1491.

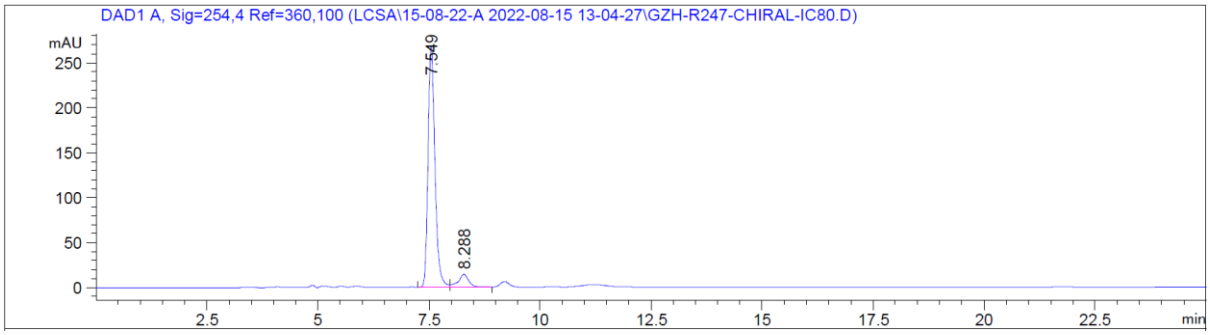
FTIR (cm^{-1}): 3381, 2930, 1512, 1454, 1238, 1179, 1085, 1035, 821, 746.

$[\alpha]_D^{20}$ = -30.11 (c = 0.65, $CHCl_3$).

Chiral HPLC (Chiralpak IA, 10 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 7.4 min, tR (minor) 11.5 min, 92.5:7.5 *er*.

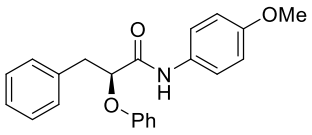


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.560	BV	0.1721	4794.96045	423.38425	51.9339
2	8.292	VV	0.1841	4437.85107	369.50461	48.0661



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.549	BV	0.1639	2894.34888	268.26691	92.4159
2	8.288	VB	0.2381	237.52493	14.27419	7.5841

(S)-N-(4-methoxyphenyl)-2-phenoxy-3-phenylpropanamide (4)



To a solution of **2a** (13.6 mg, 0.05 mmol, 1.0 equiv.), phenol (5.65 mg, 0.06 mmol, 1.2 mmol) and triphenylphosphine (15.7 mg, 0.06 mmol, 1.2 equiv.) in THF (0.1 mL) was added diethyl diazocarboxylate solution (2.2 M in toluene, 27 µL, 0.06 mol) dropwise over 14 min at 0 °C. After stirring for 48 h at the room temperature, the reaction mixture was concentrated. To this residue were added diethyl ether (1 mL) and hexane (4 mL). The resulting suspension was filtered through a pad of Celite and the filter cake was washed with a mixed solvent of diethyl ether and hexane (1:4, 5 mL). To the combined filtrates were partitioned between diethyl ether and aqueous sodium hydroxide (1 M). The aqueous phase was extracted twice with diethyl ether. The combined organic phases were dried over sodium sulfate, filtered and concentrated. The residue was purified by flash column chromatography on silica gel eluting with 10-20% ethyl acetate in hexane to give **4** (10.12 mg, 58%) as a white solid.

Analytical data for **4**:

M.P. : 113-114 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.26 – 7.15 (m, 9H), 6.98 – 6.93 (m, 1H), 6.88 – 6.83 (m, 2H), 6.81 – 6.75 (m, 2H), 4.84 (dd, *J* = 6.9, 3.9 Hz, 1H), 3.73 (s, 3H), 3.39 – 3.09 (m, 2H).

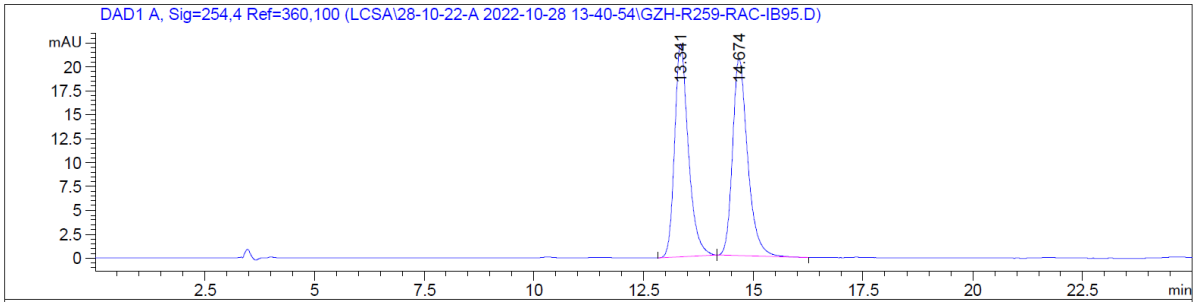
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.96, 157.26, 156.94, 136.45, 130.00, 129.96, 129.89, 128.46, 127.01, 122.57, 122.27, 115.86, 114.26, 80.11, 55.61, 39.03.

HRMS (ESI): (m/z): calculated for $C_{22}H_{22}NO_3^+$ $[M+H]^+$: 348.1594; found 348.1593.

FTIR (cm^{-1}): 2928, 1676, 1597, 1511, 1493, 1455, 1441, 1414, 1301, 1233, 1175, 1083, 1062, 1034, 828, 754, 698.

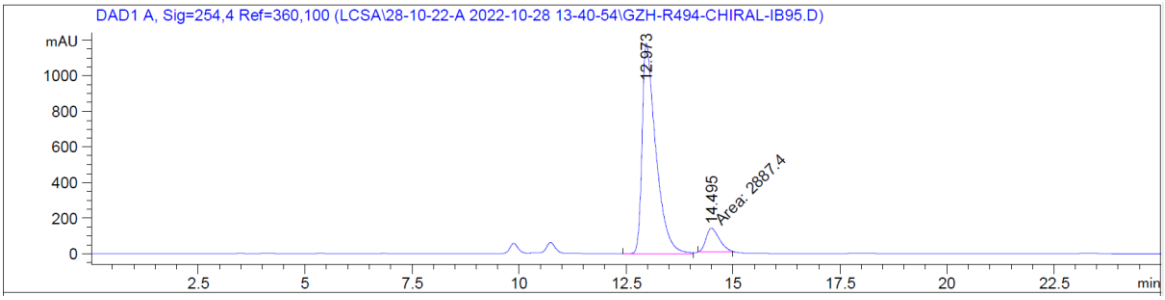
$[\alpha]_D^{20}$ = -48.44 (c = 0.32, $CDCl_3$).

Chiral HPLC (Chiralpak IB, 5 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 16.1 min, tR (minor) 18.6 min, 90:10 *er*.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

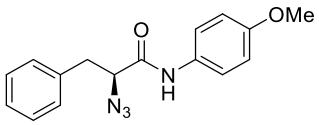
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.341	BB	0.3257	484.26846	22.27031	49.5639
2	14.674	BB	0.3587	492.79022	20.62947	50.4361



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.973	BV	0.3240	2.63416e4	1181.90613	90.1215
2	14.495	MM	0.3603	2887.39600	133.55286	9.8785

(S)-2-azido-N-(4-methoxyphenyl)-3-phenylpropanamide (5)



Step 1: Mesylation of α-hydroxy amide:

An oven-dried round-bottom flask, equipped with a magnetic stirring bar was charged with 1.0 M solution of appropriate α-hydroxy amide **2a** (1.0 equiv., 0.1 mmol, 27.1 mg) in CH_2Cl_2. This solution was treated with Et_3N (2.0 equiv., 0.4 mmol, 28 µL) and methanesulfonyl chloride (2.0 equiv., 0.4 mmol, 22.9 mg) at room temperature for 12 h or until complete as judged by TLC analysis. The reaction mixture was quenched with pH = 7 buffer solution, diluted with DCM and transferred to a separatory funnel. The organic layer was extracted and washed with saturated $NaHCO_3$, dried over $MgSO_4$ and concentrated in vacuo to afford α-methanesulfonyloxy *N*-phenylamides cleanly without the need for flash chromatography.

Step 2: Azidation of α-methanesulfonyloxy amides:

An oven-dried test tube, equipped with a magnetic stirring bar was charged with 0.5 M solution of above α-sulfonyloxy amide in DMF. This solution was treated with NaN_3 (1.1 equiv., 0.11 mmol, 7.15 mg) at 70 °C overnight. The reaction mixture was quenched with pH = 7 buffer solution, diluted with DCM and transferred to a separatory funnel. The organic layer was extracted and washed with H_2O, dried over $MgSO_4$ and concentrated in vacuo to afford α-azido *N*-phenylamide **5** as a white solid after purification by flash chromatography on silica gel (pentane:ethyl acetate = 3:1).

Analytical data for **5**:

M.P.: 67-68 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.42 – 7.24 (m, 8H), 6.92 – 6.82 (m, 2H), 4.33 (dd, *J* = 8.0, 4.3 Hz, 1H), 3.79 (s, 3H), 3.43 (dd, *J* = 14.1, 4.3 Hz, 1H), 3.12 (dd, *J* = 14.1, 8.0 Hz, 1H).

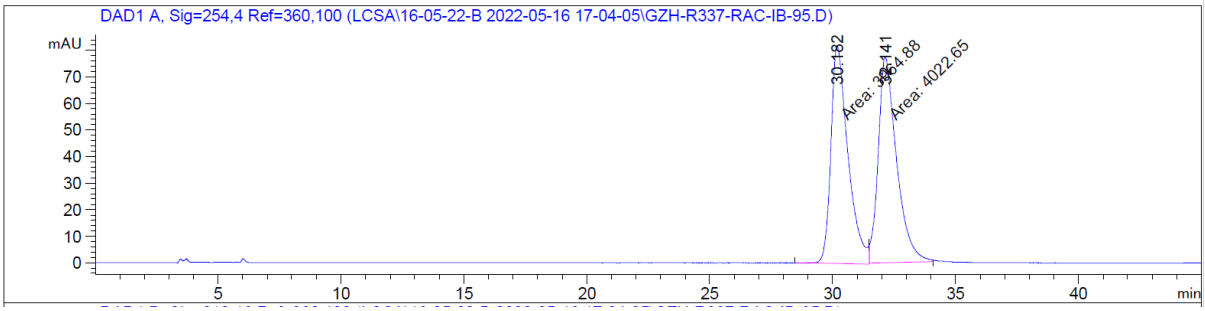
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 157.0, 136.1, 129.9, 129.7, 128.9, 127.5, 122.2, 114.3, 66.0, 55.6, 39.0.

FTIR (cm^{-1}): 3302, 2105, 1661, 1604, 1511, 1455, 1441, 1415, 1300, 1246, 1179, 1033, 828, 743.

HRMS (ESI): (m/z): calculated for $C_{16}H_{17}N_4O_2^+$ $[M+H]^+$: 297.1346; found 297.1345.

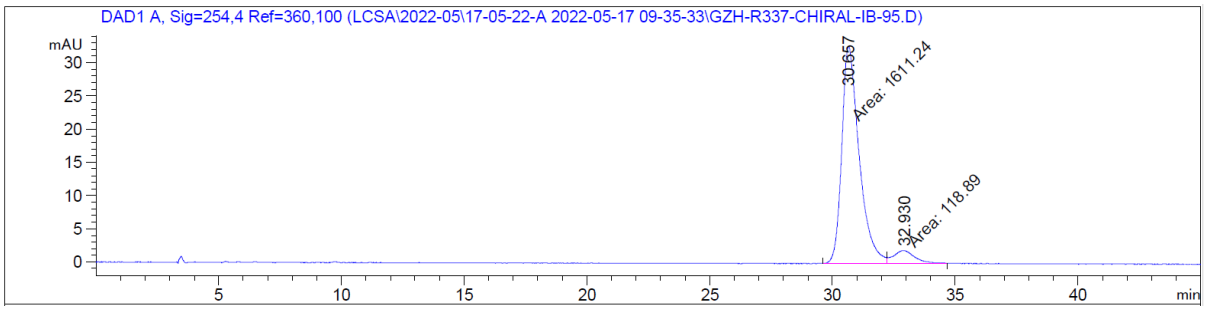
$[\alpha]_D^{20}$ = -27.87 (c = 0.88, $CHCl_3$).

Chiral HPLC (Chiralpak IB, 5 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 30.6 min, tR (minor) 32.9 min, 93:7 *er*.



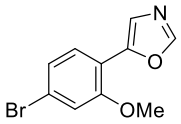
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.182	MF	0.8044	3964.88013	82.14581	49.6384
2	32.141	MM	0.8643	4022.64844	77.57420	50.3616
Totals :				7987.52856	159.72000	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.657	MF	0.8215	1611.24036	32.68917	93.1283
2	32.930	FM	1.0131	118.88955	1.95590	6.8717

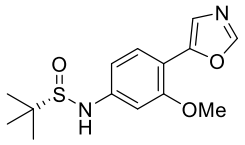
Synthesis of 5-(4-bromo-2-methoxyphenyl)oxazole (6)



A mixture of commercially available 4-bromo-2-methoxybenzaldehyde (2.15 g, 10.0 mmol), tosylmethyl isocyanide (TosMIC, 2.94 g, 15 mmol) and K_2CO_3 (5.69 g, 41.2 mmol) in anhydrous MeOH (45 mL) was heated at reflux for 24 h. After cooling to room temperature, the mixture was poured into 300 mL of ice-water and the solid precipitated was filtered. The solid was washed with water, air-dried, collected and dried in vacuo to give bromide as a yellow solid (2.09 g, 83%).

^{1}H NMR (400 M, $CDCl_3$) δ 7.91 (s, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 7.55 (s, 1H), 7.39 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H). The ^{1}H NMR spectra is consistent with literature.[2]

Synthesis of (S)-*N*-(3-methoxy-4-(oxazol-5-yl)phenyl)-2-methylpropane-2-sulfinamide (6-I)



In a sealed-tube under argon, toluene (20.0 mL) and degassed water (1.0 mL) were sequentially added to a mixture of (S)-*tert*-butanesulfinamide (1.0 equiv., 5.0 mmol, 606 mg), $Pd_2(dba)_3$•$CHCl_3$ (2 mol%, 0.1 mmol, 92 mg), ^{t}Bu-XPhos (5 mol%, 0.25 mmol, 106.2 mg), NaOH (granular, 2.4 equiv., 12 mmol, 480 mg) and 5-(4-bromo-2-methoxyphenyl)oxazole (1.26 equiv., 6.30 mmol, 1.60 g). The solution was heated at 90 ℃ for 20 h. Then the reaction mixture was cooled to room temperature, quenched by water, and extracted with EtOAc (10 mL) twice. The organic layer was combined, washed with brine (3 × 50 mL), and dried over anhydrous Na_2SO_4. The solvents was evaporated under reduced pressure to obtain the crude product, which was purified by flash chromatography. The desired product was obtained as a brown solid (1.33 g, 90% yield).

M.P.: 157-158 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 6.69 – 6.34 (m, 3H), 3.80 (s, 3H), 1.31 (s, 9H).

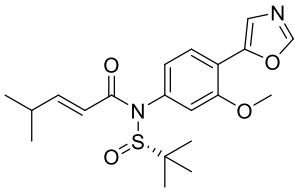
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 149.0, 147.8, 143.9, 126.7, 123.8, 111.5, 109.2, 100.8, 56.8, 55.4, 22.6.

HRMS: (m/z): calculated for $C_{14}H_{19}N_2O_3S^+$ $[M+H]^+$: 295.1111; found 295.1115.

FTIR (cm^{-1}): 1614, 1576, 1499, 1458, 1300, 1271, 1198, 1172, 1091, 1058, 1039, 966, 829, 641.

$[\alpha]_D^{20}$ = -1.96 (c = 1.02, $CDCl_3$).

Synthesis of (S,E)-*N*-(tert-butylsulfinyl)-*N*-(3-methoxy-4-(oxazol-5-yl)phenyl)-4-methylpent-2-enamide (7)



To an oven-dried BFR were added (S)-*N*-(3-methoxy-4-(oxazol-5-yl)phenyl)-2-methylpropane-2-sulfinamide (1.0 equiv., 1.0 mmol, 294.4 mg), Et_3N (6.0 equiv., 6.0 mmol, 0.84 mL), and 4-dimethylaminopyridine (0.05 equiv., 0.05 mmol, 6.11 mg) in THF (25 mL) under N_2. Then, (E)-4-methylpent-2-enoyl chloride (2.0 equiv., 2.0 mmol, 264 mg) was added dropwise. The reaction mixture was stirred at room temperature. After 24 hours, the reaction was quenched by adding water (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried over $MgSO_4$. After filtration and concentration, the crude residue was purified by flash column chromatography on silica gel (5:1 to 1:1 pentane/ethyl acetate) to yield the desired products (256.5 mg) with 66% yield as a yellow oil.

Analytical data for **7**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.63 (s, 1H), 7.08 – 6.97 (m, 2H), 6.94 (dd, *J* = 8.3, 1.9 Hz, 1H), 5.75 (d, *J* = 15.2 Hz, 1H), 3.99 (s, 3H), 2.36 (dqd, *J* = 13.7, 6.9, 1.4 Hz, 1H), 1.18 (s, 9H), 0.97 (d, *J* = 6.7 Hz, 6H).

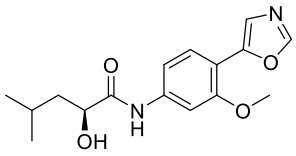
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 156.7, 155.8, 150.0, 147.3, 135.6, 126.6, 126.0, 123.4, 118.2, 117.6, 113.9, 61.0, 56.1, 31.5, 23.4, 21.5.

HRMS: (m/z): calculated for $C_{20}H_{27}N_2O_4S^+$ $[M+H]^+$: 391.1686; found 391.1682.

FTIR (cm^{-1}): 2963, 1672, 1631, 1602, 1535, 1492, 1463, 1452, 1408, 1300, 1270, 1215, 1188, 1160, 1135, 1095, 1039, 754.

$[\alpha]_D^{20}$ = -39.35 (c = 2.30, $CDCl_3$).

Synthesis of (S)-2-hydroxy-*N*-(3-methoxy-4-(oxazol-5-yl)phenyl)-4-methylpentanamide (8)



To a solution of (S,*E*)-*N*-(tert-butylsulfinyl)-*N*-(3-methoxy-4-(oxazol-5-yl)phenyl)-4-methylpent-2-(78.0 mg, 1.0 equiv., 0.2 mmol) in THF (0.4 mL) was added 2-(benzyloxy)-1,3-di-tert-butyl-2,3-dihydro-1H-1,3,2-diazaphosphole (DAP catalyst, 5 mol%, 0.01 mmol, 3.0 mg), and pinacolborane (2.1 equiv., 0.42 mmol, 71.0 uL) in the glovebox. Then the mixture was stirred at room temperature overnight. Then, the reaction was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with sodium bicarbonate and brine. The collected organic layers were dried over anhydrous $MgSO_4$. After filtration and concentration, the crude residue was purified by flash column chromatography on silica gel (5:1 to 1:1 pentane/ethyl acetate) to yield the desired α-hydroxyl amide products (39.2 mg, 64% yield).

Analytical data for **8**:

M.P. 151-152 ℃.

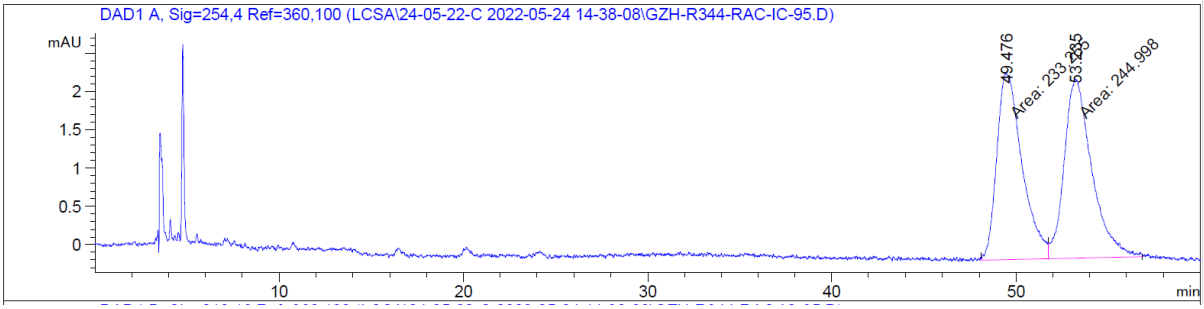
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.88 (s, 1H), 7.71 – 7.61 (m, 2H), 7.48 (s, 1H), 6.98 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.30 (dd, *J* = 9.8, 3.3 Hz, 1H), 3.96 (s, 3H), 1.96 – 1.85 (m, 1H), 1.80 (ddd, *J* = 14.1, 9.4, 3.4 Hz, 1H), 1.65 (ddd, *J* = 14.2, 9.8, 4.7 Hz, 1H), 1.00 (dd, *J* = 6.5, 2.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.74, 156.41, 149.35, 148.02, 138.77, 126.42, 124.58, 113.16, 111.52, 102.73, 71.44, 55.73, 43.79, 24.79, 23.56, 21.57.

HRMS (ESI): (m/z): calculated for $C_{16}H_{21}N_2O_4^+$ $[M+H]^+$: 305.1496; found 305.1490.

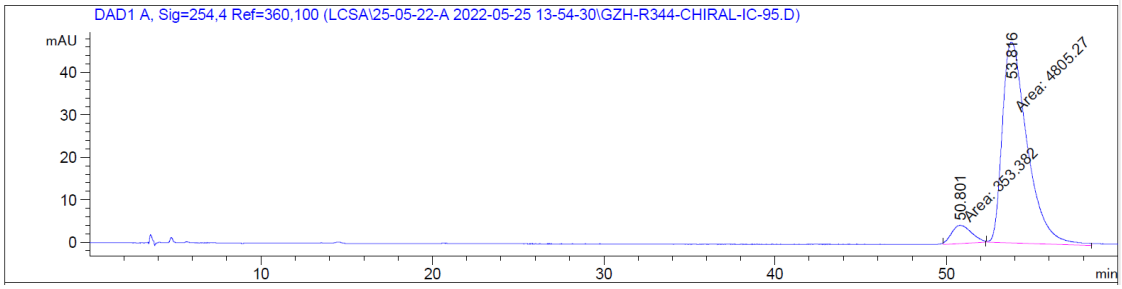
$[\alpha]_D^{20}$ = -36.67 (c = 1.00, $CHCl_3$).

Chiral HPLC (Chiralpak IC, 5 % i-PrOH/hexane, 1.0 mL/min, 254 nm): tR (major) 53.8 min, tR (minor) 50.8 min, 93:7 *er*.



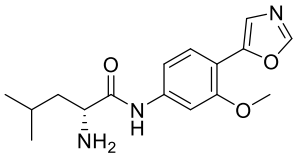
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.476	MF	1.5835	233.25542	2.45503	48.7723
2	53.235	FM	1.7410	244.99844	2.34541	51.2277



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.801	MM	1.3550	353.38205	4.34654	6.8503
2	53.816	MM	1.6940	4805.27246	47.27804	93.1497

Synthesis of (R)-2-amino-*N*-(3-methoxy-4-(oxazol-5-yl)phenyl)-4-methylpentanamide (9)



Mesylation of α-hydroxy amide:

An oven-dried round-bottom flask, equipped with a magnetic stirring bar was charged with 1.0 M solution of appropriate α-hydroxy amide (1.0 equiv., 0.02 mmol, 6.0 mg) in CH_2Cl_2. This solution was treated with Et_3N (4.0 equiv., 0.08 mmol, 11µL) and methanesulfonyl chloride (4.0 equiv., 0.08 mmol, 9.0 mg) at room temperature for 24 h or until complete as judged by TLC analysis. The reaction mixture was quenched with pH 7 buffer solution, diluted with DCM and transferred to a separatory funnel. The organic layer was extracted and washed with saturated $NaHCO_3$, dried over $MgSO_4$ and concentrated in vacuo to afford α-methanesulfonyloxy *N*-phenylamides cleanly without the need for flash chromatography.

Azidation of α-methanesulfonyloxy amides:

An oven-dried test tube, equipped with a magnetic stirring bar was charged with 0.5 M solution of above α-sulfonyloxy amide in DMF. This solution was treated with NaN_3 (2.0 equiv., 0.04 mmol, 2.57 mg) at 70 °C for 48 h or until complete as judged by TLC analysis. The reaction mixture was quenched with pH 7 buffer solution, diluted with DCM and transferred to a separatory funnel. The organic layer was extracted and washed with H_2O, dried over $MgSO_4$ and concentrated in vacuo to afford α-azido *N*-phenylamides cleanly without the need for flash chromatography.

Reduction of α-azido amides:

A 0.07 M solution of above α-azido *N*-aryl amide in EtOH was stirred with 10% by mass (based on substrate) of 5% Pd on C catalyst (10 wt%, 5.5mg) under 1 atm of H_2 at room temperature overnight. The reaction mixture was filtered over Celite and the filtrate was concentrated in vacuo. The crude product was purified through PTLC on silica gel (DCM:MeOH = 10:1) yield desired product (2.8 mg, 43% overall yield).

Analytical data for **10**:

^{1}H NMR (400 MHz, MeOD) δ 8.10 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.37 (s, 1H), 7.13 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.89 (s, 3H), 3.40 (dd, *J* = 8.3, 6.0 Hz, 1H), 3.25 (s, 2H), 1.67 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.54 (ddd, *J* = 13.8, 7.9, 6.1 Hz, 1H), 1.39 (ddd, *J* = 13.8, 8.3, 6.2 Hz, 1H), 0.89 (dd, *J* = 7.9, 6.5 Hz, 6H). The ^{1}H NMR spectra is consistent with literature.[2]

$[\alpha]_D^{20}$ = -54.85 (c = 0.50, MeOH).

NMR experiments

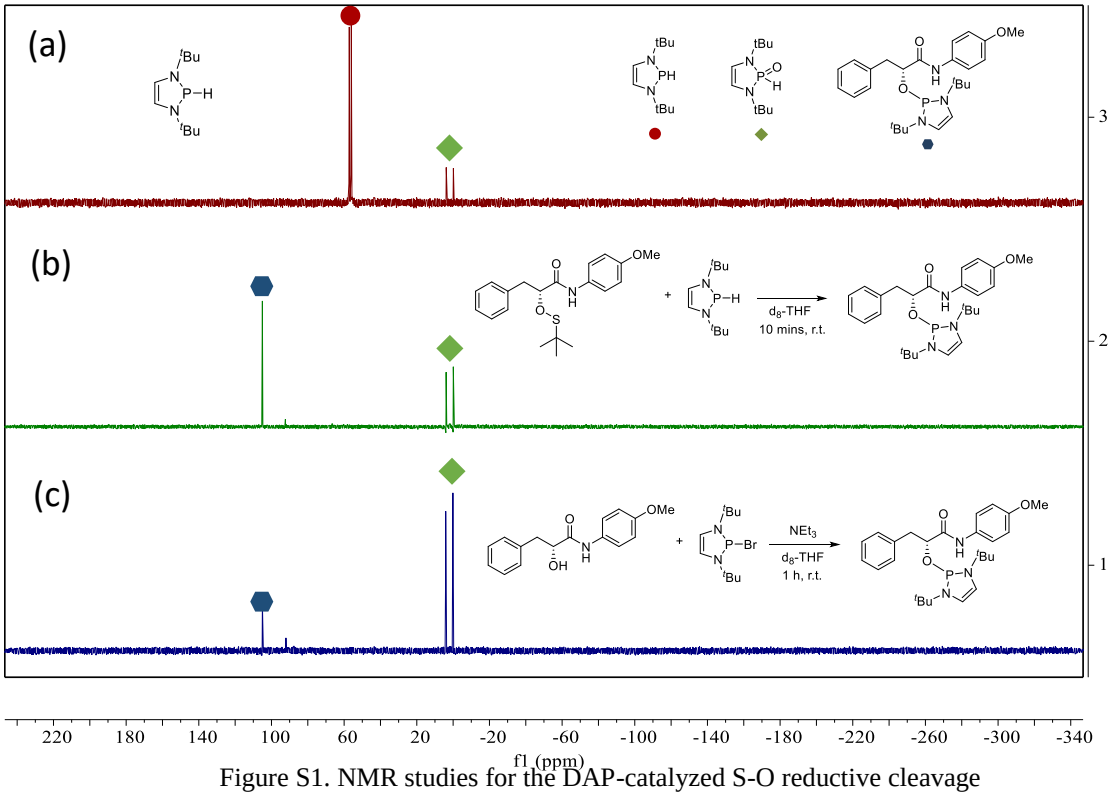


Figure S1. NMR studies for the DAP-catalyzed S-O reductive cleavage

A J-Young NMR tube inside the glovebox was charged with (R)-2-((tert-butylthio)oxy)-N-(4-methoxyphenyl)-3-phenylpropanamide (17.9 mg, 0.05 mmol) and THF-d_8 (500 µL). 1,3-di-tert-butyl-2,3-dihydro-1H-1,3,2-diazaphosphole (10.01 mg, 0.05 mmol) was then added, the tube was capped and shaken vigorously. After 10 minutes, the ^{31}P spectra was recorded, as shown in Figure S1b.

A J-Young NMR tube inside the glovebox was charged with (R)-2-hydroxy-N-(4-methoxyphenyl)-3-phenylpropanamide (13.5 mg, 0.05 mmol), trimethylamine (7.0 µL, 0.05 mmol) and THF-d_8 (500 µL). 2-bromo-1,3-di-tert-butyl-2,3-dihydro-1H-1,3,2-diazaphosphole (13.9 mg, 0.05 mmol) was then added, the tube was capped and shaken vigorously. After 10 minutes, the ^{31}P spectra was recorded, as shown in Figure S1c.

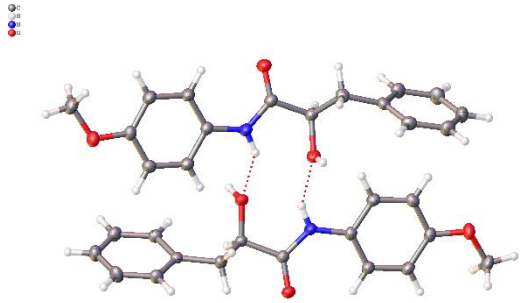
References

[1] J. H. Reed, P. A. Donets, S. Miaskiewicz, N. Cramer, *Angew. Chem. Int. Ed.* **2019**, *58*, 8893-8897.

[2] R. A. Hartz, V. T. Ahuja, S. J. Nara, C. M. V. Kumar, J. M. Brown, L. J. Bristow, R. Rajamani, J. K. Muckelbauer, D. Camac, S. E. Kiefer, L. Hunihan, M. Gulianello, M. Lewis, A. Easton, J. S. Lippy, N. Surti, S. N. Pattipati, M. Dokania, S. Elavazhagan, K. Dandapani, B. D. Hamman, J. Allen, W. Kostich, J. J. Bronson, J. E. Macor, C. D. Dzierba, *J. Med. Chem.* **2021**, *64*, 11090-11128.

Absolute configuration determination of 2a

2a (20 mg) was dissolved in $CHCl_3$ (5 mL) and allowed to slowly evaporate at -4 °C. Crystal formed after 2days. X-ray ananlysis revealed the absolute stereochemistry of **2a** to be (R). Flack parameter = 0.01(8).



Ortep-represention of (*R*)-**2a** (thermal ellipsoids set at 50% probability). CCDC2208341 contains the crystallographic data for (*R*)-**2a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Compound	**2a**
Formula	$C_{16}H_{17}NO_3$
$D_{calc.}$/ g cm^{-3}	1.337
□/mm^{-1}	0.752
Formula Weight	271.30
Colour	clear pale colourless
Shape	plate-shaped
Size/mm^3	0.31×0.26×0.05
T/K	140.01(10)
Crystal System	monoclinic
Flack Parameter	0.01(8)
Hooft Parameter	0.01(8)
Space Group	$P2_1$
a/Å	5.73113(10)
b/Å	15.7352(3)
c/Å	15.1230(3)
□/°	90
□/°	98.7304(16)
□/°	90
V/Å^3	1347.99(4)
Z	4
Z'	2
Wavelength/Å	1.54184
Radiation type	Cu K□
□$_{min}$/°	2.956
□$_{max}$/°	76.560
Measured Refl's.	15472
Indep't Refl's	5472
Refl's I≥2 □(I)	5274
R_{int}	0.0227
Parameters	380
Restraints	1
Largest Peak	0.194
Deepest Hole	-0.153
GooF	1.046
wR_2 (all data)	0.0747
wR_2	0.0731
R_1 (all data)	0.0309
R_1	0.0289

Reflection Statistics

Total reflections (after filtering)	15495	Unique reflections	5472
Completeness	0.965	Mean I/□	26.47
hkl_{max} collected	(7, 18, 19)	hkl_{min} collected	(-7, -19, -18)
hkl_{max} used	(7, 18, 19)	hkl_{min} used	(-7, -19, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	15.74	d_{min} used	0.79
Friedel pairs	2383	Friedel pairs merged	0
Inconsistent equivalents	12	R_{int}	0.0227
R_{sigma}	0.0233	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(3297, 2401, 1137, 519, 240, 67, 31, 9, 2)	Maximum multiplicity	10
Removed systematic absences	23	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	-1086(3)	6255.2(10)	1286.6(9)	31.0(3)
O2	2771(2)	6727.0(9)	5614.7(9)	25.9(3)
O3	8572(2)	5849.7(9)	5712.9(9)	24.1(3)
N1	4741(3)	6105.2(11)	4576.4(11)	23.5(3)
C1	-3015(4)	6830.7(15)	1110.3(14)	33.2(4)
C2	169(3)	6252.1(12)	2130.9(12)	23.6(4)
C3	-446(3)	6678.0(13)	2865.0(13)	25.2(4)
C4	1014(3)	6631.1(12)	3693.3(13)	24.4(4)
C5	3087(3)	6159.6(12)	3779.9(12)	22.0(4)
C6	3685(3)	5729.8(12)	3038.5(13)	24.1(4)
C7	2235(3)	5769.7(12)	2223.6(12)	25.3(4)
C8	4557(3)	6398.6(12)	5394.9(12)	20.8(3)
C9	6821(3)	6326.7(12)	6077.4(12)	20.9(3)
C10	6271(3)	5901.5(12)	6926.2(12)	22.3(3)
C11	8146(3)	5973.9(12)	7746.7(12)	21.2(3)
C12	10271(3)	6407.6(12)	7761.7(12)	23.5(4)
C13	11887(3)	6473.6(13)	8547.2(14)	28.0(4)
C14	11413(4)	6092.5(14)	9326.7(14)	30.8(4)
C15	9321(4)	5643.1(14)	9317.5(13)	30.9(4)
C16	7710(3)	5591.5(13)	8538.4(13)	25.5(4)
O4	15733(2)	3613.0(10)	8791.6(9)	28.3(3)
O5	13109(2)	3568.6(11)	4343.8(9)	32.7(3)
O6	7316(3)	4487.6(10)	4152.2(9)	28.7(3)
N2	10886(3)	4094.6(11)	5352.3(11)	25.7(3)
C17	17911(4)	3165.4(15)	8975.6(14)	33.0(4)
C18	14721(3)	3697.4(12)	7914.3(12)	23.8(4)
C19	12647(3)	4172.9(12)	7783.0(12)	24.2(4)
C20	11441(3)	4288.6(12)	6933.0(13)	24.2(4)
C21	12289(3)	3942.9(12)	6190.6(12)	23.3(4)
C22	14370(3)	3471.3(13)	6319.0(12)	25.7(4)
C23	15584(3)	3349.4(13)	7185.8(13)	26.6(4)
C24	11307(3)	3909.4(12)	4525.5(13)	24.2(4)
C25	9283(3)	4167.3(12)	3782.2(12)	24.0(4)
C26	8641(4)	3413.1(12)	3160.3(12)	26.0(4)
C27	6833(3)	3602.7(13)	2349.6(12)	24.4(4)
C28	7297(3)	4164.6(13)	1683.5(14)	28.6(4)
C29	5672(4)	4280.9(14)	912.6(14)	32.6(4)
C30	3560(4)	3832.8(15)	794.8(13)	32.8(4)
C31	3069(4)	3284.5(14)	1455.2(14)	32.4(4)
C32	4684(3)	3177.7(13)	2229.7(13)	28.2(4)

Table 2: Anisotropic Displacement Parameters (×10^4) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	32.8(7)	33.6(8)	23.5(7)	-2.3(5)	-5.4(6)	4.9(6)
O2	19.2(6)	33.1(7)	25.6(6)	-4.2(5)	4.1(5)	3.6(5)
O3	18.4(6)	28.9(7)	25.4(6)	-3.9(5)	5.0(5)	2.3(5)
N1	18.7(7)	29.6(8)	21.8(8)	-1.4(6)	1.7(6)	4.9(6)
C1	25.7(9)	42.6(13)	28.6(10)	2.6(8)	-4.3(8)	4.6(8)
C2	22.5(8)	25.0(10)	22.0(9)	0.4(7)	-1.1(7)	-2.4(7)
C3	19.9(8)	28.0(9)	26.9(9)	1.0(7)	1.0(7)	3.4(7)
C4	22.0(8)	27.7(10)	23.4(9)	-1.6(7)	3.0(7)	1.8(7)
C5	20.3(8)	23.0(9)	22.1(8)	0.9(6)	1.2(7)	-0.9(6)
C6	22.6(8)	24.6(9)	25.1(9)	0.5(7)	3.2(7)	4.0(7)
C7	29.0(9)	25.1(9)	22.0(9)	-2.8(7)	4.5(7)	0.2(7)
C8	19.3(8)	20.7(8)	22.3(8)	0.6(6)	2.9(6)	-0.1(7)
C9	17.9(8)	23.5(9)	21.6(8)	-2.0(6)	3.7(6)	1.3(7)
C10	20.4(8)	25.8(9)	20.7(8)	0.0(6)	3.1(6)	-2.3(7)
C11	19.9(8)	21.8(9)	22.1(8)	-2.8(6)	4.0(6)	1.7(7)
C12	22.5(8)	23.8(9)	24.6(9)	1.4(7)	5.4(7)	-0.6(7)
C13	22.4(8)	29.9(10)	31.1(10)	-1.4(7)	2.0(7)	-3.7(8)
C14	28.1(10)	38.5(11)	24.2(9)	-3.3(8)	-1.1(7)	-3.8(8)
C15	34.6(11)	38.4(12)	20.0(9)	1.0(7)	5.0(8)	-5.5(8)
C16	24.4(9)	28.3(9)	24.4(9)	-1.3(7)	5.8(7)	-5.6(7)
O4	28.8(7)	31.1(7)	23.4(6)	1.1(5)	-1.1(5)	1.5(6)
O5	25.0(7)	45.7(9)	27.5(7)	-2.8(6)	4.8(5)	9.4(6)
O6	24.3(7)	31.8(8)	29.0(7)	-6.1(6)	1.2(5)	8.1(6)
N2	21.4(7)	31.5(9)	23.7(8)	-1.8(6)	1.6(6)	6.9(6)
C17	27.1(9)	38.3(12)	31.3(10)	3.9(8)	-3.6(8)	1.6(8)
C18	23.5(9)	24.6(9)	22.3(8)	0.9(7)	0.1(7)	-3.2(7)
C19	24.6(9)	24.5(9)	24.4(9)	-1.6(7)	6.4(7)	-0.3(7)
C20	21.8(8)	24.3(9)	26.5(9)	-0.7(7)	3.8(7)	2.4(7)
C21	21.2(8)	24.4(9)	23.5(9)	-1.2(7)	1.3(7)	0.7(7)
C22	23.2(8)	29.0(10)	24.6(9)	-2.8(7)	2.3(7)	3.9(7)
C23	23.0(8)	26.7(10)	29.1(9)	-0.2(7)	1.3(7)	3.8(7)
C24	21.4(8)	24.9(9)	26.1(9)	-0.1(7)	2.8(7)	2.0(7)
C25	21.8(8)	26.4(9)	23.8(9)	-0.4(7)	3.2(7)	3.0(7)
C26	29.4(9)	23.4(9)	25.3(9)	-0.5(7)	4.2(7)	1.5(7)
C27	27.0(9)	24.9(9)	21.7(8)	-4.5(7)	4.9(7)	1.7(7)
C28	26.3(9)	30.5(10)	28.8(9)	-2.2(8)	3.8(7)	-5.4(7)
C29	35.8(11)	36.4(12)	25.9(9)	5.7(8)	5.8(8)	-5.2(9)
C30	28.0(10)	43.9(12)	24.9(9)	-3.0(8)	-1.5(7)	-0.8(8)
C31	25.5(9)	37.0(12)	34.8(10)	-2.8(8)	4.9(8)	-5.6(8)
C32	27.6(9)	29.2(10)	29.4(9)	2.1(7)	9.4(7)	-0.8(7)

Table 3: Bond Lengths in Å for **2a**.

Atom	Atom	Length/Å
O1	C1	1.423(2)
O1	C2	1.367(2)
O2	C8	1.236(2)
O3	C9	1.429(2)
N1	C5	1.418(2)
N1	C8	1.340(2)
C2	C3	1.387(3)
C2	C7	1.395(3)
C3	C4	1.399(3)
C4	C5	1.390(3)
C5	C6	1.396(3)
C6	C7	1.379(3)
C8	C9	1.534(2)
C9	C10	1.522(2)
C10	C11	1.517(2)
C11	C12	1.393(2)
C11	C16	1.396(3)
C12	C13	1.395(3)
C13	C14	1.386(3)
C14	C15	1.391(3)
C15	C16	1.384(3)
O4	C17	1.423(2)

Atom	Atom	Length/Å
O4	C18	1.371(2)
O5	C24	1.231(2)
O6	C25	1.425(2)
N2	C21	1.415(2)
N2	C24	1.341(2)
C18	C19	1.393(3)
C18	C23	1.387(3)
C19	C20	1.376(3)
C20	C21	1.399(3)
C21	C22	1.393(3)

Atom	Atom	Length/Å
C22	C23	1.401(3)
C24	C25	1.542(2)
C25	C26	1.524(3)
C26	C27	1.510(3)
C27	C28	1.396(3)
C27	C32	1.389(3)
C28	C29	1.390(3)
C29	C30	1.389(3)
C30	C31	1.381(3)
C31	C32	1.389(3)

Table 4: Bond Angles in ° for **2a**.

Atom	Atom	Atom	Angle/°
C2	O1	C1	117.45(15)
C8	N1	C5	128.86(16)
O1	C2	C3	125.75(17)
O1	C2	C7	114.45(16)
C3	C2	C7	119.81(17)
C2	C3	C4	120.07(17)
C5	C4	C3	119.95(17)
C4	C5	N1	124.35(16)
C4	C5	C6	119.57(17)
C6	C5	N1	116.03(16)
C7	C6	C5	120.49(17)
C6	C7	C2	120.10(17)
O2	C8	N1	125.23(16)
O2	C8	C9	120.00(16)
N1	C8	C9	114.75(15)
O3	C9	C8	110.55(14)
O3	C9	C10	109.98(15)
C10	C9	C8	109.73(14)
C11	C10	C9	116.43(15)
C12	C11	C10	123.98(16)
C12	C11	C16	117.84(17)
C16	C11	C10	118.18(16)
C11	C12	C13	121.07(17)
C14	C13	C12	120.12(18)
C13	C14	C15	119.45(18)
C16	C15	C14	120.05(18)
C15	C16	C11	121.46(18)

Atom	Atom	Atom	Angle/°
C18	O4	C17	117.82(16)
C24	N2	C21	129.83(16)
O4	C18	C19	114.61(16)
O4	C18	C23	125.49(17)
C23	C18	C19	119.89(17)
C20	C19	C18	120.06(17)
C19	C20	C21	120.78(17)
C20	C21	N2	115.73(16)
C22	C21	N2	124.96(16)
C22	C21	C20	119.30(17)
C21	C22	C23	119.77(17)
C18	C23	C22	120.19(17)
O5	C24	N2	125.36(17)
O5	C24	C25	121.03(16)
N2	C24	C25	113.61(15)
O6	C25	C24	111.06(14)
O6	C25	C26	112.72(16)
C26	C25	C24	109.23(15)
C27	C26	C25	114.77(16)
C28	C27	C26	121.91(17)
C32	C27	C26	119.76(17)
C32	C27	C28	118.24(18)
C29	C28	C27	120.79(18)
C30	C29	C28	120.07(19)
C31	C30	C29	119.60(19)
C30	C31	C32	120.17(19)
C31	C32	C27	121.09(18)

Table 5: Torsion Angles in ° for **2a**.

Atom	Atom	Atom	Atom	Angle/°
O1	C2	C3	C4	-179.18(18)
O1	C2	C7	C6	178.61(17)
O2	C8	C9	O3	173.87(17)
O2	C8	C9	C10	52.4(2)
O3	C9	C10	C11	72.8(2)
N1	C5	C6	C7	-177.59(17)
N1	C8	C9	O3	-7.8(2)
N1	C8	C9	C10	-129.31(17)
C1	O1	C2	C3	9.0(3)
C1	O1	C2	C7	-170.90(18)
C2	C3	C4	C5	0.2(3)
C3	C2	C7	C6	-1.3(3)

Atom	Atom	Atom	Atom	Angle/°
C3	C4	C5	N1	176.79(18)
C3	C4	C5	C6	-0.5(3)
C4	C5	C6	C7	-0.1(3)
C5	N1	C8	O2	5.6(3)
C5	N1	C8	C9	-172.58(17)
C5	C6	C7	C2	1.0(3)
C7	C2	C3	C4	0.7(3)
C8	N1	C5	C4	7.9(3)
C8	N1	C5	C6	-174.74(19)
C8	C9	C10	C11	-165.39(15)
C9	C10	C11	C12	0.8(3)
C9	C10	C11	C16	-179.92(17)
C10	C11	C12	C13	177.87(18)
C10	C11	C16	C15	-178.89(18)
C11	C12	C13	C14	1.1(3)
C12	C11	C16	C15	0.4(3)
C12	C13	C14	C15	0.2(3)
C13	C14	C15	C16	-1.1(3)
C14	C15	C16	C11	0.8(3)
C16	C11	C12	C13	-1.4(3)
O4	C18	C19	C20	-178.73(17)
O4	C18	C23	C22	179.15(18)
O5	C24	C25	O6	175.45(18)
O5	C24	C25	C26	50.5(2)
O6	C25	C26	C27	61.5(2)
N2	C21	C22	C23	-178.64(19)
N2	C24	C25	O6	-4.7(2)
N2	C24	C25	C26	-129.62(17)
C17	O4	C18	C19	-177.41(17)
C17	O4	C18	C23	3.1(3)
C18	C19	C20	C21	-0.9(3)
C19	C18	C23	C22	-0.3(3)
C19	C20	C21	N2	179.25(18)
C19	C20	C21	C22	0.5(3)
C20	C21	C22	C23	0.0(3)
C21	N2	C24	O5	-1.3(3)
C21	N2	C24	C25	178.81(18)
C21	C22	C23	C18	-0.1(3)
C23	C18	C19	C20	0.8(3)
C24	N2	C21	C20	174.11(19)
C24	N2	C21	C22	-7.2(3)
C24	C25	C26	C27	-174.50(15)
C25	C26	C27	C28	65.2(2)
C25	C26	C27	C32	-118.3(2)
C26	C27	C28	C29	175.22(19)
C26	C27	C32	C31	-174.49(18)
C27	C28	C29	C30	-0.3(3)
C28	C27	C32	C31	2.2(3)
C28	C29	C30	C31	1.2(3)
C29	C30	C31	C32	-0.4(3)
C30	C31	C32	C27	-1.3(3)
C32	C27	C28	C29	-1.4(3)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H1A	-3638.01	6822.8	469.99	50
H1B	-2476.94	7405.85	1286.88	50
H1C	-4258.6	6659.86	1452.65	50

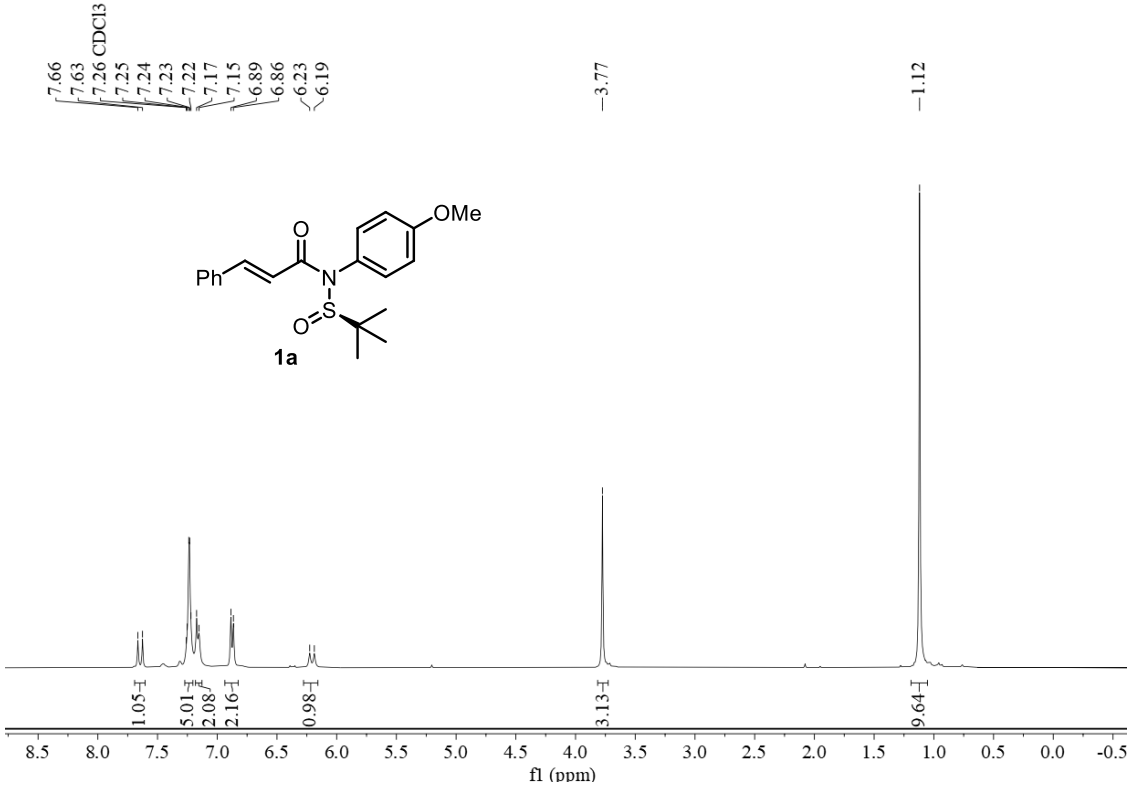
Atom	x	y	z	U_{eq}
H3A	-1860.04	7001.79	2805.12	30
H4	589.52	6921.34	4196.2	29
H6	5101.65	5407.37	3095.69	29
H7	2643.11	5468.28	1724.68	30
H9	7445.23	6910.6	6228.99	25
H10A	4788.3	6148.13	7073.55	27
H10B	5976.48	5290.66	6797.65	27
H12	10624.6	6662.51	7228.25	28
H13	13314.46	6780.47	8547.79	34
H14	12509.08	6137.84	9862.89	37
H15	8995.45	5371.33	9846.4	37
H16	6277.36	5289.14	8542.54	31
H17A	19120.59	3467.23	8704.45	50
H17B	17711.63	2591.09	8724.73	50
H17C	18400.68	3129.63	9624.15	50
H19	12064.87	4417.57	8280.78	29
H20	10016.28	4606.93	6849.25	29
H22	14964.3	3233.31	5820.51	31
H23	17002.88	3027.49	7274.96	32
H25	9876.33	4632.97	3424.92	29
H26A	10095.63	3202.04	2955.18	31
H26B	8028.34	2950.94	3505.33	31
H28	8742.1	4471.08	1758.16	34
H29	6006.07	4667.28	465.64	39
H30	2459.56	3903.16	263.13	39
H31	1621.51	2979.46	1379.56	39
H32	4313.86	2807.82	2685.02	34
H1	6070(50)	5839(19)	4561(17)	33(7)
H2	9560(50)	4385(18)	5347(16)	28(6)
H3	9840(60)	6190(20)	5700(20)	47(8)
H6A	6410(60)	4070(20)	4190(20)	43(8)

Table 7: Hydrogen Bond information for **2a**.

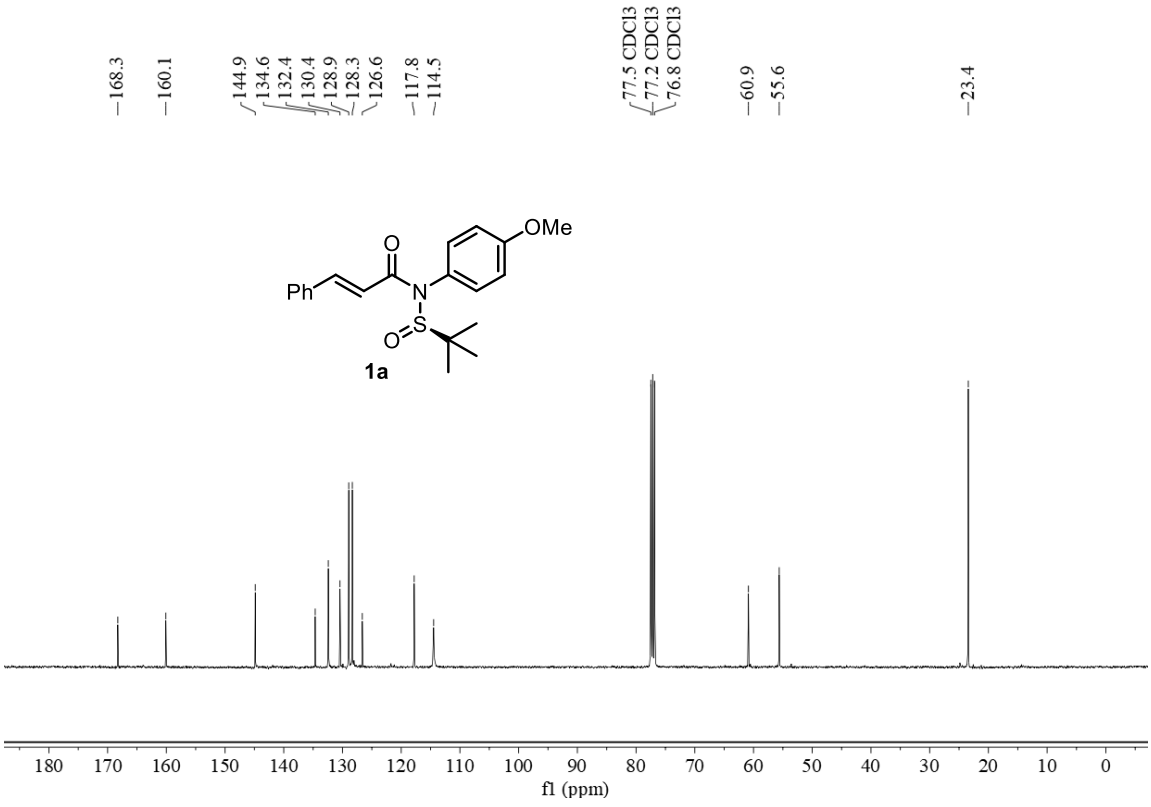
D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N1	H1	O3	0.87(3)	2.08(3)	2.606(2)	118(2)
N1	H1	O6	0.87(3)	2.36(3)	3.058(2)	138(2)
N2	H2	O3	0.88(3)	2.46(3)	3.147(2)	135(2)
N2	H2	O6	0.88(3)	2.06(2)	2.595(2)	118(2)
O3	H3	O2[1]	0.91(3)	1.90(3)	2.7979(19)	170(3)
O6	H6A	O5[2]	0.84(3)	2.10(3)	2.864(2)	152(3)

[1]1+x,+y,+z; [2]-1+x,+y,+z

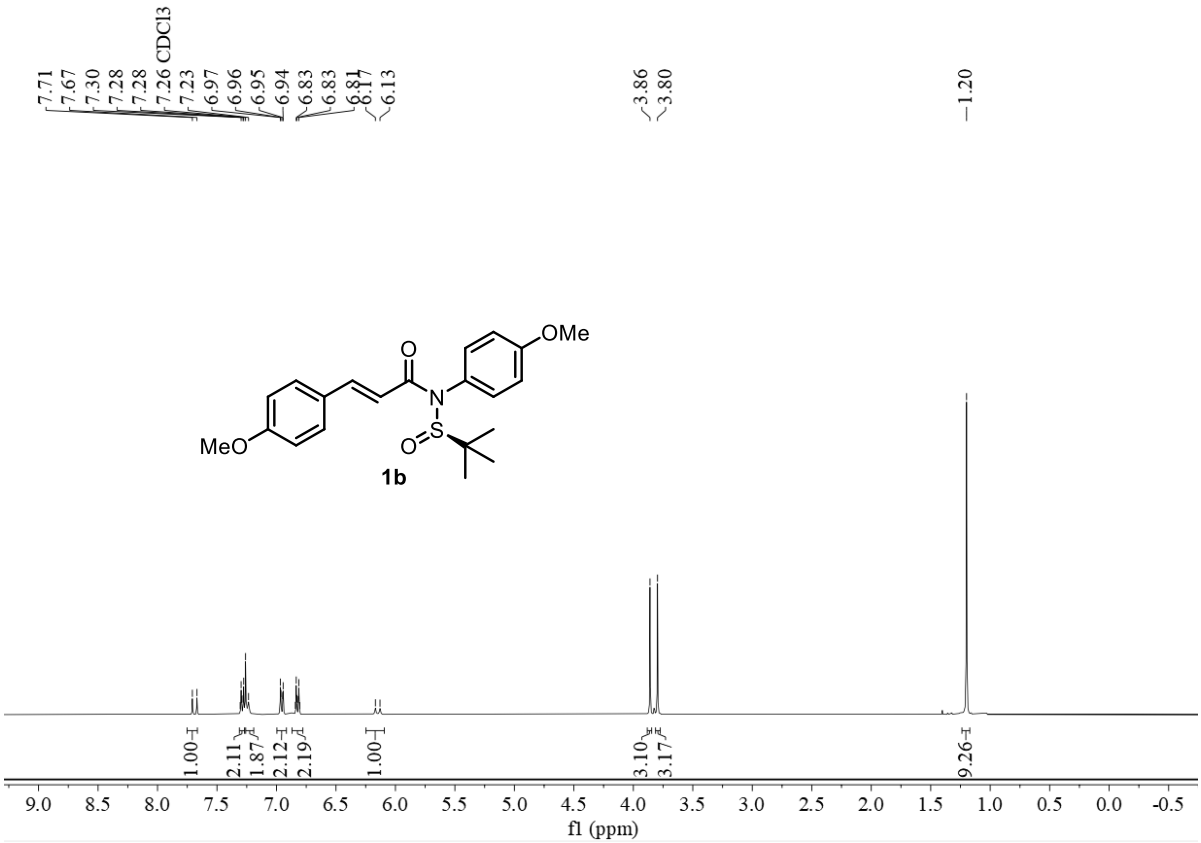
NMR Spectra



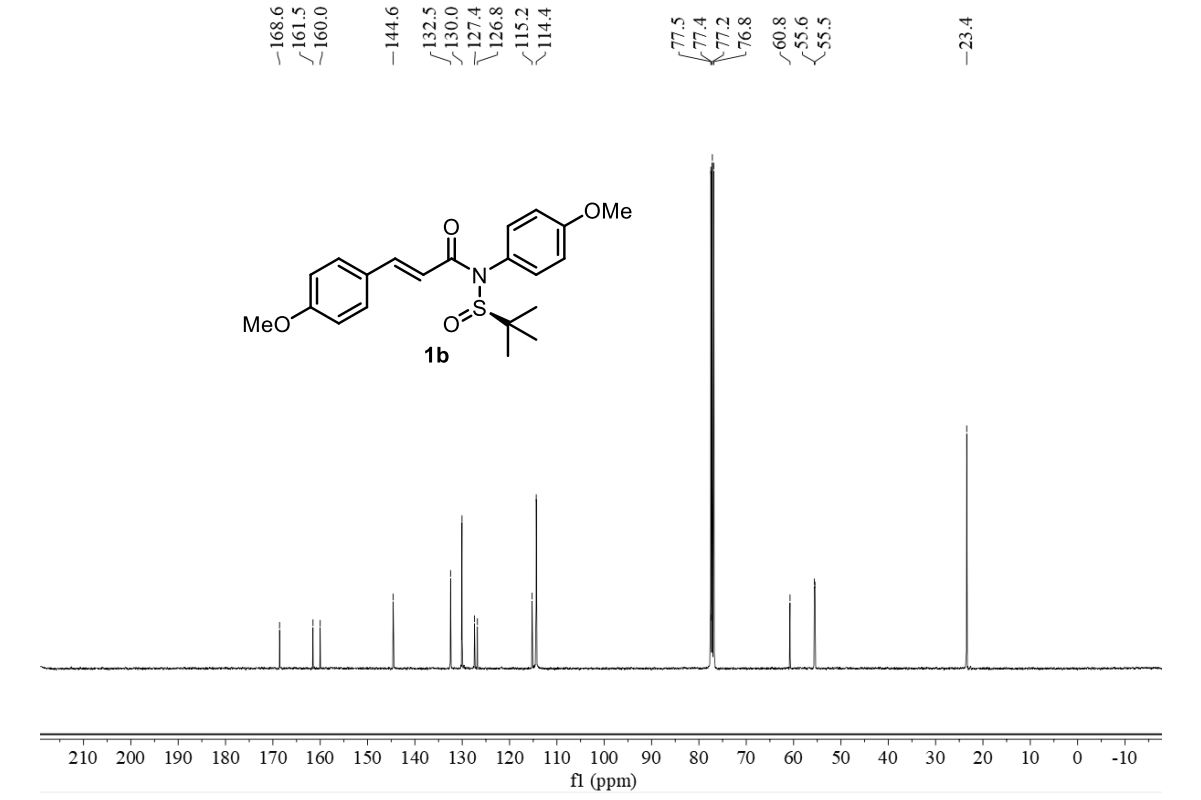
^{1}H NMR of **1a** (400 M, $CDCl_3$)



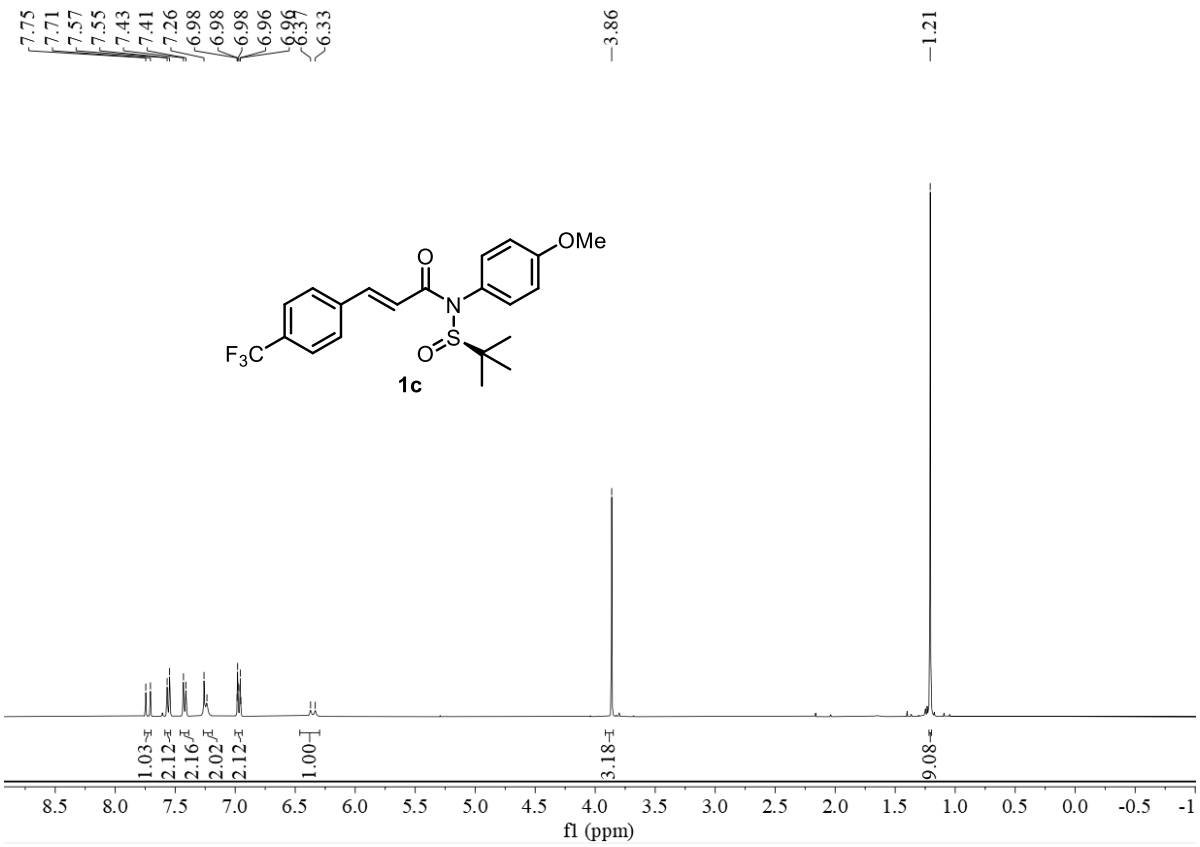
^{13}C NMR of **1a** (101 M, $CDCl_3$)



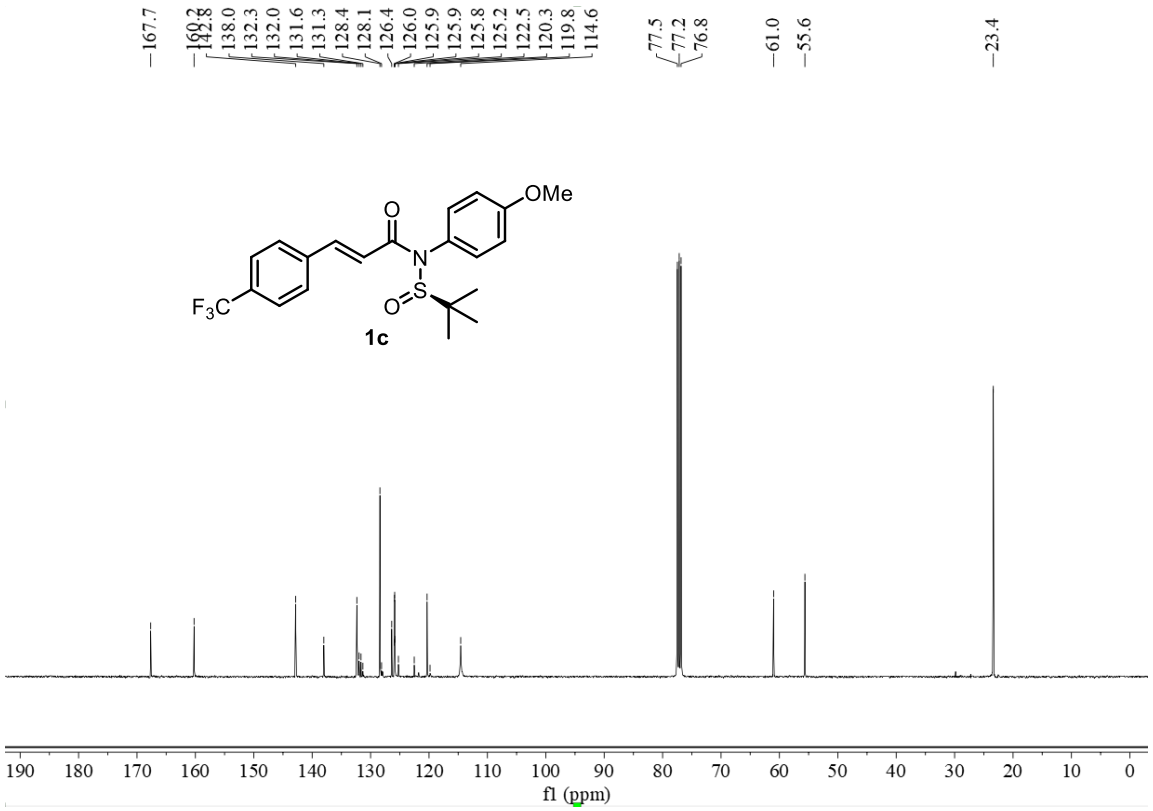
^{1}H NMR of **1b** (400 M, $CDCl_3$)



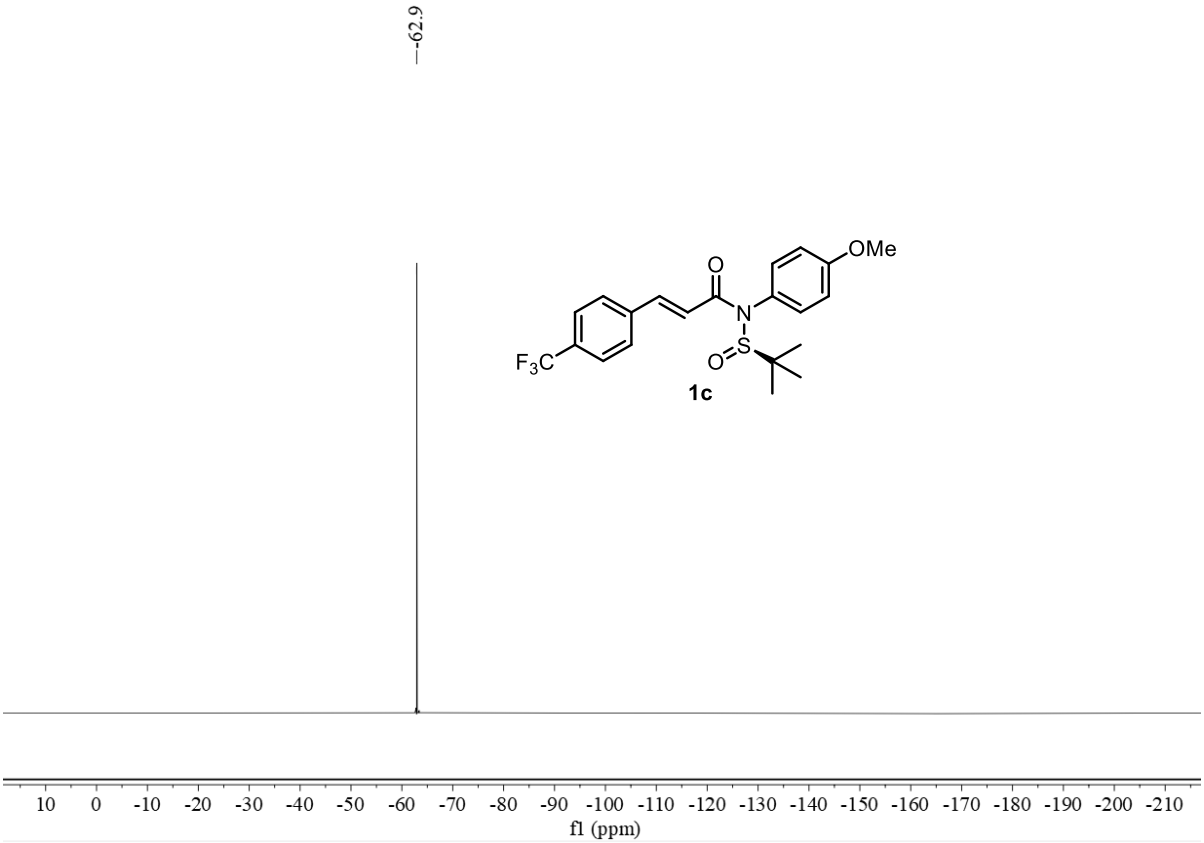
^{13}C NMR of **1b** (101 M, $CDCl_3$)



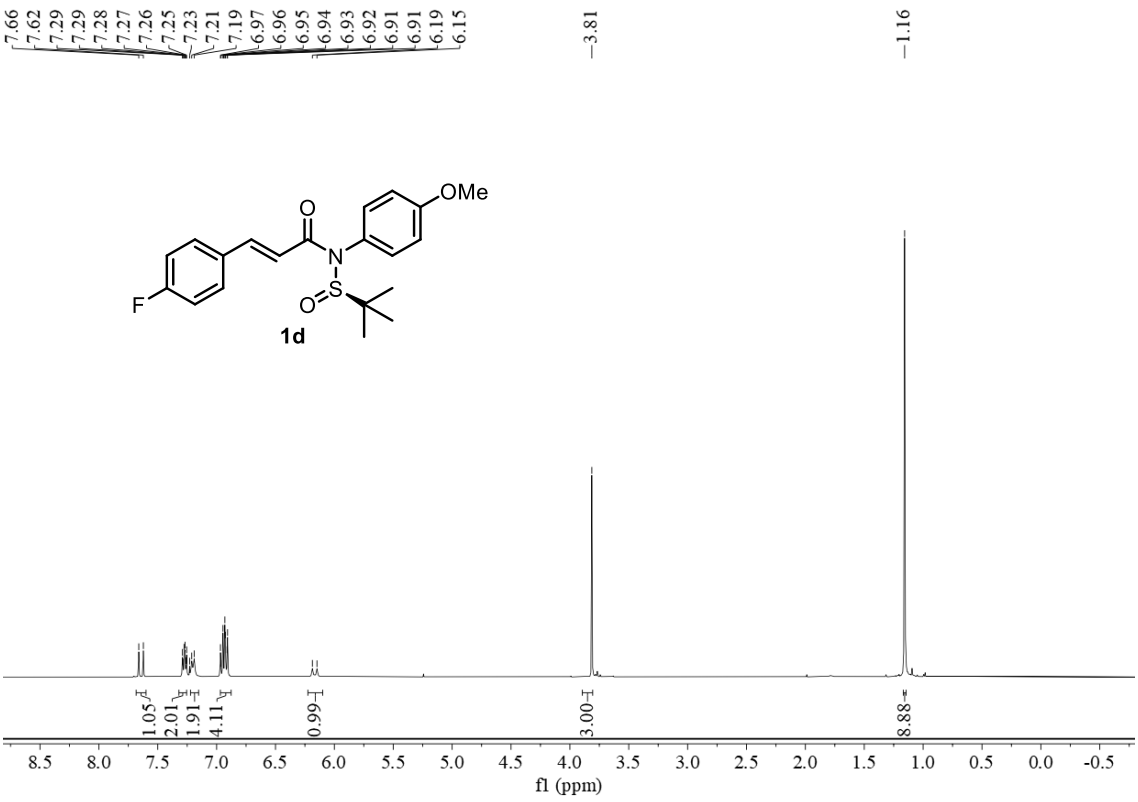
^{1}H NMR of **1c** (400 M, $CDCl_3$)



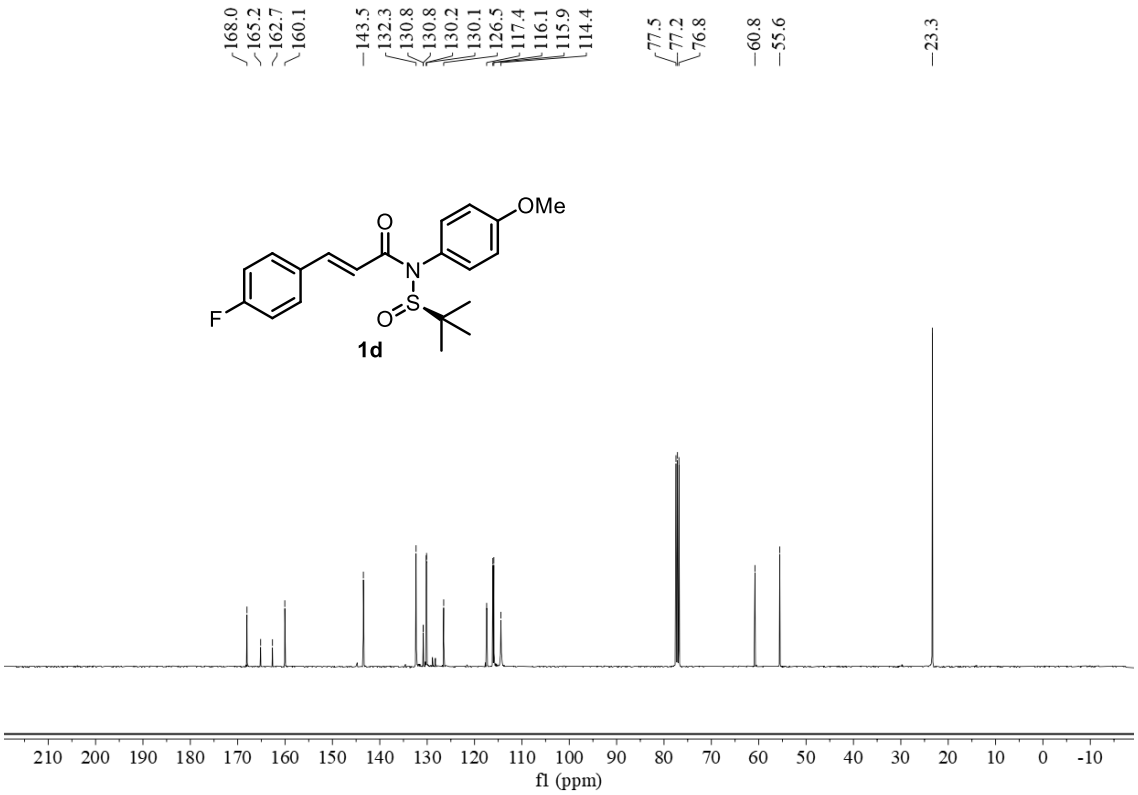
^{13}C NMR of **1c** (101 M, $CDCl_3$)



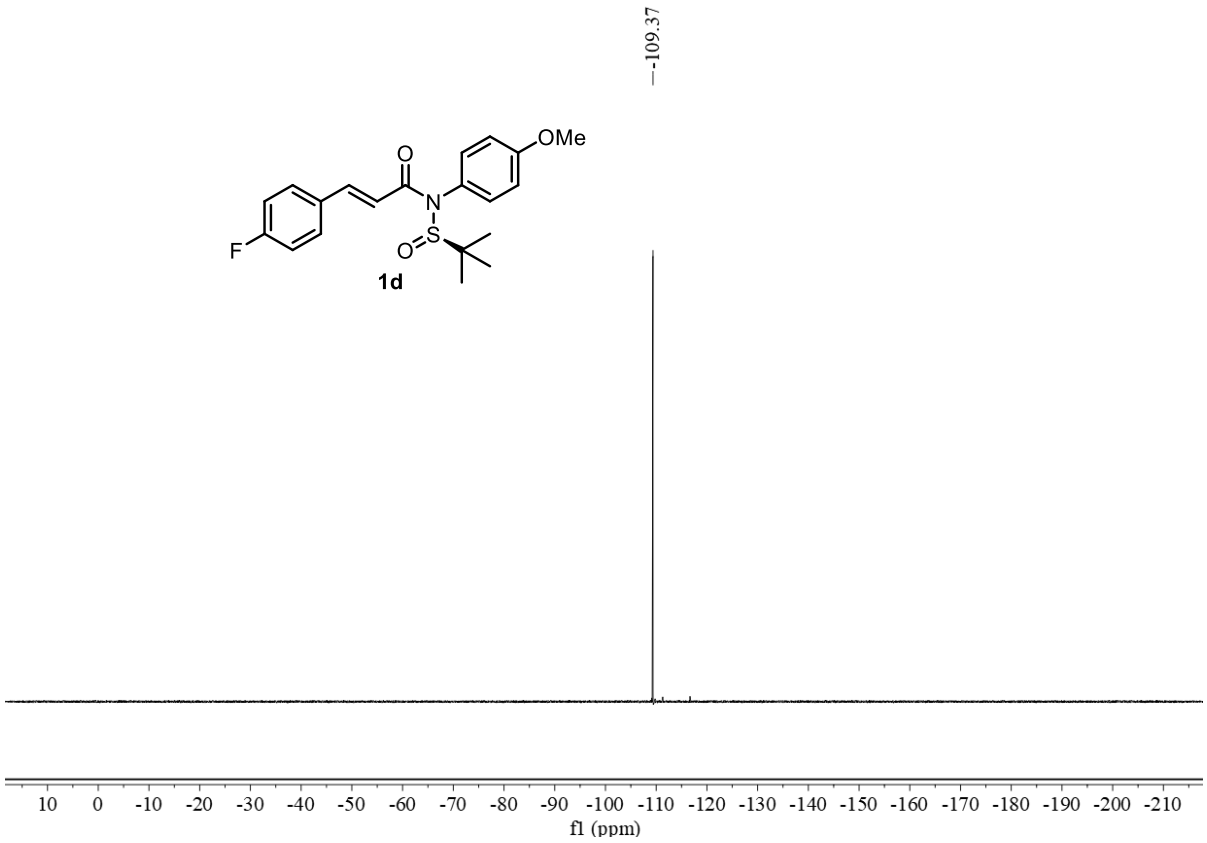
^{19}F NMR of **1c** (376 M, $CDCl_3$)



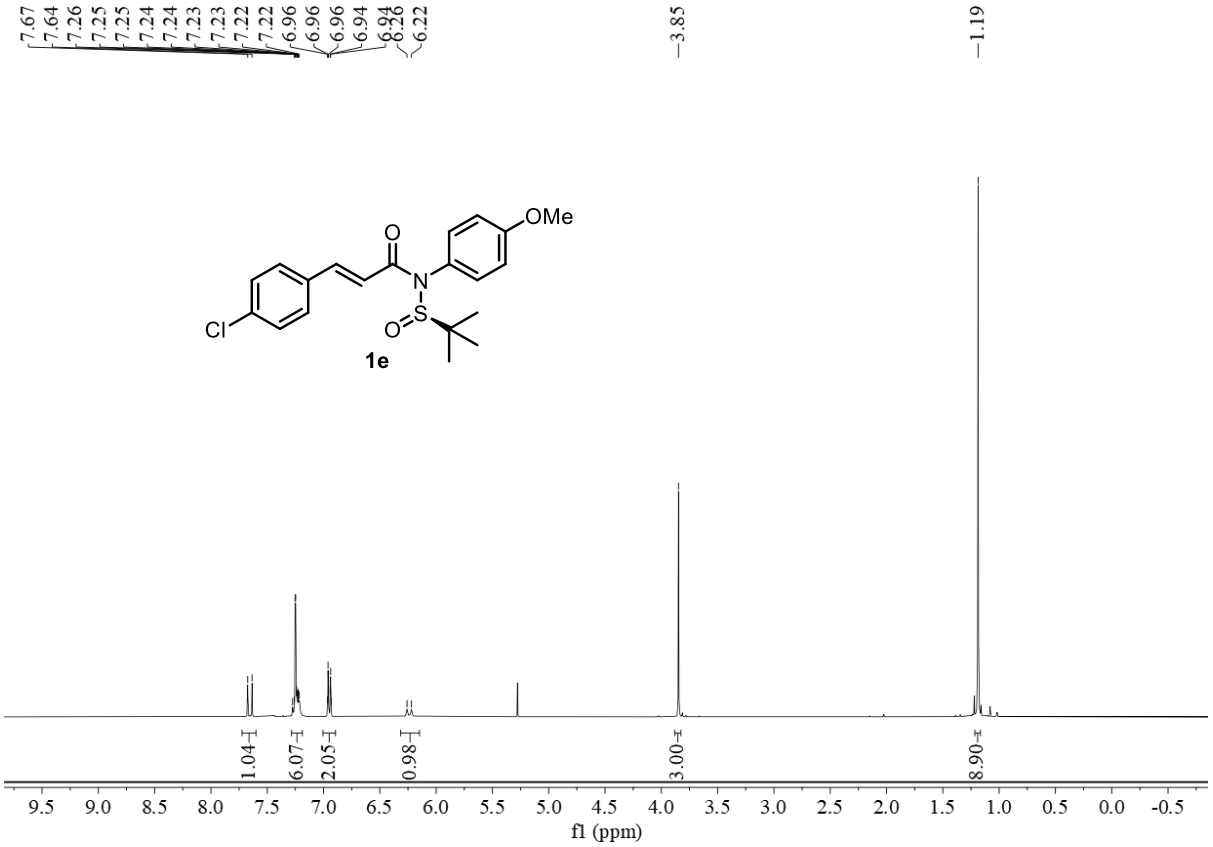
^{1}H NMR of **1d** (400 M, $CDCl_3$)



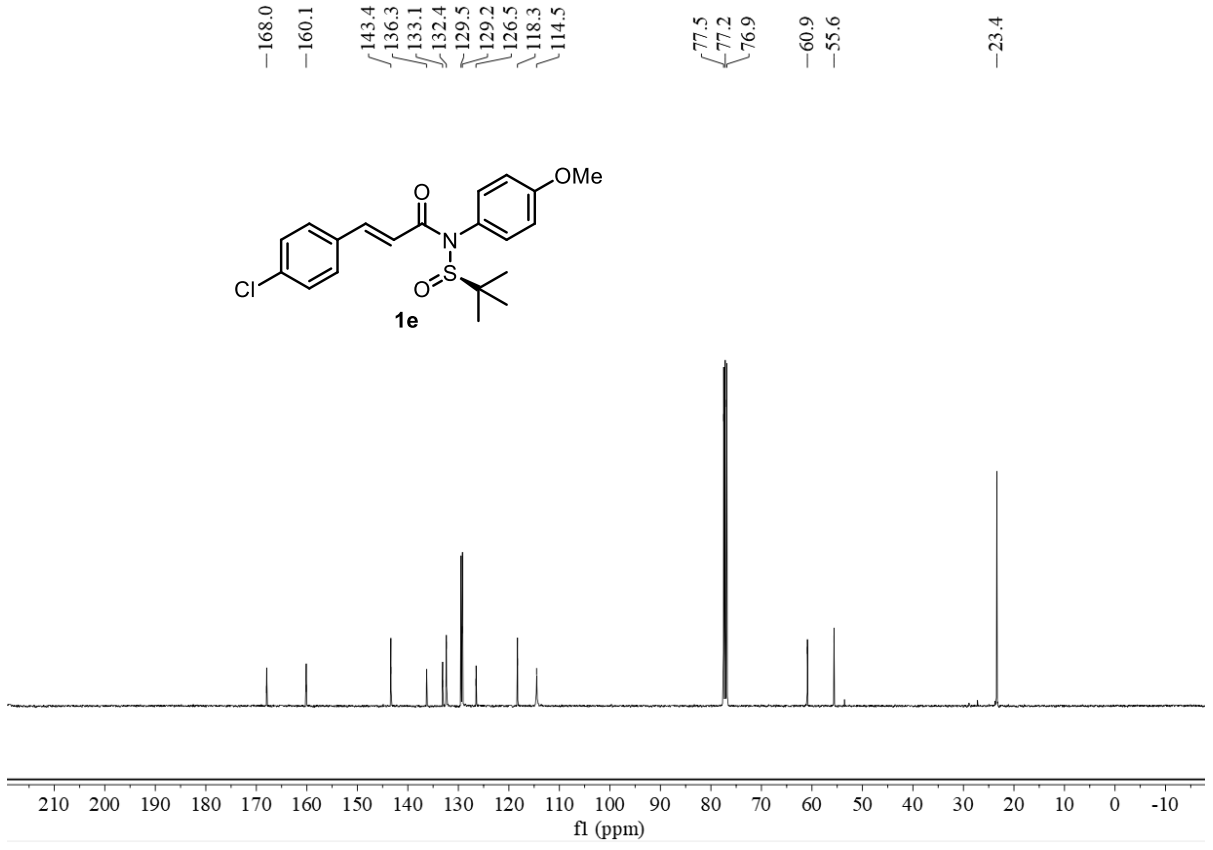
^{13}C NMR of **1d** (101 M, $CDCl_3$)



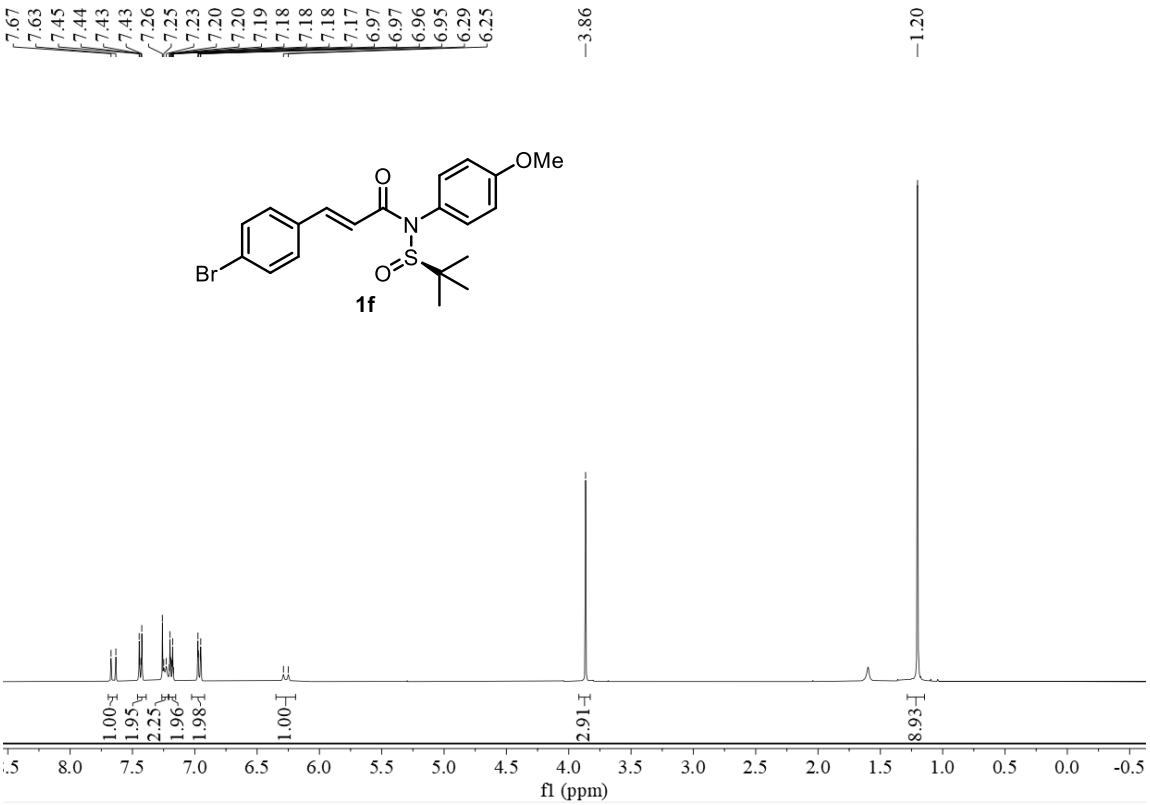
^{19}F NMR of **1d** (376 M, $CDCl_3$)



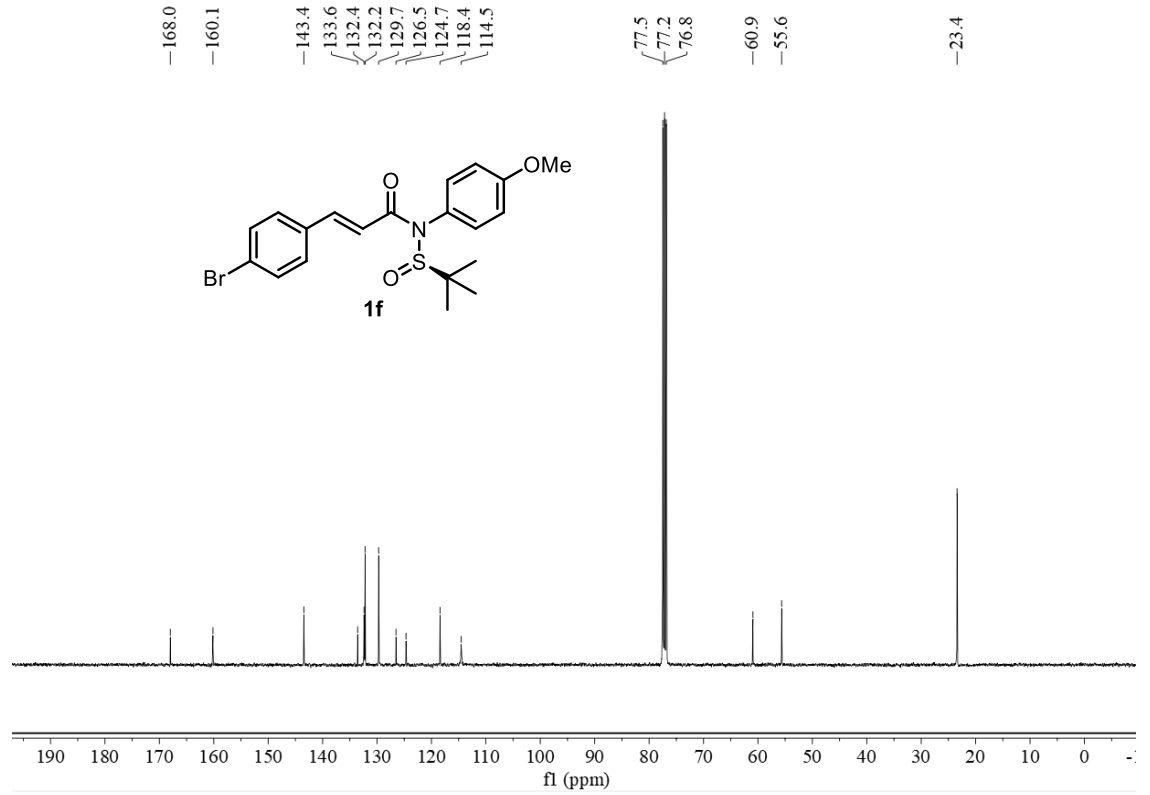
^{1}H NMR of **1e** (400 M, $CDCl_3$)



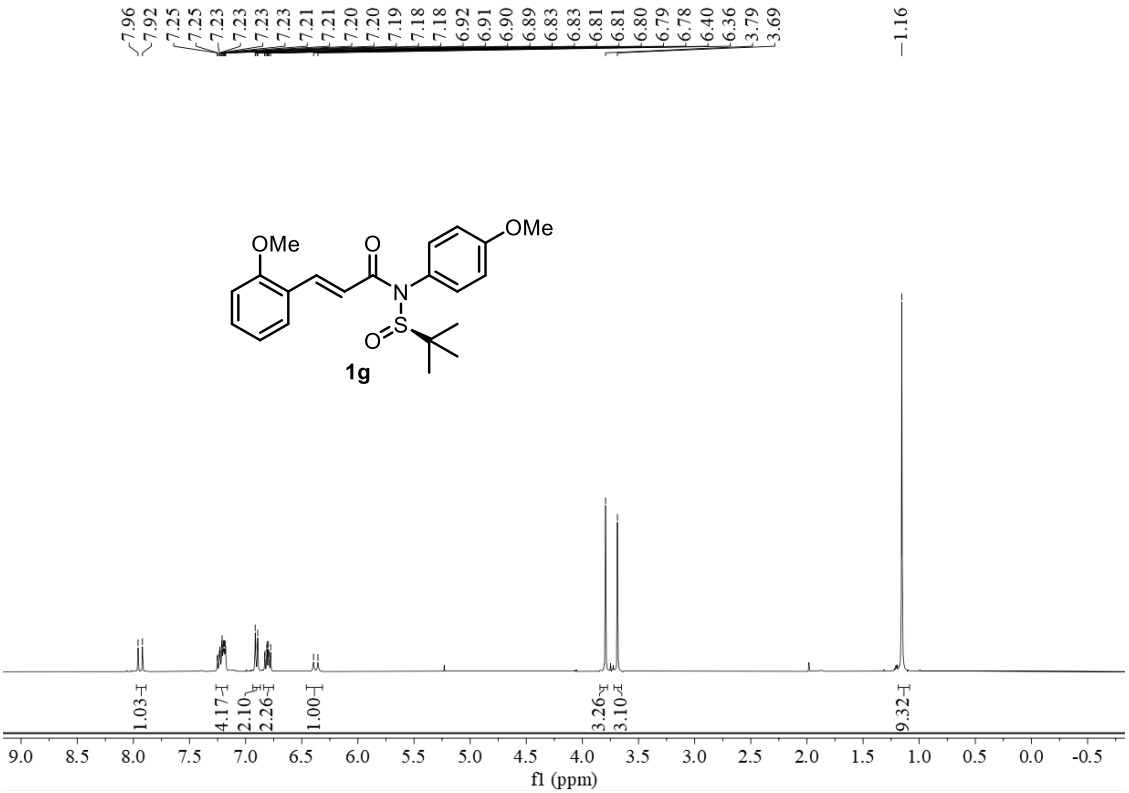
^{13}C NMR of **1e** (101 M, $CDCl_3$)



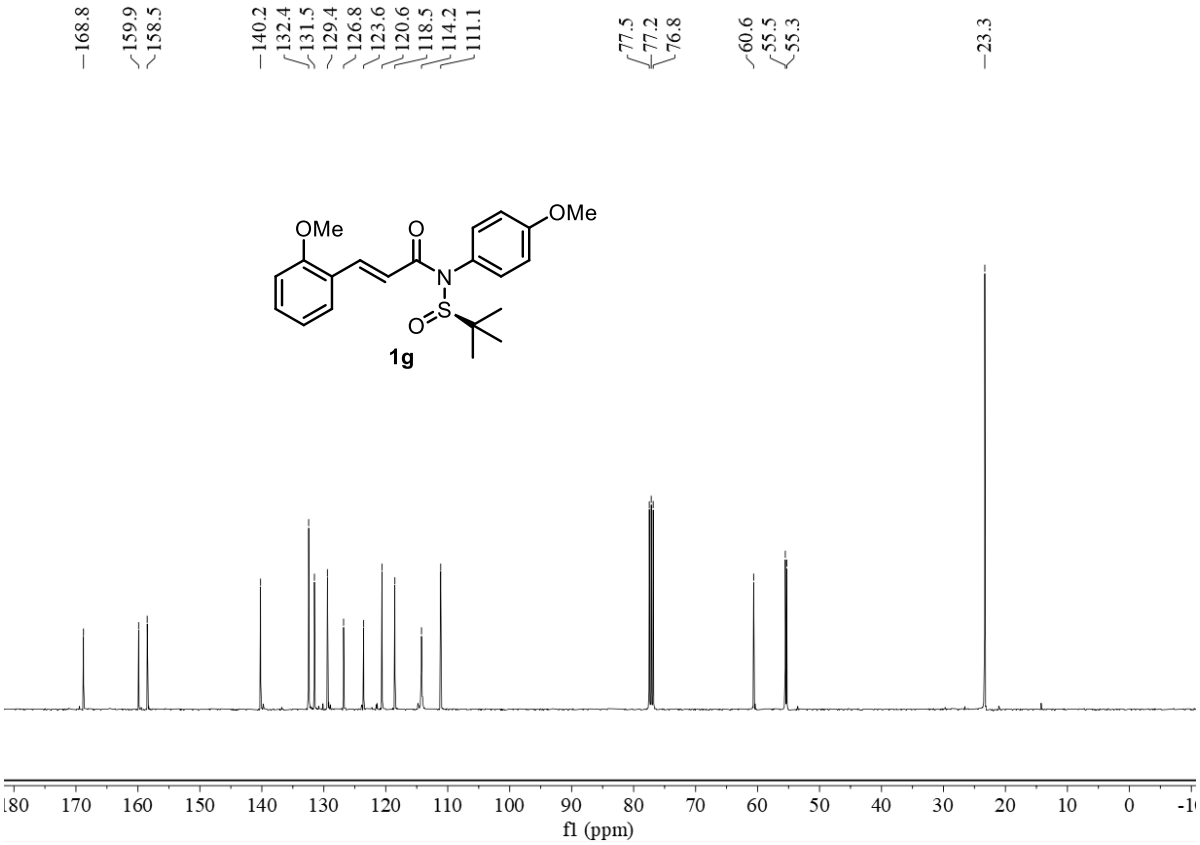
^{1}H NMR of **1f** (400 M, $CDCl_3$)



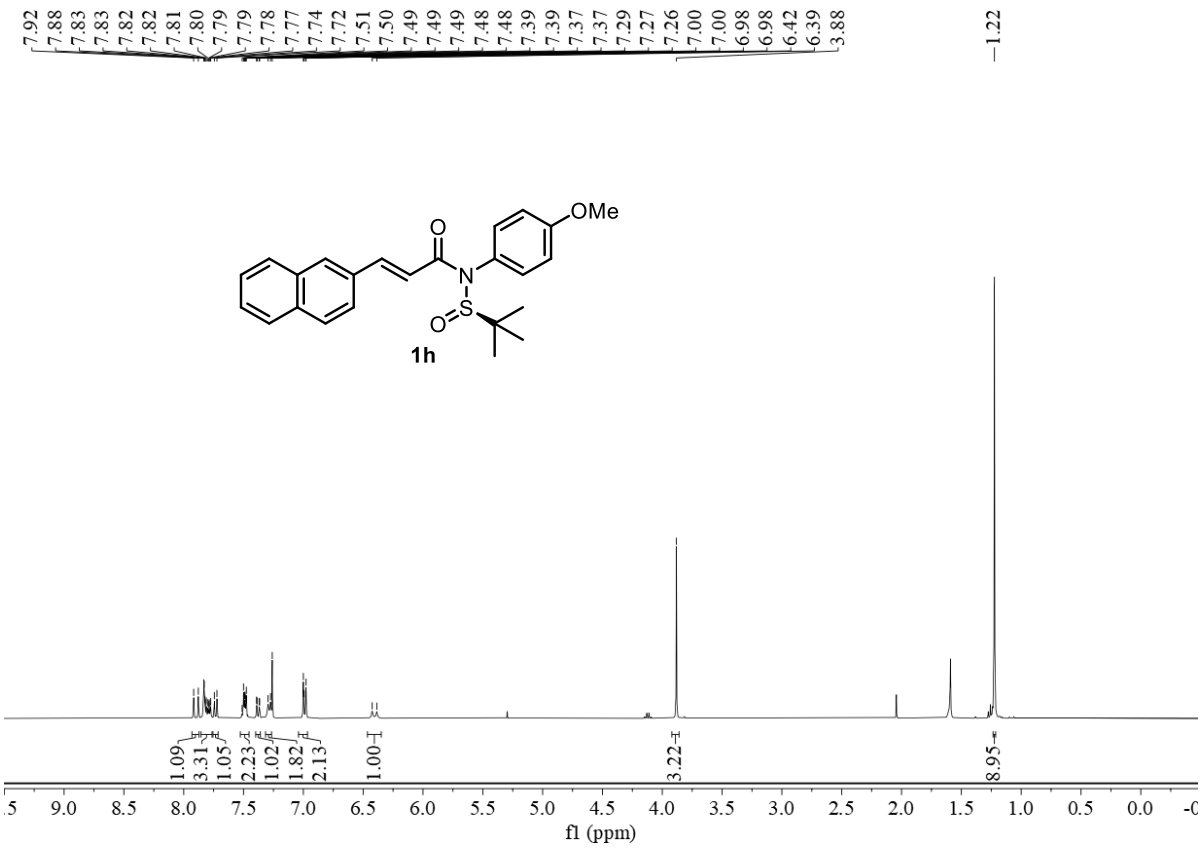
^{13}C NMR of **1f** (101 M, $CDCl_3$)



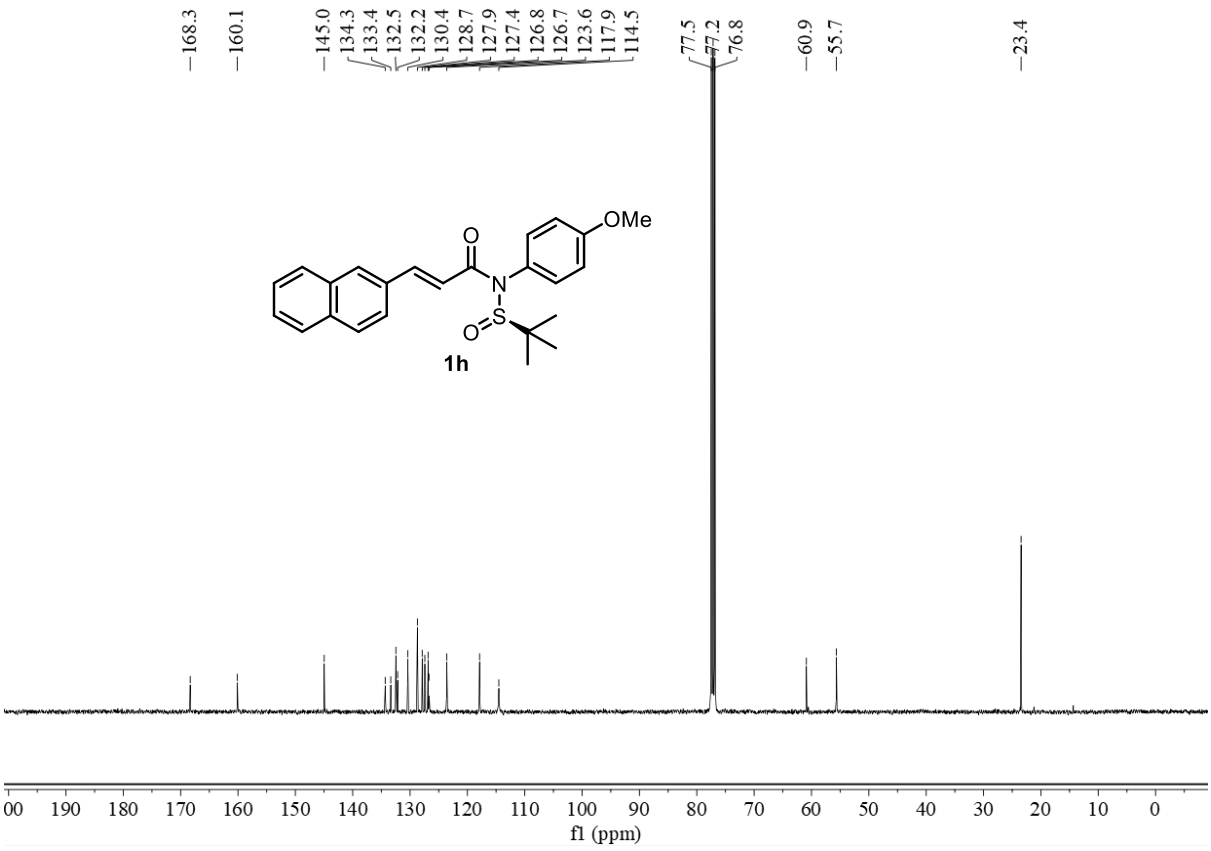
1H NMR of **1g** (400 M, $CDCl_3$)



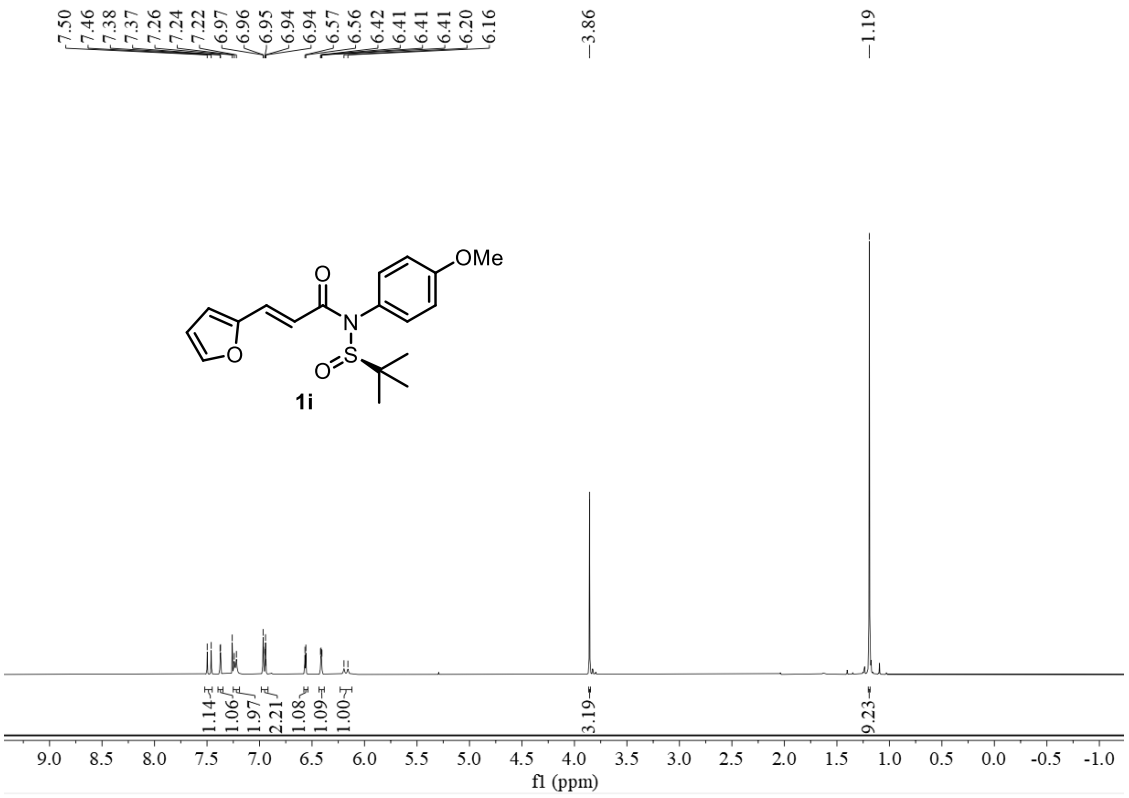
^{13}C NMR of **1g** (101 M, $CDCl_3$)



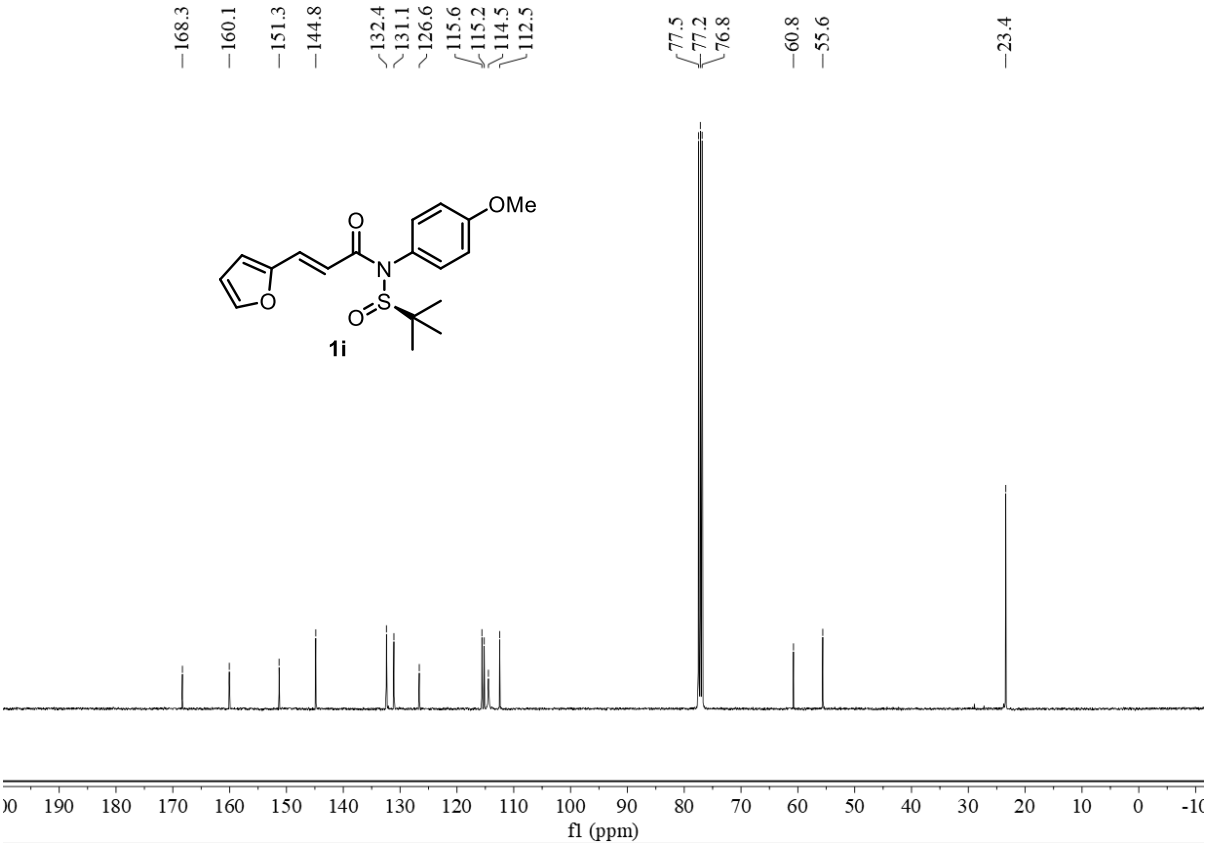
^{1}H NMR of **1h** (400 M, $CDCl_3$)



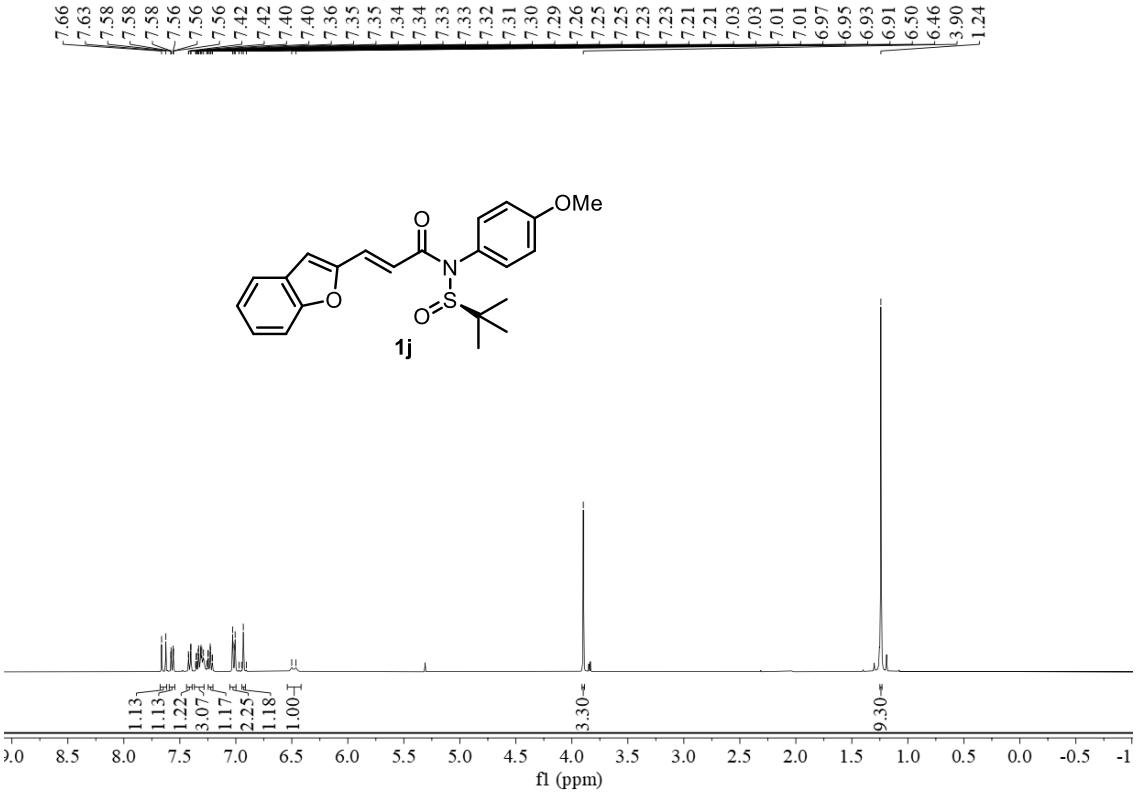
^{13}C NMR of **1h** (101 M, $CDCl_3$)



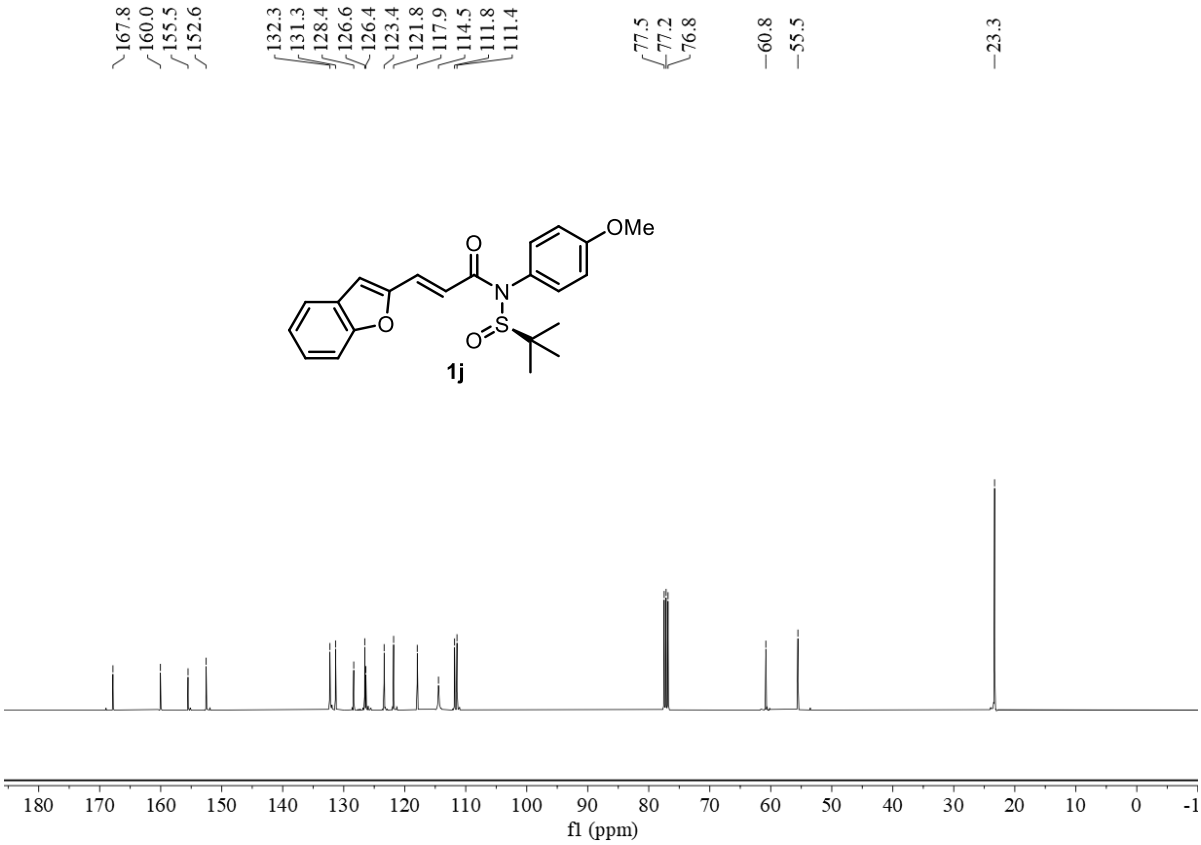
^{1}H NMR of **1i**



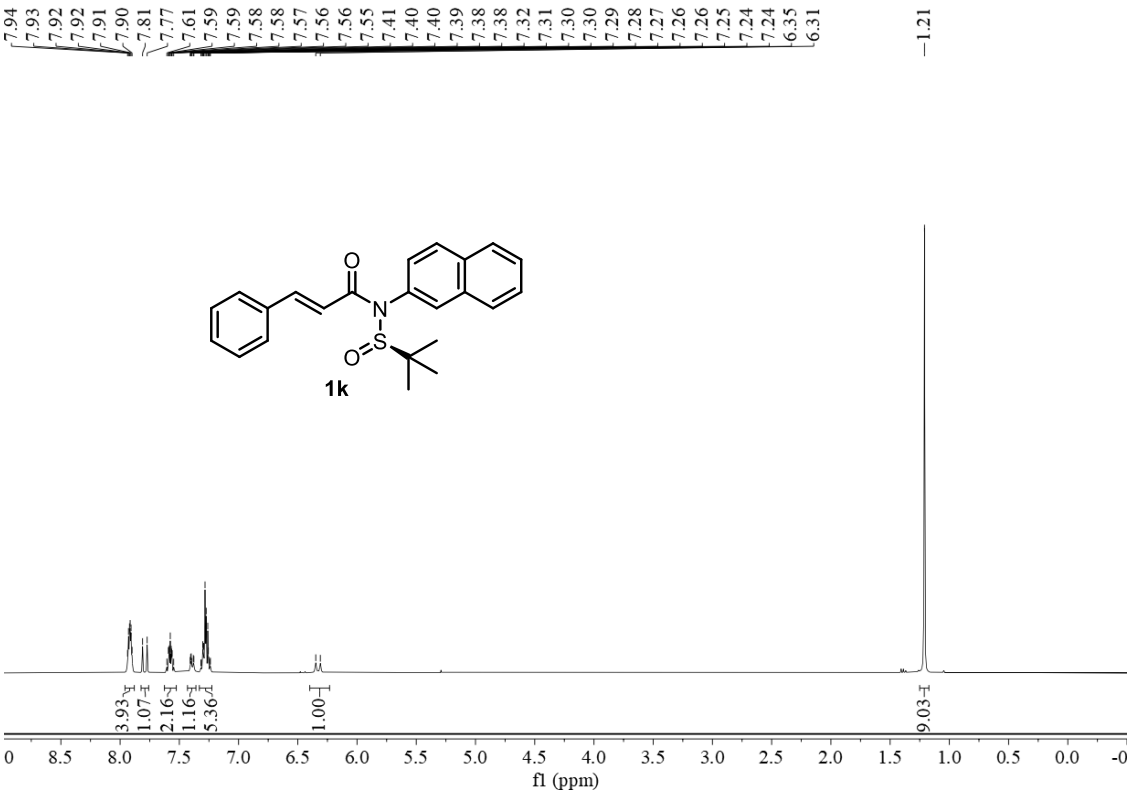
^{13}C NMR of **1i**



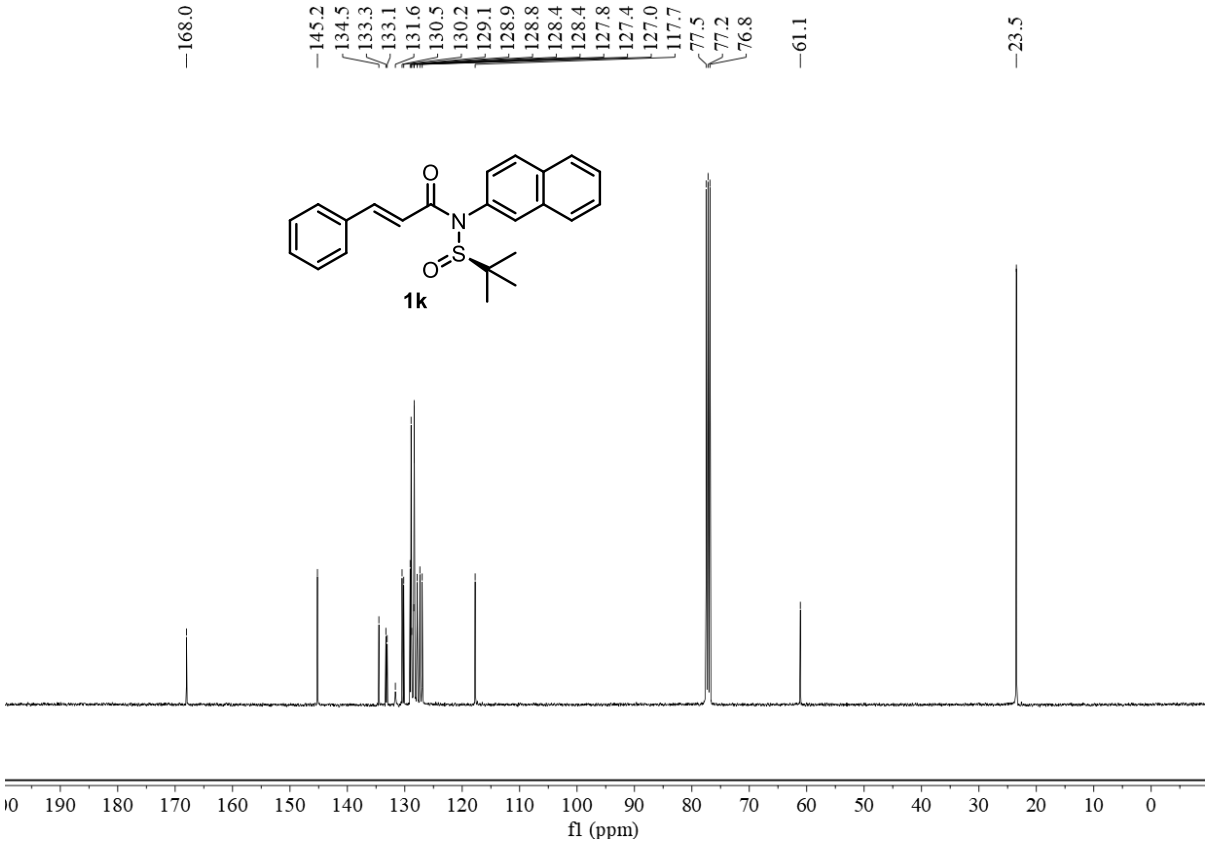
^{1}H NMR of **1j**



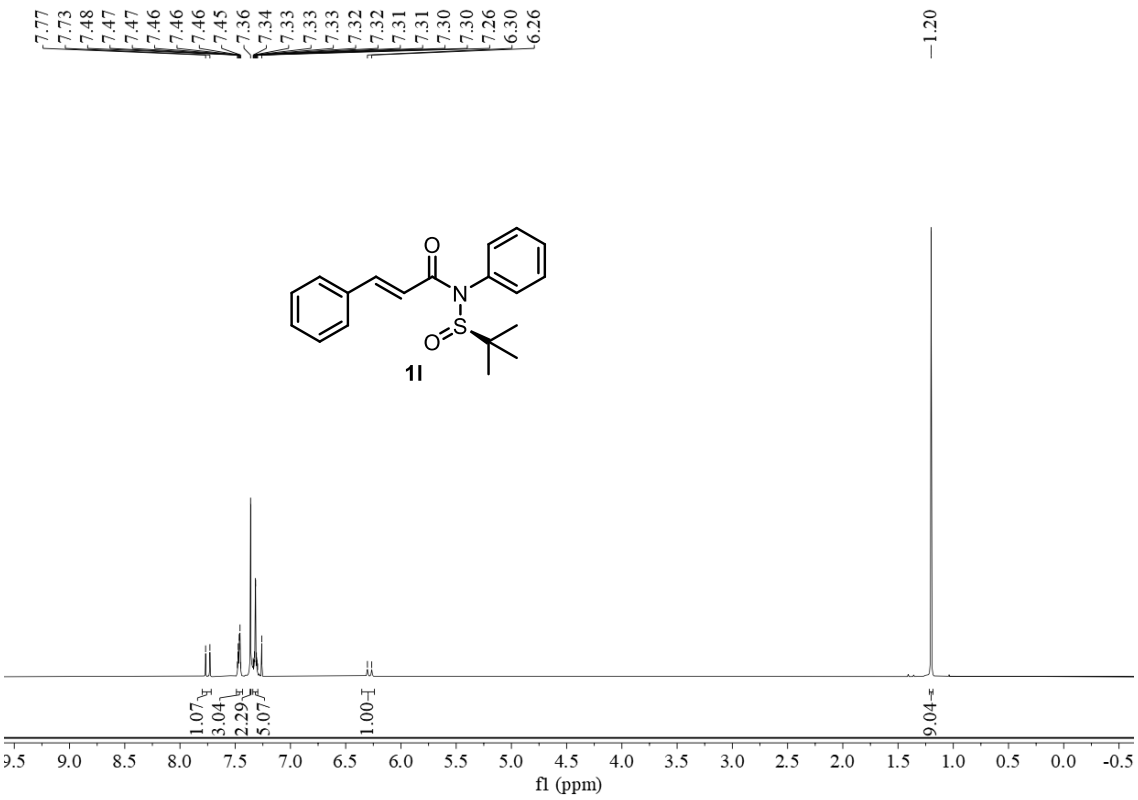
^{13}C NMR of **1j**



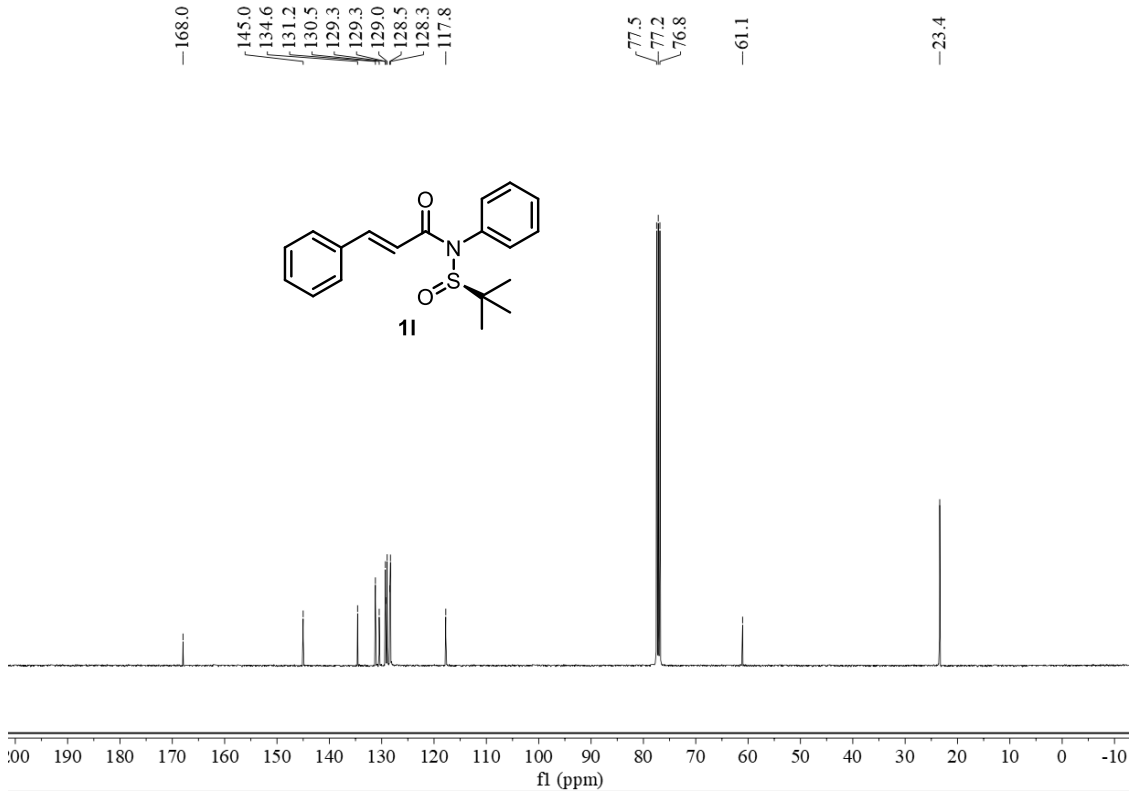
^{1}H NMR of **1k**



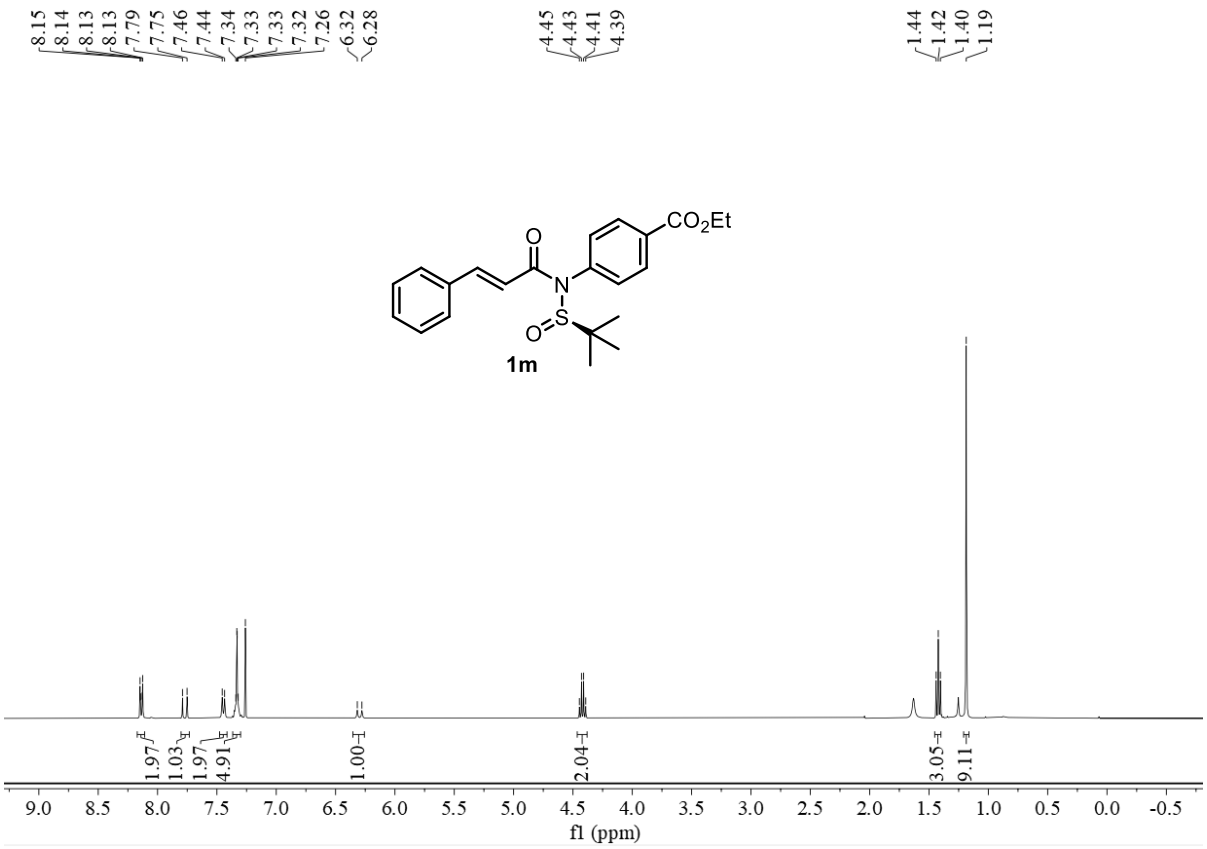
^{13}C NMR of **1k**



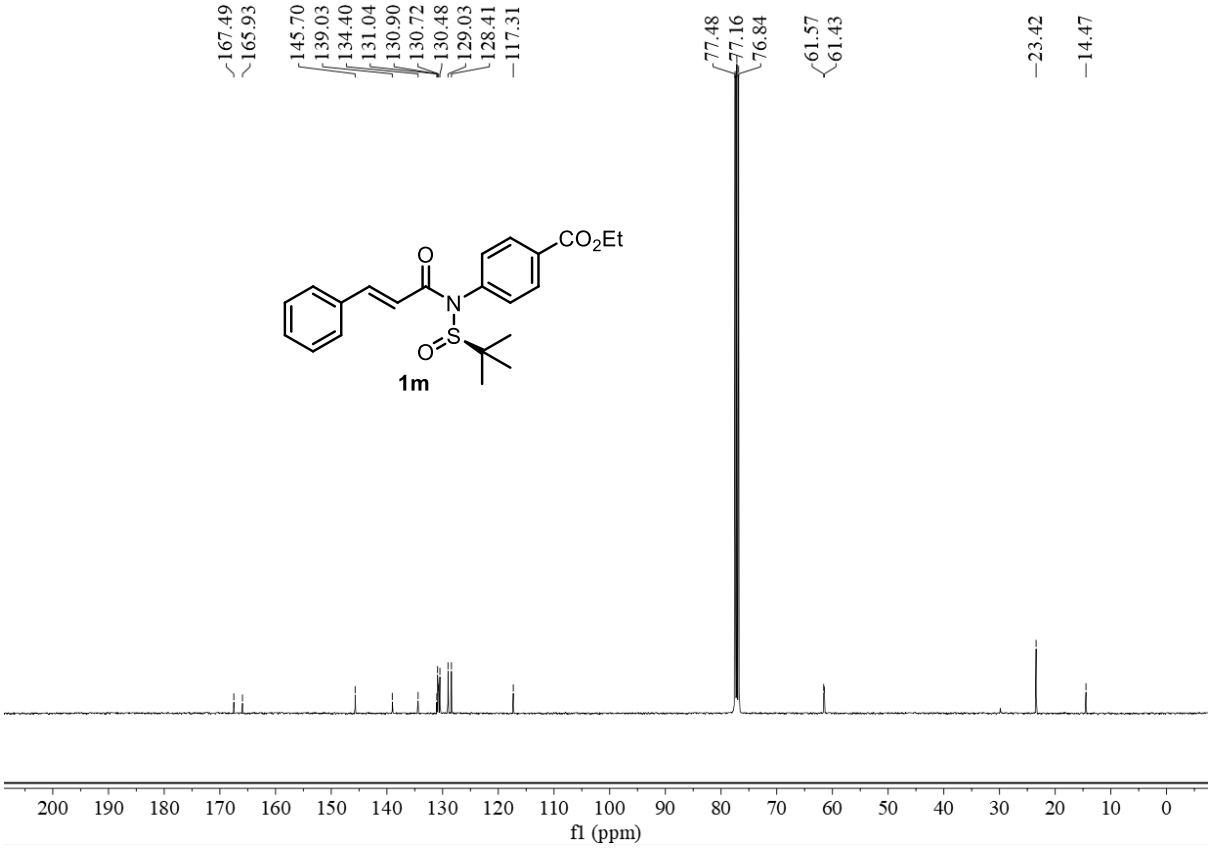
^{1}H NMR of **1l**



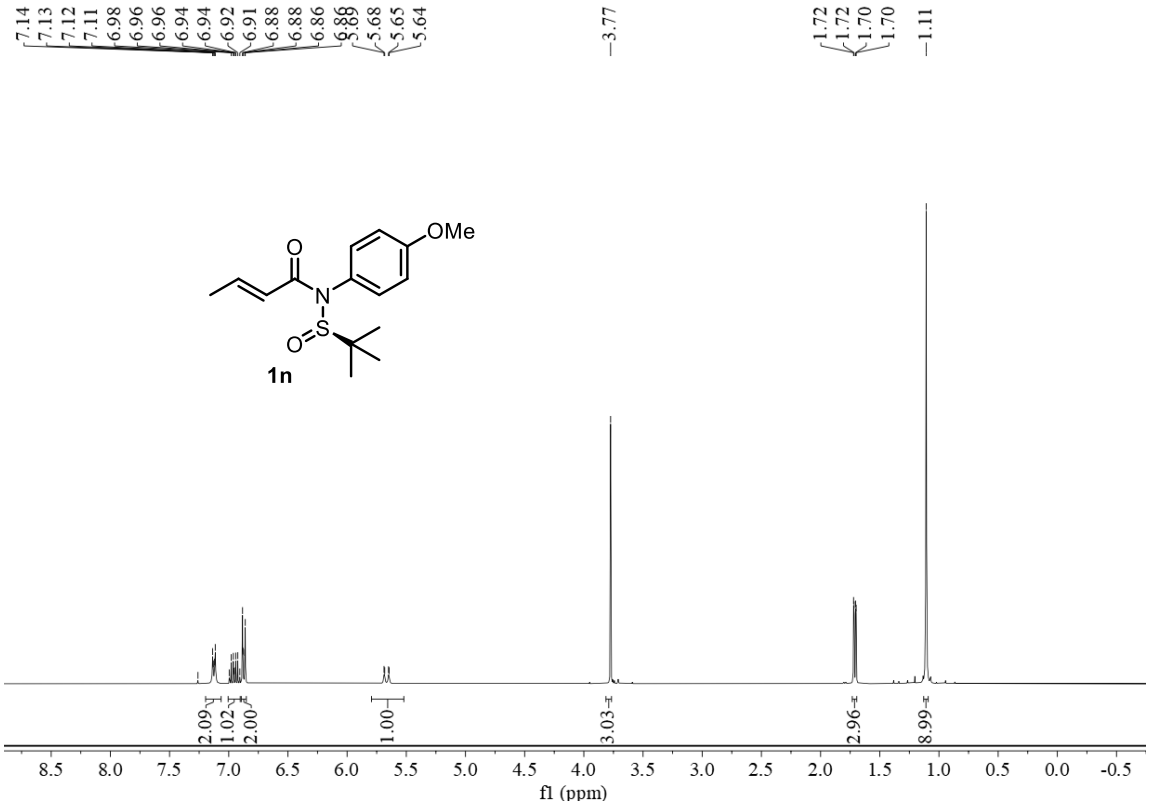
^{13}C NMR of **1l**



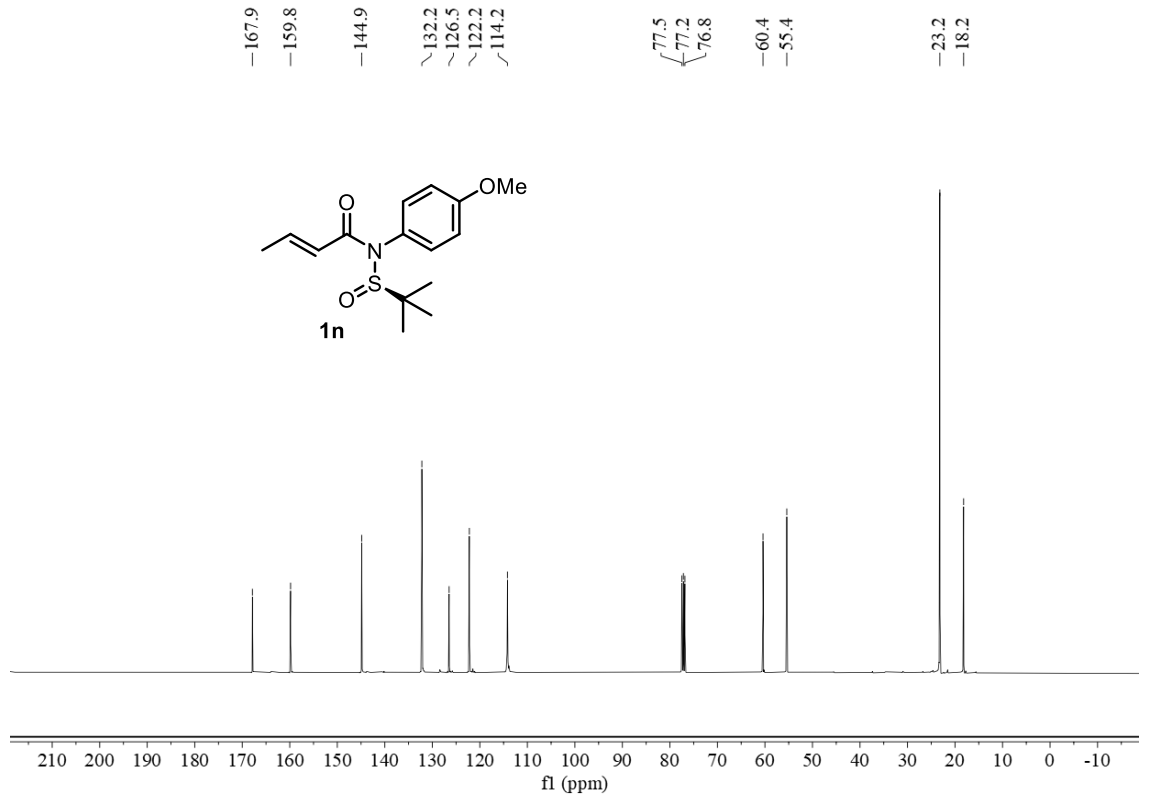
^{1}H NMR of **1m** ($CDCl_3$, 400 M)



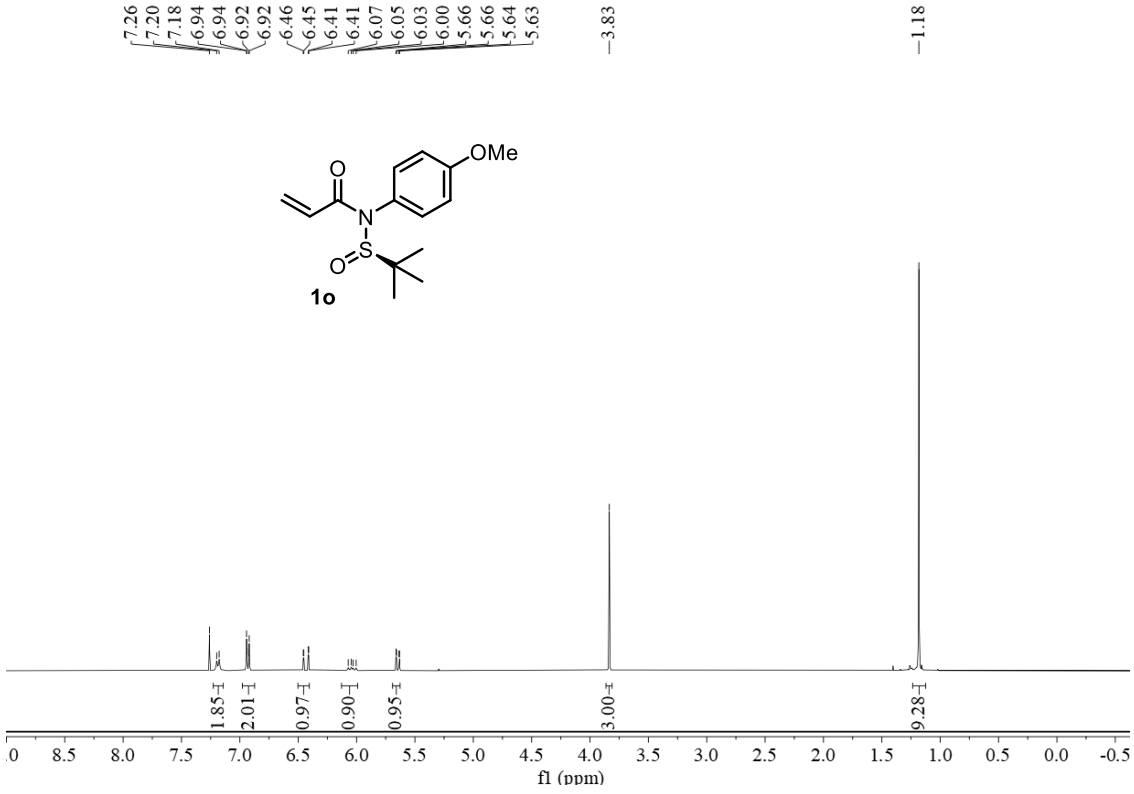
^{13}C NMR of **1m** ($CDCl_3$, 101 M)



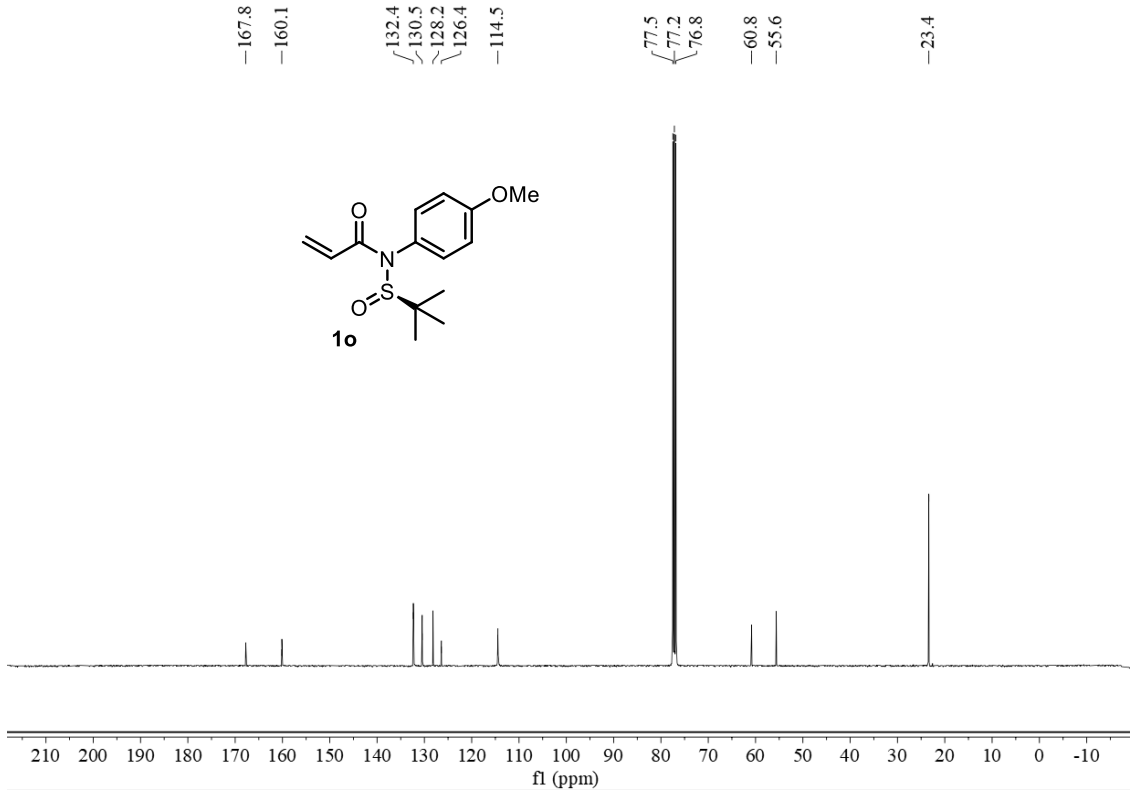
^{1}H NMR of **1n**



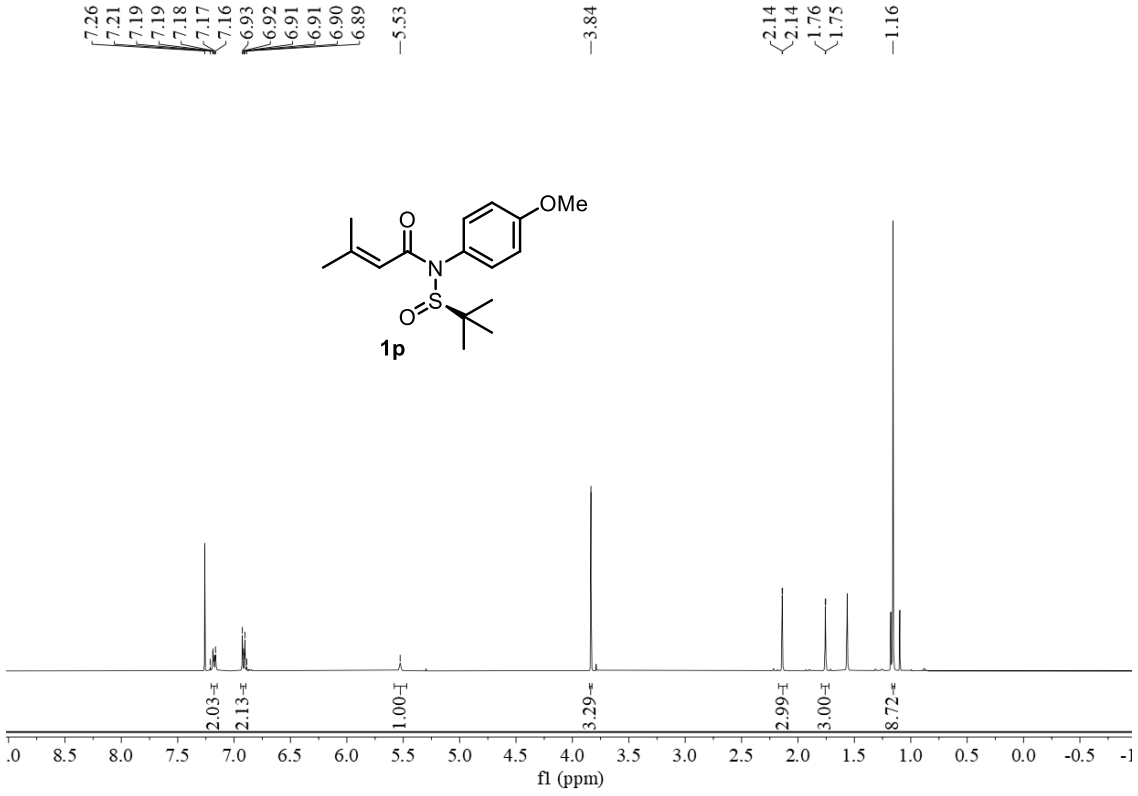
^{13}C NMR of **1n**



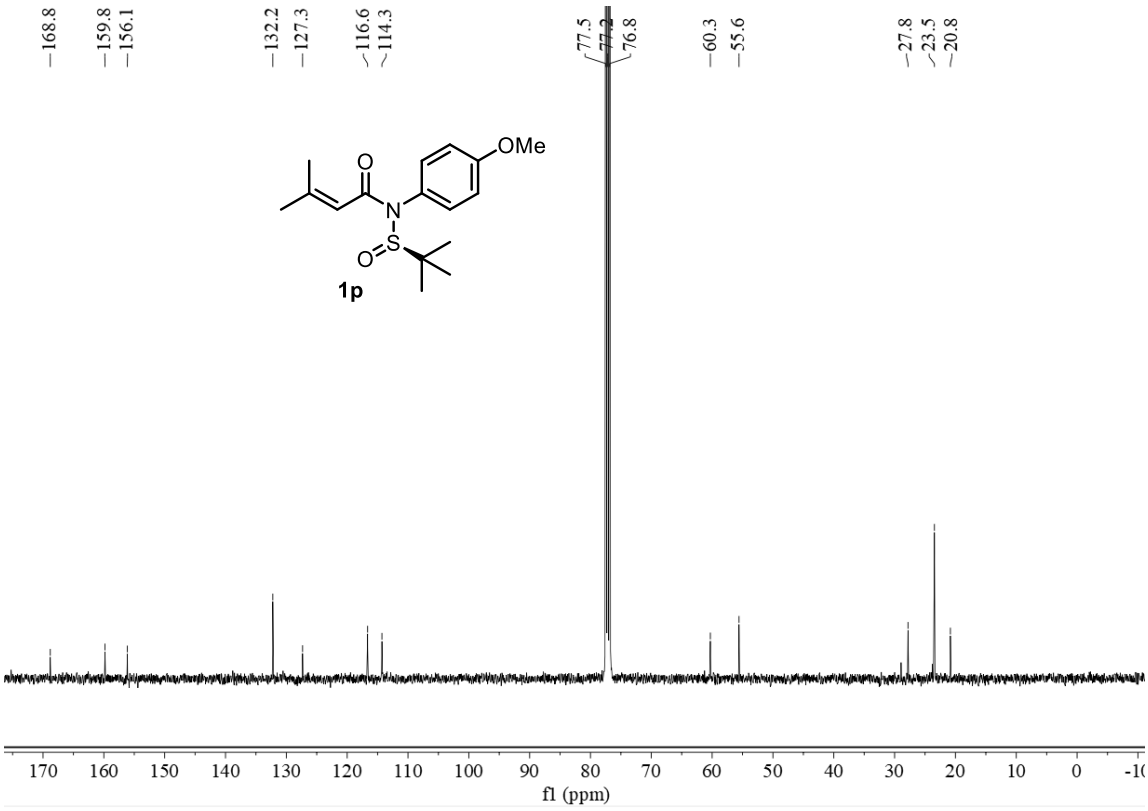
^{1}H NMR of **1o**



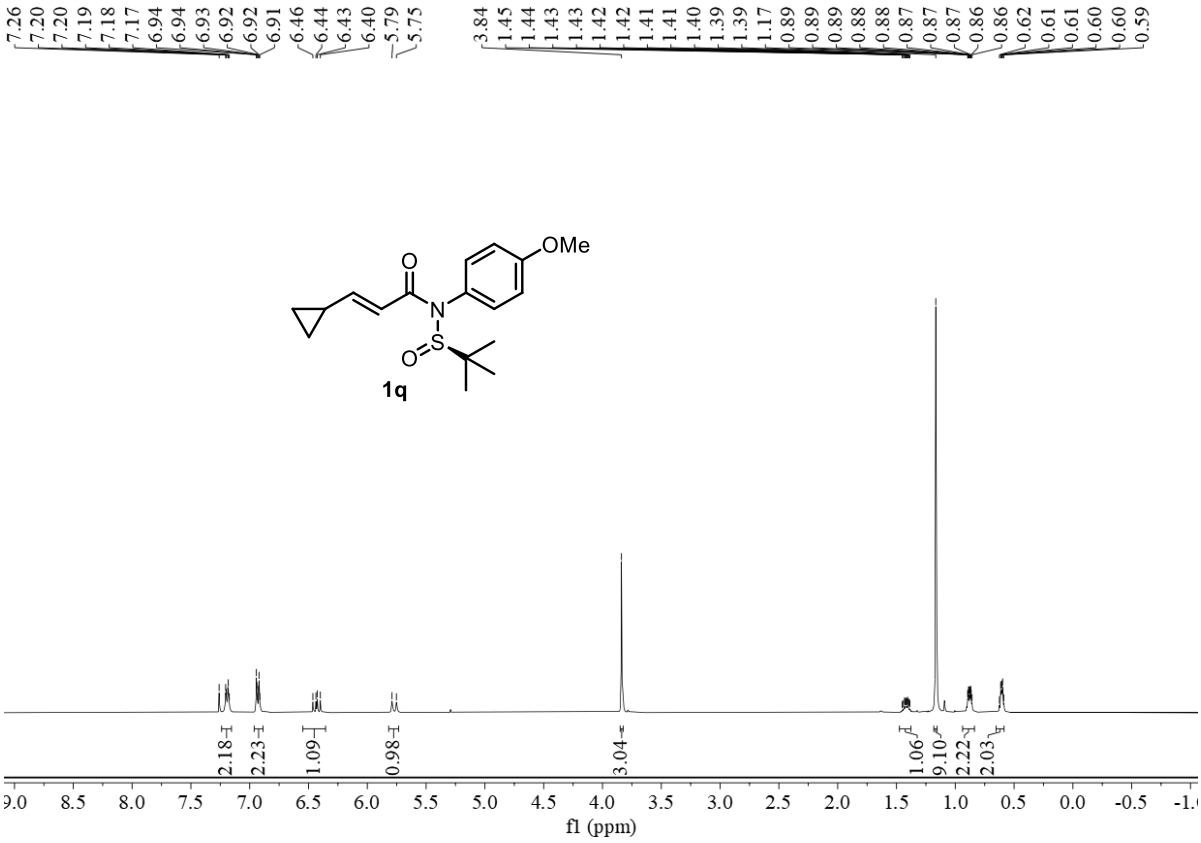
^{13}C NMR of **1o**



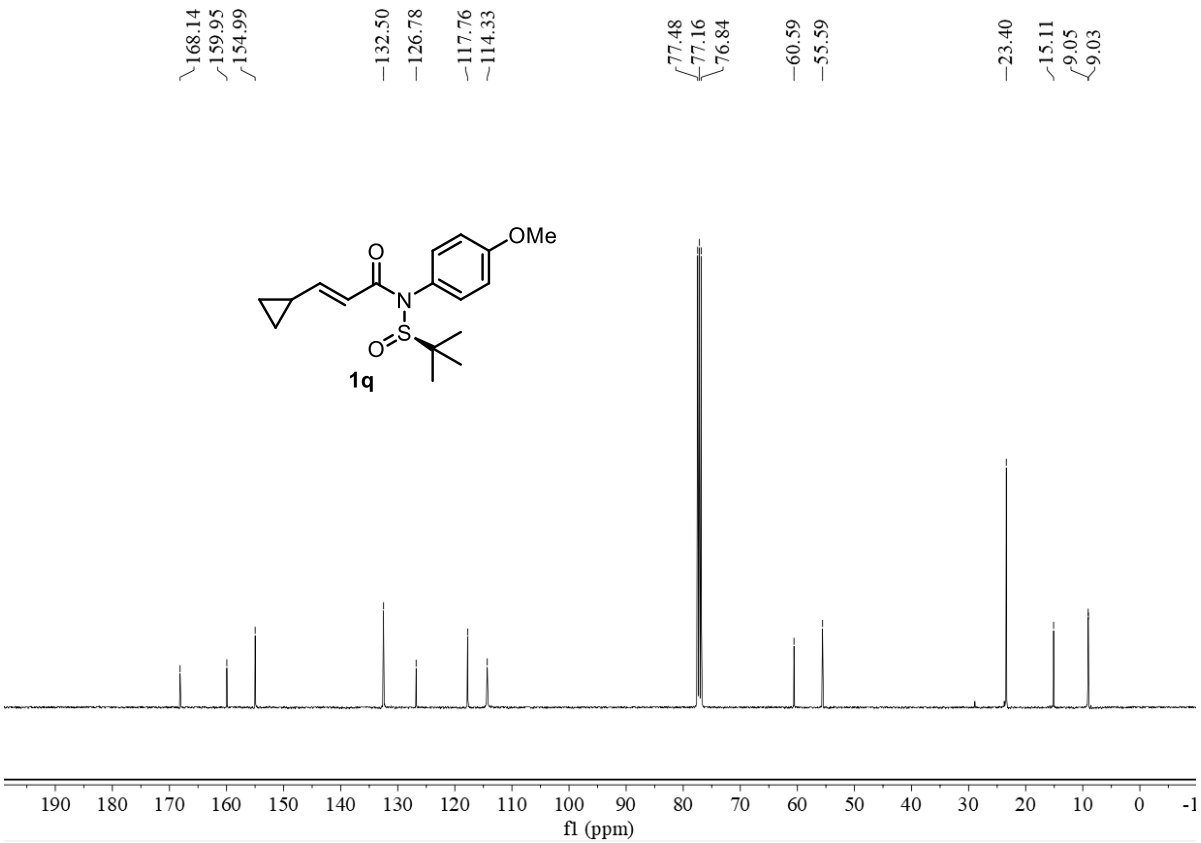
^{1}H NMR of **1p**



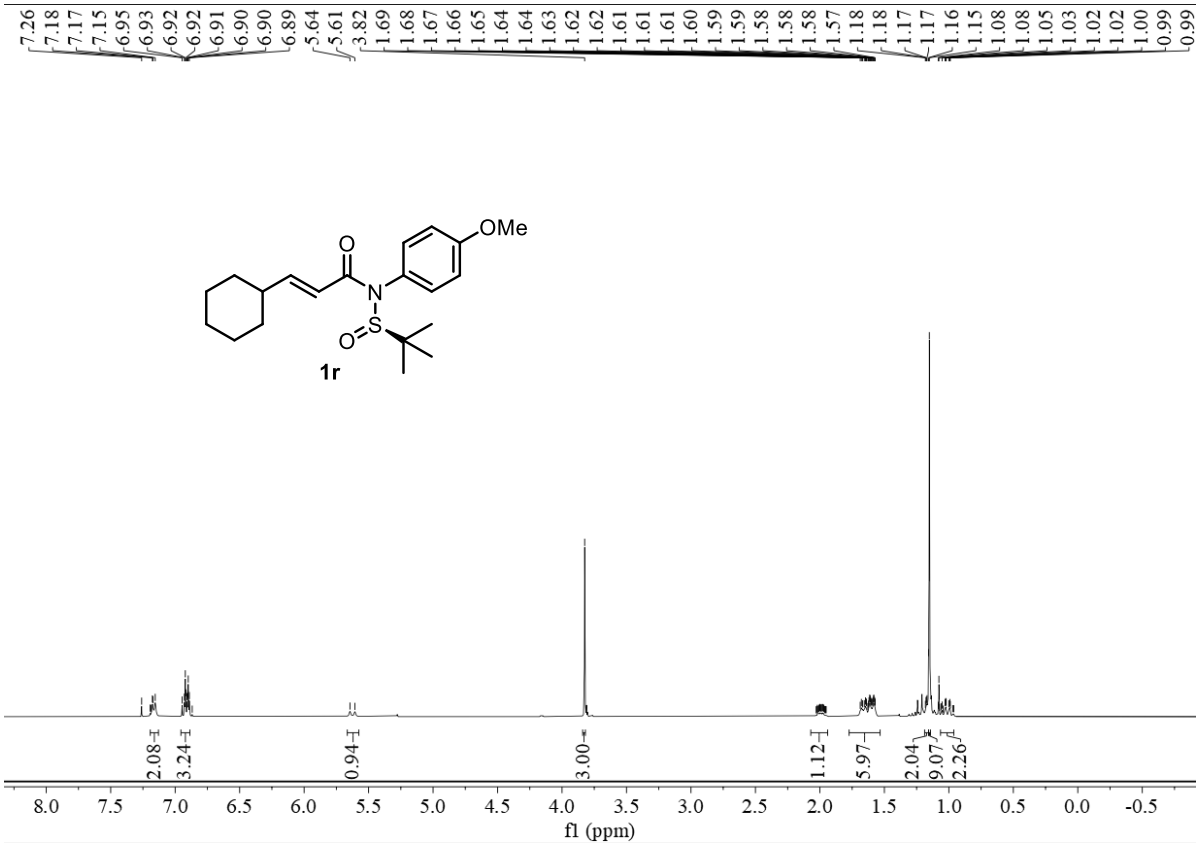
^{13}C NMR of **1p**



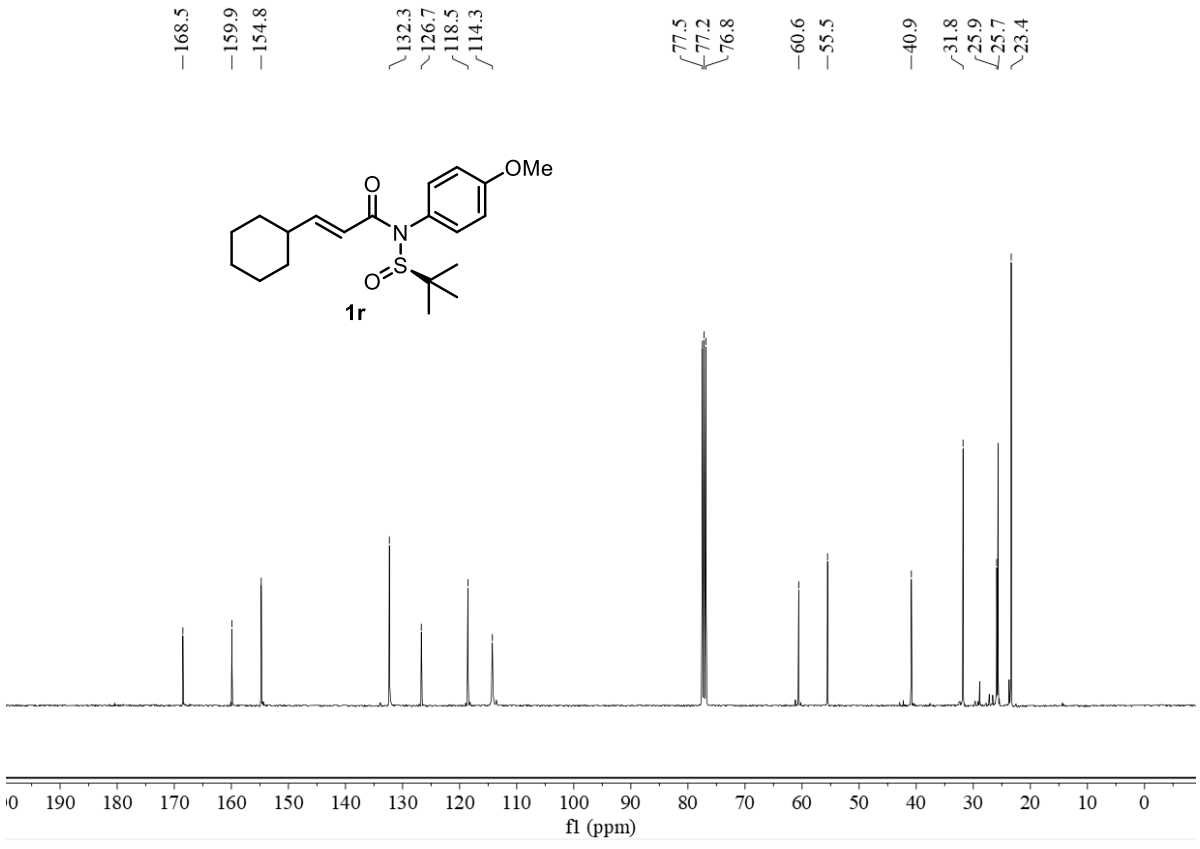
^{1}H NMR of **1q**



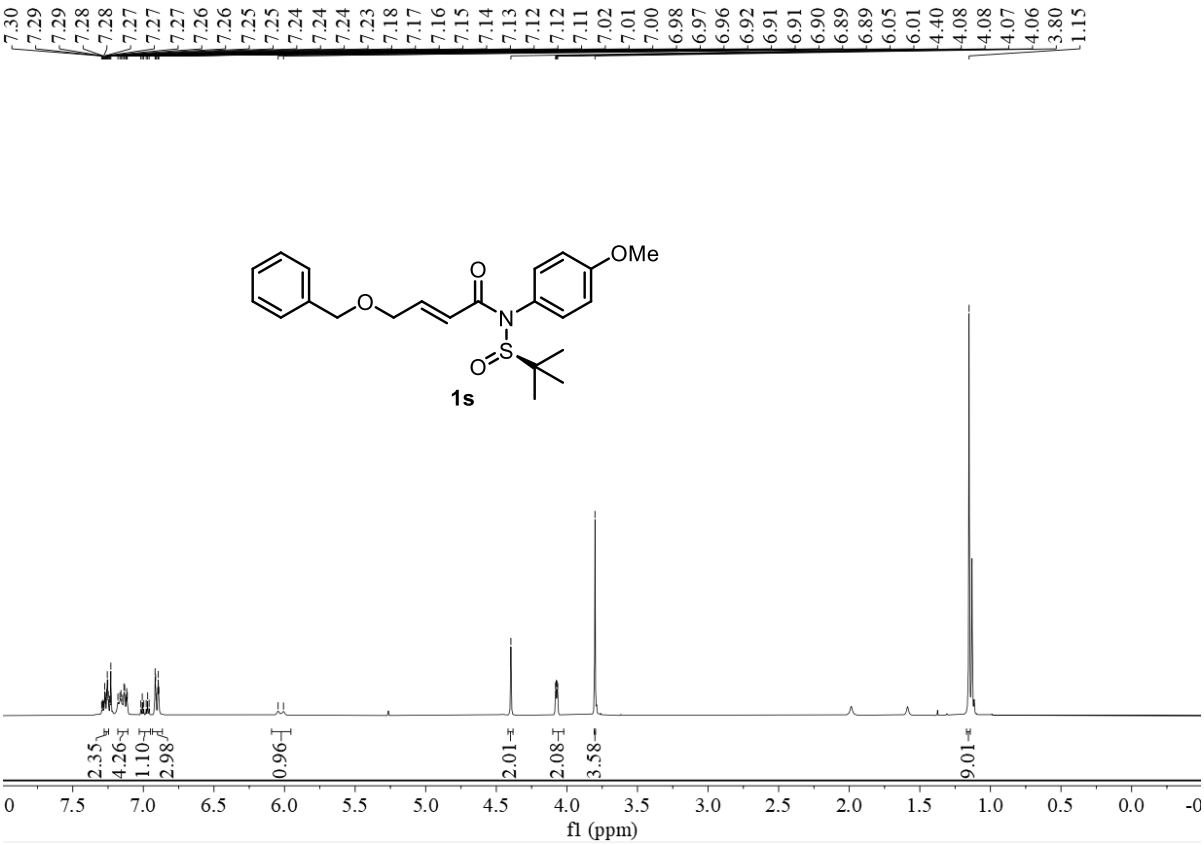
^{13}C NMR of **1q**



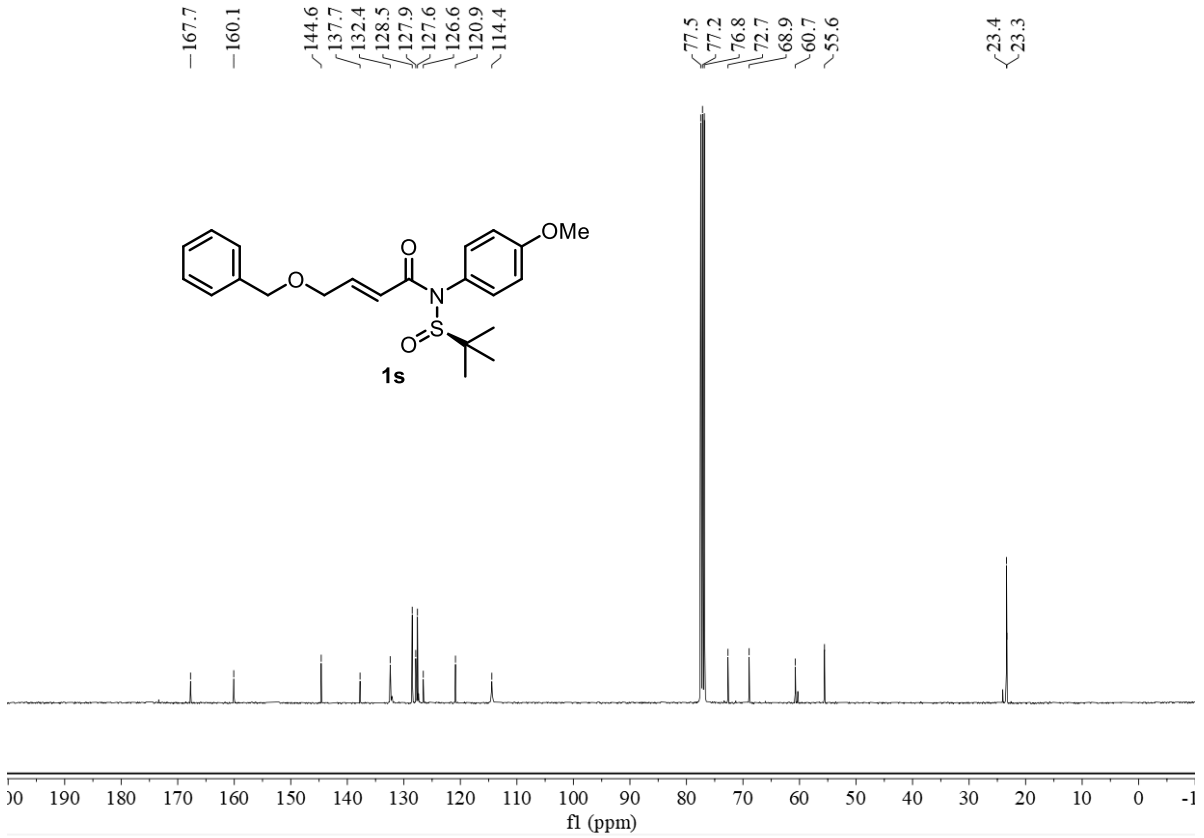
^{1}H NMR of 1r



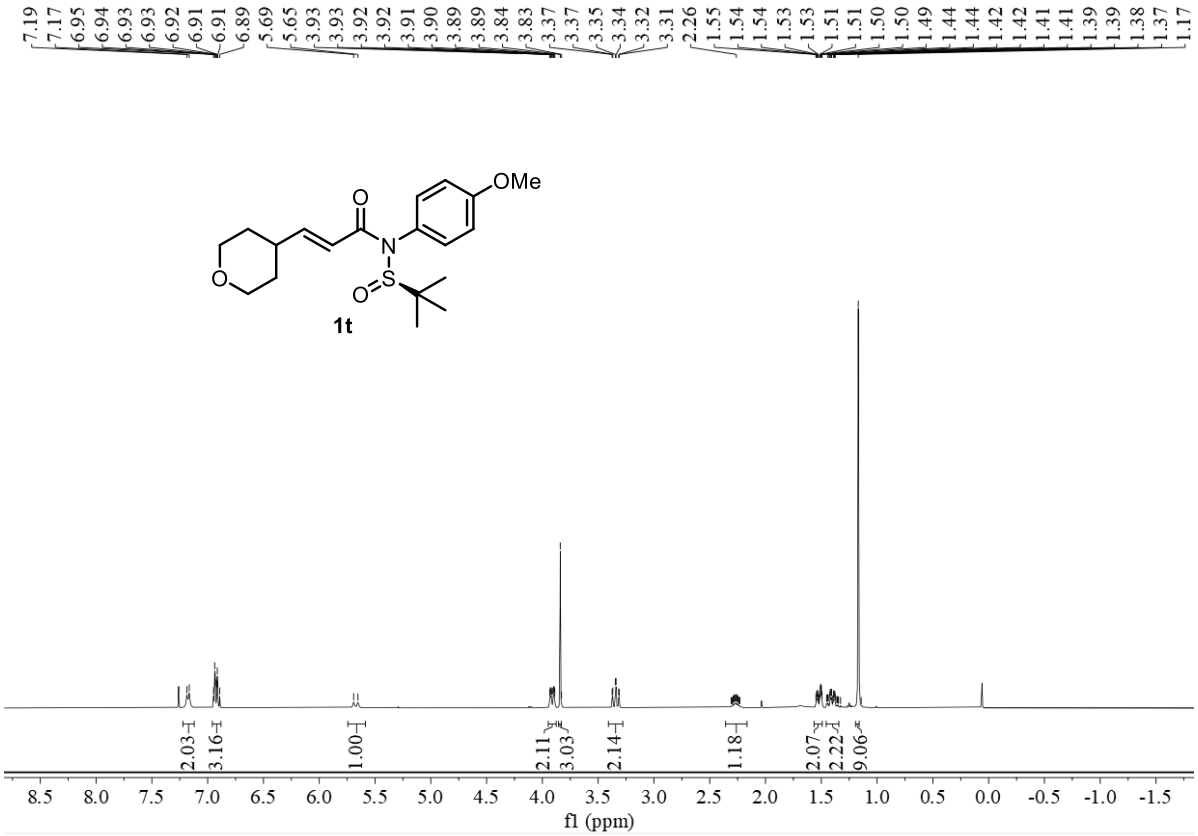
^{13}C NMR of 1r



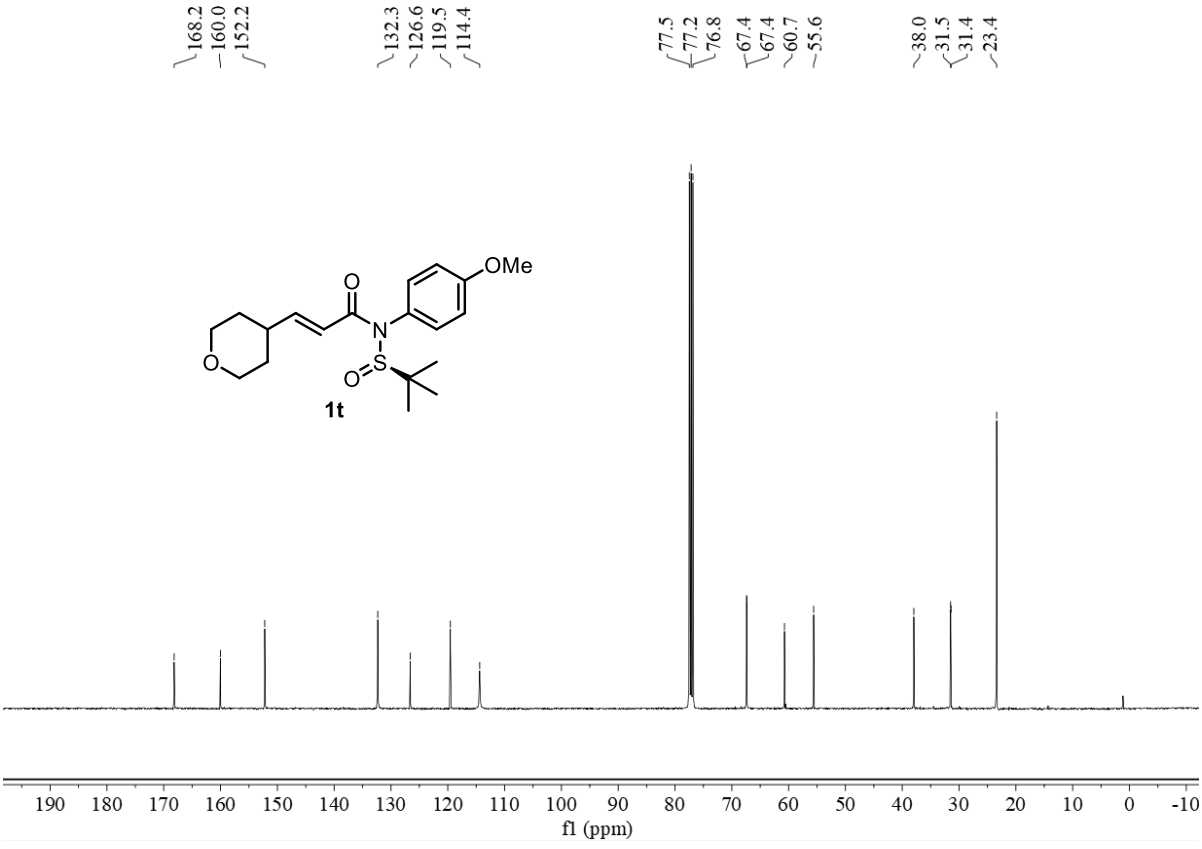
^{1}H NMR of **1s**



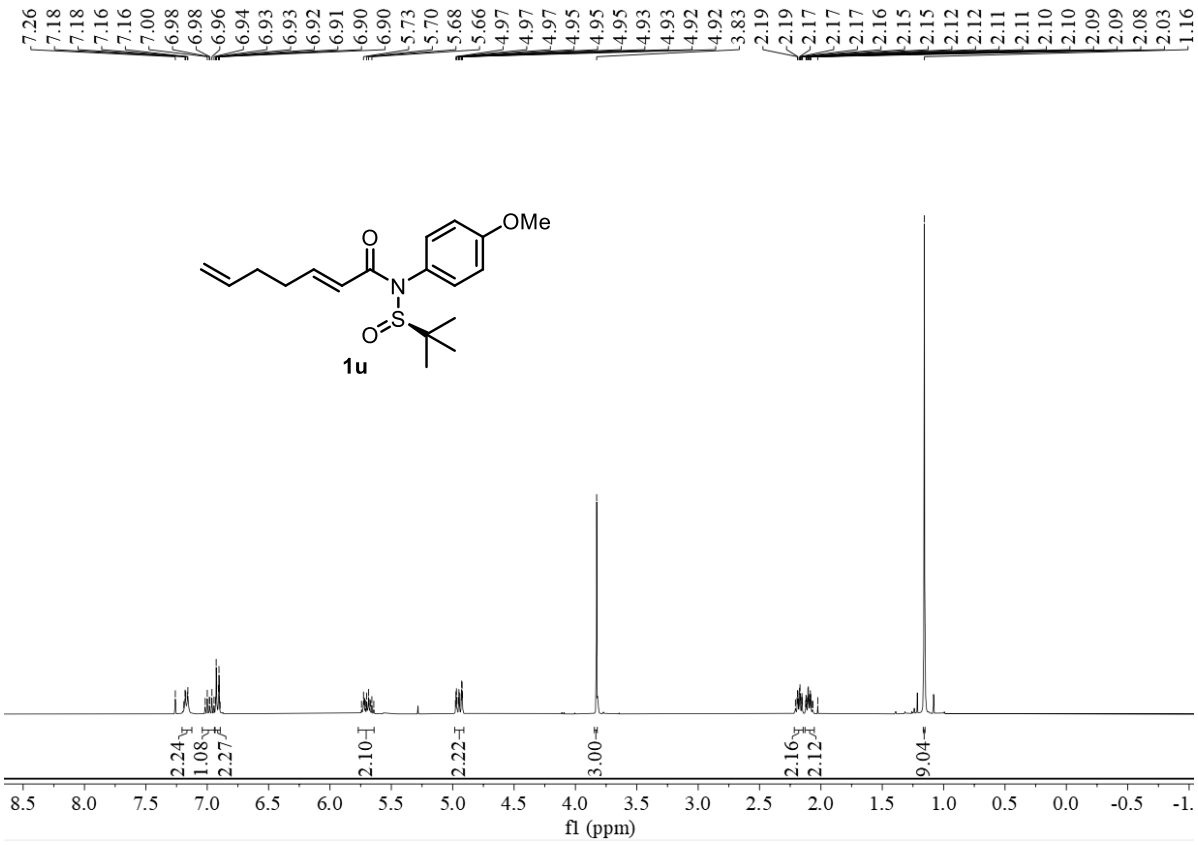
^{13}C NMR of **1s**



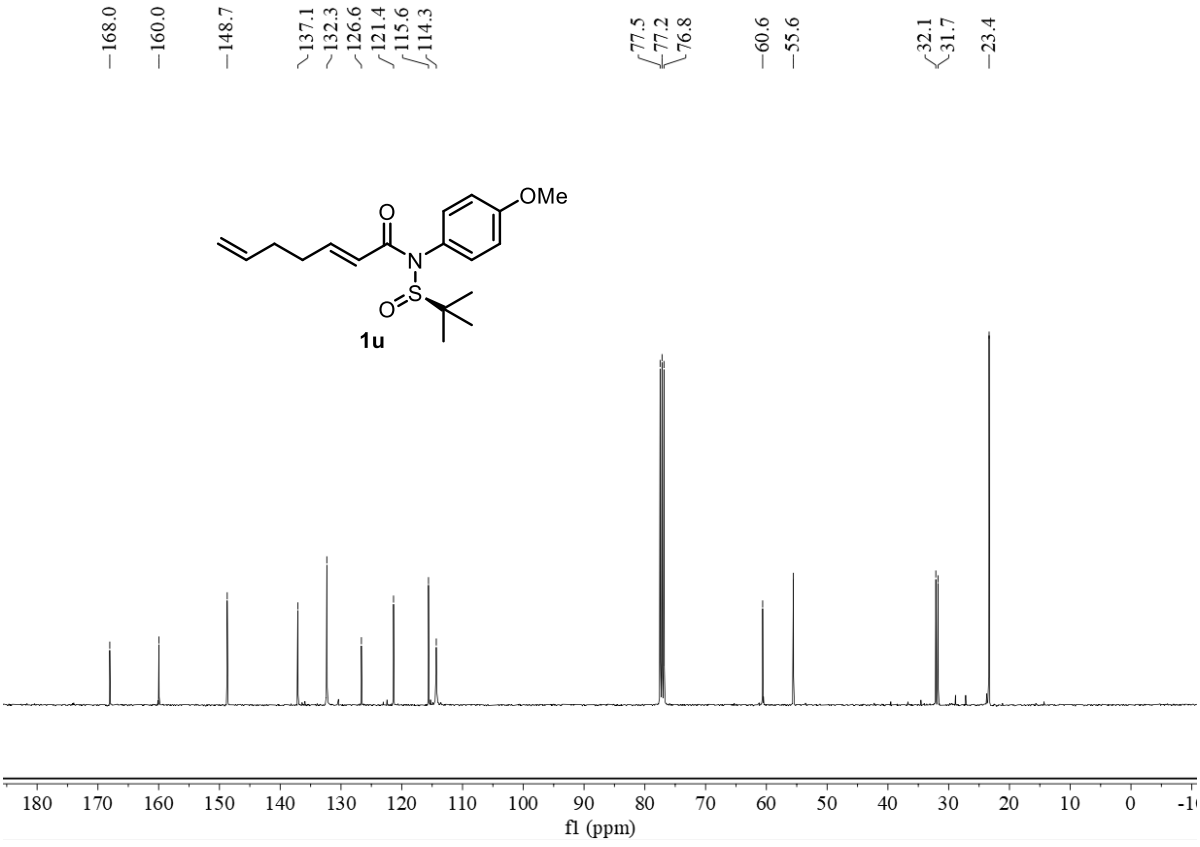
^{1}H NMR of **1t** (400 M, $CDCl_3$)



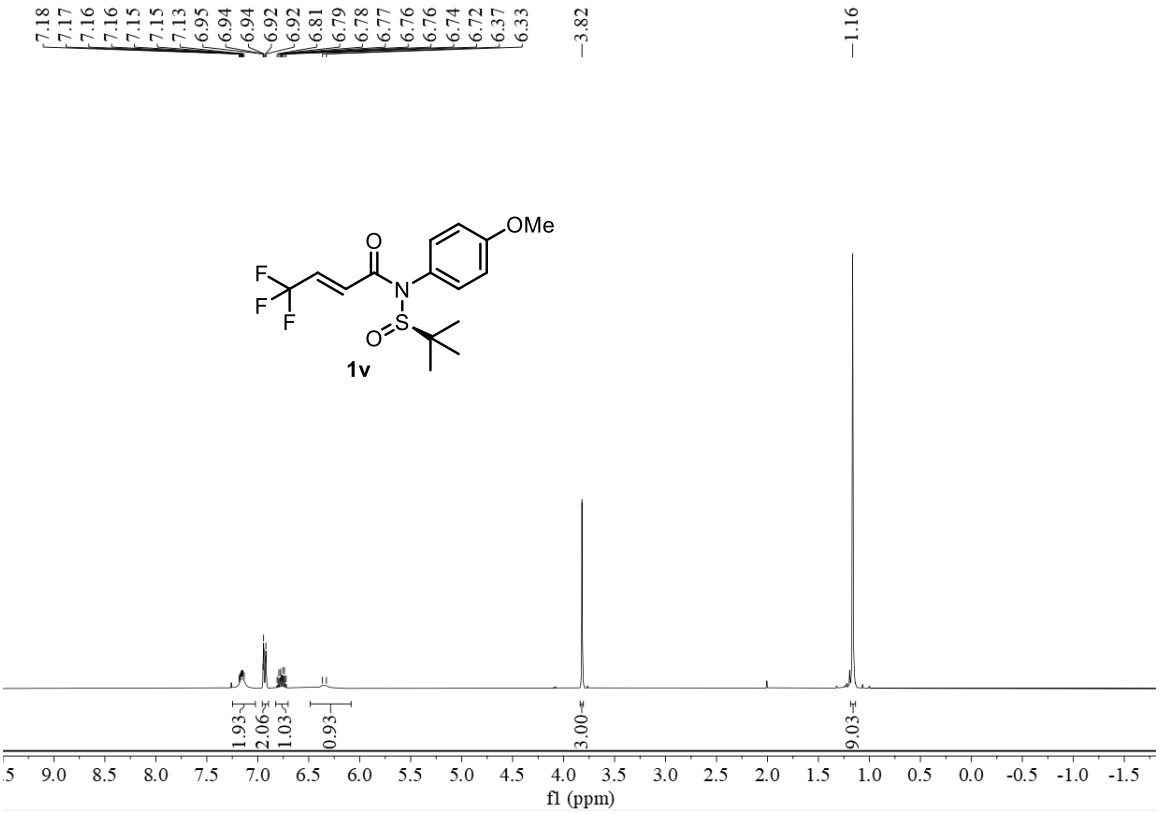
^{13}C NMR of **1t** (101 M, $CDCl_3$)



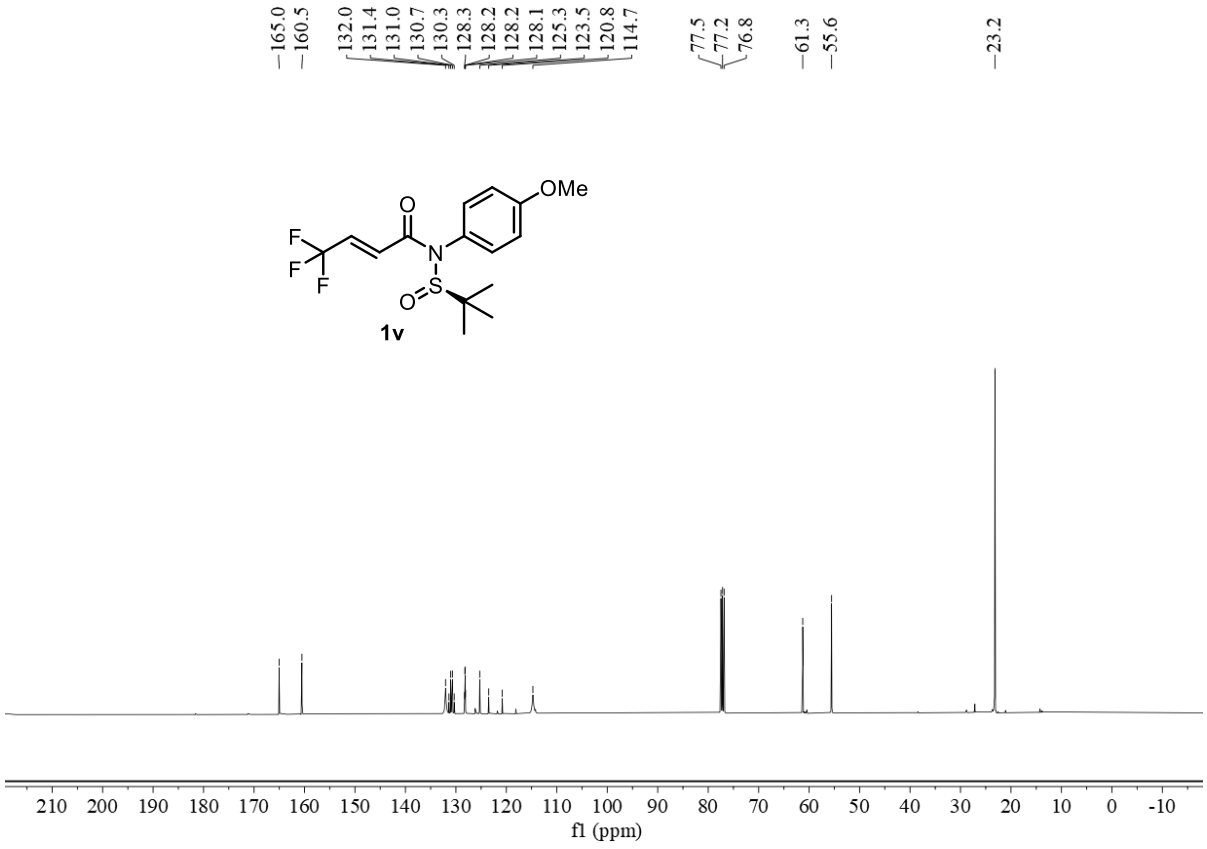
^{1}H NMR of **1u** (400 M, $CDCl_3$)



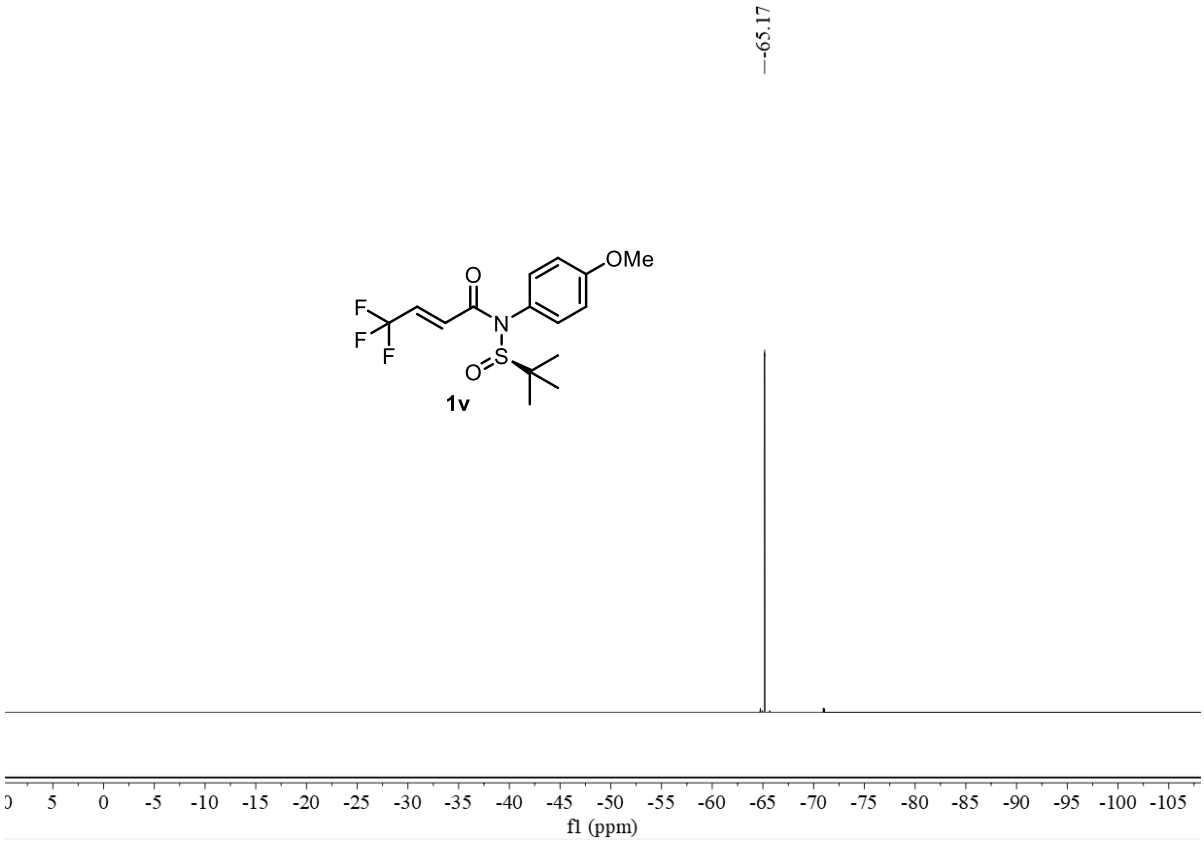
^{13}C NMR of **1u**



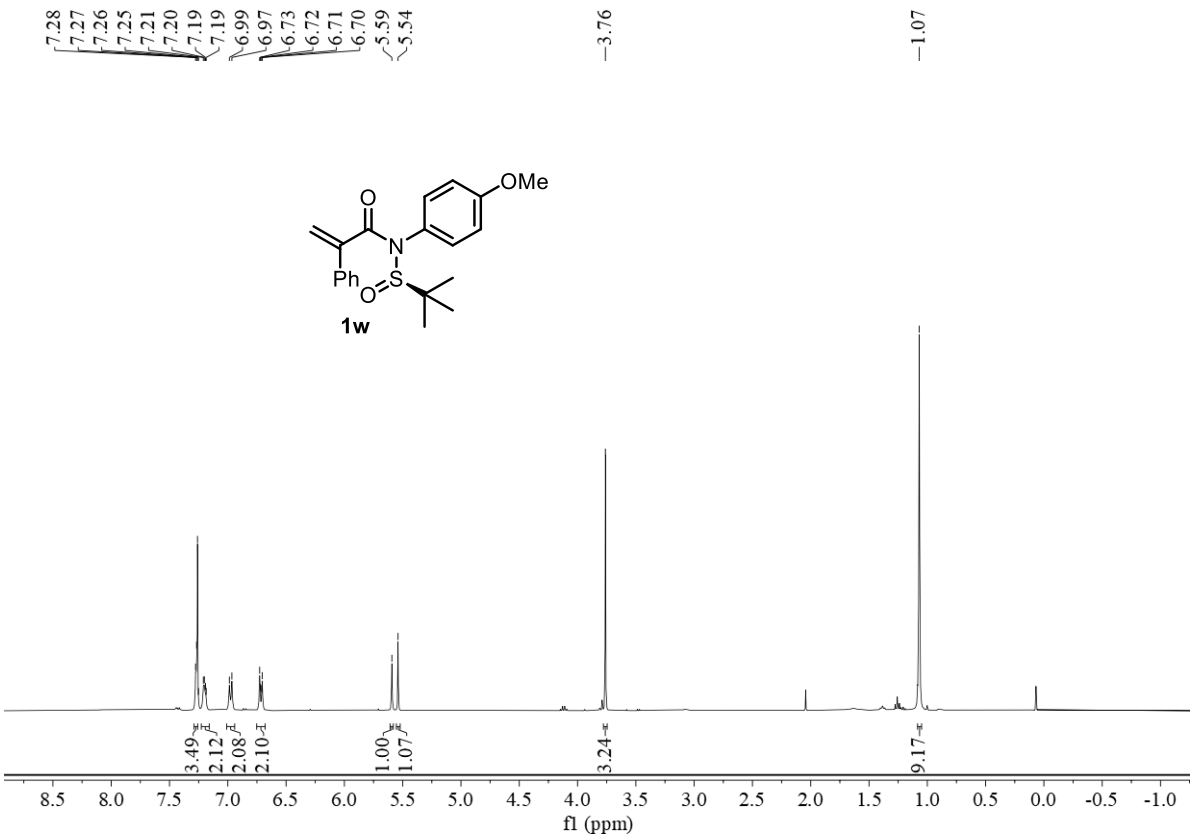
^{1}H NMR of **1v** (400M, $CDCl_3$)



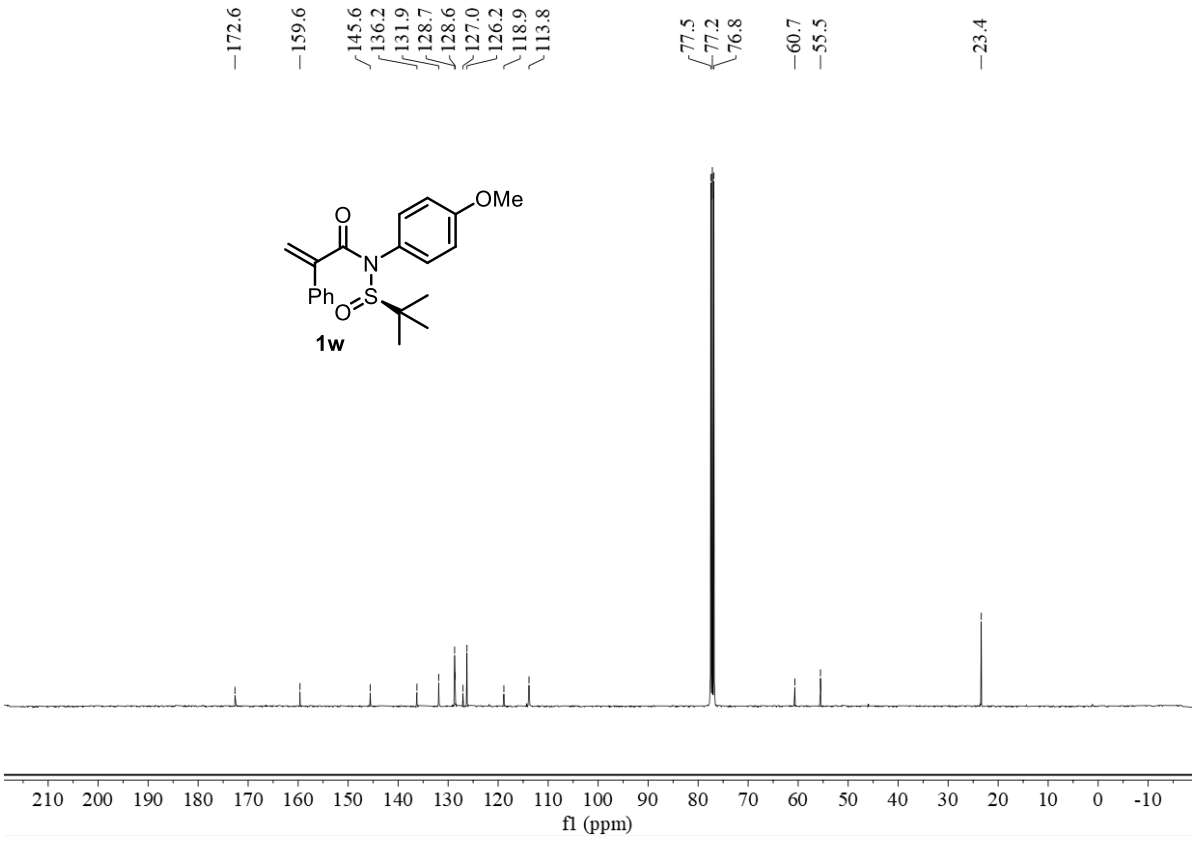
^{13}C NMR of **1v** (101M, $CDCl_3$)



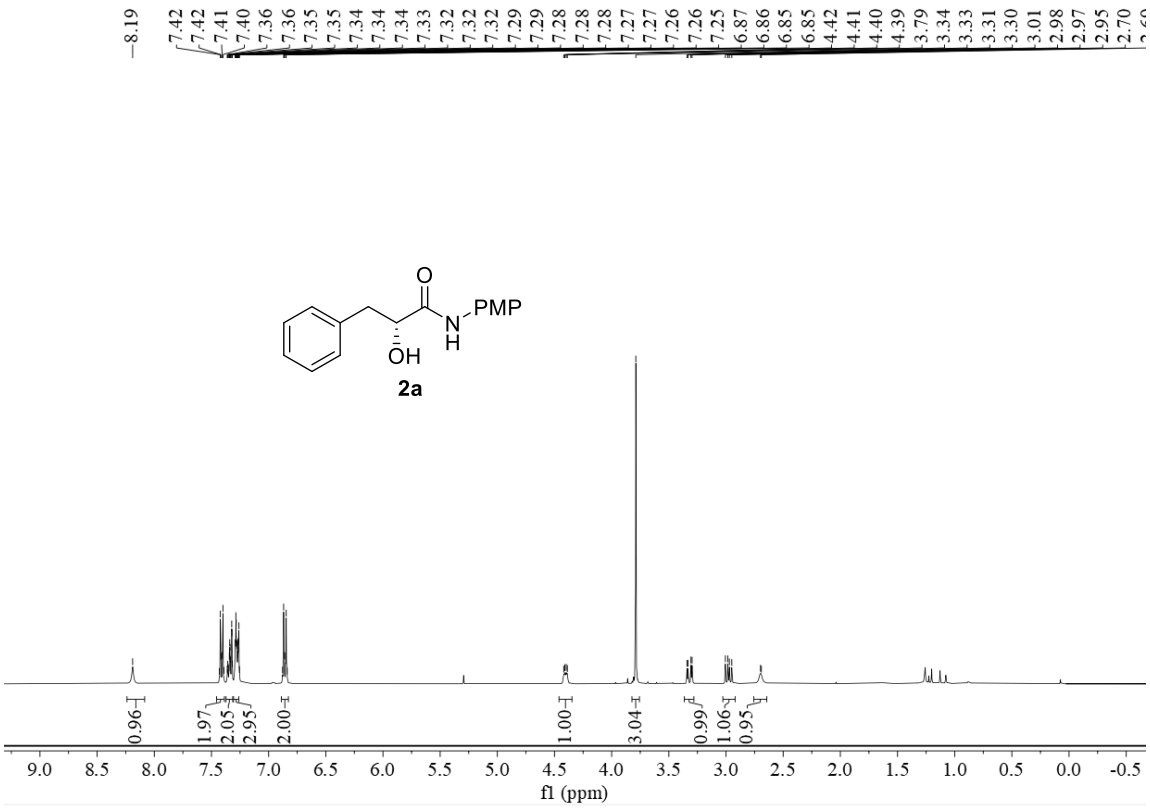
^{19}F NMR of **1v** (376M, $CDCl_3$)



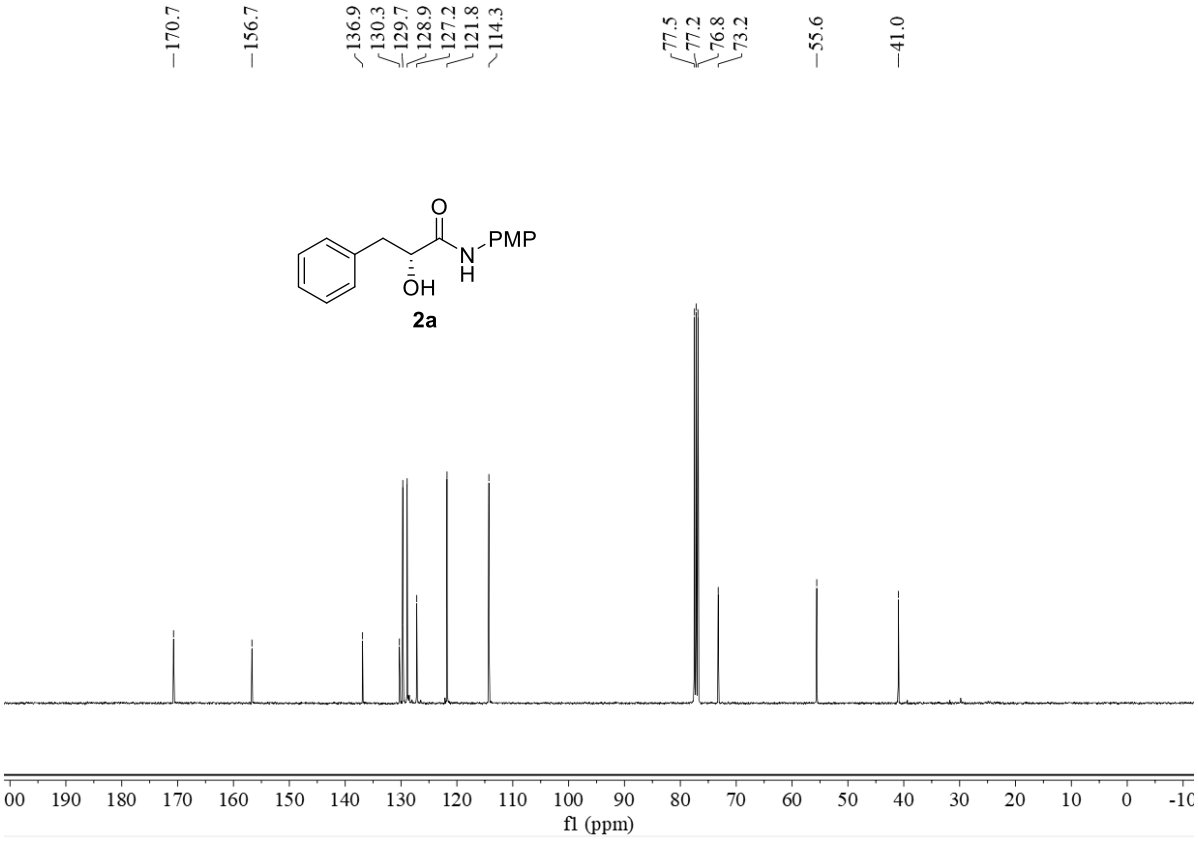
^{1}H NMR of **1w** (400M, $CDCl_3$)



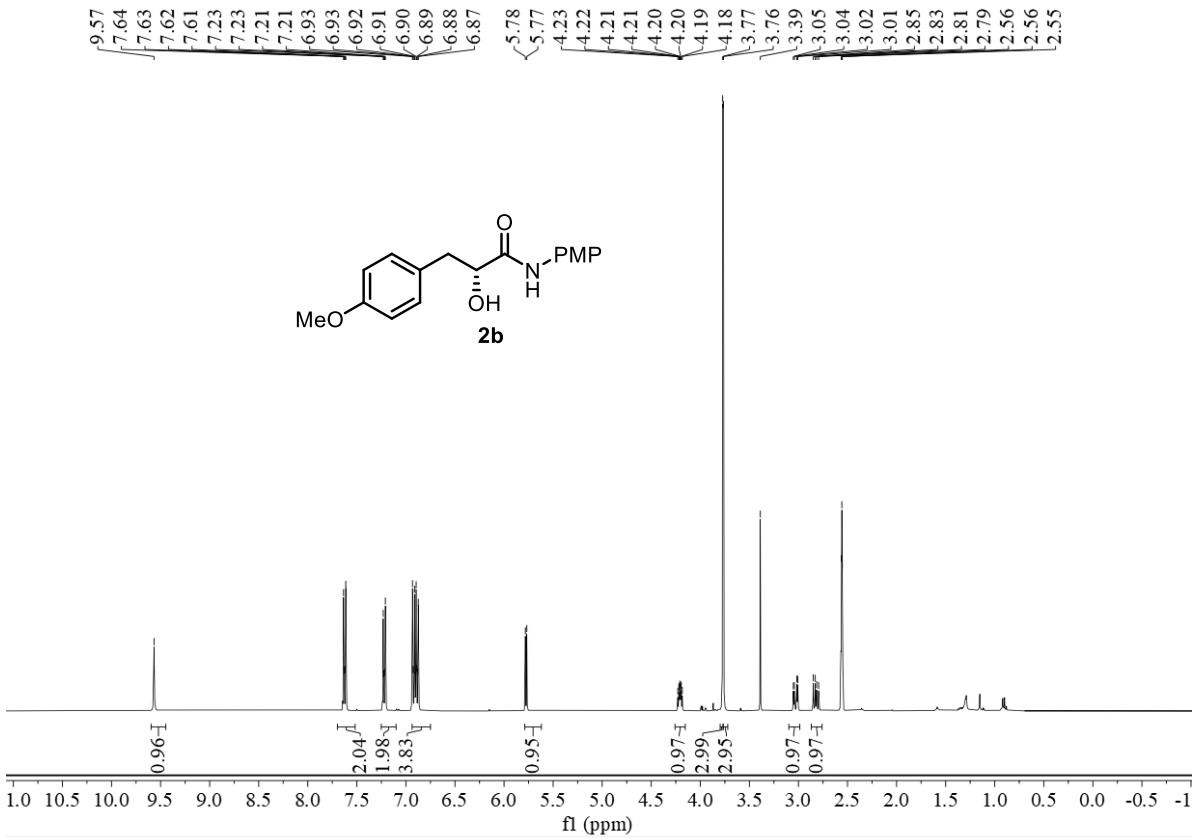
^{13}C NMR of **1w** (101M, $CDCl_3$)



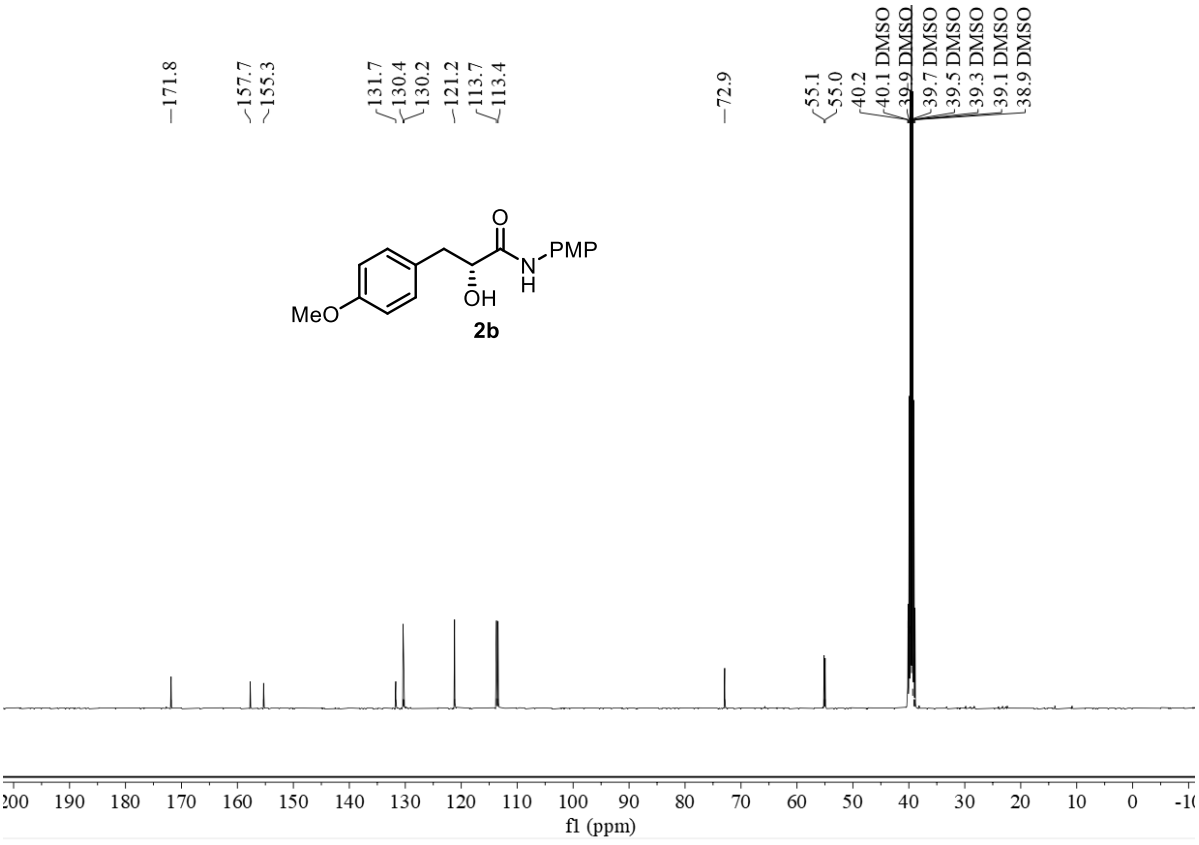
^{1}H NMR of **2a** (400M, $CDCl_3$)



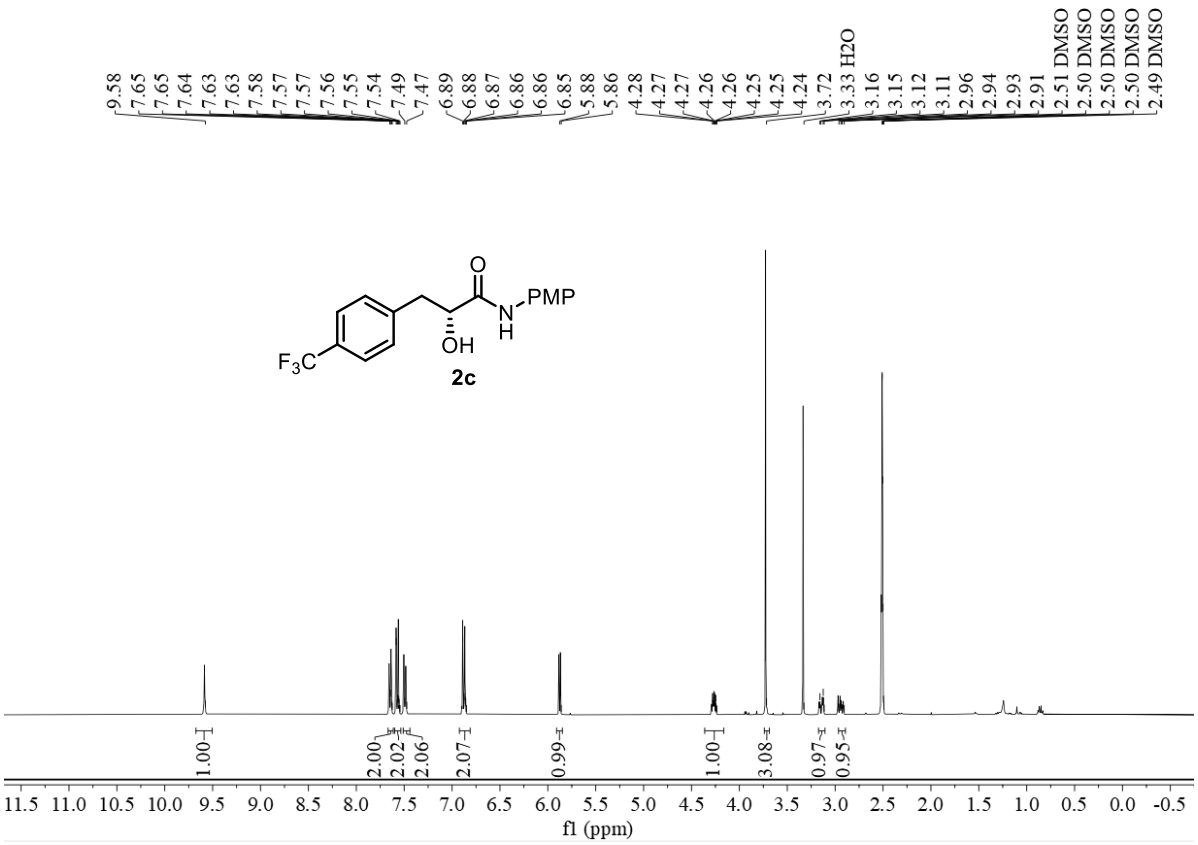
^{13}C NMR of **2a** (101M, $CDCl_3$)



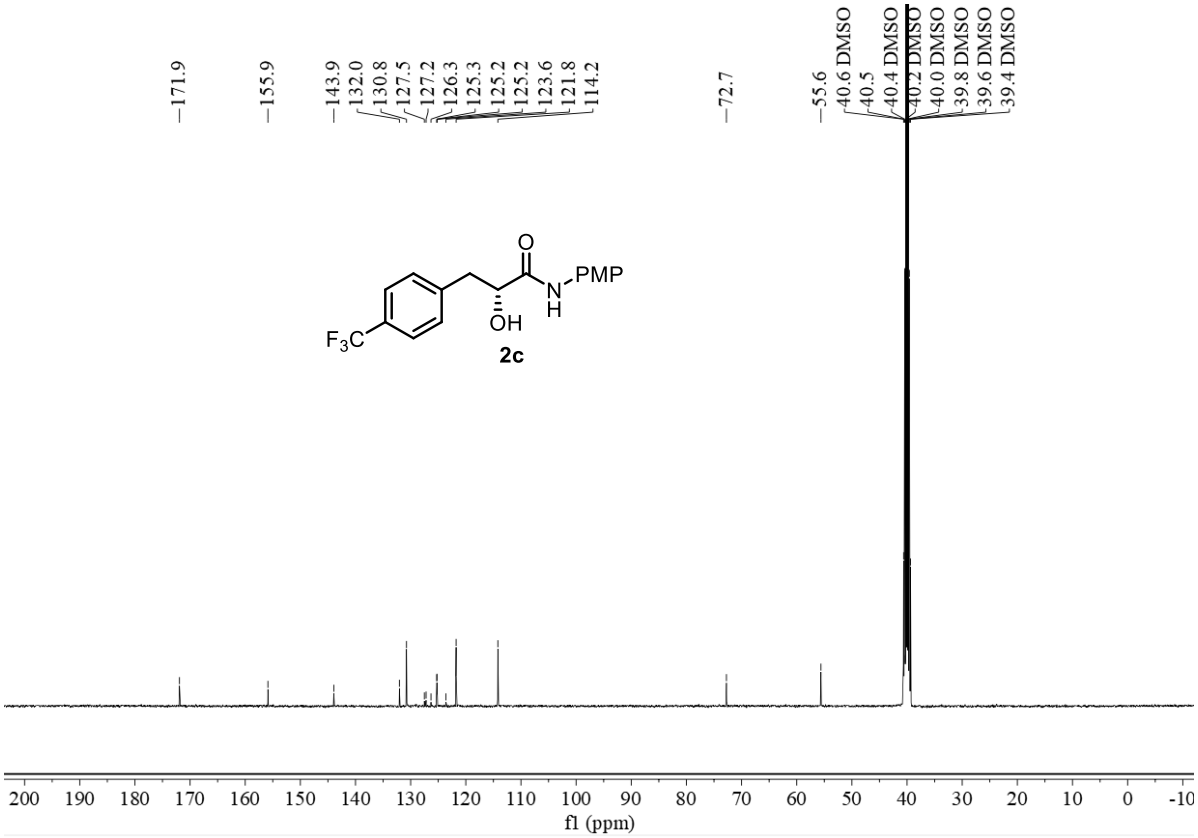
^{1}H NMR of **2b** (400 M, DMSO-d_6)



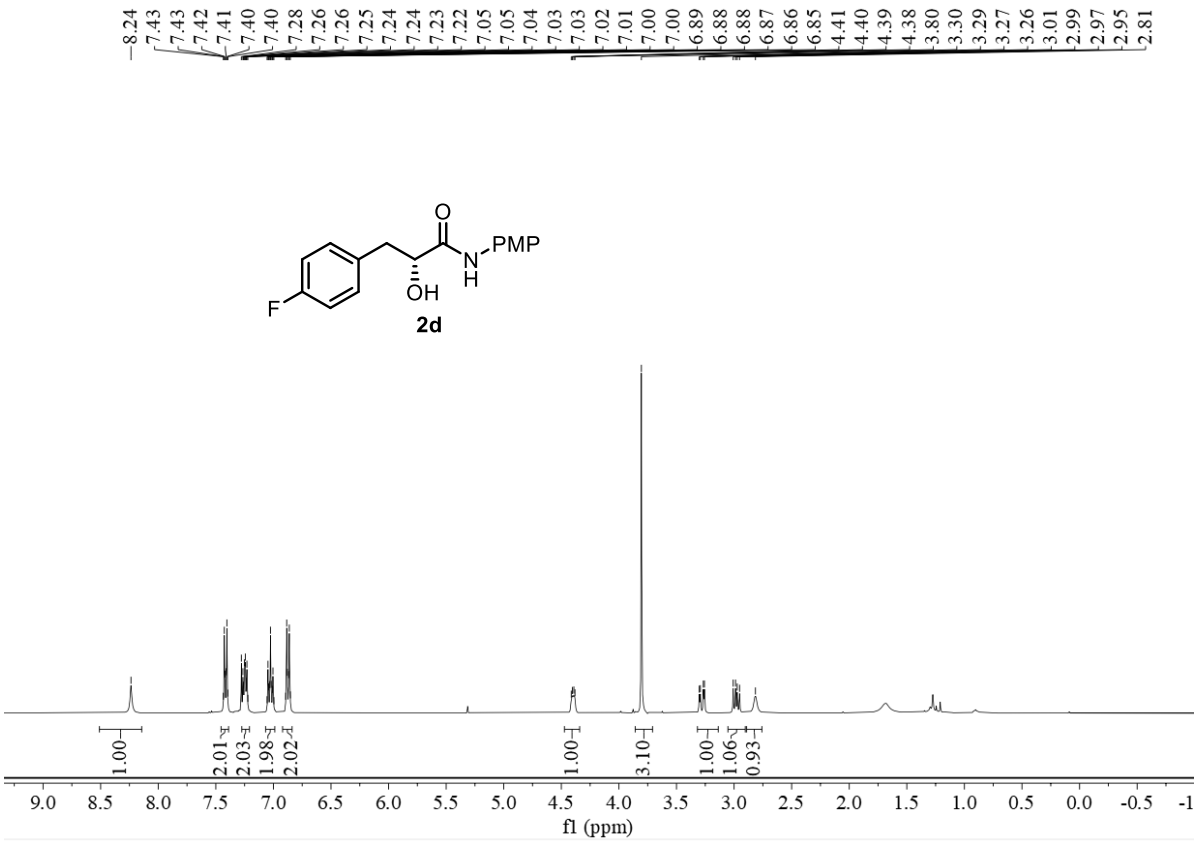
^{13}C NMR of **2b** (101 M, DMSO-d_6)



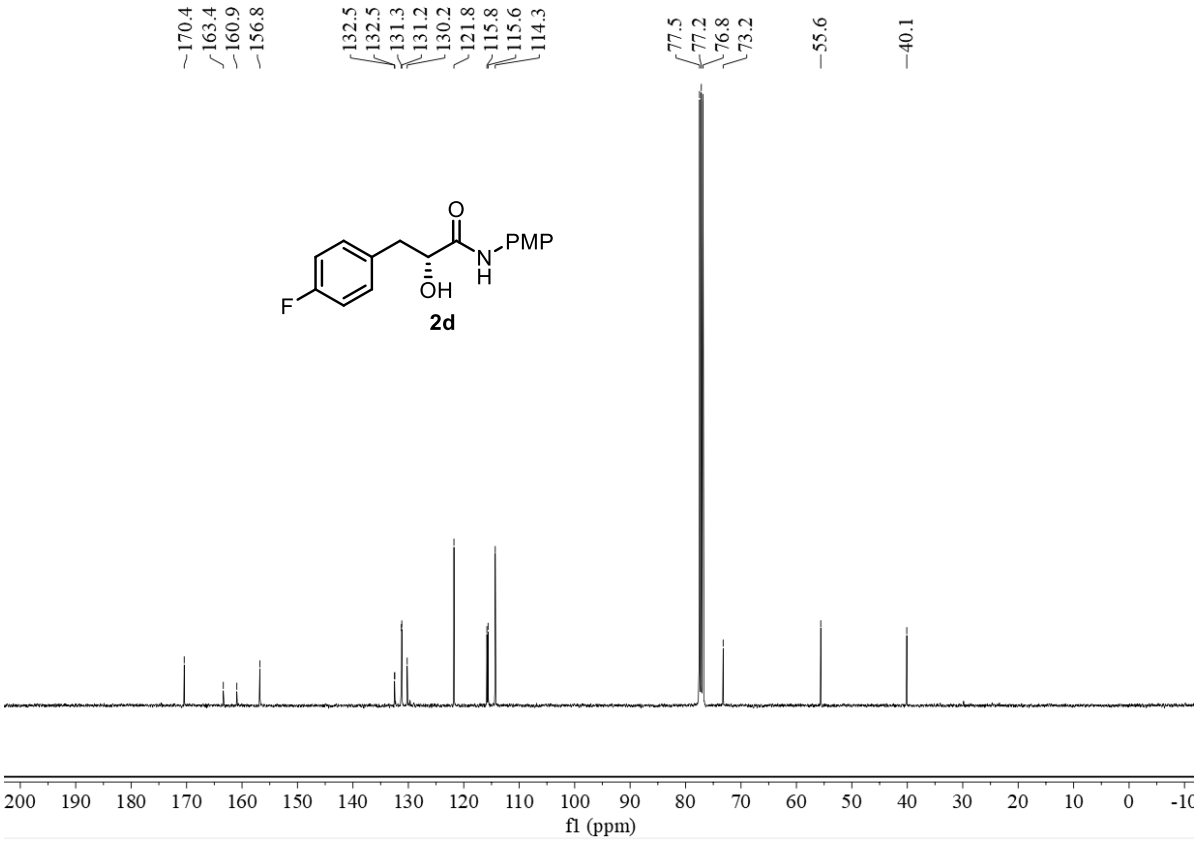
^{1}H NMR of **2c** (400 M, DMSO-d_6)



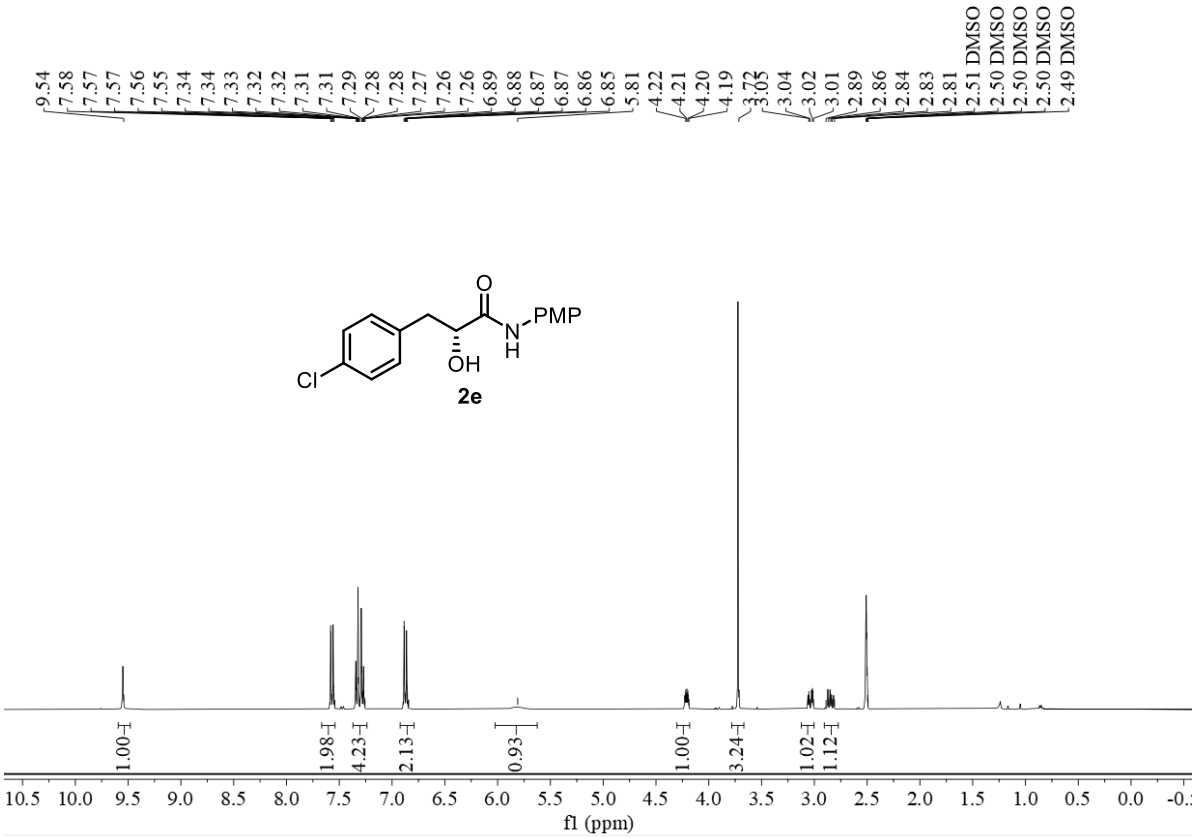
^{13}C NMR of **2c** (101 M, DMSO-d_6)



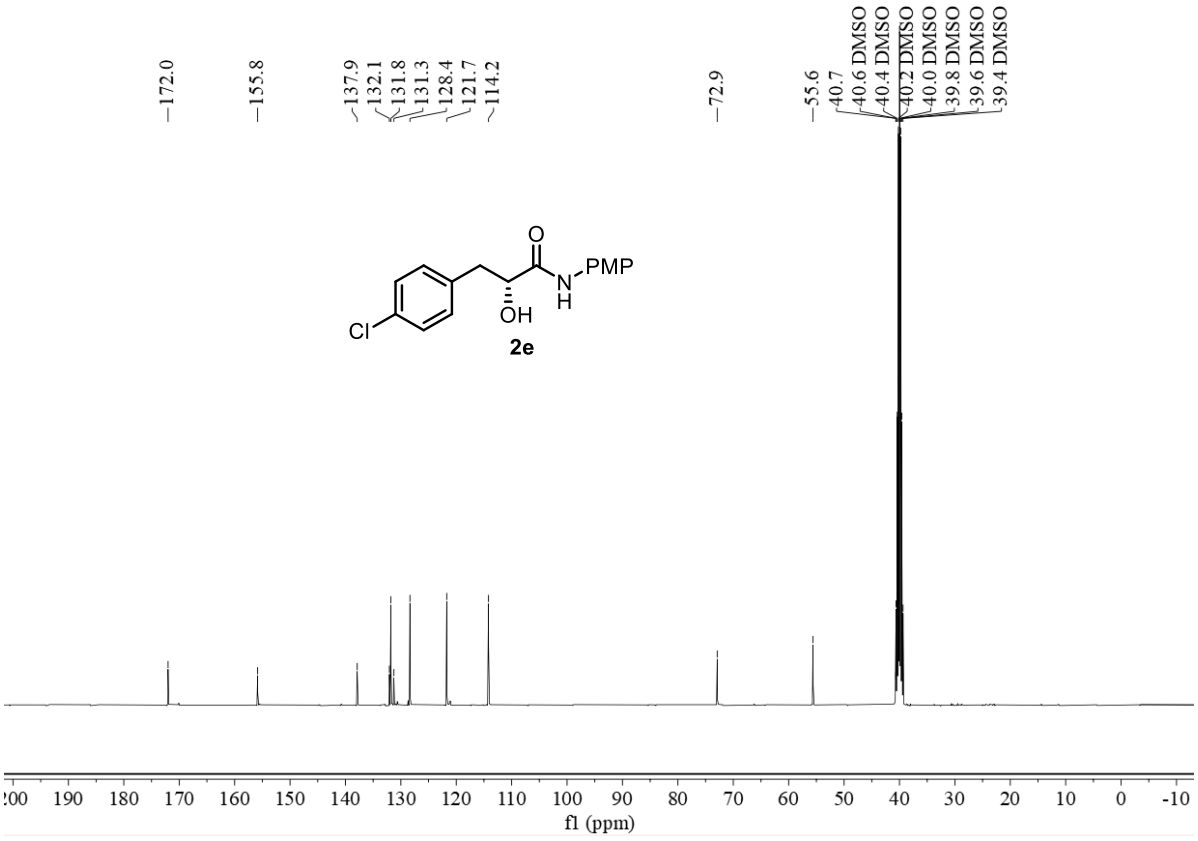
^{1}H NMR of **2d** (400 M, $CDCl_3$)



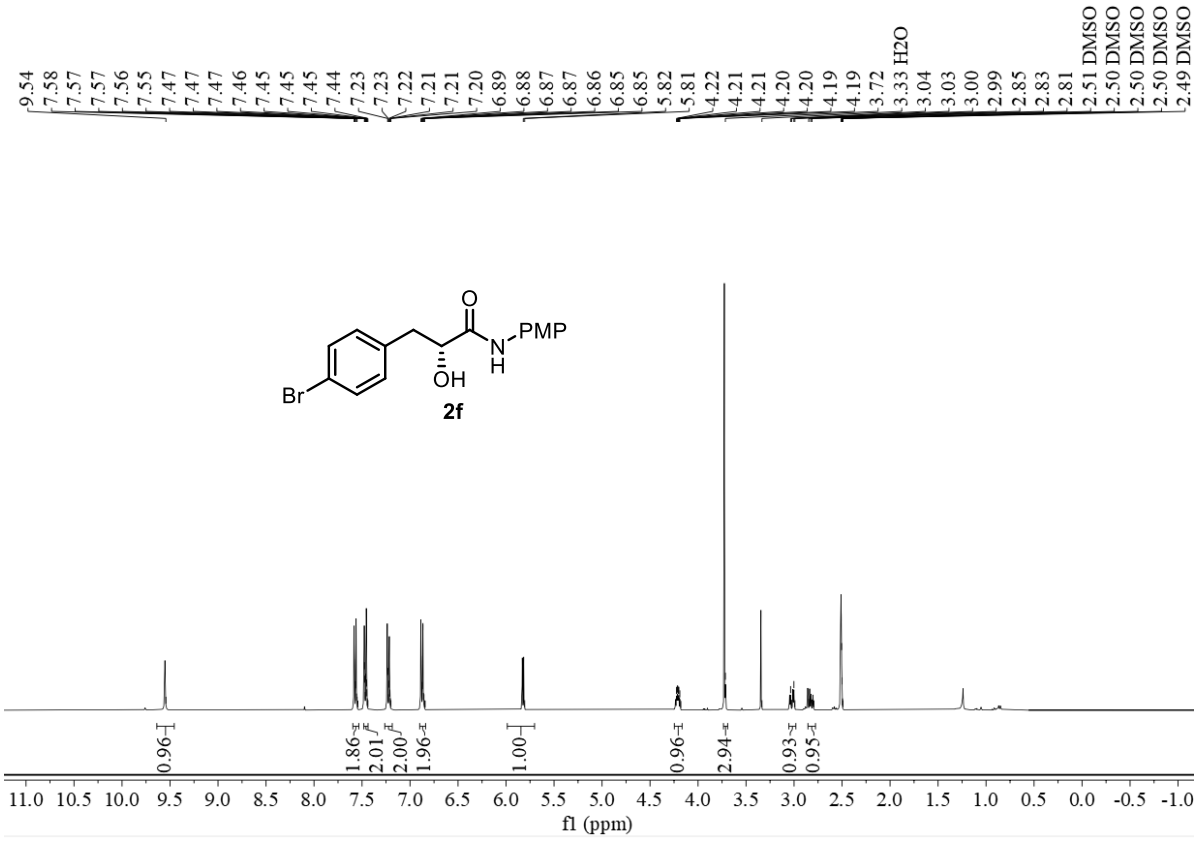
^{13}C NMR of **2d** (101 M, $CDCl_3$)



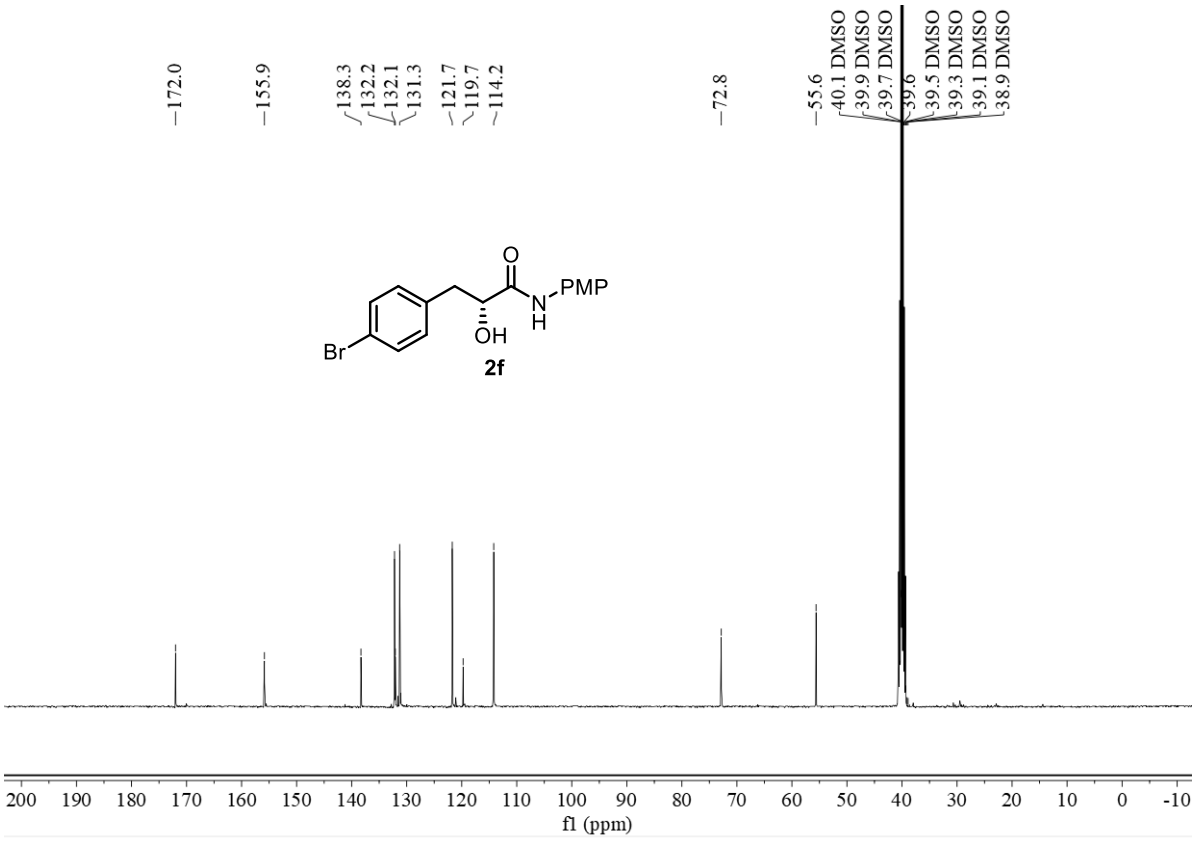
^{1}H NMR of **2e** (400 M, DMSO-d_6)



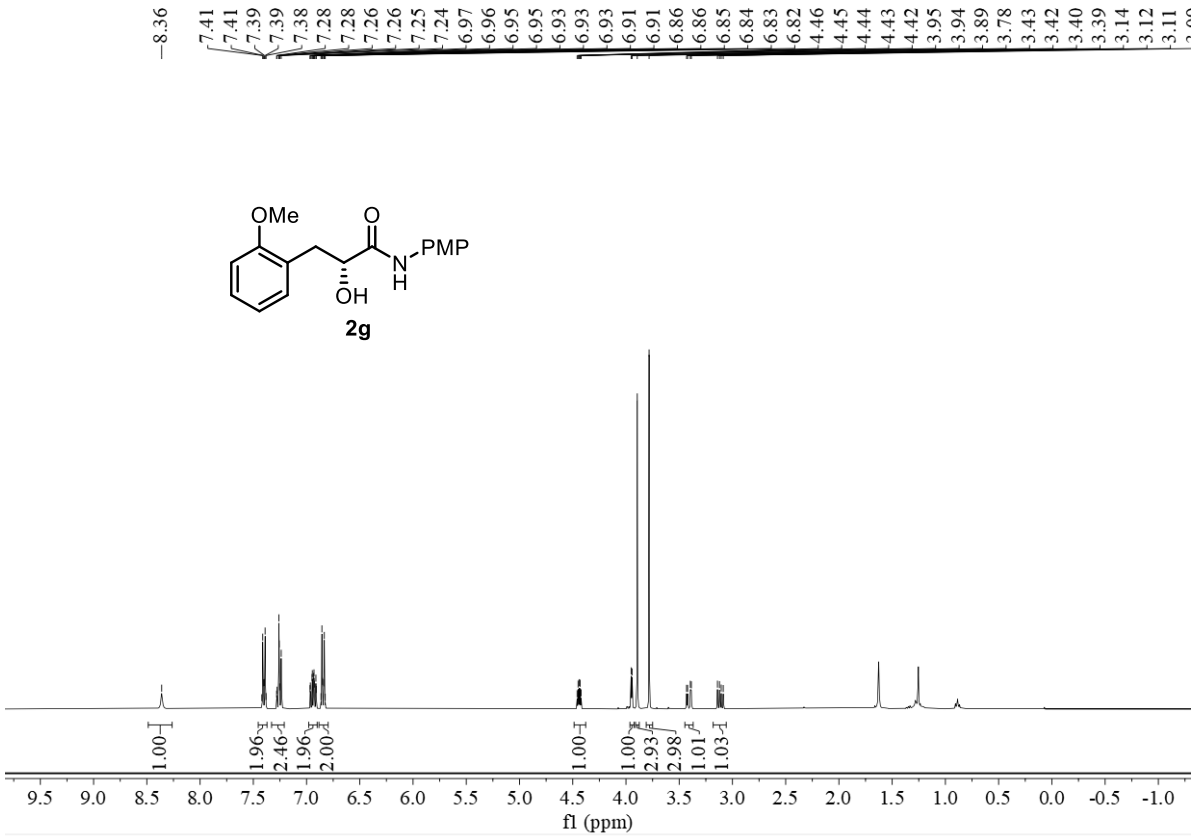
^{13}C NMR of **2e** (101 M, DMSO-d_6)



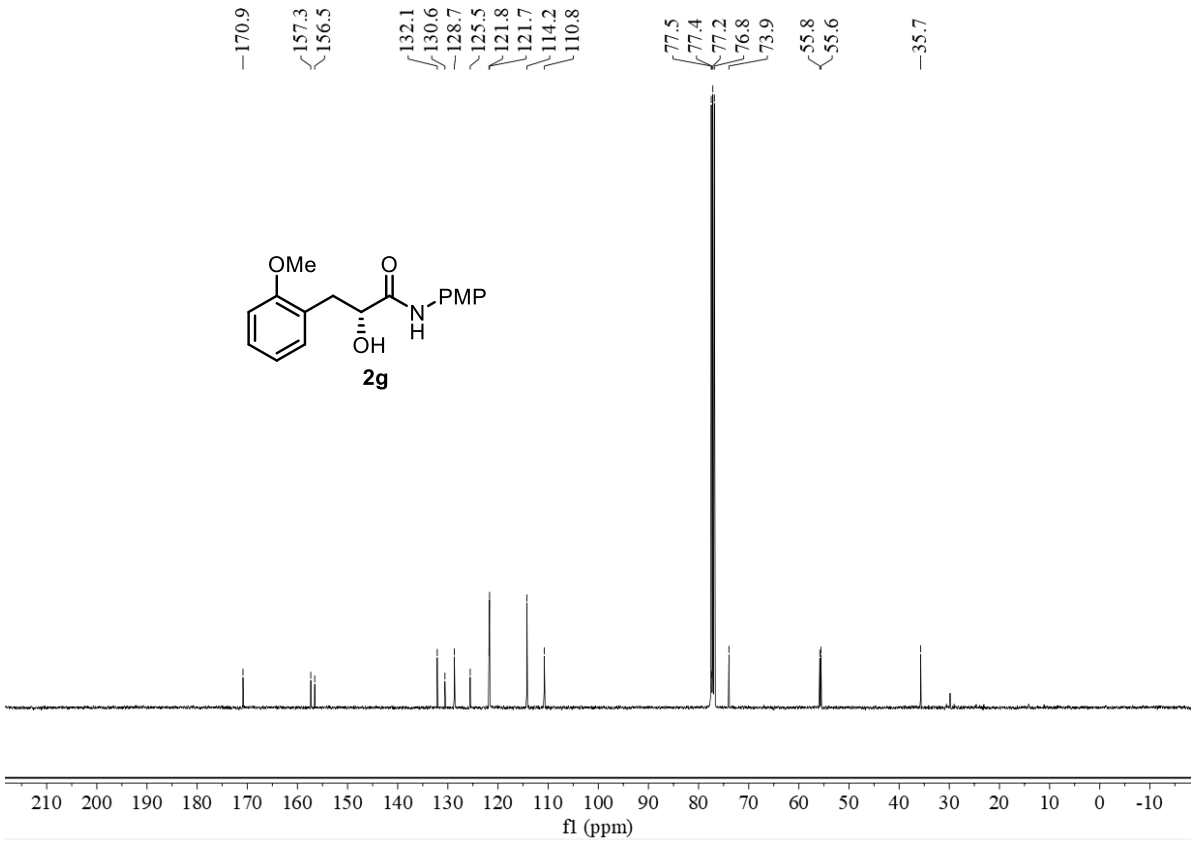
^{1}H NMR of **2f** (400 M, DMSO-d_6)



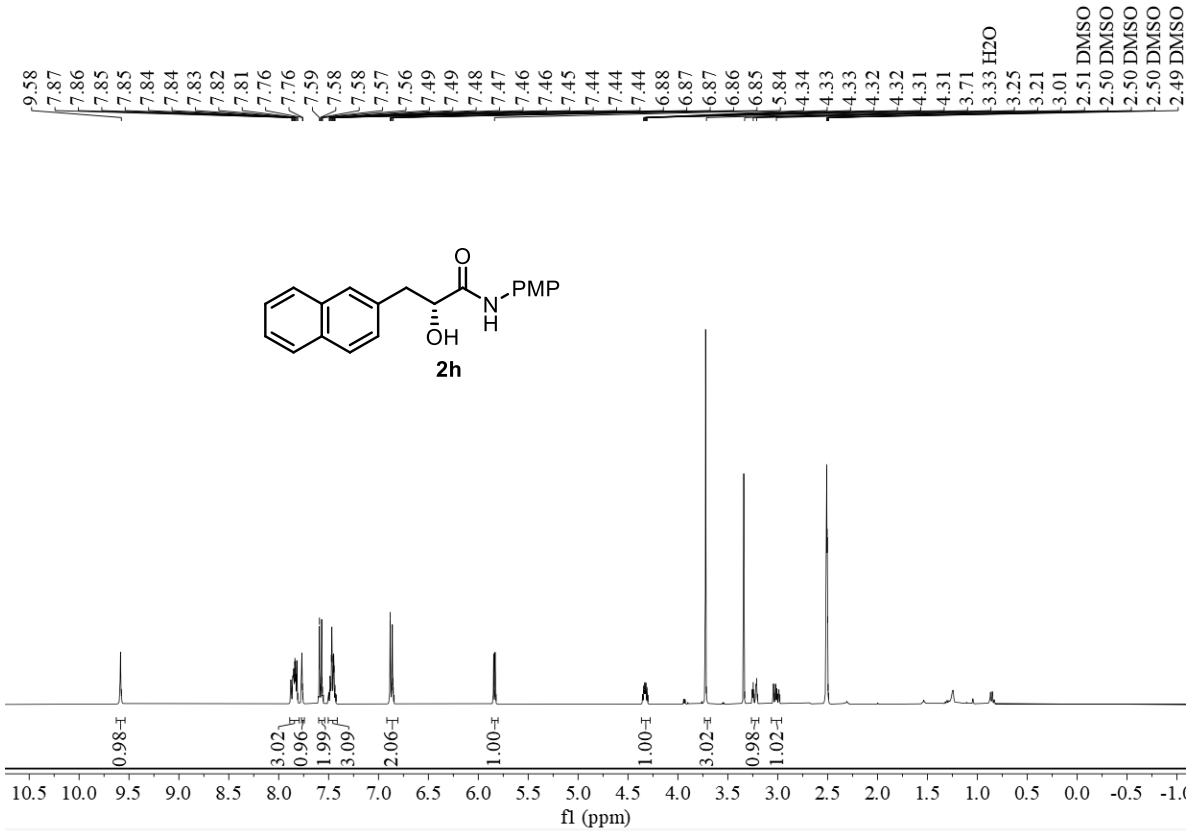
^{13}C NMR of **2f** (101 M, DMSO-d_6)



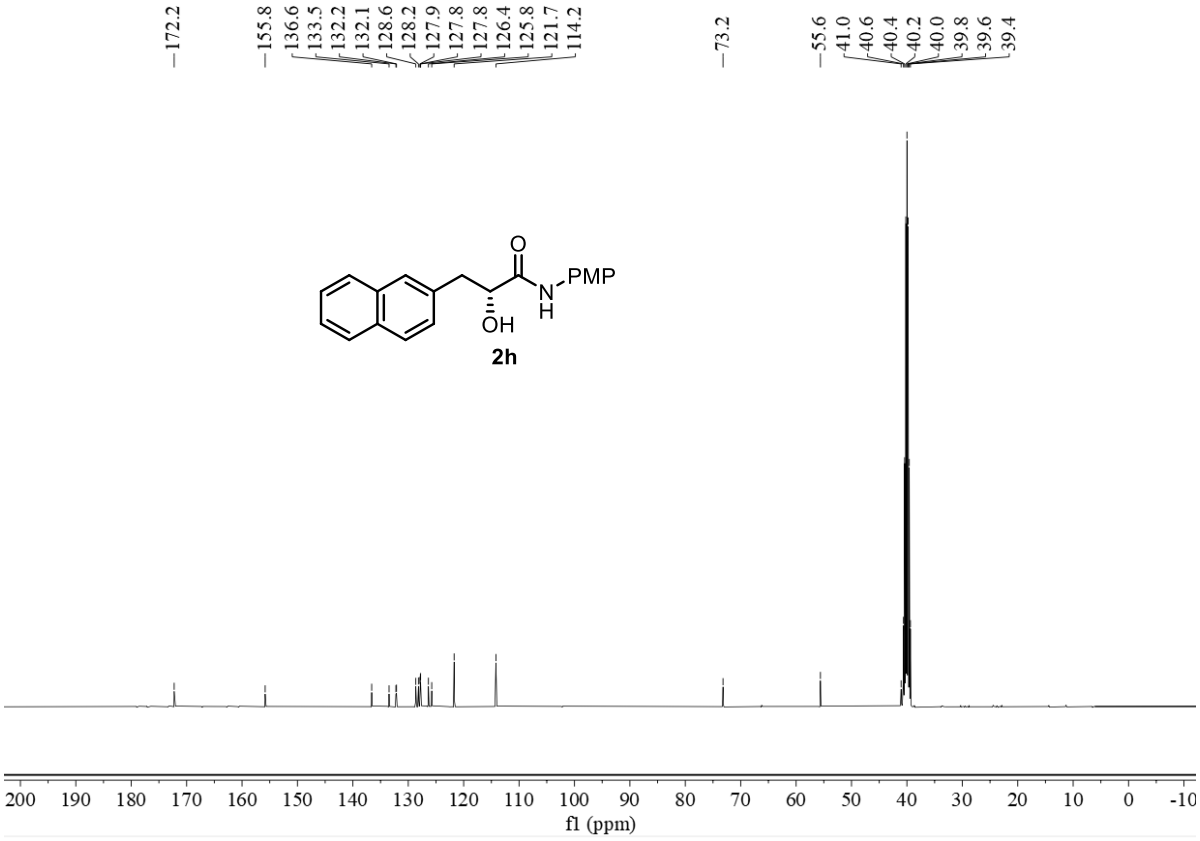
^{1}H NMR of **2g** (400M, $CDCl_3$)



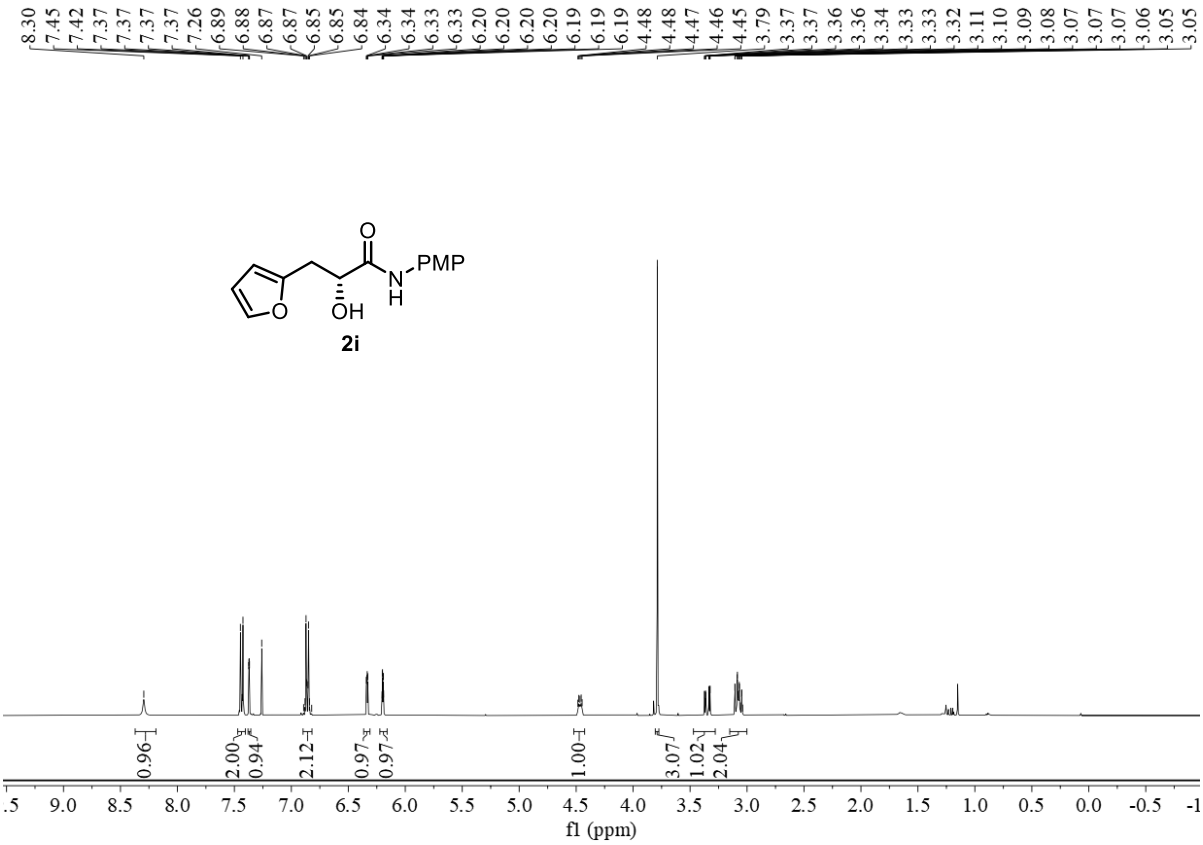
^{13}C NMR of **2g** (101M, $CDCl_3$)



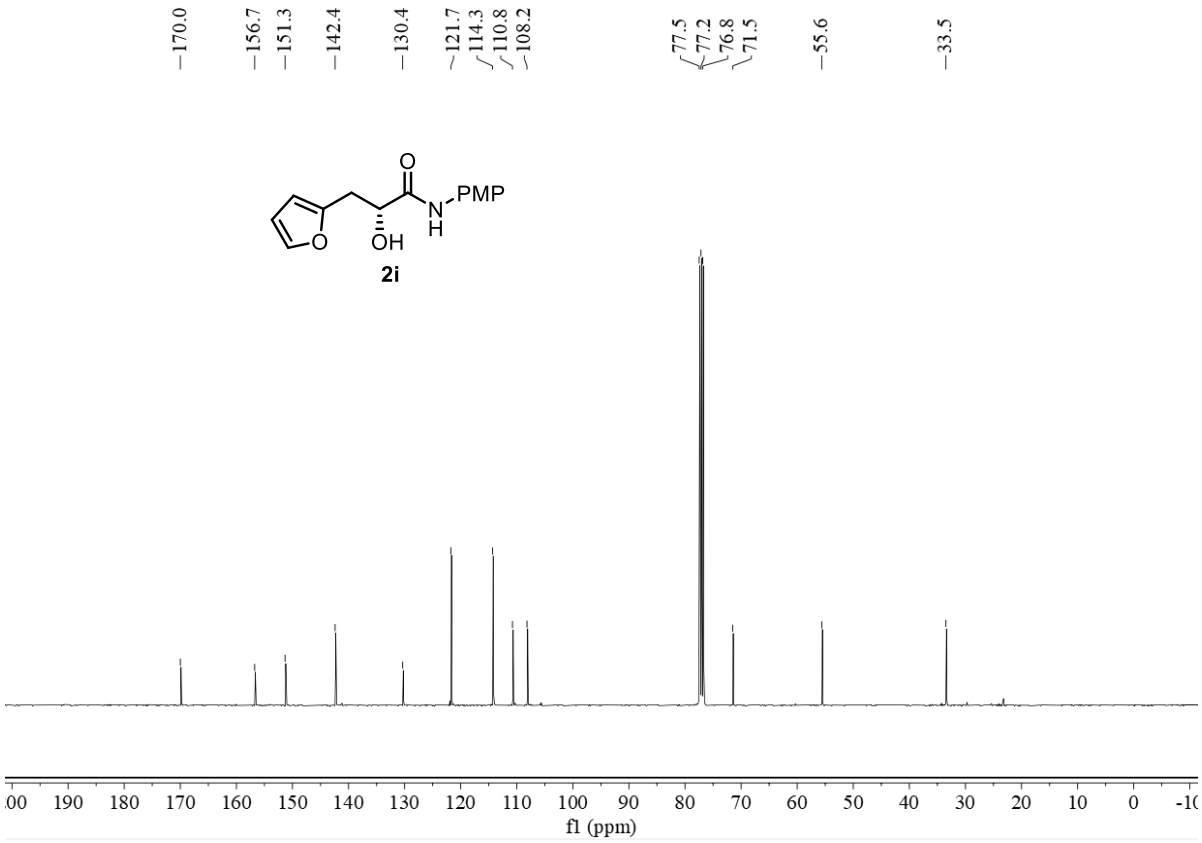
^{1}H NMR of **2h** (400 M, DMSO-d_6)



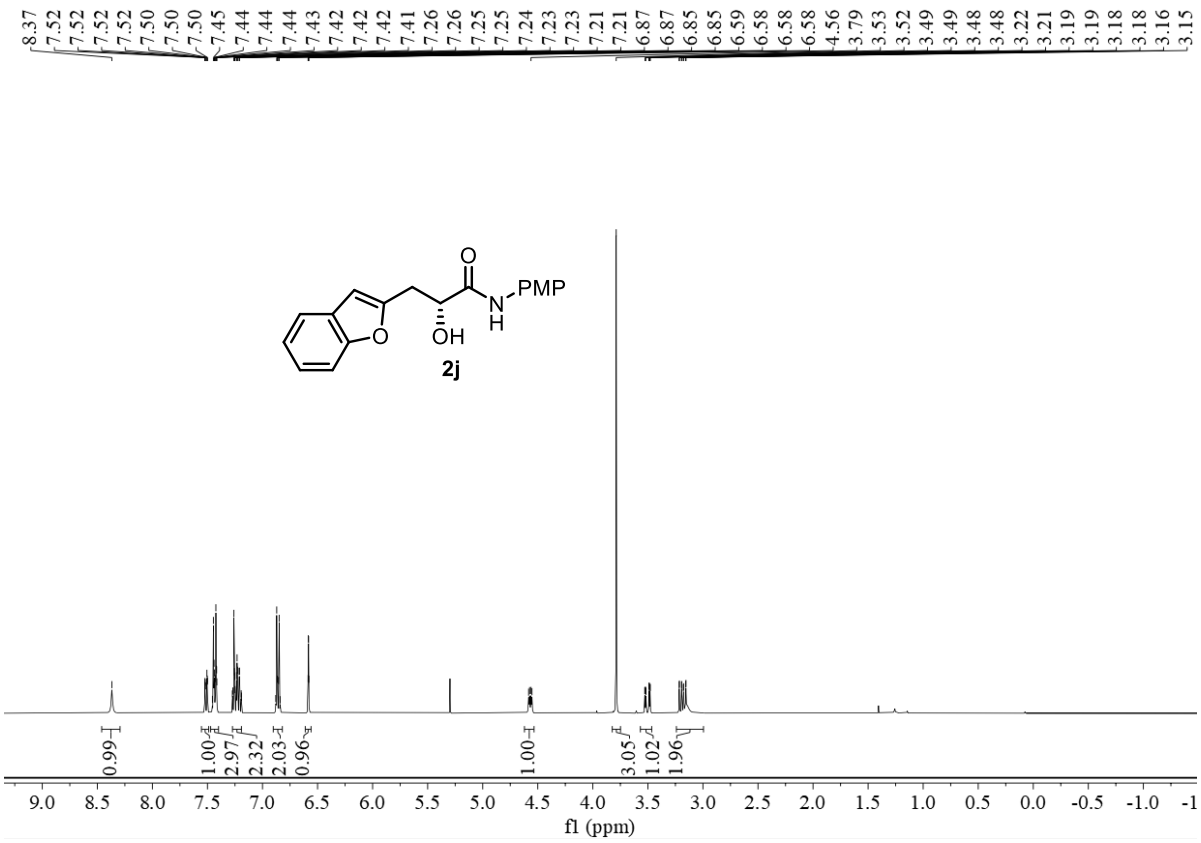
^{13}C NMR of **2h** (101 M, DMSO-d_6)



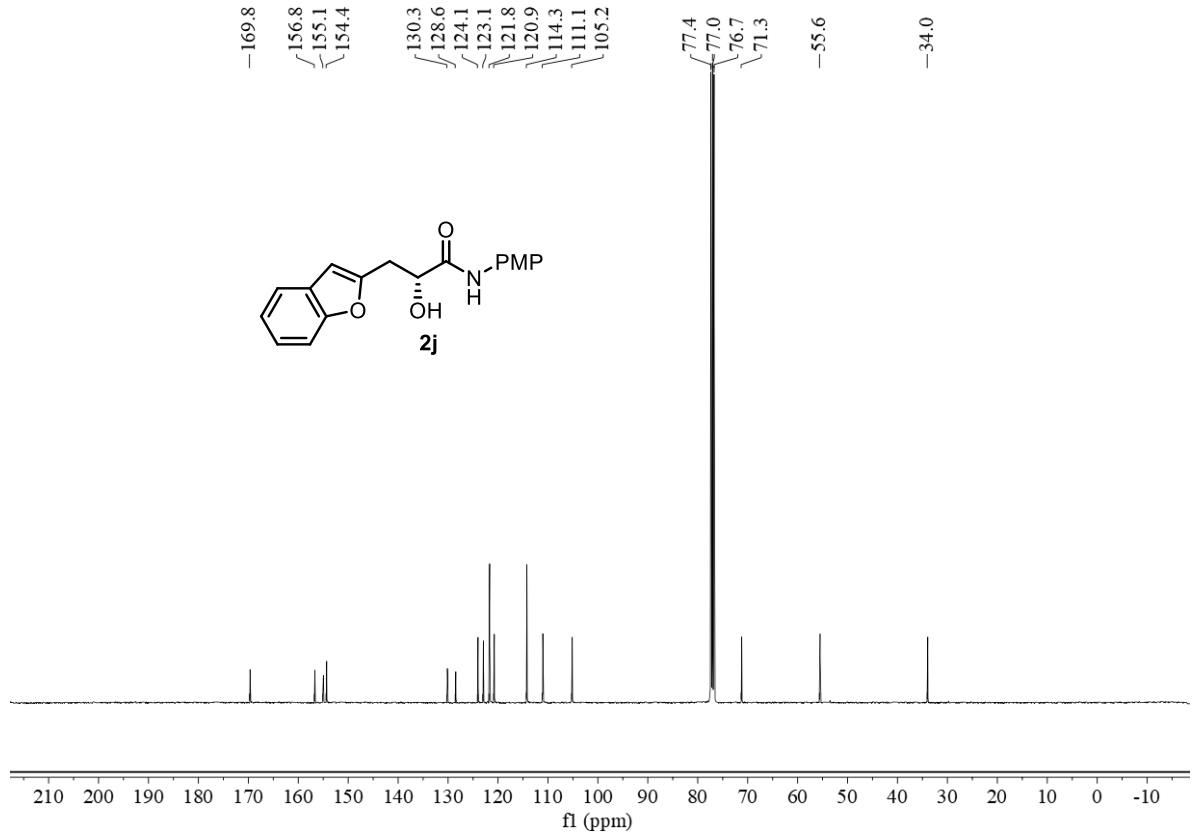
^{1}H NMR of **2i** (400 M, $CDCl_3$)



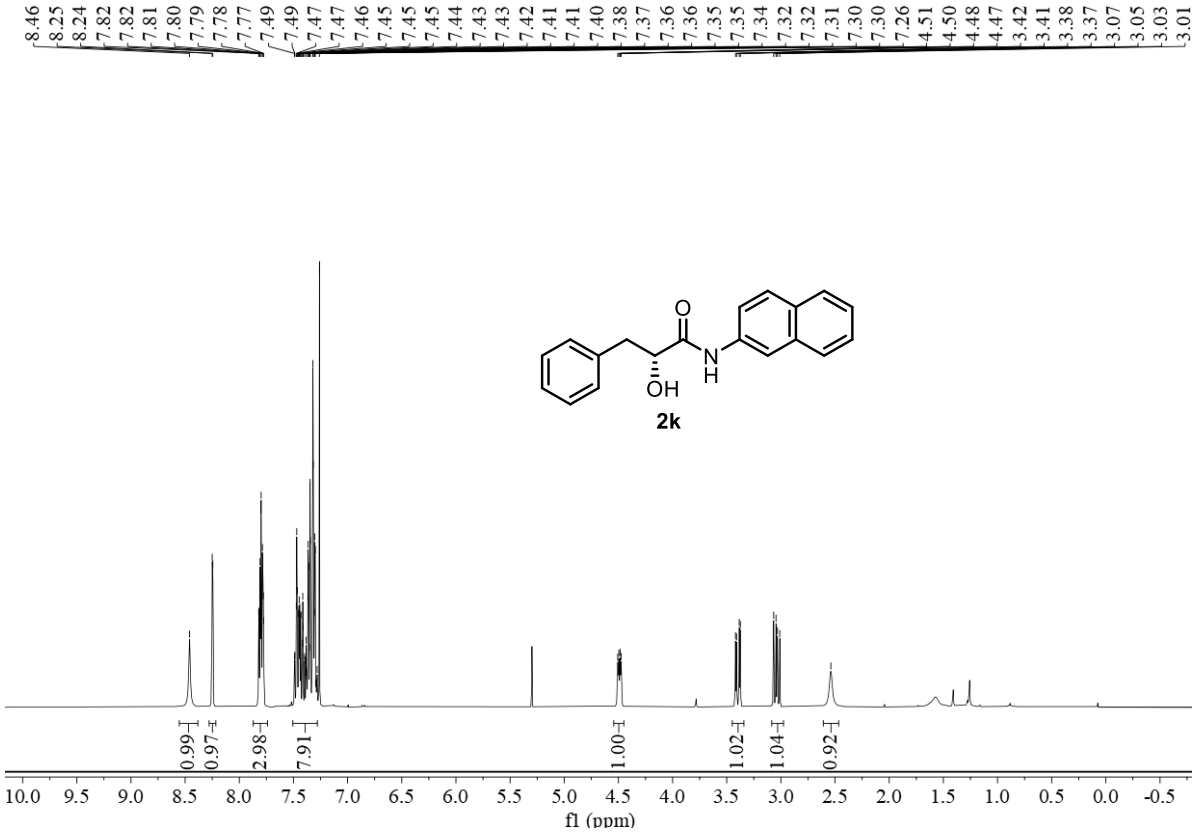
^{13}C NMR of **2i** (101 M, $CDCl_3$)



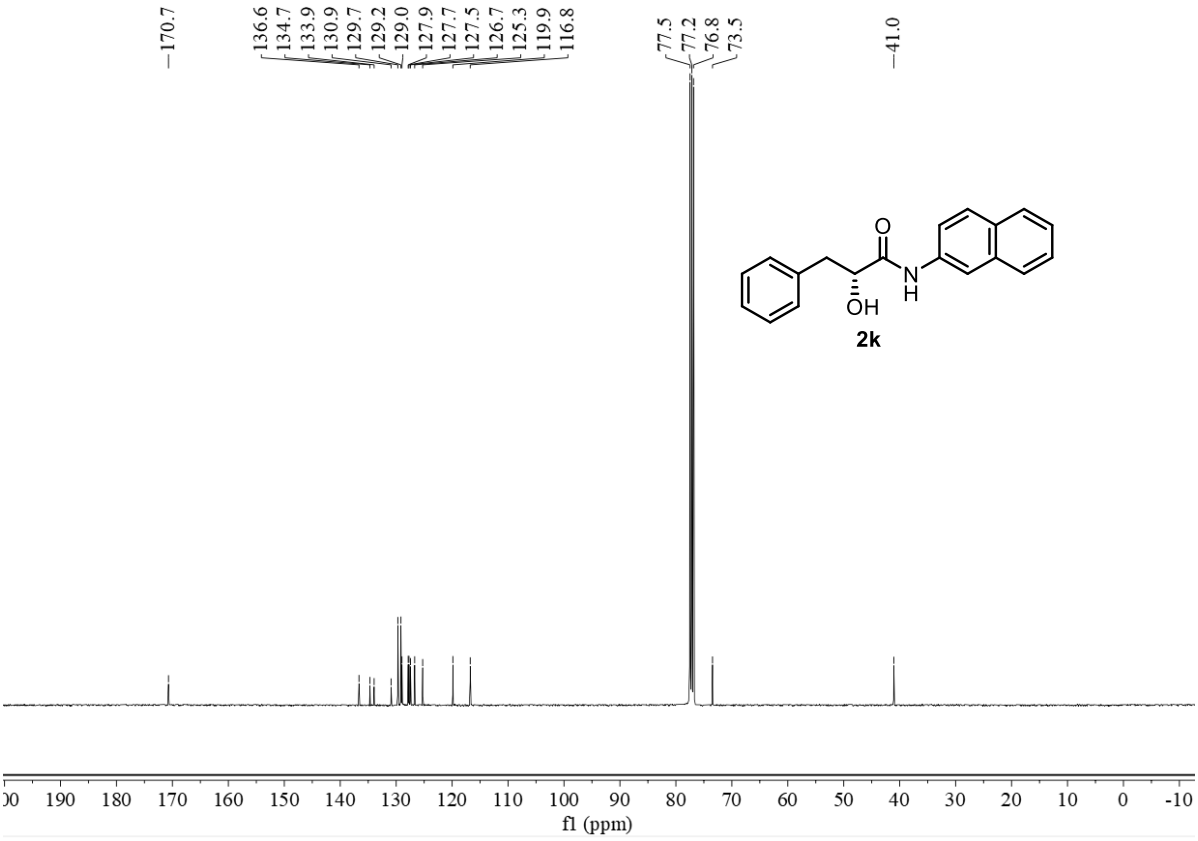
^{1}H NMR of **2j** (400 M, $CDCl_3$)



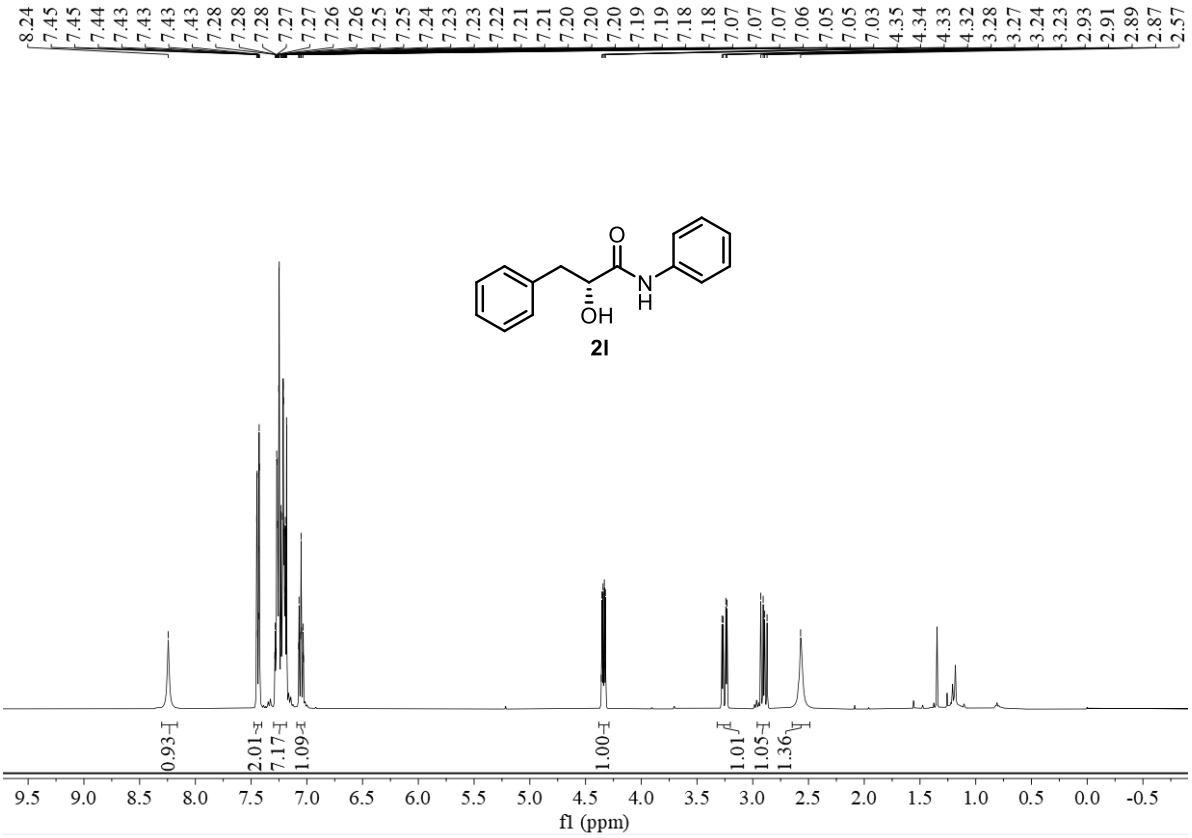
^{13}C NMR of **2j** (101 M, $CDCl_3$)



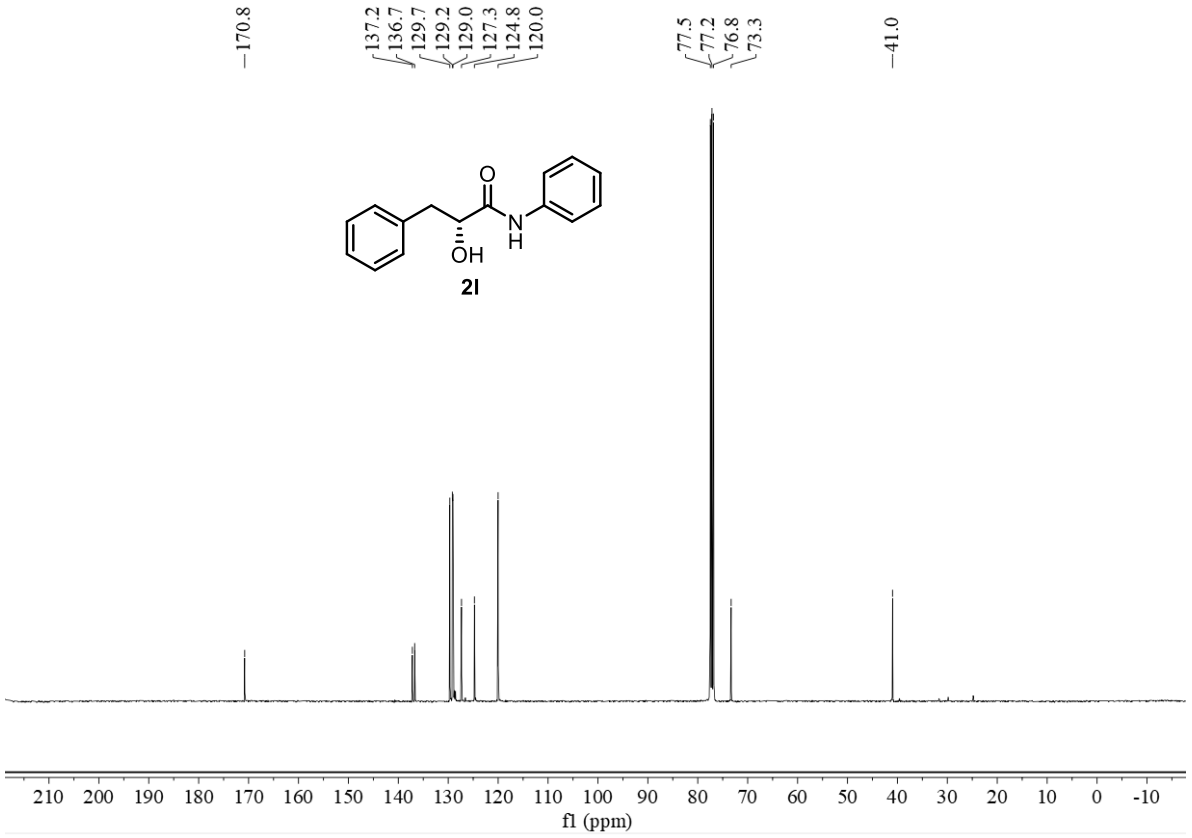
^{1}H NMR of **2k** (400 M, $CDCl_3$)



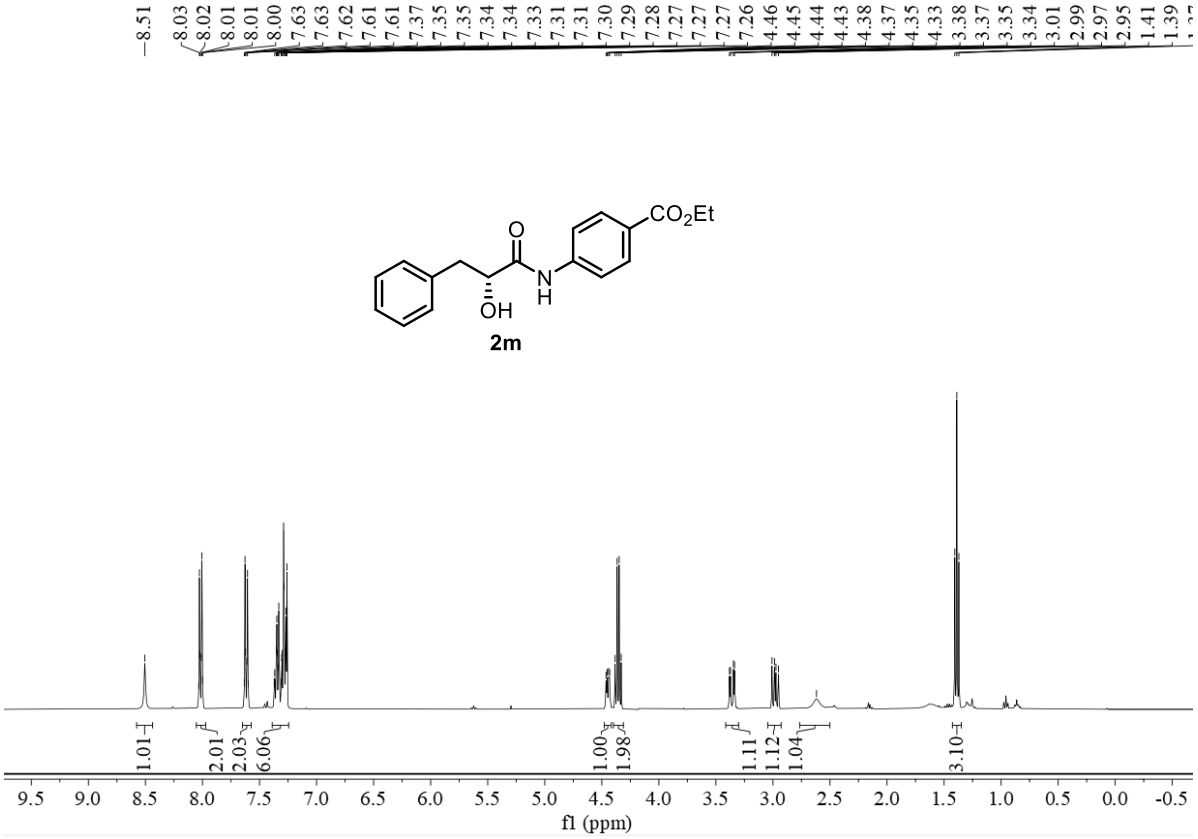
^{13}C NMR of **2k** (101 M, $CDCl_3$)



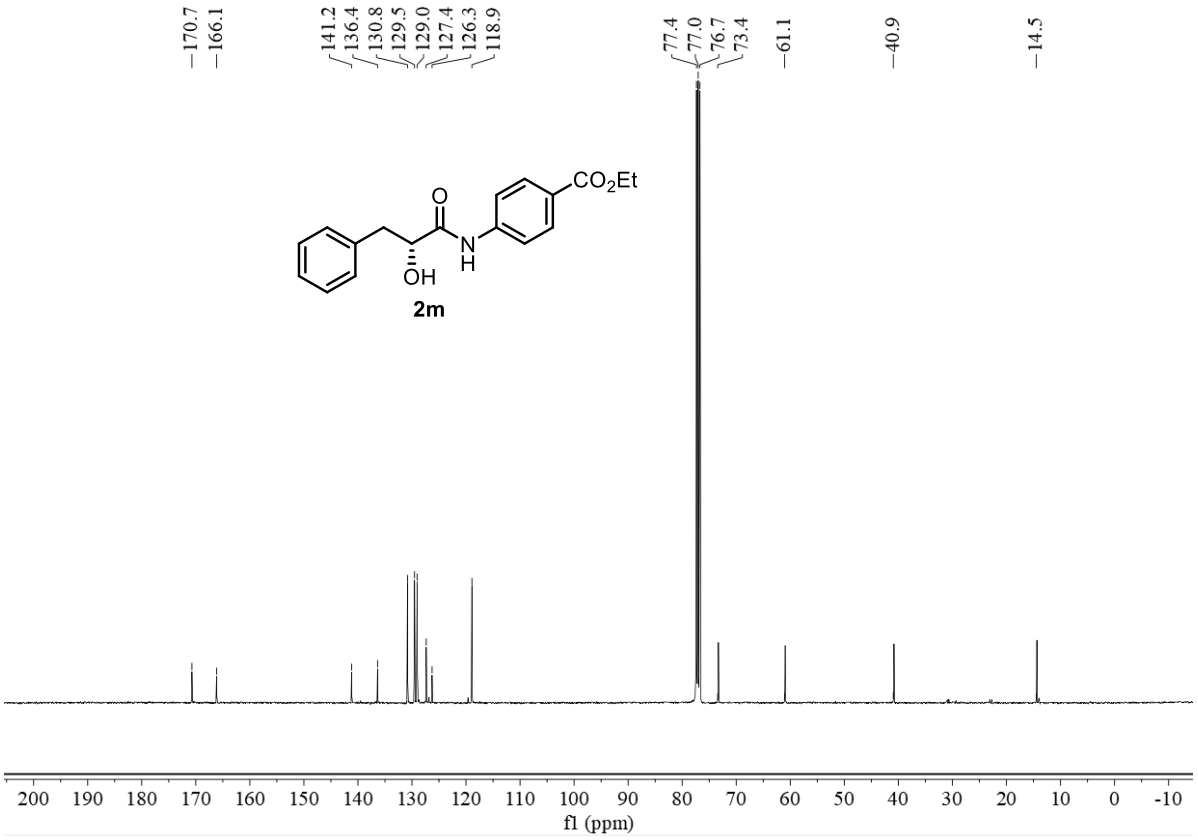
^{1}H NMR of **2l** (400 M, $CDCl_3$)



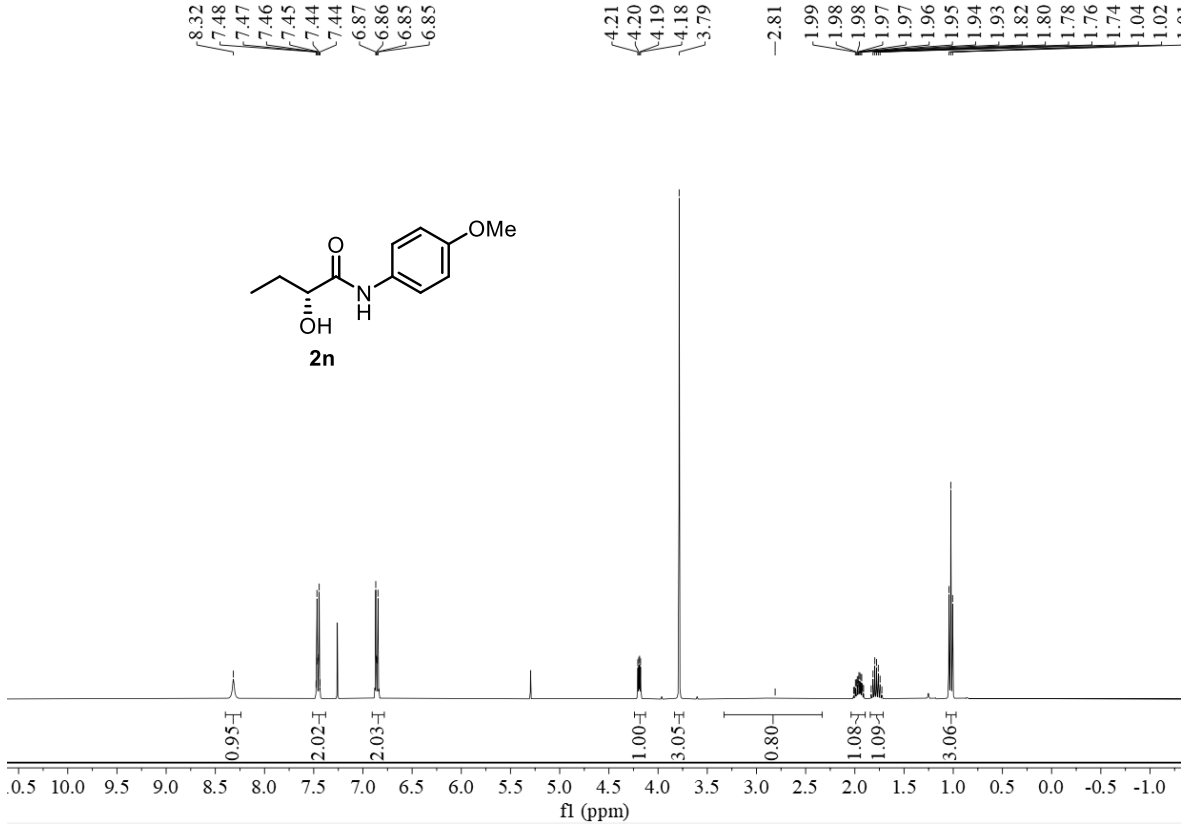
^{13}C NMR of **2l** (101 M, $CDCl_3$)



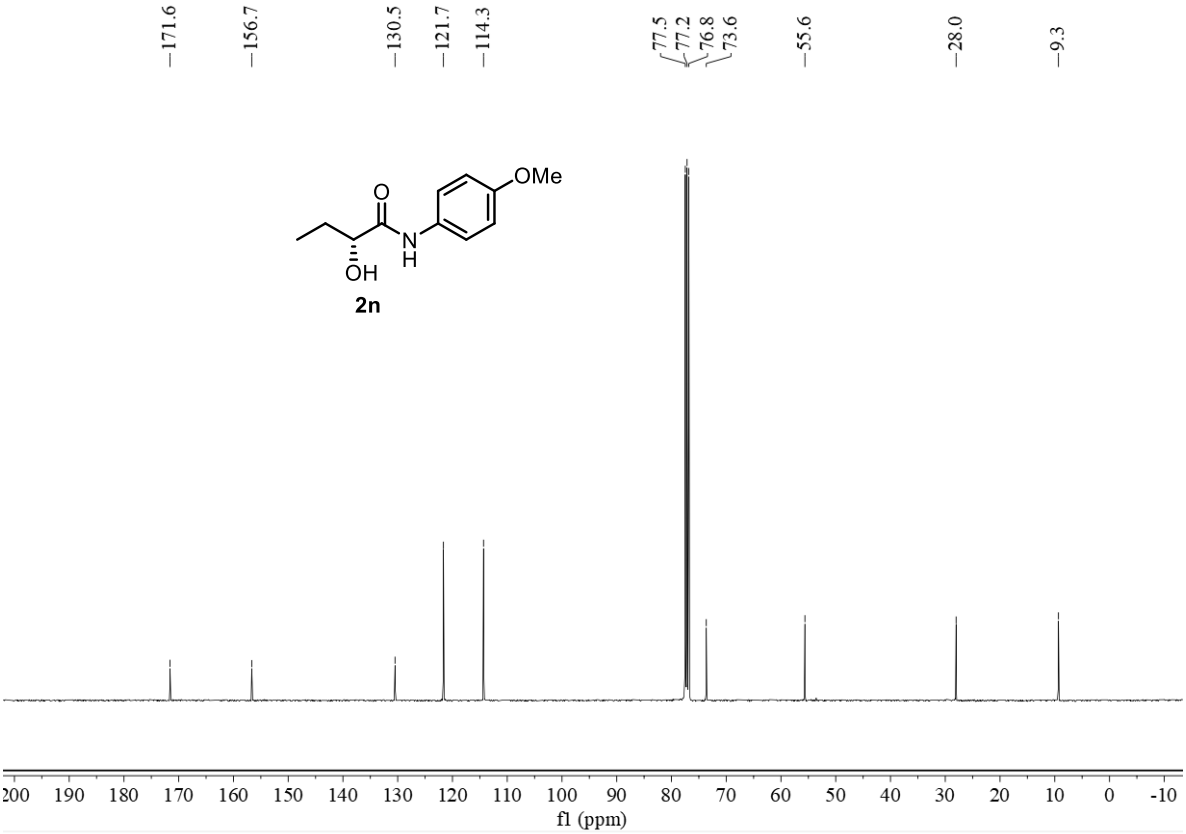
^{1}H NMR of **2m** (400 M, $CDCl_3$)



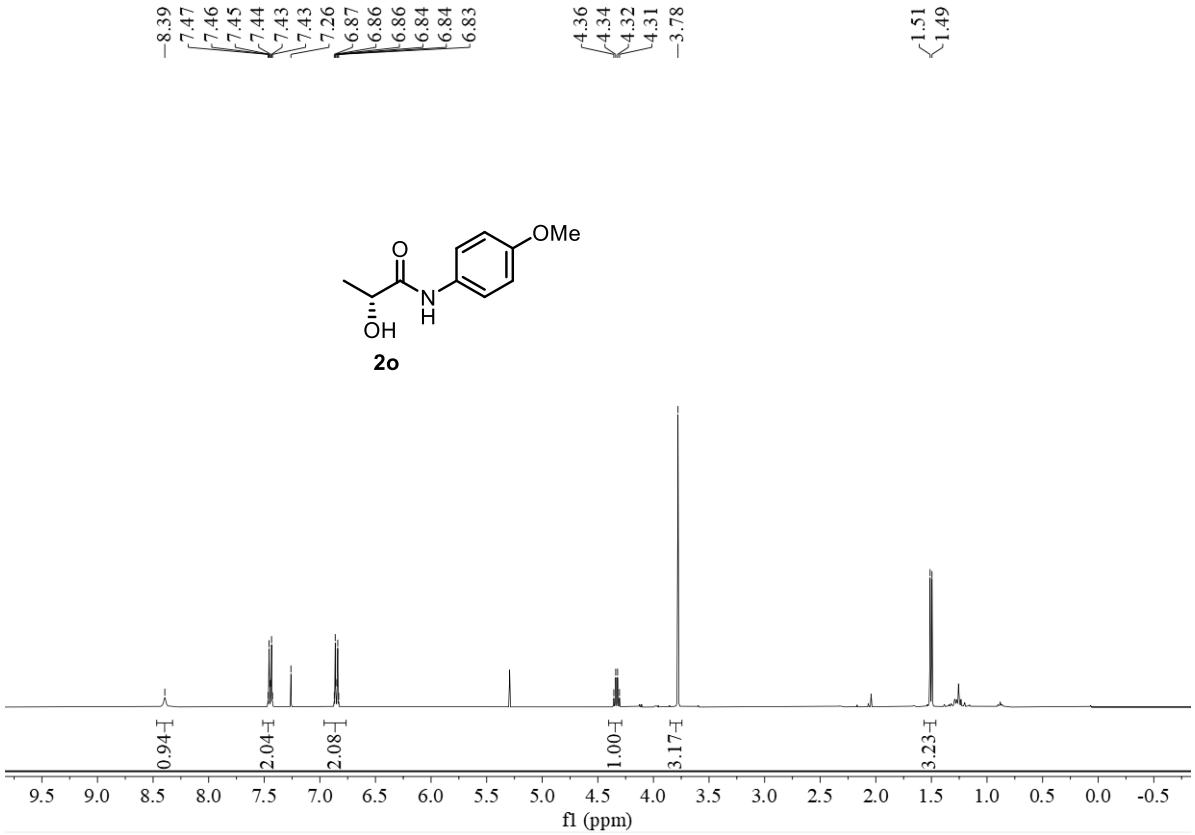
^{13}C NMR of **2m** (101 M, $CDCl_3$)



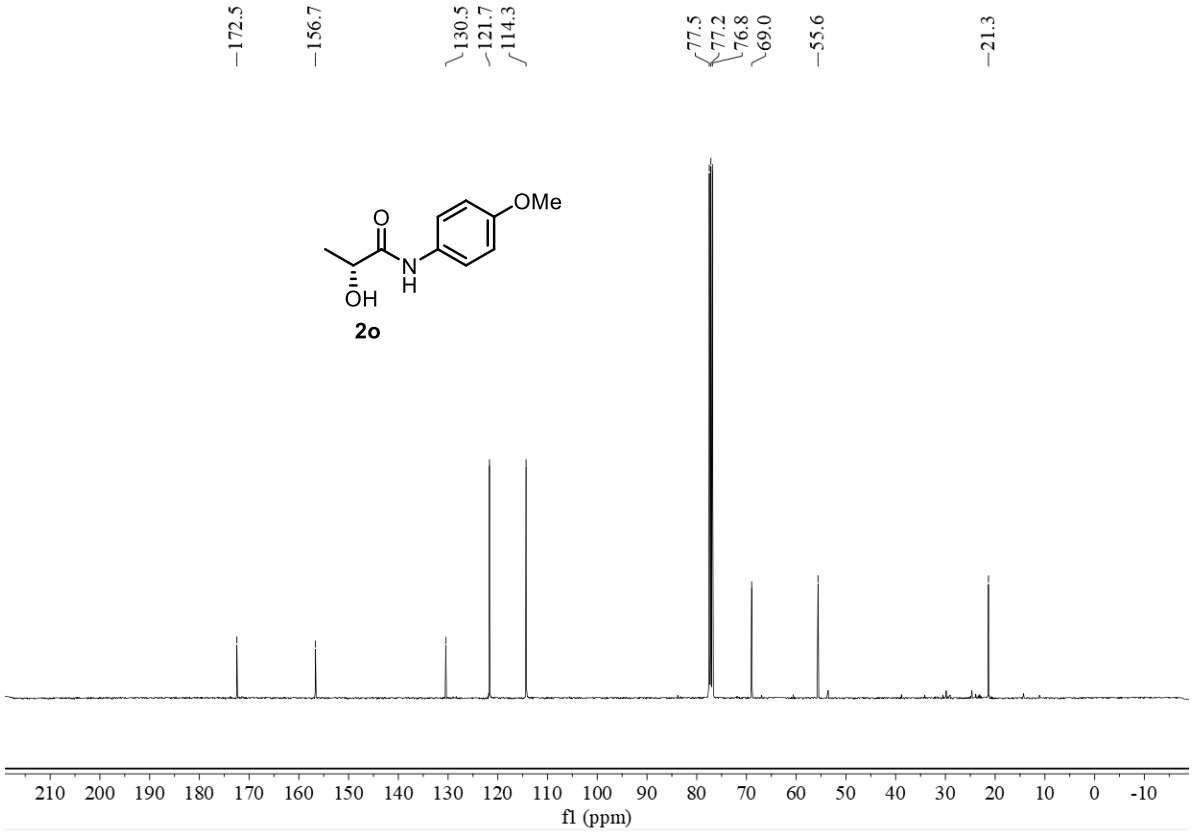
^{1}H NMR of **2n** (400 M, $CDCl_3$)



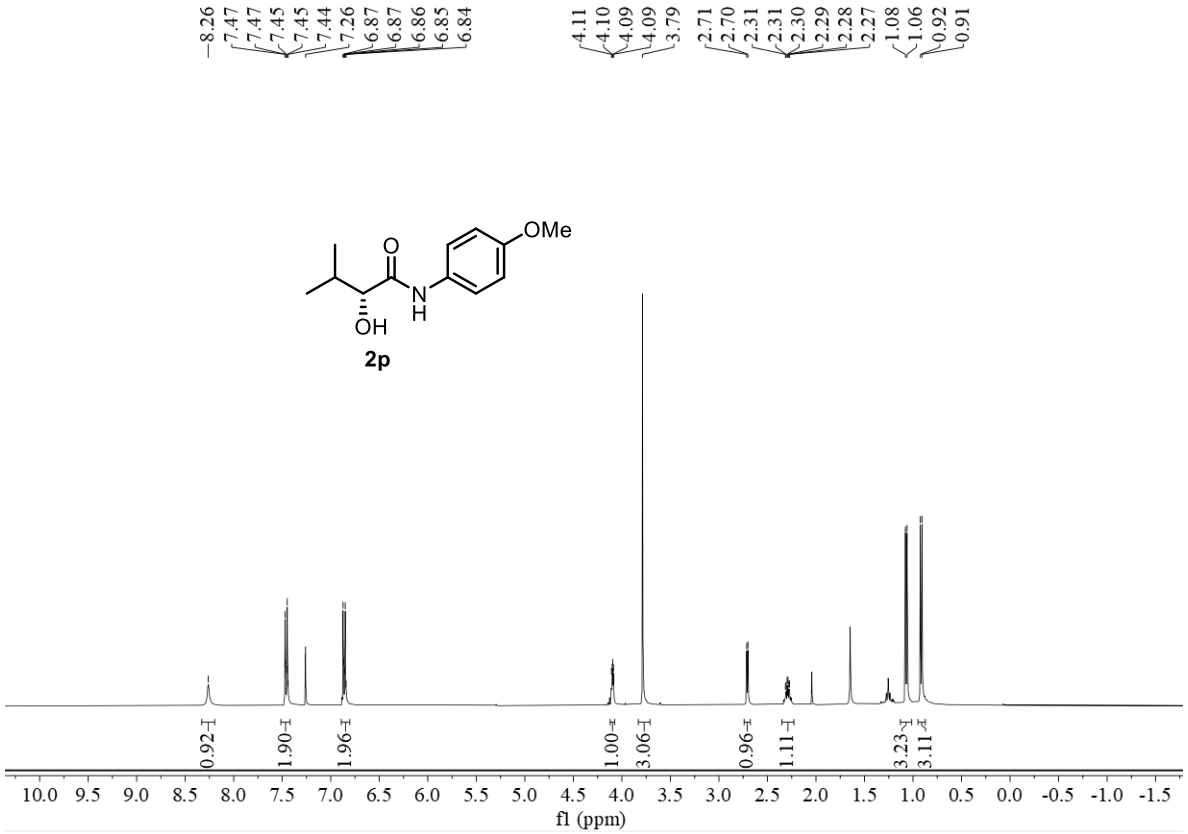
^{13}C NMR of **2n** (101 M, $CDCl_3$)



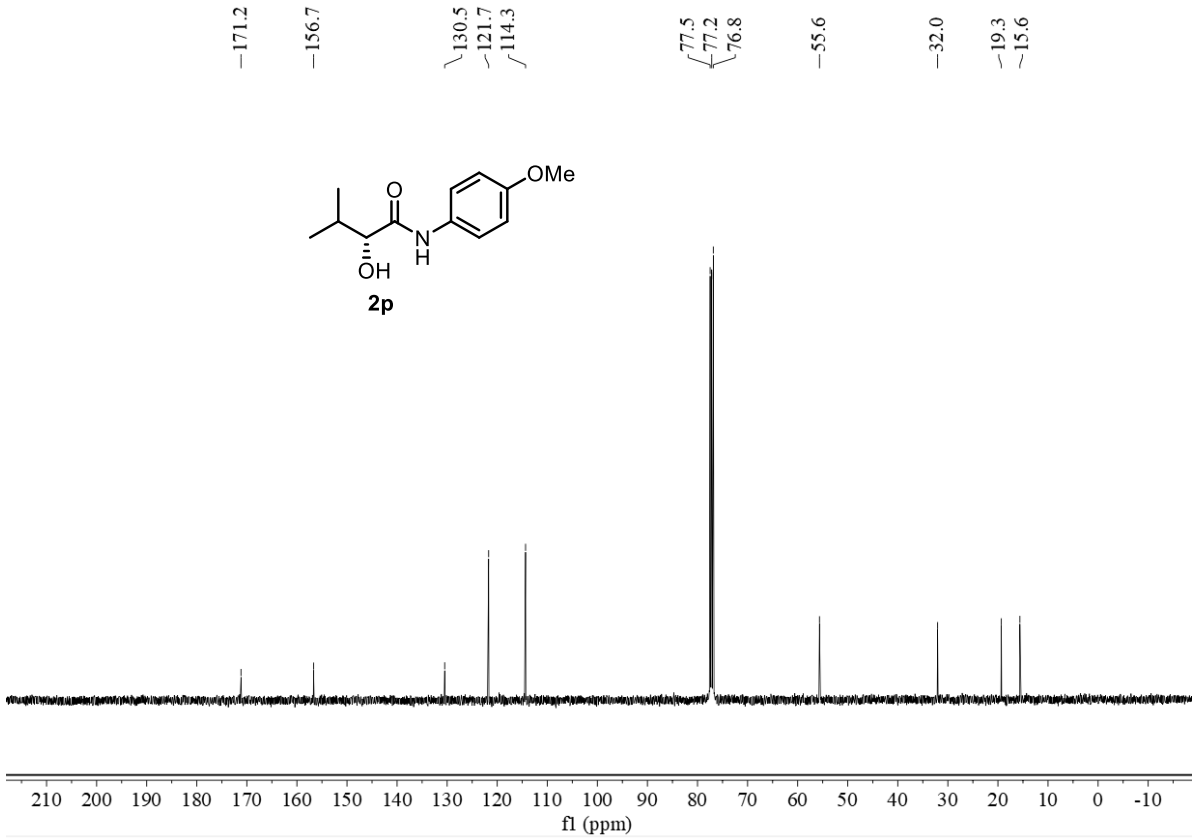
^{1}H NMR of **2o** (400 M, $CDCl_3$)



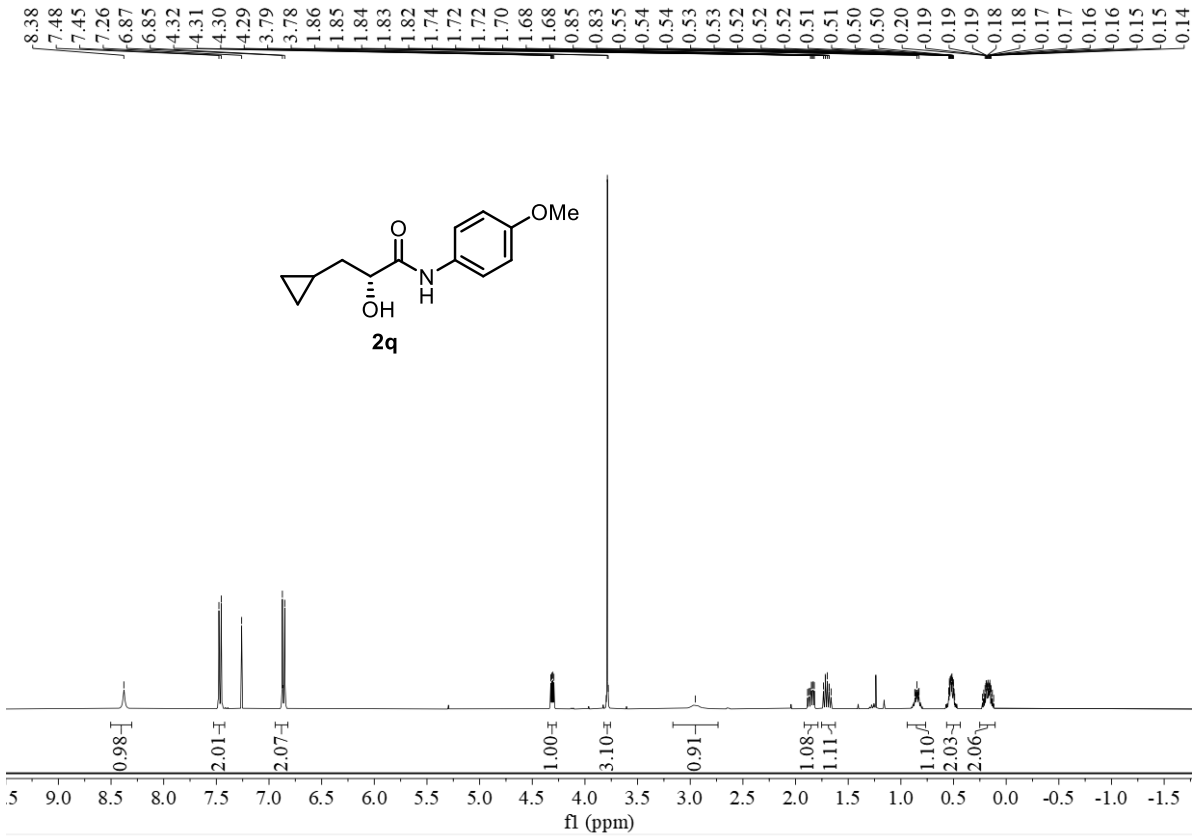
^{13}C NMR of **2o** (101 M, $CDCl_3$)



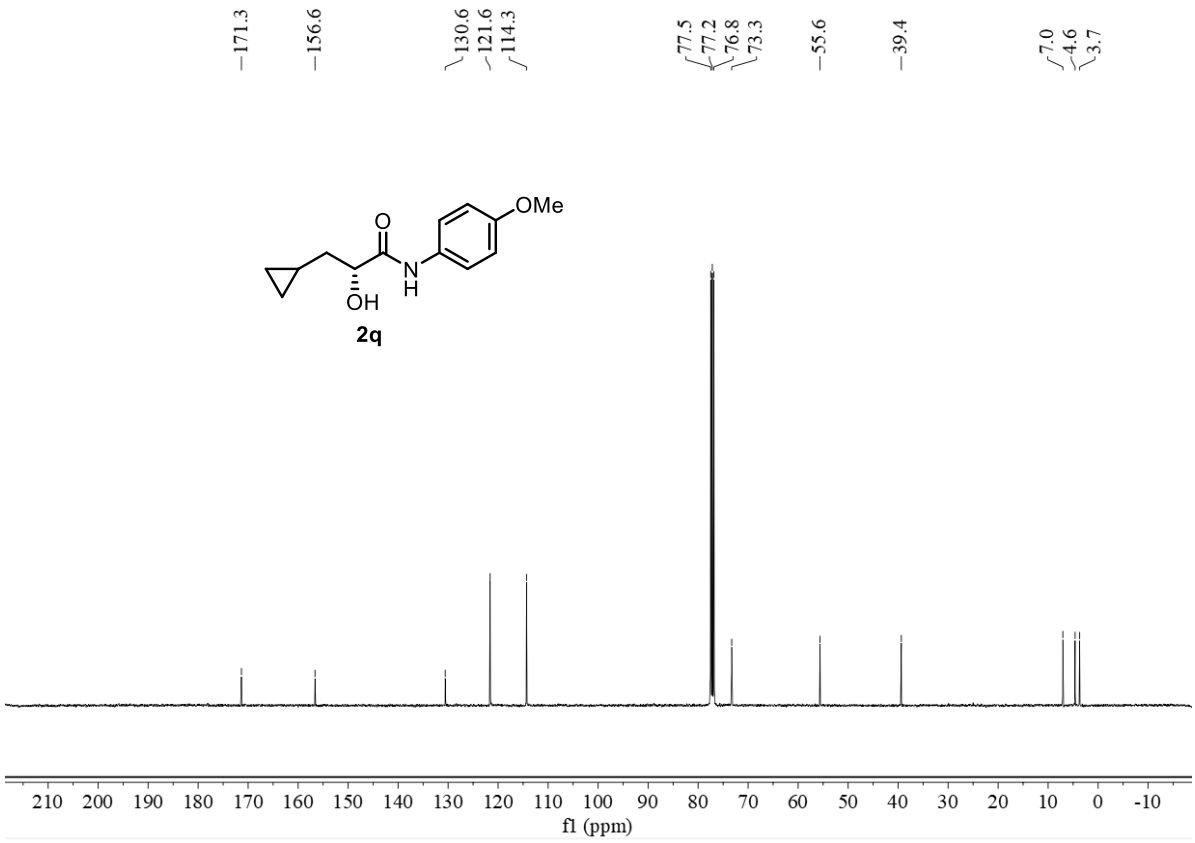
^{1}H NMR of **2p** (400 M, $CDCl_3$)



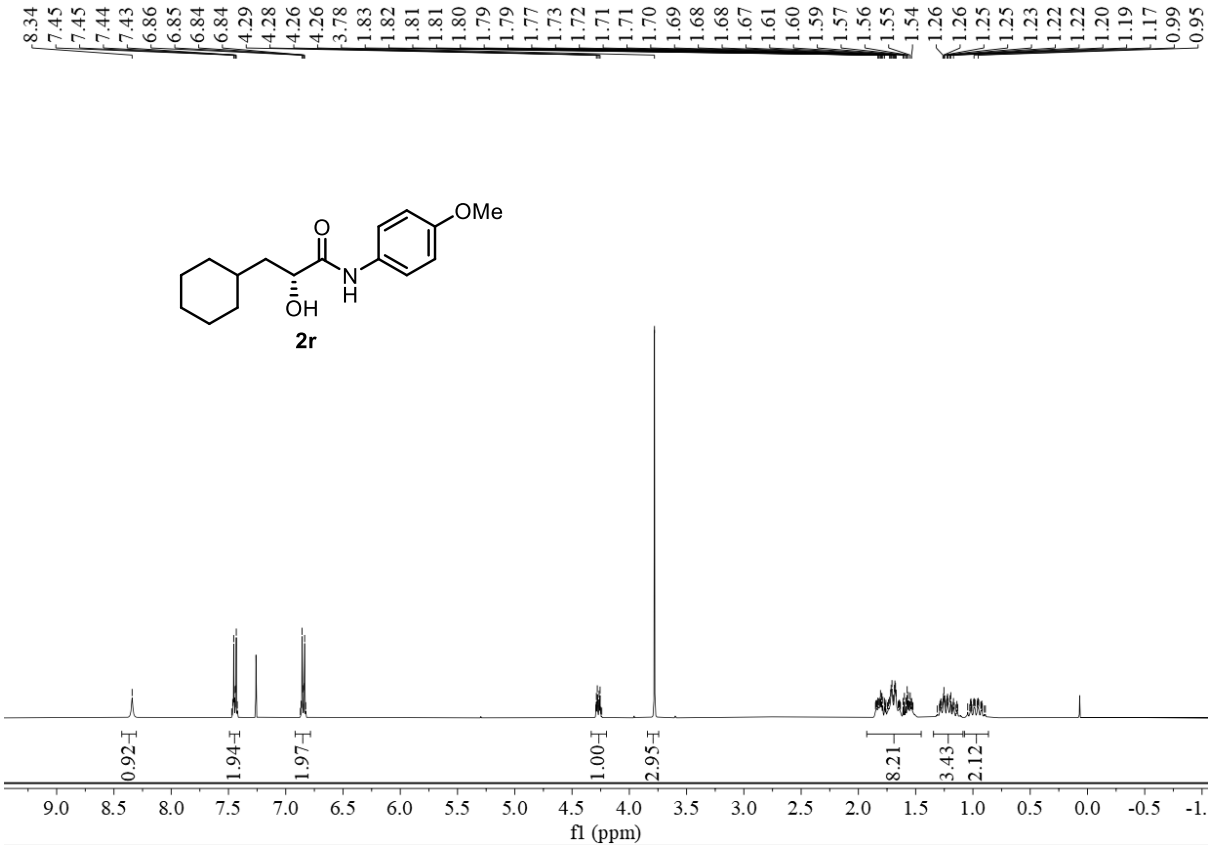
^{13}C NMR of **2p** (101 M, $CDCl_3$)



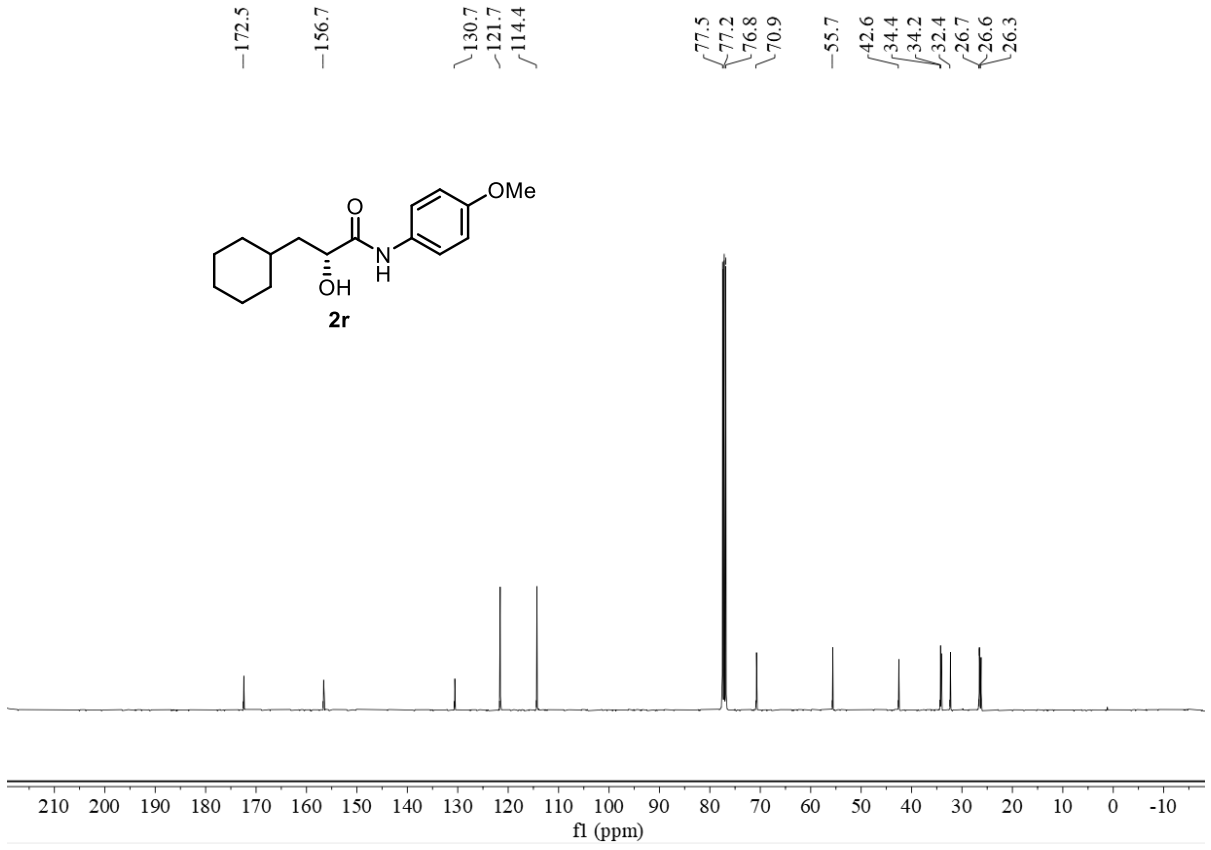
^{1}H NMR of **2q** (400 M, $CDCl_3$)



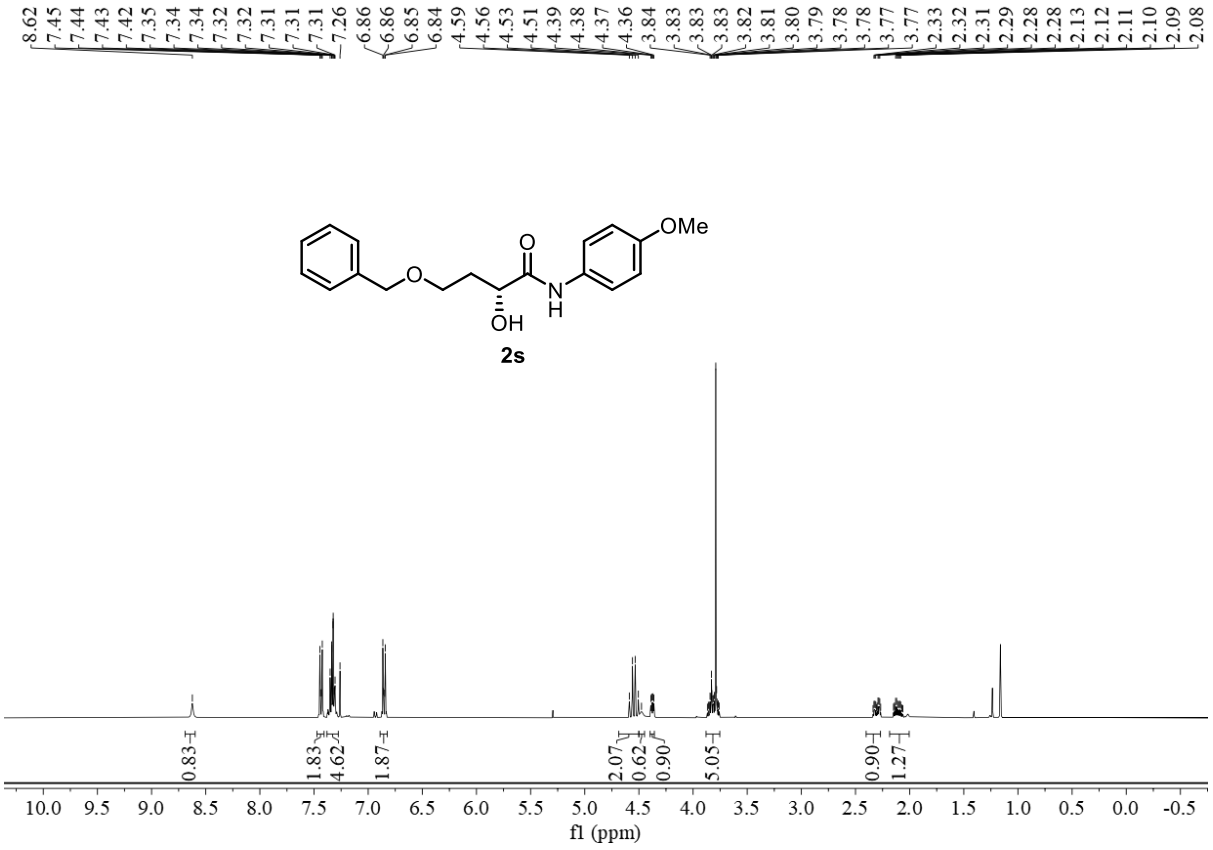
^{13}C NMR of **2q** (101 M, $CDCl_3$)



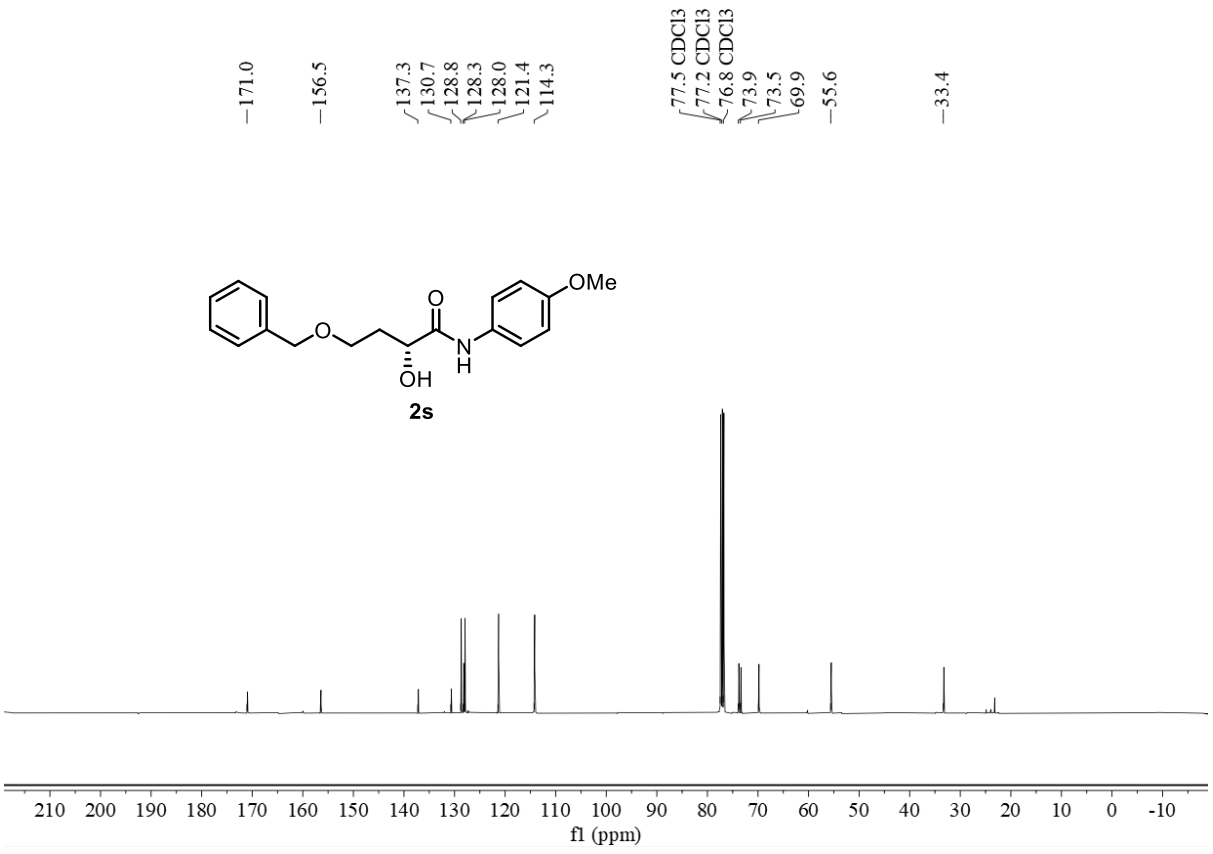
^{1}H NMR of **2r** (400 M, $CDCl_3$)



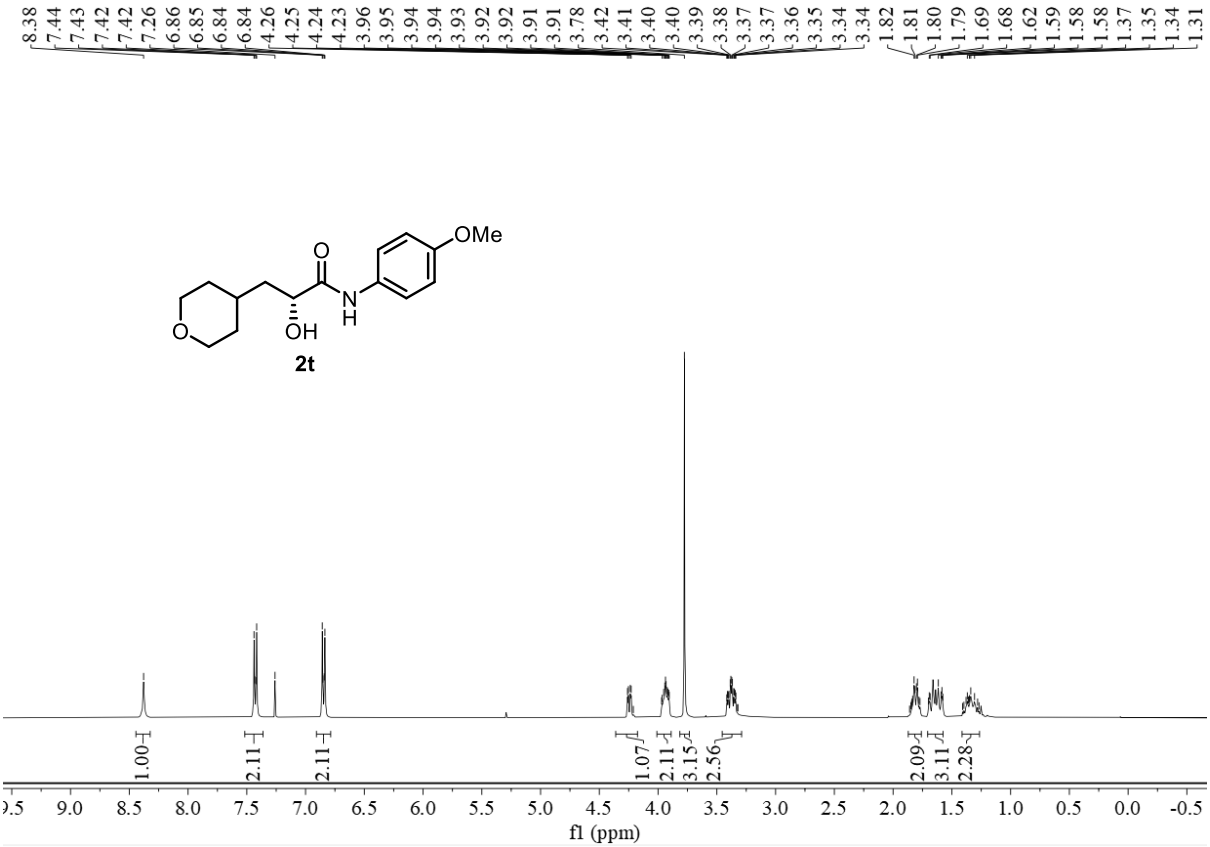
^{13}C NMR of **2r** (101 M, $CDCl_3$)



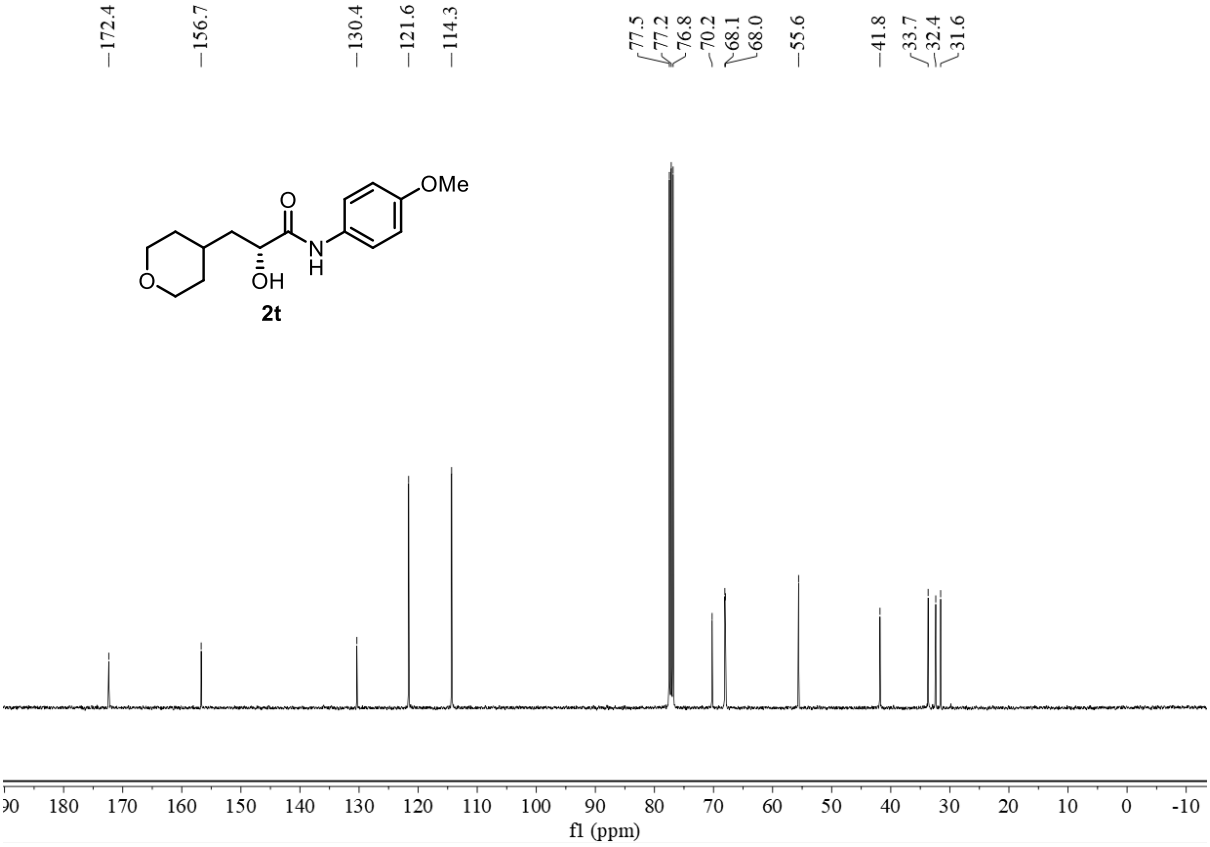
^{1}H NMR of **2s** (400 M, $CDCl_3$)



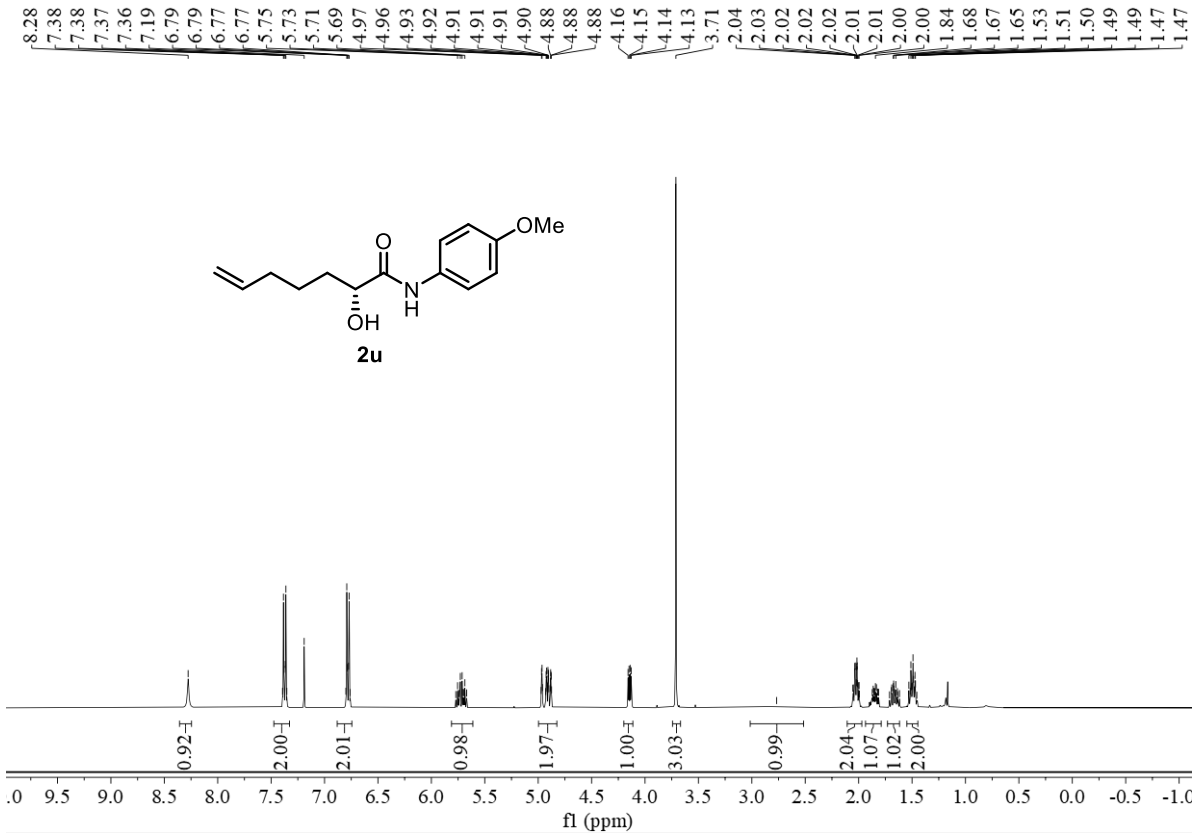
^{13}C NMR of **2s** (101 M, $CDCl_3$)



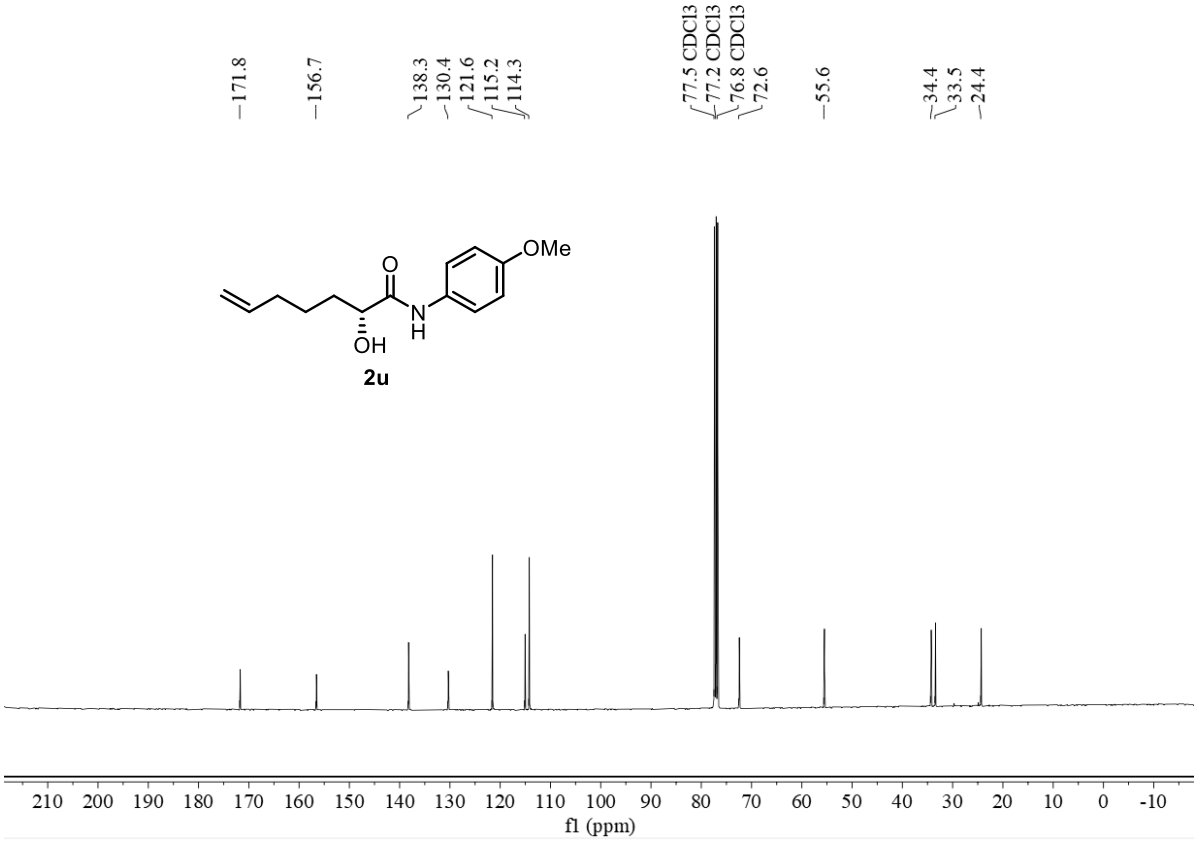
^{1}H NMR of **2t** (400 M, $CDCl_3$)



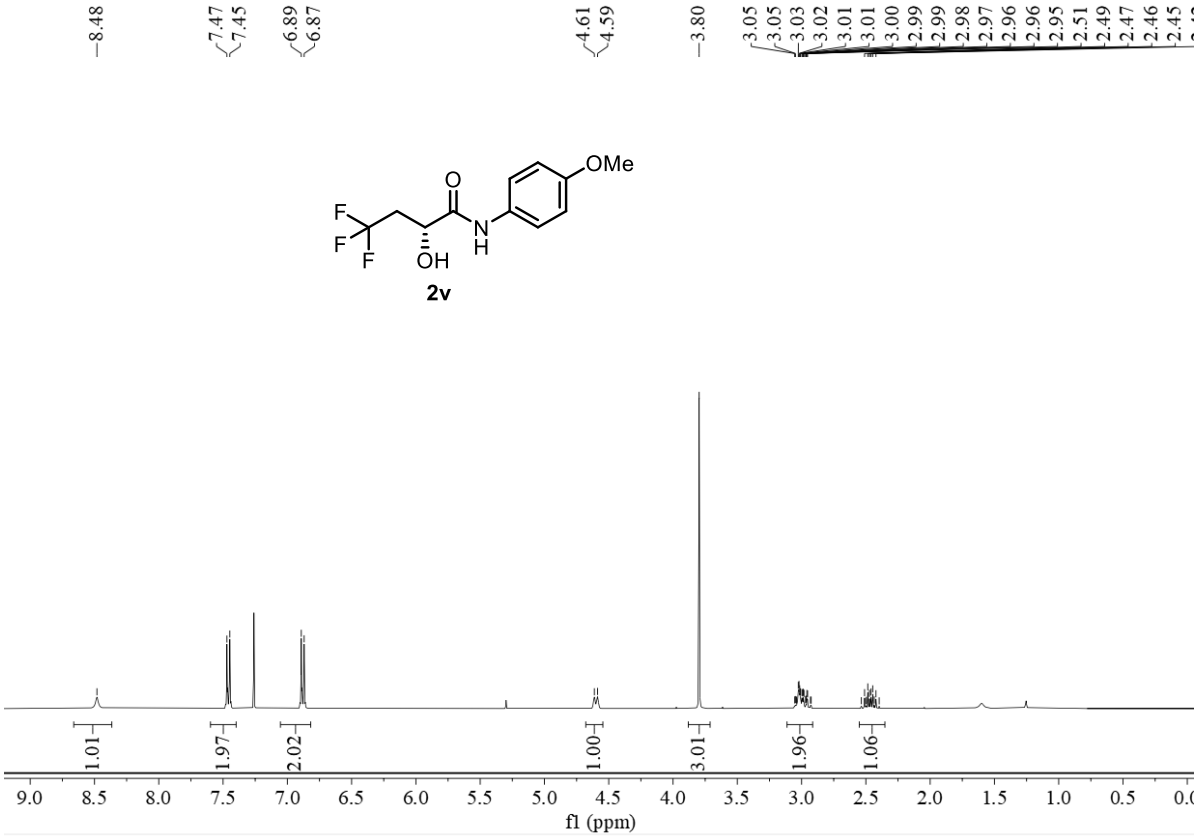
^{13}C NMR of **2t** (101 M, $CDCl_3$)



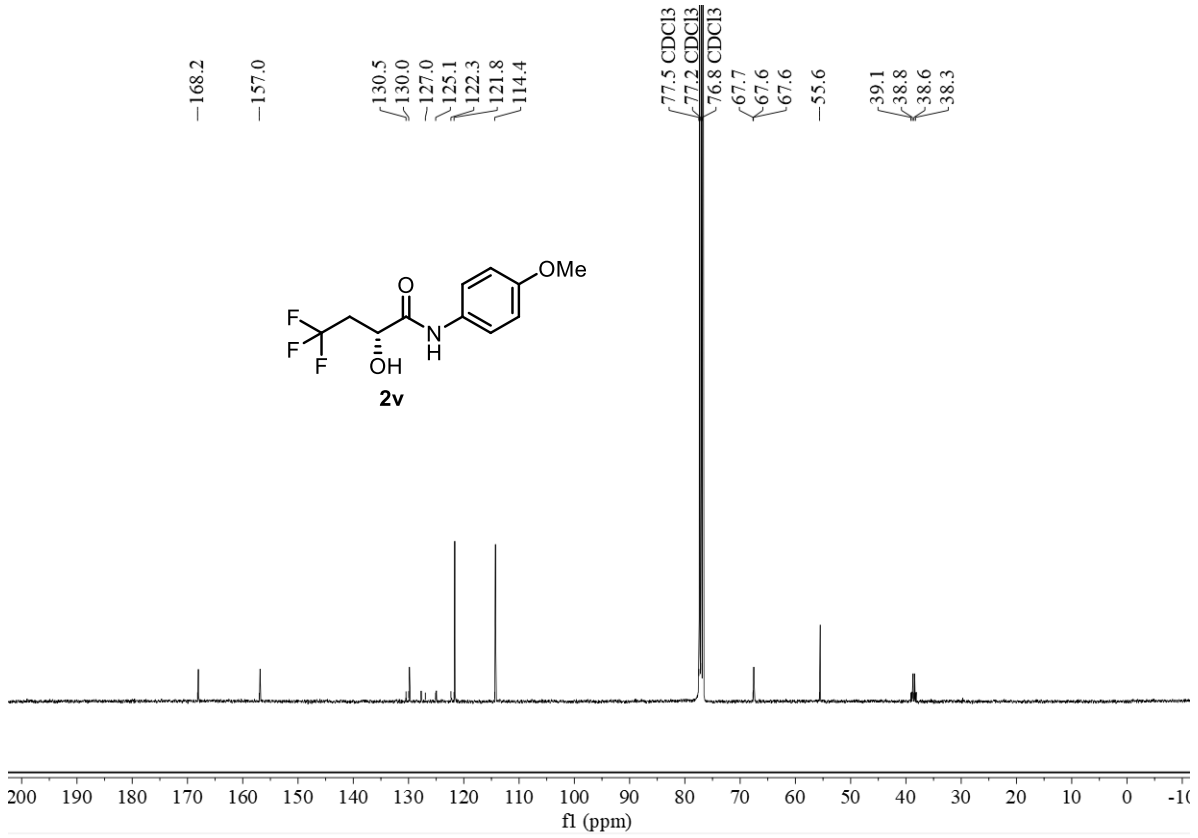
^{1}H NMR of **2u** (400 M, $CDCl_3$)



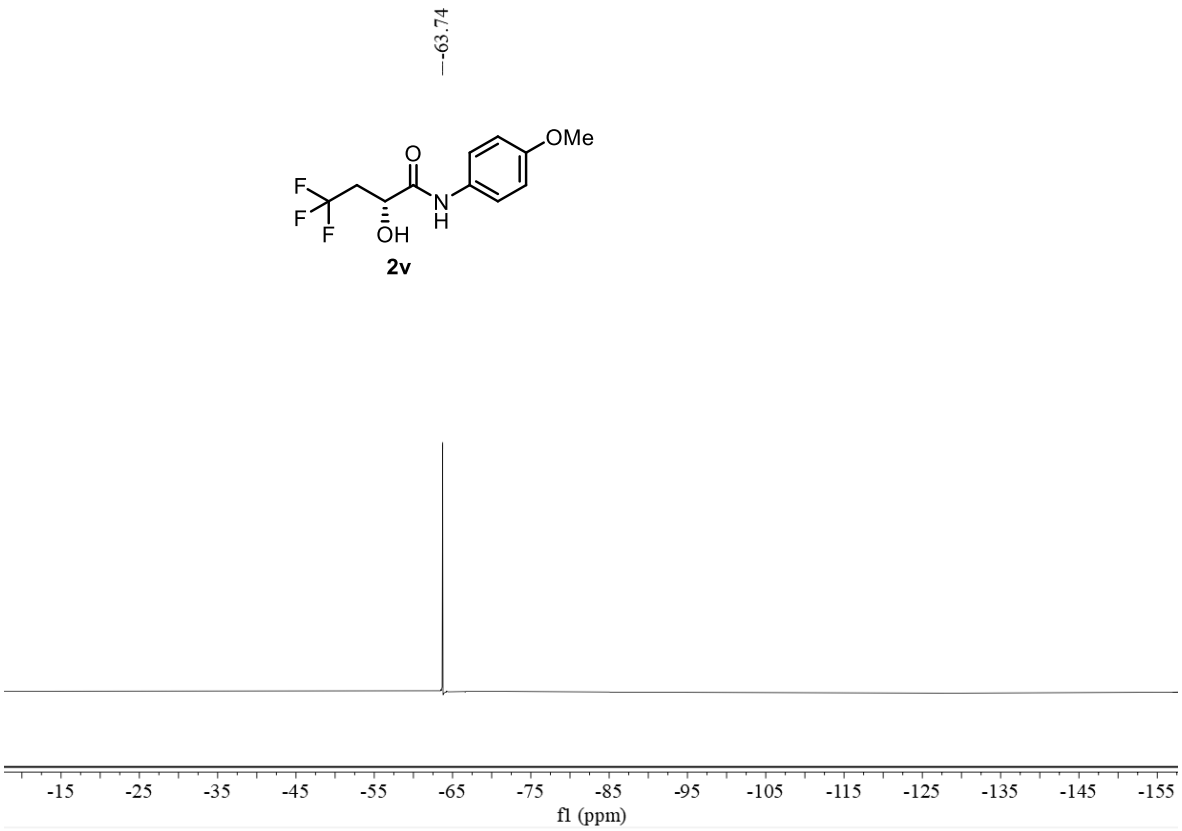
^{13}C NMR of **2u** (101 M, $CDCl_3$)



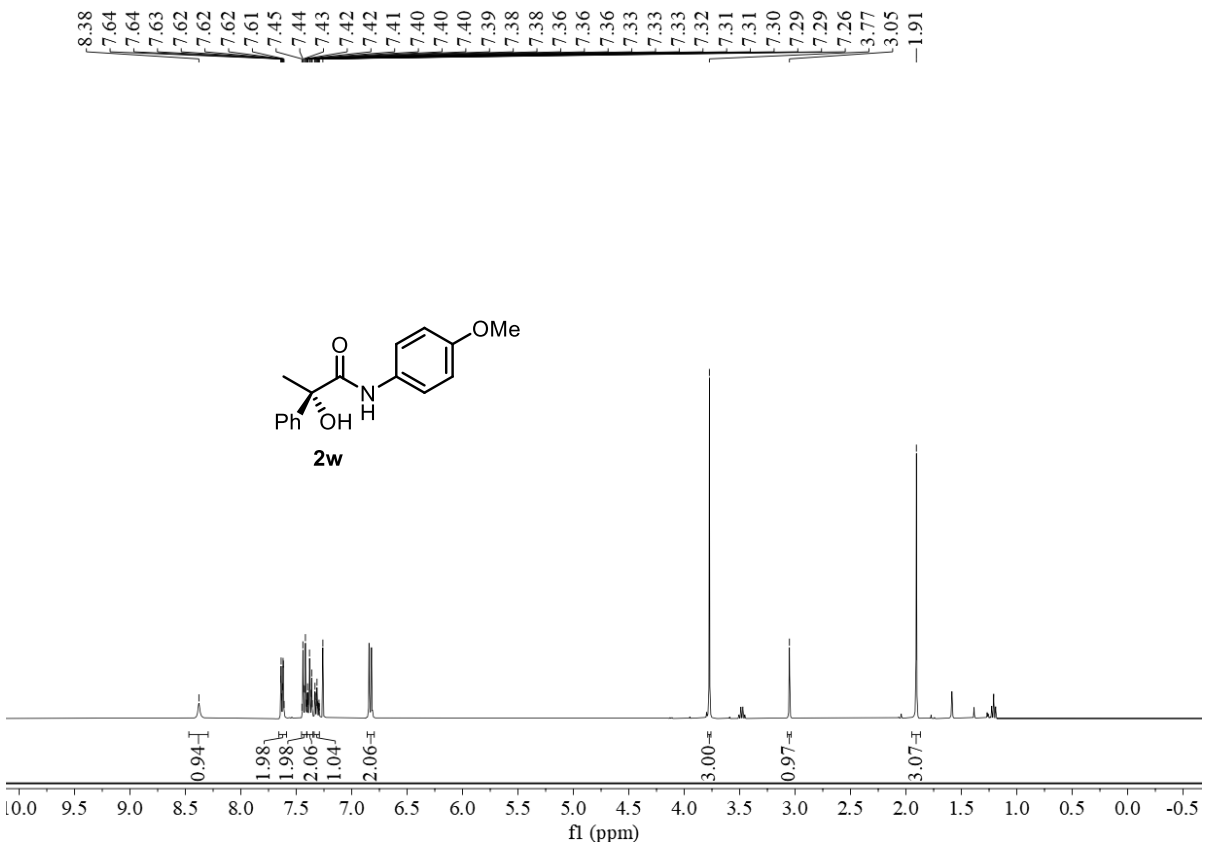
^{1}H NMR of **2v** (400 M, $CDCl_3$)



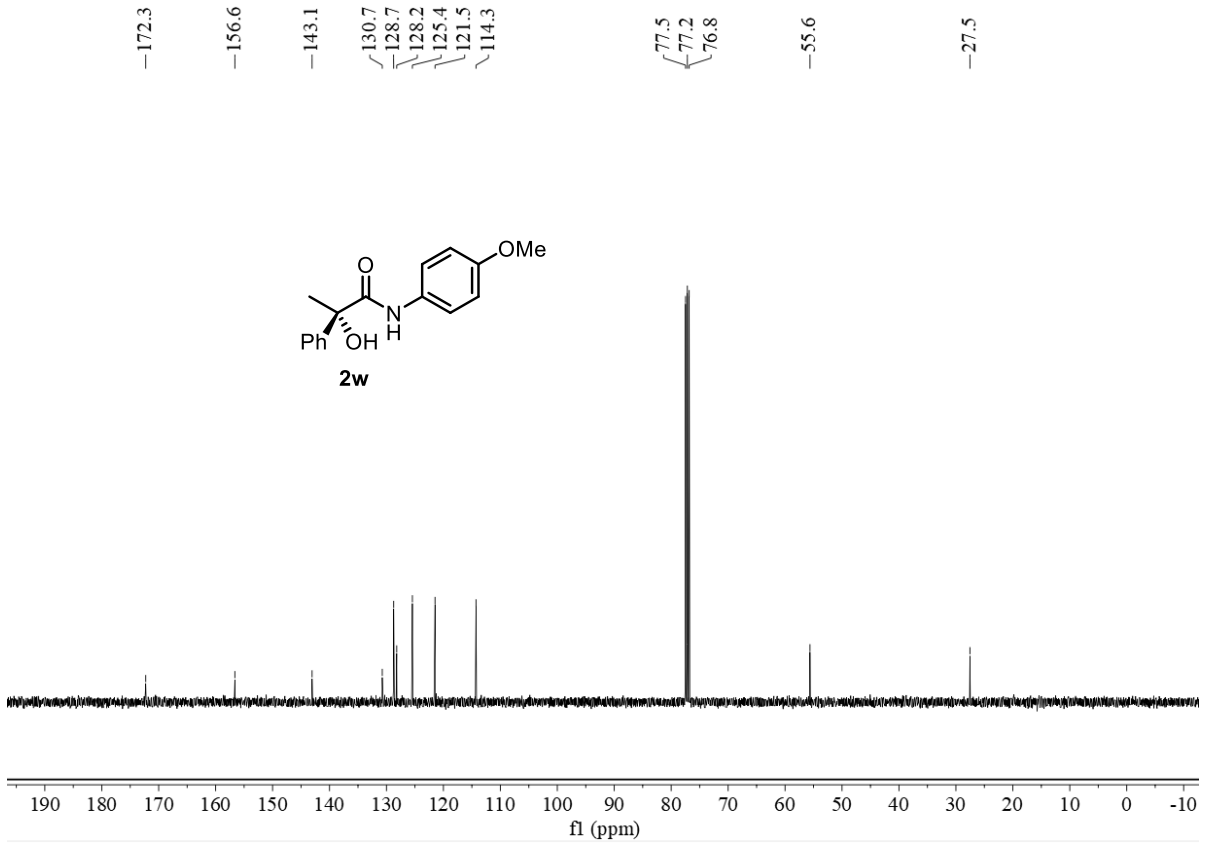
^{13}C NMR of **2v** (101 M, $CDCl_3$)



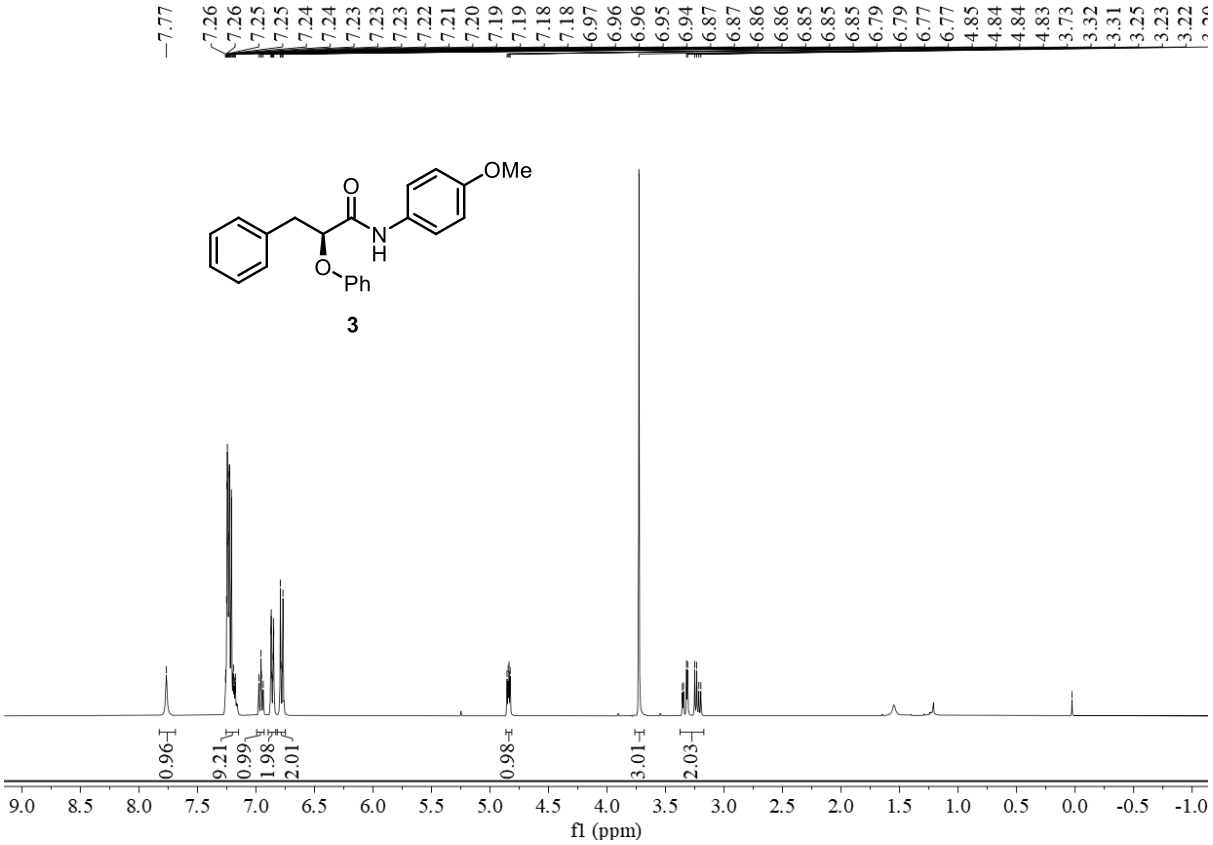
^{19}F NMR of **2v** (376 M, $CDCl_3$)



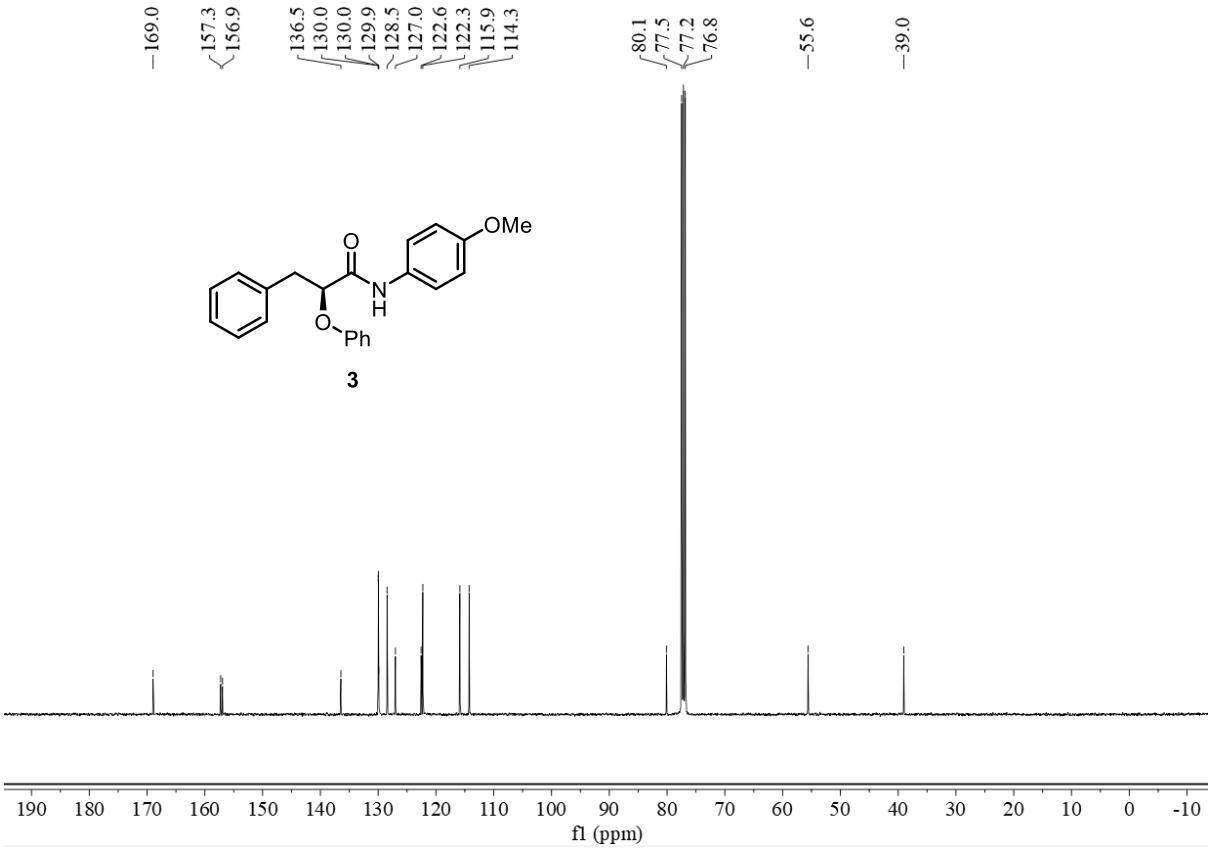
^{1}H NMR of **2w** (400 M, $CDCl_3$)



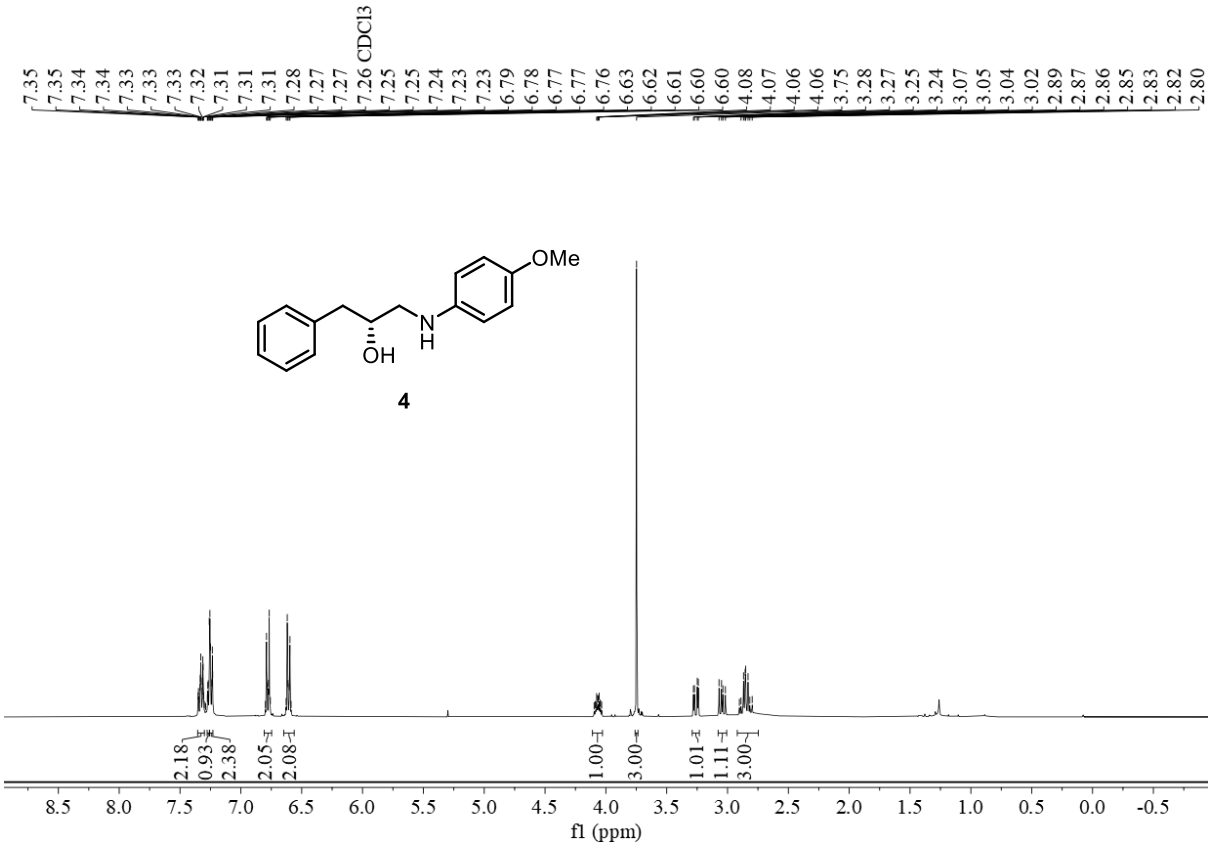
^{13}C NMR of **2w** (101 M, $CDCl_3$)



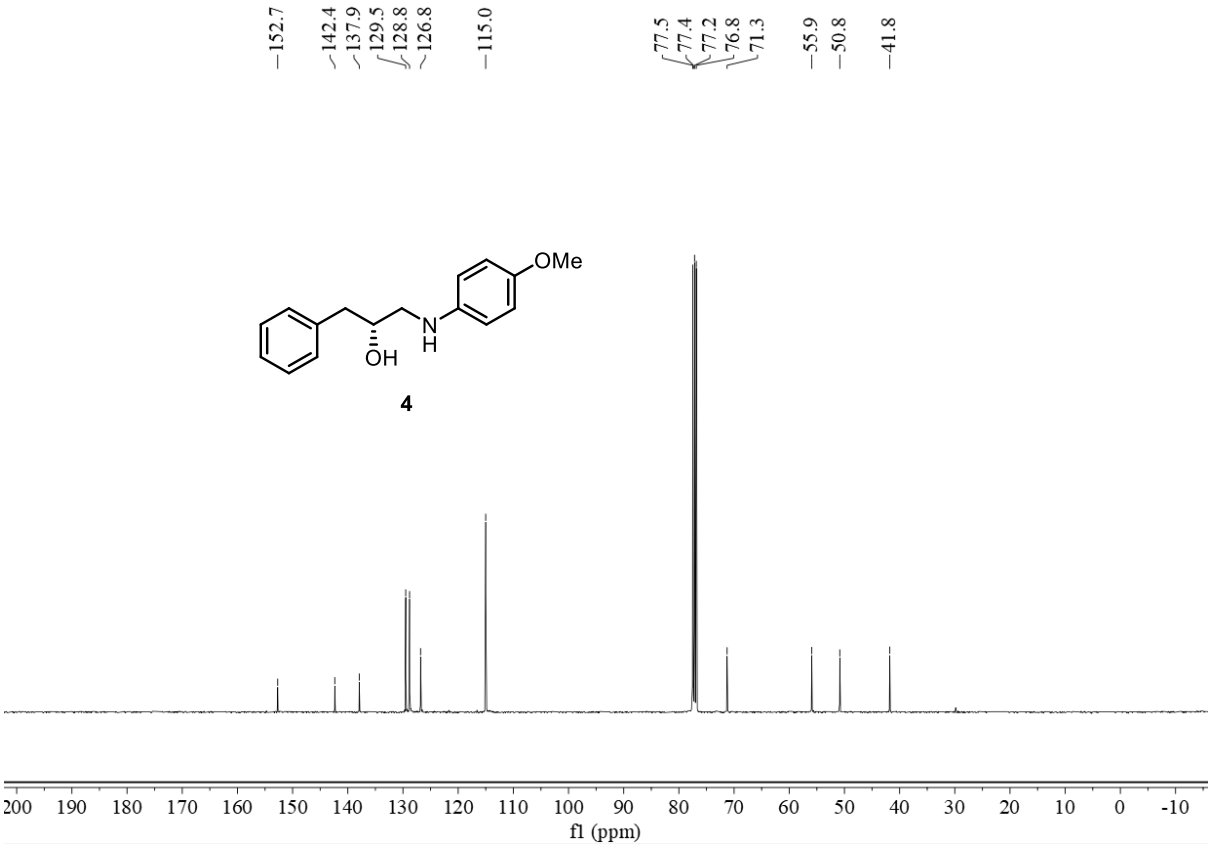
^{1}H NMR of **3** (400 M, $CDCl_3$)



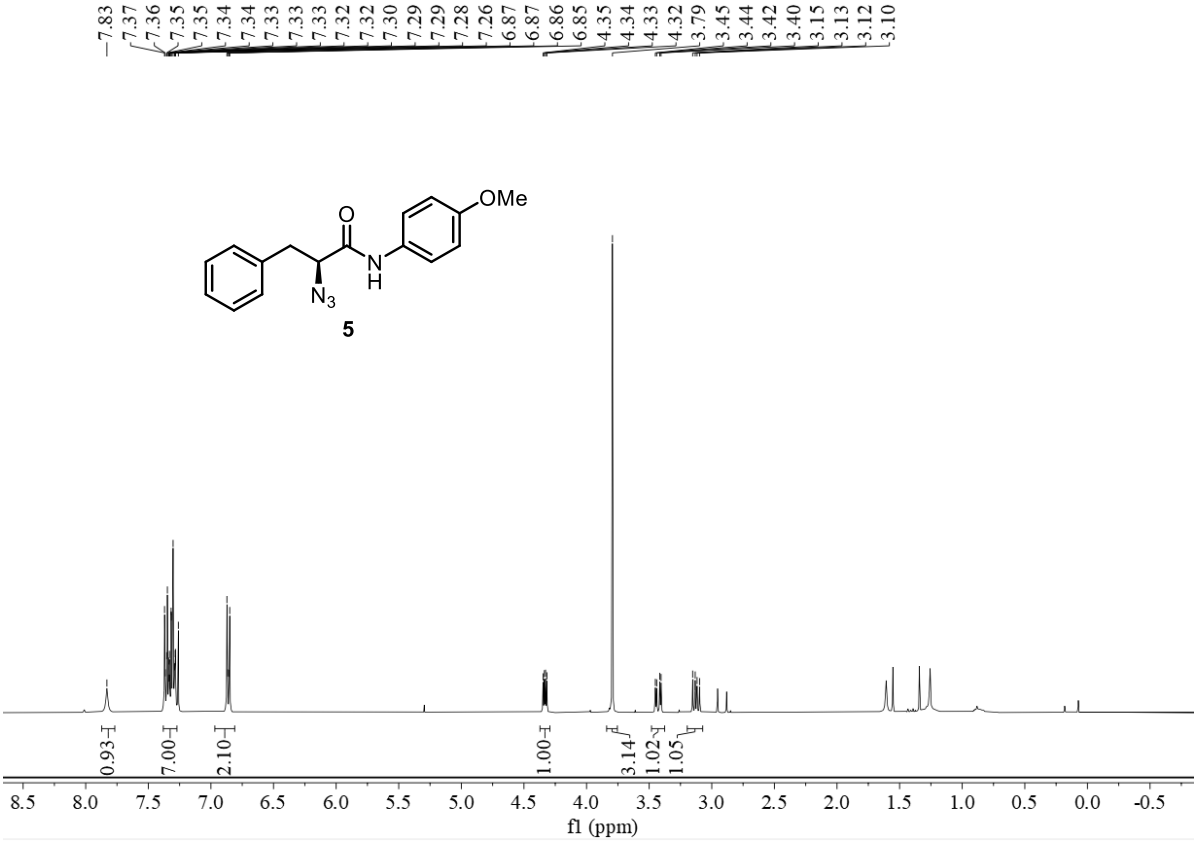
^{13}C NMR of **3** (101 M, $CDCl_3$)



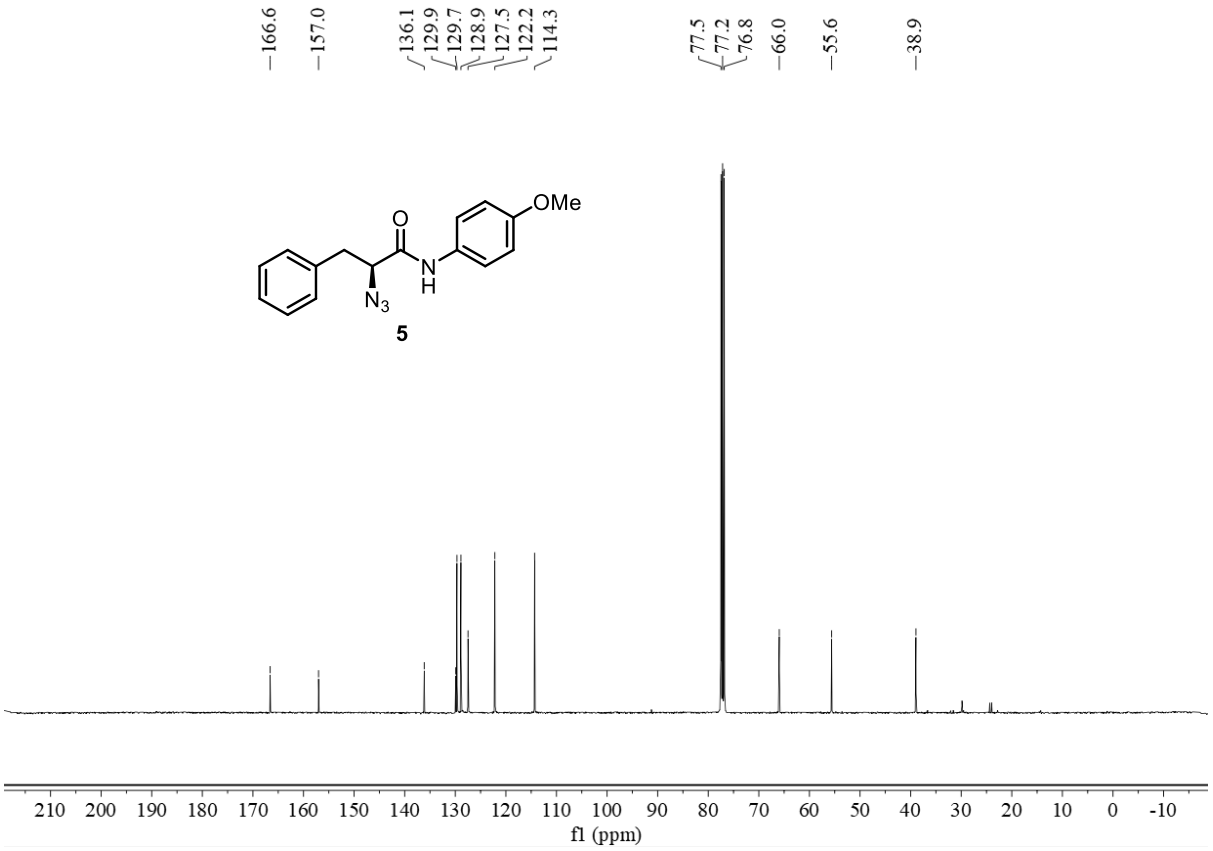
^{1}H NMR of **4** (400 M, $CDCl_3$)



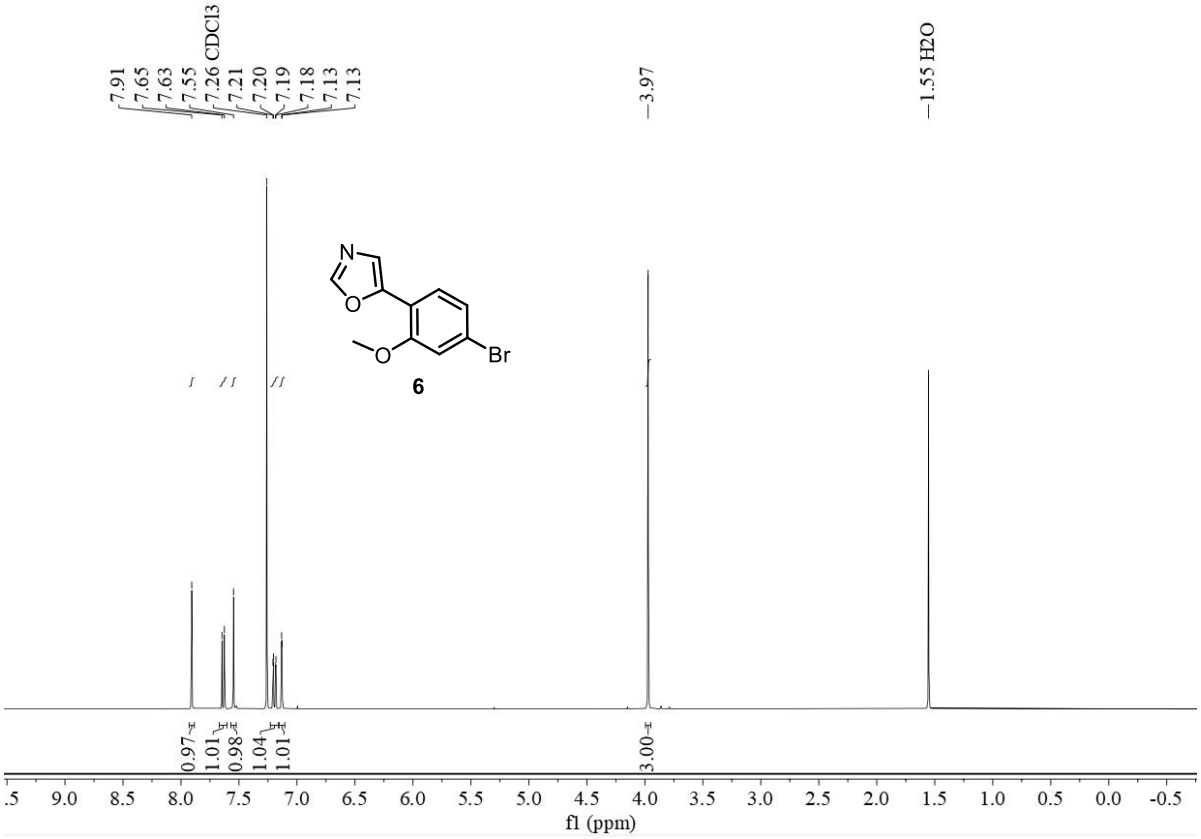
^{13}C NMR of **4** (400 M, $CDCl_3$)



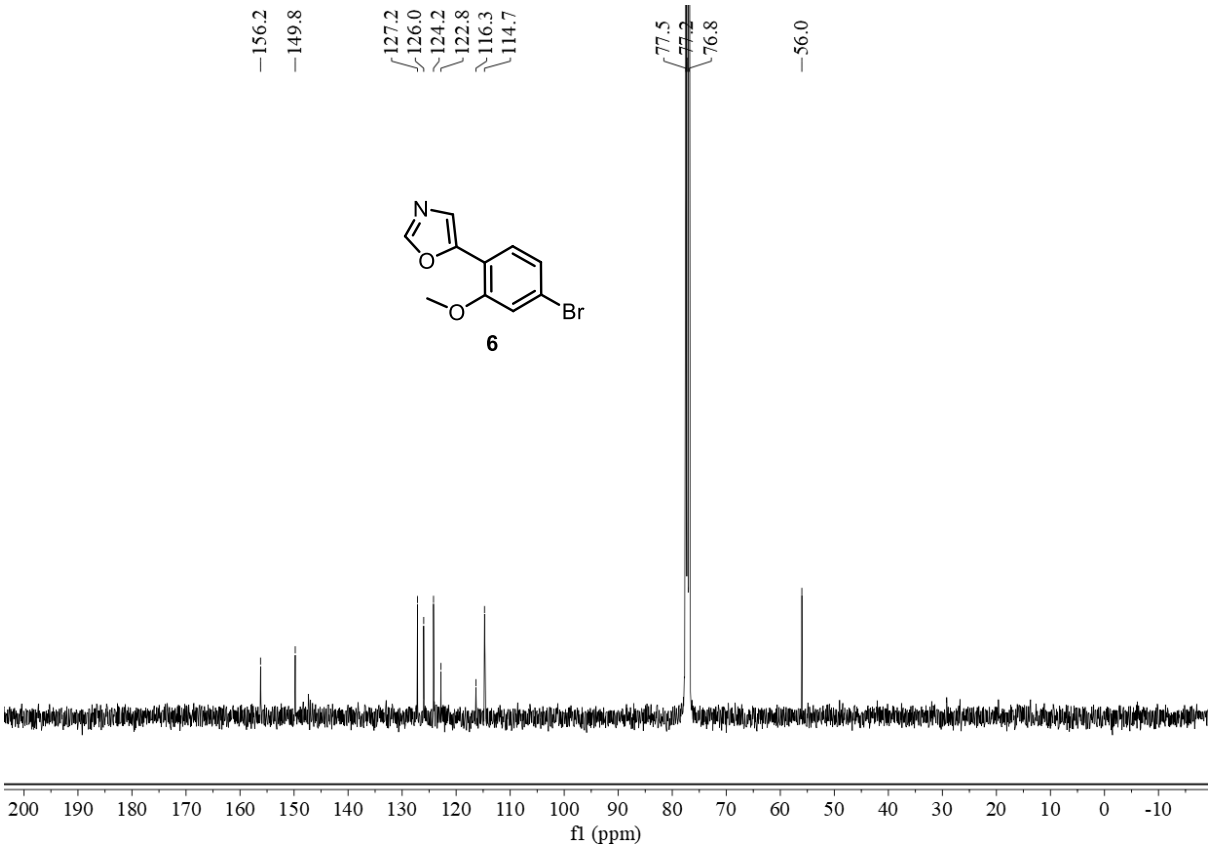
^{1}H NMR of **5** (400 M, $CDCl_3$)



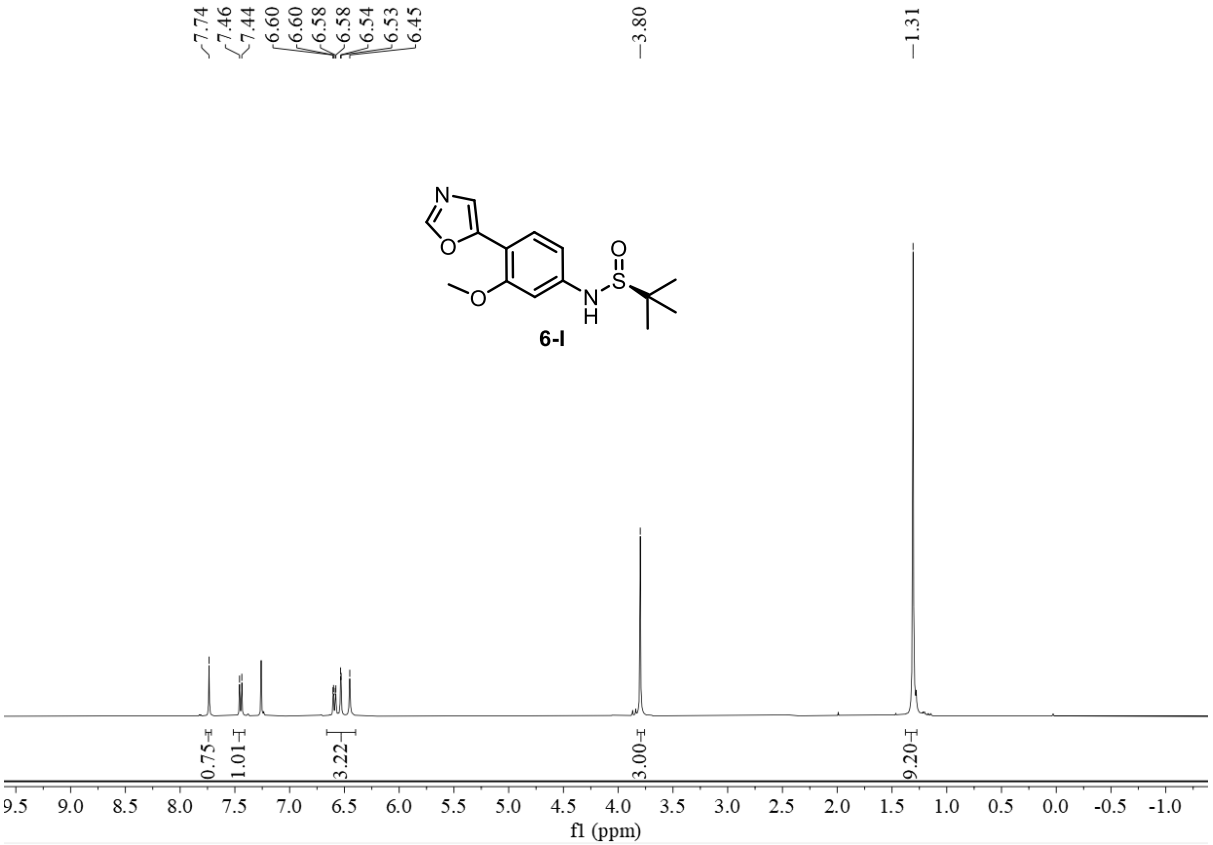
^{13}C NMR of **5** (101 M, $CDCl_3$)



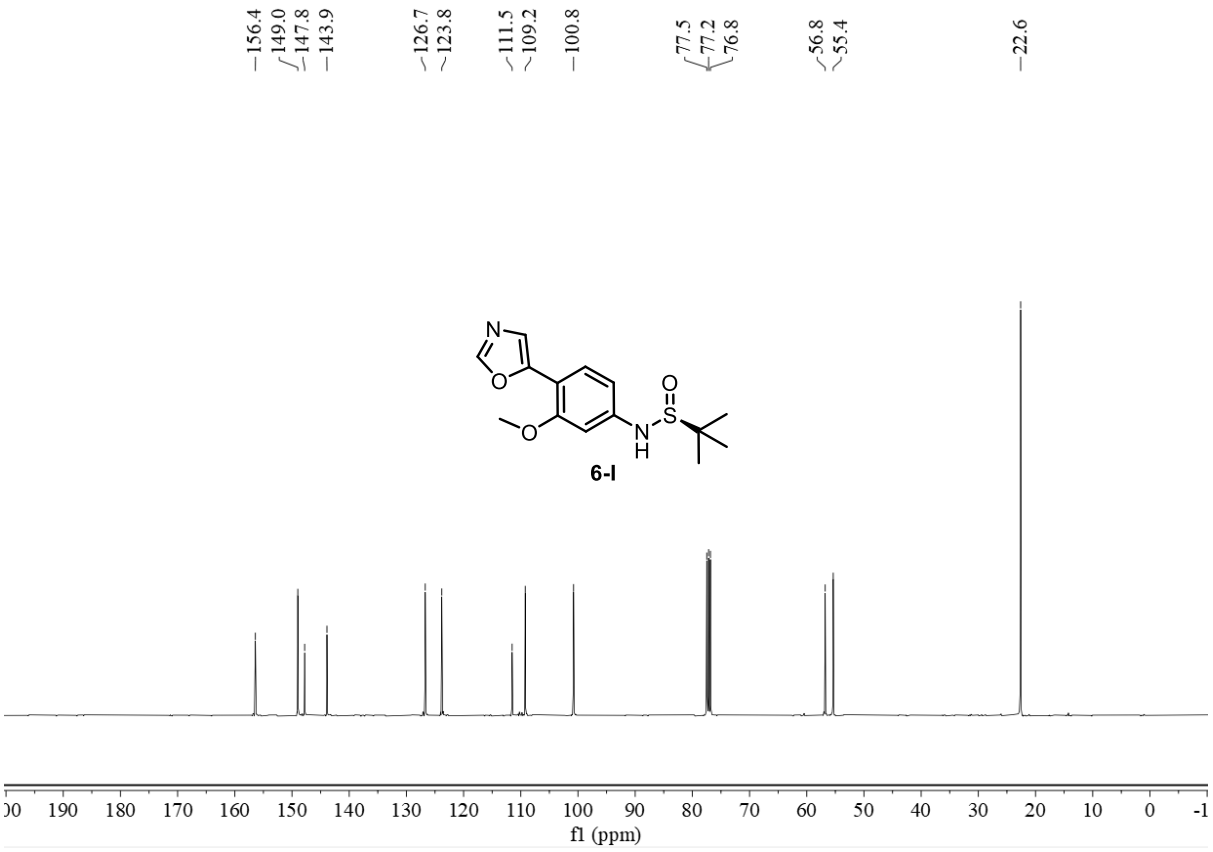
^{1}H NMR of **6** (400 M, $CDCl_3$)



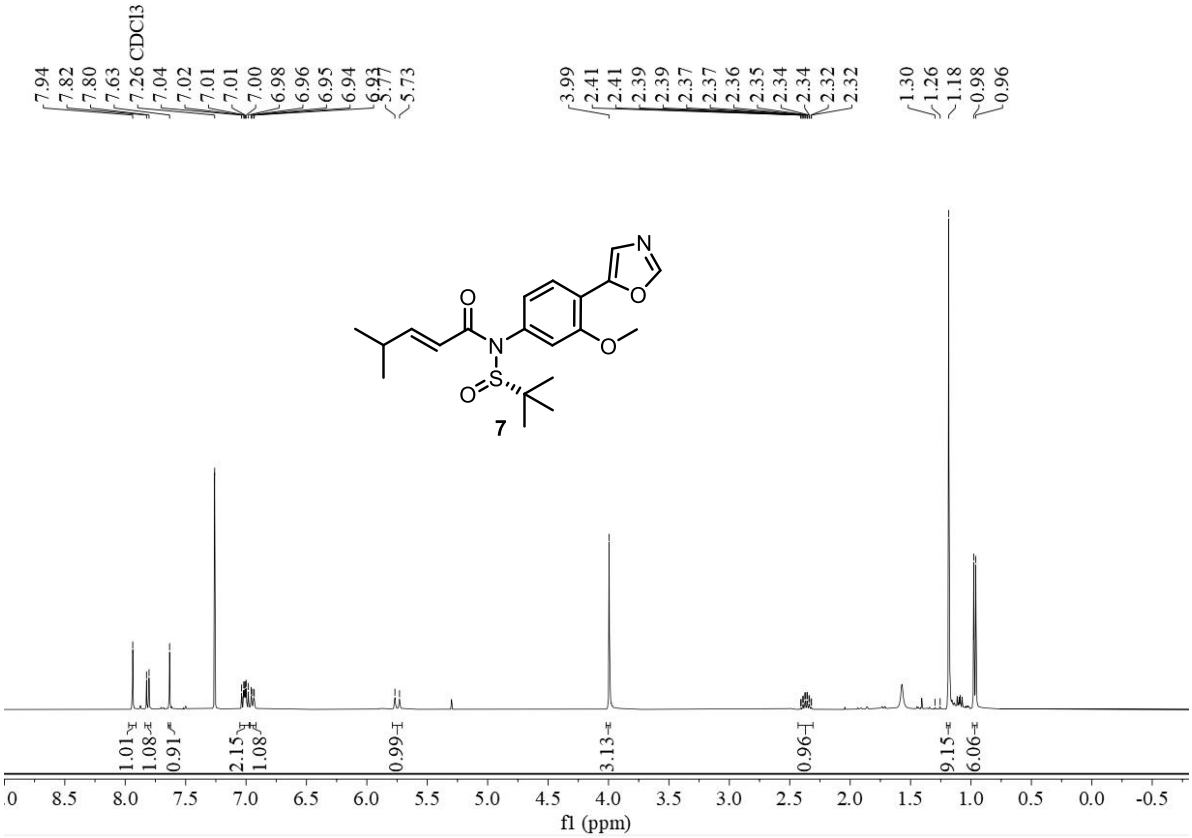
^{13}C NMR of **6** (101 M, $CDCl_3$)



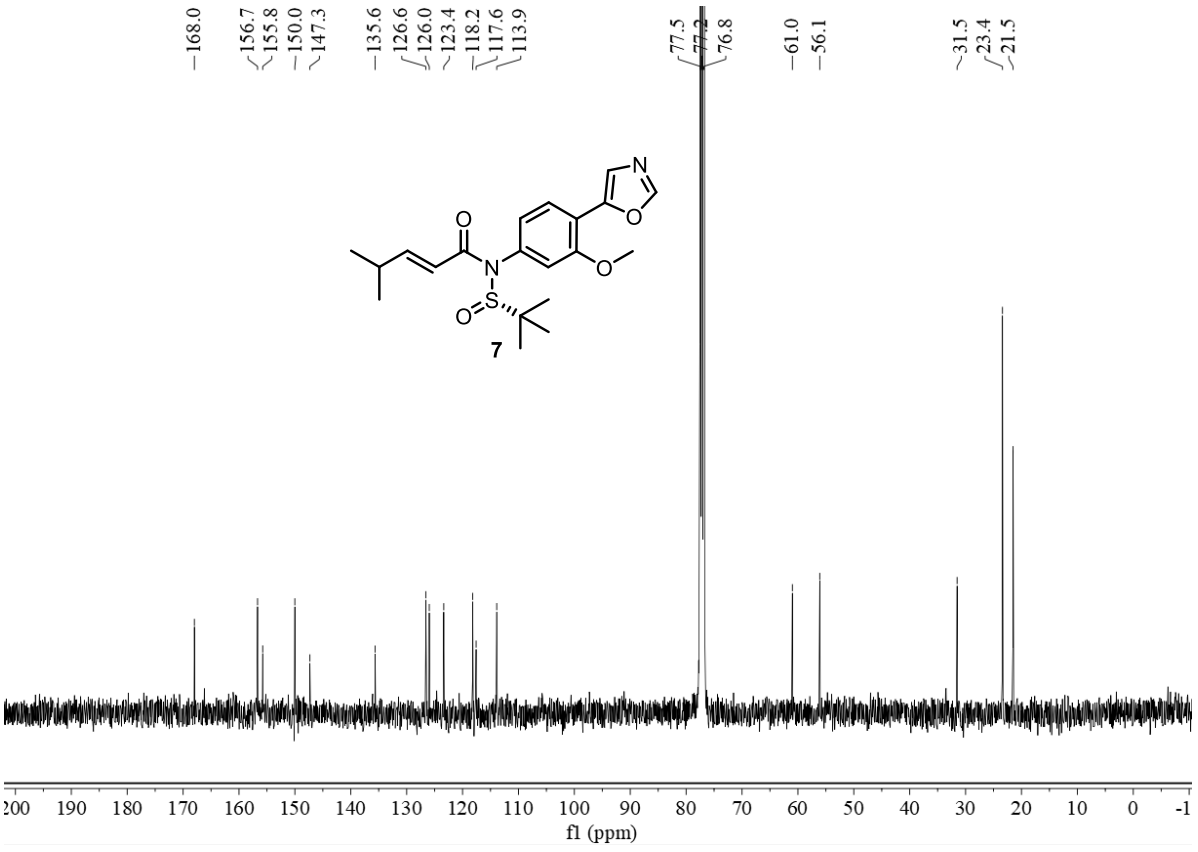
^{1}H NMR of **6-I** (400 M, $CDCl_3$)



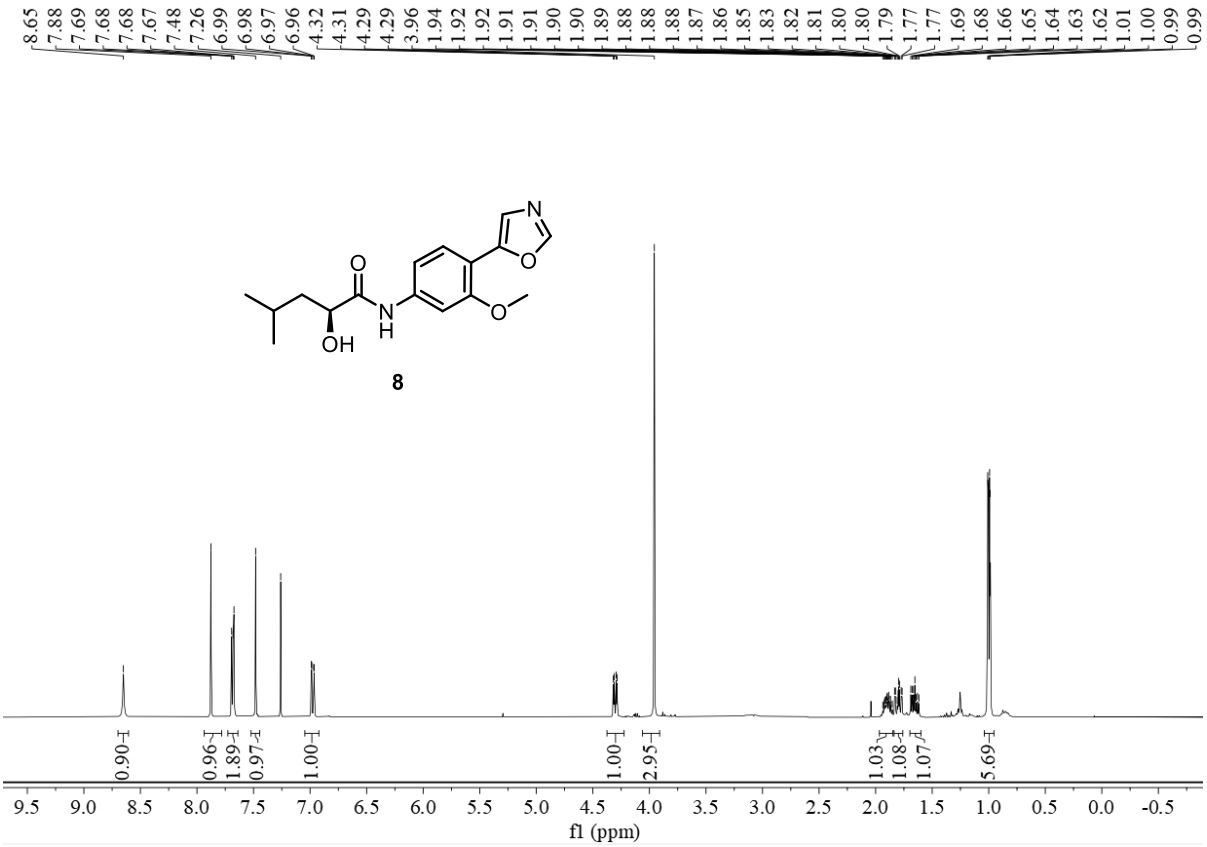
^{13}C NMR of **6-I** (101 M, $CDCl_3$)



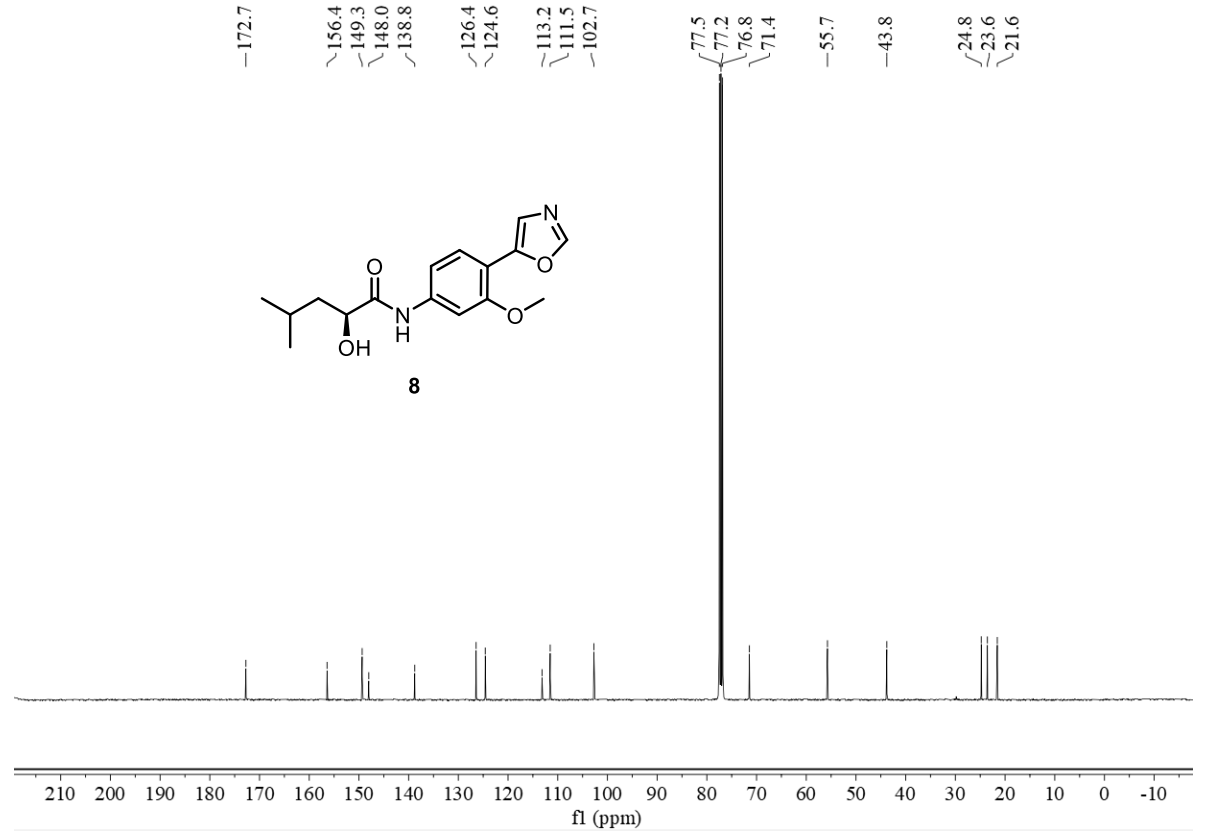
^{1}H NMR of **7** (400 M, $CDCl_3$)



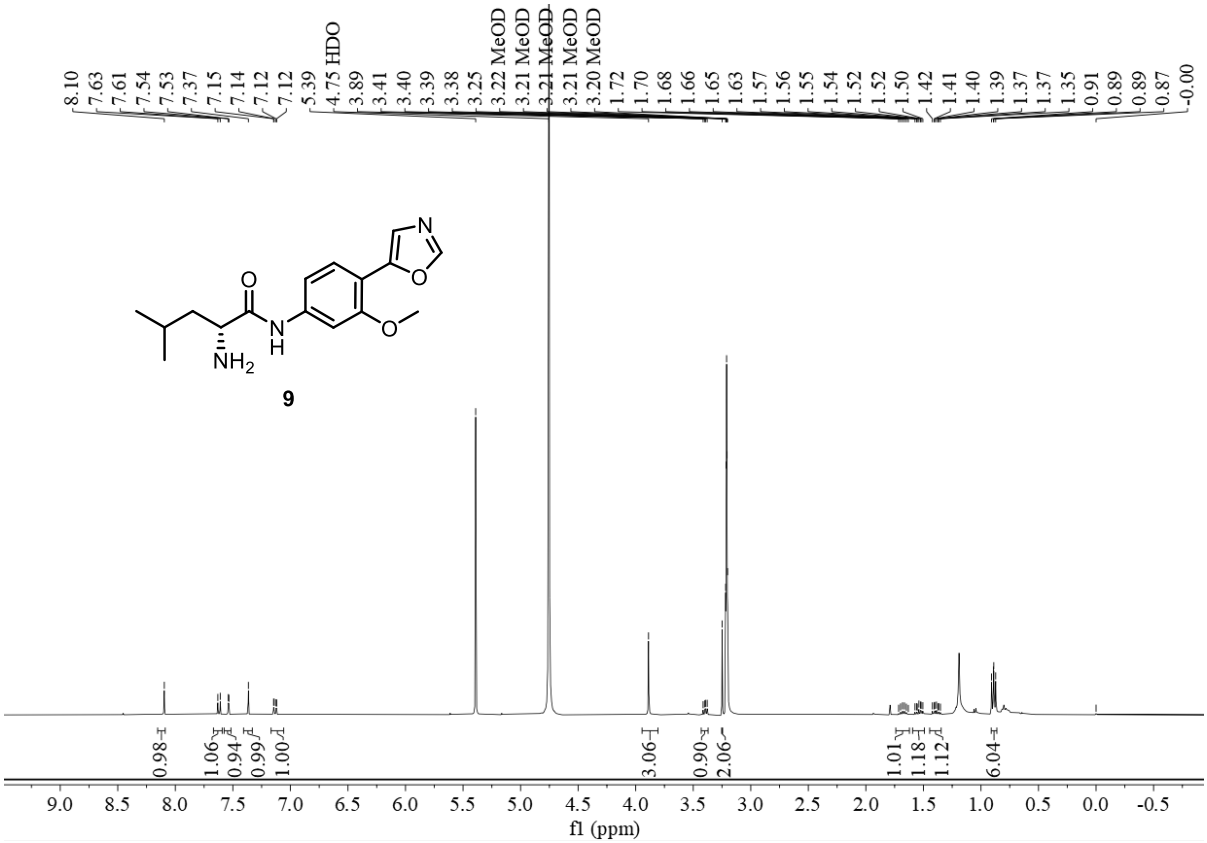
^{1}H NMR of **8** (101 M, $CDCl_3$)



^{1}H NMR of **8** (400 M, $CDCl_3$)



^{13}C NMR of **8** (400 M, $CDCl_3$)



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1H NMR of **9** (400M, CD_3OD)