Diester-Substituted Aminocyclopropanes: Synthesis and Use in [3+2] Annulation Reactions.

Eloisa Serrano, Florian de Nanteuil, Jerome Waser.*

Laboratory of Catalysis and Organic Synthesis, Ecole Polytechnique Fédérale de Lausanne, EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne, Switzerland.

Fax: +41 21 693 97 00.

E-mail: jerome.waser@epfl.ch.

Received: The date will be inserted once the manuscript is accepted.

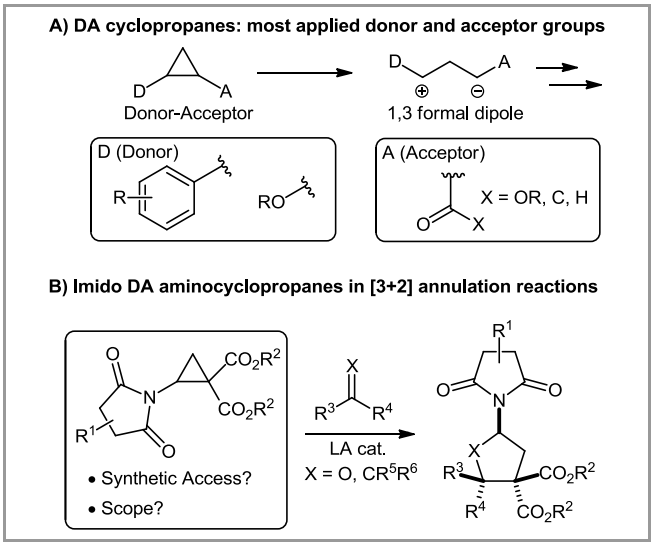
Abstract: In this article, we describe the synthesis of new donor-acceptor substituted cyclopropanes bearing various imido groups and their use in [3+2] annulation reactions. A sequence of palladium-catalyzed vinylation and rhodium-catalyzed cyclopropanation gave access to the required cyclopropanes in only two steps and high overall yields. The obtained compounds were used successfully in the tin-catalyzed [3+2] annulation with enol ethers to give cyclopentylamine derivatives in 22-95% yield.

Key words: Annulation, Carbocycles, Homogenous Catalysis, Nitrogen, Ring Opening.

Introduction

Cyclopropanes in general and donor-acceptor substituted cyclopropanes (DA cyclopropanes) in particular have found broad application in synthetic chemistry.[1] The combination of ring strain and polarizing groups allows ring-opening under mild conditions to generate reactive intermediates ideally suited for new bond formations (Scheme 1, **A**). In this respect, cyclization and annulation processes are especially useful, as they give access to ring systems constituting the core of numerous bioactive compounds. Carbon and oxygen electron-rich substituents have been most often used to direct ring cleavage. In contrast, only isolated examples of nitrogen-containing donors have been reported over the last 40 years.[2] This is surprising when considering that nitrogen-containing functionalities are especially important for the bioactivity of many synthetic and natural compounds. The use of DA aminocyclopropanes would consequently be particularly appealing for applications in synthetic and medicinal chemistry.

Driven by these considerations, our group has been working since 2009 on extending the use of DA aminocyclopropanes in cyclization, annulation and addition reactions.[3] The formal homo-Nazarov reaction of aminocyclopropanes gave a new access to *gonioma* and *aspidosperma* alkaloids.[3a-d] On the other hand, the use of imido-substituted cyclopropanes was especially successful in [3+2] annulation and Friedel-Crafts reactions.[3e-h] In our previous work, we focused on the variation of the two-atom partner, and could apply the reaction to a broad range of enol ethers, aldehydes and ketones using phthalimide-substituted cyclopropanes. In this article, we would like to report the details for the synthesis of imido-substituted cyclopropanes and their use in the [3+2] annulations with enol ethers (Scheme 1, **B**). The availability of these modified DA aminocyclopropanes was essential for our recent success in the development of a dynamic kinetic asymmetric [3+2] annulation process.[4]



Scheme 1 Most often used DA cyclopropanes (**A**) and Imido DA cyclopropanes in [3+2] annulation reactions (**B**).

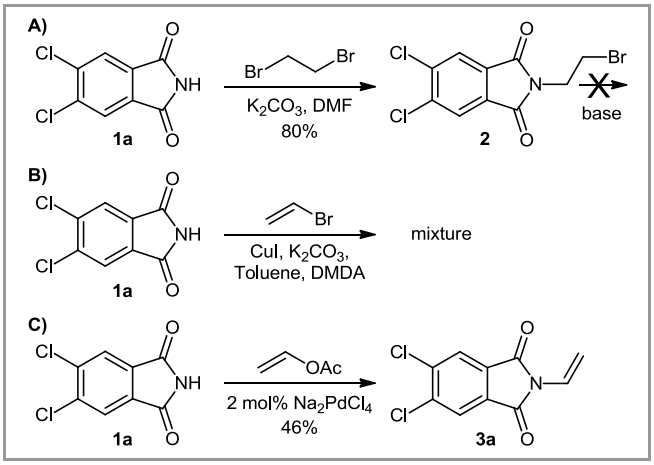
Results and Discussion

Synthesis of DA Aminocyclopropanes

In our preliminary communication, we had demonstrated that two ester groups were required on the aminocyclopropanes to allow ring-opening in presence of Lewis Acid catalysts.[3e] Furthermore, the use of a phthaloyl protecting group on the nitrogen had provided the right compromise between stability and reactivity. The required DA aminocyclopropanes were easily accessed via cyclopropanation of commercially available vinylphthalimide with diazomalonates catalyzed by Du Bois' rhodium catalyst.[5] With the goal of further examining the scope of imido groups tolerated in the [3+2] process, we needed now an efficient method to access modified vinyl phthalimide derivatives in good yields.

To reach this goal, a classical substitution-elimination procedure was first examined starting from dichlorophthalimide **1a** (Scheme 2, **A**).[6] Substitution

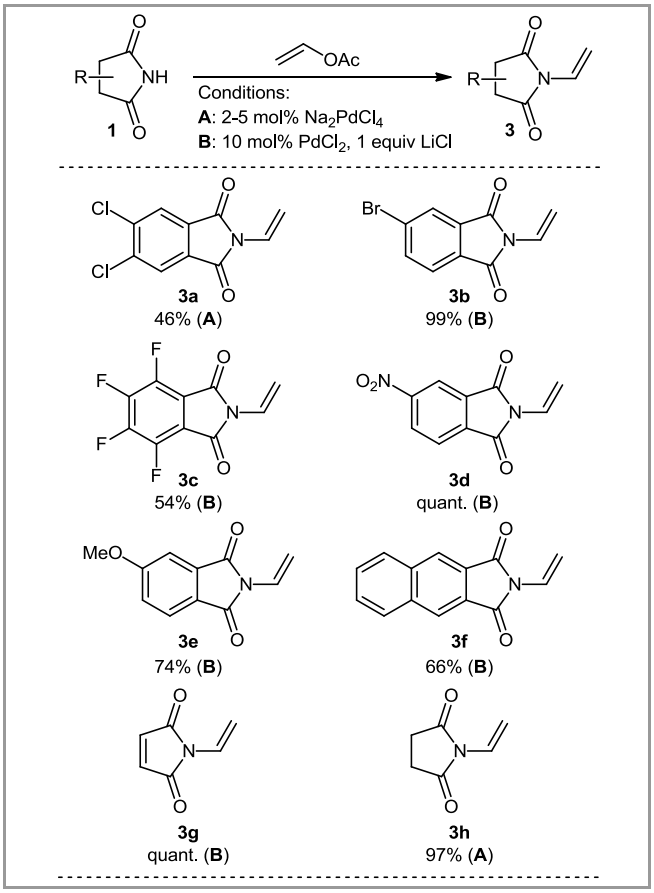
with dibromoethane proceeded smoothly in 80% yield to give product **2**. However, clean elimination of hydrogen bromide to form the desired vinyl phthalimide **3a** exclusively could not be achieved with a broad range of different bases. As a second approach, a copper-catalyzed Buchwald-Hartwig coupling with vinyl bromide was attempted (Scheme 2, **B**).[7] Although in this case the desired product **3a** was indeed observed, it could not be separated from other side products. Vinylphthalimide **3a** was finally obtained in 46% yield using a palladium-catalyzed trans-vinylation from vinyl acetate (Scheme 2, **C**).[8] Although no full conversion was achieved, product **3a** could be isolated in good purity using this protocol.



Scheme 2 Different approaches for the synthesis of dichloro-vinylphthalimide **3a**.

Nevertheless, when 5-bromophthalimide (**1b**) was used as substrate, only traces of vinylation were observed. In this case, 99% yield of vinylphthalimide **3b** could be obtained by using palladium chloride as catalyst in presence of an excess of lithium chloride (Scheme 3, conditions B). At this point, we investigated the scope of the vinylation reaction in more detail. The required phthalimides were either commercially available, or could be accessed in one step from the corresponding anhydrides by treatment with formamide under microwave heating.[9] The use of the $PdCl_2$/LiCl conditions was successful for the synthesis of vinylphthalimide derivatives **3c** and **3d** bearing electron-withdrawing fluoro and nitro groups respectively. It could also be applied to more electron-rich product **3e**, or a bulkier naphthalene derivative **3f**. Finally, the reaction was not limited to phthalimide derivatives: both vinylmaleimide (**3g**) and vinylsuccinimide (**3h**) were obtained in excellent yields. In the latter case, the use of the sodium palladate catalyst already gave 97% yield of product **3h**.

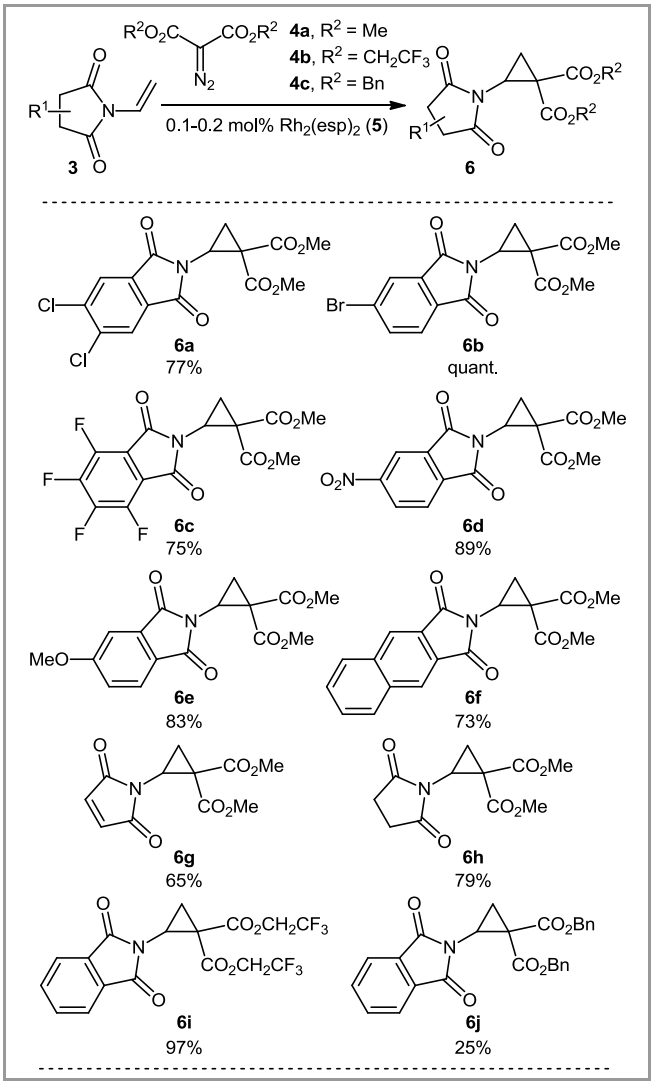
With the new vinylimides in hand, we then turned to the synthesis of the DA cyclopropanes themselves. Gratifyingly, the cyclopropanation catalyzed by Du Bois' catalyst **5** proved to be general, and proceeded from 65% up to quantitative yield for all the vinylimides synthesized using dimethyldiazomalonate (**4a**) as reagent (Scheme 4). The high stability of the rhodium catalyst allowed high turnover numbers, and 0.1 mol% catalyst loading was usually enough to provide full conversion of the vinylimides. Imido-cyclopropanes containing halogens (**6a-c**), an electron-withdrawing nitro group (**6d**), an electron-donating methoxy substituent (**6e**) or a naphthalene group (**6f**) were obtained in 73% to quantitative yield. The reaction also gave access to maleimide- and succinimide- substituted cyclopropanes **6g** and **6h**. A few other diazomalonates were also investigated in the reaction with vinylphthalimide. Ditrifluoroethylester cyclopropane **6i** was obtained in 97% yield, but the corresponding dibenzylester derivative **6j** was obtained in 25% yield only.



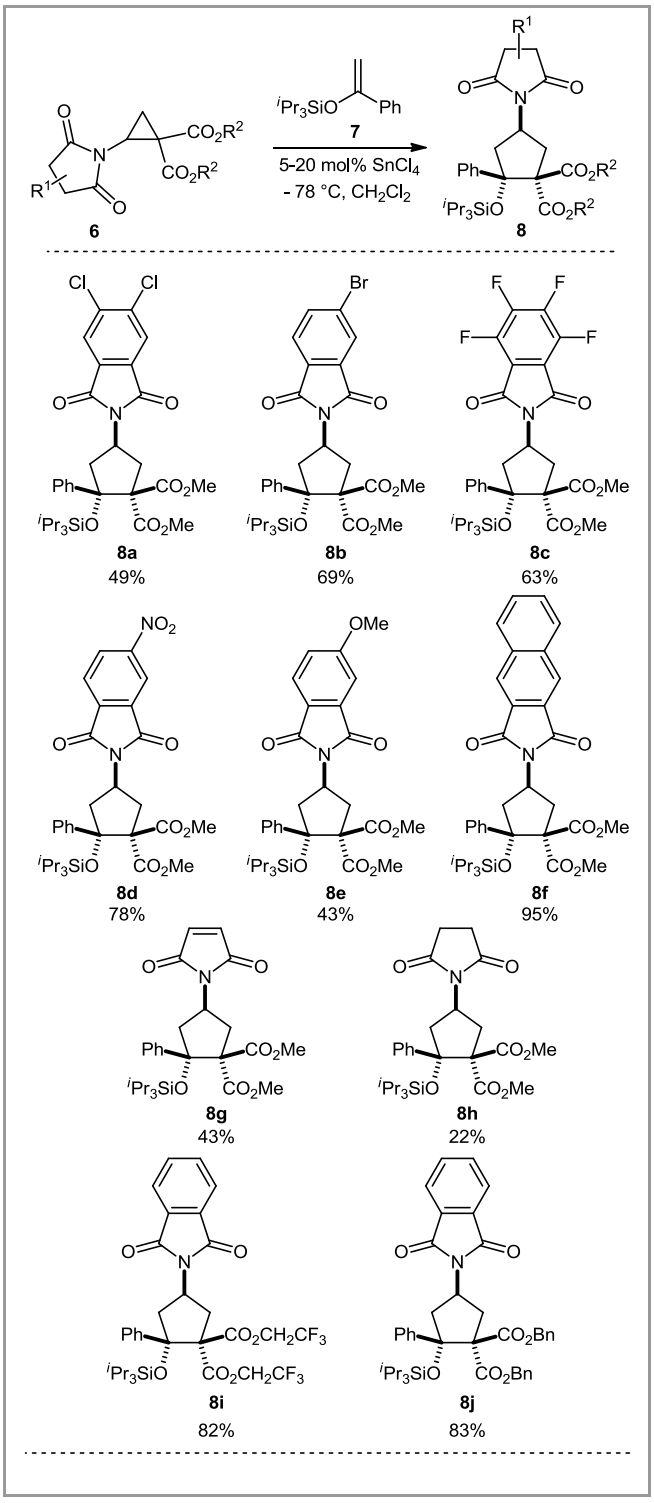
Scheme 3 Scope of the vinylation reaction. The reaction conditions used are given in parenthesis after the yield.

The DA aminocyclopropanes were then examined in the [3+2] annulation reaction with silyl enol ether **7** using the conditions developed previously in our group (Scheme 5).[3e] With phthalimide derivatives **6a-f**, the reaction gave the desired cyclopentylamines **8a-f** in 43-95% yield with excellent diastereoselectivity.[10] The lowest yield was observed for cyclopentylamine **8e**, bearing a methoxy group on the phthalimide, and the highest for product **8f** with a naphthalene imide derivative. No clear trend could be observed between yield and electronic properties of the substituents on

the phthalimide ring, demonstrating that the reaction was tolerant in this respect. When maleimide- and succinimide-substituted cyclopropanes **6g** and **6h** were used, the desired products **8g** and **8h** were also obtained, albeit in lower yields (43% and 22% respectively). It is interesting to note that substrate **8h** gave in contrast excellent results in the recently developed kinetic asymmetric [3+2] annulation using a copper bisoxazoline complex as catalyst.[4] Finally, modification of the diester group was also possible: products **8i** bearing a trifluoroethyl group and **8j** with a benzyl substituent were obtained in 82% and 83% yield respectively.



Scheme 4 Scope of the cyclopropanation reaction.



Scheme 5 Scope of the [3+2] annulation reaction.

Conclusion

In this article, we have reported the use of an efficient palladium-catalyzed method to access vinylimide derivatives in up to quantitative yields from the corresponding imides. Rhodium-catalyzed cyclopropanation with diazomalonates then occurred in good yields with only 0.1 mol% of catalyst to give DA imido-cyclopropanes with a broad variety of electronic and steric properties. All synthesized cyclopropanes could be used in the tin-catalyzed

[3+2] annulation reaction with enol ethers. The desired cyclopentylamines were obtained in 22-95% yield, whereas better results were obtained with phthalimide derivatives than with either maleimide or succinimide substituents. The ability of fine-tuning the structure of DA imido-cyclopropanes is very important for the development of new reactions, as demonstrated in the recent success in Friedel-Crafts reactions with indoles[3h] and dynamic kinetic asymmetric annulation reactions.[4]

Experimental Section

General Procedure for Vinylation

Method A: Following a modified procedure,[8b] Na_2PdCl_4 (2 mol%) was added to a stirred solution of the corresponding imide (1.00 eq) in vinyl acetate (27 equiv) and the mixture was heated under reflux for 48-96 hours. The solvent was evaporated and the residue was purified by column chromatography to obtain solid compounds.

Method B: Palladium(II) chloride (10 mol%) and lithium chloride (1.0 equiv weighted in a glovebox) were added to a stirred solution of the corresponding imide (1.00 equiv) in vinyl acetate (27 equiv) and the mixture was heated under reflux for 20-48 h. The mixture was cooled down to room temperature and the solvent was evaporated. The residue was purified by column chromatography to obtain solid compounds.

General Procedure for Cyclopropanation

Following a modified procedure,[5b] the corresponding *N*-vinyl-imide (1.00 equiv) was dissolved in dry CH_2Cl_2 (10 mL) and the solution was cooled down to 0 °C with an ice/water bath. Then, bis[rhodium(α,α,α', α'-tetramethyl-1,3-benzene-dipropionic acid)] (**5**, 0.1 mol%) was added in one portion. A solution in CH_2Cl_2 (2.0 mL) of the corresponding malonate (1.20 equiv) was added dropwise over 5 min. After the addition, the mixture was allowed to warm to rt and stirred overnight. The solvent is then removed under reduced pressure and the crude is directly purified by column chromatography.

General Procedure for [3+2] Annulation

Following a reported procedure,[3e] in an oven-dried flask sealed with a septum, the corresponding aminocyclopropane (1.00 equiv) and tri*iso*propyl((1-phenylvinyl)oxy)silane (**7**) (1.50 eq) were dissolved in dry CH_2Cl_2 (2.0 mL). The solution was then cooled down to -78 °C and 23 μL of a 0.43 M solution of tin tetrachloride (5.0 mol%)[11] in dry CH_2Cl_2 was added. The reaction was stirred for 1 to 3 h at -78 °C and then quenched at -78 °C with triethylamine (0.30 mL). The reaction was warmed up to rt and stirred for 15 min. Dichloromethane was removed under reduced pressure and the crude was directly purified by column chromatography.

Supporting Information Detailed experimental procedures and characterization data for all compounds is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Primary Data for this article are available online at http://www.thieme-connect.com/ejournals/toc/synlett and can be cited using the following DOI: (number will be inserted prior to online publication).

Acknowledgment

We thank F. Hoffmann-La Roche Ltd for an unrestricted research grant and the Swiss National Science Foundation (SNSF, grant number 200021_129874 and 200020_149494) for the support of F. d. N.

References

(1) (a) Reissig, H. U.; Zimmer, R. *Chem. Rev* **2003**, *103*, 1151. (b) Yu, M.; Pagenkopf, B. L. *Tetrahedron* **2005**, *61*, 321. (c) Carson, C. A.; Kerr, M. A. *Chem. Soc. Rev.* **2009**, *38*, 3051. (d) De Simone, F.; Waser, J. *Synthesis* **2009**, 3353. (e) Lebold, T. P.; Kerr, M. A. *Pure Appl. Chem.* **2010**, *82*, 1797. (f) Mel'nikov, M. Y.; Budynina, E. M.; Ivanova, O. A.; Trushkov, I. V. *Mendeleev Commun.* **2011**, *21*, 293. (g) Tang, P.; Qin, Y. *Synthesis* **2012**, *44*, 2969. (h) Wang, Z. W. *Synlett* **2012**, 2311. (i) Cavitt, M. A.; Phun, L. H.; France, S. *Chem. Soc. Rev.* **2014**, *43*, 804. (j) Schneider, T. F.; Kaschel, J.; Werz, D. B. *Angew. Chem., Int. Ed.* **2014**, *53*, 5504.

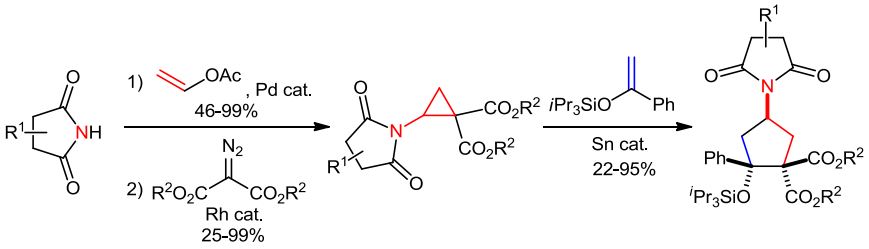
(2) Selected examples: (a) Wenkert, E.; Hudlicky, T. *J. Org. Chem.* **1988**, *53*, 1953. (b) Williams, C. M.; de Meijere, A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3699. (c) Lee, H. B.; Sung, M. J.; Blackstock, S. C.; Cha, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 11322. (d) Larquetoux, L.; Ouhamou, N.; Chiaroni, A.; Six, Y. *Eur. J. Org. Chem.* **2005**, 4654. (e) Wasilewska, A.; Woźniak, B. A.; Doridot, G.; Piotrowska, K.; Witkowska, N.; Retailleau, P.; Six, Y. *Chem. Eur. J.* **2013**, *19*, 11759. (f) Gharpure, S. J.; Vijayasree, U.; Reddy, S. R. B. *Org. Biomol. Chem.* **2012**, *10*, 1735. (g) Maity, S.; Zhu, M. Z.; Shinabery, R. S.; Zheng, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 222. Theoretical studies on the influence of different groups for the ring enlargement of cyclopropanes: (h) Schneider, T. F.; Werz, D. B. *Org. Lett.* **2011**, *13*, 1848.

(3) (a) De Simone, F.; Gertsch, J.; Waser, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 5767. (b) De Simone, F.; Saget, T.; Benfatti, F.; Almeida, S.; Waser, J. *Chem. Eur. J.* **2011**, *17*, 14527. (c) De Simone, F.; Waser, J. *Synlett* **2011**, 589. (d) Frei, R.; Staedler, D.; Raja, A.; Franke, R.; Sasse, F.; Gerber-Lemaire, S.; Waser, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 13373. (e) de Nanteuil, F.; Waser, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 12075. (f) Benfatti, F.; de Nanteuil, F.; Waser, J. *Org. Lett.* **2012**, *14*, 386. (g) Benfatti, F.; de Nanteuil, F.; Waser, J. *Chem. Eur. J.* **2012**, *18*, 4844. (h) de Nanteuil, F.; Loup, J.; Waser, J. *Org. Lett.* **2013**, *15*, 3738. Examples of annulation with imido-cyclopropanes which appeared after our first publication : (i) Rivero, A. R.; Fernandez, I.; Sierra, M. A. *Org. Lett.* **2013**, *15*, 4928. (j) Tejero, R.; Ponce, A.; Adrio, J.; Carretero, J. C. *Chem. Comm.* **2013**, *49*, 10406.

(4) de Nanteuil, F.; Serrano, E.; Perrotta, D.; Waser, J. *J. Am. Chem. Soc.* **2014**, *136*, 6239.

(5) (a) Espino, C. G.; Fiori, K. W.; Kim, M.; Du Bois, J. *J. Am. Chem. Soc.* **2004**, *126*, 15378. (b) Gonzalez-Bobes, F.; Fenster, M. D. B.; Kiau, S.; Kolla, L.; Kolotuchin, S.; Soumeillant, M. *Adv. Synth. Catal.* **2008**, *350*, 813.
(6) Muller, P. ; Albrecht, M. Bayer Aktiengesellschaft, Patent: US6232475 B1, **2001**.
(7) Nguyen, T. B.; Martel, A.; Dhal, R.; Dujardin, G. *J. Org. Chem* **2008**, *73*, 2621.
(8) (a) Bayer, E.; Geckeler, K. *Angew. Chem., Int. Ed.* **1979**, 18, 533. (b) Baret, N.; Dulcere, J. P.; Rodriguez, J.; Pons, J. M.; Faure, R. *Eur. J. Org. Chem.* **2000**, 1507.
(9) Kacprzak, K. *Synth. Commun.* **2003**, *33*, 1499.
(10) (10) All substrates were obtained with a diastereoselectivity higher than 20:1 as determined on the ^{1}H NMR of the crude reaction mixture. The *trans* relationship between the nitrogen and oxygen groups had been determined previously on phthalimido substituted products via X-ray diffraction studies (reference 3e) and was assumed to be identical for the products obtained in this work based on the similitude of the NMR data. The high diastereoselectivity observed may be due to minimization of the dipoles of the C-N and the C-O bonds during ring closing, but further studies will be required to support this hypothesis.
(11) Higher catalyst loading was required for some substrates, see the Supporting Information for more details.

Diester-Substituted Aminocyclopropanes: Synthesis and Use in [3+2] Annulation Reactions.



Supporting Information

30 pages

Diester-Substituted Aminocyclopropanes: Synthesis and Use in [3+2] Annulation Reactions.

Eloisa Serrano, Florian de Nanteuil and Jerome Waser.

Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne, Switzerland.

jerome.waser@epfl.ch

Table of Contents

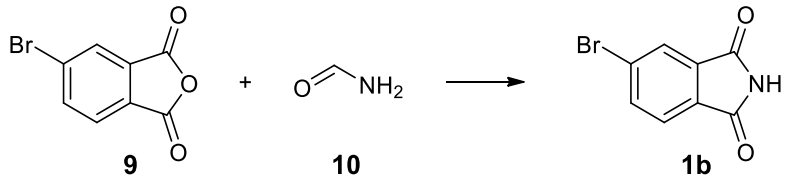
1. General Methods

All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen with magnetic stirring, unless stated otherwise. For quantitative flash chromatography, technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et_2O, CH_3CN, toluene, hexane and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 30 ppm, Karl-Fischer titration). All chemicals were purchased from Strem, Acros, Aldrich, Fluka, VWR, Aplichem or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain or p-anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, DMSO-d6, CD_2Cl_2 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm, the internal CD_2Cl_2 signal at 5.31 ppm, or the internal MeOD signal at 3.30 ppm as standard. The data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration; interpretation). ^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a Brucker DPX-400 100 MHz spectrometer in chloroform-d, DMSO-d6, CD_2Cl_2 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm, the internal CD_2Cl_2 signal at 53.5 ppm or the internal MeOD signal at 49.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm^{-1} (w = weak, m = medium, s = strong, sh = shoulder). Gas chromatography and low resolution mass spectrometry measurements were performed on a Perkin-Elmer Clarus 600 gas chromatographe and mass spectrometer using a Perkin-Elmer Elite fused silica column (length: 30 m, diameter: 0.32 mm) and Helium as carrier gas. High resolution mass spectrometry measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. HPLC measurements were done on a JASCO HPLC system with an AS2055 Autosampler, a PU 2089 Pump, a UV 2075 detector and a SEDEX 85 (SEDERE) detector using a CHIRALPAK IC, IB or IA column from DAICEL Chemical.

2. Preparation of Substrates

2.1 Synthesis of imides

5-Bromoisoindoline-1,3-dione (1b)



9 **10** **1b**

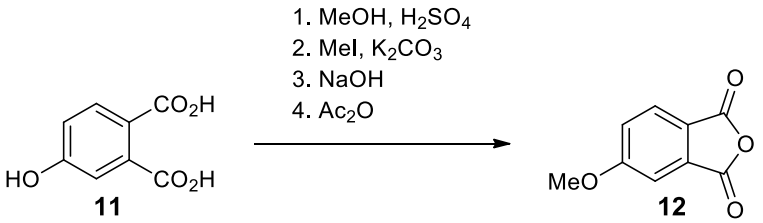
Following a modified procedure,[1] 5-bromoisobenzofuran-1,3-dione (**9**) (500 mg, 2.20 mmol, 1.00 eq) and formamide (**10**) (8.82 mL, 220 mmol, 100 eq) were added in a 20 mL microwave vial and sealed with a microwave cap. The mixture was stirred until the product was completely dissolved. The mixture was heated 2 times at 200 °C for 30 sec with 10 sec pre-stirring, using a Biotage Initiator 2.0 microwave reactor. The mixture was cooled to 0 °C to induce crystallization and 10 mL of cold water was added into the tube. The white solid

[1] K. Kacprzak, *Synth. Commun.* **2003**, *33*, 1499.

was filtrated over filter paper, washed with cold water (15 mL) and hexanes (20 mL) and dried under reduced pressure to afford 5-bromoisoindoline-1,3-dione (**1b**) as a colorless solid (394 mg, 1.75 mmol, 79% yield) which was used without further purification.

^{1}H NMR (400 MHz, DMSO) δ 11.40 (s, 1 H, *NH*), 8.04-7.99 (m, 2 H, *Ar*), 7.76 (d, 1 H, *J* = 7.7 Hz, *Ar*). HRMS (APPI) calcd for $C_8H_3{}^{79}BrNO_2^-$ [M-H]$^-$ 223.9353; found 223.9376. The ^{1}H NMR data for **1b** corresponds to the reported values.[2]

5-Methoxyisobenzofuran-1,3-dione (**12**)



Following a modified procedure,[3] a solution of 4-hydroxyphthalic acid (**11**) (2.00 g, 11.0 mmol, 1.00 eq), catalytic sulfuric acid (0.10 mL, 1.9 mmol, 0.17 eq) and MeOH (20.0 mL), was stirred at reflux for 7 h. under air. The solvent was removed under reduced pressure to afford crude dimethyl 4-hydroxyphthalate. The crude diester was dissolved in acetone (70 mL) and reacted with potassium carbonate (7.40 g, 53.5 mmol, 5.00 eq) at 50 °C for 20 min. Iodomethane (1.47 mL, 23.6 mmol, 2.20 eq) was added, and the mixture was stirred at reflux overnight. K_2CO_3 was removed by filtration and the solvent was removed under reduced pressure to afford a colorless oil.

The crude was dissolved in acetone (16.0 mL) and a 11 M solution of sodium hydroxide, (6.00 mL, 66.0 mmol, 6.20 eq) was added, and the solution was stirred for 6 h. under air at rt. The solution was then acidified with 2 M HCl to pH 3, and concentrated under reduced pressure. Then, the crude 4-methoxyphthalic acid was dissolved into acetone (50 mL) and dried over $MgSO_4$, filtered through a plug of cotton wool, and the solvent was removed in vacuo. The crude diacid was partitioned between 2 M NaOH (50 mL) and DCM (50 mL). The organic layer was extracted with NaOH 2 M (50 mL). The combined aqueous phase was cooled down to 0 °C and acidified with 37% HCl % to pH 3. The aqueous layer was then extracted five times with AcOEt (50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude diacid as a light brown solid (1.82 g).

A solution of crude 4-methoxyphthalic acid (1.82 g, 9.28 mmol, 1.00 eq) in acetic anhydride (25.0 mL, 266 mmol, 28.7 eq) was stirred at reflux for 21 h. Volatiles were removed in vacuo to afford a dark brown solid. The crude was dissolved in DCM (50 mL) and filtered through fritted glass to remove solid impurities. The solution was concentrated under reduced pressure and dried in vacuo to afford the anhydride **12** as a light brown solid (1.62 g, 9.08 mmol, 83% yield over 4 steps)

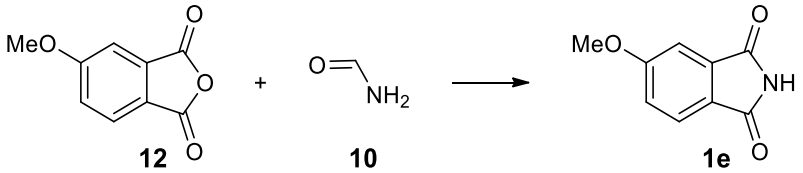
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, 1 H, *J* = 8.5, 0.4 Hz, *Ar*), 7.41 (d, 1 H, *J* = 2.2 Hz, *Ar*), 7.35 (dd, 1 H, *J* = 8.5, 2.3 Hz, *Ar*), 3.98 (s, 3 H, *OMe*). HRMS (ESI) calcd for $C_9H_7O_4^+$ [M+H]$^+$ 179.0339; found 179.0349. The ^{1}H NMR data for (**12**) corresponded to the reported values.[4]

5-Methoxyisoindoline-1,3-dione (1e)

[2] N. Delbosc, M. Reynes, O. J. Dautel, G. Wantz, J.-P. Lère-Porte, J. J. E. Moreau, *Chem. Mat.* **2010**, *22*, 5258.

[3] P. H. Mazzocchi, P. Wilson, F. Khachik, L. Klingler, S. Minamikawa, *J. Org. Chem.* **1983**, *48*, 2981.

[4] N. J. Hinde, C. D. Hall, *J. Chem. Soc., Perkin Trans. 2.* **1998**, 1249.

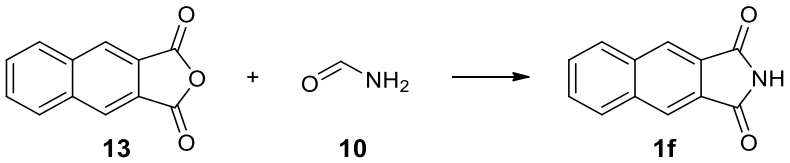


Following a modified procedure,[1] 5-methoxyisobenzofuran-1,3-dione (**12**) (1.58 g, 8.84 mmol, 1.00 eq) and formamide (35.0 mL, 880 mmol, 100 eq) were divided between four 20 mL microwave vials sealed with a microwave cap. The mixture was stirred at rt until the product was completely dissolved, then heated 2 times at 200 °C for 30 sec with 10 sec pre-stirring, using Biotage Initiator 2.0 microwave reactor. The mixture was cooled to 0 °C to induce crystallization and cold water (10 mL) was added into each vial. The obtained solid was filtrated over filter paper, washed with water (15 mL) and hexanes (20 mL) and dried under reduced pressure to afford 5-methoxyisoindoline-1,3-dione (**1e**) as a beige solid (982 mg, 5.54 mmol, 63% yield) which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, 1 H, *J* = 8.3, 0.4 Hz, *Ar*), 7.59 (br s, 1 H, *NH*), 7.33 (d, 1 H, *J* = 2.2 Hz, *Ar*), 7.20 (dd, 1 H, *J* = 8.3, 2.3 Hz, *Ar*), 3.94 (s, 3 H, *OMe*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 167.7, 165.0, 135.2, 125.4, 124.5, 120.4, 108.1, 56.2.

The NMR data for (**1e**) corresponds to the reported values.[5]

1H-Benzo[f]isoindole-1,3(2H)-dione (1f)



Following a modified procedure,[1] 2,3-naphthalene dicarboxylic anhydride (**13**) (0.250 g, 1.26 mmol, 1.00 eq) and formamide (**10**) (10.1 mL, 252 mmol, 200 eq) were added in a 20 mL microwave vial and sealed with a microwave cap. The mixture was heated at 200 °C for 30 sec with 10 sec pre-stirring, using a Biotage Initiator 2.0 microwave reactor. The desired product crystalized spontaneously from the reaction mixture as white needles. Then 10 mL of water was added and the solid was filtered, washed with cold water (10 mL) and hexanes (10 mL) and dried under reduced pressure. Compound (**1f**) was obtained as a white solid (0.172 g, 0.875 mmol, 69% yield).

R_f 0.44 (6:4 Hexane/AcOEt). m.p. 267 °C decomp. ^{1}H NMR (400 MHz, DMSO) δ 11.52 (s, 1 H, *NH*), 8.46 (s, 2 H, *Ar*), 8.29-8.23 (m, 2 H, *Ar*), 7.79-7.74 (m, 2 H, *Ar*). ^{13}C NMR (101 MHz, DMSO) δ 168.9, 135.1, 130.2, 129.1, 128.7, 124.2. IR 3224 (w), 3071 (w), 2925 (w), 2852 (w), 1707 (s), 1447 (w), 1316 (m), 1113 (m), 1012 (w), 905 (w).

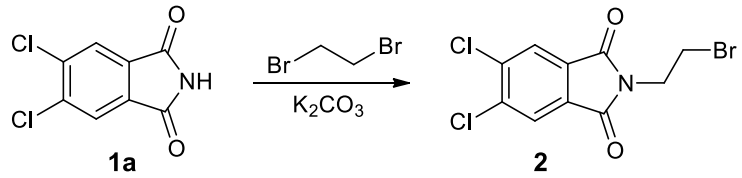
The NMR data for **1f** corresponds to the reported values.[6]

[5] F. de Nanteuil, E. Serrano, D. Perrotta, J. Waser, *J. Am. Chem. Soc.* **2014**, *136*, 6239.

[6] F. de Nanteuil, J. Loup, J. Waser, *Org. Lett.* **2013**, *15*, 3738.

2.2 Vinylation of Imides

N-(2-bromo-ethyl)-4,5-dichlorophthalimide (2)

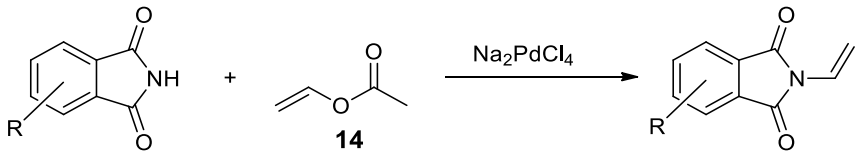


Following a modified procedure,[7] 4,5-dichlorophthalimide (1.00 g, 4.63 mmol, 1.00 eq.), anhydrous K_2CO_3 (400 mg, 2.89 mmol, 0.625 eq.) and 1,3-dibromopropane (5.0 mL, 58 mmol, 13 eq.), were dissolved in DMF (10.0 mL). The mixture was stirred and heated at reflux for 10 h, then poured into H_2O (100 mL) and extracted with CH_2Cl_2 (3 X 30 mL). The combined extracts were then washed with brine (3 X 30 mL), dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The solid residue was purified by column chromatography (9:1 Hexane/Ethyl Acetate) to obtain N-(2-bromo-ethyl)-4,5-dichlorophthalimide (1.20 g, 3.72 mmol, 80 % yield) as a white solid.

R_f 0.54 (8:2 Hexane/AcOEt). m.p. 149.6 - 150.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2 H, *Ar*), 4.10 (t, 2 H, *J* = 6.6 Hz, *CH*$_2$), 3.61 (t, 2 H, *J* = 6.5 Hz, *CH*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 139.4, 131.0, 125.8, 39.8, 28.1. IR 3085 (w), 3030 (w), 2952 (w), 1721 (s), 1388 (s), 1195 (w), 1139 (w), 1075 (m), 907 (m). HRMS (ESI) calcd for $C_{10}H_6{}^{79}Br^{35}Cl_2NO_2$ $[M+H]^+$ 321.9032; found 321.9033.

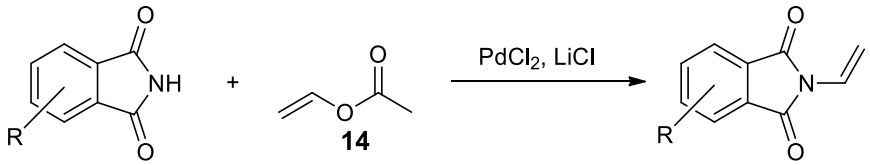
General Procedures for the Vinylation Reactions (GP1)

Method A (GP1A)



Following a modified procedure,[8] Na_2PdCl_4 (2 mol%) was added to a stirred solution of the corresponding phthalimide (1.00 eq) in vinyl acetate (**14**) (27 eq) and the mixture was heated under reflux. The solvent was evaporated and the residue was purified by column chromatography to obtain solid compounds.

Method B (GP1B)

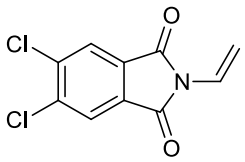


Palladium(II) chloride (10 mol%) and lithium chloride (10 mol% or 1.0 eq weighted in a glovebox), was added to a stirred solution of the corresponding phthalimide (1.00 eq) in vinyl acetate (**14**) (27 eq) and the mixture was heated under reflux. The mixture was cooled down to room temperature and the solvent was evaporated. The residue was purified by column chromatography to obtain solid compounds.

[7] C. A. Strassert, J. Awruch, *Monatsh. Chem.* **2006**, *137*, 1499.

[8] N. Baret, J.-P. Dulcere, J. Rodriguez, J.-M. Pons, R. Faure, *Eur. J. Org. Chem.* **2000**, *2000*, 1507.

5,6-Dichloro-2-vinylisoindoline-1,3-dione (3a)

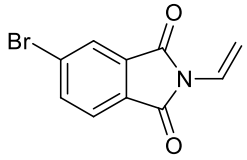


Following **GP1A**, 4,5-dichlorophthalimide (**1a**) (1.00 g, 4.63 mmol, 1.00 eq), vinyl acetate (**14**) (11.5 mL, 124 mmol, 26.8 eq) and Na_2PdCl_4 (27.0 mg, 0.093 mmol, 2 mol%) were heated under reflux for 48 h. After solvent evaporation, the crude was purified by Biotage (SNAP Cartridge KP-Sil 25 g, 8:2 Hexane/AcOEt) to obtain (**3a**) as a yellow solid (1.12 g, 2.14 mmol, 72% b.r.s.m, 46% yield) and (0.357 g, 1.65 mmol, 36% reisolated yield) of the starting material.

R_f 0.53 (6:4 Hexane/AcOEt). m.p. 164.7 – 166.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2 H, *Ar*), 6.84 (dd, 1 H, *J* = 16.4, 9.8 Hz, *=CH*), 6.09 (dd, 1 H, *J* = 16.4, 0.3 Hz, *=CH*), 5.10 (dd, 1 H, *J* = 9.8, 0.3 Hz, *=CH*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 139.7, 130.8, 125.8, 123.7, 105.6.

The NMR data for **3a** corresponds to the reported values.[6]

5-Bromo-2-vinylisoindoline-1,3-dione (3b)

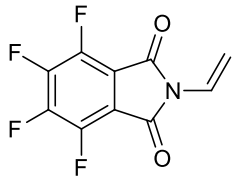


Following **GP1B**, 5-bromoisoindoline-1,3-dione (**1b**) (1.50 g, 6.64 mmol, 1.00 eq), $PdCl_2$ (118 mg, 0.664 mmol, 0.100 eq), LiCl (28.0 mg, 0.660 mmol, 0.100 eq, weighted in the glovebox) and vinyl acetate (**14**) (16.5 mL, 178 mmol, 26.8 eq) were heated under reflux for 28 h. After solvent evaporation, the crude was purified by silica gel chromatography (Hexane/AcOEt 20:1 to 15:1) to afford 5-bromo-2-vinylisoindoline-1,3-dione (**3b**) as a yellow solid (1.66 g, 6.59 mmol, 99% yield).

R_f 0.47 (9:1 Hexane/AcOEt). m.p. 74.9 - 75.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 1 H, *J* = 1.4 Hz, *Ar*), 8.07 (dd, 1 H, *J* = 8.0, 1.8 Hz, *Ar*), 7.84 (d, 1 H, *J* = 7.9 Hz, *Ar*), 6.81 (dd, 1 H, *J* = 16.3, 9.8 Hz, *=CH*), 5.93 (d, 1 H, *J* = 16.3 Hz, *=CH*), 5.08 (d, 1 H, *J* = 9.8 Hz, *=CH*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 165.1, 138.6, 133.3, 130.1, 129.5, 127.0, 125.0, 123.7, 105.1.

The NMR data for **3b** corresponds to the reported values.[6]

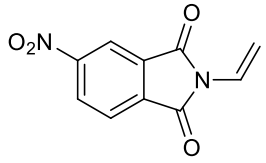
4,5,6,7-Tetrafluoro-2-vinylisoindoline-1,3-dione (3c)



Following **GP1B**, 4,5,6,7-tetrafluoroisoindoline-1,3-dione (**1c**) (500 mg, 2.82 mmol, 1.00 eq), $PdCl_2$ (40.0 mg, 0.228 mmol, 0.100 eq), LiCl (97.0 mg, 2.28 mmol, 1.00 eq, weighted in a glovebox) and vinyl acetate (**14**) (5.70 mL, 61.2 mmol, 26.8 eq) were heated under reflux for 48 h. The mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. The crude was purified by Biotage (SNAP Cartridge KP-Sil 25 g, 8:2 Hexane/AcOEt) to obtain (**3c**) as a colorless solid (302 mg, 1.23 mmol, 79% b.r.s.m, 54% yield) and (160 mg, 0.730 mmol, 32% reisolated yield) of the starting material.

R_f 0.65 (9:1 Pentane/AcOEt). m.p. 144.4 - 146.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (dd, 1 H, *J* = 16.4, 9.8 Hz, *N-CH*), 6.07 (dd, 1 H, *J* = 16.4, 0.5 Hz, *=CH₂*), 5.13 (dd, 1 H, *J* = 9.8, 0.5 Hz, *=CH₂*). IR 1732 (s), 1639 (w), 1515 (s), 1500 (m), 1402 (s), 1369 (m), 1307 (w), 1038 (w), 951 (m), 908 (s). HRMS (ESI) calcd for $C_{10}F_4H_4NO_2^+$ $[M+H]^+$ 246.0173; found 246.0174.

5-Nitro-2-vinylisoindoline-1,3-dione (3d)

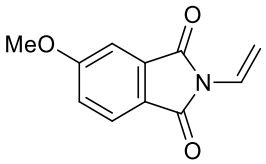


Following **GP1B**, 5-nitrosoindoline-1,3-dione (**1d**) (1.00 g, 5.20 mmol, 1.00 eq), $PdCl_2$ (92.0 mg, 0.520 mmol, 0.100 eq), LiCl (0.221 mg, 5.20 mmol, 1.00 eq, weighted in a glovebox) and vinyl acetate (**14**) (12.9 mL, 139 mmol, 26.8 eq) were heated under reflux for 20 h. The mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. The crude was purified by column chromatography using silica gel (Hexane/AcOEt 8:2 to 5:5) to afford 5-nitro-2-vinylisoindoline-1,3-dione (**3d**) as a bright yellow solid (1.14 g, 5.23 mmol, quantitative yield).

R_f 0.32 (9:1 Pentane/AcOEt). m.p. 144.3 - 148.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, 1 H, *J* = 2.0, 0.5 Hz, *Ar*), 8.63 (dd, 1 H, *J* = 8.1, 2.0 Hz, *Ar*), 8.08 (m, 1 H, *Ar*), 6.88 (dd, 1 H, *J* = 16.4, 9.8 Hz, *CH-N*), 6.14 (dd, 1 H, *J* = 16.4, 0.5 Hz, *=CH₂*), 5.16 (dd, 1 H, *J* = 9.8, 0.4 Hz, *=CH₂*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 164.2, 152.1, 136.1, 133.1, 129.8, 125.0, 123.6, 119.2, 106.3.

The NMR data for **3d** corresponds to the reported values.[5]

5-Methoxy-2-vinylisoindoline-1,3-dione (3e)

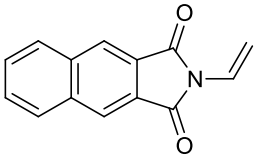


Following **GP1B**, 5-methoxyisoindoline-1,3-dione (**1e**) (980 mg, 5.53 mmol, 1.00 eq), $PdCl_2$ (98.0 mg, 0.553 mmol, 0.100 eq), LiCl (235 mg, 5.53 mmol, 1.00 eq, weighted in a glovebox) and vinyl acetate (**14**) (13.7 mL, 148 mmol, 26.8 eq) were heated under reflux for 24 h. The mixture was cooled down to room temperature and diluted with DCM/MeOH 4:1 (20 mL). Activated charcoal was added and the resulting suspension was filtered through a pad of Celite (DCM/MeOH 4:1 100 mL) and concentrated under reduced pressure. Purification by silica gel chromatography (pentane/AcOEt 90:10 to 75:25) afforded 5-methoxy-2-vinylisoindoline-1,3-dione (**3e**) as a colorless solid (828 mg, 4.08 mmol, 74% yield).

R_f 0.56 (6:4 Hexane/AcOEt). m.p. 102.2 - 105.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, 1 H, *J* = 8.3 Hz, Ar), 7.32 (d, 1 H, *J* = 2.2 Hz, Ar), 7.17 (dd, 1 H, *J* = 8.3, 2.2 Hz, Ar), 6.83 (dd, 1 H, *J* = 16.4, 9.9 Hz, =C*H*), 6.03 (d, 1 H, *J* = 16.4 Hz, =C*H*), 4.99 (d, 1 H, *J* = 9.9 Hz, =C*H*), 3.93 (s, 3 H, O*Me*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 166.3, 165.1, 134.4, 125.5, 124.0, 123.5, 120.6, 108.2, 104.0, 56.3.

The NMR data for **3e** corresponds to the reported values.[5]

2-Vinyl-1H-benzo[f]isoindole-1,3(2H)-dione (3f)

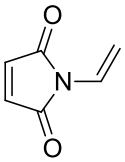


Following **GP1B**, 1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione (**1f**) (1.70 g, 8.62 mmol, 1 equiv), palladium(II) chloride (0.150 g, 0.860 mmol, 0.1 equiv), lithium chloride (0.0370 g, 0.860 mmol, 0.1 equiv) and vinyl acetate (**14**) (21.4 mL, 231 mmol, 27 equiv) were added in a microwave tube sealed with a microwave cap. After stirring for 31 h at 80 °C, the resulting mixture was cooled down to room temperature. Purification by silica gel chromatography (hexane/ethyl acetate 17/1 to 10/1) afforded 2-vinyl-1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione (**3f**) (1.26 g, 5.66 mmol, 66% yield) as a colorless solid.

R_f 0.53 (8:2 Hexane/AcOEt). m.p. 201.9 – 202.8°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 2 H, *Ar*), 8.10-8.04 (m, 2 H, *Ar*), 7.75-7.69 (m, 2 H, *Ar*), 7.01-6.93 (dd, 1 H, *J* = 16.4, 9.9 Hz, =*CH*), 6.20 (d, 1 H, *J* = 16.4 Hz, =*CH*), 5.12 (d, 1 H, *J* = 9.9 Hz, =*CH*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 135.9, 130.5, 129.6, 127.3, 125.4, 124.3, 105.3.

The NMR data for **3f** corresponds to the reported values.[6]

1-Vinyl-1*H*-pyrrole-2,5-dione (3g)

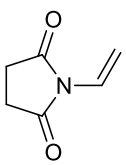


Following **GP1B**, maleimide (**1g**) (1.30 g, 13.4 mmol, 1.00 eq), $PdCl_2$ (0.237 g, 1.34 mmol, 0.100 eq), LiCl (57.0 mg, 1.34 mmol, 0.100 eq, weighted in a glovebox) and vinyl acetate (**14**) (33.2 mL, 359 mmol, 26.8 eq) were heated under reflux for 23 h. The mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. The crude was purified by Biotage (SNAP cartridge KP-Sil 50 g, 93:7 hexane/AcOEt to 40:60) afforded 1-vinyl-1*H*-pyrrole-2,5-dione (**3g**) as a bright yellow oil (1.74 g, 14.1 mmol, quantitative yield).

R_f 0.54 (7:3 Hexane/AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (s, 2 H, *CH-C=O*), 6.67 (dd, 1 H, *J* = 16.4, 9.8 Hz, *CH-N*), 5.87 (d, 1 H, *J* = 16.3 Hz, =CH_2), 4.94 (d, 1 H, *J* = 9.8 Hz, =CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 134.5, 123.1, 103.4.

The NMR data for **3g** corresponds to the reported values.[6]

1-Vinylpyrrolidine-2,5-dione (3h)



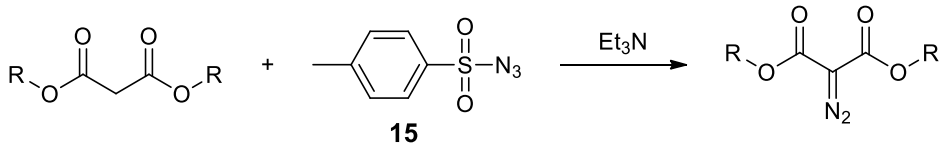
Following **GP1A**, succinimide (**1h**) (1.00 g, 10.1 mmol, 1.00 eq), vinyl acetate (**14**) (25.0 mL, 270 mmol, 26.8 eq) and Na_2PdCl_4 (59.0 mg, 0.202 mmol, 2.00 mol%) were heated under reflux for 72 h. After solvent evaporation, the crude was purified by Biotage (SNAP Cartridge KP-Sil 50 g, 7:3 Hexane/AcOEt) to obtain (**3h**) as a yellow solid (1.22 g, 9.78 mmol, 97% yield).

R_f 0.17 (8:2 Hexane/AcOEt). m.p. 47.6 – 48.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (dd, 1 H, *J* = 16.4, 9.9 Hz, =*CH*), 6.08 (d, 1 H, *J* = 16.4 Hz, =*CH*), 5.06 (d, 1 H, *J* = 9.9 Hz, =*CH*), 2.72 (s, 4 H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 124.3, 106.6, 27.8.

The NMR data for **3h** corresponds to the reported values.[5]

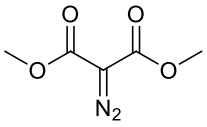
2.3 Synthesis of Diazomalonates

General Procedure for the Synthesis of Diazomalonates (GP2)



Following a modified procedure,[9] the corresponding malonate (1.00 eq), triethylamine (1.10 eq) and tosyl azide[10] (**15**) (1.10 eq) were dissolved in CH_3CN. The solution was stirred at room temperature for 24 h. The solution was concentrated under reduced pressure and partitioned between CH_2Cl_2 (30 mL) and H_2O (30 mL), the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (1 X 20 mL). The organic layers were combined and dried over $MgSO_4$. The crude was first filtered over a plug of silica gel (Hexane/Et_2O 1:1) to remove most of the tosylamide formed during the reaction, then purified by column chromatography (Hexane/Et_2O 90:10 to 80:20) to obtain the desired product.

Dimethyl-2-diazomalonate (**4a**)

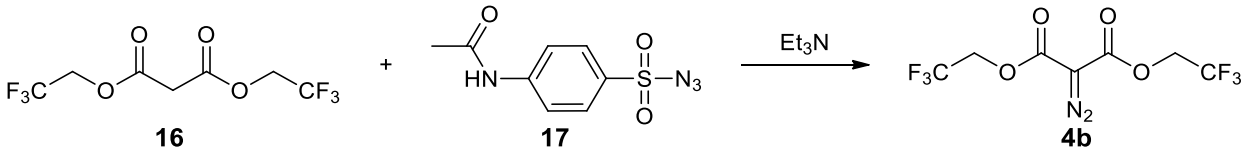


Following **GP2** and starting from dimethylmalonate (7.93 mL, 69.7 mmol, 1.00 eq), triethylamine (10.6 mL, 76.6 mmol, 1.10 eq) and tosyl azide (**15**) (15.1 g, 76.6 mmol, 1.10 eq) that were dissolved in CH_3CN (100 mL), dimethyl-2-diazomalonate (**4a**) was obtained as yellow oil which solidified under storage at 4 °C (10.4 g, 65.5 mmol, 94% yield).

R_f 0.32 (1:1 PET/Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.87 (s, 6 H, *OCH₃*). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.2, 52.4.[11]

The ^{1}H NMR data for **4a** corresponds to the reported values.[9]

Bis(2,2,2-trifluoroethyl) 2-diazomalonate (4b)



Bis(2,2,2-trifluoroethyl) malonate (**16**) (5.00 g, 18.7 mmol, 1.00 eq), triethylamine (2.8 mL, 21 mmol, 1.1 eq) and 4-acetamidobenzenesulfonyl azide (**17**) (4.93 g, 20.5 mmol, 1.10 eq) were dissolved in acetonitrile (180 mL) at room temperature. After stirring the resulting mixture overnight, the suspension was filtered through a plug of cotton wool and the solvent was removed under reduced pressure. The crude was dissolved in DCM (200 mL), filtered through a plug of cotton wool, and partitioned between dichloromethane and water (200 mL). The two layers were separated and the aqueous layer was extracted with dichloromethane (2 x 150 mL). The combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure and dried under vacuum. Filtration through a plug of silica (AcOEt/hexane 1/1 + 1% NEt_3, 500 mL) afforded bis(2,2,2-trifluoroethyl) 2-diazomalonate (**4b**) as a yellow oil (5.44 g, 18.5 mmol, 99% yield) which was not further purified.

R_f 0.67 (6:4 Hexane/AcOEt); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (q, 4 H, $J_{C\text{-}F}$ = 8.2 Hz, *CH₂*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 122.6 (q, $J_{C\text{-}F}$ = 277 Hz), 60.9 (q, $J_{C\text{-}F}$ = 37 Hz).

The NMR data for **4b** corresponds to the reported values.[6]

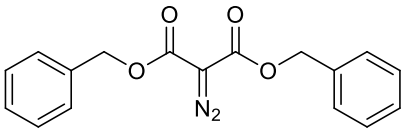
---

[9] P. Wyatt, A. Hudson, J. Charmant, A. G. Orpen, H. Phetmung, *Org. Biomol. Chem.* **2006**, *4*, 2218.

[10] P. R. Serwinski, B. Esat, P. M. Lahti, Y. Liao, R. Walton, J. Lan, *J. Org. Chem.* **2004**, *69*, 5247.

[11] The diazo carbon could not be detected.

Dibenzyl-2-diazomalonate (**4c**)



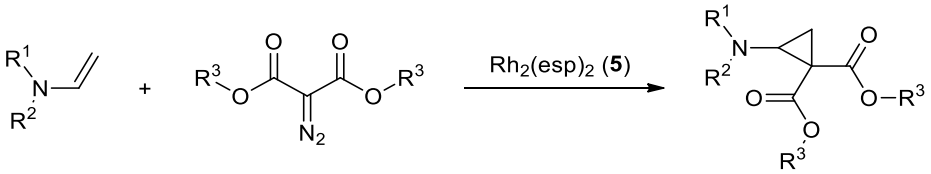
Following **GP2** and starting from dibenzylmalonate (1.03 g, 4.62 mmol, 1.00 eq), triethylamine (0.71 mL, 5.1 mmol, 1.1 eq) and tosyl azide (**15**) (1.00 g, 5.08 mmol, 1.10 eq) that were dissolved in CH_3CN (10.0 mL), dibenzyl-2-diazomalonate (**4c**) was obtained as a white-yellow solid (1.20 g, 3.72 mmol, 81% yield).

R_f 0.69 (6:4 Hexane/AcOEt). m.p. 48.2 - 51.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 10 H, *Ar*), 5.28 (s, 4 H, *CH_2*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 135.4, 128.8, 128.6, 128.4, 67.2, 41.7.

The NMR data for **4c** corresponds to the reported values.[6]

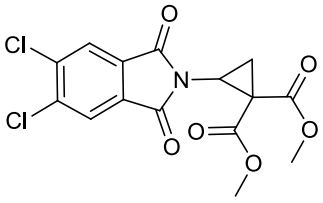
2.4 Synthesis of Aminocyclopropanes

General Procedure for the of Synthesis of Aminocyclopropanes (GP3)



Following a modified procedure,[12] the corresponding N-vinyl-imide (1.00 eq) was dissolved in dry CH_2Cl_2 (10.0 mL) and the solution was cooled down to 0 °C with an ice/water bath. Then, bis[rhodium(α,α,α', α'-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (0.1 mol%) was added in one portion. A solution in CH_2Cl_2 (2.0 mL) of the corresponding malonate (1.20 eq) was added dropwise over 5 min. After the addition, the mixture was allowed to warm to rt and stirred overnight. The solvent is then removed under reduced pressure and the crude is directly purified by column chromatography.

Dimethyl 2-(5,6-dichloro-1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (6a)

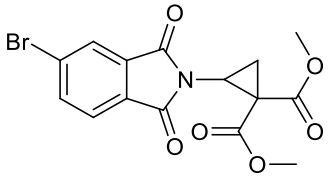


Following **GP3**, compound **6a** was synthesized starting from N-vinyl-4,5-dichlorophthalimide (**3a**) (500 mg, 2.07 mmol, 1.00 eq), dimethyl-2-diazomalonate (**4a**) (392 mg, 2.48 mmol, 1.20 eq) and bis[rhodium(α,α,α', α'-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (1.6 mg, 2.1 µmol, 0.10 mol%). After solvent evaporation, the residue was purified by Biotage (SNAP Cartridge KP-Sil 25 g, 7:3 Hexane/AcOEt), to obtain a white solid (595 mg, 1.60 mmol, 77% yield).

R_f 0.27 (8:2 Hexane/AcOEt). m.p. 145.9 – 148.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2 H, *Phth*), 3.83 (s, 3 H, *OMe*), 3.66 (dd, 1 H, *J* = 8.5, 6.5 Hz, *N-CH*), 3.63 (s, 3 H, *OMe*), 2.63 (t, 1 H, *J* = 6.5 Hz, *CH_2*), 2.04 (dd, 1 H, *J* = 8.5, 6.5 Hz, *CH_2*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 167.1, 166.0, 139.5, 130.6, 125.7, 53.3, 53.2, 35.0, 33.1, 19.8.

The NMR data for **6a** corresponds to the reported values.[6]

Dimethyl 2-(5-bromo-1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (6b)



Following **GP3**, compound **6b** was synthesized starting from 5-bromo-2-vinylisoindoline-1,3-dione (**3b**) (50.0 mg, 0.198 mmol, 1.00 eq), dimethyl 2-diazomalonate (**4a**) (47.0 mg, 0.298 mmol, 1.50 eq) and bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (0.3 mg, 0.4 µmol, 0.2 mol%). After solvent evaporation, the crude was purified by silica gel chromatography

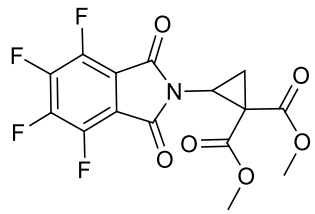
[12] F. Gonzalez-Bobes, M. D. B. Fenster, S. Kiau, L. Kolla, S. Kolotuchin, M. Soumeillant, *Adv. Synth. Catal.* **2008**, *350*, 813.

(hexane/AcOEt 75:25 to 70:30) to afford dimethyl 2-(5-bromo-1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (**6b**) as a colorless oil that solidified upon storage (77.8 mg, 0.204 mmol, quantitative yield).

R_f 0.30 (8:2 Pentane/AcOEt). m.p. 114.8 – 117.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.95 (m, 1 H, *Ar*), 7.86 (dd, 1 H, *J* = 7.9, 1.6 Hz, *Ar*), 7.70 (d, 1 H, *J* = 7.9 Hz, *Ar*), 3.82 (s, 3 H, *OMe*), 3.70-3.64 (m, 1 H, *CH-Phth*), 3.62 (s, 3 H, *OMe*), 2.66 (dd, 1 H, *J* = 6.5, 6.5 Hz, CH_2), 2.06-2.01 (m, 1 H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 167.0, 167.0, 166.5, 137.4, 133.1, 130.0, 129.4, 126.9, 124.9, 53.2, 53.0, 34.9, 33.1, 19.6.

The NMR data for **6b** corresponds to the reported values.[6]

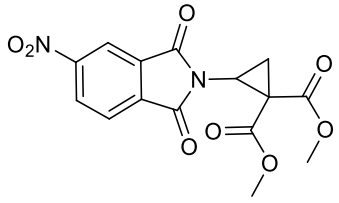
Dimethyl 2-(4,5,6,7-tetrafluoro-1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (6c)



Following **GP3**, compound **6c** was synthesized starting from 4,5,6,7-tetrafluoro-2-vinylisoindoline-1,3-dione (**3c**) (0.260 g, 1.06 mmol, 1.00 eq), dimethyl 2-diazomalonate (**4a**) (0.252 g, 1.27 mmol, 1.20 eq) and bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (0.80 mg, 1.0 µmol, 0.10 mol%). After solvent evaporation, the crude was purified by Biotage (SNAP Cartridge KP-Sil 10 g, 7:3 Hexane/AcOEt), to obtain a colorless solid (0.300 g, 0.801 mmol, 75% yield).

R_f 0.42 (8:2 Pentane/AcOEt). m.p. 86.2 – 88.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3 H, *OMe*), 3.64 (s, 3 H, *OMe*), 3.55 (dd, 1 H, *J* = 8.5, 6.5 Hz, N-*CH*), 2.50 (t, 1 H, *J* = 6.6 Hz, CH_2), 2.03 (dd, 1 H, *J* = 8.5, 6.6 Hz, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 167.3, 162.2, 145.4 (m), 143.6 (m), 113.4 (m), 53.4, 53.3, 34.7, 32.8, 19.8. IR 2957 (w), 1728 (s), 1515 (s), 1501 (s), 1410 (s), 1219 (m), 945 (s). HRMS (ESI) calcd for $C_{15}F_4H_{10}NO_6^+$ $[M+H]^+$ 376.0439; found 376.0436.

Dimethyl 2-(5-nitro-1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (6d)

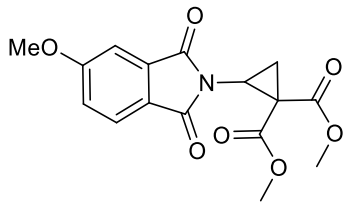


Following **GP3**, compound **6d** was synthesized starting from 5-nitro-2-vinylisoindoline-1,3-dione (**3d**) (0.500 g, 2.29 mmol, 1.00 eq), dimethyl 2-diazomalonate (**4a**) (0.544 g, 2.75 mmol, 1.20 eq) and bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] (1.7 mg, 2.3 µmol, 0.10 mol%). After solvent evaporation, the crude was purified by Biotage (SNAP Cartridge KP-Sil 50 g, 7:3 Hexane/AcOEt), to obtain **6d** as an off-white solid (712 mg, 2.04 mmol, 89% yield).

R_f 0.19 (8:2 Pentane/AcOEt). m.p. 113.0 – 115.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (m, 2 H, *Ar*), 8.03 (d, 1 H, *J* = 8.1 Hz, *Ar*), 3.83 (s, 3 H, *OMe*), 3.70 (m, 1 H, *CH-N*), 3.62 (s, 3 H, *OMe*), 2.63 (m, 1 H, CH_2), 2.07 (m, 1 H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 167.1, 165.9, 165.6, 152.0, 135.9, 132.9, 129.6, 124.9, 119.0, 53.3, 53.2, 35.0, 33.1, 19.7.

The NMR data for **6d** corresponds to the reported values.[5]

Dicarboxylate dimethyl 2-(5-methoxy-1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (6e)

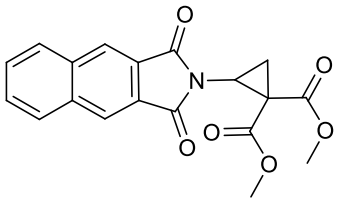


Following **GP3**, compound **6e** was synthesized starting from 5-methoxy-2-vinylisoindoline-1,3-dione (**3e**) (0.130 g, 0.640 mmol, 1.00 eq), dimethyl 2-diazomalonate (**4a**) (0.121 g, 0.768 mmol, 1.20 eq) and bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (0.5 mg, 0.6 µmol, 0.1 mol%). After solvent evaporation, the crude was purified by Biotage (SNAP Cartridge KP-Sil 10 g, 6:4 Hexane/AcOEt), to obtain **6e** as a colorless solid (176 mg, 0.528 mmol, 83% yield).

R_f 0.15 (8:2 Pentane/AcOEt). m.p. 113.5 – 117.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, 1 H, *J* = 8.3 Hz, *Phth*), 7.27 (d, 1 H, *J* = 2.2 Hz, *Phth*), 7.14 (dd, 1 H, *J* = 8.3, 2.3 Hz, *Phth*), 3.90 (s, 3 H, *OMe*), 3.80 (s, 3 H, *OMe-C=O*), 3.66 (dd, 1 H, *J* = 8.5, 6.6 Hz, *N-CH*), 3.59 (s, 3 H, *OMe-C=O*), 2.68 (t, 1 H, *J* = 6.5 Hz, CH_2), 1.99 (dd, 1 H, *J* = 8.5, 6.4 Hz, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 167.8, 167.6, 167.0, 165.0, 134.1, 125.3, 123.4, 120.4, 108.1, 56.2, 53.2, 53.0, 35.0, 33.2, 19.7.

The NMR data for **6e** corresponds to the reported values.[5]

Dimethyl 2-(1,3-dioxo-1H-benzo[f]isoindol-2(3H)-yl)cyclopropane-1,1-dicarboxylate (6f)

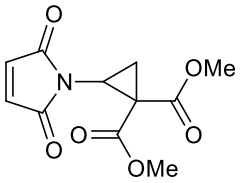


Following **GP3**, compound **6f** was synthesized starting from N-vinyl-phthalimide derivative **3f** (100 mg, 0.448 mmol, 1.00 eq), dimethyl-2-diazomalonate (**4a**) (85.0 mg, 0.538 mmol, 1.20 eq) and bis[rhodium(α,α,α', α'-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (0.4 mg, 5 µmol, 0.1 mol%). After solvent evaporation, the residue was purified by Biotage (SNAP Cartridge KP-Sil 10 g, 6:4 Hexane/AcOEt), to obtain **6f** as a white solid (115 mg, 0.325 mmol, 73% yield).

R_f 0.39 (6:4 Hexane/AcOEt). m.p. 165.6 – 167.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 2 H, *Ar*), 8.04 (dd, 2 H, *J* = 6.2, 3.3 Hz, *Ar*), 7.69 (dd, 2 H, *J* = 6.2, 3.3 Hz, *Ar*), 3.83 (s, 3 H, *OMe*), 3.76 (dd, 1 H, *J* = 8.5, 6.7 Hz, *N-CH*), 3.60 (s, 3 H, *OMe*), 2.77 (t, 1 H, *J* = 6.5 Hz, *CH_2*), 2.07 (dd, 1 H, *J* = 8.5, 6.4 Hz, *CH_2*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 167.7, 167.0, 135.7, 130.4, 129.4, 127.2, 125.1, 53.2, 53.1, 35.3, 33.3, 19.8.

The NMR data for **6f** corresponds to the reported values.[6]

Dimethyl 2-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)cyclopropane-1,1-dicarboxylate (6g)

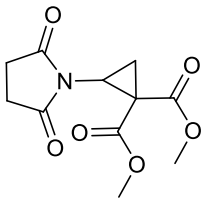


Following **GP3**, compound **6g** was synthesized starting from 1-vinyl-1*H*-pyrrole-2,5-dione (**3g**) (50.0 mg, 0.406 mmol, 1.00 eq), dimethyl 2-diazomalonate (**4a**) (96.0 mg, 0.609 mmol, 1.50 eq) and bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (0.7 mg, 0.9 µmol, 0.2 mol%). After solvent evaporation, the crude was purified by Biotage (SNAP cartridge KP-Sil 10 g, hexane/AcOEt 95:5 to 70:30) affording dimethyl 2-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)cyclopropane-1,1-dicarboxylate **(6g)** as a colorless oil that solidified upon storage (66.9 mg, 0.264 mmol, 65% yield).

R_f 0.38 (6: 4 Hexane/AcOEt). m.p. 78.4 - 80.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 2 H, *CH-C=O*), 3.79 (s, 3 H, O*Me*), 3.66 (s, 3 H, *OMe*), 3.56-3.51 (m, 1 H, *CH-N*), 2.56 (dd, 1 H, *J* = 6.4, 6.5 Hz, *CH_2*), 1.96-1.91 (m, 1 H, *CH_2*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 168.4, 167.0, 134.1, 53.1, 53.0, 34.3, 32.9, 19.3.

The NMR data for **6g** corresponds to the reported values.[6]

Dimethyl 2-(2,5-dioxopyrrolidin-1-yl)cyclopropane-1,1-dicarboxylate (6h)

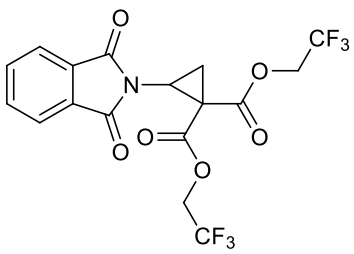


Following **GP3**, compound **6h** was synthesized starting from N-vinyl-succinimide (**3h**) (500 mg, 4.00 mmol, 1.00 eq), dimethyl-2-diazomalonate (**4a**) (300 mg, 4.80 mmol, 1.20 eq) and bis[rhodium(α,α,α', α'-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (3.0 mg, 4.0 µmol, 0.10 mol%). After solvent evaporation, the residue was purified by Biotage (SNAP Cartridge KP-Sil 50 g, 5:5 Hexane/AcOEt), to obtain **6h** as a yellow solid (801 mg, 3.14 mmol, 79% yield).

R_f 0.39 (5:5 Hexane/AcOEt). m.p. 81.9 – 85.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3 H, *OMe*), 3.68 (s, 3 H, *OMe*), 3.45 (dd, 1 H, *J* = 8.5, 6.5 Hz, *N-CH*), 2.73-2.58 (m, 4 H, O=C-*CH_2*), 2.45 (t, 1 H, *J* = 6.5 Hz, *CH_2*), 1.93 (dd, 1 H, *J* = 8.5, 6.5 Hz, *CH_2*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 168.4, 167.2, 53.2, 53.1, 35.1, 32.7, 28.1, 19.7.

The NMR data for **6h** corresponds to the reported values.[5]

Bis(2,2,2-trifluoroethyl) 2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (6i)



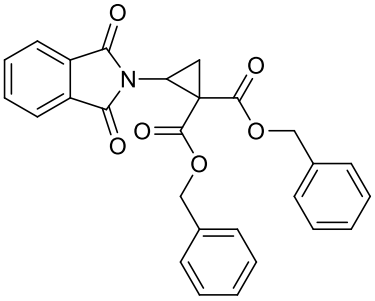
Following **GP3**, compound **6i** was synthesized starting from N-vinyl-phthalimide (535 mg, 3.09 mmol, 1.00 eq), bis(2,2,2-trifluoroethyl) 2-diazomalonate (**4b**) (1.00 g, 3.40 mmol, 1.10 eq) and bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (4.7 mg, 6.2 µmol, 0.20 mol%). After solvent evaporation, the residue was purified by silica gel chromatography (Hexane/AcOEt 95:5 to 75:25) to afford bis(2,2,2-trifluoroethyl) 2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (**6i**) as a colorless solid (1.32 g, 3.01 mmol, 97% yield).

R_f 0.61 (6:4 Hexane/AcOEt). m.p. 76.3 – 78.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 2 H, *Phth*), 7.77-7.72 (m, 2 H, *Phth*), 4.61 (q, 2 H, *J* = 8.2 Hz, *CH_2-CF_3*), 4.50-4.30 (m, 2 H, *CH_2-CF_3*), 3.83 (dd, 1 H, *J* = 8.6, 6.9 Hz, *CH-Phth*), 2.90 (dd, 1 H, *J* = 6.8, 6.8 Hz, *CH_2*), 2.19 (dd, 1 H, *J* = 8.6, 6.6 Hz, *CH_2*). ^{13}C NMR (101

MHz, $CDCl_3$) δ 167.7, 166.4, 164.5, 134.7, 131.4, 123.8, 122.7 (q, J_{C-F} = 277 Hz), 122.5 (q, J_{C-F} = 277 Hz), 61.7 (q, J_{C-F} = 37 Hz), 61.5 (q, J_{C-F} = 37 Hz), 36.4, 32.7, 21.0.

The NMR data for **6i** corresponds to the reported values.[6]

Dibenzyl 2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (6j)



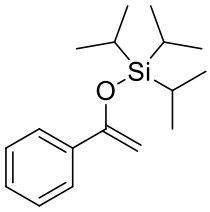
Following **GP3**, compound **6j** was synthesized starting from N-vinyl-phthalimide (180 mg, 1.04 mmol, 1.00 eq), dibenzyl-2-diazomalonate (**4b**) (387 mg, 1.25 mmol, 1.20 eq) and bis[rhodium(α,α,α', α'-tetramethyl-1,3-benzenedipropionic acid)] (**5**) (0.8 mg, 1 μmol, 0.1 mol%). After solvent evaporation, the residue was purified by Biotage (SNAP Cartridge KP-Sil 10 g, 8:2 Hexane/AcOEt), to obtain **6j** as a colorless oil (117 mg, 0.258 mmol, 25% yield).

R_f 0.36 (6:4 Hexane/AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2 H, *Phth*), 7.65-7.61 (m, 2 H, *Phth*), 7.27-7.24 (m, 5 H, *Ar*), 7.13-7.08 (m, 5 H, *Ar*), 5.18 (q, 2 H, *J* = 12.4 Hz, CH_2-*Ar*), 4.94 (q, 2 H, *J* = 12.2 Hz, CH_2-*Ar*), 3.68 (dd, 1 H, *J* = 8.5, 6.7 Hz, *N*-*CH*), 2.73 (t, 1 H, *J* = 6.5 Hz, CH_2), 1.99 (dd, 1 H, *J* = 8.5, 6.4 Hz, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 167.8, 166.2, 135.4, 135.1, 134.3, 131.5, 128.7, 128.4, 128.4, 128.3, 128.1, 123.6, 67.8, 67.7, 35.3, 33.5, 19.8.[13]

The NMR data for **6j** corresponds to the reported values.[6]

2.5 Synthesis of Enol Ether 7

Triisopropyl((1-phenylvinyl)oxy)silane (7)



In an oven-dried flask sealed with a septum and under N_2 atmosphere, acetophenone (2.06 g, 17.1 mmol, 1.00 eq) in anhydrous THF (20 mL) is cooled down to -78 °C and a 1.9 M solution of NaHMDS (10.8 mL, 20.5 mmol, 1.20 eq) is added dropwise. The cold bath is removed and the pale yellow solution is stirred for 1 hour at room temperature. The reaction is cooled again to 0 °C and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (3.96 g, 20.5 mmol, 1.20 eq) is added dropwise. The reaction is stirred at room temperature for 5 h and the solvent is directly removed under reduced pressure. The resulting orange oil is purified by plug or by column chromatography on triethylamine-deactivated silica (99% Hexane, 1% Et_3N) to obtain **7** as a colorless oil (4.7 g, 17 mmol, 99% yield)

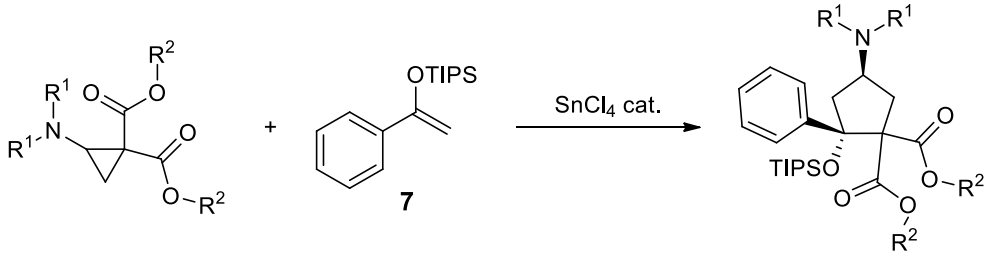
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.65 (m, 2 H, *Ar*), 7.38-7.29 (m, 3 H, *Ar*), 4.85 (d, 1 H, *J* = 1.8 Hz, C=CH_2), 4.41 (d, 1 H, *J* = 1.8 Hz, C=CH_2), 1.39-1.27 (m, 3 H, SiC*H*$(CH_3)_2$), 1.19-1.13 (m, 18 H, SiCH$(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 138.0, 128.2, 128.1, 125.4, 90.0, 18.2, 12.9.

The characterization data for **7** corresponded to the reported values.[14]

3. [3+2] Annulation

General Procedure for [3+2] Annulation (GP4)

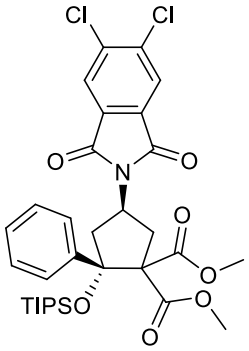


[13] One of the aromatic carbons could not be detected.

[14] J-F. Zhao, B-H. Tan, T-P. Loh, *Chem. Sci*. **2011**, *2*, 349.

Following a reported procedure,[15] in an oven-dried flask sealed with a septum and under N_2 atmosphere, the corresponding aminocyclopropane (1.00 eq) and triisopropyl((1-phenylvinyl)oxy)silane (**7**) (1.50 eq) were dissolved in dry CH_2Cl_2 (2.00 mL). The solution was then cooled down to -78 °C and 23.0 μL of a 0.43 M solution of tin tetrachloride (5.0 mol% or stated otherwise) in dry CH_2Cl_2 was added. The reaction was stirred for 1 to 3 h at -78 °C and then quenched at -78 °C with triethylamine (0.30 mL). The reaction was warmed up to rt and stirred for 15 min. Dichloromethane was removed under reduced pressure and the crude was directly purified by column chromatography (8:2 Hexane/Ethyl Acetate, 3% Et_3N).

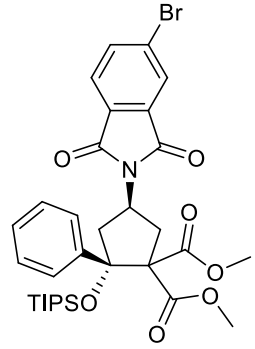
***Trans*-dimethyl-4-(5,6-dichloro-1,3-dioxoisoindolin-2-yl)-2-phenyl-2-((triisopropylsilyl)oxy)cyclopentane-1,1-dicarboxylate (8a)**



Following **GP4**, compound **8a** was synthesized starting from N-4,5-dichlorophthalimide-aminocyclopropane **6a** (74.0 mg, 0.200 mmol, 1.00 eq), triisopropylsilyl-enol ether **7** (83.0 mg, 0.300 mmol, 1.50 eq) and $SnCl_4$ (23 μL 0.43 M, 1.0 μmol, 5.0 mol%) as a white solid (64.0 mg, 99.0 μmol, 49% yield).

R_f 0.50 (8:2 Hexane/AcOEt). m.p. 57.6 – 61.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2 H, *Phth*), 7.73-7.71 (m, 2 H, *Ar*), 7.30-7.23 (m, 3 H, *Ar*), 5.25-5.16 (m, 1H, *N-CH*), 3.82 (s, 3 H, *OMe*), 3.73 (t, 1 H, *J* = 12.3 Hz, *CH₂*), 3.41 (s, 3 H, *OMe*) 3.41-3.35 (m, 2H, *CH₂*), 2.82 (dd, 1 H, *J* = 13.8, 8.6 Hz, *CH₂*), 2.42 (dd, 1 H, *J* = 12.3, 5.9 Hz, *CH₂*), 0.95-0.89 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 168.7, 166.4, 141.6, 139.1, 131.2, 128.5, 128.2, 127.3, 125.4, 87.7, 70.1, 52.5, 52.3, 48.4, 41.8, 36.3, 18.3, 18.2, 13.8. IR 2948 (w), 2867 (w), 1719 (s), 1462 (w), 1369 (s), 1256 (w), 1130 (m), 990 (w), 908 (w), 885 (w). HRMS (ESI) calcd for $C_{32}H_{39}{}^{35}Cl_2NNaO_7Si^+$ $[M+Na]^+$ 670.1765; found 670.1743

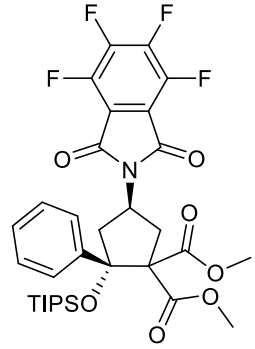
***Trans*-dimethyl 4-(5-bromo-1,3-dioxoisoindolin-2-yl)-2-phenyl-2-((triisopropylsilyl)oxy) cyclopentane-1,1-dicarboxylate (8b)**



Following **GP4**, compound **8b** was synthesized starting from N-5-bromophthalimide-aminocyclopropane **6b** (54.0 mg, 0.142 mmol, 1.00 eq), triisopropylsilyl-enol ether **7** (58.8 mg, 0.213 mmol, 1.50 eq) and $SnCl_4$ (66 μL 0.43 M, 28 μmol, 20 mol%) as a white solid (64.0 mg, 97.0 μmol, 69% yield).

R_f 0.25 (9:1 Pentane/AcOEt). m.p. 63.6 – 66.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 1 H, *J* = 1.5 Hz, *Phth*), 7.86 (dd, 1 H, *J* = 7.9, 1.7 Hz, *Phth*), 7.73 (m, 2 H, *Ar*), 7.70 (d, 1 H, *J* = 7.9 Hz, *Phth*), 7.31-7.27 (m, 3 H, *Ar*), 5.24 (m, 1 H, *N-CH*), 3.84 (s, 3 H, *OMe*), 3.75 (t, 1 H, *J* = 12.2 Hz, *CH₂*), 3.43 (s, 3 H, *OMe*), 3.43-3.36 (m, 1 H, *CH₂*), 2.85 (dd, 1 H, *J* = 13.8, 8.6 Hz, *CH₂*), 2.43 (dd, 1 H, *J* = 12.2, 5.9 Hz, *CH₂*), 0.96-0.91 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 168.8, 167.6, 167.0, 141.7, 137.2, 133.7, 130.6, 129.1, 128.5, 128.1, 127.3, 126.7, 124.7, 87.7, 70.1, 52.5, 52.3, 48.1, 41.8, 36.3, 18.3, 18.3, 13.8. IR 2948 (w), 2867 (w), 1738 (m), 1715 (s), 1371 (m), 1253 (w), 1129 (m), 984 (m), 885 (w). HRMS (ESI) calcd for $C_{32}H_{40}{}^{79}BrNNaO_7Si^+$ $[M+Na]^+$ 680.1650; found 680.1649.

***Trans*-dimethyl 2-phenyl-4-(4,5,6,7-tetrafluoro-1,3-dioxoisoindolin-2-yl)-2-((triisopropylsilyl)-oxy) cyclopentane-1,1-dicarboxylate (8c)**



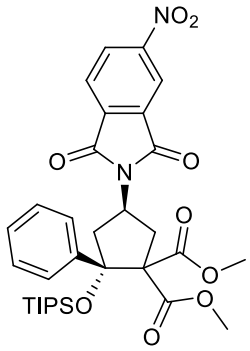
Following **GP4**, compound **8c** was synthesized starting from N-4,5,6,7-tetrafluorophthalimide-aminocyclopropane **6c** (74.8 mg, 0.200 mmol, 1.00 eq), triisopropylsilyl-enol ether **7** (83.0 mg, 0.300 mmol, 1.50 eq) and $SnCl_4$ (95 μL 0.21 M, 20 μmol, 10 mol%) as a white solid (82.0 mg, 126 μmol, 63% yield).

R_f 0.32 (9:1 Pentane/AcOEt). m.p. 143.5 – 145.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.70 (m, 2 H, *Ar*), 7.31-7.27 (m, 3 H, *Ar*), 5.21 (m, 1 H, *N-CH*), 3.84 (s, 3 H, *OMe*), 3.74 (t, 1 H, *J* = 12.2 Hz, *CH₂*), 3.40 (s, 3 H, *OMe*), 3.40-3.36 (m, 1 H, *CH₂*), 2.81 (dd, 1 H, *J* = 13.8, 8.7 Hz, *CH₂*), 2.43 (dd, 1 H, *J* = 12.3, 5.8 Hz, *CH₂*), 0.96-0.89 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 168.6, 162.5, 145.1 (m), 143.5

[15] F. de Nanteuil, J. Waser, *Angew. Chem. Int. Ed.* **2011**, *50*, 12075.

(m), 141.4, 128.4, 128.2, 127.3, 113.7 (m), 87.6, 70.1, 52.6, 52.4, 48.8, 41.6, 36.0, 18.3, 18.2, 13.8. IR 2951 (w), 2869 (w), 1723 (s), 1514 (m), 1500 (m), 1408 (m), 1363 (m), 1108 (m), 985 (m). HRMS (ESI) calcd for $C_{32}H_{37}F_4NNaO_7Si^+$ $[M+Na]^+$ 674.2168; found 674.2161

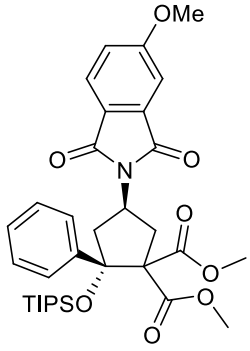
<u>*Trans*-dimethyl 4-(5-nitro-1,3-dioxoisoindolin-2-yl)-2-phenyl-2-((triisopropylsilyl)oxy) cyclopentane-1,1-dicarboxylate (8d)</u>



Following **GP4**, compound **8d** was synthesized starting from N-5-nitrophthalimide-aminocyclopropane **6d** (56.0 mg, 0.161 mmol, 1.00 eq), triisopropylsilyl-enol ether **7** (66.9 mg, 0.242 mmol, 1.50 eq) and $SnCl_4$ (67 µL 0.21 M, 14 µmol, 14 mol%) as a white solid (79.0 mg, 126 µmol, 78% yield).

R_f 0.50 (8:2 Pentane/AcOEt). m.p. 71.7 – 74.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, 1 H, *J* = 1.6 Hz, *Phth*), 8.60 (dd, 1 H, *J* = 8.1, 1.6 Hz, *Phth*), 8.04 (d, 1 H, *J* = 8.1 Hz, *Phth*), 7.73-7.71 (m, 2 H, *Ar*), 7.32-7.27 (m, 3 H, *Ar*), 5.27 (m, 1 H, *N-CH*), 3.85 (s, 3 H, *OMe*), 3.77 (t, 1 H, *J* = 12.2 Hz, *CH_2*), 3.45 (s, 3 H, *OMe*), 3.46-3.40 (m, 1 H, *CH_2*), 2.87 (dd, 1 H, *J* = 13.8, 8.5 Hz, *CH_2*), 2.47 (dd, 1 H, *J* = 12.2, 6.0 Hz, *CH_2*), 0.95-0.91 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 168.7, 166.3, 166.0, 151.9, 141.5, 136.4, 133.4, 129.5, 128.4, 128.2, 127.3, 124.6, 118.8, 87.7, 70.1, 52.6, 52.4, 48.6, 41.8, 36.3, 18.3, 18.3, 13.8. IR 2952 (w), 2869 (w), 1721 (s), 1542 (w), 1379 (w), 1346 (m), 1255 (w), 1132 (m), 1057 (m), 985 (w), 911 (w). HRMS (ESI) calcd for $C_{32}H_{40}N_2NaO_9Si^+$ $[M+Na]^+$ 647.2395; found 647.2391

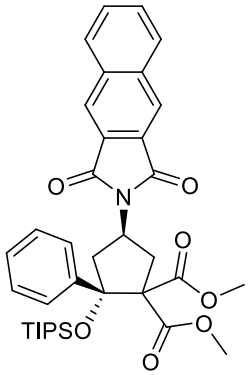
<u>*Trans*-dimethyl 4-(5-methoxy-1,3-dioxoisoindolin-2-yl)-2-phenyl-2-((triisopropylsilyl)oxy) cyclopentane-1,1-dicarboxylate (8e)</u>



Following **GP4**, compound **8e** was synthesized starting from N-5-methoxyphthalimide-aminocyclopropane **6e** (49.0 mg, 0.147 mmol, 1.00 eq), triisopropylsilyl-enol ether **7** (61.2 mg, 0.221 mmol, 1.50 eq) and $SnCl_4$ (34 µL 0.43 M, 15 µmol, 10 mol%) as a white solid (39.0 mg, 64.0 µmol, 43% yield).

R_f 0.38 (8:2 Pentane/AcOEt). m.p. 54.3 – 57.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.72 (m, 3 H, *Phth*), 7.31-7.25 (m, 4 H, *Phth + Ar*), 7.16 (dd, 1 H, *J* = 8.3, 2.3 Hz, *Ar*), 5.23 (m, 1 H, *N-CH*), 3.92 (s, 3 H, *OMe*), 3.84 (s, 3 H, *OMe*), 3.79-3.73 (m, 1 H, *CH_2*), 3.43 (s, 3 H, *OMe*), 3.40-3.35 (m, 1 H, *CH_2*), 2.87 (dd, 1 H, *J* = 13.7, 8.7 Hz, *CH_2*), 2.42 (dd, 1 H, *J* = 12.3, 5.9 Hz, *CH_2*), 0.96-0.91 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 168.9, 168.3, 168.2, 164.8, 141.9, 134.7, 128.5, 128.0, 127.2, 125.0, 124.0, 119.9, 108.0, 87.7, 70.1, 56.2, 52.5, 52.2, 47.8, 41.8, 36.3, 18.3, 18.3, 13.8. IR 2952 (w), 2868 (w), 1713 (s), 1492 (w), 1437 (m), 1375 (m), 1289 (s), 1253 (m), 1128 (m). HRMS (ESI) calcd for $C_{33}H_{43}NNaO_8Si^+$ $[M+Na]^+$ 632.2650; found 632.2648.

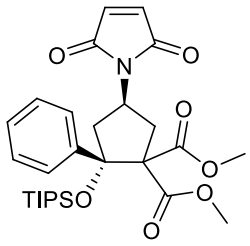
<u>*Trans*-dimethyl-4-(1,3-dioxo-1H-benzo[f]isoindol-2(3H)-yl)-2-phenyl-2-((triisopropylsilyl)oxy) Cyclopentane-1,1-dicarboxylate (8f)</u>



Following **GP4**, compound **8f** was synthesized starting from **6f** (56.4 mg, 0.160 mmol, 1.00 eq), triisopropylsilyl-enol ether **7** (66.2 mg, 0.239 mmol, 1.50 eq) and $SnCl_4$ (19 µL 0.43 M, 8.2 µmol, 5.1 mol%) as a white solid (96.0 mg, 0.152 mmol, 95% yield).

R_f 0.30 (8:2 Hexane/AcOEt). m.p. 57.5 – 63.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2 H, *Ar*), 8.06 (dd, 2 H, *J* = 6.1, 3.3 Hz, *Ar*), 7.78-7.75 (m, 2 H, *Ar*), 7.70 (dd, 2 H, *J* = 6.2, 3.3 Hz, *Ar*), 7.32-7.28 (m, 3 H, *Ar*), 5.39-5.30 (m, 1 H, *N-CH*), 3.85 (s, 3 H, *OMe*), 3.89-3.82 (m, 3 H, *CH_2*), 3.47 (s, 3 H, *OMe*), 3.47-3.40 (m, 3 H, *CH_2*), 2.96 (dd, 1 H, *J* = 13.8, 8.6 Hz, *CH_2*), 2.48 (dd, 1 H, *J* = 12.3, 5.9 Hz, *CH_2*), 0.99-0.97 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 168.9, 168.2, 141.9, 135.7, 130.5, 129.3, 128.6, 128.1, 127.8, 127.2, 124.7, 87.8, 70.2, 52.5, 52.3, 48.1, 41.8, 36.3, 18.4, 18.3, 13.9. IR 2950 (w), 2868 (w), 1765 (m), 1739 (m), 1712 (s), 1451 (w), 1369 (s), 1258 (w), 1132 (m), 1058 (w), 984 (w), 912 (w). HRMS (ESI) calcd for $C_{36}H_{43}NNaO_7Si^+$ $[M+Na]^+$ 652.2701; found 652.2700.

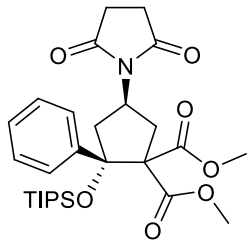
***Trans*-dimethyl 4-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)-2-phenyl-2-((triisopropylsilyl)oxy) cyclopentane-1,1-dicarboxylate (8g)**



Following **GP4**, compound **8g** was synthesized starting from N-maleimide-aminocyclopropane **6g** (43.0 mg, 0.170 mmol, 1.00 eq), triisopropylsilyl-enol ether **7** (79.0 mg, 0.286 mmol, 1.68 eq) and $SnCl_4$ (89 µL 0.21 M, 19 µmol, 11 mol%) as a white solid (38.9 mg, 73.0 µmol, 43% yield).

R_f 0.36 (8:2 Pentane/AcOEt). m.p. 150.0 – 153.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2 H, *Ar*), 7.30 – 7.26 (m, 3 H, *Ar*), 6.69 (s, 2 H, *CH-C=O*), 5.05 (m, 1 H, *CH-N*), 3.83 (s, 3 H, *OMe*), 3.62 (t, 1 H, *J* = 12.2 Hz, *CH_2*), 3.39 (s, 3 H, *OMe*), 3.32 (ddd, 1 H, *J* = 13.6, 9.4, 1.0 Hz, *CH_2*), 2.72 (dd, 1 H, *J* = 13.7, 8.7 Hz, *CH_2*), 2.38 (m, 1 H, *CH_2*), 0.95-0.89 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 170.8, 168.8, 141.8, 134.3, 128.4, 128.1, 127.3, 87.6, 70.0, 52.5, 52.2, 47.8, 41.8, 36.4, 18.3, 18.3, 13.8. IR 2949 (w), 2868 (w), 1740 (m), 1711 (s), 1383 (w), 1160 (w), 974 (w). HRMS (ESI) calcd for $C_{28}H_{39}NNaO_7Si^+$ $[M+Na]^+$ 552.2388; found 552.2390.

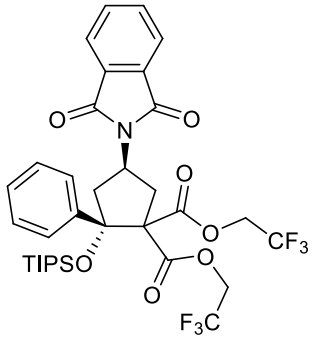
***Trans*-dimethyl-4-(2,5-dioxopyrrolidin-1-yl)-2-phenyl-2-((triisopropylsilyl)oxy)cyclopentane-1,1-dicarboxylate (8h)**



Following **GP4**, compound **8h** was synthesized starting from N-succinimide-aminocyclopropane **6h** (51.0 mg, 0.200 mmol, 1.00 eq), triisopropylsilyl-enol ether **7** (83.0 mg, 0.300 mmol, 1.50 eq) and $SnCl_4$ (23 µL 0.43 M, 1.0 µmol, 5.0 mol%) as a white solid (23.0 mg, 43.0 µmol, 22% yield).

R_f 0.34 (6:4 Hexane/AcOEt). m.p. 129.0 – 136.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2 H, *Ar*), 7.29-7.24 (m, 3 H, *Ar*), 5.14-5.05 (m, 1 H, *N-CH*), 3.81 (s, 3 H, *OMe*), 3.66 (t, 1 H, *J* = 12.2 Hz, *CH_2*), 3.41 (s, 3 H, *OMe*), 3.30 (ddd, 1 H, *J* = 13.6, 9.8, 0.7 Hz, *CH_2*), 2.79 (dd, 1 H, *J* = 13.7, 8.2 Hz, *CH_2*), 2.70 (s, 4 H, O=C-*CH_2*), 2.32 (dd, 1 H, *J* = 12.3, 6.0 Hz, *CH_2*), 0.99-0.82 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 170.9, 168.8, 141.7, 128.5, 128.1, 127.2, 87.7, 70.0, 52.5, 52.2, 48.4, 40.9, 35.3, 28.2, 18.3, 18.3, 13.8. IR 2949 (w), 2869 (w), 1737 (m), 1704 (s), 1439 (w), 1382 (m), 1257 (w), 1175 (s), 1102 (w), 1030 (w), 972 (w), 915 (w). HRMS (ESI) calcd for $C_{28}H_{41}NNaO_7Si^+$ $[M+Na]^+$ 554.2544; found 554.2541.

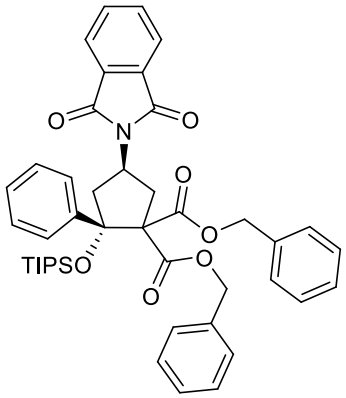
***Trans*-bis(2,2,2-trifluoroethyl) 4-(1,3-dioxoisoindolin-2-yl)-2-phenyl-2-((triisopropylsilyl)oxy) cyclopentane-1,1-dicarboxylate (8i)**



Following **GP4**, compound **8i** was synthesized starting from **6i** (60.0 mg, 0.137 mmol, 1.00 eq), triisopropylsilyl-enol ether **7** (56.8 mg, 0.205 mmol, 1.50 eq) and $SnCl_4$ (64 µL 0.21 M, 14 µmol, 10 mol%) as a white solid (80.7 mg, 113 µmol, 82% yield).

R_f 0.32 (9:1 Pentane/AcOEt). m.p. 122.5 - 124.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, 2 H, *J* = 5.4, 3.1 Hz, *Phth*), 7.73 (dd, 2 H, *J* = 5.4, 3.0 Hz, *Phth*), 7.69 (m, 2 H, *Ar*), 7.30 (m, 3 H, *Ar*), 5.31 (m, 1 H, *N-CH*), 4.59 (m, 2 H, *CH_2-CF_3*), 4.25 (m, 2 H, *CH_2-CF_3*), 3.75 (t, 1 H, *J* = 12.3 Hz, *CH_2*), 3.47 (dd, 1 H, *J* = 14.1, 10.1 Hz, *CH_2*), 2.96 (dd, 1 H, *J* = 14.2, 7.8 Hz, *CH_2*), 2.50 (dd, 1 H, *J* = 12.7, 6.4 Hz, *CH_2*), 0.97–0.92 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 168.0, 166.5, 140.5, 134.3, 132.0, 128.6, 128.4, 127.4, 123.4, 122.9 (d, J_{C-F} = 277 Hz), 122.7 (d, J_{C-F} = 277 Hz), 88.0, 69.7, 61.4 (dq, J_{C-F} = 49, 37 Hz), 61.4 (dd, J_{C-F} = 49, 37 Hz), 47.1, 41.7, 36.5, 18.3, 18.2, 13.9. IR 2949 (w), 2870 (w), 1757 (m), 1714 (s), 1379 (m), 1285 (m), 1168 (s), 1129 (s), 981 (m). HRMS (ESI) calcd for $C_{34}F_6H_{40}NO_7Si^+$ $[M+H]^+$ 716.2473; found 716.2474.

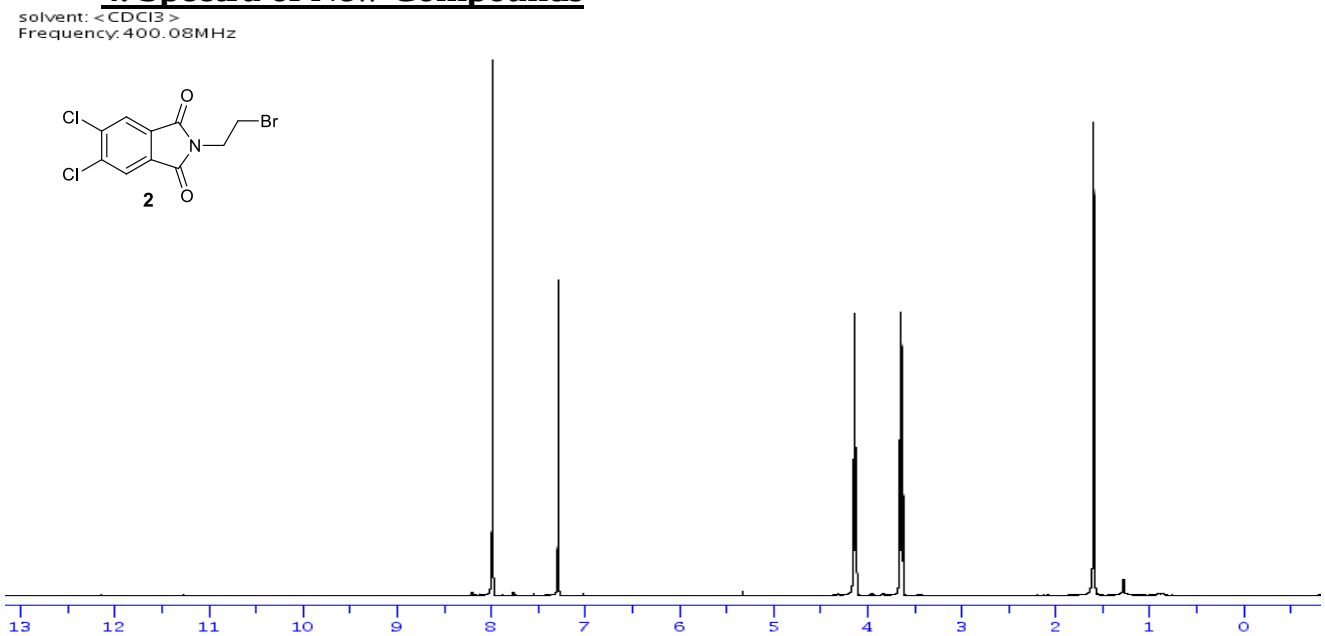
***Trans*-dibenzyl-4-(1,3-dioxoisoindolin-2-yl)-2-phenyl-2-((triisopropylsilyl)oxy)cyclopentane-1,1-dicarboxylate (8j)**

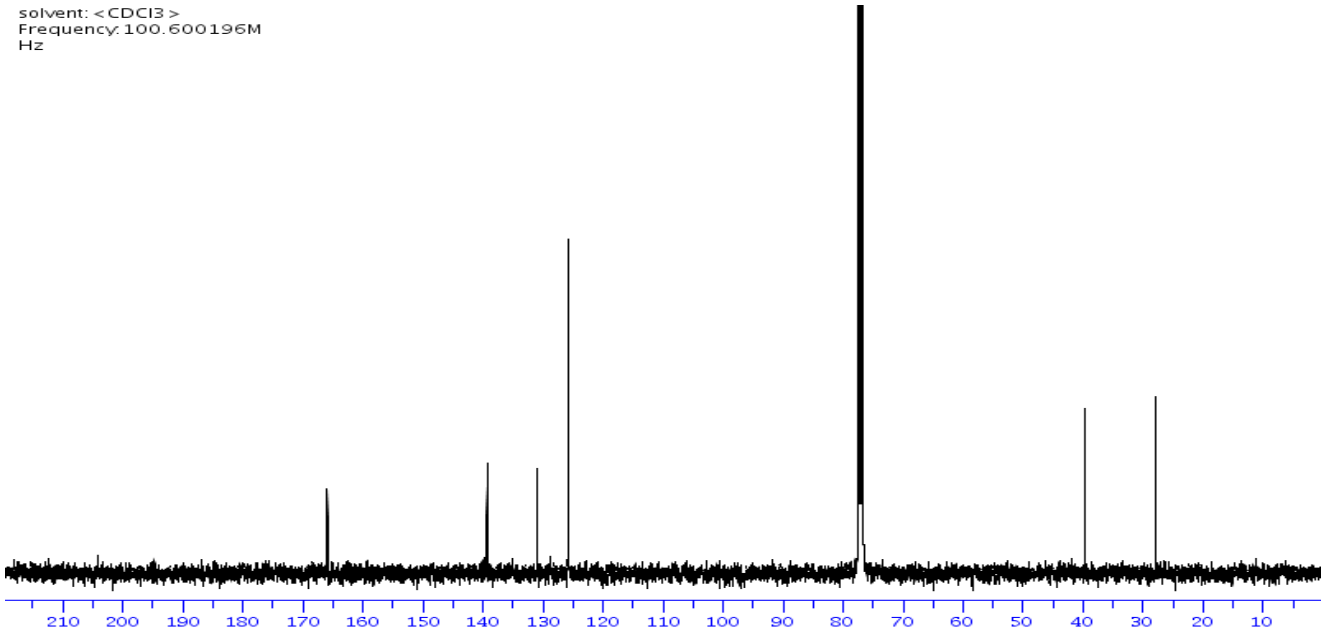


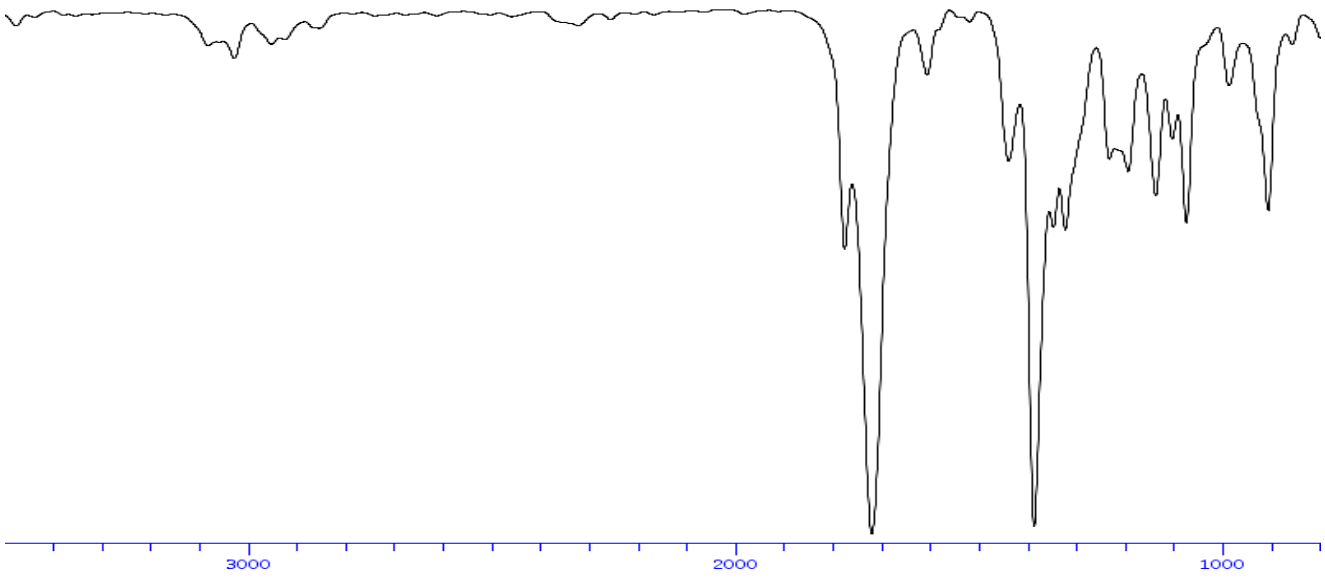
Following **GP4**, compound **8j** was synthesized starting from **6j** (45.0 mg, 99.0 μmol, 1.00 eq), triisopropylsilyl-enol ether **7** (41.0 mg, 0.148 mmol, 1.50 eq) and $SnCl_4$ (12 μL 0.43 M, 5.2 μmol, 5.2 mol%) as white solid (60.0 mg, 82.0 μmol, 83% yield).

R_f 0.72 (6:4 Hexane/AcOEt). m.p. 135.6 – 140.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, 2 H, *J* = 5.5, 3.1 Hz, *Phth*), 7.70-7.67 (m, 4 H, *Phth* + *Ar*), 7.27-7.04 (m, 13 H, *Ar*), 5.22-5.18 (m, 3 H, *CH_2-Ar* + *N-CH*), 4.86 (s, 2 H, *CH_2-Ar*), 3.81 (t, 1 H, *J* = 12.2 Hz, *CH_2*), 3.47 (dd, 1 H, *J* = 13.5, 10.3 Hz, *CH_2*), 2.92 (dd, 1 H, *J* = 14.0, 8.2 Hz, *CH_2*), 2.43 (dd, 1 H, *J* = 12.4, 6.2 Hz, *CH_2*), 0.95-0.89 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 168.4, 168.2, 141.4, 135.5, 135.4, 134.1, 132.1, 128.8, 128.5, 128.4, 128.4, 128.3, 128.2, 128.0, 127.1, 123.3, 87.8, 70.2, 67.6, 67.0, 47.6, 41.9, 36.6, 18.4, 18.3, 13.9. IR 3061 (w), 3035 (w), 2947 (w), 2867 (w), 1736 (s), 1715 (s), 1463 (w), 1379 (m), 1259 (m), 1166 (w), 1128 (m), 982 (m), 886 (w). HRMS (ESI) calcd for $C_{44}H_{49}NNaO_7Si^+$ $[M+Na]^+$ 754.3170; found 754.3158.

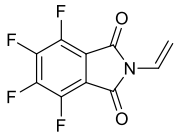
4. Spectra of New Compounds





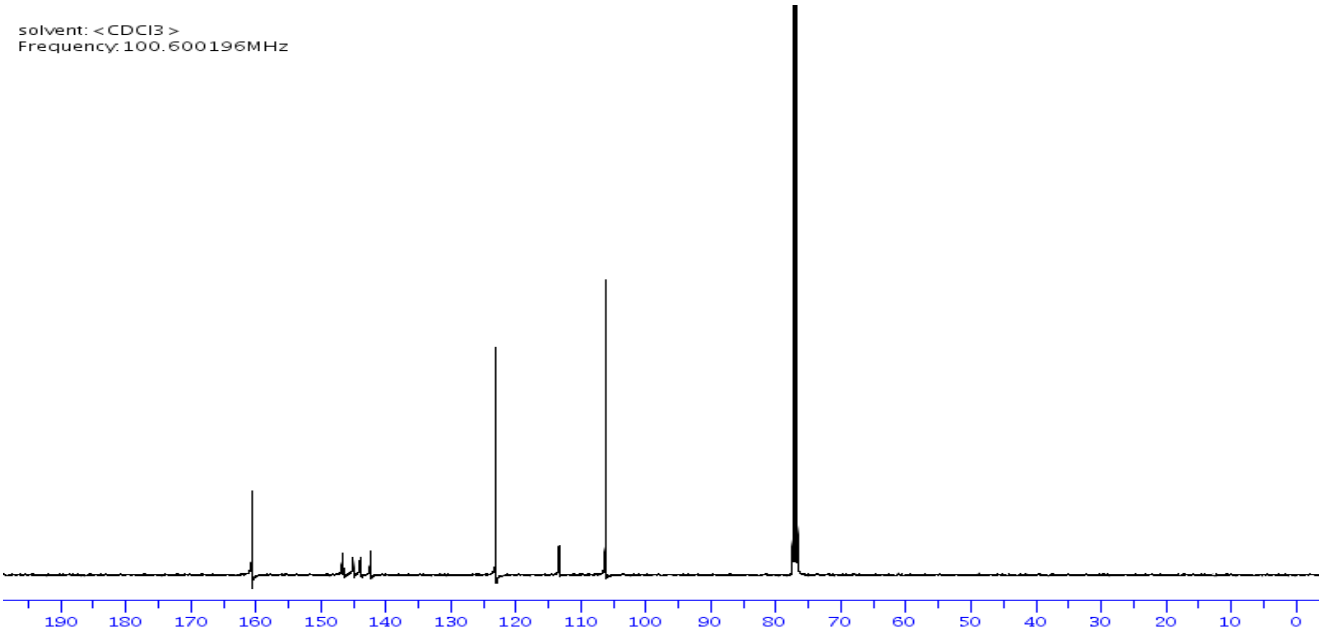


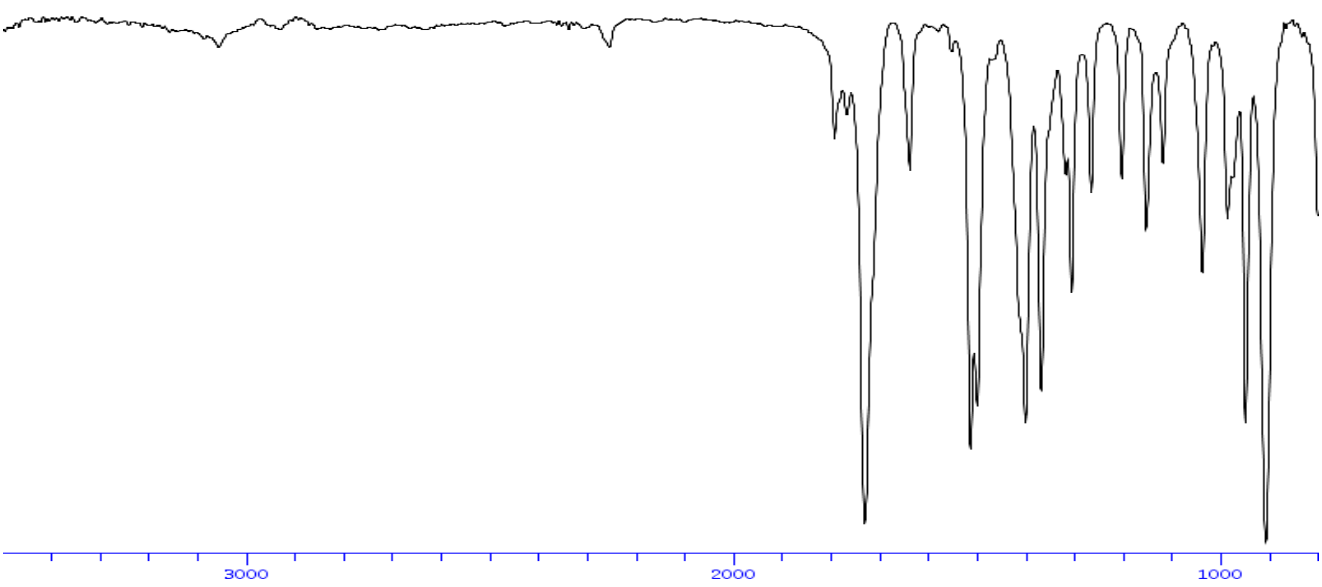
solvent: <CDCl3 >
Frequency: 400.08MHz



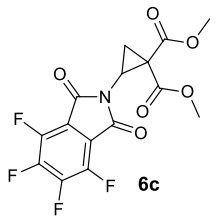
3c

solvent: <CDCl3 >
Frequency: 100.600196MHz



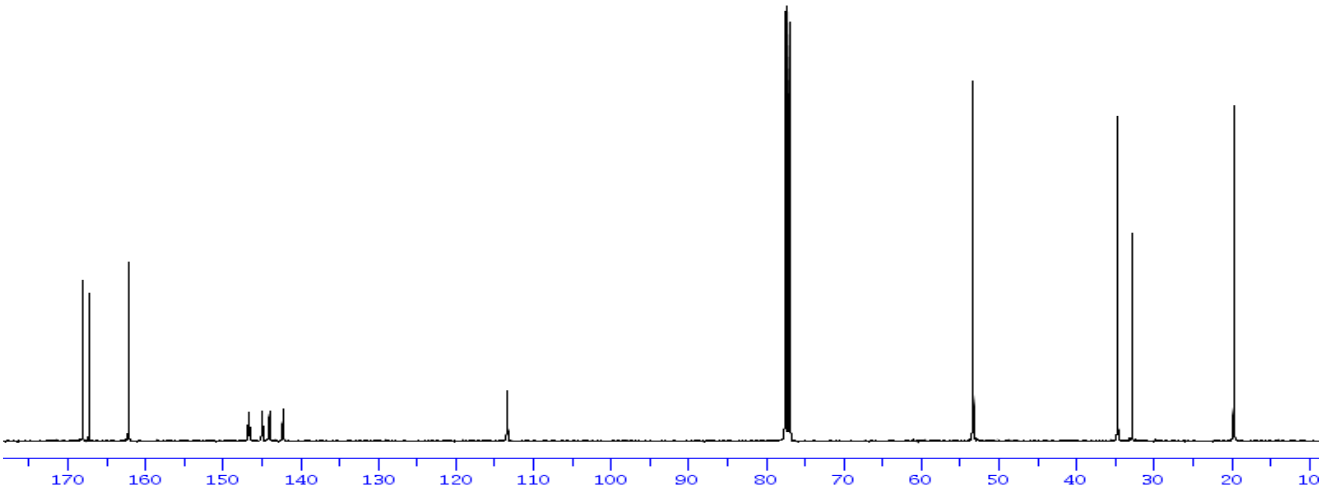


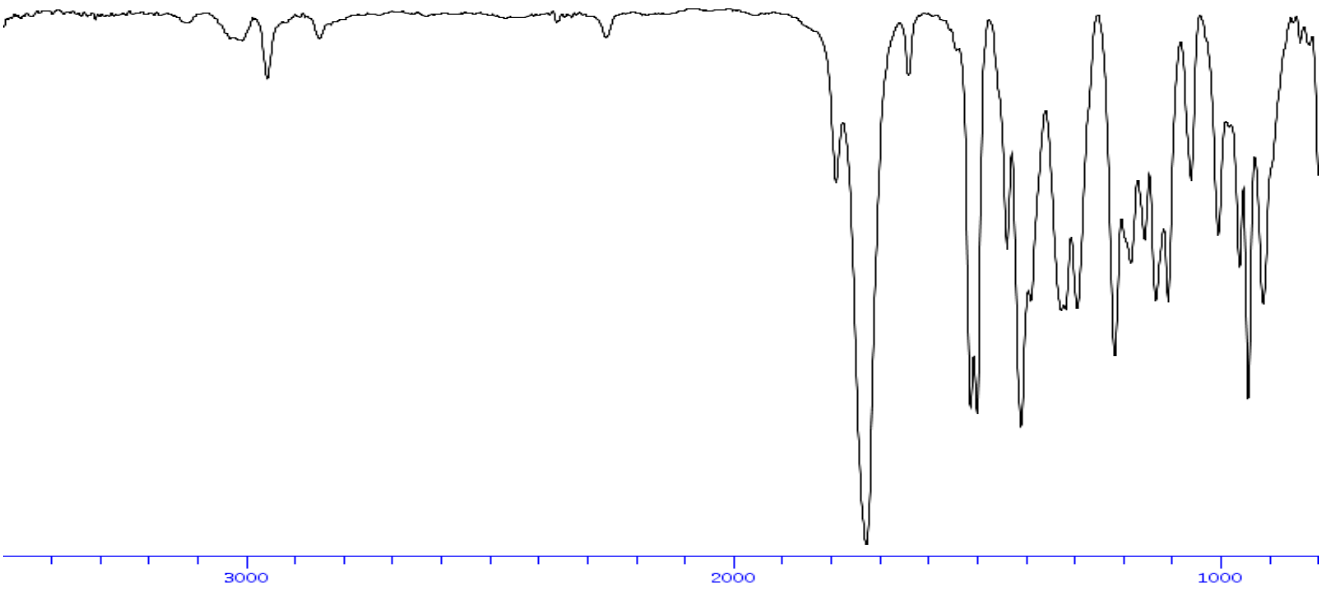
solvent: <CDCl3 >
Frequency: 400.08MHz



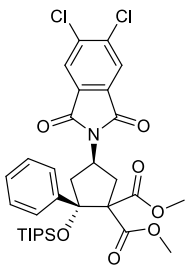
6c

solvent: <CDCl3 >
Frequency: 100.600196MHz



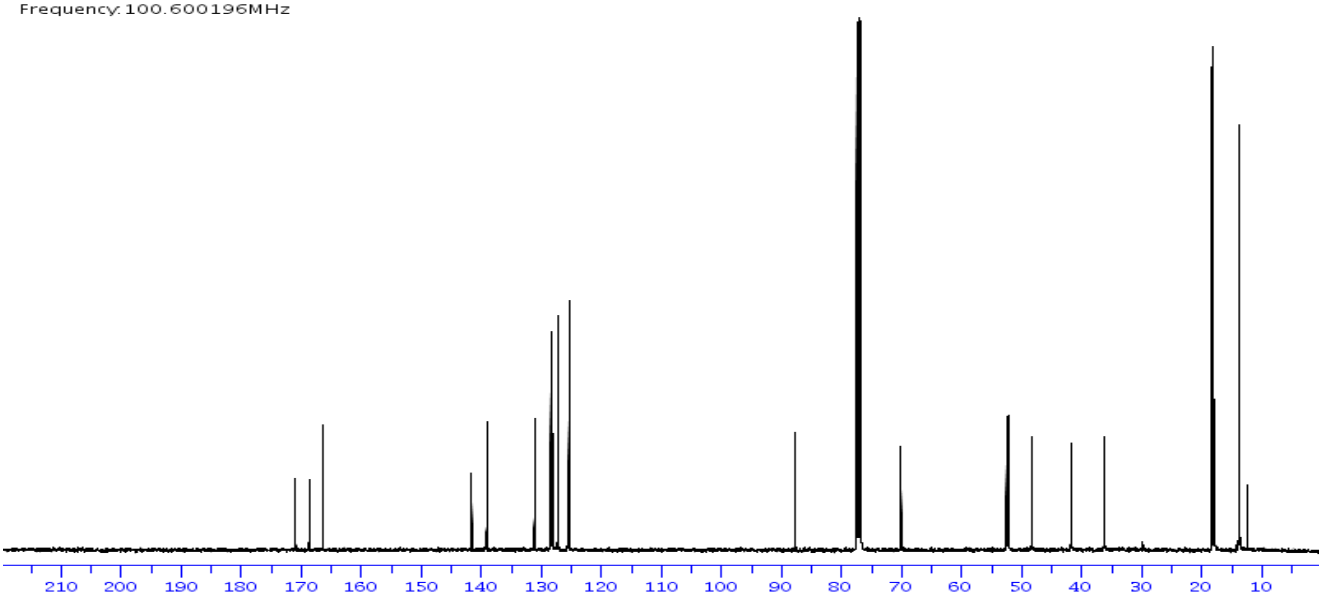


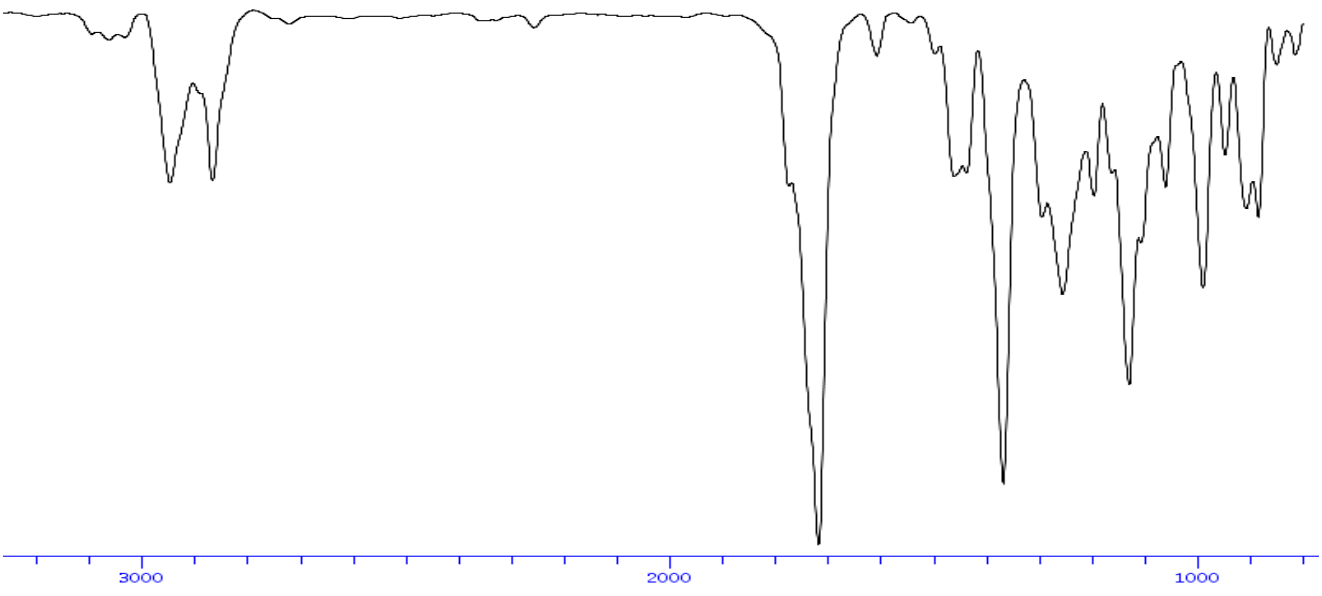
solvent: <CDCl3 >
Frequency: 400.08MHz



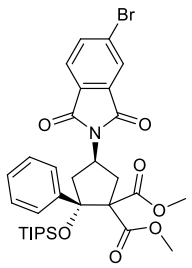
8a

solvent: <CDCl3 >
Frequency: 100.600196MHz



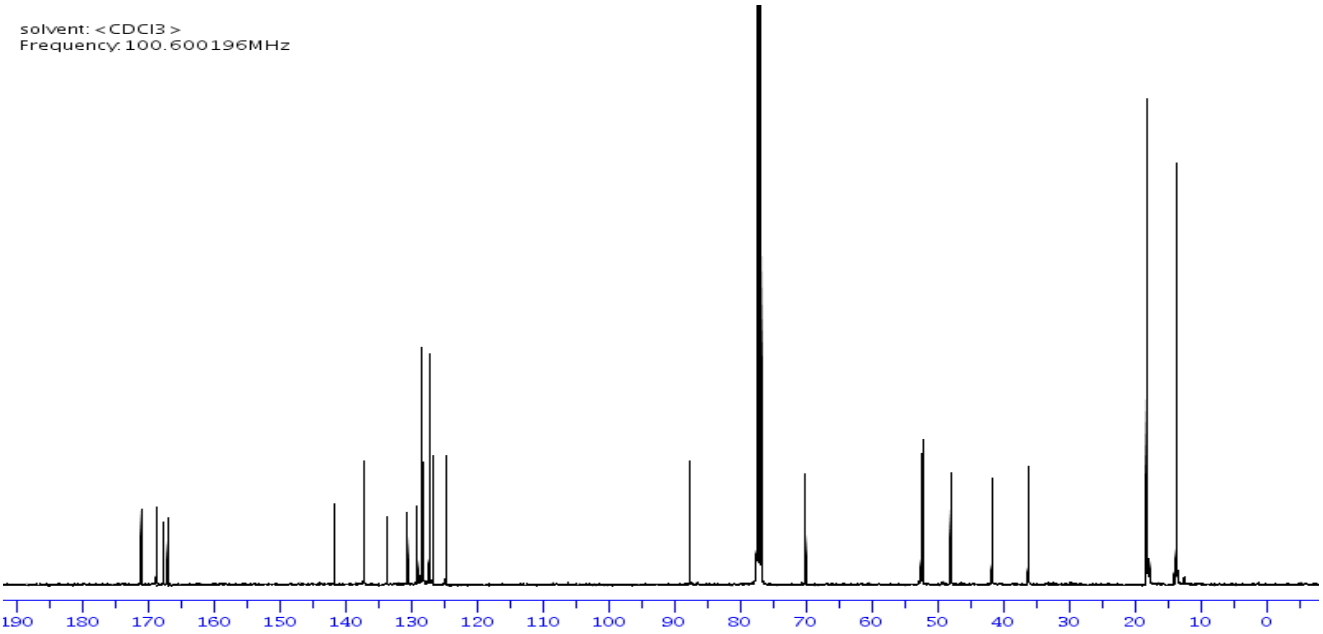


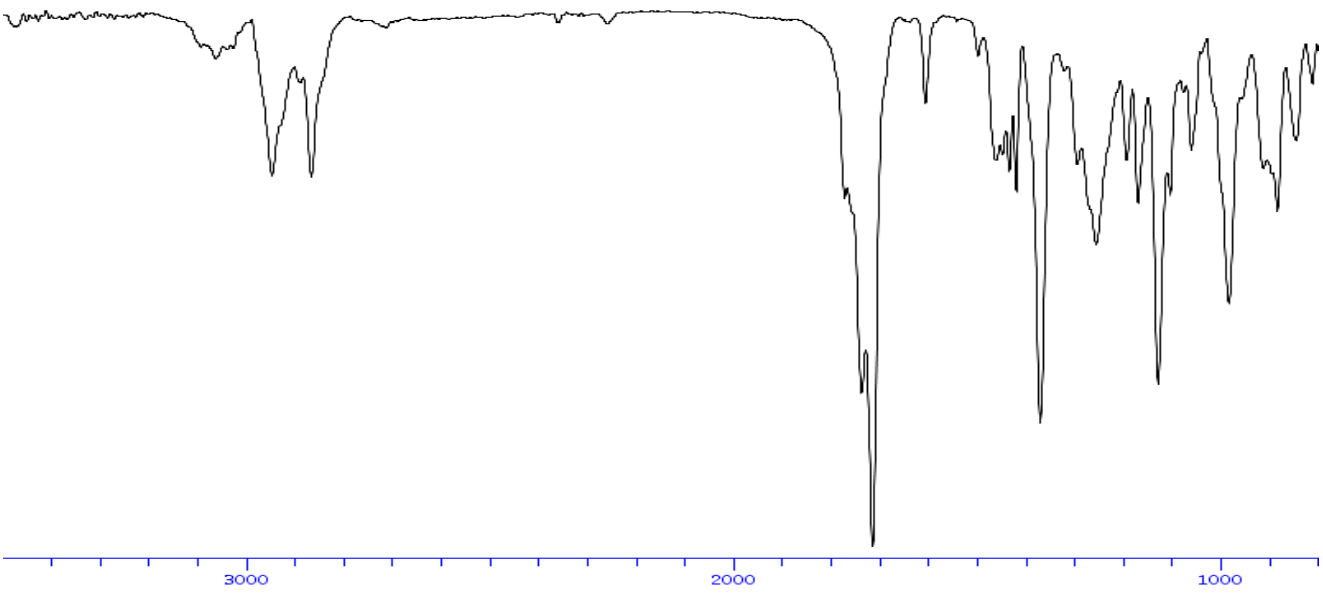
solvent: <CDCl3>
Frequency: 400.08MHz



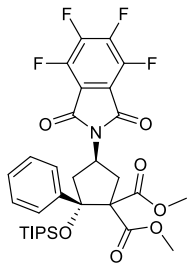
8b

solvent: <CDCl3>
Frequency: 100.600196MHz



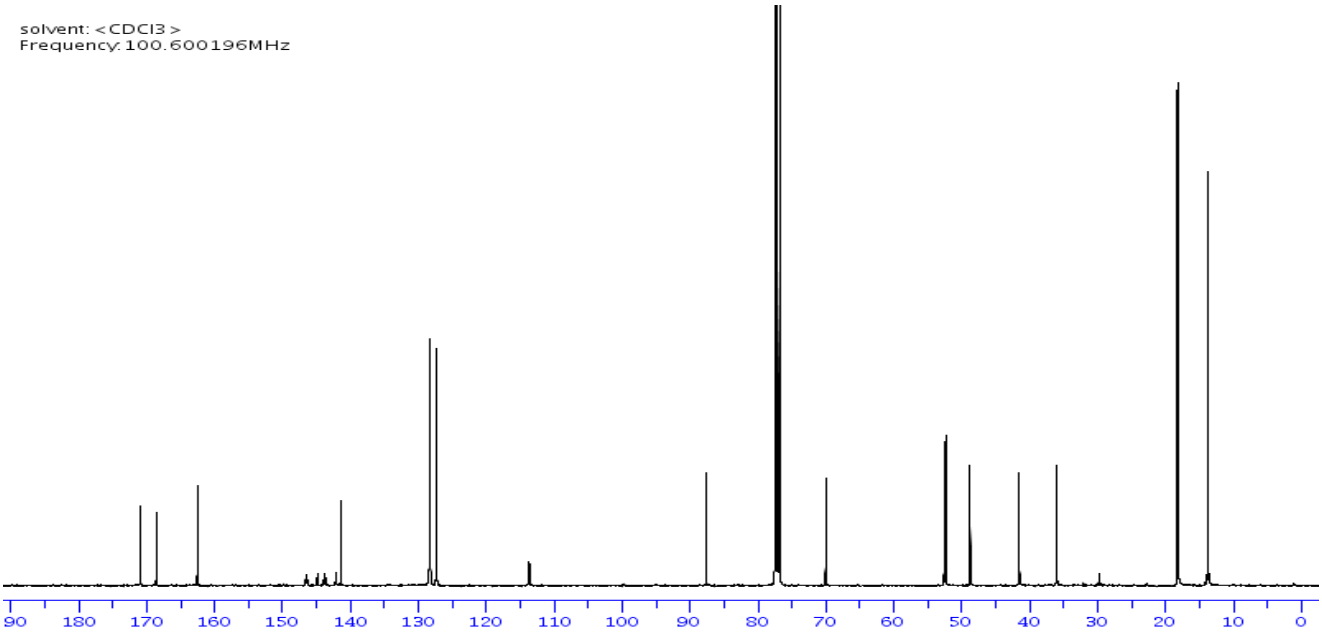


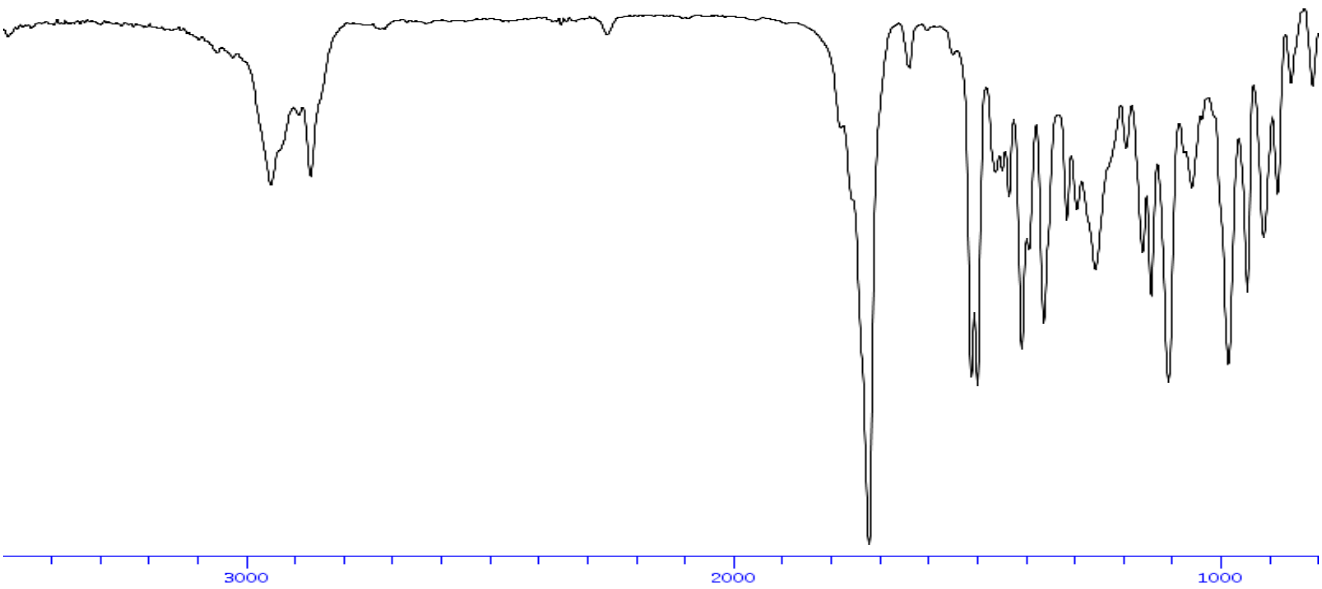
solvent: <CDCl3 >
Frequency: 400.08MHz



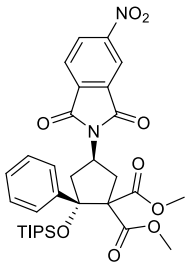
8c

solvent: <CDCl3 >
Frequency: 100.600196MHz



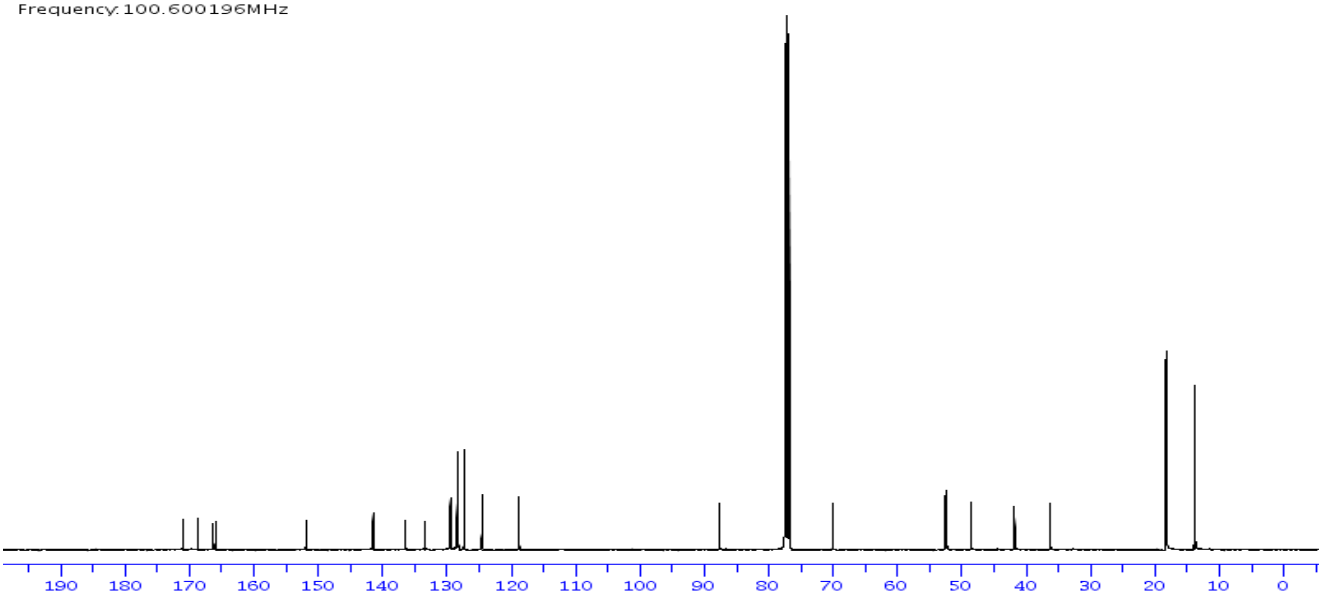


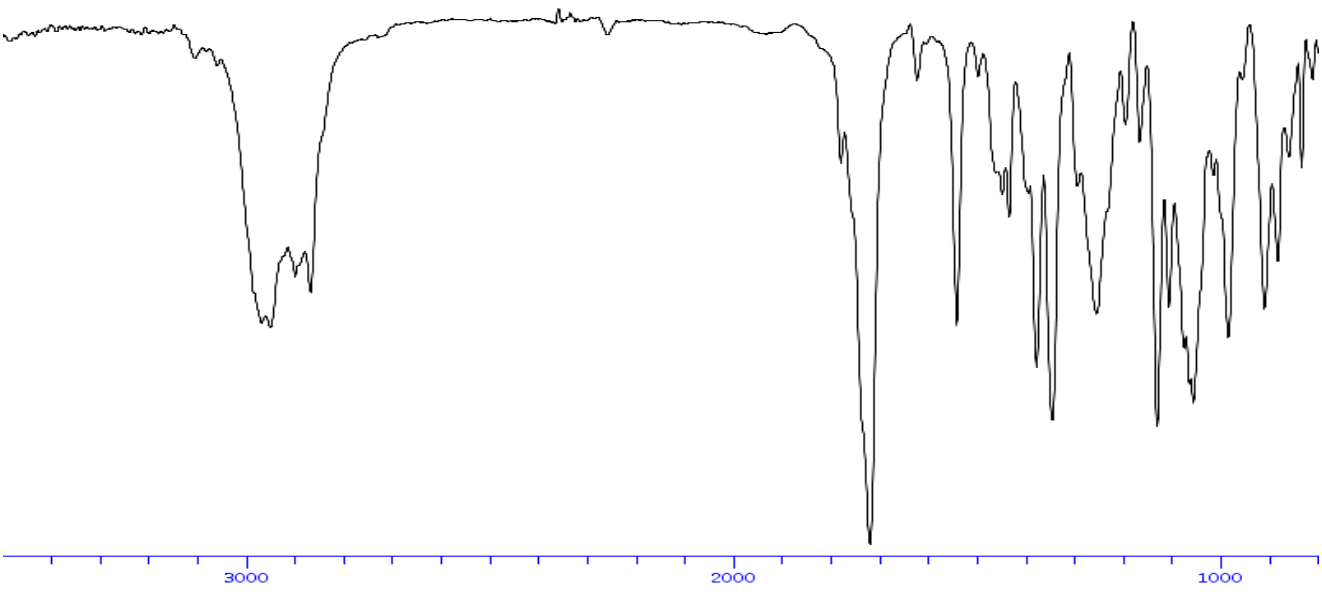
solvent: <CDCl3 >
Frequency: 400.08MHz



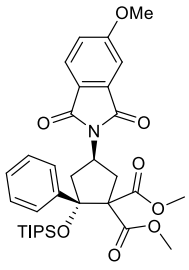
8d

solvent: <CDCl3 >
Frequency: 100.600196MHz



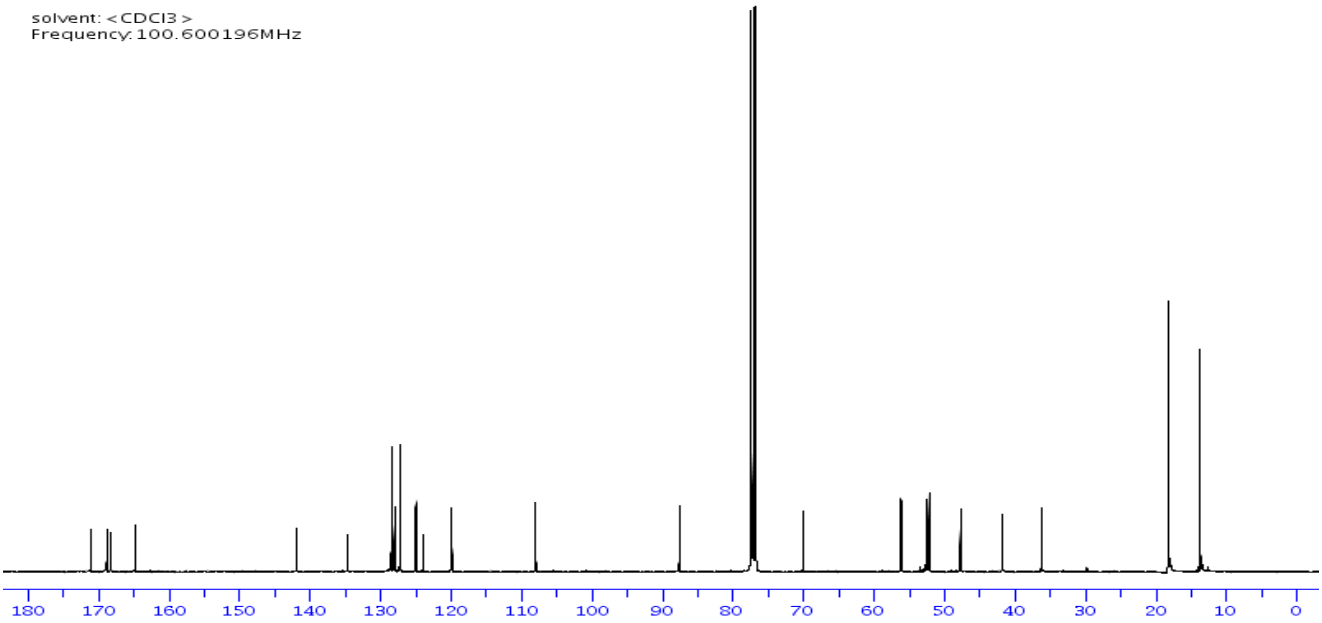


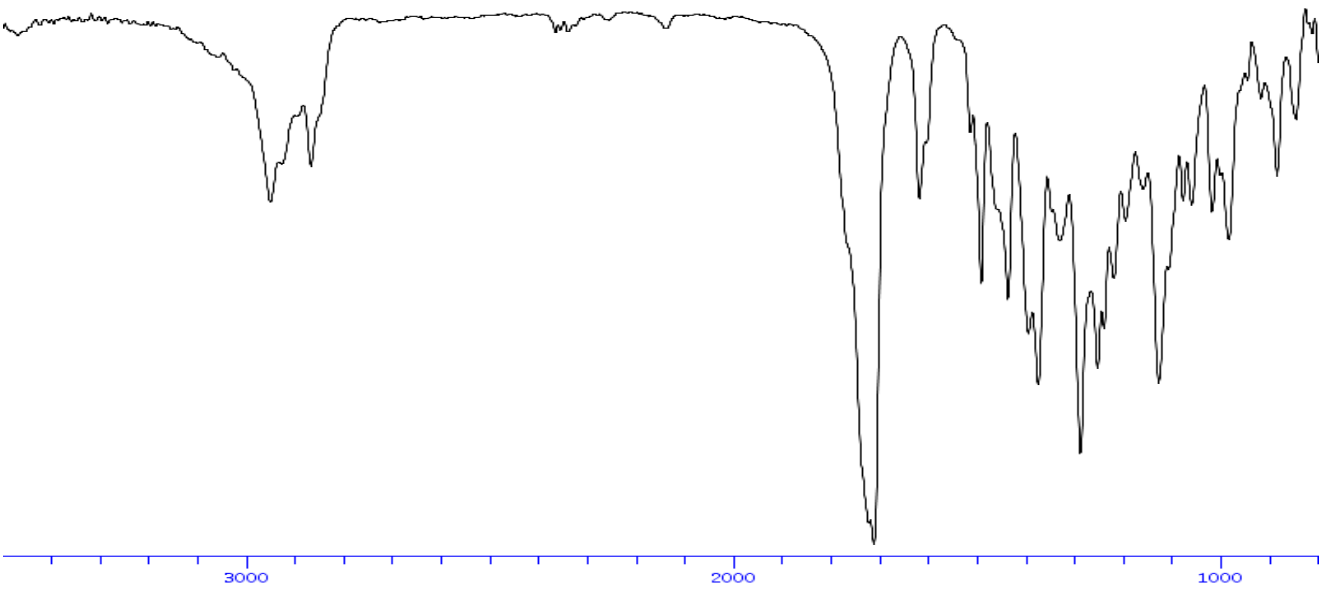
solvent: <CDCl3 >
Frequency: 400.08MHz

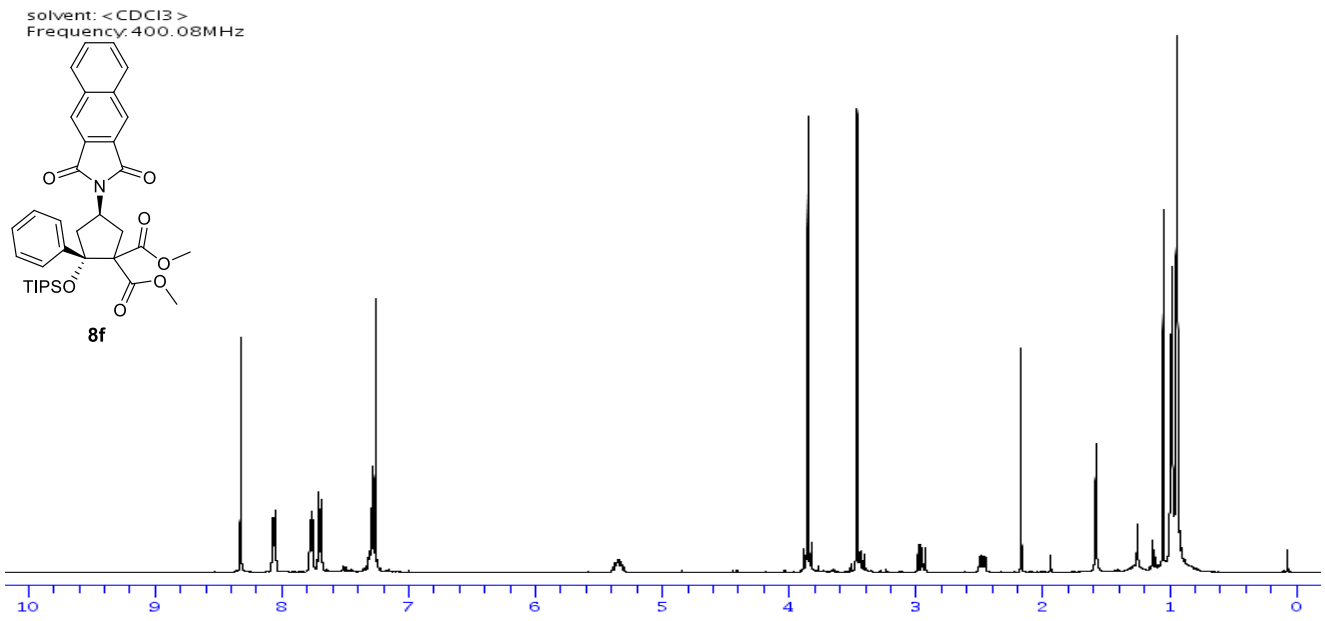


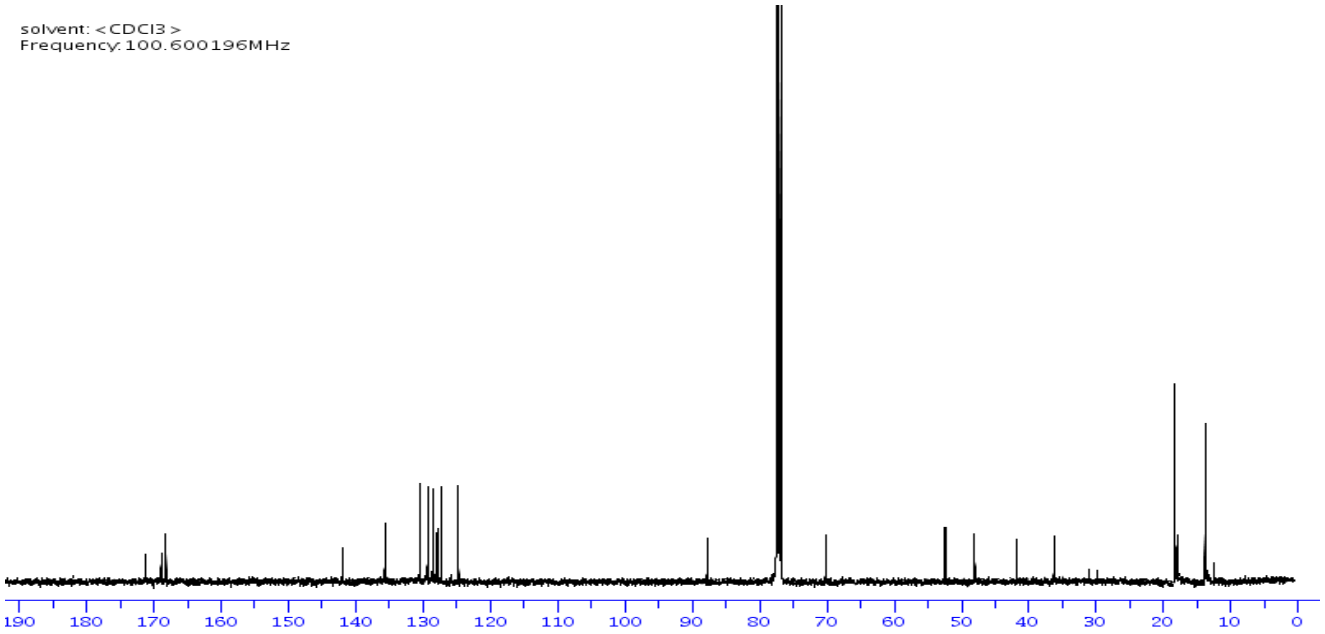
8e

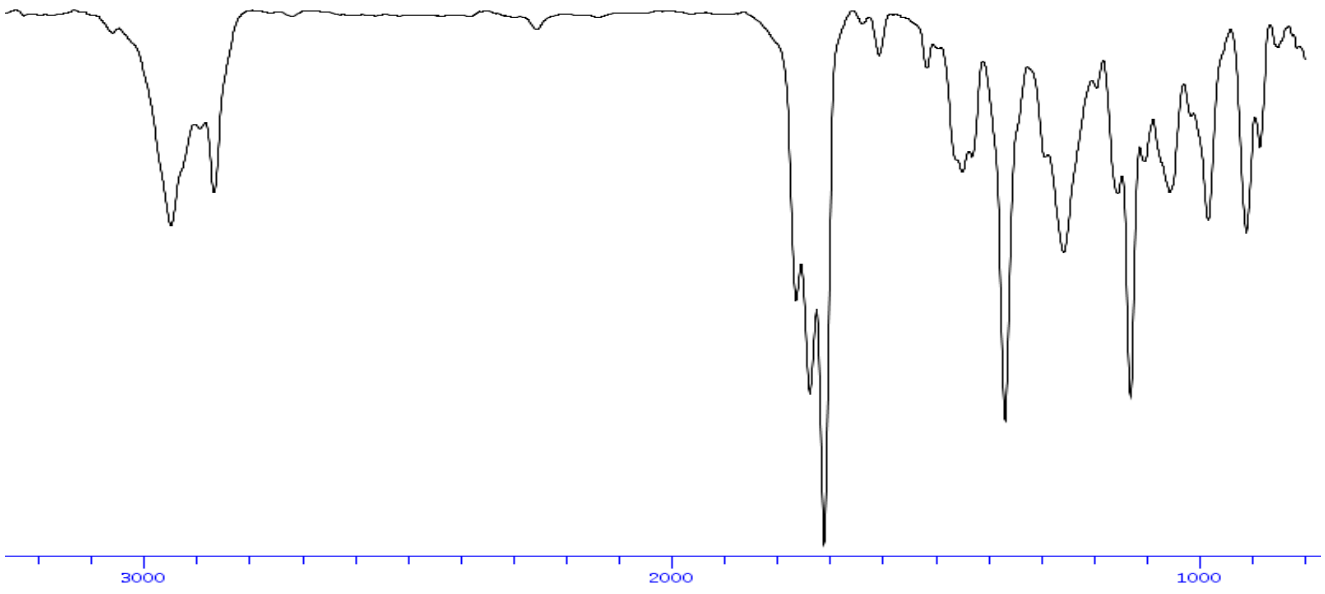
solvent: <CDCl3 >
Frequency: 100.600196MHz



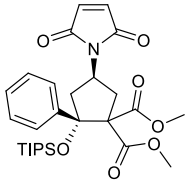



solvent: <CDCl3>
Frequency: 400.08MHz
TIPSO
8f
10
9
8
7
6
5
4
3
2
1
0


solvent: <CDCl3>
Frequency: 100.600196MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

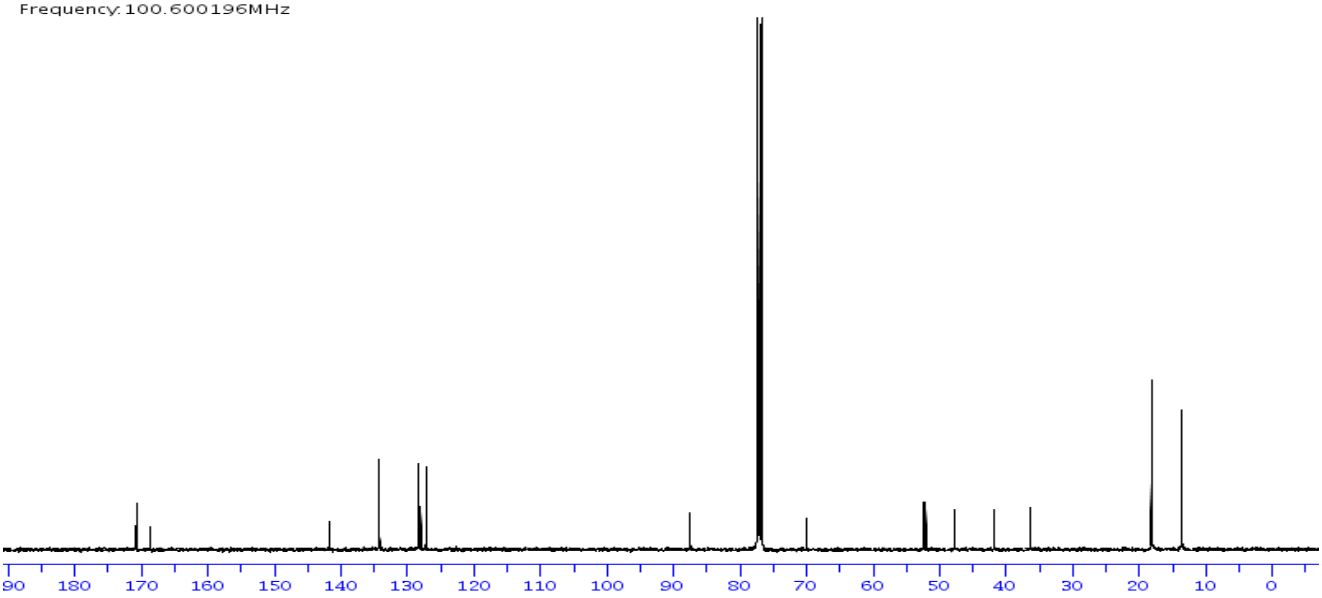

3000
2000
1000

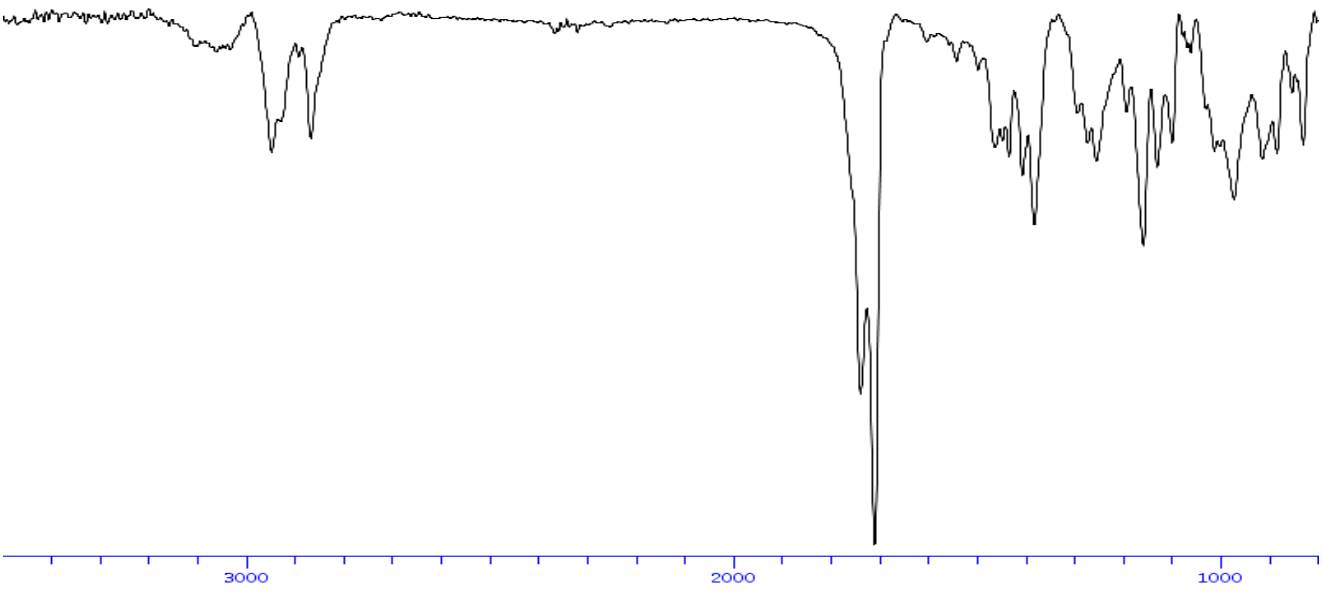
solvent: <CDCl3 >
Frequency: 400.08MHz



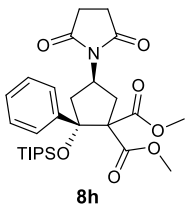
8g

solvent: <CDCl3 >
Frequency: 100.600196MHz



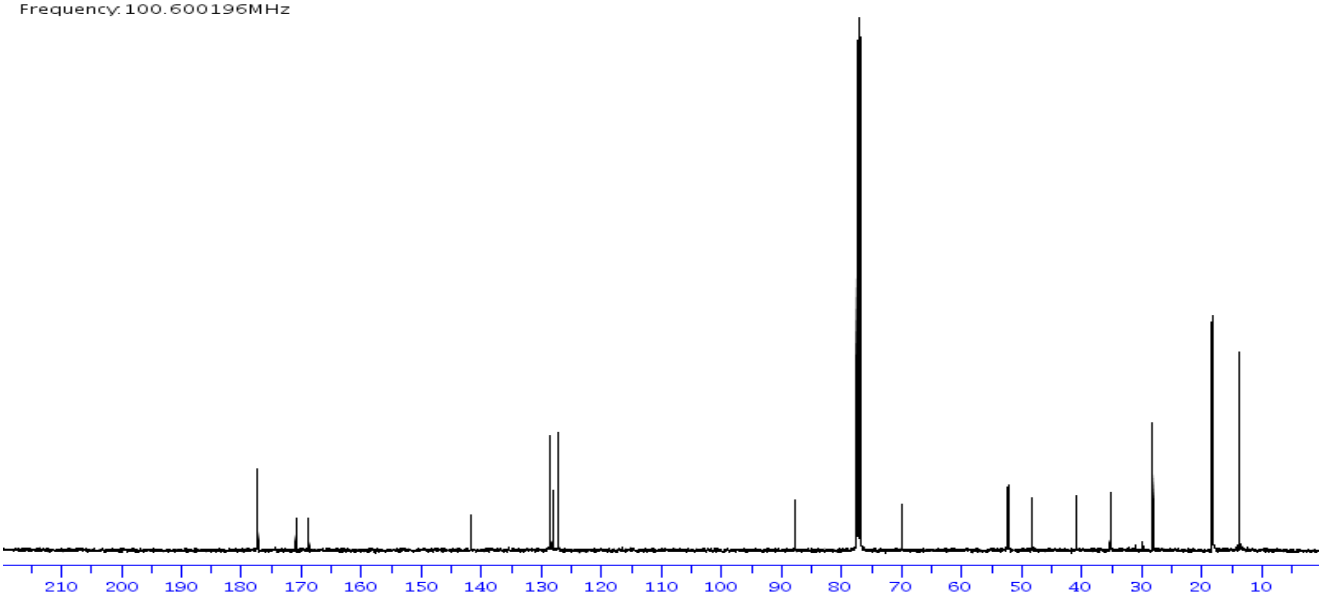


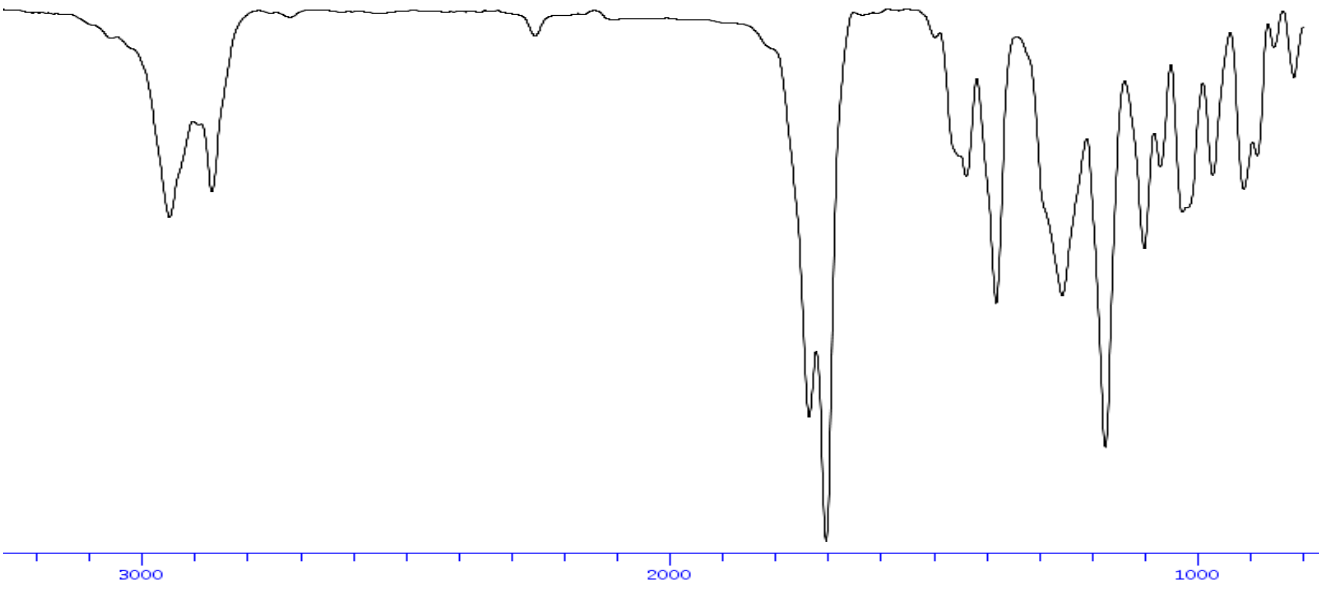
solvent: <CDCl3 >
Frequency: 400.08MHz



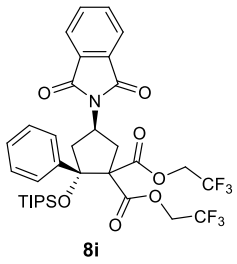
8h

solvent: <CDCl3 >
Frequency: 100.600196MHz

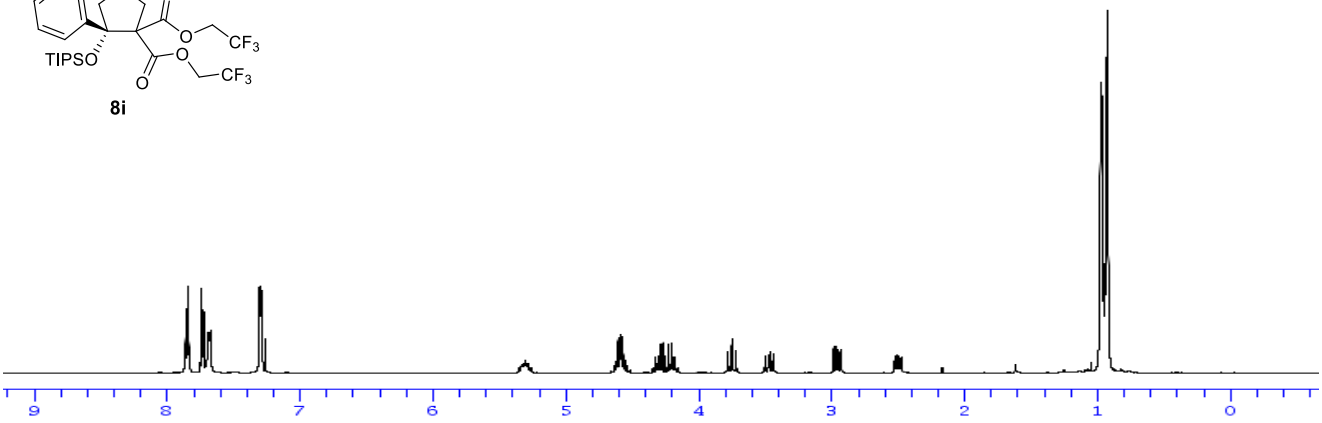




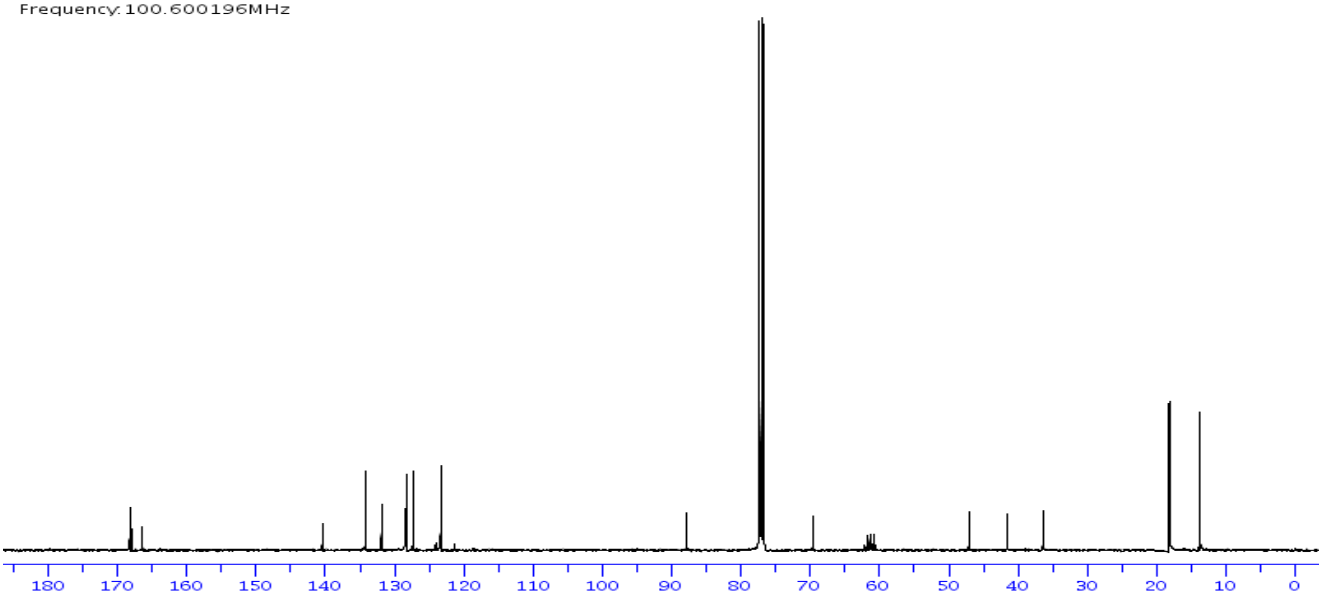
solvent: <CDCl3 >
Frequency: 400.08MHz

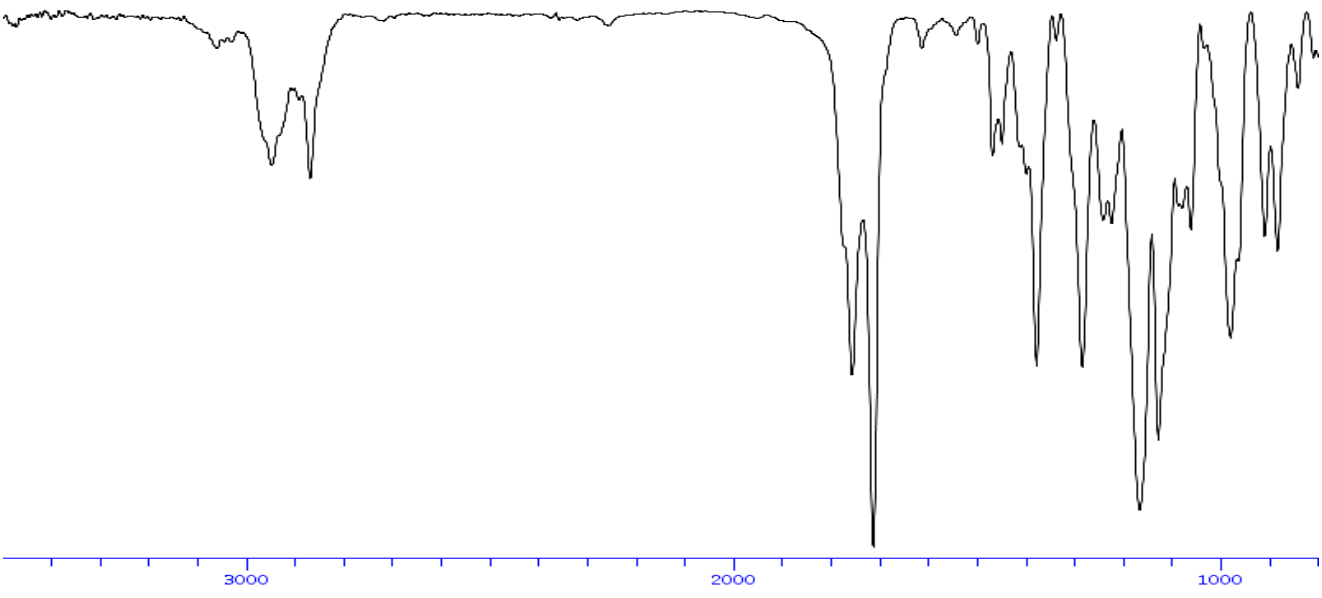


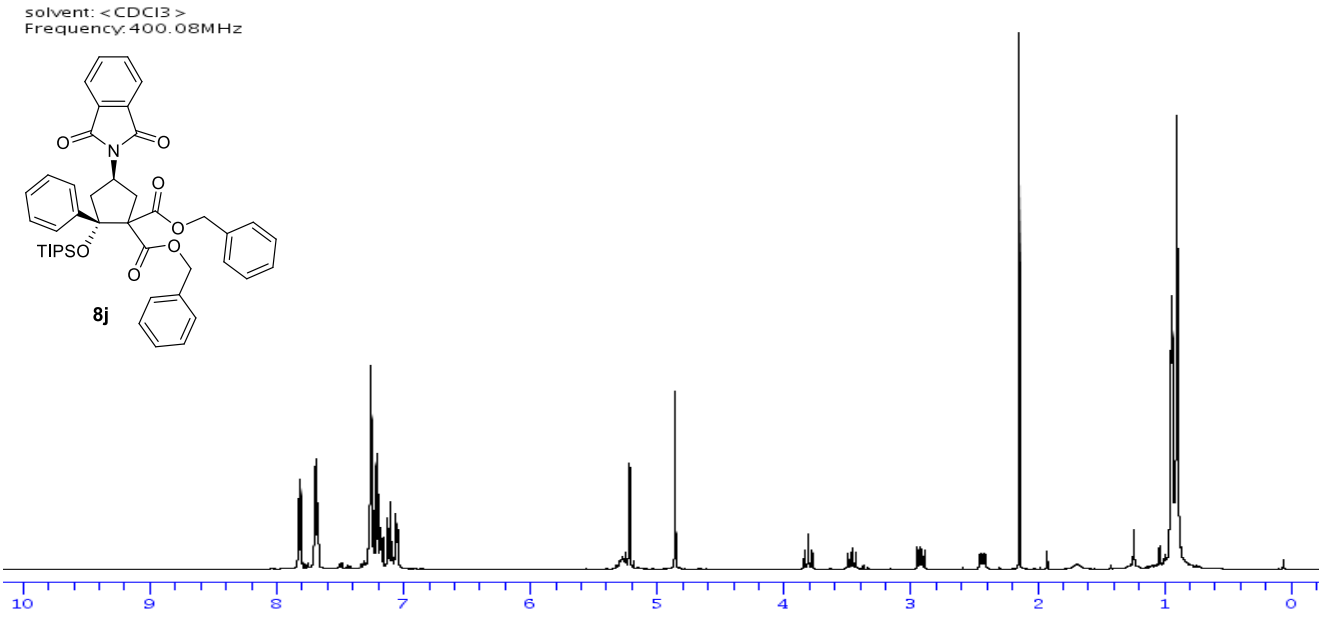
8i

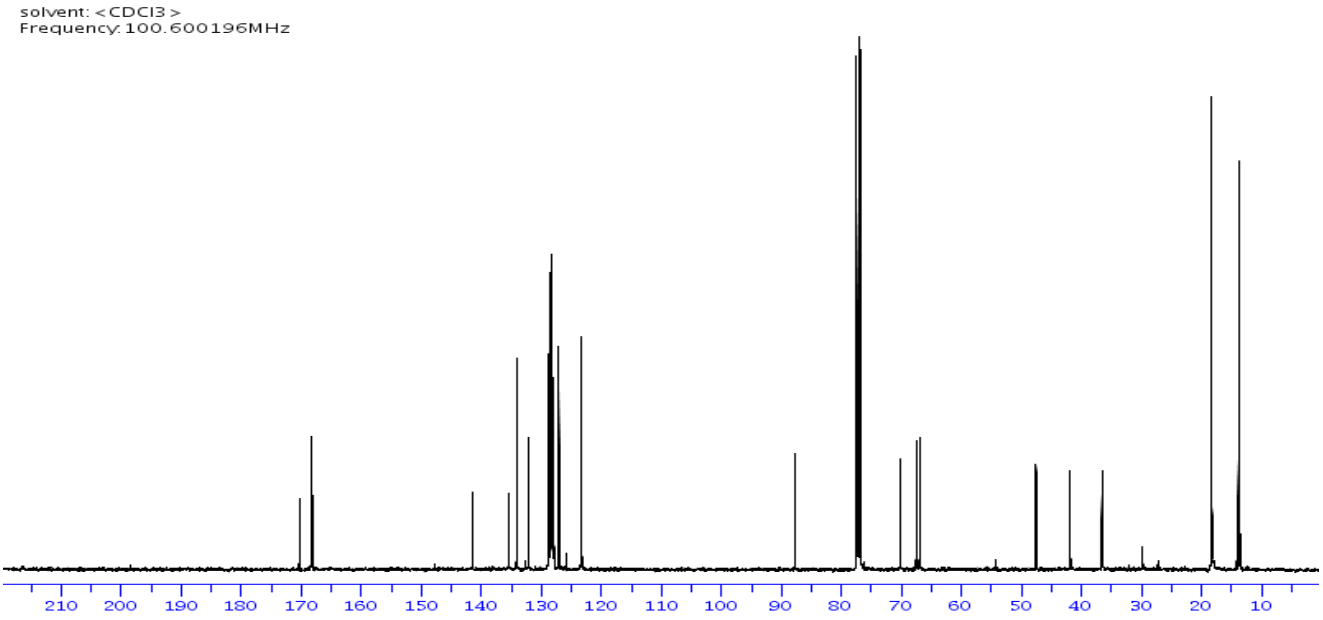


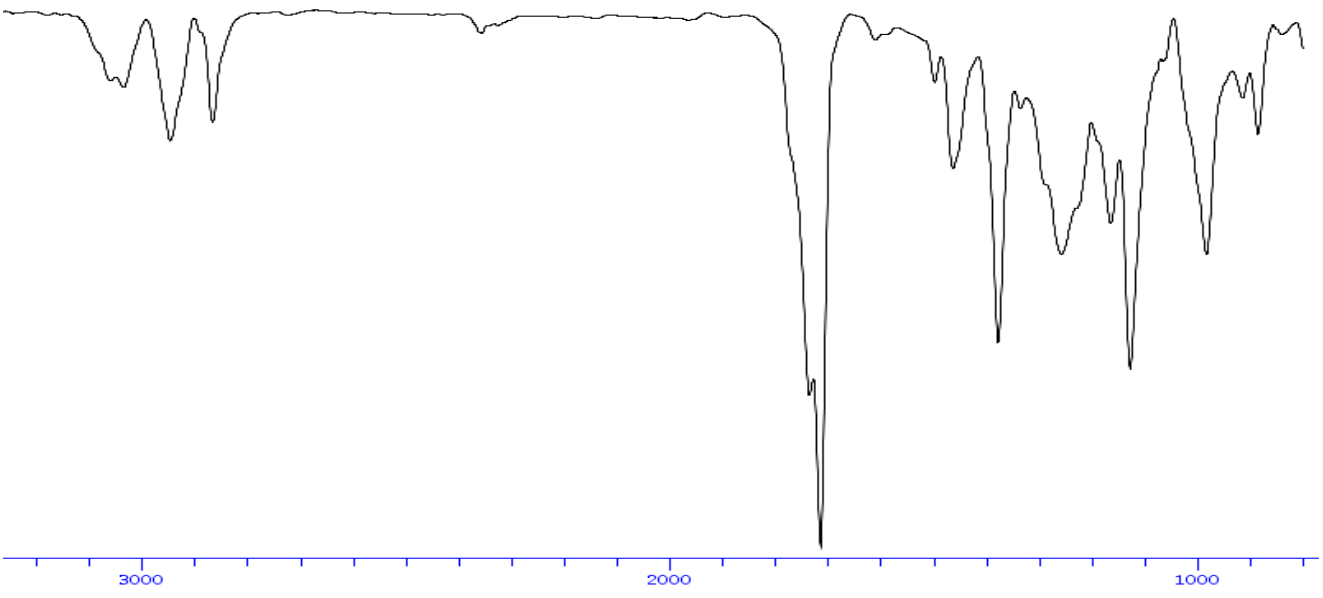
solvent: <CDCl3 >
Frequency: 100.600196MHz






solvent: <CDCl3 >
Frequency: 400.08MHz
TIPSO
8j
10
9
8
7
6
5
4
3
2
1
0


solvent: <CDCl3 >
Frequency: 100.600196MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


3000
2000
1000