Lewis acid-catalyzed diastereoselective carbofunctionalization of bicyclobutanes employing naphthols

Avishek Guin, Subrata Bhattacharjee, Mahesh Singh Harariya, and Akkattu T. Biju*

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

Email: 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. Naphthols were purchased from either Alfa Aesar, TCI, BLD pharm or Sigma-Aldrich and were used as received. All BCBs were synthesized following the literature procedure.[1] Aryl/ heteroaryl 2-naphthols were synthesized following known literature procedure via Suzuki coupling.[2]

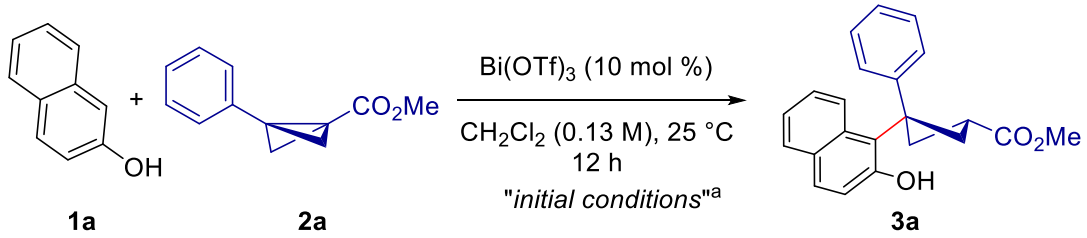
Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. All the isolated new compounds were confirmed to be single spot on TLC. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica 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. Melting points were recorded on a Buchi melting point apparatus.

[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. M. Bychek, V. Hutskalova, Y. P. Bas, O. A. Zaporozhets, S. Zozulya, V. V. Levterov and P. K. Mykhailiuk, *J. Org. Chem*., 2019, **84**, 15106; *(c)* X. Ma, D. L. Sloman, Y. Han and D. J. Bennett, *Org. Lett*., 2019, **21**, 7199.

[2] S. Zhu, Y.-H. Chen, Y.-B. Wang, P. Yu, S.-Y. Li, S.-H. Xiang, J.-Q. Wang, J. Xiao and B. Tan, *Nat. Commun*., 2019, **10**, 4268.

2. General Procedure for the Optimization of the Reaction Conditions



1a **2a** **3a**

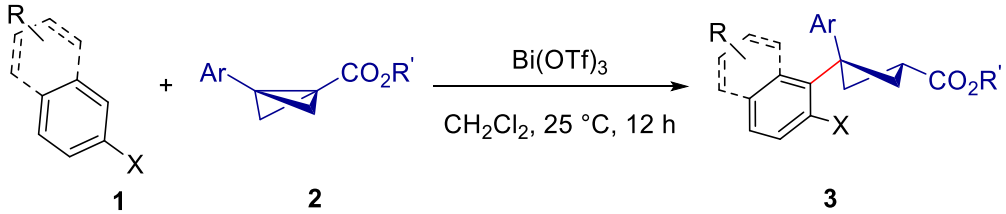
To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, 2-naphthol **1a** (0.029 g, 0.2 mmol) and 1.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the mixture was stirred for 5 minutes at 25 °C. After 5 minutes, methyl 3-phenylbicyclo [1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was stirred for 12 h at 25 °C. After 12 h, the solvent was evaporated and the crude residue was pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 80/20) on silica gel to afford **3a** as a yellow solid.

Table S1. Optimization Studies

entry	variation of the initial conditions	yield of **3a** (%)[b]
1	none	91
2	$Sc(OTf)_3$ instead of $Bi(OTf)_3$	28
3	$Yb(OTf)_3$ instead of $Bi(OTf)_3$	15
4	TfOH instead of $Yb(OTf)_3$	<5
5	DCE instead of CH_2Cl_2	78
6	THF instead of CH_2Cl_2	39
7[c]	MeCN instead of CH_2Cl_2	86
8	0 °C instead of 25 °C	84
9	1.5 equiv of **2a**	92
10	5 mol % $Bi(OTf)_3$	83
11	0.06 M CH_2Cl_2	81

[a] Initial conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), $Bi(OTf)_3$ (10 mol %), CH_2Cl_2 (1.5 mL), 25 °C for 12 h. [b] Given are the yield of chromatographically purified **3a**. [c] 3.0:1 dr was obtained in this case and the dr value was determined from ^1H NMR of the crude reaction mixture.

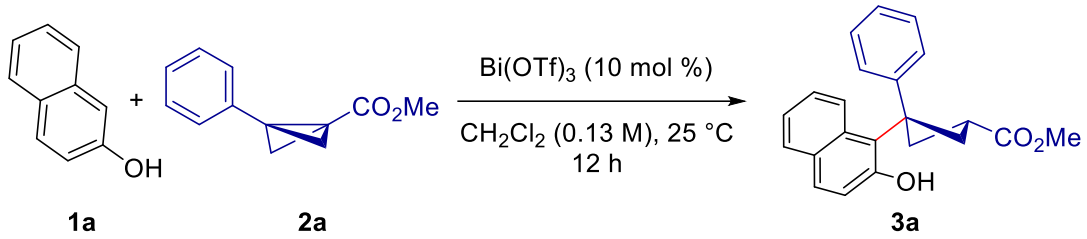
3. General Procedure for the Lewis Acid Catalyzed Diastereoselective Carbofunctionalization of Bicyclobutanes



1 **2** **3**

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, nucleophile **1** (0.2 mmol) and 1.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the mixture was stirred for 5 minutes at 25 °C. After 5 minutes, BCBs **2** (0.24 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Later the reaction mixture was stirred for 12 h at 25 °C. 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.

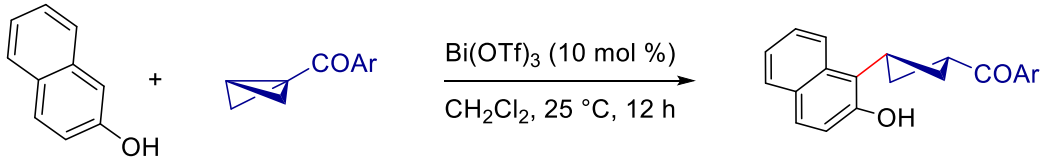
Procedure for the 2.0 mmol Scale Reaction for the synthesis of 3a



1a **2a** **3a**

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.131 g, 0.2 mmol) inside the glove box. After that, 2-naphthol **1a** (0.288 g, 2.0 mmol) and 10 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the mixture was stirred for 5 minutes at 25 °C. After 5 minutes, methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.452 g, 2.4 mmol) and 5 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was stirred for 12 h at 25 °C. 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 = 80/20) on silica gel to afford **3a** as a yellow solid (0.592 g, 89% yield).

4. General Procedure for the Reaction of Unsubstituted Ketone BCBs



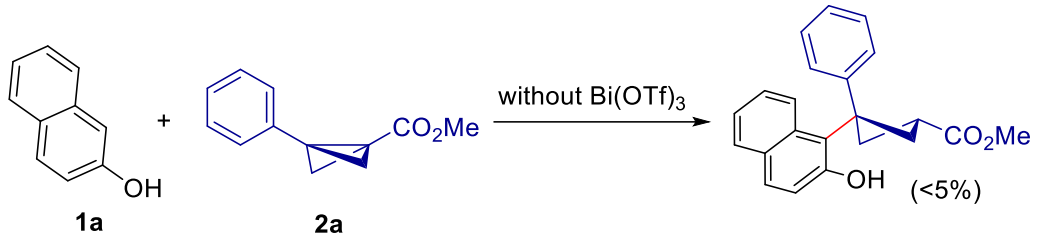
1a **2j, Ar = Ph** **2k, Ar = 2-Napthyl** **3ab, Ar = Ph, 59%, dr 2:1** **3ac, Ar = 2-Napthyl, 68%, dr 2.3:1**

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, 2-naphthol **1a** (0.029 g, 2.0 mmol) and 1.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then

the mixture was stirred for 5 minutes. After 5 minutes, keto BCBs **2j** or **2k** (0.24 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Later the reaction mixture was stirred for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography on silica gel (Pet.ether-EtOAc as eluent) to afford **3ab** or **3ac** in moderate to good yields.

5. Mechanistic Studies

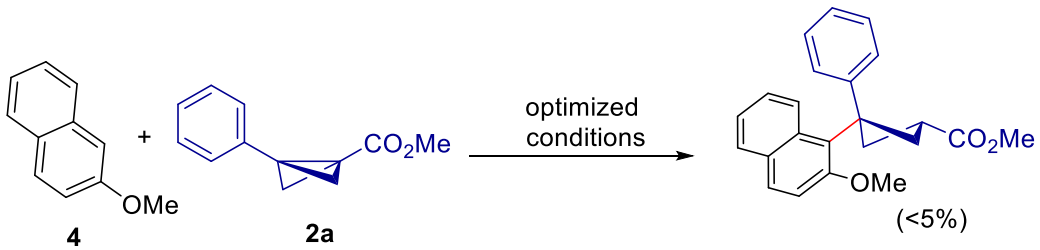
Reaction in the absence of $Bi(OTf)_3$



To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added 2-naphthol **1a** (0.029 g, 2.0 mmol) and 1.0 mL CH_2Cl_2 under nitrogen atmosphere. Then the mixture was stirred for 5 minutes at 25 °C. After 5 minutes, methyl 3-phenylbicyclo [1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Later the reaction mixture was stirred for 12 h at 25 °C. 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.

This study indicates that the 2-naphthol triggered diastereoselective BCB ring-opening is a Lewis acid catalyzed process.

Reaction using 2-methoxy napthalene

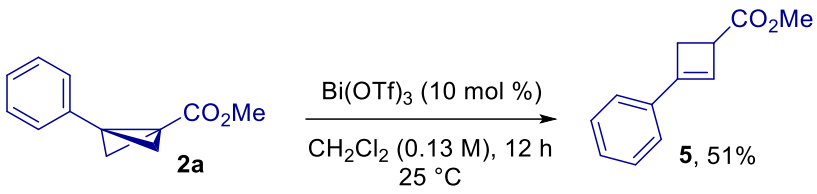


To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, 2-methoxynaphthalene **4** (0.032 g, 0.2 mmol) and 1.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the mixture was stirred for 5 minutes at 25 °C. After 5 minutes, methyl 3-

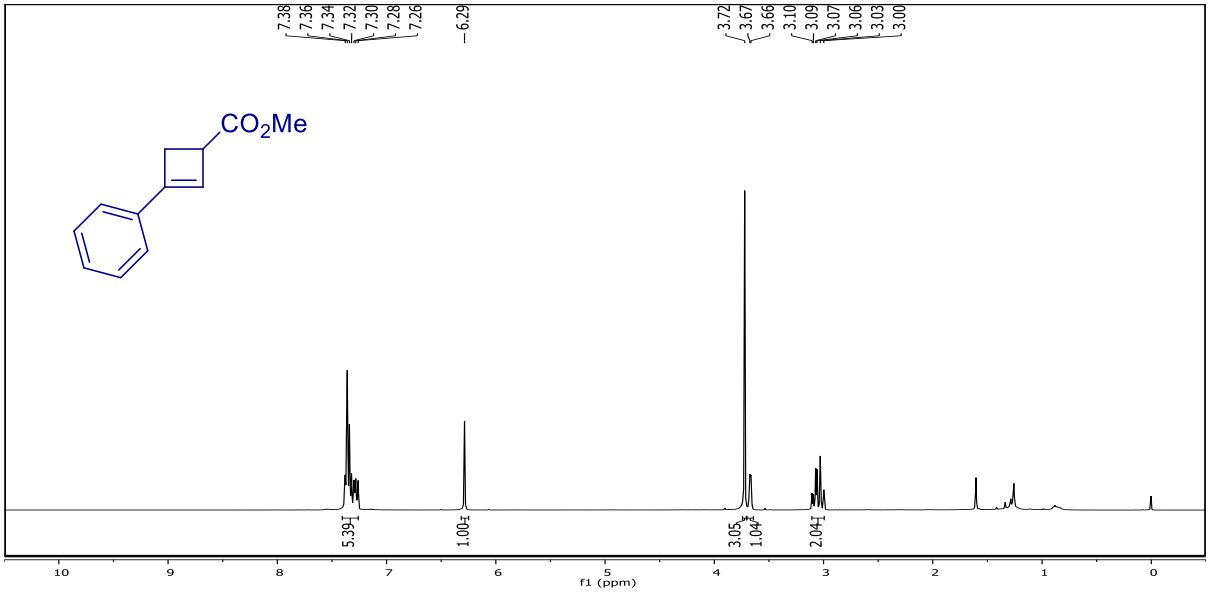
phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was stirred for 12 h at 25 °C. After 12 h, the reaction mixture was passed through a pad of silica gel and then eluted with EtOAc (3x10 mL), and the solvent was evaporated to get the crude products, which was analyzed using ^{1}H NMR spectroscopy.

This study indicates the crucial role of free -OH group in the 2-naphthol triggered, Lewis acid catalyzed diastereoselective ring-opening of BCB. In the absence of a free -OH group, the carbofunctionalization process was deemed unfavorable due to the lack of proper coordination between 2-naphthol and Bi(OTf)$_3$. (Scheme 4 of the manuscript, eq 4).

Reaction of BCB with Bi(OTf)$_3$

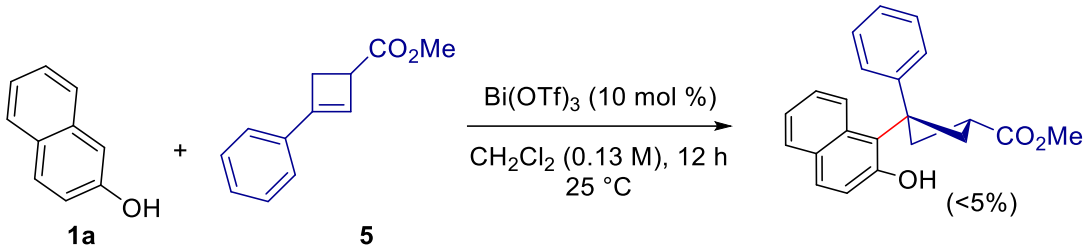


To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.038 g, 0.2 mmol) and 1.5 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was stirred for 12 h at 25 °C. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 97/03) on silica gel to afford **5** as a colorless oil (0.019 g, 51% yield).

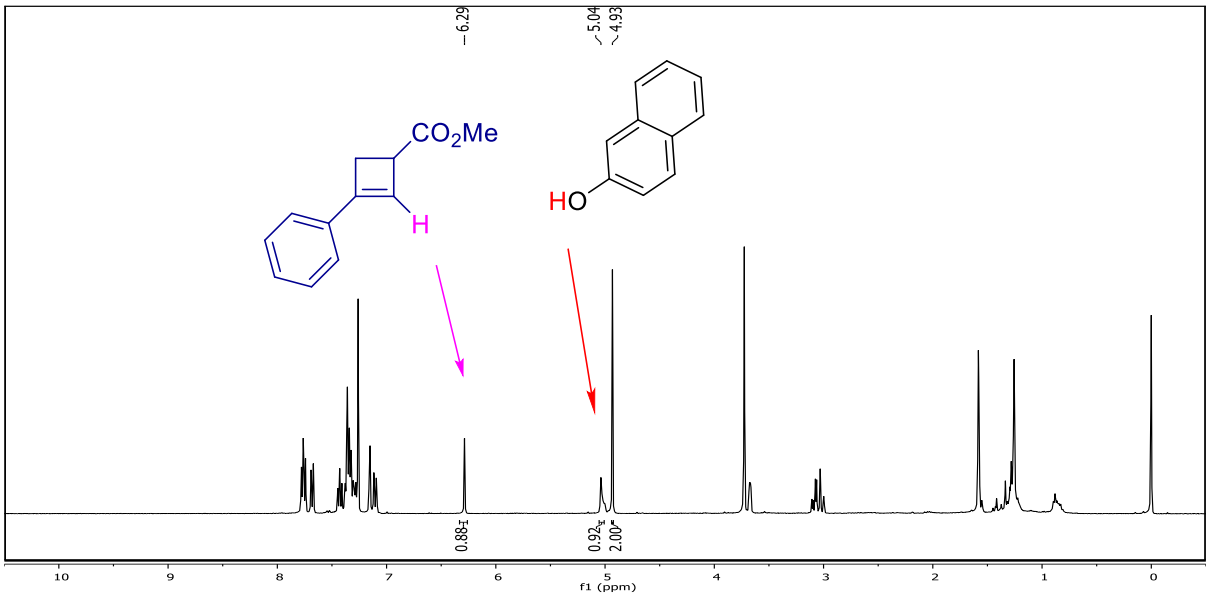


This study indicates that in the absence of 2-naphthol, BCB can directly coordinate with Lewis acid, which facilitate the decomposition of BCB. Most probably, 2-naphthol reduces the Lewis acidity of $Bi(OTf)_3$ and therefore no cyclobutene product was obtained in our optimized reaction conditions. But the question arises whether the carbofunctionalized product formation is possible via the intermediacy of cyclobutene. (Scheme 4 of the manuscript, eq 5).

Reaction of cyclobutene 5 with 2-naphthol

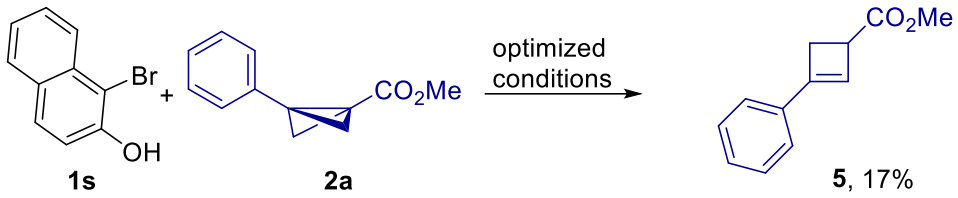


To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, 2-naphthol **1a** (0.029 g, 2.0 mmol) and 1.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the mixture was stirred for 5 minutes at 25 °C. After 5 minutes, methyl 3-phenylcyclobut-2-ene-1-carboxylate **2a** (0.038 g, 0.2 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Later the reaction mixture was stirred for 12 h at 25 °C. 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.



The findings of this study have ruled out the possibility of cyclobutene formation occurring during the present carbofunctionalization reaction. (Scheme 4 of the manuscript, eq 6).

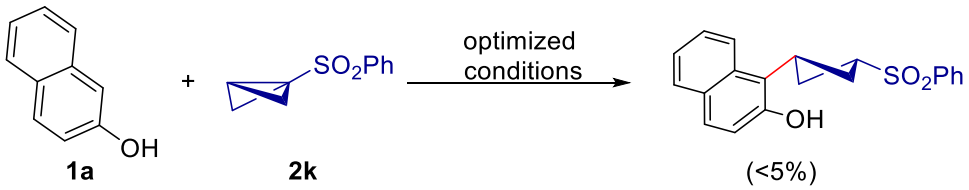
Reaction with 1-bromonaphthalen-2-ol



To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, 1-bromonaphthalen-2-ol **1s** (0.045 g, 0.2 mmol) and 1.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the mixture was stirred for 5 minutes at 25 °C. After 5 minutes, methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was stirred for 12 h at 25 °C. 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, the cyclobutene **5** was formed in 17% (crude ^{1}H NMR analysis).

This indicates that the present reaction does not work with 2-naphthols with a substituent at the 1-position. (Scheme 4 of the manuscript, eq 7).

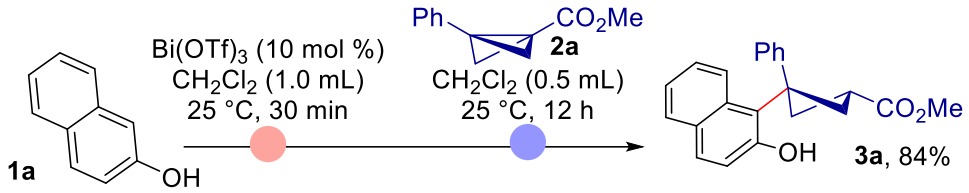
Reaction with sulfonyl BCB



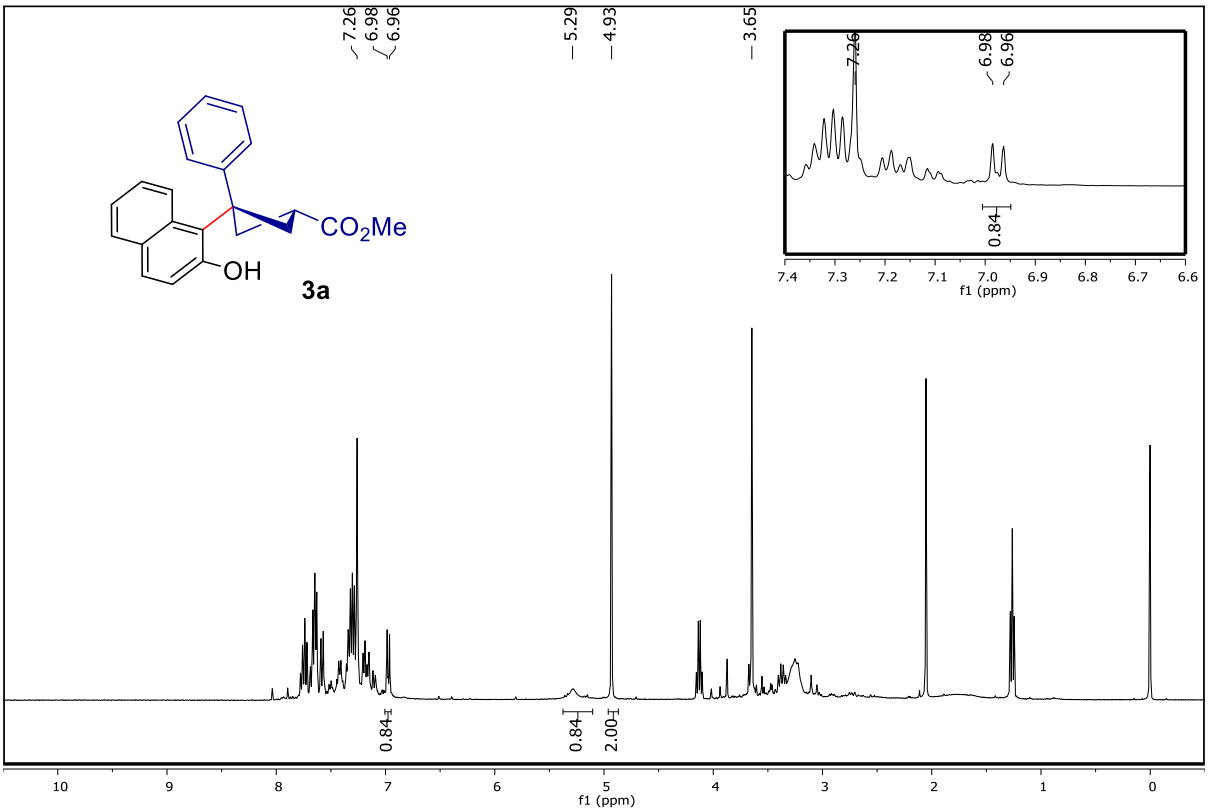
To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, 2-naphthol **1a** (0.029 g, 0.2 mmol) and 1.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the mixture was stirred for 5 minutes at 25 °C. After 5 minutes, 1-(phenylsulfonyl)bicyclo [1.1.0]butane **2k** (0.047 g, 0.24 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was stirred for 12 h at 25 °C. 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.

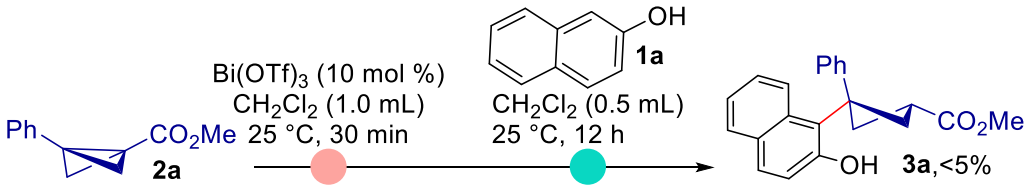
This study sheds light on the importance of ester moiety of BCB for effective Lewis acid binding in this diastereoselective ring-opening reaction (Scheme 4 of the manuscript, eq 8).

Dependence of the reaction on the mode of addition

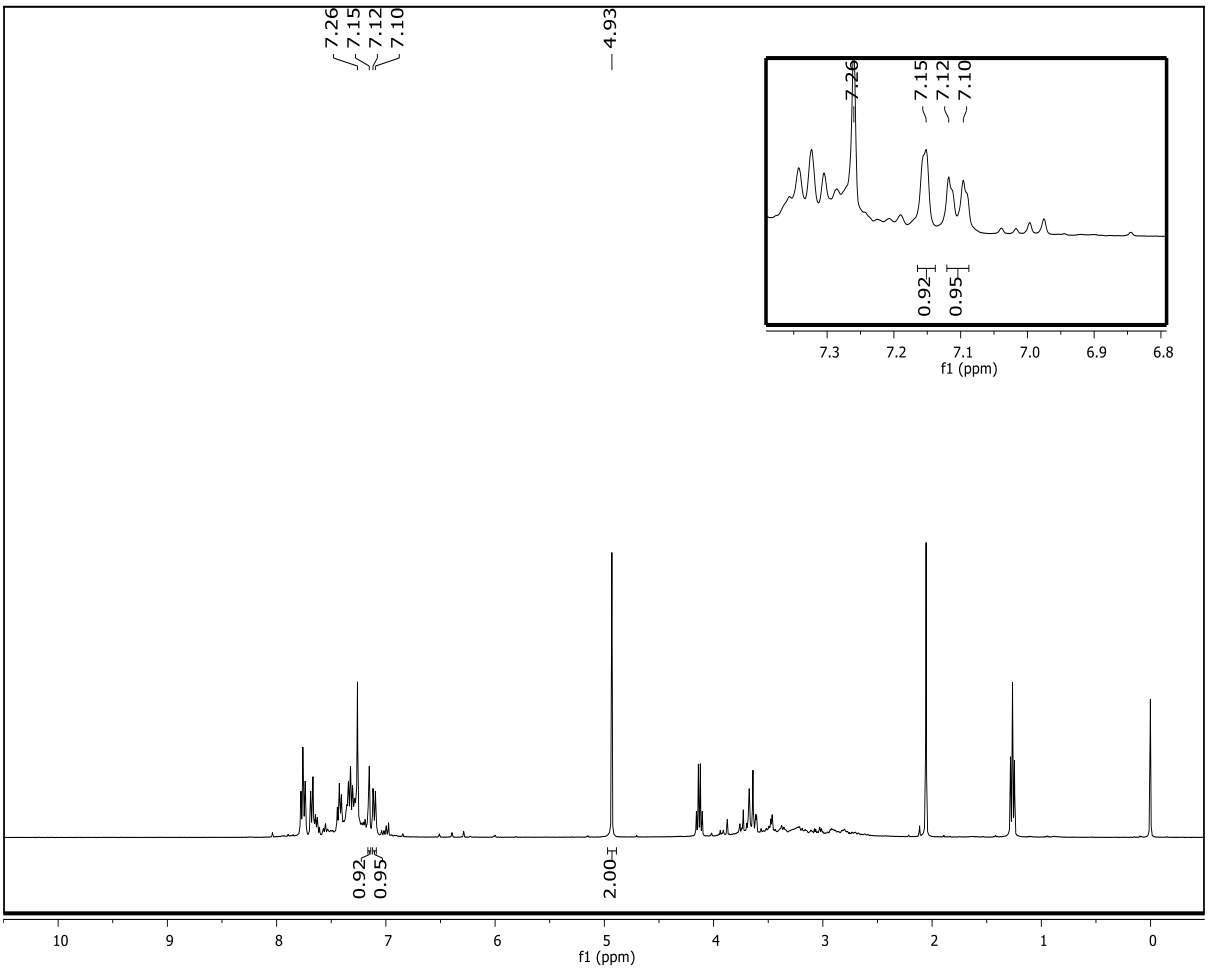


To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, 2-naphthol **1a** (0.029 g, 0.2 mmol) and 1.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the mixture was stirred for 30 minutes at 25 °C. After 30 minutes, methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was stirred for 12 h at 25 °C. 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 ^1H NMR analysis of the crude reaction products using CH_2Br_2 as the internal standard.





To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the $Bi(OTf)_3$ (0.013 g, 0.02 mmol) inside the glove box. After that, methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) and 1.0 mL CH_2Cl_2 were added outside the glove box under nitrogen atmosphere. Then the mixture was stirred for 30 minutes at 25 °C. After 30 minutes, 2-naphthol **1a** (0.029 g, 0.2 mmol) and 0.5 mL CH_2Cl_2 were added subsequently. Then, the reaction mixture was stirred for 12 h at 25 °C. 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 ^1H NMR analysis of the crude reaction products using CH_2Br_2 as the internal standard (^1H NMR revealed that naphthol was unreacted under this conditions).



These two reactions support our hypothesis about the intermediacy of bicoordinated Bi-complex for the present transformation. The pre-complexation of the Lewis acid with 2-naphthol (presumably) lowers the acidity of the Lewis acid thereby effectively halting the BCB decomposition; the soft coordination with BCB ester with the precomplexed Bi(OTf)$_3$ (with 2-naphthol) forms the bicoordinated Bi-complex, which enables the diastereoselective ring-opening of activated BCB. Reversing the mode of addition leads to decomposition of the BCB, as the acidity of Lewis acid could not be reduced by the 2-naphthol coordination (Scheme 5 of the manuscript, eq 9 and 10).

6. X-ray Data of 3k

Single crystal of **3k** (recrystallized from EtOAc/*n*-hexane at 25 °C) was mounted and the diffraction data was collected at 173 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 2233256 (**3k**) 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:

Table S2 Crystal data and structure refinement for **3k**

Compound	**3k**
Empirical formula	$C_{22}H_{19}O_3Br$
Formula weight	411.28
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Pn
Unit cell dimensions	a = 10.6120(7) Å, b = 13.2639(8) Å, c = 13.3533(8) Å, α = 90°, β = 104.195(2)°, γ = 90°
Volume	1822.2(2) $Å^3$
Z	4
Density (calculated)	1.499 g/cm^3
Absorption coefficient	2.275 mm^{-1}
F(000)	840.0
Theta range for data collection	6.414 to 58.36°
Index ranges	$-14 \leq h \leq 14$, $-18 \leq k \leq 18$, $-18 \leq l \leq 17$
Reflections collected	54631
Independent reflections	9374 [R_{int} = 0.0440, R_{sigma} = 0.0476]
Data / restraints / parameters	9374/2/477
Goodness-of-fit on F2	1.019
Final R indices [I>2sigma(I)]	R_1 = 0.0318, wR_2 = 0.0663
R indices (all data)	R_1 = 0.0410, wR_2 = 0.0688

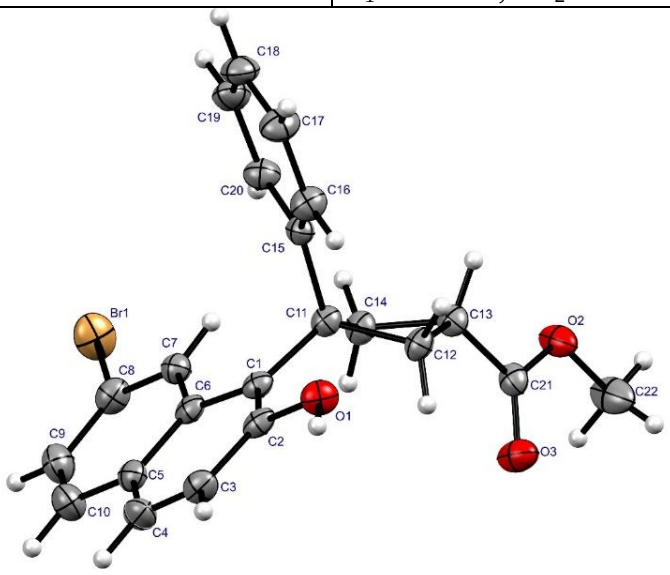


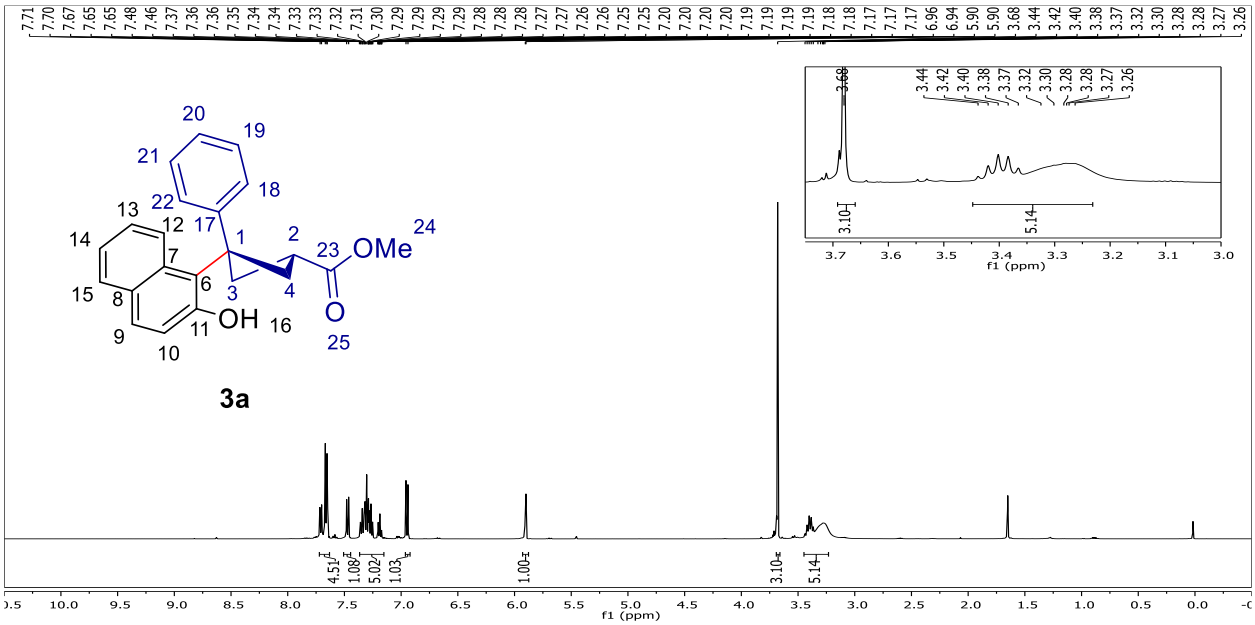
Figure S1. Crystal structure of **3k** (Thermal ellipsoids are shown with 50% probability)

7. Variable Temperature Experiment

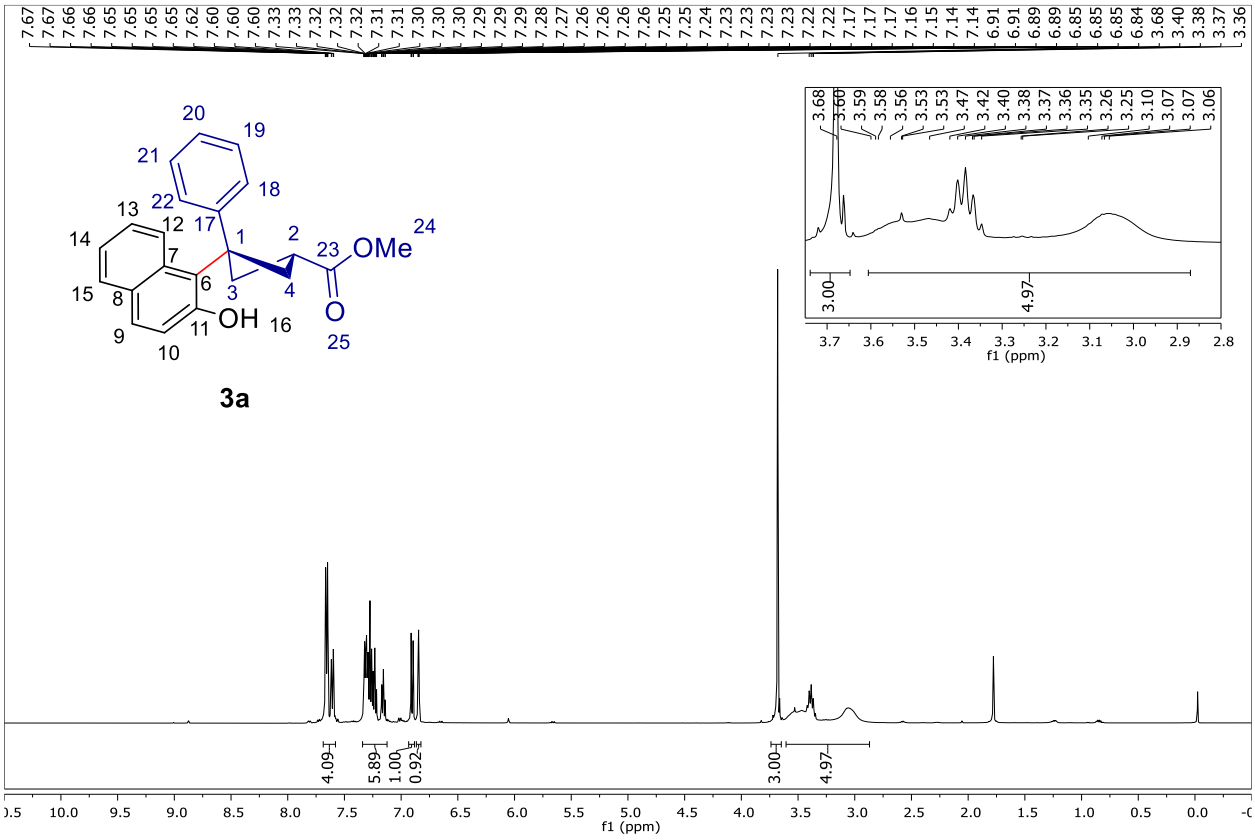
For all the synthesized 2-naphthol substituted cyclobutane derivatives the peaks for 5 protons from the cyclobutane rings appear very broad in ^{1}H NMR spectrum (3.43-3.29 for **3a**), while the signals for C3 and C4 in the ^{13}C spectra are of low intensity (40.6 for **3a**) (it is worth mentioning that no problems were observed in the ^{1}H and ^{13}C spectra for the compounds **3w-3y**.). The peak broadening in ^{1}H NMR and low intensity in ^{13}C NMR may be attributed due to the bond rotation of naphthyl substituents in the cyclobutane ring. To examine this possibility, we conducted variable temperature experiments, recording the ^{1}H NMR at 25 °C, -10 °C, -20

°C, and -35 °C. The peak broadening in the ^{1}H NMR is significantly reduced at -35 °C. Moreover, the ^{13}C spectrum at -35 °C reveals two different singlets for C3 and C4, which may be the result of restricted bond rotation in this molecule. We also checked the ^{1}H and ^{13}C NMR in 800 MHz NMR machine but the peak broadening and low intensity was similar to that of 400 MHz NMR machine.

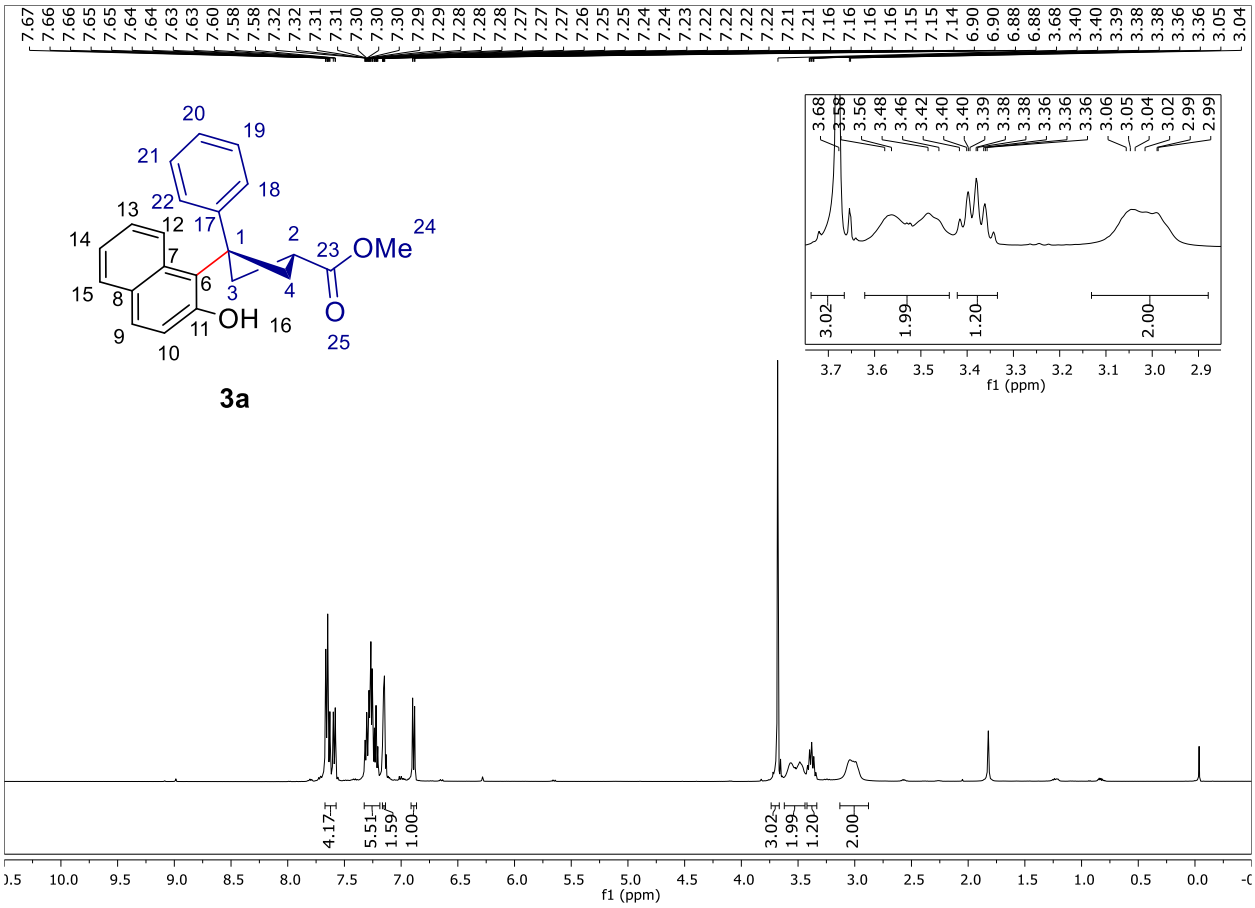
^{1}H NMR at 25 °C (500 MHz, $CDCl_3$)



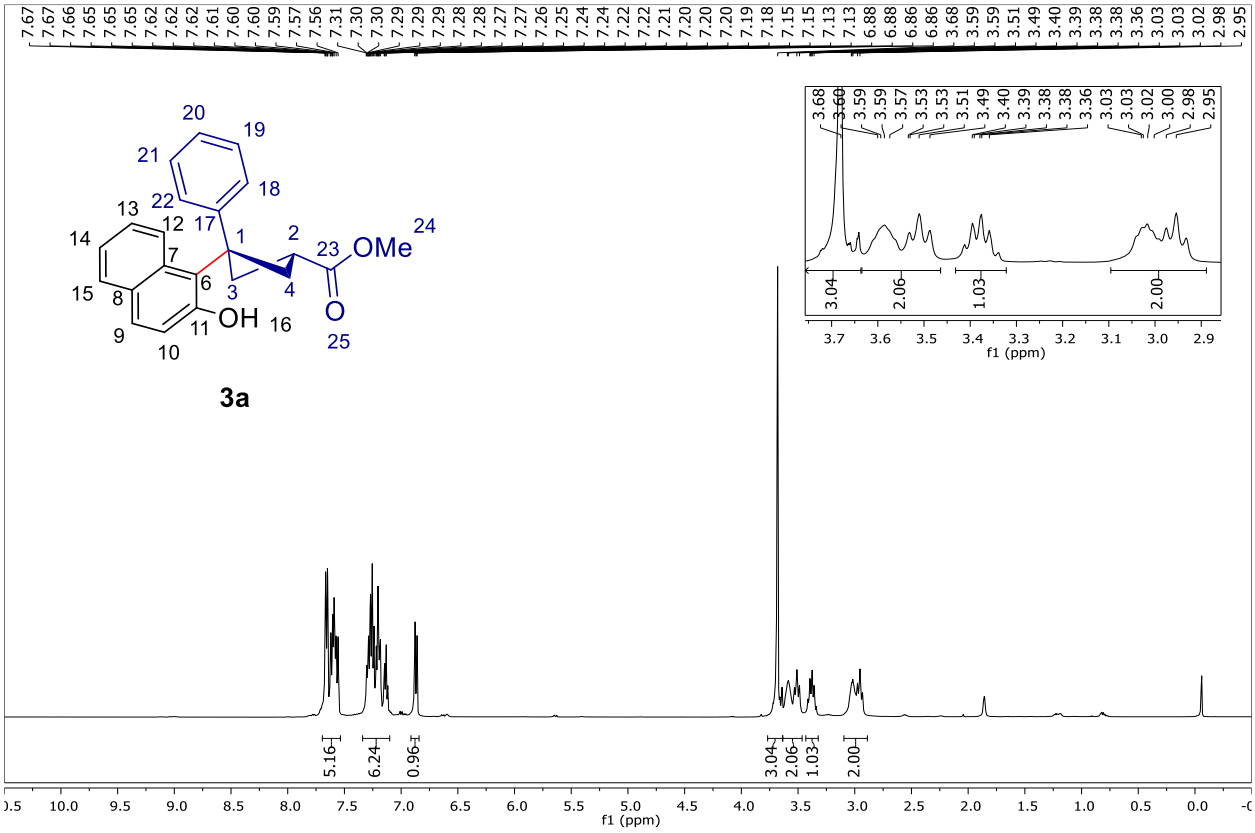
^{1}H NMR at -10 °C (500 MHz, $CDCl_3$)



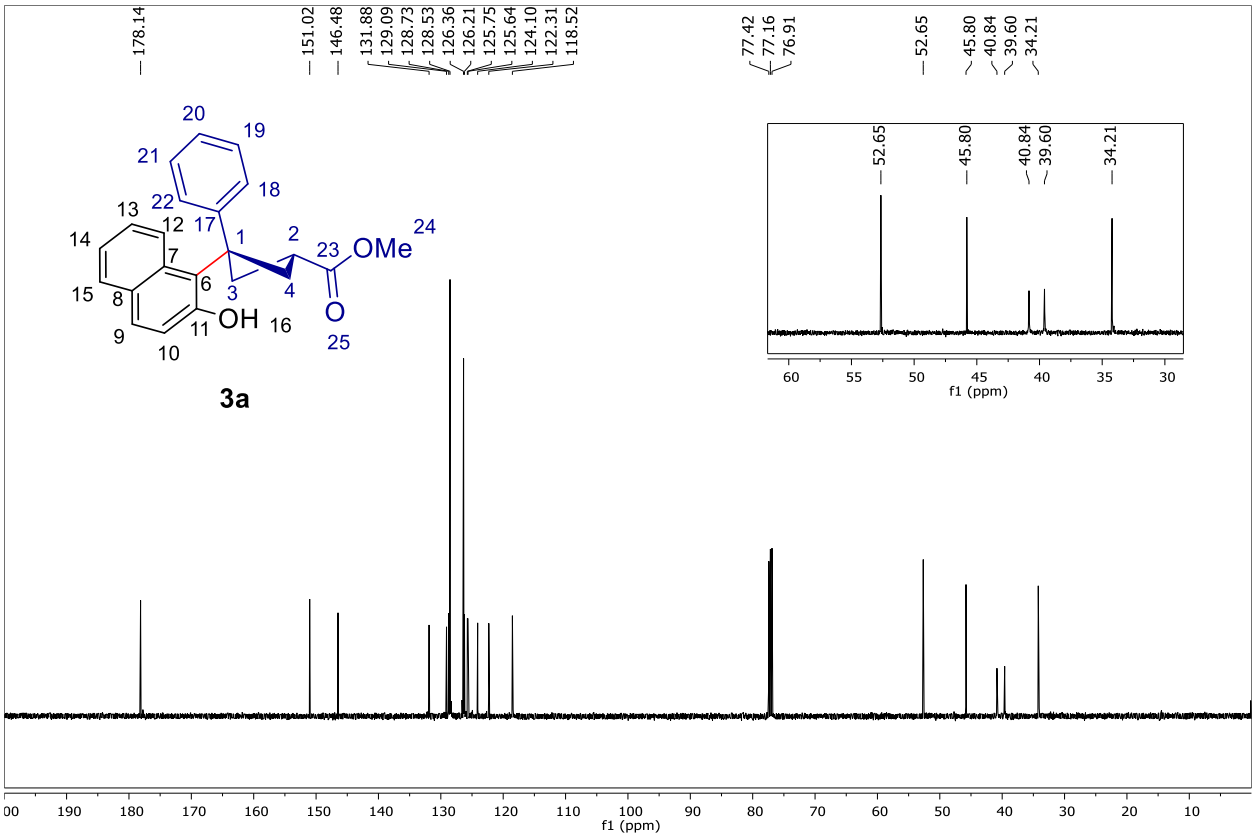
^{1}H NMR at -20 °C (500 MHz, $CDCl_3$)



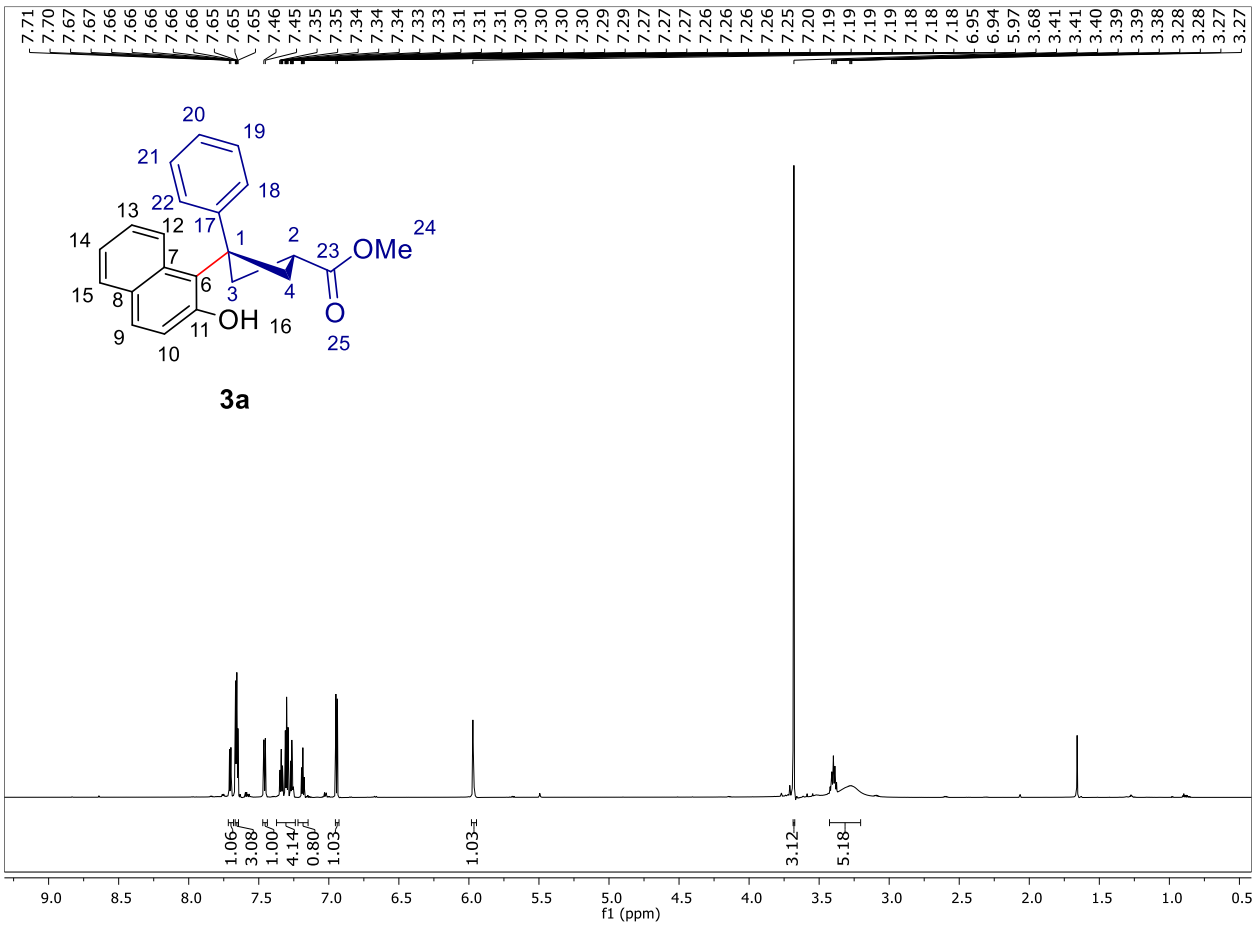
^{1}H NMR at -35 °C (500 MHz, $CDCl_3$)



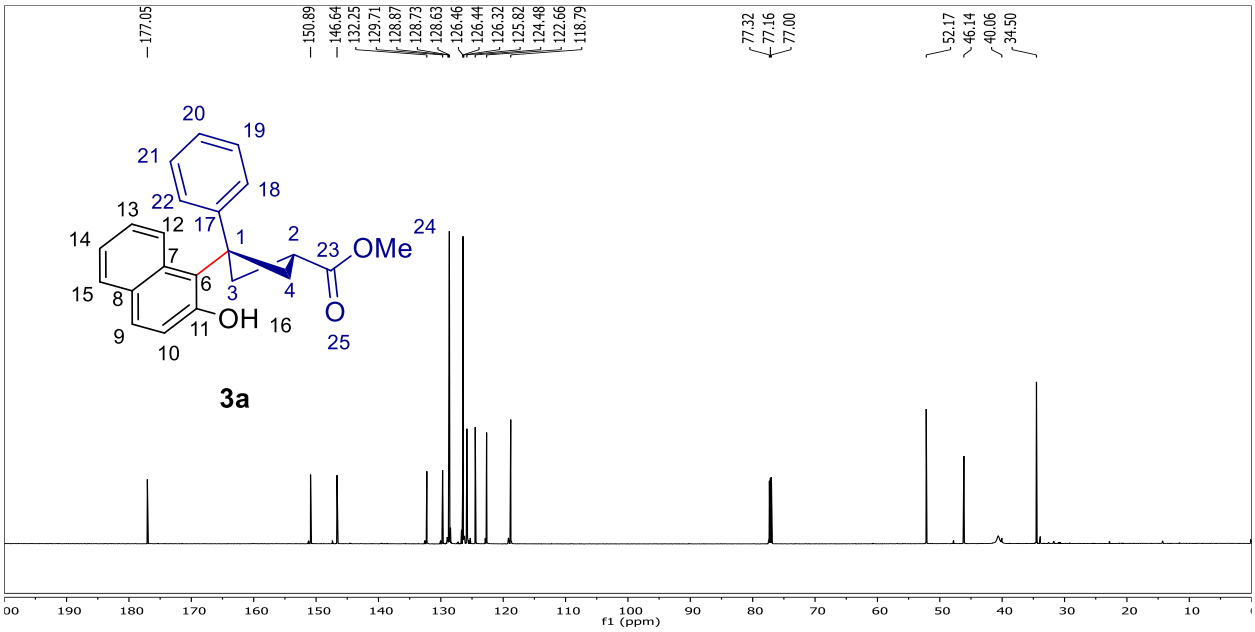
^{13}C NMR at -35 °C (125 MHz, $CDCl_3$)



^{1}H NMR at 25 °C (800 MHz, $CDCl_3$)



^{13}C NMR at 25 °C (200 MHz, $CDCl_3$)



8. DFT Studies

All DFT calculations were carried out using the Gaussian 16[3] software. All the stationary points along the reaction pathways have been optimized with the hybrid functional B3LYP-D3 and standard split valence Pople's type basis set 6-31G(d,p) except for bismuth(Bi).[4] To describe this heavy metal, LANL2DZ basis set was used with an effective core potential (ECP).[5] The vibrational frequencies were also computed at the same level of theory to identify the stationary points as minima or first order saddle points. 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[6] was used to consider the solvent effect of dichloromethane. Thermal corrections obtained from optimized geometries were added to the electronic energies obtained after single point calculations. The

[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. 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.

[5] P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

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

free energies are reported at the SMD$_{(DCM)}$/B3LYP-D3(BJ)/6-311++G(d,p),LANL2DZ(Bi)// B3LYP-D3/6-31G(d,p),LANL2DZ(Bi) level of theory.

Considering previous mechanistic studies reported in literature, we initiated our computational investigation to unravel the mechanism responsible for the formation of trisubstituted cyclobutene **3a** with notable diastereoselectivity. The desired product **3a** is obtained by reacting 2-naphthol **1a** with BCB (bicyclobutane) **2a** in the presence of Bi(OTf)$_3$. Initially, naphthol coordinates to bismuth triflate (**X**) to produce intermediate **A**, where one of the triflate ligands abstracts a proton and departs as triflic acid. From intermediate **A**, there are three different pathways through which the reaction can proceed. In pathway I, the Bi bound naphthol acts as a nucleophile and reacts via its C1 position with the incoming BCB through **TS(A-G)** to give intermediate **G**. In Pathway II, BCB coordinates to Bi displacing the initially bound naphthol ion leading to the positively charged intermediate **K**. In Pathway III, BCB coordinates to **A** displacing a triflate ion instead of the naphthol ion to yield intermediate **B**. The positive charge formed at the carbon center C3 of the cyclobutane can be stabilized by the phenyl group attached to the same carbon. In the first two cases the barrier is high as compared to the third case where we are getting the intermediate **B** (shown in Figure S2). So, for further studies we continued this pathway. Now nucleophilic attack of naphthol to the C3 of BCB happens via **TS(B-C)** to give the intermediate **C**.

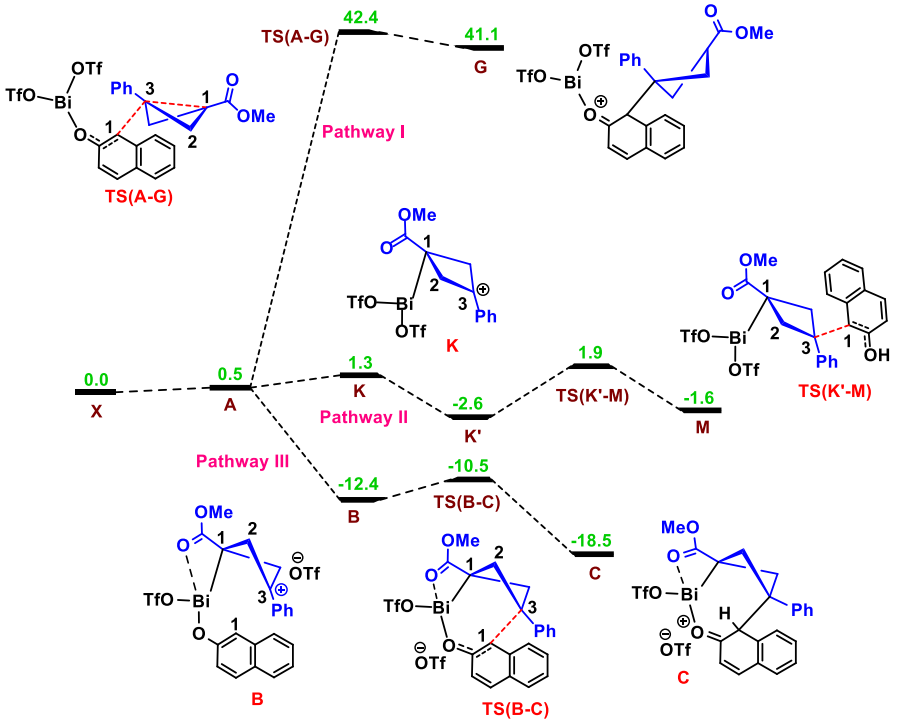


Figure S2 Free energy profile (kcal/mol) for different possible pathways. Relative free energies (ΔG) (kcal/mol) are given at the SMD$_{(DCM)}$/B3LYP-D3(BJ)/6-311++G(d,p),LANL2DZ(Bi)// B3LYP-D3/6-31G(d,p),LANL2DZ(Bi) level of theory.

The low barrier for this TS (transition state) can be explained by the high electrophilicity of BCB due to the positive charge. Subsequently, 1,3-proton transfer leads to rearomatization of naphthol via **TS(C-D)** to generate intermediate **D**. Another naphthol molecule comes and binds to Bi, resulting in the formation of enol intermediate **E**. From this intermediate hydrogen can be transferred from above face or below face of substrate giving rise to two different diastereomers (shown in Figure S4). Most likely, this proton transfer (tautomerization) is the diastereo-determining step of the reaction. Now the tautomerization via **TS(E-F)** gives the intermediate **F** where the product is weakly coordinated to Bi. Ultimately, metal dissociation results in the formation of the final product, **3a**. The presence of a highly strained four-membered ring formation during proton transfer contributes to the high energy barriers in both TSs, **TS(C-D)** and **TS(E-F)** (shown in Figure S3). This indicates the possibility of a distinct mechanism for the proton transfer step, potentially assisted by the naphthol or triflate ion present in the reaction mixture. Additional investigations are needed to further examine the proton transfer process. We also calculated the energy of both the products (diastereomers) and found that P_{major} is 1.7 kcal/mol more stable than P_{minor} which corresponds to around 17:1 diastereomeric ratio which is in good agreement with experimental value of 20:1.

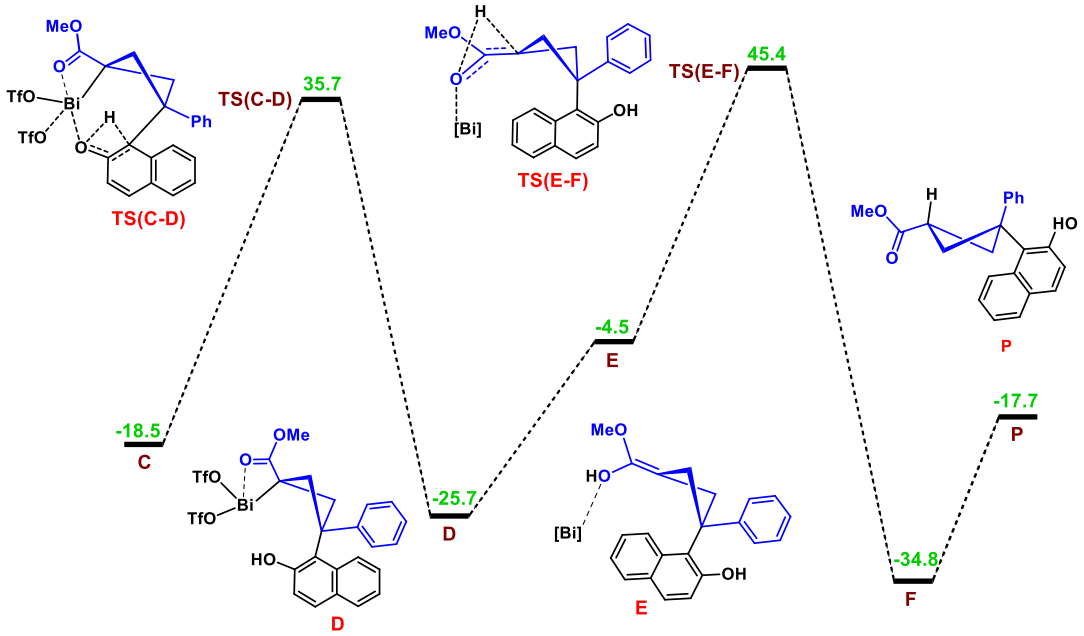


Figure S3. Free energy profile (kcal/mol) for the formation of the major product from intermediate **C**. Relative free energies (ΔG) (kcal/mol) are given at the $SMD_{(DCM)}$/B3LYP-D3BJ/6-311++G(d,p),LANL2DZ(Bi)// B3LYP-D3/6-31G(d,p),LANL2DZ(Bi) level of theory.

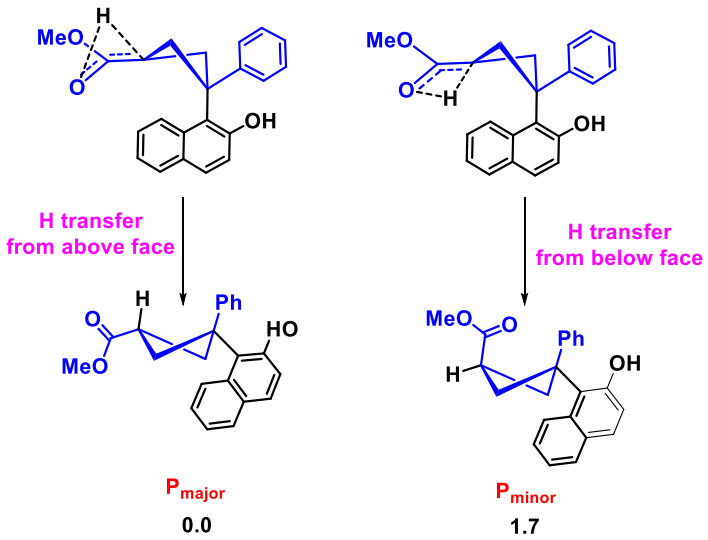


Figure S4 Formation of the diastereomers via 1,3-proton transfer. Relative energies are given in kcal/mol.

Coordinates

X

Number of imaginary frequencies : 0 Electronic energy : HF=-2889.7200833
Zero-point correction= 0.085258 (Hartree/Particle)
Thermal correction to Energy= 0.112284
Thermal correction to Enthalpy= 0.113228
Thermal correction to Gibbs Free Energy= 0.020820
Sum of electronic and zero-point Energies= -2889.634825
Sum of electronic and thermal Energies= -2889.607800
Sum of electronic and thermal Enthalpies= -2889.606855
Sum of electronic and thermal Free Energies= -2889.699263

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Cartesian Coordinates

.....

83	0.001127	0.000061	1.285094
8	1.450868	1.108307	0.329140
8	-1.684834	0.702214	0.331965
8	0.234864	-1.810686	0.330604
16	2.358430	0.813110	-0.979580
16	-0.475105	-2.447832	-0.978511
16	-1.884237	1.634128	-0.977951
8	1.775327	-0.245202	-1.784472
8	2.802531	2.082079	-1.519522
6	3.796111	0.045115	-0.064914
9	3.325706	-0.933194	0.729542
9	4.649066	-0.469572	-0.941615
9	4.407440	0.957738	0.686548
8	0.400957	-3.467398	-1.518976
8	-1.099131	-1.412754	-1.782938
6	-1.859850	-3.308627	-0.064698
9	-2.731981	-3.788990	-0.941874
9	-1.375578	-4.295072	0.686148
9	-2.471665	-2.412353	0.730273
8	-3.205535	1.382962	-1.516695
8	-0.676850	1.658301	-1.783838
6	-1.938129	3.264057	-0.064932

9	-3.032901	3.336535	0.688468
9	-0.854243	3.347867	0.727343
9	-1.921768	4.259108	-0.942721

A

Number of imaginary frequencies : 0 Electronic energy : HF=-2388.8582393
Zero-point correction= 0.198153 (Hartree/Particle)
Thermal correction to Energy= 0.225417
Thermal correction to Enthalpy= 0.226361
Thermal correction to Gibbs Free Energy= 0.134111
Sum of electronic and zero-point Energies= -2388.660087
Sum of electronic and thermal Energies= -2388.632822
Sum of electronic and thermal Enthalpies= -2388.631878
Sum of electronic and thermal Free Energies= -2388.724128

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Cartesian Coordinates

.....

83	1.099959	-0.345173	-1.478549
8	1.057395	0.585047	0.481475
8	0.064285	-1.983623	-0.681093
16	-0.897554	-2.251609	0.566505
16	1.771259	1.970780	0.350622
8	-1.810237	-3.330161	0.223831
8	-1.351279	-1.012290	1.175405
6	0.400309	-2.954585	1.708058
9	-0.126301	-3.130605	2.917496
9	0.847651	-4.119618	1.238449
9	1.426336	-2.093804	1.790631
8	1.001995	3.086868	0.865556
8	2.308330	1.998594	-1.037938
6	3.237458	1.707892	1.472646
9	2.820770	1.529001	2.719645
9	3.897357	0.621510	1.054453
9	4.033264	2.770577	1.401580
6	-1.709635	0.670158	-1.535919
6	-1.954322	1.669436	-0.622930
6	-3.190706	1.704728	0.070660
6	-4.173743	0.695848	-0.194755
6	-3.881063	-0.309089	-1.154860
6	-2.676657	-0.326260	-1.817302
1	-2.724585	3.463487	1.241602
1	-1.195960	2.415668	-0.411220
6	-3.476884	2.706567	1.036620
6	-5.403823	0.731470	0.513605
1	-4.620399	-1.079815	-1.353637
1	-2.439534	-1.099127	-2.540761
6	-5.653137	1.716473	1.442857
6	-4.679566	2.712047	1.706567
1	-6.145567	-0.037002	0.311576
1	-6.596925	1.732628	1.980103
1	-4.886125	3.481310	2.445123
8	-0.493966	0.621038	-2.212114

B

Number of imaginary frequencies : 0 Electronic energy : HF=-3003.8188874
Zero-point correction= 0.410909 (Hartree/Particle)
Thermal correction to Energy= 0.452072
Thermal correction to Enthalpy= 0.453017

Thermal correction to Gibbs Free Energy= 0.331851
Sum of electronic and zero-point Energies= -3003.407979
Sum of electronic and thermal Energies= -3003.366815
Sum of electronic and thermal Enthalpies= -3003.365871
Sum of electronic and thermal Free Energies= -3003.487037

Cartesian Coordinates

83	1.546321	1.127206	-0.305356
8	2.395805	-0.956316	-0.977570
8	-0.121169	5.238266	0.959483
16	2.645069	-2.301581	-0.294824
16	0.021190	4.183423	-0.038422
8	2.738372	-2.181693	1.171497
8	1.795138	-3.368187	-0.838270
6	4.373875	-2.660359	-0.874912
9	5.194505	-1.678829	-0.484840
9	4.789906	-3.815361	-0.345227
9	4.403811	-2.752945	-2.207353
8	0.314591	2.816666	0.614848
8	0.848892	4.391475	-1.231138
6	-1.713314	3.893799	-0.676902
9	-1.705307	3.177097	-1.801695
9	-2.445508	3.216482	0.243984
9	-2.313168	5.062440	-0.906948
6	-0.938345	-0.179530	-1.672266
6	-2.256970	-0.029040	-1.208192
6	-3.225408	-1.047352	-1.423938
6	-2.813777	-2.298385	-1.982864
6	-1.438910	-2.457682	-2.355933
6	-0.535912	-1.436337	-2.229520
1	-4.900702	0.070762	-0.641759
1	-2.560091	0.938415	-0.824750
6	-4.583464	-0.878859	-1.062650
6	-3.768603	-3.321822	-2.170313
1	-1.114515	-3.411815	-2.762848
1	0.500709	-1.561682	-2.515316
6	-5.092081	-3.128925	-1.811591
6	-5.497607	-1.899637	-1.253774
1	-3.448255	-4.265744	-2.603867
1	-5.819349	-3.920645	-1.963907
1	-6.536310	-1.753651	-0.971857
8	-0.088183	0.832792	-1.617853
8	2.562850	0.781810	2.149997
8	1.432386	-0.677302	3.448896
6	0.477545	-0.024893	1.350719
6	-0.923277	0.519484	1.801322
1	-1.002548	0.686983	2.885502
1	-1.289251	1.420275	1.305889
6	-1.520573	-0.798969	1.417439
6	-0.188532	-1.422943	1.149159
1	-0.050677	-1.961232	0.209555
1	0.084656	-2.121095	1.952747
6	1.589310	0.059212	2.356267
6	-2.784718	-1.375836	1.665129
6	-3.840668	-0.600537	2.207530
1	-3.684781	0.459888	2.382066
6	-5.049019	-1.200482	2.529774
1	-5.851166	-0.611901	2.963048
6	-5.232663	-2.568789	2.289658

1	-6.180583	-3.034776	2.541963
6	-4.215589	-3.338451	1.710795
1	-4.379926	-4.390673	1.505103
6	-2.997802	-2.752498	1.401242
1	-2.199454	-3.336435	0.955839
6	2.592393	-0.775448	4.309137
1	2.889923	0.214374	4.660971
1	2.285800	-1.410258	5.139440
1	3.408826	-1.232727	3.746360

C

Number of imaginary frequencies : 0 Electronic energy : HF=-3003.83963
Zero-point correction= 0.414769 (Hartree/Particle)
Thermal correction to Energy= 0.454872
Thermal correction to Enthalpy= 0.455817
Thermal correction to Gibbs Free Energy= 0.337091
Sum of electronic and zero-point Energies= -3003.424861
Sum of electronic and thermal Energies= -3003.384757
Sum of electronic and thermal Enthalpies= -3003.383813
Sum of electronic and thermal Free Energies= -3003.502539

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Cartesian Coordinates

.....

83	-1.730568	-0.850375	-0.269582
8	-2.222654	1.361321	-0.849113
8	-1.342217	-5.297119	0.227392
16	-2.194171	2.682671	-0.069768
16	-0.894330	-4.080249	-0.438485
8	-2.126744	2.466632	1.385686
8	-1.283294	3.661693	-0.672159
6	-3.916835	3.297378	-0.400764
9	-4.806888	2.398291	0.036434
9	-4.110181	4.452981	0.241513
9	-4.095152	3.487610	-1.711133
8	-0.946571	-2.844266	0.490073
8	-1.399617	-3.736712	-1.775397
6	0.951066	-4.282518	-0.625381
9	1.481958	-3.240431	-1.289635
9	1.533769	-4.344207	0.581374
9	1.218248	-5.401344	-1.299069
6	0.918829	0.207319	-1.672701
6	2.231373	0.127378	-0.921023
6	3.259370	1.115914	-1.422175
6	2.839114	2.298819	-2.074825
6	1.454940	2.434070	-2.465475
6	0.550979	1.425150	-2.334483
1	4.965032	0.007105	-0.731699
1	2.607509	-0.896533	-1.007548
6	4.623986	0.915918	-1.214691
6	3.780916	3.282083	-2.431447
1	1.142918	3.365962	-2.930209
1	-0.469925	1.521820	-2.680934
6	5.133172	3.083421	-2.180499
6	5.553421	1.888607	-1.587883
1	3.438858	4.188461	-2.923438
1	5.857952	3.842326	-2.457536
1	6.609710	1.713827	-1.407811
8	0.120817	-0.771463	-1.620019
8	-2.300884	-0.547429	2.077218

8	-0.863593	0.543657	3.424951
6	-0.192377	-0.020811	1.178339
6	1.109942	-0.866349	1.269680
1	1.400057	-1.046341	2.308938
1	1.123110	-1.812657	0.736784
6	1.921708	0.323466	0.672694
6	0.693263	1.237714	0.969409
1	0.398802	1.974339	0.225304
1	0.808908	1.759245	1.923010
6	-1.187323	-0.023628	2.289153
6	3.198851	0.637399	1.416137
6	4.042195	-0.402739	1.830809
1	3.758790	-1.434295	1.636243
6	5.242862	-0.128439	2.486698
1	5.884259	-0.946010	2.802956
6	5.614410	1.193740	2.741249
1	6.546799	1.409243	3.254736
6	4.777803	2.236307	2.337387
1	5.058534	3.267226	2.532391
6	3.580086	1.958661	1.678652
1	2.944324	2.775568	1.349405
6	-1.939961	0.732473	4.379917
1	-2.369020	-0.231272	4.659736
1	-1.480534	1.222131	5.236784
1	-2.701368	1.367608	3.923152

D

Number of imaginary frequencies : 1 Electronic energy : HF=-3003.7382187
Zero-point correction= 0.407880 (Hartree/Particle)
Thermal correction to Energy= 0.447944
Thermal correction to Enthalpy= 0.448888
Thermal correction to Gibbs Free Energy= 0.328882
Sum of electronic and zero-point Energies= -3003.330338
Sum of electronic and thermal Energies= -3003.290275
Sum of electronic and thermal Enthalpies= -3003.289331
Sum of electronic and thermal Free Energies= -3003.409337

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Cartesian Coordinates

.....

83	1.748445	0.701075	-0.124272
8	1.827502	-1.459039	-1.003788
8	1.449714	5.155092	0.172551
16	2.191510	-2.720988	-0.202587
16	0.953620	3.954639	-0.488518
8	2.332311	-2.416931	1.232650
8	1.402542	-3.881178	-0.612683
6	3.925259	-2.999209	-0.811569
9	4.651725	-1.892826	-0.583064
9	4.479564	-4.025891	-0.164087
9	3.922998	-3.252713	-2.122588
8	0.923801	2.728991	0.455727
8	1.459704	3.572331	-1.813203
6	-0.878721	4.235014	-0.693720
9	-1.440395	3.231037	-1.395910
9	-1.475879	4.284332	0.505946
9	-1.096059	5.378325	-1.340956
6	-0.944753	-0.420304	-1.591897
6	-2.114077	-0.284417	-0.772938
6	-3.313831	-0.893467	-1.361437

6	-3.143168	-1.838382	-2.428495
6	-1.842879	-2.102892	-2.960203
6	-0.734802	-1.372281	-2.591633
1	-4.797007	0.137902	-0.180611
1	-1.369935	0.991250	-0.935188
6	-4.630801	-0.601788	-0.951397
6	-4.272759	-2.487503	-2.986654
1	-1.752824	-2.844880	-3.749224
1	0.229711	-1.465307	-3.072944
6	-5.545814	-2.196719	-2.542142
6	-5.719211	-1.232761	-1.530991
1	-4.119102	-3.204376	-3.788719
1	-6.407498	-2.690019	-2.980504
1	-6.720530	-0.972212	-1.201192
8	-0.178787	0.683669	-1.379387
8	2.348000	0.463408	2.324347
8	0.881976	-0.644209	3.630072
6	0.251143	-0.066582	1.382459
6	-1.054498	0.770728	1.502710
1	-1.344471	0.865716	2.553105
1	-1.067830	1.764346	1.055964
6	-1.861819	-0.387162	0.827184
6	-0.626997	-1.314736	1.126316
1	-0.330872	-2.010545	0.343026
1	-0.761120	-1.876894	2.054525
6	1.238890	-0.065922	2.502349
6	-3.123427	-0.768674	1.571333
6	-3.907077	0.199526	2.212466
1	-3.614694	1.245129	2.169891
6	-5.072776	-0.161343	2.890497
1	-5.670157	0.602749	3.379443
6	-5.466254	-1.499807	2.943147
1	-6.370916	-1.782499	3.473312
6	-4.686485	-2.473917	2.315145
1	-4.983126	-3.517975	2.353135
6	-3.526019	-2.109067	1.634656
1	-2.932508	-2.869068	1.134068
6	1.912688	-0.764408	4.642079
1	2.261281	0.225338	4.943482
1	1.440293	-1.283865	5.474202
1	2.745713	-1.343482	4.238479

E

Number of imaginary frequencies : 0 Electronic energy : HF=-3464.9700678
Zero-point correction= 0.568040 (Hartree/Particle)
Thermal correction to Energy= 0.617618
Thermal correction to Enthalpy= 0.618562
Thermal correction to Gibbs Free Energy= 0.477863
Sum of electronic and zero-point Energies= -3464.402028
Sum of electronic and thermal Energies= -3464.352450
Sum of electronic and thermal Enthalpies= -3464.351505
Sum of electronic and thermal Free Energies= -3464.492204

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Cartesian Coordinates

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83	-1.046899	-0.510065	-0.439526
8	-0.058971	-2.472734	-2.575868
8	-0.309125	-1.428741	1.376417
16	-1.058906	-3.348777	-1.937448

16	-0.098474	-1.100533	2.870771
8	-1.776247	-2.534368	-0.815722
8	-1.988993	-4.120550	-2.744400
6	-0.098881	-4.579980	-0.911783
9	0.482790	-3.958854	0.121835
9	-0.907992	-5.530452	-0.456295
9	0.851878	-5.126116	-1.678615
8	-0.187491	0.346069	3.149771
8	1.053661	-1.840362	3.387567
6	-1.627688	-1.852336	3.624372
9	-1.581119	-1.683178	4.944234
9	-2.697930	-1.232998	3.125882
9	-1.677049	-3.147000	3.331517
6	3.006167	-0.478879	0.689370
6	3.282207	0.583023	-0.172318
6	3.435092	0.266261	-1.570104
6	3.051383	-1.026611	-2.063171
6	2.639292	-2.023569	-1.142550
6	2.656657	-1.767647	0.202442
1	4.401163	2.115333	-2.174255
1	2.665105	-1.042344	2.514641
6	3.987866	1.176804	-2.517657
6	3.109076	-1.306186	-3.453764
1	2.334146	-2.993636	-1.516047
1	2.379066	-2.535428	0.917037
6	3.597457	-0.377358	-4.343166
6	4.069965	0.863258	-3.857440
1	2.762183	-2.276914	-3.796253
1	3.644458	-0.601339	-5.404530
1	4.513144	1.577078	-4.546313
8	3.069369	-0.294534	2.043237
8	-0.718116	1.625948	0.894786
8	-0.431340	2.443244	-1.169433
6	1.383500	2.710812	0.357700
6	2.320339	2.337875	1.471704
1	2.645966	3.220555	2.033548
1	2.047363	1.550477	2.167163
6	3.392379	2.037089	0.331258
6	2.521949	3.023435	-0.571243
1	2.371631	2.797372	-1.624950
1	2.879873	4.052010	-0.458439
6	0.147008	2.335237	0.062285
6	4.825266	2.439651	0.648692
6	5.498798	1.798927	1.701806
1	4.984993	1.027369	2.265314
6	6.810396	2.143546	2.022176
1	7.312838	1.637487	2.841992
6	7.480052	3.131735	1.294952
1	8.503374	3.397426	1.544005
6	6.822058	3.772917	0.246860
1	7.329874	4.542360	-0.328096
6	5.504263	3.430864	-0.069624
1	5.010879	3.947113	-0.887644
6	-1.418648	3.500386	-1.255544
1	-1.924870	3.377695	-2.212975
1	-2.147155	3.416818	-0.445659
1	-0.914974	4.471407	-1.215409
6	-3.592307	0.898937	0.223574
6	-4.119445	1.351068	-0.969025
6	-4.821439	2.583936	-1.028974

6	-4.981204	3.352856	0.170790
6	-4.440244	2.843557	1.385299
6	-3.762892	1.648911	1.418102
1	-5.235900	2.508766	-3.153019
1	-4.006748	0.749918	-1.867963
6	-5.353636	3.093140	-2.244022
6	-5.665111	4.595239	0.106533
1	-4.563871	3.422769	2.296628
1	-3.333037	1.255634	2.332607
6	-6.167554	5.063813	-1.087589
6	-6.009313	4.304491	-2.272807
1	-5.785189	5.173131	1.019404
1	-6.688090	6.016077	-1.124463
1	-6.410788	4.681594	-3.208913
8	-2.919402	-0.293930	0.294039
1	-0.363528	1.451463	1.797159

F

Number of imaginary frequencies : 0 Electronic energy : HF=-3465.0214057
Zero-point correction= 0.568301 (Hartree/Particle)
Thermal correction to Energy= 0.618123
Thermal correction to Enthalpy= 0.619067
Thermal correction to Gibbs Free Energy= 0.476877
Sum of electronic and zero-point Energies= -3464.453105
Sum of electronic and thermal Energies= -3464.403282
Sum of electronic and thermal Enthalpies= -3464.402338
Sum of electronic and thermal Free Energies= -3464.544529

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Cartesian Coordinates

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83	-0.974049	-0.472924	-0.436915
8	1.776731	-0.721504	-1.524186
8	-0.962028	-2.262700	1.057230
16	1.180731	-1.818744	-2.311905
16	-1.658795	-1.675717	2.288376
8	-0.328525	-1.923789	-1.931055
8	1.396951	-1.874991	-3.751889
6	1.845557	-3.402882	-1.582247
9	1.395486	-3.533128	-0.333722
9	1.442466	-4.438927	-2.314283
9	3.177337	-3.345591	-1.575611
8	-2.291679	-0.393346	1.869667
8	-0.833478	-1.651804	3.499692
6	-3.045686	-2.877013	2.609088
9	-3.833308	-2.385290	3.563137
9	-3.749986	-3.046873	1.487503
9	-2.537970	-4.044627	2.996882
6	1.999902	-0.036906	1.739919
6	2.884898	0.682740	0.947232
6	4.108000	0.029272	0.561247
6	4.298826	-1.365795	0.831962
6	3.308596	-2.065013	1.566224
6	2.202911	-1.411225	2.037273
1	5.123075	1.790413	-0.210284
1	0.467298	0.016242	2.915736
6	5.181858	0.718749	-0.072124
6	5.476124	-2.021068	0.386551
1	3.440957	-3.125030	1.762134
1	1.449803	-1.935429	2.615726

6	6.471051	-1.329276	-0.264607
6	6.325168	0.061060	-0.472016
1	5.580301	-3.085074	0.583304
1	7.370077	-1.838714	-0.598147
1	7.126915	0.621650	-0.944318
8	0.861835	0.573484	2.224900
8	-0.395667	1.337541	-2.069486
8	1.078636	2.199605	-3.512055
6	1.394070	2.801979	-1.267095
6	1.110590	2.517264	0.217738
1	0.772417	3.371426	0.805363
1	0.403522	1.711659	0.377755
6	2.618955	2.113491	0.474698
6	2.852313	2.292041	-1.082570
1	3.041539	1.349020	-1.592220
1	3.620659	3.012058	-1.367285
6	0.598607	2.041073	-2.292019
6	3.336961	3.158655	1.333046
6	3.912882	2.823417	2.564897
1	3.877708	1.794626	2.905223
6	4.537490	3.790586	3.354893
1	4.978951	3.501168	4.304413
6	4.597474	5.117609	2.930843
1	5.084806	5.869755	3.544313
6	4.022681	5.469486	1.707803
1	4.058769	6.499370	1.363556
6	3.400320	4.500858	0.921730
1	2.957230	4.803783	-0.023212
6	0.459098	1.431789	-4.577966
1	0.902840	1.814744	-5.495432
1	0.691595	0.372552	-4.449842
1	-0.621956	1.582059	-4.572627
6	-3.810047	0.121282	-0.859424
6	-3.719955	1.461238	-1.182656
6	-4.757898	2.360939	-0.820877
6	-5.904527	1.859972	-0.122190
6	-5.961991	0.472256	0.185717
6	-4.944182	-0.379467	-0.166842
1	-3.829945	4.126181	-1.662903
1	-2.862666	1.827145	-1.741746
6	-4.698576	3.745964	-1.130950
6	-6.939386	2.761456	0.239554
1	-6.828245	0.090722	0.720109
1	-4.966290	-1.432572	0.085908
6	-6.851734	4.100334	-0.073227
6	-5.719823	4.595397	-0.765760
1	-7.805918	2.375520	0.770650
1	-7.649630	4.780606	0.209569
1	-5.659802	5.652491	-1.008744
8	-2.823773	-0.774232	-1.211939
1	1.349676	3.859889	-1.545838

G

Number of imaginary frequencies : 0 Electronic energy : HF=-3003.7322304
Zero-point correction= 0.410421 (Hartree/Particle)
Thermal correction to Energy= 0.451159
Thermal correction to Enthalpy= 0.452103
Thermal correction to Gibbs Free Energy= 0.329805
Sum of electronic and zero-point Energies= -3003.321810

Sum of electronic and thermal Energies= -3003.281072
Sum of electronic and thermal Enthalpies= -3003.280127
Sum of electronic and thermal Free Energies= -3003.402426

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Cartesian Coordinates

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83	0.849030	-0.788760	0.964942
8	2.719150	0.190009	1.197744
8	1.072457	-0.747531	-1.190528
16	3.191293	1.587316	0.601402
16	1.689566	-2.119665	-1.633380
8	3.112947	1.581741	-0.858217
8	2.649040	2.699231	1.370212
6	4.995734	1.437196	1.059239
9	5.539714	0.372340	0.471995
9	5.618145	2.541537	0.643704
9	5.115495	1.328008	2.382107
8	1.030029	-2.717781	-2.775945
8	1.847131	-2.873140	-0.355126
6	3.408234	-1.616410	-2.175518
9	3.987092	-2.673441	-2.743124
9	3.319423	-0.621608	-3.047956
9	4.110808	-1.238921	-1.110915
6	-0.774168	1.729399	-0.118414
6	-2.209555	1.904895	0.216687
6	-2.929267	2.884617	-0.660913
6	-2.316014	3.381476	-1.842797
6	-0.963050	3.023875	-2.138610
6	-0.204989	2.235165	-1.292851
1	-4.666945	2.966737	0.603546
1	-2.289077	2.247156	1.252823
6	-4.209769	3.335480	-0.311236
6	-3.044771	4.268026	-2.672734
1	-0.510864	3.418180	-3.044221
1	0.835043	2.012365	-1.503761
6	-4.318784	4.679774	-2.323440
6	-4.901427	4.221453	-1.128488
1	-2.578634	4.636259	-3.582747
1	-4.864504	5.364571	-2.965330
1	-5.895321	4.555189	-0.846267
8	-0.066972	1.048967	0.775714
8	-3.208788	-3.452719	-1.055105
8	-5.279699	-2.496650	-1.214783
6	-3.430053	-1.101867	-1.057373
6	-2.109984	-0.667841	-0.578425
1	-1.536997	-1.436773	-0.019902
1	-1.433159	-0.198808	-1.312664
6	-2.901958	0.411281	0.250210
6	-4.095864	0.192130	-0.756809
1	-4.018699	0.934480	-1.565690
1	-5.122601	0.201269	-0.379676
6	-3.909160	-2.445493	-1.116633
6	-3.191810	-0.082974	1.672100
6	-2.348516	0.248537	2.749322
1	-1.513948	0.922952	2.599306
6	-2.566658	-0.262462	4.031684
1	-1.900655	0.025494	4.840566
6	-3.633725	-1.126023	4.273663
1	-3.805380	-1.525660	5.268681
6	-4.479982	-1.465442	3.218080

1	-5.316168	-2.138430	3.384624
6	-4.264983	-0.951162	1.938495
1	-4.936331	-1.254253	1.144174
6	-5.820594	-3.820640	-1.260017
1	-5.565461	-4.380393	-0.354499
1	-6.901956	-3.699544	-1.340722
1	-5.433381	-4.372332	-2.122096

K

Number of imaginary frequencies : 0 Electronic energy : HF=-2543.0202937
Zero-point correction= 0.269804 (Hartree/Particle)
Thermal correction to Energy= 0.302081
Thermal correction to Enthalpy= 0.303025
Thermal correction to Gibbs Free Energy= 0.199771
Sum of electronic and zero-point Energies= -2542.750489
Sum of electronic and thermal Energies= -2542.718213
Sum of electronic and thermal Enthalpies= -2542.717269
Sum of electronic and thermal Free Energies= -2542.820523

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Cartesian Coordinates

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83	0.727550	-0.428449	-1.568777
8	1.503289	1.205421	-0.505824
8	3.100566	-2.113738	-0.942234
16	0.851760	1.938537	0.744587
16	2.310961	-2.508830	0.235942
8	-0.382198	2.619188	0.337676
8	0.817239	1.062178	1.911127
6	2.195756	3.215983	0.998110
9	2.304565	3.958682	-0.095979
9	1.836976	3.968197	2.032926
9	3.337058	2.591089	1.253317
8	2.135059	-3.896778	0.618204
8	0.899771	-1.782727	0.084947
6	3.004293	-1.584406	1.710347
9	3.311477	-0.342800	1.335669
9	2.091211	-1.558730	2.676196
9	4.094977	-2.215929	2.123806
8	-1.115047	1.267705	-2.435882
8	-2.912429	1.541307	-1.089606
6	-1.384460	-0.276020	-0.688462
6	-2.319789	-1.551705	-0.783651
1	-2.972779	-1.694698	-1.646478
1	-1.720006	-2.450360	-0.597259
6	-2.902084	-0.996145	0.471160
6	-1.681583	-0.250279	0.858633
1	-0.926285	-0.858677	1.369542
1	-1.789973	0.710165	1.358159
6	-1.819203	0.926814	-1.483430
6	-4.236030	-0.852673	0.880190
6	-5.278392	-1.555200	0.207161
1	-5.044462	-2.170318	-0.655363
6	-6.579933	-1.463966	0.664363
1	-7.377489	-1.999966	0.161558
6	-6.865888	-0.672006	1.789454
1	-7.890308	-0.602170	2.143558
6	-5.854626	0.029121	2.466787
1	-6.099670	0.631417	3.334768
6	-4.548400	-0.055460	2.020702

1	-3.757309	0.478428	2.536054
6	-3.192790	2.826845	-1.723218
1	-3.293206	2.696573	-2.801463
1	-4.124799	3.166824	-1.276670
1	-2.371476	3.508295	-1.495940

K'

Number of imaginary frequencies : 0 Electronic energy : HF=-3004.195701
Zero-point correction= 0.423858 (Hartree/Particle)
Thermal correction to Energy= 0.465399
Thermal correction to Enthalpy= 0.466343
Thermal correction to Gibbs Free Energy= 0.344135
Sum of electronic and zero-point Energies= -3003.771843
Sum of electronic and thermal Energies= -3003.730302
Sum of electronic and thermal Enthalpies= -3003.729358
Sum of electronic and thermal Free Energies= -3003.851566

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Cartesian Coordinates

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83	-2.117115	1.089687	-1.057797
8	-3.247616	0.175230	0.458390
8	-0.713222	4.686350	0.145668
16	-2.947675	-0.993284	1.482125
16	-0.234607	3.317334	0.205642
8	-1.776695	-1.768459	1.045039
8	-3.049177	-0.529552	2.851988
6	-4.428217	-2.064170	1.100542
9	-4.354401	-2.456493	-0.178471
9	-4.385364	-3.130268	1.894397
9	-5.548923	-1.386036	1.298481
8	0.472098	2.742133	-0.964122
8	-1.320350	2.283865	0.629837
6	0.953839	3.227152	1.652660
9	0.540778	4.020656	2.624760
9	1.041974	1.967617	2.112001
9	2.157593	3.609469	1.220641
6	3.691126	-2.001665	-1.942783
6	2.728595	-2.583327	-1.127450
6	3.016629	-2.882752	0.228809
6	4.295025	-2.525266	0.764345
6	5.247536	-1.914606	-0.102834
6	4.965069	-1.664115	-1.426479
1	1.088611	-3.767935	0.677688
1	1.770334	-2.859436	-1.552081
6	2.052622	-3.475990	1.085451
6	4.566090	-2.774485	2.131892
1	6.219868	-1.643695	0.298415
1	5.704892	-1.195774	-2.069806
6	3.604597	-3.339123	2.947426
6	2.340640	-3.689388	2.420405
1	5.540918	-2.510512	2.532836
1	3.819153	-3.522934	3.995163
1	1.594621	-4.137902	3.068782
8	3.331273	-1.724959	-3.224757
8	-2.297409	-1.238956	-2.023483
8	-0.653437	-2.697387	-1.514775
6	-0.341525	-0.342211	-1.087097
6	0.910607	0.040747	-1.962571
1	1.210038	-0.734018	-2.677424

1	0.893469	1.001598	-2.481690
6	1.722441	0.029962	-0.698006
6	0.595561	-0.496571	0.134034
1	0.357879	0.120368	1.003502
1	0.692352	-1.523963	0.495722
6	-1.169876	-1.492110	-1.570203
6	2.908047	0.689166	-0.335623
6	3.608127	1.493648	-1.276279
1	3.227404	1.583584	-2.287849
6	4.734957	2.192360	-0.885373
1	5.254850	2.831494	-1.591130
6	5.196856	2.088937	0.438404
1	6.075754	2.649762	0.742073
6	4.539708	1.277343	1.369680
1	4.912531	1.201158	2.385487
6	3.401299	0.580102	0.992616
1	2.877917	-0.046188	1.705925
6	-1.551159	-3.800781	-1.844782
1	-1.858607	-3.726972	-2.888794
1	-0.969222	-4.702736	-1.668034
1	-2.421592	-3.750691	-1.189925
1	4.085710	-1.381794	-3.723268

M

Number of imaginary frequencies : 0 Electronic energy : HF=-3004.2019671
Zero-point correction= 0.427766 (Hartree/Particle)
Thermal correction to Energy= 0.467842
Thermal correction to Enthalpy= 0.468786
Thermal correction to Gibbs Free Energy= 0.351607
Sum of electronic and zero-point Energies= -3003.774201
Sum of electronic and thermal Energies= -3003.734125
Sum of electronic and thermal Enthalpies= -3003.733181
Sum of electronic and thermal Free Energies= -3003.850360

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Cartesian Coordinates

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83	-2.188017	1.010580	-0.600669
8	-2.499052	-0.312210	1.098408
8	-1.524555	4.815871	0.628153
16	-2.495430	-1.845834	1.370658
16	-0.867610	3.567612	0.294657
8	-1.613100	-2.563912	0.430736
8	-2.379506	-2.116590	2.793009
6	-4.225359	-2.278397	0.826658
9	-4.420960	-1.779169	-0.406040
9	-4.353705	-3.601812	0.788695
9	-5.113419	-1.753449	1.660812
8	-0.826292	3.127987	-1.144052
8	-1.366224	2.315909	1.053808
6	0.929475	3.734106	0.846620
9	1.042922	4.749900	1.684495
9	1.321252	2.607388	1.446156
9	1.682922	3.944603	-0.236209
6	3.797909	-1.188843	-1.893010
6	2.578740	-1.600088	-1.156948
6	2.837893	-2.614094	-0.079861
6	4.151794	-2.759206	0.446461
6	5.229364	-2.099472	-0.207112
6	5.079883	-1.375613	-1.378784

1	0.809703	-3.342520	0.042604
1	1.833444	-1.975153	-1.859538
6	1.811914	-3.393386	0.453397
6	4.391953	-3.620527	1.542736
1	6.228671	-2.216357	0.205361
1	5.943144	-0.952791	-1.883515
6	3.349701	-4.350026	2.091132
6	2.067021	-4.246731	1.532501
1	5.400058	-3.713028	1.936223
1	3.525772	-5.010623	2.933129
1	1.252043	-4.836673	1.940259
8	3.565997	-0.545818	-3.022511
8	-2.108869	-1.004845	-2.078931
8	-0.257365	-2.271370	-2.070909
6	-0.233504	-0.095649	-0.967741
6	1.044982	0.508787	-1.626901
1	1.218006	0.265843	-2.676679
1	1.078334	1.593388	-1.508398
6	1.932185	-0.210153	-0.553765
6	0.630020	-0.471234	0.257386
1	0.532344	0.288405	1.036676
1	0.453939	-1.441938	0.706814
6	-0.928862	-1.183382	-1.743491
6	3.006230	0.594977	0.141438
6	3.678432	1.631504	-0.518822
1	3.402081	1.894768	-1.535699
6	4.681353	2.353650	0.129109
1	5.178943	3.168554	-0.387997
6	5.030519	2.042298	1.444979
1	5.803991	2.609996	1.952656
6	4.366906	1.009553	2.110557
1	4.621448	0.771617	3.138859
6	3.361516	0.290918	1.461712
1	2.839258	-0.501030	1.990919
6	-1.040077	-3.355483	-2.655777
1	-1.493039	-3.024420	-3.590874
1	-0.327756	-4.160728	-2.825157
1	-1.809045	-3.646863	-1.939355
1	4.383368	-0.205390	-3.423486

P

Number of imaginary frequencies : 0 Electronic energy : HF=-1076.1029462
Zero-point correction= 0.367965 (Hartree/Particle)
Thermal correction to Energy= 0.389143
Thermal correction to Enthalpy= 0.390087
Thermal correction to Gibbs Free Energy= 0.316376
Sum of electronic and zero-point Energies= -1075.734981
Sum of electronic and thermal Energies= -1075.713803
Sum of electronic and thermal Enthalpies= -1075.712859
Sum of electronic and thermal Free Energies= -1075.786570

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Cartesian Coordinates

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6	-0.949168	-0.433031	0.612321
6	-1.213005	-0.765436	1.934352
6	-2.360484	-1.510871	2.306582
1	-2.502753	-1.770937	3.353952
6	-3.273951	-1.900997	1.363041
1	-4.144753	-2.484420	1.648970

6	-3.105604	-1.523781	0.006704
6	-1.947479	-0.760310	-0.367466
6	-1.861639	-0.334843	-1.724518
1	-1.046428	0.304602	-2.031162
6	-2.823792	-0.676333	-2.649591
6	-3.936434	-1.466867	-2.280857
1	-4.683578	-1.735346	-3.021721
6	-4.072001	-1.872391	-0.973454
1	-4.932254	-2.461283	-0.664610
6	0.351594	0.257704	0.204030
6	1.146518	-0.424713	-0.963678
1	0.942231	-1.497766	-0.966038
1	1.052321	-0.047790	-1.983303
6	2.472773	-0.140264	-0.220165
1	2.919239	0.810521	-0.516007
6	1.631796	-0.023993	1.076458
1	1.912332	0.737363	1.805147
1	1.570744	-0.997541	1.563060
6	0.143129	1.769263	0.049524
6	0.460229	2.481734	-1.112361
1	0.869099	1.967600	-1.975555
6	0.260610	3.863920	-1.189047
1	0.512320	4.390893	-2.105341
6	-0.256895	4.560920	-0.099778
1	-0.413613	5.634166	-0.158317
6	-0.569974	3.863341	1.070664
1	-0.970418	4.394564	1.929916
6	-0.371921	2.486894	1.143177
1	-0.608826	1.954965	2.059034
6	3.492857	-1.246056	-0.242794
6	5.750638	-1.806225	-0.606171
1	6.667998	-1.287541	-0.885383
1	5.858190	-2.277749	0.374624
1	5.507752	-2.580741	-1.338958
8	-0.347533	-0.341614	2.914930
8	3.251491	-2.409519	0.009899
8	4.725555	-0.798874	-0.574636
1	-0.622225	-0.715144	3.761458
1	-2.730265	-0.324347	-3.673151

TS(A-G)

Number of imaginary frequencies : 1 Electronic energy : HF=-3003.7316373
Zero-point correction= 0.409701 (Hartree/Particle)
Thermal correction to Energy= 0.450086
Thermal correction to Enthalpy= 0.451030
Thermal correction to Gibbs Free Energy= 0.330079
Sum of electronic and zero-point Energies= -3003.321937
Sum of electronic and thermal Energies= -3003.281552
Sum of electronic and thermal Enthalpies= -3003.280607
Sum of electronic and thermal Free Energies= -3003.401558

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Cartesian Coordinates

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83	0.935244	-0.824507	0.983567
8	2.785102	0.144898	1.302418
8	1.150935	-0.755813	-1.151081
16	3.298681	1.543606	0.734470
16	1.767486	-2.110335	-1.669800
8	3.231223	1.558985	-0.724966

8	2.772287	2.651091	1.518538
6	5.094229	1.334247	1.204898
9	5.606936	0.259576	0.607896
9	5.752210	2.423337	0.806497
9	5.199283	1.205597	2.526672
8	1.094250	-2.626369	-2.844161
8	1.933768	-2.938474	-0.447303
6	3.478417	-1.560272	-2.190238
9	4.065768	-2.577869	-2.817256
9	3.378949	-0.518296	-3.003806
9	4.178941	-1.237436	-1.105408
6	-0.724077	1.663259	-0.045413
6	-2.144387	1.879356	0.208348
6	-2.789003	2.889123	-0.663521
6	-2.114414	3.379759	-1.817355
6	-0.764728	2.983665	-2.058622
6	-0.081013	2.153332	-1.188712
1	-4.593546	2.970984	0.506870
1	-2.328902	2.082183	1.264624
6	-4.087017	3.344312	-0.379630
6	-2.792376	4.282396	-2.674305
1	-0.256032	3.371644	-2.936276
1	0.958944	1.900110	-1.359079
6	-4.076689	4.704391	-2.385203
6	-4.726019	4.240242	-1.224752
1	-2.280018	4.648006	-3.560308
1	-4.583705	5.398873	-3.048206
1	-5.730865	4.580992	-0.993806
8	-0.077969	0.944534	0.890294
8	-3.493588	-3.449249	-0.683800
8	-5.395700	-2.326453	-1.264100
6	-3.395318	-1.142283	-1.198531
6	-2.094761	-0.786919	-0.588969
1	-1.652594	-1.568331	0.049688
1	-1.340676	-0.354342	-1.263436
6	-2.962583	0.325613	0.083432
6	-3.953334	0.232025	-1.121729
1	-3.621545	0.914154	-1.916798
1	-5.022714	0.371828	-0.958243
6	-4.046774	-2.408145	-1.024244
6	-3.526980	-0.085943	1.439211
6	-2.703041	-0.045470	2.577349
1	-1.687172	0.323224	2.485841
6	-3.175960	-0.435353	3.831037
1	-2.516783	-0.384311	4.693280
6	-4.489370	-0.881129	3.977407
1	-4.861257	-1.186634	4.950863
6	-5.319067	-0.929850	2.856791
1	-6.341777	-1.283569	2.951336
6	-4.846218	-0.533642	1.604833
1	-5.506774	-0.618401	0.750303
6	-6.105910	-3.554272	-1.072791
1	-6.016753	-3.899294	-0.037707
1	-7.147720	-3.337591	-1.313745
1	-5.716906	-4.337814	-1.729808

TS(B-C)

Number of imaginary frequencies : 1 Electronic energy : HF=-3003.8188557
Zero-point correction= 0.411189 (Hartree/Particle)

Thermal correction to Energy= 0.451449
Thermal correction to Enthalpy= 0.452393
Thermal correction to Gibbs Free Energy= 0.333978
Sum of electronic and zero-point Energies= -3003.407666
Sum of electronic and thermal Energies= -3003.367406
Sum of electronic and thermal Enthalpies= -3003.366462
Sum of electronic and thermal Free Energies= -3003.484878

Cartesian Coordinates

83	1.582717	1.097251	-0.263532
8	2.369264	-0.994575	-0.976901
8	0.024598	5.267851	0.907398
16	2.591418	-2.350279	-0.303253
16	0.130229	4.182839	-0.062049
8	2.656452	-2.244455	1.165420
8	1.743197	-3.401684	-0.876970
6	4.328540	-2.718234	-0.851967
9	5.148474	-1.745971	-0.437036
9	4.725540	-3.880647	-0.324323
9	4.384522	-2.799327	-2.184320
8	0.388062	2.825859	0.626739
8	0.958947	4.333382	-1.263070
6	-1.616693	3.933487	-0.688437
9	-1.637005	3.205078	-1.805631
9	-2.363963	3.288773	0.242772
9	-2.181959	5.117246	-0.928644
6	-0.924161	-0.146254	-1.656308
6	-2.238554	-0.016446	-1.152451
6	-3.221072	-1.014006	-1.429277
6	-2.815582	-2.243068	-2.033991
6	-1.442018	-2.393492	-2.420196
6	-0.532712	-1.383135	-2.264243
1	-4.891780	0.087853	-0.619571
1	-2.540794	0.949653	-0.764923
6	-4.577416	-0.847443	-1.072518
6	-3.772720	-3.255574	-2.258515
1	-1.125170	-3.333775	-2.863704
1	0.500456	-1.500698	-2.564786
6	-5.096867	-3.069371	-1.895601
6	-5.497374	-1.858011	-1.300680
1	-3.455387	-4.185068	-2.724032
1	-5.826751	-3.853001	-2.074166
1	-6.536013	-1.714844	-1.017571
8	-0.078106	0.857820	-1.577322
8	2.517274	0.703000	2.193177
8	1.332682	-0.749301	3.450400
6	0.436434	-0.047414	1.340575
6	-0.959933	0.540679	1.743715
1	-1.079605	0.676232	2.828404
1	-1.263574	1.470323	1.262659
6	-1.591597	-0.749510	1.302028
6	-0.263874	-1.421571	1.098007
1	-0.087546	-1.963436	0.168376
1	-0.060254	-2.125216	1.916630
6	1.523858	-0.002552	2.372552
6	-2.858361	-1.310023	1.613963
6	-3.885510	-0.508464	2.166784
1	-3.710590	0.553602	2.311557
6	-5.094953	-1.081339	2.536910

1	-5.874784	-0.468460	2.977536
6	-5.306523	-2.451387	2.338774
1	-6.253370	-2.896735	2.629450
6	-4.314618	-3.249196	1.755466
1	-4.495839	-4.305326	1.585792
6	-3.097926	-2.687695	1.395309
1	-2.321378	-3.295697	0.943145
6	2.472995	-0.881285	4.332630
1	2.780464	0.097661	4.705624
1	2.137790	-1.522853	5.146432
1	3.292608	-1.344777	3.779682

TS(C-D)

Number of imaginary frequencies : 1 Electronic energy : HF=-3003.7382187
Zero-point correction= 0.407880 (Hartree/Particle)
Thermal correction to Energy= 0.447944
Thermal correction to Enthalpy= 0.448888
Thermal correction to Gibbs Free Energy= 0.328882
Sum of electronic and zero-point Energies= -3003.330338
Sum of electronic and thermal Energies= -3003.290275
Sum of electronic and thermal Enthalpies= -3003.289331
Sum of electronic and thermal Free Energies= -3003.409337

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Cartesian Coordinates

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83	1.748445	0.701075	-0.124272
8	1.827502	-1.459039	-1.003788
8	1.449714	5.155092	0.172551
16	2.191510	-2.720988	-0.202587
16	0.953620	3.954639	-0.488518
8	2.332311	-2.416931	1.232650
8	1.402542	-3.881178	-0.612683
6	3.925259	-2.999209	-0.811569
9	4.651725	-1.892826	-0.583064
9	4.479564	-4.025891	-0.164087
9	3.922998	-3.252713	-2.122588
8	0.923801	2.728991	0.455727
8	1.459704	3.572331	-1.813203
6	-0.878721	4.235014	-0.693720
9	-1.440395	3.231037	-1.395910
9	-1.475879	4.284332	0.505946
9	-1.096059	5.378325	-1.340956
6	-0.944753	-0.420304	-1.591897
6	-2.114077	-0.284417	-0.772938
6	-3.313831	-0.893467	-1.361437
6	-3.143168	-1.838382	-2.428495
6	-1.842879	-2.102892	-2.960203
6	-0.734802	-1.372281	-2.591633
1	-4.797007	0.137902	-0.180611
1	-1.369935	0.991250	-0.935188
6	-4.630801	-0.601788	-0.951397
6	-4.272759	-2.487503	-2.986654
1	-1.752824	-2.844880	-3.749224
1	0.229711	-1.465307	-3.072944
6	-5.545814	-2.196719	-2.542142
6	-5.719211	-1.232761	-1.530991
1	-4.119102	-3.204376	-3.788719
1	-6.407498	-2.690019	-2.980504
1	-6.720530	-0.972212	-1.201192

8	-0.178787	0.683669	-1.379387
8	2.348000	0.463408	2.324347
8	0.881976	-0.644209	3.630072
6	0.251143	-0.066582	1.382459
6	-1.054498	0.770728	1.502710
1	-1.344471	0.865716	2.553105
1	-1.067830	1.764346	1.055964
6	-1.861819	-0.387162	0.827184
6	-0.626997	-1.314736	1.126316
1	-0.330872	-2.010545	0.343026
1	-0.761120	-1.876894	2.054525
6	1.238890	-0.065922	2.502349
6	-3.123427	-0.768674	1.571333
6	-3.907077	0.199526	2.212466
1	-3.614694	1.245129	2.169891
6	-5.072776	-0.161343	2.890497
1	-5.670157	0.602749	3.379443
6	-5.466254	-1.499807	2.943147
1	-6.370916	-1.782499	3.473312
6	-4.686485	-2.473917	2.315145
1	-4.983126	-3.517975	2.353135
6	-3.526019	-2.109067	1.634656
1	-2.932508	-2.869068	1.134068
6	1.912688	-0.764408	4.642079
1	2.261281	0.225338	4.943482
1	1.440293	-1.283865	5.474202
1	2.745713	-1.343482	4.238479

TS(E-F)

Number of imaginary frequencies : 1 Electronic energy : HF=-3464.8831845
Zero-point correction= 0.561352 (Hartree/Particle)
Thermal correction to Energy= 0.611183
Thermal correction to Enthalpy= 0.612127
Thermal correction to Gibbs Free Energy= 0.468752
Sum of electronic and zero-point Energies= -3464.321833
Sum of electronic and thermal Energies= -3464.272001
Sum of electronic and thermal Enthalpies= -3464.271057
Sum of electronic and thermal Free Energies= -3464.414432

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Cartesian Coordinates

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83	-1.465567	-0.098629	-0.624354
8	1.145542	-0.980093	-0.569456
8	-1.570629	-1.546221	1.149692
16	0.718612	-2.128090	-1.404516
16	-1.100178	-0.856214	2.447025
8	-0.814378	-1.900291	-1.644194
8	1.424387	-2.468096	-2.628841
6	0.803941	-3.665928	-0.329662
9	0.555770	-3.366864	0.937805
9	-0.080203	-4.554957	-0.774798
9	2.037096	-4.158611	-0.438983
8	-1.180647	0.606526	2.274649
8	0.137515	-1.421957	2.998674
6	-2.440419	-1.353909	3.640651
9	-2.170662	-0.828446	4.833926
9	-3.620928	-0.889598	3.210525
9	-2.492845	-2.680275	3.731488
6	3.150065	-0.204608	1.261329

6	3.841226	0.579409	0.340011
6	5.002688	-0.005906	-0.276590
6	5.272825	-1.409045	-0.120675
6	4.432384	-2.185519	0.718743
6	3.425055	-1.588458	1.424536
1	5.848456	1.821734	-1.090263
1	1.641815	-0.339076	2.473492
6	5.950287	0.747513	-1.029251
6	6.385908	-1.996280	-0.775931
1	4.615664	-3.251993	0.815588
1	2.787486	-2.164459	2.089358
6	7.251681	-1.239080	-1.531545
6	7.036698	0.153113	-1.635199
1	6.551086	-3.063934	-0.652801
1	8.104204	-1.698857	-2.022399
1	7.742611	0.767562	-2.187311
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8	1.674220	0.485995	-3.353631
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1	2.988151	2.412091	2.636481
6	4.349938	4.011668	3.106076
1	4.065840	4.039727	4.154542
6	5.325386	4.887523	2.621715
1	5.804531	5.599152	3.288010
6	5.676375	4.838497	1.273931
1	6.432591	5.512654	0.881103
6	5.055981	3.924184	0.417820
1	5.344660	3.914208	-0.628575
6	0.797603	0.033306	-4.420310
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1	-6.169372	0.260287	1.834929
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1	-8.765523	3.708288	-2.250193

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TS(K'-M)

Number of imaginary frequencies : 1 Electronic energy : HF=-3004.193019
Zero-point correction= 0.425235 (Hartree/Particle)
Thermal correction to Energy= 0.465519
Thermal correction to Enthalpy= 0.466463
Thermal correction to Gibbs Free Energy= 0.348544
Sum of electronic and zero-point Energies= -3003.767784
Sum of electronic and thermal Energies= -3003.727500
Sum of electronic and thermal Enthalpies= -3003.726556
Sum of electronic and thermal Free Energies= -3003.844475

.....

Cartesian Coordinates

.....

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9	0.778962	4.164675	2.482574
9	1.115832	2.066575	2.031474
9	2.159929	3.602827	0.893113
6	3.656631	-1.802539	-1.965712
6	2.616472	-2.234796	-1.102744
6	2.970285	-2.778974	0.188759
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8	-0.625872	-2.702662	-1.479932
6	-0.295664	-0.353899	-1.009595
6	0.955520	0.021785	-1.883516
1	1.120154	-0.600444	-2.765484
1	1.000973	1.070497	-2.182343
6	1.838494	-0.257814	-0.666706
6	0.629541	-0.579629	0.203996

1	0.501390	0.155525	1.000653
1	0.551913	-1.563862	0.660225
6	-1.123929	-1.483848	-1.540264
6	2.956380	0.562445	-0.240291
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1	3.246100	1.514046	-2.163624
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1	5.117750	2.935345	-1.399688
6	5.091507	2.163909	0.616651
1	5.907769	2.796926	0.950655
6	4.479615	1.284972	1.512850
1	4.819776	1.230002	2.541943
6	3.418907	0.488374	1.089780
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6	-1.534294	-3.783747	-1.848157
1	-1.810173	-3.694389	-2.899782
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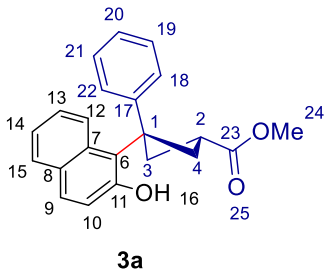
1	-2.422417	-3.722795	-1.218570
1	4.056305	-1.147967	-3.723192

9. Synthesis and Characterization of Carbofunctionalized Cyclobutanes

Methyl-3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3a)

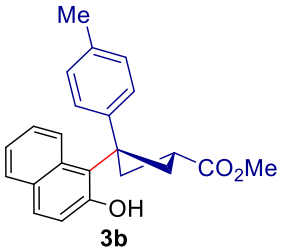


3a

Following the general procedure, treatment of naphthalen-2-ol **1a** (0.029 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3a** as yellow solid (0.060 g, 91% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.22; Melting point: 143-145 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71-7.65 (m, 4H, *12-15*), 7.44 (d, *J* = 8.9 Hz, 1H, *9*), 7.36-7.18 (m, 5H, *18-22*), 6.94 (d, *J* = 8.8 Hz, 1H, *10*), 6.20 (s, 1H, *16*), 3.68 (s, 3H, *24*), 3.43-3.29 (m, 5H, *2-4*). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.8 (*23*), 150.8 (*11*), 146.6 (*17*), 132.3 (*7*), 129.8 (*8*), 128.9 (*13*), 128.8 (*14*), 128.6 (*19,21*), 126.6 (*6*), 126.4 (*9*), 126.3 (*15*), 125.9 (*18,22*), 124.5 (*20*), 122.7 (*12*), 118.8 (*10*), 52.1 (*24*), 46.1 (*1*), 40.6 (*3,4*), 34.5 (*2*). **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{22}H_{20}NaO_3$ 355.1305; found 355.1308. **FTIR (cm^{-1})** 3351, 2947, 1691, 1615, 1432, 1259.

Methyl-3-(2-hydroxynaphthalen-1-yl)-3-(*p*-tolyl)cyclobutane-1-carboxylate (3b)

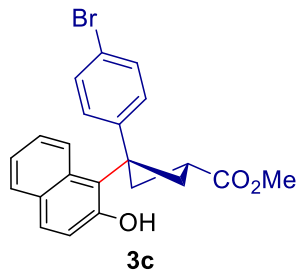


3b

Following the general procedure, treatment of naphthalen-2-ol **1a** (0.029 g, 0.2 mmol) and methyl 3-(*p*-tolyl)bicyclo[1.1.0]butane-1-carboxylate **2b** (0.048 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxynaphthalen-1-yl)-3-(*p*-tolyl)cyclobutane-1-carboxylate **3b** as yellow solid (0.055 g, 79% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 177-179 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72-7.64 (m, 2H), 7.54-7.49 (m, 3H), 7.36-7.24 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 1H), 5.75 (s, 1H), 3.66 (s, 3H), 3.44-3.25 (m, 5H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.3, 150.6, 143.6, 136.0, 132.3, 129.9, 129.4, 128.9, 128.8, 126.9, 126.3, 125.9, 124.7, 122.8, 118.9, 52.0, 45.8, 40.8, 34.5, 21.0. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}NaO_3$ 369.1461; found 369.1463. **FTIR (cm^{-1})** 3370, 2935, 1699,1511, 1437, 1194.

Methyl-3-(4-bromophenyl)-3-(2-hydroxynaphthalen-1-yl)cyclobutane-1-carboxylate (3c)

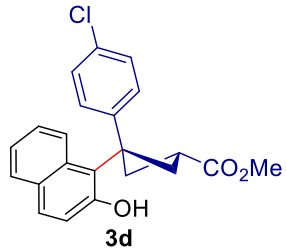


3c

Following the general procedure, treatment of naphthalen-2-ol **1a** (0.029 g, 0.2 mmol) and methyl 3-(4-bromophenyl)bicyclo [1.1.0]butane-1-carboxylate **2c** (0.064 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(4-bromophenyl)-3-(2-hydroxynaphthalen-1-yl)cyclobutane-1-carboxylate **3c** as light yellow solid (0.076 g, 78% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 211-213 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68-7.50 (m, 4H), 7.42-7.22 (m, 5H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.15 (s, 1H), 3.66 (s, 3H), 3.40-3.24 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.5, 150.6, 145.8, 132.1, 131.6, 129.8, 129.0, 128.7, 128.4, 126.4, 126.0, 124.2, 122.93, 120.2, 118.8, 52.1, 45.9, 40.6, 34.4. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}BrNaO_3$ 433.0415; found 433.0410. **FTIR (cm^{-1})** 3368, 2946, 1700, 1494, 1435, 1259.

Methyl-3-(4-chlorophenyl)-3-(2-hydroxynaphthalen-1-yl)cyclobutane-1-carboxylate (3d)

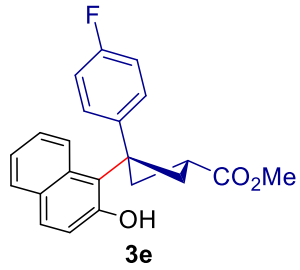


3d

Following the general procedure, treatment of naphthalen-2-ol **1a** (0.029 g, 0.2 mmol) and methyl 3-(4-chlorophenyl)bicyclo [1.1.0]butane-1-carboxylate **2d** (0.053 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(4-chlorophenyl)-3-(2-hydroxynaphthalen-1-yl)cyclobutane-1-carboxylate **3d** as yellow solid (0.061 g, 83% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 203-205 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.1 Hz, 1H), 7.60-7.58 (m, 3H), 7.40-7.22 (m, 5H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.55-6.45 (m, 1H), 3.69 (s, 3H), 3.55-3.07 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.8, 150.8, 145.3, 132.1, 132.0, 129.8, 129.0, 129.0, 128.7, 128.0, 126.0, 124.2, 122.8, 118.8, 52.2, 45.9, 40.6, 34.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}ClNaO_3$ 389.0915; found 389.0918. **FTIR (cm^{-1})** 3355, 2948, 1698, 1498, 1344, 1211.

Methyl-3-(4-fluorophenyl)-3-(2-hydroxynaphthalen-1-yl)cyclobutane-1-carboxylate (3e)

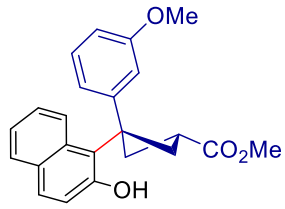


3e

Following the general procedure, treatment of naphthalen-2-ol **1a** (0.029 g, 0.2 mmol) and methyl 3-(4-fluorophenyl)bicyclo [1.1.0]butane-1-carboxylate **2e** (0.049 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(4-fluorophenyl)-3-(2-hydroxynaphthalen-1-yl)cyclobutane-1-carboxylate **3e** as yellow solid (0.066 g, 94% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 172-174 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71-7.58 (m, 5H), 7.49-7.25 (m, 4H), 6.99-6.94 (m, 2H), 6.60 (s, 1H), 3.70 (s, 3H), 3.38-3.21 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.7, 161.4 (d, *J* = 244.4 Hz), 150.8, 142.4 (d, *J* = 3.3 Hz), 132.8, 132.1, 129.2, 129.0, 128.9, 128.0 (d, *J* = 7.9 Hz), 125.9, 124.2, 122.8, 118.8, 115.2 (d, *J* = 21.1 Hz), 52.1, 45.8, 40.8, 34.4. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}FNaO_3$ 373.1216; found 373.1217. **FTIR (cm^{-1})** 3345, 2952, 1704, 1503, 1431, 1215.

Methyl-3-(2-hydroxynaphthalen-1-yl)-3-(3-methoxyphenyl)cyclobutane-1-carboxylate (3f)

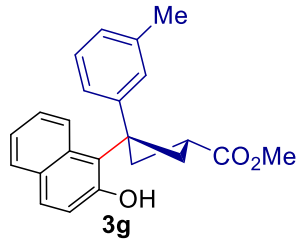


3f

Following the general procedure, treatment of naphthalen-2-ol **1a** (0.029 g, 0.2 mmol) and methyl 3-(3-methoxyphenyl)bicyclo [1.1.0]butane-1-carboxylate **2f** (0.052 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxynaphthalen-1-yl)-3-(3-methoxyphenyl)cyclobutane-1-carboxylate **3f** as yellow solid (0.055 g, 76% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.21; Melting point: 180-182 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70-7.64 (m, 2H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.36-7.22 (m, 5H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.74 (dd, *J1* = 7.7 Hz, *J2* = 1.6 Hz, 1H), 6.14 (s, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.48-3.25 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.4, 159.9, 150.8, 148.5, 132.3, 129.9, 129.6, 128.9, 128.8, 126.6, 125.9, 124.6, 122.8, 118.8, 113.6, 110.8, 55.3, 52.0, 46.2, 40.6, 34.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}NaO_4$ 385.1410; found 385.1415. **FTIR (cm^{-1})** 3366, 2947, 1704, 1591, 1434, 1213.

Methyl-3-(2-hydroxynaphthalen-1-yl)-3-(*m*-tolyl)cyclobutane-1-carboxylate (3g)

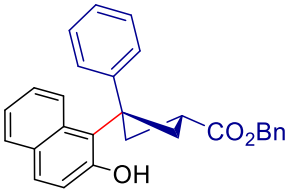


3g

Following the general procedure, treatment of naphthalen-2-ol **1a** (0.029 g, 0.2 mmol) and methyl 3-(*m*-tolyl)bicyclo[1.1.0]butane-1-carboxylate **2g** (0.048 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxynaphthalen-1-yl)-3-(*m*-tolyl)cyclobutane-1-carboxylate **3g** as yellow solid (0.062 g, 74% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 165-167 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73-7.66 (m, 2H), 7.50-7.44 (m, 3H), 7.37-7.34 (m, 1H), 7.30-7.26 (m, 1H), 7.22-7.18 (m, 1H), 7.03-6.95 (m, 2H), 5.86 (s, 1H), 3.69 (s, 3H), 3.44-3.27 (m, 5H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.5, 150.7, 146.5, 138.2, 132.3, 129.8, 128.8, 128.8, 128.6, 127.2, 127.0, 126.8, 125.8, 124.6, 123.4, 122.8, 118.8, 52.0, 46.0, 40.6, 34.5, 21.9. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}NaO_3$ 369.1467; found 369.1469. **FTIR (cm^{-1})** 3362, 2947, 1702, 1505, 1434, 1209.

Benzyl 3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3h)

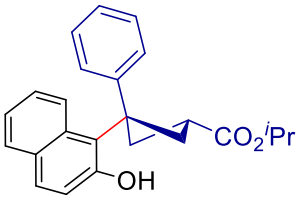


3h

Following the general procedure, treatment of naphthalen-2-ol **1a** (0.029 g, 0.2 mmol) and benzyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2h** (0.063 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded benzyl 3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3h** as sticky solid (0.063 g, 77% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75-7.70 (m, 4H), 7.46-7.29 (m, 10H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.34 (s, 1H), 5.18 (s, 2H), 3.54-3.36 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.2, 150.8, 146.6, 135.8, 132.3, 129.7, 128.9, 128.7, 128.7, 128.6, 128.4, 128.3, 126.4, 126.3, 125.9, 124.5, 122.7, 118.8, 66.8, 46.2, 40.6, 34.7. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}NaO_5$ 431.1618; found 431.1623. **FTIR (cm^{-1})** 3052, 2358, 1704, 1505, 1261, 1025.

Isopropyl 3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3i)

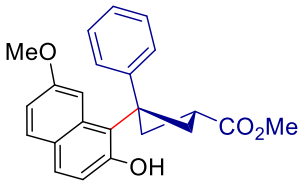


3i

Following the general procedure, treatment of naphthalen-2-ol **1a** (0.029 g, 0.2 mmol) and isopropyl 3-phenylbicyclo[1.1.0] butane-1-carboxylate **2i** (0.051 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded isopropyl 3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3i** as sticky solid (0.048 g, 66% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72-7.66 (m, 4H), 7.43-7.26 (m, 5H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.53 (s, 1H), 5.10-5.01 (m, 1H), 3.52-3.28 (m, 5H), 1.26 (s, 3H), 1.25 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.0, 150.9, 146.7, 132.3, 129.8, 128.9, 128.7, 128.6, 126.6, 126.5, 125.8, 124.6, 122.7, 118.9, 68.3, 46.1, 40.6, 34.9, 21.9. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{24}H_{24}NaO_3$ 383.1618; found 383.1625. **FTIR (cm^{-1})** 3315, 2926, 2356, 1703, 1502, 1215.

Methyl-3-(2-hydroxy-7-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3j)

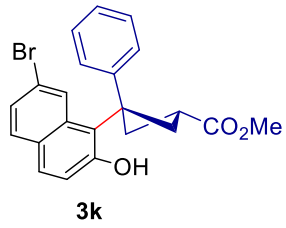


3j

Following the general procedure, treatment of 7-methoxynaphthalen-2-ol **1b** (0.035 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxy-7-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3j** as yellow solid (0.061 g, 84% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.21; Melting point: 178-180 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69-7.67 (m, 2H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.33-7.29 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.96-6.92 (m, 2H), 6.81 (d, *J* = 8.7 Hz, 1H), 5.77 (s, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 3.41-3.27 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.3, 157.6, 151.2, 146.5, 133.5, 130.2, 128.7, 128.5, 126.4, 126.4, 125.7, 125.2, 116.4, 114.9, 104.1, 55.2, 52.0, 46.2, 36.9, 34.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}NaO_4$ 385.1410; found 385.1413. **FTIR (cm^{-1})** 3358, 2937, 1701, 1620, 1444, 1216.

Methyl-3-(7-bromo-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3k)

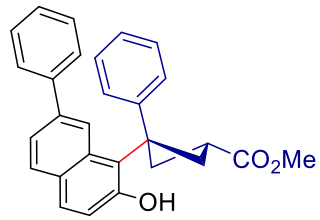


3k

Following the general procedure, treatment of 7-bromonaphthalen-2-ol **1c** (0.045 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(7-bromo-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3k** as yellow solid (0.076 g, 93% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 209-211 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 1.2 Hz, 1H), 7.67-7.65 (m, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.34-7.30 (m, 3H), 7.28-7.19 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.74 (s, 1H), 3.72 (s, 3H), 3.51-3.08 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.2, 151.7, 146.1, 133.4, 130.4, 128.8, 128.6, 128.0, 126.7, 126.5, 126.3, 125.9, 125.8, 120.3, 119.1, 52.3, 46.0, 40.6, 34.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}BrNaO_3$ 433.0410; found 433.0411. **FTIR (cm^{-1})** 3352, 2950, 1704, 1613, 1495, 1204.

Methyl-3-(2-hydroxy-7-phenylnaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3l)

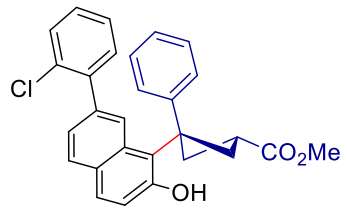


3l

Following the general procedure, treatment of 7-phenylnaphthalen-2-ol **1d** (0.044 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0] butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxy-7-phenylnaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3l** as orange solid (0.060 g, 73% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 130-132 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (s, 1H), 7.79-7.73 (m, 3H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.65-7.46 (m, 4H), 7.40-7.31 (m, 3H), 7.22-7.18 (m, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.27 (s, 1H), 3.70 (s, 3H), 3.52-3.35 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.8, 151.1, 146.6, 141.8, 138.4, 132.5, 129.4, 129.0, 129.0, 128.7, 128.4, 127.5, 127.3, 126.8, 126.4, 126.4, 122.8, 122.4, 118.9, 52.1, 46.2, 40.6, 34.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}NaO_3$ 431.1623; found 431.1622. **FTIR (cm^{-1})** 3368, 2949, 1708, 1489, 1437, 1210.

Methyl-3-(7-(2-chlorophenyl)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3m)

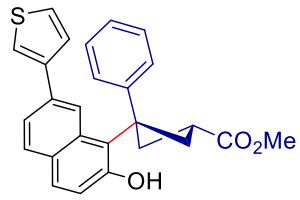


3m

Following the general procedure, treatment of 7-(2-chlorophenyl)naphthalen-2-ol **1e** (0.051 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(7-(2-chlorophenyl)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3m** as yellow solid (0.063 g, 71% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 205-207 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78-7.68 (m, 4H), 7.51-7.45 (m, 2H), 7.40-7.26 (m, 6H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.19 (s, 1H), 3.69 (s, 3H), 3.37-3.35 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.7, 151.1, 146.5, 141.1, 136.7, 132.7, 132.0, 131.8, 130.2, 129.0, 128.7, 128.6, 128.6, 127.0, 127.0, 126.5, 126.4, 125.4, 124.5, 119.3, 52.1, 46.2, 40.9, 34.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{23}ClNaO_3$ 465.1228; found 465.1233. **FTIR (cm^{-1})** 3241, 2948, 1690, 1434, 1334, 1221.

Methyl-3-(2-hydroxy-7-(thiophen-3-yl)naphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3n)



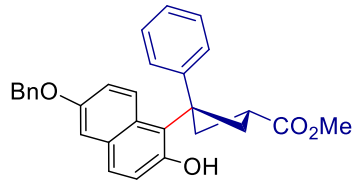
3n

Following the general procedure, treatment of 7-(thiophen-3-yl)naphthalen-2-ol **1f** (0.045 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxy-7-(thiophen-3-yl)naphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3n** as yellow solid (0.065 g, 78% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 204-206 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (s, 1H), 7.78-7.71 (m, 3H), 7.54-7.39 (m, 7H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.39 (s, 1H), 3.70 (s, 3H), 3.57-3.12 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.8, 151.2, 146.6, 143.0, 133.0, 132.5, 132.3, 129.4, 128.9, 128.8, 128.5, 126.7, 126.5, 126.5, 126.4,

121.9, 121.8, 120.5, 118.7, 52.2, 46.3, 40.6, 34.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{26}H_{22}NaO_3S$ 437.1182; found 437.1184. **FTIR (cm^{-1})** 3343, 2950, 1699, 1618, 1443, 1213.

Methyl-3-(6-(benzyloxy)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3o)

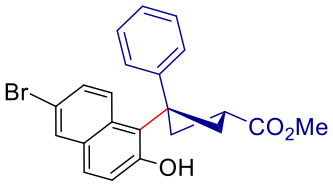


3o

Following the general procedure, treatment of 6-(benzyloxy)naphthalen-2-ol **1g** (0.050 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(6-(benzyloxy)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3o** as yellow solid (0.081 g, 92% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 167-169 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65-7.58 (m, 3H), 7.48-7.28 (m, 8H), 7.21-7.10 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 1H), 5.67 (s, 1H), 5.13 (s, 2H), 3.68 (s, 3H), 3.43-3.07 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.3, 154.6, 149.2, 146.6, 137.2, 132.3, 130.9, 129.2, 128.7, 128.7, 128.1, 127.6, 127.6, 127.2, 126.4, 126.1, 119.4, 118.6, 108.8, 70.2, 52.0, 46.2, 40.7, 34.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{29}H_{26}NaO_4$ 461.1723; found 461.1727. **FTIR (cm^{-1})** 3401, 2946, 1709, 1607, 1367, 1228.

Methyl 3-(6-bromo-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3p)



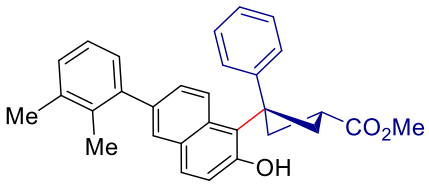
3p

Following the general procedure, treatment of methyl 6-bromonaphthalen-2-ol **1h** (0.045 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl 3-(6-bromo-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3p** as yellow solid (0.062 g, 76% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 203-205 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.53-7.50 (m, 1H), 7.41-7.38 (m, 1H), 7.32-7.17 (m, 4H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.79 (s, 1H), 3.72 (s, 3H), 3.43-3.28 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.1, 151.2, 146.3, 131.0, 130.8, 130.7, 129.0, 128.7, 127.7,

126.8, 126.5, 126.3, 126.2, 119.9, 116.4, 52.2, 46.1, 40.6, 34.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for **$C_{22}H_{19}BrNaO_3$** 433.0410; found 433.0412. **FTIR (cm^{-1})** 3320, 2939, 2356, 1702, 1589, 1209.

Methyl-3-(6-(2,3-dimethylphenyl)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3q)

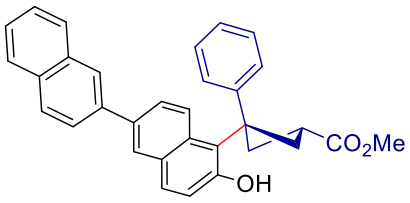


3q

Following the general procedure, treatment of 6-(2,3-dimethylphenyl)naphthalen-2-ol **1i** (0.050 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(6-(2,3-dimethylphenyl)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3q** as yellow solid (0.087 g, 97% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 141-143 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71-7.53 (m, 5H), 7.35-7.32 (m, 3H), 7.23-7.12 (m, 4H), 7.00 (d, *J* = 8.7 Hz, 1H), 5.63 (s, 1H), 3.69 (s, 3H), 3.43-3.31 (m, 5H), 2.36 (s, 3H), 2.18 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.2, 150.6, 146.5, 142.1, 137.3, 137.2, 134.4, 131.0, 129.8, 129.0, 128.9, 128.9, 128.8, 128.1, 128.0, 126.8, 126.5, 125.4, 124.2, 119.1, 52.0, 46.2, 40.6, 34.5, 20.8, 17.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{30}H_{28}NaO_3$ 459.1931; found 459.1937. **FTIR (cm^{-1})** 3349, 2946, 1689, 1486, 1440, 1208.

Methyl-3-(6-hydroxy-[2,2'-binaphthalen]-5-yl)-3-phenylcyclobutane-1-carboxylate (3r)



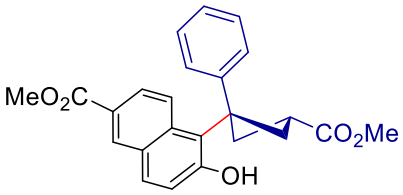
3r

Following the general procedure, treatment of [2,2'-binaphthalen]-6-ol **1j** (0.054 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(6-hydroxy-[2,2'-binaphthalen]-5-yl)-3-phenylcyclobutane-1-carboxylate **3r** as yellow solid (0.076 g, 83% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 111-113 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (s, 1H), 7.98 (s, 1H), 7.89-7.87 (m, 3H), 7.82-7.73 (m, 5H), 7.51-7.49 (m, 2H), 7.42 (d,

J = 8.9 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.46 (s, 1H), 3.73 (s, 3H), 3.58-3.37 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.0, 151.0, 146.6, 138.3, 135.0, 133.9, 132.6, 131.5, 130.1, 129.1, 128.7, 128.6, 128.3, 127.8, 127.0, 126.5, 126.4, 126.4, 126.4, 125.9, 125.6, 125.6, 125.5, 125.1, 119.3, 52.2, 46.2, 40.6, 34.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{32}H_{26}NaO_3$ 481.1774; found 481.1780. **FTIR (cm^{-1})** 3359, 2947, 1700, 1602, 1436, 1200.

Methyl 6-hydroxy-5-(3-(methoxycarbonyl)-1-phenylcyclobutyl)-2-naphthoate (3s)

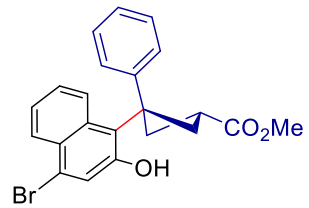


3s

Following the general procedure, treatment of methyl 6-hydroxy-2-naphthoate **1k** (0.04 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl 6-hydroxy-5-(3-(methoxycarbonyl)-1-phenylcyclobutyl)-2-naphthoate **3s** as yellow solid (0.062 g, 79% yield).

***R*$_f$** (Pet. ether /EtOAc = 90/10): 0.25; Melting point: 229-231 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (s, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.69-7.64 (m, 3H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.32-7.26 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.0 (d, *J* = 8.8 Hz, 1H), 6.72 (s, 1H), 3.96 (s, 3H), 3.70 (s, 3H), 3.40-3.25 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.9, 167.6, 153.0, 146.2, 134.8, 132.0, 130.3, 128.7, 126.8, 126.5, 126.4, 125.3, 124.6, 124.2, 119.6, 52.3, 52.2, 46.0, 40.5, 34.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{24}H_{22}NaO_5$ 413.1359; found 413.1365. **FTIR (cm^{-1})** 3384, 2951, 2356, 1722, 1434, 1300.

Methyl-3-(4-bromo-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3t)

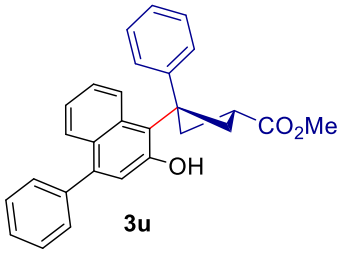


3t

Following the general procedure, treatment of 4-bromonaphthalen-2-ol **1l** (0.045 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0] butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(4-bromo-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3t** as yellow solid (0.067 g, 81% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 202-204 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08-8.06 (m, 1H), 7.67-7.61 (m, 3H), 7.38-7.29 (m, 5H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 3.75 (s, 3H), 3.49-3.29 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.4, 150.7, 146.2, 133.1, 128.7, 128.0, 127.9, 126.8, 126.6, 126.5, 126.3, 124.8, 124.1, 122.6, 122.2, 52.4, 46.0, 40.7, 34.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}BrNaO_3$ 433.0410; found 433.0412. **FTIR (cm^{-1})** 3220, 2942, 1693, 1500, 1429, 1224.

Methyl-3-(2-hydroxy-4-phenylnaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3u)

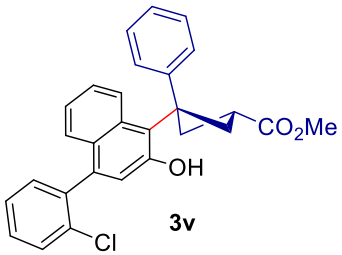


3u

Following the general procedure, treatment of 4-phenylnaphthalen-2-ol **1m** (0.044 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxy-4-phenylnaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3u** as yellow solid (0.069 g, 85% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 189-191 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73-7.68 (m, 4H), 7.40-7.31 (m, 6H), 7.26-7.17 (m, 4H), 6.92 (s, 1H), 6.15 (s, 1H), 3.68 (s, 3H), 3.49-3.32 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.7, 150.1, 146.7, 141.0, 140.2, 132.7, 130.0, 128.7, 128.3, 128.2, 127.3, 127.0, 126.5, 126.4, 126.1, 125.8, 124.8, 122.9, 119.8, 52.1, 46.1, 40.6, 34.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}NaO_3$ 431.1618; found 431.1620. **FTIR (cm^{-1})** 3365, 2945, 1697, 1602, 1434, 1214.

Methyl-3-(4-(2-chlorophenyl)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3v)

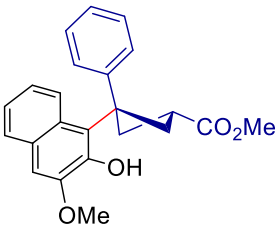


3v

Following the general procedure, treatment of 4-(2-chlorophenyl)naphthalen-2-ol **1n** (0.051 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(4-(2-chlorophenyl)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3v** as yellow solid (0.063 g, 71% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.23; Melting point: 193-195 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76-7.73 (m, 3H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.38-7.17 (m, 9H), 6.92 (s, 1H), 6.43 (bs, 1H), 3.68 (s, 3H), 3.56-3.14 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.7, 150.0, 146.6, 138.9, 138.0, 134.1, 132.5, 132.1, 129.6, 129.0, 128.7, 128.5, 128.1, 126.8, 126.7, 126.6, 126.4, 125.8, 124.8, 123.0, 120.2, 52.1, 46.2, 40.7, 34.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{23}ClNaO_3$ 465.1228; found 465.1235. **FTIR (cm^{-1})** 3350, 2948, 1702, 1434, 1369, 1208.

Methyl-3-(2-hydroxy-3-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3w)

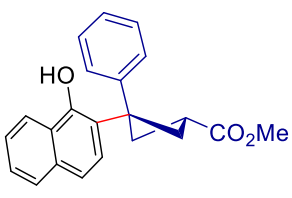


3w

Following the general procedure, treatment of 3-methoxynaphthalen-2-ol **1o** (0.035 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxy-3-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3w** as sticky solid (0.056 g, 78% yield, 2:1 dr).

***R*f** (Pet. ether /EtOAc = 90/10): 0.21; **^{1}H NMR (400 MHz, $CDCl_3$) of Major isomer** δ 7.73-7.64 (m, 4H), 7.34-7.12 (m, 5H), 7.02 (s, 1H), 6.34 (s, 1H), 3.98 (s, 3H), 3.65 (s, 3H), 3.57-3.04 (m, 5H). **Representative peaks of minor isomer ^{1}H NMR (400 MHz, $CDCl_3$)** 7.57 (d, *J* = 8.3 Hz, 1H), 7.06 (s, 1H), 6.45 (s, 1H), 4.02 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) of Major isomer** δ 175.7, 147.1, 146.6, 142.9, 129.4, 128.5, 127.62, 127.60, 126.6, 126.4, 125.2, 124.4, 123.8, 123.4, 104.8, 56.0, 51.7, 46.3, 39.7, 34.4. **Representative peaks of minor isomer ^{13}C NMR (100 MHz, $CDCl_3$)** 176.3, 147.6, 143.4, 129.5, 125.2, 105.0, 56.1, 51.8, 48.1, 33.9. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}NaO_4$ 385.1410; found 385.1415. **FTIR (cm^{-1})** 3412, 2944, 1717, 1428, 1246, 1187.

Methyl-3-(1-hydroxynaphthalen-2-yl)-3-phenylcyclobutane-1-carboxylate (3x)



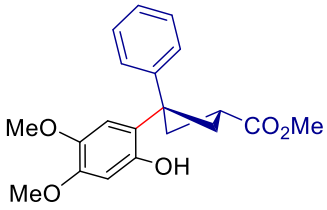
3x

Following the general procedure, treatment of naphthalen-1-ol **1p** (0.029 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction

mixture using silica gel afforded methyl-3-(1-hydroxynaphthalen-2-yl)-3-phenylcyclobutane-1-carboxylate **3x** as white solid (0.032 g, 48% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.22; Melting point: 187-189 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10-8.08 (m, 1H), 7.84-7.82 (m, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.49-7.42 (m, 2H), 7.37-7.32 (m, 4H), 7.24-7.20 (m, 1H), 4.95 (s, 1H), 3.70 (s, 3H), 3.15-3.03 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.4, 149.5, 146.2, 134.0, 129.2, 127.6, 127.1, 126.2, 126.1, 125.7, 125.6, 125.4, 124.3, 121.5, 120.3, 52.0, 45.5, 37.2, 33.0. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{22}H_{20}NaO_3$ 355.1305; found 355.1310. **FTIR (cm^{-1})** 3359, 2949, 1701, 1434, 1344, 1213.

Methyl-3-(2-hydroxy-4,5-dimethoxyphenyl)-3-phenylcyclobutane-1-carboxylate (3y)

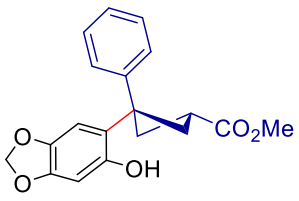


3y

Following the general procedure, treatment of 3,4-dimethoxyphenol **1q** (0.031 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(2-hydroxy-4,5-dimethoxyphenyl)-3-phenylcyclobutane-1-carboxylate **3y** as yellow oil (0.040 g, 58% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.28 (m, 4H), 7.20-7.16 (m, 1H), 7.06 (s, 1H), 6.41 (s, 1H), 4.35 (s, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 3.68 (s, 3H), 3.12-3.06 (m, 1H), 2.99-2.91 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.6, 149.2, 148.4, 146.8, 142.9, 128.9, 126.7, 126.0, 122.8, 111.4, 102.8, 57.3, 56.1, 52.0, 45.1, 37.1, 33.0. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{20}H_{22}NaO_5$ 365.1359; found 365.1360. **FTIR (cm^{-1})** 3311, 2940, 1692, 1517, 1352, 1197.

Methyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-phenylcyclobutane-1-carboxylate (3z)



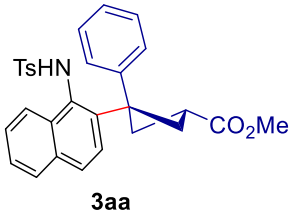
3z

Following the general procedure, treatment of benzo[*d*][1,3]dioxol-5-ol **1r** (0.028 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0] butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude

reaction mixture using silica gel afforded methyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-phenylcyclobutane-1-carboxylate **3z** as yellow oil (0.036 g, 55% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.20; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.28-7.23 (m, 4H), 7.17-7.13 (m, 1H), 7.01 (s, 1H), 6.33 (s, 1H), 5.90 (s, 2H), 4.44 (s, 1H), 3.64 (s, 3H), 3.10-3.01 (m, 1H), 2.90-2.88 (m, 4H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 175.6, 148.9, 147.0, 146.8, 141.6, 128.8, 126.6, 126.0, 124.1, 106.5, 101.3, 100.1, 52.0, 45.4, 37.1, 33.1. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}NaO_5$ 349.1046; found 349.1054. **FTIR (cm^{-1})** 3389, 2918, 1706, 1495, 1432, 1167.

Methyl-3-(1-((4-methylphenyl)sulfonamido)naphthalen-2-yl)-3-phenylcyclobutane-1-carboxylate (3aa)



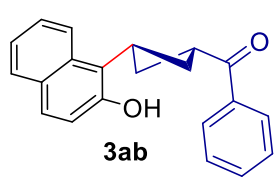
3aa

Following the general procedure, treatment of 4-methyl-*N*-(naphthalen-1-yl)benzenesulfonamide **1s** (0.059 g, 0.2 mmol) and methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **2a** (0.045 g, 0.24 mmol) with Bi(OTf)$_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded methyl-3-(1-((4-methylphenyl)sulfonamido)naphthalen-2-yl)-3-phenylcyclobutane-1-carboxylate **3aa** as white solid (0.051 g, 52% yield, 3:1 dr).

***R*f** (Pet. ether /EtOAc = 90/10): 0.20; Melting point: 159-161 °C. **^{1}H NMR (400 MHz, CDCl$_3$) of Major isomer** δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.45-7.36 (m, 3H), 7.31-7.13 (m, 8H), 7.05 (s, 1H), 3.66 (s, 3H), 3.12-3.05 (m, 5H), 2.36 (s, 3H). **Representative peaks of minor isomer ^{1}H NMR (400 MHz, CDCl$_3$)** 7.92 (d, *J* = 8.3 Hz, 1H), 3.70 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$) of Major isomer** δ 175.2, 146.3, 144.2, 143.9, 136.7, 131.2, 130.6, 130.0, 129.7, 128.7, 128.5, 127.5, 126.3, 126.1, 126.0, 125.9, 124.1, 122.6, 122.2, 52.0, 47.4, 38.9, 33.2, 21.6. **Representative peaks of minor isomer ^{13}C NMR (100 MHz, CDCl$_3$)** 175.5, 47.8, 38.7, 33.1. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{29}H_{27}NNaO_4S$ 508.1553; found 508.1561. **FTIR (cm^{-1})** 3354, 2791, 1710, 1595, 1210, 1149.

3-(2-Hydroxynaphthalen-1-yl)cyclobutyl)(phenyl)methanone (3ab)

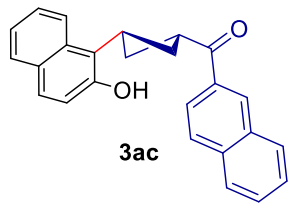
Following the general procedure, treatment of naphthalen-2-ol **2a** (0.029 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(phenyl)methanone **2j** (0.038 g, 0.24 mmol) with Bi(OTf)$_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography



3ab

(Pet. ether/ EtOAc = 84/16) of the crude reaction mixture using silica gel afforded 3-(2-hydroxynaphthalen-1-yl)cyclobutyl)(phenyl)methanone **3ab** as colorless oil (0.042 g, 70% yield, 2:1 dr). ***R*f** (Pet. ether /EtOAc = 90/10): 0.24; **^{1}H NMR (400 MHz, $CDCl_3$) of Major isomer** δ 8.02-7.96 (m, 3H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.63-7.56 (m, 2H), 7.50-7.41 (m, 3H), 7.32-7.28 (m, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 6.53 (s, 1H), 4.46-4.37 (m, 1H), 4.22-4.09 (m, 1H), 3.21-3.11 (m, 2H), 2.99-2.88 (m, 2H). **Representative peaks of minor isomer ^{1}H NMR (400 MHz, $CDCl_3$)** 7.05 (d, *J* = 9.0 Hz, 1H), 5.62 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) of Major isomer** δ 202.8, 152.5, 135.8, 133.4, 133.3, 133.1, 129.4, 128.8, 128.7, 128.5, 126.2, 123.2, 123.0, 120.6, 119.5, 39.0, 32.3, 29.8. **Representative peaks of minor isomer ^{13}C NMR (100 MHz, $CDCl_3$)** 202.1, 151.9, 135.6, 129.5, 126.3, 121.8, 39.1, 29.8. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{21}H_{18}NaO_2$ 325.1199; found 325.1204. **FTIR (cm^{-1})** 3354, 2926, 1663, 1325, 1221, 1079.

3-(2-Hydroxynaphthalen-1-yl)cyclobutyl)(naphthalen-2-yl)methanone (3ac)



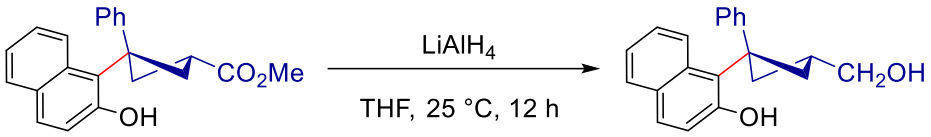
3ac

Following the general procedure, treatment of naphthalen-2-ol **2a** (0.029 g, 0.2 mmol) and bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **2k** (0.050 g, 0.24 mmol) with $Bi(OTf)_3$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (1.5 mL) at 25 °C for 12 h followed by flash column chromatography (Pet. ether/ EtOAc = 80/20) of the crude reaction mixture using silica gel afforded 3-(2-hydroxynaphthalen-1-yl)cyclobutyl)(naphthalen-2-yl)methanone **3ac** as yellow solid (0.048 g, 68% yield, 2.3:1 dr).

***R*f** (Pet. ether /EtOAc = 90/10): 0.24; Melting point: 180-182 °C. **^{1}H NMR (400 MHz, $CDCl_3$) of Major isomer** δ 8.52 (s, 1H), 8.11-7.87 (m, 5H), 7.76-7.74 (m, 1H), 7.63-7.53 (m, 3H), 7.48-7.41 (m, 1H), 7.33-7.29 (m, 1H), 7.11-7.06 (m, 1H), 6.57 (s, 1H), 4.54-4.25 (m, 2H), 3.28-3.17 (m, 2H), 3.06-2.91 (m, 2H). **Representative peaks of minor isomer ^{1}H NMR (400 MHz, $CDCl_3$)** 5.64 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) of Major isomer** δ 202.7, 152.6, 135.9, 133.3, 132.7, 130.5, 130.2, 129.8, 129.5, 128.8, 128.7, 128.5, 128.0, 126.9, 126.3, 124.3, 123.3, 123.0, 120.7, 119.5, 118.9, 39.0, 32.4, 31.2 **Representative peaks of minor isomer ^{13}C NMR (100 MHz, $CDCl_3$)** 202.0, 151.9, 39.2, 31.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{25}H_{21}O_2$ 353.1536; found 353.1542. **FTIR (cm^{-1})** 3330, 2921, 1662, 1509, 1358, 1219.

10.Product Functionalization

a) Reduction of the ester to alcohol

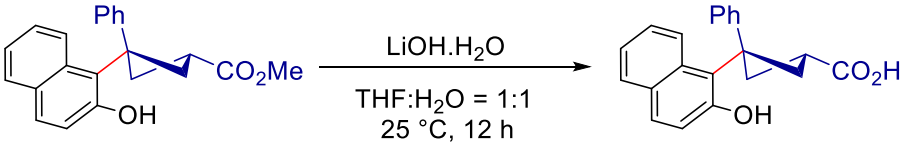


3a **6**, 94%

Compound **6** was prepared using the literature procedure.[7] To a 25 mL two neck round bottom flask equipped with stir bar, $LiAlH_4$ (0.015 g, 0.4 mmol) was dissolved in dry THF (1.0 mL). The reaction mixture was cooled to 0 °C with ice bath. Then, the solution of methyl-3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3a** (0.066 g, 0.2 mmol) in dry THF (1.0 mL) was added slowly and reaction mixture was allowed to stir for 12h at room temperature. After this time, the reaction was cooled to 0 °C and quenched with 10% KOH solution (2.0 mL). The resulting suspension was filtered through celite, washed with ethyl acetate. The combined filtrate was dried, concentrated and purified by flash column chromatography (Pet. ether /EtOAc = 80/20) of the crude reaction mixture afforded 1-(3-(hydroxymethyl)-1-phenylcyclobutyl)naphthalen-2-ol **6** as a white solid (0.057 g, 94% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.17; Melting point: 190-192 °C. **^{1}H NMR (400 MHz, $(CD_3)_2CO$)** δ 8.64 (s, 1H), 7.82-7.72 (m, 4H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.32-7.18 (m, 5H), 7.11 (t, *J* = 7.3 Hz, 1H), 3.56-3.52 (m, 3H), 3.11 (bs, 3H), 2.62-2.60 (m, 2H). **^{13}C NMR (100 MHz, $(CD_3)_2CO$)** δ 152.7, 149.5, 133.6, 130.4, 129.4, 128.9, 128.8, 128.6, 127.4, 126.3, 126.0, 125.6, 123.0, 120.0, 67.1, 47.1, 41.5, 34.2, **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{21}H_{20}NaO_2$ 327.1356; found 327.1361. **FTIR (cm^{-1})** 3458, 2926, 2359, 1436, 1338, 1230.

b) Conversion of ester to acid



3a **7**, 78%

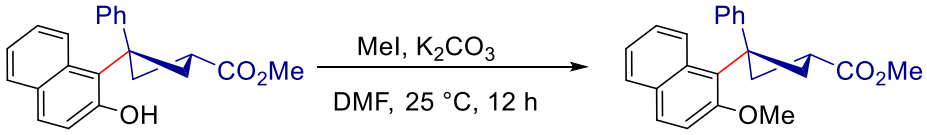
Following the general procedure,[8] methyl-3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3a** (0.066 g, 0.2 mmol) and lithium hydroxide monohydrate (0.017 g, 0.4 mmol) were dissolved in THF:H_2O (1+1 mL) at 25 °C and stirred for 12 h. The

[7] A. O. Chagarovskiy, V. S. Vasin, V. V. Kuznetsov, O. A. Ivanova, V. B. Rybakov, A. N. Shumsky, N. N. Makhova and I. V. Trushkov, *Angew. Chem., Int. Ed.*, 2018, **57**, 10338.
[8] K. Dhake, K. J. Woelk, J. Becia, A. Un, S. E. Jenny and D. C. Leitch, *Angew. Chem., Int. Ed.*, 2022, **61**, e202204719.

mixture was then concentrated under reduced pressure. The resulting residue was dissolved in water (5 mL) and acidified with 1 M HCl to adjust the pH to 4-6. Once the solution reached the desired pH range, the aqueous phase was extracted with DCM (5 mL). The organic layer was dried using anhydrous Na_2SO_4 and concentrated under reduced pressure, followed by purification via silica gel flash column chromatography (Pet. ether /EtOAc = 70/30) of the crude reaction mixture afforded 3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylic acid **7** as white solid (0.050 g, 78% yield).

***R*f** (Pet. ether /EtOAc = 70/30): 0.28; Melting point: 243-245 °C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 12.02 (s, 1H), 9.73 (s, 1H), 7.76-7.65 (m, 4H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.32-7.13 (m, 6H), 3.37-2.87 (m, 5H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 176.0, 151.9, 147.3, 131.8, 128.7, 128.6, 128.2, 128.1, 126.2, 126.1, 125.8, 125.5, 123.9, 122.0, 119.2, 45.6, 33.8. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{21}H_{18}NaO_3$ 341.1148; found 341.1153. **FTIR (cm$^-$)^1** 3375, 2354, 1650, 1220, 991.

c) Conversion of alcohol to methyl ether



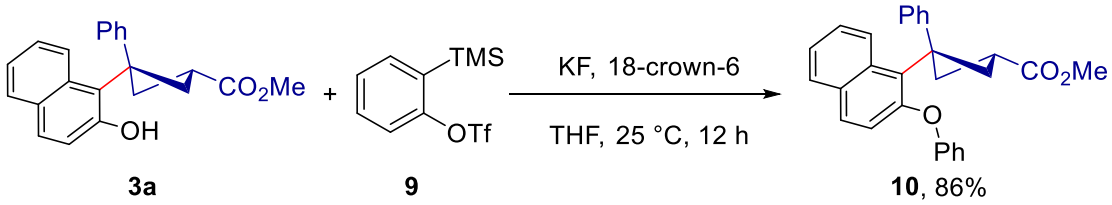
3a **8**, 93%

Compound **8** was synthesized following the modified literature procedure.[9] To a solution of **3a** (0.066 g, 0.2 mmol) in 2.0 mL DMF was added K_2CO_3 (0.041 g, 0.3 mmol) and methyl iodide (0.042 g, 0.3 mmol) then the mixture was stirred at 25 °C for 12 h. Then the solvent was evaporated, and the residue was purified by column chromatography to give methyl-3-(2-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **8** as a white solid (0.064 g, 93% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.25; Melting point: 105-107 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.79-7.65 (m, 5H), 7.39-7.18 (m, 6H), 3.98 (s, 3H), 3.65 (s, 3H), 3.38-3.13 (m, 5H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 175.7, 154.3, 146.8, 132.0, 130.1, 129.8, 128.9, 128.8, 128.5, 126.5, 126.2, 125.9, 124.8, 123.1, 114.2, 56.2, 51.7, 46.5, 41.0, 34.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}NaO_3$ 369.1461; found 369.1464. **FTIR (cm$^-$)^1** 2954, 1727, 1598, 1439, 1251, 1153.

[9] P. Alvarez-Bercedo and R. Martin, *J. Am. Chem. Soc*., 2010, **132**, 17353.

d) Arylation of 3a

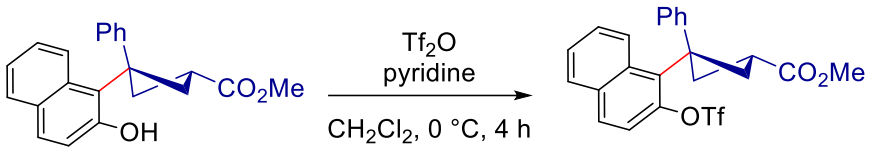


3a **9** **10**, 86%

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added KF (0.035 g, 0.6 mmol) and 18-crown-6 (0.158 g, 0.6 mmol) in a nitrogen filled glove box. After that **3a** (0.066 g, 0.2 mmol) was added outside the glove-box in nitrogen atmosphere. Then THF (1.0 mL) was added followed by the addition of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **9** (0.090 g, 0.3 mmol). The mixture was stirred at 25 °C for 12 h. Then the solvent was evaporated, and the residue was purified by column chromatography to give methyl-3-(2-phenoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **10** as a colorless oil (0.082 g, 86% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.24; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.89 (d, *J* = 8.5 Hz, 1H), 7.81-7.74 (m, 3H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.46-7.31 (m, 6H), 7.22-7.18 (m, 1H), 7.14-7.07 (m, 4H), 3.62 (s, 3H), 3.46-3.19 (m, 5H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 175.4, 157.3, 151.2, 146.2, 133.6, 132.2, 131.3, 129.9, 129.0, 128.9, 128.6, 126.6, 126.3, 126.1, 125.3, 124.4, 123.0, 120.2, 118.6, 51.7, 46.6, 40.9, 34.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}NaO_3$ 431.1618; found 431.1622. **FTIR (cm^{-})**[1] 2948, 1727, 1587, 1487, 1367, 1218.

e) Triflyl protection of 3a



3a **11**, 93%

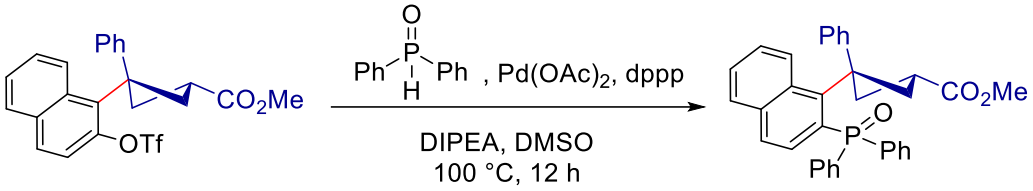
Compound **11** was synthesized following the literature procedure.[10] To a solution of methyl-3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **3a** (0.066 g, 0.2 mmol) and pyridine (0.043g, 0.54 mmol) in CH_2Cl_2 (2 mL) was added Tf_2O (0.073 g, 0.26 mmol) dropwise at 0 °C under argon. The mixture was stirred at 0 °C for 3 h, then the reaction was quenched by the addition of water (1 mL). The organic layer was washed with water and brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue

[10] D. Xu, T. M. Penning, I. A. Blair and R. G. Harvey, *J. Org. Chem*., 2009, **74**, 597.

was purified by chromatography on a silica gel column eluted with hexane/EtOAc (10:1) to afford **11** as a colorless oil (0.086 g, 93% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.24; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.93-7.87 (m, 2H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.55-7.46 (m, 5H), 7.38-7.34 (m, 2H), 7.30-7.26 (m, 1H), 3.69 (s, 3H), 3.61-3.54 (m, 1H), 3.36-3.24 (m, 4H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 175.2, 145.6, 145.3, 136.5, 133.1, 132.2, 130.0, 129.1, 128.9, 127.02, 126.99, 126.7, 126.5, 126.3, 129.4 (unresolved quartet), 118.4 (*q*, *J* = 320 Hz), 52.0, 46.0, 40.0 (unresolved quartet), 34.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{19}F_3NaO_5S$ 487.0798; found 487.0802. **FTIR (cm$^-$)[1]** 3055, 1729, 1585, 1489, 1369, 1217.

f) Conversion of -OTf to diphenylphosphine oxide



11 **12**, 82%

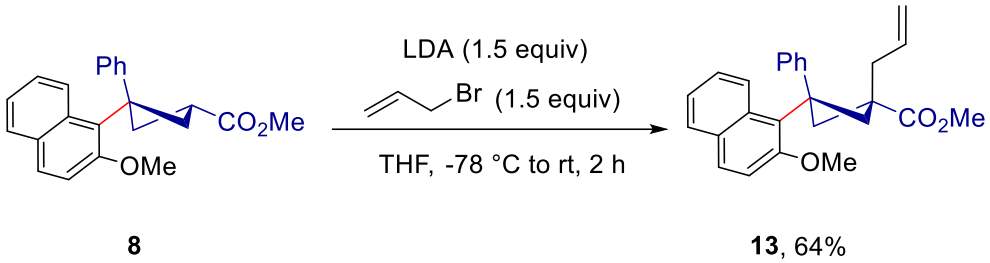
Compound **12** was synthesized following the literature procedure.[11] A solution of $Pd(OAc)_2$ (2 mg, 10 mol%), dppp (4 mg, 10 mol%) in DMSO (0.5 mL) was vigorously stirred at room temperature for 30 min under Ar atmosphere. Then **11** (0.050 g, 0.1 mmol), DIPEA (0.052 g, 4.0 equiv) and diphenylphosphine oxide (0.045 g, 0.22 mmol) were added sequentially before heating at 100 °C in an oil bath for 12 h. The reaction was removed to room temperature and quenched by water, extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo and the residue was purified by chromatography on a silica gel column eluted with hexane/EtOAc (1:1) to afford **12** as a colorless oil (0.042 g, 82% yield).

***R*f** (Pet. ether /EtOAc = 70/30): 0.12; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.94-7.89 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.65-7.54 (m, 7H), 7.48-7.22 (m, 11H), 3.44-3.20 (m, 4H), 3.38 (s, 3H), 2.90-2.87 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 175.6, 155.6 (d, *J* = 5.3 Hz), 148.2, 137.3 (d, *J* = 107.0 Hz), 135.4 (d, *J* = 2.5 Hz), 133.6 (d, *J* = 99.4 Hz), 132.2 (d, *J* = 9.8 Hz), 132.1 (d, *J* = 11.8 Hz), 131.86 (d, *J* = 9.2 Hz), 131.84 (d, *J* = 3.8 Hz), 131.3 (d, *J* = 2.8 Hz), 130.2 (d, *J* = 14.2 Hz), 128.8 (d, *J* = 11.9 Hz), 128.6, 128.4 (d, *J* = 11.9 Hz), 127.6 (d, *J* = 41.0 Hz), 126.7, 126.1 (d, *J* = 16.1 Hz), 125.7 (d, *J* = 13.3 Hz), 51.6, 49.1 (d, *J* = 3.6 Hz), 44.0 (d, *J* = 45.9 Hz),

[11] J. Zhang, Z. Gao, J. Qian, H. Yang, M. He and G. Jiang, *Org. Lett*., 2021, **23**, 7814.

33.5. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{34}H_{30}O_3P$ 517.1927; found 517.1930. **FTIR (cm^-)[1]** 3055, 2223, 1726, 1436, 1193, 1031.

g) Allylation of 8

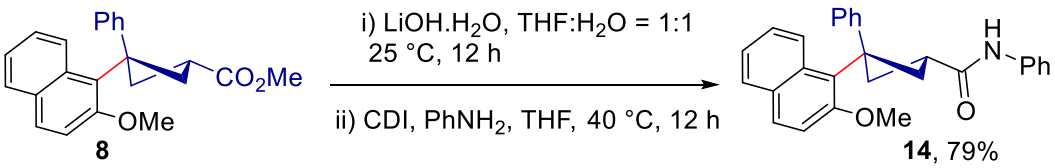


8 **13**, 64%

Compound **13** was synthesized following the literature procedure.[12] To a -78 °C solution of **8** (0.052 g, 0.15 mmol) in THF (1.0 mL), was slowly added LDA (0.11 mL, 1.5 equiv (2M in THF)). The reaction mixture was stirred for 30 min. Allyl bromide (0.027 g, 1.5 equiv) was then added dropwise into the reaction mixture. The reaction mixture was then warmed naturally to room temperature and stirred for 1.5 h. The reaction mixture was quenched by the addition of saturated aq. NH_4Cl and extracted with Et_2O three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo and the residue was purified by chromatography on a silica gel column eluted with hexane/EtOAc (9:1) to afford **13** as a colorless oil (0.037 g, 64% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.27; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 8.9 Hz, 1H), 7.78-7.73 (m, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 8.4 Hz, 1H), 7.31-7.22 (m, 4H), 7.11 (t, *J* = 7.3 Hz, 1H), 5.69-5.58 (m, 1H), 4.97-4.93 (m, 2H), 3.99 (s, 3H), 3.70 (bs, 2H), 3.52 (s, 3H), 2.99 (bs, 2H), 2.37 (d, *J* = 7.3 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.4, 154.2, 147.1, 133.5, 131.9, 130.4, 129.9, 128.9, 128.8, 128.1, 126.9, 125.9, 125.8, 125.2, 123.1, 117.5, 114.4, 56.2, 51.8, 45.6, 45.2, 44.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{26}H_{26}NaO_3$ 409.1774; found 409.1783. **FTIR (cm^-)[1]** 2190, 2129, 1696, 1212, 1083.

h) Amidation of 8



8 **14**, 79%

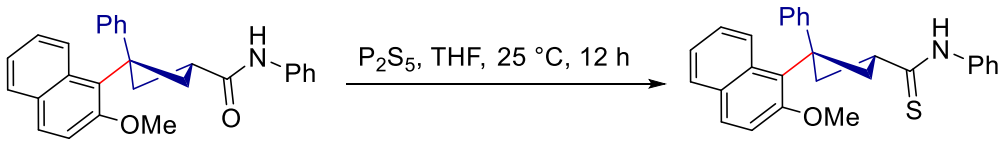
[12] X. He, Y. Zhao, Z. Zhang and X. Shen, *Org. Lett.*, 2022, **24**, 1991.

Methyl-3-(2-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate **8** (0.069 g, 0.15 mmol) and lithium hydroxide monohydrate (0.017 g, 0.4 mmol) were dissolved in THF:H_2O (1+1 mL) at 25 °C and stirred for 12 h. The mixture was then concentrated under reduced pressure. The resulting residue was dissolved in water (5 mL) and acidified with 1 M HCl to adjust the pH to 4-6. Once the solution reached the desired pH range, the aqueous phase was extracted with DCM (5 mL). The organic layer was dried using anhydrous Na_2SO_4 and concentrated under reduced pressure to furnish the acid derivative. The acid derivative was used directly for the next step without purification.

Compound **14** was synthesized following the literature procedure.[13] Carbonyldiimidazole (0.036 g, 0.22 mmol) was added to the solution of the acid derivative (0.2 mmol) in THF (1.0 mL), and the solution was stirred at 40 °C for 2 h. The reaction mixture was cooled to rt, aniline (0.020 g, 0.22 mmol) was added, and the reaction mixture was stirred at 40 °C for 10 h. The obtained mixture was concentrated under vacuum, the residue was dissolved in CH_2Cl_2, washed with 5% aq HCl, $NaHCO_3$, and brine. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo and the residue was purified by chromatography on a silica gel column eluted with hexane/EtOAc (5:1) to afford **14** as a white solid (0.064 g, 79% yield) (over two steps).

***R*f** (Pet. ether /EtOAc = 90/10): 0.27; Melting point: 249-251 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77-7.67 (m, 5H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.37-7.26 (m, 7H), 7.21-7.19 (m, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 3.96 (s, 3H), 3.31-3.21 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.8, 154.3, 146.9, 138.1, 132.0, 129.9, 129.8, 129.1, 128.9, 128.8, 128.5, 126.6, 126.2, 125.9, 124.7, 124.2, 123.1, 119.7, 114.2, 56.2, 46.2, 40.7, 37.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}NNaO_2$ 430.1778; found 430.1783. **FTIR (cm^-)[1]** 3246, 2124, 1976, 1651, 1499, 1253.

i) Thioamide formation of 14



14 **15**, 84%

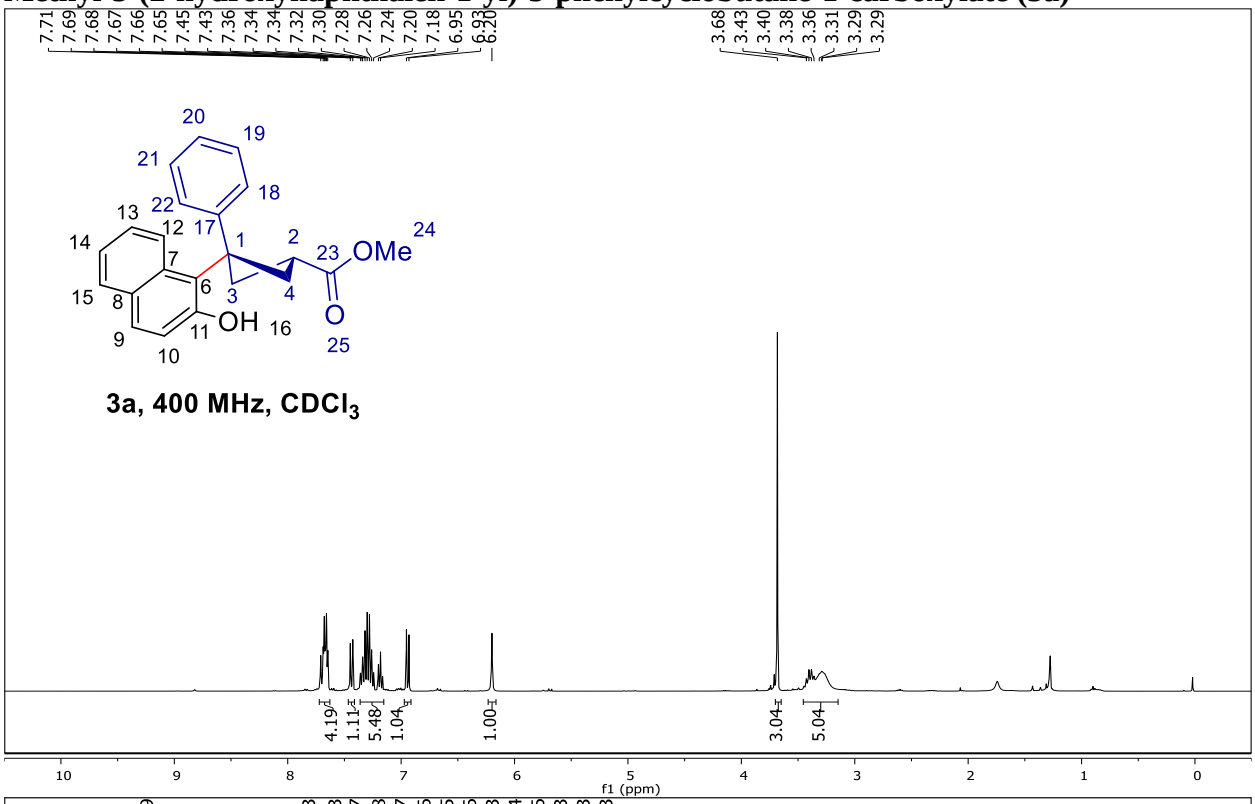
[13] . V. Chernykh, K. P. Melnykov, N. A. Tolmacheva, I. S. Kondratov, D. S. Radchenko, C. G. Daniliuc, D. M. Volochnyuk, S. V. Ryabukhin, Y. O. Kuchkovska, and O. O. Grygorenko, *J. Org. Chem.*, 2019, **84**, 8487.

Compound **15** was synthesized following the literature procedure.[14] Compound **15** (0.043 g, 0.1 mmol) and P_2S_5 (0.111 g, 0.25 mmol) were dissolved in THF (2.0 mL) under argon atmosphere and stirred for 12 h at 25 °C. 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 = 90/10) to afford **15** as a sticky solid (0.036 g, 84% yield).
***R*f** (Pet. ether /EtOAc = 90/10): 0.29; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (s, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.78-7.74 (m, 4H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.46-7.29 (m, 7H), 7.26-7.17 (m, 2H), 4.00 (s, 3H), 3.66-3.23 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.0, 154.2, 146.7, 138.5, 132.0, 129.9, 129.8, 129.0, 128.9, 128.9, 128.5, 126.9, 126.7, 126.3, 126.0, 124.7, 123.8, 123.2, 114.2, 56.3, 46.0, 45.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}NNaOS$ 446.1549; found 446.1556. **FTIR (cm^-)^1** 3243, 2130, 1979, 1932, 1788, 1334.

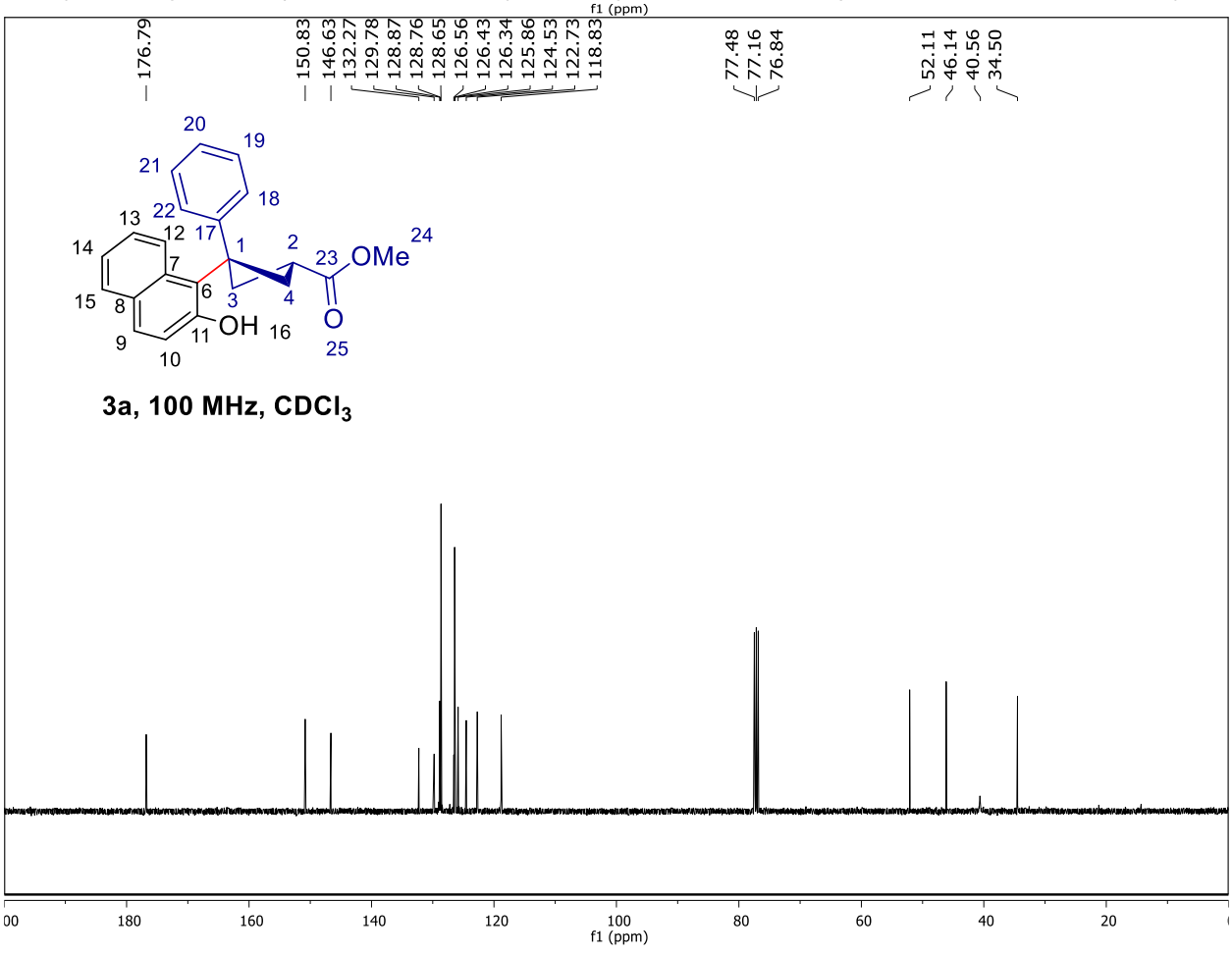
[14] A. Ghosh, S. Barik and A. T. Biju, *Org. Lett*., 2019, **21**, 8598.

11. ^{1}H and ^{13}C NMR Spectra of Products

Methyl-3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3a)

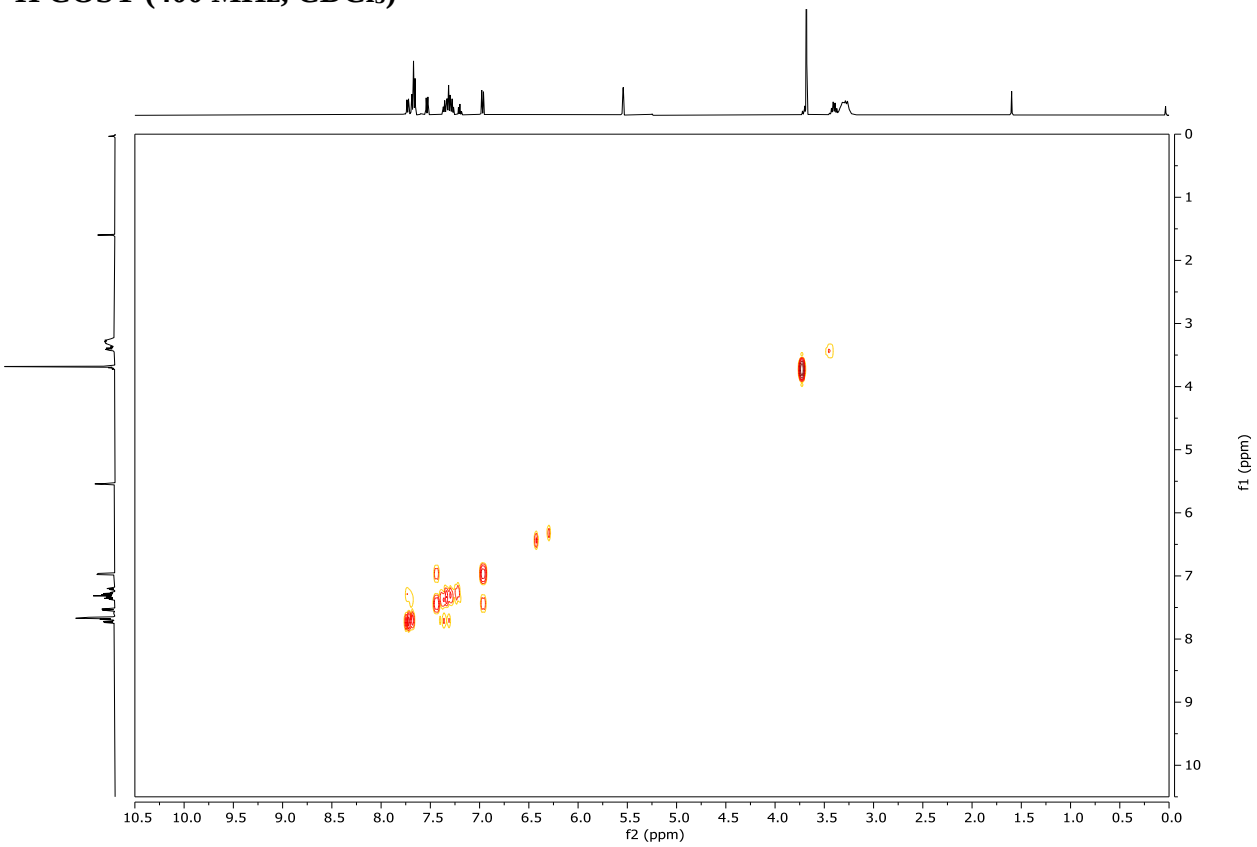


3a, 400 MHz, $CDCl_3$

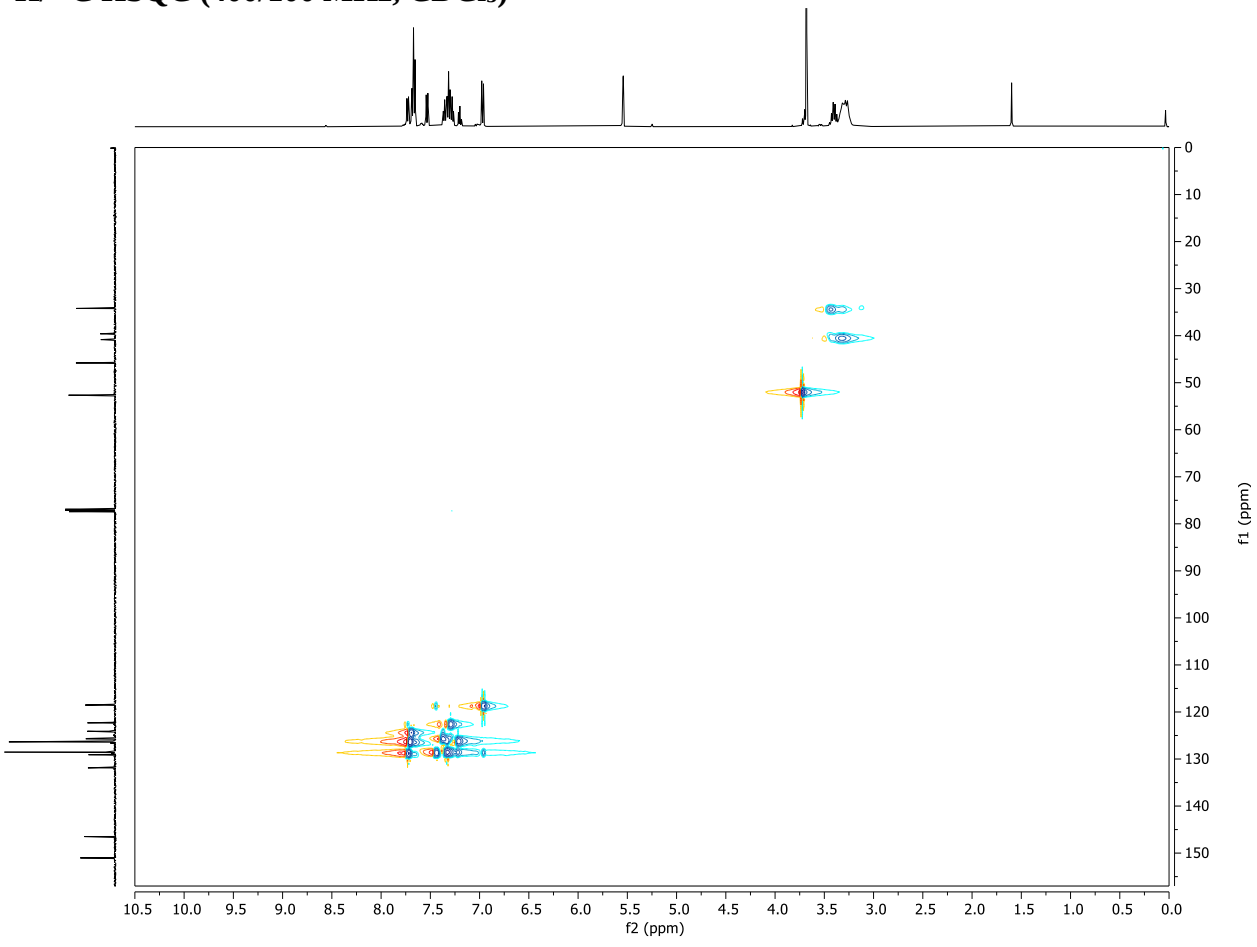


3a, 100 MHz, $CDCl_3$

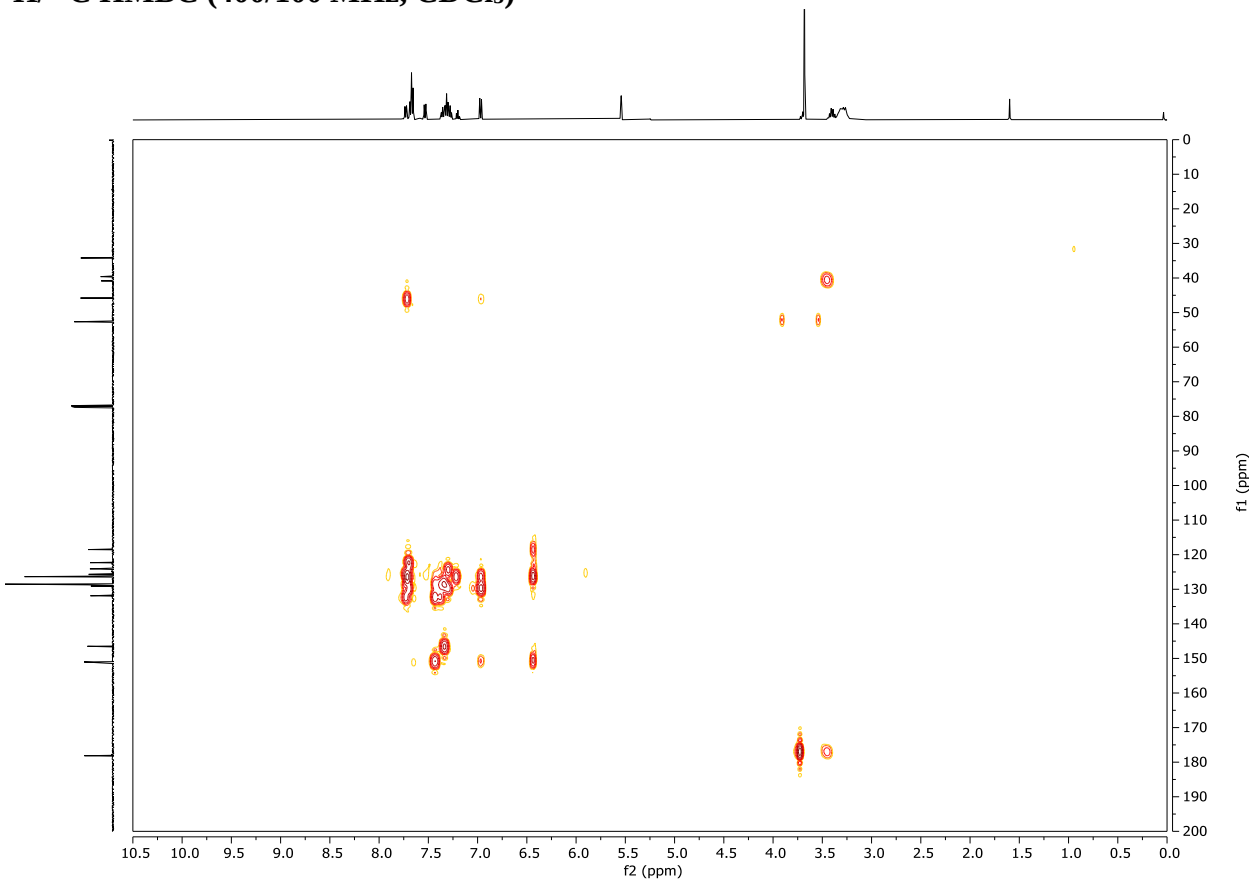
^{1}H COSY (400 MHz, $CDCl_3$)



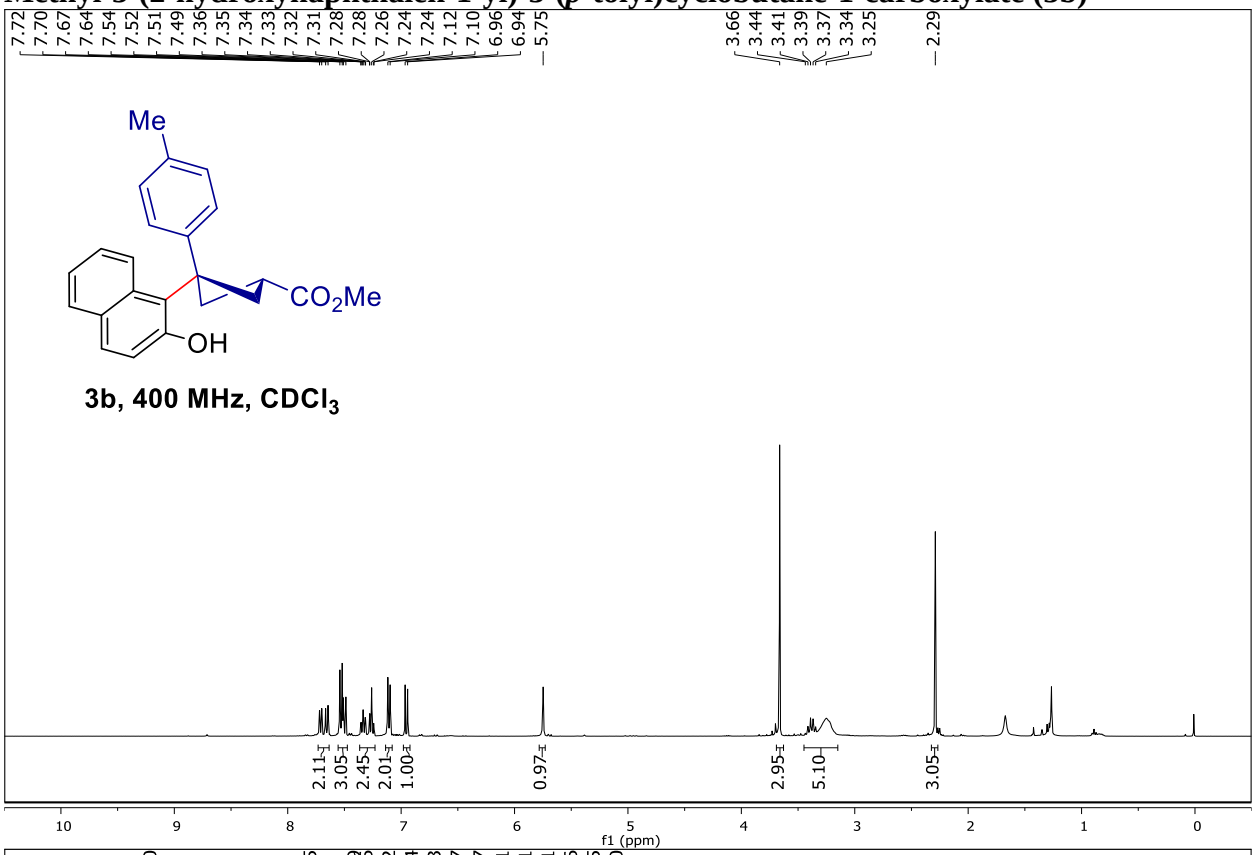
^{1}H/^{13}C HSQC (400/100 MHz, $CDCl_3$)

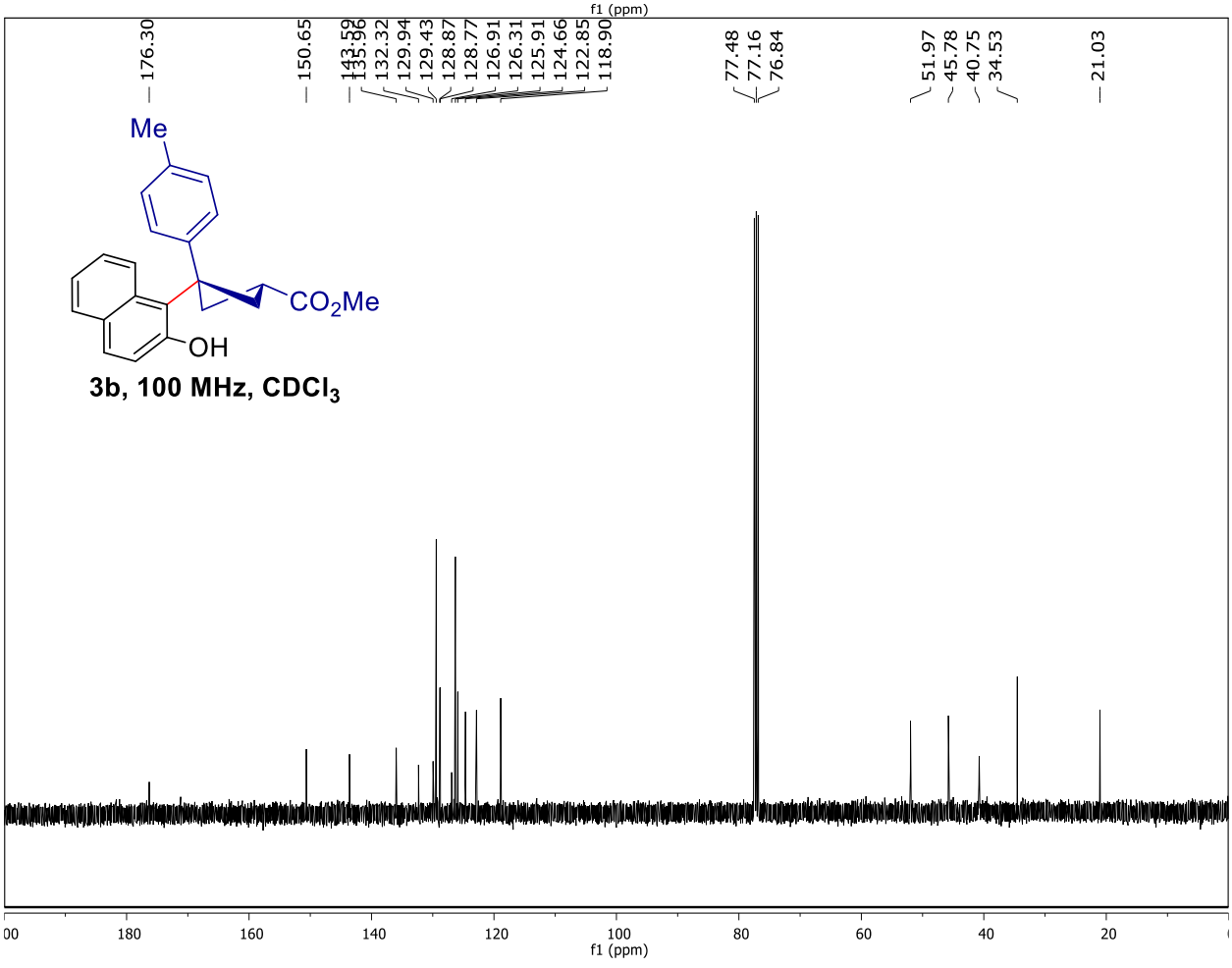


$^{1}H/^{13}C$ HMBC (400/100 MHz, $CDCl_3$)

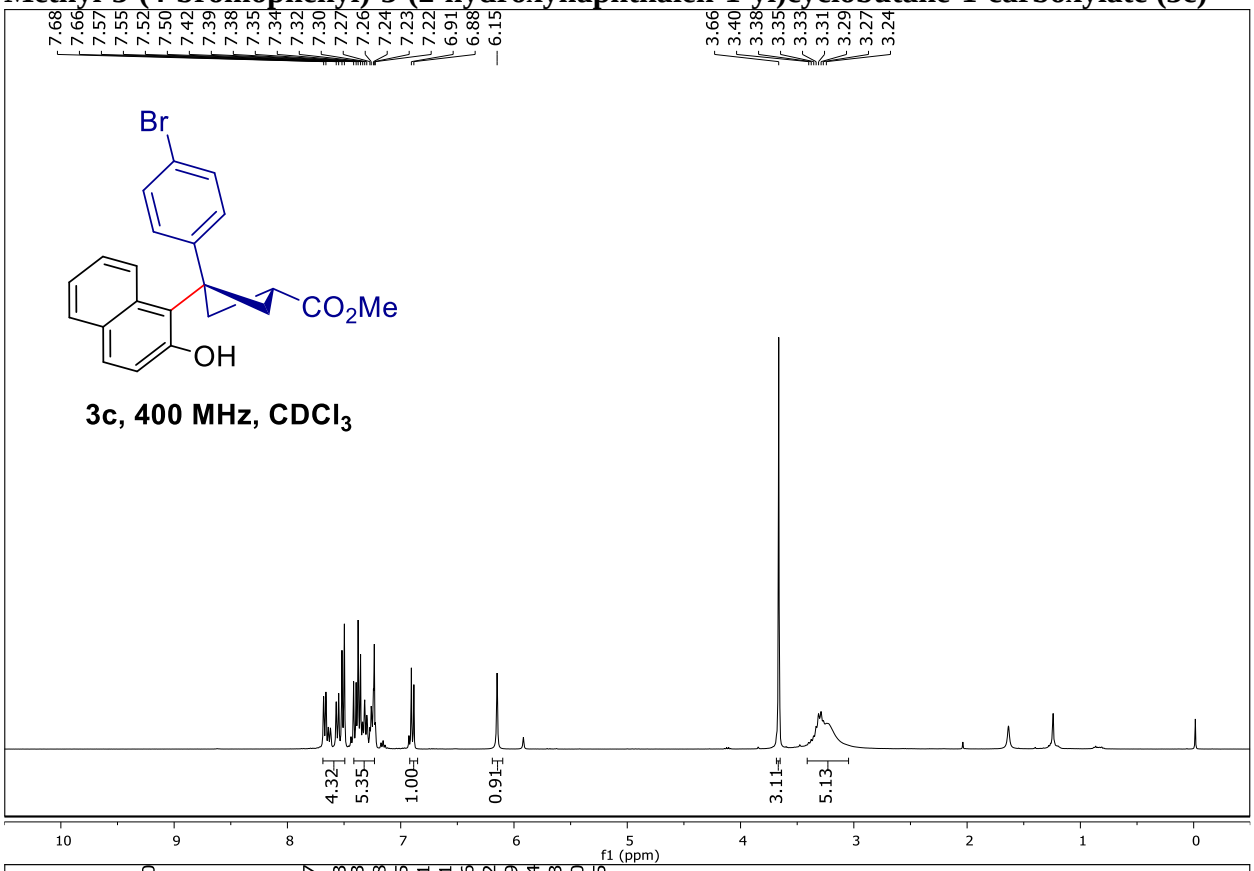


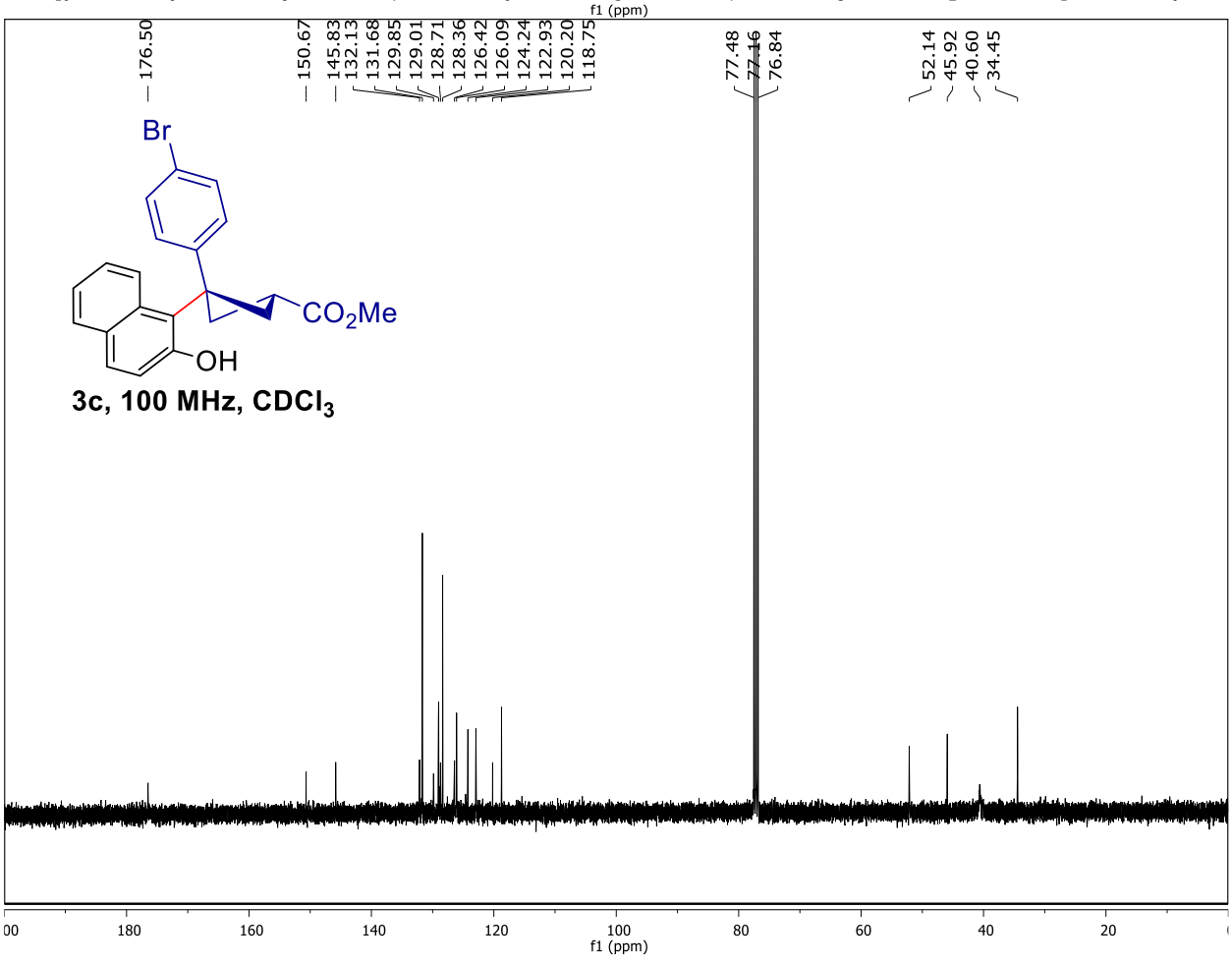
Methyl-3-(2-hydroxynaphthalen-1-yl)-3-(*p*-tolyl)cyclobutane-1-carboxylate (3b)



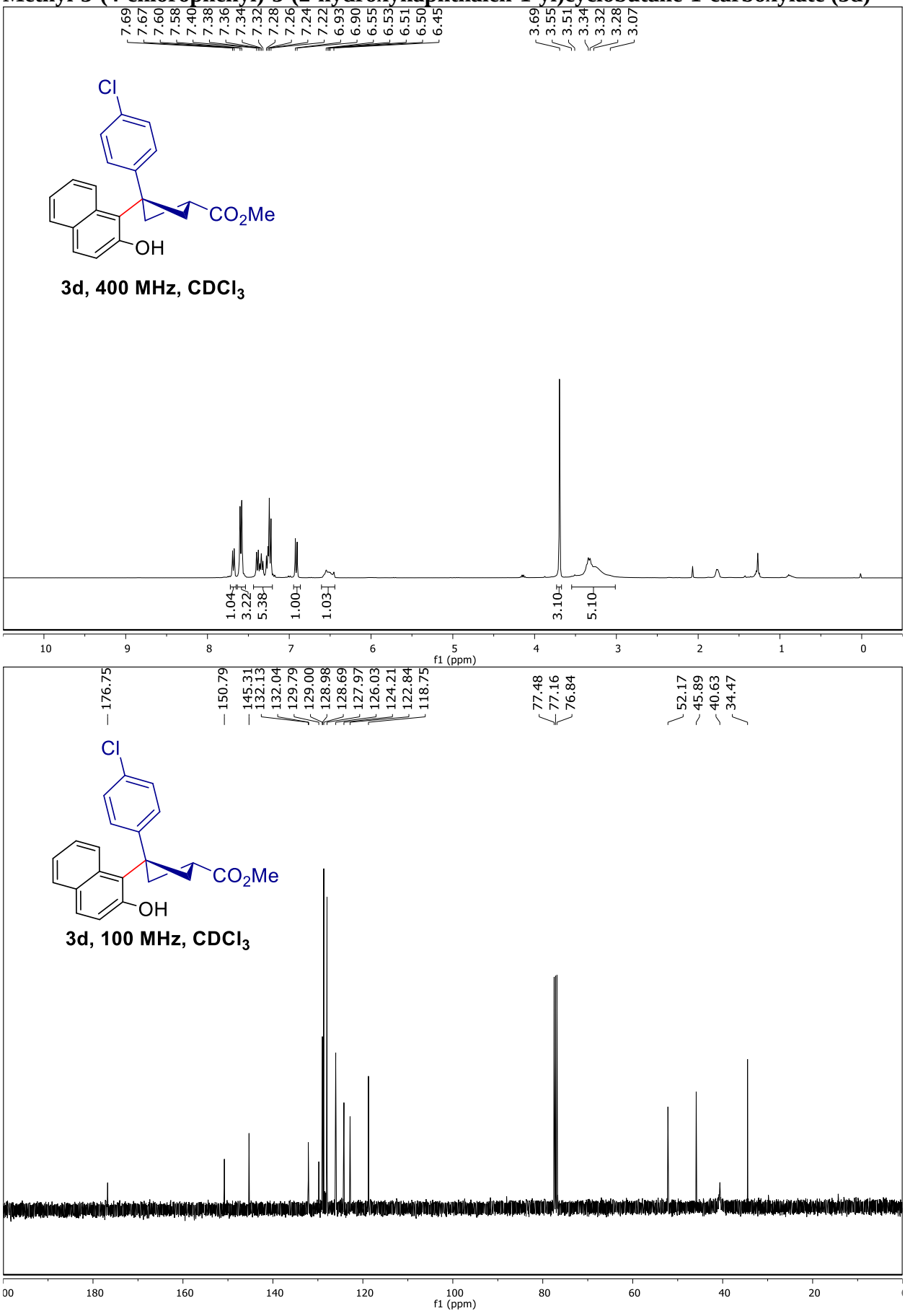


Methyl-3-(4-bromophenyl)-3-(2-hydroxynaphthalen-1-yl)cyclobutane-1-carboxylate (3c)

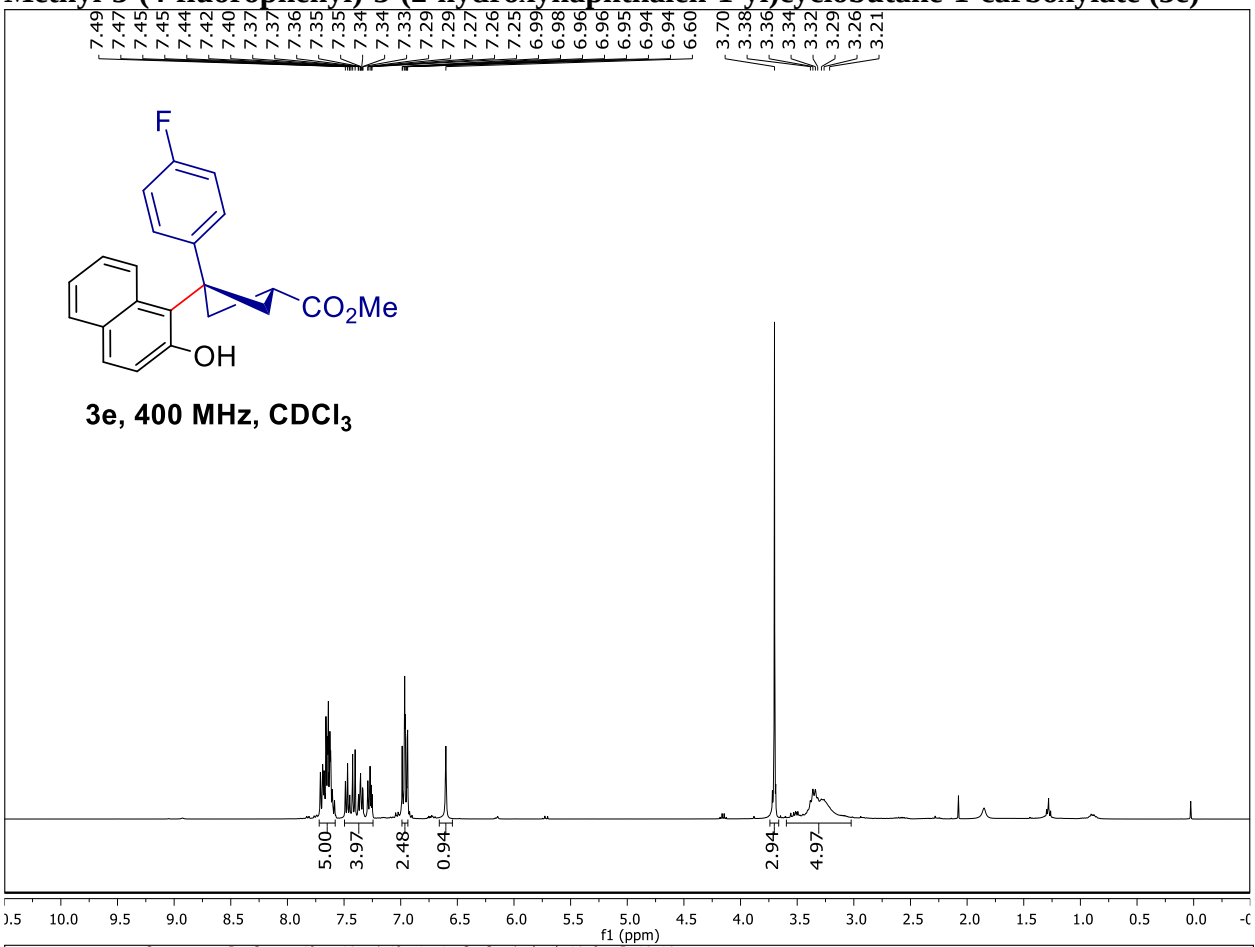


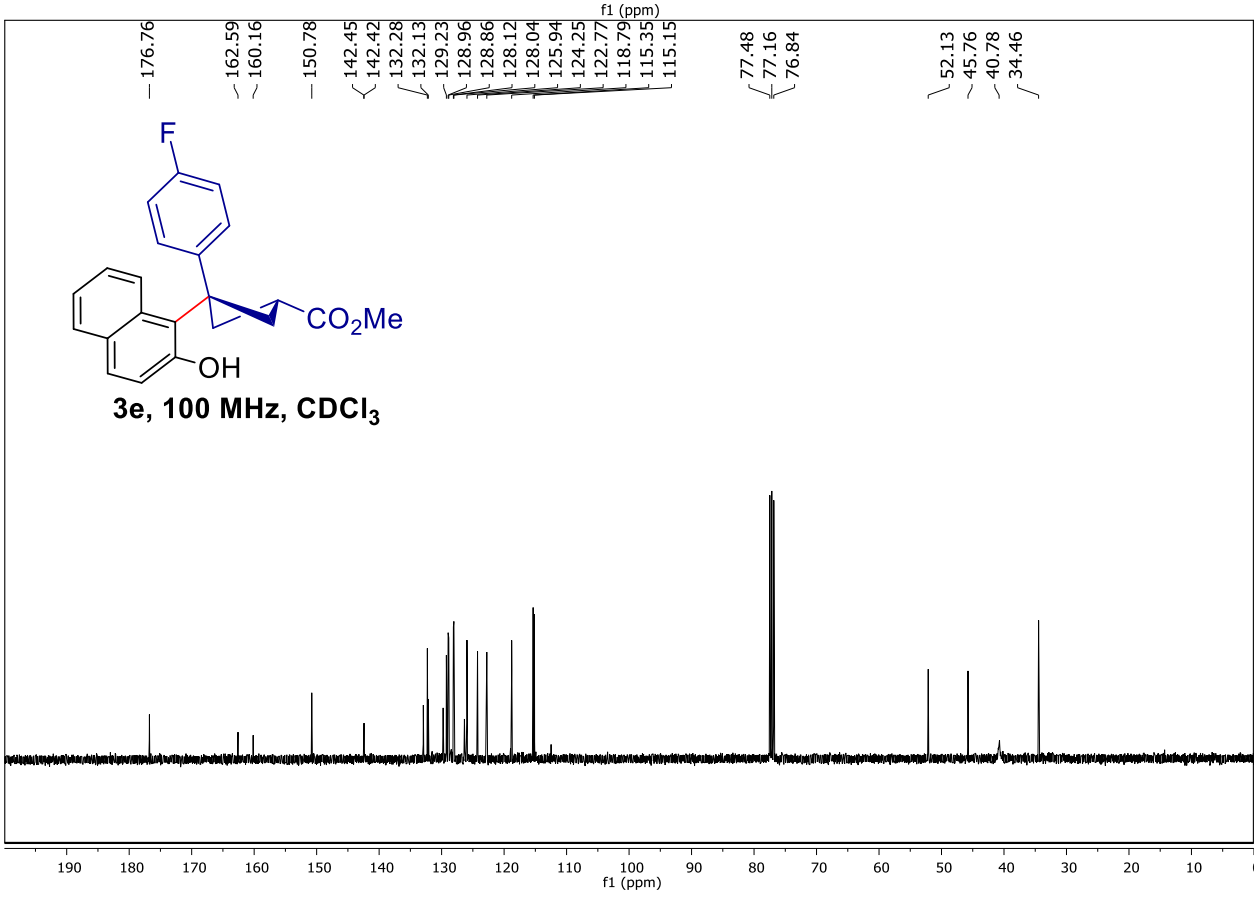


Methyl-3-(4-chlorophenyl)-3-(2-hydroxynaphthalen-1-yl)cyclobutane-1-carboxylate (3d)

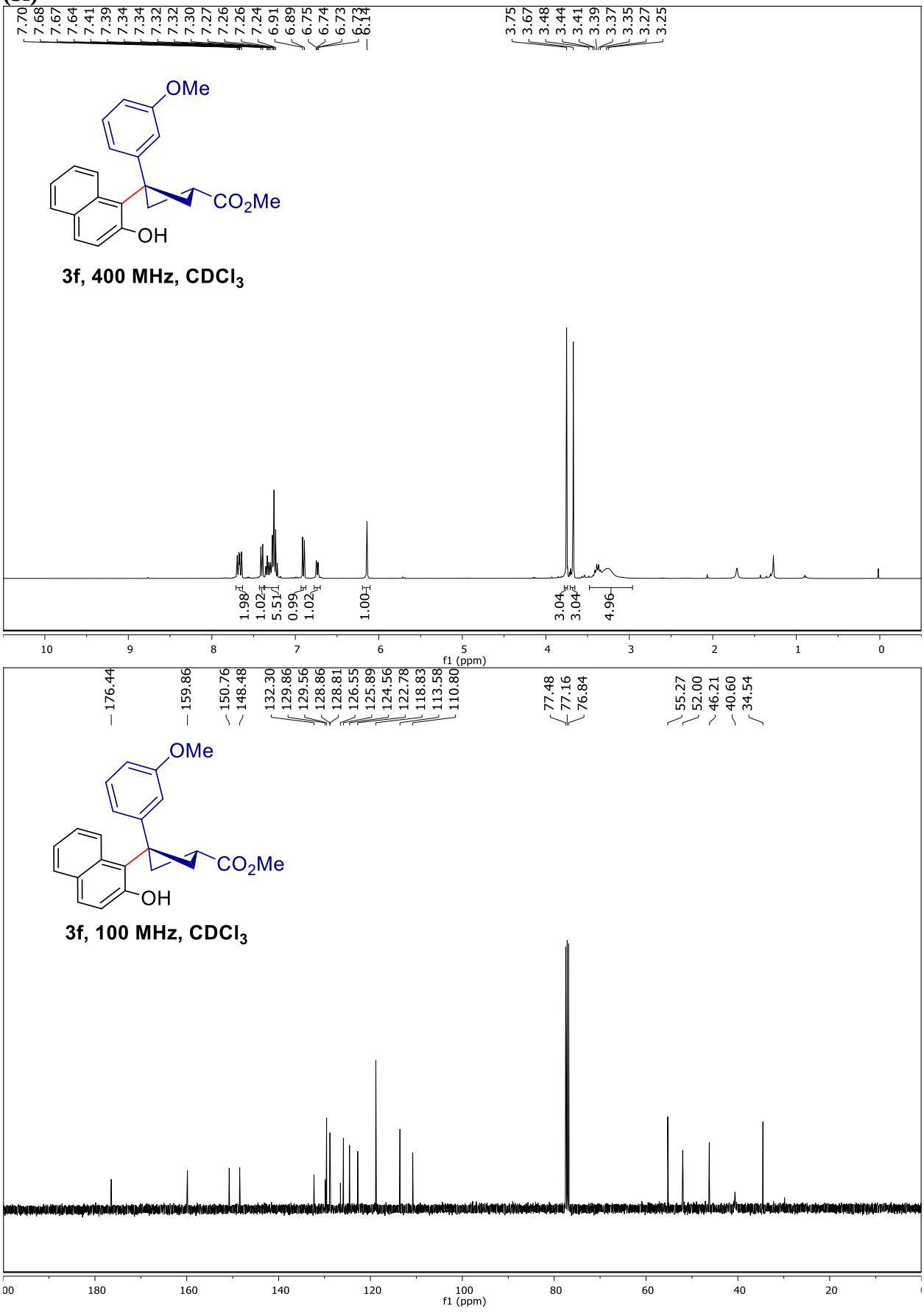


Methyl-3-(4-fluorophenyl)-3-(2-hydroxynaphthalen-1-yl)cyclobutane-1-carboxylate (3e)

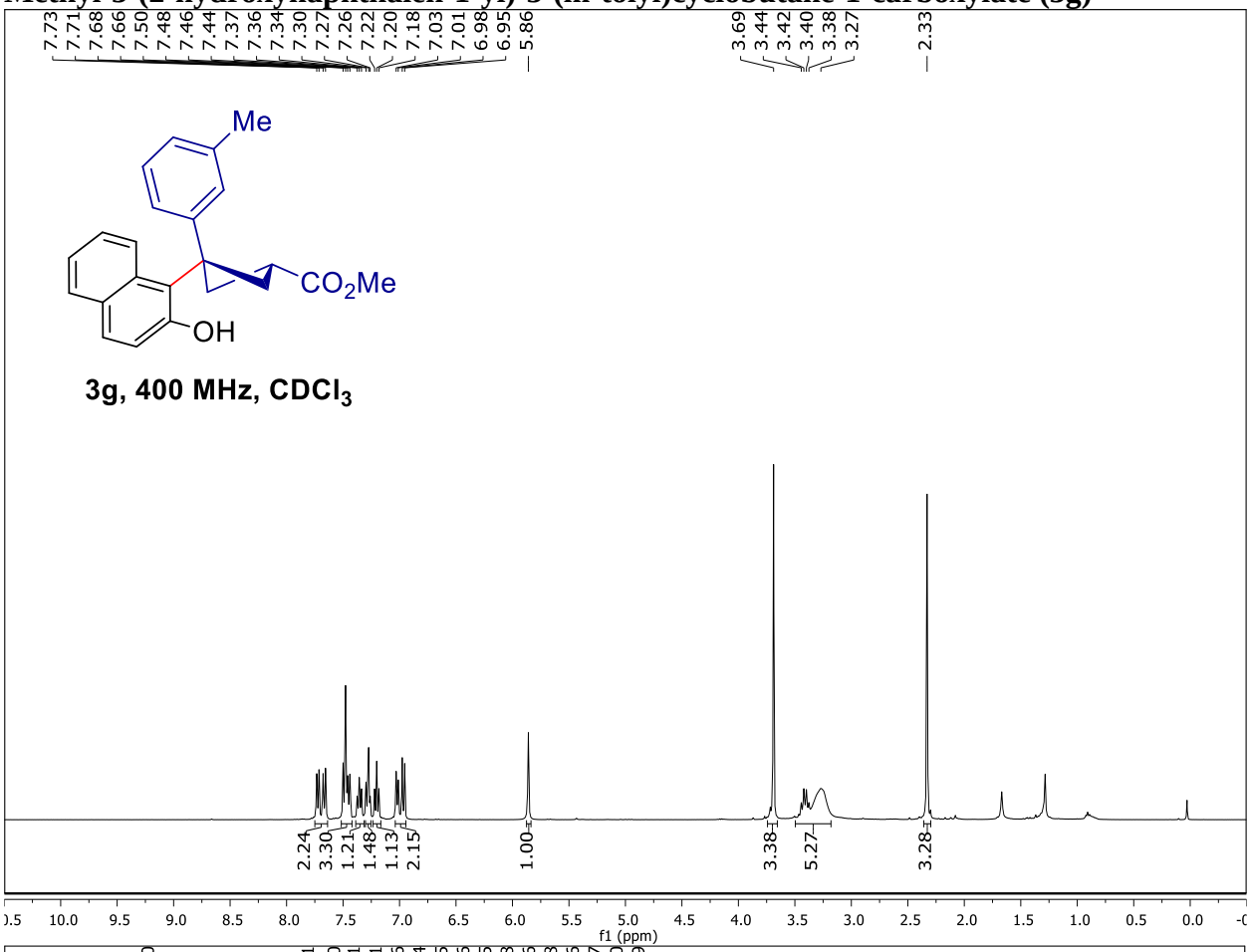


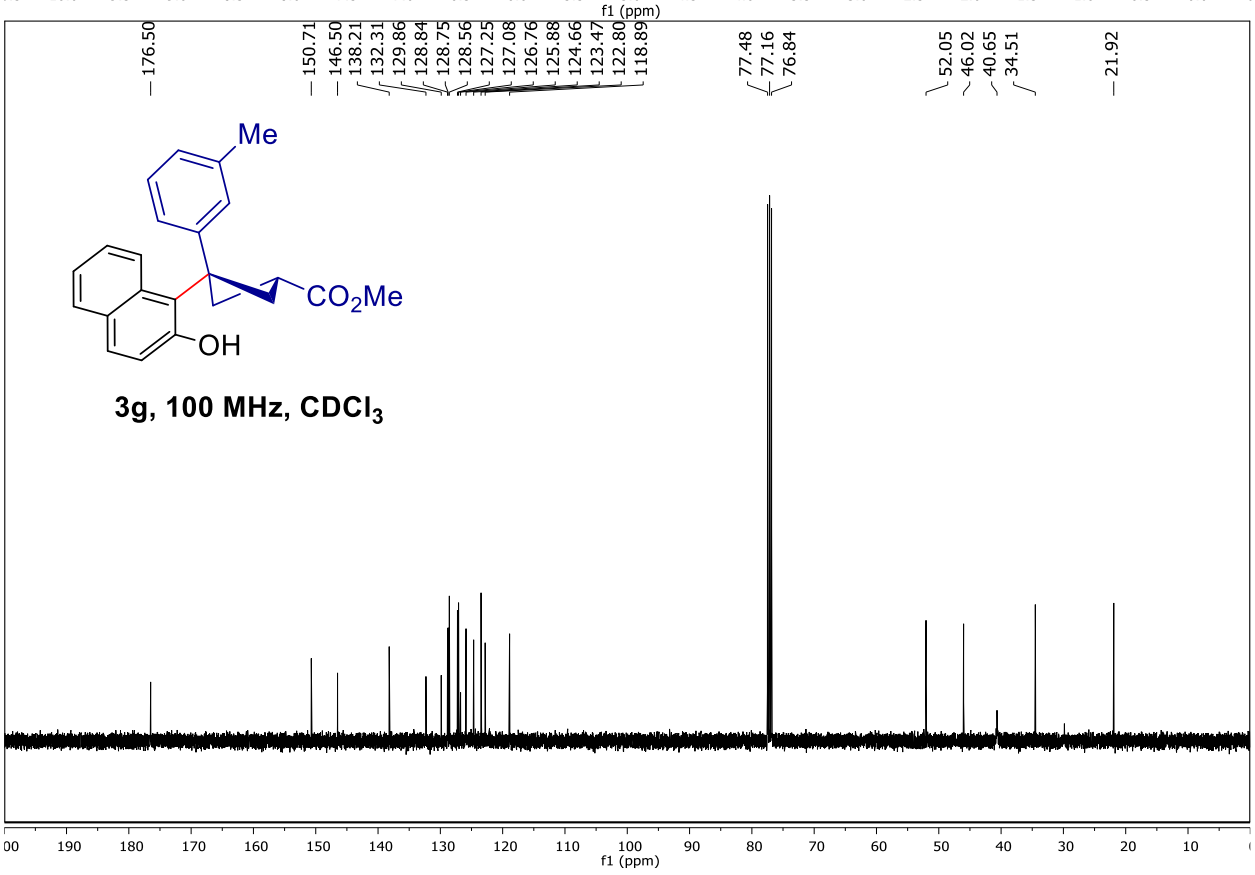


Methyl-3-(2-hydroxynaphthalen-1-yl)-3-(3-methoxyphenyl)cyclobutane-1-carboxylate (3f)

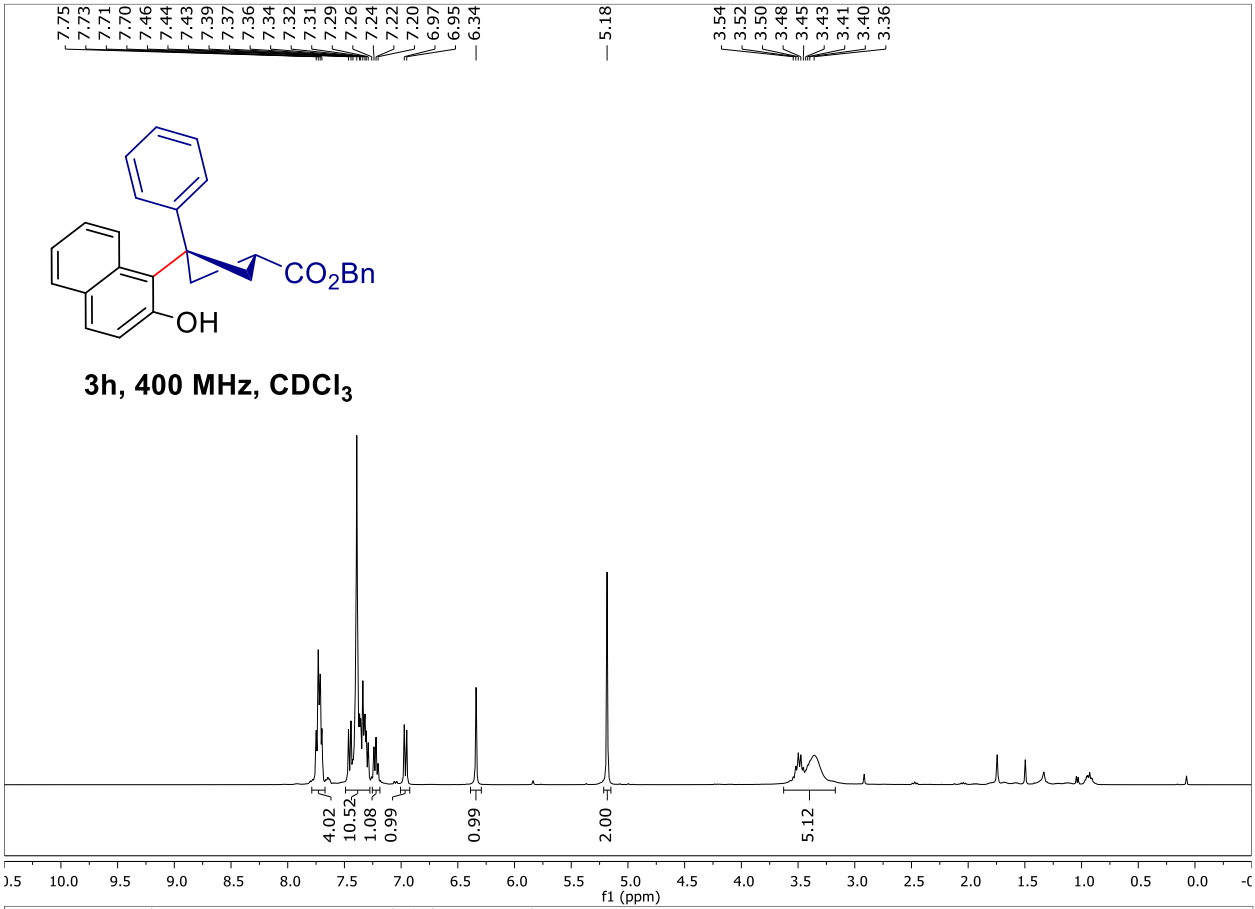


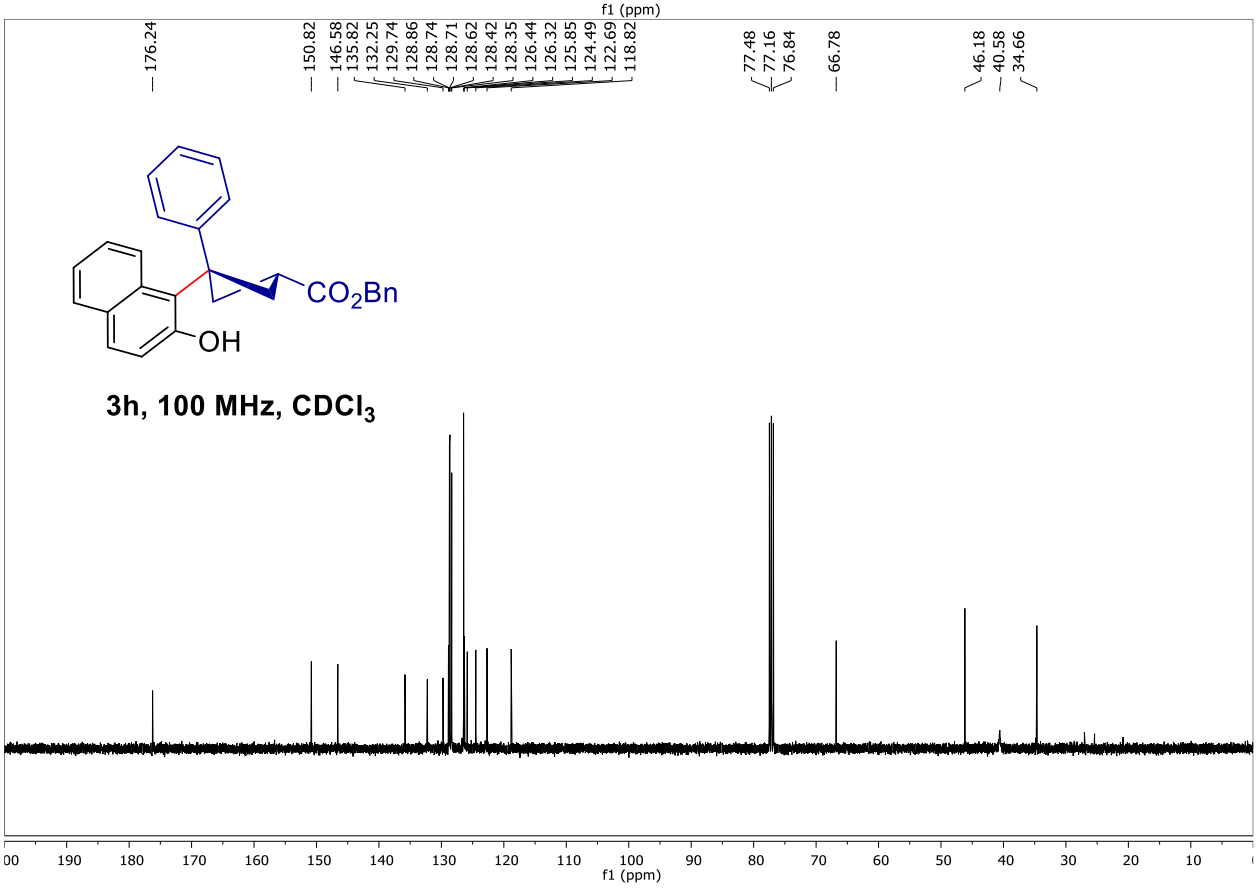
Methyl-3-(2-hydroxynaphthalen-1-yl)-3-(m-tolyl)cyclobutane-1-carboxylate (3g)



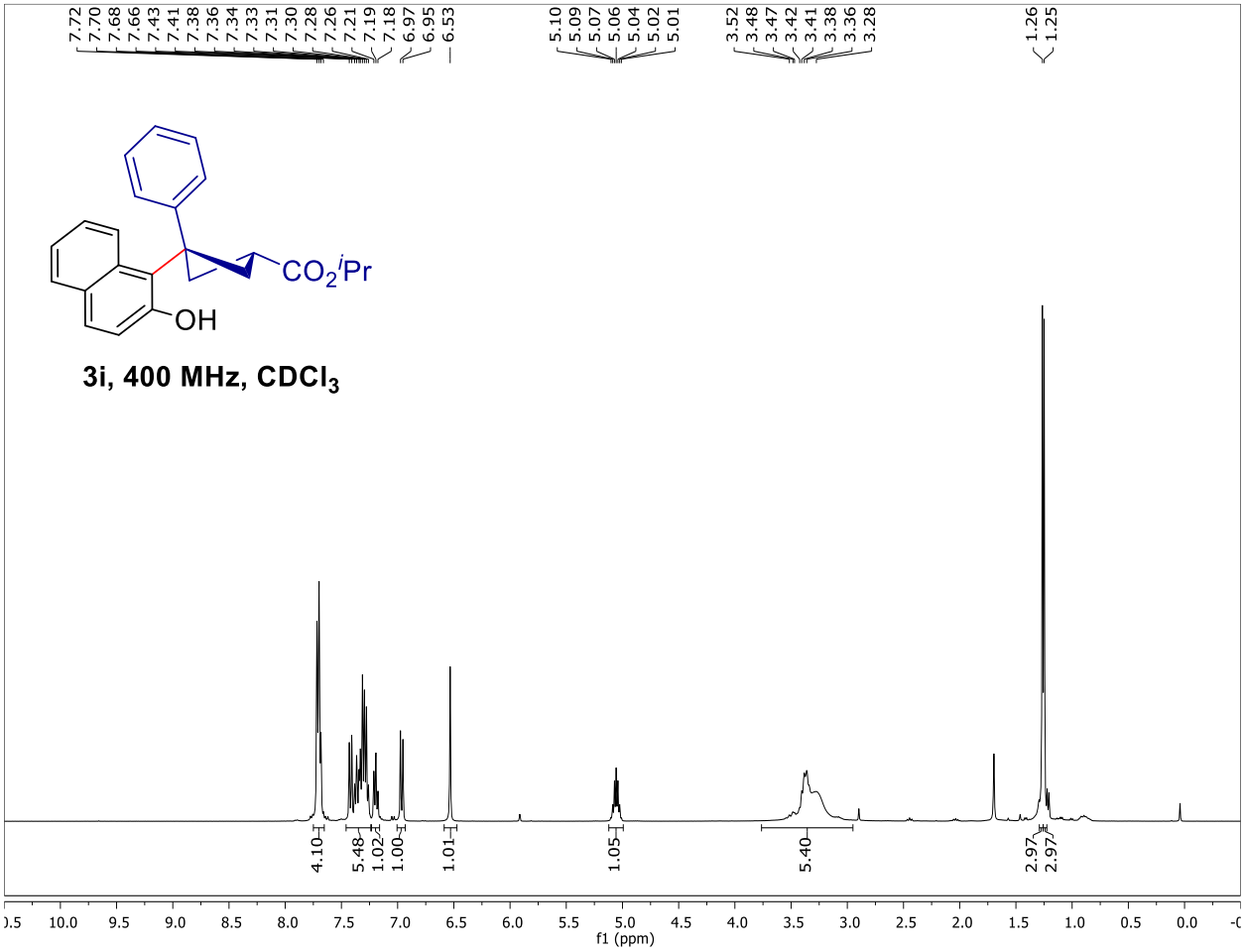


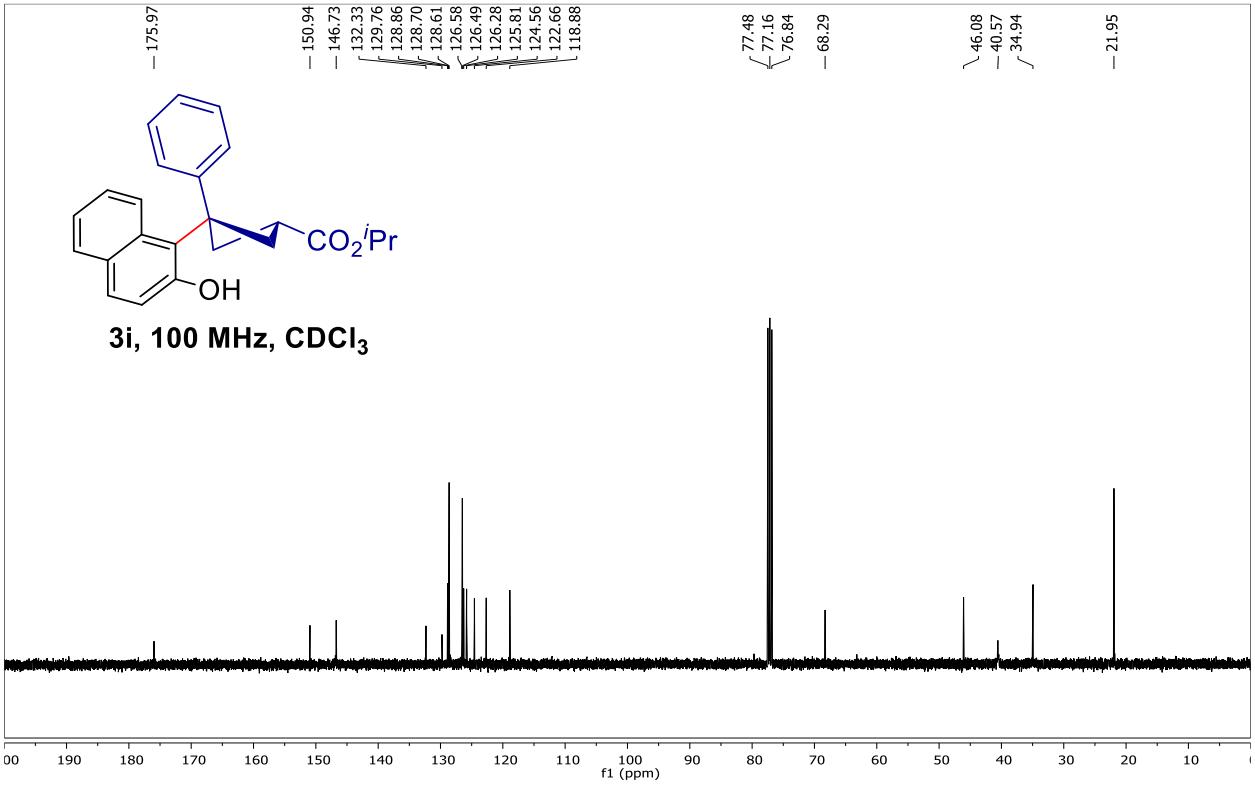
Benzyl 3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3h)



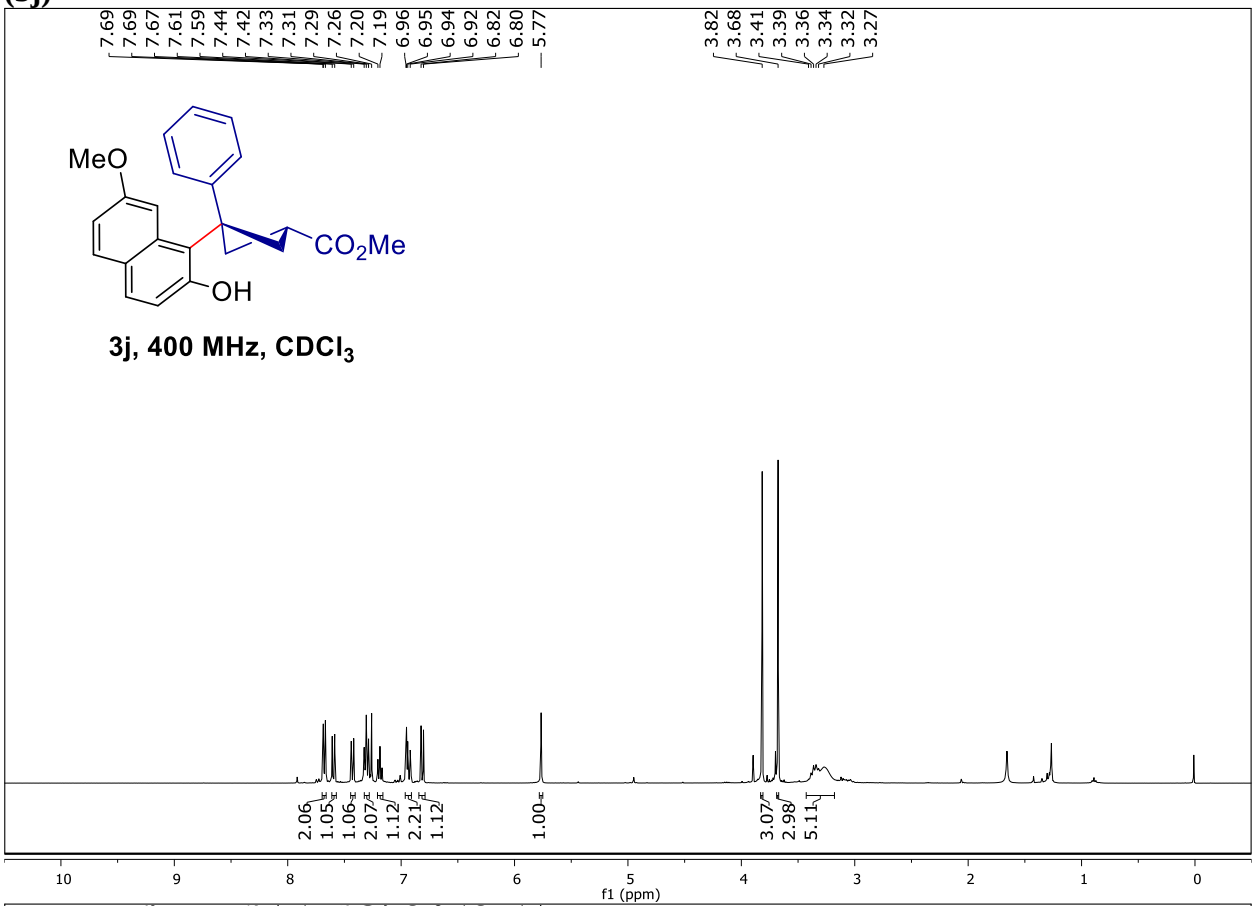


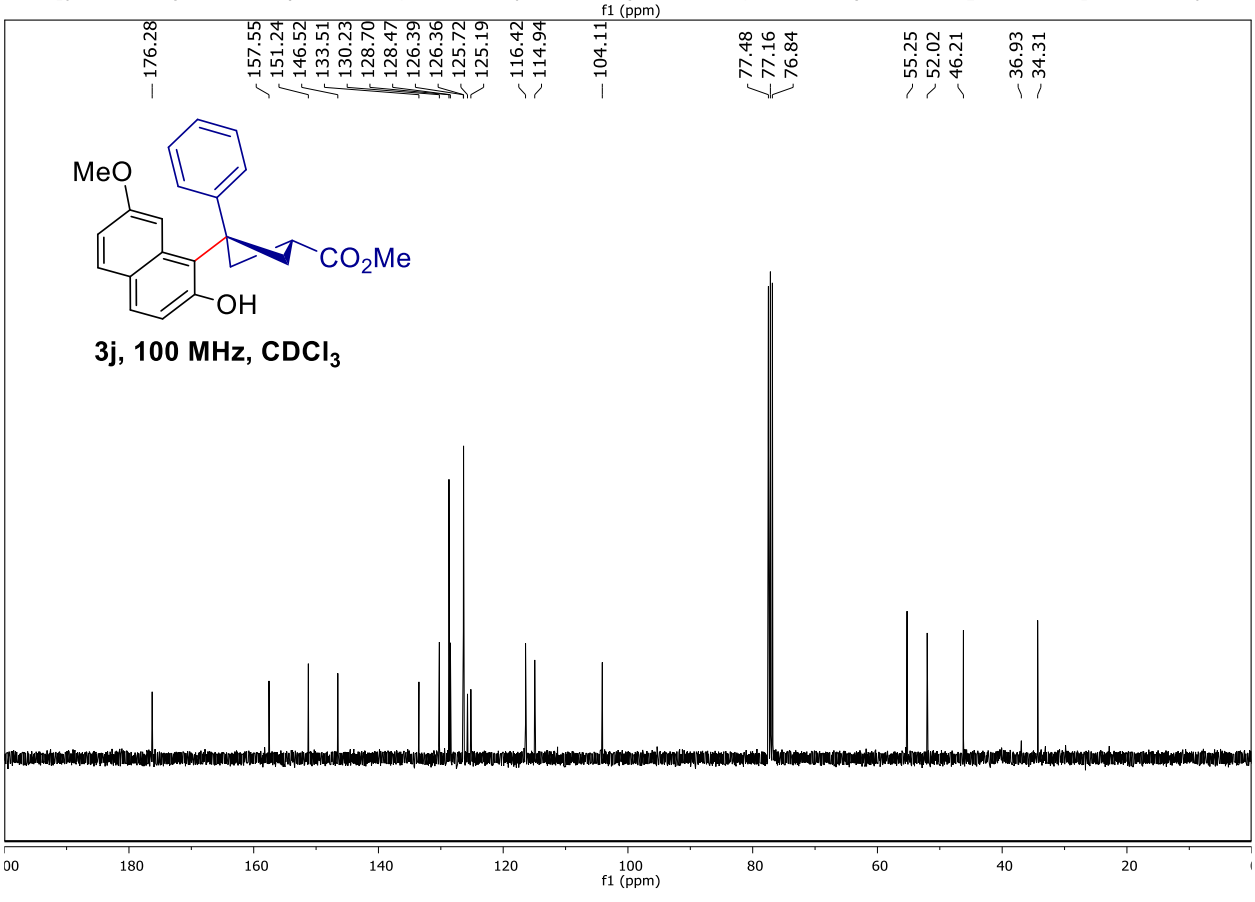
Isopropyl 3-(2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3i)



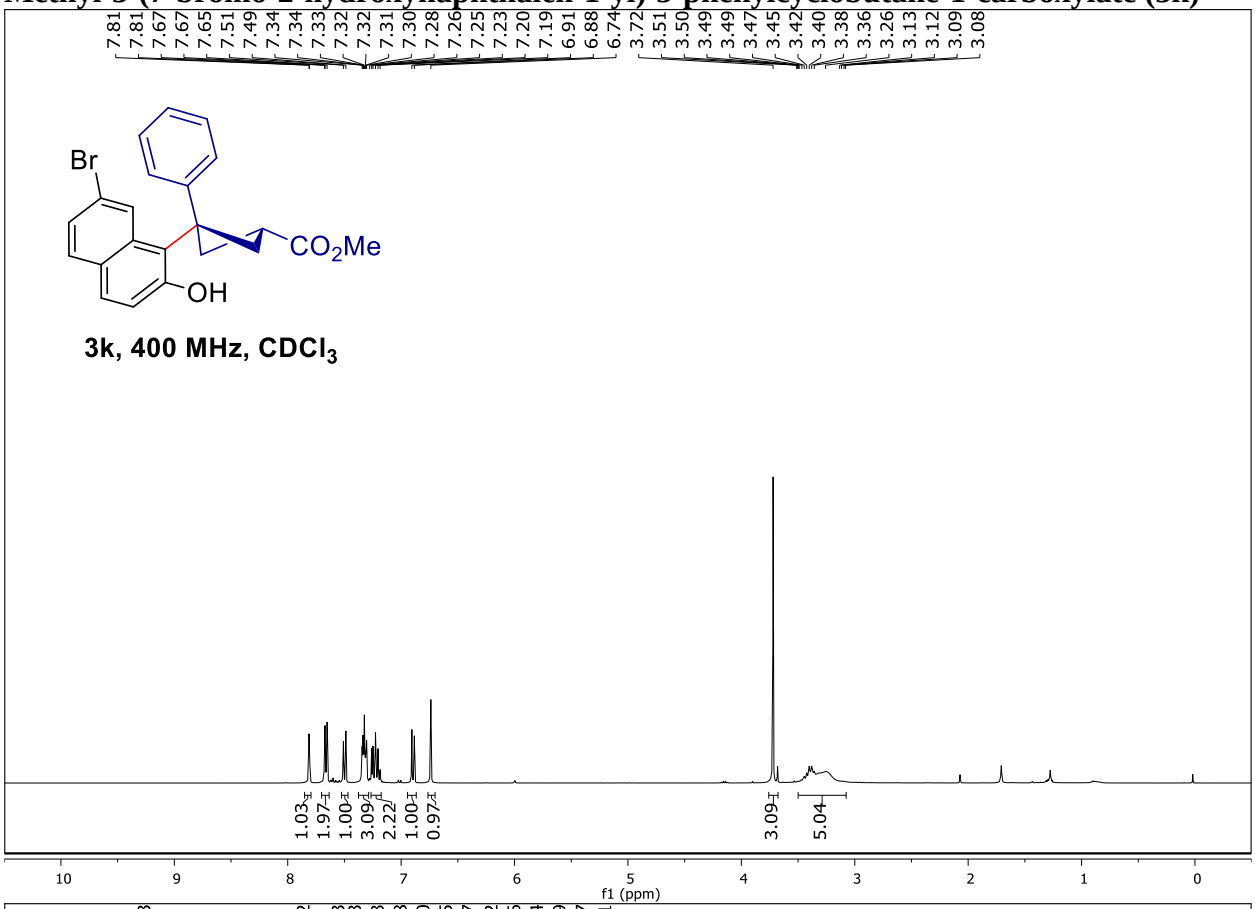


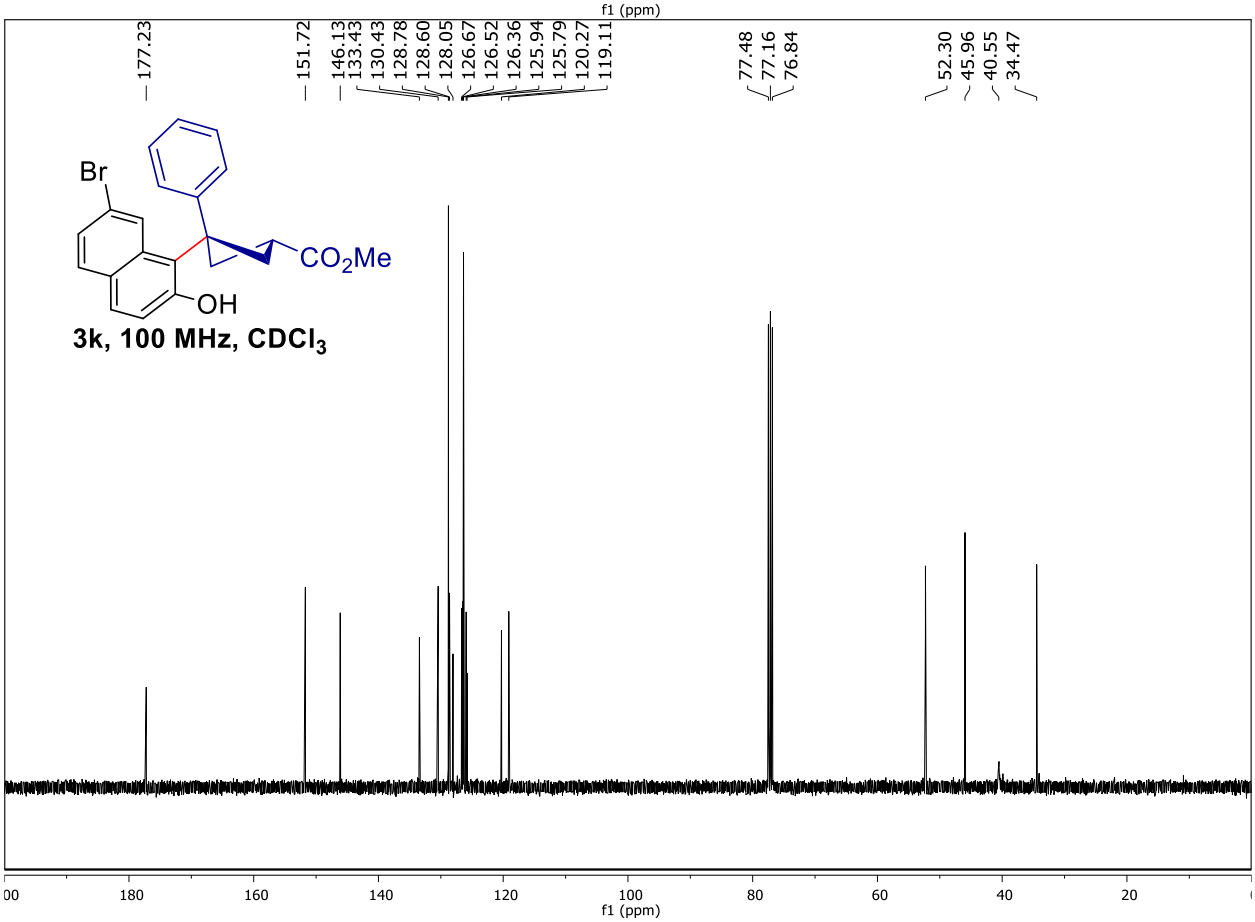
Methyl-3-(2-hydroxy-7-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3j)



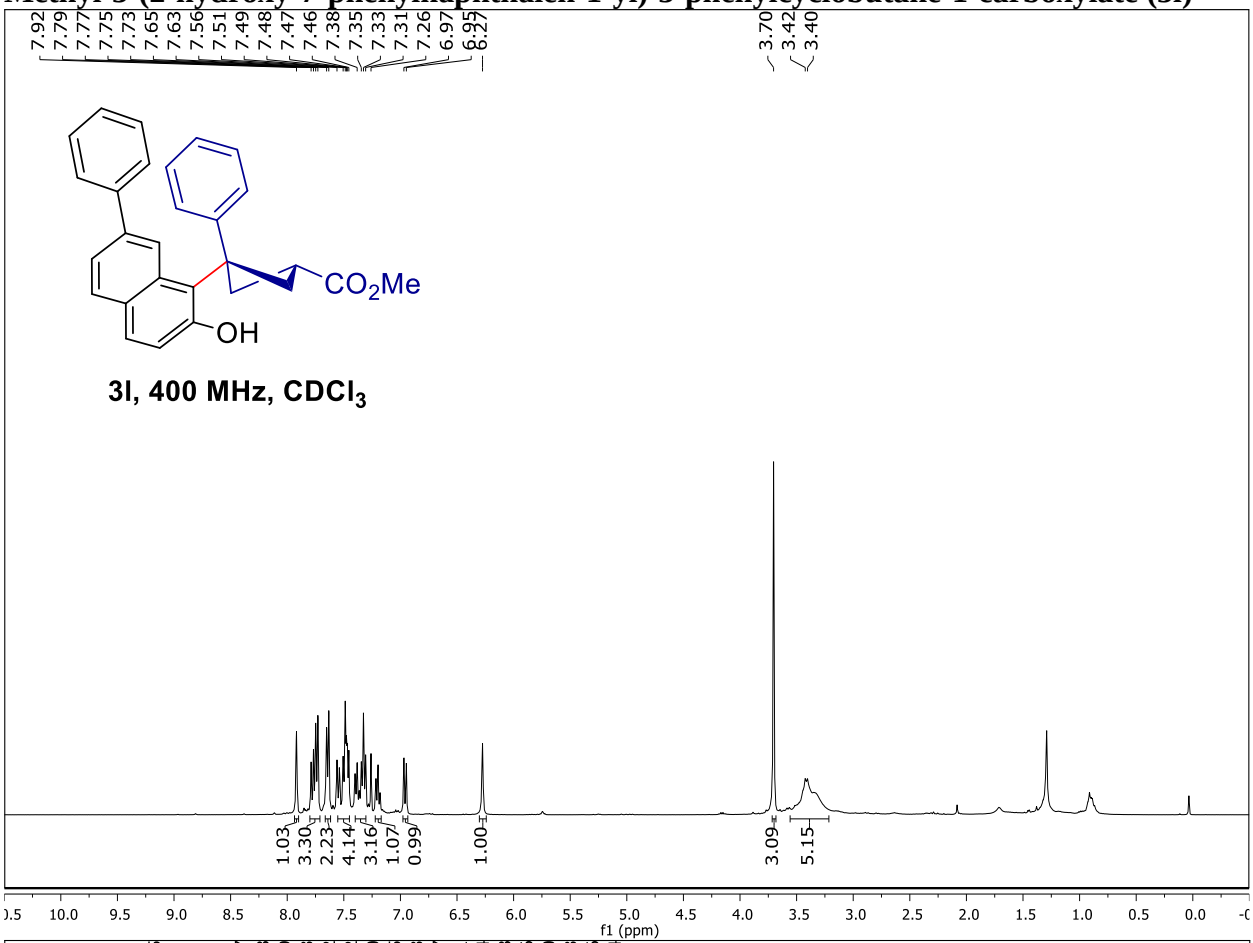


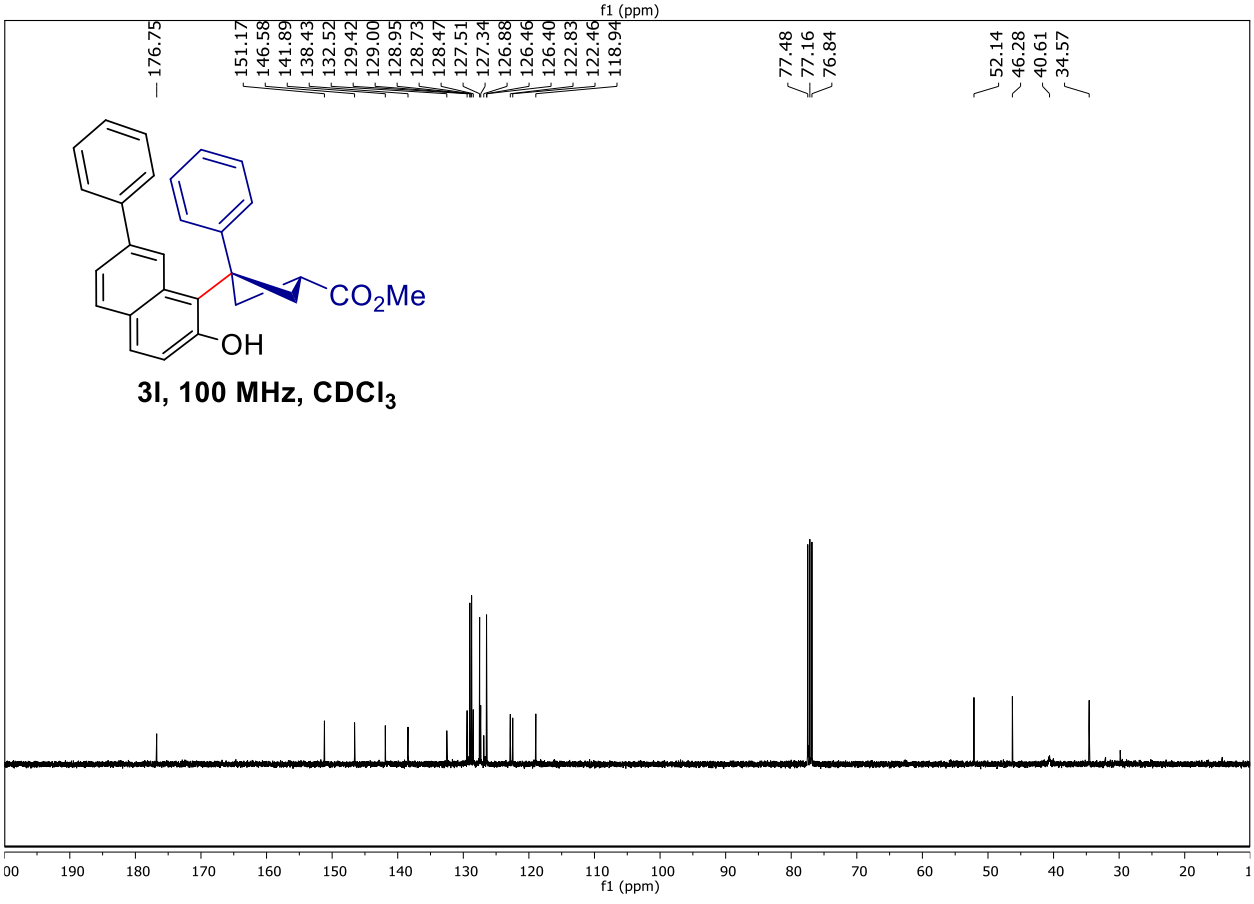
Methyl-3-(7-bromo-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3k)



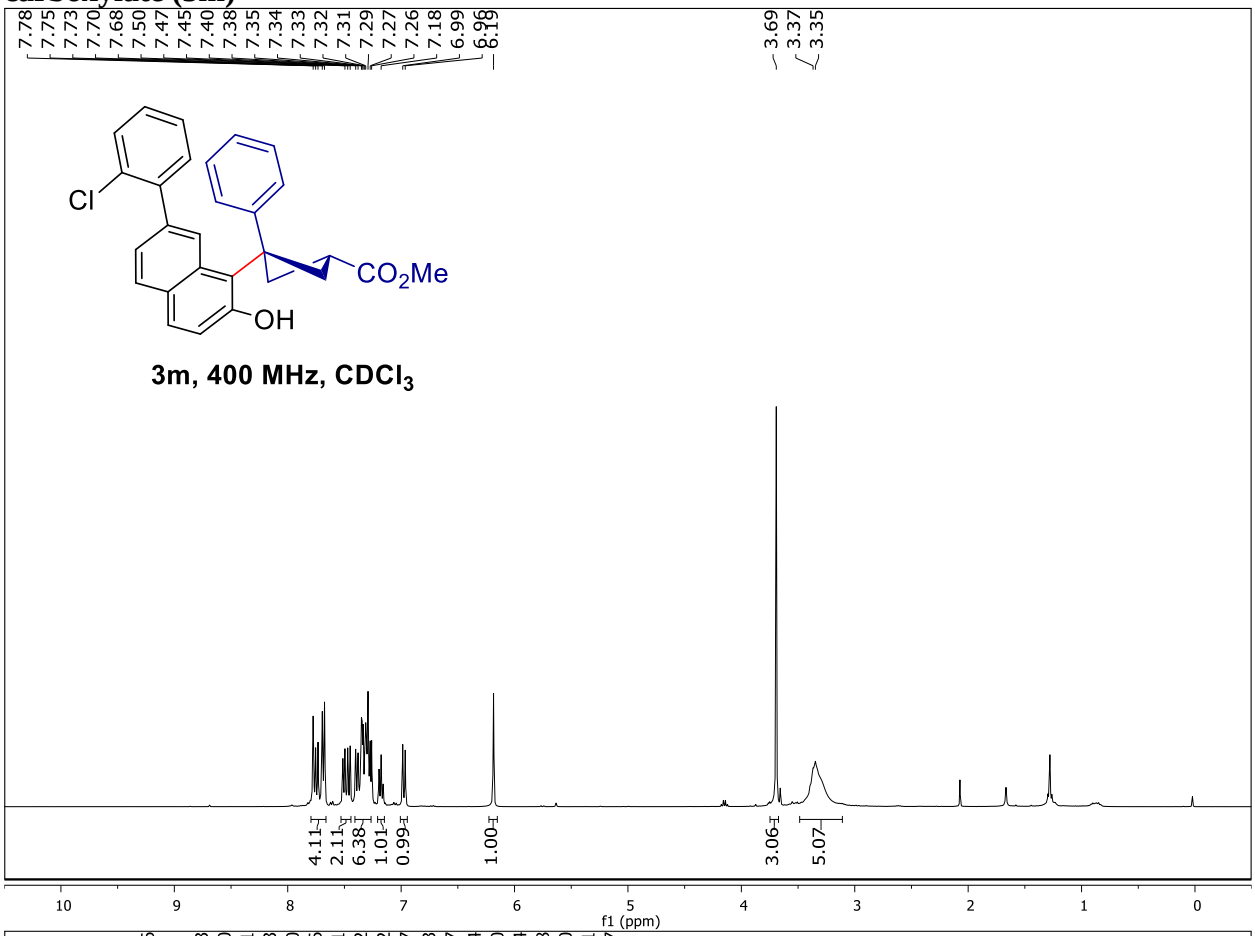


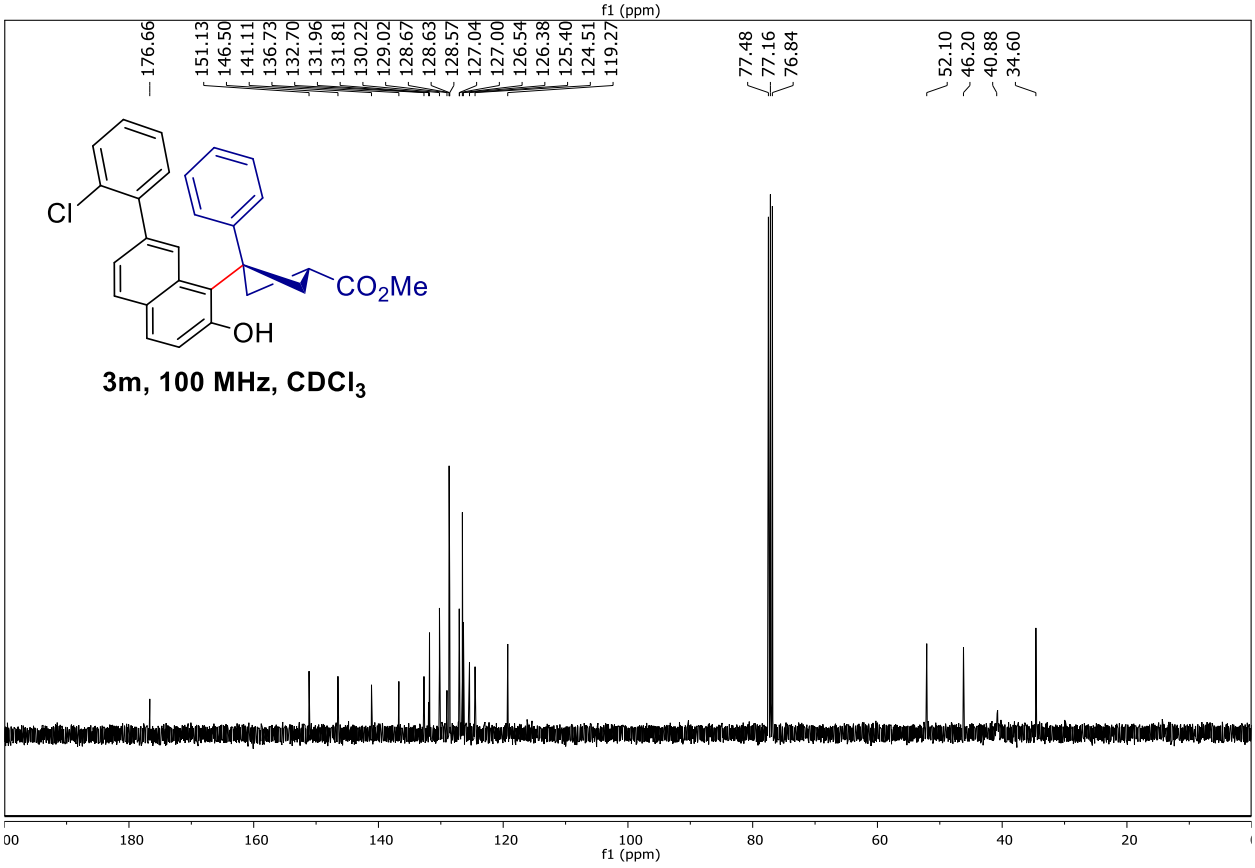
Methyl-3-(2-hydroxy-7-phenylnaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3l)



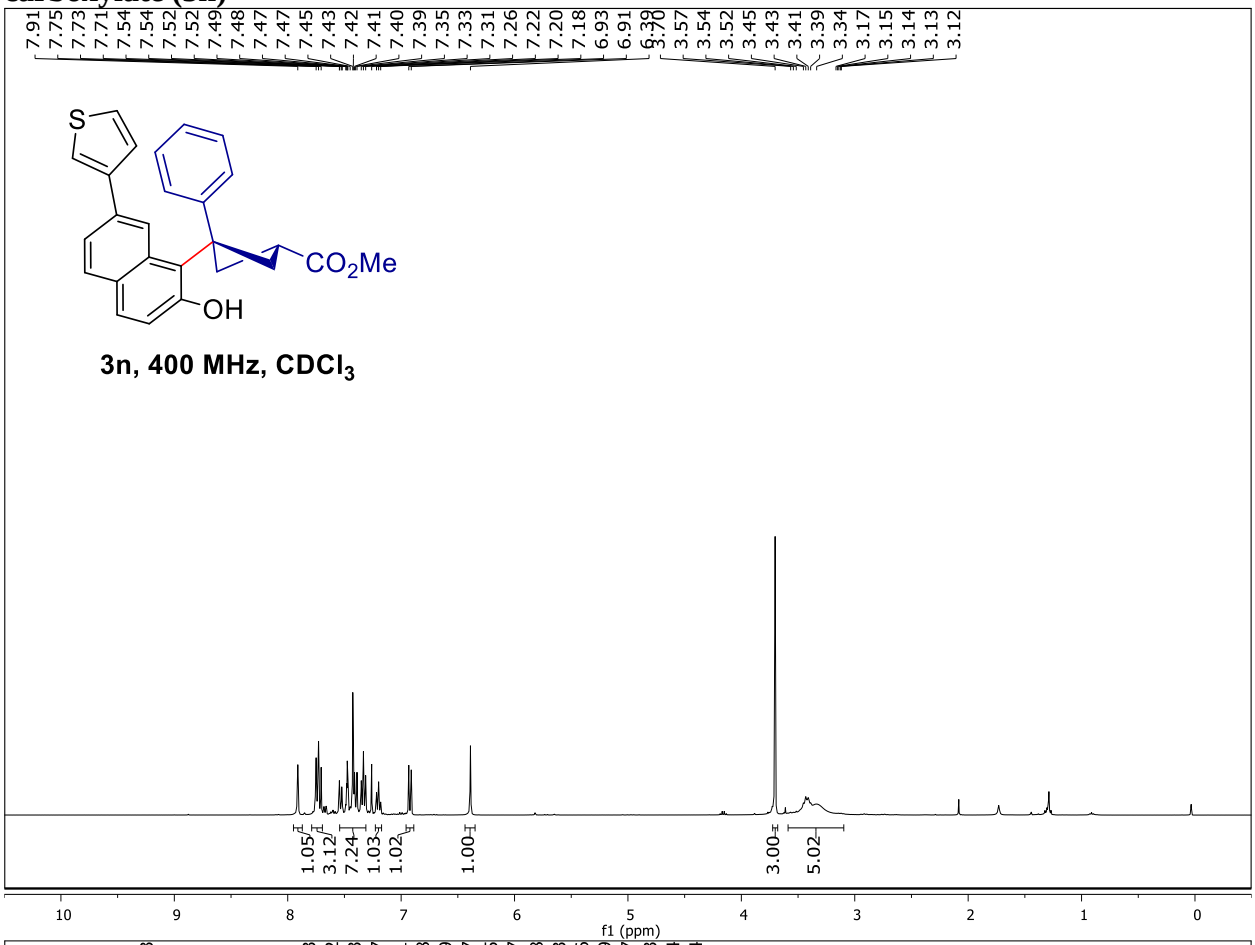


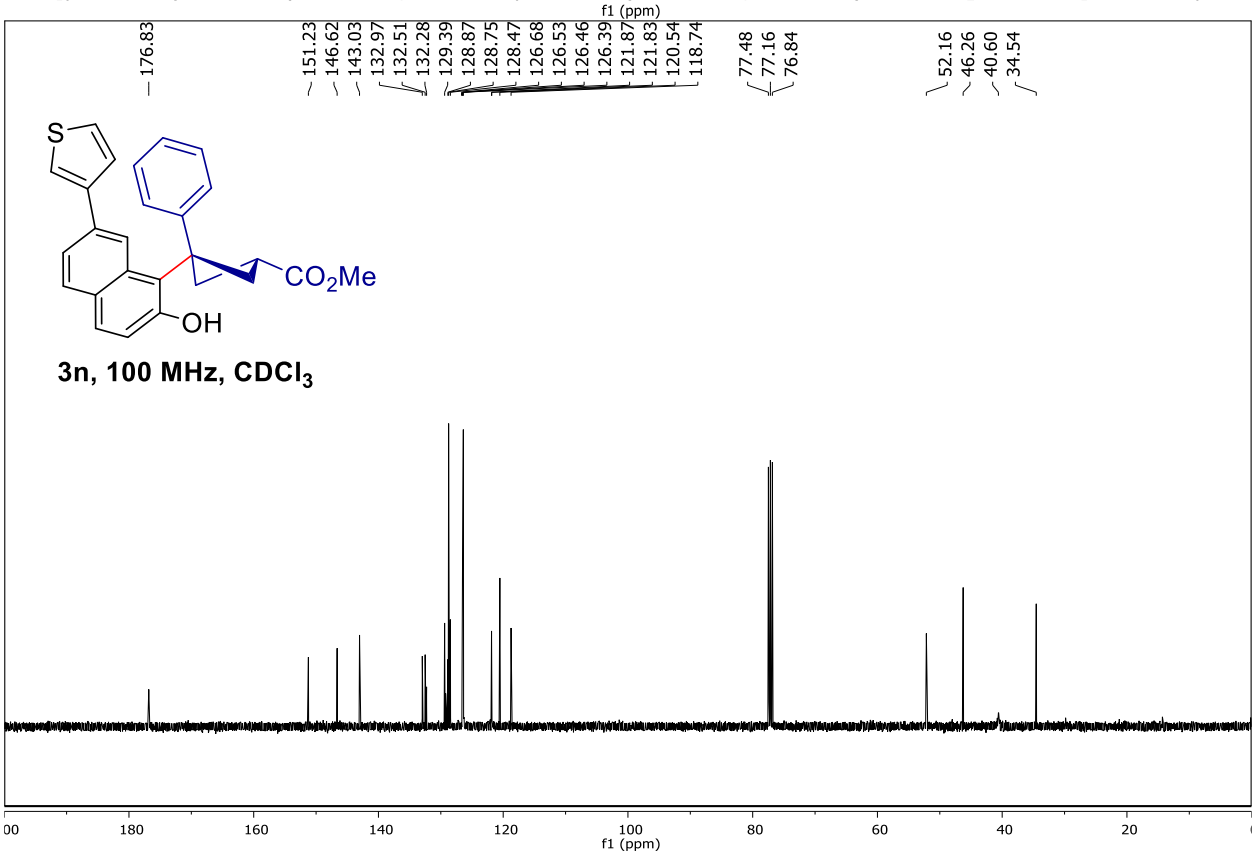
Methyl-3-(7-(2-chlorophenyl)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3m)



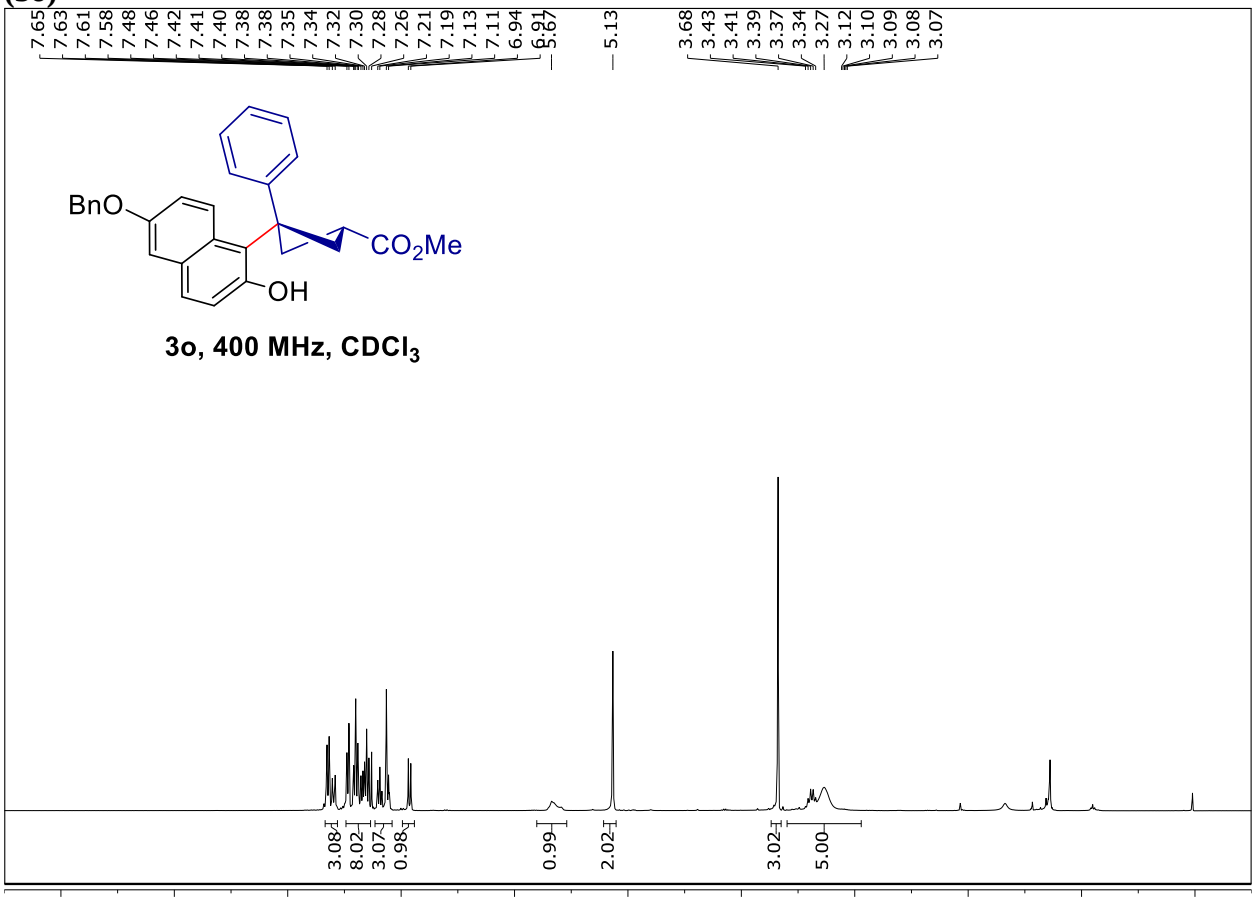


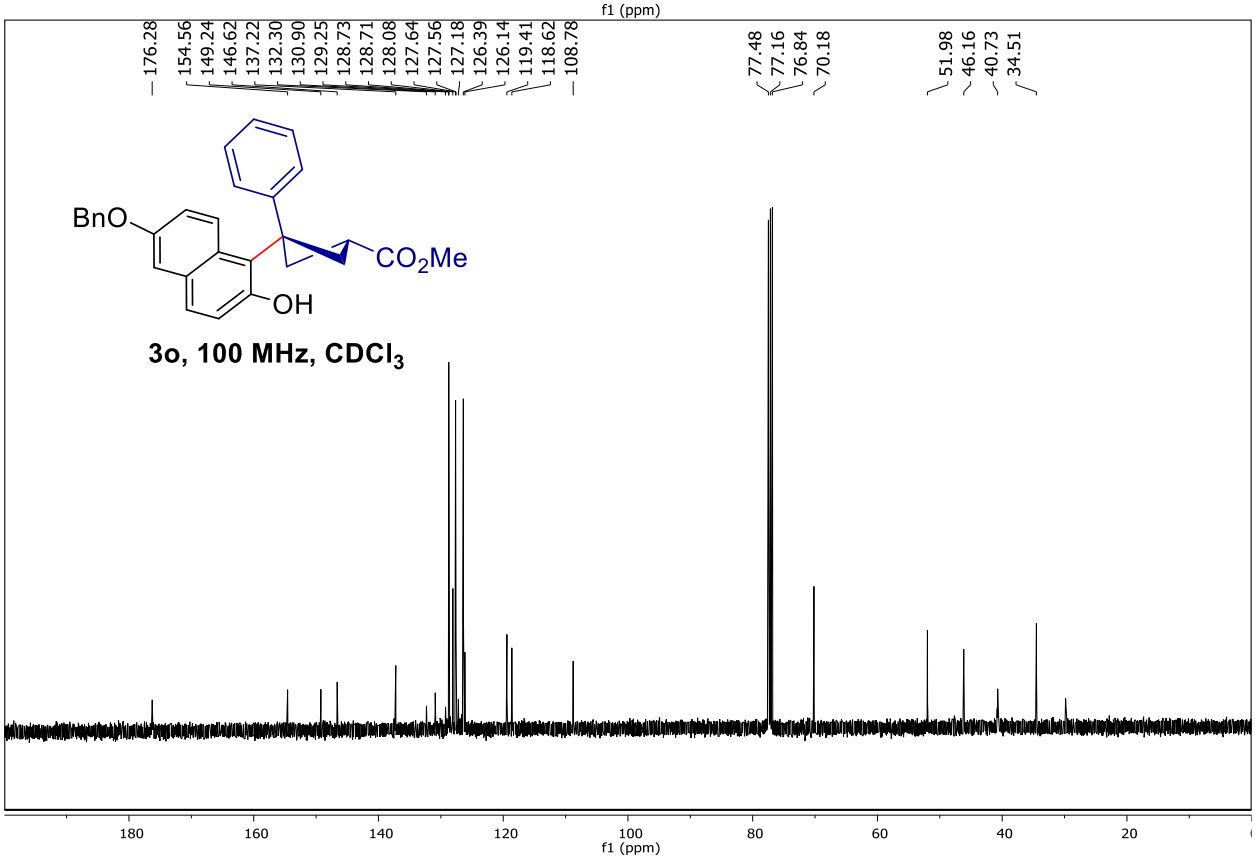
Methyl-3-(2-hydroxy-7-(thiophen-3-yl)naphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3n)



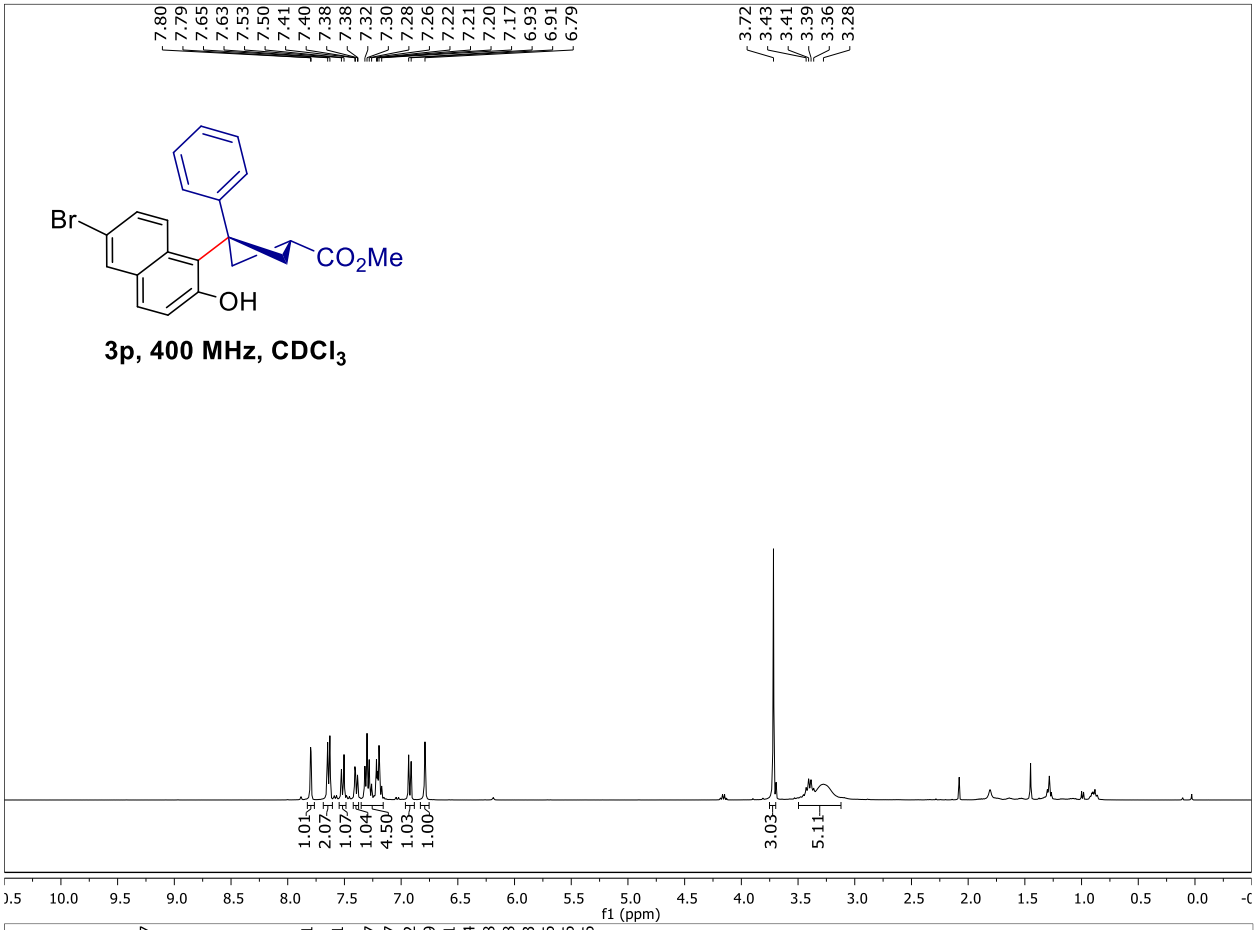


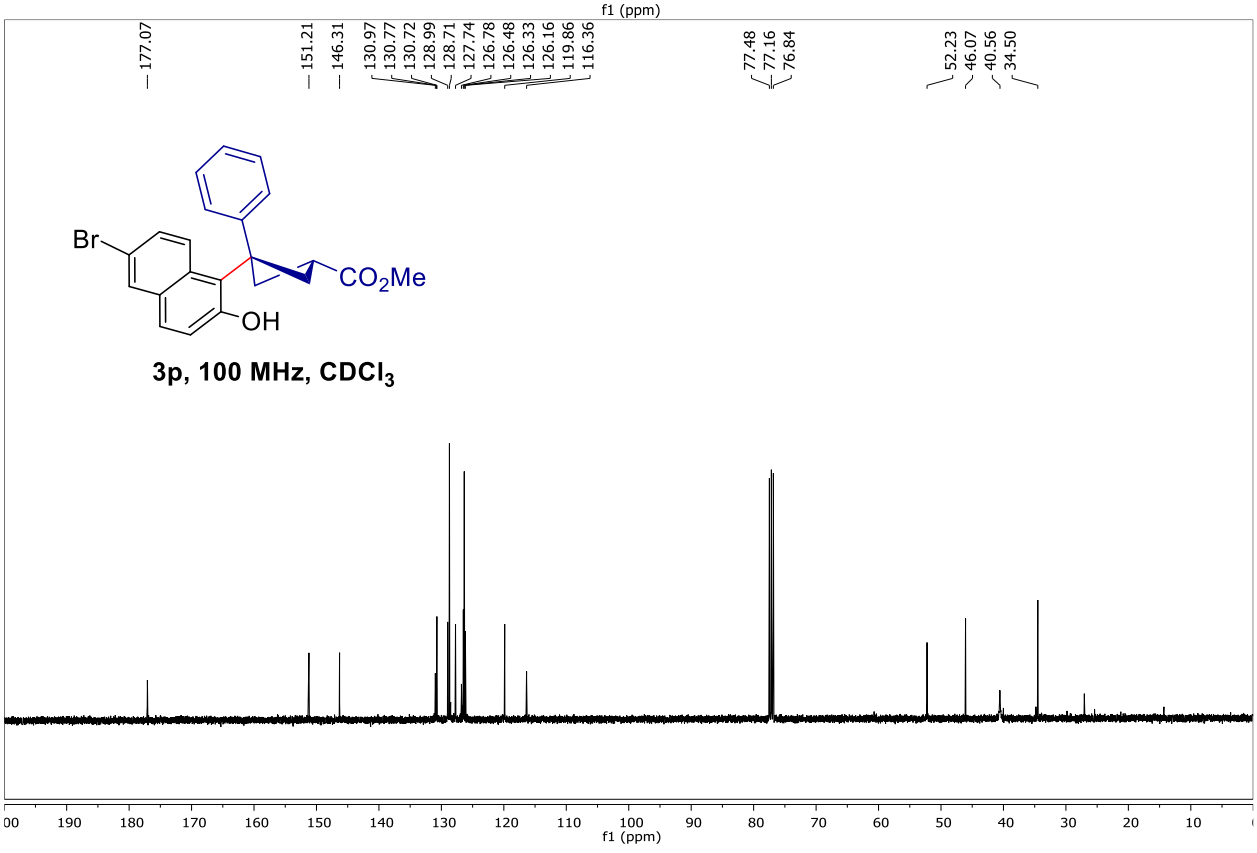
Methyl-3-(6-(benzyloxy)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3o)



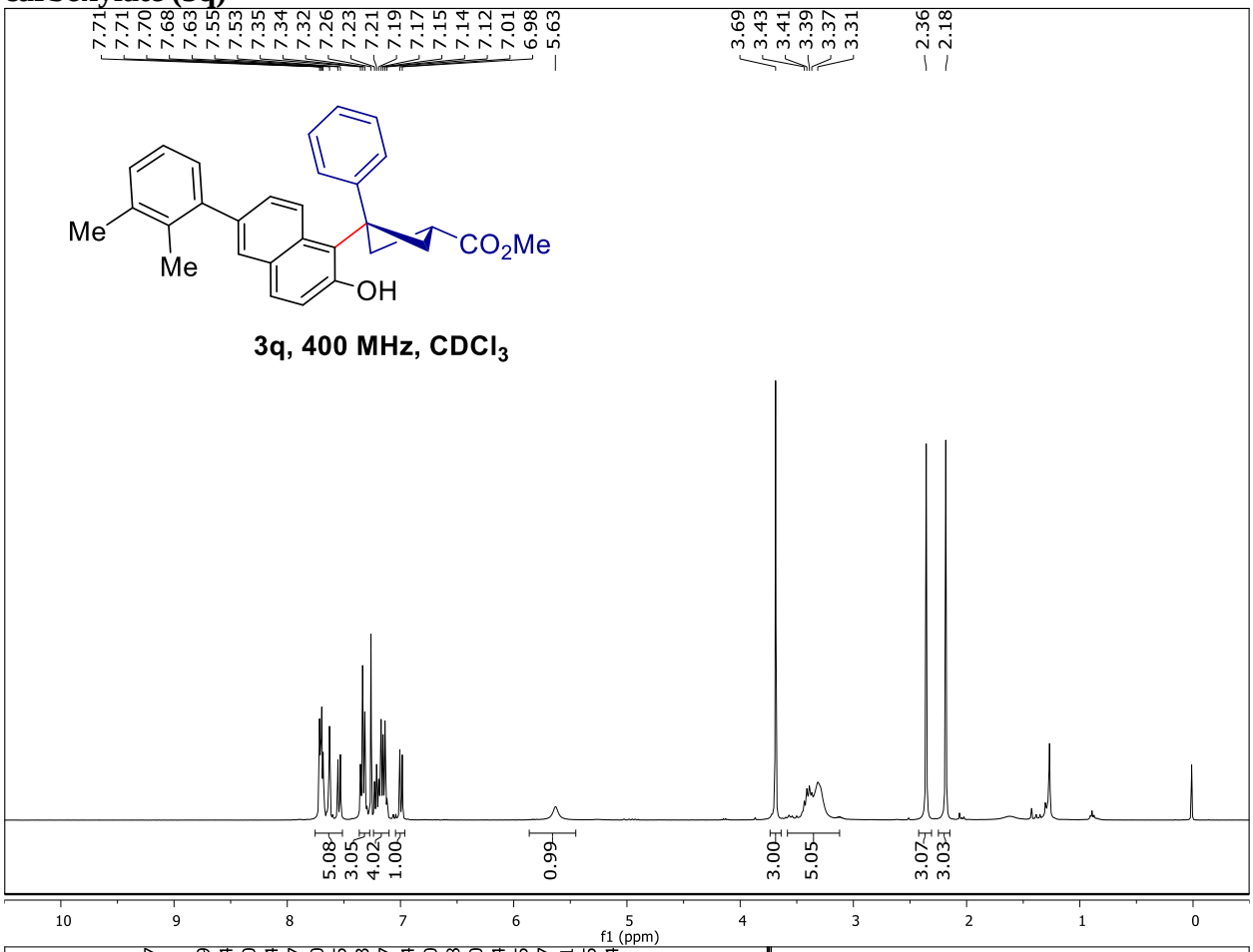


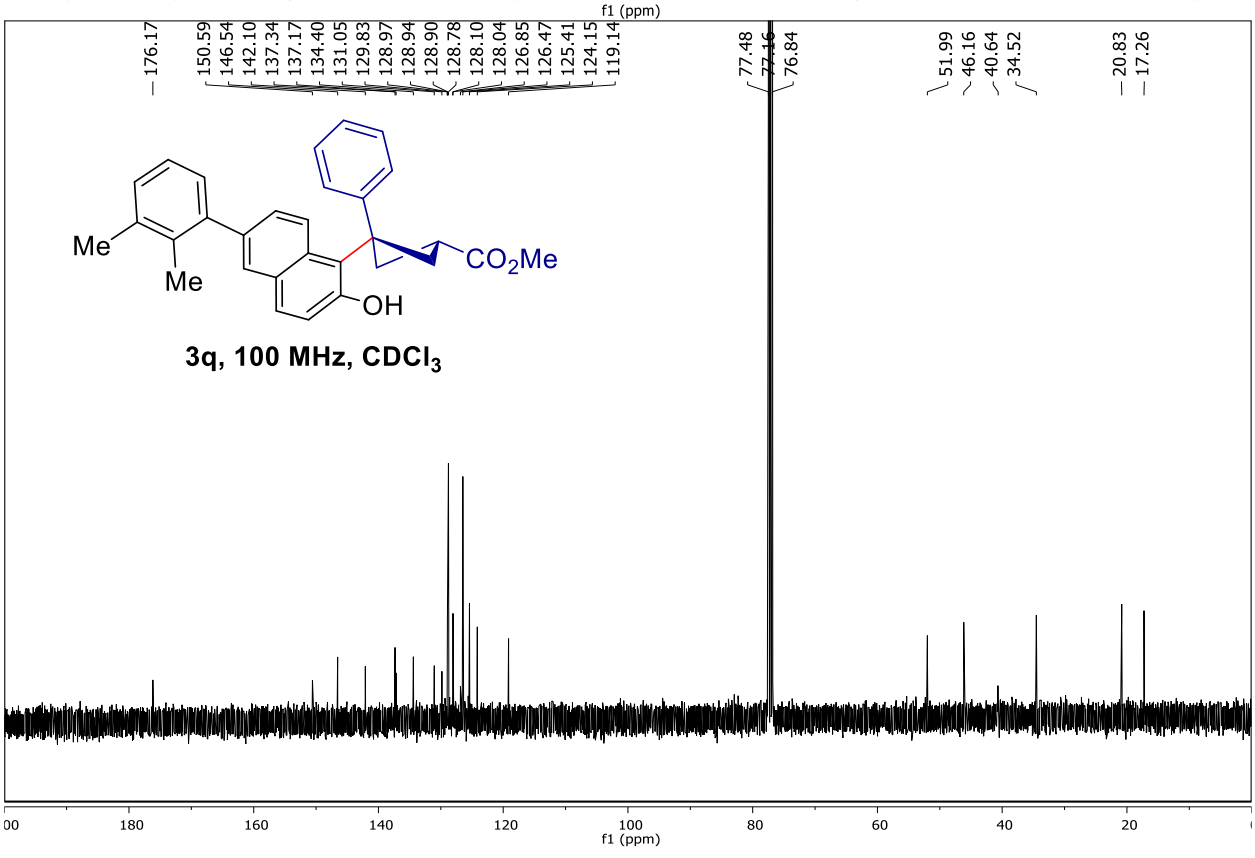
Methyl 6-hydroxy-5-(3-(methoxycarbonyl)-1-phenylcyclobutyl)-2-naphthoate (3p)



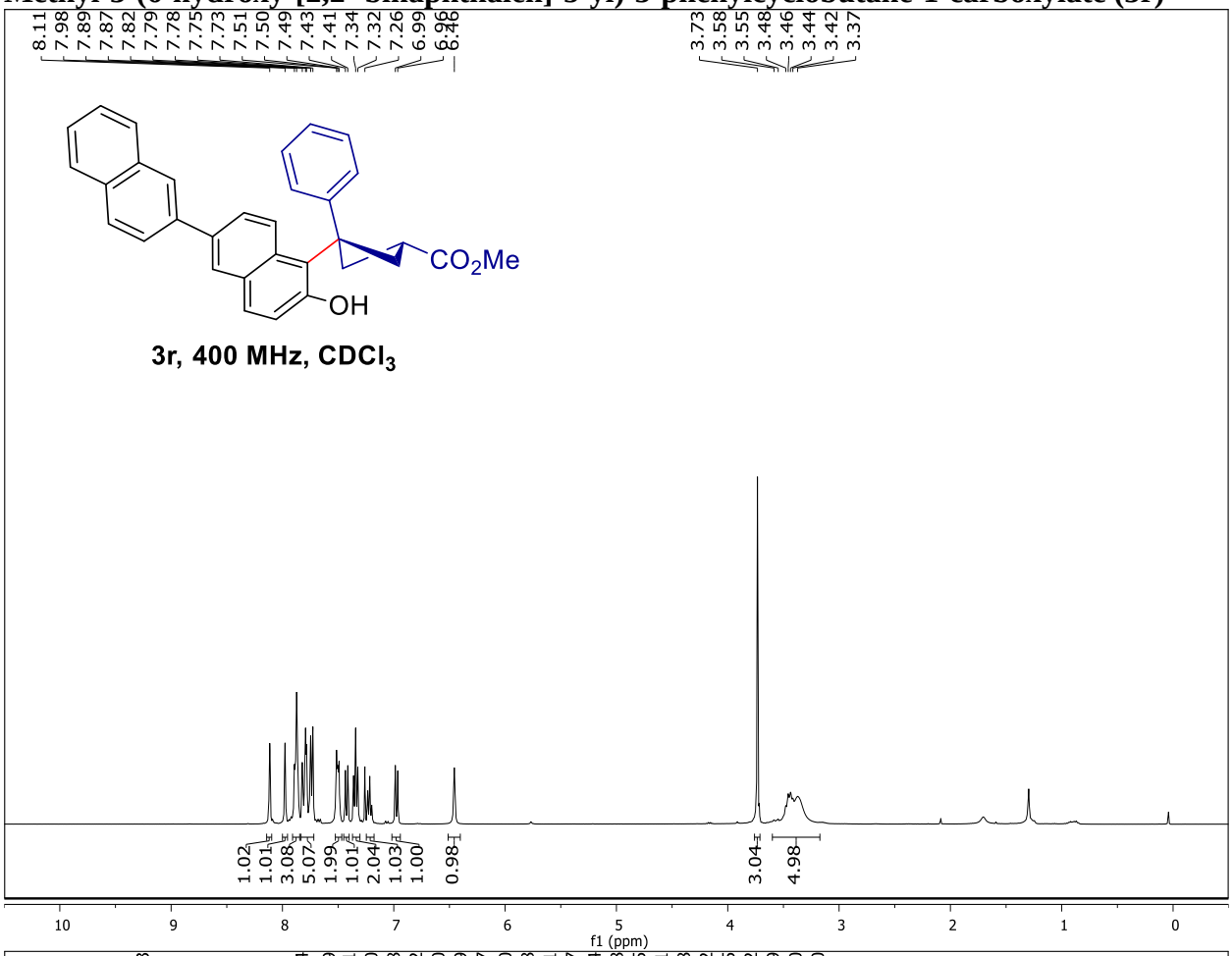


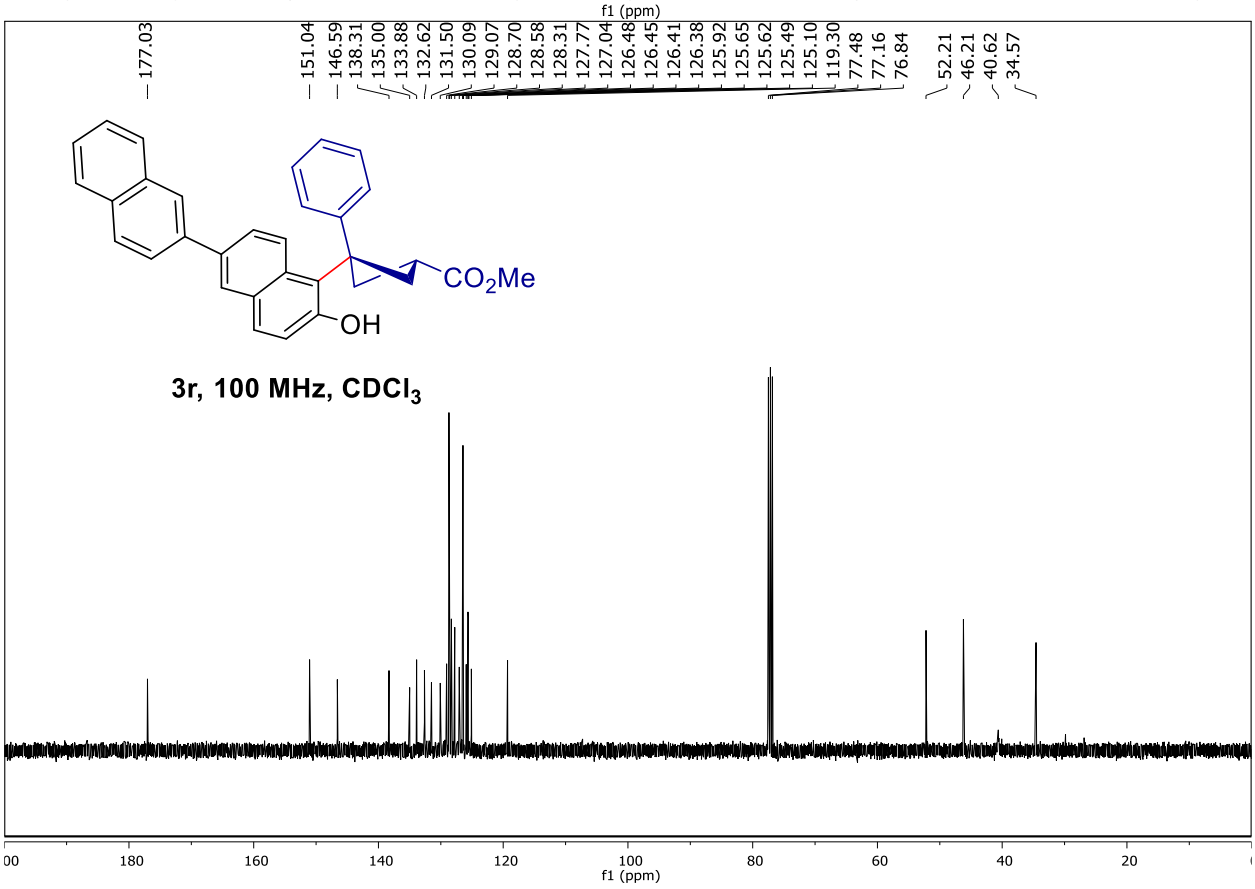
Methyl-3-(6-(2,3-dimethylphenyl)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3q)



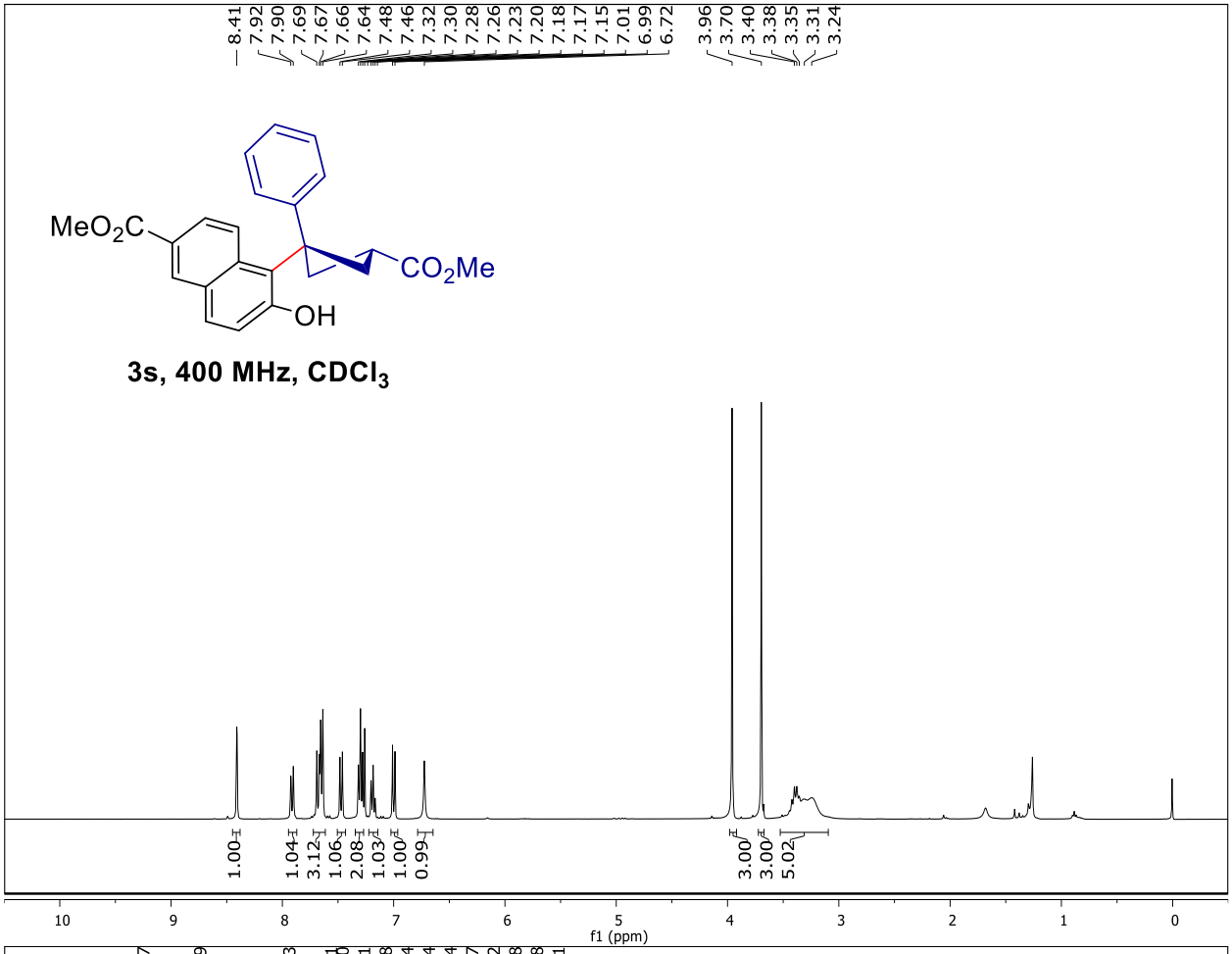


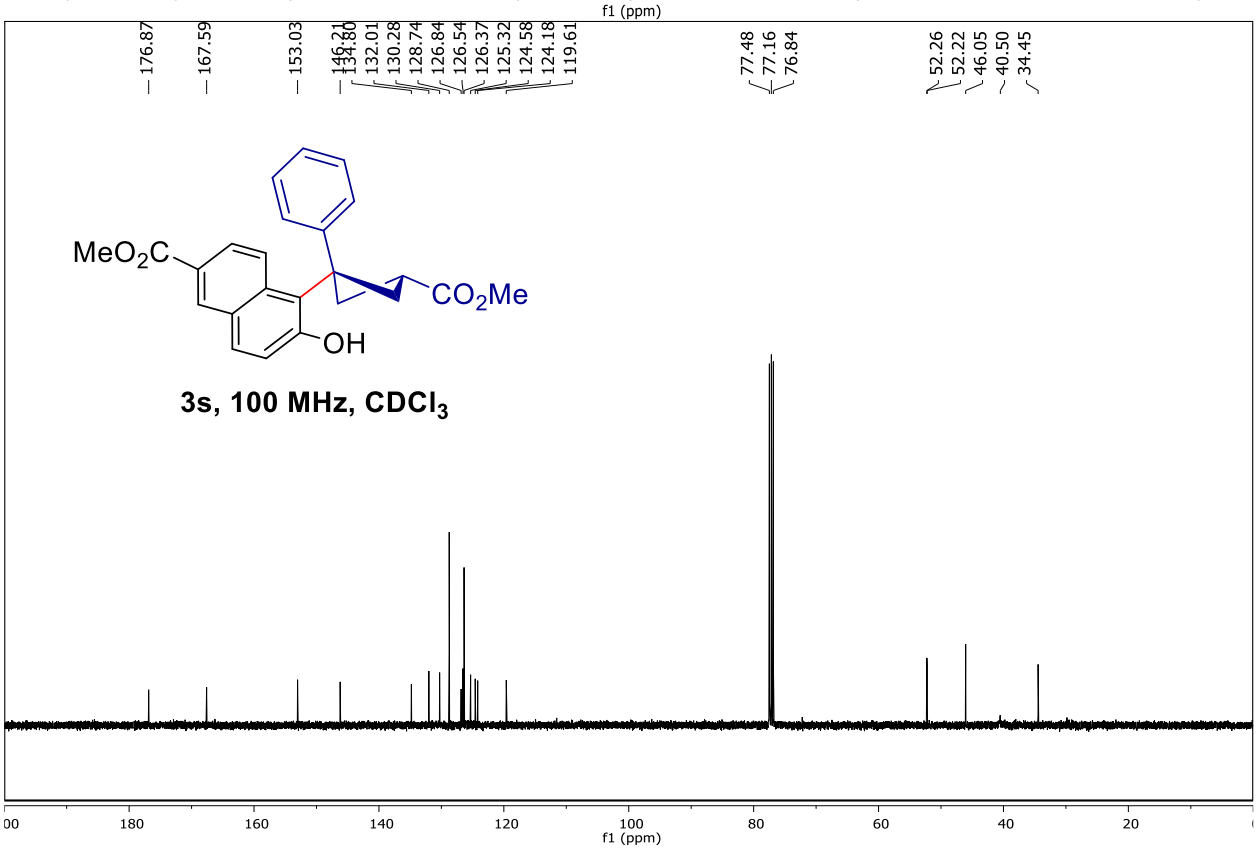
Methyl-3-(6-hydroxy-[2,2'-binaphthalen]-5-yl)-3-phenylcyclobutane-1-carboxylate (3r)



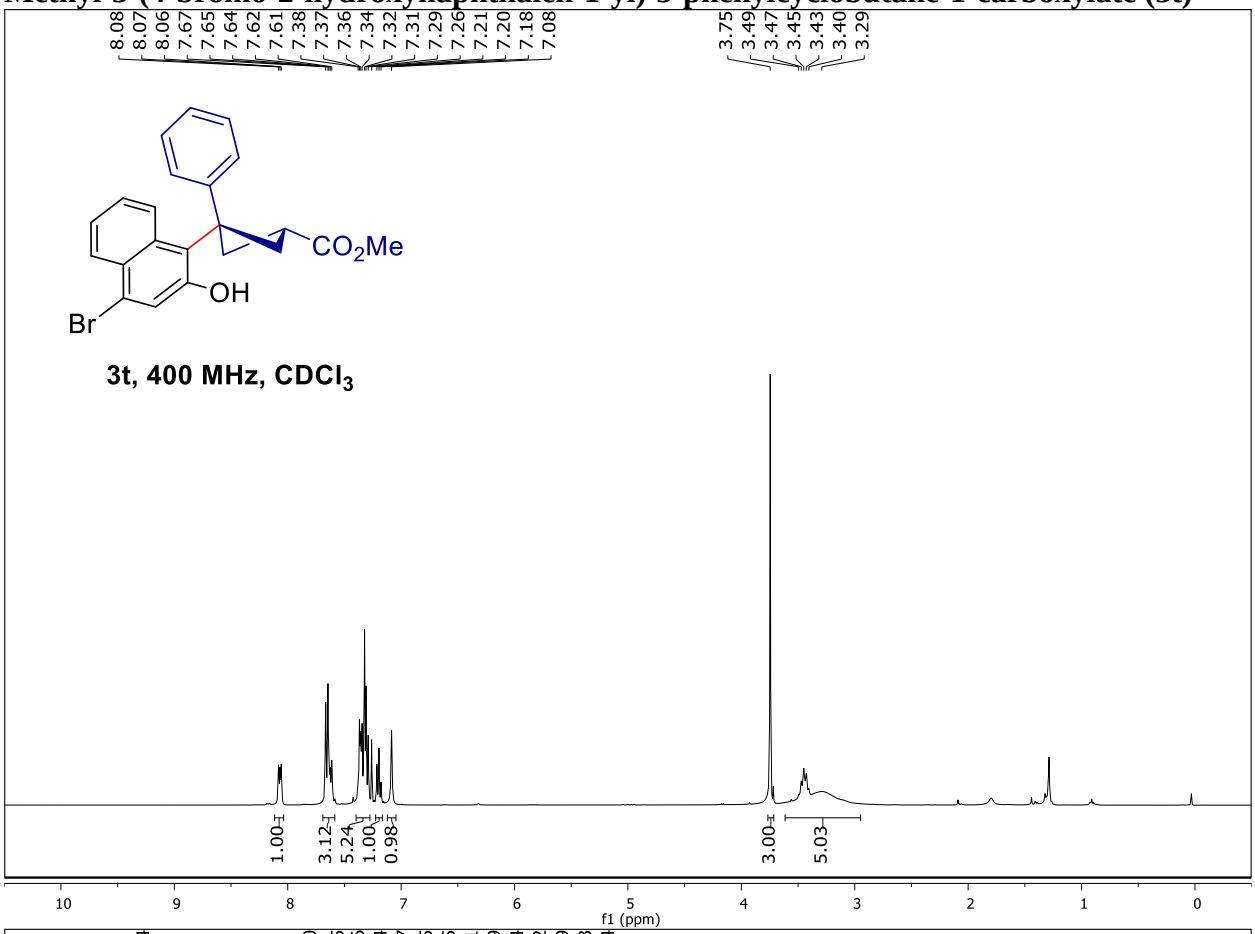


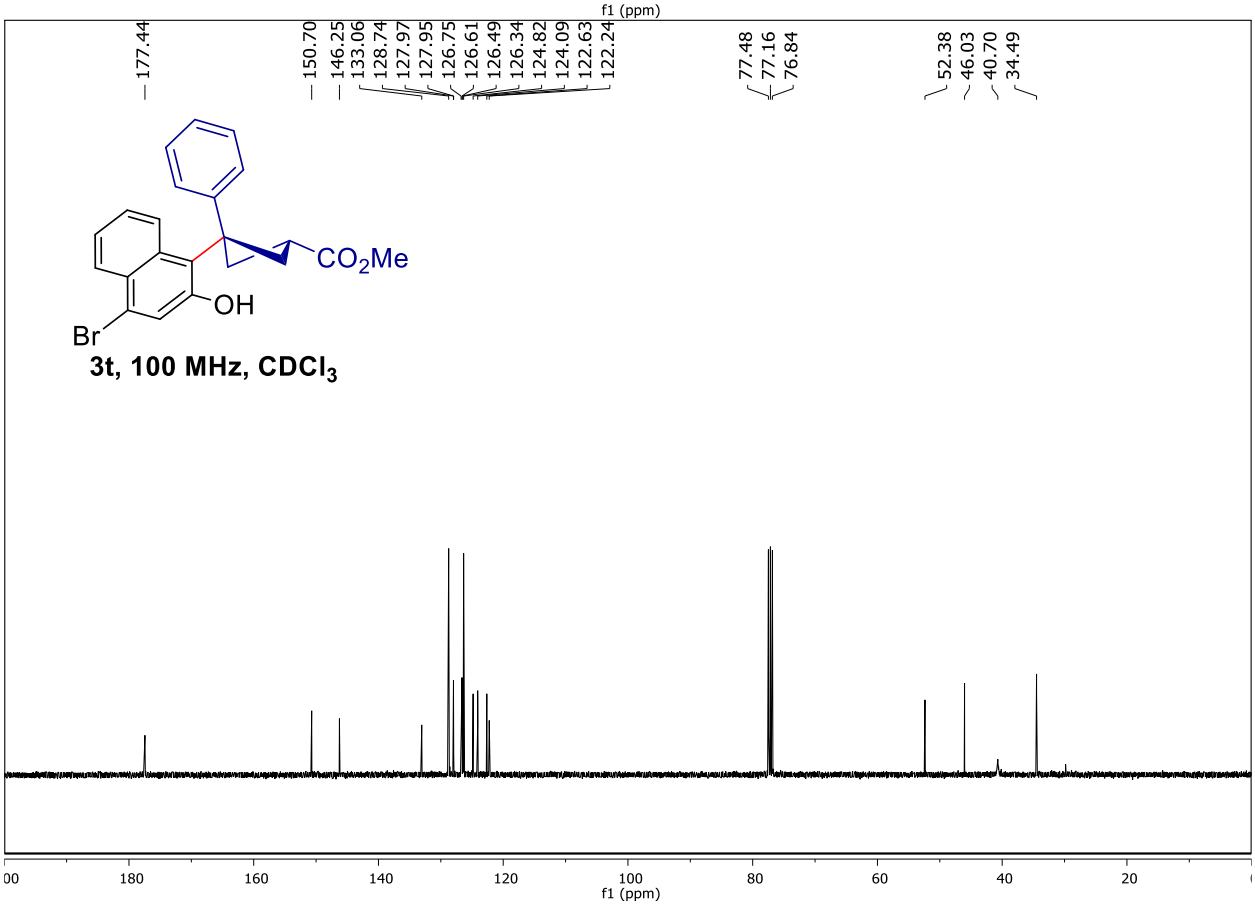
Methyl 6-hydroxy-5-(3-(methoxycarbonyl)-1-phenylcyclobutyl)-2-naphthoate (3s)



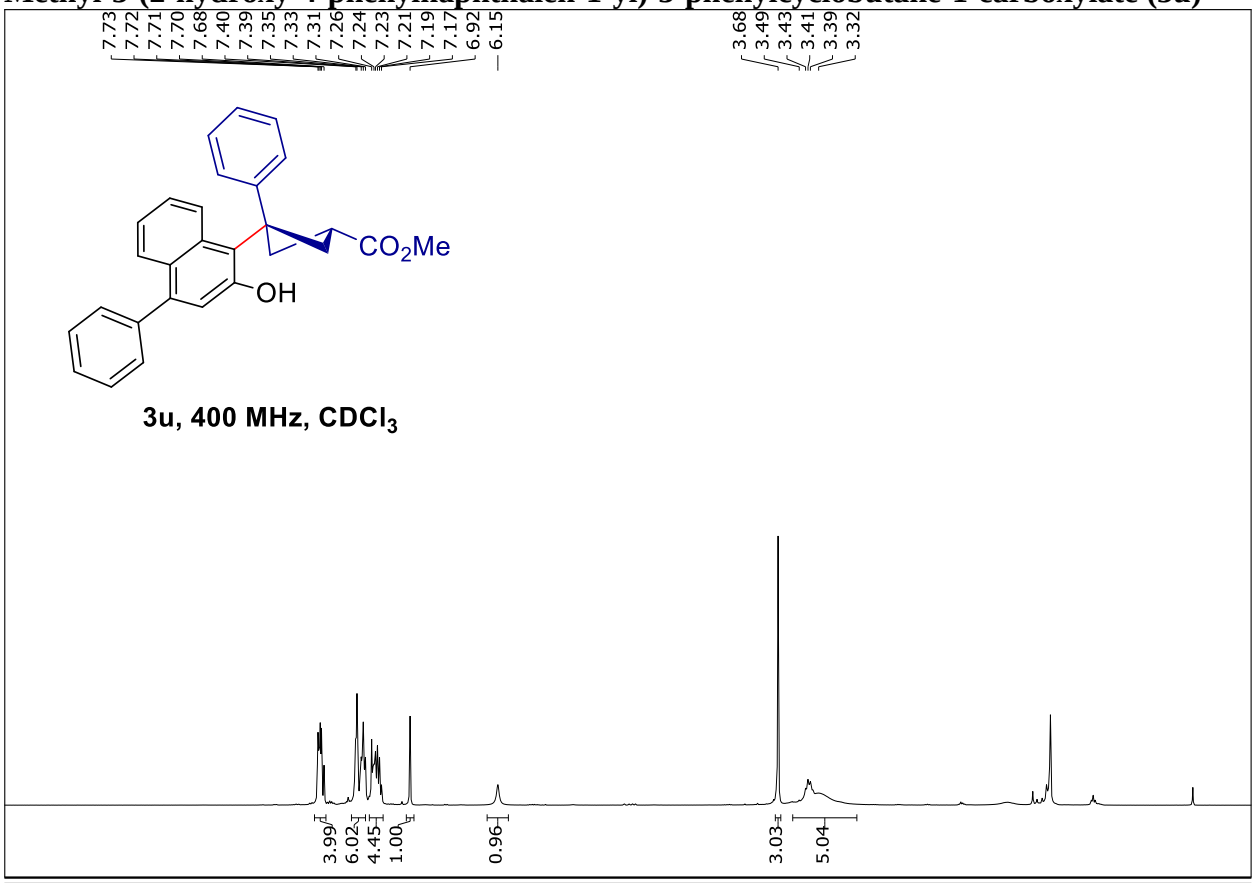


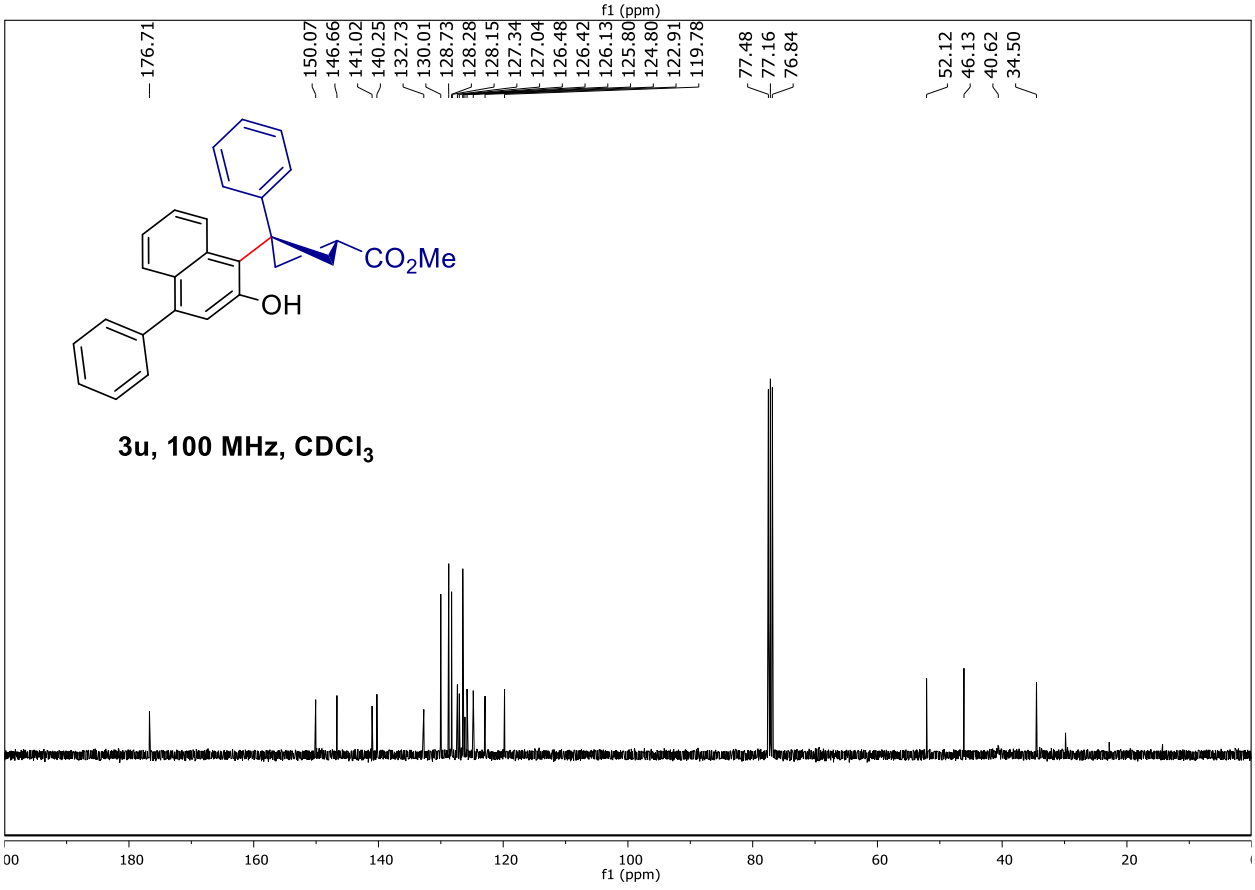
Methyl-3-(4-bromo-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3t)



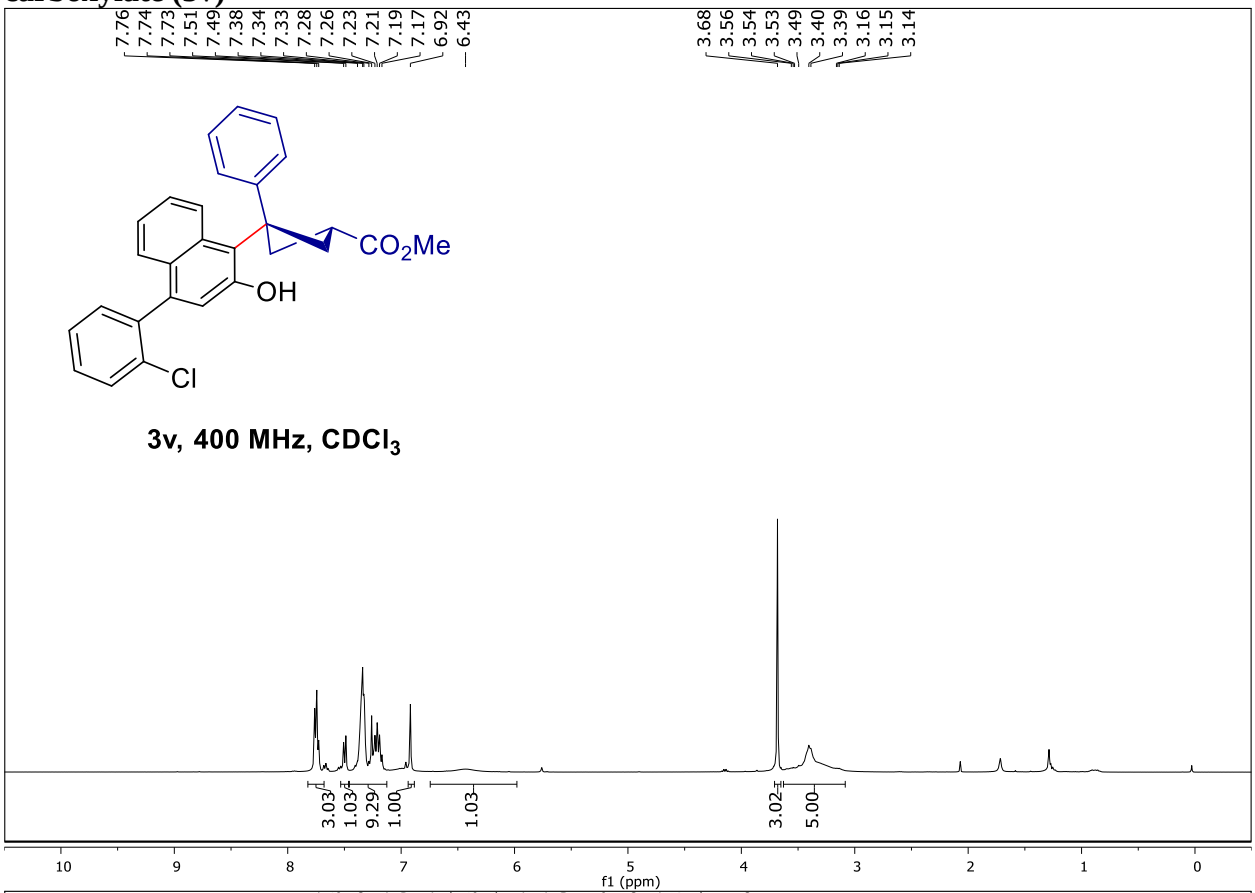


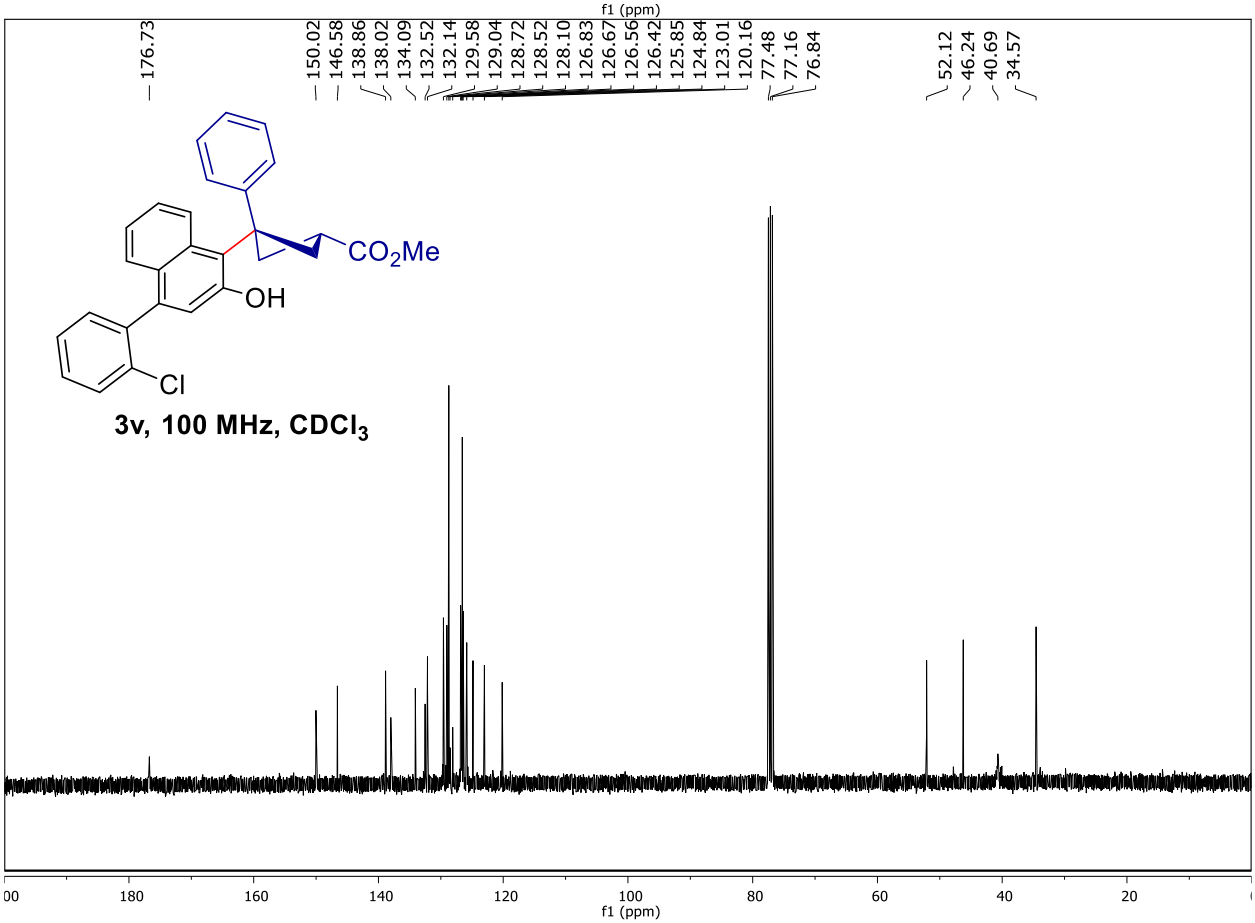
Methyl-3-(2-hydroxy-4-phenylnaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3u)



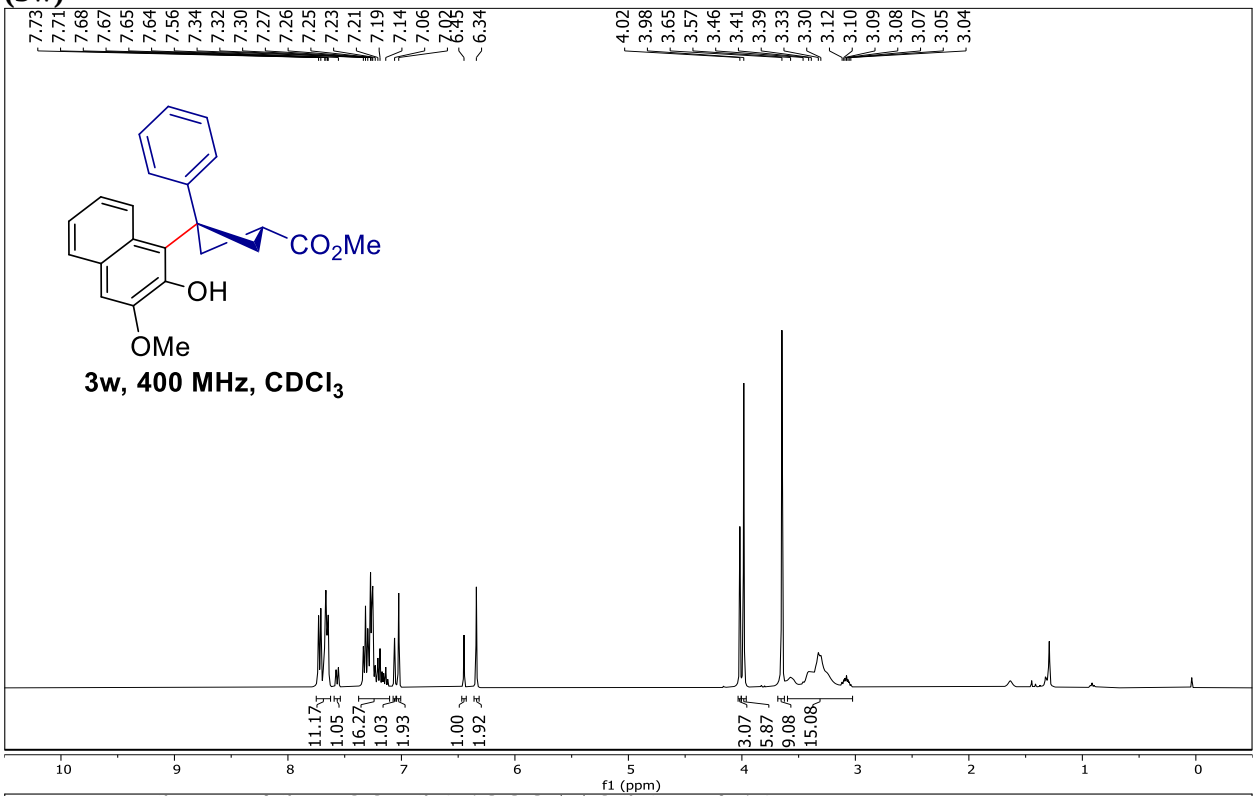


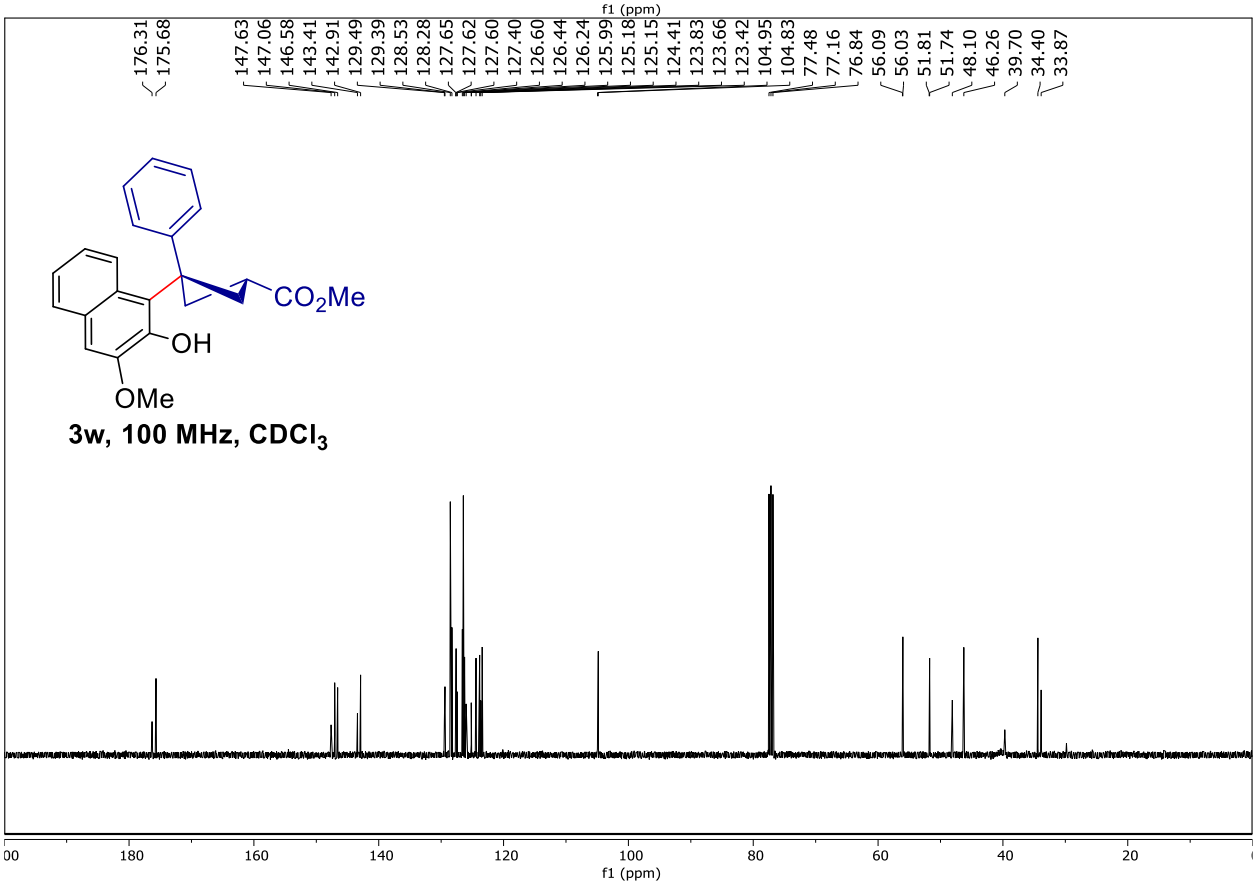
Methyl-3-(4-(2-chlorophenyl)-2-hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3v)



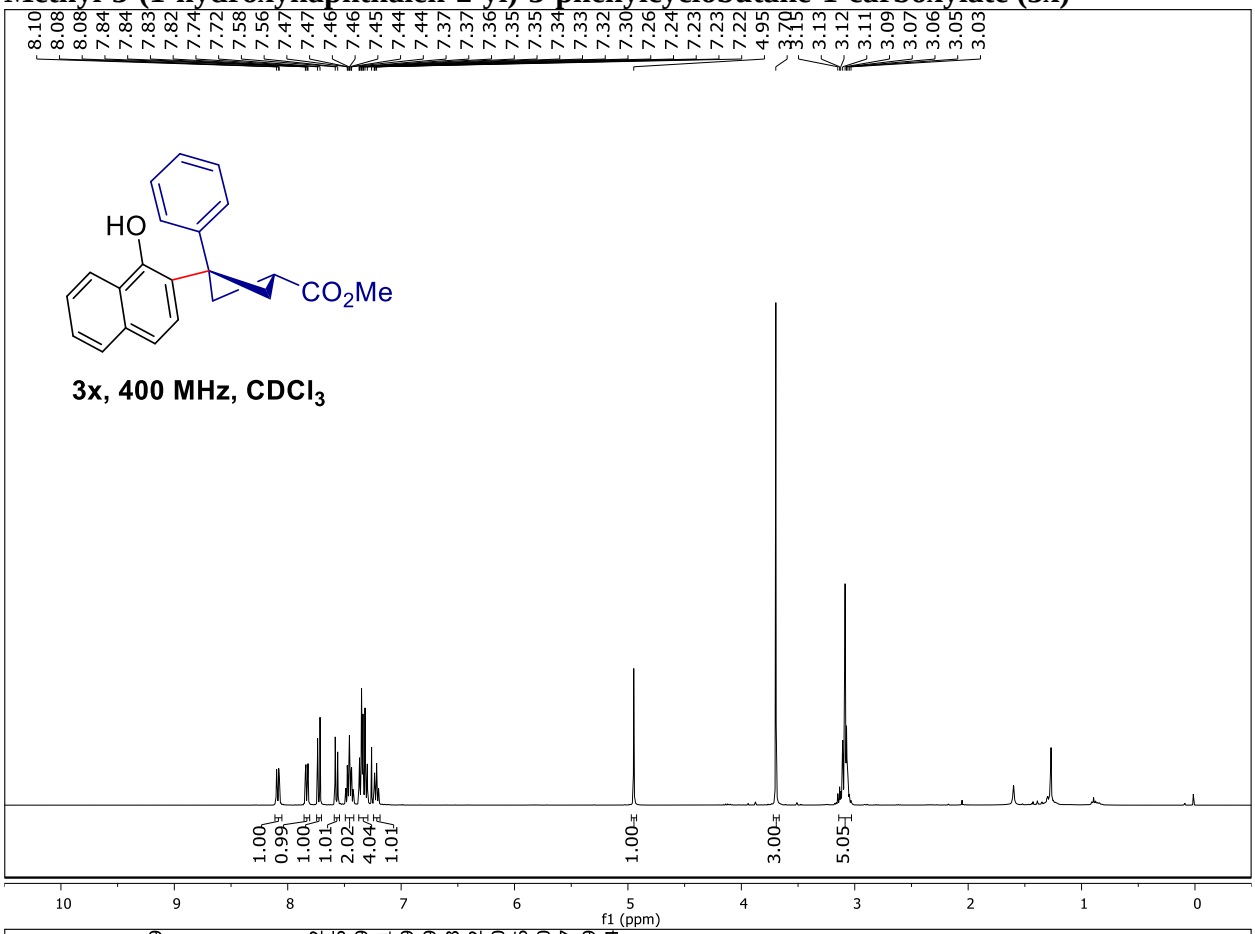


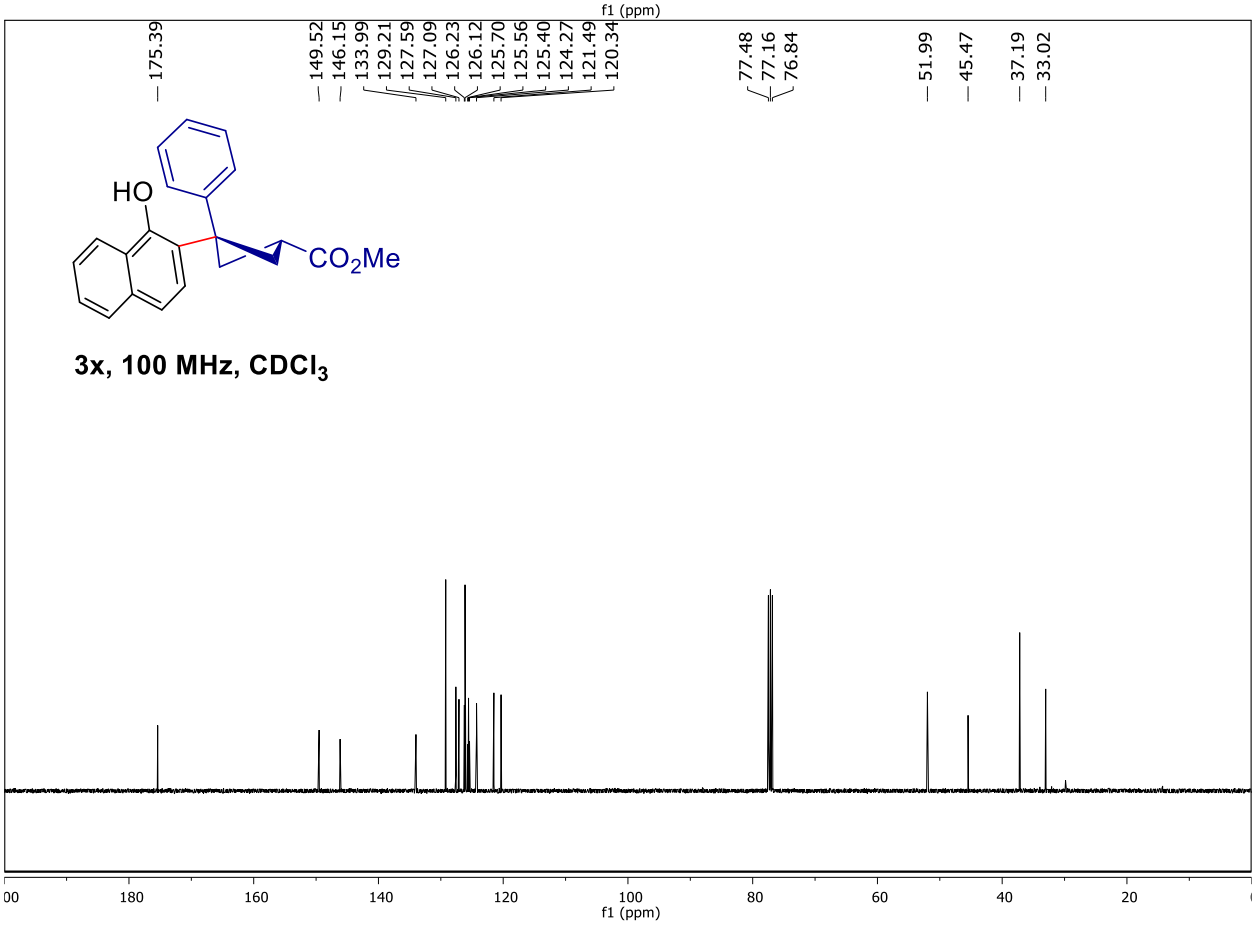
Methyl-3-(2-hydroxy-3-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (3w)



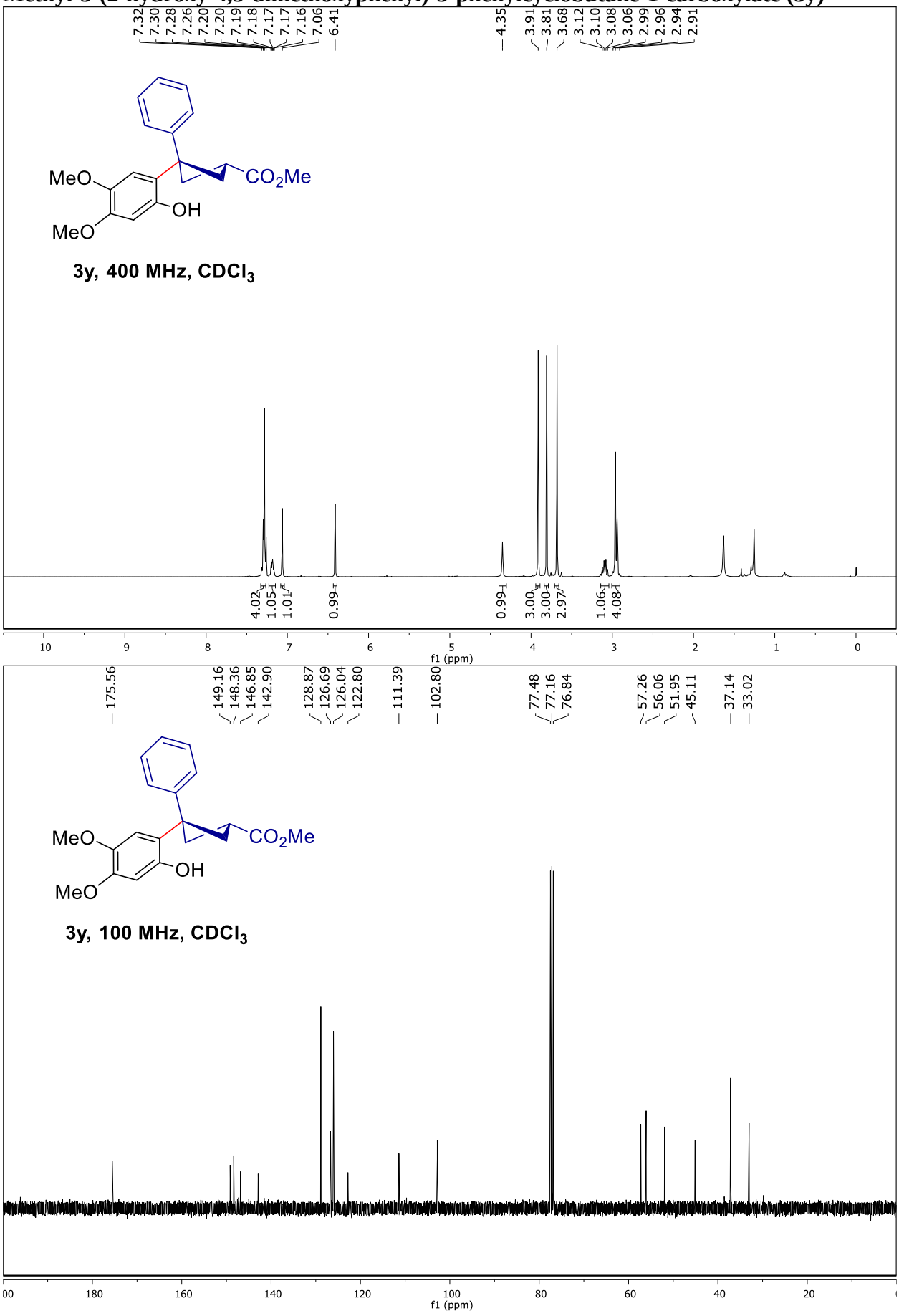


Methyl-3-(1-hydroxynaphthalen-2-yl)-3-phenylcyclobutane-1-carboxylate (3x)

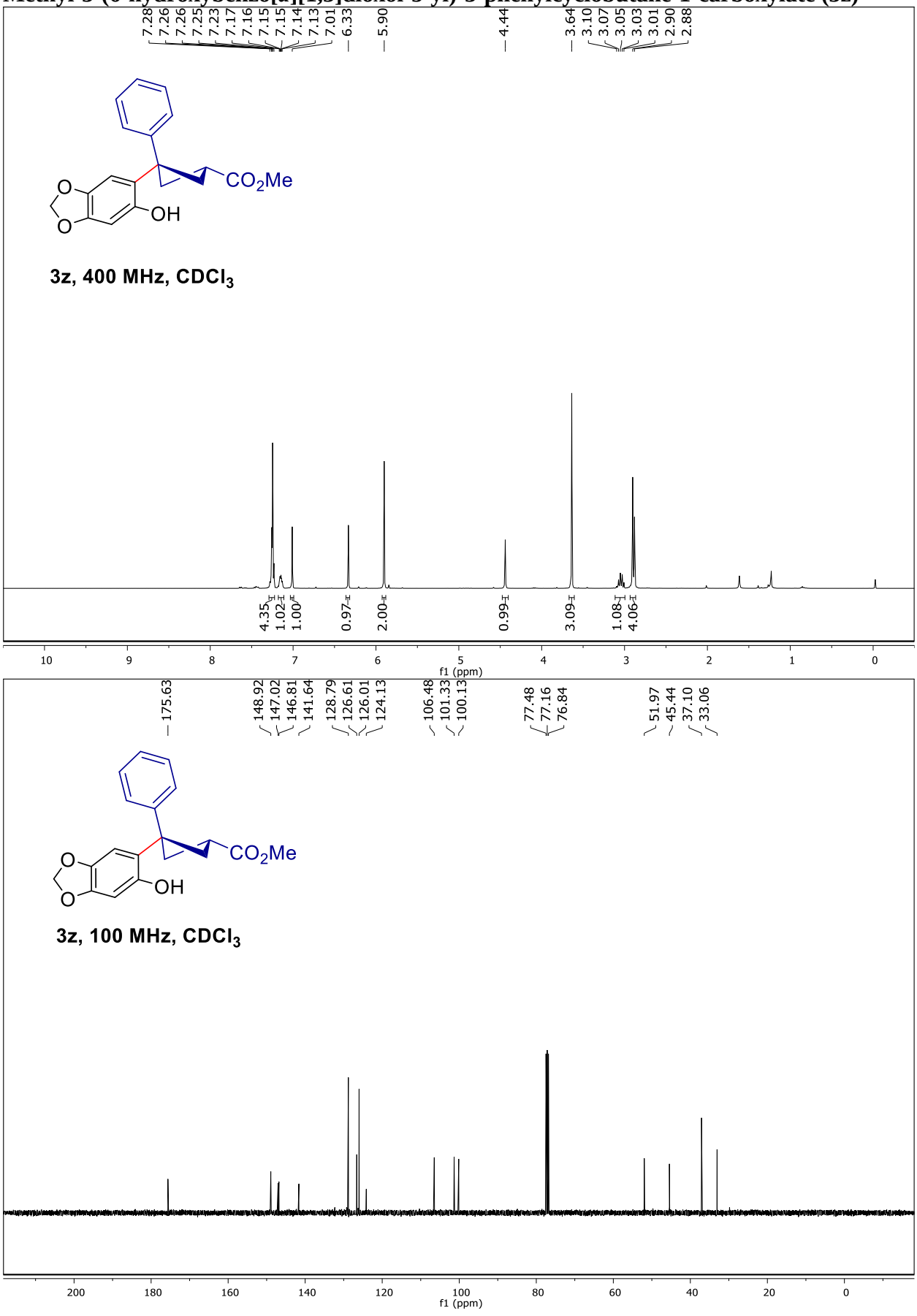




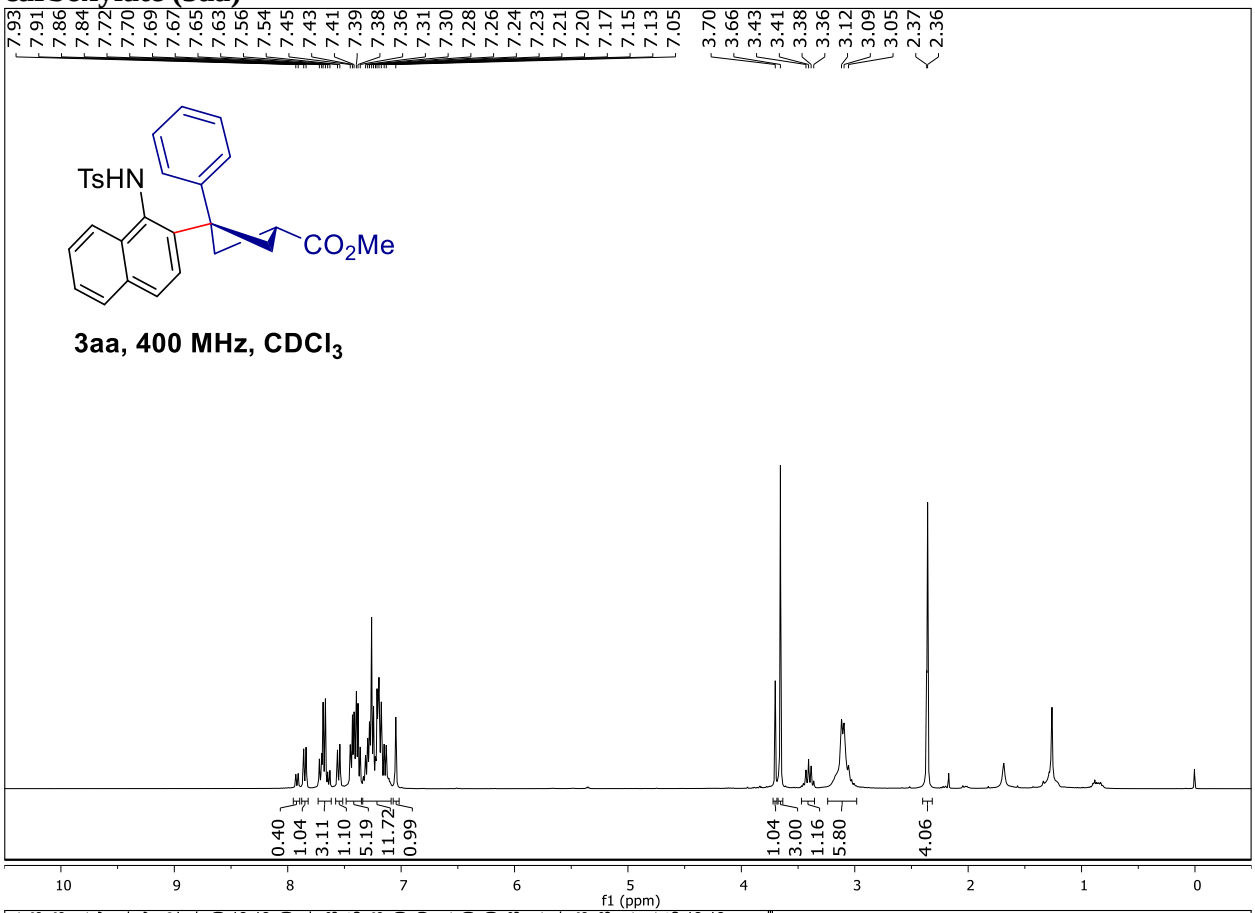
Methyl-3-(2-hydroxy-4,5-dimethoxyphenyl)-3-phenylcyclobutane-1-carboxylate (3y)

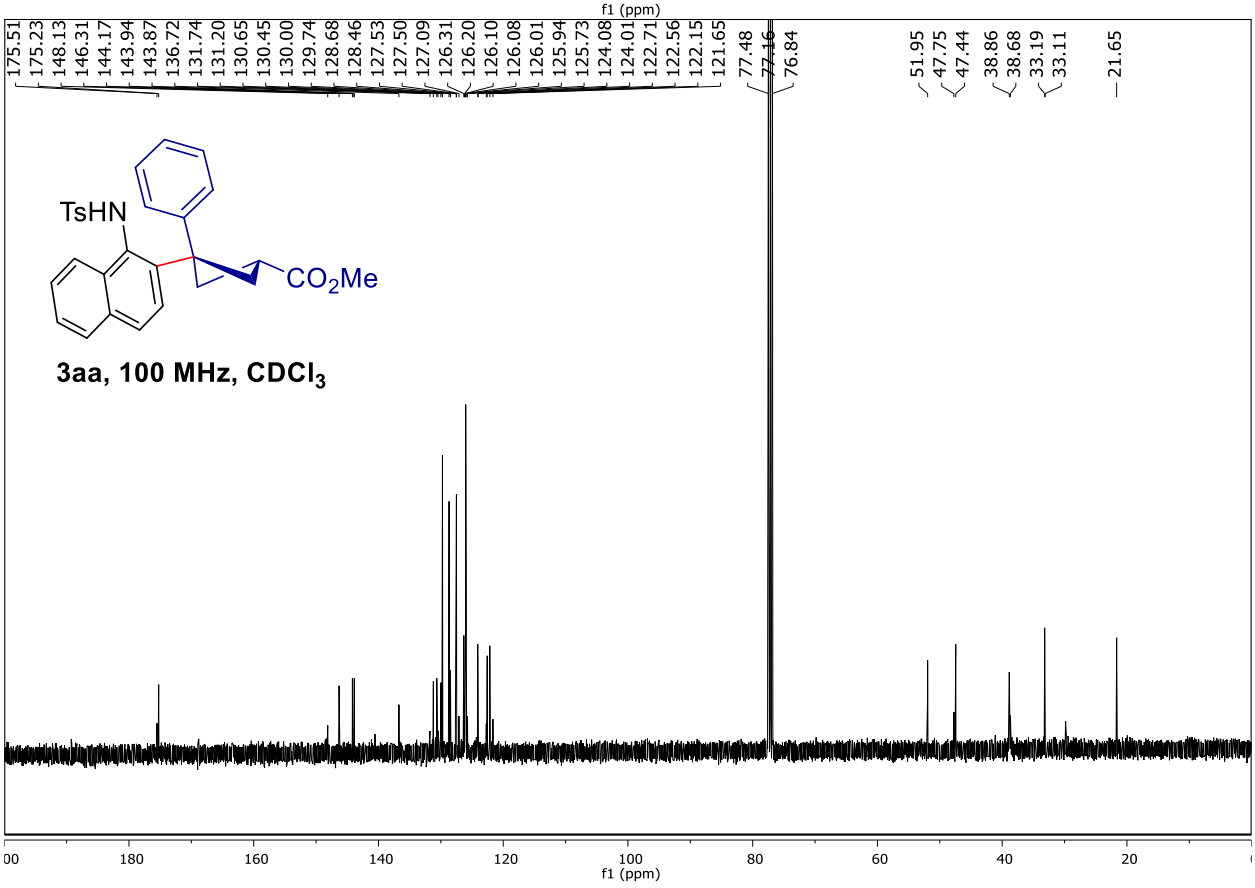


Methyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-phenylcyclobutane-1-carboxylate (3z)

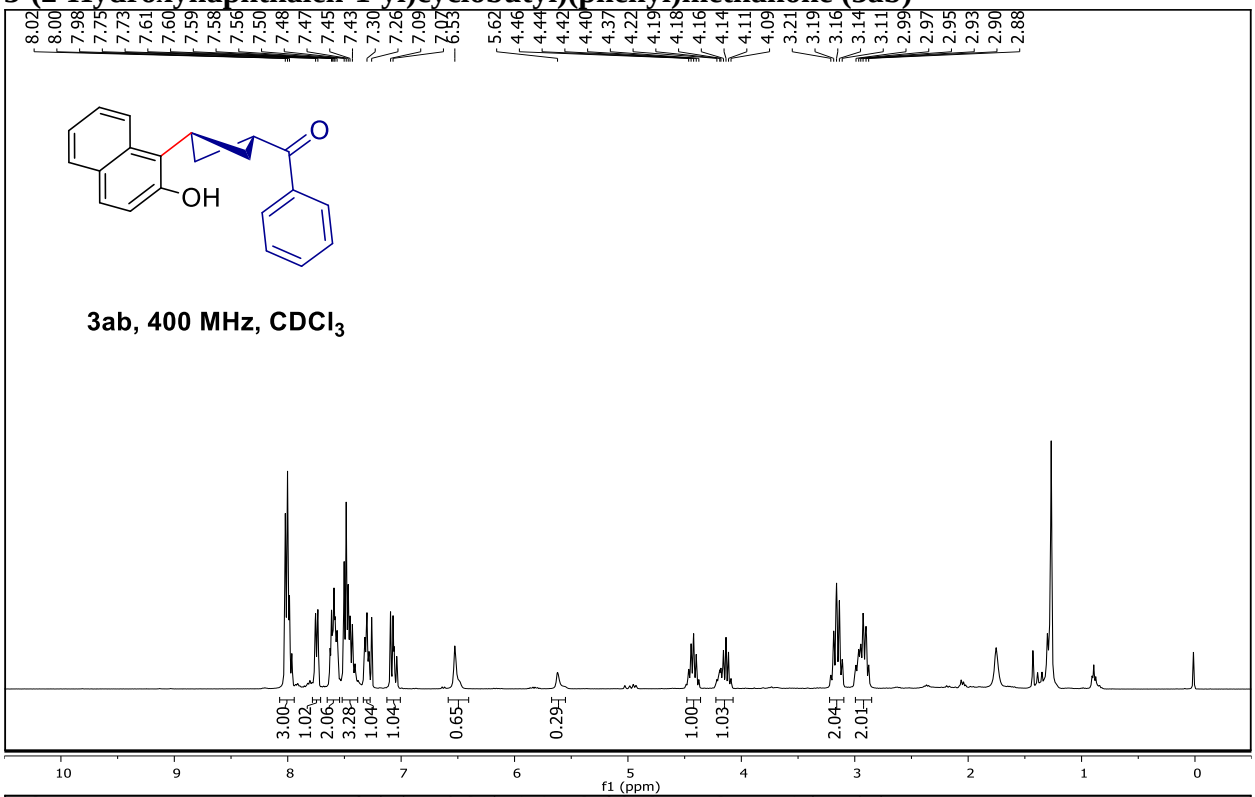


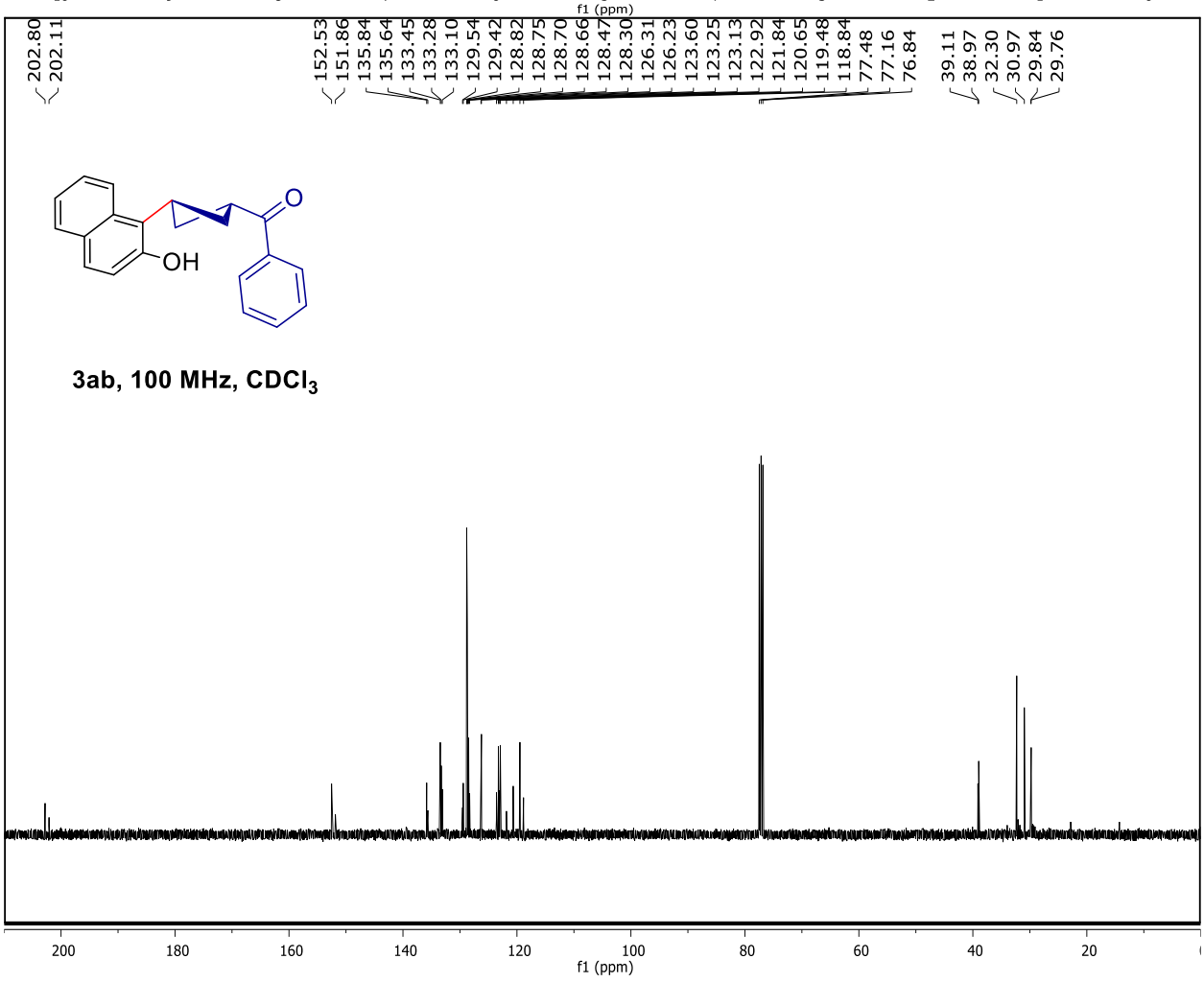
Methyl-3-(1-((4-methylphenyl)sulfonamido)naphthalen-2-yl)-3-phenylcyclobutane-1-carboxylate (3aa)



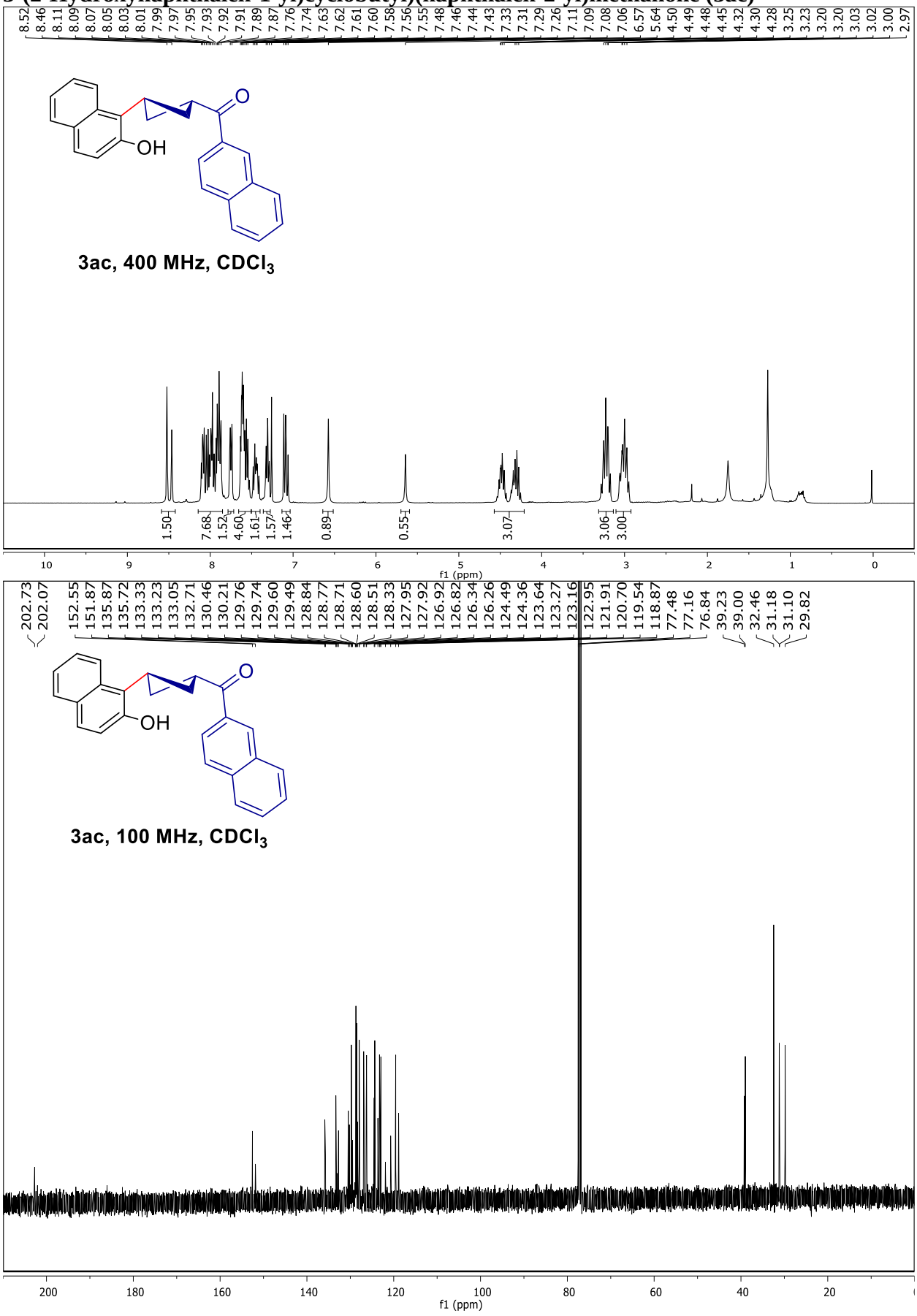


3-(2-Hydroxynaphthalen-1-yl)cyclobutyl)(phenyl)methanone (3ab)

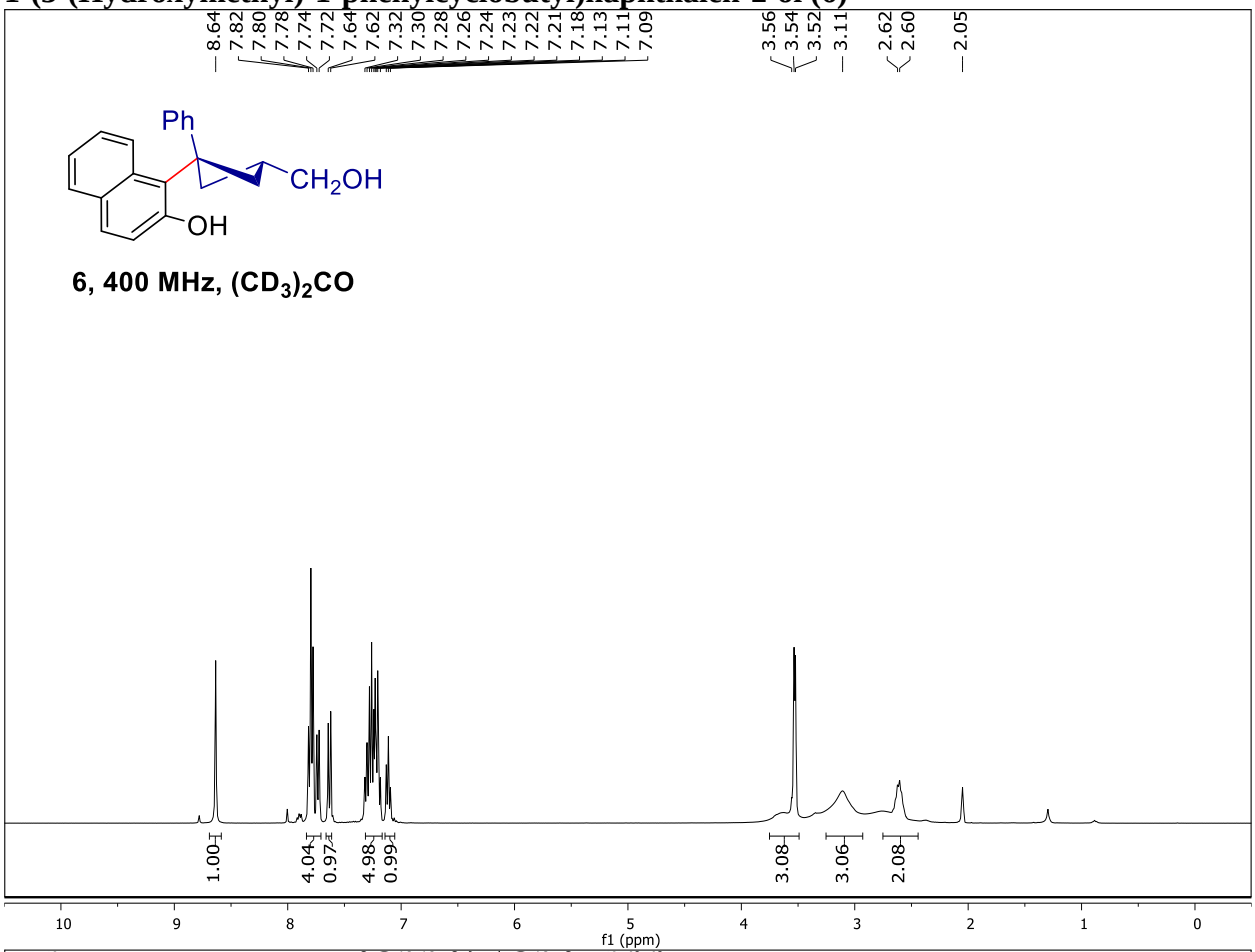


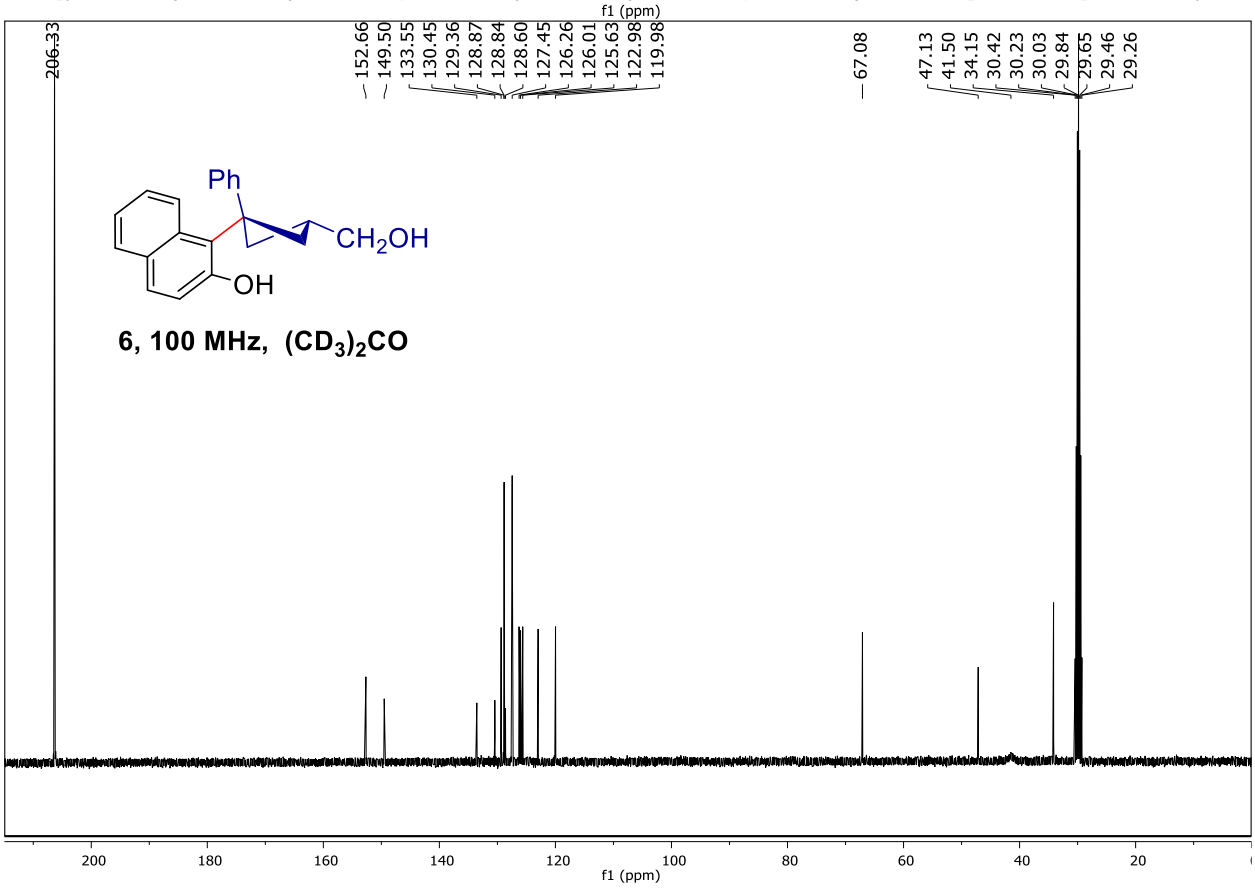


3-(2-Hydroxynaphthalen-1-yl)cyclobutyl)(naphthalen-2-yl)methanone (3ac)

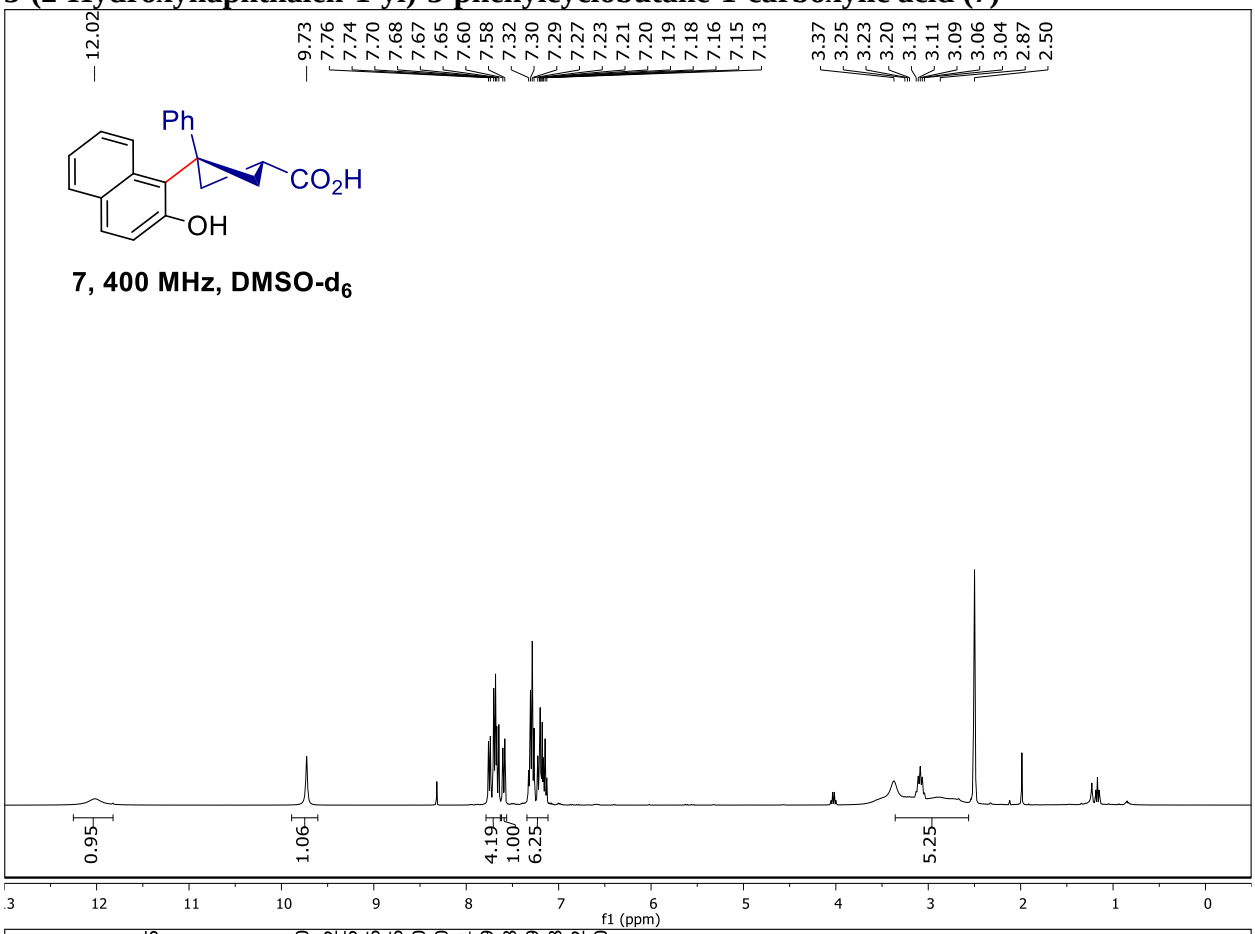


1-(3-(Hydroxymethyl)-1-phenylcyclobutyl)naphthalen-2-ol (6)

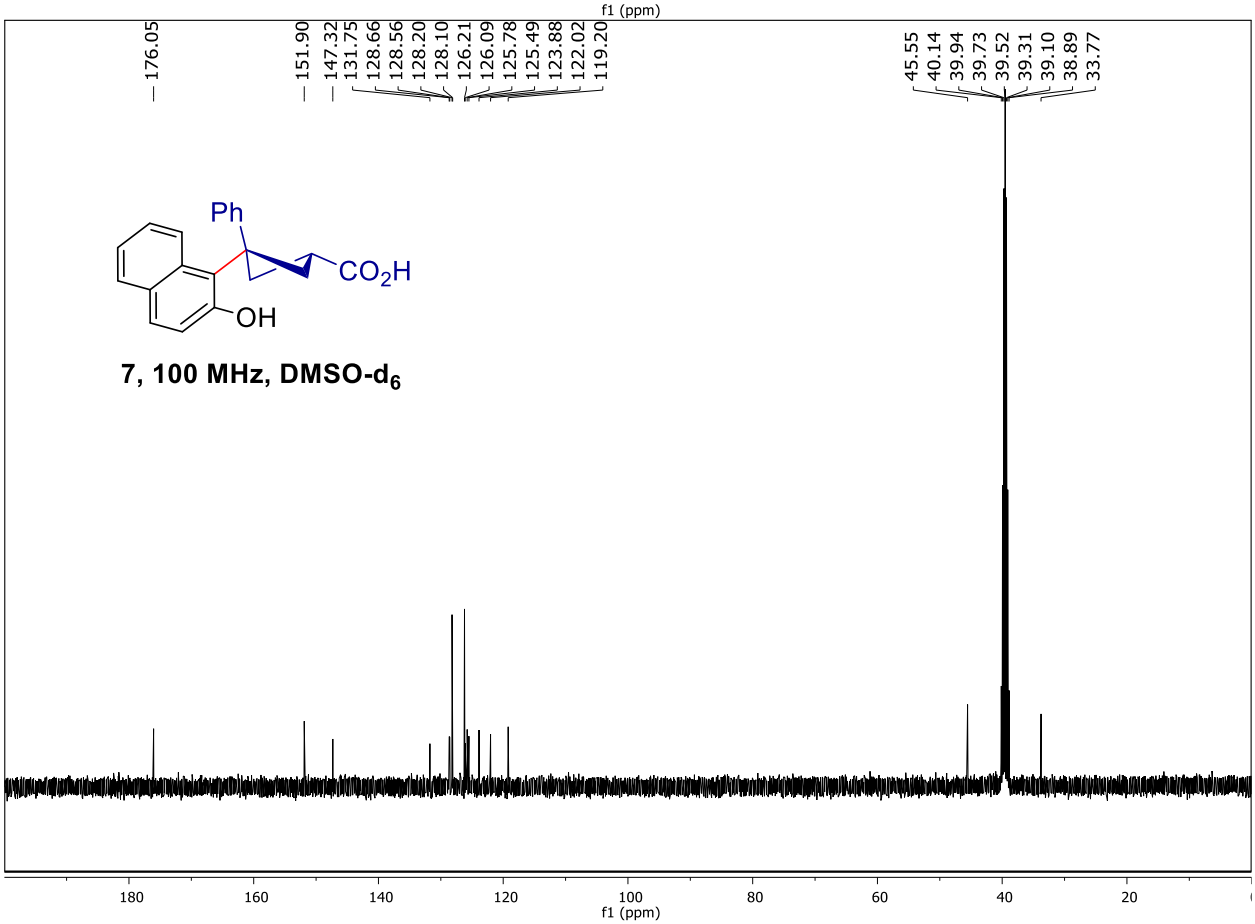




3-(2-Hydroxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylic acid (7)

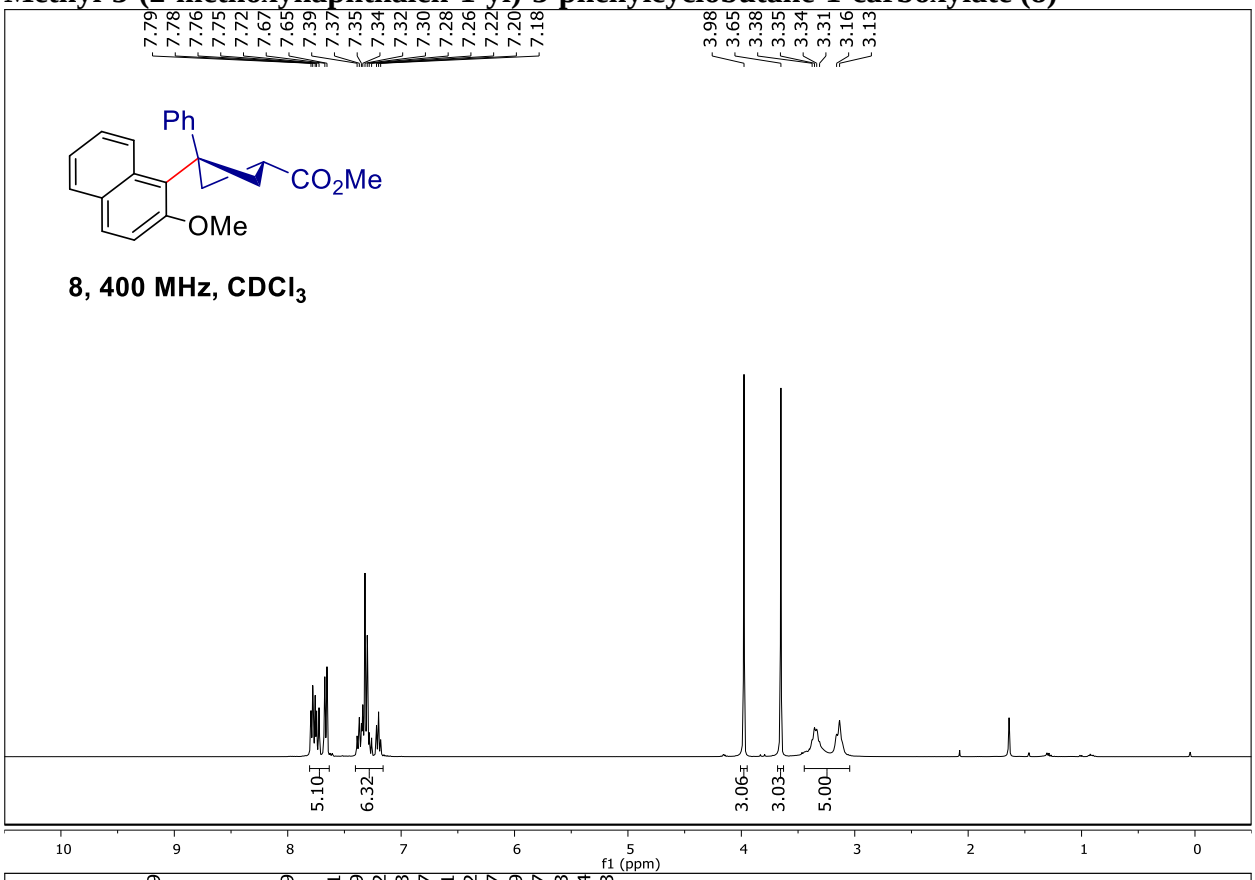


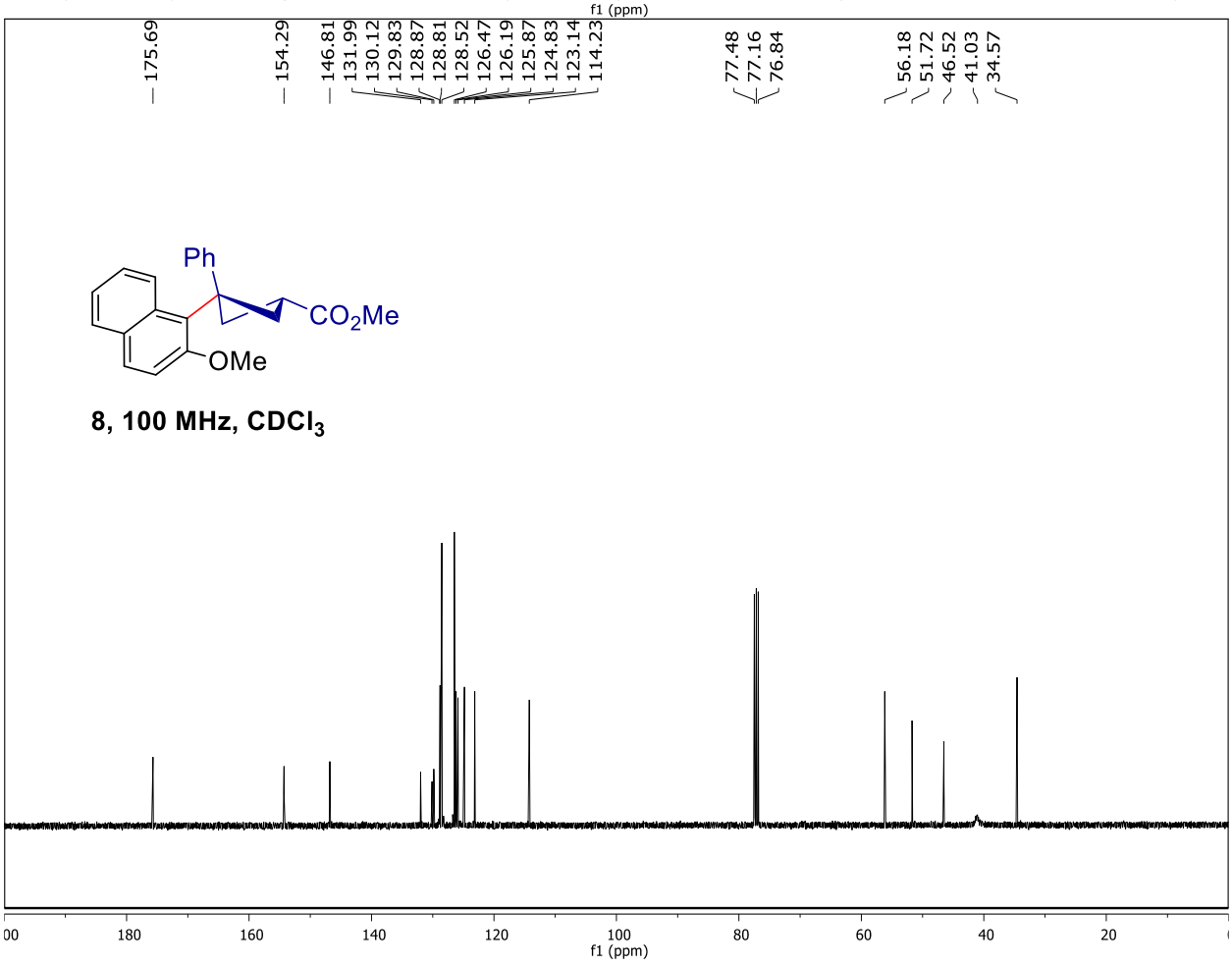
7, 400 MHz, DMSO-d_6



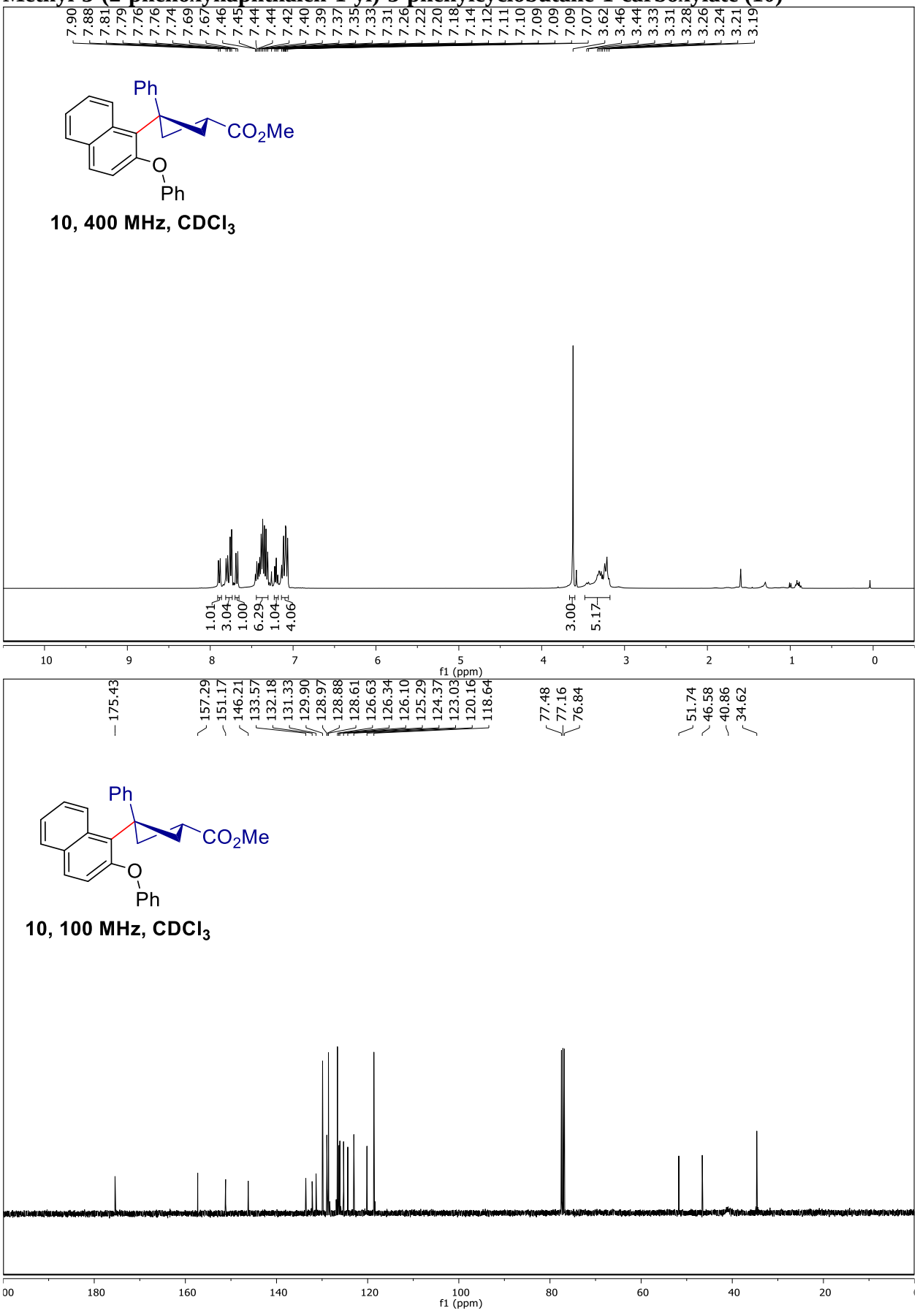
7, 100 MHz, DMSO-d_6

Methyl-3-(2-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (8)

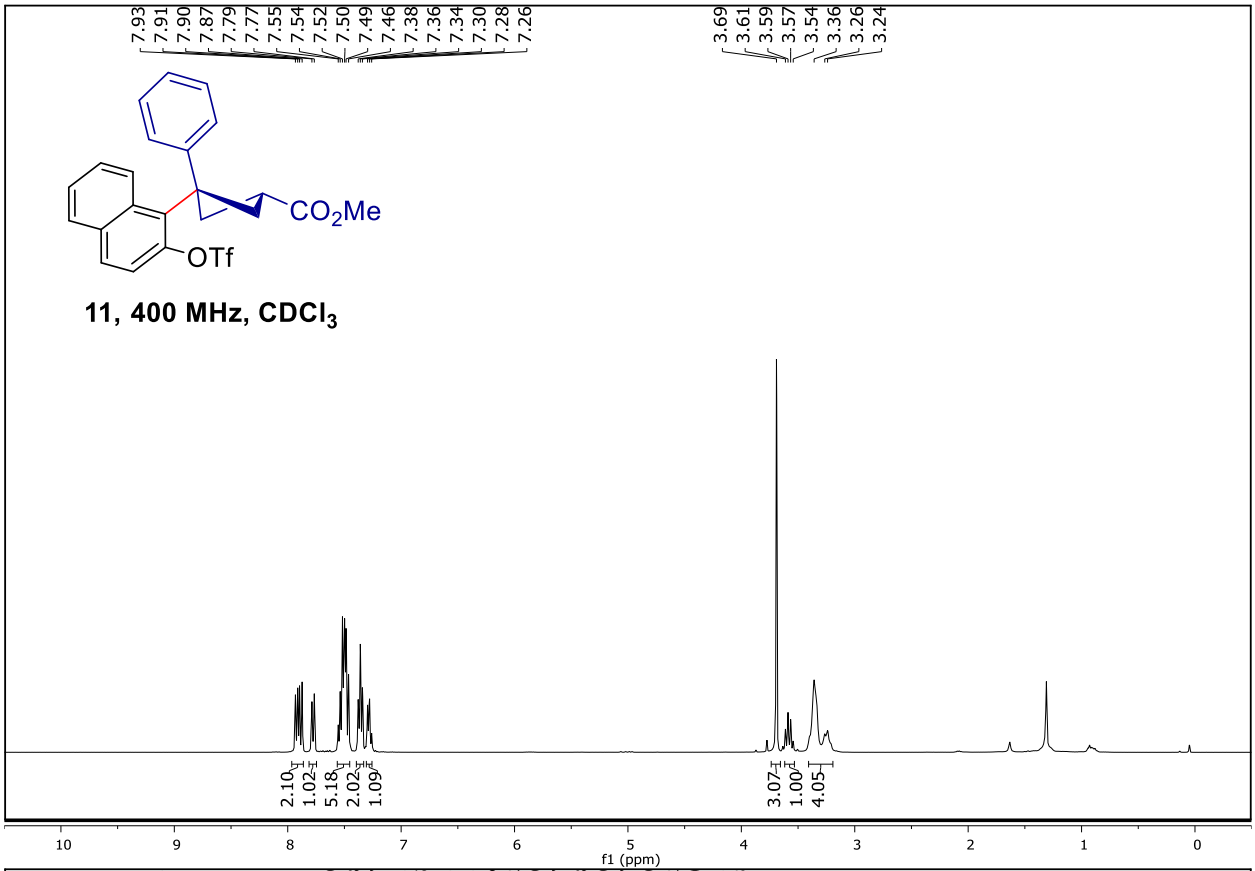


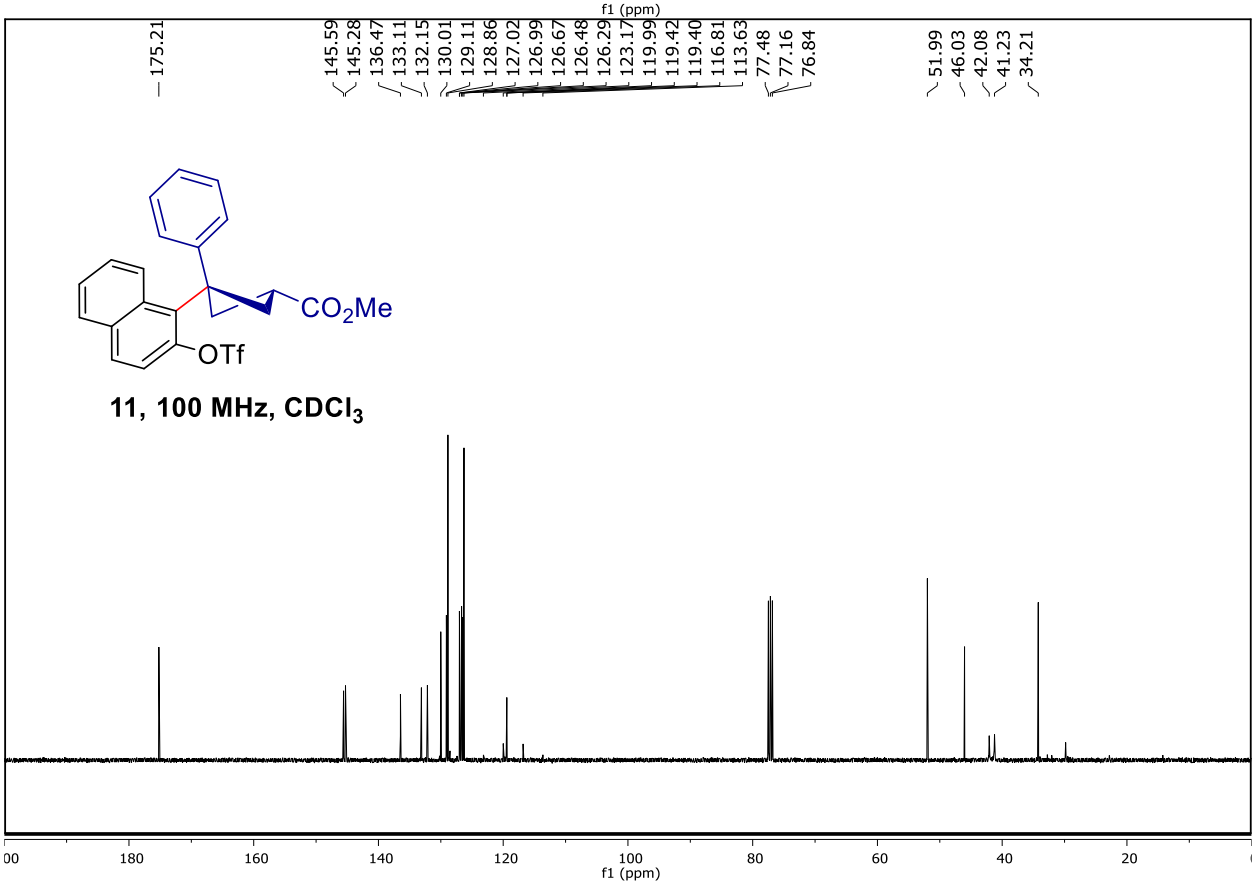


Methyl-3-(2-phenoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (10)

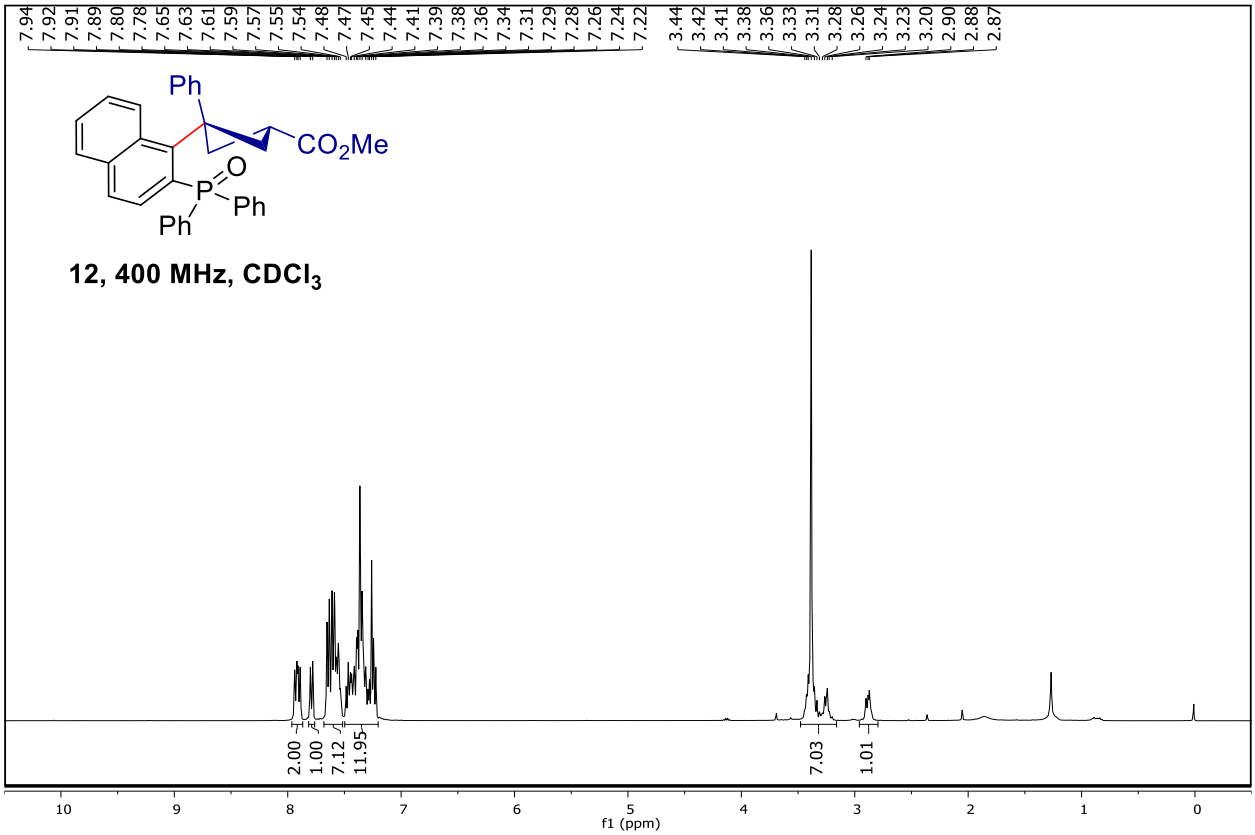


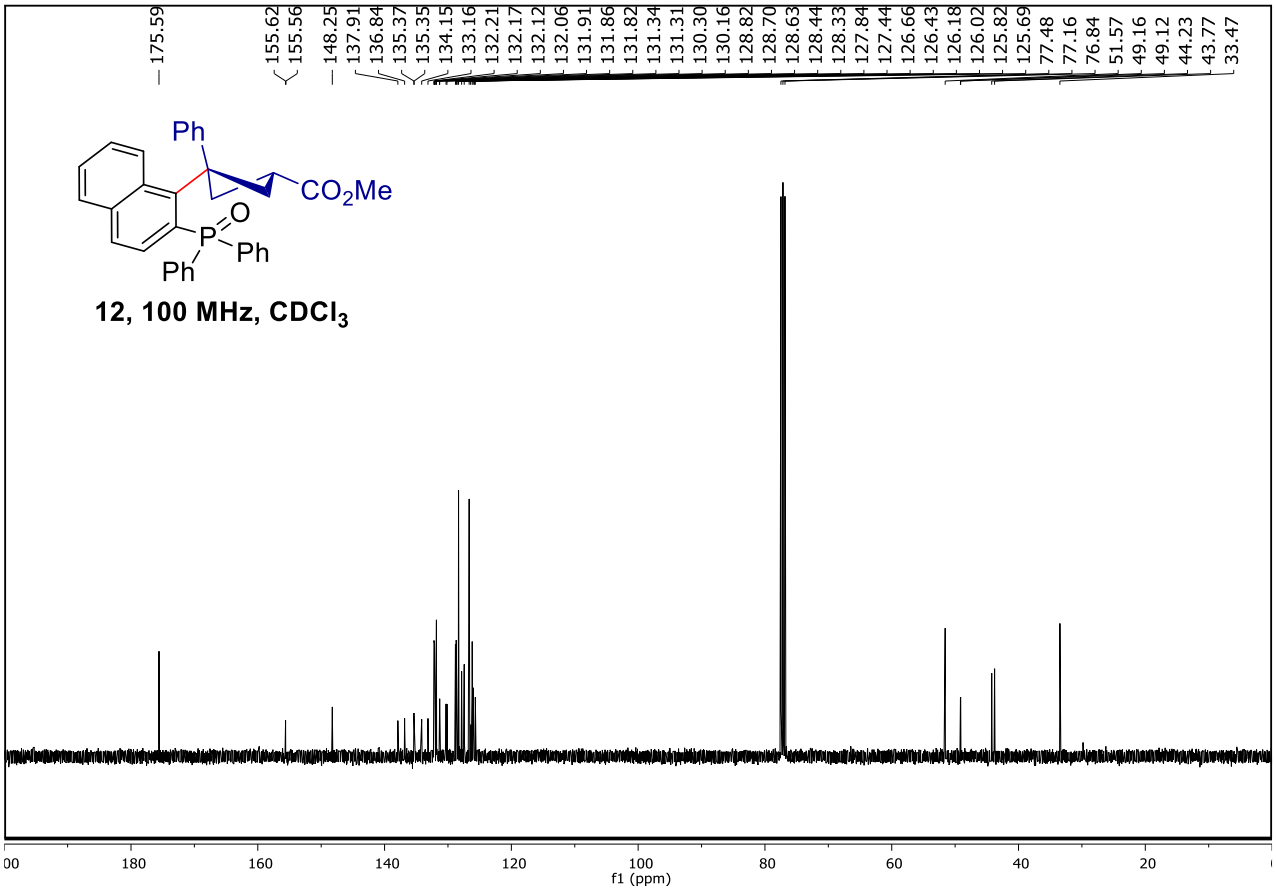
Methyl-3-phenyl-3-(2-(((trifluoromethyl)sulfonyl)oxy)naphthalen-1-yl)cyclobutane-1-carboxylate (11)

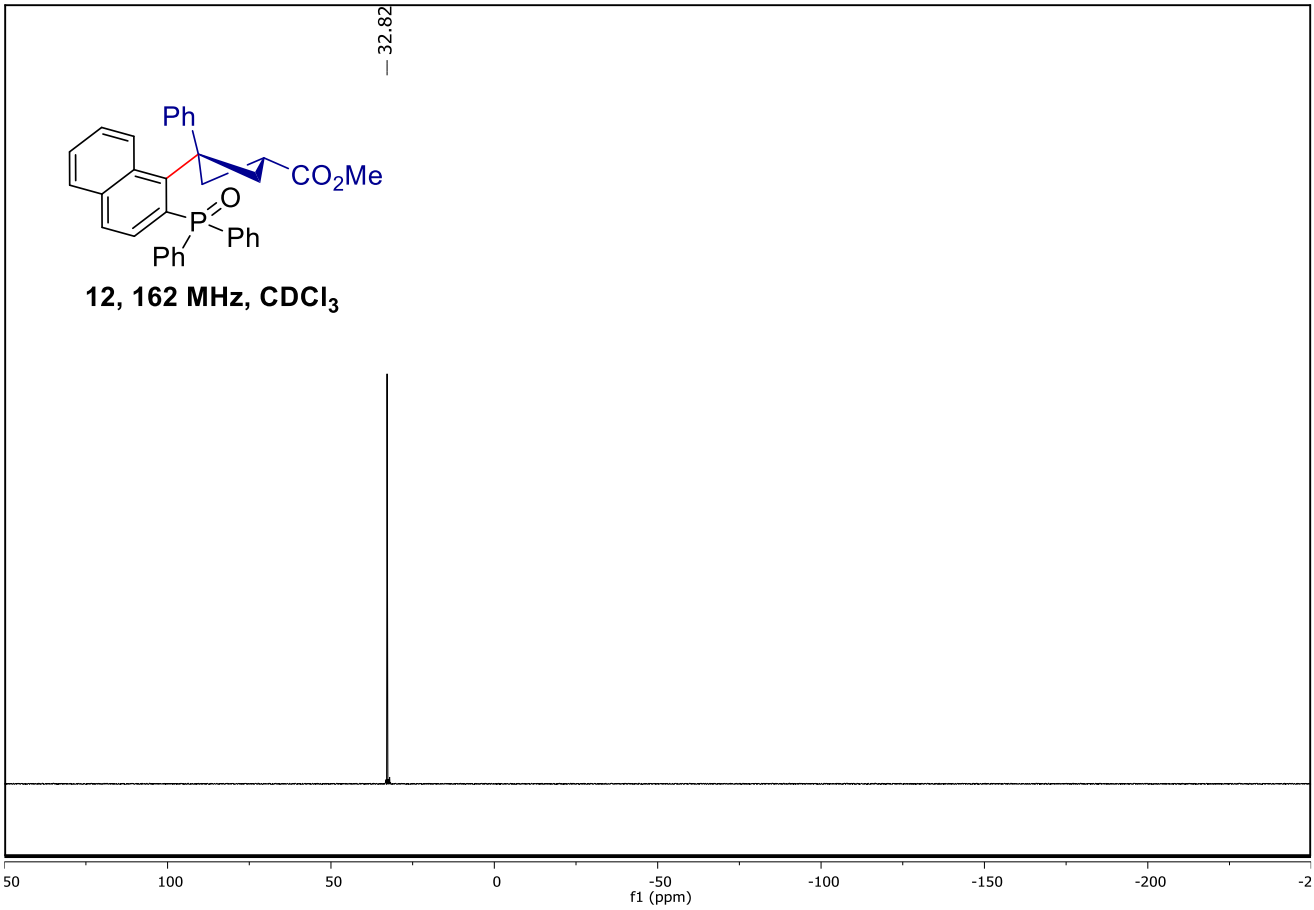




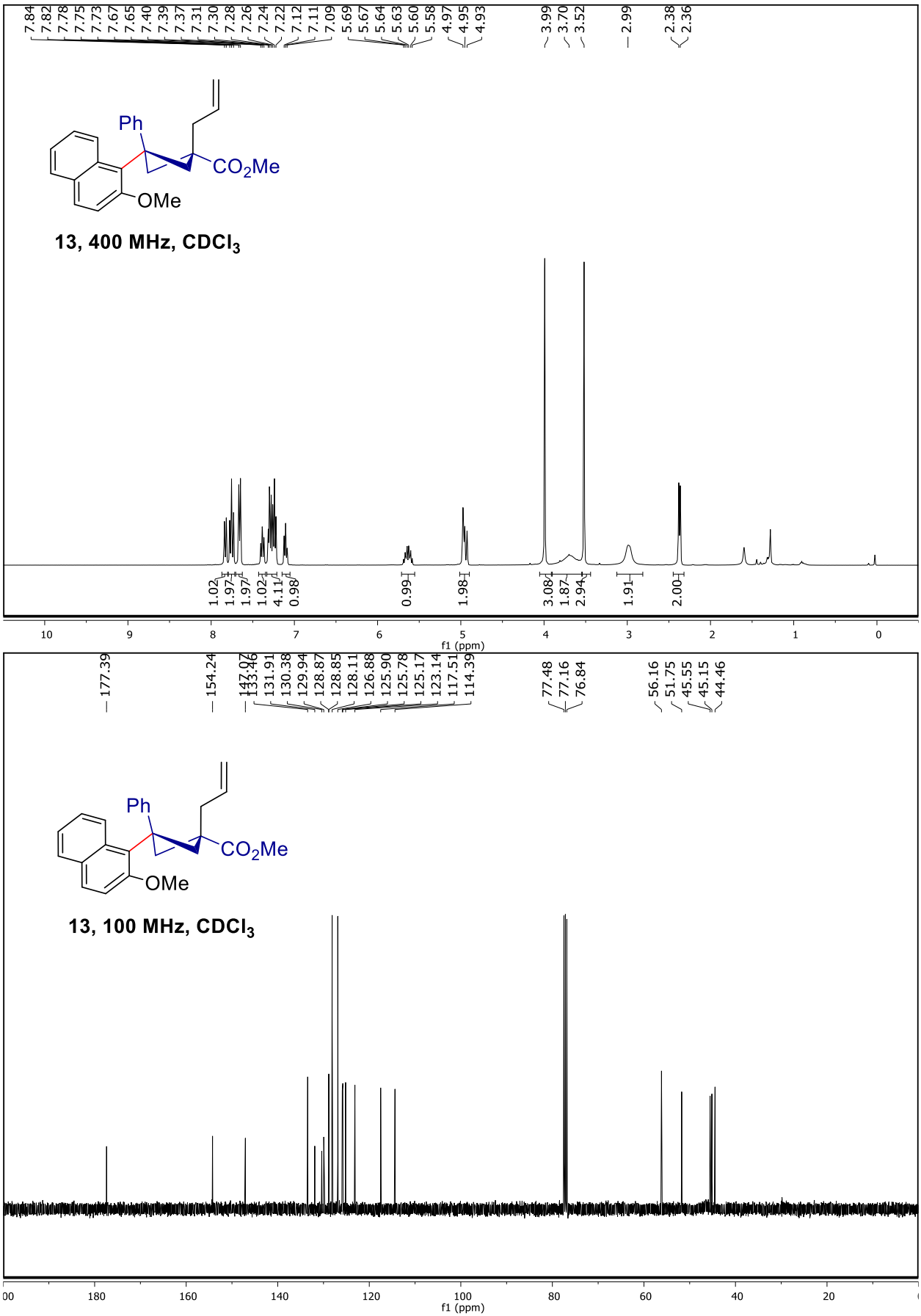
Methyl-3-(2-(diphenylphosphoryl)naphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (12)



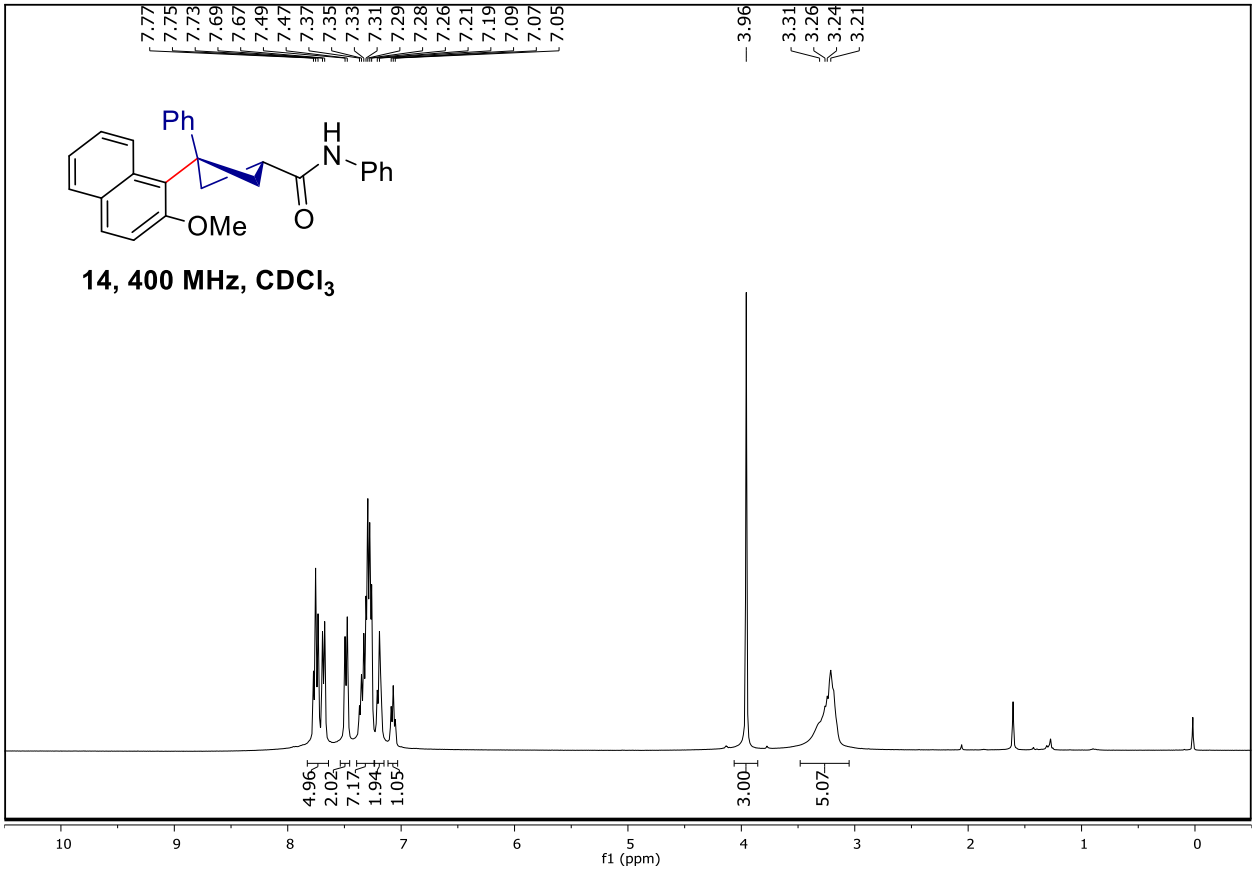


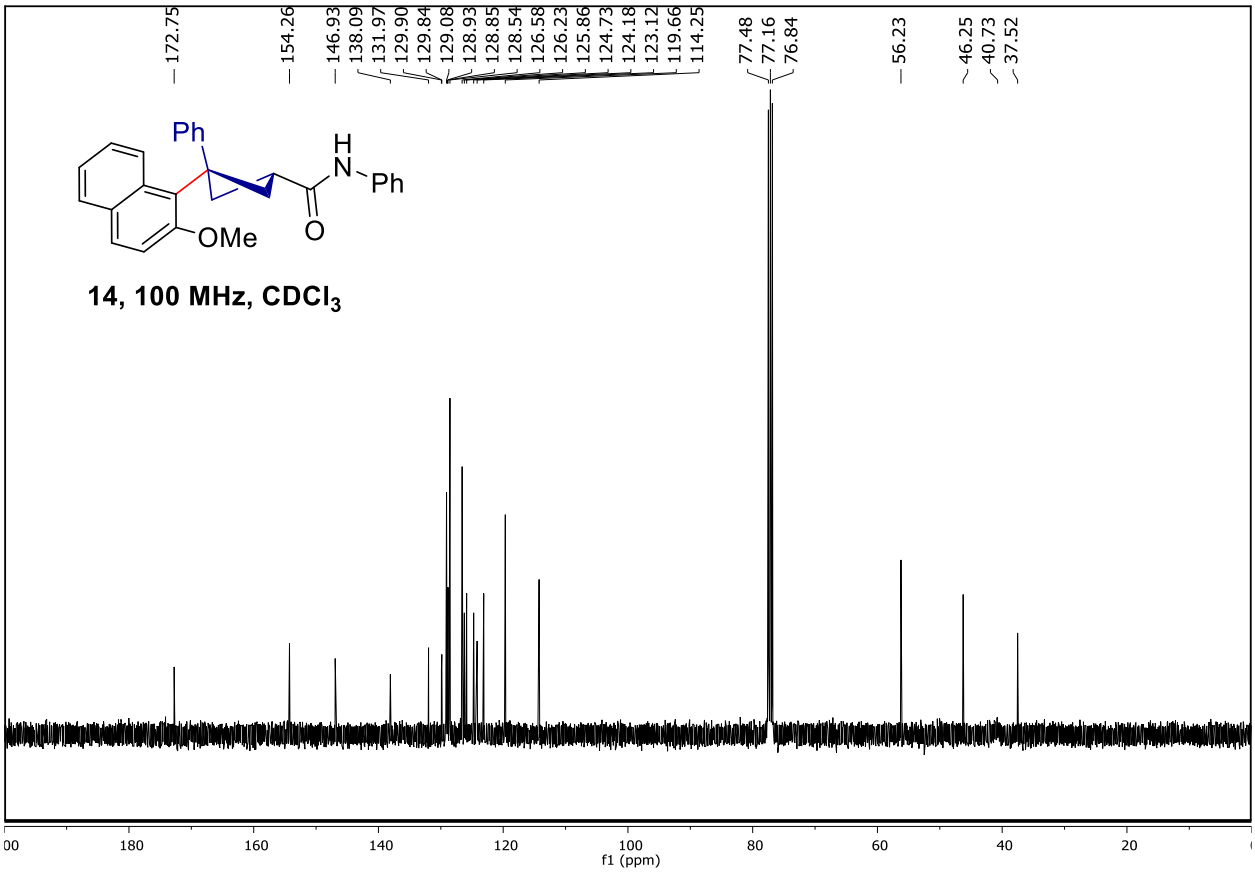

32.82
Ph
CO2Me
O
P
Ph
Ph
12, 162 MHz, CDCl3
50
100
50
0
-50
f1 (ppm)
-100
-150
-200
-2

Methyl-1-allyl-3-(2-methoxynaphthalen-1-yl)-3-phenylcyclobutane-1-carboxylate (13)



3-(2-Methoxynaphthalen-1-yl)-*N*,3-diphenylcyclobutane-1-carboxamide (14)





3-(2-Methoxynaphthalen-1-yl)-N,3-diphenylcyclobutane-1-carbothioamide (15)