Lewis acid-catalyzed diastereoselective formal ene reaction of thioindolinones/thiolactams with bicyclobutanes

Avishek Guin,* Shiksha Deswal, Mahesh Singh Harariya and Akkattu T. Biju*

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012, India

Email: avishekguin@iisc.ac.in ; atbiju@iisc.ac.in

Supporting Information

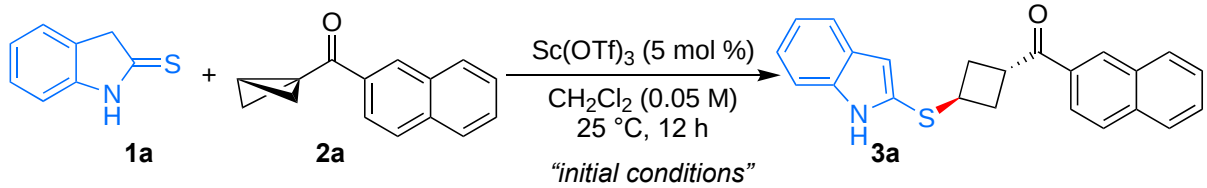
1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of nitrogen in oven-dried reaction vessels with Teflon screw caps. 25 °C Corresponds to the room temperature (rt) of the lab when the experiments were carried out. CH_2Cl_2 was freshly purified by distillation over CaH_2 under nitrogen atmosphere. BCBs were prepared following the reported literature procedures.[1] All thioindolinone and other thione derivatives were prepared from the corresponding amides following the literature procedure.[2]

Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. All the isolated new compounds were confirmed to be single spot on TLC. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded on Bruker Ultrashield spectrometer in $CDCl_3$ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). Infrared (FT-IR) spectra were recorded on a Bruker Alfa FT-IR, ν-max in cm^{-1}. HRMS (ESI) data were recorded on a Waters Xevo G2-XS Q-TOF instrument.

2. General Procedure for the Optimization of the Reaction Conditions



To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added $Sc(OTf)_3$ (0.002 g, 0.005 mmol) inside the glove box. After that, indoline-2-thione **1a** (0.015 g, 0.1 mmol) and 1.5 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere

[1] *(a)* K. Dhake, K. J. Woelk, J. Becia, A. Un, S. E. Jenny and D. C. Leitch, *Angew. Chem., Int. Ed*., 2022, **61**, e202204719; *(b)* R. Guo, Y. Chang, L. Herter, C. Salome, S. E. Braley, T. C. Fessard and M. K. Brown, *J. Am. Chem. Soc*., 2022, **144**, 7988.

[2] B. Gopal, P. R. Singh, M. Kumar and A. Goswami, *J. Org. Chem.*, 2023, **88**, 132.

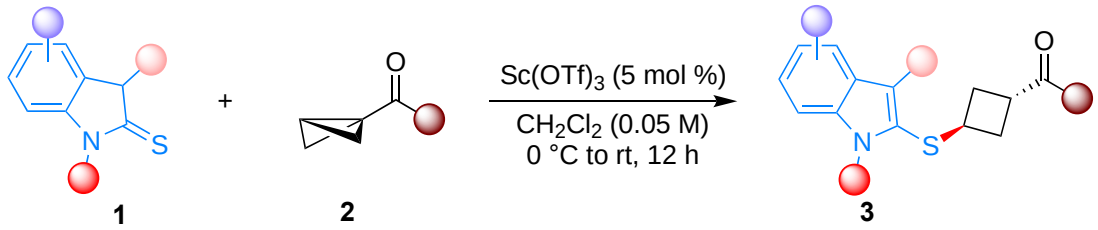
at 25 °C and stirred for 5 minutes. After 5 minutes, bicyclo[1.1.0]butan-1-yl(naphthalene-2-yl)methanone **2a** (0.025 g, 0.12 mmol) and 0.5 mL CH_2Cl_2 was added subsequently. Then, the reaction mixture was stirred for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated, and the crude mixture was passed through a pad of silica gel and eluted with EtOAc (3x10 mL). The reaction mixture was concentrated under reduced pressure and then the yield of **3a** was determined by the ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 as the internal standard.

Table S1. Optimization Studies

entry	variation of the initial conditions[a]	yield of **3a** (%)[b]	dr[c]
1	none	63	>20:1
2	$Bi(OTf)_3$ instead of $Sc(OTf)_3$	40	>20:1
3	$Cu(OTf)_2$ instead of $Sc(OTf)_3$	60	2:1
4	TMSOTf instead of $Sc(OTf)_3$	47	1:1
5	10 mol % $Sc(OTf)_3$ instead of 5 mol %	62	>20:1
6	1.4 equiv of **2a**	57	>20:1
7	1.2 equiv of **1a**	51	>20:1
8	0 °C instead of 25 °C	71	>20:1
9	*0 °C to rt instead of 25 °C*	*71 (70)*	*>20:1*
10[d]	DCE instead of CH_2Cl_2	60	>20:1
11[d]	THF instead of CH_2Cl_2	69	1:1

[a] Initial conditions: **1a** (0.10 mmol), **2a** (0.12 mmol), $Sc(OTf)_3$ (5 mol %), CH_2Cl_2 (2.0 mL), 25 °C for 12 h. [b] The ^{1}H NMR yield of the crude products was determined using CH_2Br_2 as the internal standard and the isolated yield was given in parenthesis. [c] dr value was determined from ^{1}H NMR of the crude reaction mixture. [d] The reaction was performed at 0 °C to rt.

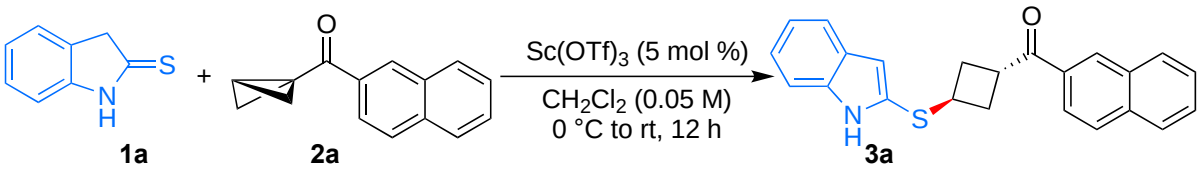
3. General Procedure for the Lewis Acid-Catalyzed Ene Reaction of Thioindolinones with Bicyobutanes



To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added $Sc(OTf)_3$ (0.005 g, 0.01 mmol) inside the glove box. After that, thioindolinones **1** (0.2 mmol) and 3.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the reaction mixture was cooled at 0 °C and stirred for 5 minutes. After 5 minutes, BCBs **2** (0.24 mmol) and 1.0 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was slowly warmed to rt while stirring for 12 h. After 12 h, the solvent was evaporated, and the crude

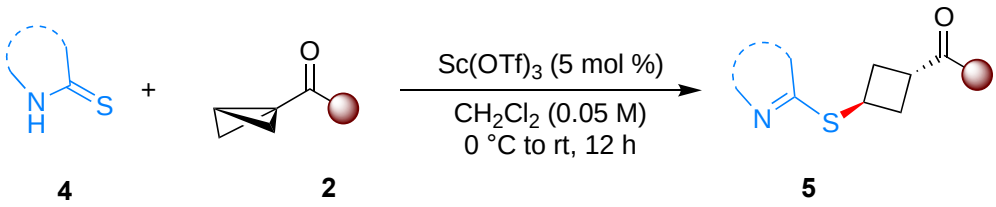
residue was pre-adsorbed on silica gel and purified by flash column chromatography on silica gel (Pet.ether-EtOAc as eluent) to afford **3** in good to excellent yields.

Procedure for the 2.0 mmol Scale Reaction for the synthesis of 3a



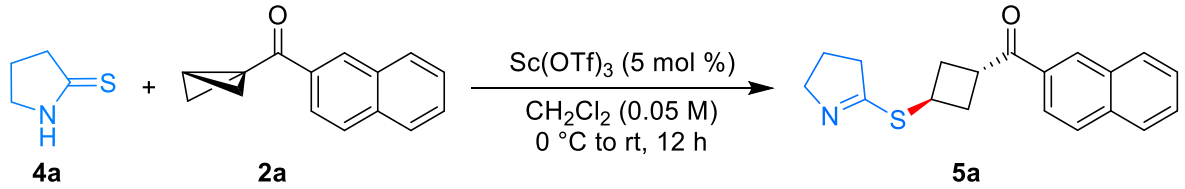
To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added $Sc(OTf)_3$ (0.049 g, 0.1 mmol) inside the glove box. After that, indoline-2-thione **1a** (0.298 g, 2.0 mmol) and 30 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then, the reaction mixture was cooled at 0 °C and stirred for 5 minutes. After 5 minutes, bicyclo[1.1.0]butan-1-yl(naphthalene-2-yl)methanone **2a** (0.500 g, 2.4 mmol) and 10 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was slowly warmed to rt while stirring for 12 h. After 12 h, the solvent was evaporated, and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 90/10) on silica gel to afford **3a** as a purple solid (0.515 g, 72% yield).

4. General Procedure for the Reaction of Thiones with BCBs



To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added $Sc(OTf)_3$ (0.005 g, 0.01 mmol) inside the glove box. After that, thiones **4** (0.2 mmol) and 3.0 mL CH_2Cl_2 were added outside the glove box under a nitrogen atmosphere. Then, the reaction mixture was cooled at 0 °C and stirred for 5 minutes. After 5 minutes, BCBs **2** (0.24 mmol) and 1.0 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was slowly warmed to rt while stirring for 12 h. After 12 h, the solvent was evaporated, and the crude residue was pre-adsorbed on silica gel and purified by flash column chromatography on silica gel (Pet.ether-EtOAc as eluent) to afford **5** in good to excellent yields and single diastereomeric ratio.

Procedure for the 1.0 mmol Scale Reaction for the synthesis of 5a

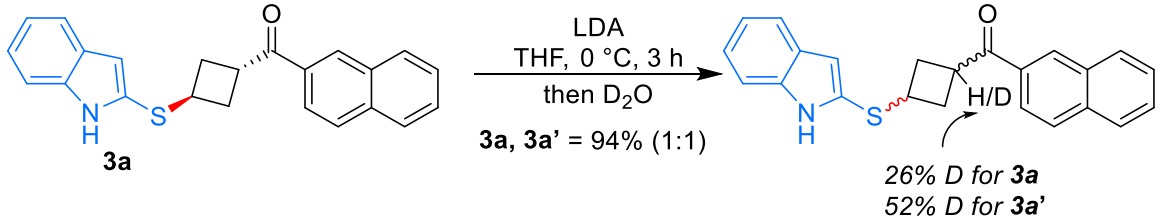


4a **2a** **5a**

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added $Sc(OTf)_3$ (0.025 g, 0.05 mmol) inside the glove box. After that, pyrrolidine-2-thione **4a** (0.101 g, 1.0 mmol) and 15 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then, the reaction mixture was cooled at 0 °C and stirred for 5 minutes. After 5 minutes, bicyclo[1.1.0]butan-1-yl(naphthalene-2-yl)methanone **2a** (0.250 g, 1.2 mmol) and 5 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was slowly warmed to rt while stirring for 12 h. After 12 h, the solvent was evaporated, and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 90/10) on silica gel to afford **5a** as a white solid (0.204 g, 66% yield).

5. Mechanistic Studies

Epimerization of the product 3a

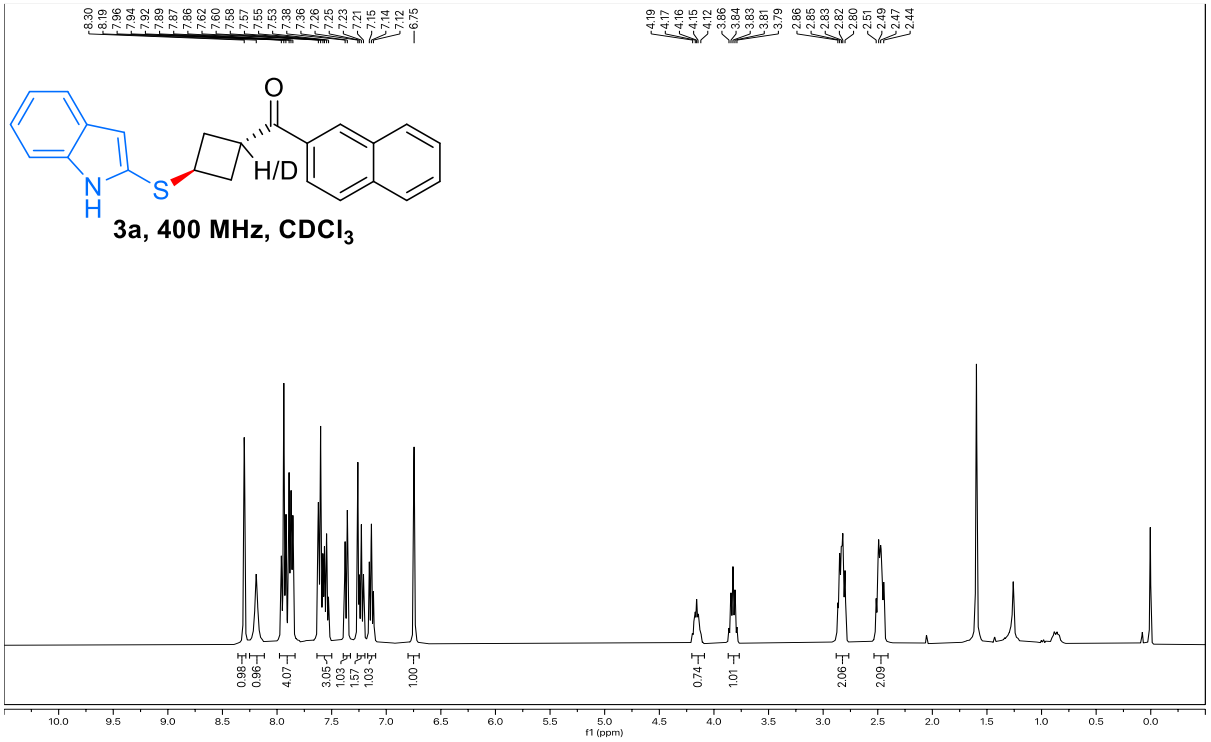


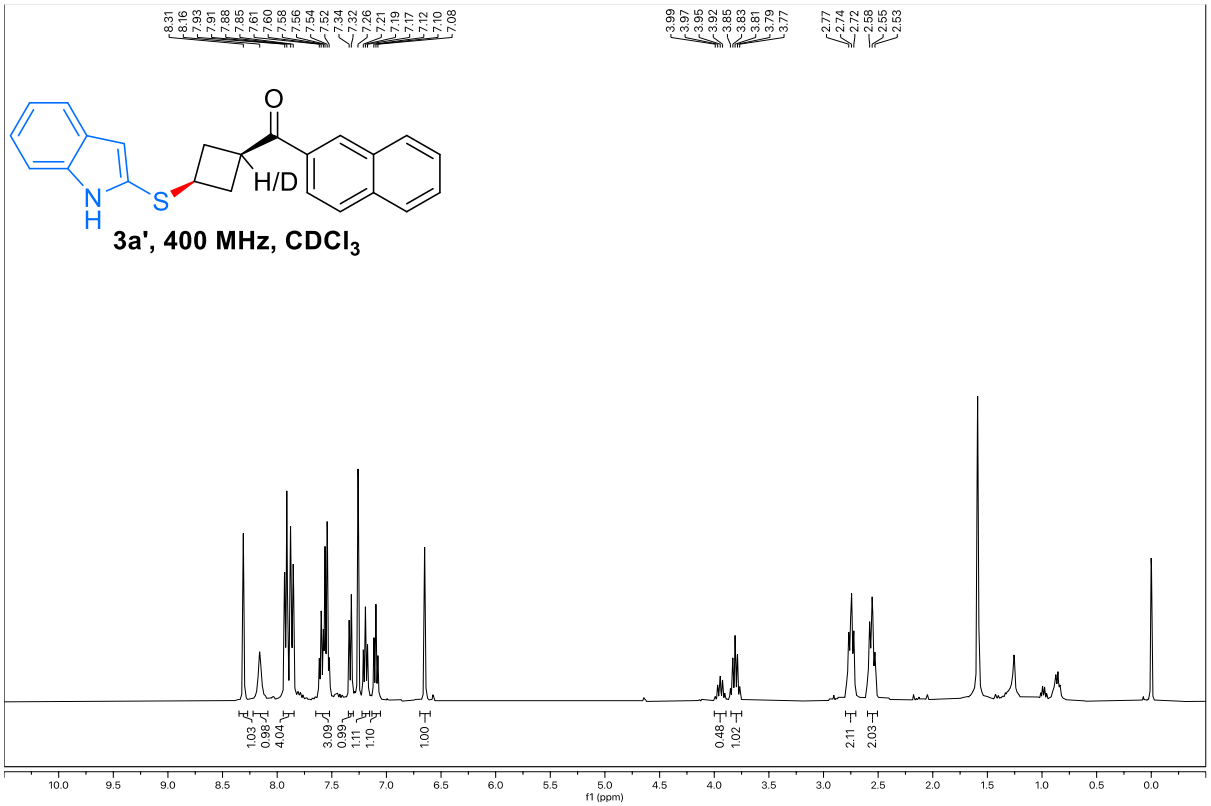
3a

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added **3a** (0.036 g, 0.1 mmol) in 1.0 mL THF under nitrogen atmosphere at 0 °C. Then, the reaction mixture was stirred for 5 minutes at 0 °C. After 5 minutes, LDA (0.3 mL, 1 M solution in THF) was added and then the reaction mixture was stirred for 3 hour while maintaining the same temperature. After 3 h, the reaction was quenched with D_2O (0.020 g, 1.0 mmol) and stirred for 15 minutes. After 15 min, and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 90/10) on silica gel to afford **3a** and **3a'** in 94% isolated yield with 1:1 separable dr.

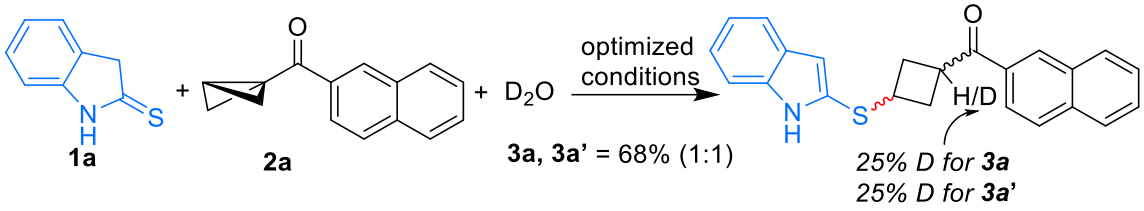
This study reveals that the proton adjacent to the 2-naphthyl ketone exhibits acidity and is susceptible to deprotonation by LDA. Furthermore, following the deprotonation and subsequent re-protonation, both diastereomers were formed in equal proportions, suggesting that the observed diastereoselectivity in the described ene reaction is not governed by

thermodynamic parameters. If thermodynamic parameters were decisive in determining diastereoselectivity, then minimal change would be expected in diastereoselectivity after the deprotonation and re-protonation steps (Scheme 4 of the manuscript, eq 4).



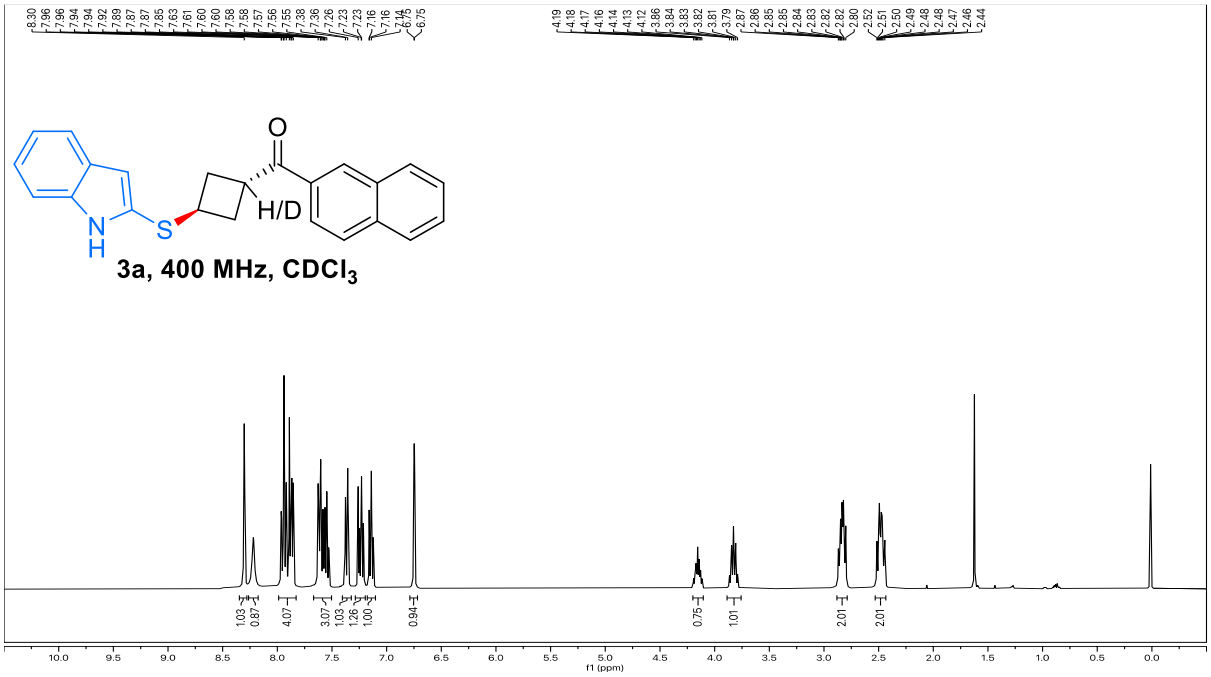


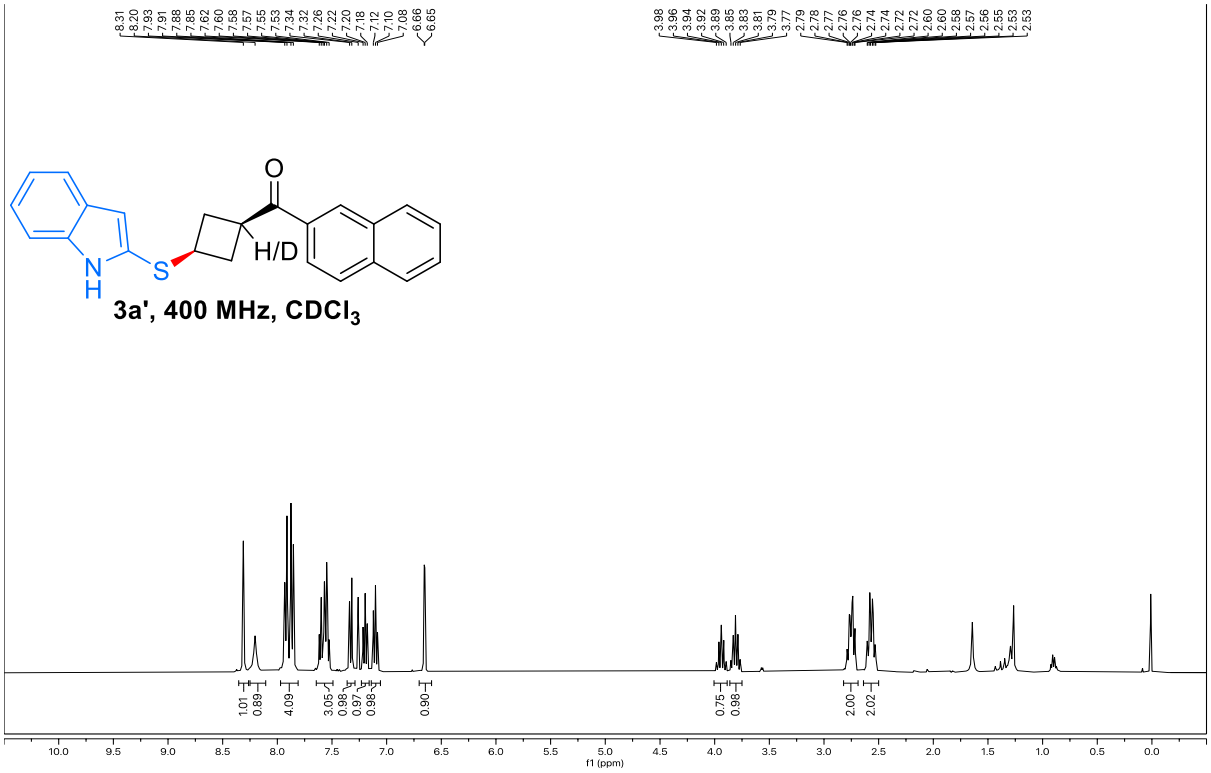
Reaction in the presence of D_2O



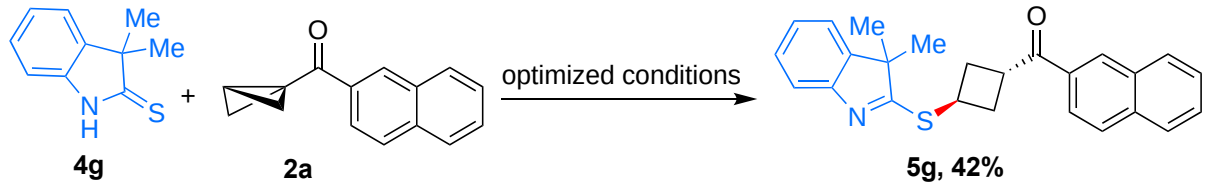
To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added $Sc(OTf)_3$ (0.005 g, 0.01 mmol) inside the glove box. After that, indoline-2-thione **1a** (0.030 g, 0.2 mmol) and 3.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the reaction mixture was cooled at 0 °C and stirred for 5 minutes. After 5 minutes, bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol), D_2O (0.016 g, 0.8 mmol) and 1.0 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was slowly warmed to rt while stirring for 12 h. After 12 h, the solvent was evaporated, and the crude residue was pre-adsorbed on silica gel and purified by flash column chromatography on silica gel (Pet.ether-EtOAc as eluent) to afford **3a** and **3a'** in 68% isolated yield with 1:1 separable dr.

The findings of this study suggest that the introduction of an external proton source can modify the diastereoselectivity of the product. Given that the presence of such a proton source can influence diastereoselectivity, it is likely that intramolecular proton transfer occurs under the optimized reaction conditions, possibly originating from the same side of the thioindolinones (Scheme 4 of the manuscript, eq 5).





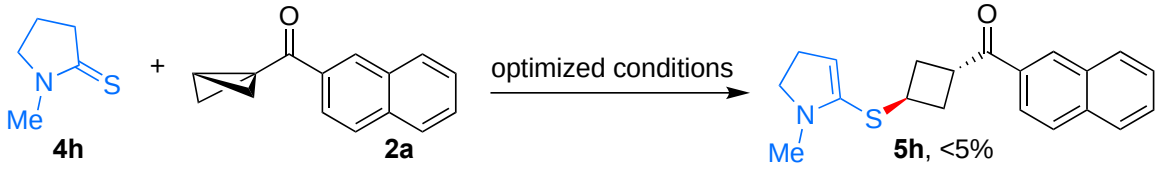
Reaction with 3,3-dimethylindoline-2-thione



To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added $Sc(OTf)_3$ (0.005 g, 0.01 mmol) inside the glove box. After that, 3,3-dimethylindoline-2-thione **4g** (0.035 g, 0.2 mmol) and 3.0 mL CH_2Cl_2 were added outside the glove box under a nitrogen atmosphere. Then, the reaction mixture was cooled at 0 °C and stirred for 5 minutes. After 5 minutes, bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) and 1.0 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was slowly warmed to rt while stirring for 12 h. After 12 h, the solvent was evaporated, and the crude residue was pre-adsorbed on silica gel and purified by flash column chromatography on silica gel (Pet.ether-EtOAc as eluent) to afford **5g** as yellow solid (0.032 g, 42% yield).

This study suggests that even without the favourable aromatization process, thiones can still undergo reactions. If there is potential for aromatization, the imine bearing product can convert to desired product via tautomerization. Therefore, it's possible that the cyclobutane bearing imine serves as an intermediate in the developed ene reaction (Scheme 4 of the manuscript, eq 6).

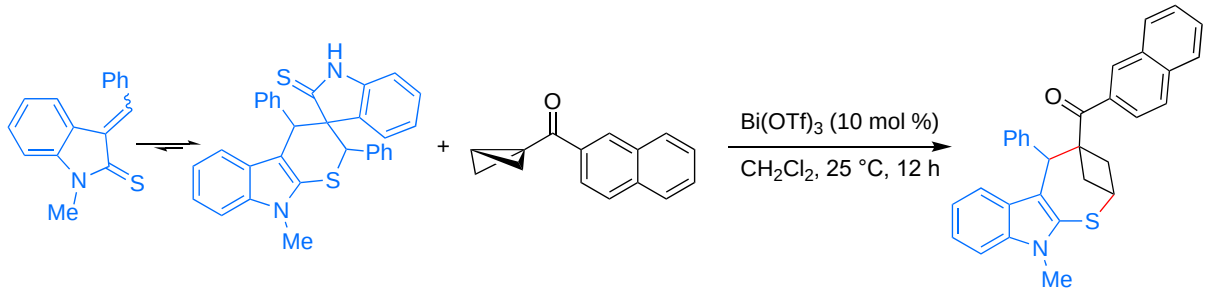
Reaction with 1-methylpyrrolidine-2-thione



To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added $Sc(OTf)_3$ (0.005 g, 0.01 mmol) inside the glove box. After that, 1-methylpyrrolidine-2-thione **4h** (0.023 g, 0.2 mmol) and 3.0 mL CH_2Cl_2 were added outside the glove box under a nitrogen atmosphere. Then, the reaction mixture was cooled at 0 °C and stirred for 5 minutes. After 5 minutes, bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) and 1.0 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was slowly warmed to rt while stirring for 12 h. After 12 h, the reaction mixture was passed through a pad of silica gel and then eluted with EtOAc (3x10 mL), and the solvent was evaporated to get the crude products, which was analyzed using ^{1}H NMR spectroscopy. In this case, no desired product formation was observed.

This study highlights the significance of the N-H proton in facilitating the formation of the BCB ring-open product from 1-methylpyrrolidine-2-thione. However, in the case of 1-methylindoline-2-thione, the expected product was still formed in moderate yield even in the absence of the N-H proton. This disparity in outcomes may be attributed to the potential influence of aromaticity, which could serve as an additional driving force for product formation in 1-methylindoline-2-thione, a feature lacking in 1-methylpyrrolidine-2-thione. (Scheme 4 of the manuscript, eq 7).

Reaction with benzylidene-1-methylindoline-2-thione



4i **2a** **5i, 55%**

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added $Bi(OTf)_3$ (0.006 g, 0.01 mmol) inside the glove box. After that, 3-benzylidene-1-methylindoline-2-thione **4i** (0.050 g, 0.2 mmol), bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.021 g, 0.1 mmol) and 4.0 mL CH_2Cl_2 were added outside the glove box

under a nitrogen atmosphere at 25 °C. Then, the reaction mixture was stirred for 12 h at the same temperature. After 12 h, the solvent was evaporated, and the crude residue was pre-adsorbed on silica gel and purified by flash column chromatography on silica gel (Pet.ether-EtOAc as eluent) to afford (10-methyl-5-phenyl-2,3,5,10-tetrahydro-4*H*-2,4-methanothiepino[2,3-*b*]indol-4-yl)(naphthalen-2-yl)methanone **5i** as white solid (0.025 g, 55% yield).

Once more, this study highlighted the essential role of aromaticity. While the addition of thioamide to BCB could potentially yield the ring-open product in this scenario, it is the driving force of aromatization that propels the reaction towards the formation of the annulated product (Scheme 4 of the manuscript, eq 8).

6. X-ray Data of 8

Single crystal of **8** (recrystallized from EtOAc/*n*-hexane at 25 °C) was mounted and the diffraction data was collected at 120 K on a Bruker APEX-II CCD diffractometer using SMART/SAINT software. Intensity data were collected using MoKα radiation (λ=0.71073 A°). The single crystal was affixed to a Hampton Research cryoloop using Paratone-N oil. Data collection and reduction was performed using Bruker APEX2 and Bruker SAINT, respectively. The structure was solved by direct methods using the SHELX-97 and refined by full-matrix leastsquares on F2. Empirical absorption corrections were applied with SADABS. All Nonhydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and Mercury-3. CCDC 2335481 (**8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic refinement parameters are given below:

Compound	**8**
Empirical formula	$C_{23}H_{19}NO_3S$
Formula weight	389.478
Temperature	120.15 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.8830(5) Å, b = 10.7359(6) Å, c = 10.9008(6) Å, α = 84.098(2)°, β = 80.590(2)°, γ = 65.900(1)°
Volume	935.44(9) $Å^3$
Z	2
Density (calculated)	1.383 g/cm^3
Absorption coefficient	0.198 mm^{-1}
F(000)	408.4
Theta range for data collection	3.8 to 68.24°
Index ranges	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-15 \leq l \leq 16$
Reflections collected	26876
Independent reflections	6247 [R_{int} = 0.0302, R_{sigma} = 0.0279]
Data / restraints / parameters	6247/0/253
Goodness-of-fit on F2	1.044
Final R indices [I>2sigma(I)]	R_1 = 0.0377, wR_2 = 0.0960
R indices (all data)	R_1 = 0.0498, wR_2 = 0.1030

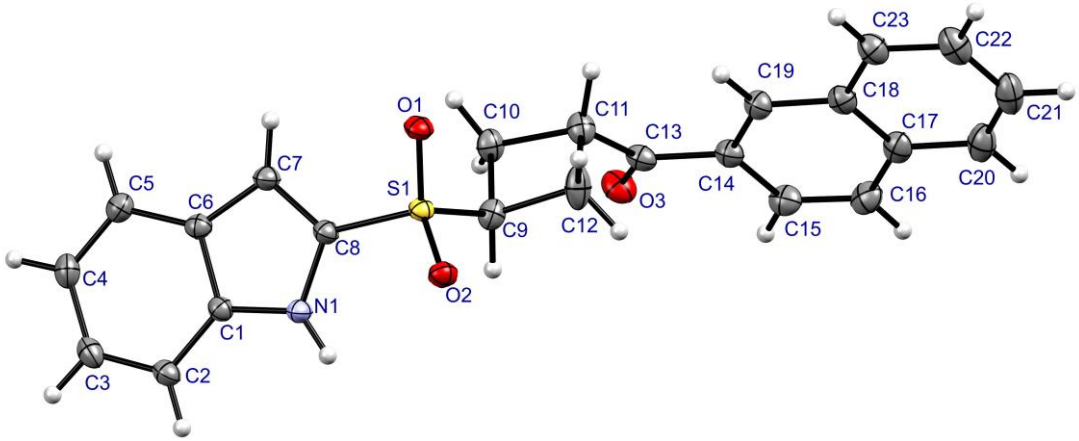


Figure S1. Crystal structure of **8** (Thermal ellipsoids are shown with 50% probability)

7. DFT Studies

All DFT calculations were performed using Gaussian 16 software.[3] Geometry optimizations were carried out in gas phase using hybrid functional B3LYP-D3 along with

[3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.

LANL2DZ basis set with an effective core potential (ECP) for Sc and split valence Pople's type basis set 6-31G(d,p) for all other atoms.[4] Vibrational frequency calculations were done to verify the nature of stationay points as minima or first-order saddle points with the same functional and basis set to obtain thermal energy corrections at 1 atm and 298K.[5] Single point energies of B3LYP-D3 optimized structures were calculated using the B3LYP-D3(BJ) functional and triple zeta basis set; 6-311++G(d,p). SMD solvation model was used to consider the solvent effect of dichloromethane.[6] Thermal corrections obtained from optimized geometries were added to the electronic energies obtained after single point calculations. The free energies are reported at the $SMD_{(DCM)}$/B3LYP-D3(BJ)/6-311++G(d,p),LANL2DZ(Sc)//B3LYP-D3/6-31G(d,p), LANL2DZ(Sc) level of theory. All the Gibbs free energies reported here are calculated using GoodVibes package at room temperature and 1M concentration.[7] Grimme's quasi-harmonic approximation[8] is employed to compute the entropic contributions for frequencies below the defined cut-off (100 cm^{-1}), with entropy terms for these lower frequencies being estimated using the free-rotor approximation.

Based on the mechanistic studies and DFT calculations a catalytic cycle for diastereoselective ene reaction of thioindolinones is presented in Figure S2. Reaction begins with the coordination of BCB **2a** with $Sc(OTf)_3$ to form the intermediate **A'**. Now, 2-thioindolinone **1a** attacks the intermediate **A'** at C3 position via **TS(A'-B)** to give the intermediate **B** (please see Figure S4). From this intermediate several pathways can be followed, but the major pathway goes via the **TS(B-C)** as shown in Figure S5. Depending upon the position of triflate, two different diastereomers can be formed. Triflate t_1 abstracts the proton from thioindolinone via **TS(B-C)** to from the intermediate **C**, while proton abstraction from triflate t_2 via **TS(B-C')** lead to intermediate **C'**. In the final step, the proton is transferred from triflate to the C1 position of the BCB to give the product.

Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[4] (*a*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785; (*b*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*c*) W. J. Hehre, R. Ditchfield and J. A. People, *J. Chem. Phys.*, 1972, **56**, 2257; (*d*) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*., 1973, **28**, 213; (*e*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

[5] A. P. Scott, L. Radom, *J. Phys. Chem.* 1996, **100**, 16502.

[6] A. V. Marenich, C. J. Cramer and D. G. Truhlar *J. Phys. Chem.* B, 2009, **113**, 6378.

[7] G. Luchini, J. V. Alegre-REquena, I. Funes-Ardoiz, R. S. Paton, *F1000 Research* **2020**, *9*, 291.

[8] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955.

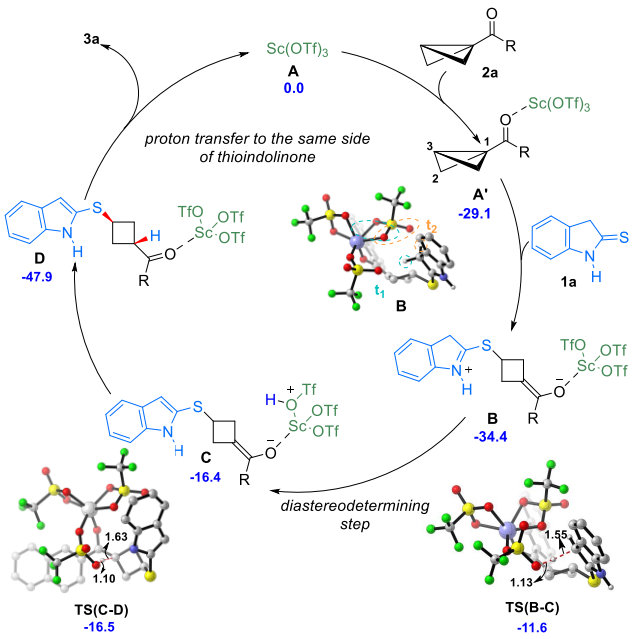
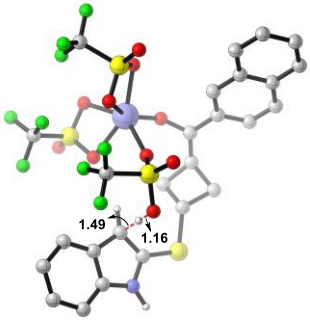


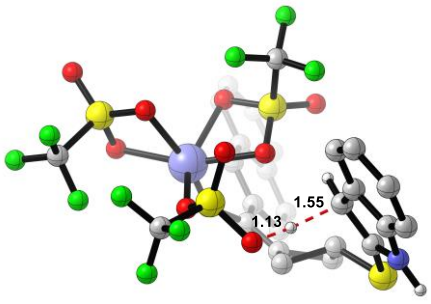
Figure S2. Proposed catalytic cycle. Relative Gibbs free energies (ΔG) are given in kcal/mol. Distances are given in Å.

This proton transfer is barrierless and very facile. Since the diastereomeric product formation depends upon the proton abstraction by triflate, the formation of **C** via **TS(B-C)** becomes the diastereodetermining step of the reaction. After subsequent steps, proton abstraction by triflate t_1 leads to the major product while abstraction by triflate t_2 gives the minor product. The **TS(B-C)** is more stable than **TS(B-C')** by 1.6 kcal mol^{-1} which corresponds to the dr of 1:14. This is in good agreement with experimental value of 1:20. Furthermore, the energy difference between diastereomeric products was found to be only 0.2 kcal mol^{-1} which suggests that the diastereoselectivity is not governed by thermodynamic stability of the products. The mechanistic study also validates this result where 1:1 mixture of products **3a** and **3a'** is found when the reaction is carried out in the presence of LDA and D_2O. From the free energy values and mechanistic studies, it is established that reaction is kinetically controlled.



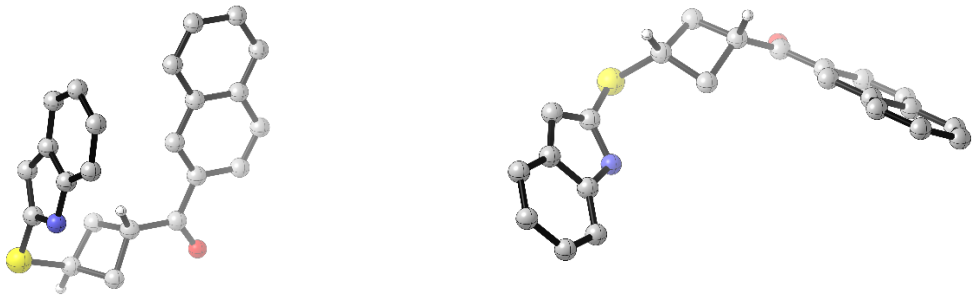
TS(B-C)

0.0



TS(B-C')

1.6



3a	**3a'**
0.0	-0.2

Figure S3. Structures of the diastereodetermining TSs and products with their relative free energies. Energies are given in kcal mol^{-1}. Some hydrogen atoms are removed for clarity.

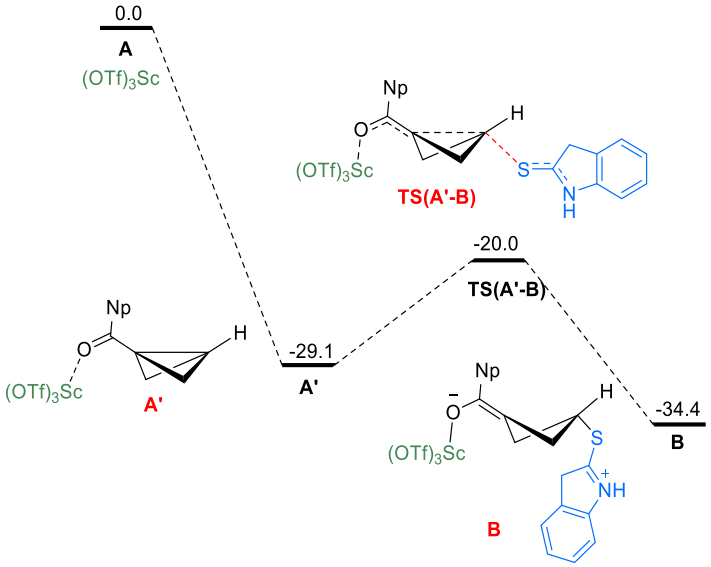


Figure S4. Formation of the intermediate **B**.

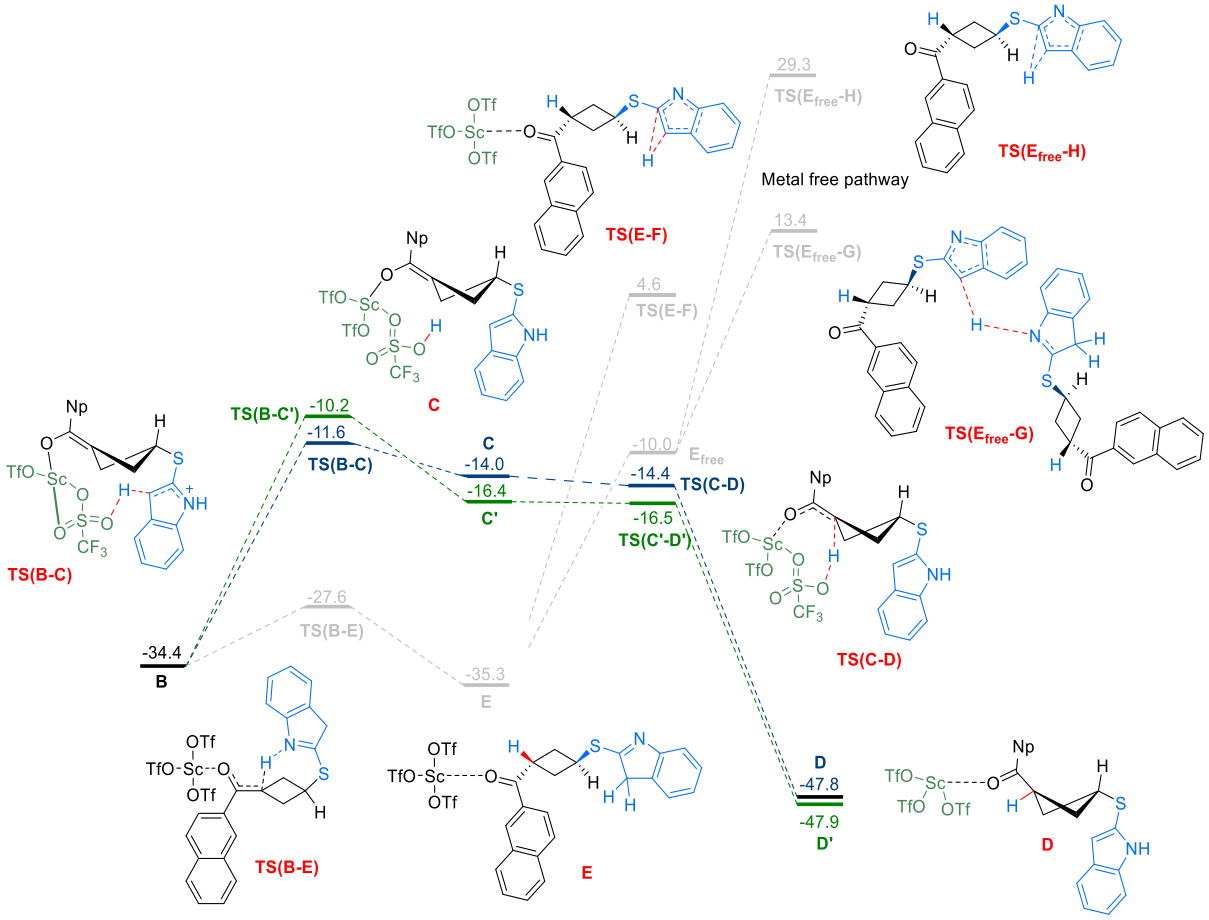


Figure S5. Different possible pathways from intermediate **B**.

Coordinates

A

Number of imaginary frequencies : 0 Electronic energy : HF=-2930.9756952
Zero-point correction= 0.087442 (Hartree/Particle)
Thermal correction to Energy= 0.113374
Thermal correction to Enthalpy= 0.114318
Thermal correction to Gibbs Free Energy= 0.025038
Sum of electronic and zero-point Energies= -2930.888254
Sum of electronic and thermal Energies= -2930.862321
Sum of electronic and thermal Enthalpies= -2930.861377
Sum of electronic and thermal Free Energies= -2930.950658

.....

Cartesian Coordinates

.....

21	0.000033	0.000023	-0.268164
8	1.568004	0.913943	-1.373246
8	0.008823	-1.814847	-1.373228
8	-1.068124	1.453918	0.867995
16	2.589481	0.896189	-0.234442
16	-2.071126	1.794219	-0.234604
16	-0.518391	-2.690657	-0.235032
8	3.930070	0.432995	-0.513736
8	1.793013	0.198194	0.868257
8	-1.576107	0.899808	-1.372898
8	-2.340565	3.186583	-0.514728

8	-0.725574	-1.651880	0.867480
8	-1.589401	-3.620242	-0.515270
6	0.981517	-3.665881	0.315686
6	2.684247	2.683208	0.315154
6	-3.665899	0.982956	0.315554
9	3.274459	3.390075	-0.640934
9	3.387726	2.745500	1.439327
9	1.448388	3.135482	0.522283
9	-3.438773	-0.312852	0.525370
9	-4.572613	1.138115	-0.641475
9	-4.072646	1.563112	1.438283
9	0.682024	-4.309123	1.437748
9	1.301826	-4.527891	-0.641644
9	1.989561	-2.820859	0.526968

A'

Number of imaginary frequencies : 0 Electronic energy : HF=-3585.0485447
Zero-point correction= 0.314890 (Hartree/Particle)
Thermal correction to Energy= 0.354919
Thermal correction to Enthalpy= 0.355864
Thermal correction to Gibbs Free Energy= 0.234816
Sum of electronic and zero-point Energies= -3584.733655
Sum of electronic and thermal Energies= -3584.693625
Sum of electronic and thermal Enthalpies= -3584.692681
Sum of electronic and thermal Free Energies= -3584.813728

Cartesian Coordinates

21	0.957734	-0.475361	0.106004
8	-0.684446	-2.039588	-0.150663
8	4.489744	1.681961	1.725680
8	1.796459	-1.279486	-1.737693
16	-0.100234	-2.939778	0.907982
16	1.026052	-0.351564	-2.659418
16	3.038619	1.585936	1.713690
8	-0.979115	-3.404489	1.972042
8	1.170637	-2.212400	1.338337
8	0.209359	0.486629	-1.680477
8	0.333317	-0.917119	-3.800457
8	2.555211	0.522428	0.676101
8	2.285025	1.477146	2.962758
6	2.399226	3.118426	0.860358
6	0.514443	-4.453521	0.003816
6	2.310651	0.839339	-3.308421
9	-0.527697	-5.059650	-0.561478
9	1.095227	-5.269524	0.880035
9	1.389050	-4.089131	-0.927436
9	2.956401	1.392657	-2.284386
9	1.696714	1.783561	-4.018996
9	3.165677	0.172740	-4.078831
9	1.088168	2.978429	0.598801
9	2.573016	4.173673	1.656191
9	3.048228	3.311794	-0.288596
8	-0.385940	0.434866	1.263384
6	-1.500360	0.574949	3.296561
6	-0.320900	0.143988	4.156546
1	0.609231	-0.086125	3.648483
1	-0.205015	0.704011	5.085326

6	-1.450696	-0.799141	4.032817
6	-2.601699	0.124668	4.231043
1	-2.686352	0.654615	5.181487
1	-3.551794	-0.168007	3.791331
6	-1.487741	0.658584	1.865563
6	-2.682841	0.991746	1.088916
6	-3.787123	1.692942	1.665477
6	-2.733425	0.618771	-0.250584
6	-4.891902	1.986453	0.906711
1	-3.730177	2.030038	2.693538
6	-3.863789	0.899652	-1.045043
1	-1.905893	0.087014	-0.697963
6	-4.973217	1.595989	-0.460161
1	-5.721168	2.536095	1.343231
6	-6.102551	1.877956	-1.269084
1	-6.946142	2.405223	-0.832221
6	-3.918743	0.514560	-2.413832
1	-3.066722	-0.003944	-2.845177
6	-5.030024	0.805322	-3.170828
1	-5.070444	0.513073	-4.215472
6	-6.128762	1.489903	-2.592007
1	-6.999506	1.711272	-3.202227
1	-1.457762	-1.748233	3.510618

TS(A'-B).log

Number of imaginary frequencies : 1 Electronic energy : HF=-4347.1003006
Zero-point correction= 0.448433 (Hartree/Particle)
Thermal correction to Energy= 0.497079
Thermal correction to Enthalpy= 0.498023
Thermal correction to Gibbs Free Energy= 0.357795
Sum of electronic and zero-point Energies= -4346.651867
Sum of electronic and thermal Energies= -4346.603221
Sum of electronic and thermal Enthalpies= -4346.602277
Sum of electronic and thermal Free Energies= -4346.742505

.....

Cartesian Coordinates

.....

21	0.718402	1.013410	-0.096392
8	1.271337	-0.321641	1.698463
8	-2.546498	3.399735	-1.834968
8	1.153931	2.655001	1.336212
16	-0.162896	-0.626580	2.020397
16	2.594647	2.807369	0.903456
16	-1.916664	2.088147	-1.867481
8	-0.558374	-2.025318	2.159219
8	-0.957810	0.196375	1.018775
8	2.742167	1.738879	-0.179215
8	3.630229	2.882338	1.916019
8	-0.509271	2.110727	-1.216448
8	-2.679749	0.901650	-1.460742
6	-1.408151	1.769216	-3.631416
6	-0.544917	0.190060	3.653321
6	2.628033	4.406945	-0.057606
9	0.112849	-0.438611	4.623857
9	-1.863468	0.089727	3.862212
9	-0.194766	1.468920	3.616601
9	1.722925	4.351069	-1.034815
9	3.842274	4.575694	-0.578680

9	2.343259	5.414128	0.764570
9	-0.740500	0.605767	-3.705016
9	-2.497261	1.692757	-4.399603
9	-0.619609	2.750100	-4.070092
8	1.066713	-0.515973	-1.233584
6	0.200038	-2.531263	-1.994287
6	-1.219518	-2.008644	-2.098841
1	-1.425631	-0.987712	-1.798514
1	-1.725658	-2.285780	-3.027366
6	-1.193499	-3.077057	-1.061466
6	-0.201411	-3.975790	-1.736734
1	-0.579092	-4.514714	-2.610832
1	0.433549	-4.591539	-1.102537
6	1.255277	-1.795740	-1.458537
6	2.578370	-2.363787	-1.159289
6	3.004594	-3.607265	-1.720414
6	3.445510	-1.671652	-0.323921
6	4.235454	-4.129935	-1.411037
1	2.366659	-4.120615	-2.430149
6	4.715531	-2.190457	0.013629
1	3.153756	-0.718294	0.093818
6	5.124062	-3.451611	-0.531001
1	4.553772	-5.070154	-1.853433
6	6.400636	-3.964379	-0.186185
1	6.713137	-4.919983	-0.598929
6	5.597160	-1.487207	0.880500
1	5.278286	-0.530053	1.284670
6	6.829136	-2.013032	1.196218
1	7.498697	-1.472781	1.858582
6	7.232475	-3.261553	0.658885
1	8.207597	-3.664217	0.917310
1	-1.076552	-2.843198	-0.009805
6	-4.626147	-0.698053	1.123077
6	-5.825557	-1.307907	0.741563
6	-7.072378	-0.769014	1.028071
6	-7.085564	0.442372	1.730472
6	-5.896028	1.069484	2.117564
6	-4.650233	0.504028	1.813726
6	-3.490340	-1.544650	0.626879
6	-4.180327	-2.707790	-0.055400
1	-7.992815	-1.255876	0.721682
1	-8.038292	0.901957	1.974400
1	-5.939500	2.010525	2.656624
1	-3.724274	0.985869	2.108917
7	-5.504911	-2.498171	0.045051
1	-6.186470	-3.137037	-0.343506
16	-3.473950	-4.043398	-0.791387
1	-2.829504	-1.912021	1.417271
1	-2.863881	-0.989443	-0.076860

B.log

Number of imaginary frequencies : 0 Electronic energy : HF=-4347.1120422
Zero-point correction= 0.450078 (Hartree/Particle)
Thermal correction to Energy= 0.498678
Thermal correction to Enthalpy= 0.499622
Thermal correction to Gibbs Free Energy= 0.359681
Sum of electronic and zero-point Energies= -4346.661964
Sum of electronic and thermal Energies= -4346.613364

Sum of electronic and thermal Enthalpies= -4346.612420
Sum of electronic and thermal Free Energies= -4346.752361

Cartesian Coordinates

21	0.851097	1.045551	-0.160916
8	1.311559	-0.270269	1.705650
8	-2.461932	3.416401	-1.900057
8	1.055845	2.730309	1.342525
16	-0.131406	-0.578251	1.955929
16	2.478233	3.032873	0.946625
16	-1.890923	2.076343	-1.882950
8	-0.534920	-1.975337	2.128224
8	-0.892187	0.198496	0.900058
8	2.777906	1.986885	-0.127647
8	3.473749	3.229979	1.983730
8	-0.465044	2.060346	-1.301593
8	-2.711104	0.959978	-1.386724
6	-1.494443	1.637119	-3.648508
6	-0.624758	0.260484	3.546770
6	2.369359	4.621885	-0.024248
9	-0.026893	-0.341768	4.572190
9	-1.958149	0.132347	3.671615
9	-0.306638	1.545840	3.523390
9	1.510306	4.467232	-1.032866
9	3.574430	4.926169	-0.505792
9	1.946429	5.596544	0.779862
9	-0.870873	0.449032	-3.695273
9	-2.629141	1.555780	-4.351756
9	-0.702985	2.563579	-4.188701
8	1.327854	-0.427937	-1.248982
6	0.309632	-2.443748	-1.752339
6	-1.092461	-1.887410	-1.764633
1	-1.263068	-0.903049	-1.341204
1	-1.580499	-1.949798	-2.745319
6	-1.406971	-3.119352	-0.889396
6	-0.185467	-3.863636	-1.494884
1	-0.438642	-4.414997	-2.411068
1	0.385645	-4.505251	-0.820559
6	1.424689	-1.763696	-1.393271
6	2.737753	-2.368161	-1.094215
6	3.076179	-3.671594	-1.565671
6	3.662803	-1.669665	-0.335582
6	4.283594	-4.244669	-1.248515
1	2.383873	-4.199673	-2.212707
6	4.914689	-2.235765	0.007670
1	3.430624	-0.670650	0.014184
6	5.236167	-3.555337	-0.449256
1	4.532416	-5.234798	-1.622319
6	6.492194	-4.116737	-0.100122
1	6.735049	-5.117192	-0.449702
6	5.862805	-1.529365	0.797577
1	5.612845	-0.528763	1.140626
6	7.071885	-2.102671	1.121262
1	7.789164	-1.555253	1.725818
6	7.389540	-3.407848	0.668359
1	8.347483	-3.847863	0.930675
1	-1.229447	-2.927955	0.168839
6	-4.731192	-0.859570	1.123016
6	-5.831922	-1.605495	0.694300

6	-7.144877	-1.286299	1.011692
6	-7.328587	-0.149320	1.805845
6	-6.238985	0.613188	2.247300
6	-4.925045	0.267773	1.908570
6	-3.486257	-1.480464	0.565896
6	-4.010099	-2.673364	-0.184284
1	-7.984886	-1.879232	0.664721
1	-8.335722	0.145719	2.081893
1	-6.418255	1.490328	2.860548
1	-4.077705	0.853239	2.248681
7	-5.337317	-2.684842	-0.088698
1	-5.928777	-3.382158	-0.525186
16	-3.119857	-3.873649	-1.017107
1	-2.753929	-1.785387	1.321628
1	-2.958283	-0.788298	-0.104899

TS(B-C)

Number of imaginary frequencies : 1 Electronic energy : HF=-4347.0879653
Zero-point correction= 0.445480 (Hartree/Particle)
Thermal correction to Energy= 0.493181
Thermal correction to Enthalpy= 0.494125
Thermal correction to Gibbs Free Energy= 0.358287
Sum of electronic and zero-point Energies= -4346.642485
Sum of electronic and thermal Energies= -4346.594785
Sum of electronic and thermal Enthalpies= -4346.593840
Sum of electronic and thermal Free Energies= -4346.729678

.....

Cartesian Coordinates

.....

21	0.845892	1.234713	-0.263392
8	1.796811	0.597633	1.597820
8	-2.676691	0.925316	0.745274
8	-0.152205	2.922629	0.981327
16	0.924287	-0.619837	1.840148
16	0.778678	3.960500	0.421332
16	-2.452745	0.892657	-0.689694
8	1.566572	-1.880471	2.160572
8	-0.030824	-0.599235	0.662084
8	1.718138	3.154681	-0.484791
8	1.384608	4.932113	1.310502
8	-1.085728	1.242783	-1.200300
8	-2.944350	-0.402438	-1.379936
6	-3.538803	2.164309	-1.520839
6	-0.191363	-0.175998	3.271635
6	-0.260608	4.914101	-0.804268
9	0.501539	-0.204008	4.406518
9	-1.171510	-1.087688	3.316333
9	-0.712381	1.029086	3.081726
9	-0.652193	4.097288	-1.791466
9	0.452312	5.913449	-1.315878
9	-1.336475	5.395379	-0.181843
9	-3.316191	2.153906	-2.829847
9	-4.809159	1.868842	-1.266167
9	-3.233600	3.353589	-1.010688
8	1.867448	0.197752	-1.448881
6	1.435745	-2.001166	-2.108465
6	-0.066780	-1.897230	-2.181416
1	-0.550671	-1.029717	-1.751200

1	-0.460425	-2.071147	-3.191134
6	-0.051965	-3.211868	-1.363947
6	1.372923	-3.513644	-1.917021
1	1.339989	-4.074387	-2.860665
1	2.086614	-3.979925	-1.234610
6	2.309580	-1.070617	-1.671166
6	3.719482	-1.342738	-1.325644
6	4.425003	-2.416888	-1.944637
6	4.371082	-0.572879	-0.376890
6	5.721147	-2.704953	-1.592611
1	3.935430	-2.990135	-2.724918
6	5.706539	-0.847360	0.007935
1	3.849125	0.245551	0.105430
6	6.401416	-1.939426	-0.606942
1	6.250008	-3.520544	-2.079406
6	7.739445	-2.210175	-0.217690
1	8.264779	-3.037635	-0.688115
6	6.377589	-0.072897	0.993511
1	5.845239	0.751873	1.460173
6	7.674822	-0.362774	1.351683
1	8.177596	0.235126	2.106280
6	8.362760	-1.440617	0.739859
1	9.386360	-1.657940	1.031274
1	0.021821	-3.003329	-0.296181
6	-3.945325	-2.465395	0.814787
6	-4.749756	-3.449181	0.199230
6	-6.101871	-3.612435	0.495977
6	-6.642759	-2.759030	1.456655
6	-5.856190	-1.777593	2.087810
6	-4.509118	-1.614323	1.772196
6	-2.624693	-2.536083	0.198491
6	-2.662478	-3.650652	-0.671004
1	-6.705613	-4.370915	0.007126
1	-7.690775	-2.855917	1.722610
1	-6.311220	-1.134447	2.834871
1	-3.901812	-0.851775	2.247520
7	-3.933160	-4.145548	-0.696688
1	-4.243907	-4.888624	-1.305313
16	-1.409116	-4.433024	-1.609971
1	-1.717085	-2.146811	0.641629
1	-2.810991	-1.333814	-0.757294

C

Number of imaginary frequencies : 0 Electronic energy : HF=-4347.1017874
Zero-point correction= 0.447240 (Hartree/Particle)
Thermal correction to Energy= 0.495693
Thermal correction to Enthalpy= 0.496637
Thermal correction to Gibbs Free Energy= 0.358999
Sum of electronic and zero-point Energies= -4346.654548
Sum of electronic and thermal Energies= -4346.606095
Sum of electronic and thermal Enthalpies= -4346.605150
Sum of electronic and thermal Free Energies= -4346.742788

.....

Cartesian Coordinates

.....

21	0.146392	1.249192	-0.779764
8	1.565933	2.036505	-2.163363
8	0.672872	-1.135018	2.988518

8	-0.210085	2.950318	0.594105
16	2.805217	1.454498	-1.481131
16	-1.419825	3.472716	-0.151492
16	-0.271219	-1.069711	1.890648
8	3.771629	0.756346	-2.302930
8	2.197455	0.720820	-0.296295
8	-1.503786	2.542659	-1.355203
8	-1.550723	4.898740	-0.366484
8	-0.297196	0.134255	1.025579
8	-0.201069	-2.374906	1.029287
6	-2.007629	-1.140572	2.585851
6	3.627856	2.972488	-0.758708
6	-2.875992	2.939314	0.891216
9	3.861267	3.828730	-1.751525
9	4.768202	2.634922	-0.172861
9	2.801422	3.524151	0.129983
9	-2.874792	1.604122	1.011834
9	-4.004853	3.321901	0.292006
9	-2.791729	3.493532	2.095633
9	-2.873873	-1.219869	1.583479
9	-2.109014	-2.207098	3.369908
9	-2.211288	-0.029480	3.285021
8	-0.521795	-0.233496	-1.752250
6	-0.009820	-2.473133	-1.747152
6	1.476767	-2.293452	-1.988773
1	1.708309	-1.869260	-2.972744
1	2.039653	-1.718285	-1.249023
6	1.632117	-3.840191	-1.933067
6	0.075613	-3.991643	-1.858826
1	-0.293608	-4.580723	-1.012667
1	-0.370394	-4.388655	-2.778826
6	-0.964750	-1.498687	-1.703228
6	-2.419211	-1.668783	-1.495558
6	-3.007821	-2.953904	-1.298796
6	-3.223142	-0.542549	-1.417050
6	-4.345154	-3.074055	-1.012321
1	-2.398656	-3.846203	-1.367289
6	-4.602582	-0.637870	-1.113772
1	-2.791631	0.438435	-1.575512
6	-5.182481	-1.929747	-0.900065
1	-4.781025	-4.057913	-0.859790
6	-6.561671	-2.018860	-0.579284
1	-7.002343	-2.999706	-0.420939
6	-5.420043	0.518199	-0.988146
1	-4.971139	1.495258	-1.137356
6	-6.754291	0.398611	-0.670518
1	-7.372394	1.286267	-0.573974
6	-7.330222	-0.880403	-0.467118
1	-8.384737	-0.959348	-0.219551
1	2.092480	-4.288965	-2.814200
6	4.933012	-1.476703	0.460356
6	3.915934	-1.382565	1.453282
6	3.914474	-0.381778	2.433054
6	4.957770	0.533626	2.406598
6	5.979489	0.459199	1.432733
6	5.973559	-0.528668	0.459519
6	4.617426	-2.609809	-0.356002
6	3.451603	-3.156378	0.133950
1	3.119617	-0.323188	3.168501
1	4.988258	1.326699	3.148180

1	6.775283	1.198079	1.443764
1	6.755343	-0.574676	-0.292868
7	3.019888	-2.401255	1.221200
1	2.227999	-2.633624	1.799104
16	2.506193	-4.525036	-0.435634
1	5.169857	-2.978819	-1.207755
1	-0.228970	-2.247212	-0.016748

TS(B-C')

Number of imaginary frequencies : 1 Electronic energy : HF=-4347.0879814
Zero-point correction= 0.445587 (Hartree/Particle)
Thermal correction to Energy= 0.493148
Thermal correction to Enthalpy= 0.494092
Thermal correction to Gibbs Free Energy= 0.359414
Sum of electronic and zero-point Energies= -4346.642394
Sum of electronic and thermal Energies= -4346.594834
Sum of electronic and thermal Enthalpies= -4346.593890
Sum of electronic and thermal Free Energies= -4346.728567

.....

Cartesian Coordinates

.....

21	0.705884	0.853174	-0.919297
8	0.041505	-0.594884	0.535577
8	-2.198496	1.839262	-3.562560
8	0.858033	2.066404	0.947717
16	-0.400555	-0.893874	1.935052
16	2.248353	2.594308	0.650509
16	-1.464876	1.949259	-2.317997
8	0.619303	-1.174443	2.923566
8	-1.485181	-1.988945	1.867725
8	2.574125	1.954355	-0.687213
8	3.253574	2.517906	1.694263
8	-1.475635	0.767027	-1.365164
8	0.003155	2.328692	-2.366239
6	-2.268254	3.303980	-1.314650
6	-1.391532	0.607003	2.523821
6	1.981841	4.402202	0.269633
9	-0.613292	1.394622	3.244691
9	-2.410727	0.171750	3.262113
9	-1.869665	1.266899	1.463933
9	1.062258	4.528089	-0.687419
9	3.131075	4.934818	-0.136984
9	1.562486	5.015357	1.375878
9	-1.561174	3.513383	-0.201972
9	-2.322547	4.422099	-2.030609
9	-3.504287	2.915467	-0.985091
8	1.484150	-0.546218	-1.895371
6	0.833405	-2.762744	-2.165094
6	-0.631285	-2.459723	-2.377128
1	-0.975867	-1.436166	-2.240629
1	-1.022695	-2.859632	-3.320824
6	-0.828016	-3.476790	-1.224716
6	0.516906	-4.151494	-1.616138
1	0.386647	-4.913483	-2.395453
1	1.133414	-4.546060	-0.806201
6	1.782249	-1.869743	-1.806476
6	3.094018	-2.211995	-1.222162
6	3.688391	-3.490443	-1.443925

6	3.759091	-1.301404	-0.417494
6	4.876820	-3.829140	-0.843380
1	3.207487	-4.187534	-2.121913
6	4.979496	-1.624661	0.222987
1	3.355460	-0.308224	-0.267062
6	5.555097	-2.919464	0.013691
1	5.322047	-4.803295	-1.029623
6	6.779055	-3.238247	0.657609
1	7.217386	-4.219902	0.495894
6	5.643613	-0.698717	1.073735
1	5.194414	0.277943	1.236951
6	6.827575	-1.041387	1.687140
1	7.327693	-0.330566	2.338435
6	7.401109	-2.320586	1.475849
1	8.336436	-2.575712	1.965830
1	-0.693928	-2.984933	-0.263361
6	-4.377072	-1.337098	0.449104
6	-5.207355	-2.440502	0.739471
6	-6.424678	-2.316549	1.405959
6	-6.812563	-1.028177	1.771753
6	-6.008103	0.087300	1.476618
6	-4.786169	-0.052184	0.821331
6	-3.165254	-1.857295	-0.179681
6	-3.385643	-3.249196	-0.345819
1	-7.045168	-3.179549	1.626803
1	-7.755774	-0.884671	2.289435
1	-6.349097	1.076633	1.766047
1	-4.170438	0.809720	0.589502
7	-4.567317	-3.581333	0.239282
1	-4.889863	-4.529176	0.371879
16	-2.378909	-4.474889	-1.080884
1	-2.220897	-1.931294	0.971160
1	-2.533674	-1.271576	-0.834956

C'

Number of imaginary frequencies : 0 Electronic energy : HF=-4347.1074228
Zero-point correction= 0.448547 (Hartree/Particle)
Thermal correction to Energy= 0.496754
Thermal correction to Enthalpy= 0.497698
Thermal correction to Gibbs Free Energy= 0.361093
Sum of electronic and zero-point Energies= -4346.658876
Sum of electronic and thermal Energies= -4346.610669
Sum of electronic and thermal Enthalpies= -4346.609725
Sum of electronic and thermal Free Energies= -4346.746330

.....

Cartesian Coordinates

.....

21	1.083581	0.480388	-0.572199
8	1.261127	-0.617475	-2.412710
8	2.940748	-1.077934	2.544386
8	2.185601	2.208260	-1.441211
16	1.127901	-1.966645	-3.028774
16	0.953089	3.079743	-1.563295
16	2.912422	-0.138122	1.435199
8	1.074447	-2.049673	-4.468617
8	-0.065547	-2.791723	-2.412529
8	-0.160229	2.153969	-1.077265
8	0.735506	3.822235	-2.787503

8	2.864498	-0.692037	0.026463
8	1.791360	0.887502	1.447122
6	4.480293	0.873970	1.498315
6	2.618909	-2.926853	-2.408515
6	1.099391	4.329346	-0.181089
9	3.694582	-2.165892	-2.543362
9	2.735481	-4.032025	-3.133824
9	2.426574	-3.240907	-1.129254
9	1.382935	3.702286	0.964249
9	-0.062031	4.972453	-0.057256
9	2.068701	5.192101	-0.469717
9	4.478396	1.744241	0.492210
9	4.523480	1.521634	2.659870
9	5.523944	0.055566	1.391122
8	-0.292750	-0.676049	-0.099459
6	-0.932556	-2.827760	0.448435
6	0.307269	-3.226269	1.228174
1	0.971793	-3.903212	0.680261
1	0.911418	-2.427919	1.660250
6	-0.642653	-4.017187	2.180420
6	-1.779251	-3.904156	1.111950
1	-2.761038	-3.581744	1.467561
1	-1.887473	-4.831125	0.536596
6	-1.263114	-1.603787	-0.041673
6	-2.590559	-1.188470	-0.537210
6	-3.572731	-2.148397	-0.921151
6	-2.882562	0.160032	-0.644751
6	-4.806739	-1.745051	-1.368829
1	-3.334040	-3.205512	-0.887021
6	-4.144684	0.601940	-1.109215
1	-2.150179	0.899064	-0.344309
6	-5.135940	-0.365407	-1.472260
1	-5.546383	-2.484077	-1.665551
6	-6.401482	0.086843	-1.929542
1	-7.153417	-0.647814	-2.206082
6	-4.453989	1.984889	-1.218076
1	-3.695069	2.707919	-0.934985
6	-5.690616	2.391980	-1.664729
1	-5.919603	3.450555	-1.745730
6	-6.673142	1.434322	-2.022347
1	-7.645206	1.769539	-2.372409
1	-0.326811	-5.030109	2.443682
6	-2.822938	0.170018	2.795672
6	-1.448384	0.544606	2.746897
6	-1.042412	1.831601	2.367807
6	-2.033968	2.741421	2.020956
6	-3.401726	2.392285	2.068712
6	-3.802153	1.121153	2.455010
6	-2.865452	-1.206376	3.186664
6	-1.563659	-1.627422	3.354821
1	0.004378	2.103340	2.339614
1	-1.744279	3.736880	1.697570
1	-4.149063	3.126455	1.784107
1	-4.854424	0.853498	2.472982
7	-0.706261	-0.559603	3.102789
1	0.301141	-0.605544	3.135739
16	-0.974733	-3.223836	3.817342
1	-0.348524	-2.641470	-1.441887
1	-3.741018	-1.823228	3.326275

TS(C-D)

Number of imaginary frequencies : 1 Electronic energy : HF=-4347.1016891
Zero-point correction= 0.445609 (Hartree/Particle)
Thermal correction to Energy= 0.493424
Thermal correction to Enthalpy= 0.494369
Thermal correction to Gibbs Free Energy= 0.358422
Sum of electronic and zero-point Energies= -4346.656080
Sum of electronic and thermal Energies= -4346.608265
Sum of electronic and thermal Enthalpies= -4346.607321
Sum of electronic and thermal Free Energies= -4346.743267

.....

Cartesian Coordinates

.....

21	0.116297	1.252245	-0.774639
8	1.530818	2.067220	-2.144125
8	0.719629	-1.079091	2.950476
8	-0.259642	2.951860	0.588789
16	2.774548	1.489720	-1.464844
16	-1.481206	3.453672	-0.152489
16	-0.244659	-1.078734	1.866644
8	3.750086	0.810942	-2.291599
8	2.168383	0.736047	-0.291358
8	-1.554396	2.518280	-1.353137
8	-1.633879	4.876760	-0.372008
8	-0.330969	0.120221	0.989509
8	-0.152256	-2.377174	1.020689
6	-1.965640	-1.178538	2.592004
6	3.579790	3.005917	-0.719300
6	-2.926010	2.901828	0.897249
9	3.817381	3.873471	-1.701147
9	4.715853	2.668733	-0.125542
9	2.740831	3.542963	0.166523
9	-2.907573	1.567686	1.019597
9	-4.061504	3.269893	0.300967
9	-2.843949	3.459872	2.099900
9	-2.848222	-1.281802	1.604417
9	-2.035677	-2.241622	3.385109
9	-2.183506	-0.067219	3.287640
8	-0.535827	-0.228230	-1.789272
6	0.008860	-2.458333	-1.681655
6	1.489013	-2.266820	-1.972403
1	1.679629	-1.837951	-2.962913
1	2.075861	-1.693155	-1.251095
6	1.654515	-3.812537	-1.933713
6	0.101325	-3.976972	-1.835111
1	-0.249560	-4.591796	-0.999888
1	-0.356854	-4.348776	-2.759372
6	-0.962405	-1.487779	-1.703039
6	-2.412356	-1.674701	-1.489133
6	-2.981414	-2.963714	-1.262589
6	-3.230657	-0.557086	-1.429205
6	-4.315375	-3.095617	-0.966805
1	-2.359333	-3.848089	-1.312422
6	-4.606227	-0.664675	-1.115677
1	-2.812420	0.425915	-1.609471
6	-5.167142	-1.960106	-0.873344
1	-4.737291	-4.081552	-0.790785
6	-6.543062	-2.060855	-0.542733

1	-6.970045	-3.043892	-0.362431
6	-5.437681	0.483224	-1.007259
1	-5.001939	1.462822	-1.177289
6	-6.768169	0.352348	-0.679103
1	-7.397465	1.233330	-0.595235
6	-7.325534	-0.930238	-0.447951
1	-8.377399	-1.018201	-0.192309
1	2.105456	-4.251196	-2.824814
6	4.992492	-1.459351	0.423887
6	3.972029	-1.350185	1.411987
6	3.970783	-0.338398	2.380699
6	5.018987	0.571009	2.349345
6	6.045318	0.480719	1.381276
6	6.038465	-0.517010	0.418409
6	4.673264	-2.598080	-0.383017
6	3.503029	-3.133897	0.108745
1	3.171721	-0.267550	3.110503
1	5.049820	1.372362	3.081979
1	6.845102	1.215403	1.388537
1	6.823779	-0.575240	-0.329501
7	3.073453	-2.367990	1.188772
1	2.270888	-2.582952	1.758714
16	2.552753	-4.502393	-0.452606
1	5.226569	-2.978919	-1.228985
1	-0.161373	-2.271421	-0.074737

D

Number of imaginary frequencies : 0 Electronic energy : HF=-4347.1518187
Zero-point correction= 0.451548 (Hartree/Particle)
Thermal correction to Energy= 0.499563
Thermal correction to Enthalpy= 0.500507
Thermal correction to Gibbs Free Energy= 0.363502
Sum of electronic and zero-point Energies= -4346.700271
Sum of electronic and thermal Energies= -4346.652256
Sum of electronic and thermal Enthalpies= -4346.651312
Sum of electronic and thermal Free Energies= -4346.788316

.....

Cartesian Coordinates

.....

21	-0.076358	-0.802400	-0.226680
8	0.265550	-2.290757	-1.815665
16	1.713779	-1.940101	-2.068337
8	1.969184	-0.839179	-1.044140
8	2.143371	-1.701095	-3.433231
6	2.686931	-3.398141	-1.419069
9	2.447164	-3.550792	-0.117312
9	2.313808	-4.492282	-2.078105
9	3.983602	-3.167217	-1.612189
8	-0.972481	0.265131	-1.727141
6	-1.609236	1.258955	-2.176587
6	-2.960567	1.528836	-1.703270
6	-3.584302	0.587030	-0.886328
6	-4.863480	0.821205	-0.346338
6	-5.488988	-0.130094	0.506940
6	-6.734741	0.125209	1.031988
6	-7.403014	1.336625	0.722927
6	-6.819239	2.278921	-0.098695
6	-5.535632	2.051147	-0.652089

6	-4.883584	2.998469	-1.493668
6	-3.637779	2.751635	-2.008071
1	-3.155461	3.502083	-2.623491
1	-5.389432	3.933503	-1.716710
1	-7.335570	3.207295	-0.326279
1	-8.386512	1.524102	1.143853
1	-7.210132	-0.597608	1.687488
1	-4.957377	-1.048202	0.740864
1	-3.085643	-0.344207	-0.650944
6	-0.901077	2.180247	-3.119168
1	-1.600860	2.618475	-3.832296
6	0.442467	1.641789	-3.691112
1	0.668139	2.143117	-4.636512
1	0.554010	0.562809	-3.812594
6	1.163509	2.292448	-2.491229
1	1.229289	1.579696	-1.675582
6	-0.050407	3.221714	-2.271473
1	0.033975	4.160655	-2.824516
1	-0.356040	3.419555	-1.242081
16	2.850307	2.983936	-2.691380
6	3.353849	2.862878	-1.002270
6	3.516353	3.850319	-0.057281
6	3.826872	3.198793	1.182825
6	4.068006	3.643400	2.495703
6	4.274309	2.703799	3.497360
6	4.242721	1.319692	3.219044
6	4.020453	0.848237	1.930645
6	3.828350	1.798223	0.921217
7	3.590764	1.623827	-0.421932
1	3.336000	0.741995	-0.845739
1	3.989173	-0.214773	1.710437
1	4.392616	0.610096	4.027642
1	4.453700	3.034992	4.516182
1	4.080169	4.706164	2.721118
1	3.410726	4.910480	-0.235323
8	0.830552	1.011284	0.503976
16	-0.332862	1.501382	1.352775
8	-1.344804	0.388465	1.185674
8	-0.784016	2.867300	1.143855
6	0.292099	1.368824	3.109269
9	-0.750314	1.459284	3.935246
9	0.897398	0.195477	3.270737
9	1.141731	2.361383	3.335968
8	0.244992	-2.167427	1.375349
16	-1.139032	-2.816430	1.356083
8	-1.871521	-2.884413	2.605106
8	-1.802517	-2.163152	0.161555
6	-0.810715	-4.585573	0.845730
9	-0.104789	-5.177075	1.807743
9	-0.134504	-4.632751	-0.298958
9	-1.983331	-5.200917	0.698793

TS(C'-D')

Number of imaginary frequencies : 1 Electronic energy : HF=-4347.1072555
Zero-point correction= 0.446878 (Hartree/Particle)
Thermal correction to Energy= 0.494314
Thermal correction to Enthalpy= 0.495259
Thermal correction to Gibbs Free Energy= 0.360703

Sum of electronic and zero-point Energies= -4346.660378
Sum of electronic and thermal Energies= -4346.612941
Sum of electronic and thermal Enthalpies= -4346.611997
Sum of electronic and thermal Free Energies= -4346.746553

.....

Cartesian Coordinates

.....

21	1.079369	0.543867	-0.577643
8	1.246360	-0.628008	-2.336786
8	2.827976	-0.844560	2.660020
8	2.088668	2.308678	-1.459537
16	1.170404	-1.982324	-2.967323
16	0.810910	3.109042	-1.620687
16	2.865336	0.020435	1.490228
8	1.062071	-2.028721	-4.407473
8	0.093896	-2.887918	-2.296187
8	-0.256755	2.128195	-1.142442
8	0.581945	3.818915	-2.861937
8	2.831411	-0.624366	0.120761
8	1.786733	1.085598	1.404437
6	4.469323	0.974533	1.527815
6	2.770746	-2.814413	-2.451233
6	0.850503	4.385673	-0.254993
9	3.771045	-1.966530	-2.653170
9	2.933372	-3.906916	-3.188208
9	2.697176	-3.142708	-1.163213
9	1.113306	3.790756	0.911315
9	-0.341888	4.977930	-0.189321
9	1.792547	5.285304	-0.521362
9	4.521341	1.773400	0.464769
9	4.511855	1.697844	2.643462
9	5.483129	0.113475	1.500854
8	-0.291238	-0.598351	-0.006706
6	-0.775748	-2.827711	0.347741
6	0.464423	-3.171270	1.164631
1	1.194904	-3.776288	0.618104
1	0.992284	-2.347480	1.643864
6	-0.457622	-4.056622	2.056782
6	-1.576918	-3.970180	0.968699
1	-2.578189	-3.707951	1.319125
1	-1.630616	-4.882656	0.364198
6	-1.190048	-1.577724	-0.028936
6	-2.528066	-1.224393	-0.537615
6	-3.439557	-2.220040	-0.998142
6	-2.897329	0.109497	-0.582377
6	-4.682536	-1.865989	-1.461137
1	-3.137933	-3.261191	-1.013388
6	-4.171660	0.500001	-1.057869
1	-2.215276	0.871476	-0.225548
6	-5.091838	-0.504105	-1.500451
1	-5.367883	-2.629629	-1.819202
6	-6.369778	-0.103654	-1.970449
1	-7.068179	-0.865215	-2.307605
6	-4.561149	1.866113	-1.102712
1	-3.855203	2.616218	-0.759778
6	-5.807976	2.222591	-1.563963
1	-6.099119	3.268343	-1.596259
6	-6.720016	1.228671	-2.000223
1	-7.701074	1.523928	-2.360974
1	-0.086268	-5.059458	2.284169

6	-2.799508	0.024919	2.826499
6	-1.436274	0.441775	2.827570
6	-1.060874	1.754632	2.510356
6	-2.071760	2.649845	2.181639
6	-3.429856	2.260594	2.188521
6	-3.799983	0.962335	2.509404
6	-2.808311	-1.370918	3.144198
6	-1.498092	-1.761281	3.321806
1	-0.021177	2.054116	2.506589
1	-1.805543	3.665666	1.903886
1	-4.193210	2.985910	1.924067
1	-4.843888	0.663708	2.492621
7	-0.668496	-0.656730	3.145825
1	0.338687	-0.675996	3.215713
16	-0.869786	-3.360702	3.719673
1	-0.258266	-2.746449	-1.291978
1	-3.667191	-2.020308	3.229201

D'

Number of imaginary frequencies : 0 Electronic energy : HF=-4347.1593312
Zero-point correction= 0.451366 (Hartree/Particle)
Thermal correction to Energy= 0.499339
Thermal correction to Enthalpy= 0.500283
Thermal correction to Gibbs Free Energy= 0.364935
Sum of electronic and zero-point Energies= -4346.707965
Sum of electronic and thermal Energies= -4346.659993
Sum of electronic and thermal Enthalpies= -4346.659048
Sum of electronic and thermal Free Energies= -4346.794396

.....

Cartesian Coordinates

.....

21	1.186503	0.075374	-0.766320
8	0.892056	-1.036329	-2.364818
8	3.072235	-1.222174	2.470516
8	2.376181	1.573801	-1.813526
16	0.286528	-2.343230	-2.956568
16	1.274313	2.615417	-1.874143
16	3.017939	-0.386824	1.283679
8	0.400731	-2.371401	-4.404956
8	-0.986764	-2.669241	-2.305923
8	0.125645	1.914874	-1.154091
8	0.989543	3.269229	-3.133637
8	2.886261	-1.068779	-0.067439
8	1.926394	0.668457	1.240955
6	4.615100	0.578299	1.189563
6	1.513754	-3.571186	-2.274654
6	1.827329	3.953321	-0.690156
9	2.753180	-3.241231	-2.628569
9	1.221251	-4.788563	-2.733530
9	1.426841	-3.579714	-0.931807
9	2.246977	3.410610	0.454959
9	0.797547	4.766051	-0.446418
9	2.820457	4.636056	-1.249774
9	4.592282	1.367358	0.119134
9	4.723907	1.315506	2.293090
9	5.630287	-0.275561	1.107010
8	-0.342304	-0.807707	0.187014
6	-1.219242	-2.915128	0.825466

6	0.007132	-3.142234	1.747566
1	0.616754	-3.999084	1.455989
1	0.666472	-2.284101	1.869820
6	-0.948911	-3.424836	2.938646
6	-2.175259	-3.328157	1.991730
1	-2.918810	-2.577662	2.263312
1	-2.677256	-4.284665	1.825885
6	-1.374937	-1.532139	0.261817
6	-2.648480	-1.020621	-0.210031
6	-3.768498	-1.884674	-0.411566
6	-2.764083	0.338413	-0.490389
6	-4.948893	-1.380884	-0.889573
1	-3.672743	-2.946427	-0.218240
6	-3.969378	0.876267	-0.985239
1	-1.927563	1.002839	-0.310049
6	-5.090514	0.005480	-1.188986
1	-5.795093	-2.040573	-1.058971
6	-6.297965	0.556434	-1.685042
1	-7.151233	-0.097706	-1.841340
6	-4.091790	2.260360	-1.288934
1	-3.232862	2.902947	-1.125129
6	-5.277184	2.762547	-1.773720
1	-5.368211	3.818449	-2.008850
6	-6.387368	1.903118	-1.969956
1	-7.317776	2.313117	-2.351947
1	-0.813048	-4.400420	3.412162
6	-2.502634	1.069761	2.835636
6	-1.107355	1.265598	2.611599
6	-0.609099	2.414087	1.983284
6	-1.530638	3.368874	1.571486
6	-2.915974	3.197373	1.788013
6	-3.408203	2.060773	2.413523
6	-2.643430	-0.198905	3.480728
6	-1.377364	-0.733057	3.623843
1	0.452384	2.544299	1.820414
1	-1.173342	4.260724	1.067113
1	-3.605534	3.965040	1.450277
1	-4.475125	1.929628	2.568079
7	-0.449711	0.163576	3.109390
1	0.541978	-0.004916	3.033301
16	-0.902138	-2.257887	4.370747
1	-1.259184	-3.578193	-0.045729
1	-3.555744	-0.664554	3.823898

TS(B-E)

Number of imaginary frequencies : 1 Electronic energy : HF=-4347.1129719
Zero-point correction= 0.444689 (Hartree/Particle)
Thermal correction to Energy= 0.492600
Thermal correction to Enthalpy= 0.493544
Thermal correction to Gibbs Free Energy= 0.356711
Sum of electronic and zero-point Energies= -4346.668283
Sum of electronic and thermal Energies= -4346.620372
Sum of electronic and thermal Enthalpies= -4346.619428
Sum of electronic and thermal Free Energies= -4346.756261

.....

Cartesian Coordinates

.....

21	-2.014768	-0.372433	-0.015456

8	-3.259457	-1.555594	1.368404
8	0.342241	-0.830890	-3.666458
8	-3.730036	0.658003	-0.938782
16	-2.996812	-2.880814	0.682951
16	-3.770093	1.804051	0.050284
16	0.392375	-0.311788	-2.306803
8	-2.589922	-4.010037	1.502074
8	-2.103373	-2.493875	-0.484614
8	-2.688601	1.430863	1.050628
8	-5.055191	2.253257	0.546791
8	-1.014920	-0.043120	-1.729696
8	1.273726	-0.946531	-1.319433
6	0.975461	1.454848	-2.439100
6	-4.622270	-3.321325	-0.119736
6	-2.996836	3.245749	-0.850306
9	-5.533912	-3.530506	0.827781
9	-4.464450	-4.424522	-0.848562
9	-5.006821	-2.313663	-0.902971
9	-1.749337	2.930122	-1.211684
9	-2.954599	4.295580	-0.019992
9	-3.713893	3.552995	-1.925381
9	1.114067	1.982255	-1.208195
9	2.163837	1.494335	-3.054439
9	0.102236	2.188719	-3.127908
8	-0.434269	-0.359498	1.101443
6	1.404385	-1.531312	1.851510
6	0.810534	-2.911153	1.569277
1	-0.151287	-3.095497	2.059724
1	0.720573	-3.202554	0.519698
6	1.987878	-3.511584	2.392734
6	2.290317	-2.098580	2.979825
1	3.341876	-1.800865	3.031962
1	1.845163	-1.985145	3.973893
6	0.727094	-0.319031	1.670903
6	1.303022	1.010314	1.937580
6	2.677488	1.175693	2.283839
6	0.509644	2.133610	1.758155
6	3.212444	2.431359	2.434229
1	3.314180	0.307301	2.402641
6	1.037490	3.436951	1.897235
1	-0.533744	2.016793	1.493272
6	2.418364	3.597334	2.246131
1	4.262716	2.548944	2.687316
6	2.942714	4.908915	2.375690
1	3.988701	5.033879	2.643071
6	0.235138	4.590067	1.675857
1	-0.804534	4.457324	1.390603
6	0.776466	5.848890	1.805144
1	0.161514	6.726982	1.632625
6	2.139229	6.008352	2.161885
1	2.551378	7.008185	2.262652
1	1.739616	-4.297523	3.109881
6	5.243640	-1.922649	-1.217231
6	4.253176	-1.095755	-0.669851
6	4.097553	0.235185	-1.030396
6	4.984049	0.735112	-1.988769
6	5.980016	-0.074239	-2.547220
6	6.120043	-1.416503	-2.166399
6	5.097468	-3.286934	-0.587141
6	3.934321	-3.046727	0.363026

1	3.309508	0.842967	-0.604398
1	4.883765	1.765345	-2.314133
1	6.651292	0.341265	-3.292345
1	6.892891	-2.038831	-2.607681
7	3.491739	-1.823993	0.276173
1	2.412608	-1.465578	0.898632
16	3.354758	-4.294983	1.419466
1	5.987316	-3.623517	-0.042980
1	4.842079	-4.071871	-1.309360

E

Number of imaginary frequencies : 0 Electronic energy : HF=-4347.13146
Zero-point correction= 0.449325 (Hartree/Particle)
Thermal correction to Energy= 0.497934
Thermal correction to Enthalpy= 0.498878
Thermal correction to Gibbs Free Energy= 0.358344
Sum of electronic and zero-point Energies= -4346.682135
Sum of electronic and thermal Energies= -4346.633526
Sum of electronic and thermal Enthalpies= -4346.632582
Sum of electronic and thermal Free Energies= -4346.773116

.....

Cartesian Coordinates

.....

21	1.387295	-1.444480	-0.088629
8	1.281943	-3.264203	-1.284344
8	-0.449719	0.107010	3.405215
8	3.295308	-1.894340	0.839091
16	0.152206	-3.886433	-0.480823
16	4.156670	-1.220065	-0.215340
16	-0.108354	0.685976	2.115258
8	-0.994580	-4.411534	-1.195927
8	-0.094546	-2.840939	0.601174
8	3.127698	-0.766496	-1.240359
8	5.348194	-1.900773	-0.676598
8	0.942917	-0.163522	1.351824
8	-1.171537	1.137959	1.209658
6	0.949445	2.183443	2.447856
6	0.959552	-5.298945	0.435905
6	4.706768	0.386721	0.567734
9	1.372072	-6.206335	-0.445038
9	0.073864	-5.839120	1.267786
9	2.000164	-4.827999	1.123411
9	3.638951	1.126079	0.875461
9	5.458580	1.050753	-0.316948
9	5.414207	0.133619	1.661955
9	1.341426	2.732419	1.291092
9	0.234245	3.076451	3.135511
9	2.026824	1.835312	3.152724
8	0.227402	-0.452004	-1.407889
6	-1.985280	0.289833	-1.700197
6	-2.478584	-1.147474	-1.984468
1	-1.723880	-1.795883	-2.435530
1	-2.918933	-1.660414	-1.129830
6	-3.466919	-0.568555	-3.039814
6	-2.809501	0.836708	-2.906316
1	-3.484351	1.659908	-2.669376
1	-2.206686	1.101521	-3.779618
6	-0.533636	0.544130	-1.580121

6	0.030920	1.889302	-1.599304
6	-0.800020	3.041291	-1.452933
6	1.410570	2.039043	-1.688777
6	-0.236718	4.288846	-1.385406
1	-1.871807	2.922961	-1.349198
6	2.011485	3.312320	-1.618212
1	2.040534	1.164995	-1.806553
6	1.174850	4.466779	-1.460558
1	-0.866222	5.164063	-1.252298
6	1.786782	5.741678	-1.368700
1	1.158731	6.620452	-1.251674
6	3.424392	3.469963	-1.660575
1	4.047366	2.585972	-1.754353
6	3.986096	4.721824	-1.560465
1	5.064917	4.840017	-1.586842
6	3.159488	5.864728	-1.418360
1	3.616667	6.846967	-1.342818
1	-3.363862	-1.012296	-4.033702
6	-6.620082	0.497342	0.827299
6	-5.242622	0.783634	0.841814
6	-4.616273	1.339599	1.953027
6	-5.416103	1.619706	3.067193
6	-6.789148	1.349036	3.059262
6	-7.406065	0.780185	1.934276
6	-6.922723	-0.118407	-0.516627
6	-5.528758	-0.084695	-1.140058
1	-3.547110	1.526464	1.946569
1	-4.961142	2.049070	3.955047
1	-7.385416	1.575426	3.938302
1	-8.471233	0.565335	1.939901
7	-4.618728	0.426293	-0.378515
1	-2.440022	0.649572	-0.769481
16	-5.274324	-0.721534	-2.756066
1	-7.641039	0.455427	-1.114664
1	-7.302908	-1.144752	-0.450725

E_{free}

Number of imaginary frequencies : 0 Electronic energy : HF=-1416.094461
Zero-point correction= 0.360438 (Hartree/Particle)
Thermal correction to Energy= 0.381318
Thermal correction to Enthalpy= 0.382262
Thermal correction to Gibbs Free Energy= 0.307404
Sum of electronic and zero-point Energies= -1415.734023
Sum of electronic and thermal Energies= -1415.713143
Sum of electronic and thermal Enthalpies= -1415.712199
Sum of electronic and thermal Free Energies= -1415.787057

.....

Cartesian Coordinates

.....

8	1.839257	-2.505570	1.484685
6	0.043300	-1.201066	0.583301
6	-0.973983	-2.265737	1.056739
1	-0.518823	-3.105730	1.584769
1	-1.793744	-1.852157	1.642699
6	-1.330700	-2.570042	-0.423839
6	-0.360004	-1.460280	-0.911052
1	-0.844938	-0.605593	-1.381019
1	0.443218	-1.823270	-1.558795

6	1.500363	-1.493921	0.884303
6	2.525498	-0.517492	0.386892
6	2.176535	0.654612	-0.343479
6	3.859396	-0.778710	0.649720
6	3.149556	1.520118	-0.784269
1	1.135857	0.869505	-0.560539
6	4.883419	0.094085	0.212655
1	4.109751	-1.677502	1.205638
6	4.524283	1.272371	-0.522549
1	2.875935	2.411549	-1.342758
6	5.553257	2.146949	-0.961695
1	5.280549	3.039580	-1.518723
6	6.257323	-0.161027	0.478605
1	6.523224	-1.055155	1.036145
6	7.230687	0.706644	0.039006
1	8.277088	0.503525	0.246788
6	6.874499	1.871030	-0.687712
1	7.652726	2.547630	-1.028929
1	-1.025207	-3.571660	-0.739814
6	-5.050033	0.891883	-0.202559
6	-3.741790	1.118203	0.266113
6	-3.379359	2.331666	0.843170
6	-4.359013	3.326392	0.943926
6	-5.660016	3.106748	0.479258
6	-6.017335	1.879927	-0.101016
6	-5.073681	-0.510815	-0.752628
6	-3.625125	-0.919670	-0.491942
1	-2.367080	2.489645	1.201120
1	-4.105124	4.283545	1.390398
1	-6.402607	3.894049	0.568879
1	-7.029862	1.715294	-0.459574
7	-2.901629	-0.005737	0.072455
1	-0.218115	-0.188809	0.900366
16	-3.084277	-2.519151	-0.960300
1	-5.315908	-0.559928	-1.821013
1	-5.773621	-1.174594	-0.231197

TS(E_{free}-G)

Number of imaginary frequencies : 1 Electronic energy : HF=-2832.1629527
Zero-point correction= 0.718974 (Hartree/Particle)
Thermal correction to Energy= 0.761697
Thermal correction to Enthalpy= 0.762641
Thermal correction to Gibbs Free Energy= 0.638806
Sum of electronic and zero-point Energies= -2831.443979
Sum of electronic and thermal Energies= -2831.401256
Sum of electronic and thermal Enthalpies= -2831.400311
Sum of electronic and thermal Free Energies= -2831.524147

.....

Cartesian Coordinates

.....

16	-0.465670	-0.856984	-1.421225
6	0.363313	0.573330	-0.877439
6	0.390203	1.886059	-1.618117
6	1.525276	2.599176	-0.928754
6	2.130324	3.829432	-1.142676
6	3.169851	4.218452	-0.286301
6	3.582200	3.398264	0.771278
6	2.969667	2.160801	1.001355

6	1.950858	1.793521	0.133273
7	1.201399	0.586851	0.156166
1	3.272504	1.517770	1.820862
1	4.388460	3.723335	1.421278
1	3.663621	5.172230	-0.444979
1	1.809548	4.477799	-1.952097
1	0.515101	1.746391	-2.695686
6	0.866227	-2.154201	-1.371917
1	0.419177	-2.916699	-2.016044
6	2.297469	-1.699070	-1.771873
1	2.747378	-2.376606	-2.503212
1	2.417530	-0.673203	-2.128099
6	2.769441	-1.983074	-0.307987
6	4.049810	-2.782057	-0.197270
8	4.034106	-3.999522	-0.076940
6	5.338902	-2.025548	-0.292907
6	5.381069	-0.648487	-0.441786
6	6.613124	0.047518	-0.520751
6	6.666535	1.461650	-0.659650
6	7.878347	2.111285	-0.729801
6	9.088070	1.375603	-0.664657
6	9.066866	0.004434	-0.528059
6	7.835501	-0.697136	-0.451404
6	7.767051	-2.112016	-0.305807
6	6.558783	-2.757868	-0.228413
1	6.496751	-3.834746	-0.114518
1	8.694670	-2.676319	-0.254675
1	9.995095	-0.558493	-0.476350
1	10.037281	1.900442	-0.721808
1	7.912820	3.191721	-0.835022
1	5.734656	2.020053	-0.702370
1	4.470054	-0.061605	-0.500741
1	2.858729	-1.054927	0.253013
6	1.421302	-2.678953	-0.018709
1	1.518776	-3.767816	-0.018496
1	0.901052	-2.364842	0.887434
16	-0.977529	-1.807999	2.954512
6	-1.104103	-0.191651	2.230230
6	-0.108045	0.812820	2.544811
6	-0.631685	2.015721	1.952443
6	-0.211128	3.353660	1.881665
6	-0.912966	4.239343	1.067013
6	-2.021042	3.808975	0.308979
6	-2.465478	2.485695	0.373404
6	-1.773750	1.593150	1.200491
7	-2.049095	0.244281	1.405516
1	-3.316369	2.145635	-0.209382
1	-2.548012	4.521410	-0.320006
1	-0.595460	5.276350	1.005811
1	0.659358	3.691567	2.436909
1	0.613081	0.745652	3.352005
6	-2.313412	-2.886891	2.284152
1	-2.309593	-3.695169	3.021574
6	-3.696134	-2.241648	1.999469
1	-4.506468	-2.918035	2.290615
1	-3.879687	-1.245581	2.400942
6	-3.365270	-2.330507	0.474860
6	-4.485915	-2.720205	-0.450517
8	-4.570304	-3.843383	-0.933827
6	-5.515481	-1.670090	-0.740890

6	-5.420691	-0.389278	-0.220767
6	-6.406519	0.589933	-0.507174
6	-6.330866	1.906428	0.025563
6	-7.297311	2.840924	-0.272863
6	-8.384316	2.498900	-1.115116
6	-8.487617	1.229619	-1.642102
6	-7.508802	0.242506	-1.355151
6	-7.580519	-1.080629	-1.876460
6	-6.616142	-2.009914	-1.577201
1	-6.660061	-3.021346	-1.967290
1	-8.417780	-1.343666	-2.518264
1	-9.323372	0.966812	-2.285673
1	-9.140910	3.244472	-1.342812
1	-7.231352	3.843672	0.139169
1	-5.497236	2.160945	0.674628
1	-4.585103	-0.104207	0.412551
1	-2.932268	-1.373877	0.178494
6	-2.248270	-3.339567	0.798119
1	-2.593021	-4.371273	0.679788
1	-1.298810	-3.216501	0.274900
1	-0.563743	2.422174	-1.454448
1	0.819891	0.301070	1.166262

TS(E_{free}-H)

Number of imaginary frequencies : 1 Electronic energy : HF=-1416.0184744
Zero-point correction= 0.355750 (Hartree/Particle)
Thermal correction to Energy= 0.376579
Thermal correction to Enthalpy= 0.377523
Thermal correction to Gibbs Free Energy= 0.301311
Sum of electronic and zero-point Energies= -1415.662724
Sum of electronic and thermal Energies= -1415.641896
Sum of electronic and thermal Enthalpies= -1415.640952
Sum of electronic and thermal Free Energies= -1415.717163

.....

Cartesian Coordinates

.....

16	-2.223950	-2.389761	-0.553209
8	0.615484	1.746472	0.560953
7	-4.111182	-0.548282	-1.412870
1	-4.626810	-2.121079	-0.026040
6	-5.031849	0.263795	-0.846242
6	-5.785564	1.281406	-1.491873
1	-5.625595	1.477992	-2.546774
6	-6.693944	1.994170	-0.744131
1	-7.272314	2.784785	-1.214247
6	-6.907498	1.725323	0.641936
1	-7.637219	2.318945	1.184704
6	-6.212427	0.731385	1.292358
1	-6.380729	0.524162	2.345226
6	-5.252354	-0.004801	0.554179
6	-4.367911	-1.049927	0.875339
1	-4.153571	-1.530588	1.820345
6	-3.695699	-1.379406	-0.414851
6	-1.000990	-1.074546	-0.186526
1	-1.176840	-0.254638	-0.886634
6	-0.826962	-0.554130	1.262805
1	-1.253072	0.426054	1.480814
1	-1.153514	-1.288131	2.004067

6	0.707186	-0.597348	1.051337
1	1.294509	-1.043845	1.859505
6	0.478927	-1.526664	-0.192824
1	0.598753	-2.581167	0.074545
1	1.059136	-1.319854	-1.095440
6	1.311622	0.745112	0.659935
6	2.777571	0.804778	0.362196
6	3.336440	2.068663	0.015832
1	2.672096	2.925389	-0.009346
6	4.671761	2.187341	-0.274317
1	5.092578	3.154965	-0.535318
6	5.532234	1.053920	-0.243240
6	4.977784	-0.222759	0.098946
6	3.594303	-0.312349	0.398198
1	3.190258	-1.288062	0.650549
6	6.917287	1.140977	-0.540304
1	7.337195	2.109323	-0.799486
6	7.717486	0.019922	-0.502569
1	8.775951	0.100008	-0.732548
6	7.169537	-1.242672	-0.165577
1	7.812327	-2.117564	-0.140513
6	5.829734	-1.360159	0.128264
1	5.404429	-2.326505	0.387179

TS(E-F)

Number of imaginary frequencies : 1 Electronic energy : HF=-4347.0599774
Zero-point correction= 0.444969 (Hartree/Particle)
Thermal correction to Energy= 0.493238
Thermal correction to Enthalpy= 0.494183
Thermal correction to Gibbs Free Energy= 0.354543
Sum of electronic and zero-point Energies= -4346.615008
Sum of electronic and thermal Energies= -4346.566739
Sum of electronic and thermal Enthalpies= -4346.565795
Sum of electronic and thermal Free Energies= -4346.705435

.....

Cartesian Coordinates

.....

21	-1.328408	1.429403	-0.109672
8	-1.291741	3.238862	-1.325356
8	0.753552	-0.153020	3.248208
8	-3.201142	1.881013	0.889160
16	-0.139343	3.881771	-0.571294
16	-4.101428	1.201094	-0.128393
16	0.264589	-0.720476	1.998521
8	0.969514	4.420804	-1.333380
8	0.164208	2.845162	0.505242
8	-3.111874	0.734061	-1.185064
8	-5.306644	1.882127	-0.552274
8	-0.817744	0.171676	1.335898
8	1.223324	-1.216326	1.007334
6	-0.812827	-2.176522	2.435042
6	-0.929562	5.287014	0.371338
6	-4.628961	-0.396455	0.686540
9	-1.391825	6.183476	-0.496159
9	-0.018704	5.844976	1.163336
9	-1.933978	4.805004	1.103902
9	-3.552219	-1.129007	0.979267
9	-5.397964	-1.074419	-0.172967

9	-5.312944	-0.132815	1.793197
9	-1.297672	-2.730811	1.316121
9	-0.078663	-3.079721	3.088106
9	-1.828603	-1.784651	3.205352
8	-0.235419	0.419358	-1.463522
6	1.974444	-0.237810	-1.859724
6	2.377654	1.206609	-2.237436
1	1.611263	1.731974	-2.813804
1	2.701700	1.834261	-1.408308
6	3.490863	0.613472	-3.150445
6	2.850825	-0.799341	-3.017489
1	3.525299	-1.621606	-2.765972
1	2.276177	-1.077234	-3.905942
6	0.539751	-0.554648	-1.694678
6	-0.000842	-1.909072	-1.715071
6	0.854554	-3.049773	-1.651354
6	-1.381125	-2.080093	-1.705464
6	0.317143	-4.307806	-1.567864
1	1.928485	-2.914713	-1.619899
6	-1.956102	-3.363803	-1.614179
1	-2.031082	-1.214246	-1.757206
6	-1.093227	-4.507459	-1.542190
1	0.967669	-5.174974	-1.497976
6	-1.677862	-5.793613	-1.430530
1	-1.030091	-6.664293	-1.378268
6	-3.365882	-3.543190	-1.552843
1	-4.007045	-2.667587	-1.581203
6	-3.899979	-4.805577	-1.435954
1	-4.975854	-4.940659	-1.383306
6	-3.048425	-5.937652	-1.379643
1	-3.484302	-6.928331	-1.289714
1	3.511694	1.012896	-4.168061
6	6.273977	-0.775948	0.882655
6	4.904418	-0.361064	1.062465
6	4.279511	-0.497414	2.331036
6	5.033089	-1.003725	3.365013
6	6.391265	-1.408943	3.188904
6	7.012975	-1.317157	1.964304
6	6.562094	-0.553181	-0.476839
6	5.294799	-0.025130	-1.048499
1	3.243477	-0.208092	2.461612
1	4.583089	-1.105728	4.348489
1	6.935832	-1.802225	4.042285
1	8.042982	-1.634216	1.829605
7	4.340524	0.102250	-0.075435
1	2.443884	-0.474938	-0.890834
16	5.240378	0.821029	-2.623586
1	5.535256	-1.231140	-1.233477
1	7.476818	-0.705392	-1.034761

3a

Number of imaginary frequencies : 0 Electronic energy : HF=-1416.1065832
Zero-point correction= 0.361592 (Hartree/Particle)
Thermal correction to Energy= 0.382413
Thermal correction to Enthalpy= 0.383357
Thermal correction to Gibbs Free Energy= 0.309841
Sum of electronic and zero-point Energies= -1415.744992
Sum of electronic and thermal Energies= -1415.724171

Sum of electronic and thermal Enthalpies= -1415.723226
Sum of electronic and thermal Free Energies= -1415.796742

.....

Cartesian Coordinates

.....

16	4.339606	-0.440696	0.698442
6	3.133996	0.806737	0.397823
6	2.330184	1.481269	1.290625
6	1.448168	2.315714	0.530416
6	0.413288	3.210305	0.863635
6	-0.271149	3.857140	-0.156793
6	0.056003	3.632725	-1.512652
6	1.077086	2.763697	-1.875180
6	1.766041	2.111465	-0.844924
7	2.797053	1.200554	-0.894511
1	3.257204	0.860434	-1.723772
1	1.328962	2.592155	-2.917519
1	-0.502559	4.150145	-2.286676
1	-1.073138	4.547776	0.086569
1	0.157324	3.387167	1.904422
1	2.370374	1.374124	2.364583
6	3.324821	-1.990139	0.551881
1	4.010283	-2.760059	0.917612
6	1.918618	-1.943678	1.204373
1	1.658051	-2.912031	1.642356
1	1.716928	-1.148569	1.924035
6	1.299917	-1.774288	-0.224295
6	0.063583	-2.605413	-0.495867
8	0.170637	-3.780572	-0.827894
6	-1.282396	-1.985749	-0.293883
6	-1.454254	-0.656364	0.057456
6	-2.749599	-0.104195	0.229480
6	-2.938452	1.262382	0.571962
6	-4.206772	1.773894	0.732259
6	-5.340440	0.942108	0.557474
6	-5.188008	-0.385804	0.221067
6	-3.895515	-0.944723	0.046295
6	-3.692664	-2.308681	-0.308422
6	-2.428843	-2.813645	-0.476062
1	-2.264313	-3.849968	-0.750123
1	-4.561748	-2.946856	-0.447147
1	-6.057721	-1.023053	0.083450
1	-6.335508	1.357987	0.687700
1	-4.343388	2.819832	0.991431
1	-2.064466	1.896009	0.691859
1	-0.604411	0.001288	0.211483
1	1.131522	-0.720989	-0.442125
6	2.644190	-2.258896	-0.816711
1	2.600863	-3.328155	-1.042041
1	3.030757	-1.720574	-1.686184

3a'

Number of imaginary frequencies : 0 Electronic energy : HF=-1416.0999872
Zero-point correction= 0.360906 (Hartree/Particle)
Thermal correction to Energy= 0.382081
Thermal correction to Enthalpy= 0.383025
Thermal correction to Gibbs Free Energy= 0.306413
Sum of electronic and zero-point Energies= -1415.739081

Sum of electronic and thermal Energies= -1415.717906
Sum of electronic and thermal Enthalpies= -1415.716962
Sum of electronic and thermal Free Energies= -1415.793574

.....

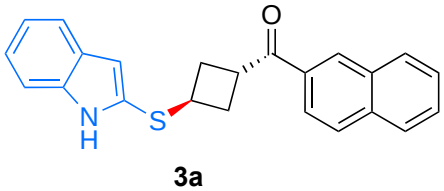
Cartesian Coordinates

.....

8	-2.219356	3.267276	0.687224
7	3.295039	-0.076645	0.982680
1	2.616668	-0.023123	1.725431
6	4.126117	-1.139920	0.710196
6	4.188053	-2.414983	1.284944
1	3.515653	-2.704318	2.087499
6	5.143020	-3.294387	0.789558
1	5.219357	-4.291415	1.213482
6	6.016470	-2.917618	-0.254150
1	6.749098	-3.633279	-0.615527
6	5.953378	-1.652167	-0.821012
1	6.629243	-1.368407	-1.622779
6	4.999650	-0.735775	-0.341117
6	4.656172	0.615357	-0.673900
1	5.108586	1.241372	-1.429113
6	3.619996	0.990815	0.150193
6	1.283412	2.093831	-0.797689
6	0.173164	3.168708	-0.884513
1	0.096654	3.773347	0.023307
1	0.180879	3.826960	-1.755619
6	-0.871982	2.028220	-0.844858
1	-1.178858	1.715065	-1.848144
6	0.237291	1.077993	-0.279216
1	0.290158	0.056770	-0.664148
1	0.208038	1.050745	0.814406
6	-2.091308	2.238613	0.037323
6	-3.107027	1.144282	0.129722
6	-4.238361	1.351731	0.970548
1	-4.310602	2.297260	1.496674
6	-5.198257	0.381078	1.103342
1	-6.060131	0.545791	1.744874
6	-5.089124	-0.857676	0.410445
6	-3.952886	-1.076231	-0.435512
6	-2.979204	-0.051873	-0.554999
1	-2.123493	-0.235278	-1.197343
6	-6.062402	-1.883885	0.527447
1	-6.924059	-1.717589	1.168599
6	-5.920197	-3.070829	-0.157837
1	-6.672178	-3.848313	-0.059480
6	-4.796639	-3.287638	-0.993560
1	-4.697893	-4.228174	-1.527273
6	-3.835235	-2.311522	-1.128658
1	-2.971463	-2.472873	-1.768676
16	2.739658	2.514264	0.246427
1	1.654774	1.808801	-1.785731

8. Synthesis and Characterization of Substituted Cyclobutane Derivatives

(3-((1*H*-Indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3a)

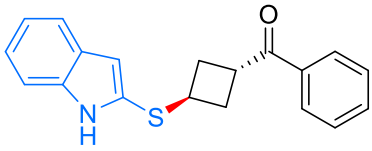


3a

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded (3-((1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3a** as purple solid (0.050 g, 70% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 8.27 (s, 1H), 7.97 – 7.85 (m, 4H), 7.63 – 7.53 (m, 3H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.17 – 7.13 (m, 1H), 6.75 – 6.75 (m, 1H), 4.19 – 4.11 (m, 1H), 3.87 – 3.79 (m, 1H), 2.87 – 2.80 (m, 2H), 2.52 – 2.44 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.3, 137.3, 135.7, 132.6, 132.6, 130.1, 129.7, 128.7, 128.7, 128.7, 127.9, 126.9, 126.8, 124.1, 123.0, 120.5, 120.3, 110.8, 110.3, 39.8, 38.2, 32.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NOS$ 358.1260; found 358.1269. **FTIR (cm^{-1})** 3342, 1668, 1442, 1346, 1224, 1127.

3-((1*H*-Indol-2-yl)thio)cyclobutyl)(phenyl)methanone (3b)

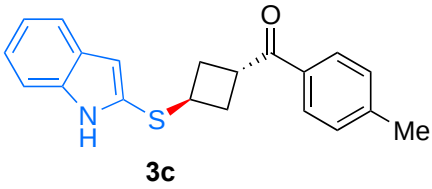


3b

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(phenyl)methanone **2b** (0.038 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3-((1*H*-indol-2-yl)thio)cyclobutyl)(phenyl)methanone **3b** as greenish sticky solid (0.037 g, 61% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (s, 1H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.72 (s, 1H), 4.05 – 3.97 (m, 1H), 3.82 – 3.74 (m, 1H), 2.81 – 2.74 (m, 2H), 2.45 – 2.37 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 137.3, 135.3, 133.4, 128.8, 128.7, 128.5, 126.9, 123.0, 120.5, 120.4, 110.8, 110.3, 39.7, 38.2, 32.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NOS$ 308.1104; found 308.1108. **FTIR (cm^{-1})** 3369, 2937, 1672, 1443, 1342, 1222.

(3-((1*H*-Indol-2-yl)thio)cyclobutyl)(*p*-tolyl)methanone (3c)

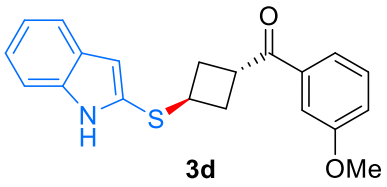


3c

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(*p*-tolyl)methanone **2c** (0.041 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded (3-((1*H*-indol-2-yl)thio)cyclobutyl)(*p*-tolyl)methanone **3c** as purple solid (0.046 g, 71% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.71 – 6.71 (m, 1H), 4.02 – 3.95 (m, 1H), 3.81 – 3.74 (m, 1H), 2.80 – 2.73 (m, 2H), 2.44 – 2.34 (m, 2H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.9, 144.2, 137.3, 132.7, 129.5, 128.7, 128.6, 126.9, 122.9, 120.5, 120.3, 110.8, 110.2, 39.8, 38.1, 32.3, 21.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NOS$ 322.1260; found 322.1270. **FTIR (cm^{-1})** 3351, 2932, 1669, 1447, 1346, 1184.

3-((1*H*-Indol-2-yl)thio)cyclobutyl)(3-methoxyphenyl)methanone (3d)

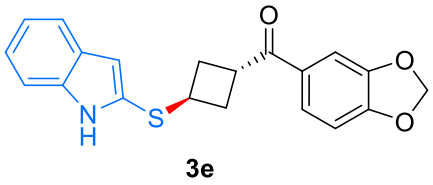


3d

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(3-methoxyphenyl)methanone **2d** (0.045 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3-((1*H*-indol-2-yl)thio)cyclobutyl)(3-methoxyphenyl)methanone **3d** as green sticky solid (0.050 g, 74% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.72 – 6.2 (m, 1H), 4.01 – 3.94 (m, 1H), 3.84 (s, 3H), 3.81 – 3.74 (m, 1H), 2.80 – 2.73 (m, 2H), 2.44 – 2.37 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 159.9, 137.3, 136.6, 129.8, 128.7, 126.8, 122.9, 121.0, 120.4, 120.3, 119.7, 112.7, 110.8, 110.2, 55.5, 39.7, 38.3, 32.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO_2S$ 338.1209; found 338.1219. **FTIR (cm^{-1})** 3354, 2936, 1674, 1589, 1441, 1259.

3-((1*H*-Indol-2-yl)thio)cyclobutyl)(benzo[*d*][1,3]dioxol-5-yl)methanone (3e)

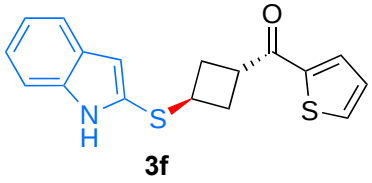


3e

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and benzo[*d*][1,3]dioxol-5-yl(bicyclo[1.1.0]butan-1-yl)methanone **2e** (0.049 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3-((1*H*-indol-2-yl)thio)cyclobutyl)(benzo[*d*][1,3]dioxol-5-yl)methanone **3e** as greenish sticky solid (0.047 g, 67% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.32; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.23 – 7.19 (m, 1H), 7.14 – 7.10 (m, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.71-6.70 (m, 1H), 6.03 (s, 2H), 3.95 – 3.88 (m, 1H), 3.80 – 3.73 (m, 1H), 2.78 – 2.71 (m, 2H), 2.41 – 2.34 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.4, 151.9, 148.4, 137.3, 130.1, 128.7, 126.9, 124.7, 122.9, 120.5, 120.3, 110.8, 110.2, 108.2, 108.1, 102.0, 39.7, 38.1, 32.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{18}NO_3S$ 352.1002; found 352.1004. **FTIR (cm^{-1})** 3384, 2930, 1665, 1440, 1348, 1250.

(3-((1*H*-Indol-2-yl)thio)cyclobutyl)(thiophen-2-yl)methanone (3f)

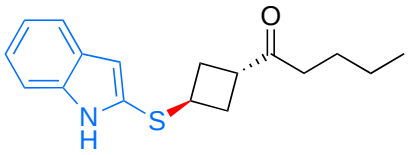


3f

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(thiophen-2-yl)methanone **2f** (0.039 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded (3-((1*H*-indol-2-yl)thio)cyclobutyl)(thiophen-2-yl)methanone **3f** as purple solid (0.047 g, 75% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 7.63 – 7.55 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.15 – 7.09 (m, 2H), 6.72 – 6.72 (m, 1H), 3.92 – 3.79 (m, 2H), 2.81 – 2.75 (m, 2H), 2.43 – 2.35 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.8, 142.7, 137.3, 133.9, 132.2, 128.7, 128.3, 126.7, 122.9, 120.4, 120.3, 110.9, 110.3, 39.9, 38.9, 32.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NOS_2$ 314.0668; found 314.0672. **FTIR (cm^{-1})** 3346, 2148, 1650, 1511, 1415, 1232.

1-(3-((1*H*-Indol-2-yl)thio)cyclobutyl)pentan-1-one (3g)

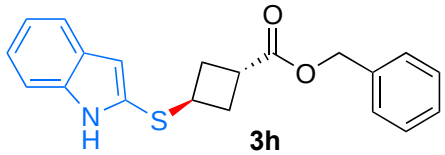


3g

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and 1-(bicyclo[1.1.0]butan-1-yl)pentan-1-one **2g** (0.033 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 1-(3-((1*H*-indol-2-yl)thio)cyclobutyl)pentan-1-one **3g** as yellow liquid (0.053 g, 92% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.68 – 6.68 (m, 1H), 3.71 (p, *J* = 7.3 Hz, 1H), 3.29 – 3.23 (m, 1H), 2.61 – 2.55 (m, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.26 – 2.19 (m, 2H), 1.54 (p, *J* = 7.4 Hz, 2H), 1.28 (q, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 211.8, 137.3, 128.6, 126.9, 122.9, 120.4, 120.2, 110.8, 110.1, 41.4, 40.6, 39.6, 31.6, 25.9, 22.5, 14.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{22}NOS$ 288.1417; found 288.1423. **FTIR (cm^{-1})** 3350, 2945, 2065, 1699, 1444, 1343.

Benzyl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3h)

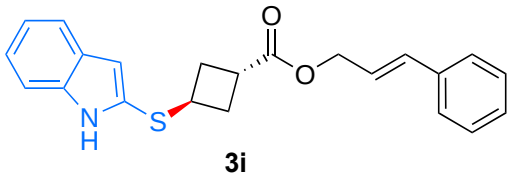


3h

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and benzyl bicyclo[1.1.0]butane-1-carboxylate **2h** (0.045 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded benzyl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate **3h** as yellow liquid (0.055 g, 82% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.73 – 7.32 (m, 6H), 7.24 – 7.20 (m, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.71 – 6.65 (m, 1H), 5.14 (s, 2H), 3.86 (p, *J* = 7.4 Hz, 1H), 3.22 – 3.15 (m, 1H), 2.69 – 2.63 (m, 2H), 2.36 – 2.29 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.1, 137.3, 135.9, 128.7, 128.7, 128.4, 128.3, 126.7, 122.9, 120.5, 120.3, 110.8, 110.3, 66.6, 40.2, 34.8, 32.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{20}NO_2S$ 338.1209; found 338.1219. **FTIR (cm^{-1})** 3385, 2947, 1721, 1445, 1254, 1177.

Cinnamyl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3i)

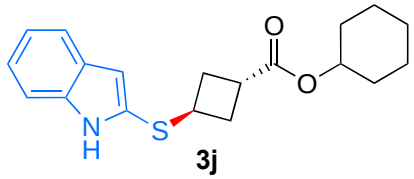


3i

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and cinnamyl bicyclo[1.1.0]butane-1-carboxylate **2i** (0.051 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded cinnamyl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate **3i** as yellow liquid (0.049 g, 68% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.25 (m, 6H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.69 – 6.62 (m, 2H), 6.27 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.75 (d, *J* = 6.5 Hz, 2H), 3.87 (p, *J* = 7.4 Hz, 1H), 3.21 – 3.13 (m, 1H), 2.70 – 2.64 (m, 2H), 2.37 – 2.30 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.1, 137.3, 136.2, 134.5, 128.8, 128.7, 128.3, 126.8, 126.7, 123.1, 123.0, 120.5, 120.3, 110.8, 110.4, 65.5, 40.3, 34.9, 32.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{22}NO_2S$ 364.1366; found 364.1371. **FTIR (cm^{-1})** 3377, 1720, 1443, 1340, 1250, 1179.

Cyclohexyl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3j)

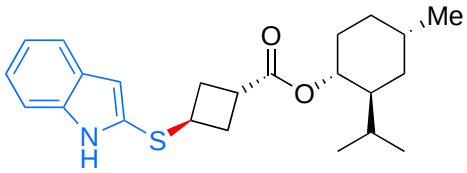


3j

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and cyclohexyl bicyclo[1.1.0]butane-1-carboxylate **2j** (0.043 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded cyclohexyl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate **3j** as yellow liquid (0.058 g, 88% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.67 (s, 1H), 4.77 – 4.75 (m, 1H), 3.85 (p, *J* = 7.4 Hz, 1H), 3.14 – 3.06 (m, 1H), 2.62 (dt, *J* = 13.4, 7.6 Hz, 2H), 2.34 – 2.27 (m, 2H), 1.80 – 1.70 (m, 7H), 1.43 – 1.34 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.8, 137.3, 128.7, 126.9, 122.9, 120.5, 120.3, 110.8, 110.2, 72.9, 40.3, 35.1, 32.8, 31.7, 25.5, 23.8, 16.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{24}NO_2S$ 330.1522; found 330.1532. **FTIR (cm^{-1})** 3355, 2072, 1707, 1445, 1343, 1132.

(1*R*,2*S*,4*S*)-2-Isopropyl-4-methylcyclohexyl 3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3k)

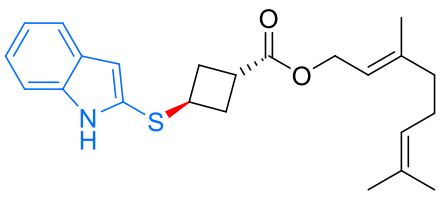


3k

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and (1*R*,2*S*,4*S*)-2-isopropyl-4-methylcyclohexyl bicyclo[1.1.0]butane-1-carboxylate **2k** (0.057 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded (1*R*,2*S*,4*S*)-2-isopropyl-4-methylcyclohexyl 3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate **3k** as yellow liquid (0.062 g, 80% yield with 12:1 dr).

***R*f** (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.68 – 6.68 (m, 1H), 4.69 (td, *J* = 10.8, 4.3 Hz, 1H), 3.85 (p, *J* = 7.4 Hz, 1H), 3.15 – 3.08 (m, 1H), 2.66 – 2.60 (m, 2H), 2.36 – 2.27 (m, 2H), 1.97 (d, *J* = 11.8 Hz, 1H), 1.83 (dtd, *J* = 13.9, 7.0, 2.6 Hz, 1H), 1.71 – 1.65 (m, 3H), 1.41 – 1.27 (m, 2H), 1.11 – 0.99 (m, 2H), 0.91 – 0.88 (m, 6H), 0.75 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.9, 137.3, 128.7, 126.8, 122.9, 120.4, 120.3, 110.8, 110.2, 74.5, 47.1, 40.9, 40.2, 35.1, 34.3, 32.7, 31.5, 26.4, 23.5, 22.1, 20.9, 16.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{32}NO_2S$ 386.2148; found 386.2151. **FTIR (cm^{-1})** 3353, 2943, 1710, 1448, 1344, 1191.

(*E*)-3,7-Dimethylocta-2,6-dien-1-yl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3l)



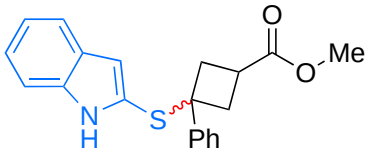
3l

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and (*E*)-3,7-dimethylocta-2,6-dien-1-yl bicyclo[1.1.0]butane-1-carboxylate **2l** (0.056 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded (*E*)-3,7-dimethylocta-2,6-dien-1-yl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate **3l** as greenish liquid (0.042 g, 55% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.67 – 6.67 (m, 1H), 5.33 – 5.29 (m, 1H), 5.08 – 5.05 (m, 1H), 4.60 (d, *J* = 7.1 Hz, 2H), 3.89 – 3.81 (m, 1H), 3.15 – 3.08 (m, 1H), 2.67 – 2.60 (m, 2H), 2.34 – 2.27 (m, 2H), 2.10 – 2.01 (m, 4H),

1.68 (d, *J* = 6.6 Hz, 6H), 1.59 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.3, 142.6, 137.3, 132.0, 128.7, 126.8, 123.8, 122.9, 120.5, 120.3, 118.2, 110.8, 110.3, 61.8, 40.3, 39.6, 34.9, 32.8, 26.4, 25.8, 17.8, 16.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{29}NO_2SNa$ 406.1811; found 406.1814. **FTIR (cm^{-1})** 3375, 2927, 1717, 1444, 1343, 1182.

Methyl 3-((1*H*-indol-2-yl)thio)-3-phenylcyclobutane-1-carboxylate (3m)

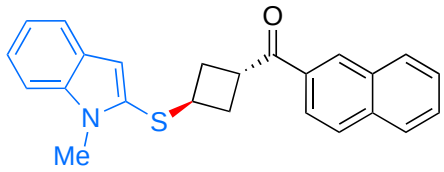


3m

Following the general procedure, treatment of indoline-2-thione **1a** (0.030 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2m** (0.045 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded methyl 3-((1*H*-indol-2-yl)thio)-3-phenylcyclobutane-1-carboxylate **3m** as yellow liquid (0.059 g, 88% yield with 2:1 dr).

***R*$_f$** (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$) of major isomer** δ 7.60 – 7.58 (m, 1H), 7.43 (s, 1H), 7.32 – 7.22 (m, 4H), 7.20 – 7.09 (m, 3H), 6.95 – 6.93 (m, 1H), 6.69 – 6.68 (m, 1H), 3.68 (s, 3H), 3.67 – 3.60 (m, 1H), 3.05 – 2.90 (m, 2H), 2.87 – 2.79 (m, 2H). **Representative peaks of minor isomer ^{1}H NMR (400 MHz, $CDCl_3$)** 7.92 (s, 1H), 7.60 – 7.60 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) of major isomer** δ 174.9, 147.3, 137.3, 128.3, 128.1, 126.9, 126.2, 125.5, 123.2, 120.8, 120.1, 112.5, 110.8, 53.6, 52.0, 37.2, 32.9. **Representative peaks of minor isomer ^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.4, 145.5, 112.5, 111.0, 54.2, 52.3, 37.8, 32.9. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{20}H_{19}NNaO_2S$ 360.1029; found 360.1056. **FTIR (cm^{-1})** 3379, 1725, 1497, 1439, 1344, 1217.

(3-((1-Methyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3n)



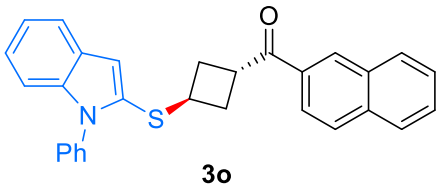
3n

Following the general procedure, treatment of 1-methylindoline-2-thione **1b** (0.033 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 92/08) of the crude reaction mixture using silica gel afforded (3-((1-methyl-1*H*-indol-2-yl)thio)cyclobutyl) (naphthalen-2-yl)methanone **3n** as white solid (0.044 g, 59% yield).

***R*$_f$** (Pet. ether /EtOAc = 90/10): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 7.97 – 7.86 (m, 4H), 7.63 – 7.53 (m, 3H), 7.34 – 7.25 (m, 2H), 7.16 – 7.12 (m, 1H), 6.78 (s, 1H), 4.23 –

4.15 (m, 1H), 3.83 (s, 3H), 3.81 – 3.75 (m, 1H), 2.85 – 2.78 (m, 2H), 2.49 – 2.41 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 138.5, 135.7, 132.6, 132.6, 130.1, 129.7, 129.7, 128.7, 128.7, 127.9, 127.5, 126.9, 124.1, 122.5, 120.5, 120.0, 109.8, 109.6, 39.6, 38.5, 32.0, 30.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NOS$ 372.1417; found 372.1420. **FTIR (cm^{-1})** 2926, 1675, 1498, 1444, 1360, 1183.

Naphthalen-2-yl(3-((1-phenyl-1*H*-indol-2-yl)thio)cyclobutyl)methanone (3o)

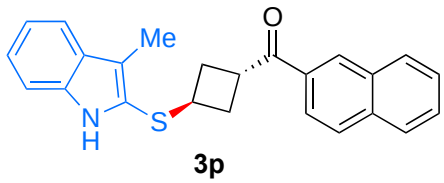


3o

Following the general procedure, treatment of 1-phenylindoline-2-thione **1c** (0.046 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded naphthalen-2-yl(3-((1-phenyl-1*H*-indol-2-yl)thio)cyclobutyl)methanone **3o** as yellowish sticky liquid (0.056 g, 65% yield).

***R*$_f$** (Pet. ether /EtOAc = 90/10): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (s, 1H), 7.95 – 7.86 (m, 4H), 7.62 – 7.44 (m, 8H), 7.17 – 7.17 (m, 3H), 6.79 (s, 1H), 4.26 – 4.18 (m, 1H), 3.66 – 3.61 (m, 1H), 2.80 – 2.74 (m, 2H), 2.37 – 2.31 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.1, 139.2, 137.5, 135.7, 132.6, 132.6, 131.8, 130.1, 129.7, 129.4, 128.7, 128.7, 128.6, 128.2, 127.9, 126.9, 124.1, 122.7, 120.7, 120.1, 110.5, 108.6, 38.9, 38.7, 32.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{29}H_{24}NOS$ 434.1573; found 434.1582. **FTIR (cm^{-1})** 2928, 1675, 1498, 1446, 1361, 1183.

(3-((3-Methyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3p)



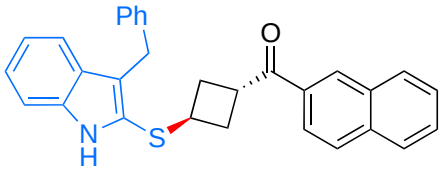
3p

Following the general procedure, treatment of 3-methylindoline-2-thione **1d** (0.033 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 92/08) of the crude reaction mixture using silica gel afforded (3-((3-methyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3p** as yellow liquid (0.055 g, 74% yield).

***R*$_f$** (Pet. ether /EtOAc = 90/10): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (s, 1H), 8.14 (s, 1H), 8.02 – 7.85 (m, 4H), 7.62 – 7.53 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.17

(t, *J* = 7.4 Hz, 1H), 4.16 – 4.09 (m, 1H), 3.78 (p, *J* = 7.4 Hz, 1H), 2.81 – 2.75 (m, 2H), 2.48 (s, 3H), 2.46 – 2.40 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.3, 136.6, 135.7, 132.6, 130.1, 129.6, 128.7, 128.7, 128.6, 127.9, 126.9, 124.1, 123.3, 123.2, 119.6, 119.4, 119.2, 110.8, 40.6, 38.4, 32.6, 10.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NOS$ 372.1417; found 372.1420. **FTIR (cm^{-1})** 3362, 2931, 1670, 1450, 1349, 1242.

(3-((3-Benzyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3q)

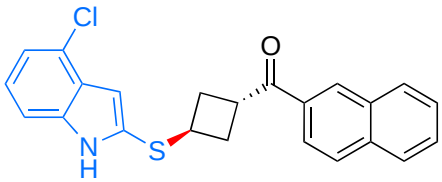


3q

Following the general procedure, treatment of 3-benzylindoline-2-thione **1e** (0.048 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 92/08) of the crude reaction mixture using silica gel afforded (3-((3-benzyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3q** as yellow liquid (0.080 g, 89% yield).

***R*$_f$** (Pet. ether /EtOAc = 90/10): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (s, 1H), 8.26 (s, 1H), 7.94 – 7.87 (m, 4H), 7.63 – 7.54 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.16 (m, 6H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.35 (s, 2H), 4.19 – 4.09 (m, 1H), 3.81 – 3.74 (m, 1H), 2.79 – 2.72 (m, 2H), 2.44 – 2.37 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.3, 141.3, 136.9, 135.7, 132.6, 132.5, 130.1, 129.7, 128.7, 128.5, 128.5, 128.4, 128.1, 127.9, 126.9, 126.0, 124.6, 124.1, 123.3, 121.7, 119.9, 119.9, 110.9, 40.4, 38.4, 32.6, 31.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}NNaOS$ 470.1549; found 470.1558. **FTIR (cm^{-1})** 3394, 1670, 1443, 1348, 1257, 1130.

(3-((4-Chloro-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3r)

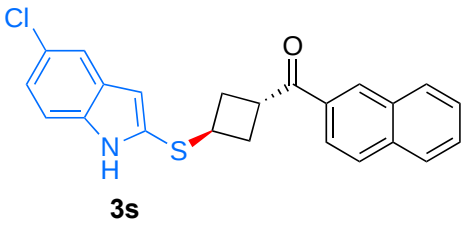


3r

Following the general procedure, treatment of 4-chloroindoline-2-thione **1f** (0.037 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded (3-((4-chloro-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3r** as yellow solid (0.069 g, 88% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (s, 1H), 8.31 (s, 1H), 7.97 – 7.85 (m, 4H), 7.62 – 7.53 (m, 2H), 7.26 – 7.23 (m, 1H), 7.14 – 7.10 (m, 2H), 6.81 (d, *J* = 2.1 Hz, 1H), 4.23 – 4.15 (m, 1H), 3.86 (p, *J* = 7.3 Hz, 1H), 2.89 – 2.83 (m, 2H), 2.52 – 2.45 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 137.8, 135.8, 132.6, 132.5, 130.2, 129.7, 128.7, 128.7, 128.3, 127.9, 127.7, 127.0, 125.6, 124.1, 123.4, 120.1, 109.4, 108.1, 39.7, 38.3, 32.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{19}ClNOS$ 392.0870; found 392.0873. **FTIR (cm^{-1})** 3327, 2938, 1667, 1476, 1422, 1183.

(3-((5-Chloro-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3s)

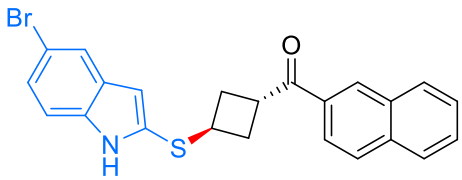


3s

Following the general procedure, treatment of 5-chloroindoline-2-thione **1g** (0.037 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded (3-((5-chloro-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3s** as yellow solid (0.051 g, 65% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (s, 1H), 8.22 (s, 1H), 7.96 – 7.86 (m, 4H), 7.62 – 7.53 (m, 3H), 7.26 (t, *J* = 4.3 Hz, 1H), 7.16 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.64 (d, *J* = 1.3 Hz, 1H), 4.22 – 4.15 (m, 1H), 3.89 – 3.81 (m, 1H), 2.88 – 2.82 (m, 2H), 2.51 – 2.43 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 135.8, 135.6, 132.6, 132.5, 130.1, 129.7, 129.7, 128.9, 128.7, 128.7, 127.9, 127.0, 126.1, 124.1, 123.2, 119.8, 111.8, 109.3, 39.7, 38.3, 32.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{19}ClNOS$ 392.0870; found 392.0875. **FTIR (cm^{-1})** 3346, 2941, 1670, 1624, 1448, 1184.

3-((5-Bromo-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3t)



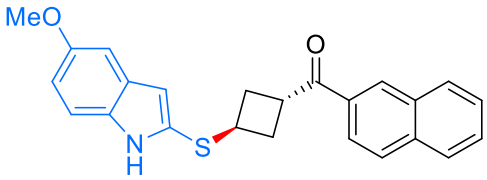
3t

Following the general procedure, treatment of 5-bromoindoline-2-thione **1h** (0.046 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using

silica gel afforded 3-((5-bromo-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3t** as brown sticky solid (0.060 g, 69% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 – 8.27 (m, 2H), 7.96 – 7.92 (m, 2H), 7.89 – 7.85 (m, 2H), 7.72 (s, 1H), 7.62 – 7.55 (m, 2H), 7.30 – 7.28 (m, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 6.64 – 6.63 (m, 1H), 4.22 – 4.14 (m, 1H), 3.88 – 3.81 (m, 1H), 2.88 – 2.81 (m, 2H), 2.50 – 2.43 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 135.8, 135.8, 132.6, 132.5, 130.4, 130.2, 129.7, 128.82, 128.75, 128.7, 127.9, 127.0, 125.7, 124.1, 122.8, 113.6, 112.2, 109.1, 39.7, 38.3, 32.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{19}BrNOS$ 436.0365; found 436.0377. **FTIR (cm^{-1})** 3328, 2936, 1667, 1438, 1338, 1220.

3-((5-Methoxy-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3u)

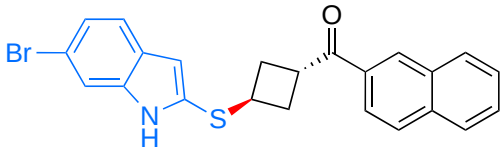


3u

Following the general procedure, treatment of 5-methoxyindoline-2-thione **1i** (0.036 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3-((5-methoxy-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3u** as yellow greenish solid (0.059 g, 76% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (s, 2H), 7.96 – 7.91 (m, 2H), 7.88 – 7.85 (m, 2H), 7.61 – 7.52 (m, 2H), 7.25 (d, *J* = 9.1 Hz, 1H), 7.07 (d, *J* = 2.2 Hz, 1H), 6.91 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.68 – 6.67 (m, 1H), 4.17 – 4.10 (m, 1H), 3.86 (s, 1H), 3.83 – 3.77 (m, 1H), 2.86 – 2.79 (m, 2H), 2.51 – 2.43 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.4, 154.4, 135.7, 132.6, 132.5, 130.1, 129.6, 129.1, 128.7, 128.7, 127.9, 127.2, 126.9, 124.1, 113.4, 111.7, 110.0, 101.7, 55.9, 39.8, 38.2, 32.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NO_2S$ 388.1366; found 388.1374. **FTIR (cm^{-1})** 3343, 2939, 1669, 1445, 1348, 1218.

(3-((6-Bromo-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3v)



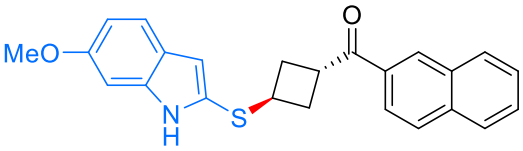
3v

Following the general procedure, treatment of 6-bromoindoline-2-thione **1j** (0.046 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g,

0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded (3-((6-bromo-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3v** as yellow solid (0.078 g, 89% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 – 8.26 (m, 2H), 7.96 – 7.85 (m, 4H), 7.62 – 7.43 (m, 4H), 7.26 – 7.21 (m, 1H), 6.68 (dd, *J* = 2.1, 0.9 Hz, 1H), 4.21 – 4.13 (m, 1H), 3.87 – 3.80 (m, 1H), 2.87 – 2.81 (m, 2H), 2.50 – 2.43 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.3, 137.9, 135.7, 132.6, 132.5, 130.2, 129.7, 128.7, 128.0, 127.9, 127.5, 127.0, 124.1, 123.7, 121.6, 116.5, 113.7, 110.0, 39.7, 38.3, 32.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{19}BrNOS$ 436.0365; found 436.0379. **FTIR (cm^{-1})** 3331, 2852, 1668, 1442, 1258, 1185.

3-((6-Methoxy-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3w)



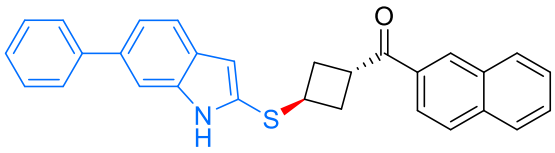
3w

Following the general procedure, treatment of 6-methoxyindoline-2-thione **1k** (0.036 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3-((6-methoxy-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3w** as grey solid (0.058 g, 75% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.32; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.29 (s, 1H), 8.23 (s, 1H), 7.93 (t, J = 10.1 Hz, 2H), 7.88 – 7.85 (m, 2H), 7.61 – 7.52 (m, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 6.84 – 6.81 (m, 2H), 6.71 (s, 1H), 4.15 – 4.08 (m, 1H), 3.84 (s, 3H), 3.80 – 3.73 (m, 1H), 2.83 – 2.77 (m, 2H), 2.50 – 2.43 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.4, 157.1, 138.2, 135.7, 132.6, 130.1, 129.7, 128.7, 127.9, 126.9, 124.6, 124.1, 123.0, 121.2, 111.0, 110.6, 94.1, 55.7, 39.9, 38.2, 32.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NO_2S$ 388.1366; found 388.1372. **FTIR (cm^{-1})** 3349, 2939, 1669, 1448, 1355, 1181.

Naphthalen-2-yl(3-((6-phenyl-1*H*-indol-2-yl)thio)cyclobutyl)methanone (3x)

Following the general procedure, treatment of 6-phenylindoline-2-thione **1l** (0.046 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column

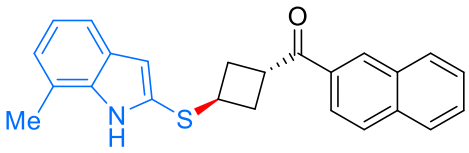


3x

chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded naphthalen-2-yl(3-((6-phenyl-1*H*-indol-2-yl)thio)cyclobutyl)methanone **3x** as brown sticky solid (0.055 g, 64% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 8.25 (s, 1H), 7.97 – 7.85 (m, 4H), 7.67 – 7.52 (m, 6H), 7.47 – 7.40 (m, 3H), 7.34 (t, *J* = 7.3 Hz, 1H), 6.76 (s, 1H), 4.21 – 4.14 (m, 1H), 3.89 – 3.81 (m, 1H), 2.89 – 2.82 (m, 2H), 2.53 – 2.46 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.3, 142.1, 137.9, 136.5, 136.4, 135.8, 132.6, 130.1, 129.7, 128.9, 128.7, 128.7, 128.1, 127.9, 127.6, 127.5, 127.0, 124.2, 120.7, 120.4, 110.2, 109.3, 39.9, 38.3, 32.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{29}H_{24}NOS$ 434.1573; found 434.1581. **FTIR (cm^{-1})** 3335, 2928, 1670, 1443, 1355, 1182.

3-((7-Methyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3y)



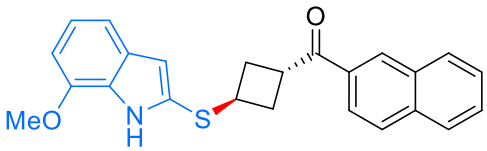
3y

Following the general procedure, treatment of 7-methylindoline-2-thione **1m** (0.032 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3-((7-methyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3y** as blue sticky solid (0.040 g, 51% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 8.09 (s, 1H), 7.96 – 7.92 (m, 2H), 7.89 – 7.85 (m, 2H), 7.61 – 7.53 (m, 2H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.76 – 6.76 (m, 1H), 4.20 – 4.13 (m, 1H), 3.87 – 3.80 (m, 1H), 2.87 – 2.80 (m, 2H), 2.51 (s, 3H), 2.51 – 2.45 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.3, 137.1, 135.7, 132.6, 130.1, 129.7, 128.7, 128.7, 128.3, 127.9, 126.9, 126.4, 124.1, 123.5, 120.6, 120.1, 118.2, 111.0, 39.9, 38.2, 32.4, 16.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NOS$ 372.1417; found 372.1425. **FTIR (cm^{-1})** 3352, 2933, 1669, 1446, 1346, 1185.

3-((7-Methoxy-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3z)

Following the general procedure, treatment of 7-methoxyindoline-2-thione **1n** (0.036 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with

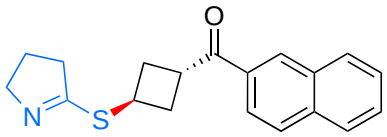


3z

$Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3-((7-methoxy-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **3z** as green solid (0.055 g, 70% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.40 (s, 1H), 8.30 (s, 1H), 7.96 – 7.92 (m, 2H), 7.88 – 7.85 (m, 2H), 7.61 – 7.53 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.73-6.72 (m, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.17 – 4.10 (m, 1H), 3.97 (s, 3H), 3.84 – 3.77 (m, 1H), 2.85 – 2.79 (m, 2H), 2.51 – 2.43 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 145.7, 135.7, 132.6, 132.6, 130.1, 129.9, 129.7, 128.6, 128.6, 128.1, 127.9, 126.9, 126.2, 124.1, 120.7, 113.1, 110.8, 102.5, 55.5, 39.8, 38.2, 32.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NO_2S$ 388.1366; found 388.1376. **FTIR (cm^{-1})** 3344, 2842, 1672, 1579, 1357, 1254.

(3-((3,4-Dihydro-2*H*-pyrrol-5-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (5a)



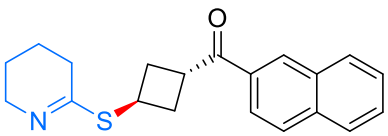
5a

Following the general procedure, treatment of pyrrolidine-2-thione **4a** (0.020 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 92/08) of the crude reaction mixture using silica gel afforded (3-((3,4-dihydro-2*H*-pyrrol-5-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **5a** as white solid (0.042 g, 68% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.34 (s, 1H), 7.99 – 7.85 (m, 4H), 7.61 – 7.52 (m, 2H), 4.38 – 4.30 (m, 1H), 4.20 – 4.13 (m, 1H), 3.82 (t, *J* = 7.2 Hz, 2H), 3.07 – 3.00 (m, 2H), 2.61 (t, *J* = 8.2 Hz, 2H), 2.51 – 2.44 (m, 2H), 1.96 (p, *J* = 7.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.0, 171.9, 135.7, 132.6, 132.6, 130.1, 129.7, 128.6, 128.6, 127.9, 126.9, 124.2, 61.3, 39.5, 38.7, 35.6, 32.5, 23.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{20}NOS$ 312.1260; found 312.1262. **FTIR (cm^{-1})** 2942, 2315, 1675, 1589, 1538, 1217.

Naphthalen-2-yl(3-((3,4,5,6-tetrahydropyridin-2-yl)thio)cyclobutyl)methanone (5b)

Following the general procedure, treatment of piperidine-2-thione **4b** (0.023 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$

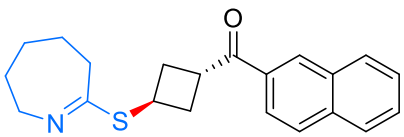


5b

(0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded naphthalen-2-yl(3-((3,4,5,6-tetrahydropyridin-2-yl)thio)cyclobutyl)methanone **5b** as sticky solid (0.043 g, 67% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 7.99 – 7.93 (m, 2H), 7.90 – 7.85 (m, 2H), 7.61 – 7.52 (m, 2H), 4.35 – 4.25 (m, 1H), 4.13 – 4.06 (m, 1H), 3.68 – 3.57 (m, 2H), 3.01 – 2.94 (m, 2H), 2.44 – 2.37 (m, 2H), 2.27 (t, *J* = 6.4 Hz, 2H), 1.73 – 1.69 (m, 2H), 1.63 – 1.57 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 165.1, 135.7, 132.8, 132.7, 130.1, 129.7, 128.6, 128.5, 127.9, 126.8, 124.3, 50.7, 39.5, 36.5, 34.0, 32.4, 31.3, 22.6, 20.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{22}NOS$ 324.1417; found 324.1422. **FTIR (cm^{-1})** 2935, 1673, 1351, 1260, 1181, 1127.

Naphthalen-2-yl(3-((3,4,5,6-tetrahydro-2*H*-azepin-7-yl)thio)cyclobutyl)methanone (5c)



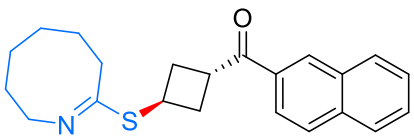
5c

Following the general procedure, treatment of azepane-2-thione **4c** (0.026 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded naphthalen-2-yl(3-((3,4,5,6-tetrahydro-2*H*-azepin-7-yl)thio)cyclobutyl)methanone **5c** as yellowish sticky solid (0.055 g, 79% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 7.98 – 7.94 (m, 2H), 7.90 – 7.85 (m, 2H), 7.62 – 7.52 (m, 2H), 4.35 – 4.25 (m, 1H), 4.05 – 3.98 (m, 1H), 3.60 – 3.58 (m, 2H), 3.02 – 2.93 (m, 2H), 2.49 – 2.35 (m, 4H), 1.79 – 1.73 (m, 2H), 1.55 – 1.47 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 171.1, 135.7, 132.8, 132.7, 130.0, 129.7, 128.7, 128.6, 128.5, 127.9, 126.9, 126.8, 124.3, 124.2, 53.0, 39.6, 36.6, 34.9, 32.1, 31.4, 27.1, 24.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{21}H_{24}NOS$ 338.1573; found 338.1578. **FTIR (cm^{-1})** 2928, 1674, 1457, 1356, 1263, 1182.

3-(((*E*)-3,4,5,6,7,8-Hexahydroazocin-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (5d)

Following the general procedure, treatment of azocane-2-thione **4d** (0.029 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$

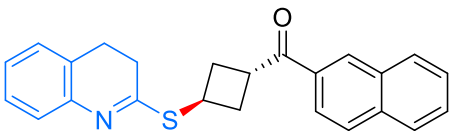


5d

(0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3-(((*E*)-3,4,5,6,7,8-hexahydroazocin-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **5d** as yellowish sticky solid (0.048 g, 71% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 7.99 – 7.93 (m, 2H), 7.89 – 7.85 (m, 2H), 7.60 – 7.51 (m, 2H), 4.35 – 4.27 (m, 1H), 4.11 – 4.04 (m, 1H), 3.59 (t, *J* = 5.8 Hz, 2H), 3.02 – 2.95 (m, 2H), 2.43 – 2.36 (m, 4H), 1.70 – 1.62 (m, 4H), 1.51 – 1.45 (m, 2H), 1.37 – 1.31 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 168.9, 135.7, 132.8, 132.6, 130.0, 129.6, 128.6, 128.5, 127.9, 126.8, 124.2, 49.7, 39.6, 34.4, 32.1, 32.1, 30.5, 29.2, 25.9, 24.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{26}NOS$ 352.1730; found 352.1734. **FTIR (cm^{-1})** 2925, 1674, 1445, 1356, 1221. 1182.

(3-((3,4-Dihydroquinolin-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (5e)

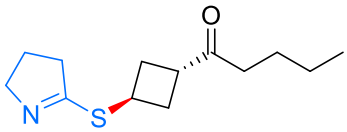


5e

Following the general procedure, treatment of 3,4-dihydroquinoline-2(1*H*)-thione **4e** (0.033 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded (3-((3,4-dihydroquinolin-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **5e** as white solid (0.048 g, 65% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.37 (s, 1H), 8.02 – 7.87 (m, 4H), 7.62 – 7.53 (m, 2H), 7.19 – 7.18 (m, 2H), 7.08 – 7.03 (m, 2H), 4.42 – 4.34 (m, 2H), 3.14 – 3.07 (m, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.59 – 2.46 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 168.4, 144.5, 135.7, 132.7, 132.7, 130.1, 129.7, 128.7, 128.6, 127.9, 127.6, 127.5, 126.9, 126.6, 125.7, 125.6, 124.3, 39.6, 34.9, 32.1, 29.7, 24.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NOS$ 372.1417; found 372.1422. **FTIR (cm^{-1})** 2941, 1676, 1572, 1473, 1357, 1189.

3-((3,4-Dihydro-2*H*-pyrrol-5-yl)thio)cyclobutyl)pentan-1-one (5f)

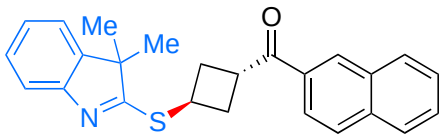


5f

Following the general procedure, treatment of pyrrolidine-2-thione **5a** (0.020 g, 0.2 mmol) and 1-(bicyclo[1.1.0]butan-1-yl)pentan-1-one **2g** (0.033 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3-((3,4-dihydro-2*H*-pyrrol-5-yl)thio)cyclobutyl)pentan-1-one **5f** as white sticky solid (0.035 g, 73% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.38; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.06 – 4.00 (m, 1H), 3.81 – 3.78 (m, 2H), 3.45 – 3.37 (m, 1H), 2.79 – 2.72 (m, 2H), 2.57 – 2.53 (m, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.23 – 2.16 (m, 2H), 1.96 – 1.88 (m, 2H), 1.56 – 1.48 (m, 2H), 1.32-1.22 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 211.1, 171.8, 61.3, 42.4, 40.2, 38.7, 35.3, 31.7, 25.9, 23.2, 22.5, 13.9. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{13}H_{22}NOS$ 240.1417; found 240.1421. **FTIR (cm^{-1})** 2946, 1706, 1589, 1365, 1294, 1081.

(3-((3,3-Dimethyl-3*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (5g)

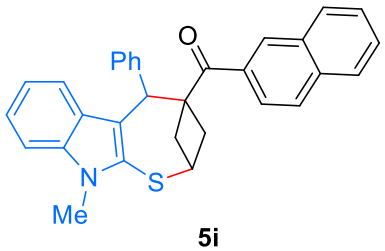


5g

Following the general procedure, treatment of 3,3-dimethylindoline-2-thione **4g** (0.035 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.050 g, 0.24 mmol) with $Sc(OTf)_3$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 92/08) of the crude reaction mixture using silica gel afforded (3-((3,3-dimethyl-3*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **5g** as white solid (0.032 g, 42% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.37 (s, 1H), 8.02 – 7.87 (m, 4H), 7.62 – 7.53 (m, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.46 – 4.37 (m, 2H), 3.18 (dt, *J* = 14.9, 8.4 Hz, 2H), 2.62 – 2.55 (m, 2H), 1.37 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.0, 188.0, 154.1, 145.7, 135.8, 132.7, 130.2, 129.7, 128.7, 128.6, 127.9, 127.8, 126.9, 124.3, 124.2, 121.1, 119.0, 55.2, 39.6, 35.5, 32.6, 25.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{25}H_{24}NOS$ 386.1573; found 386.1575. **FTIR (cm^{-1})** 2929, 1675, 1506, 1458, 1188, 1036.

(10-Methyl-5-phenyl-2,3,5,10-tetrahydro-4*H*-2,4-methanothiepino[2,3-*b*]indol-4-yl)(naphthalen-2-yl)methanone (5i)



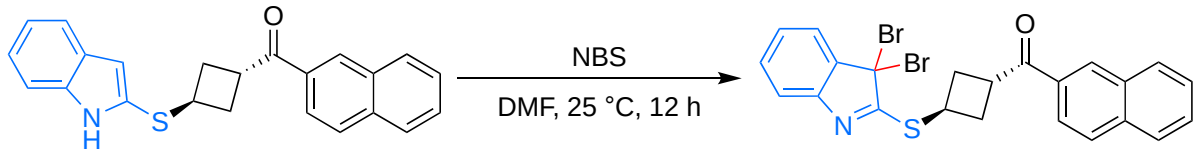
5i

Following the general procedure, treatment of 3-benzylidene-1-methylindoline-2-thione **4i** (0.050 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2a** (0.021 g, 0.1 mmol) with $Bi(OTf)_3$ (0.006 g, 0.01 mmol) in CH_2Cl_2 (4.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 95/5) of the crude reaction mixture using silica gel afforded (10-methyl-5-phenyl-2,3,5,10-tetrahydro-4*H*-2,4-methanothiepino[2,3-*b*]indol-4-yl)(naphthalen-2-yl)methanone **5i** as white solid (0.025 g, 55% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (s, 1H), 7.91 – 7.85 (m, 4H), 7.64 – 7.60 (m, 1H), 7.56 – 7.52 (m, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.13 – 7.07 (m, 4H), 6.92 – 6.81 (m, 4H), 5.50 (s, 1H), 3.81 (s, 3H), 3.76 – 3.71 (m, 1H), 3.46 – 3.40 (m, 1H), 3.28 – 3.23 (m, 1H), 3.12 (d, *J* = 12.6 Hz, 1H), 2.79 – 2.75 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 202.5, 140.6, 137.9, 135.3, 132.5, 132.3, 131.2, 130.7, 129.9, 129.1, 128.9, 128.7, 128.5, 128.2, 127.8, 127.0, 126.9, 125.4, 121.0, 119.2, 118.5, 111.0, 108.0, 55.6, 49.6, 39.0, 36.6, 33.5, 30.8. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{31}H_{25}NOSNa$ 482.1549; found 482.1556. **FTIR (cm^{-1})** 3059, 1672, 1464, 1353, 1268, 1187.

9. Product Functionalization

a) Dearomatization of Indoles via dibromation at C3

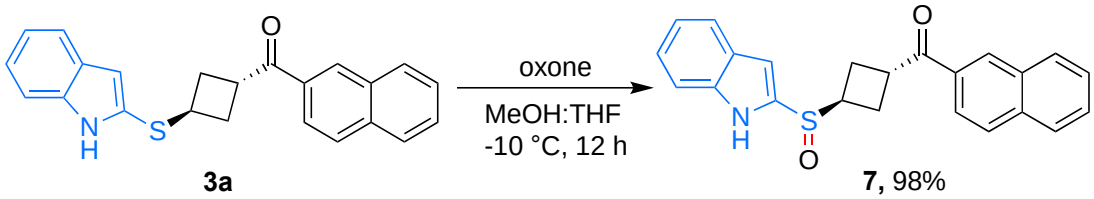


3a **6**, 81%

To a solution of **3a** (0.021 g, 0.06 mmol) in 2.0 mL DMF was added NBS (0.107 g, 0.18 mmol) and then the reaction mixture was stirred at 25 °C for 12 h. After completion, the reaction mixture was diluted with EtOAc (10 mL), washed with H_2O (5 mL × 3), brine (5 mL × 2) and the organic layer was separated and dried over Na_2SO_4. The crude residue was purified using flash silica gel column chromatography (Pet. ether /EtOAc = 94/06) to afford (3-((3,3-dibromo-3*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **6** as a yellow solid (0.025 g, 81% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.39; **^{1}H NMR (400 MHz, CD_3Cl_3)** δ 8.38 (s, 1H), 8.02 – 7.87 (m, 4H), 7.64 – 7.54 (m, 3H), 7.35 – 7.29 (m, 2H), 7.26 – 7.22 (m, 1H), 4.51 – 4.42 (m, 2H), 3.22 – 3.15 (m, 2H), 2.69 – 2.62 (m, 2H). **^{13}C NMR (100 MHz, CD_3Cl_3)** δ 199.7, 180.4, 148.6, 140.5, 135.8, 132.7, 132.5, 131.4, 130.2, 129.7, 128.8, 128.7, 127.9, 127.0, 126.4, 124.2, 123.9, 119.7, 50.7, 39.4, 36.5, 32.4. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{17}Br_2NNaOS$ 535.9290; found 535.9296. **FTIR (cm^{-1})** 2938, 2065, 1672, 1503, 1451, 1186.

b) Conversion to sulfoxide 7

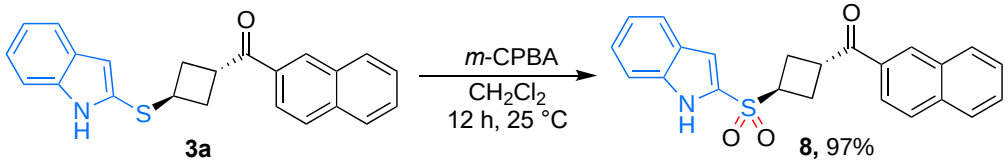


Following the general procedure,[9] into the stirred solution of **3a** (0.021 g, 0.06 mmol) in methanol: THF (1:1, 2 mL) was added solution of oxone (0.018 g, 0.03 mmol, 0.5 equiv.) in methanol: THF (1:1, 1 mL) dropwise at 0 °C. After addition, the reaction was stirred at -10 °C for 12 h. Then the reaction mixture was poured into the ice water and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified with column chromatography (Pet. ether /EtOAc = 70/30) to give the (3-(1*H*-indol-2-yl)sulfinyl)cyclobutyl) (naphthalen-2-yl)methanone **7** as a white solid (0.022 g, 98% yield) (*The relative configuration of the newly generated stereocentre was not unequivocally determined*).

***R*f** (Pet. ether /EtOAc = 80/20): 0.12; **^{1}H NMR (400 MHz, CD_3Cl_3)** δ 10.71 (s, 1H), 8.23 (s, 1H), 7.87 (dt, *J* = 17.1, 7.5 Hz, 4H), 7.64 – 7.52 (m, 4H), 7.31 – 7.26 (m, 1H), 7.16 – 7.12 (m, 1H), 6.82 – 6.82 (m, 1H), 4.16 – 4.09 (m, 1H), 3.90 (p, *J* = 7.7 Hz, 1H), 3.20 – 3.12 (m, 1H), 2.83 – 2.73 (m, 2H), 2.66 – 2.59 (m, 1H). **^{13}C NMR (100 MHz, CD_3Cl_3)** δ 199.4, 137.7, 135.8, 133.3, 132.6, 132.2, 130.2, 129.7, 128.8, 128.8, 127.9, 127.5, 127.0, 124.4, 124.0, 121.7, 120.9, 112.3, 104.7, 54.5, 37.8, 25.2, 24.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NO_2S$ 374.1209; found 374.1212. **FTIR (cm^{-})[1]** 3191, 2315, 2148, 1741, 1674, 1026.

[9] A. Saputra, R. Fan, T. Yao, J. Chen and J. Tan, *Adv. Synth. Catal.*, 2020, **362**, 2683.

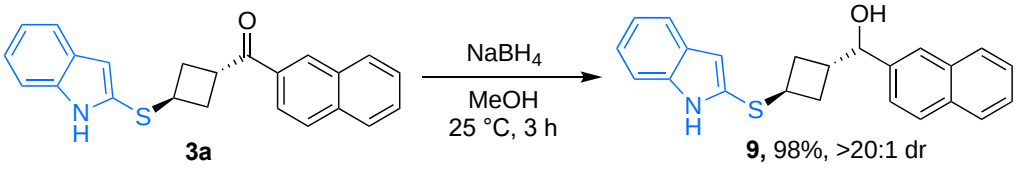
c) Conversion to sulfone 8



Compound **8** was synthesized following the modified literature procedure.[10] To a dry Schlenk tube containing compound **3a** (0.021 g, 0.06 mmol) in CH_2Cl_2 (2.0 mL), *m*-CPBA (0.047 g, 0.15 mmol) was added at 0 °C and the resulting mixture was allowed to stir overnight at 25 °C. After the completion of the reaction, the reaction mixture was quenched with aqueous $NaHCO_3$ solution, and extracted with CH_2Cl_2 for three times, then the combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. CH_2Cl_2 was removed under reduced pressure, and crude reaction mixture was purified by flash column chromatography using silica gel (Pet. ether /EtOAc = 60/40) to afford (3-((1*H*-indol-2-yl)sulfonyl)cyclobutyl) (naphthalen-2-yl)methanone **8** as a white solid (0.023 g, 97% yield).

***R*f** (Pet. ether /EtOAc = 80/20): 0.19; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.26 (s, 1H), 8.32 (s, 1H), 7.96 – 7.86 (m, 4H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.50 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.21 (m, 2H), 4.33 (p, *J* = 8.2 Hz, 1H), 3.96 (p, *J* = 9.5 Hz, 1H), 3.02 – 2.95 (m, 2H), 2.83 – 2.76 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.2, 137.3, 135.9, 132.6, 132.0, 130.4, 130.4, 129.8, 128.9, 128.9, 127.9, 127.2, 127.1, 126.5, 124.0, 122.9, 121.9, 112.5, 110.1, 55.4, 37.4, 25.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NO_3S$ 390.1158; found 390.1162. **FTIR (cm^{-1})** 3321, 2313, 1918, 1673, 1511, 1364.

d) Reduction of the ketone

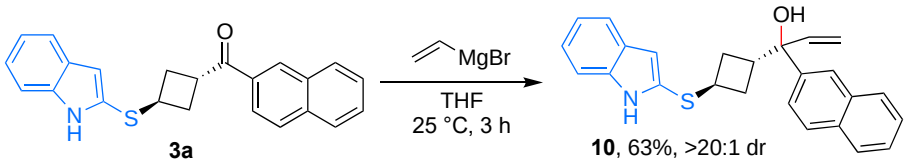


Following the general procedure,[11] treatment of **3a** (0.021 g, 0.06 mmol), $NaBH_4$ (0.009 g, 0.24 mmol) in MeOH (1 mL) at 25 °C for 3 h followed by purification via silica gel flash column chromatography (Pet. ether /EtOAc = 80/20) of the crude reaction mixture afforded (3-((1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanol **9** as a colorless oil (0.021 g, 98% yield) (*The relative configuration of the newly generated stereocentre was not unequivocally determined*).

[10] S. Barik, S. Shee, R. G. Gonnade, and A. T. Biju *Org. Lett*., 2022, **24**, 8848.
[11] A. Guin, R. N. Gaykar, S. Deswal and A. T. Biju, *Org. Lett*., 2021, **23**, 7456.

***R*f** (Pet. ether /EtOAc = 80/20): 0.18; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (s, 1H), 7.82 (dd, *J* = 9.1, 6.7 Hz, 3H), 7.72 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.49 (ddt, *J* = 10.1, 6.3, 3.5 Hz, 2H), 7.41 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.21 – 7.17 (m, 1H), 7.12 – 7.08 (m, 1H), 6.62 (d, *J* = 1.4 Hz, 1H), 4.79 (d, *J* = 7.6 Hz, 1H), 3.78 – 3.71 (m, 1H), 2.89 – 2.80 (m, 1H), 2.58 – 2.52 (m, 1H), 2.30 – 2.01 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.2, 137.1, 133.2, 133.2, 128.7, 128.5, 128.0, 127.9, 127.8, 126.4, 126.1, 125.1, 124.3, 122.7, 120.3, 120.2, 110.7, 109.5, 77.2, 39.8, 38.3, 31.8, 31.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{22}NOS$ 360.1417; found 360.1421. **FTIR (cm^{-})[1]** 3403, 2934, 1508, 1337, 1250.

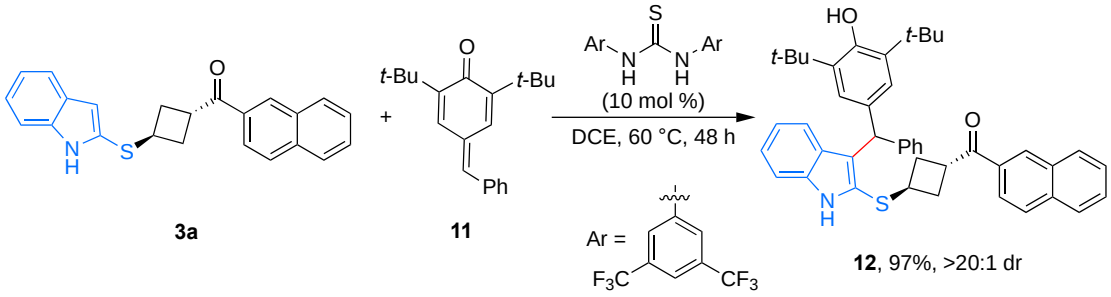
e) Vinyl magnesium bromide addition to 3a



To a solution of **3a** (0.021 g, 0.06 mmol) in THF (1.0 mL) vinyl magnesium bromide solution (0.24 mL, 1M solution in THF) was added dropwise at 0 °C under argon. After that, the reaction mixture was stirred at 25 °C for 3 h, then the reaction was quenched by the addition of water (1 mL). The organic layer was washed with water, brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by chromatography on a silica gel (Pet. ether /EtOAc = 75/25) of the crude reaction mixture to afford 1-(3-((1*H*-indol-2-yl)thio)cyclobutyl)-1-(naphthalen-2-yl)prop-2-en-1-ol **10** as a colorless oil (0.014 g, 63% yield) (*The relative configuration of the newly generated stereocentre was not unequivocally determined*).

***R*f** (Pet. ether /EtOAc = 80/20): 0.26; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (s, 1H), 7.86 – 7.78 (m, 4H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 1.2 Hz, 1H), 6.15 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.31 – 5.20 (m, 2H), 3.76 – 3.67 (m, 1H), 3.15 (p, *J* = 8.7 Hz, 1H), 2.58 – 2.51 (m, 1H), 2.45 – 2.38 (m, 1H), 2.19 – 2.13 (m, 1H), 2.01 (s, 1H), 1.93- 1.87 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.9, 141.5, 137.1, 133.2, 132.5, 128.7, 128.3, 128.1, 127.6, 126.3, 126.1, 124.1, 122.7, 120.3, 120.2, 114.2, 110.7, 109.2, 77.5, 39.9, 39.3, 30.1, 29.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{25}H_{24}NOS$ 386.1573; found 386.1577. **FTIR (cm^{-})[1]** 3391, 2938, 1669, 1506, 1345, 1255.

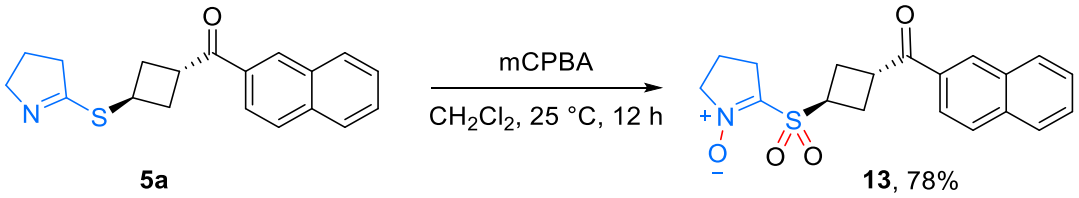
f) 1,6-Conjugate addition of 3a to para-quinone methides



To a solution of *p*-QM **11** (0.015 g, 0.06 mmol) and **3a** (0.021 g, 0.06 mmol) in anhydrous DCE (2 mL) was added thiourea catalyst (0.003 g, 10 mol%) and stirred at 60 °C for 48 h. Evaporation of the solvent under reduced pressure and further purification of the residue by flash chromatography on silica gel (petro ether / EtOAc = 85/15) furnished the 3-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone **12** as a white solid (0.032 g, 97% yield) (*The relative configuration of the newly generated stereocentre was not unequivocally determined*).[12]

***R*f** (Pet. ether /EtOAc = 90/10): 0.29; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.20 – 8.17 (m, 2H), 7.88 – 7.83 (m, 5H), 7.56 (dddd, *J* = 21.6, 8.1, 6.9, 1.4 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.19 – 7.11 (m, 5H), 6.91 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 6.02 (s, 1H), 5.05 (s, 1H), 4.07 – 3.99 (m, 1H), 3.72 – 3.65 (m, 1H), 2.66 – 2.57 (m, 2H), 2.34 – 2.25 (m, 2H), 1.31 (s, 18H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 200.3, 152.1, 144.7, 137.1, 135.7, 135.5, 134.2, 132.6, 132.5, 130.0, 129.7, 129.2, 128.7, 128.1, 127.9, 127.2, 126.9, 126.1, 126.0, 125.9, 124.8, 124.1, 122.9, 121.7, 119.6, 110.8, 48.3, 40.2, 38.5, 34.4, 32.6, 32.5, 30.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{44}H_{45}NNaO_2S$ 674.3063; found 674.3070. **FTIR (cm^{-})[1]** 3341, 2934, 1668, 1442, 1346, 1182.

g) m-CPBA oxidation to 5a



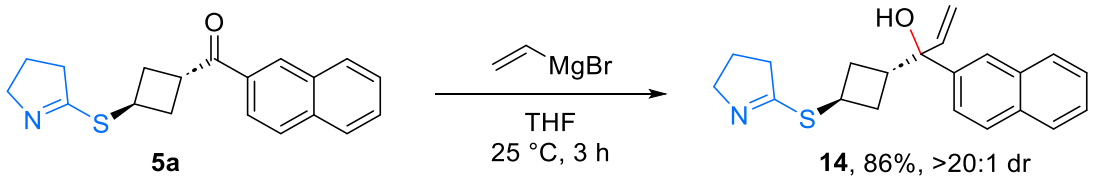
Compound **13** was synthesized following the modified literature procedure.[10] To a dry Schlenk tube containing compound **5a** (0.031 g, 0.1 mmol) in CH_2Cl_2 (2.0 mL), *m*-CPBA (0.078 g, 0.25 mmol) was added at 0 °C and the resulting mixture was allowed to stir overnight at 25 °C. After the completion of the reaction, the reaction mixture was quenched with aqueous

[12] G. Wu, T. Li, F. Liu, Y. Zhao, S. Ma, S. Tang, X. Xie and X. She, *Tetrahedron Lett.*, 2021, **81**, 153315.

$NaHCO_3$ solution, and extracted with CH_2Cl_2 three times, then the combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. CH_2Cl_2 was removed under reduced pressure, and the crude reaction mixture was purified by flash column chromatography using silica gel (Pet. ether /EtOAc = 60/40) to afford 5-((3-(2-naphthoyl)cyclobutyl)sulfonyl)-3,4-dihydro-2*H*-pyrrole 1-oxide **13** as a sticky solid (0.027 g, 79% yield).

***R*f** (Pet. ether /EtOAc = 80/20): 0.08; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.92 – 7.87 (m, 2H), 7.64 – 7.55 (m, 2H), 4.42 – 4.31 (m, 2H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.01 – 2.84 (m, 4H), 2.57 (t, *J* = 8.0 Hz, 2H), 2.16 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.9, 174.6, 135.9, 132.6, 132.0, 130.4, 129.7, 129.0, 128.0, 127.1, 124.0, 77.5, 77.2, 76.8, 52.9, 47.9, 37.8, 32.4, 25.8, 18.9. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}NO_4SNa$ 380.0927; found 380.0937. **FTIR (cm^-)^1** 2950, 1732, 1676, 1348, 1155.

h) Vinyl magnesium bromide addition to 5a

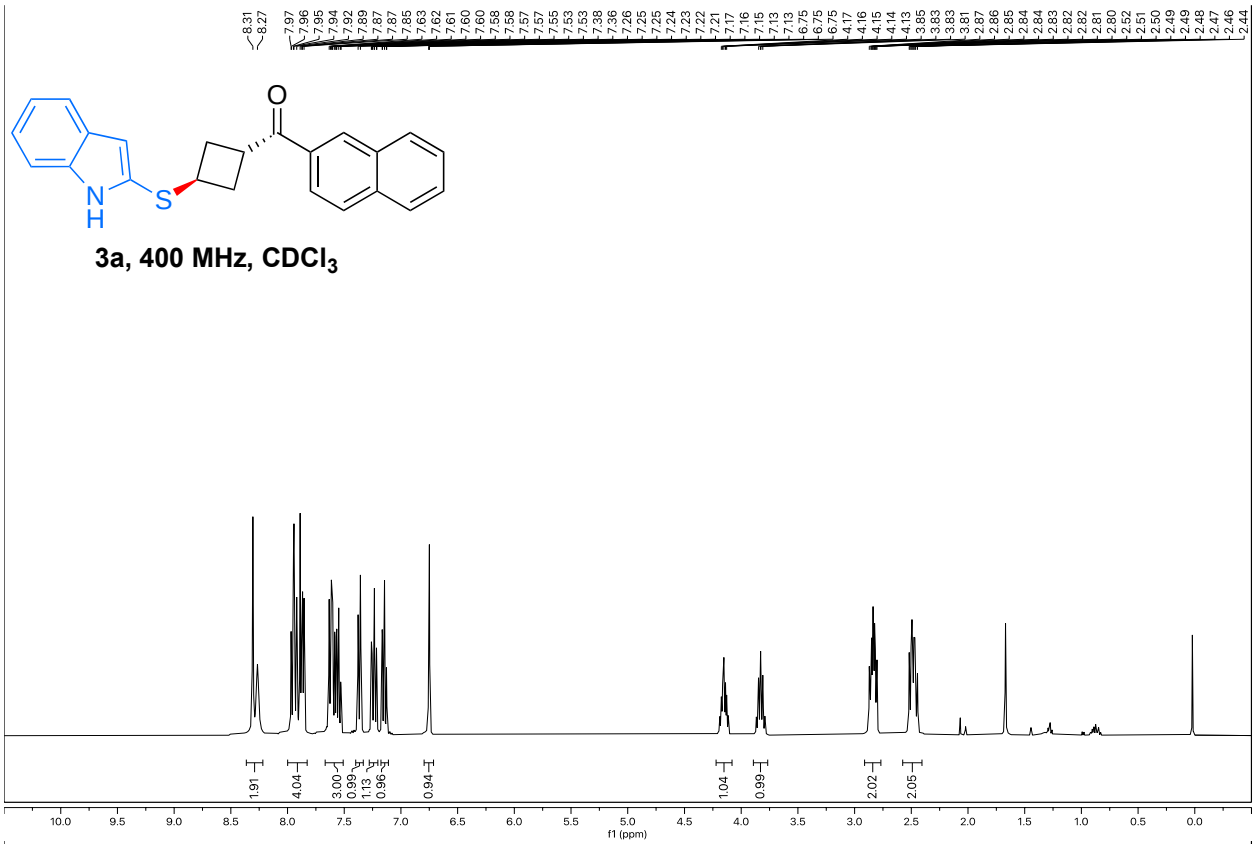


To a solution of **5a** (0.031 g, 0.1 mmol) in THF (2.0 mL) vinyl magnesium bromide solution (0.4 mL, 1M solution in THF) was added dropwise at 0 °C under argon. After that, the reaction mixture was stirred at 25 °C for 3 h, then the reaction was quenched by the addition of water (1 mL). The organic layer was washed with water, brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by chromatography on a silica gel (Pet. ether /EtOAc = 75/25) of the crude reaction mixture to afford 1-(3-((3,4-dihydro-2*H*-pyrrol-5-yl)thio)cyclobutyl)-1-(naphthalen-2-yl)prop-2-en-1-ol **14** as a white solid (0.029 g, 86% yield) (The relative configuration of the newly generated stereocentre was not unequivocally determined).

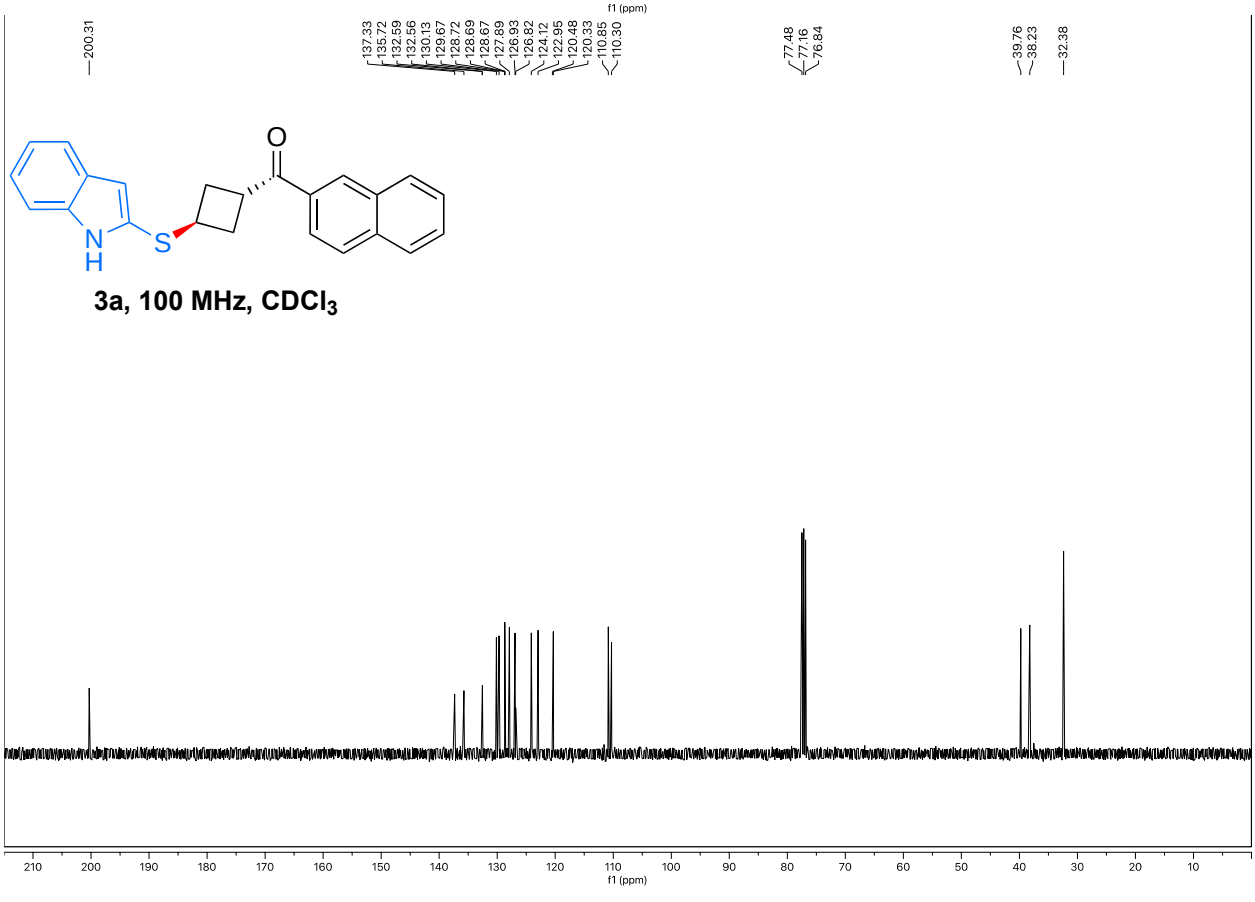
***R*f** (Pet. ether /EtOAc = 80/20): 0.18; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (s, 1H), 7.81 – 7.77 (m, 3H), 7.51 – 7.43 (m, 3H), 6.17 (dd, J_1 = 17.3 Hz, J_2 = 10.7 Hz, 1H), 5.32 (d, *J* = 17.3 Hz, 1H), 5.20 (d, *J* = 10.7 Hz, 1H), 4.16 – 4.10 (m, 1H), 3.70 (t, *J* = 6.9 Hz, 2H), 3.28 – 3.16 (m, 2H), 2.82 – 2.75 (m, 1H), 2.64 – 2.52 (m, 3H), 2.14 (t, *J* = 12.7 Hz, 1H), 1.86 (p, *J* = 7.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.8, 142.0, 141.8, 133.2, 132.5, 128.3, 127.9, 127.5, 126.1, 125.9, 124.4, 124.3, 114.0, 77.4, 61.1, 40.7, 38.7, 34.9, 30.7, 29.8, 23.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{21}H_{24}NOS$ 338.1573; found 338.1573. **FTIR (cm^-)^1** 3206, 2936, 1582, 14221, 1295, 1085.

10. ^{1}H and ^{13}C NMR Spectra of Products

(3-((1*H*-Indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3a)

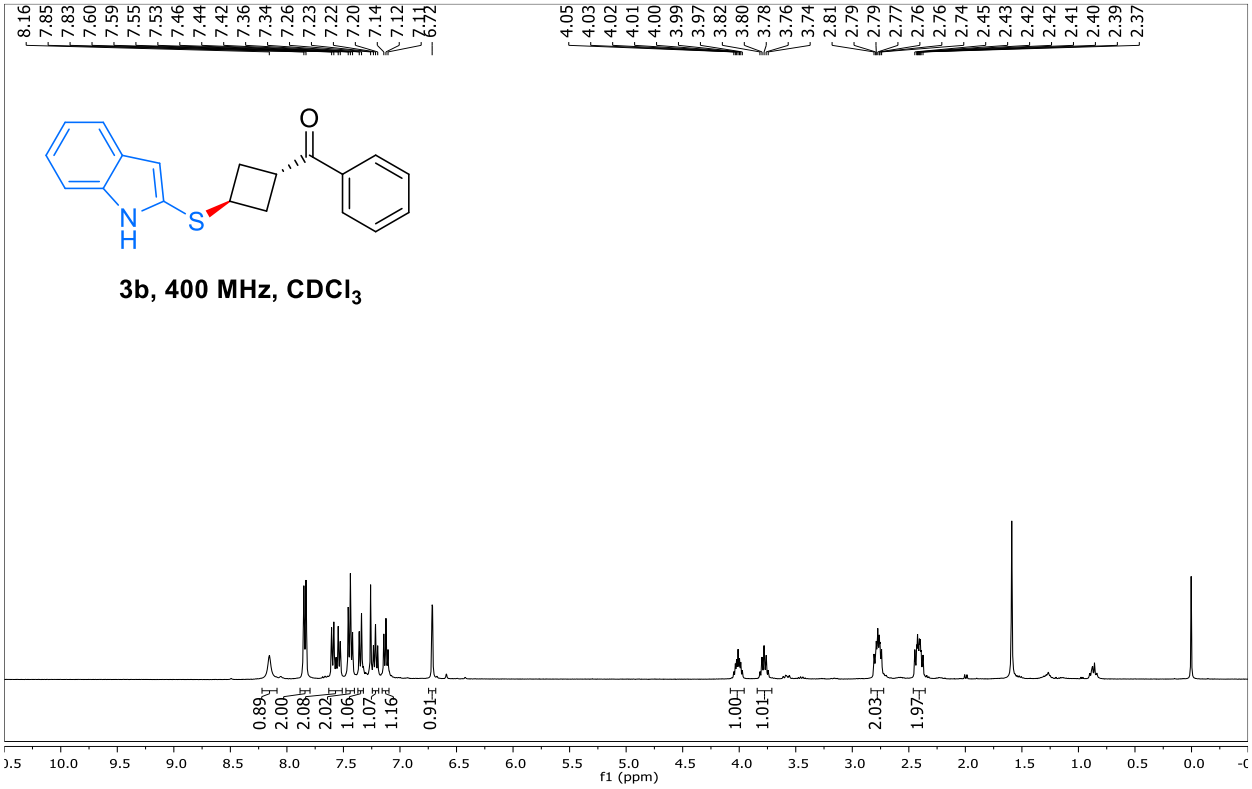


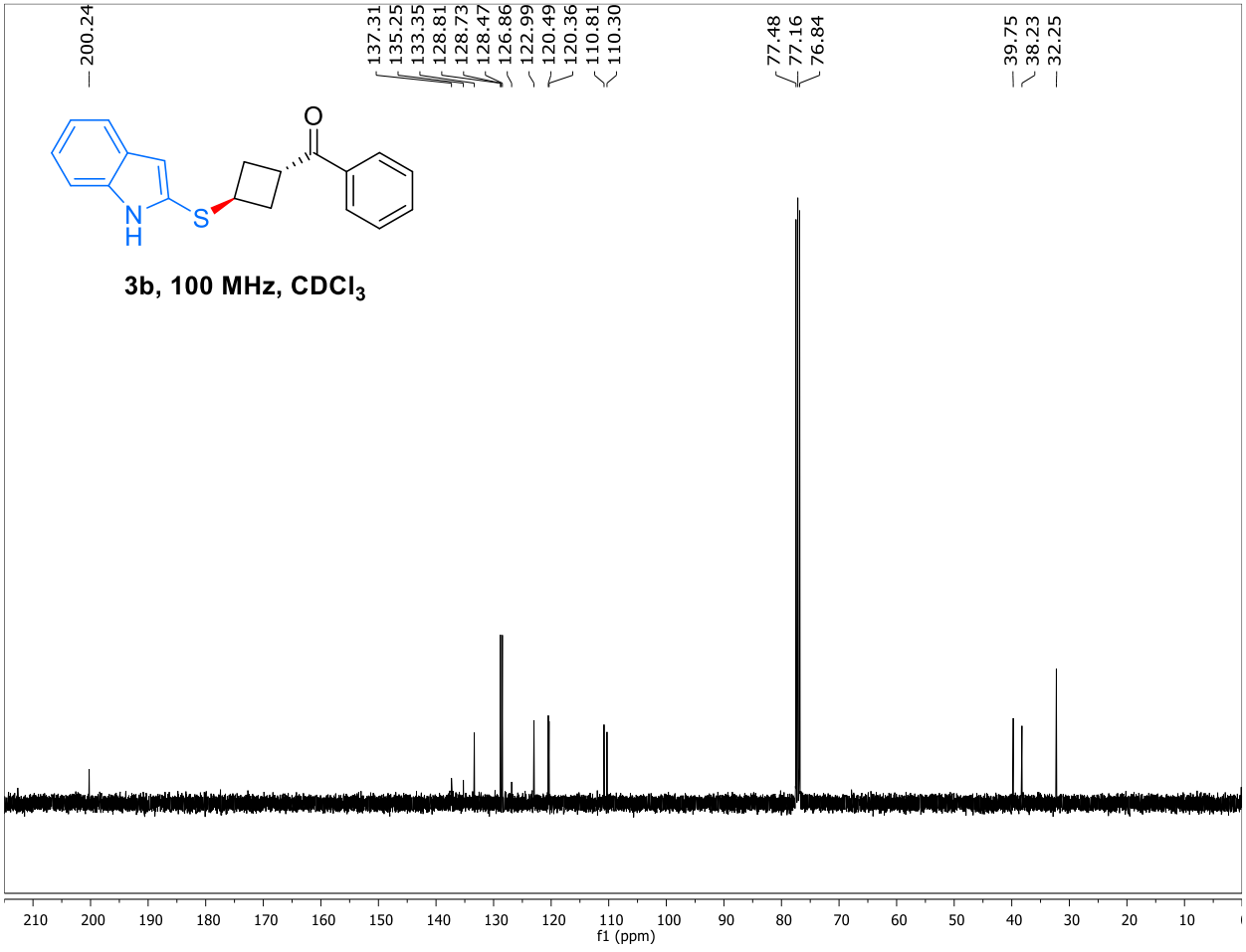
3a, 400 MHz, $CDCl_3$



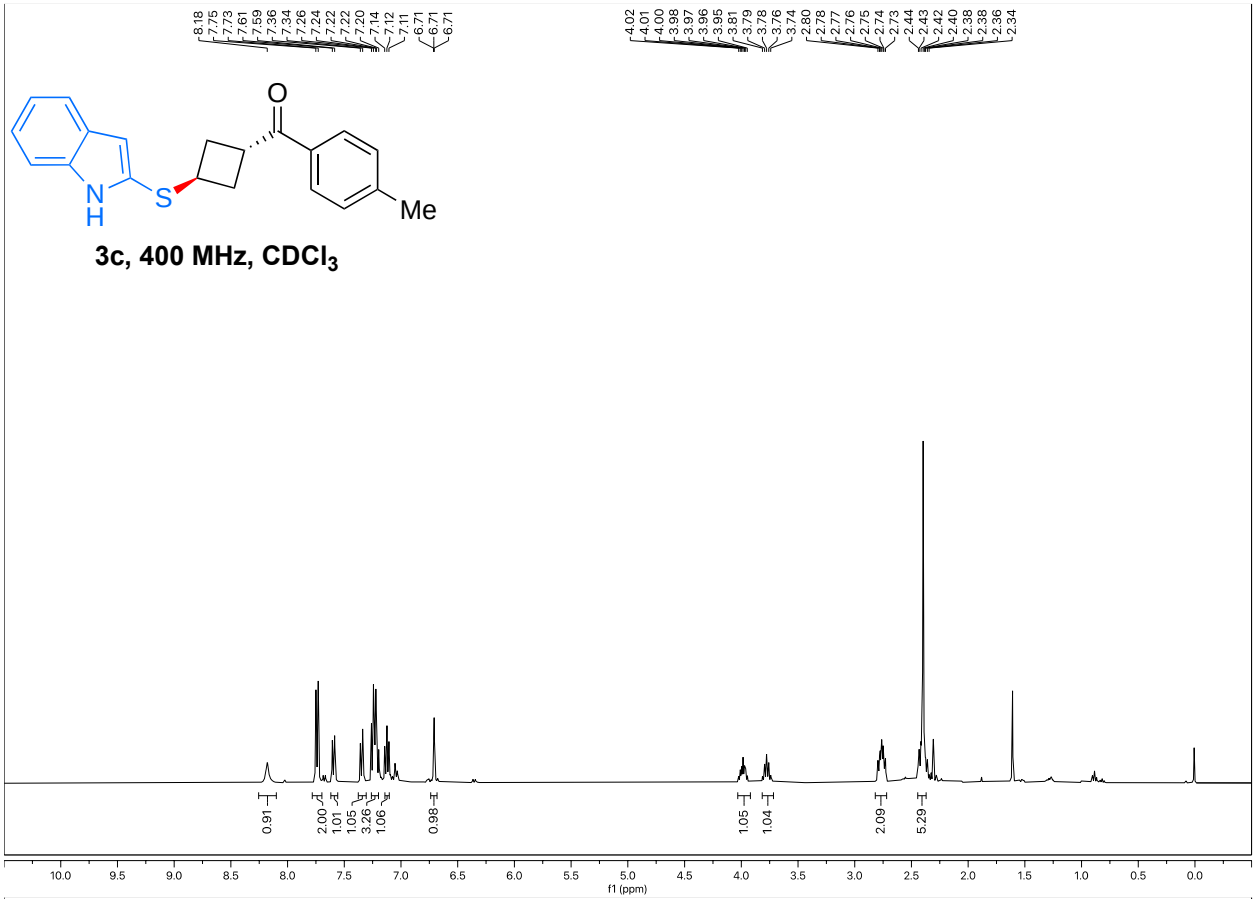
3a, 100 MHz, $CDCl_3$

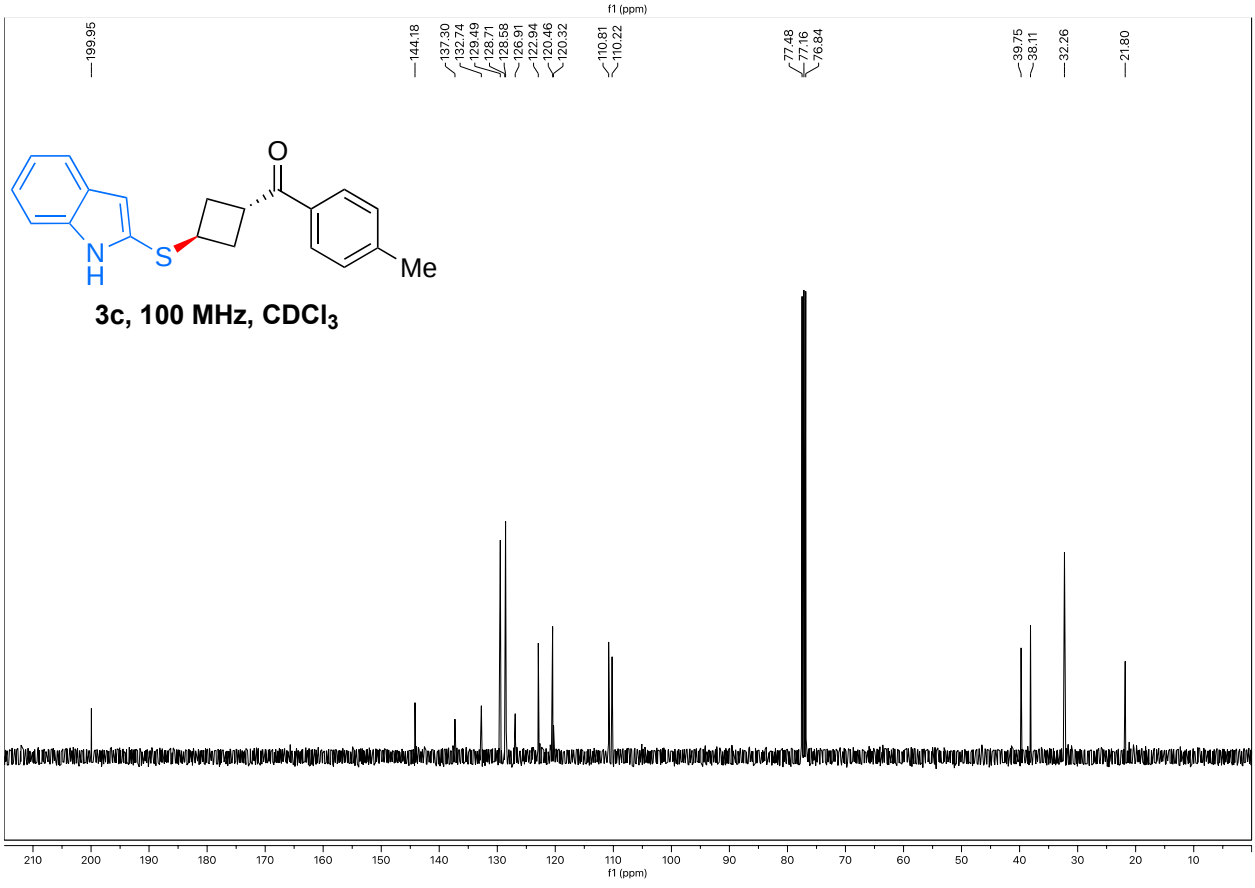
3-((1*H*-Indol-2-yl)thio)cyclobutyl)(phenyl)methanone (3b)



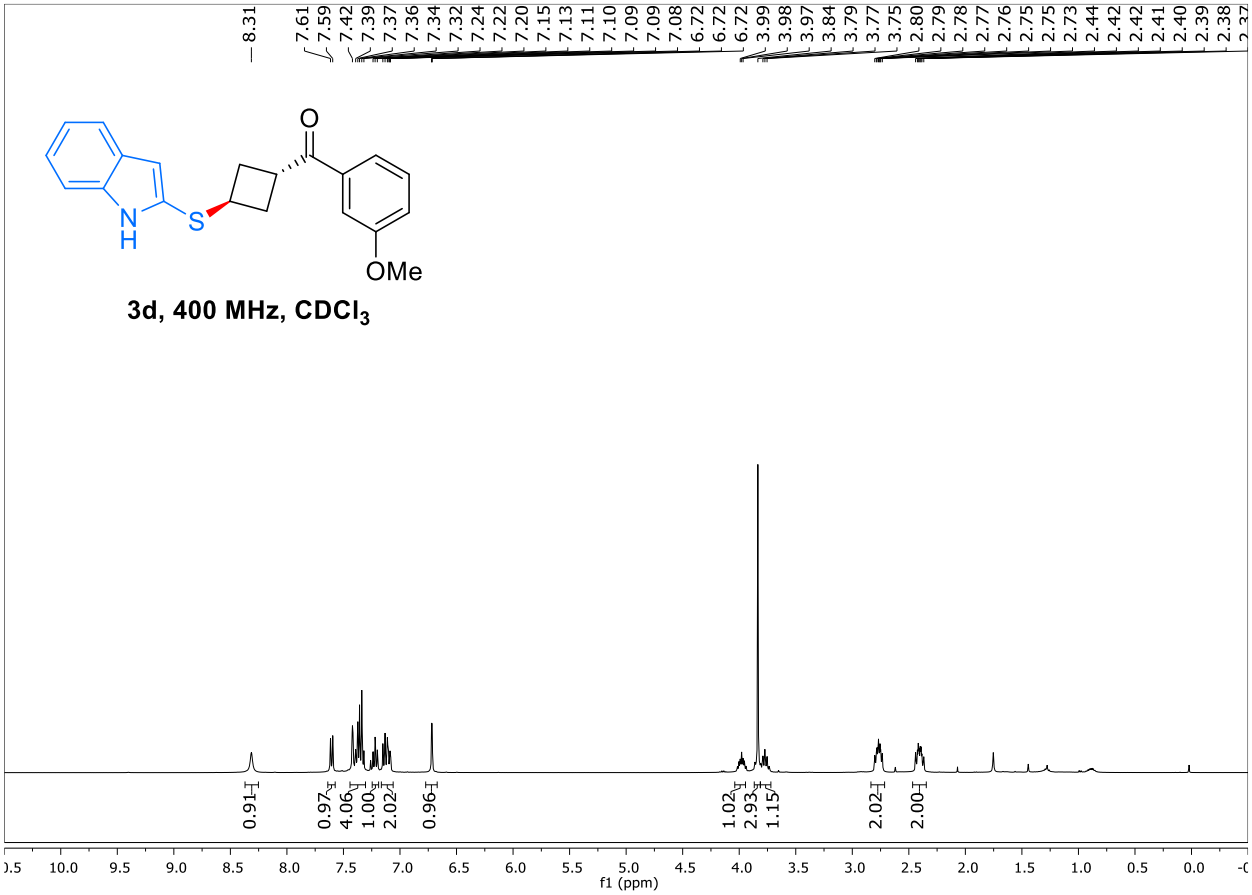


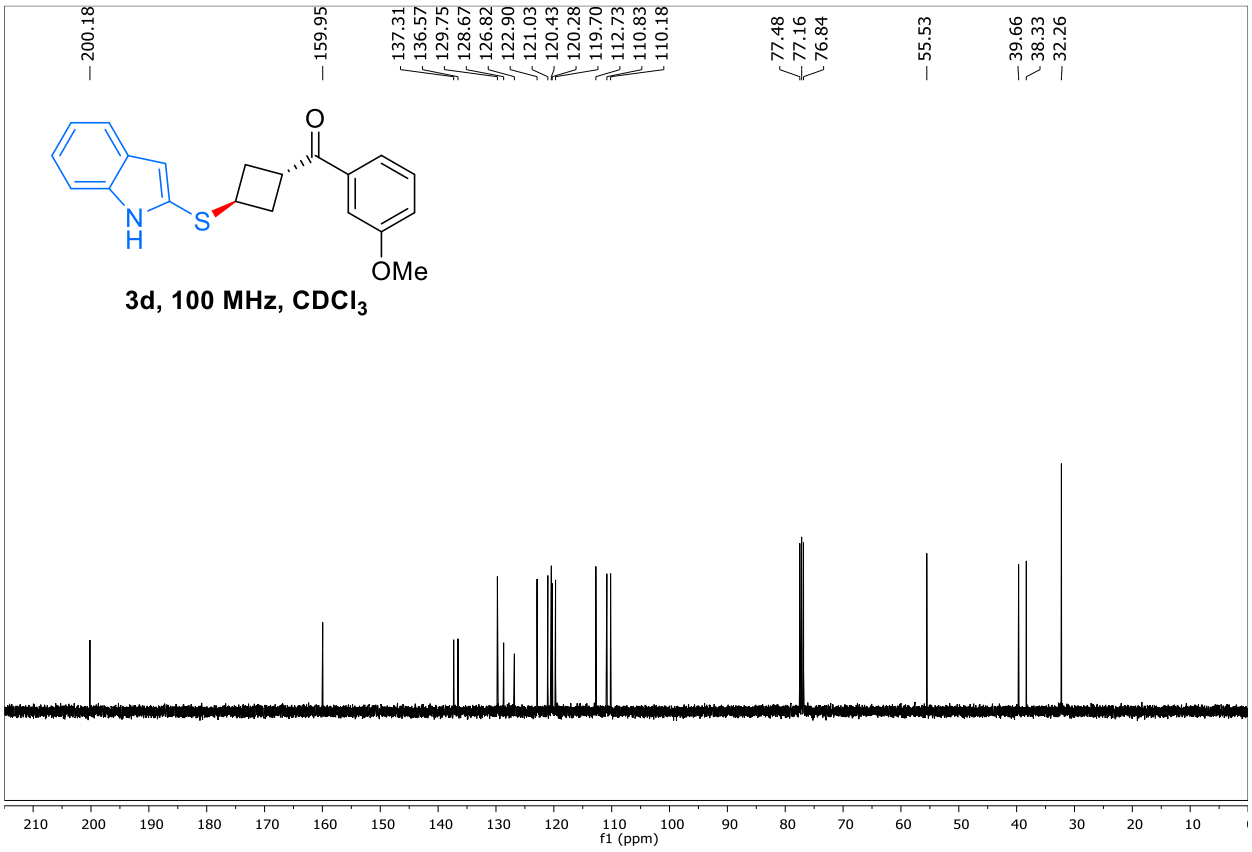
(3-((1*H*-Indol-2-yl)thio)cyclobutyl)(*p*-tolyl)methanone (3c)



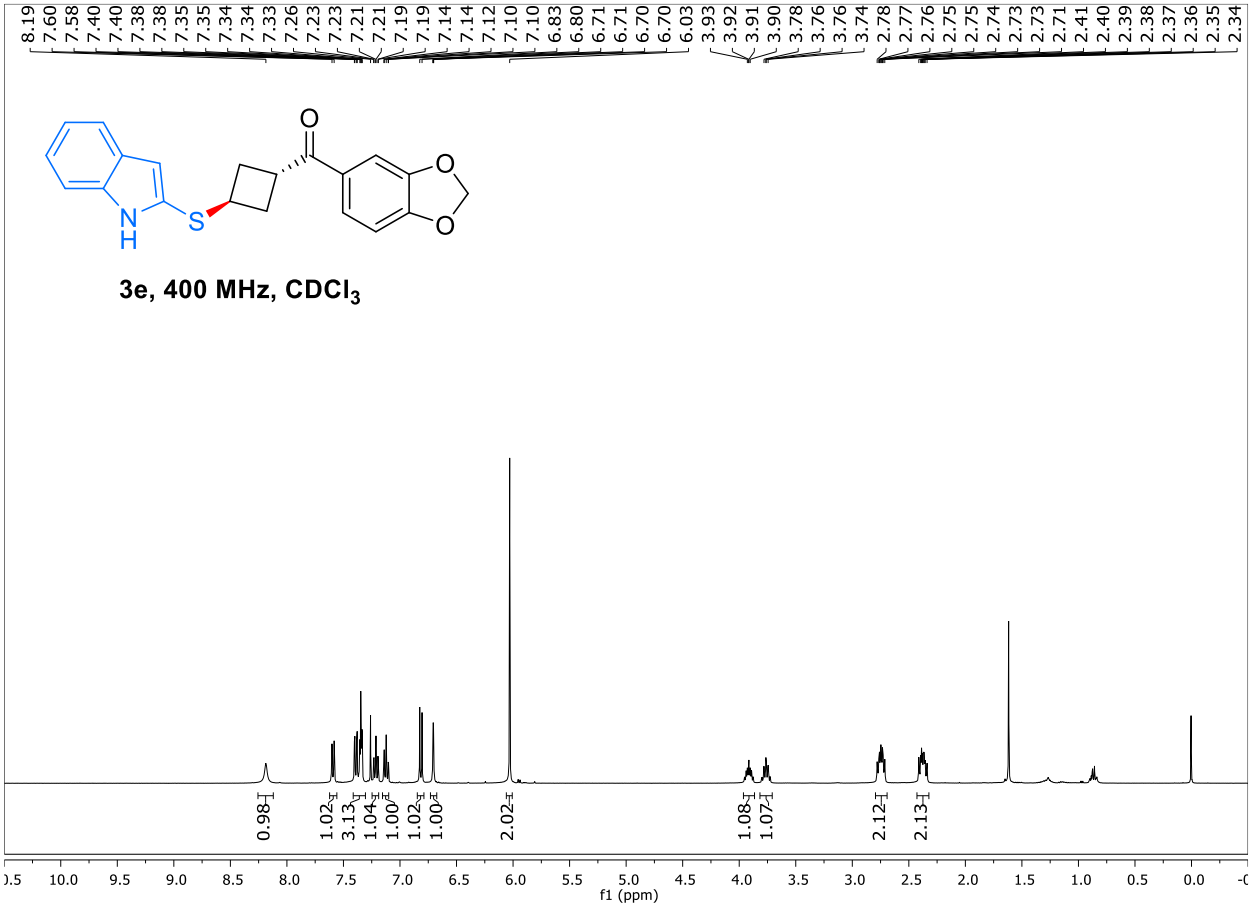


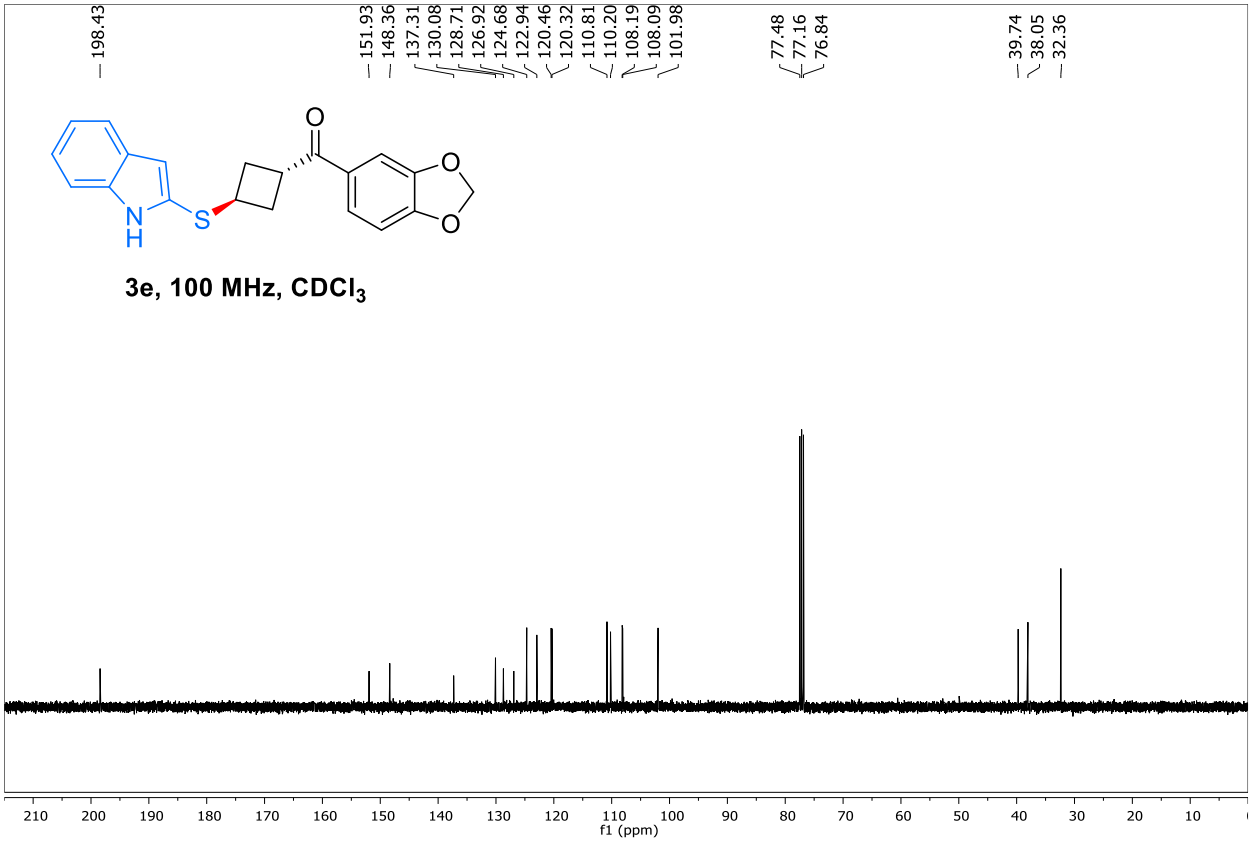
3-((1*H*-Indol-2-yl)thio)cyclobutyl)(3-methoxyphenyl)methanone (3d)



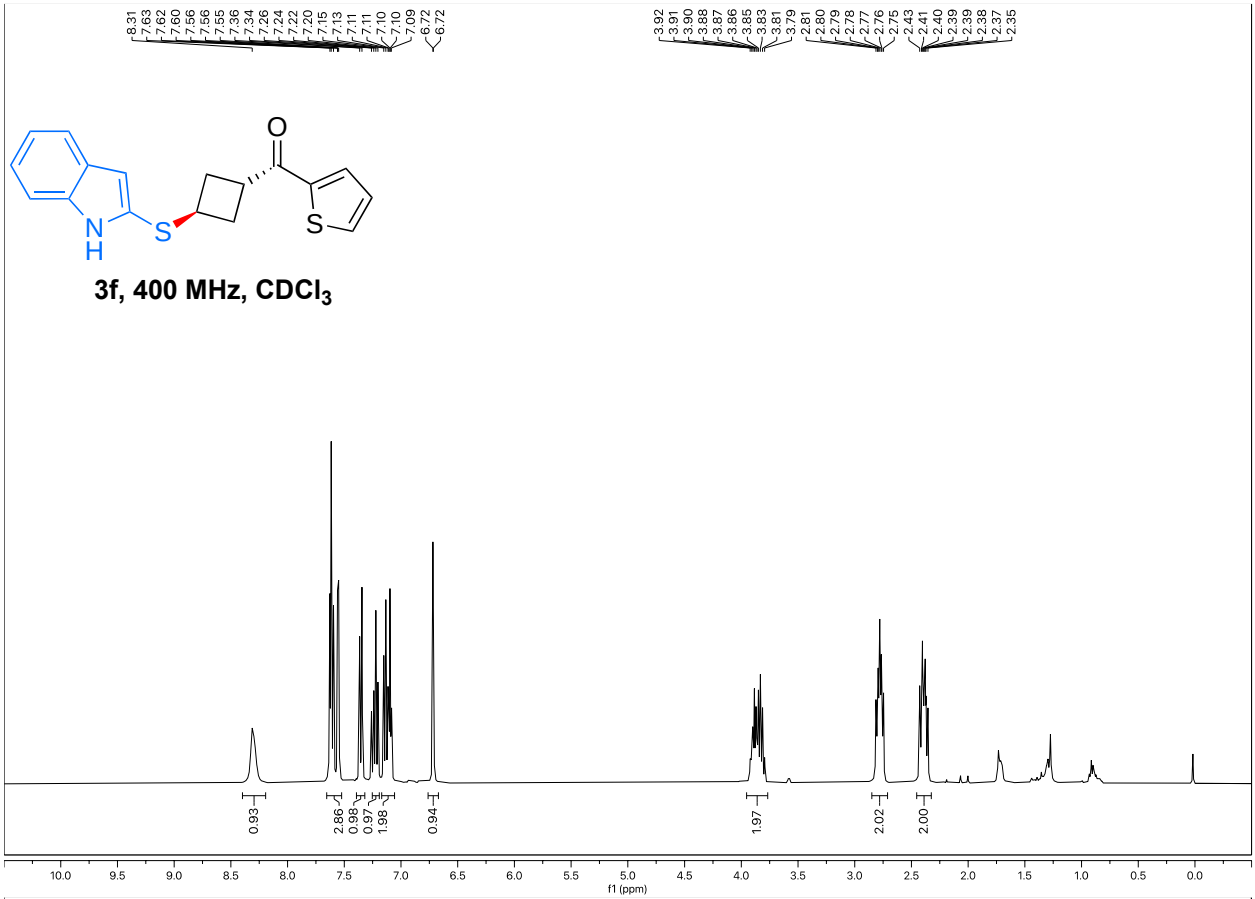


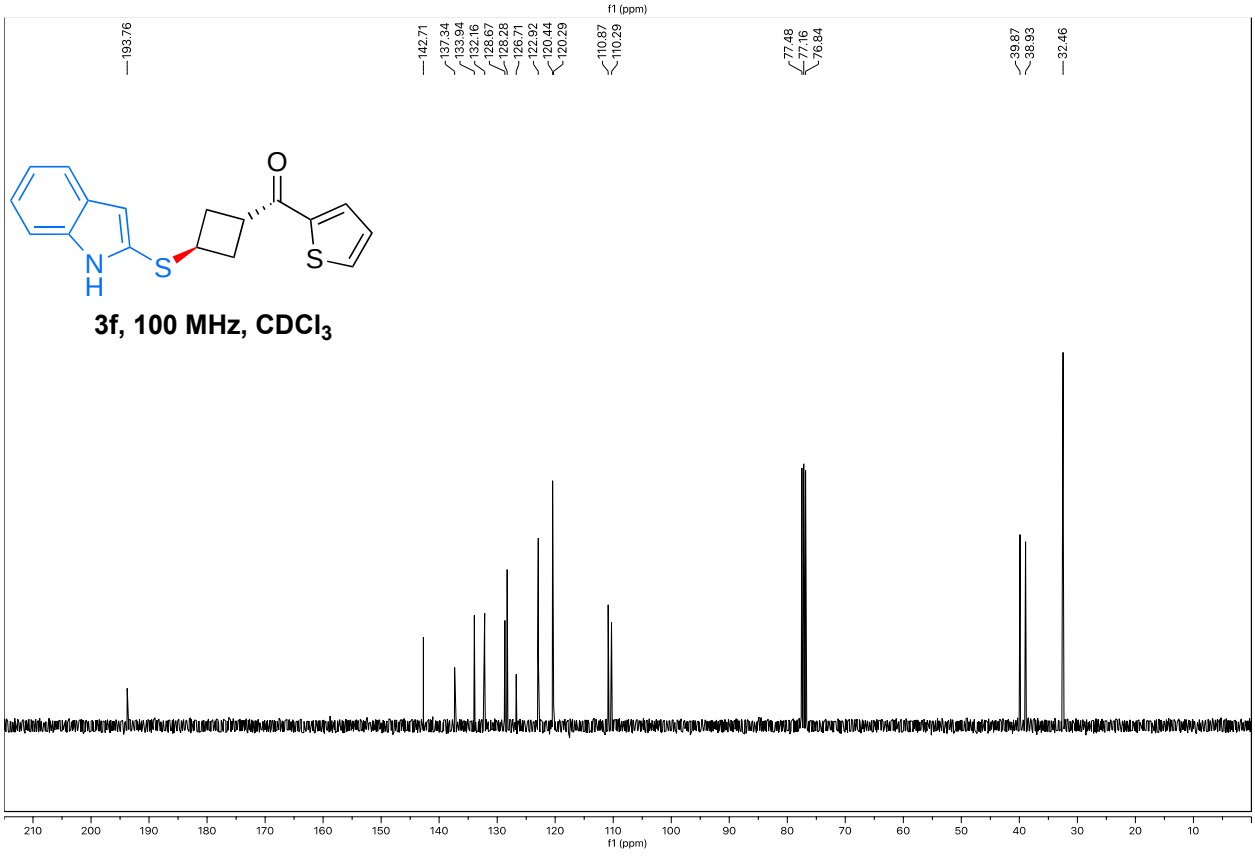
3-((1*H*-Indol-2-yl)thio)cyclobutyl)(benzo[*d*][1,3]dioxol-5-yl)methanone (3e)



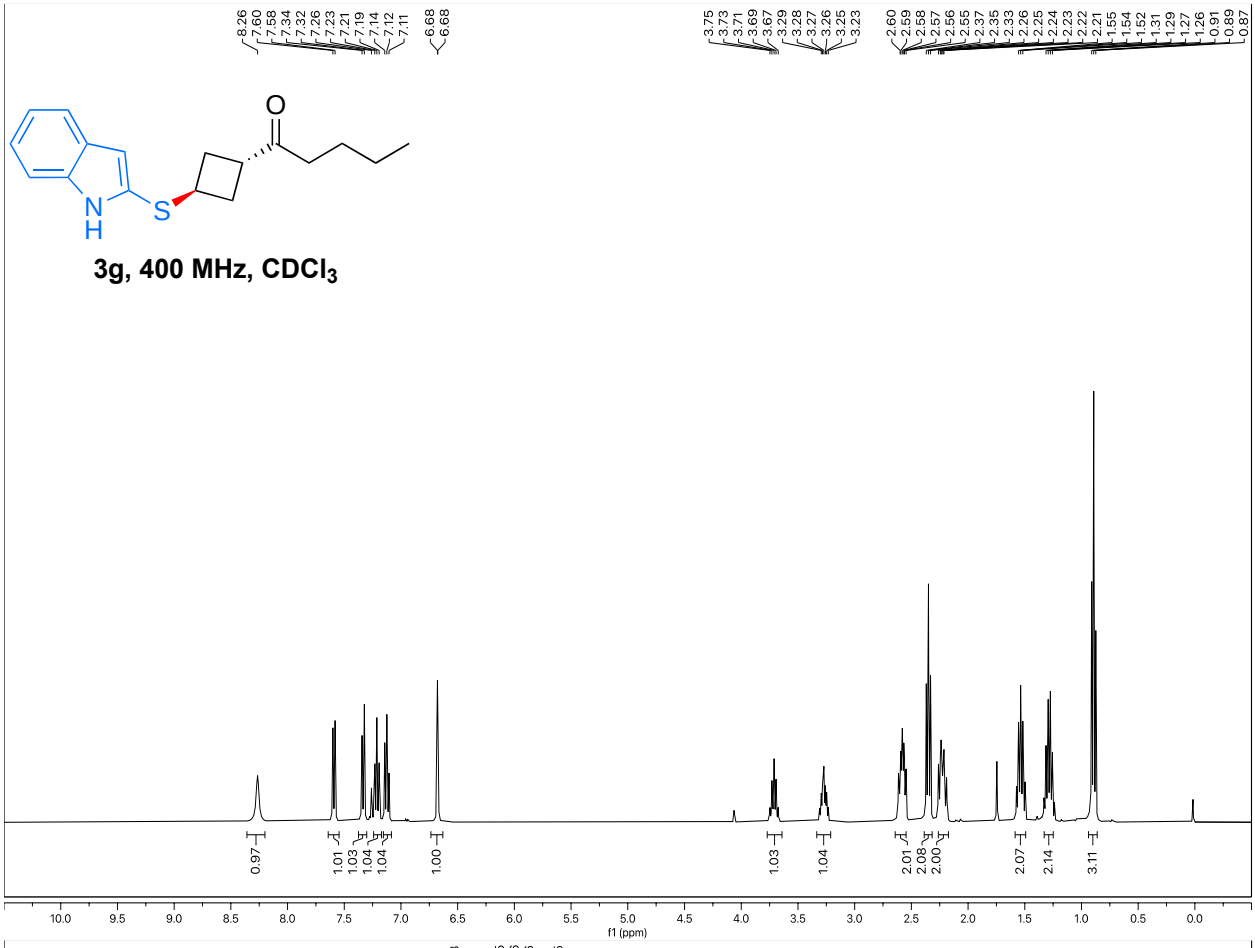


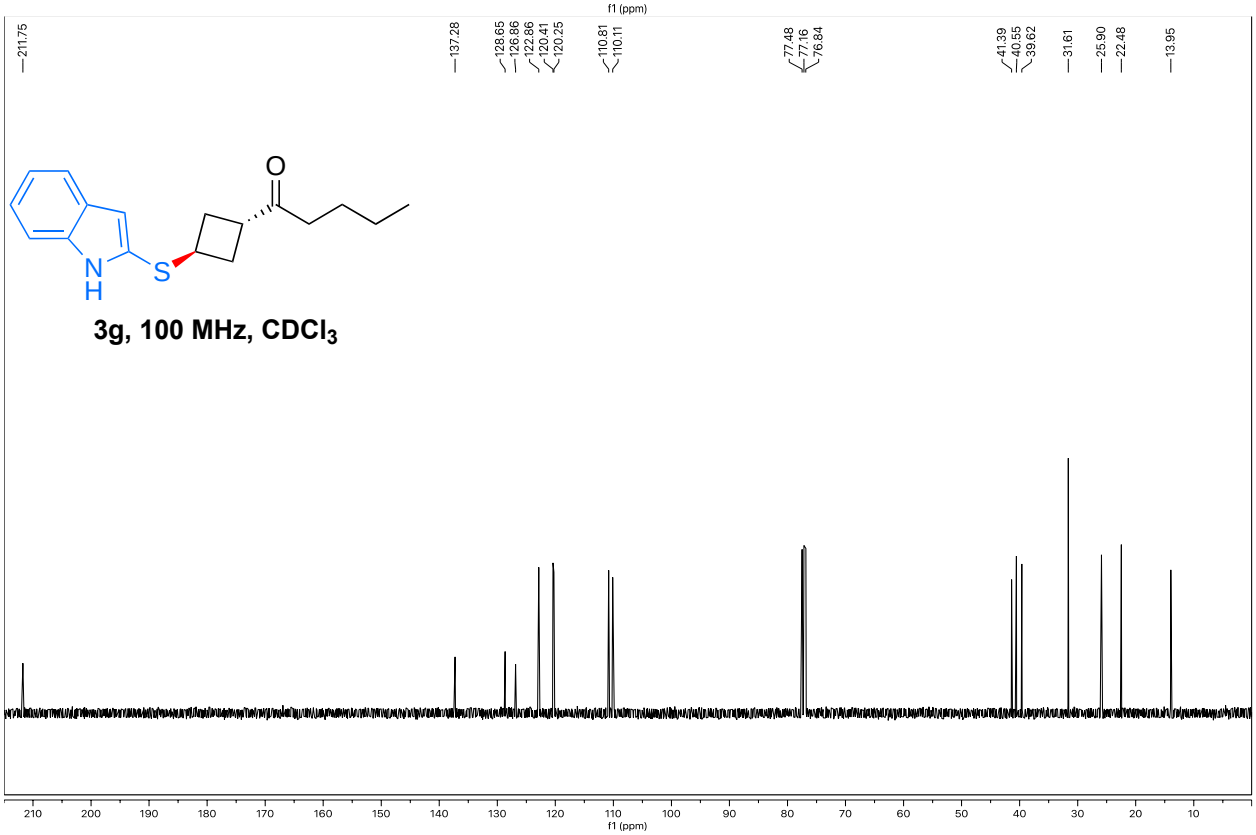
(3-((1*H*-Indol-2-yl)thio)cyclobutyl)(thiophen-2-yl)methanone (3f)



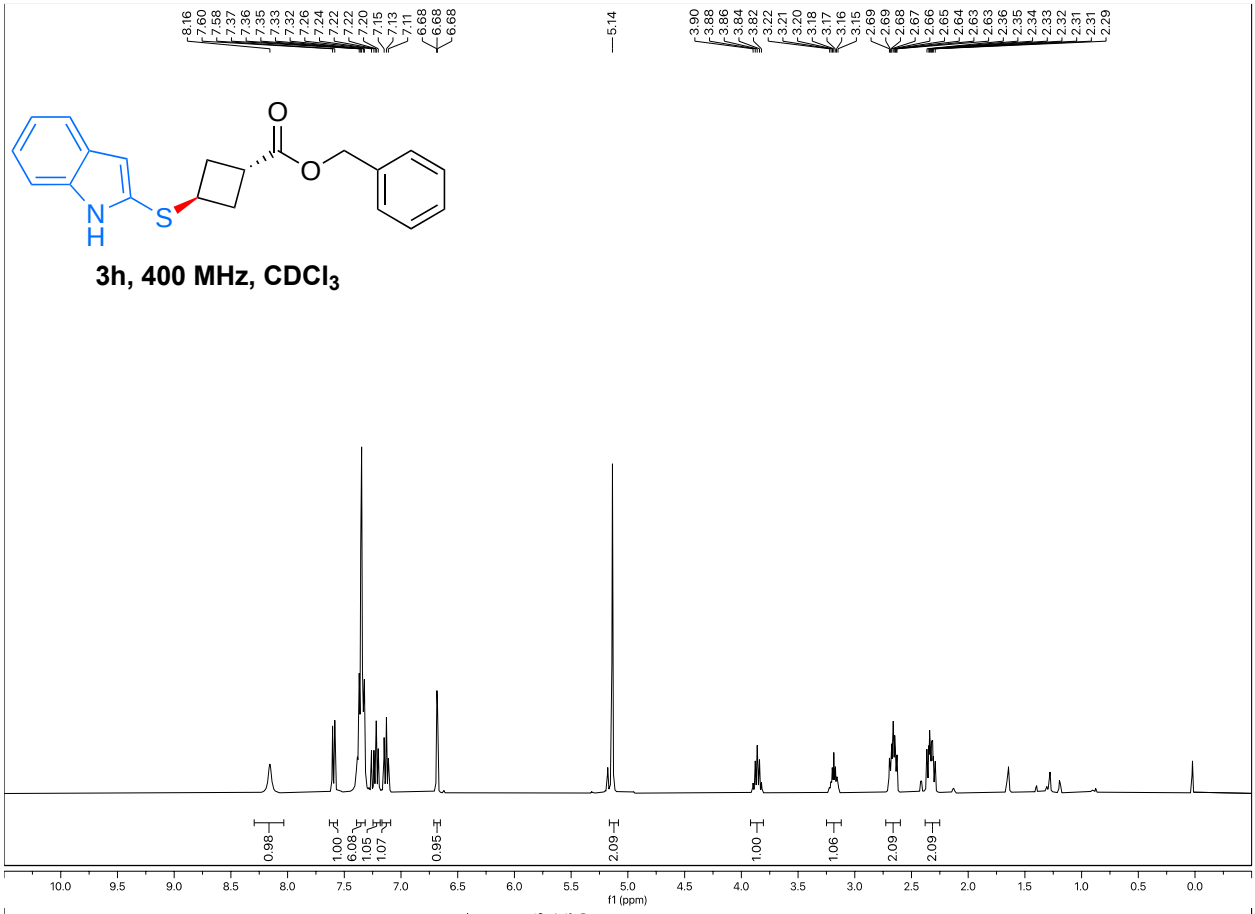


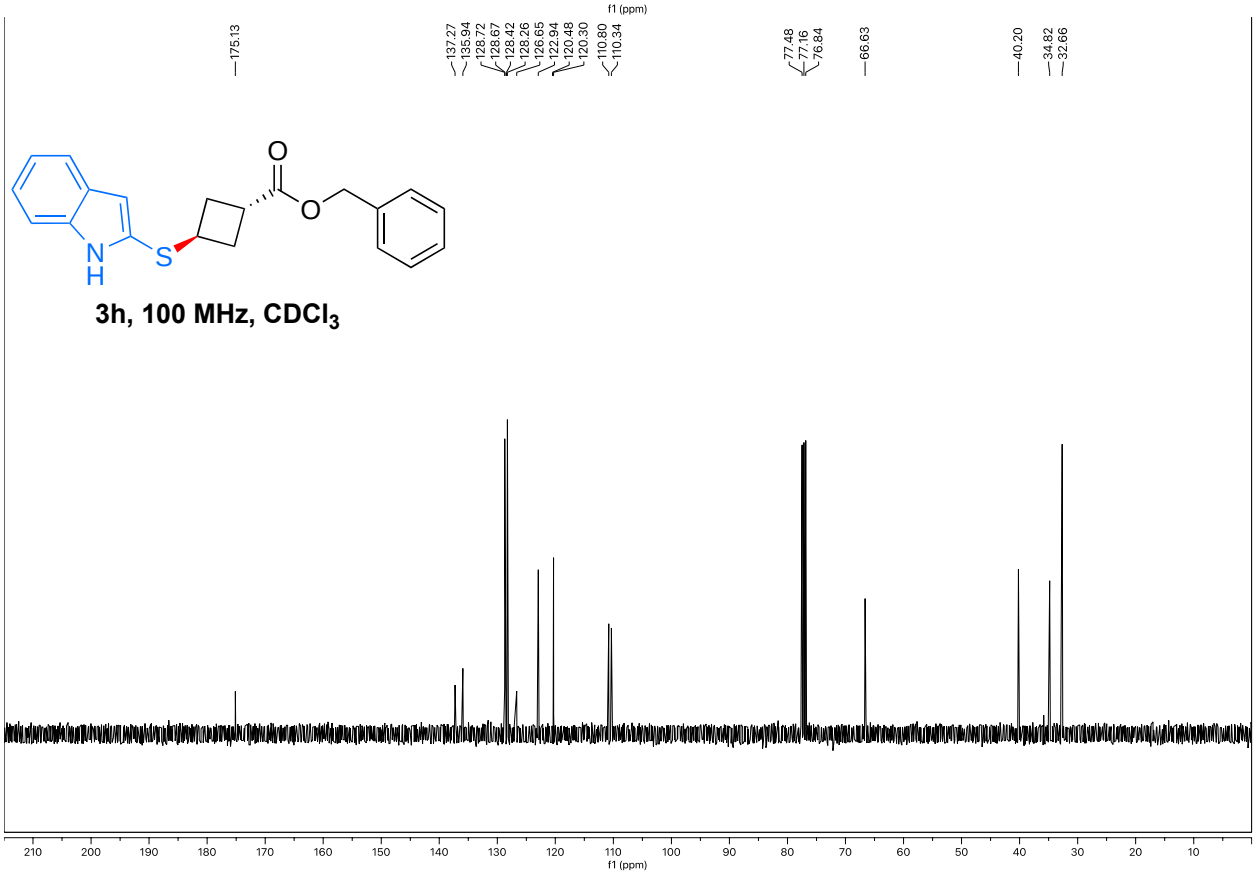
1-(3-((1*H*-Indol-2-yl)thio)cyclobutyl)pentan-1-one (3g)



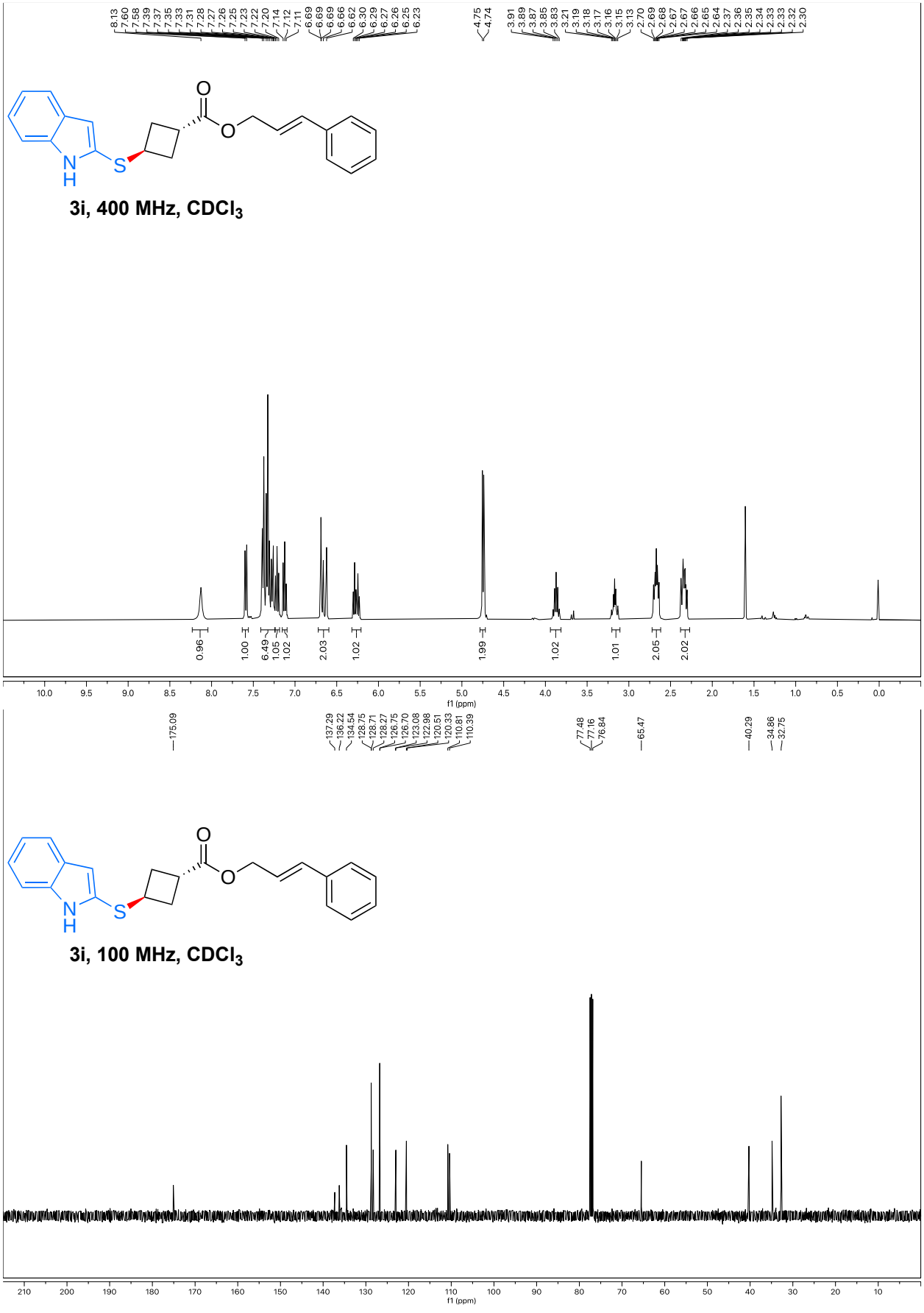


Benzyl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3h)

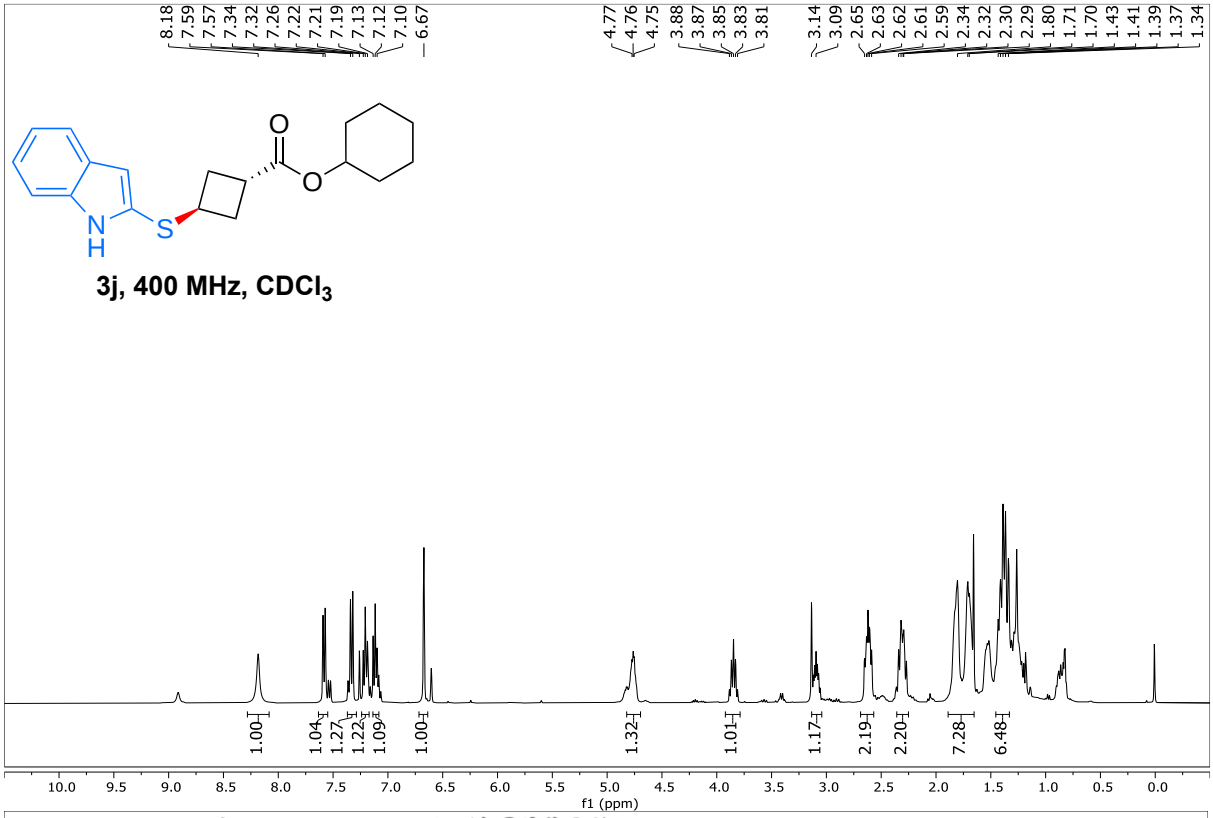


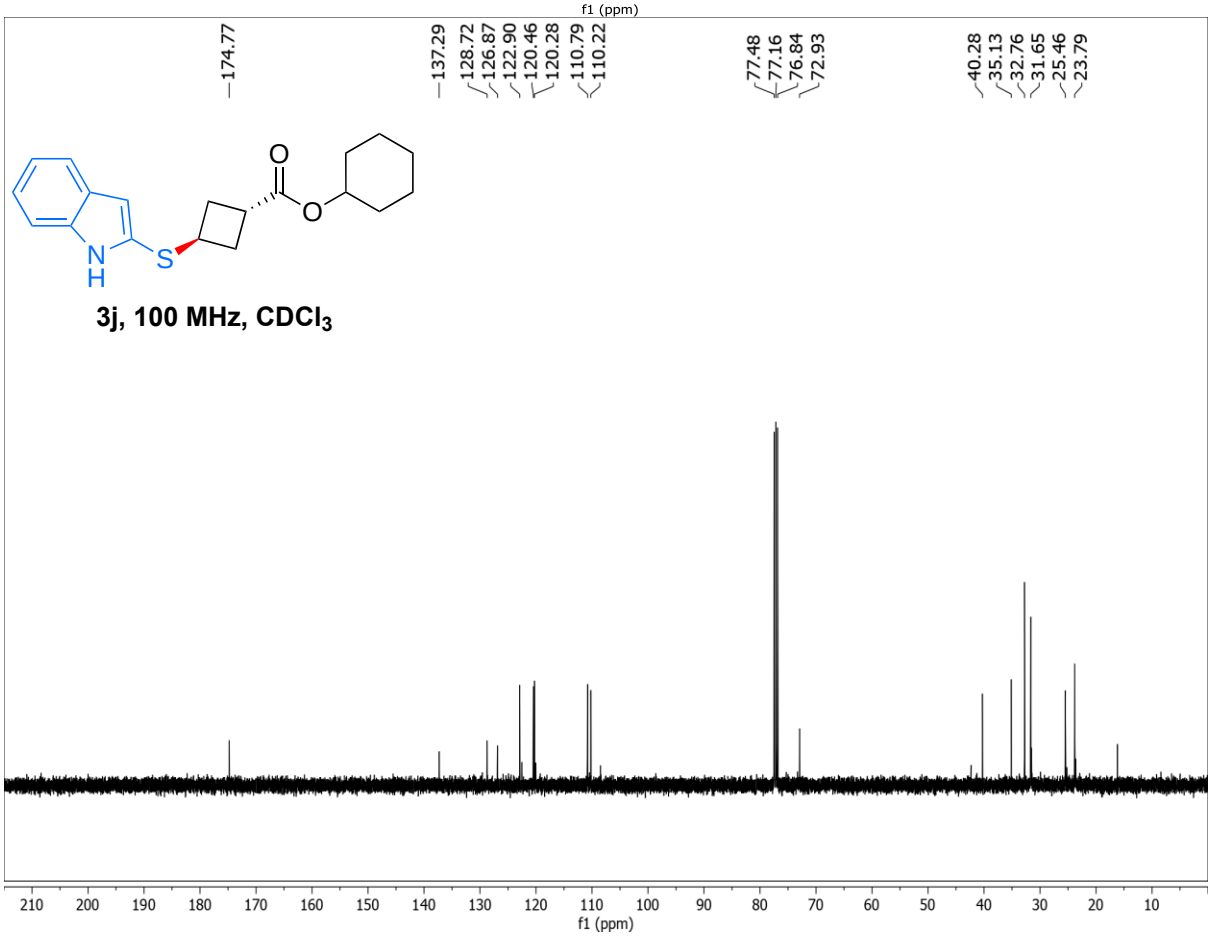


Cinnamyl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3i)

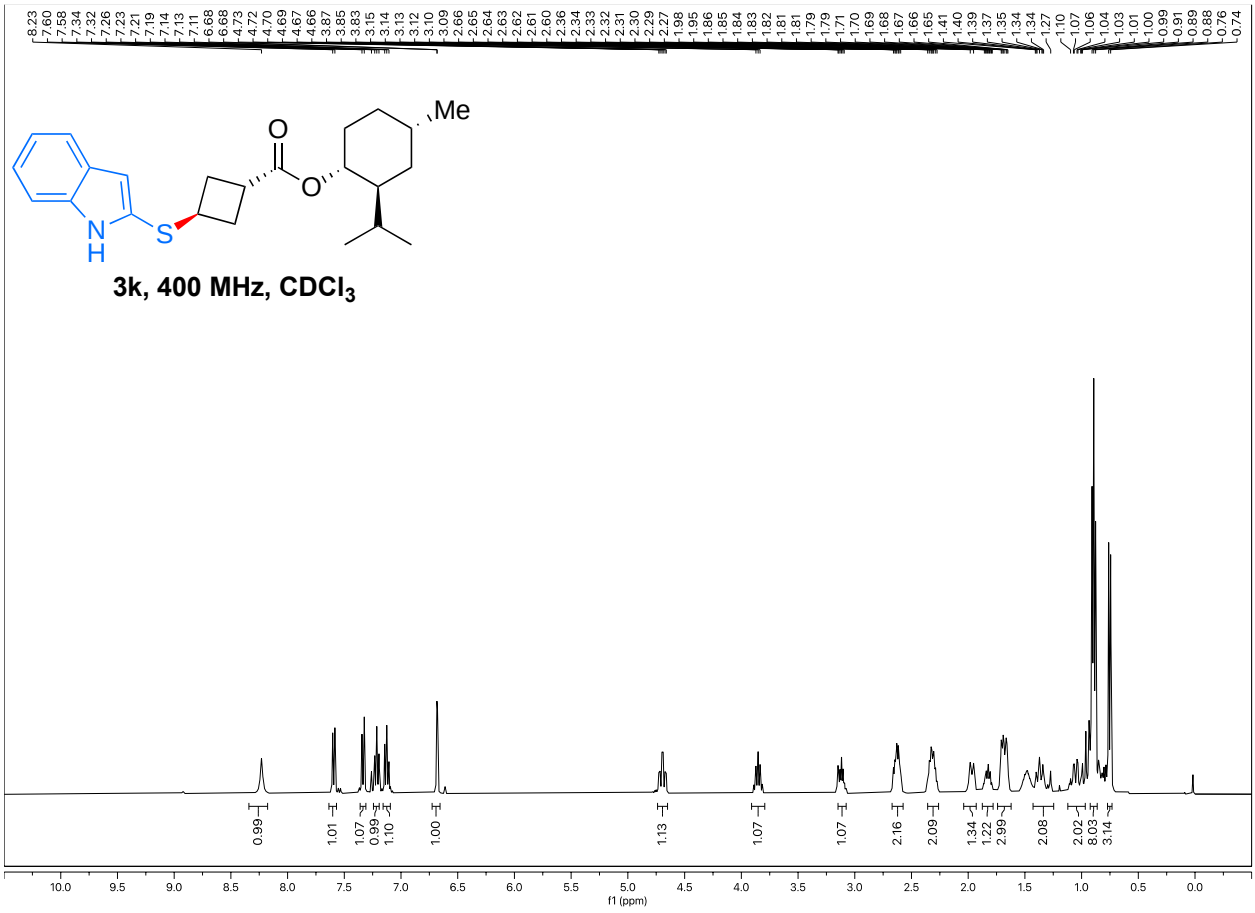


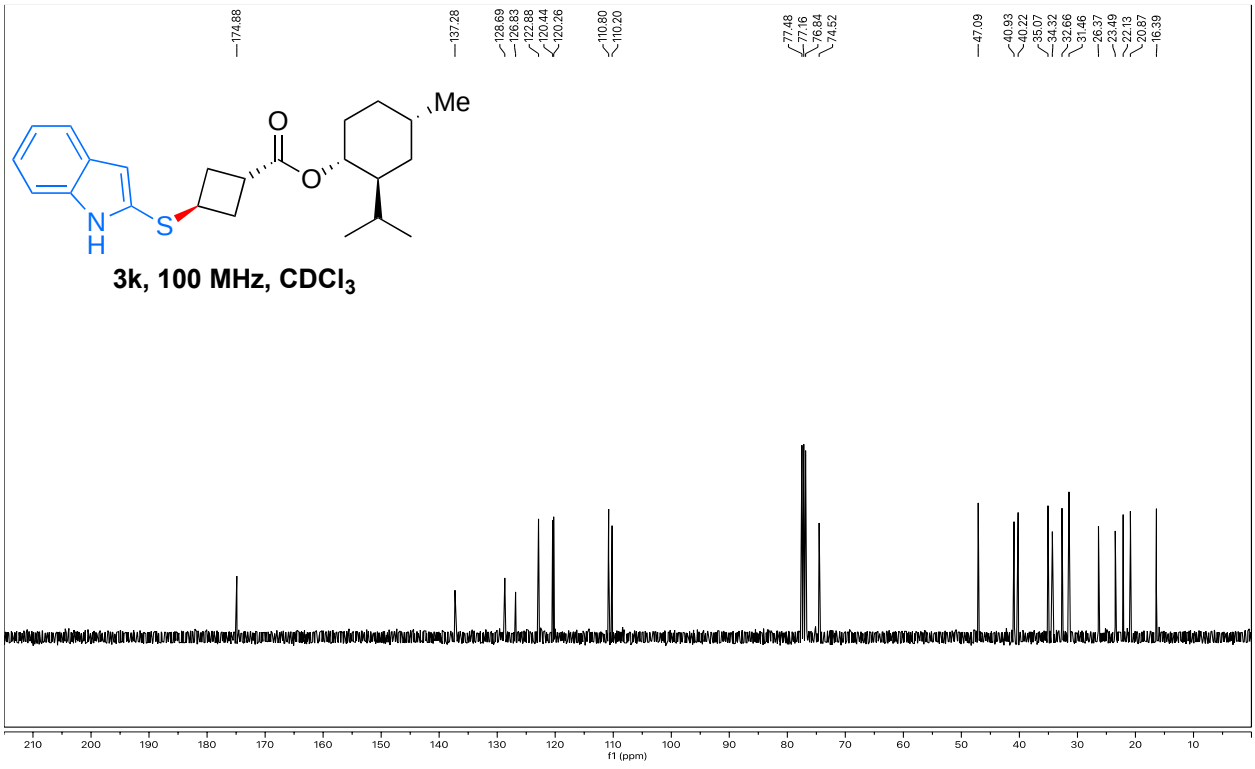
Cyclohexyl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3j)



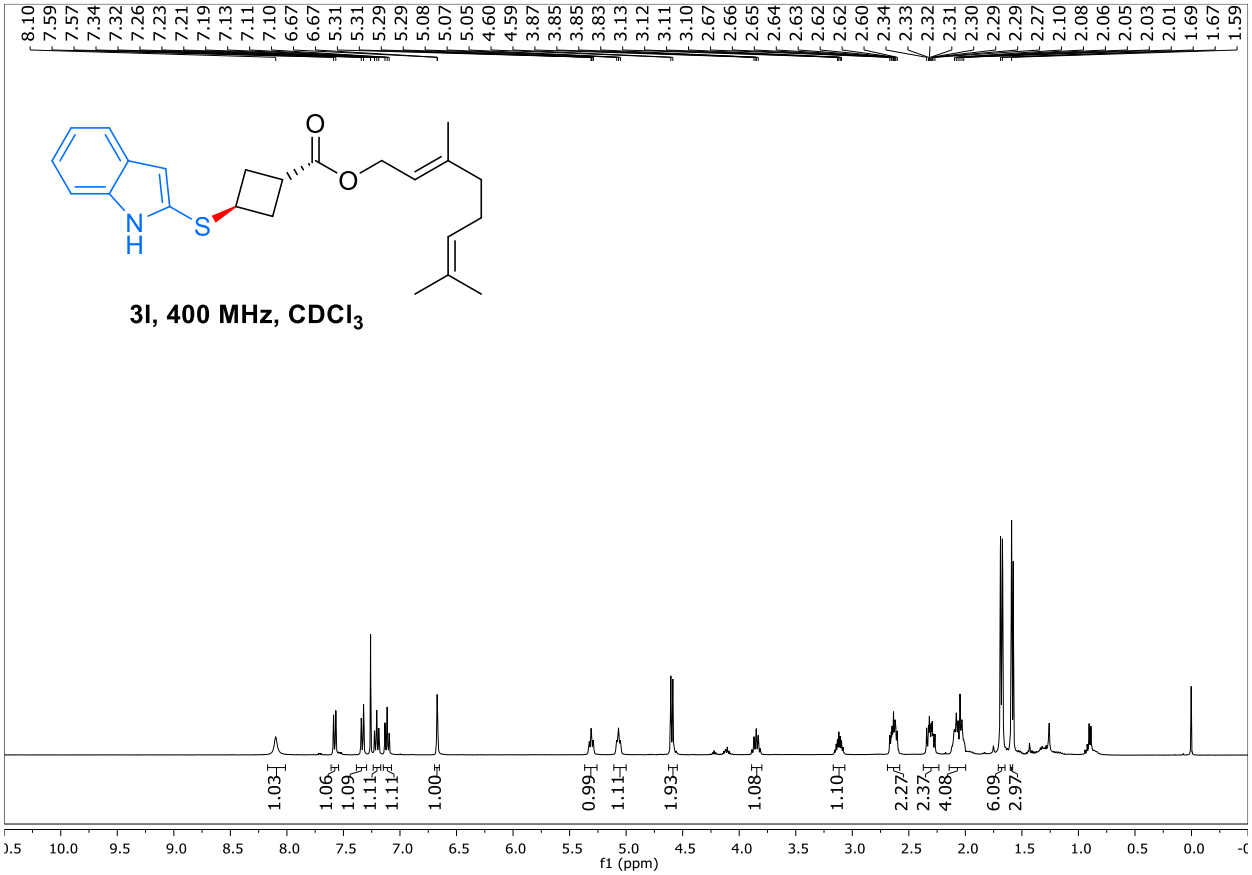


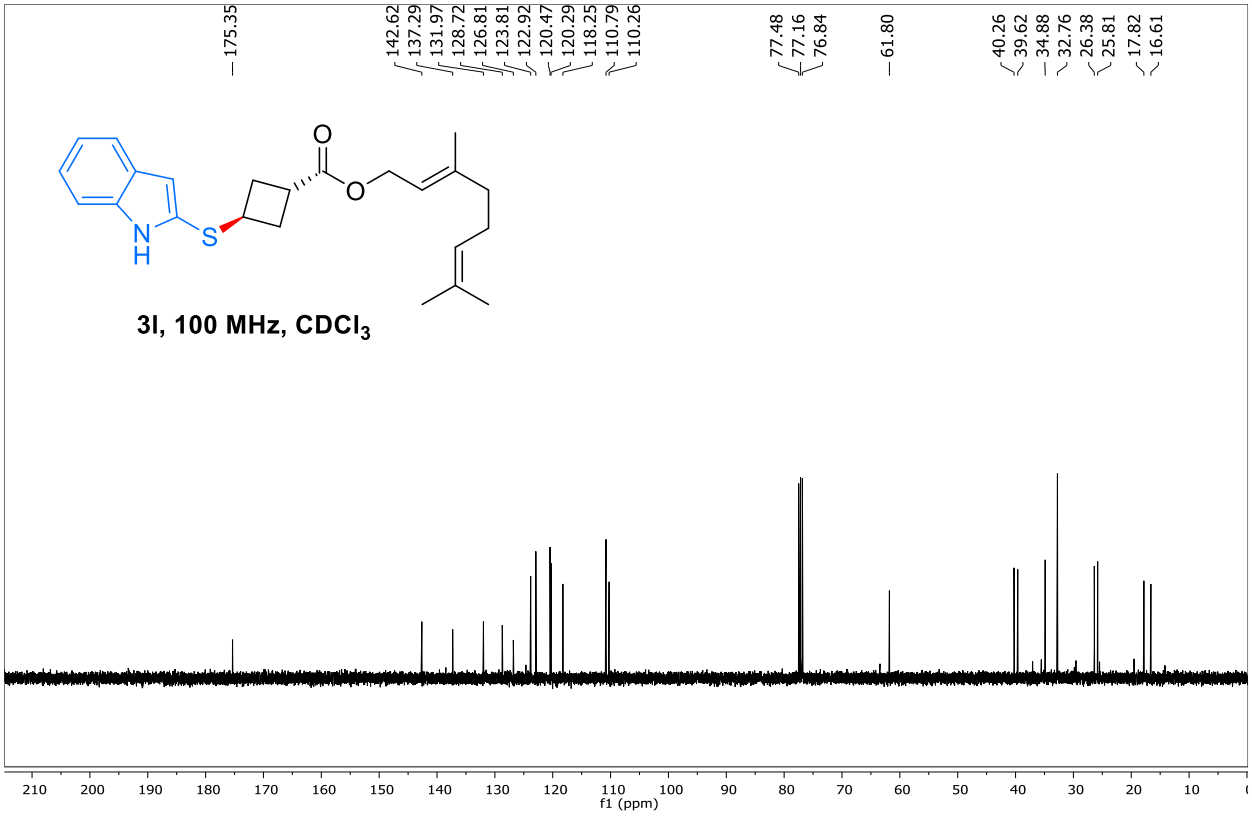
(1*R*,2*S*,4*S*)-2-Isopropyl-4-methylcyclohexyl 3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3k)



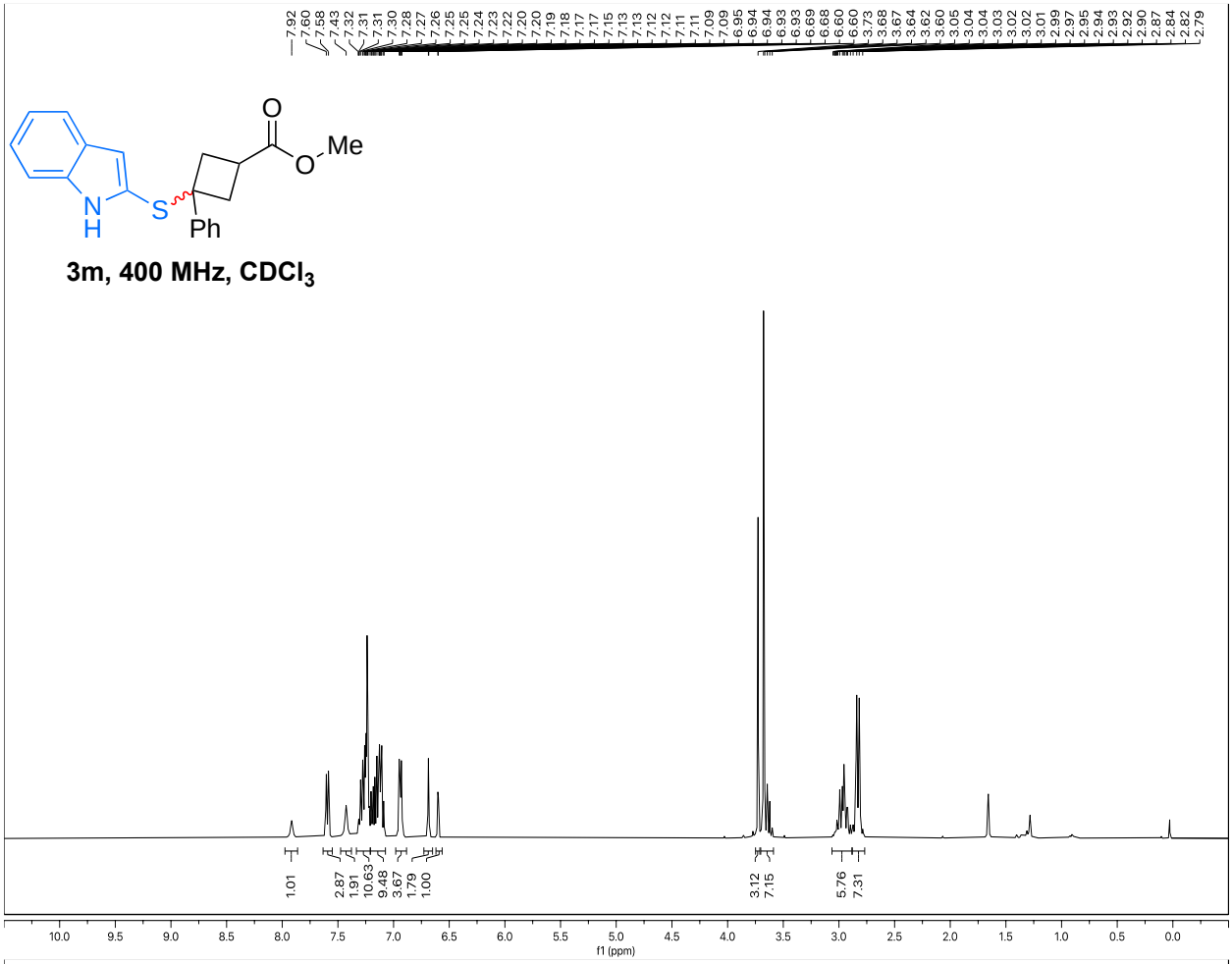


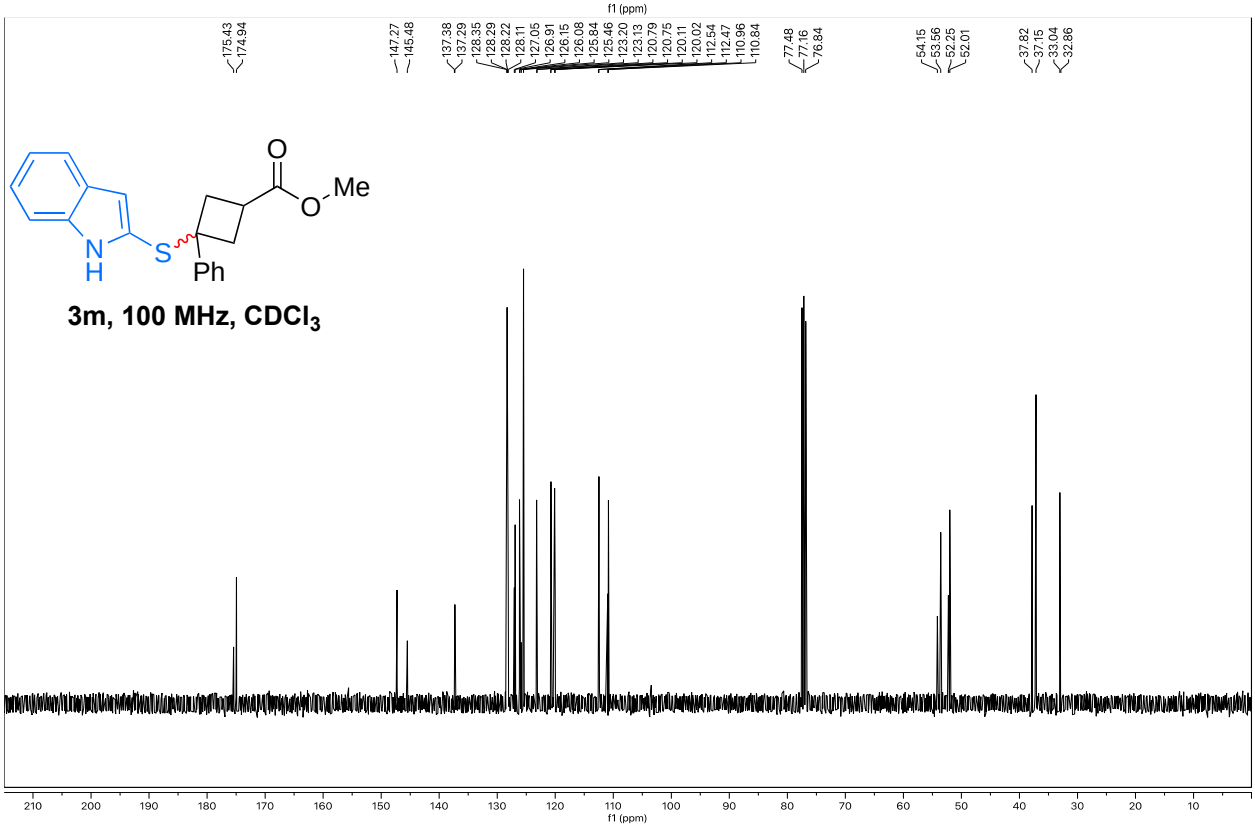
(*E*)-3,7-Dimethylocta-2,6-dien-1-yl-3-((1*H*-indol-2-yl)thio)cyclobutane-1-carboxylate (3l)



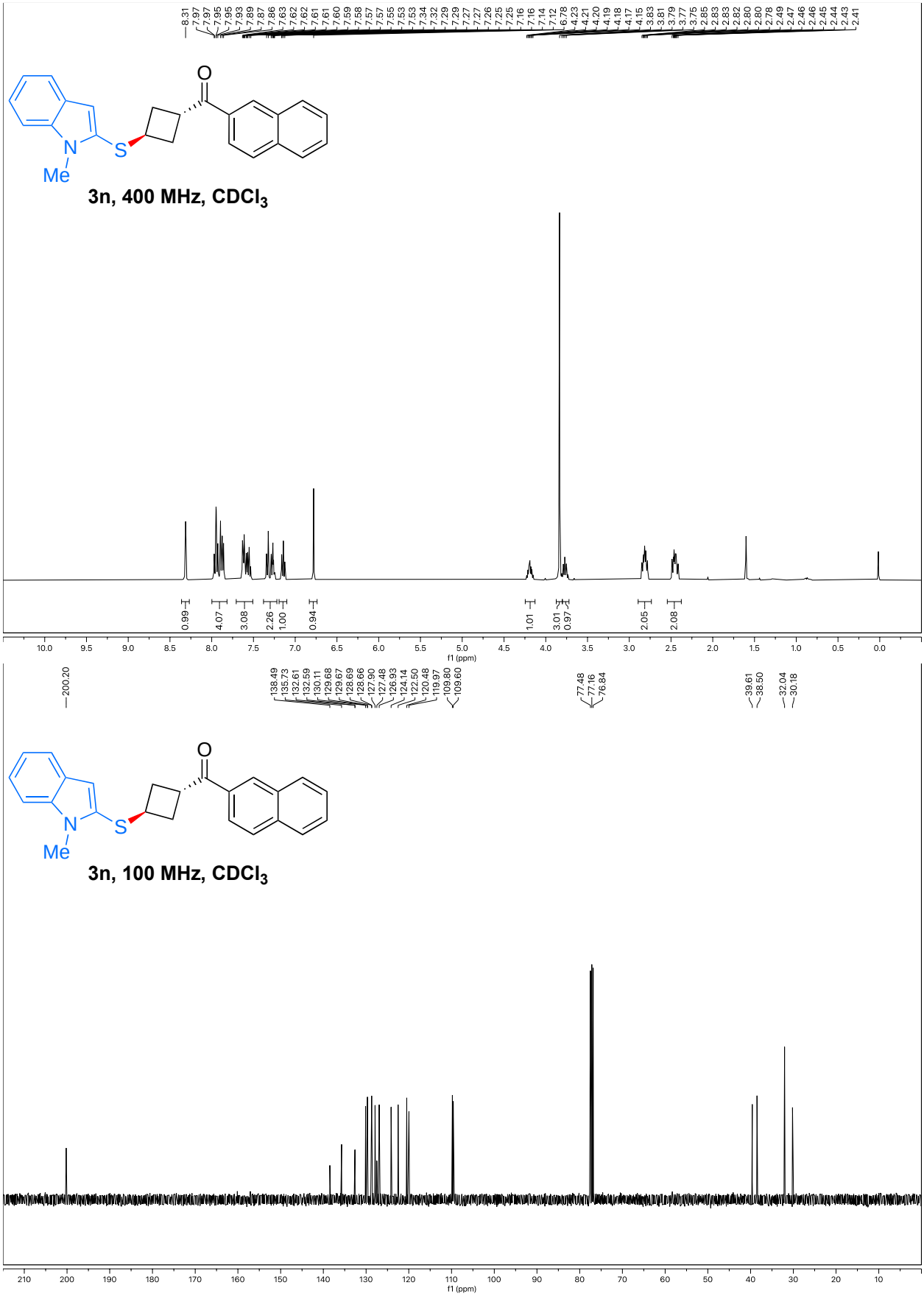


Methyl 3-((1*H*-indol-2-yl)thio)-3-phenylcyclobutane-1-carboxylate (3m)

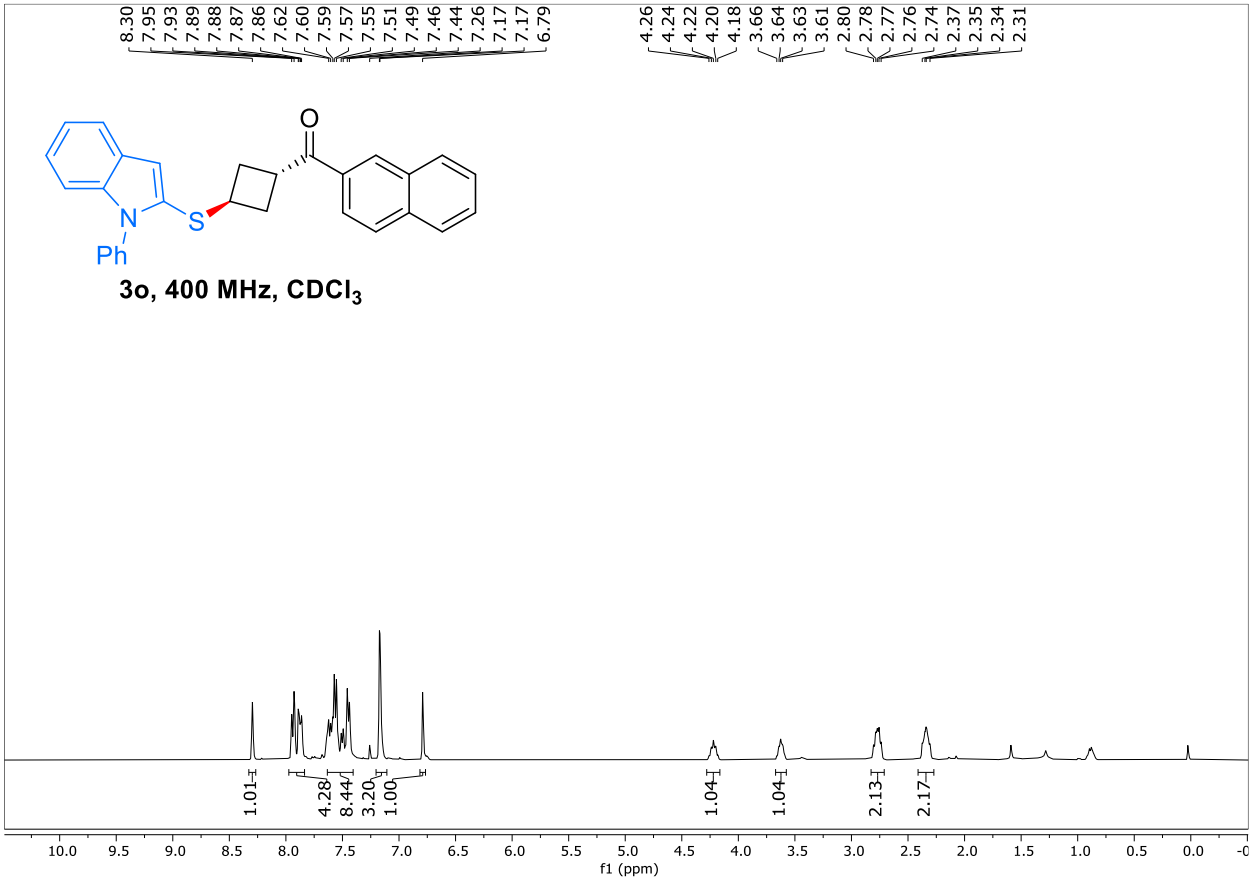


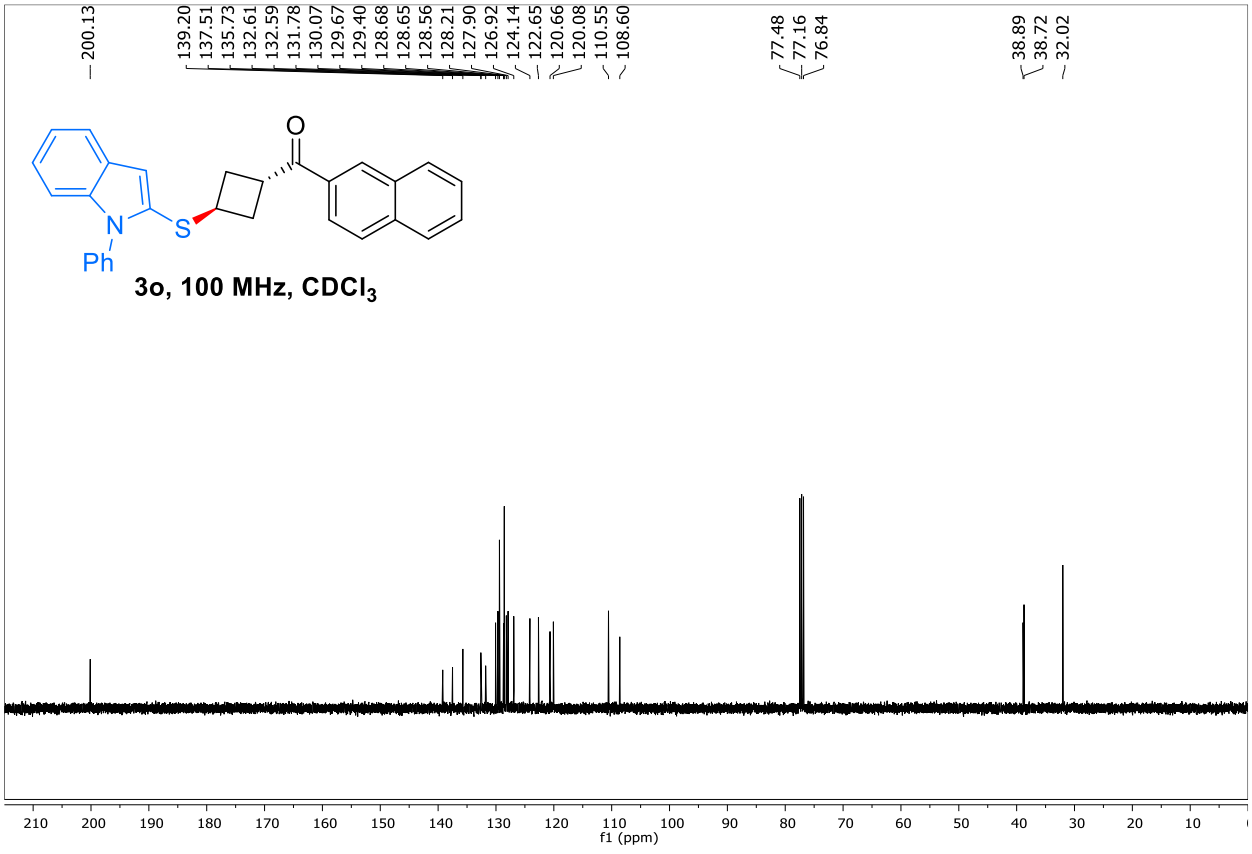


(3-((1-Methyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3n)

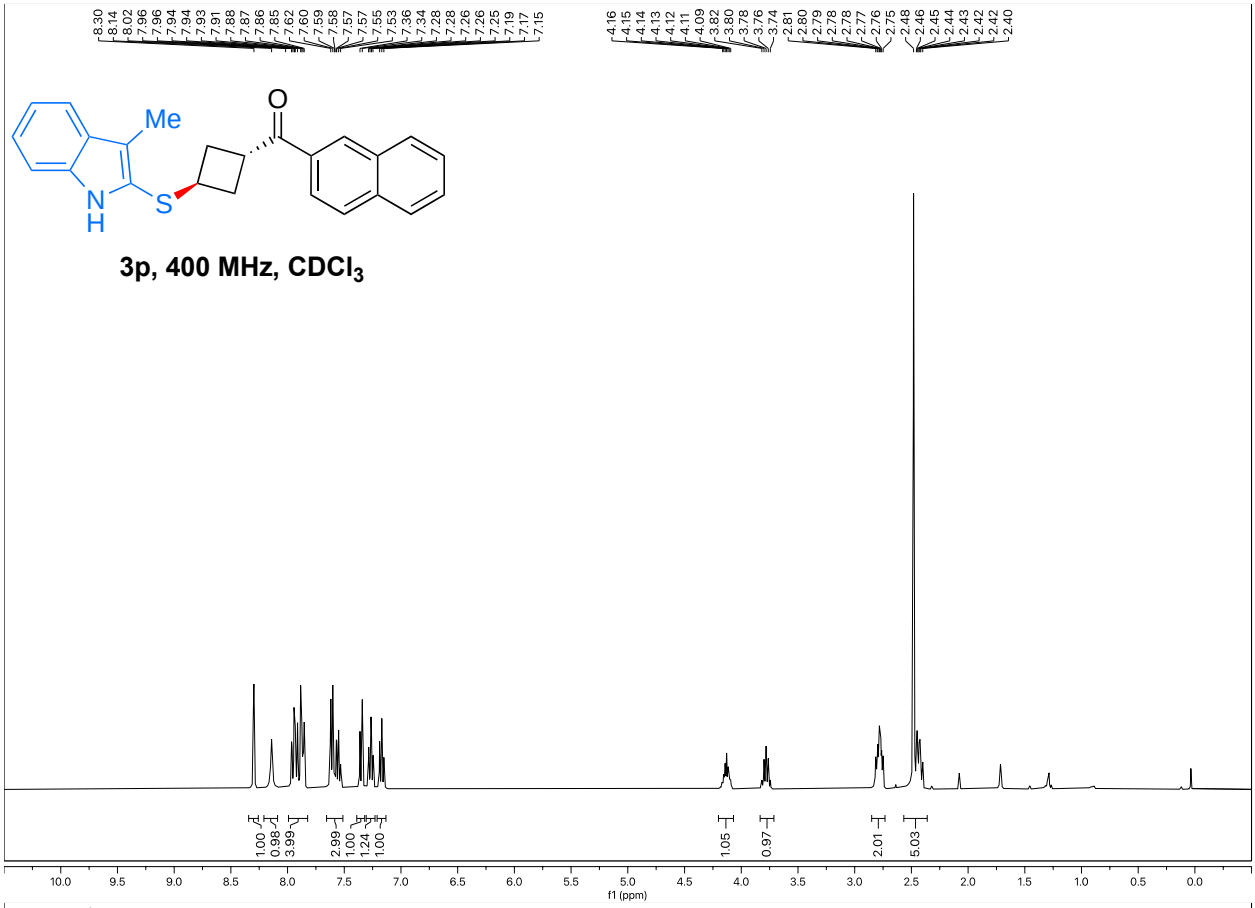


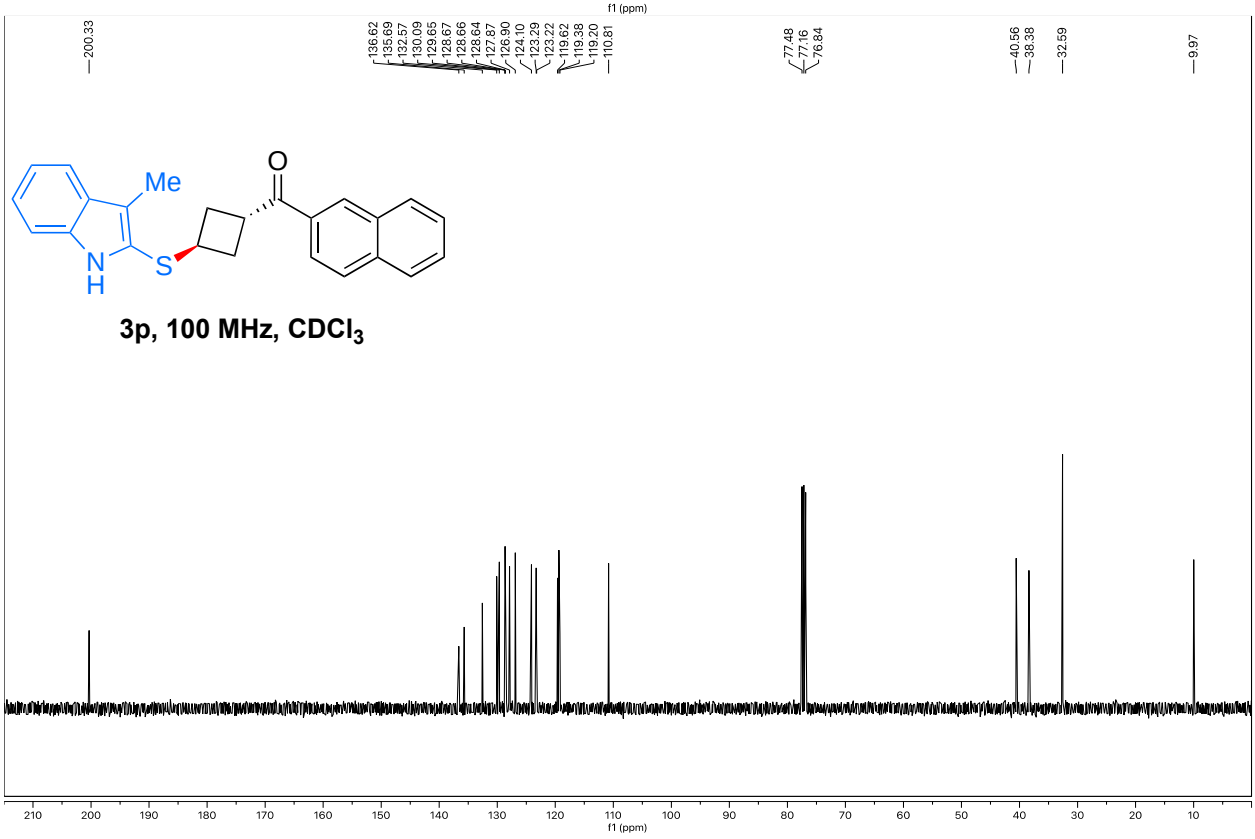
Naphthalen-2-yl(3-((1-phenyl-1*H*-indol-2-yl)thio)cyclobutyl)methanone (3o)



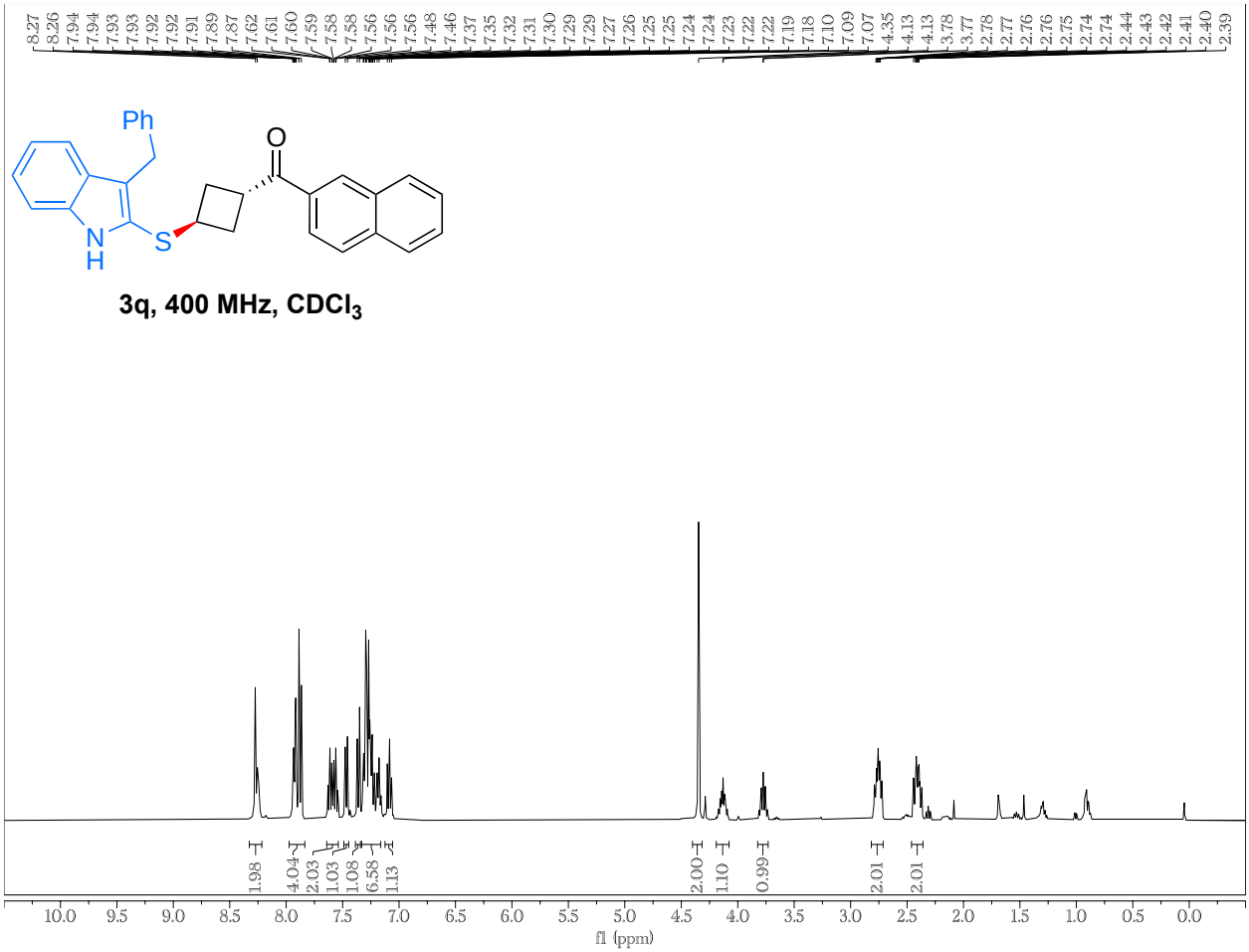


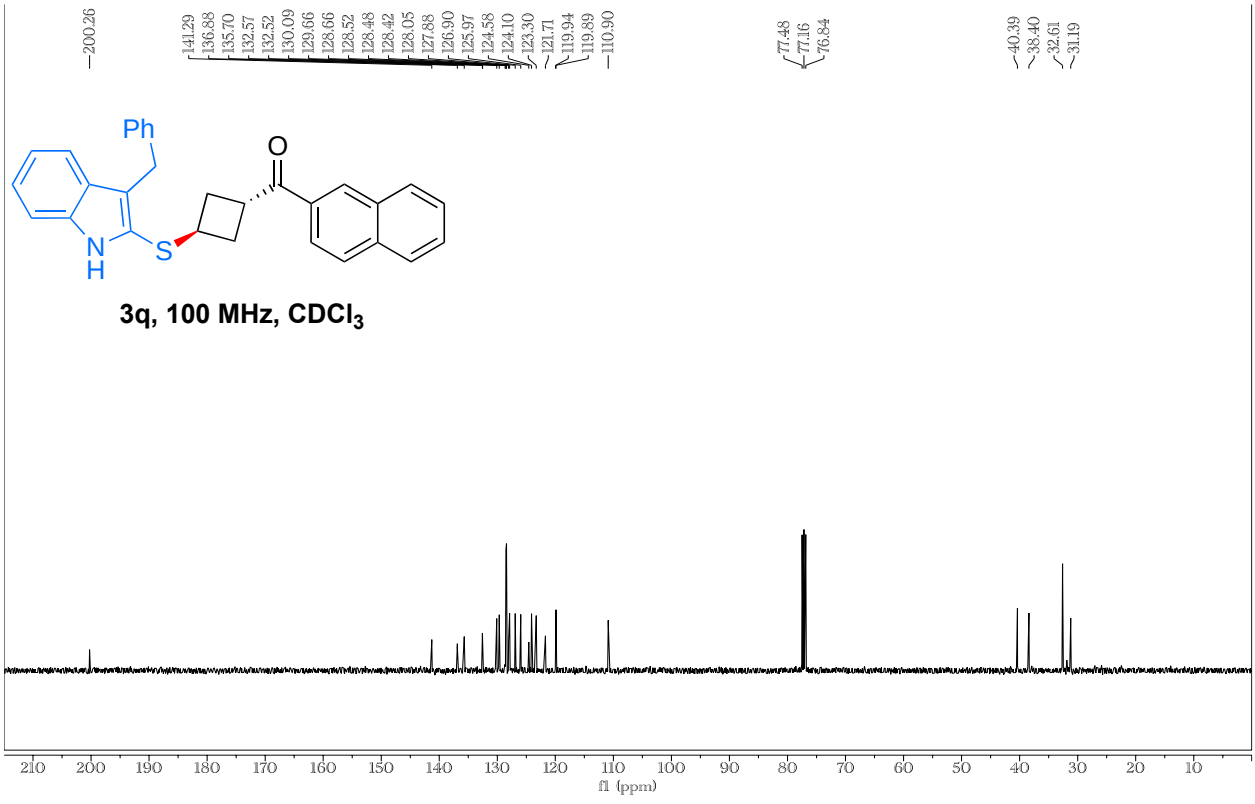
(3-((3-Methyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3p)



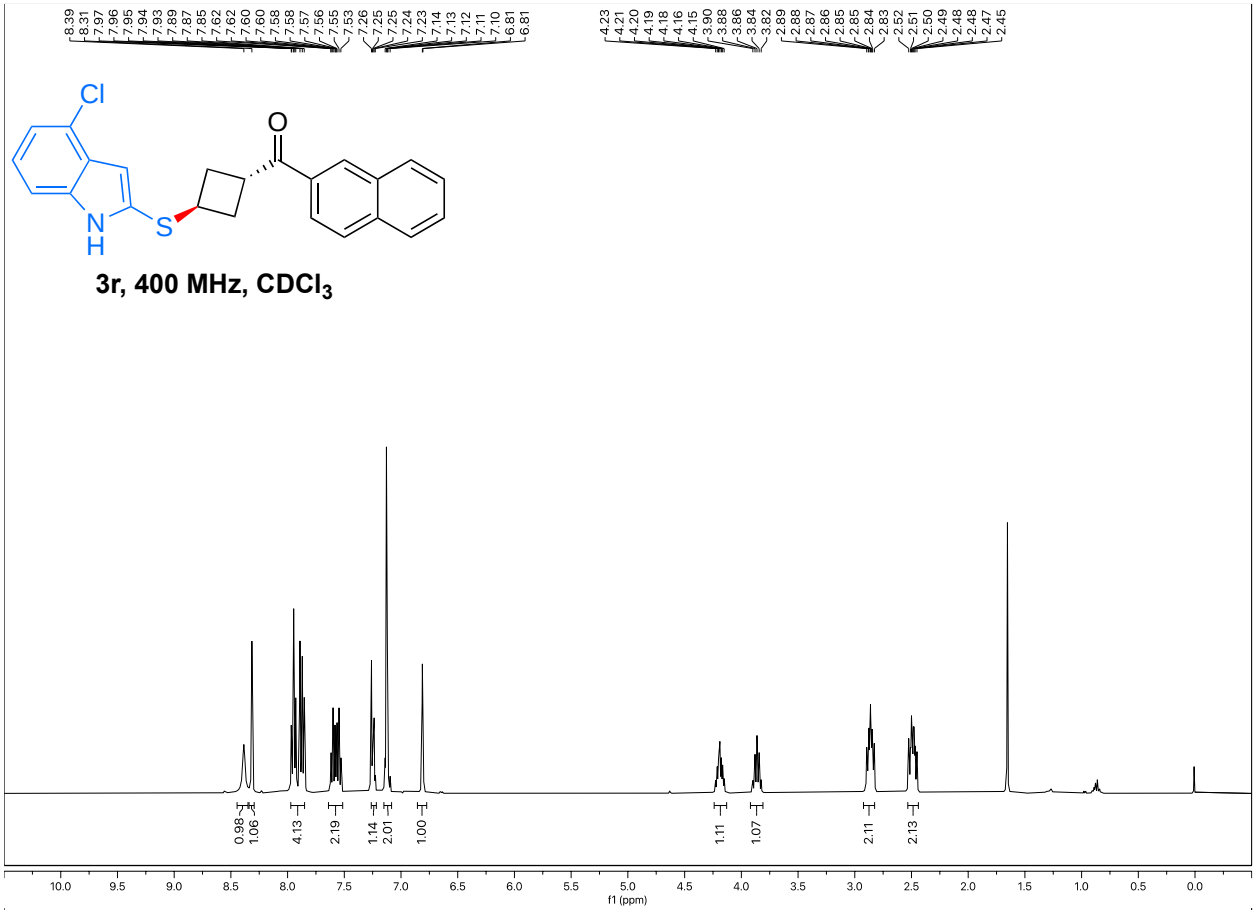


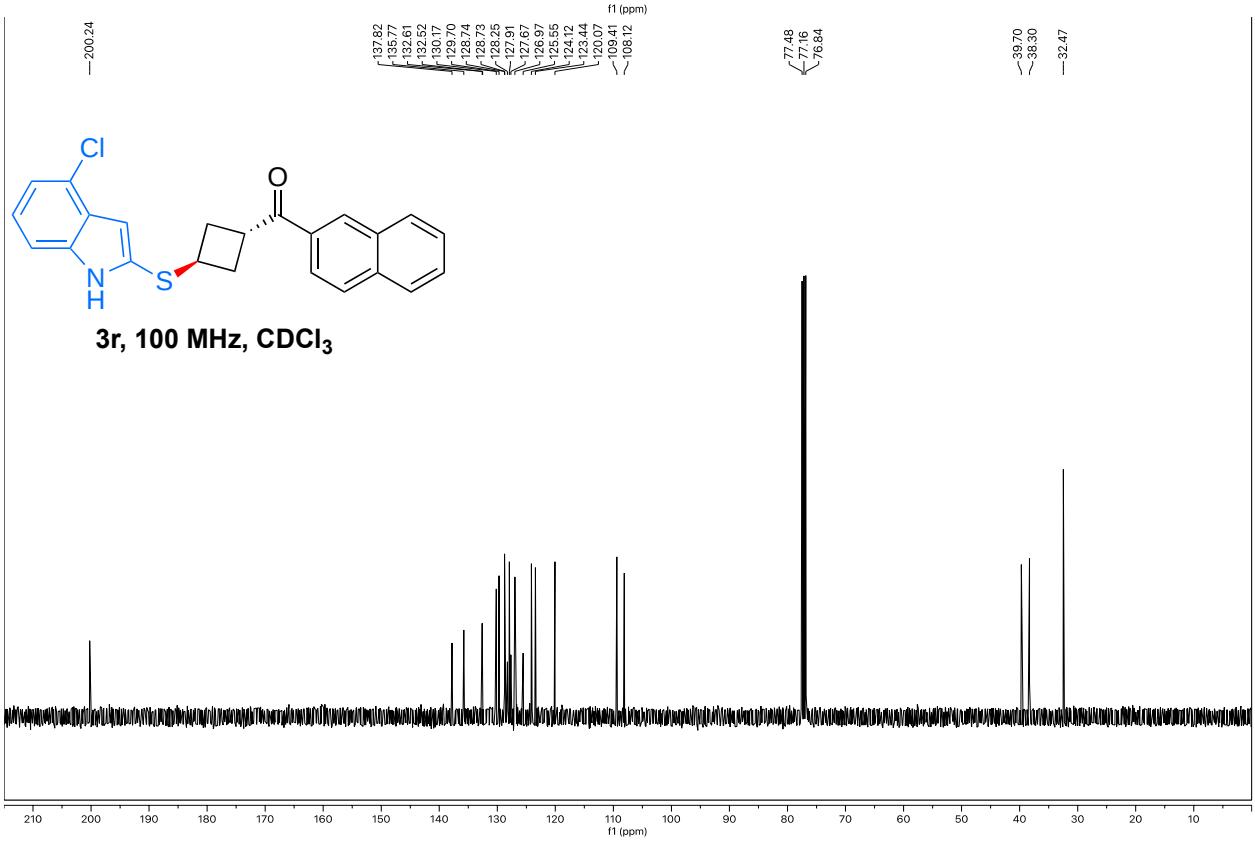
(3-((3-Benzyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3q)



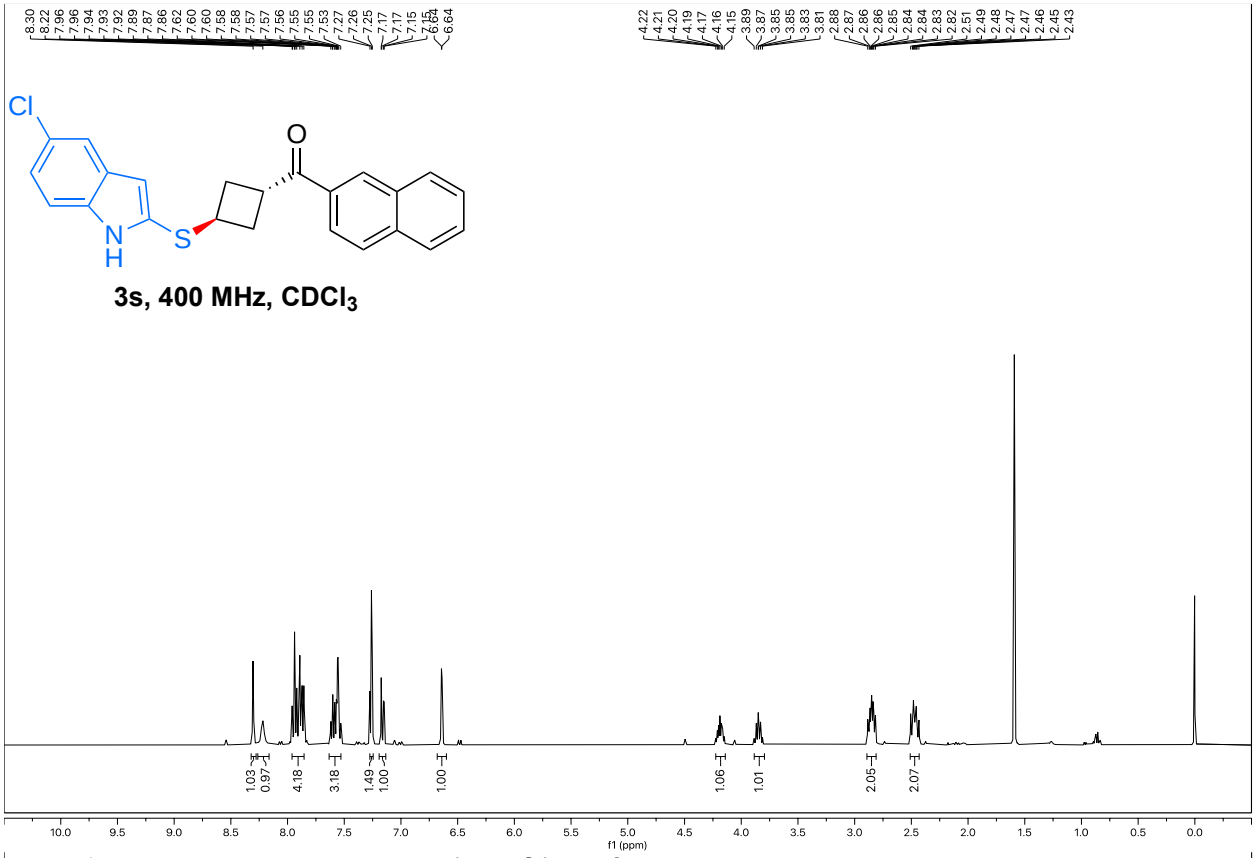


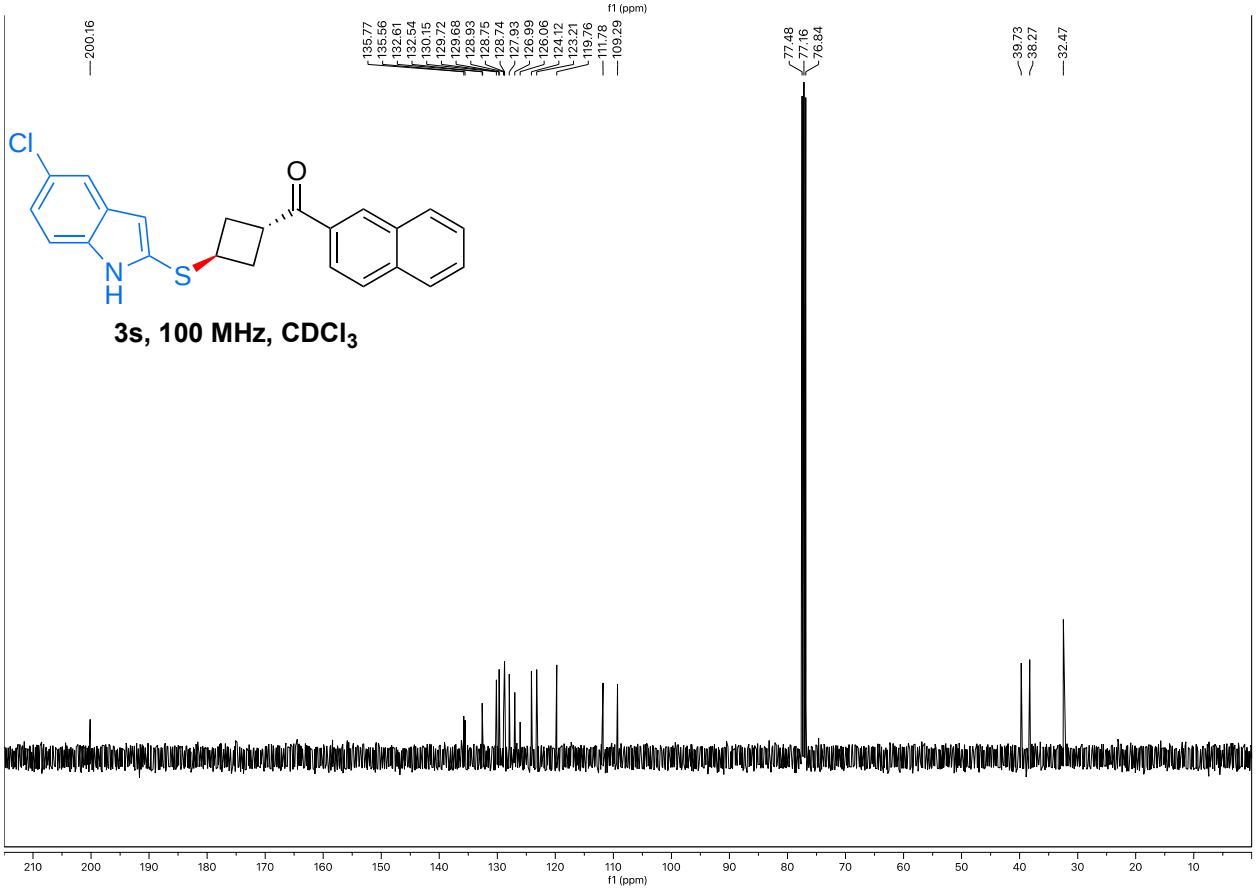
(3-((4-Chloro-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3r)



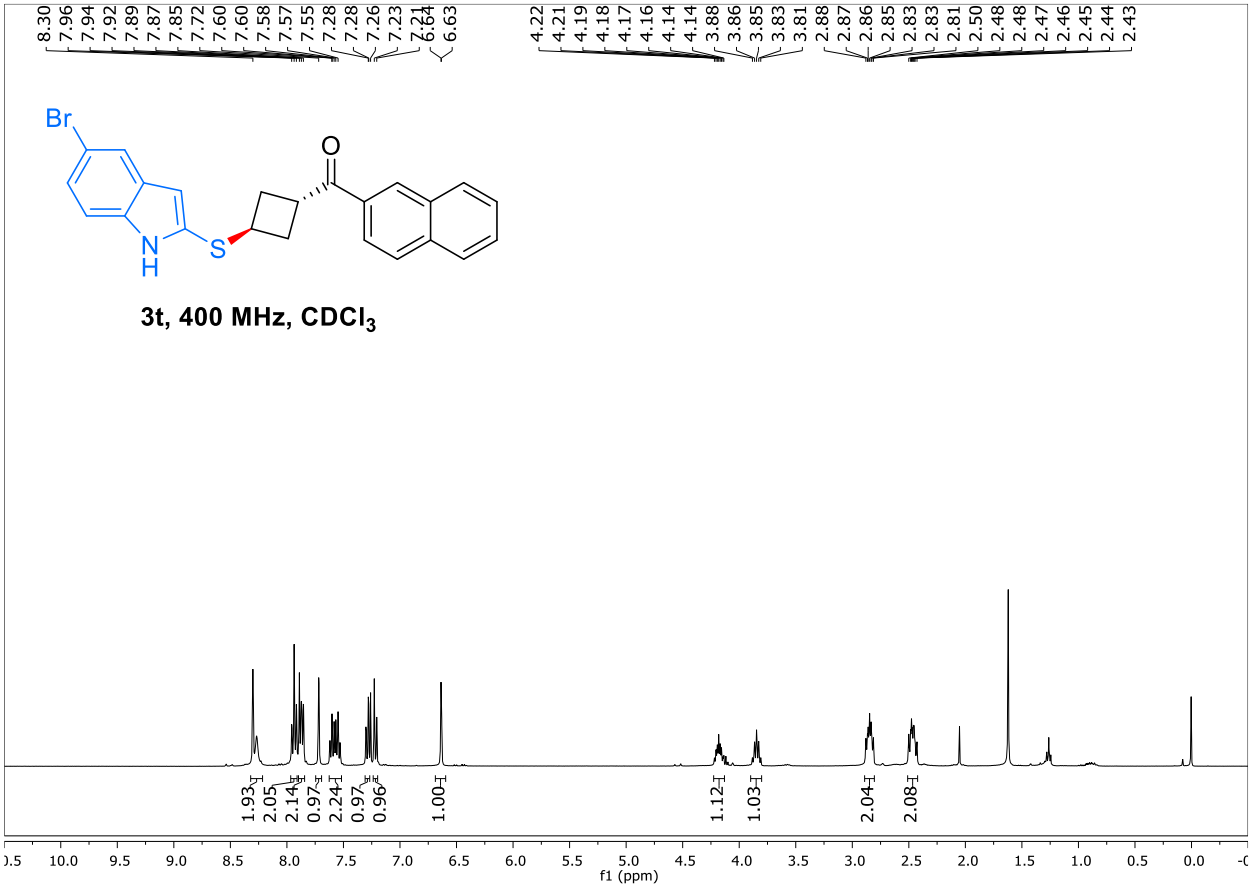


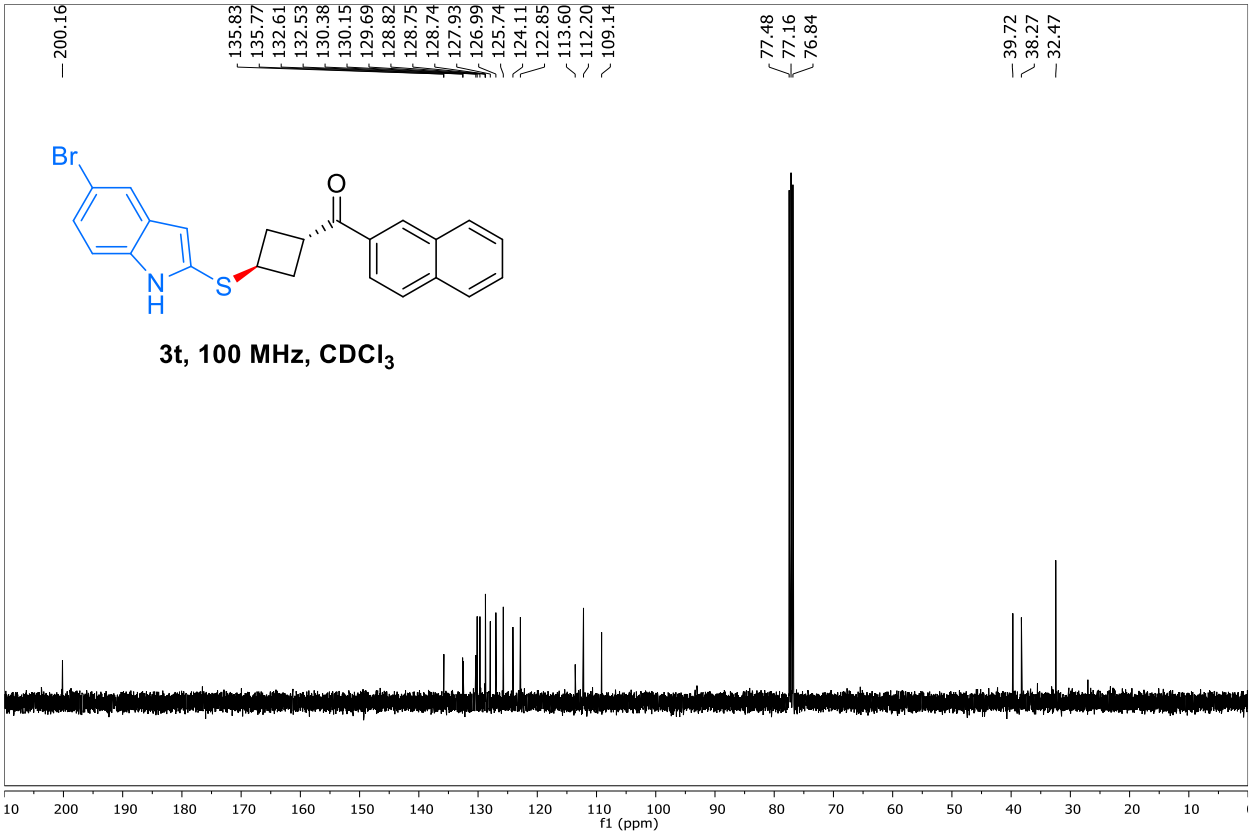
(3-((5-Chloro-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3s)



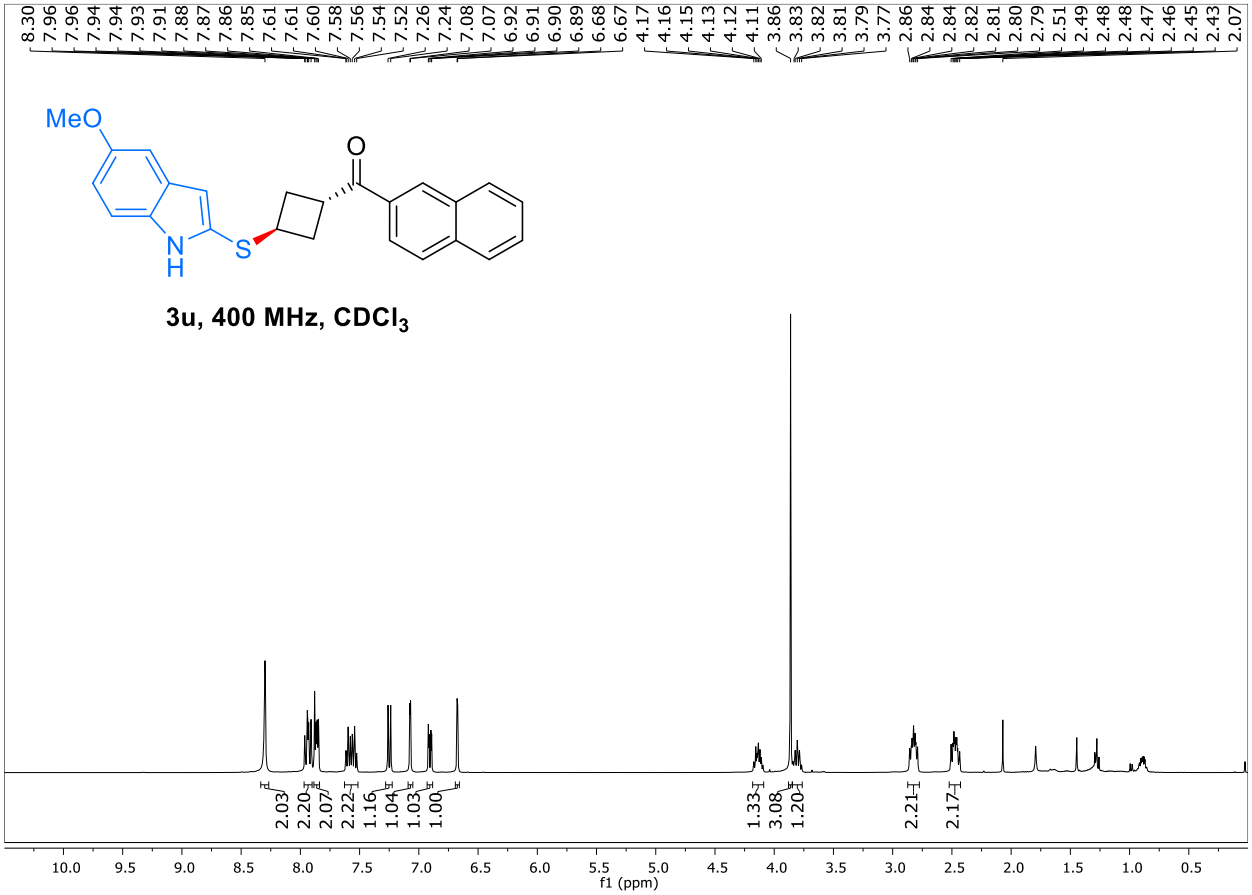


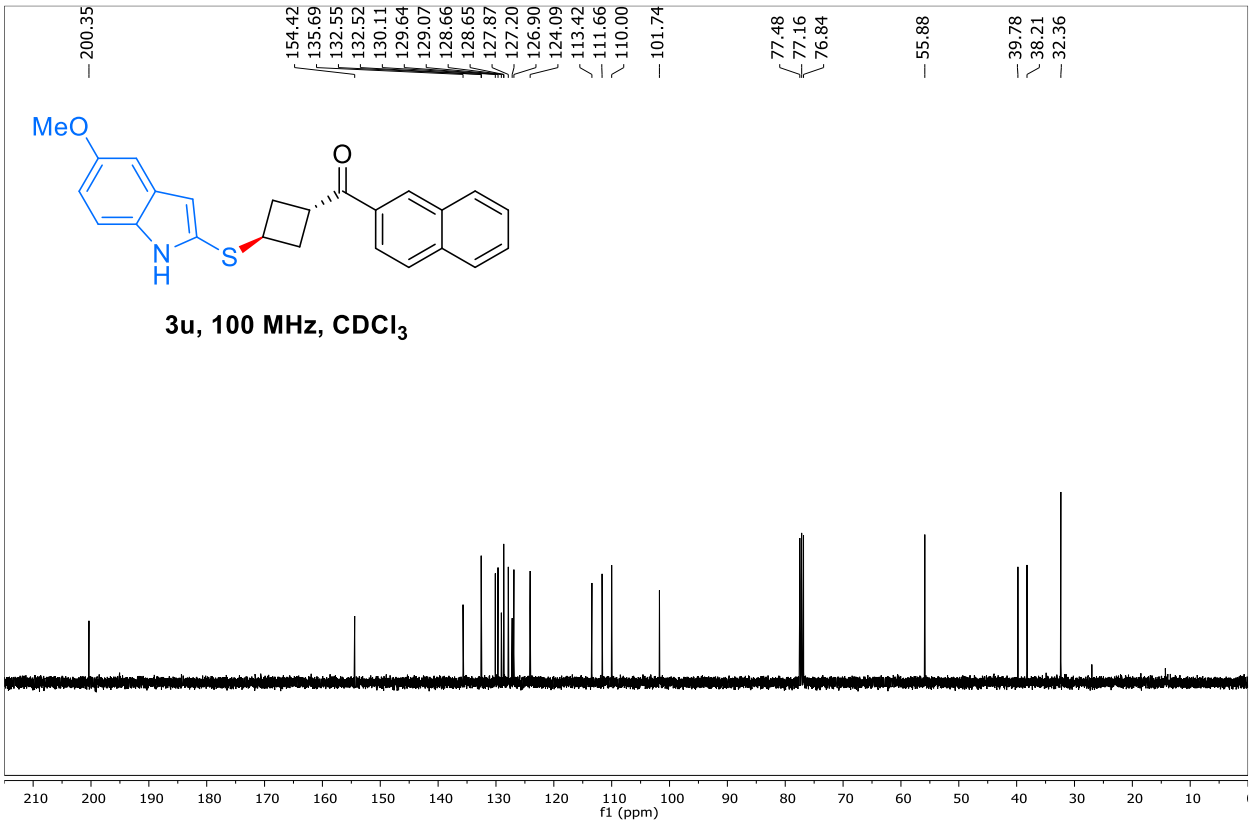
3-((5-Bromo-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3t)



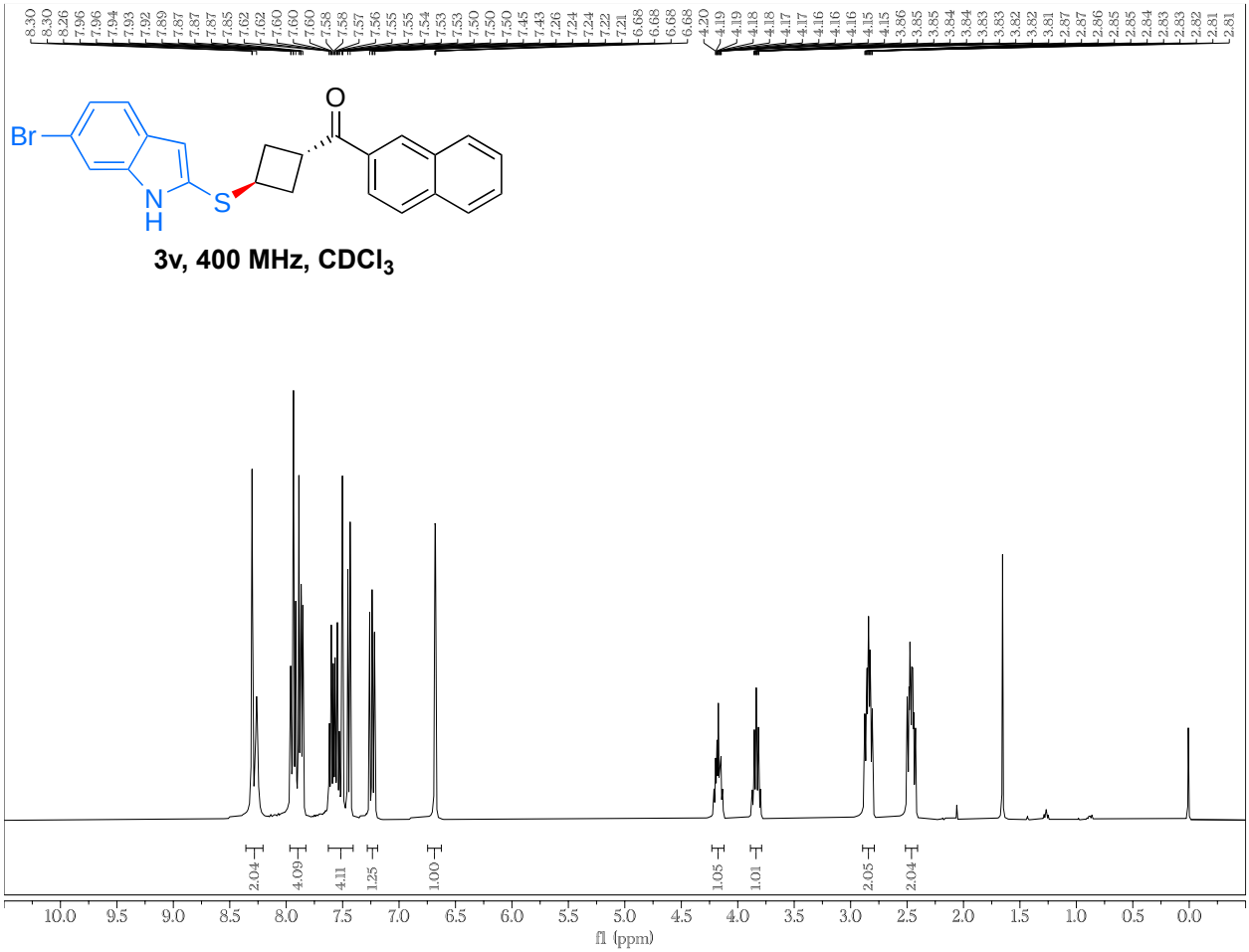


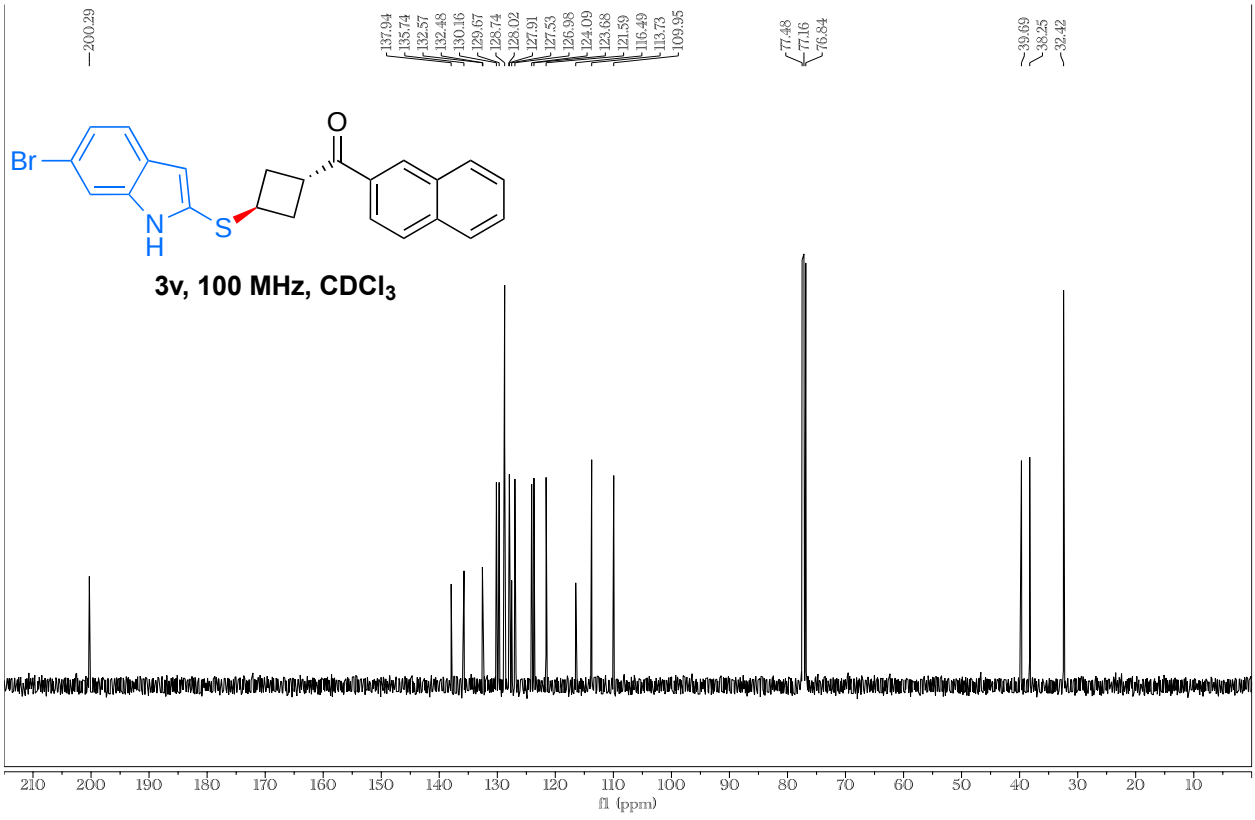
3-((5-Methoxy-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3u)



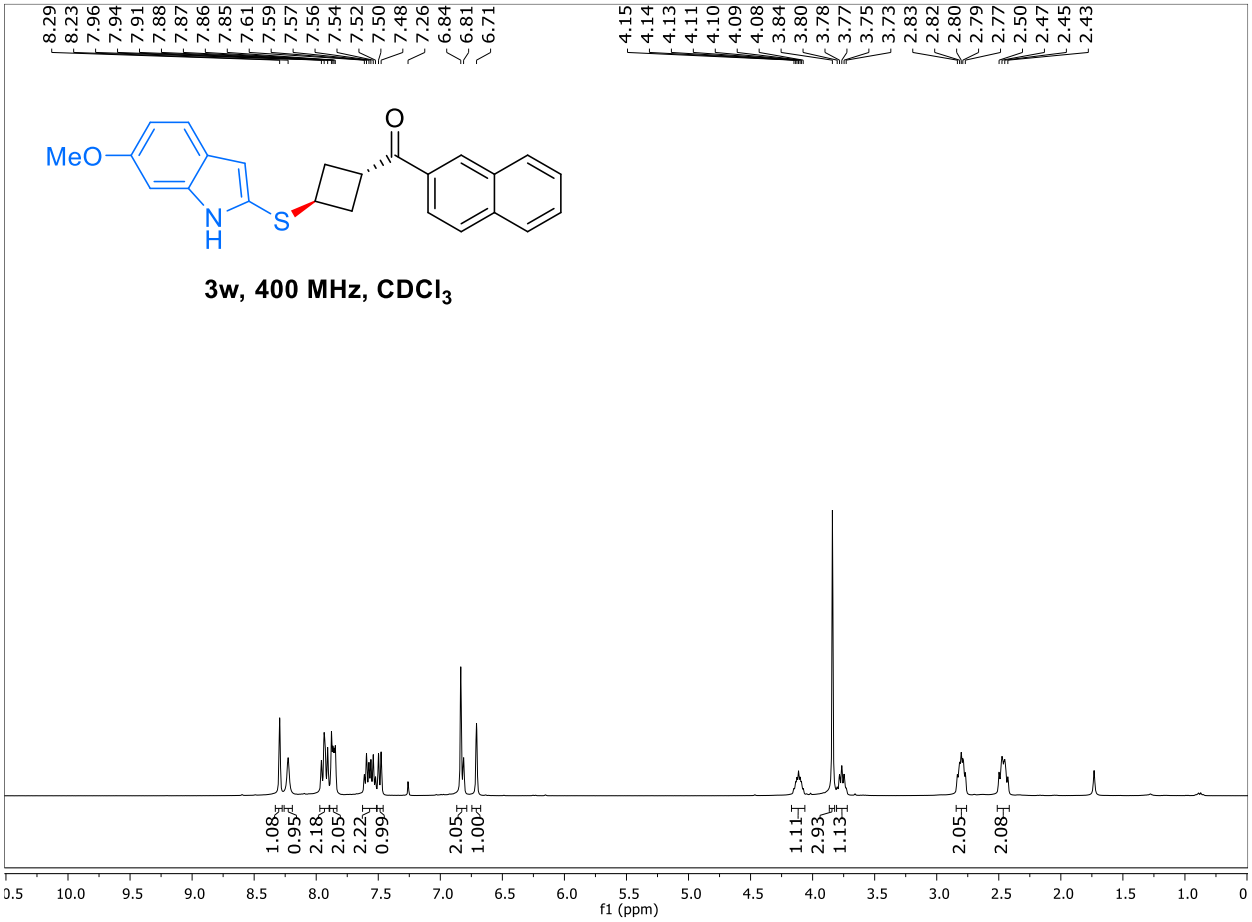


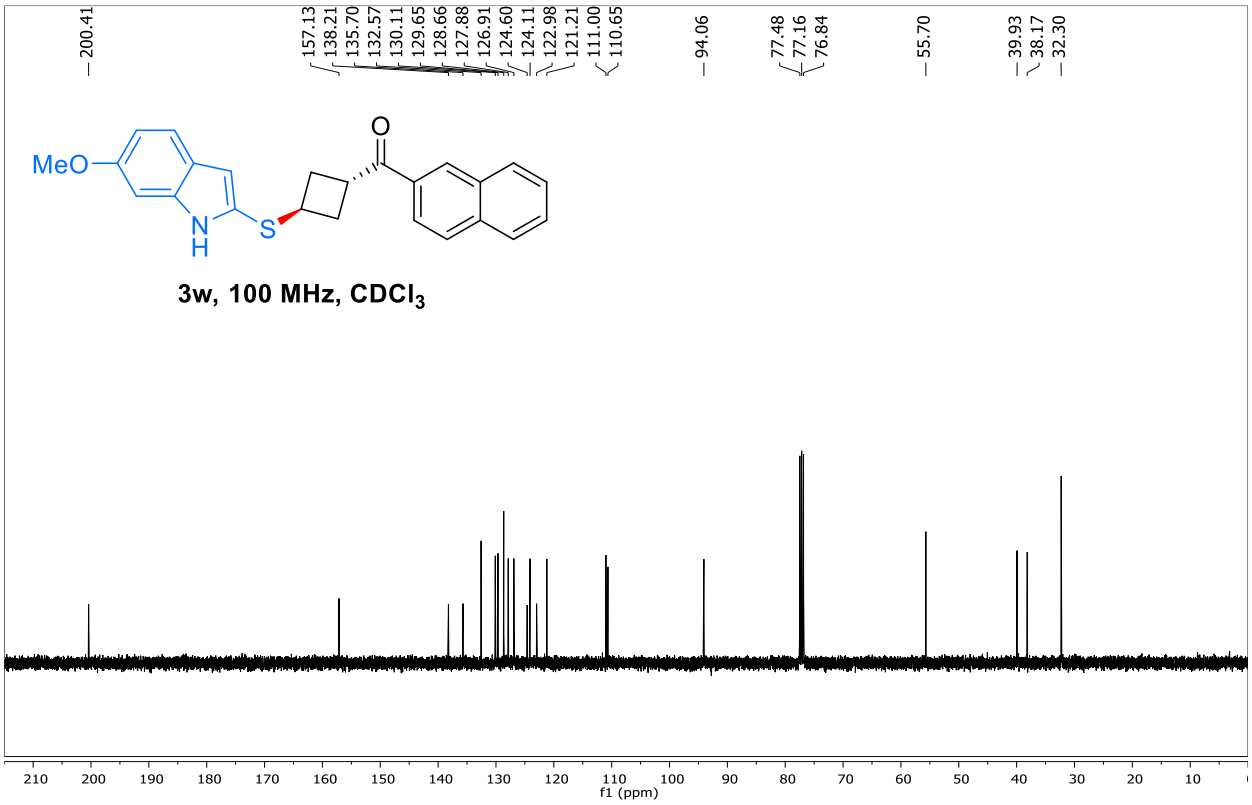
(3-((6-Bromo-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3v)



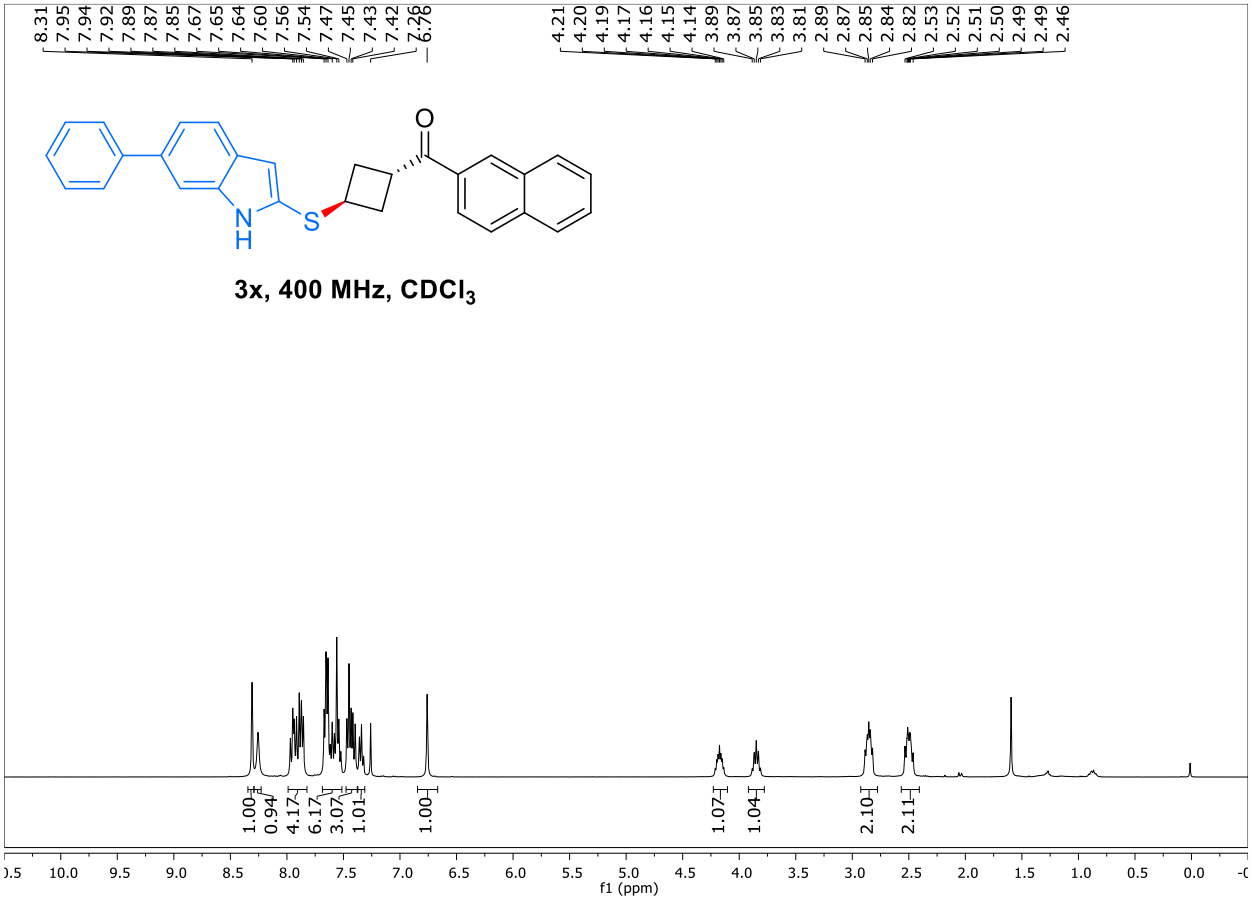


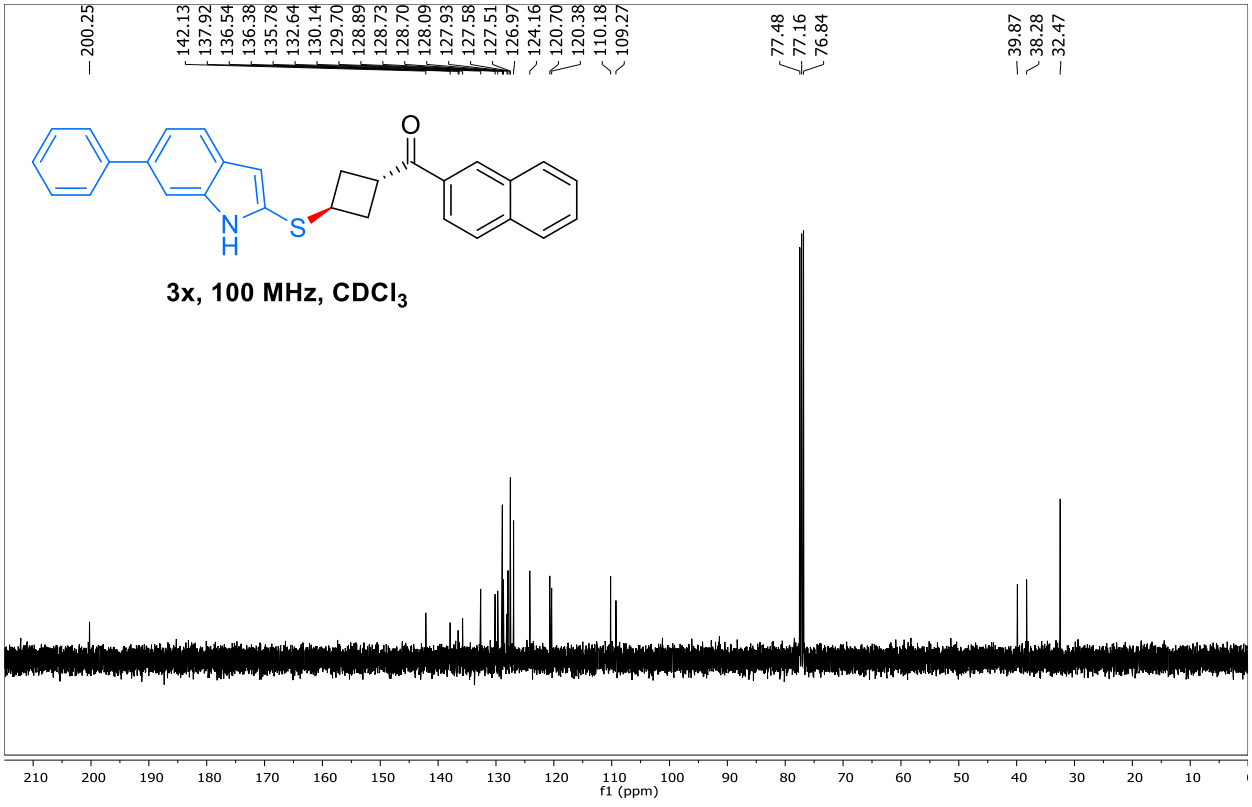
3-((6-Methoxy-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3w)



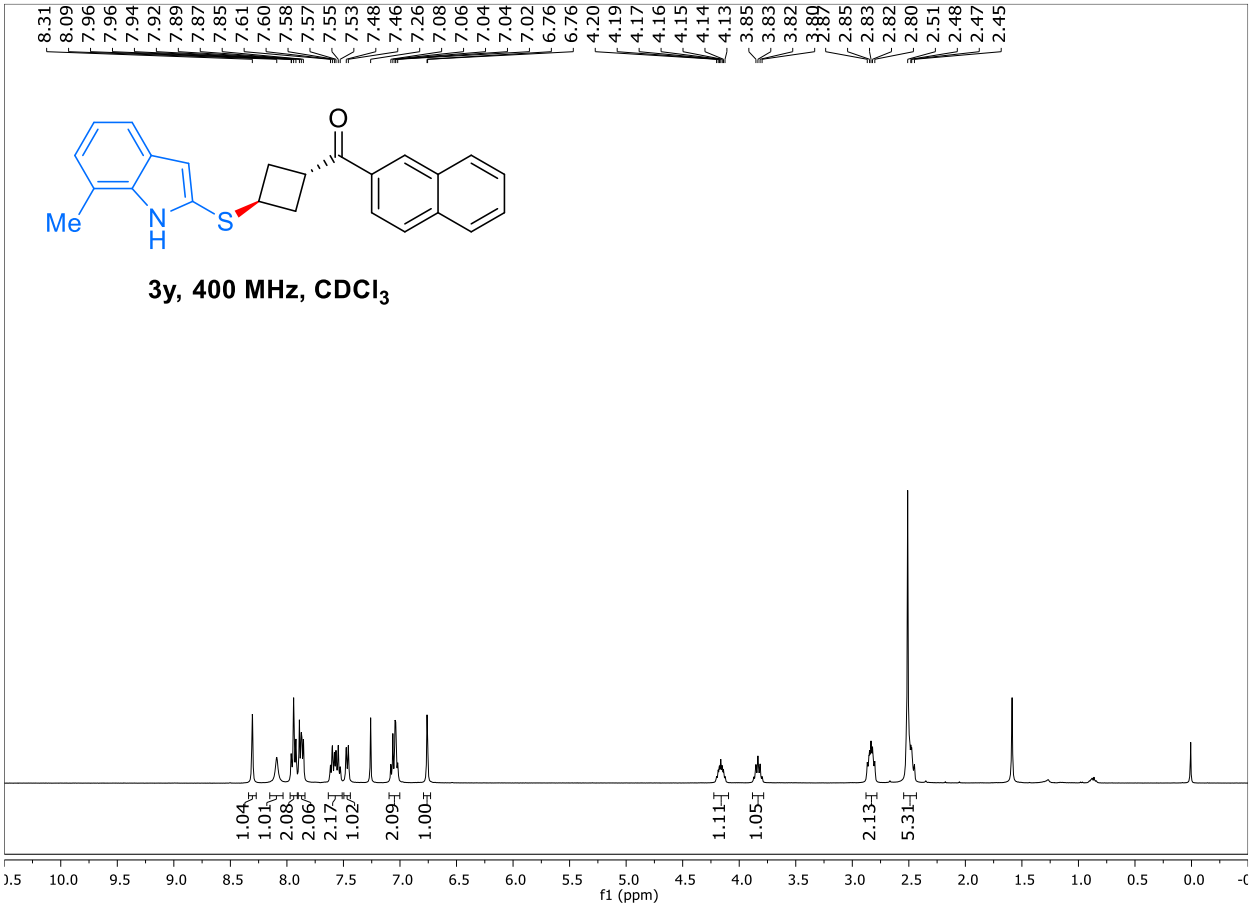


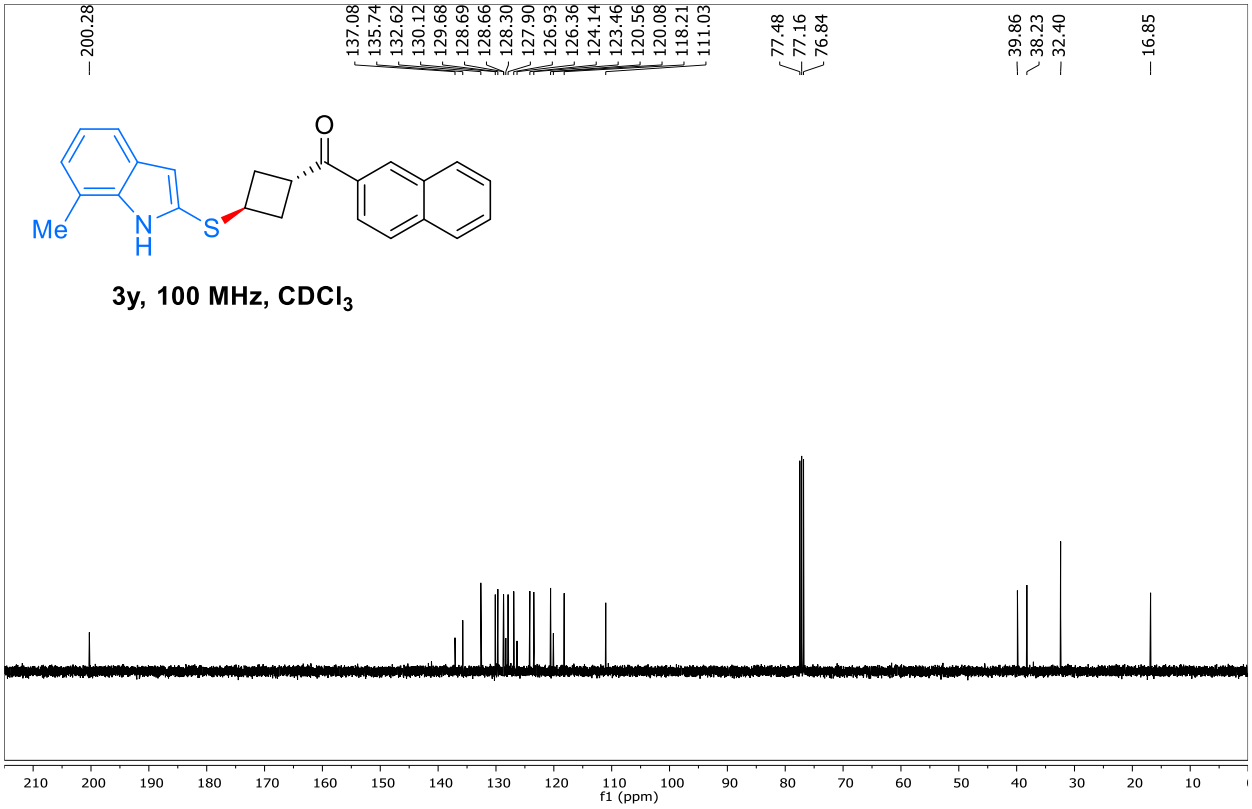
Naphthalen-2-yl(3-((6-phenyl-1*H*-indol-2-yl)thio)cyclobutyl)methanone (3x)



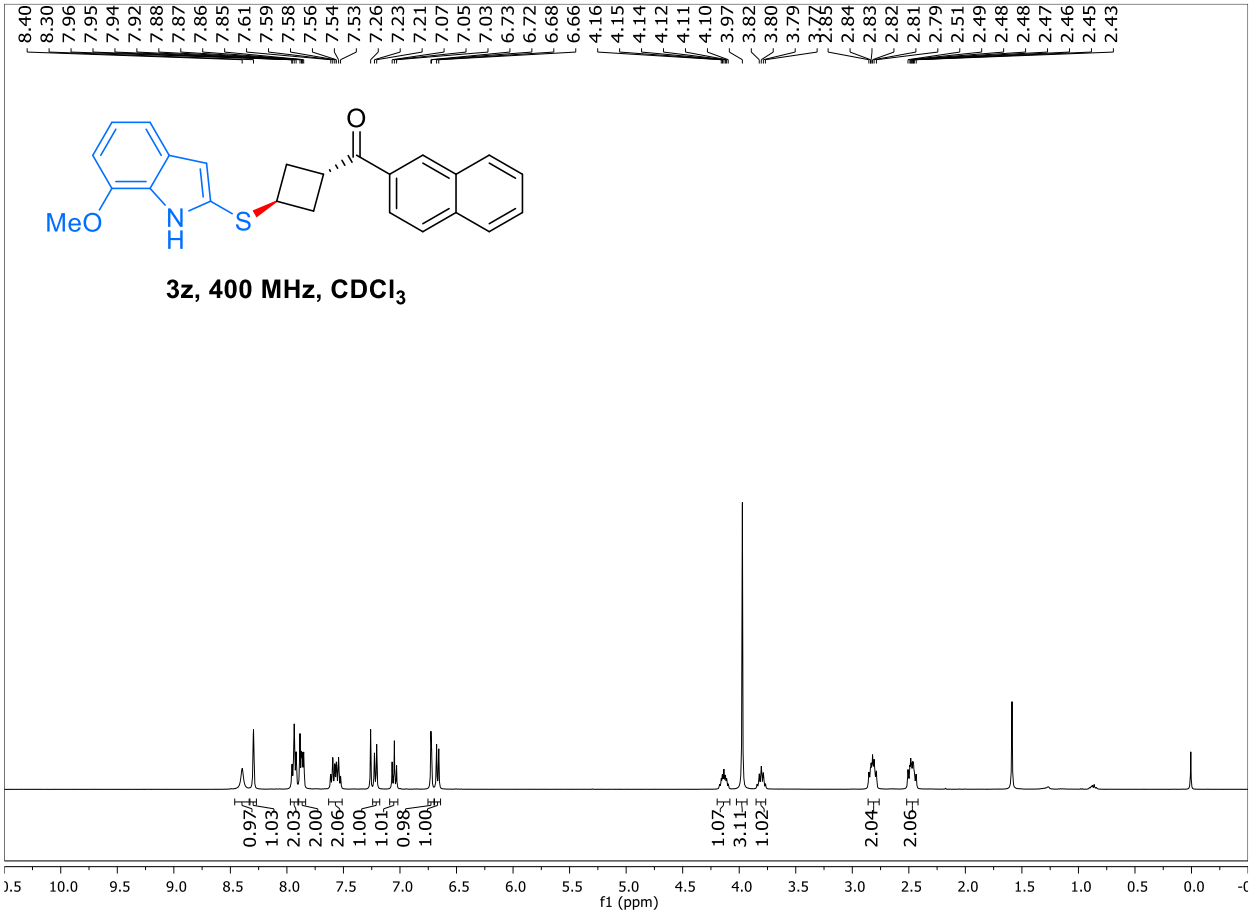


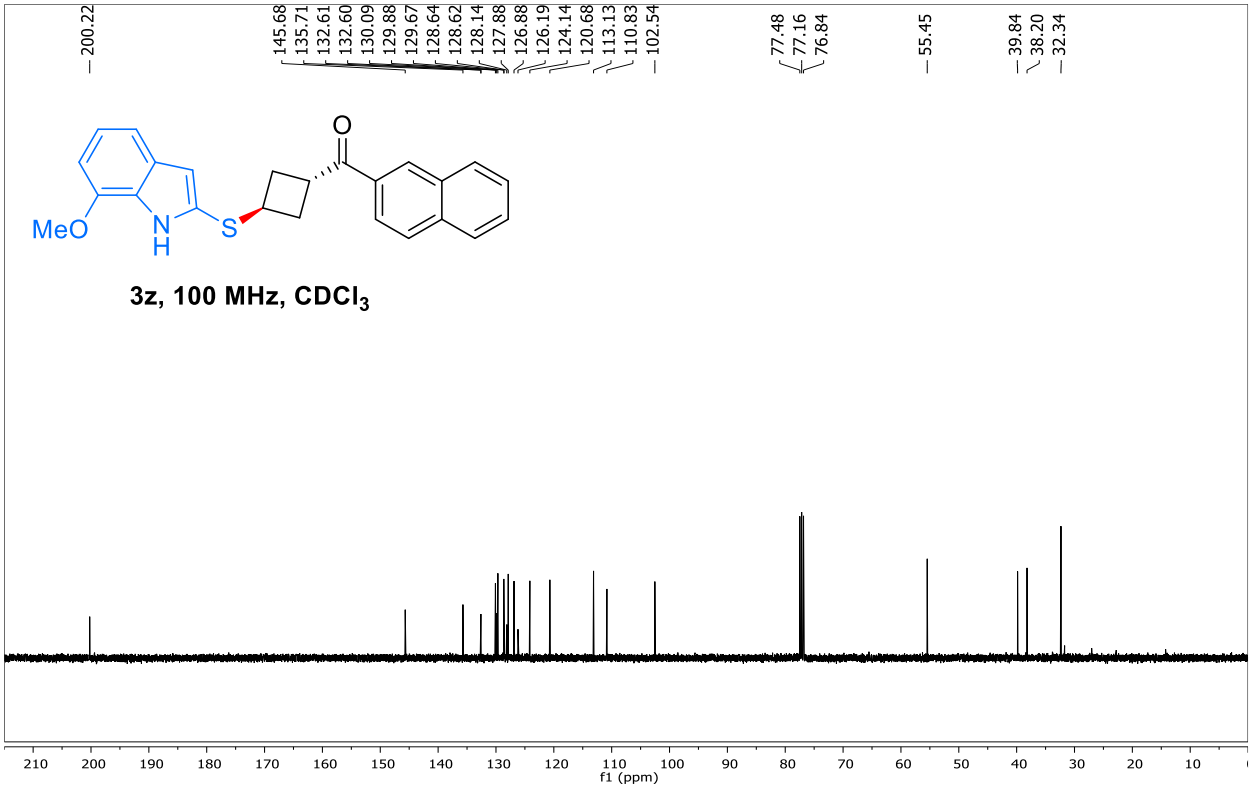
3-((7-Methyl-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3y)



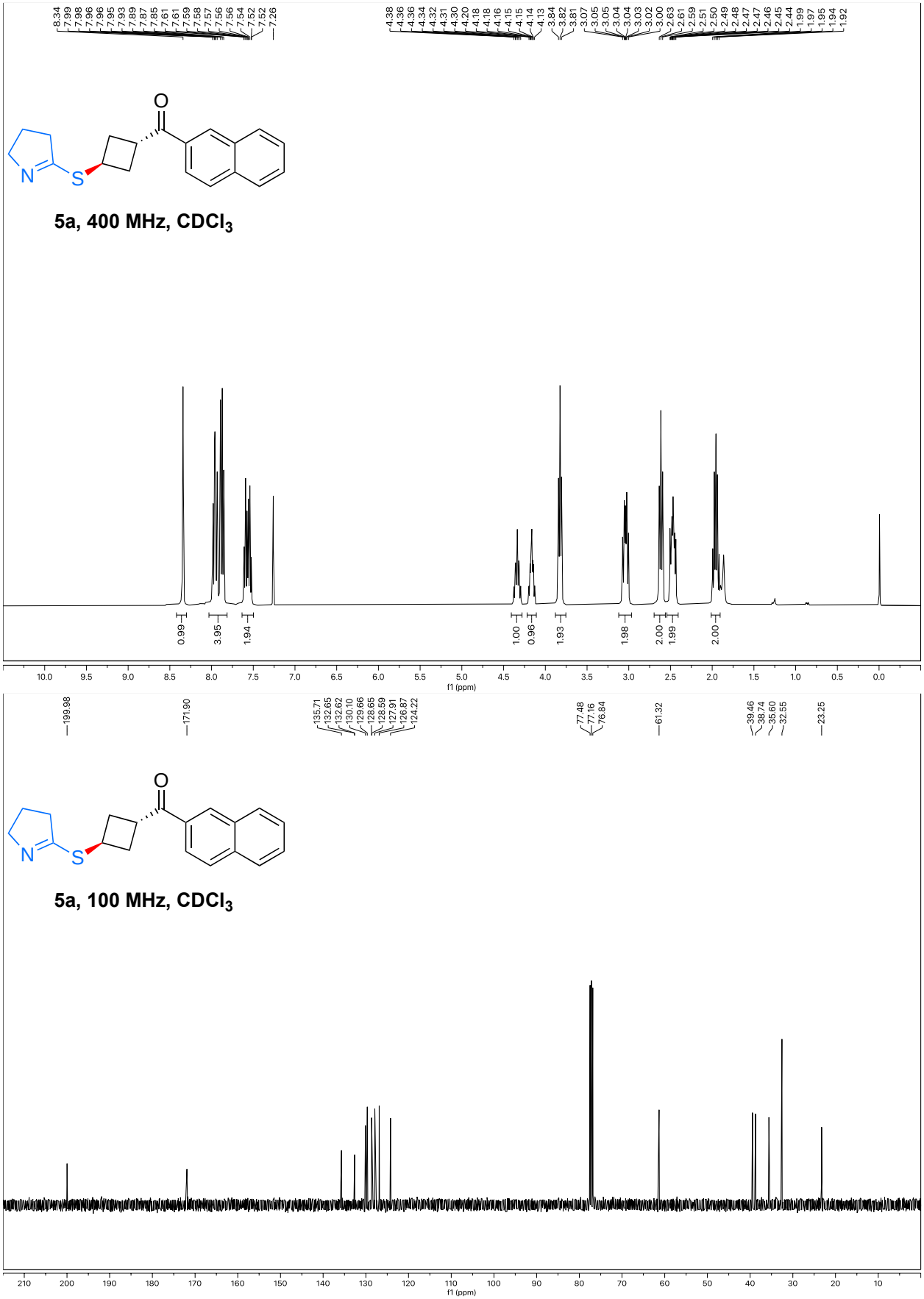


3-((7-Methoxy-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (3z)

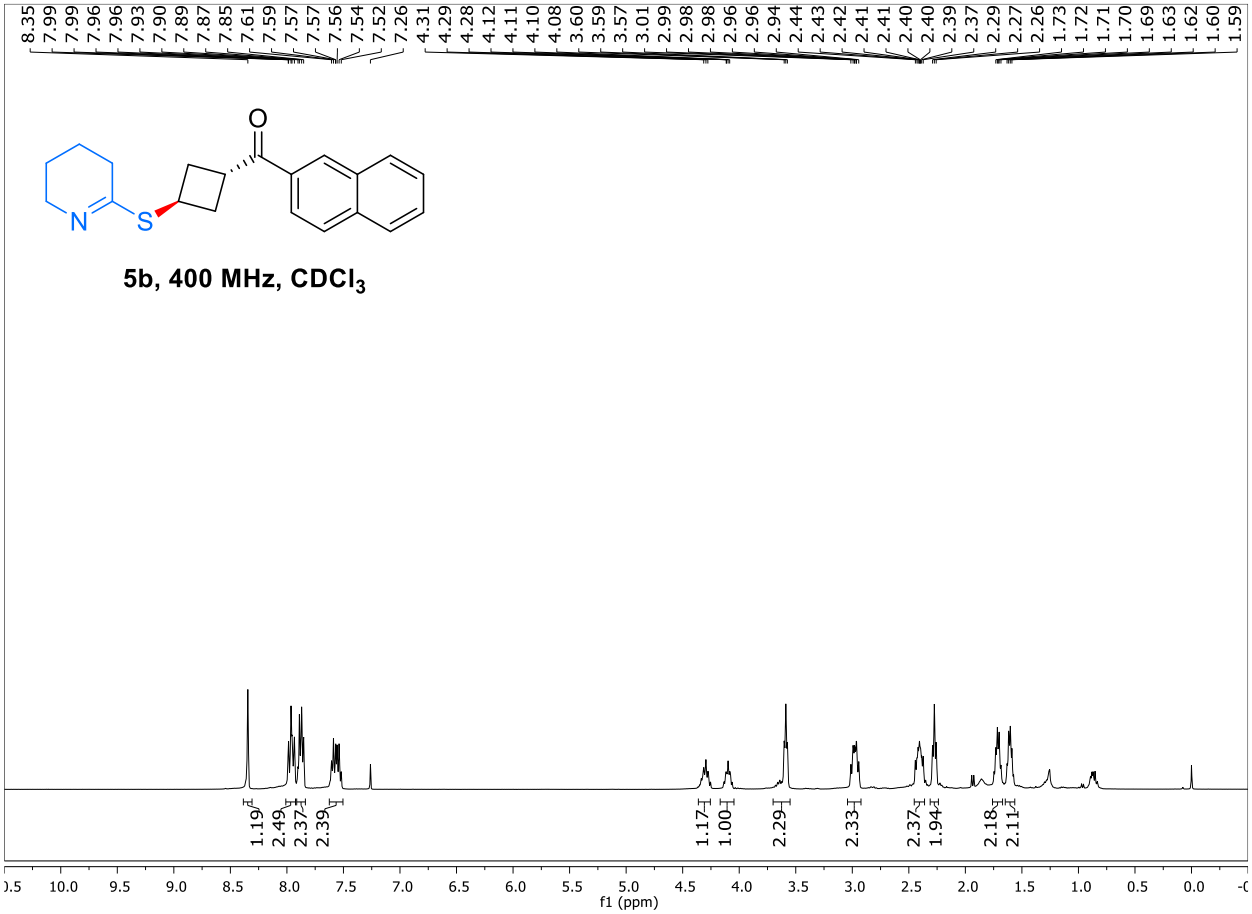


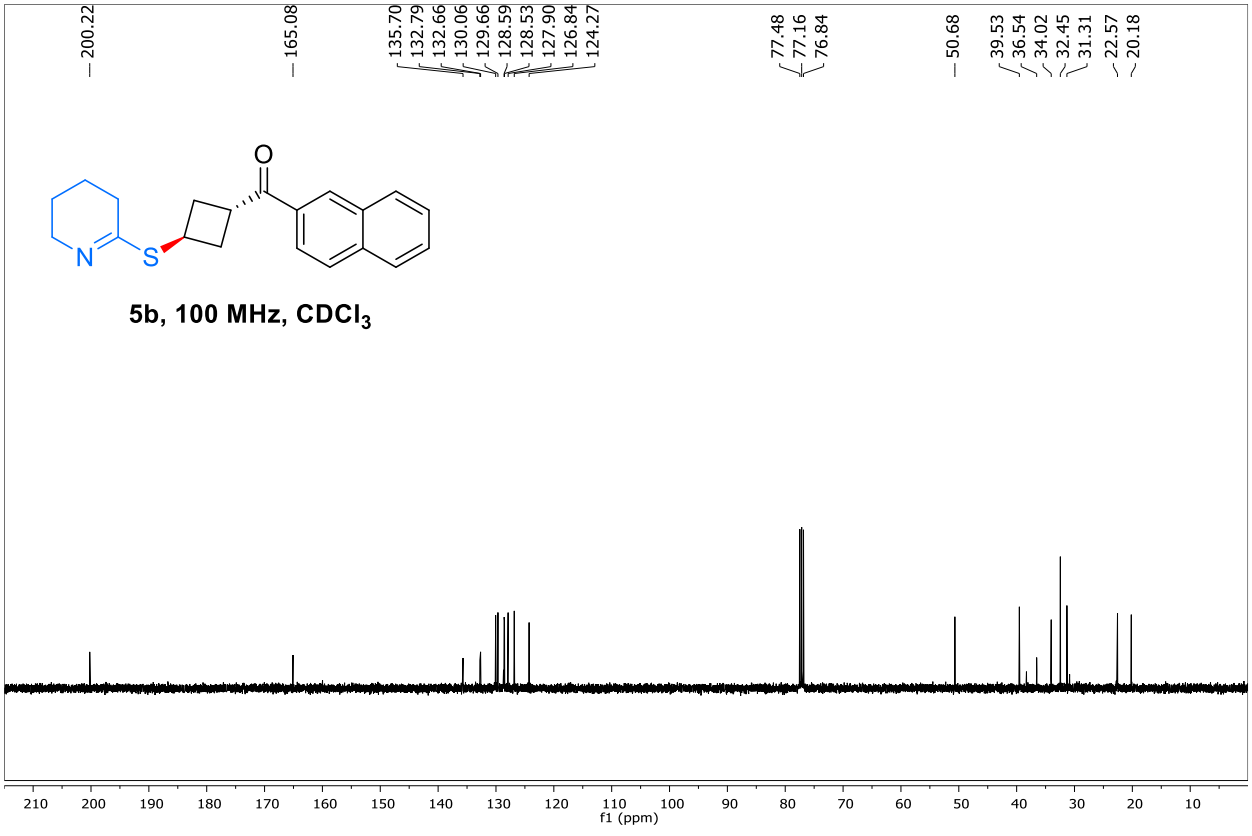


(3-((3,4-Dihydro-2*H*-pyrrol-5-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (5a)

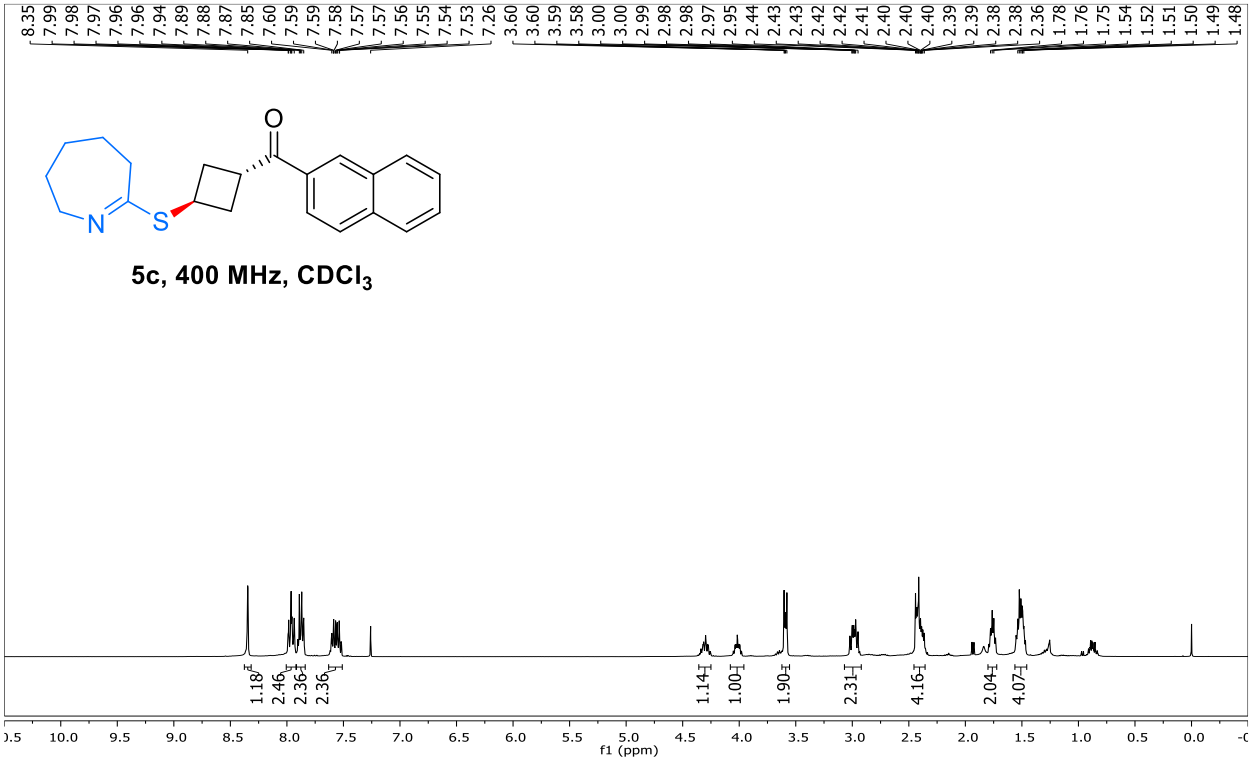


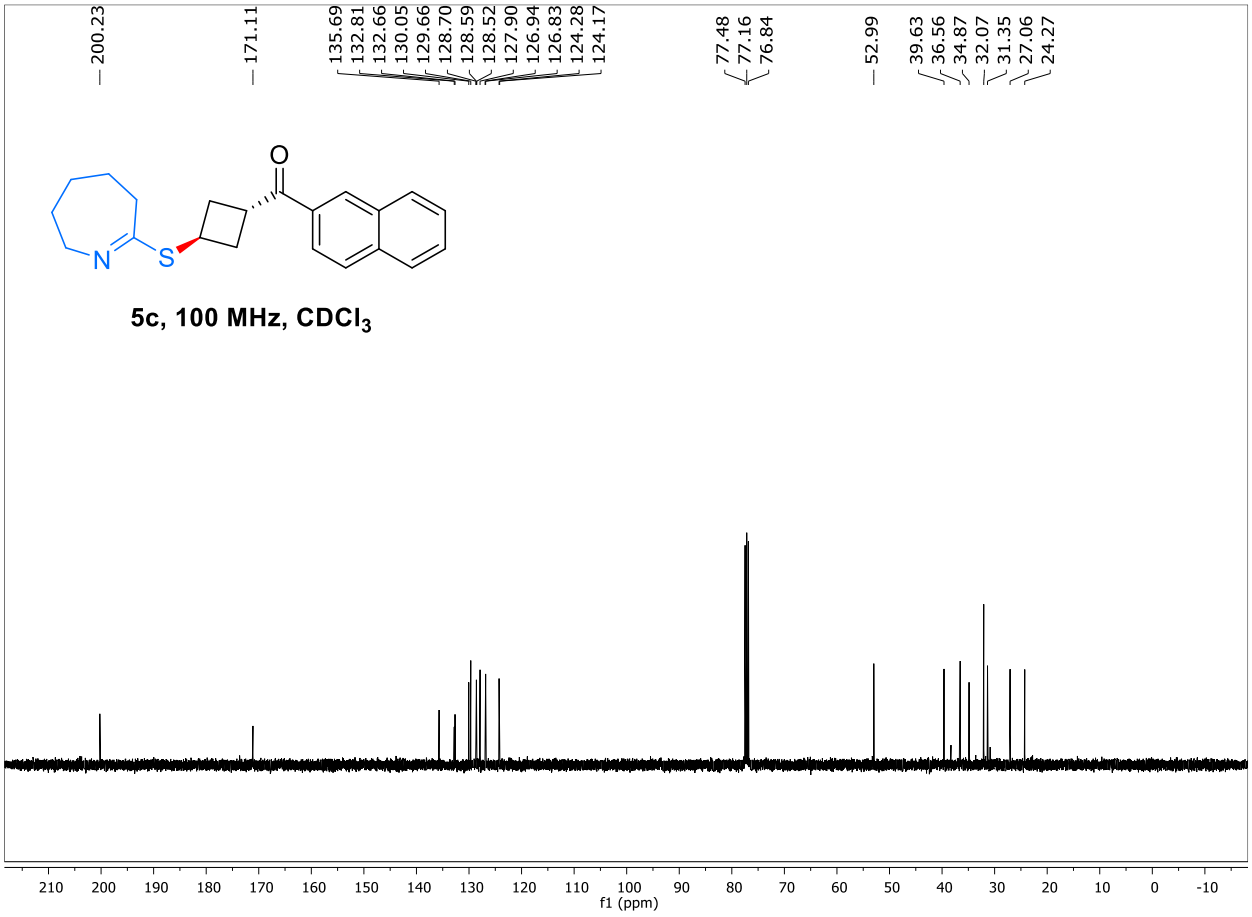
Naphthalen-2-yl(3-((3,4,5,6-tetrahydropyridin-2-yl)thio)cyclobutyl)methanone (5b)



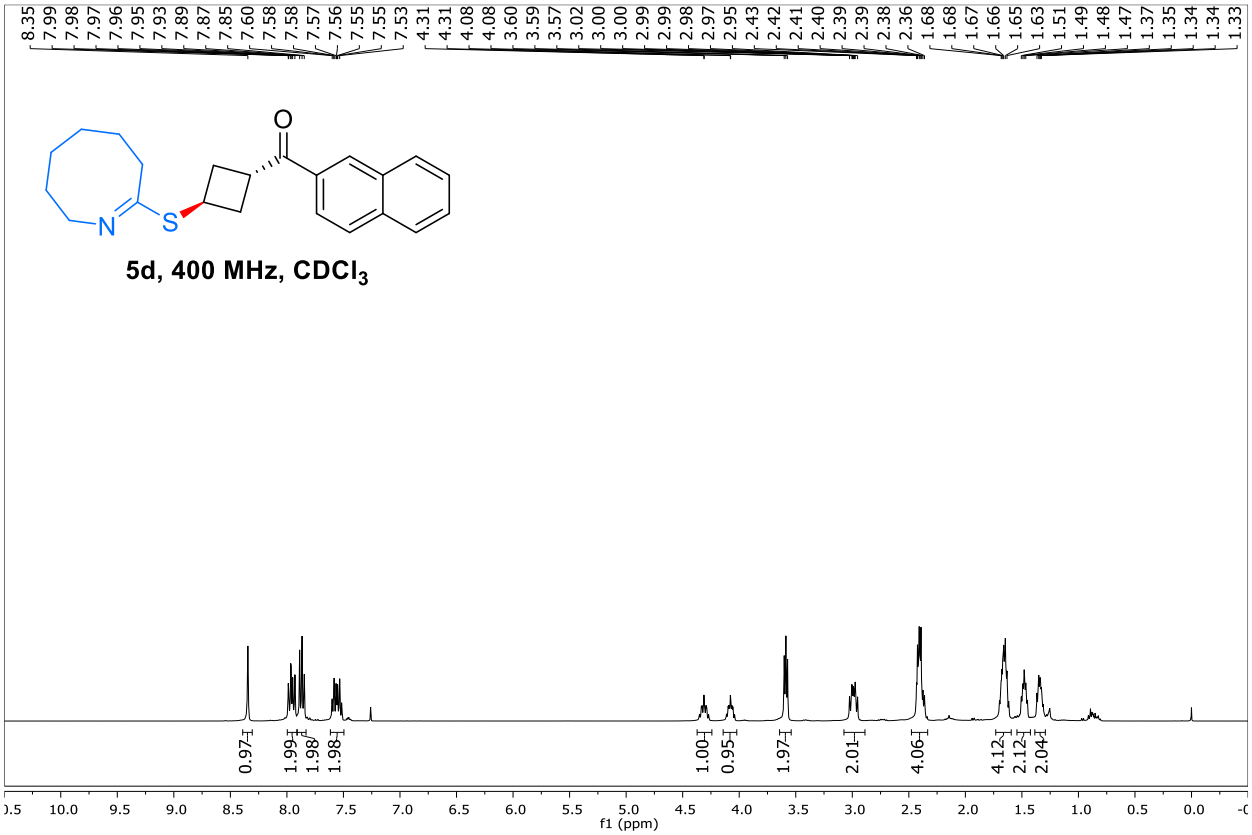


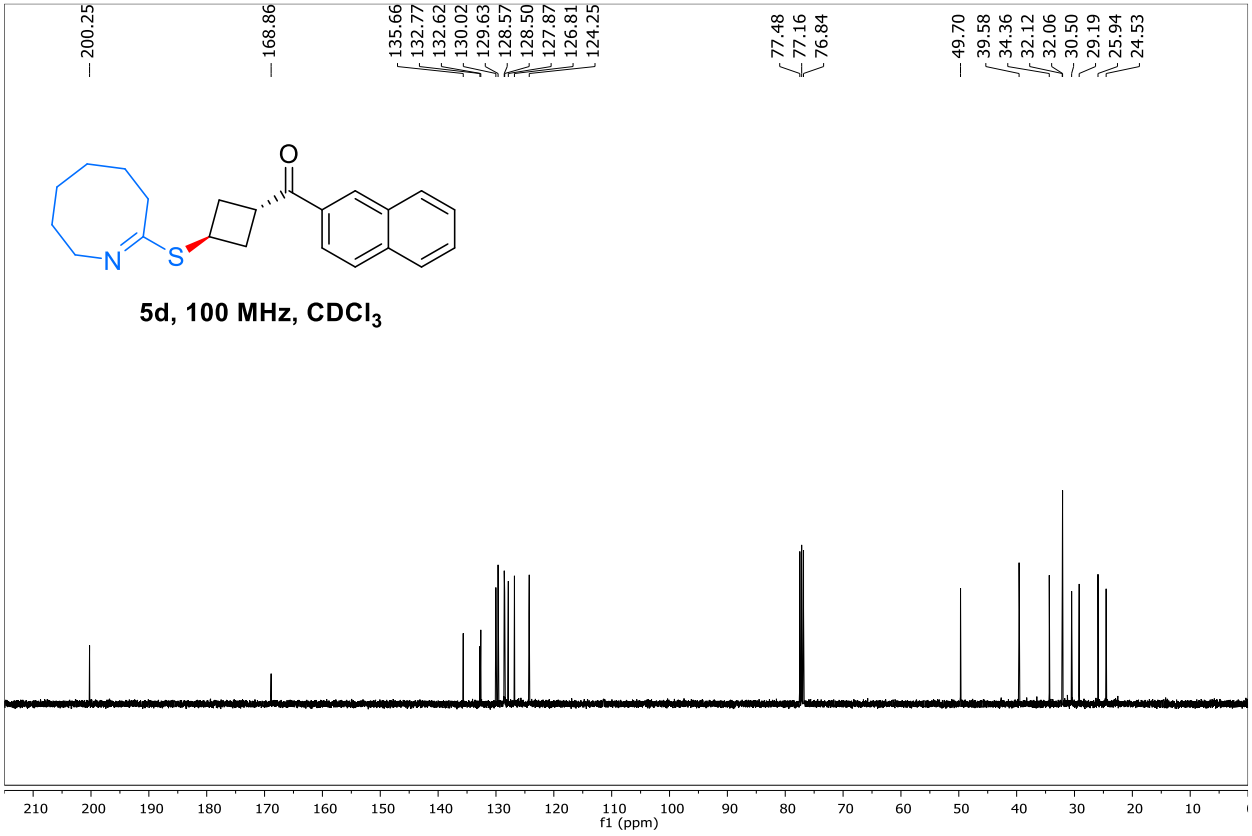
Naphthalen-2-yl(3-((3,4,5,6-tetrahydro-2*H*-azepin-7-yl)thio)cyclobutyl)methanone (5c)



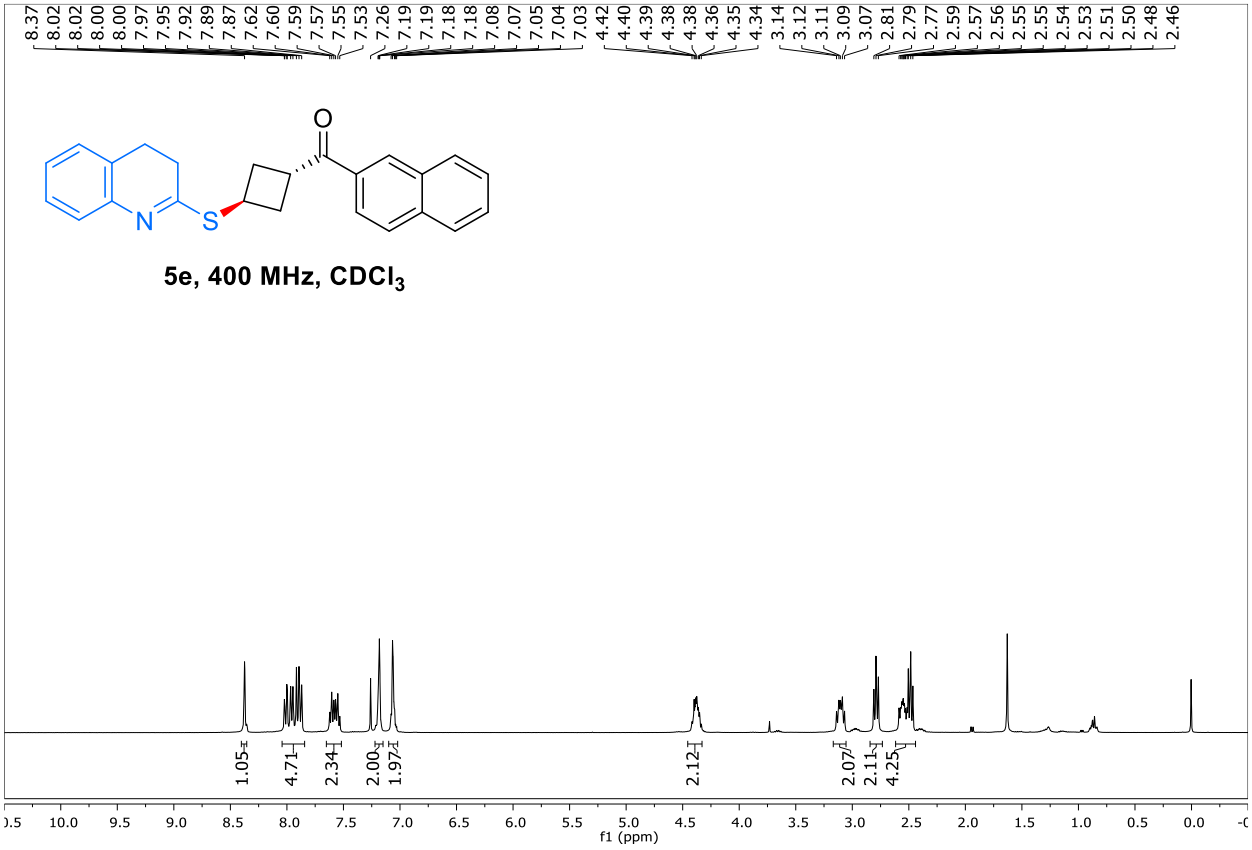


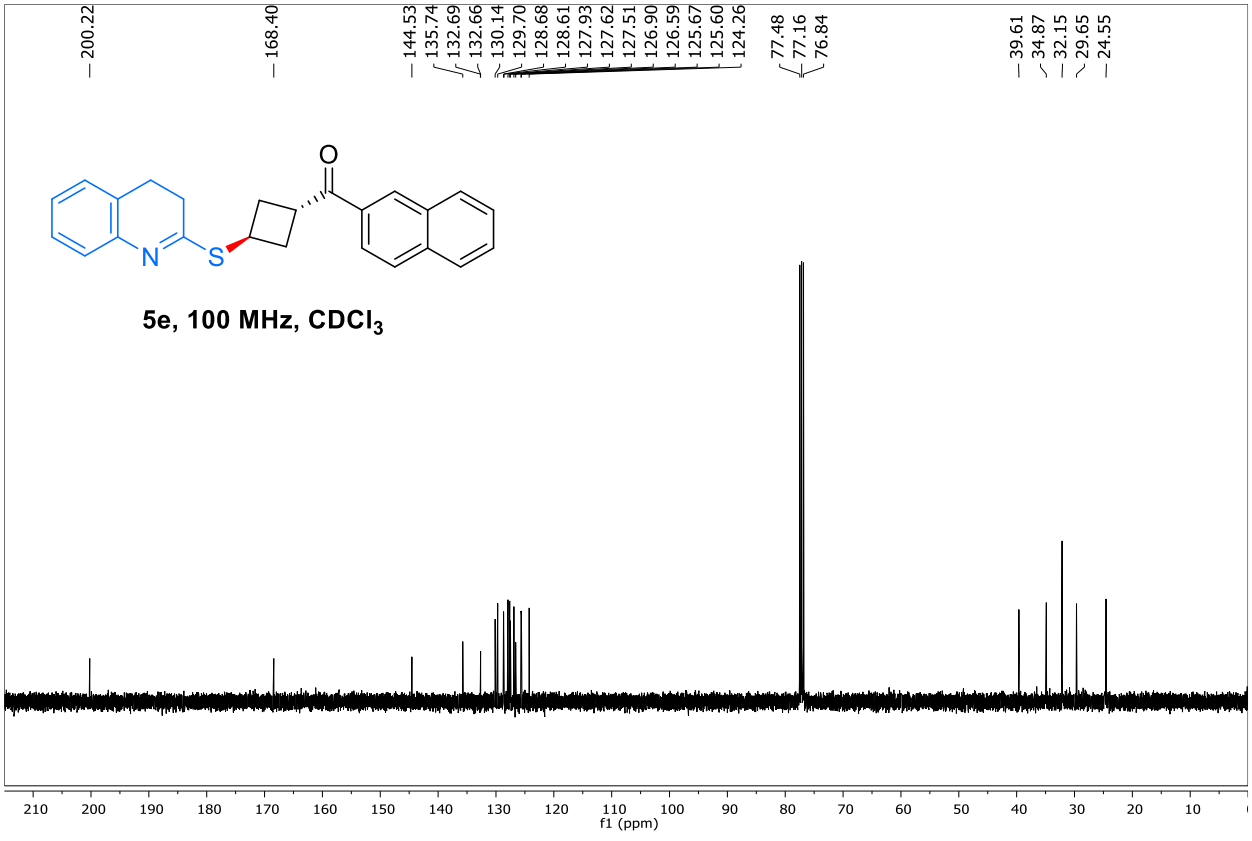
3-(((*E*)-3,4,5,6,7,8-Hexahydroazocin-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (5d)



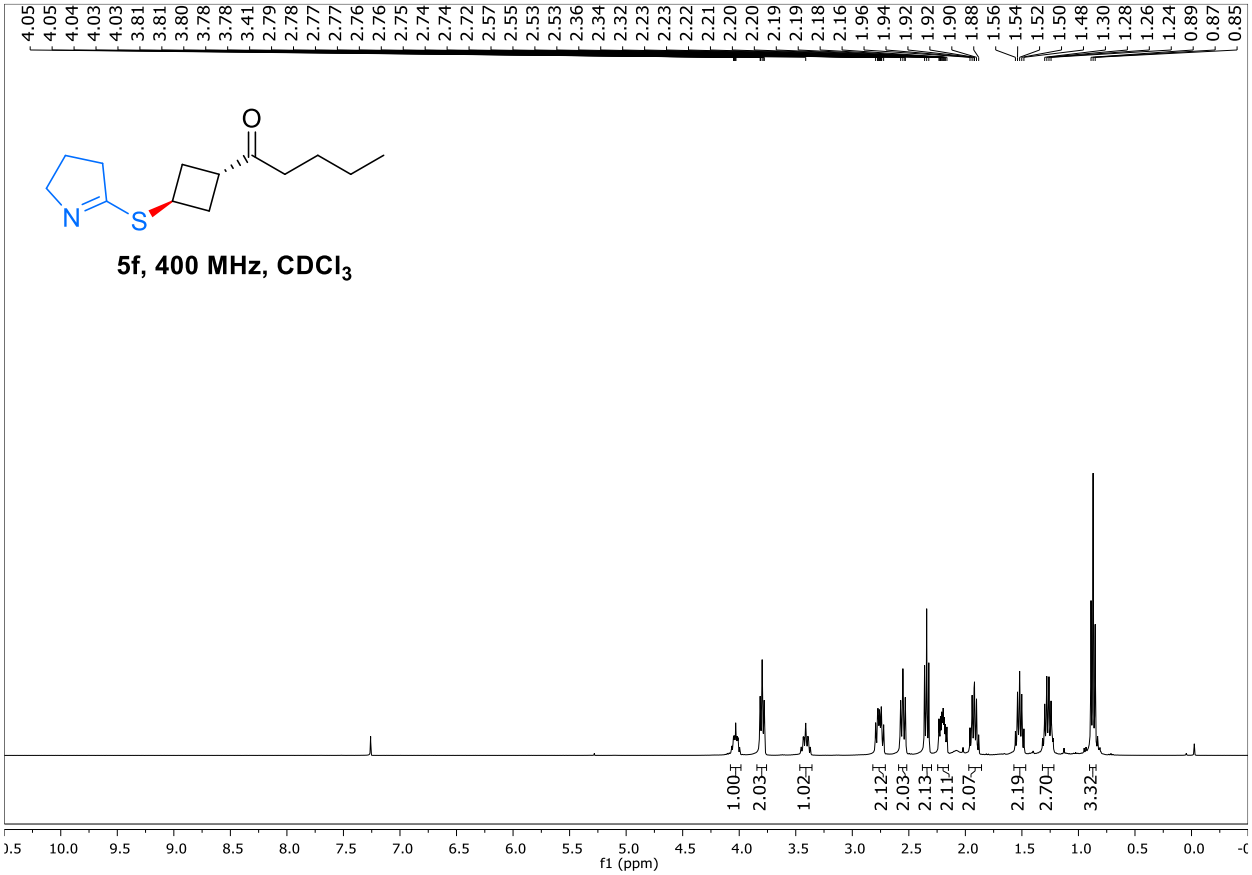


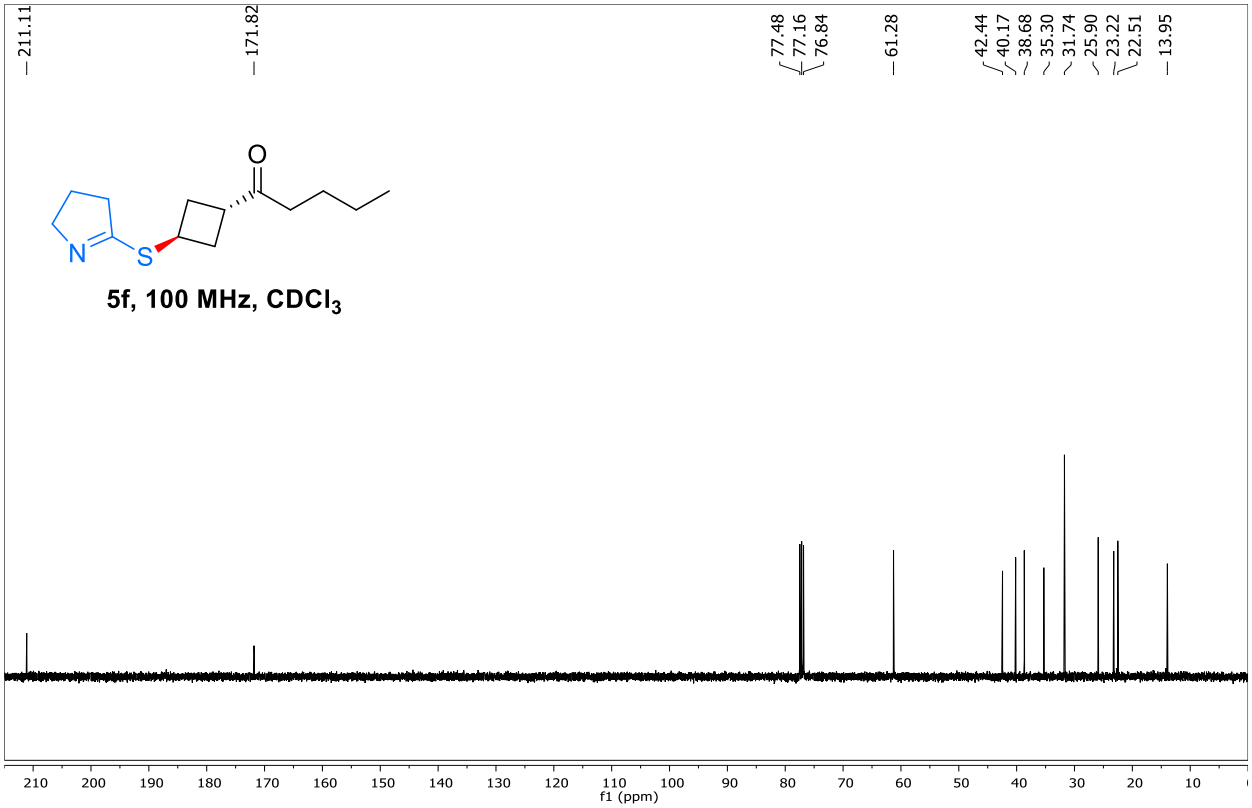
(3-((3,4-Dihydroquinolin-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (5e)



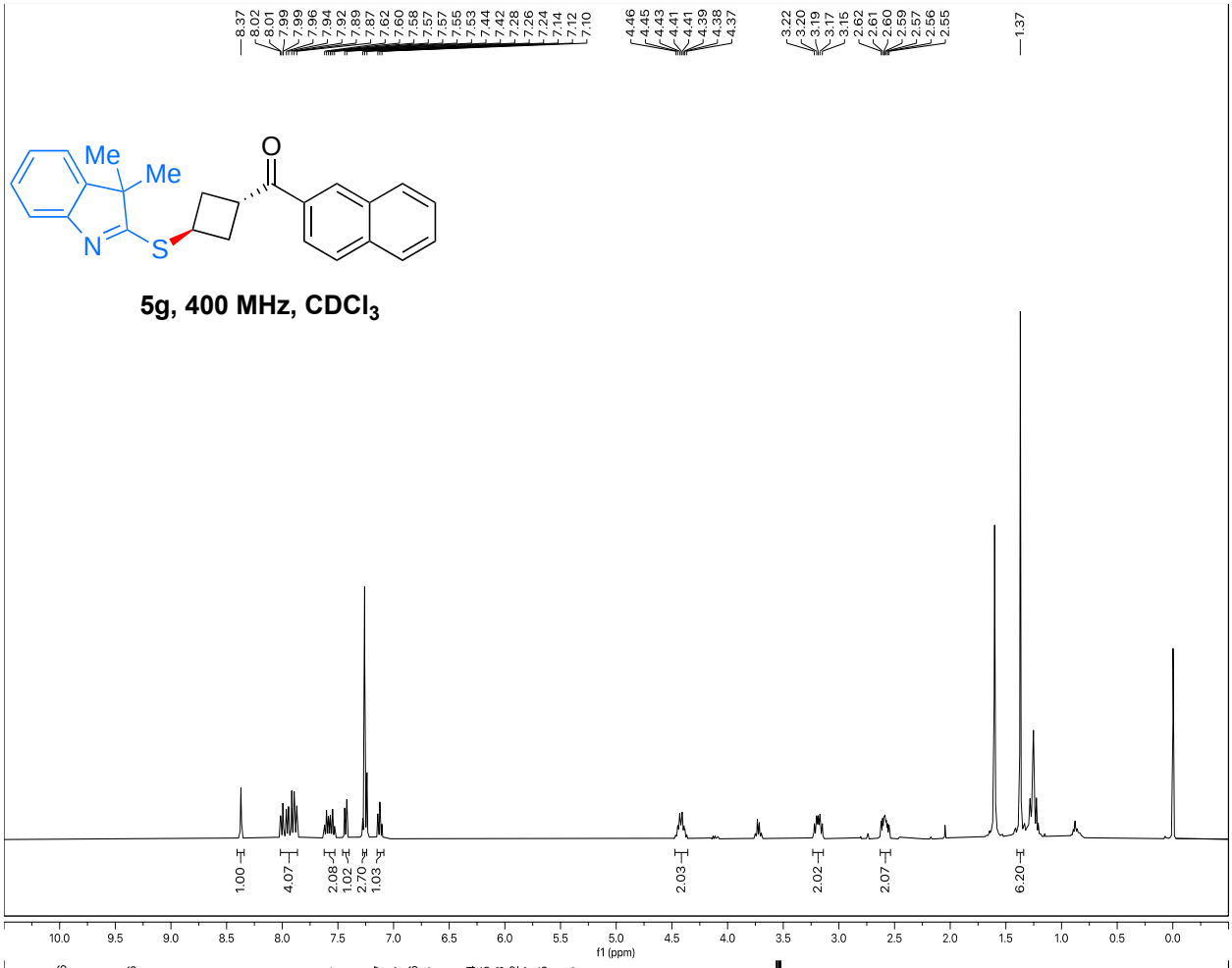


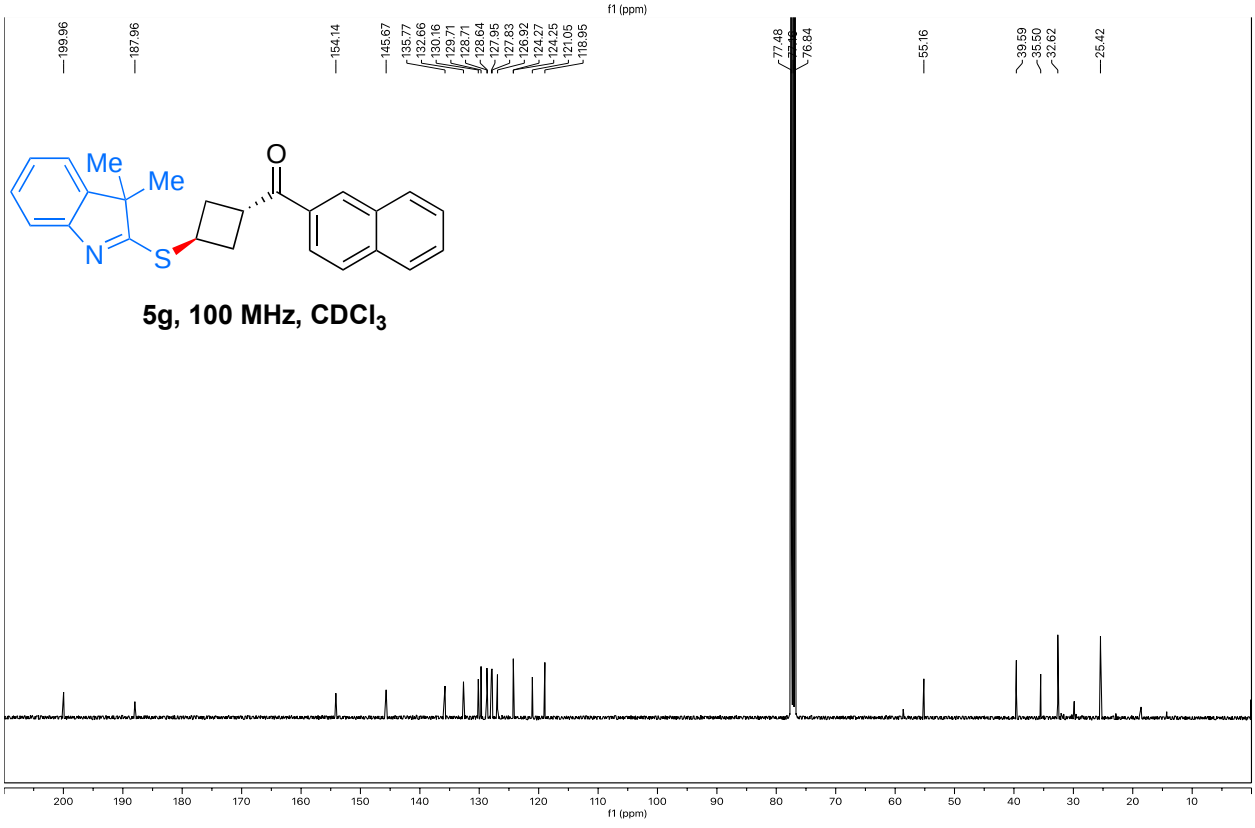
3-((3,4-Dihydro-2*H*-pyrrol-5-yl)thio)cyclobutyl)pentan-1-one (5f)



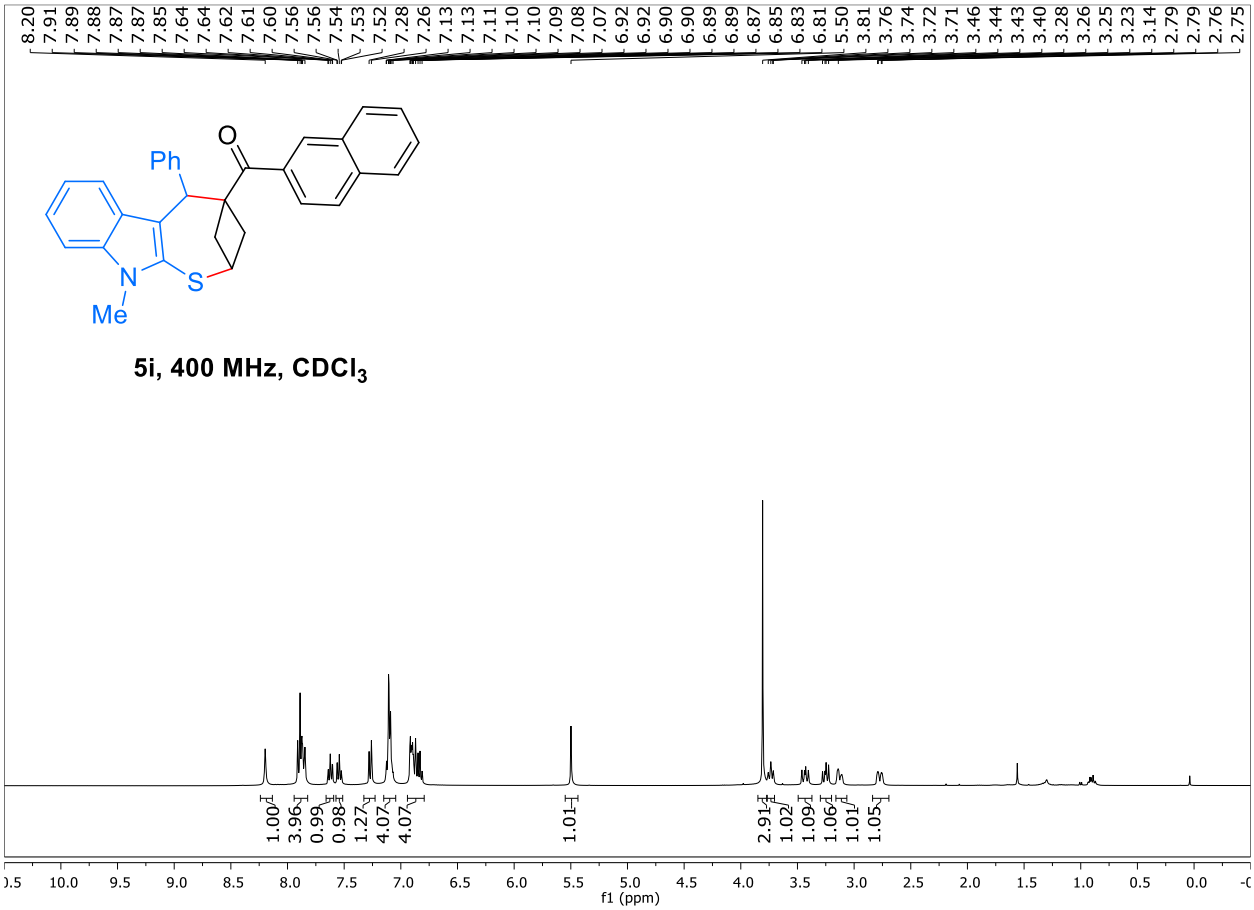


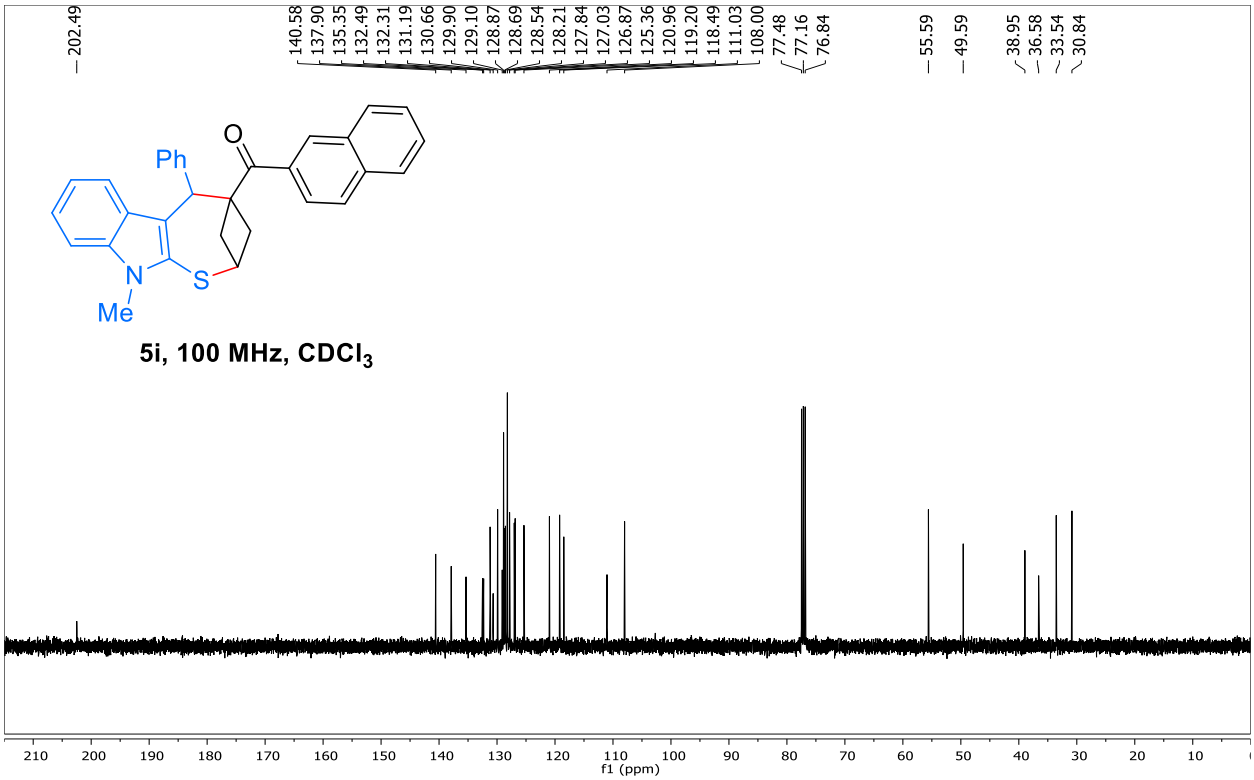
(3-((3,3-Dimethyl-3*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (5g)



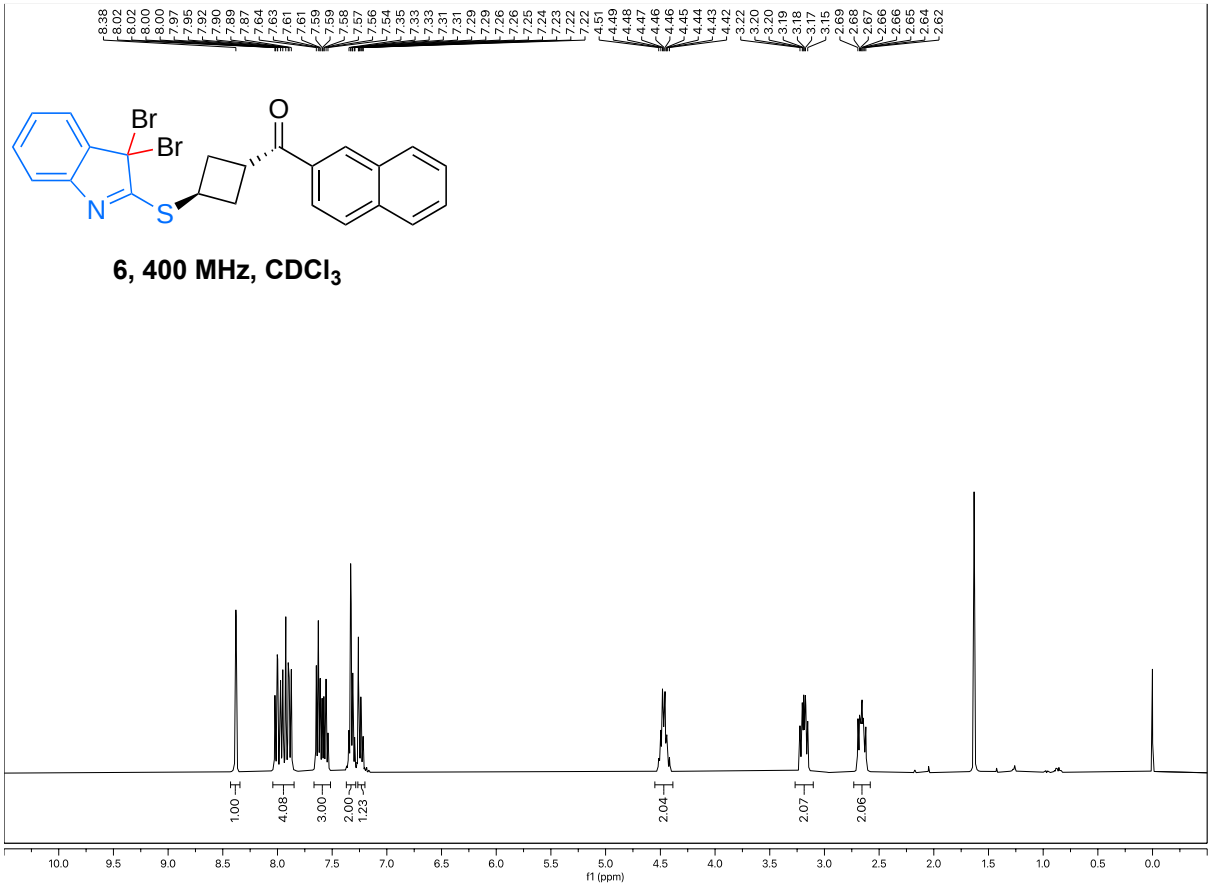


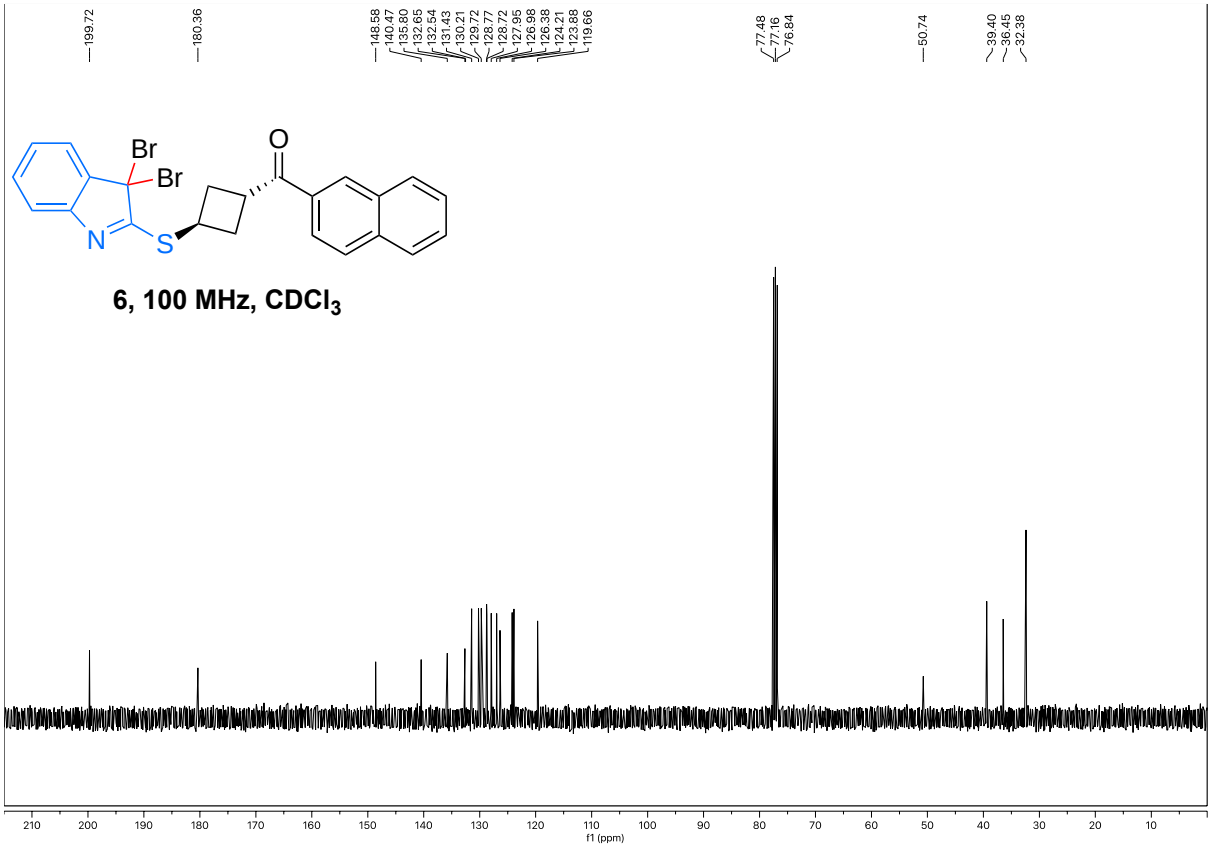
(10-Methyl-5-phenyl-2,3,5,10-tetrahydro-4*H*-2,4-methanothiepino[2,3-*b*]indol-4-yl)(naphthalen-2-yl)methanone (5i)



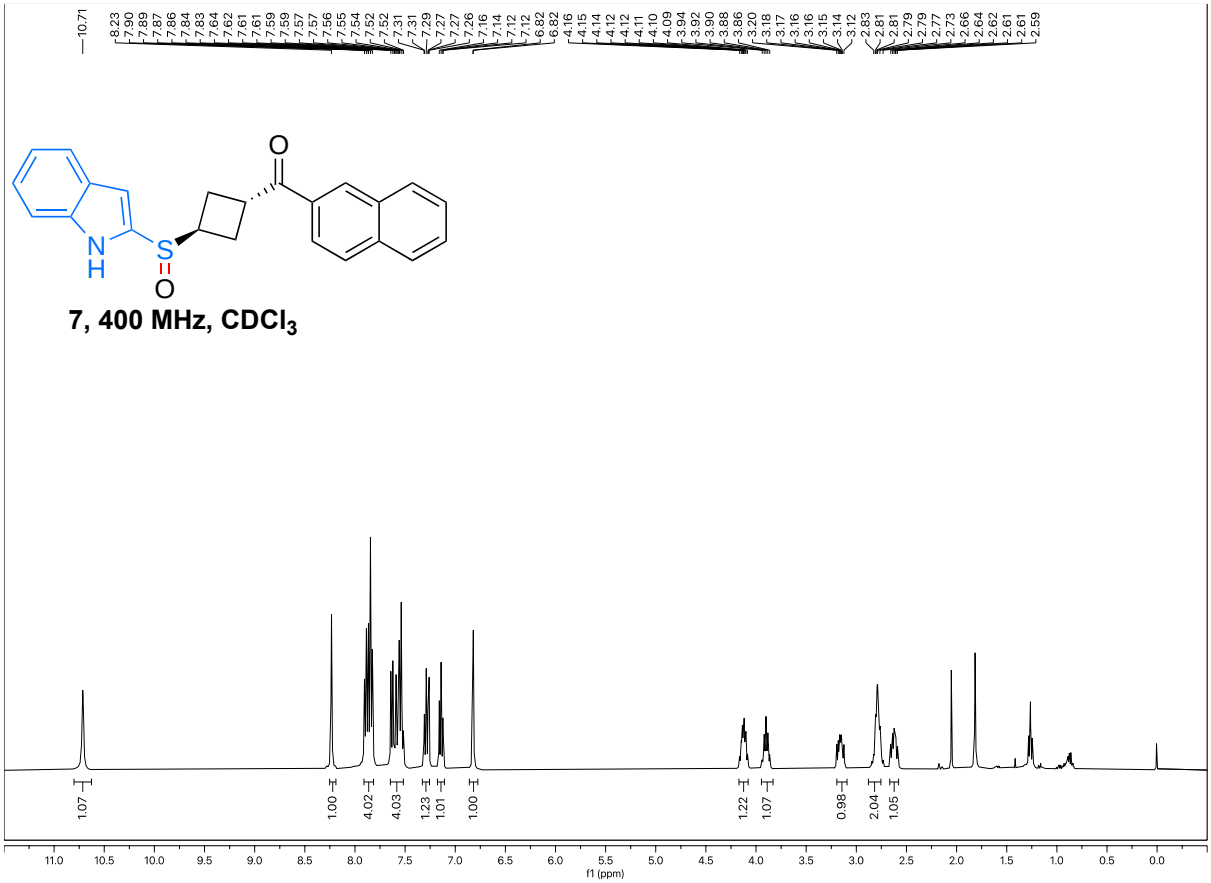


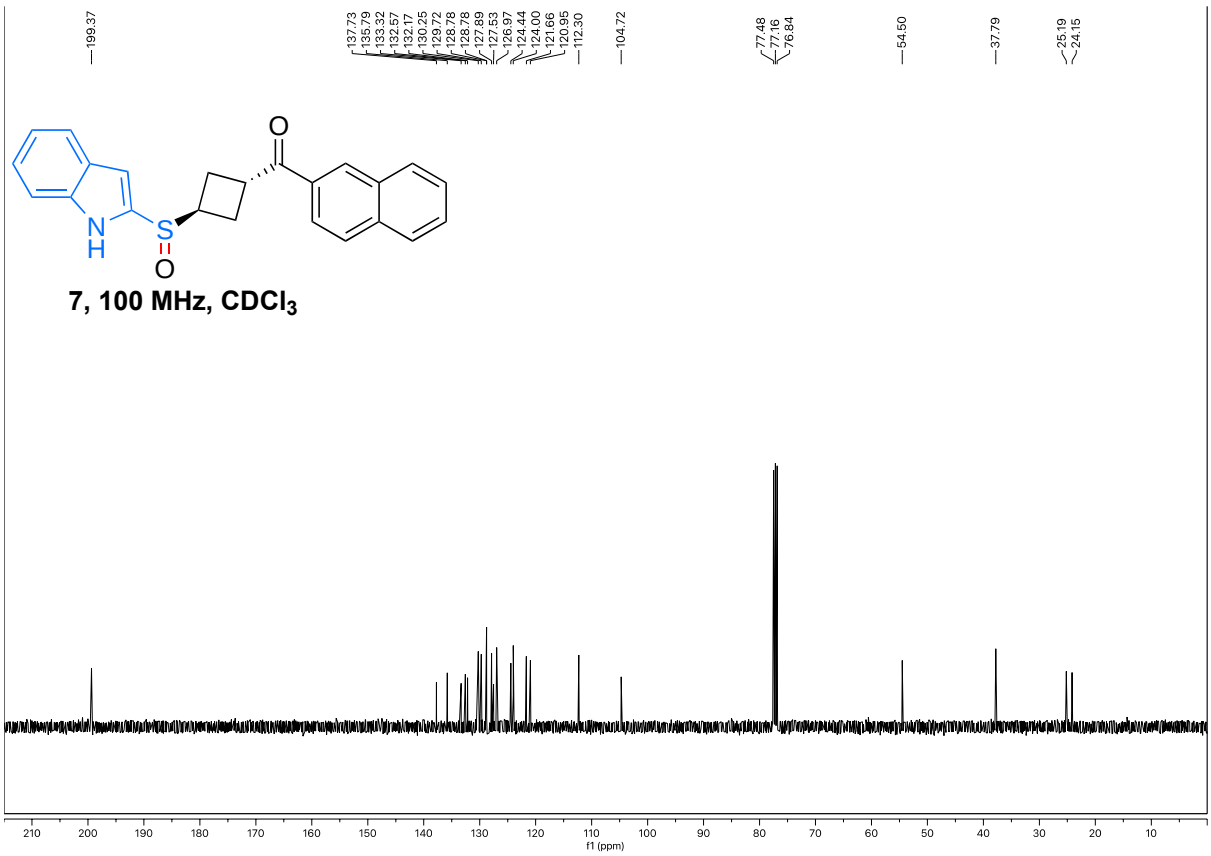
(3-((3,3-Dibromo-3*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (6)



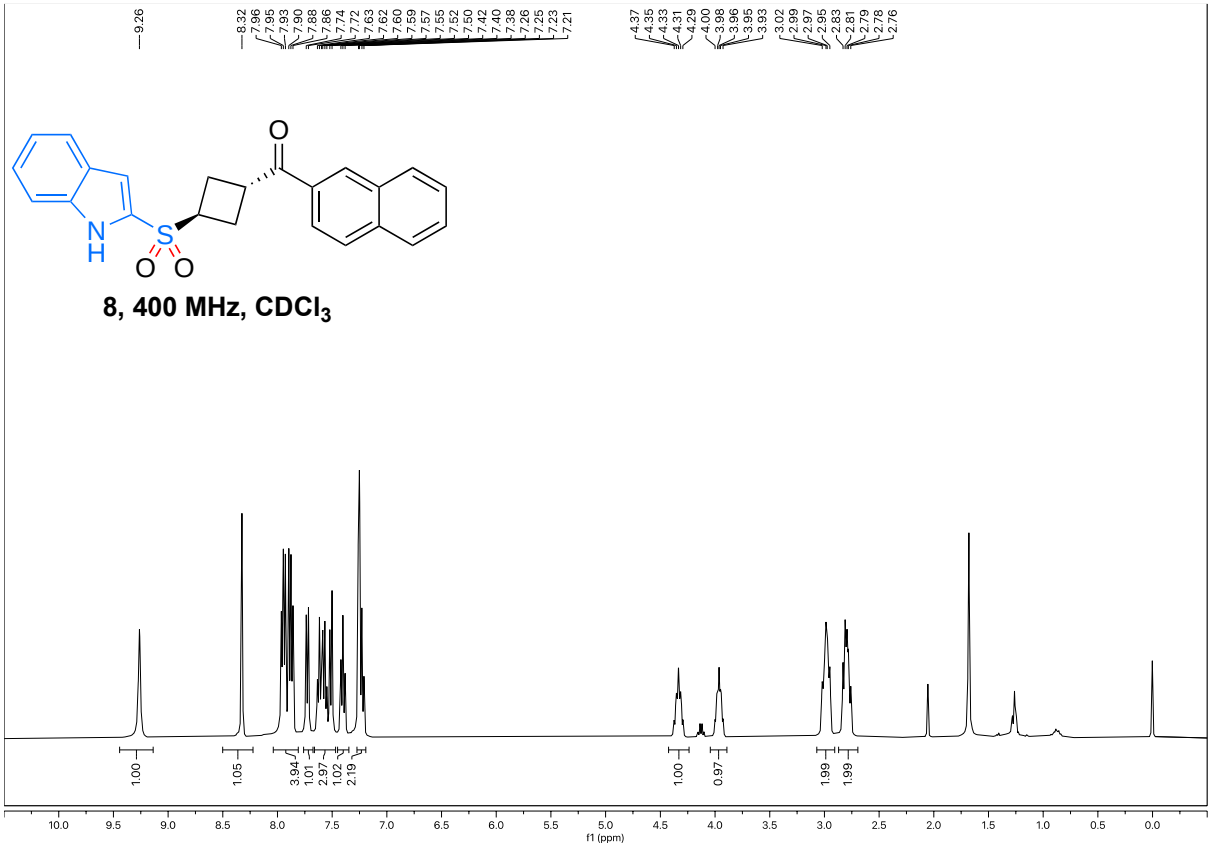


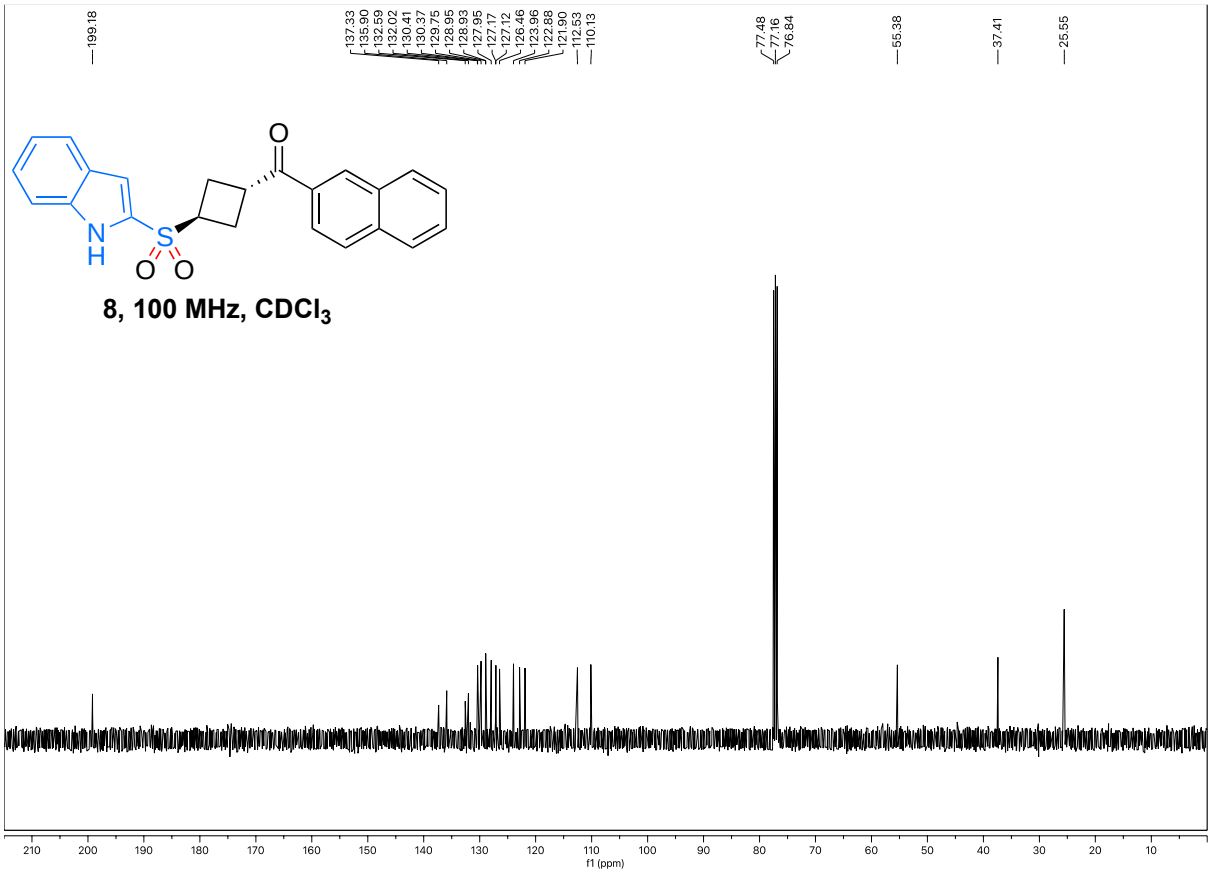
(3-(1*H*-Indol-2-yl)sulfinyl)cyclobutyl)(naphthalen-2-yl)methanone (7)



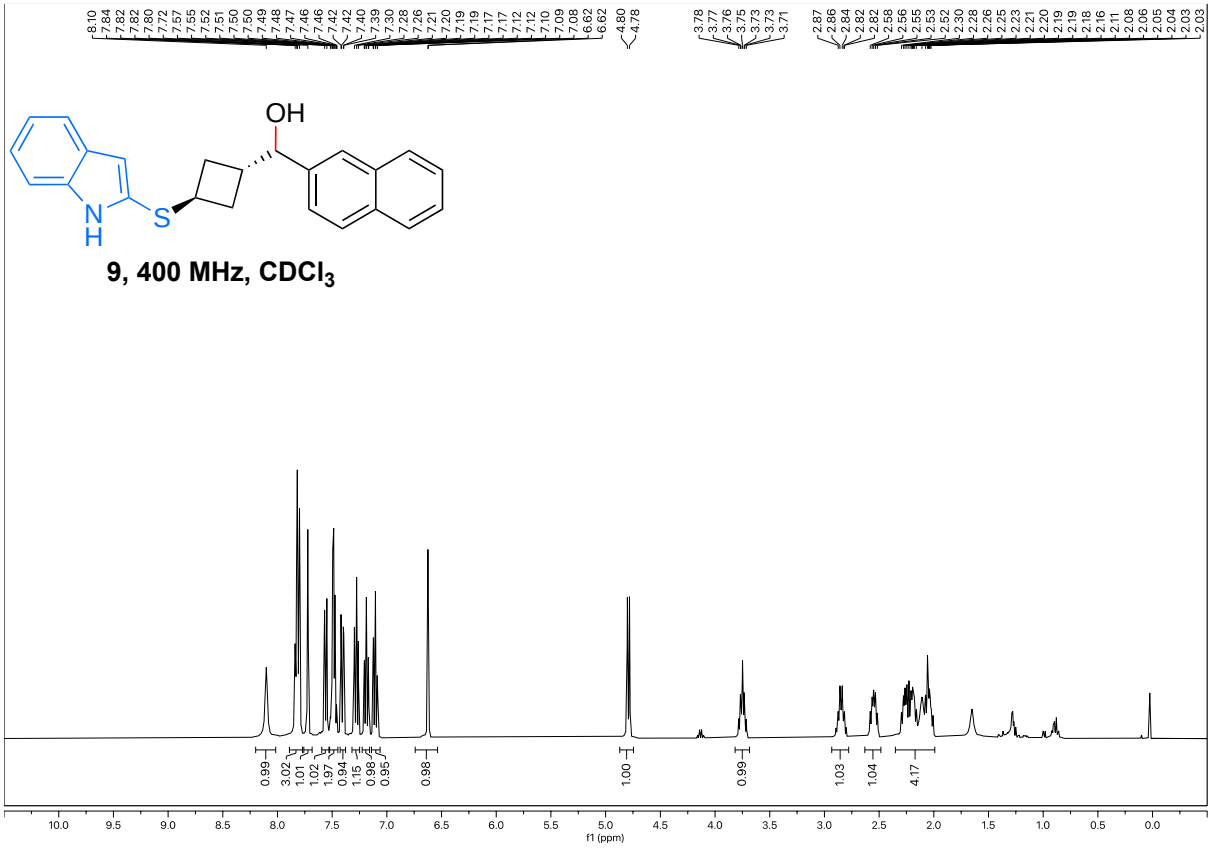


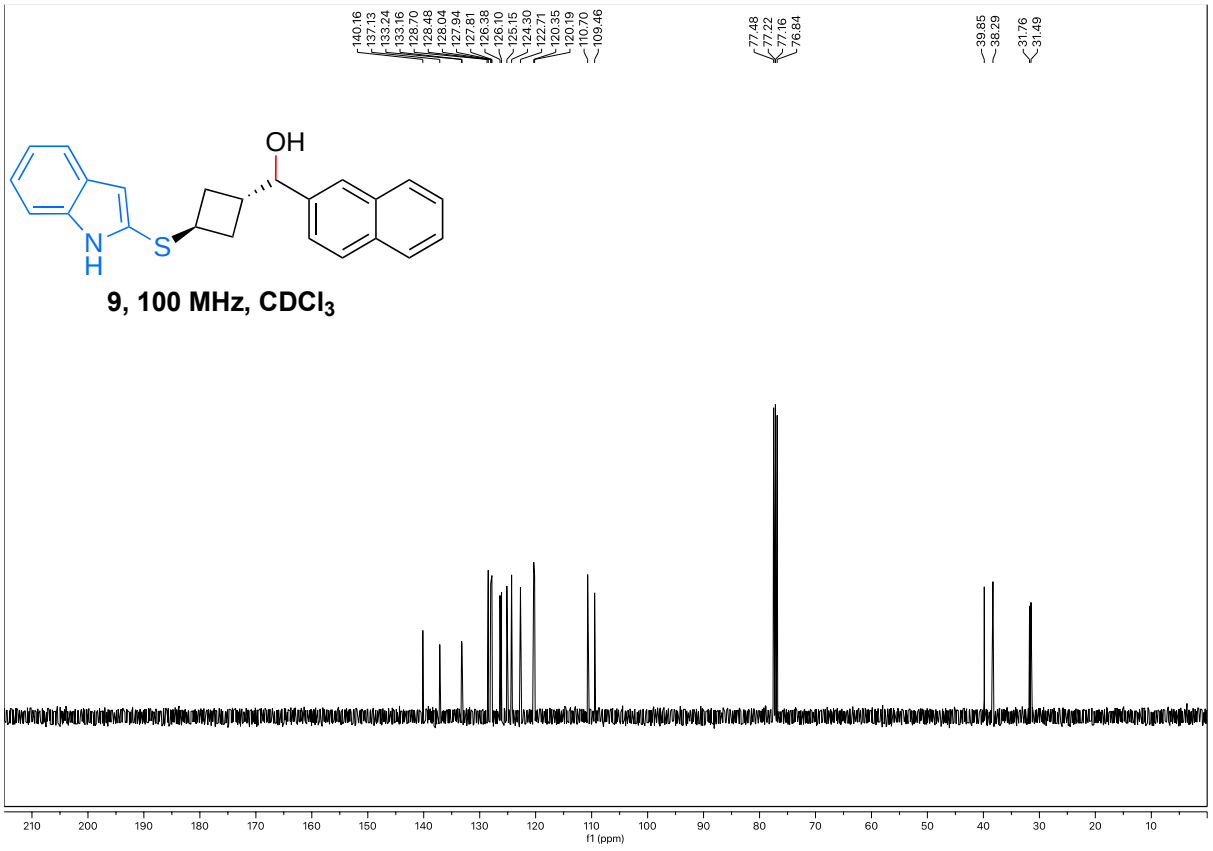
(3-((1*H*-Indol-2-yl)sulfonyl)cyclobutyl)(naphthalen-2-yl)methanone (8)



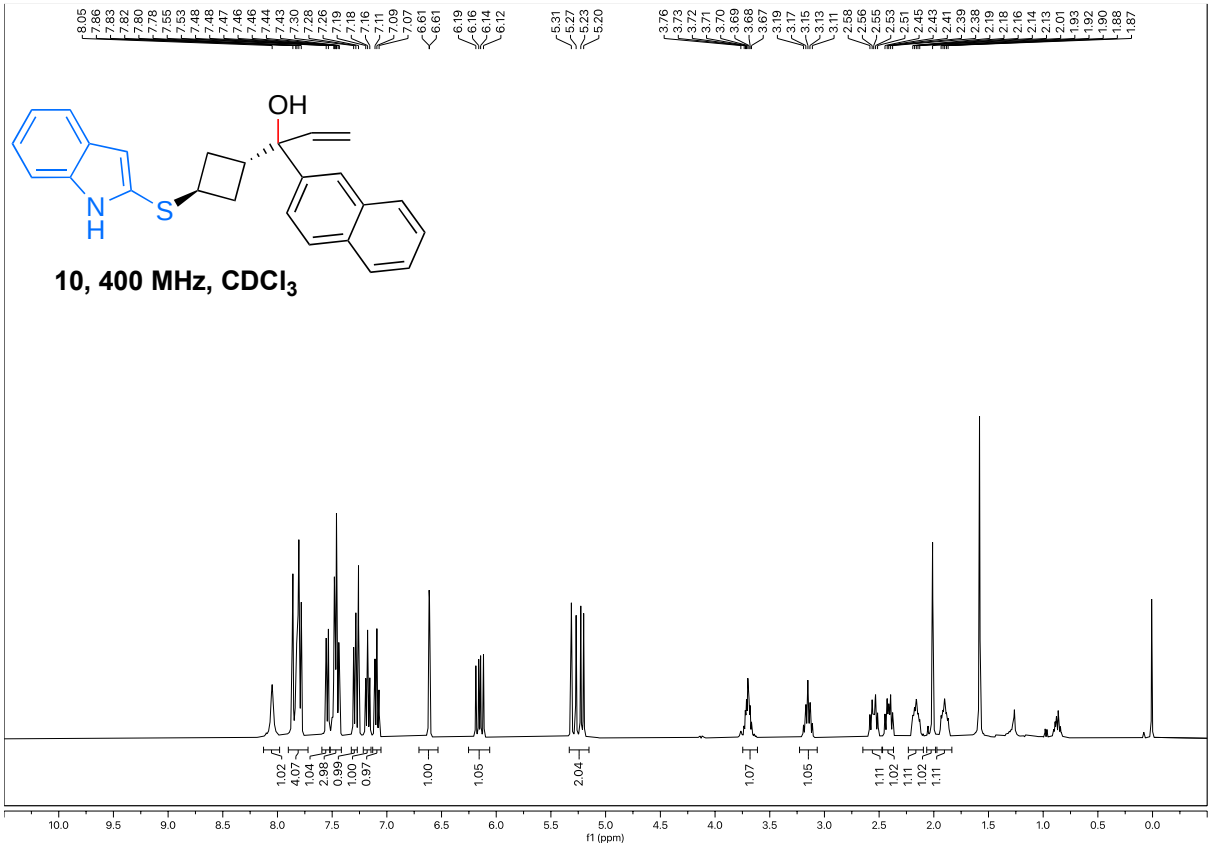


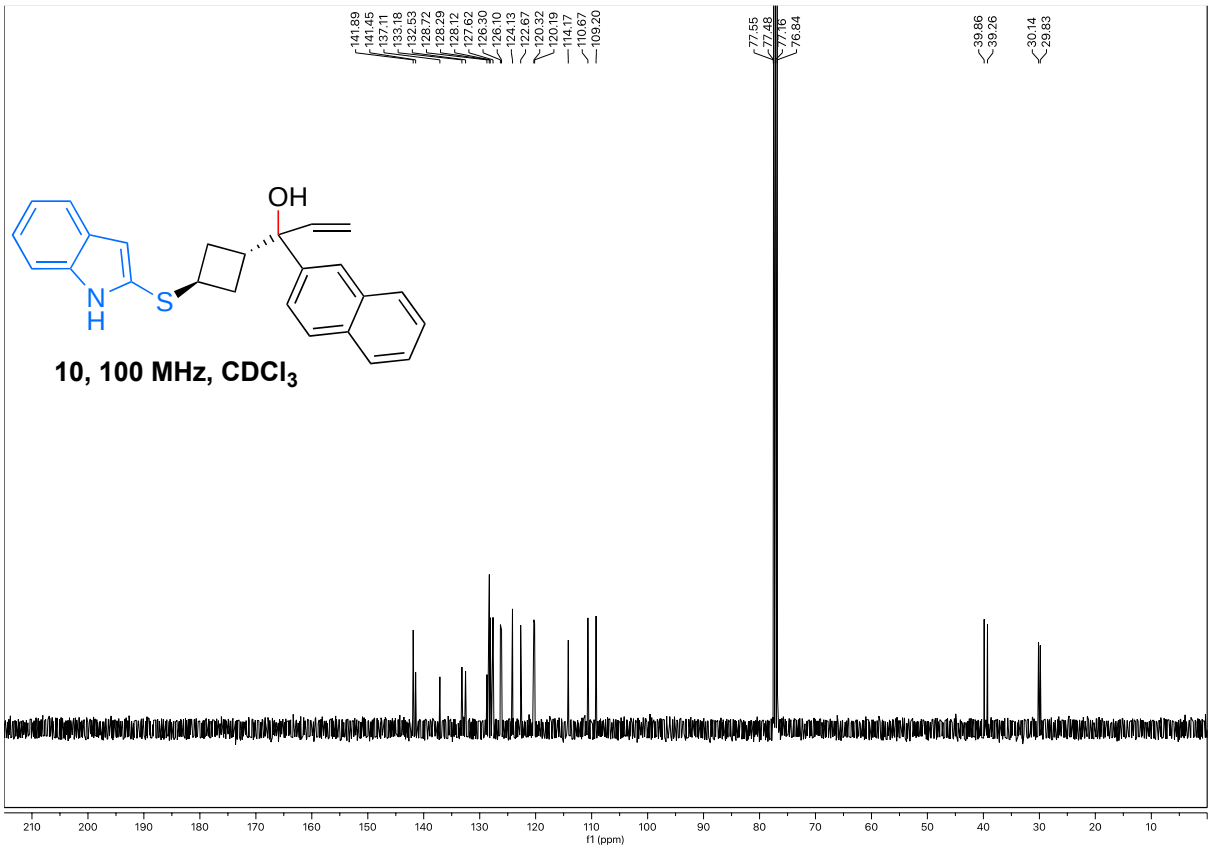
(3-((1*H*-Indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanol (9)



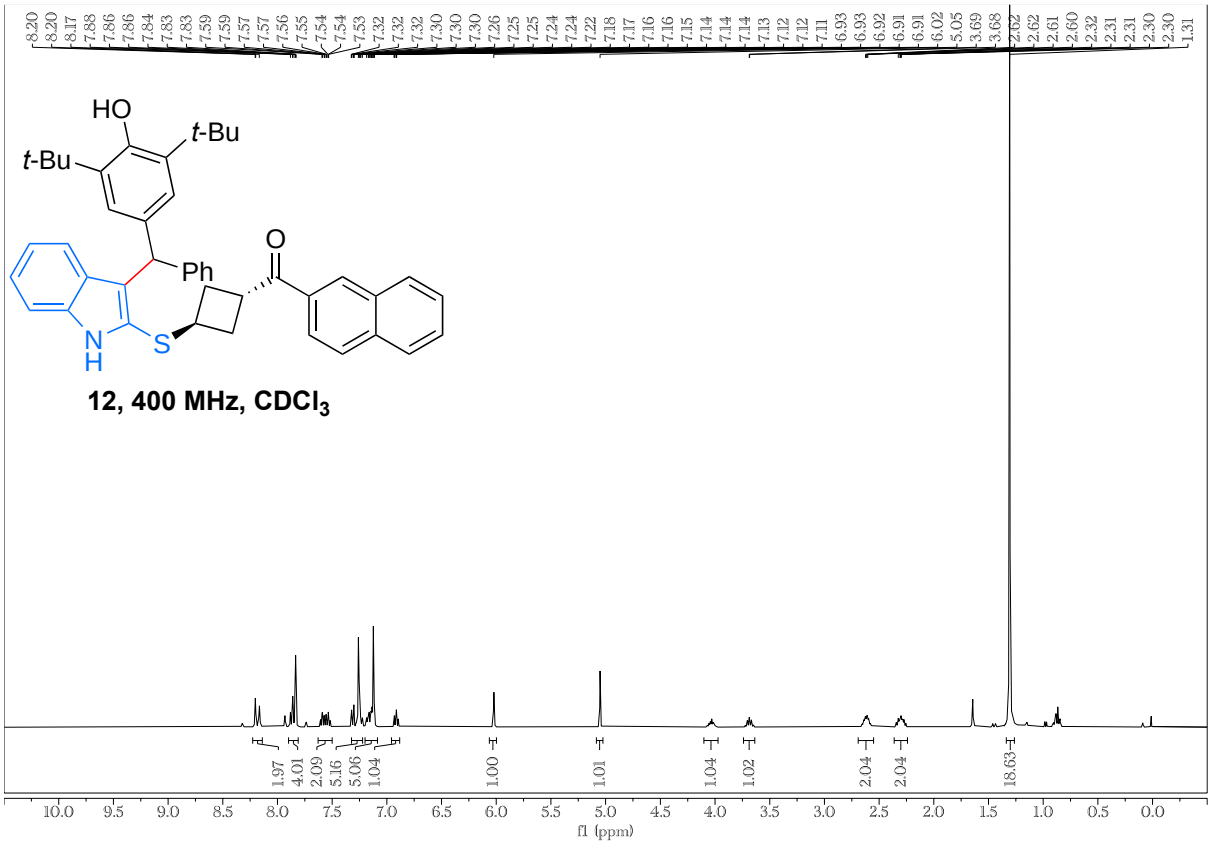


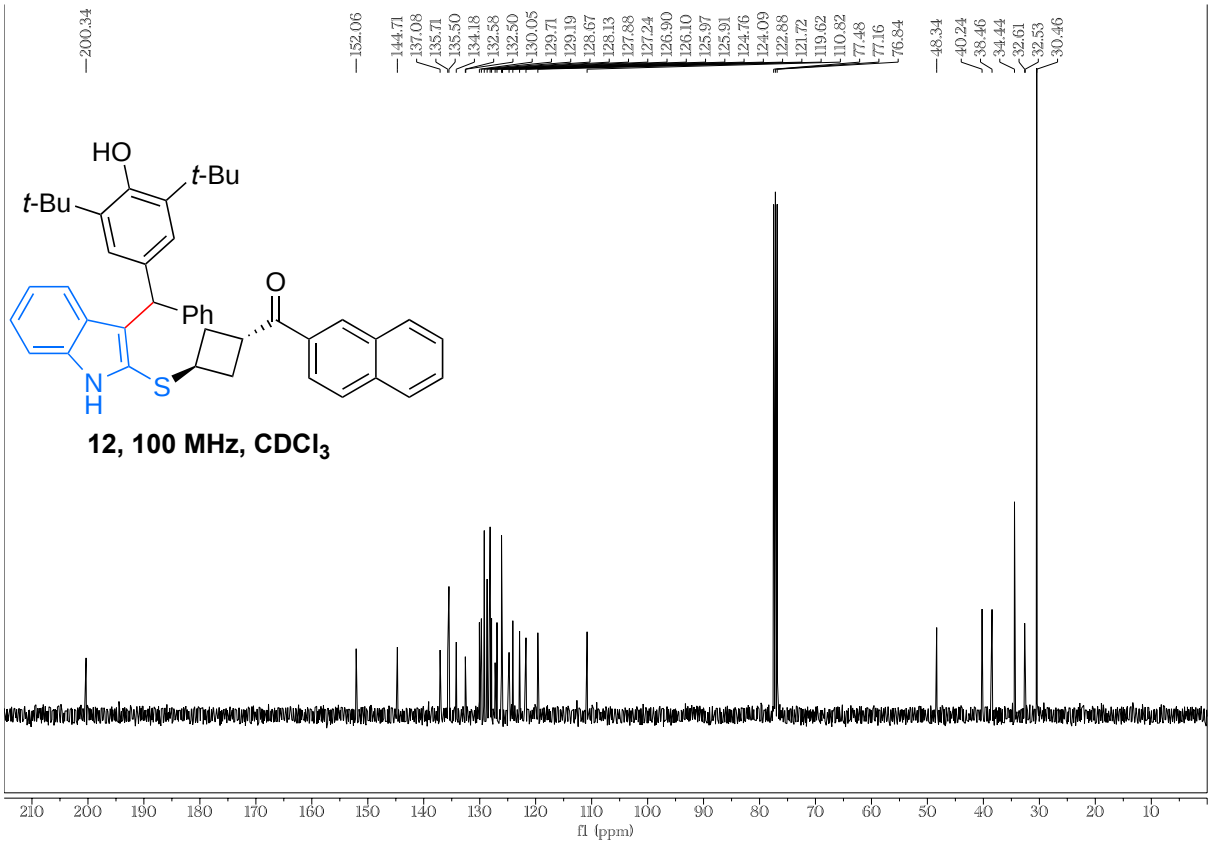
1-(3-((1*H*-Indol-2-yl)thio)cyclobutyl)-1-(naphthalen-2-yl)prop-2-en-1-ol (10)



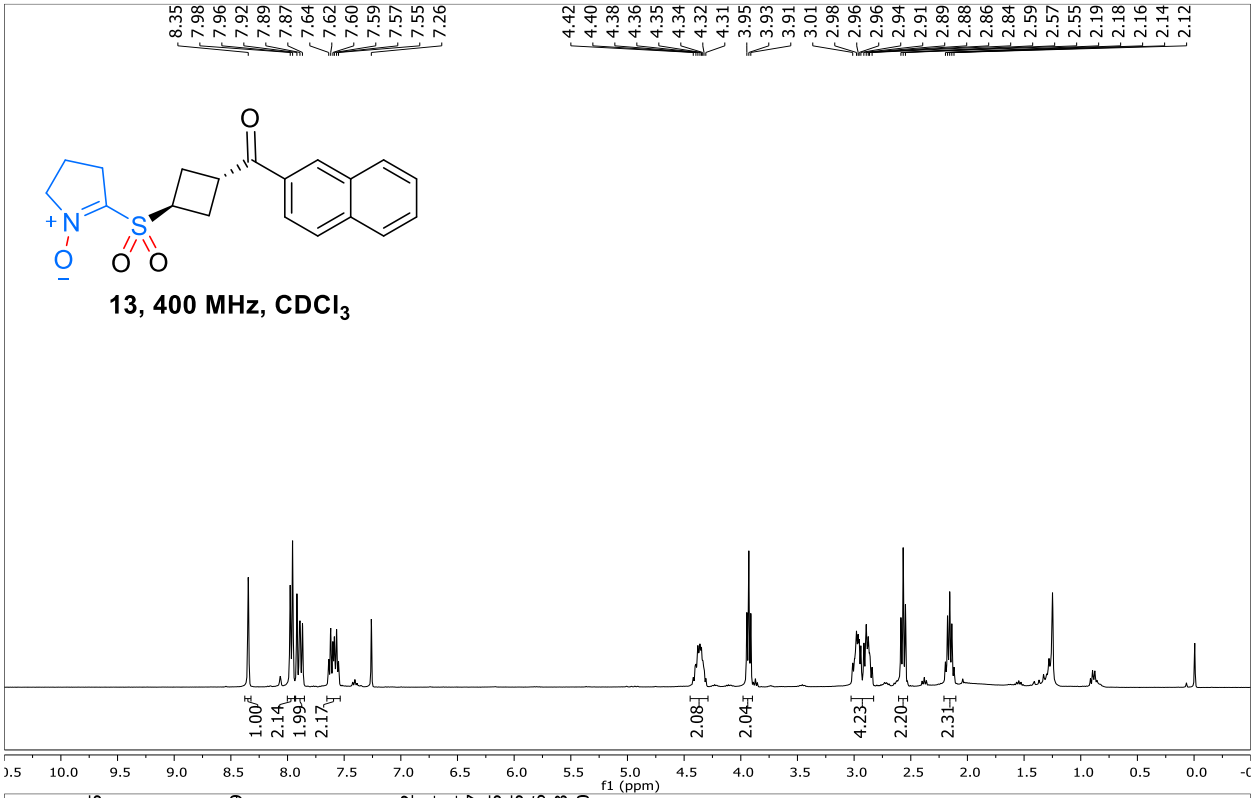


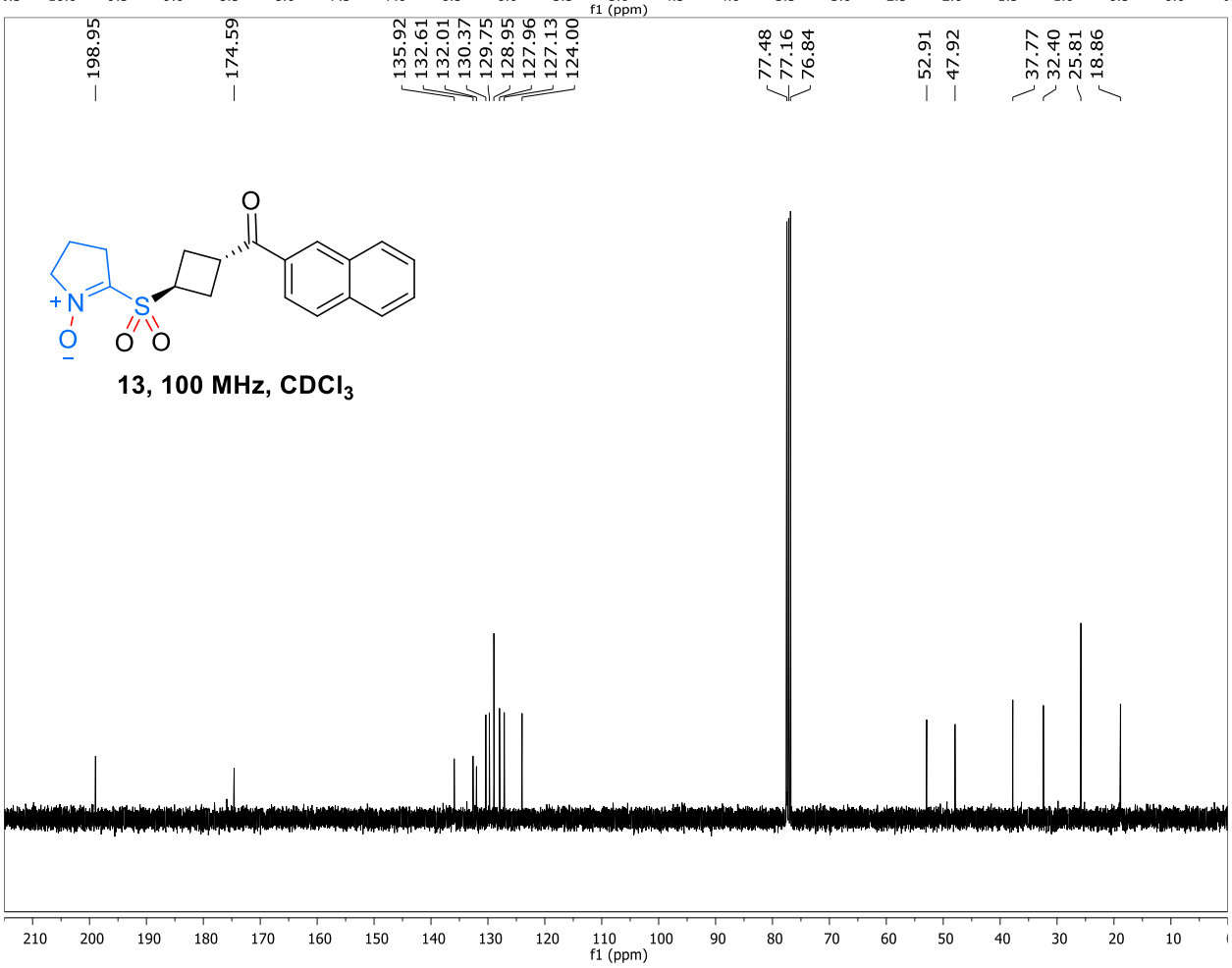
3-(3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-1*H*-indol-2-yl)thio)cyclobutyl)(naphthalen-2-yl)methanone (12)





5-((3-(2-Naphthoyl)cyclobutyl)sulfonyl)-3,4-dihydro-2*H*-pyrrole 1-oxide (13)





1-(3-((3,4-Dihydro-2*H*-pyrrol-5-yl)thio)cyclobutyl)-1-(naphthalen-2-yl)prop-2-en-1-ol (5b)