Triazene-Activated Donor-Acceptor Cyclopropanes: Ring-Opening and (3+2) Annulation Reactions

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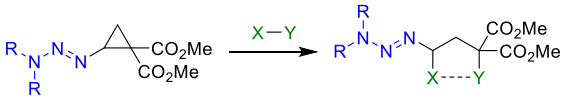
Supporting Information Placeholder

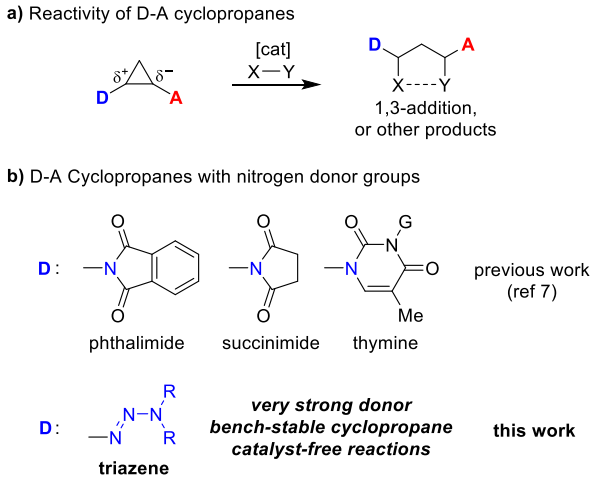


ABSTRACT: Donor-acceptor cyclopropanes substituted with 3,3-dialkyltriazenyl groups are described herein. The strong electron-donating character of the triazene renders the cyclopropanes highly reactive, allowing for catalyst-free ring-opening reactions with methanol and tetracyanoethylene under mild conditions. The triazene-substituted cyclopropanes could also be used as substrates in Lewis acid catalyzed (3+2) annulations with silyl enol ethers.

Cyclopropanes substituted with both electron-withdrawing and electron-donating groups in vicinal position display a high reactivity, which can be accentuated by using catalysts.[1,2] Typically, catalytic activation is achieved by coordination of a Lewis or Brønsted acid to the acceptor group.[2] The acid facilitates heterolytic C-C bond cleavage of the strained ring, allowing for reactions with electrophiles or nucleophiles, as well as cycloaddition and rearrangement reactions (Scheme 1a). Alternatively, formyl-acceptor groups can be activated by amine catalysts via iminium formation.[3] The catalytic activation of donor-acceptor (D-A) cyclopropanes via interaction of the donor group with Lewis bases is less common.[4] Examples of isolable D-A cyclopropanes, which are able to undergo ring-opening reactions without external catalysts, remain scarce.[5] The paucity of such cyclopropanes is related to the difficulty of finding donor/acceptor pairs, which provide the right amount of activation, while insuring sufficient stability of the three-membered ring. Indeed, too much activation can result in spontaneous rearrangement of cyclopropanes into larger 5-membered heterocycles.[6]

A good balance between stability and reactivity has traditionally been realized with carbon and oxygen-based donor groups, whereas nitrogen-based substituents were less investigated, despite their synthetic relevance.[2] To address this limitation, the Waser group has introduced phthalimide-, succinimide- and nucleobase-substituted cyclopropanes (Scheme 1b).[2e,7] In this work we introduce 3,3-dialkyltriazenes as new nitrogen-based donors. We show that triazenes provide an exceptional activation of the cyclopropane ring, allowing for ring-opening and expansion reactions under mild conditions.

Scheme 1. Reactivity of D-A Cyclopropanes (A) and Nitrogen-Based Donor Groups (B).[2-7]



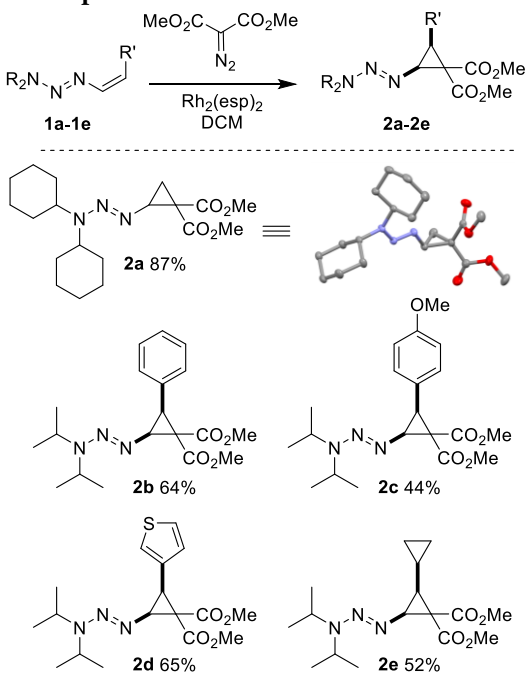
Over the last five years, we have studied the chemistry of 1-alkynyl triazenes.[8] These investigations have revealed that the triazene group is a very good electron donor, enabling an electrophilic attack to the triple bond. In view of these results, we were interested to explore if triazenes could be

used as donors in D-A cyclopropanes to expand the range of useful nitrogen substituents.

A common procedure for the synthesis of diester-substituted cyclopropanes is the Rh-catalyzed cyclopropanation of olefins with diazomalonates.[9] This approach could be implemented for the synthesis of cyclopropanes bearing triazene groups. The required vinyl triazenes starting materials **1a–1e** were accessed by coupling of vinyl Grignard reagents with nitrous oxide and lithium amides,[8g,10] or by hydrogenation of alkynyl triazenes.[11]

Cyclopropane **2a** could then be prepared by reaction of (*E*)-3,3-dicyclohexyl-1-vinyltriaz-1-ene (**1a**) with dimethyl diazomalonate (1.2 equiv.) in the presence of commercially available $Rh_2(esp)_2$ (0.2 mol %) as catalyst (Scheme 2). The desired product was obtained in good yield, and the procedure was further optimized to gram scale with an isolated yield of 87%. Compound **2a** is a colorless crystalline solid, and its structure could be confirmed by single crystal X-ray diffraction. Using this optimized procedure, we could prepare cyclopropanes **2b–2e** having additional phenyl, 4-anisyl, 2-thienyl or cyclopropyl groups in C3 position from the corresponding *cis*-1,2-disubstituted vinyl triazenes **1b–1e**. The isolated yields of **2b–2e** varied from 52% to 65%. According to the ^{1}H NMR spectra, the *cis* stereochemistry is conserved in the products.

Scheme 2. Synthesis of D-A Cyclopropanes with Triazene Groups.[a]



[a] Reaction conditions: vinyl triazene (1 equiv.), diazomalonate (1.2 equiv.), $Rh_2(esp)_2$ (0.2–0.5 mol %), DCM (0.1 M), 0 °C – RT.

The ^{13}C NMR spectrum of cyclopropane **2a** in $CDCl_3$ shows a chemical shift for the C2 atom next to the triazene group at 55.6 ppm. Calculation of ^{13}C NMR chemical shifts for DFT-optimized structures of **2a** gave a similar value.[12] For comparison, the corresponding values for 'standard' D-A cyclopropanes having aryl, cyclopropyl, or phthalimidyl donor groups lie in the range of 31–35 ppm, and cyclopropanes with poor donor groups such as *n*-butyl and hydrogen show a C2 signal at 24 ppm and 17 ppm, respectively (Figure 1a).[13] The strongly shifted C2 signal of **2a** was a first indication for the pronounced electronic effect of the triazene group.

Figure 1. ^{13}C NMR Chemical Shifts of Different D-A Cyclopropanes (a) and (b) Relative Stability of Carbocations (ΔG^{298} (kcal·mol^{-1})).[a]

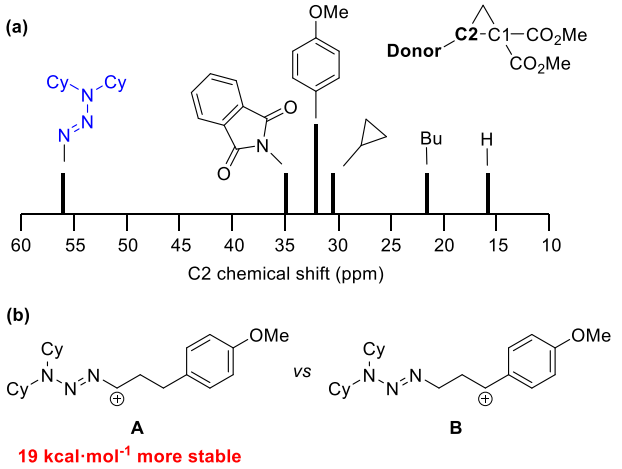


Figure 1. ^{13}C NMR Chemical Shifts of Different D-A Cyclopropanes (a) and (b) Relative Stability of Carbocations (ΔG^{298} (kcal·mol^{-1})). The reference values were taken from the literature (ref. 13). All spectra were measured in $CDCl_3$. The calculations for the carbocations were performed on M06-2X/6–311+G(d,p) level.

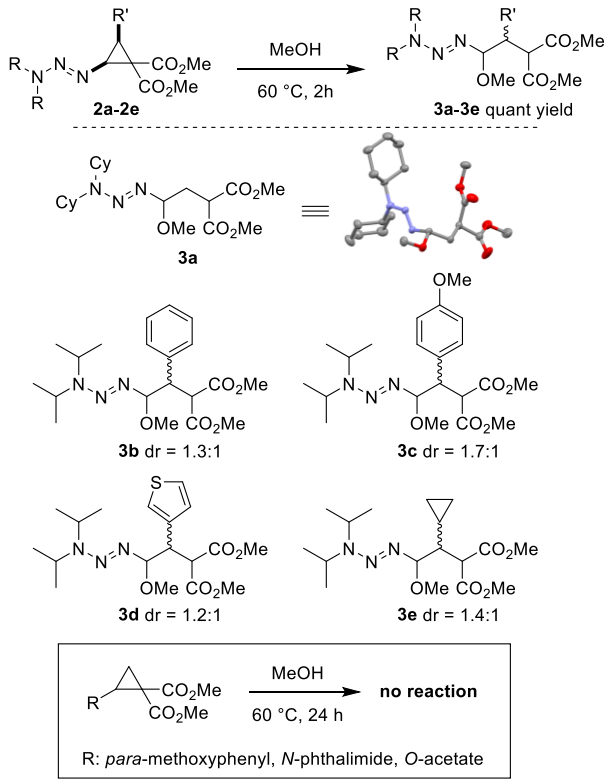
Further evidence for the strong electron-donating properties of the triazene group were obtained by calculating the relative stability of carbocations **A** and **B** (Figure 1b). This approach, which was developed by Werz,[14] allows comparing the donor capabilities of different substituents. As a reference, we used the *p*-methoxyphenyl group, which is known to be one of the strongest donors amongst the reported stable D-A cyclopropanes, both from a thermodynamic[14] as well as a kinetic[15] point of view. The calculations on M06-2X/6–311+G(d,p) level showed that carbocation **A** is 19 kcal·mol^{-1} more stable than **B**. Accordingly, the triazene group was expected to provide a very strong activation of the cyclopropane ring.

Diverse reactivity studies with these new cyclopropanes **2** were then carried out. When **2a** was dissolved in methanol, the ring-opened adduct **3a** (Scheme 3) could be isolated in quantitative yield after heating to 60 °C for 2 h, followed by evaporation of the solvent. The structure of **3a** could be confirmed by X-ray crystallography. Analogously, reaction of methanol with cyclopropanes **2b–2e** gave the addition products **3b–3e** in quantitative yields as a mixture of two diastereoisomers (ratio: ~ 1:1). In all cases, the bond between the triazene and the diester was broken, showing again that it was a better donor than a (hetero)arene or a

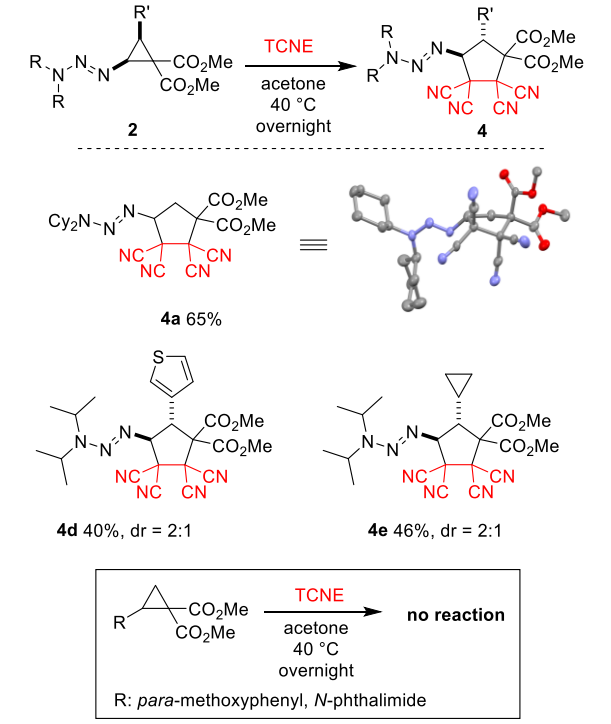
cyclopropyl group. Preliminary mechanistic investigations indicate that methanol addition proceeds with participation of the ester group: more details are given in the Supporting Information.

For comparison, we have attempted reactions with methanol using three literature-known D-A cyclopropanes (donor = *p*-methoxyphenyl, *N*-phthalimide, or *O*-acetate). No reaction was observed, even after prolonged (24 h) heating at 60 °C. These results underline the unique donor properties of the triazene group.

Scheme 3. Methanol Addition Reactions.



Scheme 4. (3+2) Annulation with TCNE.[a]



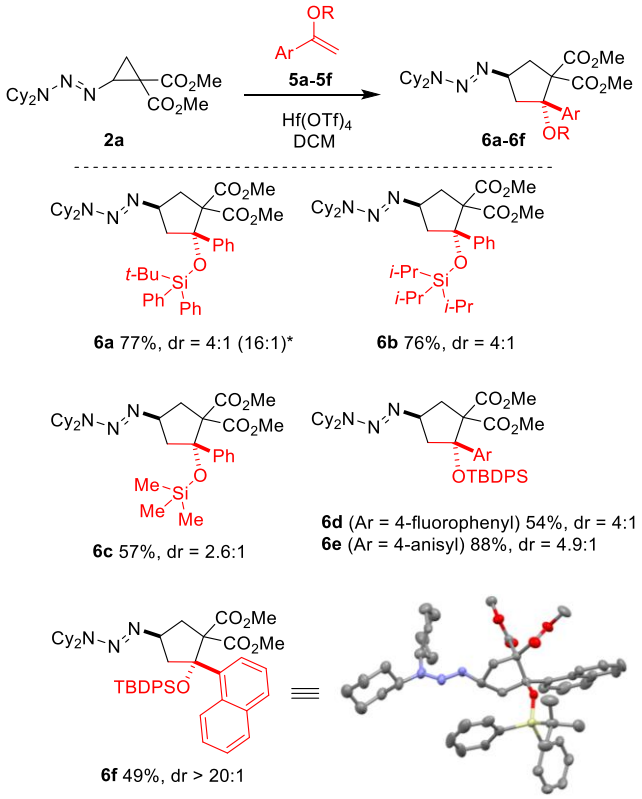
[a] Reaction conditions: **2a** (1 equiv.), TCNE (1.2 equiv.), acetone (0.1 M), 40 °C, 12 h.

Next, we have explored the reactivity of **2a** towards electrophiles. Ring-opening of D-A cyclopropanes with electrophiles is generally more challenging.[2] Cyclopropane **2a** reacted with tetracyanoethylene (TCNE) in a formal (3+2) cycloaddition reaction, in the absence of any external catalyst, to give the highly functionalized cyclopentane **4a** in 65% yield (Scheme 4).[16] Similarly, we were able to prepare the addition products **4d** and **4e**, albeit with reduced yields of 40% and 46%, respectively. The cyclopentanes **4d** and **4e** were isolated as mixtures of diastereoisomers, with prevalence of the *trans* isomer (dr = 2:1). As for the reactions with methanol, we found that D-A cyclopropanes with *p*-methoxyphenyl or *N*-phthalimide donor groups did not react with TCNE under these conditions.

After having established catalyst-free reactions with methanol and TCNE, we turned our attention to less reactive reaction partners, which require activation of the acceptor group by a catalyst. A priori, it was not clear if cyclopropanes bearing triazene groups could be activated by Lewis or Brønsted acids, because the triazene groups are known to be acid-sensitive.[17]

As a benchmark reaction, we have examined the addition of silyl enol ethers to cyclopropane **2a**. For D-A cyclopropanes with N-donor groups, this reaction is known to occur with a Lewis acid catalyst such as $SnCl_4$.[7] Screening of different LA catalysts and reaction conditions revealed that hafnium triflate[18] can catalyze the desired reaction between **2a** and silyl enol ethers at − 40 °C (see SI for details).

Scheme 5. (3+2) Annulation with Silyl Enol Ethers.[a]



[a] Reaction conditions: **2a** (1 equiv.), enol ether (1.2 equiv.), $Hf(OTf)_4$ (10 mol %), DCM (0.1 M), − 40 °C, 20 h. * After recrystallization from MeOH.

Using the optimized reaction conditions, we have tested different acetophenone-based silyl enol ethers (**5a–5c**, Scheme 5). Bulky TBDPS and TIPS groups allowed isolation

of the cyclopentanes **6a** and **6b** in good yields with a dr of 4:1. Recrystallization of **6a** from methanol improved the dr to 16:1. Analysis of **6a** by NOESY NMR spectroscopy revealed that the major diastereoisomer has a *trans* configuration of the triazene and the $OSiR_3$ group. The same selectivity had been observed for reactions with *N*-phthalimide D-A cyclopropanes.[7a] Utilization of a silyl enol ether with a less bulky TMS group (**5c**) gave cyclopentane **6c** in lower yield (57%) and a dr of 2.6:1. Next, we tested silyl enol ethers with different aryl groups. Electron-withdrawing 4-fluorophenyl and electron-donating 4-anisyl led to the formation of **6d** and **6e** in 54% and 88% yield, respectively. Interestingly, the dr of the products was only slightly influenced by the electronic properties of the aryl groups. On the other hand, using a substrate with a bulky 1-naphtyl substituent gave **6f** almost exclusively as one diastereoisomer (dr > 20:1) in 49% yield. Cyclopentane **6f** was additionally characterized by single crystal X-ray diffraction.

In conclusion, we report the first synthesis of D-A cyclopropanes substituted with dialkyltriazene groups by a simple Rh-catalyzed reaction of vinyl triazenes with dimethyl diazomalonate. The triazene group was found to provide an exceptionally strong activation of the cyclopropane ring, allowing for catalyst-free reactions with methanol and TCNE. Combined with the good stability of the new cyclopropanes, this type of reactivity is unique, as evidenced by the fact that 'standard' D-A cyclopropanes with 4-methoxyphenyl or *N*-phthalimide donor groups do not react under these conditions. The usefulness of the new triazenyl cyclopropanes was further highlighted by their compatibility with Lewis acid catalysts in a (3+2) cycloaddition with silyl enol ethers, which delivered highly-functionalized cyclopentanes. Taken together, our findings highlight the potential of the triazene group in activating cyclopropane ring systems. The results are also relevant from the more general perspective of triazene chemistry. So far, most investigations about triazenes have focused on 1-aryl triazenes,[18] with studies about 1-vinyl[11,20] and 1-alkynyl triazenes[8] as recent additions. There are very few reports about 1-alkyl triazenes, and no examples of alkyl triazenes with additional functional groups.[21] The D-A cyclopropane chemistry described above offers a means to prepare structurally and functionally complex alkyl triazenes. Further reactivity studies are ongoing in our laboratories.

ASSOCIATED CONTENT

Supporting Information

Experimental details and analytical data of the new compounds (PDF). Crystallographic data for compounds **2a**, **3a**, **4a** and **6f** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Triazene-Activated Donor-Acceptor Cyclopropanes: Ring-Opening and (3+2) Annulation Reactions

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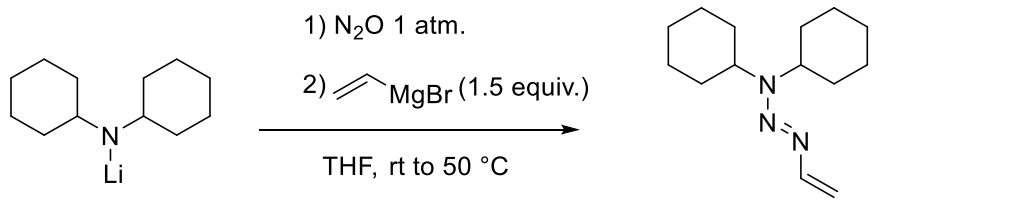
1. Materials and methods

All *reactions* were carried out in oven dried glassware under an atmosphere of dry nitrogen or nitrous oxide (purity: 99.999%, Messer Schweiz AG), unless stated otherwise. For flash chromatography for analysis, HPLC grade *solvents* were used. Dry THF, Et_2O, CH_3CN, toluene, hexane and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere using solvent purification system. All *chemicals* were purchased from commercial suppliers and used as such unless stated otherwise. *TLC* was performed on Merck silica gel 60 F254 TLC glass plates or aluminium oxide plates were 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. *NMR* spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in $CDCl_3$, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm (^1H) and 77.16 ppm (^{13}C) 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). *High resolution mass* spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL. Electrospray-ionisation HRMS data were acquired on a Q-Tof Ultima mass spectrometer (Waters) or a Q-Tof 6530 Accurate mass spectrometer (Agilent) operated in the positive ionization mode and fitted with a standard Z-spray ion source equipped with the Lock-Spray interface. Data from the Lock-Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. Atmospheric pressure photo-ionisation (APPI) HRMS measurements were done on a LTQ-Orbitrap Elite instrument (Thermofisher) operated in the positive ionization mode. *Column chromatography* was carried out employing silica gel 230–460 mesh (100 g) deactivated by adding dichloromethane containing 5 vol% triethylamine (300 mL), removal of the solvent under reduced pressure, and drying at room temperature under oil pump vacuum overnight.

2. Synthesis of vinyl triazenes

*Safety note: N_2O-lithium amide intermediate generated in the synthesis of **1a** poses a risk of explosion, so a protective blast shield is recommended during the synthesis.*



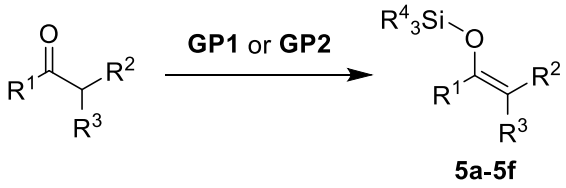
(*E*)-3,3-dicyclohexyl-1-vinyltriaz-1-ene
1a

Following the reported procedure,[1] a Schlenk flask was charged with lithium dicyclohexylamide (1.9 g, 10 mmol, 1.0 equiv.) dissolved in THF (24 mL). The resulting solution was stirred vigorously under N_2O (1 atm) for 1 h at room temperature. A white precipitate formed. The N_2O atmosphere was then replaced by an atmosphere of dry N_2 and vinyl magnesium bromide (15 mL, 1 M in THF, 15 mmol, 1.5 equiv.) was added resulting in the formation of a yellow solution. The solution was stirred for 2 h at 50 °C (oil bath heating). The mixture was then cooled down to room temperature and quenched with water (35 mL), extracted with ethyl acetate (3 x 35 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. After filtration and removal of the solvent under reduced pressure, the crude product was purified by flash chromatography with a gradient of hexane to hexane/ethyl acetate (5%) as eluent. Compound **1a** was obtained as a white solid. Yield = 1.7 g (73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 15.5, 7.8 Hz, 1H, C*H*olef), 5.17 (d, *J* = 15.5 Hz, 1H, C*H*), 5.00–4.82 (m (br), 1H, C*H*), 4.76 (d, *J* = 8.1 Hz, 1H, C*H*olef), 3.53–3.22 (m (br), 1H, C*H*), 1.84–1.64 (m, 12H, 6 x CH_2), 1.49–1.25 (s, 6H, 3 x CH_2), 1.19–1.07 (d, 2H, CH_2); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 149.2, 104.5, 56.9, 53.5, 34.1, 29.9, 26.2, 25.7, 25.4. The characterization data corresponded to the reported values.[1]

*Triazenes **1b-1f** were prepared following the reported procedure by hydrogenation of corresponding 1-alkynyl triazenes.*[2]

3. Synthesis of silyl enol ethers

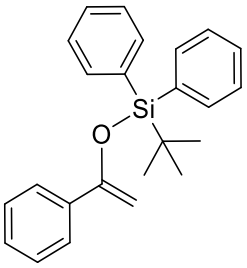


General Procedure 1 (GP1):

Following a slightly modified procedure.[3] A flame-dried 50 mL round bottom flask was charged with the ketone (2.8 mmol, 1.0 equiv.) and THF (12 mL) under N_2. The reaction mixture was cooled to –78 °C and KHMDS (6.7 mL, 0.5M in toluene, 3.4 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was then stirred for 1 h at room temperature. The reaction mixture was cooled again to –78 °C and the corresponding silyl chloride (3.4 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was then stirred at room temperature for 6 h. The reaction was quenched by adding 2.0 mL of a saturated solution of $NaHCO_3$ and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by column chromatography (pentane) to give the title compound.

General Procedure 2 (GP2):

Following a slightly modified procedure.[4] In a 100 mL flame-dried round-bottom flask equipped with a stirring bar and filled with THF (20 ml), acetophenone (1.0 equiv.) and Et_3N (1.8 equiv.) were added. The solution was stirred at room temperature for 15 min before cooling down to 0 °C. Triisopropylsilyl-trifluoromethanesulfonate (1.2 equiv.) was added *via* a syringe slowly over 2 min at 0 °C. The resulting mixture was stirred under N_2 atmosphere at 0 °C for 24 h. The reaction was then quenched by saturated $NaHCO_3$ solution (20 mL) and diluted with cooled CH_2Cl_2 (10mL). The organic layer was washed with cooled saturated $NaHCO_3$ solution twice, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography (pentane) to give the title compound.

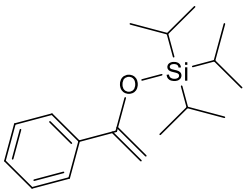


tert-butyldiphenyl((1-phenylvinyl)oxy)silane

5a

Following GP1, starting from acetophenone (0.36 g, 2.8 mmol), compound **5a** was obtained as a white solid. Yield = 0.82 g (82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.72 (m, 6H, Ar*H*), 7.43–7.30 (m, 9H, Ar*H*), 4.75 (d, *J* = 1.5 Hz, 1H, CH_2), 4.02 (d, *J* =1.5 Hz, 1H, CH_2), 1.10 (s, 9H, TBDPS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 137.5, 135.5, 134.8, 132.4, 129.8, 128.24, 128.20, 127.7, 125.2, 92.2, 26.6, 19.5. The characterization data corresponded to the reported values.[5]

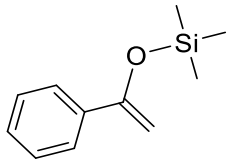


triisopropyl((1-phenylvinyl)oxy)silane

5b

Following GP2, starting from acetophenone (0.580 g, 4.82 mmol), compound **5b** was obtained as a colorless oil. Yield = 1.3 g (93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.65 (m, 2 H, Ar*H*), 7.38–7.29 (m, 3 H, Ar*H*), 4.85 (d, 1 H, *J* = 1.8 Hz, CH_2), 4.41 (d, 1 H, *J* = 1.8 Hz, CH_2), 1.39–1.27 (m, 3 H, SiC*H*(CH_3)$_2$), 1.19–1.13 (m, 18 H, TIPS); **^{13}C {^{1}H} 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 corresponded to the reported values.[4]

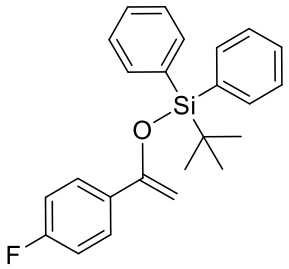


trimethyl((1-phenylvinyl)oxy)silane

5c

Following GP1, starting from acetophenone (0.36 g, 2.8 mmol), compound **5c** was obtained as a colorless oil. Yield = 0.31 g (58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.39 (m, 5H, Ar*H*), 4.91 (d, *J* = 1.7 Hz, 1H, C=CH_2), 4.43 (d, *J* = 1.7 Hz, 1H, C=CH_2), 0.27 (s, 9H, TMS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 157.7, 136.5, 128.6, 125.9, 125.3, 91.1, 0.17. The characterization data corresponded to the reported values.[6]

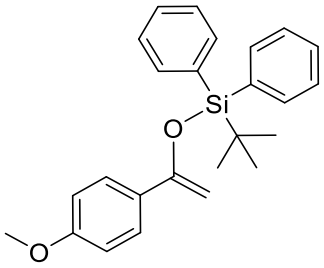


tert-butyl((1-(4-fluorophenyl)vinyl)oxy)diphenylsilane

5d

Following GP1, starting from 4-fluoroacetophenone (0.39 g, 2.8 mmol), compound **5d** was obtained as a white solid. Yield = 0.76 g (71%).

Rf 0.24 (Pentane); **Mp** 58-60 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 6.7, 1.6 Hz, 4H, Ar*H*), 7.74–7.68 (m, 2H, Ar*H*), 7.47–7.37 (m, 6H, Ar*H*), 7.06 (t, *J* = 8.7 Hz, 2H, Ar*H*), 4.67 (d, *J* = 2.4 Hz, 1H, CH_2), 4.01 (d, *J* = 2.4 Hz, 1H, CH_2), 1.10 (s, 9H, TBDPS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.4 Hz), 154.4, 135.6, 134.9, 133.8 (d, *J* = 3.2 Hz), 132.4, 130.0, 127.9, 127.1 (d, *J* = 8.1 Hz), 115.1 (d, *J* = 21.6 Hz), 92.0 (d, *J* = 1.7 Hz), 26.7, 19.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.96; **IR** 3072 (w), 2954 (w), 2932 (w), 2858 (w), 1621 (m), 1604 (w), 1505 (m), 1427 (w), 1310 (m), 1220 (m), 1154 (w), 1114 (s), 1098 (m), 1018 (m), 1003 (m), 845 (m), 821 (s), 768 (s), 744 (m); **HRMS** (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}FOSi^+$ 377.1731; Found 377.1723.

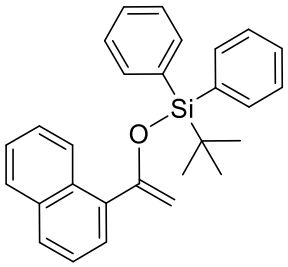


tert-butyl((1-(4-methoxyphenyl)vinyl)oxy)diphenylsilane

5e

Following GP1, starting from 4-methoxyacetophenone (0.42 g, 2.8 mmol), compound **5e** was obtained as a yellowish oil. Yield = 1.0 g (94%).

Rf 0.1 (Pentane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81–7.76 (m, 4H, Ar*H*), 7.72–7.67 (m, 2H, Ar*H*), 7.47–7.36 (m, 6H, Ar*H*), 6.95–6.88 (m, 2H, Ar*H*), 4.64 (d, *J* = 2.2 Hz, 1H, CH_2), 3.93 (d, *J* = 2.3 Hz, 1H, CH_2), 3.85 (s, 3H, OCH_3), 1.10 (s, 9H, TBDPS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 159.8, 154.9, 135.6, 132.6, 130.3, 129.9, 127.8, 126.6, 113.6, 90.6, 55.4, 26.7, 19.6; **IR** 3074 (w), 2959 (w), 2931 (w), 2856 (w), 1608 (m), 1509 (m), 1313 (m), 1291 (s), 1247 (s), 1172 (m), 1110 (s), 1031 (m), 1003 (m), 820 (m), 764 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{29}O_2Si^+$ 389.1931; Found 389.1930.



tert-butyl((1-(naphthalen-1-yl)vinyl)oxy)diphenylsilane

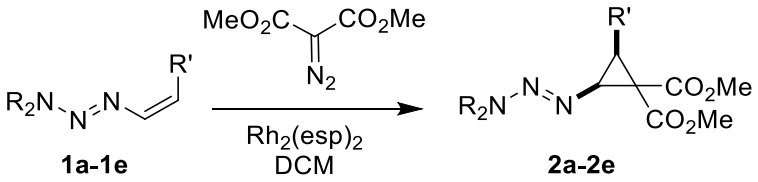
5f

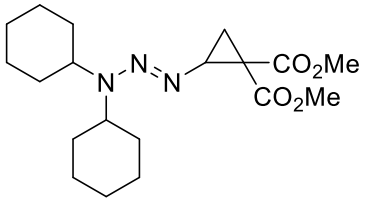
Following GP1, starting from 1-acetonaphtone (0.48 g, 2.8 mmol), compound **5f** was obtained as a white solid. Yield = 1.1 g (96%).

Rf 0.25 (Pentane); **Mp** 43-45 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48–8.37 (m, 1H, Ar*H*), 7.89–7.76 (m, 6H, Ar*H*), 7.55–7.35 (m, 10H, Ar*H*), 4.52 (d, *J* = 1.5 Hz, 1H, CH_2), 4.46 (d, *J* = 1.4 Hz, 1H, CH_2), 1.02 (s, 9H, TBDPS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 156.6, 137.2, 135.8, 133.8, 132.8, 131.0, 129.9, 128.6, 128.2, 127.7, 126.6, 126.2, 126.0, 125.7, 125.1, 97.9, 26.7, 19.5; **IR**

3071 (w), 2950 (w), 2929 (w), 2856 (w), 1625 (w), 1611 (w), 1470 (w), 1427 (m), 1287 (m), 1248 (m), 1199 (m), 1141 (m), 1111 (m), 1017 (s), 997 (m), 854 (w), 838 (m), 825 (m), 806 (m), 777 (s), 742 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{29}OSi^+$ 409.1982; Found 409.1979.

4. Synthesis of D-A cyclopropanes





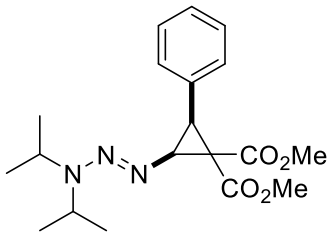
dimethyl (*E*)-2-(3,3-dicyclohexyltriaz-1-en-1-yl)cyclopropane-1,1-dicarboxylate

2a

To a solution of (*E*)-3,3-dicyclohexyl-1-vinyltriaz-1-ene (**1a**) (1.4 g, 6.0 mmol, 1.0 equiv.) and $Rh_2(esp)_2$ (9.0 mg, 0.0118 mmol, 0.2 mol%) in 14 mL of DCM at 0 °C, was added dropwise a solution of dimethyl 2-diazomalonate (1.1 g, 7.2 mmol, 1.2 equiv.) in 8 mL of DCM. The resulting mixture was allowed to slowly warm to room temperature and was stirred overnight. The solvent was removed under vacuum, and the residue was purified by column chromatography using pentane/EtOAc (10:1) to give compound **2a** as a colorless solid. Yield = 1.9 g (87%).

*Single crystals suitable for X-ray analysis were obtained from an oily non-solidified batch of **2a** upon storage at – 20 °C (freezer).*

Rf 0.67 (5:1 Pentane/EtOAc); **Mp** 62–64 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.44–4.25 (br m, 1H, C*H*$_{(cyclohexyl)}$), 4.09–4.05 (m, 1H, NC*H*$_{(cyclopropyl)}$), 3.72 (s, 3H, CO_2CH_3), 3.69 (s, 3H, CO_2CH_3), 3.43–3.24 (br m, 1H, C*H*$_{(cyclohexyl)}$), 2.15–2.12 (m, 1H, C*H*$_{(cyclopropyl)}$), 1.80–1.78 (m, 1H, C*H*$_{(cyclopropyl)}$), 1.76–1.61 (m, 11H, C*H*$_{2(cyclohexyl)}$), 1.33–1.10 (m, 9H, C*H*$_{2(cyclohexyl)}$); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 170.2, 167.5, 55.6, 52.7, 52.4, 36.0, 34.0, 29.8, 26.2, 25.8, 21.0; **IR** 2921 (m), 2854 (m), 1722 (s), 1448 (s), 1330 (s), 1274 (s), 1201 (s), 1128 (s), 887 (m); **HRMS** (ESI-TOF): m/z $[M+H]^+$ calcd for $C_{19}H_{32}N_3O_4^+$ 366.2393; Found 366.2396.

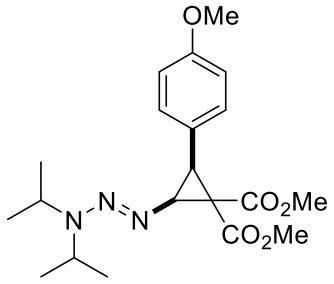


dimethyl (2*S*,3*S*)-2-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-3-phenylcyclopropane-1,1-dicarboxylate

2b

Cyclopropane **2b** was prepared following the procedure for **2a** using **1b** (115 mg, 0.5 mmol), dimethyl 2-diazomalonate (95 mg, 0.6 mmol) and $Rh_2(esp)_2$ (2 mg, 0.05 mmol). Yield (colorless oil) = 140 mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.21 (m, 5H), 4.81–4.37 (br m, 1H) 4.64 (d, *J* = 6.6 Hz, 1H), 4.22–3.58 (br m, 1H), 3.79 (d, *J* = 6.6 Hz, 1H), 3.74 (s, 3H), 3.44 (s, 3H), 1.34–1.10 (br m, 12H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.5, 167.1, 134.6, 129.0, 128.3, 127.3, 57.6, 52.7, 52.3, 47.5 (br), 46.4, 44.6, 36.5, 22.9 (br), 19.9 (br). **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{28}N_3O_4^+$ 362.2074; Found 362.2076.

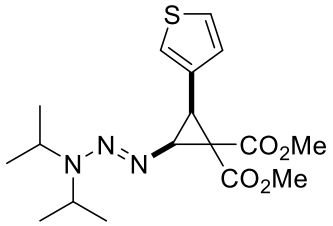


dimethyl (2*S*,3*S*)-2-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate

2c

Cyclopropane **2c** was prepared following the procedure for **2a** using **1c** (130 mg, 0.5 mmol), dimethyl 2-diazomalonate (119 mg, 0.75 mmol) and $Rh_2(esp)_2$ (2 mg, 0.05 mol). Yield (colorless oil) = 86 mg (44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.80–4.40 (br m, 1H), 4.59 (d, *J* = 6.5 Hz, 1H), 4.10–3.60 (br m, 1H), 3.78 (s, 3H), 3.75–3.73 (m, 1H), 3.73 (s, 3H), 3.46 (s, 3H), 1.20 (s, 12H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.1, 158.8, 130.0, 126.4, 113.7, 57.7, 55.3, 52.6, 52.4, 49.2 (br), 46.4 (br), 44.5, 36.0, 23.4 (br), 19.5 (br). **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{30}N_3O_5^+$ 392.2180; Found 392.2163.

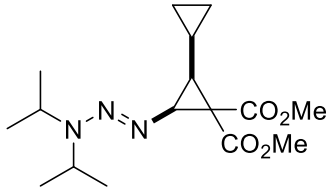


dimethyl (2*S*,3*R*)-2-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-3-(thiophen-3-yl)cyclopropane-1,1-dicarboxylate

2d

Cyclopropane **2d** was prepared following the procedure for **2a** using **1d** (118 mg, 0.5 mmol), dimethyl 2-diazomalonate (119 mg, 0.75 mmol) and $Rh_2(esp)_2$ (2 mg, 0.05 mol). Yield (pale-yellow oil) = 119 mg (65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.21 (m, 1H), 7.14–7.13 (m, 1H), 7.02–7.01 (m, 1H), 4.80–4.38 (br m, 1H), 4.55 (d, *J* = 6.5 Hz, 1H), 4.01–3.50 (br m, 1H), 3.73 (s, 3H), 3.69 (d, *J* = 6.4 Hz, 1H), 3.51 (s, 3H), 1.38–1.01 (br m, 12H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.3, 167.1, 135.1, 128.3, 125.2, 122.9, 58.4, 52.7, 52.5, 48.8 (br), 46.3 (br), 44.5, 31.9, 23.3 (br), 18.9 (br). **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{26}N_3O_4S^+$ 368.1639; Found 368.1637.



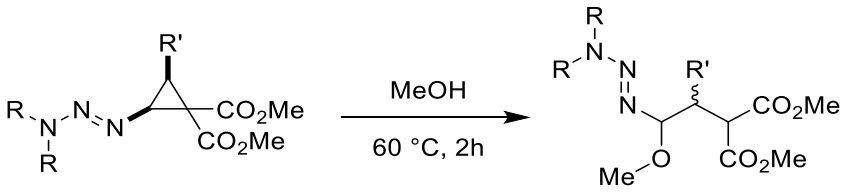
dimethyl (1*S*,3*S*)-3-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-[1,1'-bi(cyclopropane)]-2,2-dicarboxylate

2e

Cyclopropane **2e** was prepared following the procedure for **2a** using **1e** (103 mg, 0.53 mmol), dimethyl 2-diazomalonate (125 mg, 0.8 mmol) and $Rh_2(esp)_2$ (2 mg, 0.05 mol). Yield (colorless oil) = 85 mg (52%). Compound **2e** solidified upon storage at –20 °C.

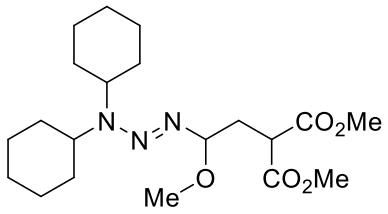
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57–3.50 (br m, 2H), 4.13 (d, *J* = 6.3 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 2.14 (t, *J* = 6.9 Hz, 1H), 1.30–1.06 (br m, 12H), 0.81–0.73 (m, 1H), 0.60–0.40 (m, 3H), 0.34–0.28 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 168.6, 167.8, 59.3, 52.5, 52.4, 47.1 (br, iPr), 42.2, 36.6, 20.6 (br, iPr), 7.6, 5.3, 4.2. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{28}N_3O_4^+$ 326.2074; Found 326.2060.

5. Alcohol addition reactions



General Procedure 3 (GP3).

An oven-dried vial was charged with the cyclopropane **2** and MeOH (0.3 M). The reaction mixture was stirred at 60 °C in an aluminum heating block for 2 h. The solvent was removed under reduced pressure to give the desired compound in analytically pure form.



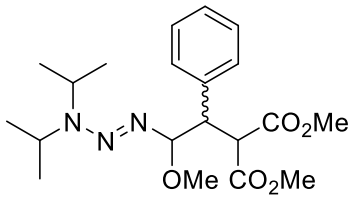
dimethyl (*E*)-2-(2-(3,3-dicyclohexyltriaz-1-en-1-yl)-2-methoxyethyl)malonate

3a

Following GP3, compound **3a** was obtained from **2a** (110 mg, 0.3 mmol) as a white solid (118 mg, 99% yield).

*Single crystals of **3a** suitable for X-ray analysis were obtained from saturated MeOH solution at 4 °C (fridge).*

Rf 0.45 (Pentane/EtOAc 10:2); **Mp** 42–44 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.71 (br m, 1H, NC*H*$_{cyclohexyl}$), 4.36 (dd, *J* = 6.9, 5.4 Hz, 1H, NC*H*O), 3.73 (s, 3H, CO_2CH_3), 3.72 (s, 3H, CO_2CH_3), 3.58 (t, *J* = 7.3 Hz, 1H, $(CO_2CH_3)_2CH$), 3.35 (br m, 1H, NC*H*$_{cyclohexyl}$), 3.17 (s, 3H, OC*H*$_3$), 2.39 (dt, *J* = 14.4, 7.3 Hz, 1H, C*H*$_2$), 2.23 (ddd, *J* = 14.0, 7.0, 5.4 Hz, 1H, C*H*$_2$), 1.83-1.13 (m, 20H, C*H*$_{2(cyclohexyl)}$); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) 170.1, 170.0, 96.8, 55.4, 52.6, 52.5, 48.0, 34.2, 29.8, 26.0, 25.7; **IR** 2927 (s), 2854 (m), 1750 (s), 1725 (s), 1435 (s), 1331 (m), 1312 (m), 1269 (s), 1192 (s), 1142 (s), 1111 (s), 1068 (s), 1007 (m), 980 (m), 941 (m), 891 (m), 844 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{36}N_3O_5^+$ 398.2649; Found 398.2659.

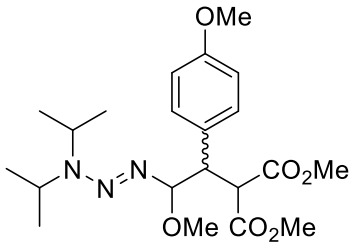


dimethyl (*E*)-2-(2-(3,3-diisopropyltriaz-1-en-1-yl)-2-methoxy-1-phenylethyl)malonate

3b

Following GP3, compound **3b** was obtained from **2b** (20 mg, 0.045 mmol) as a colorless oil (20 mg, 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.08 (m, 2x5H), 4.92–4.75 (br m, 2x1H), 4.67 (t, *J* = 3.9 Hz, 1H), 4.61 (d, *J* = 5.0 Hz, 1H), 4.17 (d, *J* = 10.7 Hz, 1H), 3.96 (m, 2x1H), 3.83 (dd, *J* = 10.7, 4.9 Hz, 1H), 3.77–3.55 (br m, 2x1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.45 (s, 3H), 3.39 (s, 3H), 3.17 (s, 3H), 3.17 (s, 3H), 1.18–0.81 (br m, 2x12H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 169.0, 168.95, 168.64, 168.62, 138.20, 138.13, 129.84, 129.81, 127.98, 127.87, 126.80, 126.75, 100.9, 99.4, 55.93, 55.71, 55.52, 54.2, 52.7, 52.5, 52.3, 52.3, 50.7, 50.6, 47.8 (br), 45.3 (br), 23.3 (br), 19.3 (br). **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{32}N_3O_5^+$ 394.2336; Found 394.2333.



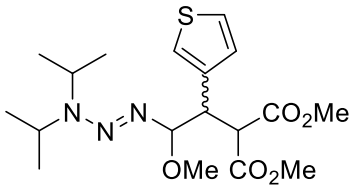
dimethyl (*E*)-2-(2-(3,3-diisopropyltriaz-1-en-1-yl)-2-methoxy-1-(4-methoxyphenyl)ethyl)malonate

3c

Following GP3, compound **3c** was obtained from **2c** (39 mg, 0.1 mmol) as a colorless oil (40 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–7.09 (m, 2x2H), 6.79–6.68 (m, 2x2H), 4.97–4.74 (br m, 2x1H), 4.63 (d, *J* = 5.7 Hz, 1H), 4.57 (d, *J* = 4.9 Hz, 1H), 4.12 (d, *J* = 10.6 Hz, 1H), 3.92–3.89 (m, 2H), 3.78–3.76 (m, 1H), 3.75–3.72 (m, 4x3H), 3.80–3.58 (br m, 2x1H), 3.47 (s, 3H), 3.42 (s, 3H), 3.17 (s, 2x3H), 1.25–0.85 (br m, 2x12H). **^{13}C {^{1}H} NMR** (101 MHz, CDCl3) δ 169.1, 169.00, 168.7, 158.42, 158.38, 130.84, 130.81, 130.26, 130.12, 113.43, 113.33, 100.8, 99.4, 55.90, 55.70,

55.5, 55.29, 55.25, 54.3, 52.6, 52.5, 52.3, 49.8, 47.8 (br), 45.4 (br), 23.3 (br), 19.4 (br). **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{34}N_3O_6^+$ 424.2442; Found 424.2423.

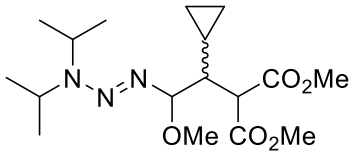


dimethyl (*E*)-2-(2-(3,3-diisopropyltriaz-1-en-1-yl)-2-methoxy-1-(thiophen-3-yl)ethyl)malonate

3d

Following GP3, compound **3d** was obtained from **2d** (39 mg, 0.1 mmol) as pale yellow oil (40 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 4.8, 3.1 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.06–7.01 (m, 3H), 6.96 (dd, *J* = 4.9, 1.3 Hz, 1H), 4.93–4.77 (br m, 2x1H), 4.68 (d, *J* = 7.6 Hz, 1H), 4.59 (d, *J* = 4.8 Hz, 1H), 4.13–4.06 (m, 2H), 4.00–3.88 (m, 2H), 3.78–3.68 (br m, 2x1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.52 (s, 3H), 3.46 (s, 3H), 3.19 (s, 3H), 3.18 (s, 3H), 1.21–0.89 (br m, 2x12H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 169.00, 168.94, 168.8, 168.7, 138.4, 138.3, 129.1, 128.8, 124.4, 124.2, 123.4, 123.1, 100.2, 98.8, 55.9, 55.7, 55.0, 54.2, 52.7, 52.5, 52.38, 52.36, 47.4 (br), 46.0, 45.8, 44.8 (br), 23.8 (br), 19.2 (br). **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{30}N_3O_5S^+$ 400.1901; Found 400.1887.



dimethyl (*E*)-2-(1-cyclopropyl-2-(3,3-diisopropyltriaz-1-en-1-yl)-2-methoxyethyl)malonate

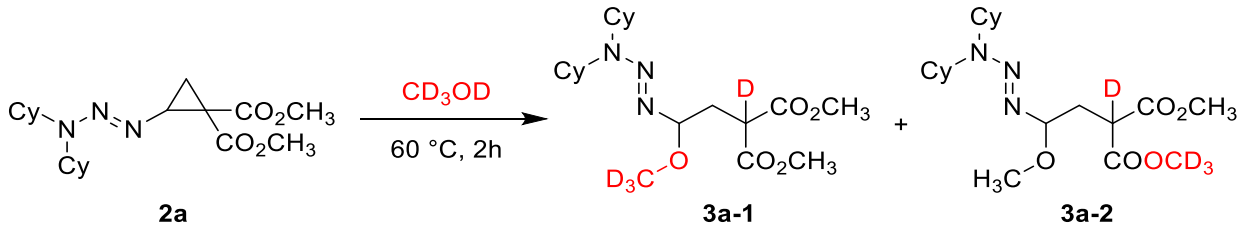
3e

Following GP3, compound **3e** was obtained from **2e** (10 mg, 0.03 mmol) as a colorless oil (10 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10–4.92 (br m, 2x1H), 4.51 (d, *J* = 6.7 Hz, 1H), 4.45 (d, *J* = 3.8 Hz, 1H), 3.95 (d, *J* = 7.8 Hz, 1H), 3.90–3.66 (br m, 2x1H), 3.86 (d, *J* = 6.8 Hz, 1H), 3.72 (s, 3H), 3.72 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 3.16 (s, 3H), 3.15 (s, 3H), 1.91–1.76 (m, 2x1H), 1.19 (br m, 2x12H), 0.94–0.69 (m, 2H), 0.54–0.29 (m, 4H), 0.26–0.01 (m, 4H). **^{13}C {^{1}H} NMR** (101 MHz,

$CDCl_3$) δ 170.1, 169.9, 169.8, 169.7, 100.8, 100.0, 55.61, 55.56, 52.8, 52.6, 52.4, 52.2, 52.1, 49.1, 48.8, 47.6 (br), 44.9 (br), 23.6 (br), 19.5 (br), 10.4, 9.8, 5.0, 4.3, 3.7. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{32}N_3O_5^+$ 358.2336; Found 358.2321.

5.1. Mechanistic study of alcohol addition: deuterium labeling experiment



ratio **3a-1** : **3a-2** ~ 1 : 1

Cyclopropane **2a** (ca. 10 mg) was dissolved in CD_3OD (0.5 mL) and heated at 60 °C for 2 h. The solvent was removed under reduced pressure, and the product was analyzed by NMR spectroscopy. The mass spectrum (ESI-MS) of the product shows a peak corresponding to **2a**+**CD_3OD**+**H^+**.

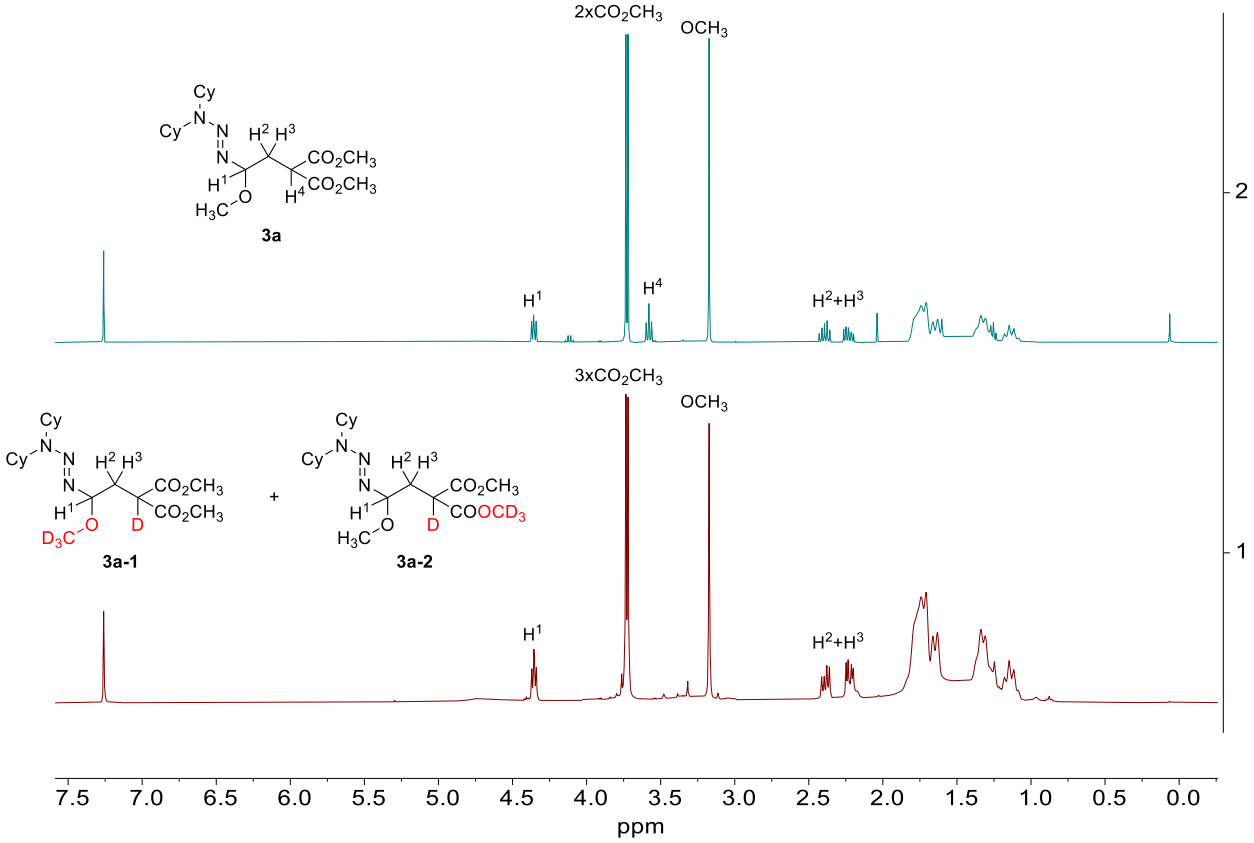


Figure 5.1. ^1H NMR (400 MHz, $CDCl_3$) spectra of **3a** (top) and **3a-1** + **3a-2** (bottom).

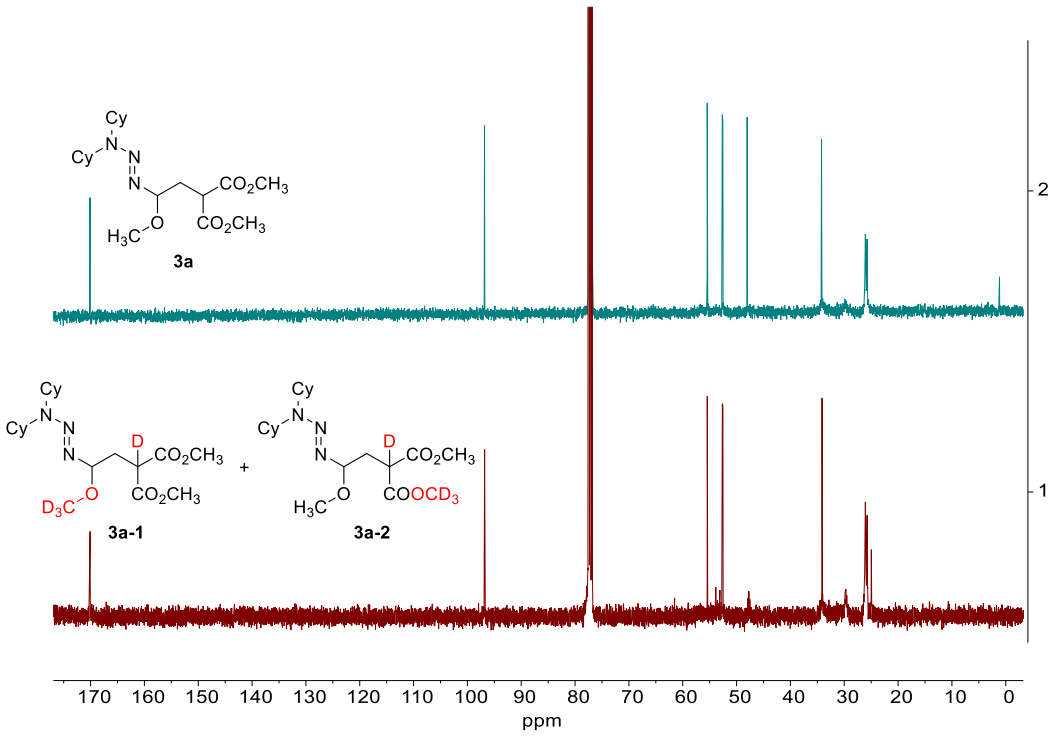


Figure 5.2. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3a** (top) and **3a-1** + **3a-2** (bottom).

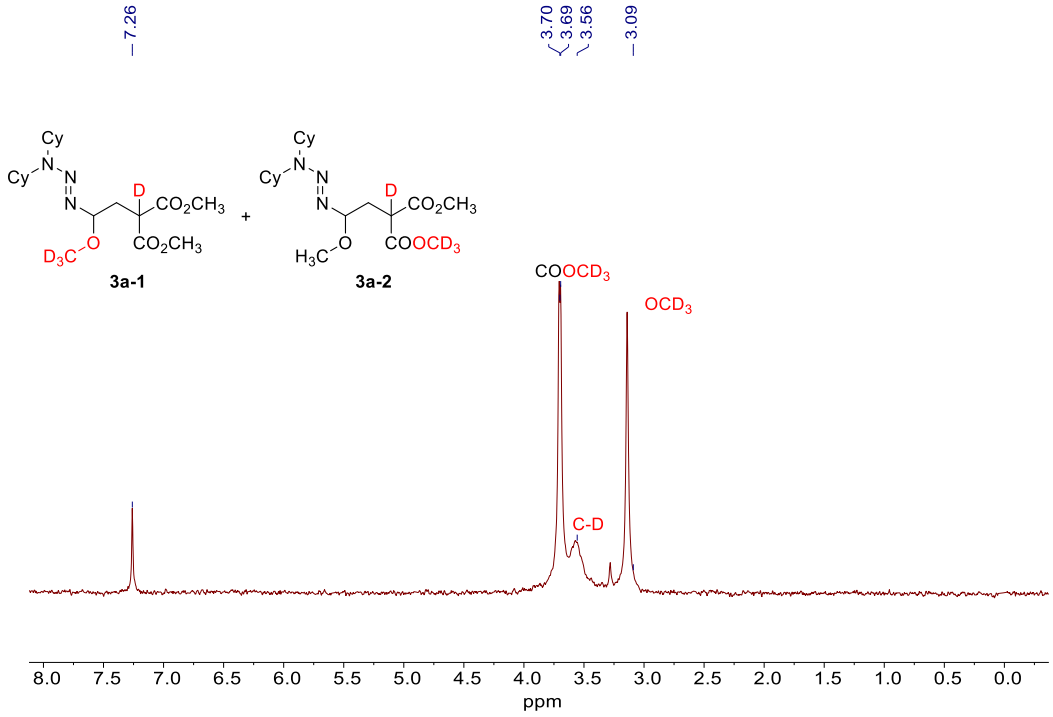
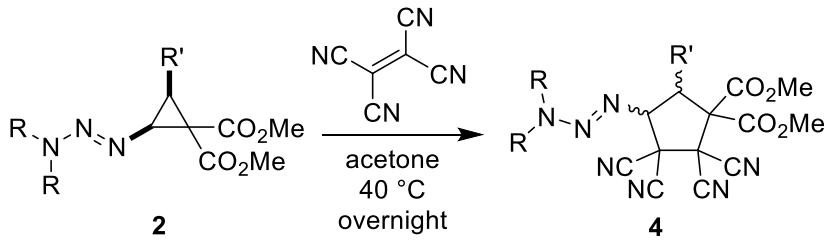


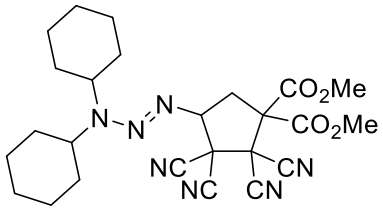
Figure 5.3. ^{2}H NMR (400 MHz, $CHCl_3$) spectrum of **3a-1** + **3a-2**.

6. (3+2) cycloaddition with TCNE



General Procedure 4 (GP4).

A solution of tetracyanoethylene (1.25–2.00 equiv.) in acetone (0.25 M) was added to a stirred solution of a cyclopropane **2** (1.00 equiv.) in acetone (1.00 M) at room temperature. The mixture was then closed with a cap and heated to 40 °C in an aluminum heating block overnight. The solvent was removed under reduced pressure, and the residue was extracted several times with pentane. Evaporation of pentane afforded the desired product in analytically pure form.



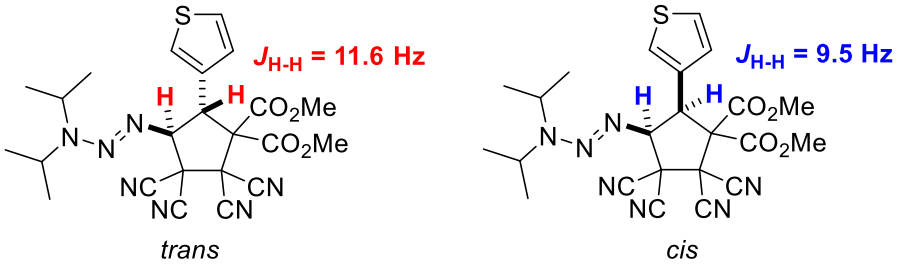
dimethyl (*E*)-2,2,3,3-tetracyano-4-(3,3-dicyclohexyltriaz-1-en-1-yl)cyclopentane-1,1-dicarboxylate

4a

Following GP4, product **4a** was obtained from **2a** (46.0 mg, 0.126 mmol) and TCNE (32.0 mg, 0.25 mmol) as a colorless solid. Yield = 40 mg (65%).

*Single crystals of **4a** suitable for X-ray analysis were obtained from saturated hexane solution at – 20 °C (freezer).*

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (t, *J* = 7.8 Hz, 1H), 4.69–4.62 (m, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.48–3.40 (m, 1H), 3.21 (dd, *J* = 14.9, 7.8 Hz, 1H), 2.95 (dd, *J* = 14.9, 7.9 Hz, 1H), 1.89–1.09 (m, 22 H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 165.2, 164.8, 110.9, 109.8, 109.4, 108.7, 73.2, 66.4, 58.3, 56.4, 55.2, 54.9, 51.6, 48.7, 36.3, 34.9, 33.7, 29.5, 29.3, 26.2, 26.1, 25.8, 25.74, 25.70, 25.4. **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{25}H_{32}N_7O_4^+$ 494.2510; Found 494.2488.

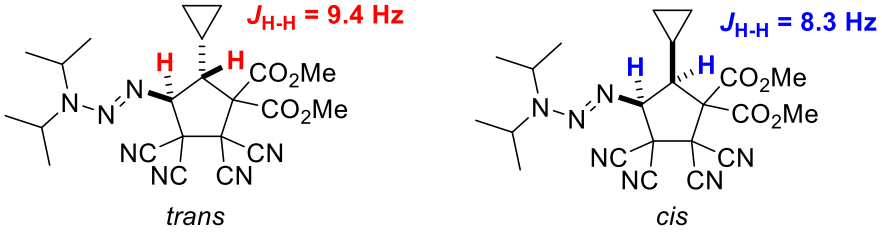


dimethyl (*E*)-2,2,3,3-tetracyano-4-(3,3-diisopropyltriaz-1-en-1-yl)-5-(thiophen-3-yl)cyclopentane-1,1-dicarboxylate

4d trans:cis = 2:1

Following GP4, product **4d** was obtained from **2d** (63.0 mg, 0.170 mmol) and TCNE (28.0 mg, 0.21 mmol) as a yellow solid. Yield = 33 mg (40%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, $4H_{trans}$ + $1H_{cis}$), 7.21–7.19 (m, $1H_{cis}$), 7.06–7.01 (m, $2H_{trans}$ + $1H_{cis}$), 5.15 (d, *J* = 9.5 Hz, $1H_{cis}$), 5.13 (d, *J* = 11.6 Hz, $2x1H_{trans}$), 5.00 (d, *J* = 9.5 Hz, $1H_{cis}$), 4.91–4.84 (m, $2x1H_{trans}$ + $1H_{cis}$), 4.55 (d, *J* = 11.6 Hz, $2x1H_{trans}$), 3.98 (s, $3H_{cis}$), 3.96 (s, $2x3H_{trans}$), 3.87–3.77 (m, $2x1H_{trans}$ + $1H_{cis}$), 3.66 (s, $2x3H_{trans}$), 3.42 (s, $3H_{cis}$), 1.29–1.04 (m, $2x12H_{trans}$ + $12H_{cis}$). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 165.7, 164.5, 132.30, 130.25, 127.7, 127.6, 126.0, 125.7, 124.9, 112.0, 111.6, 110.3, 109.8, 109.6, 109.1, 109.0, 75.2, 70.7, 55.2, 54.8, 54.5, 54.0, 49.6, 49.5, 49.1, 48.9, 48.1, 47.6, 47.5, 23.4, 23.21, 23.17, 19.2, 19.0, 18.81, 18.75. **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{25}N_7NaO_4S^+$ 518.1581; Found 518.1556.



dimethyl (*E*)-2,2,3,3-tetracyano-5-cyclopropyl-4-(3,3-diisopropyltriaz-1-en-1-yl)cyclopentane-1,1-dicarboxylate

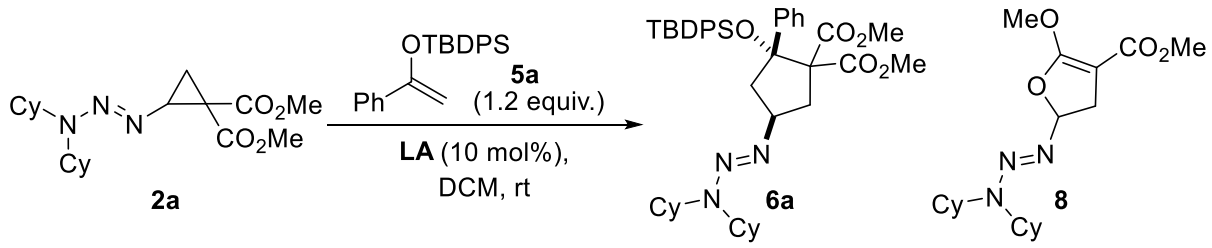
4e trans:cis = 2:1

Following GP4, product **4e** was obtained from **2e** (18.0 mg, 0.055 mmol) and TCNE (14.0 mg, 0.11 mmol) as a colorless solid. Yield = 11 mg (46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (p, *J* = 6.8 Hz, 2x1H_{trans}), 4.90 (p, *J* = 6.9 Hz, 1H_{cis}), 4.75 (d, *J* = 8.3 Hz, 1H_{cis}), 4.65 (d, *J* = 9.4 Hz, 2x1H_{trans}), 3.98–3.95 (m, 2x1H_{trans} + 1H_{cis}), 3.97 (m, 3H_{cis} + 2x3H_{trans}), 3.96 (s, 2x3H_{trans}), 3.90 (s, 3H_{cis}), 2.79 (t, *J* = 9.2 Hz, 2x1H_{trans}), 2.70 (dd, *J* = 11.0, 8.3 Hz, 1H_{cis}), 1.35–1.17 (m, 2x12H_{trans} + 12H_{cis}), 0.98–0.46 (m, 7$H_{cyclopropyl}$) 0.26–0.20 (m, 2$H_{cyclopropyl}$), 0.16–0.11 (m, 1$H_{cyclopropyl}$). **^{13}C {^{1}H} NMR** (101 MHz, CDCl3) δ 165.51, 165.45, 164.7, 164.3, 111.5, 110.0, 109.8, 109.6, 109.4, 109.1, 76.3, 70.5, 70.4, 55.0, 54.8, 54.4, 53.8, 53.4, 52.1, 50.4, 49.8, 49.7, 49.6, 49.1, 47.6, 47.4, 23.7, 23.5, 23.3, 23.3, 19.3, 19.2, 19.1, 19.0, 11.2, 9.0, 5.9, 5.7, 4.2, 3.2, 1.2. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{28}N_7O_4^+$ 454.2197; Found 454.2211.

7. (3+2) cycloaddition reaction with silyl enol ethers

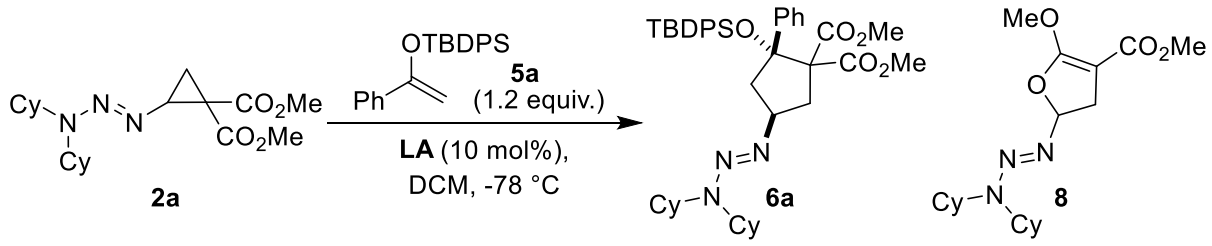
Table S7.1. Optimization of Lewis acid with **5a** at room temperature.



Entry[a]	LA	Yield[b]	Ratio 6a/8[c]	d.r. [c]
1	none	NR		
2	$Yb(OTf)_3$	23%	33:67	3.5:1
3	$FeCl_3$-Al_2O_3	15%	91:9	3:1
4	$In(OTf)_3$	47%	ND	4:1
5	**$Hf(OTf)_4$**	**50%**	**91:9**	**3:1**
6	$Sc(OTf)_3$	55%	67:33	3:1

[a] Reaction conditions: 0.05 mmol of **2a**, 0.06 mmol of **5a**, 0.005 mmol of LA in DCM (0.05 M) at RT. [b] NMR yields determined for **6a** using 3,4,5-trichloropyridine as internal standard. [c] Determined by ^{1}H NMR of the crude reaction mixture.

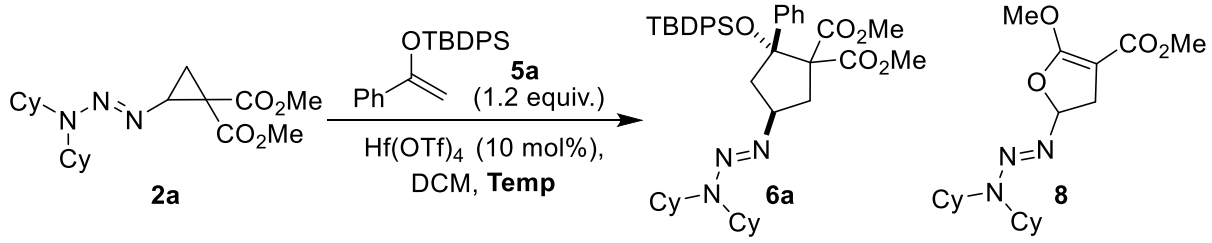
Table S7.2. Optimization of Lewis acid with **5a** at –78 °C.



Entry[a]	LA	Yield[b]	Ratio 6a/8[c]	d.r. [c]
1	$In(OTf)_3$	<5%	ND	ND
2	$Sc(OTf)_3$	<5%	ND	ND
3	**$Hf(OTf)_4$**	**40%**	**>20:1**	**4.4:1**

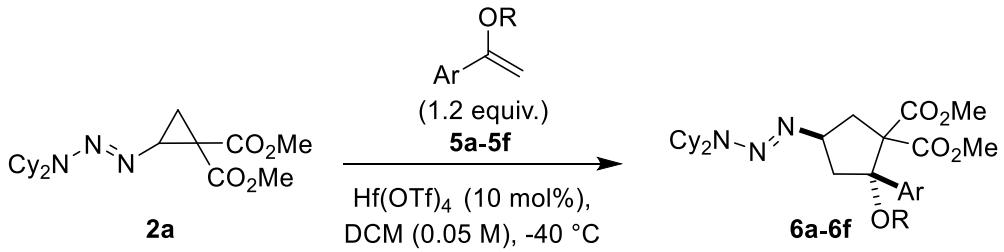
[a] Reaction conditions: 0.05 mmol of **2a**, 0.06 mmol of **5a**, 0.005 mmol of LA in DCM (0.05 M) at –78 °C. [b] NMR yields determined for **6a** using 3,4,5-trichloropyridine as internal standard. [c] Determined by ^{1}H NMR of the crude reaction mixture.

Table S7.3. Temperature optimization with **5a** and $Hf(OTf)_4$.



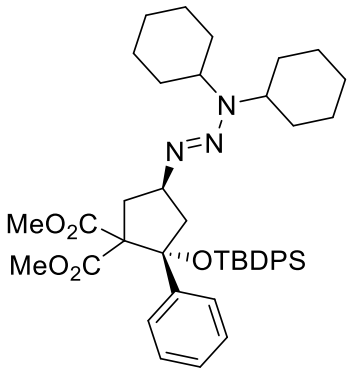
Entry[a]	Temp	Yield[b]	Ratio 6a/8[c]	d.r. [c]
1	–78 °C	40%	>20:1	4.4:1
2	**–40 °C**	**84%**	**>20:1**	**4.3:1**
3	–20 °C	66%	>20:1	3.5:1
4	0 °C	62%	>20:1	3.8:1

[a] Reaction conditions: 0.05 mmol of **2a**, 0.06 mmol of **5a**, 0.005 mmol of LA in DCM (0.05 M) at –78 °C. [b] NMR yields determined for **6a** using 3,4,5-trichloropyridine as internal standard. [c] Determined by ^{1}H NMR of the crude reaction mixture.



General Procedure 5 (GP5):

An oven-dried flask sealed with a septum was charged in the glovebox with $Hf(OTf)_4$ (23 mg, 0.030 mmol, 0.1 equiv.) and 3.0 mL of dry DCM. The solution was cooled down to –40 °C. A solution of the silyl enol ether (0.36 mmol, 1.2 equiv.) in 1.5 mL of dry DCM was then added, followed by a solution of (*E*)-dimethyl 2-(3,3-dicyclohexyltriaz-1-en-1-yl)cyclopropane-1,1-dicarboxylate (**2a**) (0.11 g, 0.30 mmol, 1.0 equiv.) in 1.5 mL of dry DCM. The reaction mixture was stirred at –40 °C for 20 h, and then filtered through a short plug of basic alumina eluting with EtOAc. The filtrate was evaporated under reduced pressure. The crude mixture was purified by column chromatography (pentane/EtOAc, 30:1) to give the desired product.



dimethyl (2*R*,4*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-phenylcyclopentane-1,1-dicarboxylate

6a

Following GP5, compound **6a** was obtained as an inseparable mixture of diastereoisomers (4:1) as a white foam (166 mg, 0.229 mmol, 77% yield). A recrystallization from MeOH gave a d.r. of 16:1 in favor of the *trans* product.

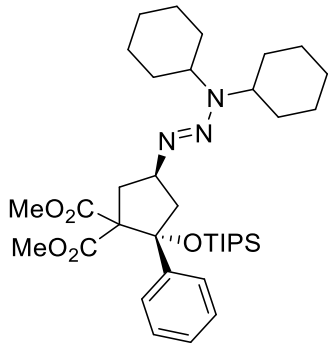
*This procedure was carried out in 1 mmol scale using the same general procedure (GP5) with the reagent and solvent loadings multiplied accordingly. The product **6a** was isolated in 55% yield (400 mg, 0.55 mmol).*

Rf 0.64 (pentane/EtOAc 10:1);

Major diastereoisomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 8.1, 2.6, 1.3 Hz, 2H, Ar*H*), 7.45 (dt, *J* = 8.1, 1.6 Hz, 3H, Ar*H*), 7.38 (ddt, *J* = 14.9, 7.0, 1.5 Hz, 1H, Ar*H*), 7.33–7.27 (m, 1H, Ar*H*), 7.25–7.10 (m, 5H, Ar*H*), 7.03 (tq, *J* = 7.0, 1.5 Hz, 1H, Ar*H*), 6.99–6.93 (m, 2H, Ar*H*), 4.30 (qd, *J* = 8.4, 6.7 Hz, 1H, C*H*$N_{cyclopentane}$), 3.96–3.88 (br m, 1H, NC*H*$_{cyclohexyl}$), 3.86 (s, 3H, OC*H*$_3$), 3.42 (s, 3H, OC*H*$_3$), 2.85–2.75 (m, 2H, $(CO_2Me)_2CCH_2$ and OCC*H*$_2$), 2.75–2.66 (m, 1H, NC*H*$_{cyclohexyl}$), 2.55 (dd, *J* = 13.8, 6.7 Hz, 1H, OCC*H*$_2$), 2.37–2.28 (m, 1H, $(CO_2Me)_2CCH_2$), 1.84–1.60 (m, 10H, C*H*$_{2\ cyclohexyl}$), 1.54–1.40 (m, 3H, C*H*$_{2\ cyclohexyl}$), 1.38–1.26 (m, 3H, C*H*$_{2\ cyclohexyl}$), 1.21–1.10 (m, 3H, C*H*$_{2\ cyclohexyl}$), 1.04 (s, 9H, TBDPS), 0.92–0.80 (m, 1H, C*H*$_{2\ cyclohexyl}$);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.9, 170.3, 143.0, 136.7, 136.3, 134.8, 134.2, 129.3, 129.0, 128.7, 127.3, 127.1, 126.9, 126.8, 89.5, 70.7, 64.9, 55.1, 52.5, 51.8, 46.2, 45.7, 40.1,32.1, 27.5, 26.4, 26.3, 25.9,19.8;

Minor diastereoisomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 8.1, 2.6, 1.3 Hz, 2H, Ar*H*), 7.45 (dt, *J* = 8.1, 1.6 Hz, 3H, Ar*H*), 7.38 (ddt, *J* = 14.9, 7.0, 1.5 Hz, 1H, Ar*H*), 7.33–7.27 (m, 1H, Ar*H*), 7.25–7.10 (m, 5H, Ar*H*), 7.03 (tq, *J* = 7.0, 1.5 Hz, 1H, Ar*H*), 6.99–6.93 (m, 2H, Ar*H*), 4.17 (p, J = 8.2 Hz, 1H, C*H*$N_{cyclopentane}$), 3.99 (m, 1H, NC*H*$_{cyclohexyl}$), 3.83 (s, 3H, OC*H*$_3$), 3.47 (s, 3H, OC*H*$_3$), 2.98 (dd, *J* = 13.8, 8.6 Hz, 1H, $(CO_2Me)_2CCH_2$), 2.85–2.75 (m, 1H, OCC*H*$_2$), 2.75–2.66 (m, 1H, NC*H*$_{cyclohexyl}$), 2.48 (dd, J = 13.8, 7.7 Hz, 1H, $(CO_2Me)_2CCH_2$), 2.37–2.28 (m, 1H, OCC*H*$_2$), 1.84–1.60 (m, 10H, C*H*$_{2\ cyclohexyl}$), 1.54–1.40 (m, 3H, C*H*$_{2\ cyclohexyl}$), 1.38–1.26 (m, 3H, C*H*$_{2\ cyclohexyl}$), 1.21–1.10 (m, 3H, C*H*$_{2\ cyclohexyl}$), 1.04 (s, 9H, TBDPS), 0.92–0.80 (m, 1H, C*H*$_{2\ cyclohexyl}$); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 170.9, 169.8, 143.1, 136.8, 136.2, 134.6, 134.5, 129.3, 128.9, 128.3, 127.3, 127.1, 127.0, 126.8, 89.5, 70.5, 65.5, 55.1, 52.3, 52.2, 47.1, 40.9, 32.1, 24.6, 23.9, 23.1, 19.8, 14.3, 14.2; **IR**: 2981 (m), 2944 (m), 2860 (m), 1734 (m), 1454 (w), 1258 (m), 1136 (s), 846 (w); **HRMS** (APPI/LTQ-Orbitrap) m/z: [M+H]+ Calcd for C43H58N3O5Si+ 724.4140; Found 724.4163.



dimethyl (2*R*,4*R*)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-phenyl-2-((triisopropylsilyl)oxy)cyclopentane-1,1-dicarboxylate

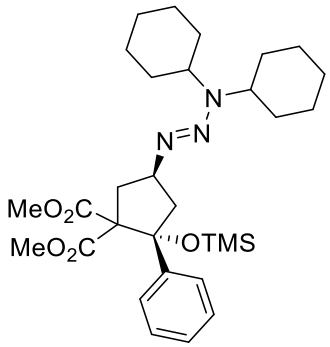
6b

Following GP5, compound **6b** was obtained as an inseparable mixture of diastereoisomers (4:1) as a colorless oil (146 mg, 0.228 mmol, 76% yield).

Rf 0.60 (pentane/EtOAc 10:1);

Major diastereoisomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.85 (m, 2H, Ar*H*), 7.25–7.19 (m, 3H, Ar*H*), 4.42 (td, *J* = 8.6, 7.3 Hz, 1H, C*H*$N_{cyclopentane}$), 4.07–3.87 (br m, 2H, NC*H*$_{cyclohexyl}$), 3.78 (s, 3H, OC*H*$_3$), 3.40 (s, 3H, OC*H*$_3$), 2.85 (dd, *J* = 7.9, 2.3 Hz, 2H, $(CO_2Me)_2CCH_2$), 2.72 (dd, *J* = 14.0, 8.4 Hz, 1H, OCC*H*$_2$), 2.42–2.33 (m, 1H, OCC*H*$_2$), 1.84–1.01 (m, 20H, C*H*$_{2\ cyclohexyl}$), 0.96 (m, 21H, TIPS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 171.0, 170.3, 144.2, 128.4, 127.7, 127.1, 88.1, 70.9, 65.2, 52.4, 51.8, 46.2, 39.7, 32.2, 31.9, 26.3, 25.9, 18.3, 13.7;

Minor diastereoisomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.66 (m, 2H, Ar*H*), 7.25–7.19 (m, 3H, Ar*H*), 4.38–4.29 (m, 1H, C*H*$N_{cyclopentane}$), 4.07–3.87 (br m, 2H, NC*H*$_{cyclohexyl}$), 3.74 (s, 3H, OC*H*$_3$), 3.43 (s, 3H, OC*H*$_3$), 3.31–3.20 (m, 1H, $(CO_2Me)_2CCH_2$), 3.00 (dd, *J* = 13.6, 9.5 Hz, 1H, OCC*H*$_2$), 2.57 (dd, *J* = 14.8, 6.4 Hz, 1H, $(CO_2Me)_2CCH_2$), 2.46–2.40 (m, 1H, OCC*H*$_2$), 1.84–1.01 (m, 20H, C*H*$_{2\ cyclohexyl}$), 0.96 (m, 21H, TIPS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 170.8, 169.4, 143.2, 128.5, 127.5, 126.9, 88.3, 71.6, 65.7, 52.1, 52.0, 46.8, 40.6, 32.2, 31.9, 26.4, 25.9, 18.5, 13.8; **IR** 2930 (s), 2861 (m), 1731 (s), 1455 (s), 1255 (s), 1186 (s), 1135 (s), 1015 (m), 884 (s), 753 (s), 698 (s), 673 (s); **HRMS** (ESI-TOF): m/z $[M+H]^+$ calcd for $C_{36}H_{60}N_3O_5Si^+$ 642.4297; Found 642.4302.



dimethyl (2*R*,4*R*)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-phenyl-2-((trimethylsilyl)oxy)cyclopentane-1,1-dicarboxylate

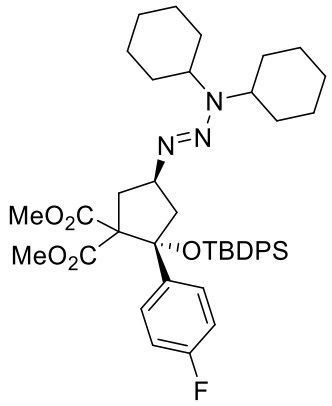
6c

Following GP5, compound **6c** was obtained as an inseparable mixture of diastereoisomers (2.6:1) as a white foam (95 mg, 0.17 mmol, 57% yield).

Rf 0.41 (pentane/EtOAc 20:1);

Major diastereoisomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82–7.76 (2H, m, Ar*H*), 7.36–7.26 (3H, m, Ar*H*), 4.45 (1H, p, *J* = 8.3 Hz, C*H*$N_{cyclopentane}$), 3.97 (2H, m, NC*H*$_{cyclohexyl}$), 3.84 (3H, s, OC*H*$_3$), 3.43 (3H, s, OC*H*$_3$), 2.98 (dd, *J* = 13.4, 8.6 Hz, 2H, $(CO_2Me)_2CCH_2$ and OCC*H*$_2$), 2.66–2.58 (m, 1H, $(CO_2Me)_2CCH_2$), 2.42 (dd, *J* = 13.9, 8.4 Hz, 1H, OCC*H*$_2$), 1.90–1.14 (m, 20H, C*H*$_{2\ cyclohexyl}$), 0.00 (s, 9H, TMS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 171.1, 170.2, 143.6, 128.1, 127.5, 127.1, 88.0, 70.8, 65.7, 65.6, 52.1, 51.8, 46.1, 39.9, 32.1, 26.3, 26.3, 25.9, 22.4, 1.8;

Minor diastereoisomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65–7.62 (m, 2H, Ar*H*), 7.36–7.26 (m, 3H, Ar*H*), 4.45 (p, *J* = 8.3 Hz, 1H, C*H*$N_{cyclopentane}$), 3.97 (m, 2H, NC*H*$_{cyclohexyl}$), 3.74 (s, 3H, OC*H*$_3$), 3.54 (s, 3H, OC*H*$_3$), 3.33 (dd, *J* = 15.0, 10.6 Hz, 1H, $(CO_2Me)_2CCH_2$), 3.03 (m, 1H, OCC*H*$_2$), 2.65 (m, 1H, $(CO_2Me)_2CCH_2$), 2.53–2.45 (m, 1H, OCC*H*$_2$), 1.90–1.14 (m, 20H, C*H*$_{2\ cyclohexyl}$), 0.12 (s, 9H); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 170.8, 169.7, 142.4, 128.3, 127.3, 126.9, 88.5, 72.2, 65.6, 52.1, 51.7, 46.1, 40.9, 32.1, 29.8, 26.3, 26.3, 25.9, 22.4, 2.2; **IR** 2924 (m), 2850 (w), 1734 (s), 1449 (m), 1249 (s), 1182 (m), 1134 (s), 1082 (m), 891 (m), 839 (s), 754 (m), 700 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{48}N_3O_5Si^+$ 558.3358; Found 558.3365.



dimethyl (2*R*,4*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-(4-fluorophenyl)cyclopentane-1,1-dicarboxylate

6d

Following GP5, compound **6d** was obtained as an inseparable mixture of diastereoisomers (4:1) as a white foam (121 mg, 0.163 mmol, 54% yield).

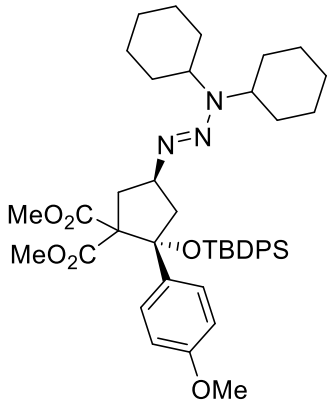
Rf 0.7 (pentane/EtOAc 10:1);

The signal of $NCH_{cyclohexyl}$ was overlapping with other signals and could not be properly attributed.

Major diastereoisomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57–7.49 (m, 2H, Ar*H*), 7.49–7.44 (m, 4H, Ar*H*), 7.38–7.27 (m, 2H, Ar*H*), 7.20 (q, *J* = 8.0 Hz, 4H, Ar*H*), 6.62 (q, *J* = 9.2, 8.8 Hz, 2H, Ar*H*), 4.38–4.27 (m, 1H, C*H*$N_{cyclopentane}$), 3.86 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 2.81 (ddd, *J* = 16.6, 14.1, 8.7 Hz, 2H, $(CO_2Me)_2CCH_2$ and OCCH_2), 2.49 (ddd, *J* = 18.7, 13.7, 7.1 Hz, 1H, $(CO_2Me)_2CCH_2$), 2.30 (dd, *J* = 14.1, 7.9 Hz, 1H, OCCH_2), 1.84–1.10 (m, 20H, C$H_{2\ cyclohexyl}$), 1.05 (s, 9H, TBDPS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 170.6, 170.0, 163.1, 160.6, 136.4, 136.1, 130.4, 130.3, 129.3, 129.0, 127.0, 126.9, 113.3, 113.1, 88.8, 70.4, 64.7, 54.9, 52.4, 51.7, 45.7, 39.9, 31.9, 27.3, 27.2, 26.2, 26.1, 25.7, 19.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.03;

Minor diastereoisomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57–7.49 (m, 2H, Ar*H*), 7.49–7.44 (m, 4H, Ar*H*), 7.38–7.27 (m, 2H, Ar*H*), 7.20 (q, *J* = 8.0 Hz, 4H, Ar*H*), 6.62 (q, *J* = 9.2, 8.8 Hz, 2H, Ar*H*), 4.15 (p, *J* = 8.2 Hz, 1H, C*H*$N_{cyclopentane}$), 3.84 (s, 1H, OCH_3), 3.48 (s, 1H, OCH_3), 3.03 (dd, *J* = 13.8, 9.0 Hz, 1H, $(CO_2Me)_2CCH_2$), 2.81 (ddd, *J* = 16.6, 14.1, 8.7 Hz, 1H, OCCH_2), 2.68 (dd, *J* = 14.7, 9.5 Hz, 1H, OCCH_2), 2.49 (ddd, *J* = 18.7, 13.7, 7.1 Hz, 1H, $(CO_2Me)_2CCH_2$), 1.84–1.10 (m, 20H, C$H_{2\ cyclohexyl}$), 1.03 (s, 9H, TBDPS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 170.7, 169.5, 163.0, 160.6, 138.8, 138.8, 136.6, 136.0, 134.3, 134.1, 133.9, 130.1, 130.1, 128.9, 126.7, 113.5,

113.3, 88.7, 70.4, 65.2, 54.9, 52.2, 52.0, 47.0, 46.2, 40.8, 31.9, 27.3, 26.1, 25.7, 19.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.01; **IR** 2931 (m), 2855 (w), 1737 (s), 1513 (m), 1454 (m), 1427 (m), 1253 (m), 1134 (m), 1102 (s), 824 (m), 741 (m), 703 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{43}H_{57}FN_3O_5Si^+$ 742.4046; Found 742.4048.



dimethyl (2*R*,4*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-(4-methoxyphenyl)cyclopentane-1,1-dicarboxylate

6e

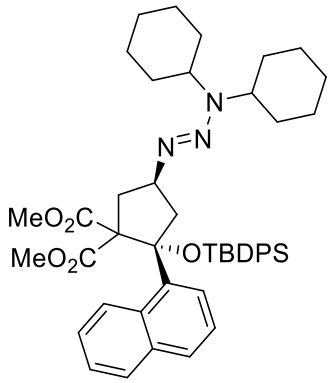
Following GP5, compound **6e** was obtained as an inseparable mixture of diastereoisomers (4.9:1) as a white foam (198 mg, 0.262 mmol, 88% yield).

Rf 0.5 (pentane/EtOAc 10:1);

The signal of $NCH_{cyclohexyl}$ was overlapping with other signals and could not be properly attributed.

Major diastereoisomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49–7.43 (m, 6H, Ar*H*), 7.34–7.27 (m, 2H, Ar*H*), 7.20 (q, *J* = 7.7 Hz, 4H, Ar*H*), 6.50–6.45 (m, 2H, Ar*H*), 4.28 (p, *J* = 8.0 Hz, 1H, C*H*$N_{cyclopentane}$), 3.85 (s, 3H, OCH_3), 3.71 (s, 3H, ArOCH_3), 3.44 (s, 3H, OCH_3), 2.84 (dd, *J* = 14.1, 8.5 Hz, 1H, $(CO_2Me)_2CCH_2$), 2.73 (dd, *J* = 13.8, 8.7 Hz, 1H, OCCH_2), 2.58–2.49 (m, 1H, OCCH_2), 2.31 (dd, *J* = 14.1, 7.8 Hz, 1H, $(CO_2Me)_2CCH_2$), 1.83–1.08 (m, 20H, C$H_{2\ cyclohexyl}$), 1.04 (s, 9H, TBDPS); **^{13}C NMR {^{1}H}** (101 MHz, $CDCl_3$) δ 171.0, 170.3, 158.6, 136.6, 136.3, 135.3, 134.8, 134.3, 129.9, 129.3, 129.0, 127.1, 126.9, 112.0, 89.2, 70.6, 64.9, 55.1, 52.5, 51.8, 46.4, 45.7, 40.1, 32.1, 27.4, 26.3, 26.3, 25.9, 19.7;

Minor diastereoisomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H, Ar*H*), 7.43–7.39 (m, 2H, Ar*H*), 7.34–7.26 (m, 4H, Ar*H*), 7.20 (q, *J* = 7.7 Hz, 4H, Ar*H*), 6.51–6.47 (m, 2H, Ar*H*), 4.15 (p, *J* = 8.1 Hz, 1H, C*H*$N_{cyclopentane}$), 3.82 (s, 3H, OCH_3), 3.69 (s, 3H, ArOCH_3), 3.49 (s, 3H, OCH_3), 2.99 (dd, *J* = 13.8, 8.6 Hz, 1H, $(CO_2Me)_2CCH_2$), 2.78 (d, *J* = 6.7 Hz, 1H, OCCH_2), 2.69–2.63 (m, 1H, OCCH_2), 2.49–2.43 (m, 1H, $(CO_2Me)_2CCH_2$), 1.84–1.06 (m, 20H, C$H_{2\ cyclohexyl}$), 1.01 (s, 9H, TBDPS); **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 171.0, 169.9, 158.6, 136.8, 136.2, 135.4, 134.7, 134.5, 129.9, 129.6, 128.8, 127.0, 126.7, 112.2, 89.2, 70.6, 65.4, 55.2, 52.2, 52.1, 47.1, 40.9, 32.1, 27.4, 26.3, 26.3, 25.9, 19.7; **IR** 2931 (m), 2856 (w), 1735 (m), 1514 (m), 1453 (m), 1252 (s), 1186 (m), 1106 (s), 1031 (m), 820 (m), 740 (m), 703 (s); **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{44}H_{60}N_3O_6Si^+$ 754.4246; Found 754.4229.



dimethyl (2*R*,4*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-(naphthalen-1-yl)cyclopentane-1,1-dicarboxylate

6f

Following GP5, compound **6f** was obtained as a single diastereoisomer as a white foam (115 mg, 0.149 mmol, 49% yield). Product was recrystallized from MeOH at – 20 °C. *Recrystallized product contained single crystals suitable for X-ray analysis of **6f**.*

Rf 0.63 (pentane/EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.74 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.70–7.57 (m, 4H, Ar*H*), 7.30 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.17 (ddt, *J* = 23.8, 16.3, 7.4 Hz, 6H, Ar*H*), 6.95 (t, *J* = 7.4 Hz, 2H, Ar*H*), 3.97–3.78 (br m, 2H, NC$H_{cyclohexyl}$), 3.72 (t, *J* = 6.2 Hz, 1H, C*H*$N_{cyclopentane}$), 3.63 (s, 3H, OCH_3), 3.20 (s, 3H, OCH_3), 3.05 (dt, *J* = 13.2, 6.5 Hz, 2H, $(CO_2Me)_2CCH_2$ and OCCH_2), 2.90 (dd, *J* = 14.3, 9.1 Hz, 1H, OCCH_2), 2.43 (dd, *J* = 13.7, 5.2 Hz, 1H, $(CO_2Me)_2CCH_2$), 1.85–1.04 (m, 20H, C$H_{2\ cyclohexyl}$), 0.96 (s, 9H, TBDPS); **^{13}C**

{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.6, 170.5, 138.0, 136.6, 136.0, 134.8, 134.2, 133.9, 132.2, 129.3, 129.2, 128.8, 128.5, 128.1, 127.1, 126.6, 124.6, 124.2, 124.1, 93.0, 63.5, 55.0, 54.7, 52.5, 51.7, 46.9, 41.9, 32.1, 29.8, 27.9, 26.3, 25.9, 20.1; **IR** 2927 (m), 2854 (w), 1730 (s), 1455 (m), 1430 (m), 1255 (m), 1191 (m), 1104 (s), 1074 (m), 1027 (m), 963 (m), 778 (m), 741 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{47}H_{60}N_3O_5Si^+$ 774.4297; Found 774.4278.

8. Computational details

All quantum chemical calculations were carried out using the Gaussian16 package.[7] The molecular structure optimizations were performed using the M06-2X functional[8] along with the 6-311+G(d,p) basis set for all elements.[9] Stationary points were verified as minima by subsequent frequency calculations (Number of imaginary frequencies (NIMAG): 0).

NMR chemical shift computations were performed using the GIAO method as implemented in Gaussian 16 and the M06-L functional along with the 6-311(2d,p) basis set for molecular structure obtained at the M06-2X/6-311+G(d,p) level of theory.[10, 11]

Table S5.1. Calculated absolute energies, E(SCF), and free enthalpies at 298 K, G^{298}, for compounds of interest.

Compound	Method/basis set	E(SCF) [a.u.]	NIMAG ZPVE [kJ mol^{-1}]	G^{298} [a.u.]
2a	M06-2X/6-311+G(d,p)	-1207.62880	0, 1313	-1207.18664
Carbocation **A**	M06-2X/6-311+G(d,p)	-1097.82201	0, 1418	-1097.34144
Carbocation **B**	M06-2X/6-311+G(d,p)	-1097.79210	0, 1417	-1097.31200

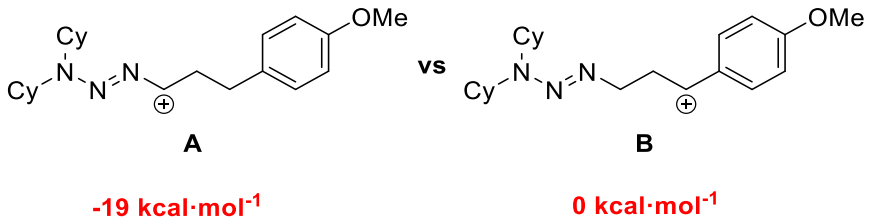


Figure S5.1. Calculated differences in Gibbs energy at 298 K, ΔG^{298} for carbocation **A** and carbocation **B** (in kcal·mol^{-1}, at M06-2X/6-311+G(d,p) level).

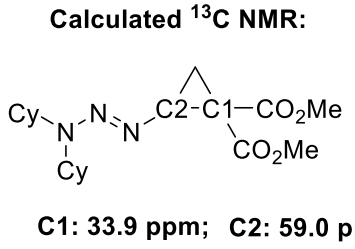


Figure S5.2. Calculated ^{13}C NMR chemical shifts of **2a** (at GIAO/M06L/6-311G(2d,p)//M06-2X/6–311+G(d,p) level).

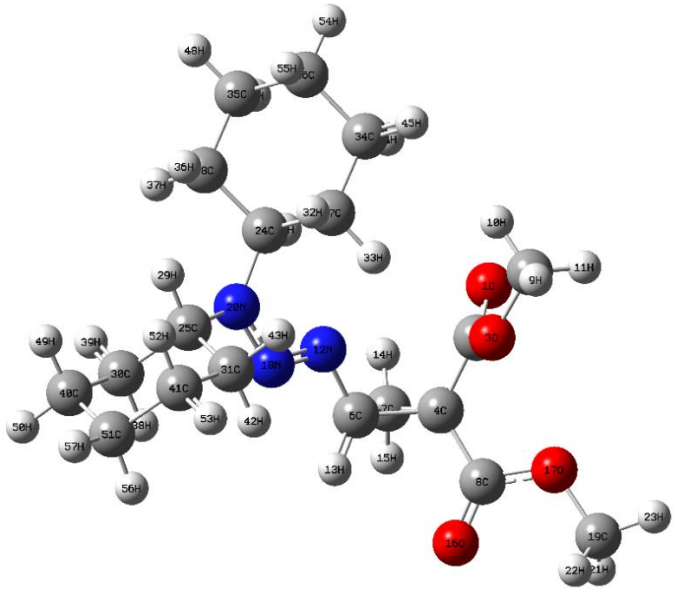


Figure S5.3. Optimized structure of **2a** at M06-2X/6-311+G(d,p) level. Color code: blue, nitrogen; gray, carbon; white: hydrogen; red: oxygen.

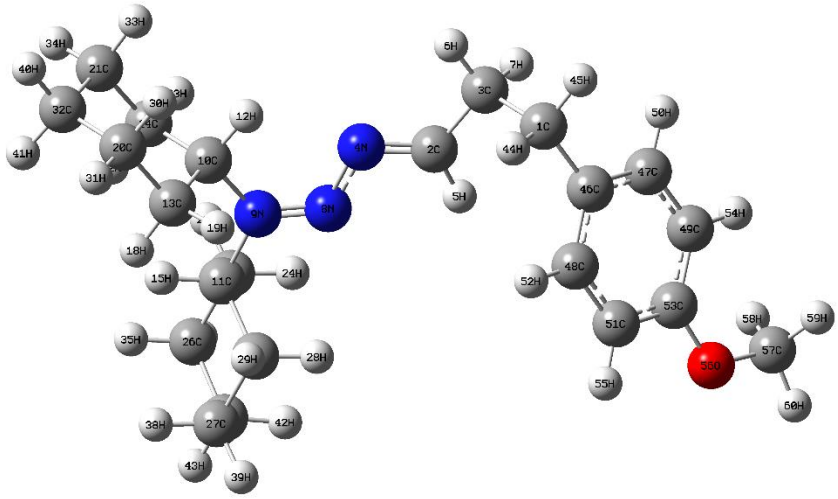


Figure S5.4. Optimized structure of carbocation **A** at M06-2X/6-311+G(d,p) level. Color code: blue, nitrogen; gray, carbon; white: hydrogen; red: oxygen.

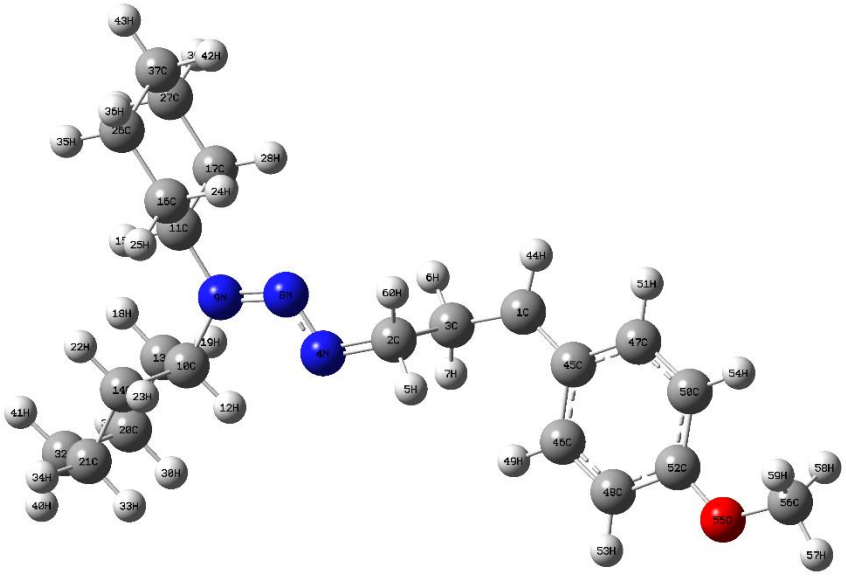


Figure S5.5. Optimized structure of carbocation **B** at M06-2X/6-311+G(d,p) level. Color code: blue, nitrogen; gray, carbon; white: hydrogen; red: oxygen.

Cartesian Coordinates of Computed Structures

2a, M06-2X/6-311+G(d,p)

O	2.89125315	2.07587532	-0.62044255
C	2.73376799	1.00999757	-0.09251096
O	2.39448232	0.85974696	1.19329384
C	2.85732116	-0.32307117	-0.77398255
C	2.31464285	2.07116688	1.94438875
C	1.56133793	-0.92132695	-1.31712580
C	2.57756719	-0.37520298	-2.25582905
C	3.85534320	-1.30229217	-0.26414789
H	1.99011268	1.78107469	2.94053792
H	1.59837724	2.75506348	1.48812064
H	3.29260358	2.55257131	1.98375632
N	0.40477603	-0.11947504	-1.07789092
H	1.46049662	-1.99721630	-1.21737783

H	2.36215202	0.58434210	-2.70779960
H	3.16247275	-1.08155680	-2.82876290
O	3.92620767	-2.44443866	-0.63715022
O	4.69786293	-0.75813643	0.61992180
N	-0.59919821	-0.81425652	-0.81935772
C	5.69949747	-1.63959441	1.13190681
N	-1.73147223	-0.15277225	-0.60509096
H	6.32425858	-2.01304487	0.32049392
H	5.23368522	-2.48278945	1.64187857
H	6.28577210	-1.04539340	1.82730299
C	-1.72534491	1.31123806	-0.52607091
C	-2.79343646	-0.97984825	-0.02066358
H	-0.99158676	1.62885800	-1.27177245
C	-1.24889002	1.81782359	0.84056590
C	-3.06594350	1.93982431	-0.90373171
H	-3.62454314	-0.30003126	0.18284850
C	-3.27959047	-2.03686854	-1.01545084
C	-2.37185221	-1.62885508	1.30355364
H	-1.98589822	1.53126807	1.60200827
H	-0.30153243	1.33364848	1.09366755
C	-1.10412771	3.34141257	0.81130347
C	-2.91397484	3.46444214	-0.95229126
H	-3.83319855	1.69604354	-0.16077954
H	-3.40216884	1.54783568	-1.86788964
H	-2.43423251	-2.68602462	-1.26663469
H	-3.59574561	-1.54246881	-1.93810023
C	-4.41902487	-2.86667231	-0.41966175
C	-3.51776036	-2.45207243	1.89613102
H	-1.51188285	-2.27772082	1.10774770
H	-2.04244622	-0.85686383	2.00460860

H	-0.31316797	3.60789980	0.09901402
H	-0.78950185	3.71187757	1.79122212
C	-2.41510184	4.01079699	0.38860034
H	-2.20136749	3.73176852	-1.74088472
H	-3.86899534	3.92513386	-1.21701060
H	-5.28686706	-2.21819456	-0.24525313
H	-4.73595852	-3.63054403	-1.13410126
C	-4.00280388	-3.51117105	0.90415780
H	-4.35287487	-1.78640152	2.14846983
H	-3.19574050	-2.92080283	2.82947161
H	-2.28550651	5.09447513	0.32951757
H	-3.17618666	3.82266780	1.15590129
H	-3.19195292	-4.22508349	0.71713070
H	-4.83552401	-4.07760290	1.32921402

Carbocation **A**, M06-2X/6-311+G(d,p)

C	2.63980582	-2.90295930	-0.23422568
C	0.86219500	-1.44180457	0.72646198
C	1.57849448	-2.72258686	0.88560990
N	-0.41504505	-1.40892859	0.53640973
H	1.43391493	-0.51023051	0.74645278
H	0.86939492	-3.55032714	0.90146882
H	2.10394418	-2.68297300	1.84747908
N	-0.82172152	-0.10973884	0.40876523
N	-2.03133852	0.05142433	0.18879882
C	-3.04620969	-1.03750803	0.04336373
C	-2.46585681	1.47804137	0.05976955
H	-2.50465070	-1.96672386	0.20191140
C	-3.61494827	-1.01991709	-1.38001291
C	-4.12923907	-0.89401413	1.11787107

H	-3.53115406	1.43029365	-0.16647980
C	-2.26093450	2.21276216	1.38630307
C	-1.73338044	2.15868250	-1.09797814
H	-4.10884297	-0.06386475	-1.58310822
H	-2.80360115	-1.13737177	-2.10328063
C	-4.63679049	-2.15407765	-1.51876626
C	-5.14319611	-2.03182010	0.94977592
H	-4.64760772	0.06516389	1.01709703
H	-3.67219791	-0.92494699	2.11041216
H	-1.19430763	2.19630882	1.63150609
H	-2.79906856	1.69687881	2.18650295
C	-2.74422946	3.65894660	1.24381857
C	-2.22301457	3.60434162	-1.22441203
H	-0.65921114	2.14467728	-0.89001849
H	-1.90512929	1.60399622	-2.02491557
H	-4.12416554	-3.11681858	-1.41653998
H	-5.06380613	-2.12784824	-2.52279934
C	-5.73538342	-2.04250519	-0.46039321
H	-4.64924785	-2.98914649	1.14880335
H	-5.92998401	-1.92036786	1.69784768
H	-3.82673449	3.66590140	1.07122224
H	-2.57296009	4.18744760	2.18329556
C	-2.03598303	4.36756565	0.08795817
H	-3.28303325	3.60764983	-1.50371019
H	-1.68315106	4.09523596	-2.03607927
H	-6.43895278	-2.87040073	-0.56374729
H	-6.30550883	-1.12037626	-0.62285310
H	-0.96618032	4.44649535	0.31207454
H	-2.41423769	5.38624566	-0.01441850
H	2.12841866	-3.01085490	-1.19349258

H	3.15547279	-3.84514790	-0.03788990
C	3.62152538	-1.75880826	-0.29408101
C	4.62119415	-1.62476407	0.66389543
C	3.52842532	-0.77966304	-1.28910792
C	5.50931313	-0.55135090	0.64807045
H	4.72941791	-2.37909822	1.43789163
C	4.39900422	0.29529706	-1.32129194
H	2.77213399	-0.87158855	-2.06329161
C	5.39754073	0.41842160	-0.34931853
H	6.28131627	-0.49013037	1.40281879
H	4.34189876	1.04865945	-2.09718711
O	6.20126530	1.49702826	-0.46296977
C	7.26376252	1.63832265	0.46321178
H	6.88439397	1.73935906	1.48425354
H	7.94893111	0.78789147	0.40555545
H	7.78853923	2.54687512	0.18002835

Carbocation **B**, M06-2X/6-311+G(d,p)

C	2.84929086	1.23388434	-0.82356579
C	0.93510306	0.33215405	0.43454885
C	1.58375642	0.52647072	-0.99605360
N	-0.31449425	-0.37257553	0.27519442
H	1.61462057	-0.28146971	1.02970114
H	0.88029707	1.11529070	-1.58480141
H	1.69186487	-0.46450316	-1.43689602
N	-1.27231940	0.44452751	0.21593508
N	-2.47445971	-0.02951620	0.06249777
C	-2.78092540	-1.46824498	0.00265967
C	-3.54884298	0.97716295	0.07488963
H	-1.81421346	-1.97208978	-0.02204880

C	-3.54326893	-1.82249100	-1.27777997
C	-3.53207440	-1.92166029	1.25926143
H	-4.47928360	0.40935663	-0.00795444
C	-3.58429054	1.75648196	1.39183353
C	-3.45141260	1.91538977	-1.12967784
H	-4.49529648	-1.28048817	-1.31298990
H	-2.95888861	-1.50929813	-2.14743029
C	-3.82728632	-3.32693215	-1.32443696
C	-3.82256325	-3.42353741	1.19498167
H	-4.47913376	-1.37412481	1.33987212
H	-2.93723563	-1.67652344	2.14356414
H	-2.63155047	2.28372919	1.50771586
H	-3.67568561	1.05628804	2.22735795
C	-4.73774055	2.76255061	1.38950618
C	-4.60192717	2.92491750	-1.12265183
H	-2.49287799	2.44351281	-1.07703468
H	-3.45335702	1.32542825	-2.05098935
H	-2.87804369	-3.87190959	-1.38811404
H	-4.39114740	-3.56728818	-2.22847444
C	-4.58896406	-3.78404615	-0.07888711
H	-2.87483532	-3.97435879	1.21511966
H	-4.38444514	-3.72896216	2.08039352
H	-5.69138228	2.22251247	1.34788099
H	-4.73774682	3.32696776	2.32465307
C	-4.64158032	3.70832594	0.19084713
H	-5.55150057	2.39214140	-1.25369687
H	-4.50398945	3.60426477	-1.97244116
H	-4.76774282	-4.86081278	-0.12009638
H	-5.57253817	-3.29964568	-0.05884762
H	-3.72962350	4.31079455	0.27958639

H	-5.48324305	4.40456581	0.18993666
H	2.81085094	2.32218162	-0.85073059
C	4.07256868	0.67075448	-0.51752489
C	4.26842119	-0.74667854	-0.40844756
C	5.19395000	1.52641371	-0.28665517
C	5.48733000	-1.25468054	-0.08914269
H	3.43542466	-1.41836524	-0.57745517
C	6.42693532	1.02686736	0.02656519
H	5.05348415	2.59918820	-0.36522881
C	6.58642664	-0.37735830	0.12970706
H	5.66596552	-2.31819456	0.00346961
H	7.26115759	1.69308338	0.19438316
O	7.71723815	-0.96455918	0.42380351
C	8.90161743	-0.19065735	0.66302431
H	9.67868633	-0.91685645	0.87817070
H	9.16067091	0.38313662	-0.22779895
H	8.75336641	0.46555520	1.52171767
H	0.80124153	1.30579610	0.91567974

9. Crystallographic data

Bragg-intensities of **2a**, **3a** and **4a** were collected at 140(1) K using Cu *Kα* radiation. A Rigaku SuperNova dual system diffractometer with an Atlas S2 CCD detector was used. The dataset was reduced and corrected for absorption, with the help of a set of faces enclosing the crystal as snugly as possible, with *CrysAlis*^{Pro}.[12] The diffraction data of compound **6f** were measured at low temperature [120(2) K] using Mo K_α radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The datasets were reduced by EvalCCD[13] and then corrected for absorption.[14]

The solution and refinements were performed by the latest available version of *ShelXT*[15] and *ShelXL*.[16] All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on $|F|^2$. The hydrogen atoms were placed at calculated positions by means of the "riding" model in which each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the methyl groups). For compound **2a**, the major problems found during the refinement of the crystal structure dealt with the disorder of the -COOMe moiety. It was treated by the splitting method and some restraints (SADI and SIMU cards) were applied to bond distances and to the adp's, in order to obtain acceptable values. In the structure **3a**, some moieties are disordered over two orientations each, found in difference maps. These were anisotropically refined by imposing distance and similarity restraints (SADI and SIMU) on the least-squares refinement yielding site occupancies of 0.9298(14)/0.0702(14). In the case of compound **4a** some restraints (ISOR and RIGU cards) were used for the displacement parameters of some atoms. Finally, compound **6f** displayed clear disorder for the -N(cyclohexyl)$_2$; the substituent was refined by splitting it and by applying restraints (DFIX, SADI, DANG, SIMU) in order to get reasonable adp's and geometric parameters.

Crystallographic and refinement data are summarized in **Table S9.1**. Crystallographic data have been deposited with the CCDC and correspond to the following codes: **2a** (1995416), **3a** (1995157), **4a** (1995417) and **6f** (1995418). Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44-1223-336033; E-mail, deposit@ccdc.cam.ac.uk).

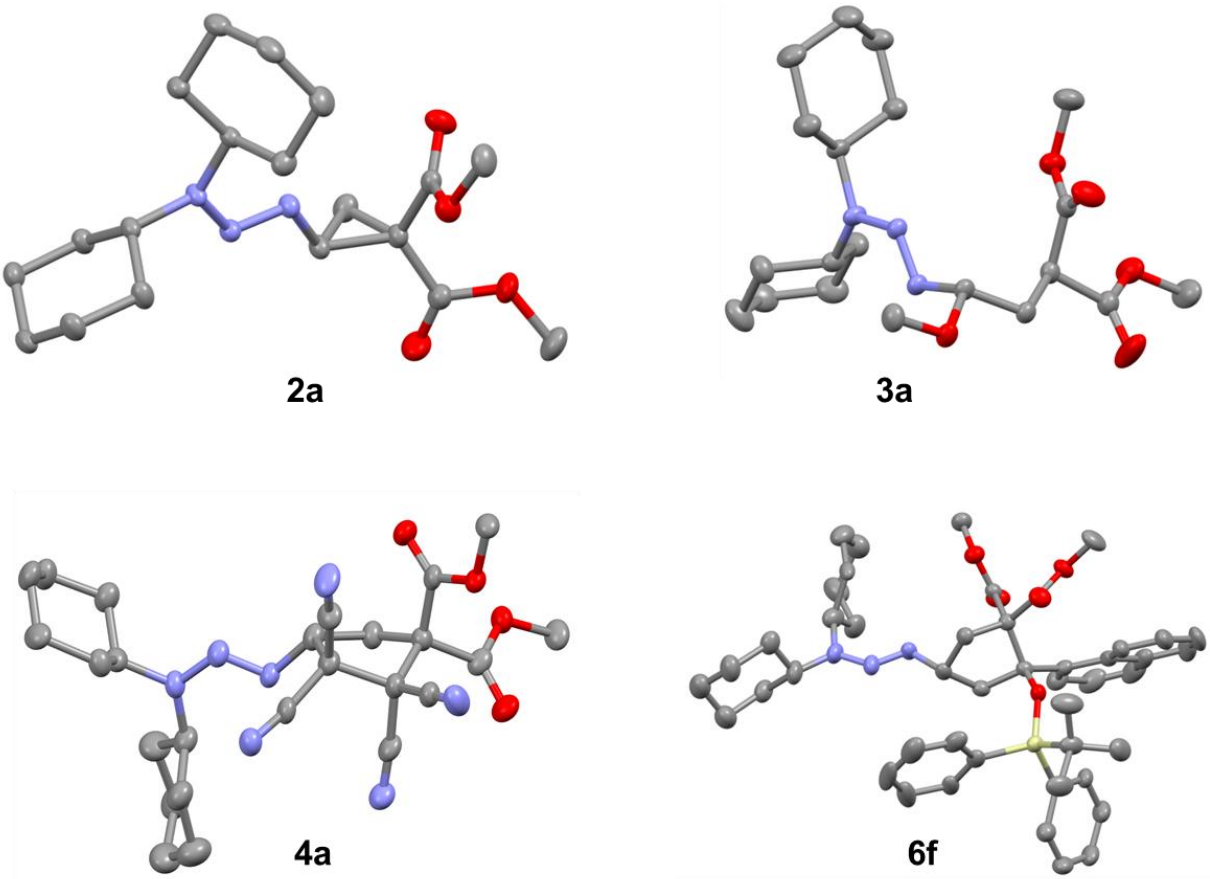
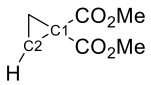
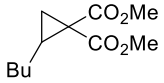
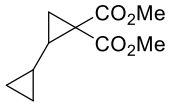
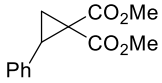
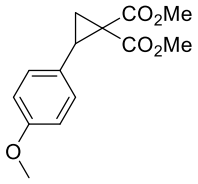
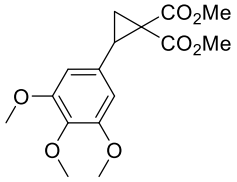
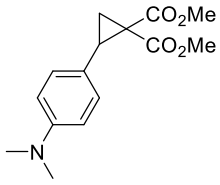
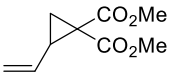
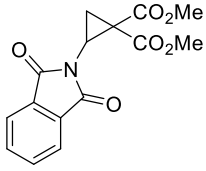
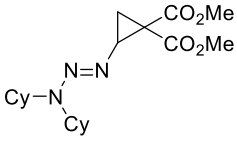


Figure S9.1. X-ray structures of **2a**, **3a**, **4a** and **6f** (hydrogen atoms are omitted for clarity, probability level 50%).

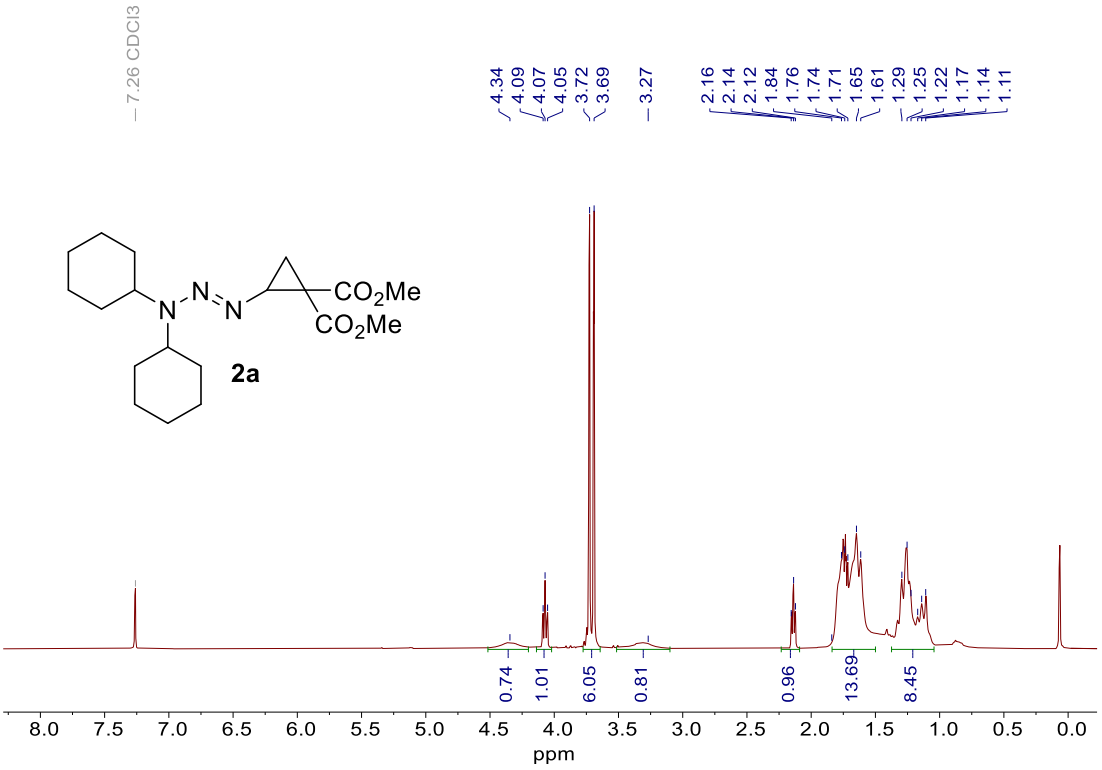
Table S9.1. Crystallographic and refinement data for **2a**, **3a**, **4a** and **6f**.

Compound	**2a**	**3a**	**4a**	**6f**
Formula	$C_{19}H_{31}N_3O_4$	$C_{20}H_{35}N_3O_5$	$C_{25}H_{31}N_7O_4$	$C_{47}H_{59}N_3O_5Si$
$D_{calc.}$/ g cm^{-3}	1.229	1.214	1.235	1.192
μ/mm^{-1}	0.702	0.710	0.708	0.103
Formula Weight	365.47	397.51	493.57	774.06
Colour	clear pale yellow	clear colourless	clear pale colourless	colourless
Shape	irregular	prism	plate	prism
Size/mm^3	0.871x0.377x0.346	0.72×0.55×0.14	0.42×0.08×0.06	0.382x0.278x0.072
T/K	140.00(10)	140.00(10)	140.00(10)	120(2)
Crystal System	monoclinic	triclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P\bar{1}$	$I2/a$	$P2_1$/n
a/Å	14.2084(3)	8.7504(2)	43.268(5)	16.9645(15)
b/Å	9.04241(18)	8.8246(2)	6.7588(6)	14.2356(18)
c/Å	15.5363(3)	16.0455(4)	40.361(3)	18.3540(19)
α/°	90	82.937(2)	90	90
β/°	98.371(2)	82.375(2)	115.909(11)	103.404(10)
γ/°	90	62.604(3)	90	90
V/Å^3	1974.81(8)	1087.63(6)	10616.6(19)	4311.8(8)
Z	4	2	16	4
Z'	1	1	2	1
Wavelength/Å	1.54184	1.54184	1.54184	0.71073
Radiation type	Cu$K\alpha$	Cu$K\alpha$	Cu Kα	Mo K_α
Θ_{min}/°	5.677	5.577	3.991	1.473
Θ_{max}/°	75.460	76.101	66.597	24.997
Measured Refl.	13869	9387	34567	42887
Independent Refl.	4032	4471	9322	7573
Reflections with I > 2σ(I)	3714	4372	3615	5490
R_{int}	0.0244	0.0131	0.1226	0.0465
Parameters	377	350	653	628
Restraints	112	181	612	450
Largest Peak/e Å^{-3}	0.263	0.446	0.576	1.167
Deepest Hole/e Å^{-3}	-0.194	-0.212	-0.239	-0.535
GooF	1.038	1.120	0.840	1.077
wR_2 (all data)	0.0955	0.1239	0.2326	0.2139
wR_2	0.0926	0.1234	0.1938	0.1879
R_1 (all data)	0.0395	0.0494	0.1564	0.1197
R_1	0.0361	0.0487	0.0738	0.0833
CCDC code	1995416	1995157	1995417	1995418

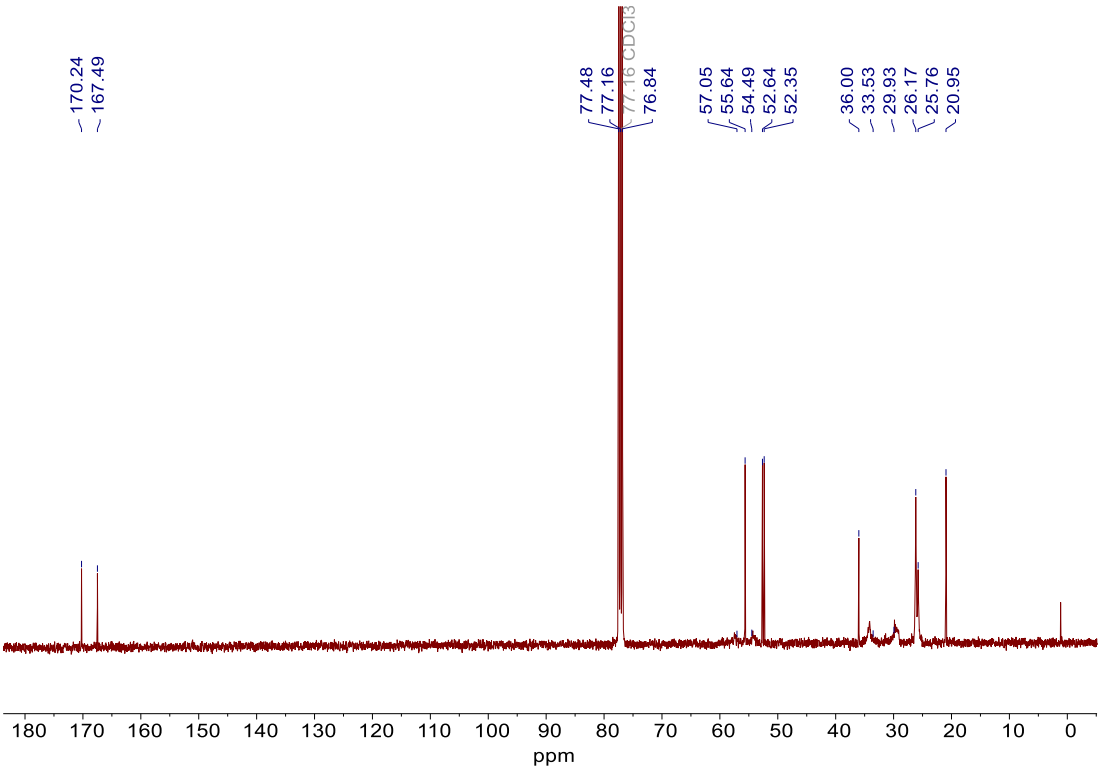
10. ^{13}C NMR of reported D-A cyclopropanes

D-A cyclopropane	C2 (ppm)	C1 (ppm)	Reference
	16.5	27.7	*Org. Biomol. Chem.* **2018**, *16*, 9472-9476 (600 MHz, $CDCl_3$)
	23.5	34.5	*J. Org. Chem.* **2009**, 470 (300 MHz, $CDCl_3$)
	31.8	34.1	*J. Am. Chen. Soc.* **2006**, *128*, 5600-5601 (400 MHz, $CDCl_3$)
	32.4	37.1	*Chem. Eur. J.* **2018**, *24*, 6062- 6066 (500 MHz, $CDCl_3$)
	32.2	37.1	*Chem. Eur. J.* **2018**, *24*, 6062- 6066 (500 MHz, $CDCl_3$)
	32.8	37.2	*Eur. J. Org. Chem.* **2019**, 5475–5485 (500 MHz, $CDCl_3$)
	32.2	36.6	*Eur. J. Org. Chem.* **2019**, 5475–5485 (500 MHz, $CDCl_3$)
	31.5	35.8	*Chem. Eur. J.* **2018**, *24*, 6062- 6066 (500 MHz, $CDCl_3$)
	34.9	33.1	*Chem. Eur. J.* **2018**, *24*, 6062- 6066 (500 MHz, $CDCl_3$)
	55.6	36.0	***This work***

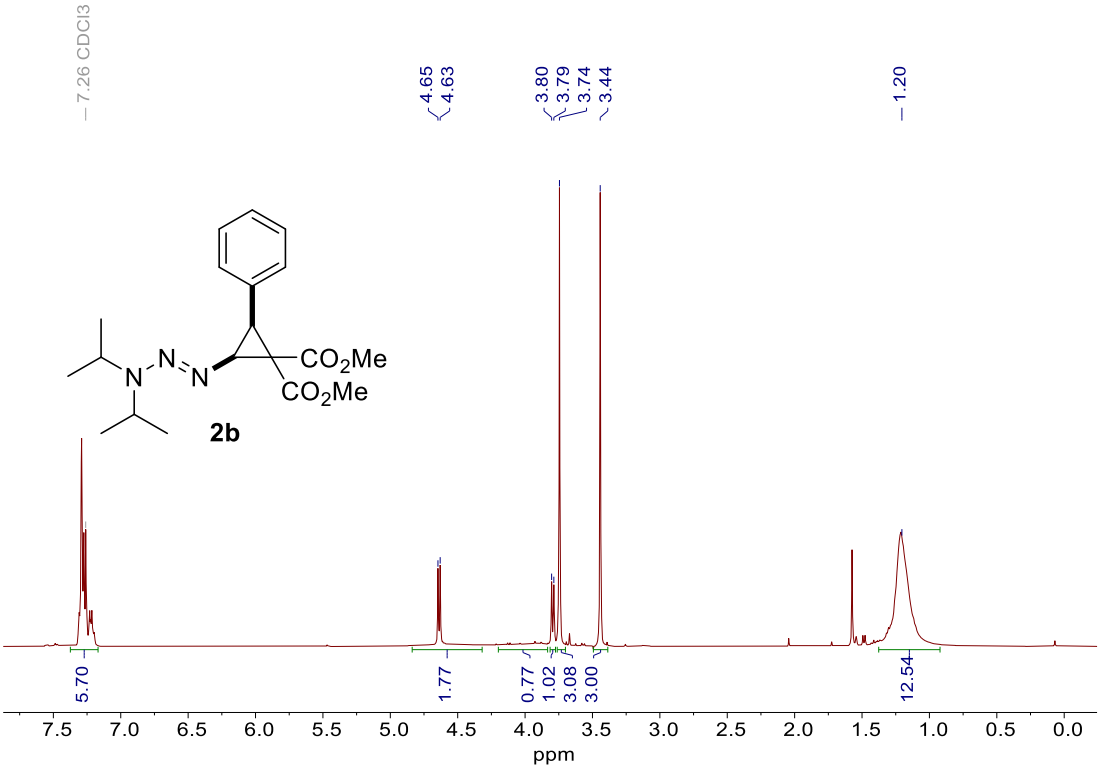
11. NMR spectra



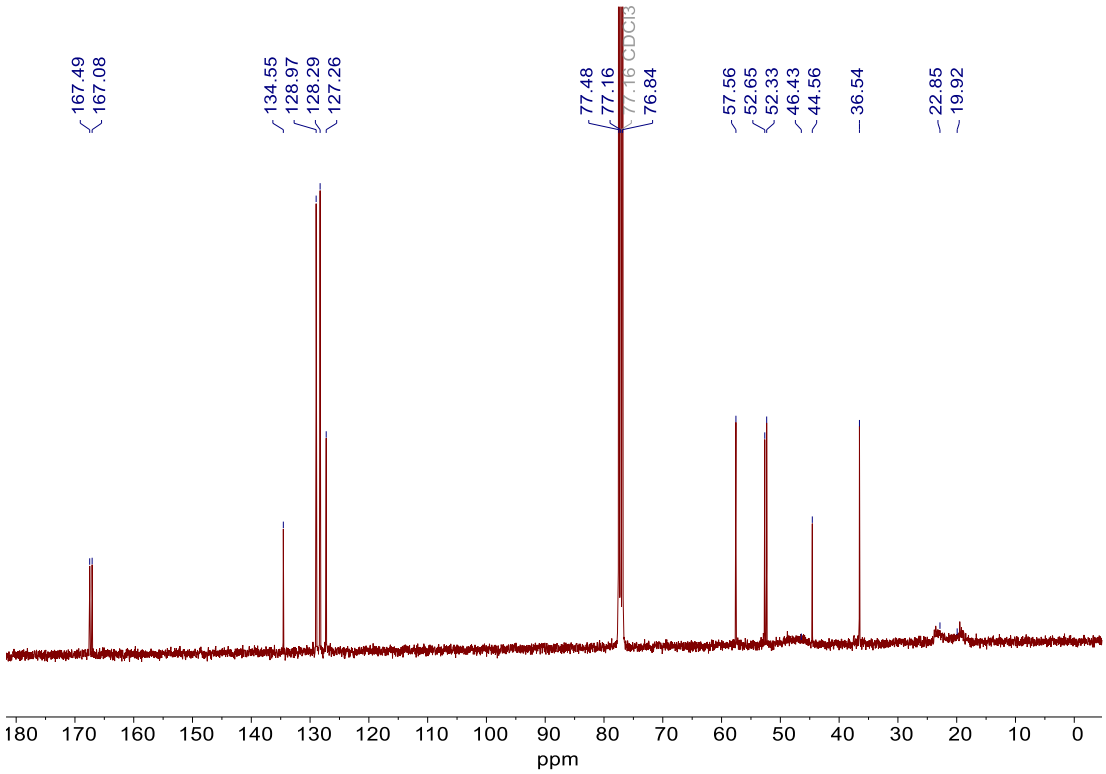
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2a**.



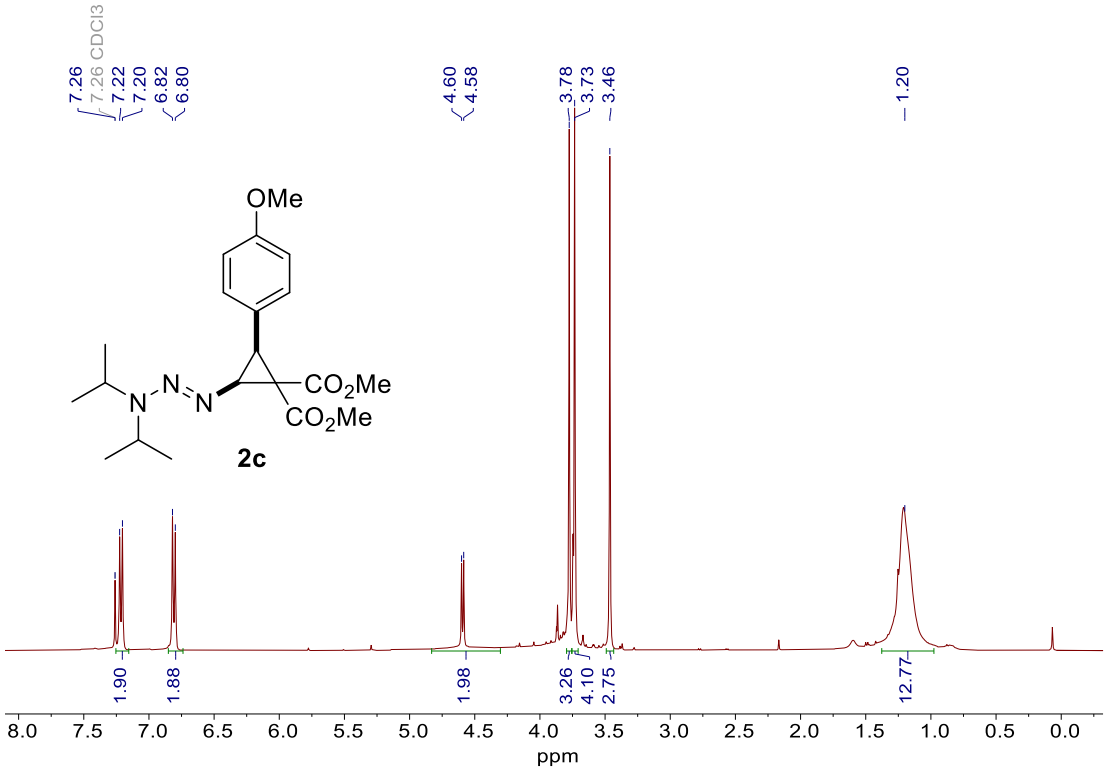
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **2a**.



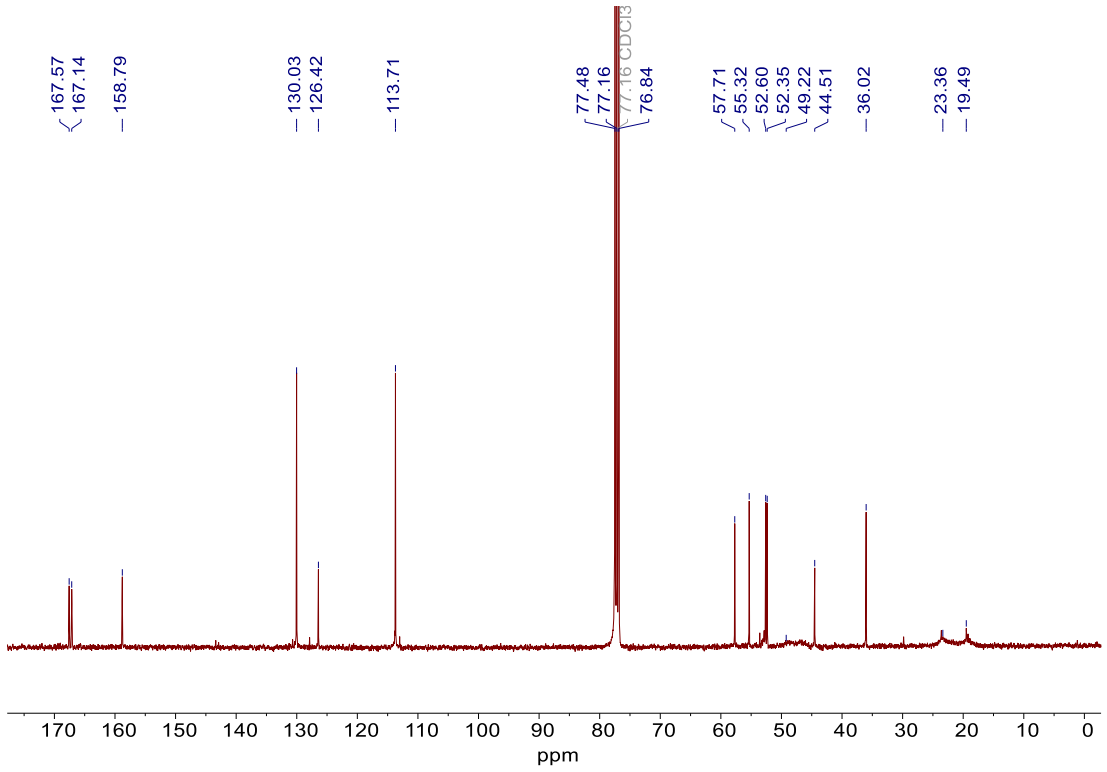
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2b**.



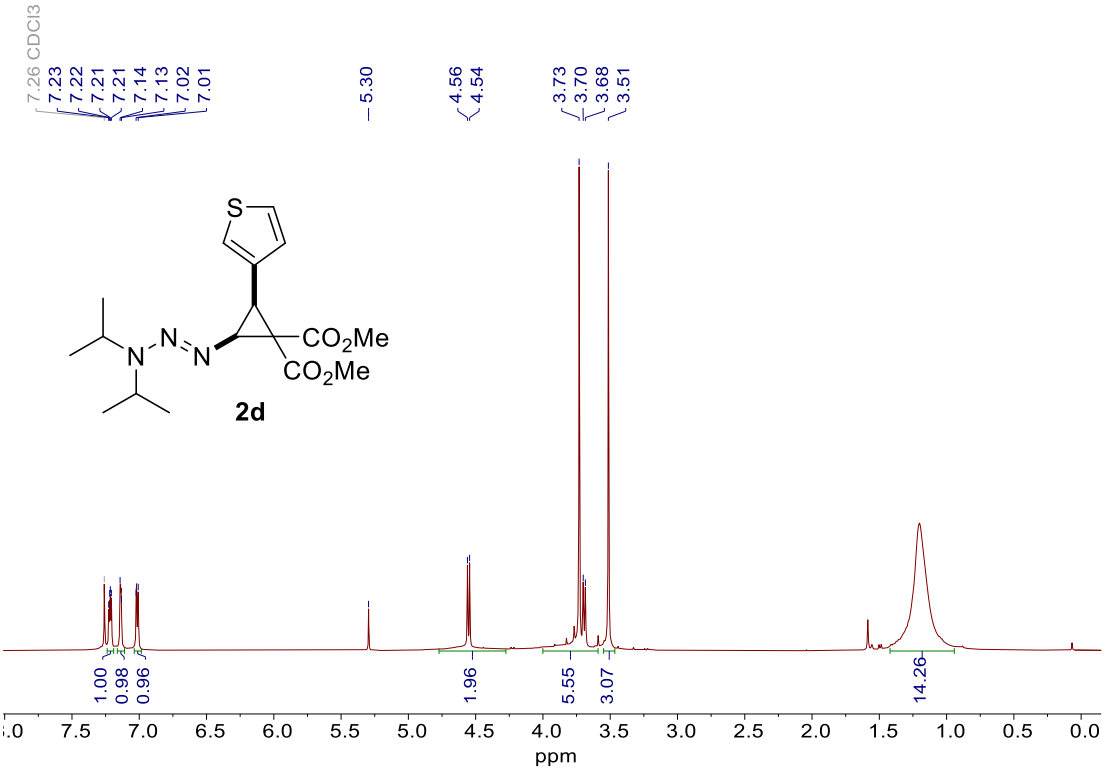
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **2b**.



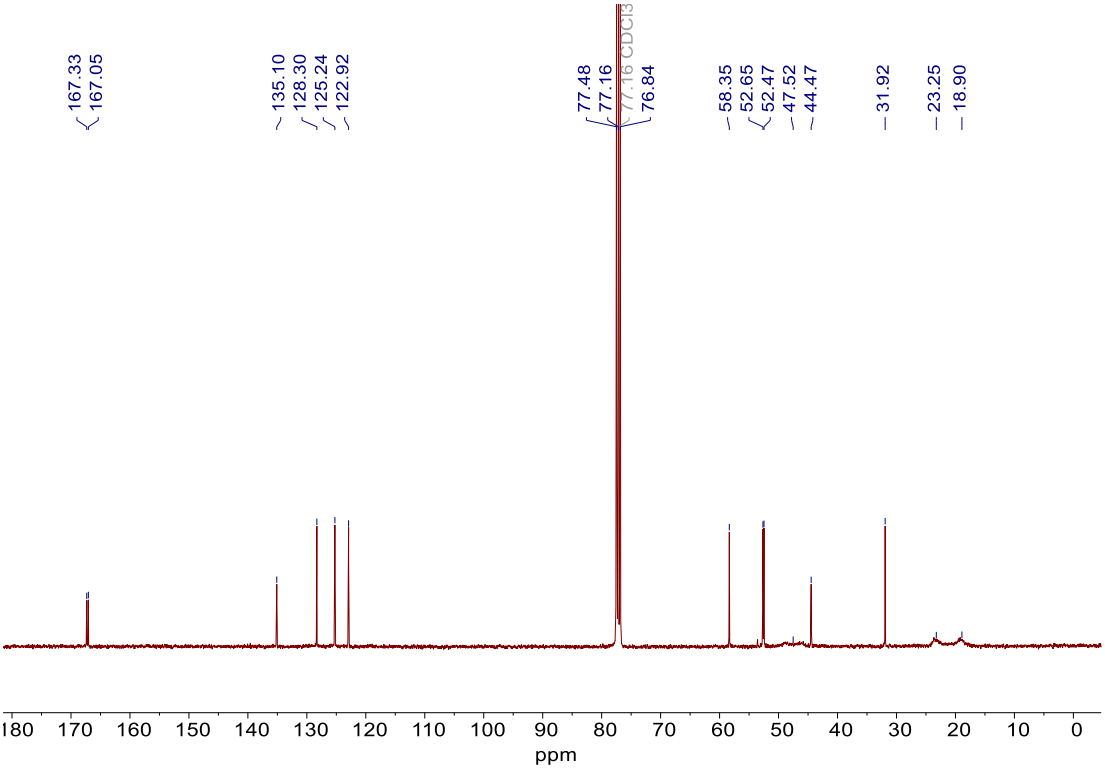
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2c**.



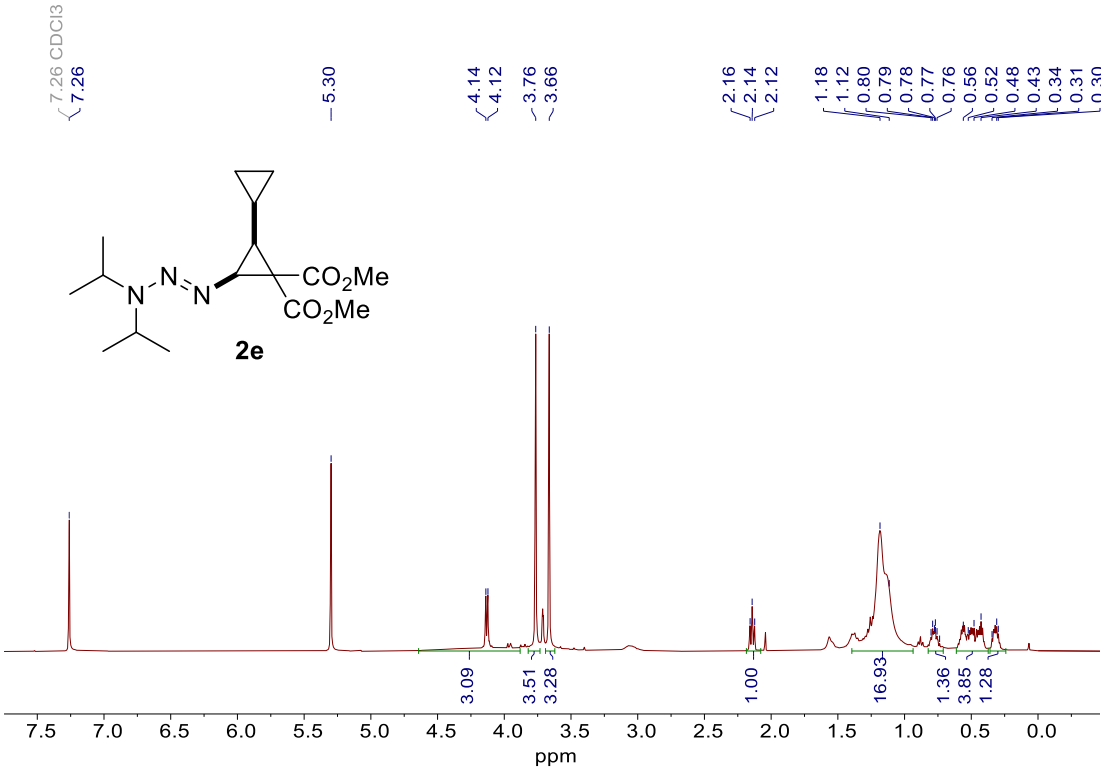
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **2c**.



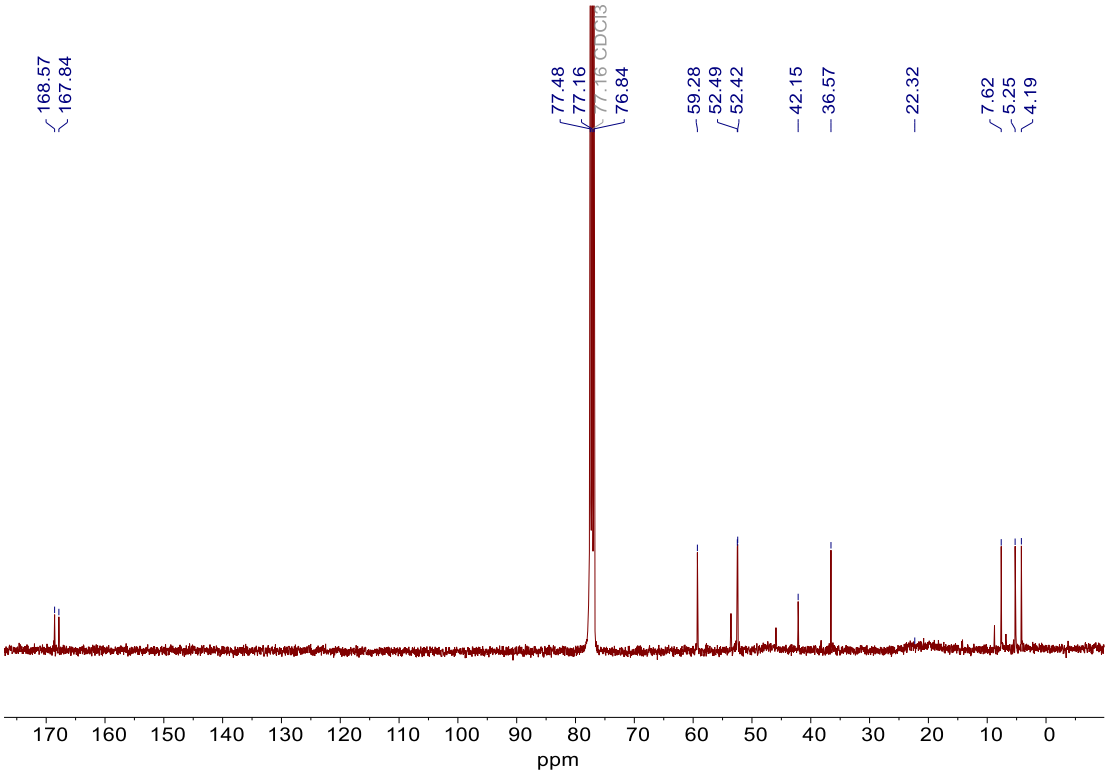
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2d**.



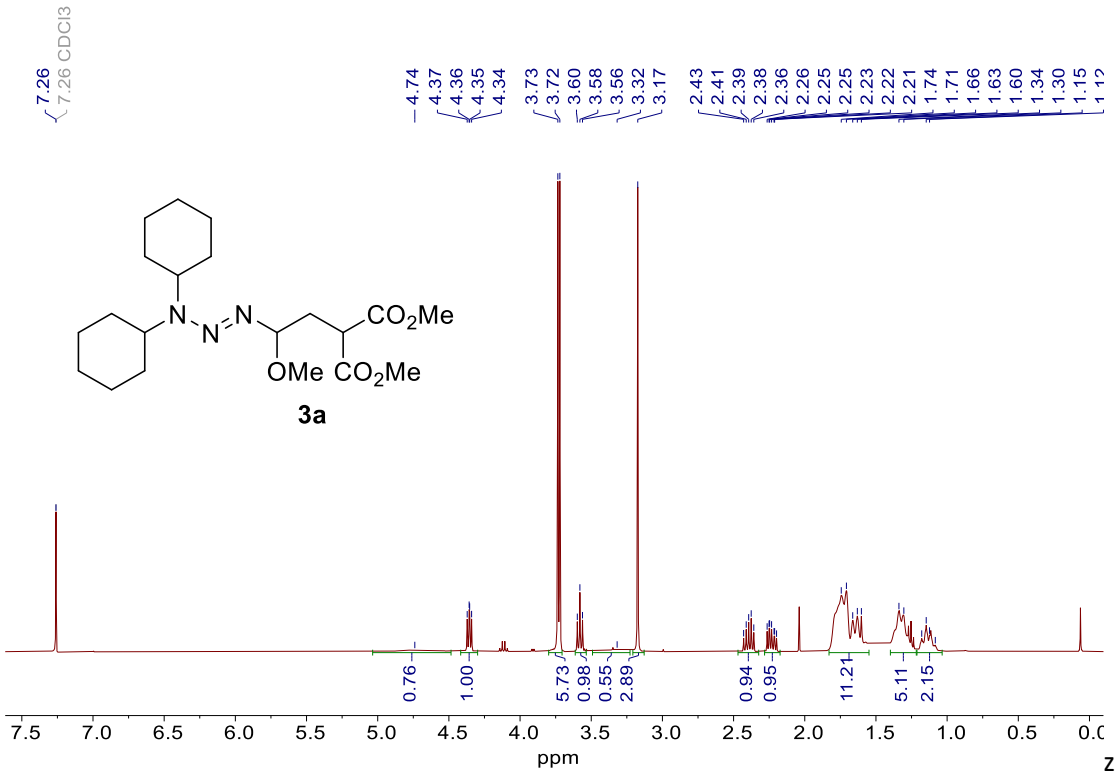
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **2d**.



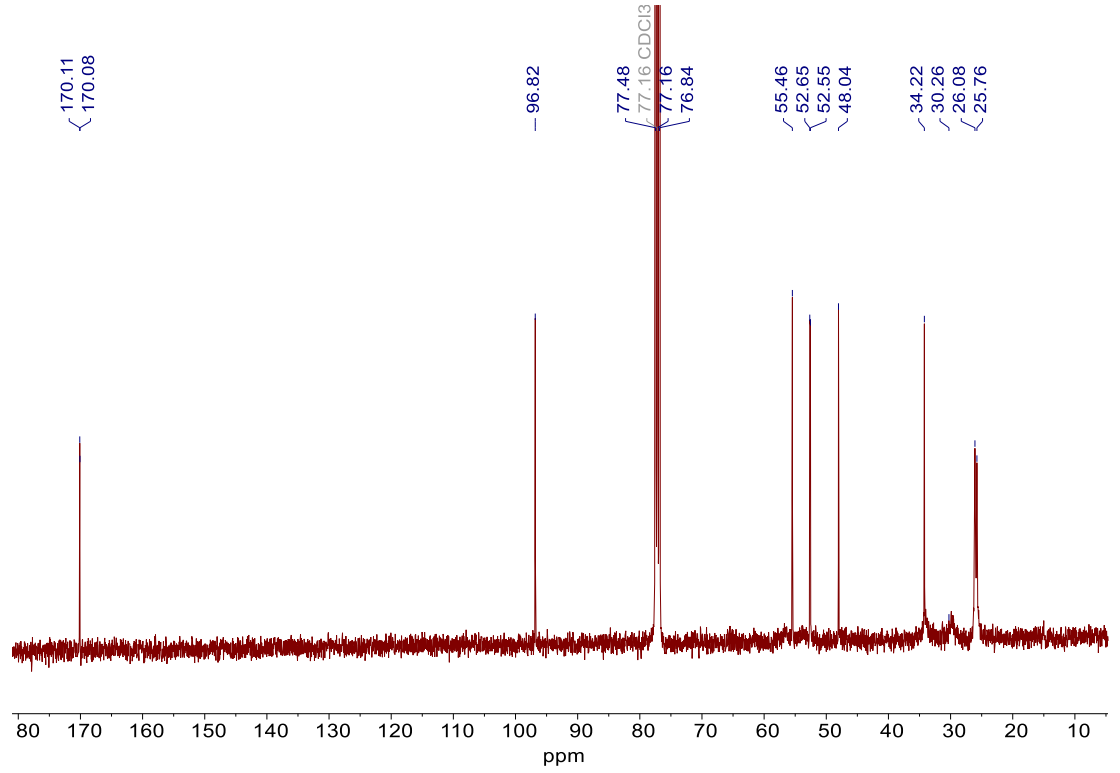
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2e**.



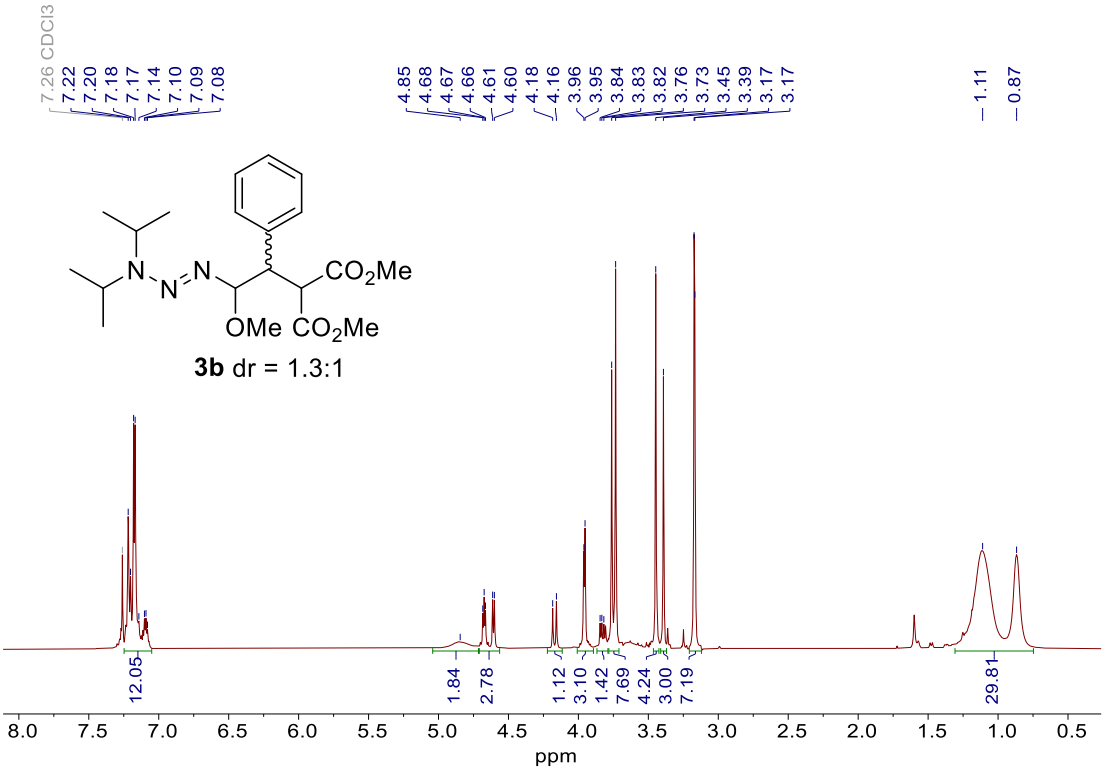
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **2e**.



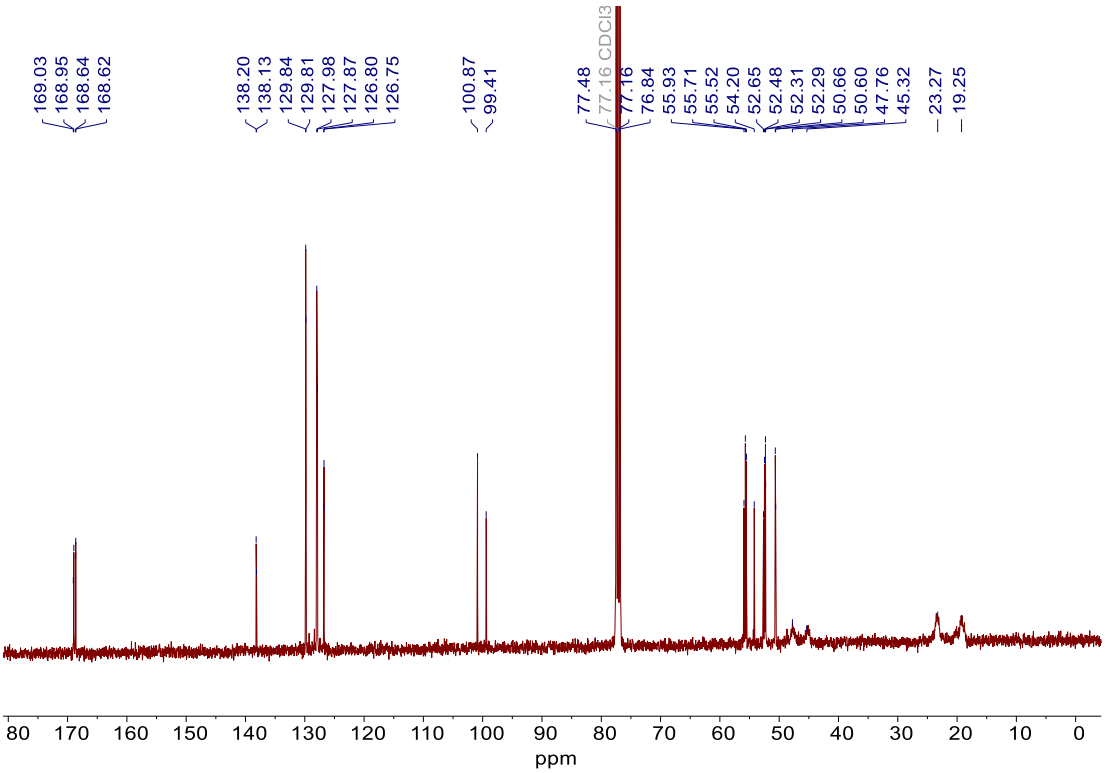
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**.



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3a**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**.



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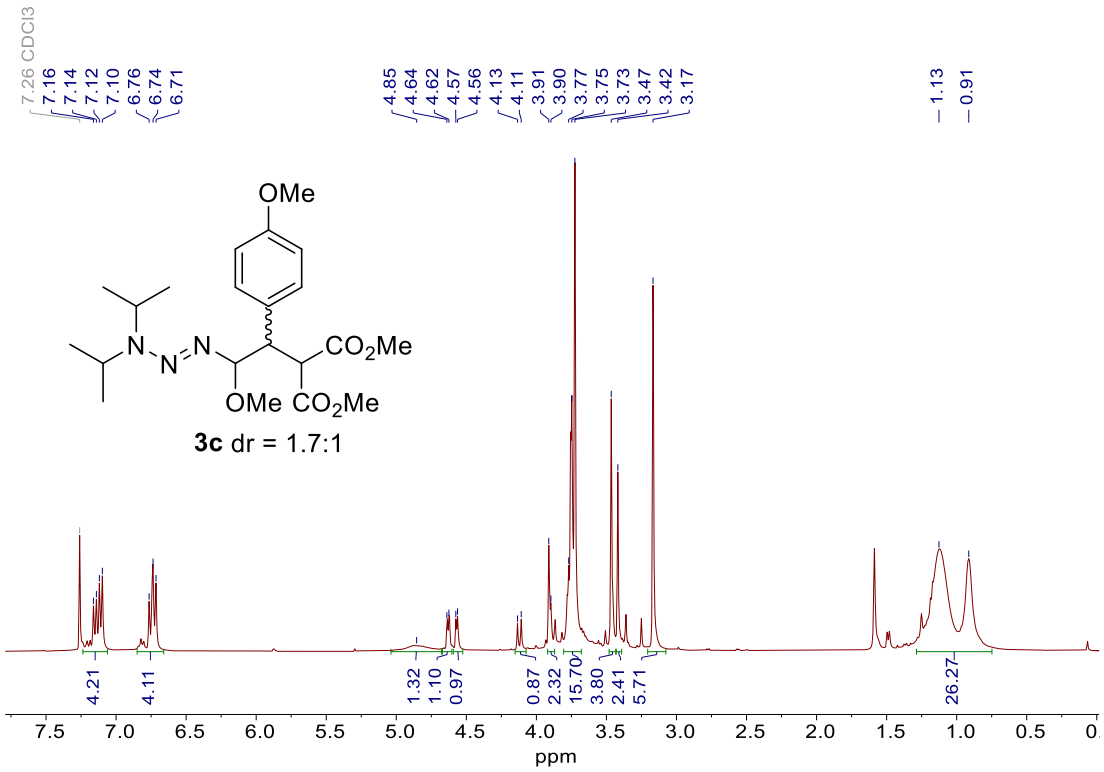
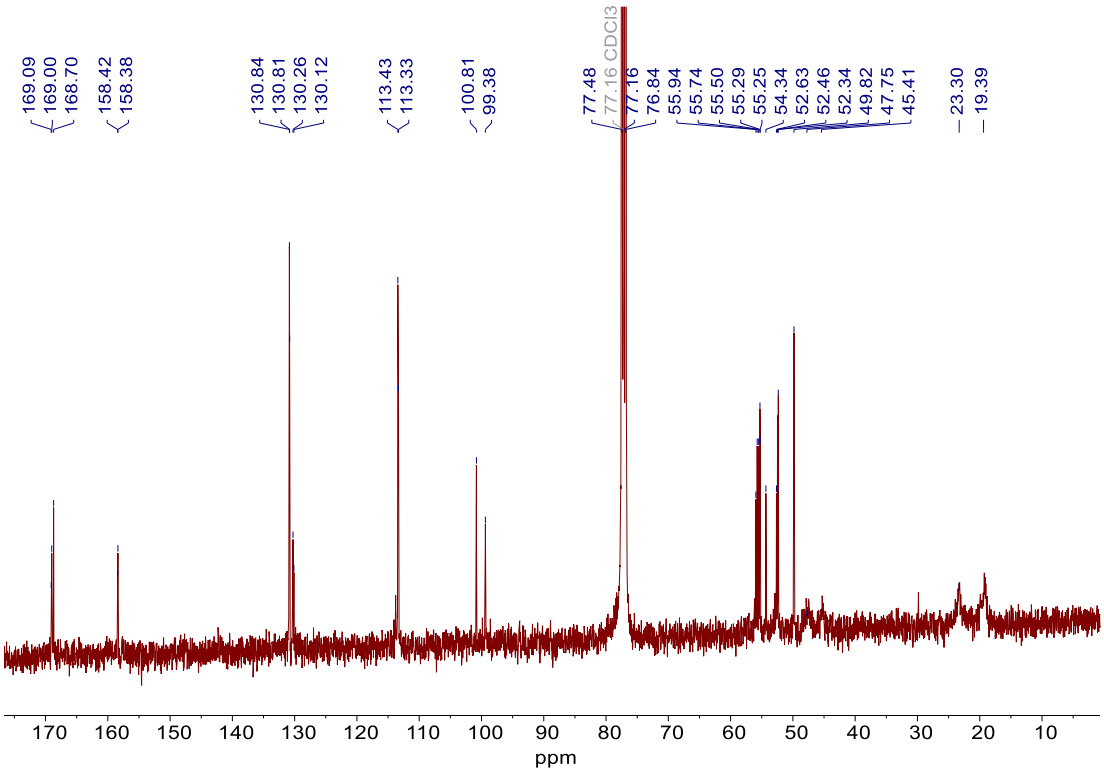


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**.



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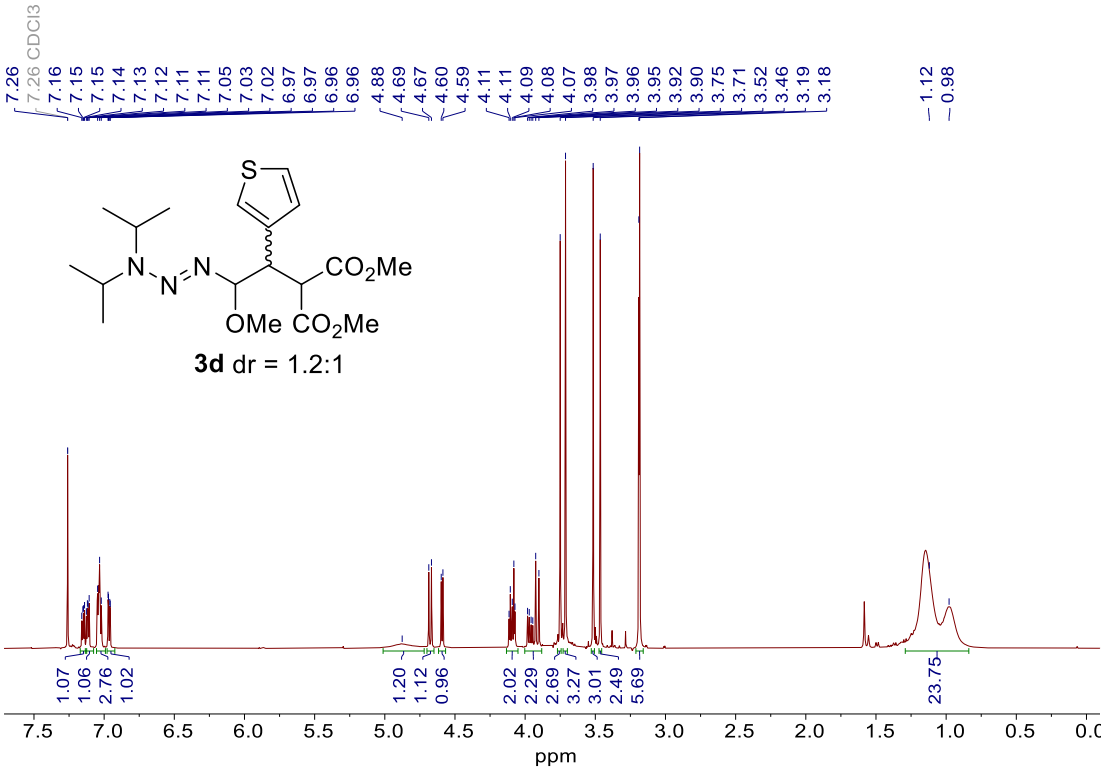
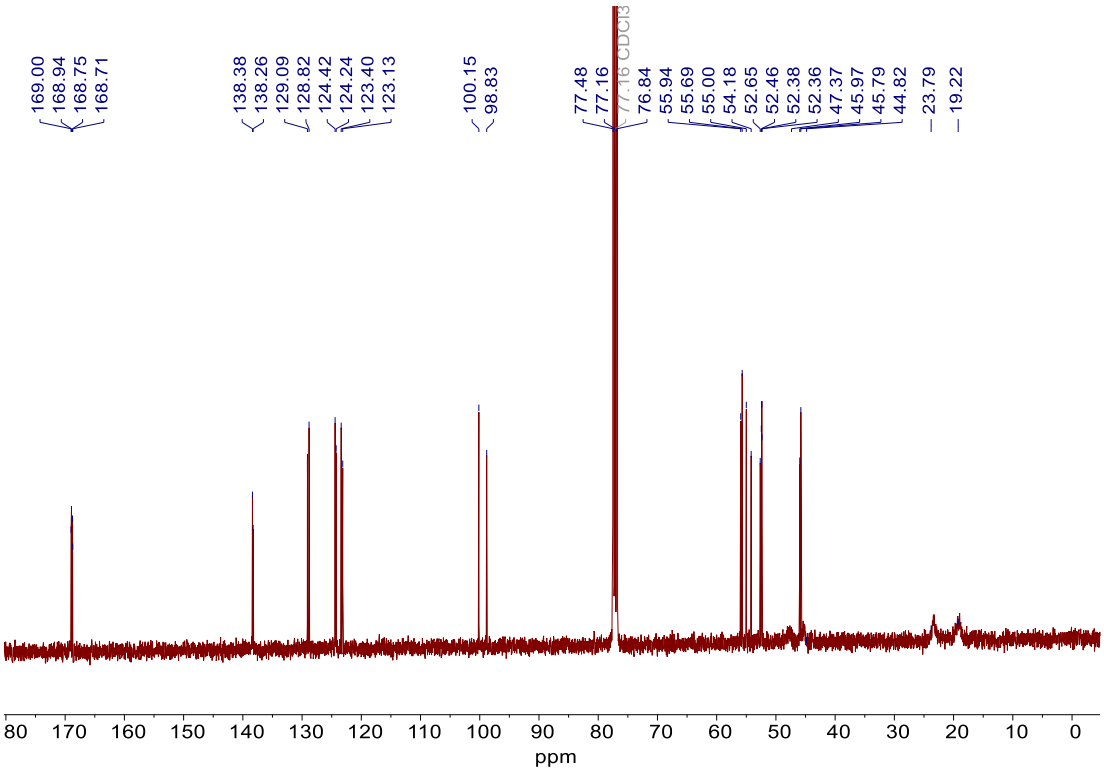
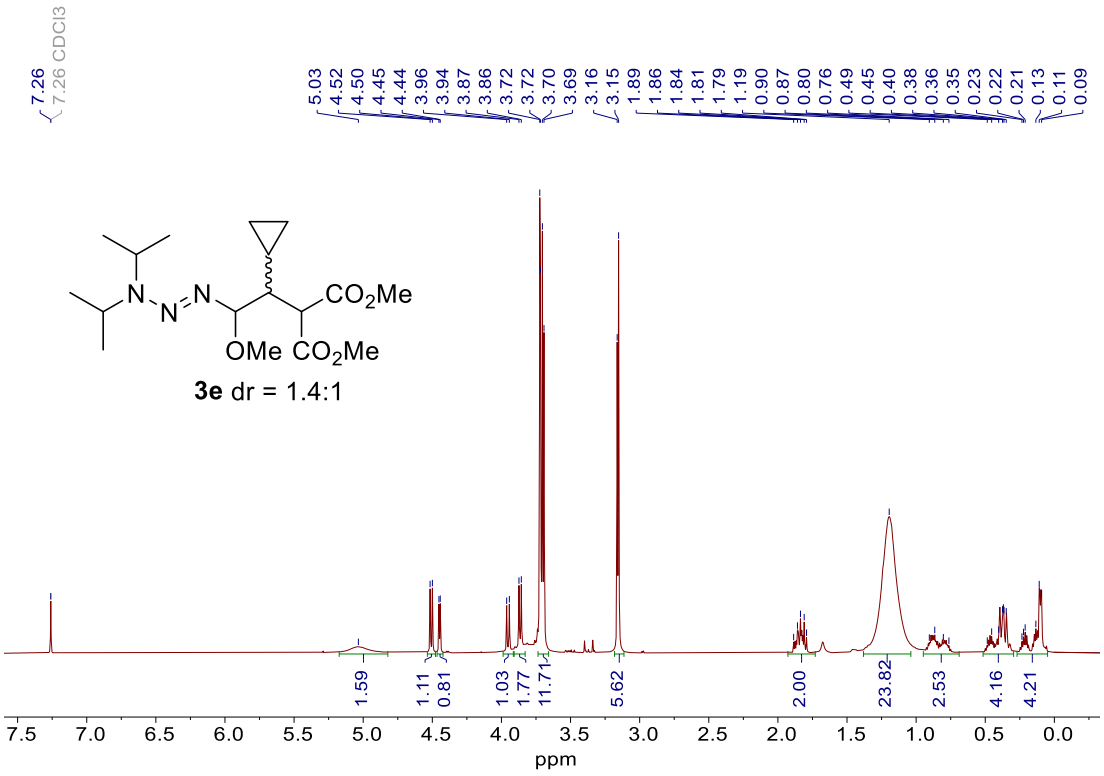


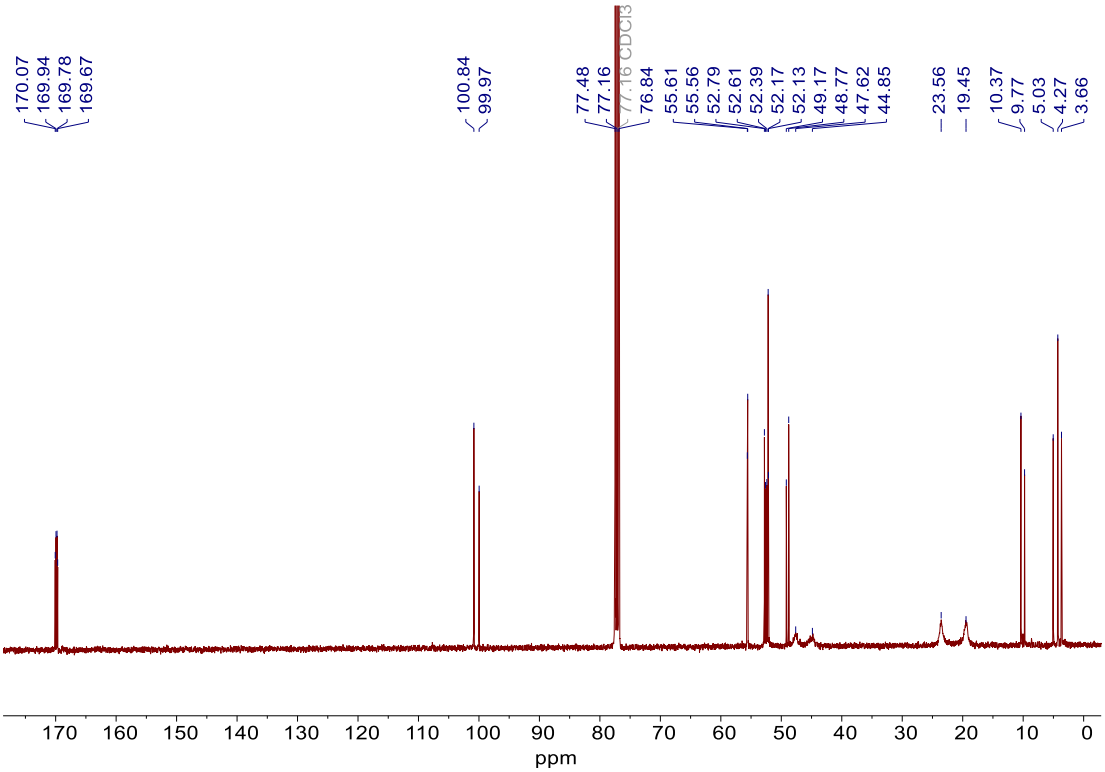
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**.



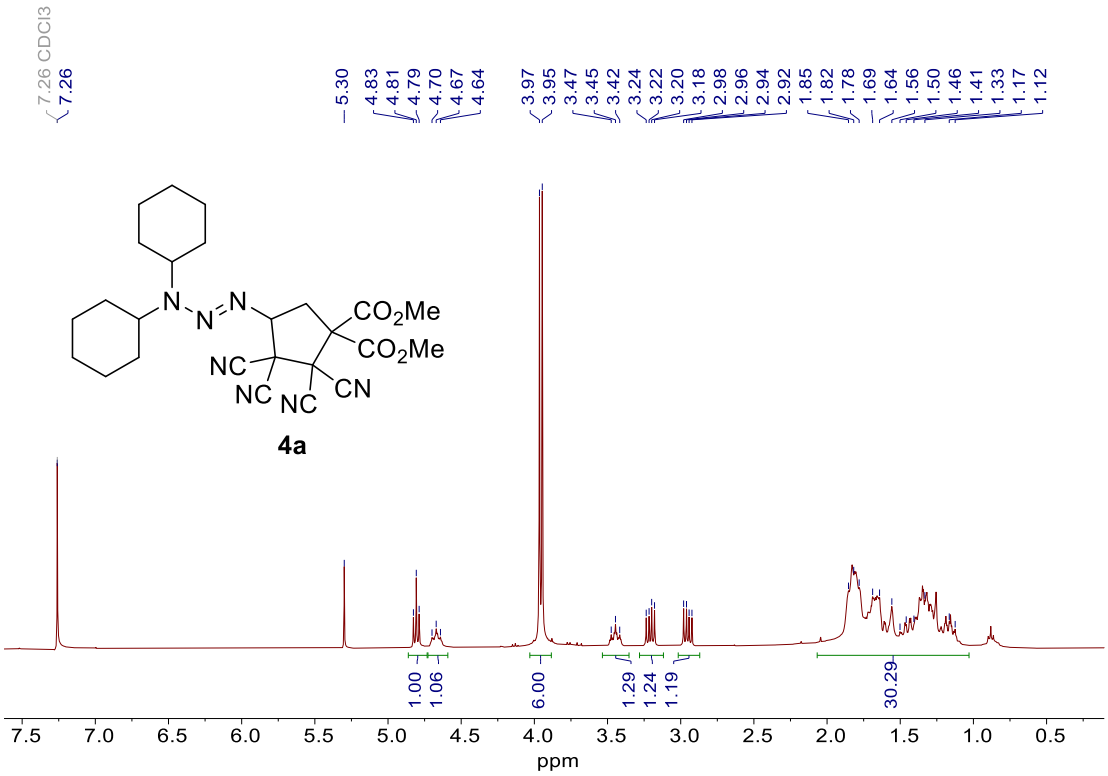
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3d**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**.



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3e**.



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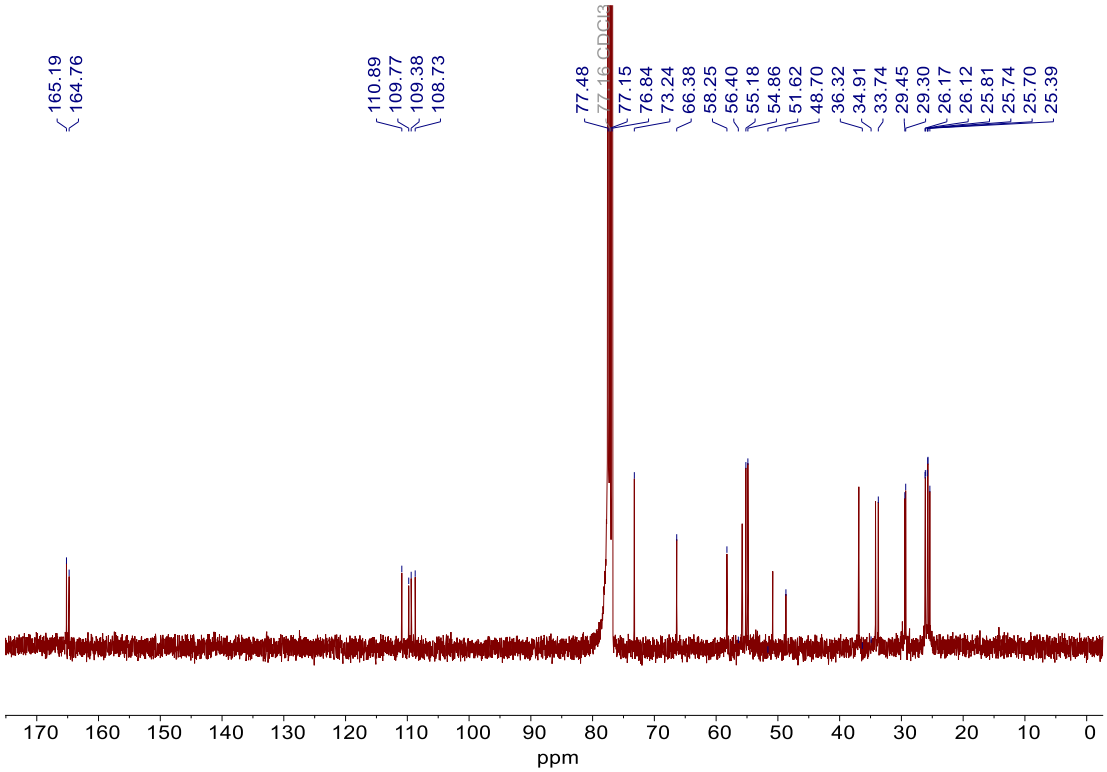
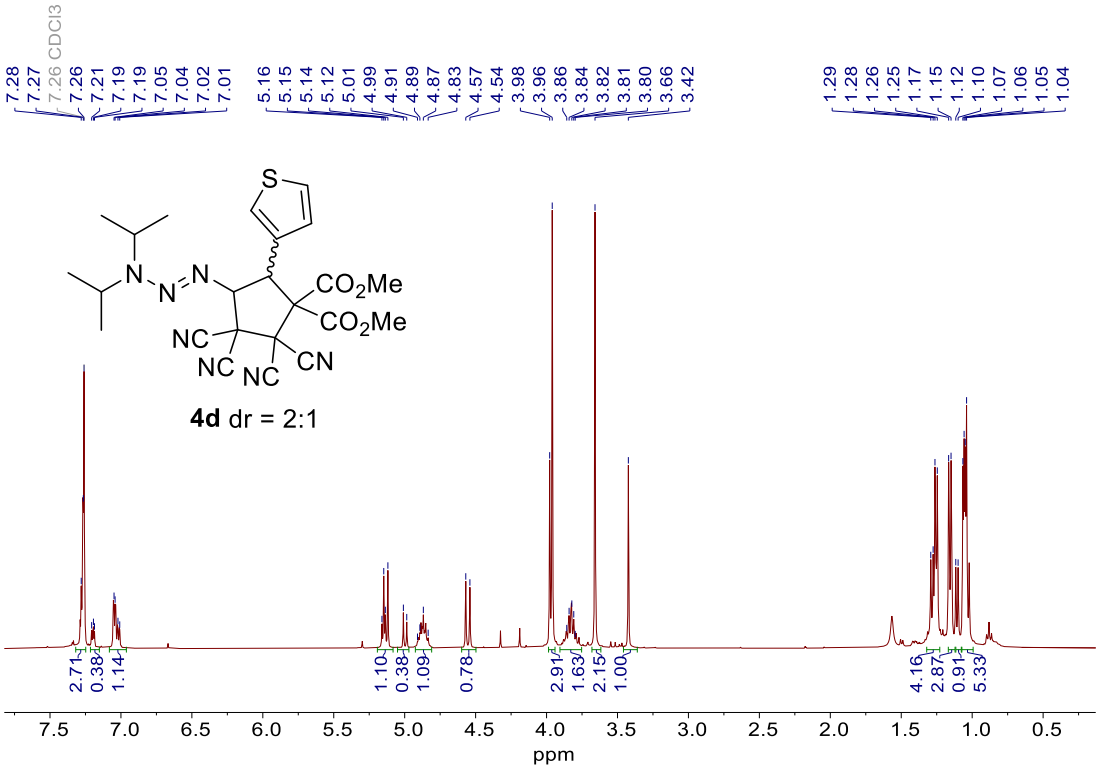
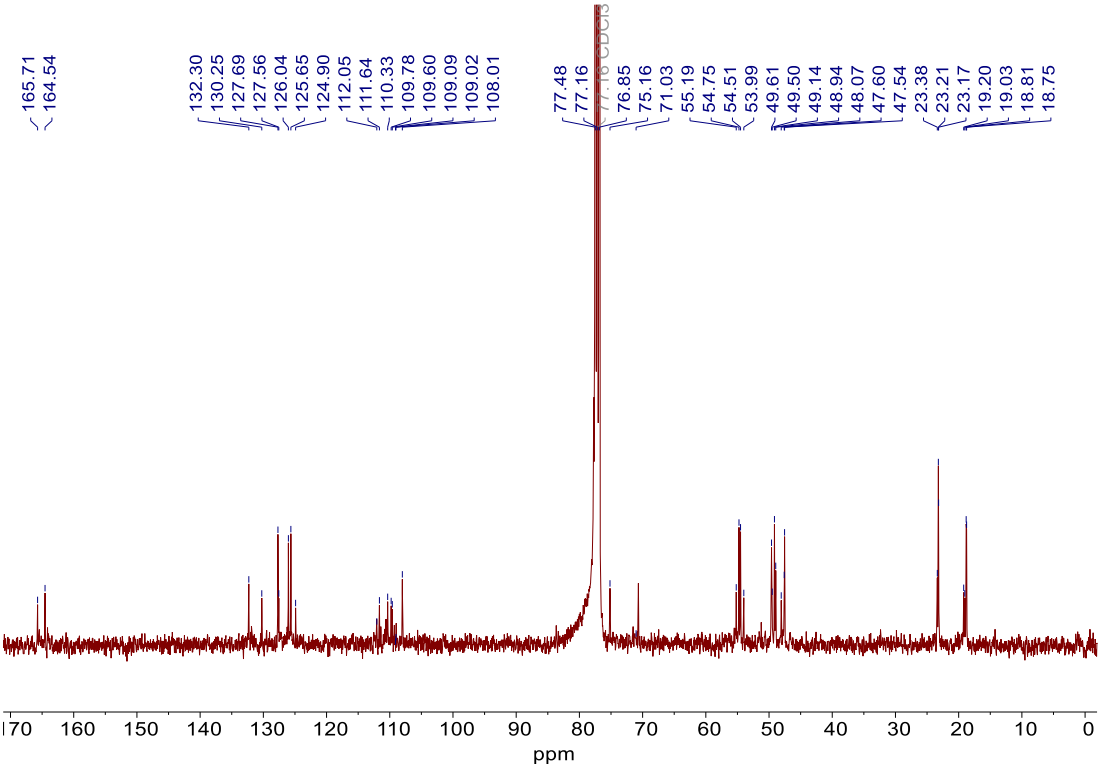


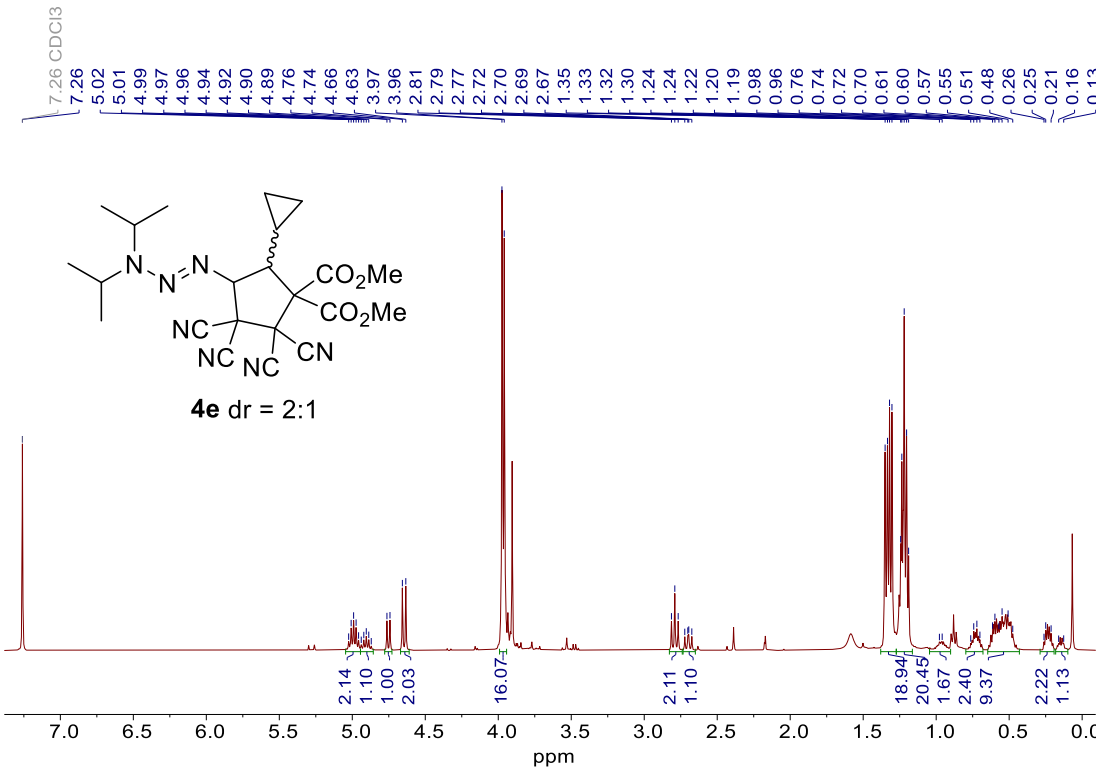
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4a**.



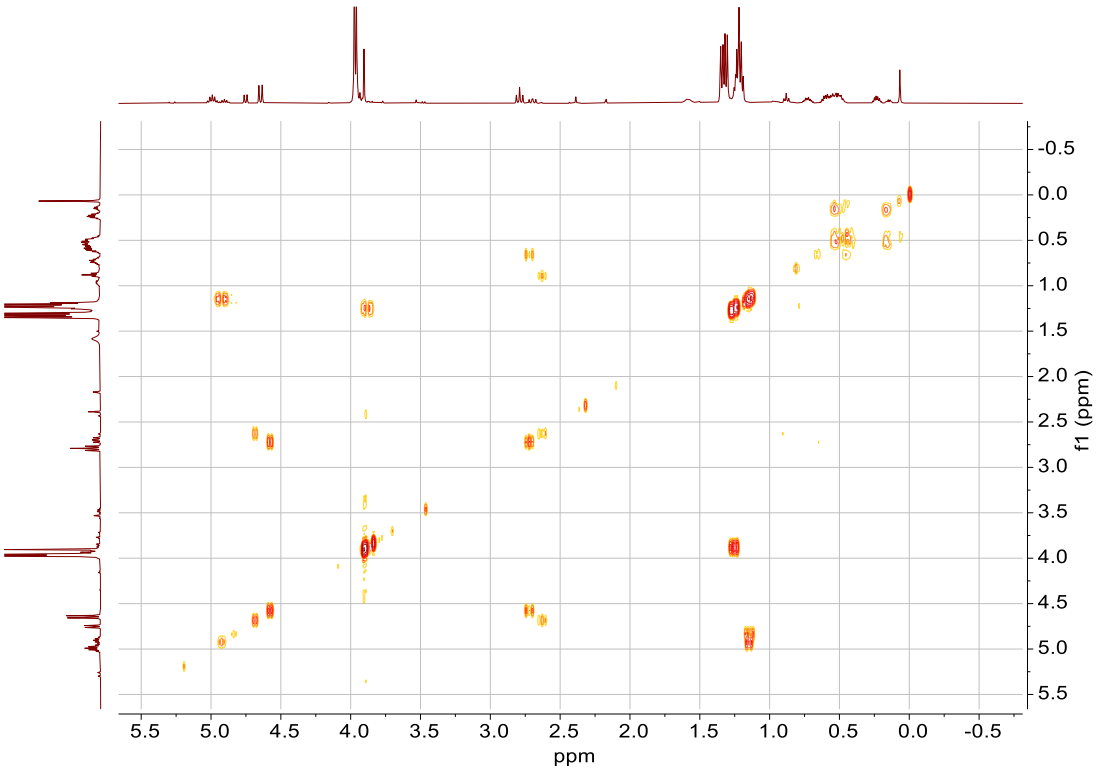
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**.



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4d**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**.



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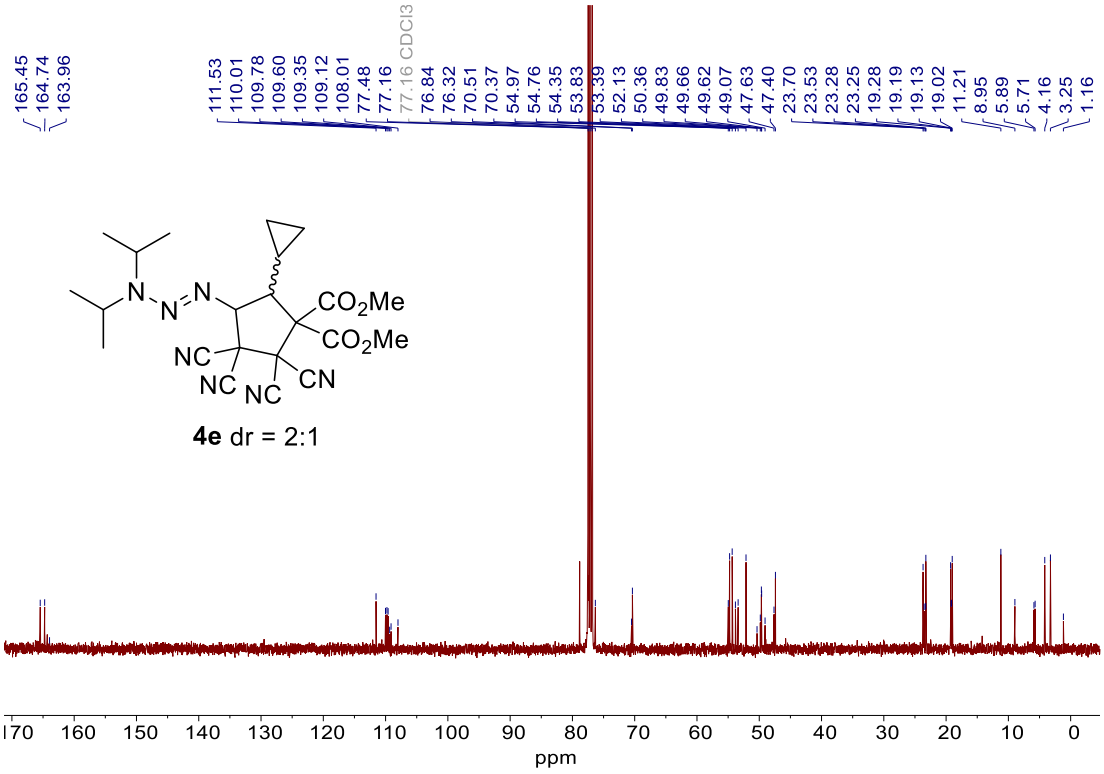
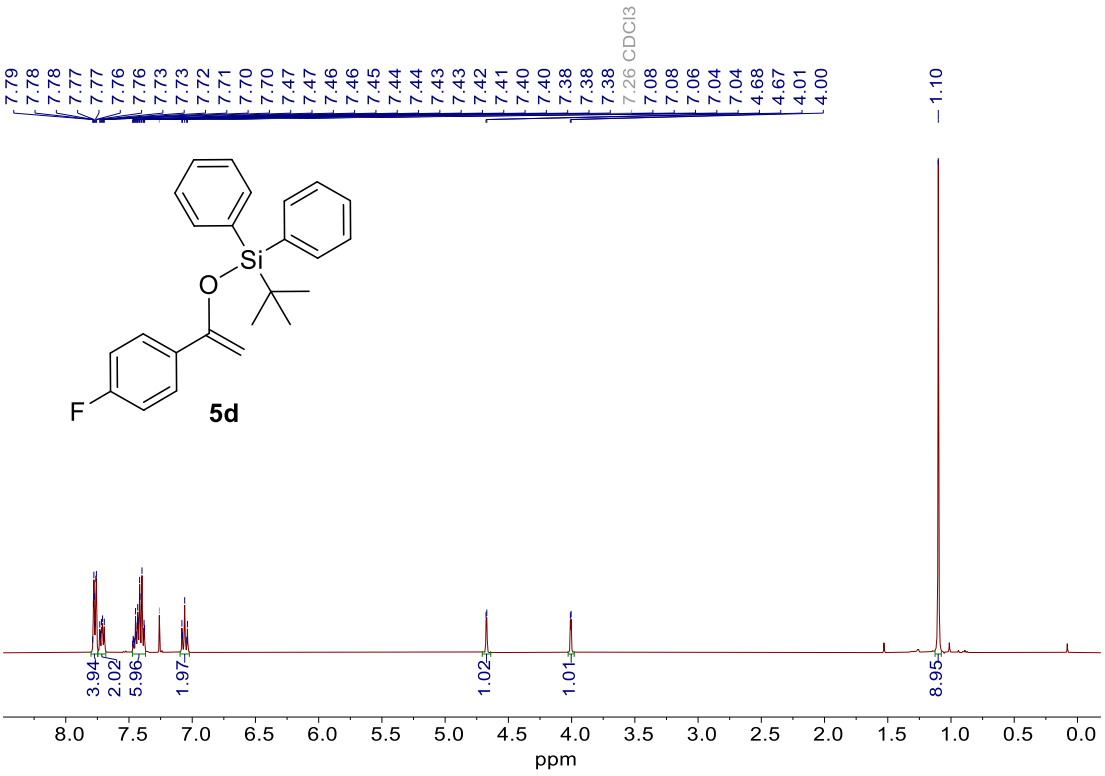
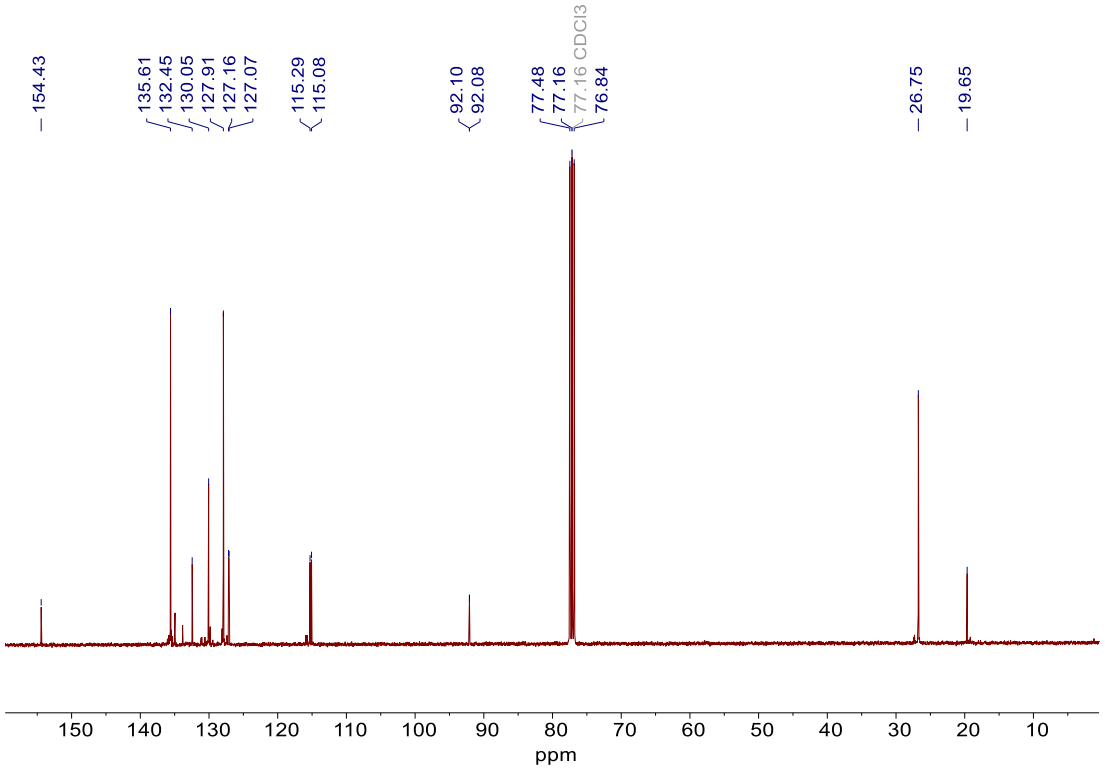


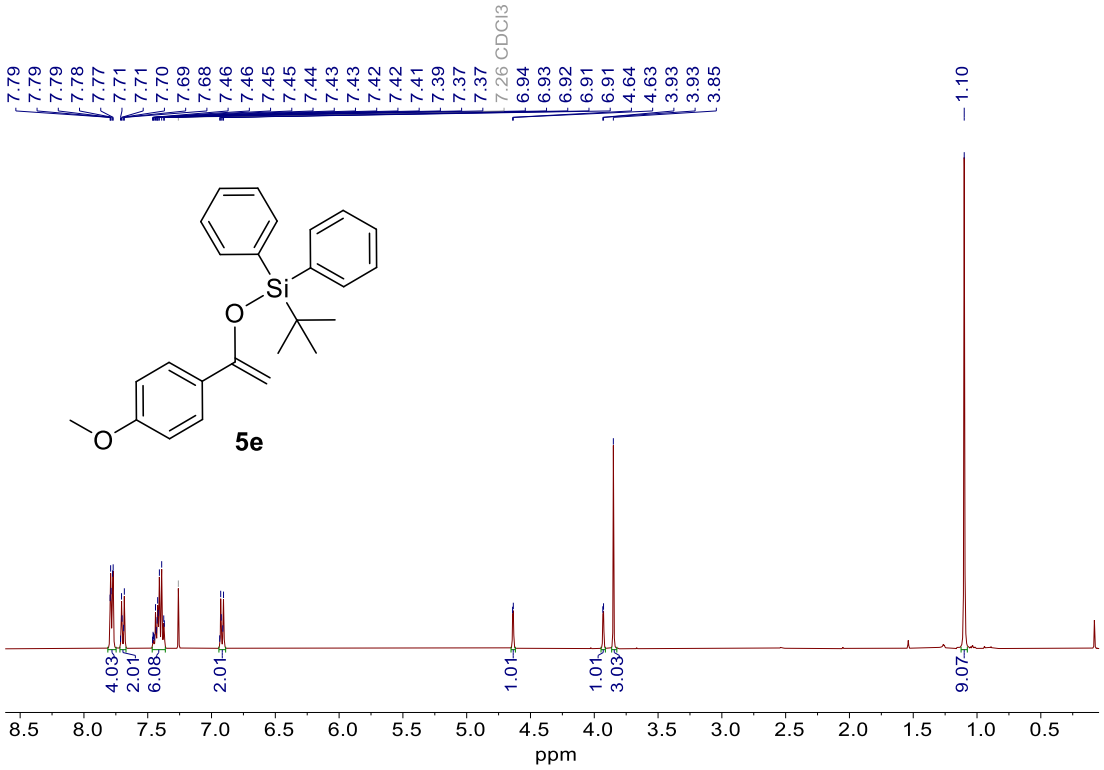
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4e**.



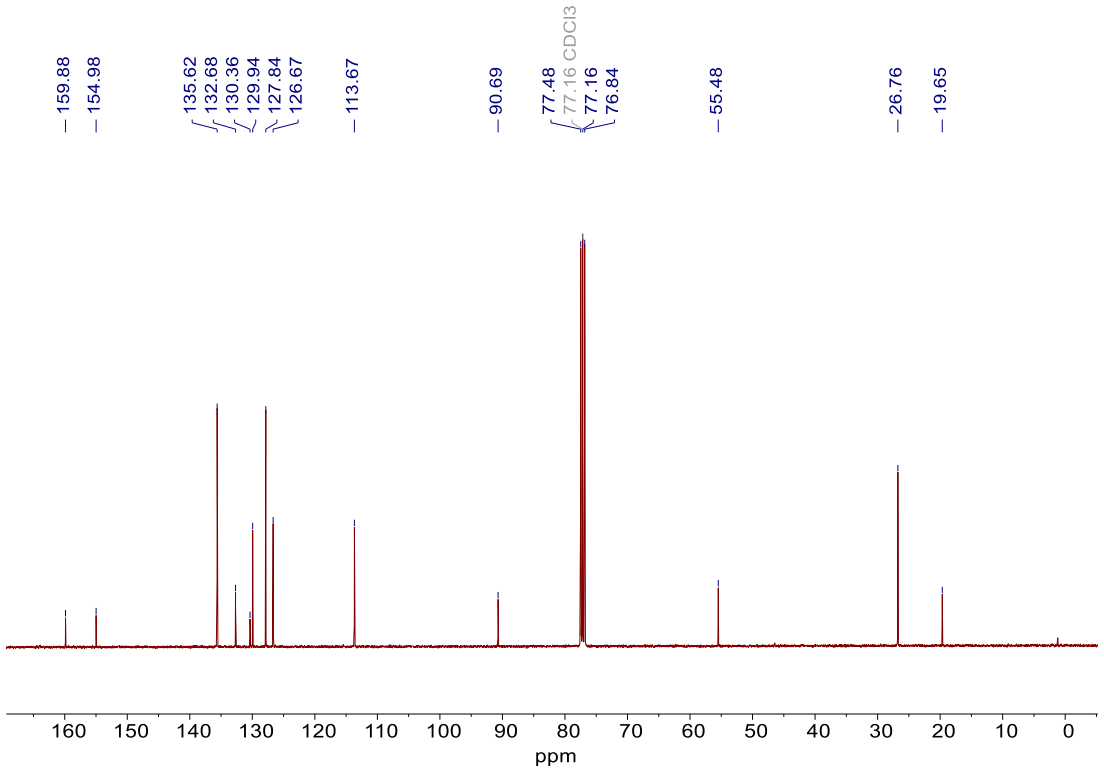
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5d**.



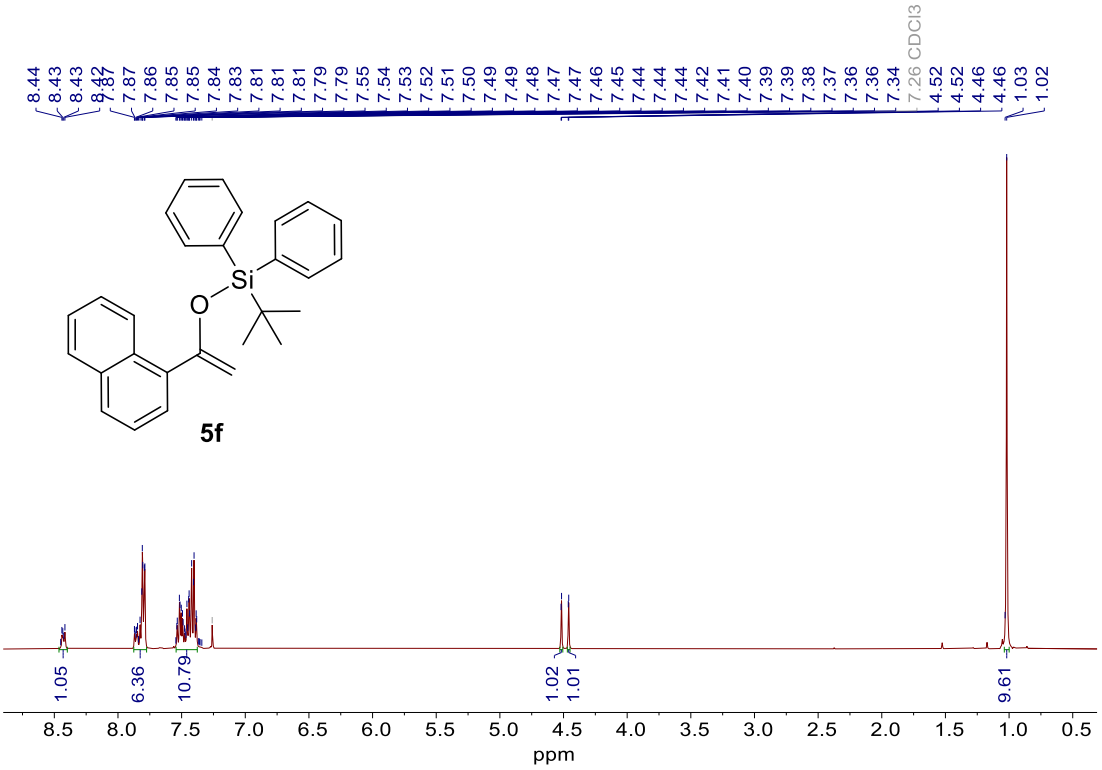
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **5d**.



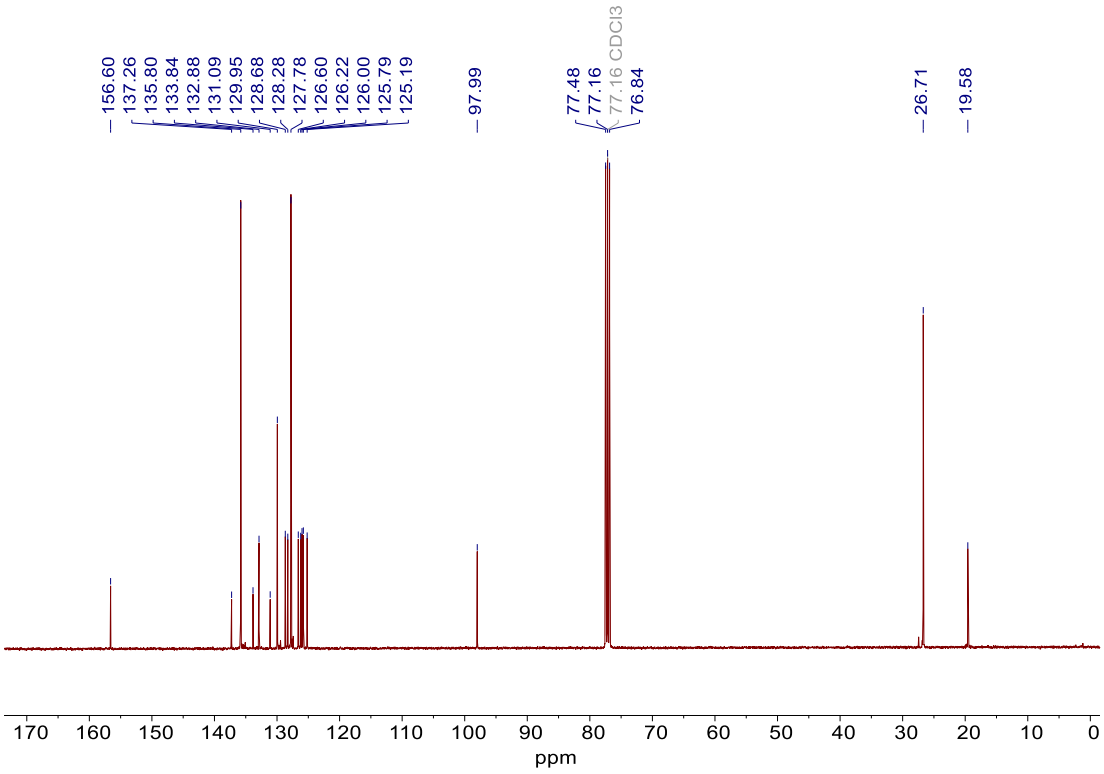
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5e**.



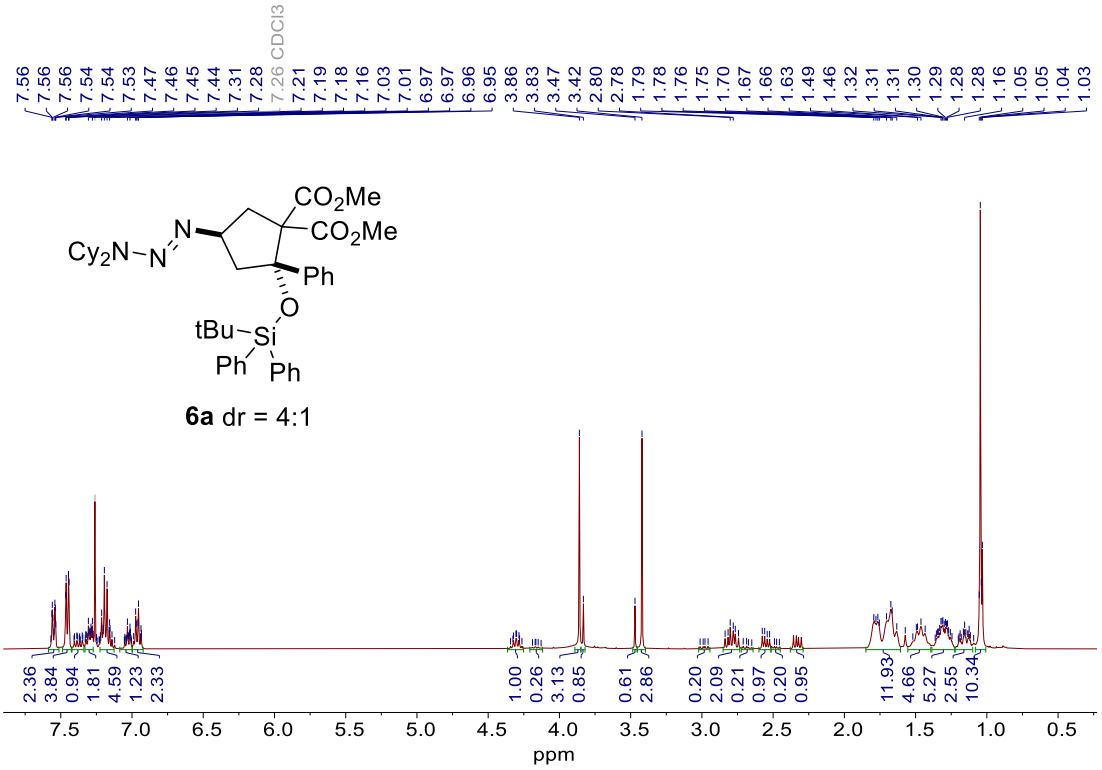
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **5e**.



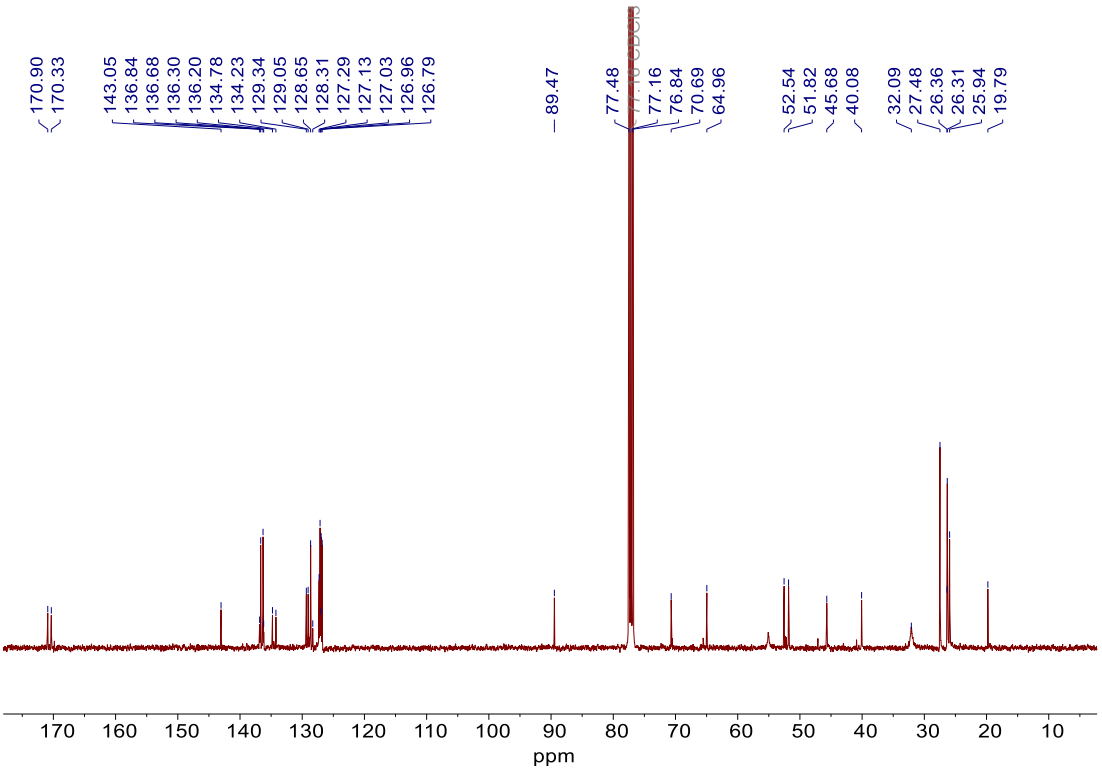
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5f**.



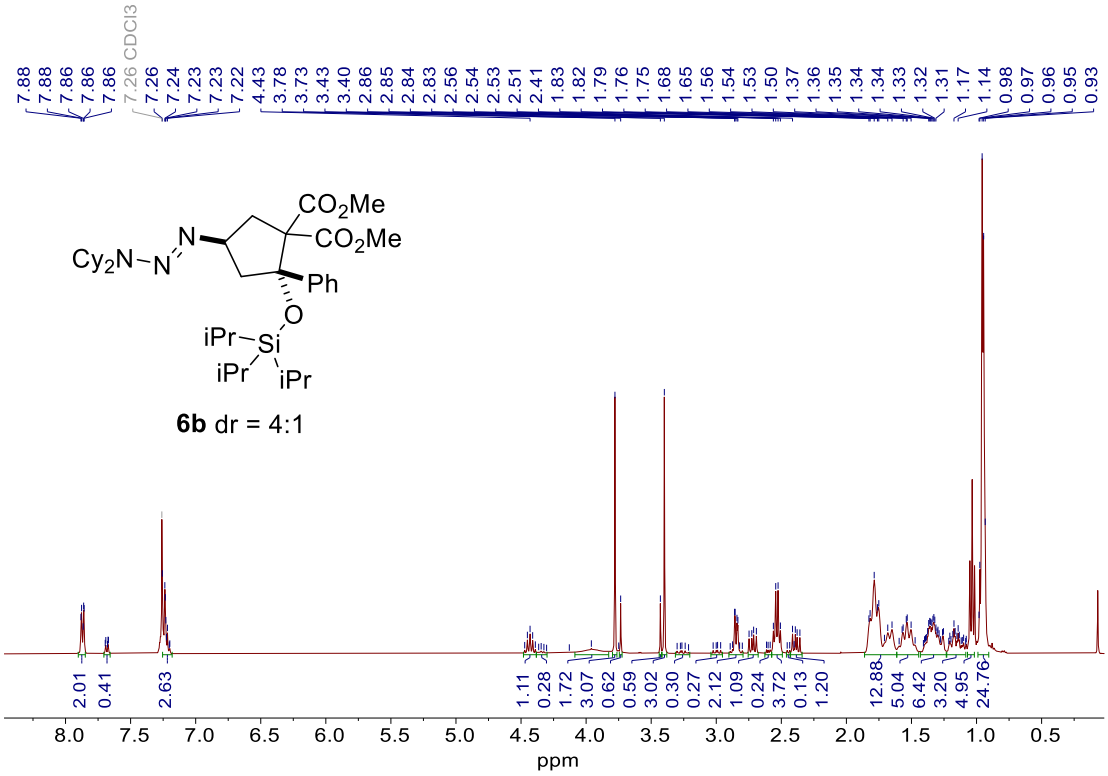
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **5f**.



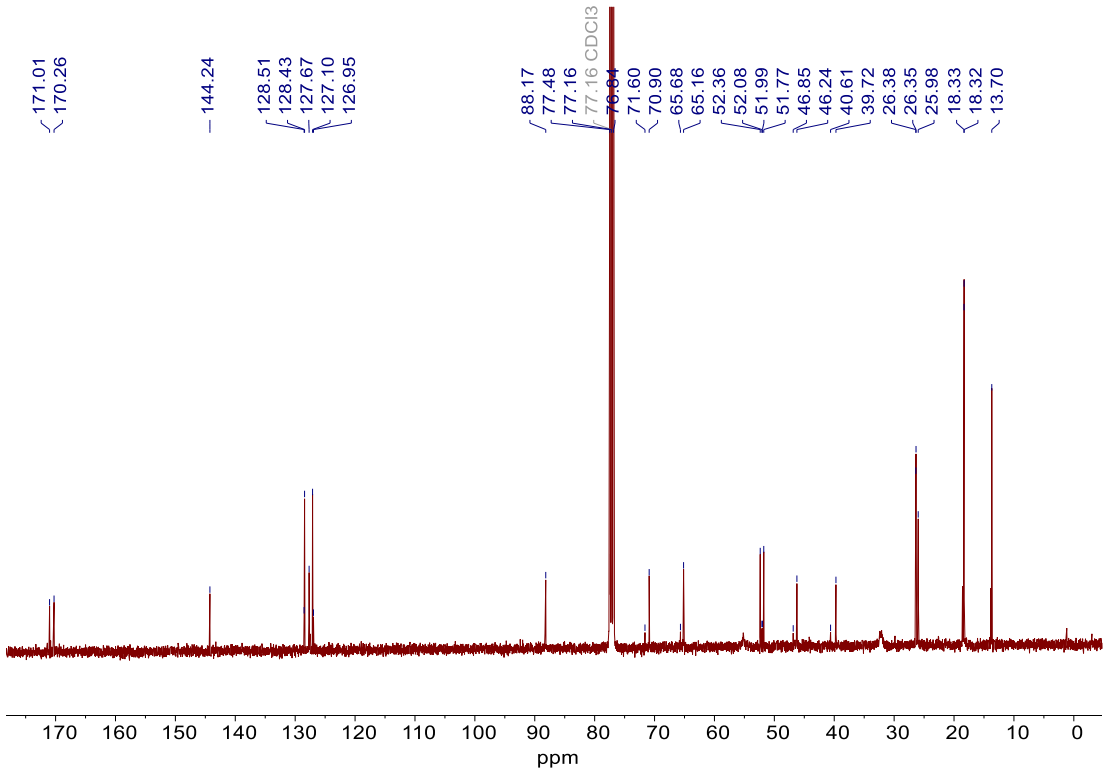
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6a**.



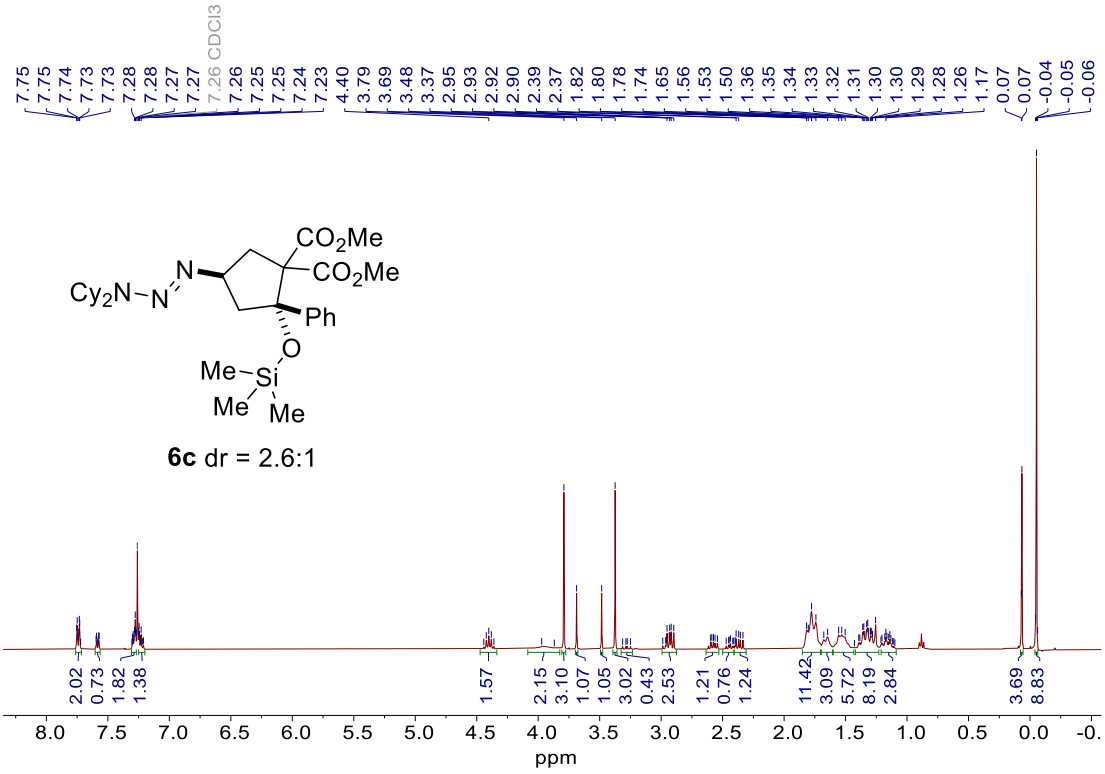
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **6a**.



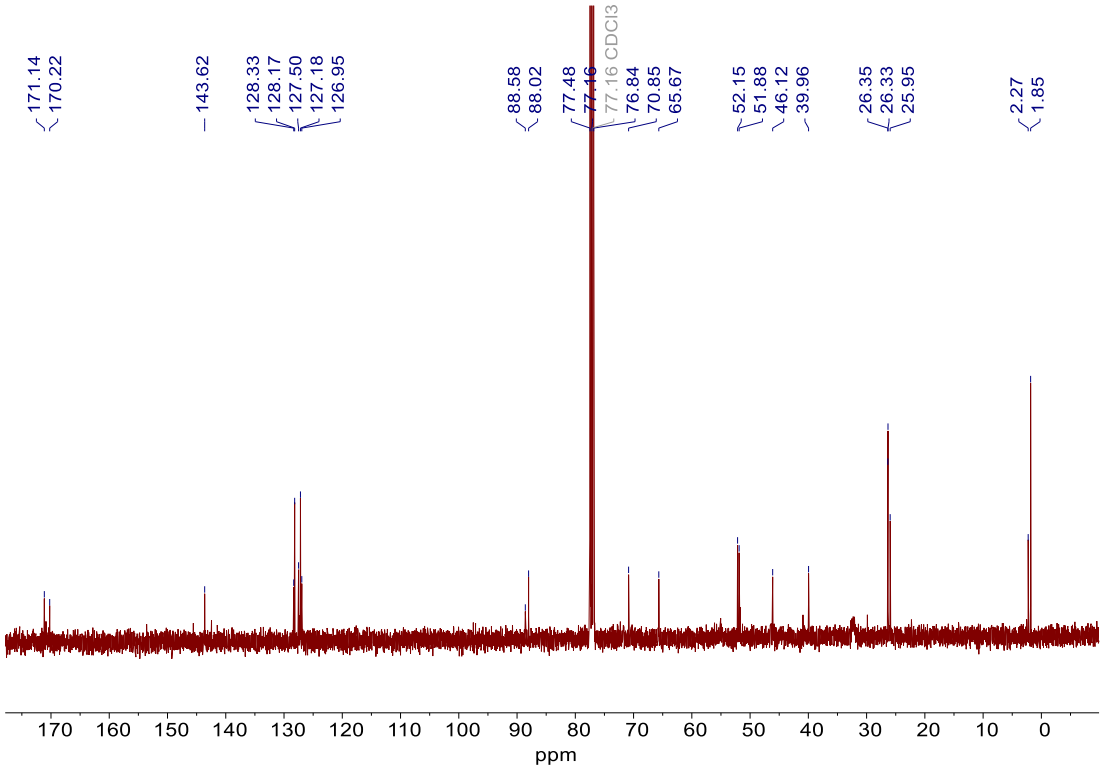
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6b**.



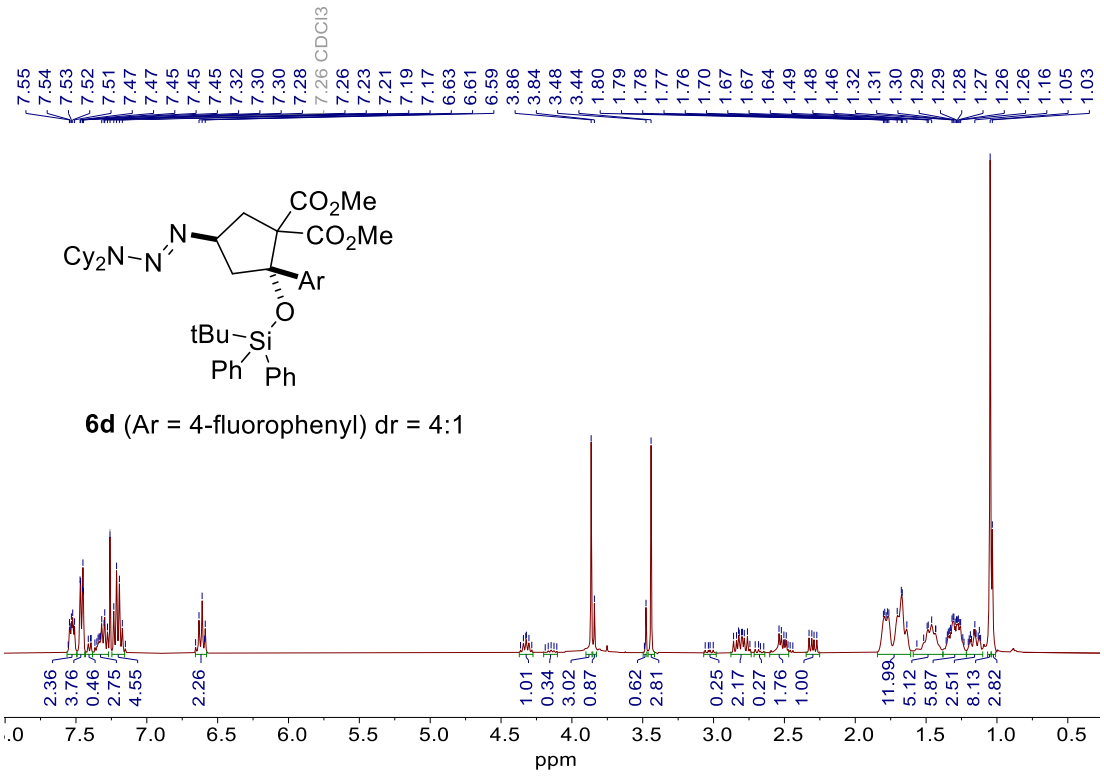
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **6b**.



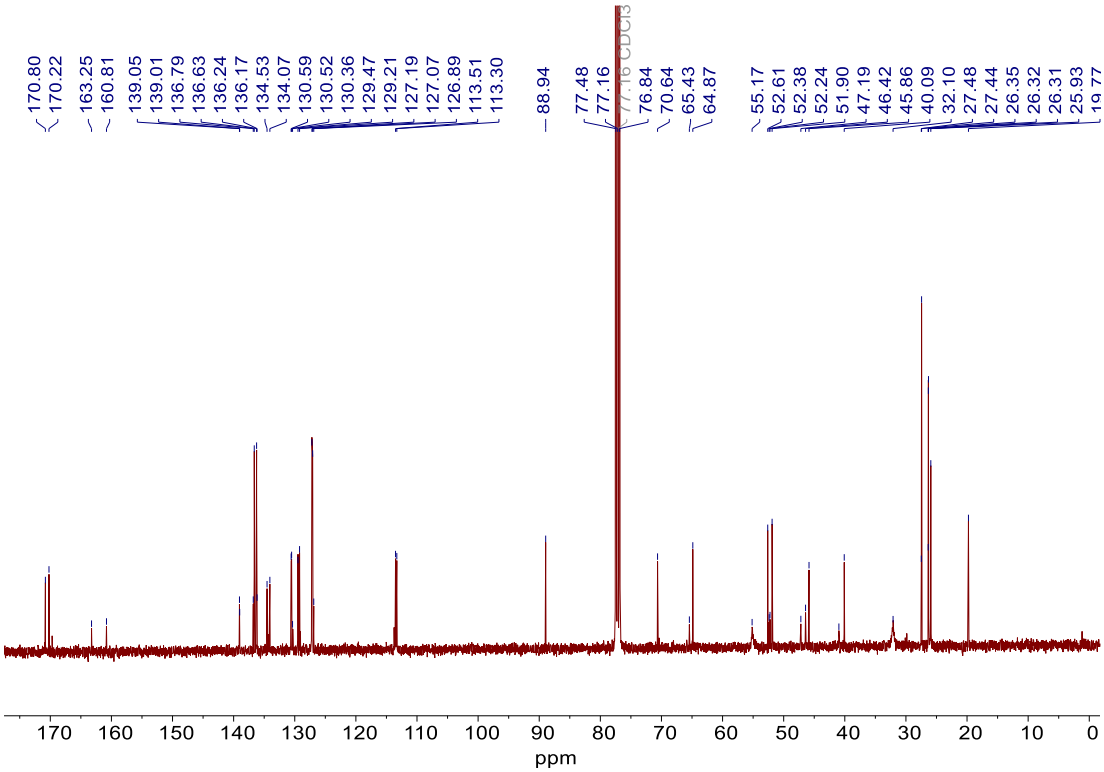
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6c**.



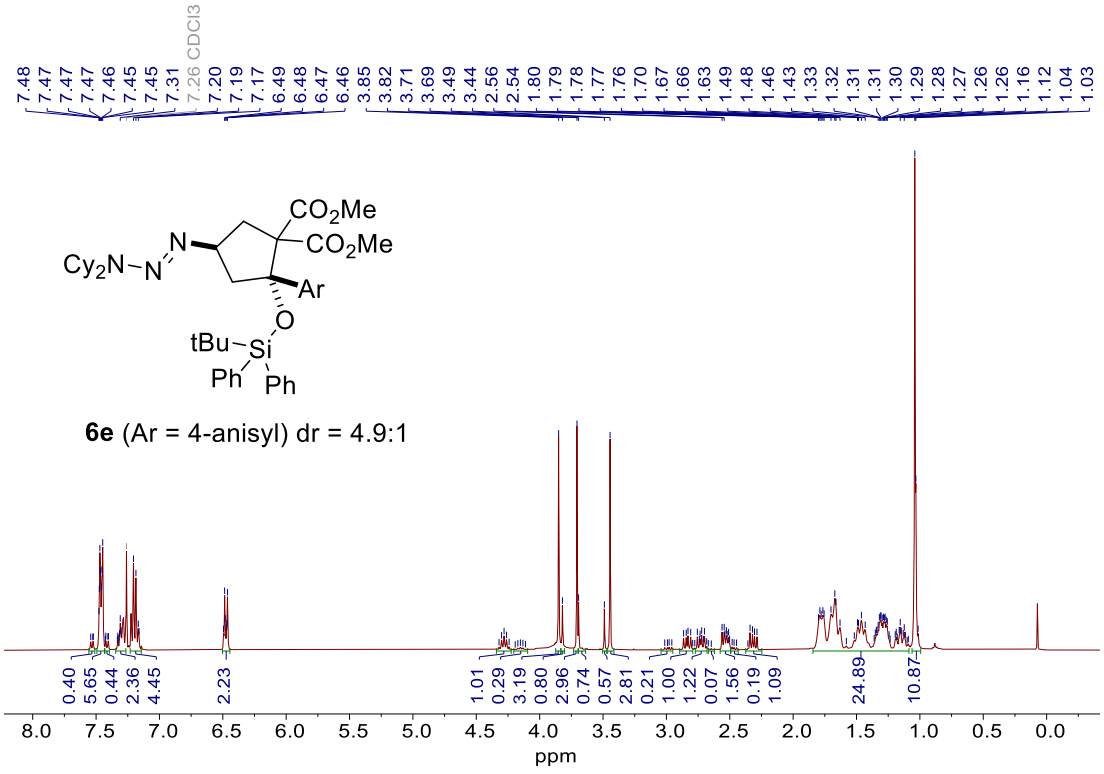
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **6c**.



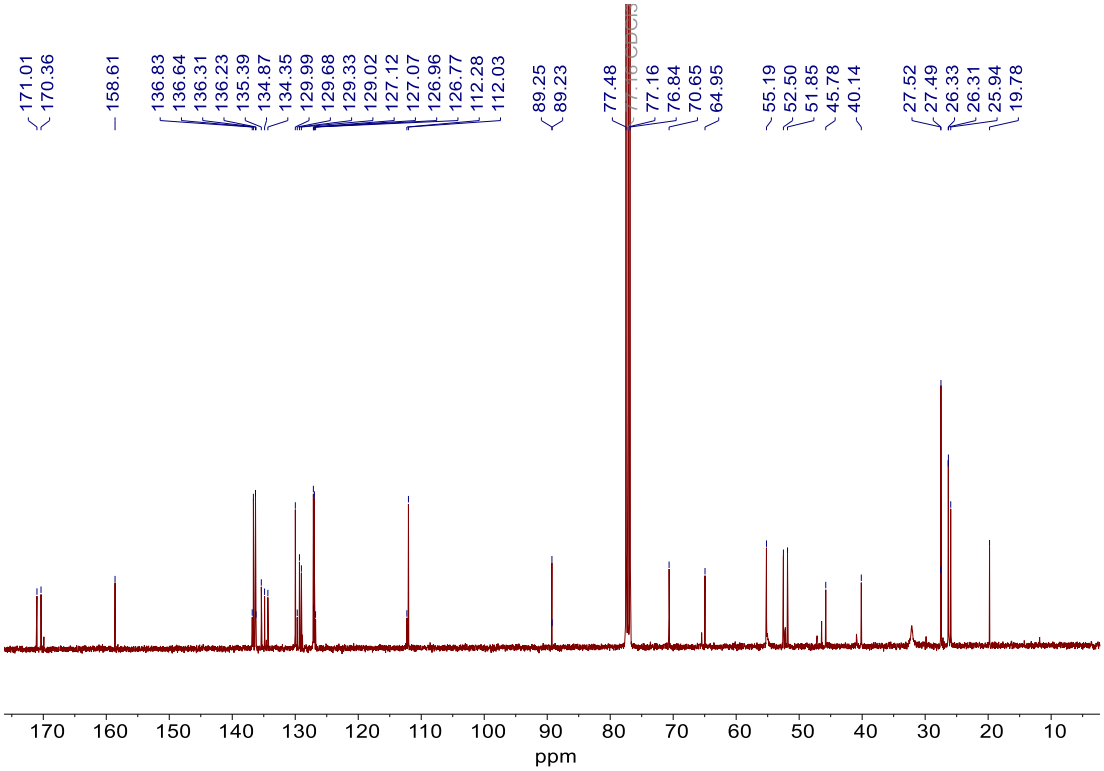
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6d**.



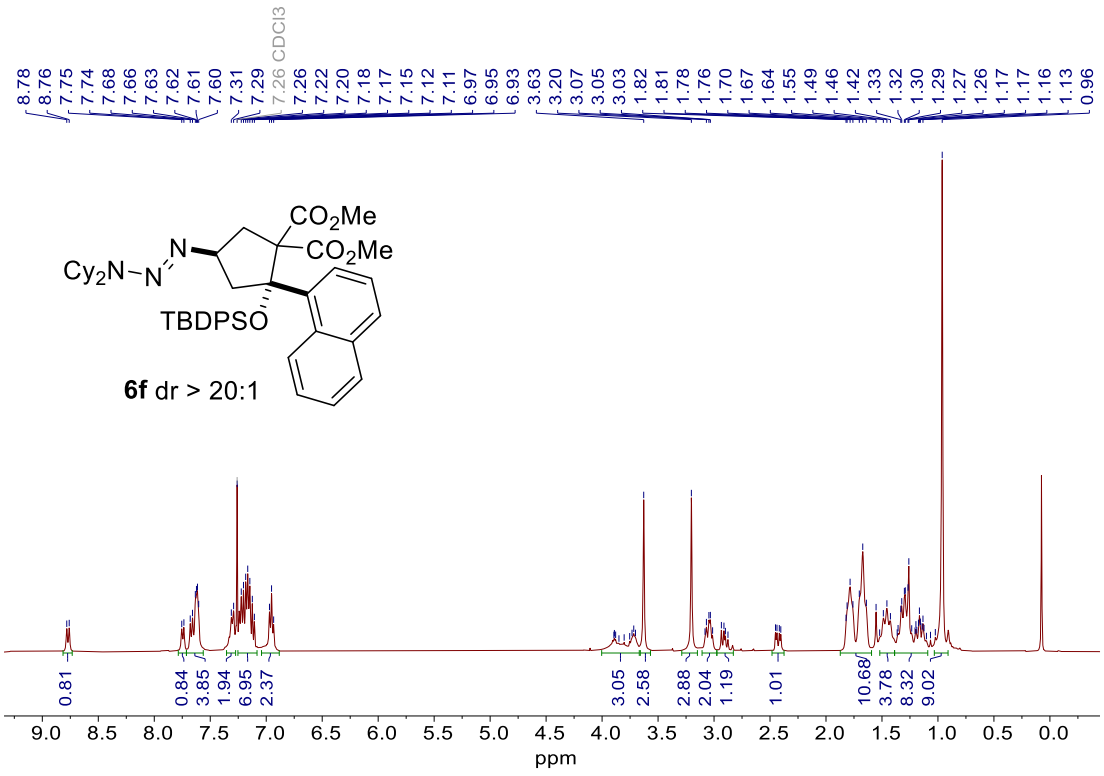
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **6d**.



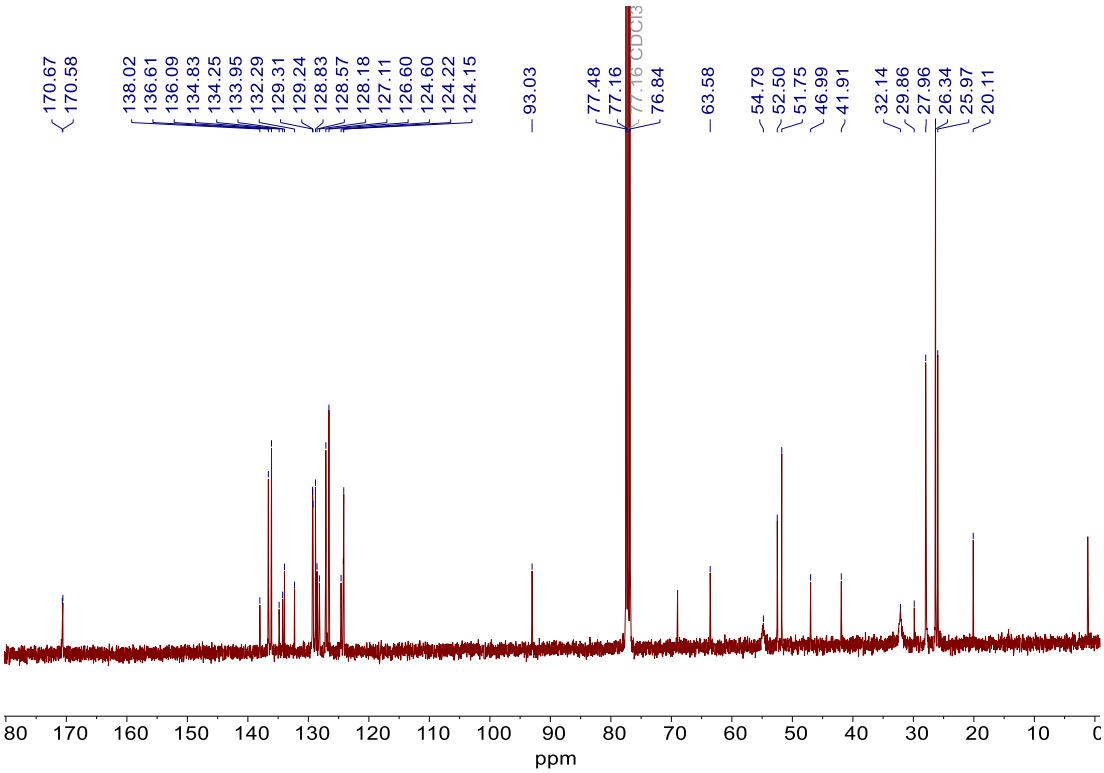
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6e**.



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **6e**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6f**.



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **6f**.

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