Synthesis of Quinolines via the Metal-Free Visible-Light-Mediated Radical Azidation of Cyclopropenes

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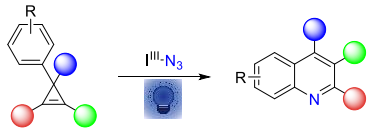
Supporting Information Placeholder

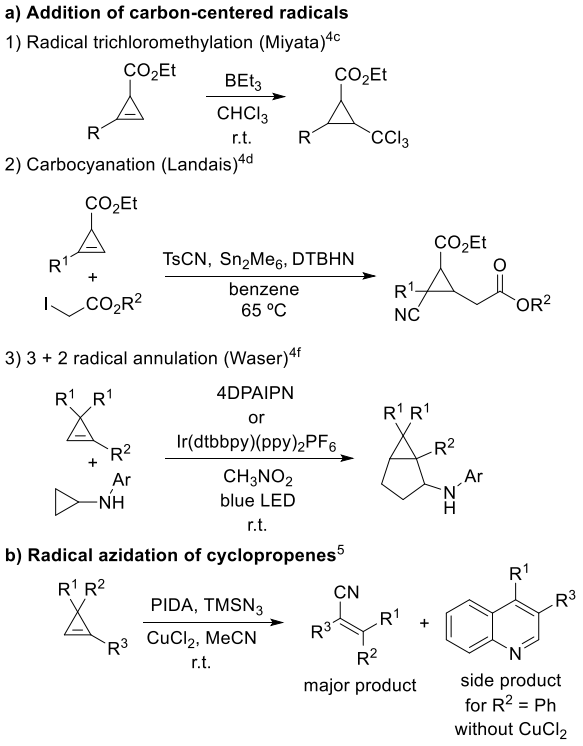


ABSTRACT: We report the synthesis of quinolines using cyclopropenes and an azidobenziodazolone (ABZ) hypervalent-iodine reagent as azide radical source under visible light irradiation. Multi-substituted quinoline products were obtained in 34-81% yield. The reaction was most efficient for 3-trifluoromethylcyclopropenes, affording valuable 4-trifluoromethylquinolines. The transformation probably proceeds through cyclization of an iminyl radical formed by addition of the azide radical on the cyclopropene double bond, followed by ring-opening and fragmentation.

As the smallest cyclic alkenes, cyclopropenes contain a substantial ring strain (ca 228 kJ. Mol-1).[1] Nevertheless, cyclopropenes bearing one or two substituents on the third position are generally stable. Due to the presence of the ring strain, cyclopropenes are useful intermediates in organic synthesis.[2] However, reports of reactions relying on the addition of radicals to cyclopropenes remain scarce, despite the fast growing use of radicals for alkene functionalization (Scheme 1a). The first example of such a reaction was a radical hydrostannylation reported by Nakamura in 1994.[3] Different research groups then reported the addition of carbon-centered radicals to the strained double bond,[4] resulting in hydrotrichloromethylation (eq. 1), carbocyanation (eq. 2), and 3+2 annulation of cyclopropenes (eq. 3) among other transformations (Scheme 1a).

In particular, the addition of heteroatom-centered radicals has been mostly neglected. Recently, our group reported the radical azidation of cyclopropenes to give alkenylnitriles (Scheme 1b).[5] During optimization of this work, small amounts of quinolines were observed as side products for aryl-substituted cyclopropenes, in the absence of $CuCl_2$. Quinolines have found numerous applications in medicine, industry,[6] and material sciences.[7] This heterocycle is present in the structure of many natural products[8] and synthetic bioactive compounds, including examples of approved drugs.[9] For instance, the structures of the antimalarial drugs quinine (**1**), chloroquine (**2**), and the acetylcholinesterase inhibitor tacrine (**3**) are based on the quinoline core (Scheme 2a). Many classical synthetic methods exist for the synthesis of quinolines, such as the Skraup, Friedlander, Doebner-von-Miller, Conrad-Limpach and Pfitzinger reactions.[10] Most of these methods require strongly acidic or basic conditions, not compatible with sensitive functionalities. Therefore, the use of radical-based methods for quinoline synthesis is particularly attractive.[11] A special subclass of such methods are transformations based on cyclizations of iminyl radicals onto the aryl ring.

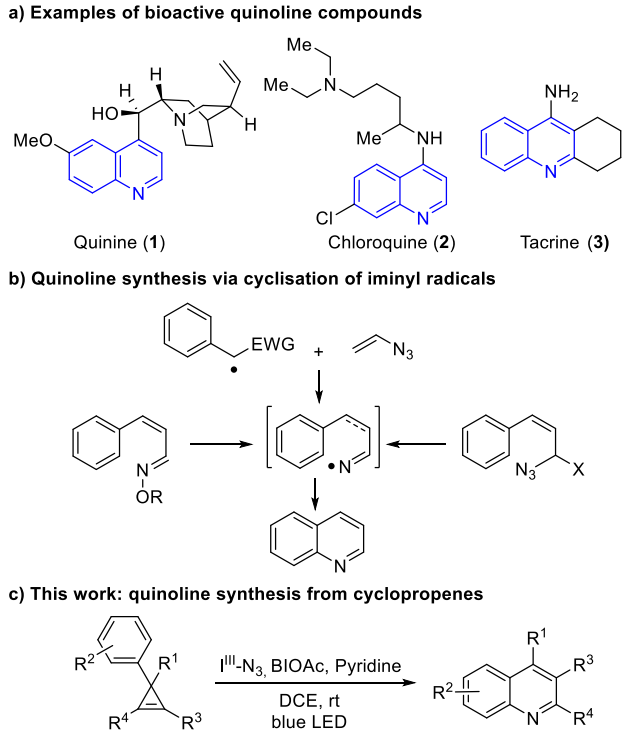
Scheme 1. Radical-mediated transformations of cyclopropenes



These radicals can be accessed via the homolysis of the N-O bond in oxime derivatives,[12] or by fragmentation of α-azidorad-

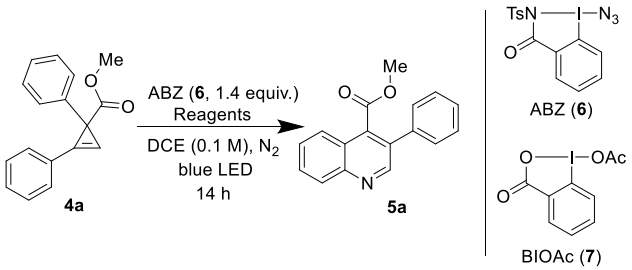
ical species (Scheme 2b).[13] Methods to generate the desired iminyl radical remain limited and new approaches are highly desirable to give access to different substitution patterns. Therefore, we decided to optimize the formation of the quinoline product resulting from the radical azidation of cyclopropenes (Scheme 1b), and report herein a new synthesis of quinolines from cyclopropenes, which is particularly efficient for the synthesis of trifluoromethylated derivatives (Scheme 2c).

Scheme 2. Quinolines: bioactive compounds and radical-based synthetic strategies



Using cyclopropene (**4a**) as the model substrate, we were pleased to find that the use of the safe hypervalent iodine reagent azidobenziodazolone (ABZ, **6**),[14] in the presence of the organic dyes 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)[15] and 1,3-dicyano-2,4,5,6-tetrakis(diphenylamino)-benzene (4DPAIPN)[16] in DCE gave the desired quinoline (**5a**) as the single product albeit in low yield (Table 1, entries 1, 2). A control experiment revealed that in the absence of a photocatalyst the reaction proceeded even slightly better (entry 3). However, we found that the reaction outcome was strongly dependent on the batch of ABZ we used, resulting in no product formation in the worst case. We thought that traces of iodine(III) impurities could act as initiator for the reaction. Indeed, the use of 20 mol% of acetoxybenziodoxolone (BIOAc, **7**)[17] as an additive made the reaction reproducible, giving the product in 34% yield (entry 4). No improvement was seen when using one equivalent of BIOAc (entry 5). The addition of bases to the reaction mixture was examined (entries 6-8), resulting in improved yield, with pyridine performing the best (entry 8). Despite numerous attempts to increase the reaction yield by fine-tuning the reaction conditions, no improvement could be achieved. As quinoline **5a** was the only product isolable in a substantial amount, we speculate that polymerization of cyclopropene **1a** was occurring as the main side reaction.

Table 1. Optimization of the reaction conditions with cyclopropene 4a[a]



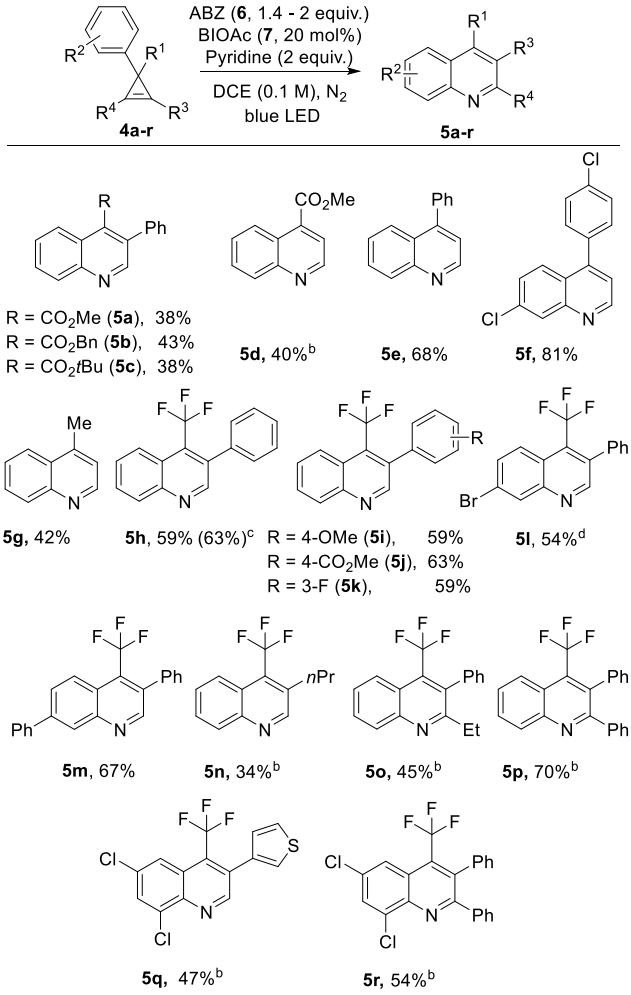
entry	reagents	yield[b]
1	4CzIPN (5 mol%)	28%
2	4DPAIPN (5 mol%)	26%
3	none	0-32%[c]
4	BIOAc (20 mol%)	34%
5	BIOAc (1 equiv.)	34%
6	BIOAc (20 mol%), K_2HPO_4 (2 equiv.)	40%
7	BIOAc (20 mol%), 2,6-lutidine (2 equiv.)	42%
8	BIOAc (20 mol%), pyridine (2 equiv.)	44%

[a]The reactions were performed on 0.1 mmol scale. [b]The yield was determined by ^{1}H NMR of the concentrated reaction mixture using CH_2Br_2 as an internal standard. [c]The reaction outcome was dependent on the batch of ABZ.

Despite the moderate yield obtained for the synthesis of **5a**, we turned to explore the scope of the reaction, as we expected that the reaction efficiency would be highly dependent on the structure of the cyclopropene. Starting materials were prepared by metal-catalyzed cyclopropenation of alkynes with diazo compounds, using Rh catalyst for terminal alkynes[18] and Ag catalyst for internal ones.[19] Cyclopropenes **4e-g** were prepared by 1,2-elimination of the corresponding cyclopropylbromides.[20] We started by evaluating the influence of the substituent at position 3 of the cyclopropene ring. Different ester substituted cyclopropenes **4a-d** were converted to the corresponding quinoline products **5a-d** in 38-43% yield. For mono-substituted cyclopropene **4d**, an increased amount of ABZ (**6**) and prolonged reaction time were required for full conversion. 3-Aryl (**4e, 4f**) and 3-alkyl (**4g**) substituted cyclopropenes were also found to be suitable substrates for the transformation. Aryl substituted quinolines **5e** and **5f** could be obtained in higher yields (68% and 81% respectively). To our delight, 3-trifluoromethyl cyclopropene **4h** was converted to quinoline **5h** in 59% yield. The trifluoromethyl group is very popular in medicinal chemistry.[21] Despite the attractiveness of such heterocycles, to the best of our knowledge, there are only two reported examples of the synthesis of 3-aryl, 4-trifluoromethylquinolines without the substituent at position 2 of the heterocyclic ring.[22] Therefore, we focused on the synthesis of trifluoromethyl-substituted quinolines for further exploring the scope of the transformation. Different substituents on the aryl groups in 1 and 3 positions of the cyclopropenes were tolerated (products **5i-5m)**, including electron-rich, electron-poor and halogen substituents. 1-Alkyl-substituted cyclopropene **4n** gave quinoline **5n** in 34% yield. Interestingly, tetrasubstituted cyclopropenes **4o** and **4p** gave a single regioisomer of quinoline **5o** and **5p**. This method can also be used for the synthesis of tetra- and pentasubstituted quinolines **5q** and **5r**. 1,2-Dialkylcyclopropenes were found to be inert to

reaction conditions, representing a limitation of our methodology. Scale-up of the transformation was straightforward: **5h** was obtained in 63% on a 1.5 mmol scale.

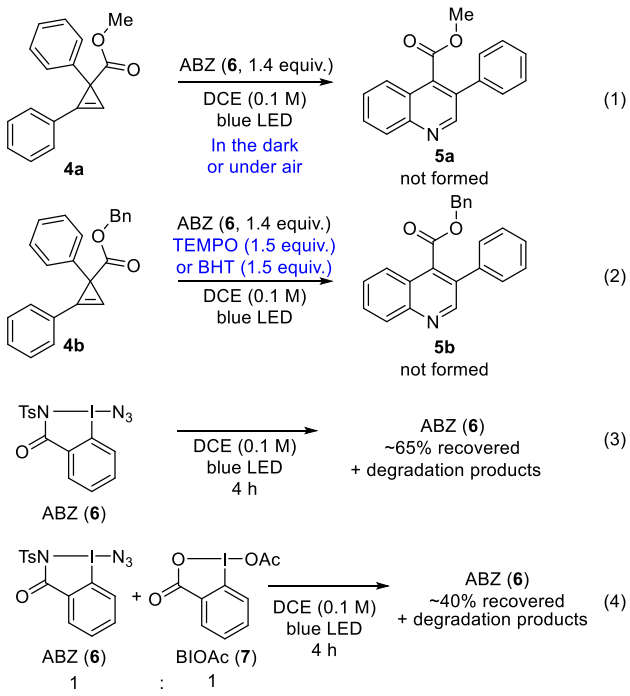
Scheme 3. Substrate scope[a]



[a] Reaction conditions: 0.2 mmol of cyclopropene, 1.4 equiv. ABZ (**6**), 2 equiv. of pyridine, 20 mol% BIOAc (**7**), DCE (0.1 M), room temperature, 14 h. [b] Reaction conditions: 0.2 mmol of cyclopropene, 2 equiv. ABZ (**6**), 2 equiv. of pyridine, 20 mol% BIOAc (**7**), DCE (0.1 M), room temperature, 48 h. [c] 1.5 mmol scale. [d] 0.1 mmol scale.

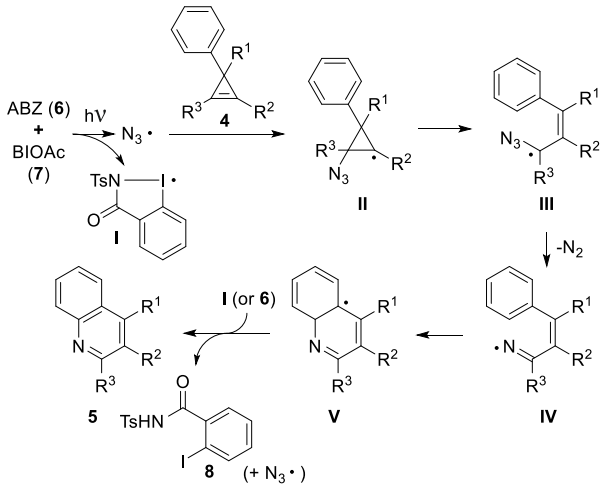
Several experiments were then performed in order to get insight into the reaction mechanism (Scheme 4). It was found that the reaction does not proceed in the dark or under air (Eq. 1). Performing the reaction in the presence of TEMPO and BHT as radical scavengers fully inhibits the formation of the product **5b** (Eq. 2). It was found that ABZ (**6**) slowly degrades under blue LED irradiation (Eq. 3), while the presence of BIOAc significantly accelerates this process (Eq. 4). Other control experiments showed that cyclopropene **2a** as well as BIOAc (**7**) are stable when irradiated by blue LEDs as a solution in DCE.

Scheme 4. Control experiments



Based on these results and our previous investigations,[5] we can suggest the following mechanism for the transformation (Scheme 5). Irradiation of ABZ (**6**) in presence of BIOAc (**7**) would result in the formation of an excited form, prone to homolytic cleavage of the weak I-N_3 bond, forming an iodanyl radical **I** and an azidyl radical. Once formed, the azidyl radical would add to the cyclopropene double bond forming the reactive cyclopropyl radical **II**, which would undergo an electrocyclic ring-opening to give the α-azidoallyl radical **III**. α-azido radicals are known to quickly lose N_2 forming the corresponding iminyl radicals **IV**,[23] which could then cyclize to the adjacent arene ring giving rise to the intermediate **V**. Subsequent oxidation-deprotonation of **IV** with either iodanyl radical **I** or ABZ (**6**) would result in formation of product **2** and tosylamide **8**. In the latter case, an azido radical would also be generated, leading to a chain process.

Scheme 5. Mechanism proposal



In summary, a protocol for the metal-free radical azidation of cyclopropenes leading to the formation of quinolines was developed. The hypervalent iodine reagent ABZ (**6**) was used as the source of azidyl radical under visible-light irradiation. The resulting transformation represents the first method for the synthesis of quinolines via the addition of a radical to a cyclopropene. The overall synthetic strategy is highly convergent as, starting from different alkynes and diazo compounds for accessing the cyclopropenes, multi-substituted quinolines can be obtained, especially valuable trifluoromethylated heterocycles. These results further demonstrate the potential of radical-based reactions with cyclopropenes as useful methods in organic synthesis.

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Supporting information

Synthesis of quinolines via metal-free visible-light-mediated radical azidation of cyclopropenes

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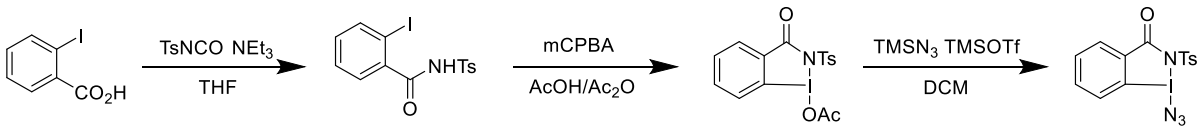
1. General information

HPLC grade or technical grade solvents were used for flash chromatography. For non-air-sensitive reactions, analytical or reagent grade solvents purchased from Merck or Sigma-Aldrich were used unless specified. THF, Et_2O, CH_3CN, toluene, hexane and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 10 ppm, Karl-Fischer titration). Solvents were degassed by bubbling with a balloon of argon when mentioned. Reagents were purchased from Sigma-Aldrich, Acros, TCI, Fluorochem, Fluka, VWR or Merck, unless specified. Chromatographic purification was performed as flash chromatography using Silicycle silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure or using Biotage Isolera Spektra One with pre-packaged silica cartridges purchased from Buchi, models: Sepacore or GraceResolve (4 g, 12 g, 25 g, 40g, 80g, 120g). TLC was performed on Merck silica gel 60 F254 TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, p-anisaldehyde stain. ^{1}H NMR spectra were recorded on a Brucker DPX-400, 400 MHz, in chloroform-d, DMSO-d6 and CD_3CN. All signals are reported in ppm using the residual solvent signal as internal reference (chloroform-d: 7.26 ppm, DMSO-d6: 2.50 ppm, CD_3CN: 1.96 ppm). The data is reported as (multiplicity, coupling constants in Hz, integration, interpretation) using these abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, bs = broad signal. ^{13}C NMR spectra were carried out with 1H decoupling on a Brucker DPX-400, 101 MHz. All signals are reported in ppm using the residual solvent signal as internal reference (chloroform-d: 77.0 ppm or DMSO-d6: 39.5 ppm). Infrared spectra were obtained on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported in cm-1 as (w = weak, m = medium, s = strong). 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 LTQOrbitrap Elite instrument (Thermofisher) operated in the positive ionization mode. Reactions under blue LED irradiation were performed in test tubes (1.0 to 10 mL) which were hold using a rack for test-tubes placed at the centre of a crystallization flask. On this flask were attached the blue LEDs (RUBAN LED 5MÈTRES-60LED/M-3528BLEU-IP65 with Transformateur pour Ruban LED 24W/2A/12V, bought directly on RubanLED.com). The distance between the LEDs and the test tubes was approximatively 5 cm. Long irradiation resulted in temperature increasing up to 35°C during overnight reactions.

2. Synthesis of starting materials

2.1 Synthesis of azidating reagent (ABZ)



9 10 11 6

1-Azido-2-tosyl-1,2-dihydro-3*H*-1λ3-benzo[*d*][1,2]iodazol-3-one(ABZ)(6)

Following a modified reported procedure[1], to a solution of 2-iodobenzoic acid (**9**) (10.0 g, 40.3 mmol, 1.00 equiv) and tosyl isocyanate (7.95 g, 40.3 mmol, 1.00 equiv) in THF (115 mL) NEt_3(4.08 g, 40.3 mmol, 1.00 equiv) was added dropwise. The reaction mixture was stirred at r.t. for 2h. The reaction mixture was diluted with EtOAc(175ml) and washed with HCl(1N) (2x70ml) and brine(100ml). The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum to give 2-iodo-N-(4-methylphenyl)sulfonylbenzamide(**10**) (17.8g, 90% purity, 39.9 mmol, 99% yield) as a yellow thick oil. The compound was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H, N*H*), 8.01 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.80 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar*H*), 7.43−7.31 (m, 4H, Ar*H*), 7.10 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1H, Ar*H*), 2.44 (s, 3H, ArC*H*$_3$) ppm. Spectral data of the obtained compound is corresponding to the reported values[1].

A solution of 2-iodo-N-(4-methylphenyl)sulfonylbenzamide(**10**) (17.8 g, 44.5 mmol, 1.00 equiv) and 3-chloroperbenzoic acid acid (9.97 g, 44.5 mmol, 1equiv, ca 75% purity) in acetic acid (150 mL) and acetic anhydride(150 mL) was heated at 80°C for 72h. The reaction mixture was diluted with ether(140ml), cooled to -20°C. The formed solid was filtered off, washed with ether and dried under vacuum to give 3-oxo-2-tosyl-2,3-dihydro-1*H*-1λ3-benzo[*d*][1,2]iodazol-1-yl acetate (**11**)(9.00 g, 95% purity, 19.6 mmol, 44% yield) as a white solid. The compound was used without further purification.

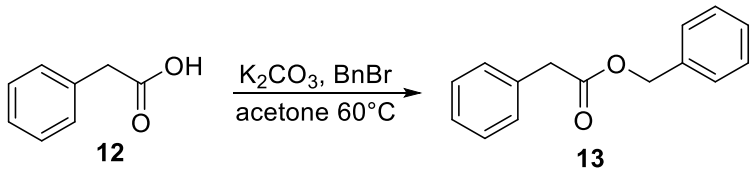
^{1}H NMR (400 MHz, d_6-DMSO) δ 8.02−7.95 (m, 2H, Ar*H*), 7.95−7.89 (m, 2H, Ar*H*), 7.86 (dd, *J* = 8.8, 0.9 Hz, 1H, Ar*H*), 7.80−7.71 (m, 1H, Ar*H*), 7.44 (d, *J* = 8.1 Hz, 2H, Ar*H*), 2.38 (s, 3H, ArC*H*$_3$), 2.26 (s, 3H, COC*H*$_3$) ppm. Spectral data of the obtained compound is corresponding to the reported values[1].

Caution: For safety reasons, the reaction was carried out behind an antiblast shield. To a solution of **11** (2.76 g, 6.00 mmol, 1.00 equiv) in dichloromethane (30.0 mL), cooled to 0°C azido(trimethyl)silane (1.04 g, 9.00 mmol, 1.50 equiv) was added dropwise, followed by 1 drop of trimethylsilyl trifluoromethanesulfonate (6.67 mg, 30.0 µmol, 0.00500 equiv). The reaction mixture was stirred at 20°C for 60 minutes, then cooled back to 0°C. The reaction mixture was dilutedwith cold pentane(12ml), stirred for 5 minutes, then filtered. The precipitate was washed with cold pentane(10ml) and dried on the frite to give ABZ (**6**) (2.05 g, 4.61 mmol, 77% yield) as a light-yellow solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.17 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar*H*), 8.03−7.93 (m, 2H, Ar*H*), 7.93−7.87 (m, 2H, Ar*H*), 7.75 (td, *J* = 7.4, 0.9 Hz, 1H, Ar*H*), 7.46−7.37 (m, 2H, Ar*H*), 2.38 (s, 3H, ArC*H*$_3$) ppm. Spectral data of the obtained compound is corresponding to the reported values[1].

2.2 Synthesis of diazo compounds

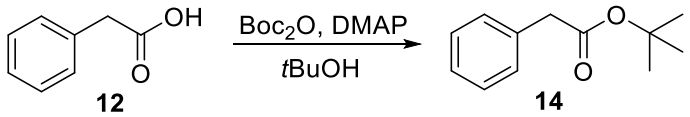
[1] Alazet, S.; Preindl, J.; Simonet-Davin, R.; Nicolai, S.; Nanchen, A.; Meyer, T.; Waser, J., *J. Org. Chem.* **2018,** *83* (19), 12334-12356.

Benzyl 2-phenylacetate (13)



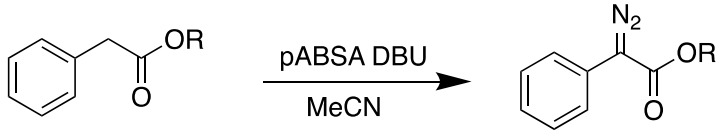
Following a reported procedure[2], a solution of 2-phenylacetic acid(**12)** (3.00 g, 22.0 mmol, 1.00 equiv), potassium carbonate (3.35 g, 24.2 mmol, 1.10 equiv) and bromomethylbenzene (4.52 g, 26.4 mmol, 1.20 equiv) in acetone (45.0 mL) was heated at reflux overnight. The reaction mixture was concentrated under vacuum, diluted with water(60ml) and extracted with DCM(260ml). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give benzyl 2-phenylacetate (**13**) (5.47g, 90% purity, 21.8 mmol, 99% yield) which was used without further purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (m, 10H, Ar*H*), 5.15 (s, 2H, PhCH_2O), 3.68 (s, 2H, C(O)CH_2Ph). Spectral data of the obtained compound is corresponding to the reported values[2].

***Tert*-butyl 2-phenylacetate (14)**



Following a reported procedure[3], a solution of 2-phenylacetic acid (1.00 g, 7.34 mmol, 1.00 equiv), *tert*-butyl (2-methylpropan-2-yl)oxycarbonyl carbonate (3.37 g, 15.4 mmol, 2.10 equiv) and N,N-dimethylpyridin-4-amine (269 mg, 2.20 mmol, 0.300 equiv) in 2-methylpropan-2-ol (20.0 mL) was heated at 30°C overnight. The reaction mixture was concentrated under vacuum to give crude *tert*-butyl 2-phenylacetate (**14**) (950 mg, 90% purity, 4.94 mmol, 67% yield), which was used without further purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.15 (m, 5H, Ar*H*), 3.53 (s, 2H, CH_2), 1.44 (s, 9H, CH_3). Spectral data of the obtained compound is corresponding to the reported values[3].

General procedure for the preparation of diazo compounds(GP1)



Following a reported procedure[4], DBU (1.6 equiv.) and the indicated α-arylacetate (1.0 equiv.) were added to a solution of pABSA (1.5 equiv.) in CH_3CN (0.5 M) at room temperature and the resulting mixture was stirred for 18 hours. The reaction mixture was then diluted with distilled water and extracted with diethyl ether. The combined organic layers were washed with a 10% $NaHCO_3$ solution and brine, then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography with the indicated solvents.

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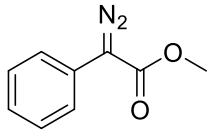
[2] Chapman, R. S.; Francis, M.; Lawrence, R.; Tibbetts, J. D.; Bull, S. D., *Tetrahedron* **2018**, *74* (44), 6442–6452.

[3] Gao, M.; Zhao, Y.; Zhong, C.; Liu, S.; Liu, P.; Yin, Q.; Hu, L., *Org. Lett.* **2019,** *21* (14), 5679-5684.

[4] B. Muriel, J. Waser, *Angew. Chem. Int. Ed.* **2021**, *60*, 4075-4079.

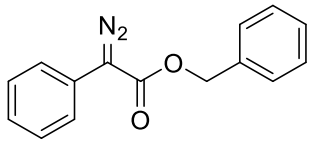
Methyl 2-diazo-2-phenylacetate (15)



15

Following the GP1, starting from methyl 2-phenylacetate (5.00 g, 33.2 mmol), the title compound **15** was obtained after purification by flash column chromatography (SiO_2, Et_2O/Pentane 2/98 to 10/90) as a red oil (4.25 g, 24.1 mmol, 72 % yield). Rf=0.36 (Et_2O:Pentane 1:20).
^1H NMR (400 MHz, $CDCl_3$): δ 7.52–7.45 (m, 2H, Ar*H*), 7.42–7.34 (m, 2H, Ar*H*), 7.19 (td, *J* = 7.3, 1.2 Hz, 1H, Ar*H*), 3.87 (s, 3H, OCH_3). Spectral data of the obtained compound is corresponding to the reported values[4].

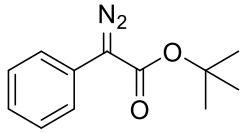
Benzyl 2-diazo-2-phenylacetate (16)



16

Following the GP1, starting from benzyl 2-phenylacetate (**13**) (5.47g, 24.1 mmol), the title compound **16** was obtained after purification by flash column chromatography (SiO_2, Et_2O/Pentane 2/98 to 10/90) as an orange solid (4.70 g, 18.6 mmol, 77% yield). Rf=0.47 (EtOAc:Pentane 10:90).
^1H NMR (400 MHz; $CDCl_3$): δ 7.48 (dd, *J* = 8.5, 1.1 Hz, 2H, Ar*H*), 7.41–7.32 (m, 7H, Ar*H*), 7.17 (t, *J* = 7.4 Hz, 1H, Ar*H*), 5.30 (s, 2H, CH_2). Spectral data of the obtained compound is corresponding to the reported values[5].

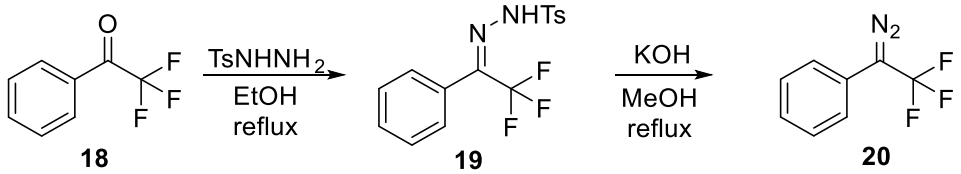
Tert-butyl 2-diazo-2-phenylacetate (17)



17

Following the GP1, starting from tert-butyl 2-phenylacetate (**14**) (950mg, 4.94 mmol), the title compound **17** was obtained after purification by flash column chromatography (SiO_2, EtOAc/Pentane 2/98 to 10/90) as an orange oil (530 mg, 2.43 mmol, 49% yield). Rf=0.5 (Et_2O:Pentane 1:8). ^1H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.37 (m, 2H, Ar*H*), 7.37 – 7.32 (m, 2H, Ar*H*), 7.21 – 7.13 (m, 1H, Ar*H*), 1.55 (s, 9H, CH_3). Spectral data of the obtained compound is corresponding to the reported values[4].

(1-Diazo-2,2,2-trifluoroethyl)benzene (20)



18 **19** **20**

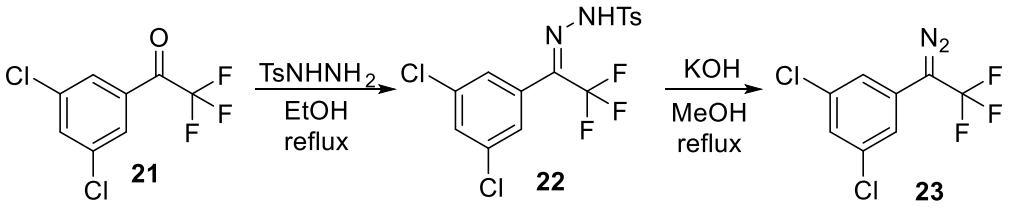
[5] Ye, F.; Qu, S.; Zhou, L.; Peng, C.; Wang, C.; Cheng, J.; Hossain, M. L.; Liu, Y.; Zhang, Y.; Wang, Z.-X., *J. Am. Chem. Soc.* **2015,** *137* (13), 4435-4444.

Following a reported procedure[6], a solution of 2,2,2-trifluoro-1-phenylethanone (**18)** (35.17g, 202.0 mmol, 1.00 equiv) and 4-methylbenzenesulfonohydrazide (37.62 g, 202.0 mmol, 1.00 equiv) in ethanol (400mL) was heated at reflux for 14h. The reaction mixture was cooled to r.t., concentrated under vacuum. The resulting crude was triturated with pentane(200ml), filtered. The precipitate was washed with pentane and dried under vacuum to give N-[(E)-(2,2-dimethyl-1-phenylpropylidene)amino]-4-methylbenzenesulfonamide (**19**) (28.3 g, 85.6 mmol, 42% yield) as a white solid(95% purity), which was used without further purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H, N*H*), 7.82 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.57 – 7.50 (m, 3H, Ar*H*), 7.36 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.27 – 7.22 (m, 2H, Ar*H*), 2.46 (s, 3H, C*H*$_3$). Spectral data of the obtained compound is corresponding to the reported values[4].

Following a reported procedure[7], KOH (10.19 g, 181.6 mmol, 2.000 equiv.) was dissolved in MeOH (270mL) by stirring at room temperature. 4-Methyl-N'-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (**19**) (31.1 g, 90.7 mmol) was added in one portion and the solution was heated to reflux for ~1 h and then cooled to room temperature. Water (300 mL) was added and the resulting mixture was extracted with pentane (3x150 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under low vacuum (900 mbar, 40 ºC) until no more pentane condensed to give (1-diazo-2,2,2-trifluoroethyl)benzene (**20**) (30.6 mmol, 34% yield) as a 1.3 M solution in pentane (concentration was measured by ^{19}F NMR using $PhCF_3$ as an internal standard). The solution was stored at -20 ºC and used for the next reactions as such.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H, Ar*H*), 7.25 – 7.19 (m, 1H, Ar*H*), 7.17 – 7.08 (m, 2H, Ar*H*). Spectral data of the obtained compound is corresponding to the reported values[4].

1,3-Dichloro-5-(1-diazo-2,2,2-trifluoroethyl)benzene (23)



A solution of 1-(3,5-dichlorophenyl)-2,2,2-trifluoroethan-1-one (**21)** (3.75 g, 15.4 mmol, 1.00 equiv) and 4-methylbenzenesulfonohydrazide (2.87 g, 15.4 mmol, 1.00 equiv) in toluene (15 mL) was heated at 90 °C for 14 h. The mixture was cooled to r.t. and filtered. The precipitate was washed with pentane and dried under vacuum to give N'-(1-(3,5-dichlorophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (**22**) as an off-white solid (3.81 g, 9.27 mmol, 60% yield).

Rf = 0.43 (EtOAc:Pentane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H, N*H*), 7.85 – 7.77 (m, 2H, Ar*H*), 7.53 (t, *J* = 1.9 Hz, 1H, Ar*H*), 7.37 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.13 (d, *J* = 1.9 Hz, 2H, Ar*H*), 2.47 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 138.1 (q, *J* = 36.4 Hz), 137.1, 134.1, 131.9, 130.0, 128.1, 127.9, 126.7, 119.6 (q, *J* = 275.0 Hz), 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.0. HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{11}Cl_2F_3N_2NaO_2S^+$ 432.9763; Found 432.9753. M.p. 173-175°C.

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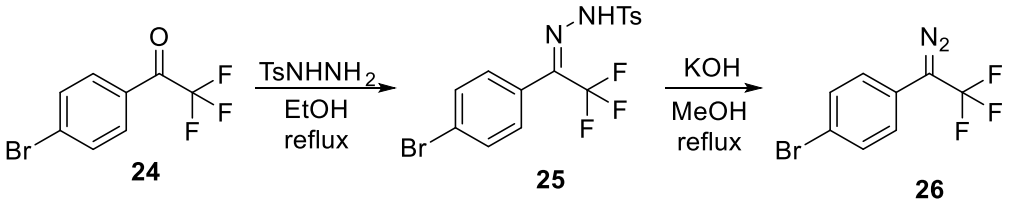
[6] Liang, X.; Guo, P.; Yang, W.; Li, M.; Jiang, C.; Sun, W.; Loh, T.-P.; Jiang, Y. *Chem. Commun.* **2020**, *56* (13), 2043–2046.

[7] Denton, J. R.; Sukumaran, D.; Davies, H. M., *Org. Lett.* **2007,** *9* (14), 2625-2628.

KOH (1.01 g, 18.0 mmol, 2.00 equiv) was dissolved in MeOH (40 mL) by stirring at room temperature. 4-Methyl-N'-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (**22**) (3.71 g, 9.02 mmol, 1.00 equiv) was added in one portion and the solution was heated to reflux for ~1 h and then cooled to room temperature. Water (100 mL) was added and the resulting mixture was extracted with pentane (3x50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum to give 1,3-dichloro-5-(1-diazo-2,2,2-trifluoroethyl)benzene **(23)** as a red oil ((780 mg, 3.06 mmol, 34% yield).

Rf = 0.83(pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 1.8 Hz, 1H, Ar*H*), 6.95 (d, *J* = 1.7 Hz, 2H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 127.4, 125.8, 124.8 (q, *J* = 269.9 Hz), 120.0 (one carbon is not resolved). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.3.

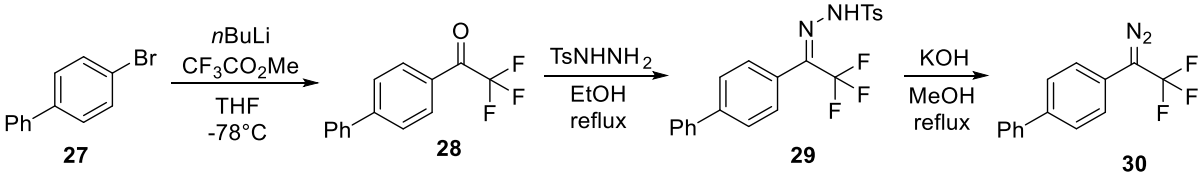
1-Bromo-4-(1-diazo-2,2,2-trifluoroethyl)benzene (26)



Following a reported procedure[8], 1-(4-bromophenyl)-2,2,2-trifluoroethanone (**24**) (633 mg, 2.50 mmol, 1.05 equiv.) was added to EtOH (4.7 mL) at room temperature followed by *p*-toluenesulfonylhydrazide (0.443 g, 2.38 mmol, 1.00 equiv.) in one portion. A condenser was then attached and the contents were heated to reflux for 12 h. After this time, the solvent was removed under reduced pressure until the beginning of the formation of a solid. Then, pentane (100 mL) was added and the precipitate was collected by filtration and washed with pentane. The solid obtained was used in the next step without purification.

N'-(1-(4-bromophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (**25**) was dissolved in a 0.4 M solution of potassium hydroxide (281 mg, 5.00 mmol, 2.00 equiv.) in MeOH (12.5 mL). A condenser was attached and the reaction mixture was stirred at reflux for 0.5 h. Then, the reaction was cooled to room temperature and diluted with water (15 mL). The crude product was extracted with pentane (3 x 20 mL), dried over MgSO4, filtered and concentrated under reduced pressure. The crude oil was purified by silica gel chromatography using pentane as eluent to afford 1-bromo-4-(1-diazo-2,2,2-trifluoroethyl)benzene (**26**) as a orange oil (146 mg, 0.551 mmol, 22%). The compound was kept as a 0.6 M solution in DCM at -18 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H, Ar*H*), 7.01 – 6.91 (m, 2H, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.8, 125.7 (q, *J* = 270.3 Hz), 124.0, 123.0, 119.7 (one carbon is not resolved); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.5. Spectral data of the obtained compound is corresponding to the reported values.[8]

4-(1-Diazo-2,2,2-trifluoroethyl)-1,1'-biphenyl (**30**)



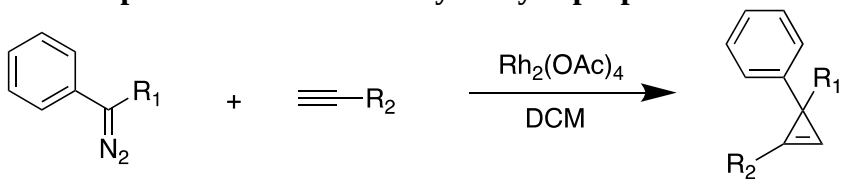
[8] G. Pisella, A. Gagnebin, J. Waser, *Chem. Eur. J.* **2020**, *26*, 10199.

Following a reported procedure,[8] a solution of 4-bromo-biphenyl (**27**) (4.66 g, 20.0 mmol, 1.00 equiv.) in anhydrous THF (100 mL) was cooled to -78 °C. Then, a 2.5 M solution of n-butyllithium (9.60 mL, 24.0 mmol, 1.20 equiv.) in hexanes was added dropwise. The mixture was stirred for 1 h, followed by the dropwise addition of methyl 2,2,2-trifluoroacetate (2.21 mL, 22.0 mmol, 1.10 equiv.) in 30 min. The mixture was allowed to warm up to room temperature, stirred for 18 h and then quenched with saturated aqueous ammonium chloride solution (50 mL). Diethyl ether (50 mL) was added and the layers were separated. The aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO4, filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography using pentane/EtOAc 90:10 as eluent to afford 1-([1,1'-biphenyl]- 4-yl)-2,2,2-trifluoroethanone (**28**) as a light-yellow oil (3.37 g, 13.5 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.10 (m, 2H, Ar*H*), 7.81 – 7.74 (m, 2H, Ar*H*), 7.68 – 7.62 (m, 2H, Ar*H*), 7.54 – 7.41 (m, 3H, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.3 (q, *J* = 34.8 Hz), 148.4, 139.3, 130.9 (q, *J* = 2.2 Hz), 129.3, 129.1, 128.7, 127.8, 127.5, 116.9 (q, *J* = 291.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.32. Spectral data of the obtained compound is corresponding to the reported values.[8]

Following a reported procedure, 1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethanone (**28**) (3.36 g, 13.5 mmol, 1.05 equiv.) was added to EtOH (9 mL) at room temperature followed by *p*-toluenesulfonylhydrazide (2.40 g, 12.9 mmol, 1.00 equiv.) in one portion. A condenser was then attached and the contents were heated to reflux for 12 h. After this time, the solvent was removed under reduced pressure until the beginning of the formation of a solid. Then, pentane (200 mL) was added and the precipitate was collected by filtration and washed with pentane. The solid obtained was used in the next step without purification.

Following a reported procedure, N'-(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (**29**) was dissolved in a 0.4 M solution of potassium hydroxide (3.37 g, 60.0 mmol, 2.00 equiv.) in MeOH (17.5 mL). A condenser was attached and the reaction mixture was stirred at reflux for 0.5 h. Then, the reaction was cooled to room temperature and diluted with water (20 mL). The product was extracted with Et_2O (3 x 30 mL), dried over MgSO4, filtered and concentrated under reduced pressure. The crude oil was purified by silica gel chromatography using pentane as eluent to afford 4-(1-Diazo-2,2,2-trifluoroethyl)-1,1'-biphenyl (**30**) as a red solid (1.42 g, 5.44 mmol, 50%). The compound was kept at -18 °C. Rf = 0.70 (pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H, Ar*H*), 7.62 – 7.55 (m, 2H, Ar*H*), 7.45 (dd, *J* = 8.4, 6.9 Hz, 2H, Ar*H*), 7.41 – 7.34 (m, 1H, Ar*H*), 7.17 (d, J = 8.2 Hz, 2H, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.0, 129.1, 128.2, 127.7, 127.0, 125.8 (q, *J* = 269.6 Hz), 122.7, 122.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.32. Spectral data of the obtained compound is corresponding to the reported values.[8]

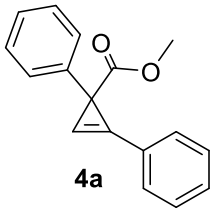
General procedure for Rh-catalysed cyclopropenation of terminal alkynes (GP2)



Following a modified reported procedure[4], the diazo compound was dissolved in DCM (0.25 M) and the resulting solution was added via syringe pump to a suspension of $Rh_2(OAc)_4$ (0.01 equiv.) in indicated alkyne(3.0 equiv.) at room temperature over 10 hours. After the addition was complete, the reaction mixture was allowed to stir for another 4 hours. The reaction mixture was then filtered through a small pad of silica eluting with CH_2Cl_2 and the filtrate was

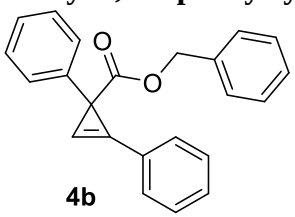
concentrated under reduced pressure. The crude residue was purified by column chromatography with the indicated solvents.

Methyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (4a)



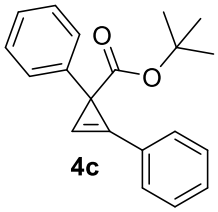
Following the GP2, starting from methyl 2-diazo-2-phenylacetate (**15**) (1.40 g, 7.95 mmol, 1.00 equiv) and phenylacetylene (2.43 g, 23.8 mmol, 3.00 equiv), the title compound **4a** was obtained after purification by column chromatography (SiO_2, Pentane:EtOAc 95:5 to 80:20) as a pale yellow oil (1.37 g, 5.47 mmol, 69 % yield).
Rf=0.21 (EtOAc:Pentane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H, Ar*H*), 7.45 – 7.37 (m, 5H, Ar*H*), 7.33 – 7.26 (m, 2H, Ar*H*), 7.23 – 7.18 (m, 2H, Ar*H* & C=C*H*), 3.72 (s, 3H, CO_2CH_3). Spectral data of the obtained compound is corresponding to the reported values[4].

Benzyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (4b)



Following the GP2, starting from benzyl 2-diazo-2-phenylacetate **(16)** (4.70 g, 18.6 mmol, 1.00 equiv) and phenylacetylene (5.71 g, 55.9 mmol, 3.00 equiv), the title compound **4b** was obtained after purification by column chromatography (SiO_2, Pentane:EtOAc 90:10) as a white solid (3.37 g, 10.3 mmol, 55% yield).
Rf=0.25 (EtOAc:Pentane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H, Ar*H*), 7.44 – 7.36 (m, 5H, Ar*H*), 7.32 – 7.20 (m, 7H, Ar*H*), 7.21 (s, 1H, C=C*H*), 7.21 – 7.16 (m, 1H, Ar*H*), 5.18 (s, 2H, CH_2). Spectral data of the obtained compound is corresponding to the reported values[9].

***Tert*-butyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (4c)**

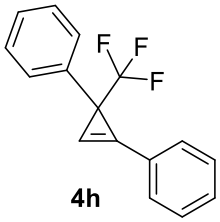


Following the GP2, starting from *tert*-butyl 2-diazo-2-phenylacetate **(17)** (530 mg, 2.43 mmol, 1.00 equiv) and phenylacetylene (2.43 g, 23.8 mmol, 3.00 equiv), the title compound **4c** was obtained after purification by column chromatography (SiO_2, Pentane:EtOAc 93:7 to 70:30) as an off-white solid (247 mg, 0.845 mmol, 35% yield).

[9] Hommelsheim, R.; Guo, Y.; Yang, Z.; Empel, C.; Koenigs, R. M., *Angew. Chem. Int. Ed.* **2019,** *58* (4), 1203-1207.

Rf =0.36 (Pentane:EtOAc 80:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H, Ar*H*), 7.45 – 7.36 (m, 5H, Ar*H*), 7.29 – 7.25 (m, 2H, Ar*H*), 7.21 – 7.17 (m, 2H, Ar*H* & C=C*H*), 1.44 (s, 9H, CH_3). Spectral data of the obtained compound is corresponding to the reported values[4].

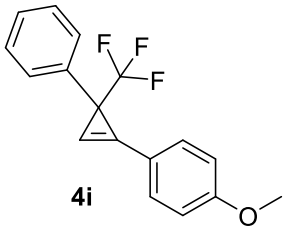
(1-(Trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (4h)



4h

Following the GP2, starting from (1-diazo-2,2,2-trifluoroethyl)benzene (**20**) (1.86 g, 10.0 mmol, 1.00 equiv.) and phenylacetylene (3.64 g, 30.0 mmol, 3.00 equiv), the title compound **4h** was obtained after purification by column chromatography (SiO_2, Pentane) as a colorless oil (1.98 g, 6.82 mmol, 68% yield).
Rf=0.39 (Pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H, Ar*H*), 7.50 – 7.39 (m, 5H, Ar*H*), 7.35 – 7.29 (m, 2H, Ar*H*), 7.29 – 7.24 (m, 1H, Ar*H*), 7.17 (q, *J* = 1.6 Hz, 1H, C=C*H*). Spectral data of the obtained compound is corresponding to the reported values[4].

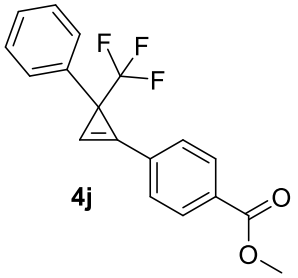
1-Methoxy-4-(3-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene (4i)



4i

Following the GP2, starting from (1-diazo-2,2,2-trifluoroethyl)benzene (**20**) (372 mg, 2.00 mmol, 1.00 equiv) and 1-ethynyl-4-methoxybenzene (793 mg, 6.00 mmol, 3.00 equiv) the title compound **4i** was obtained after purification by column chromatography(SiO_2, Et_2O:Pentane 2:98) as a yellow oil (423 mg, 1.46 mmol, 73% yield).
Rf=0.53 (Et_2O:Pentane 1:19). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.42 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.33-7.20 (m, 3H, Ar*H*), 6.97 (s, 1H, C=C*H*), 6.94 (d, *J* = 8.8 Hz, 2H, Ar*H*), 3.81 (s, 3H, CH_3). Spectral data of the obtained compound is corresponding to the reported values[10].

Methyl 4-(3-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzoate (4j)



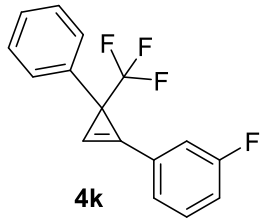
4j

Following the GP2, starting from (1-diazo-2,2,2-trifluoroethyl)benzene (**20**) (372 mg, 2.00 mmol, 1.00 equiv) and methyl 4-ethynylbenzoate (961 mg, 6.00 mmol, 3.00 equiv) the title compound **4j** was obtained after purification by column chromatography (SiO_2, Et_2O:Pentane 1:99 to 10:90) as a light-yellow oil (425 mg, 1.46 mmol, 73% yield).

[10] Uehara, M.; Suematsu, H.; Yasutomi, Y.; Katsuki, T., *J. Am. Chem. Soc.* **2011,** *133* (2), 170-171.

Rf=0.76 (EtOAc:Pentane 10:90) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 2H, Ar*H*), 7.75 – 7.67 (m, 2H, Ar*H*), 7.44 – 7.37 (m, 2H, Ar*H*), 7.35 – 7.26 (m, 4H, Ar*H* & C=C*H*), 3.94 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 137.6, 131.6, 130.2, 129.8, 129.2, 128.5, 127.6, 127.5, 125.1 (q, *J* = 277.5 Hz), 117.0, 102.1, 52.4, 32.5 (q, *J* = 35.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.1. IR (ν_{max}, cm^{-1}) 3139 (w), 2956 (w), 1722 (s), 1605 (w), 1496 (w), 1441 (m), 1410 (w), 1278 (s), 1163 (s), 1114 (s), 1024 (w), 971 (w), 921 (m), 861 (w), 833 (w), 774 (m), 723 (s), 708 (s), 658 (w). HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}F_3O_2^+$ 319.0940; Found 319.0955.

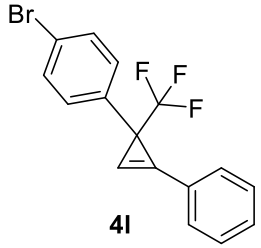
1-Fluoro-3-(3-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene (4k)



4k

Following the GP2, starting from (1-diazo-2,2,2-trifluoroethyl)benzene (**20**) (372 mg, 2.00 mmol, 1.00 equiv) and 1-ethynyl-3-fluorobenzene (721 mg, 6.00 mmol, 3.00 equiv) the title compound **4k** was obtained after purification by column chromatography (SiO_2, Pentane) as a colorless oil (453 mg, 1.63 mmol, 81% yield).
Rf=0.34(pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H, Ar*H*), 7.28 – 7.13 (m, 5H, Ar*H* & C=C*H*), 7.11 – 6.98 (m, 1H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.9 Hz), 137.7, 130.7 (d, *J* = 8.2 Hz), 128.5, 127.6, 127.4, 127.1 (d, *J* = 8.2 Hz), 125.8 (d, *J* = 3.1 Hz), 125.1 (q, *J* = 277.6 Hz), 117.6 (d, *J* = 21.4 Hz), 116.8, 116.6 (d, *J* = 22.3 Hz), 100.6 (d, *J* = 2.9 Hz), 32.5 (q, 36 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.1, -111.9. IR (ν_{max}, cm^{-1}) 3144 (w), 3068 (w), 3034 (w), 1589 (m), 1490 (m), 1441 (m), 1304 (m), 1256 (m), 1160 (s), 1129 (s), 969 (w), 919 (m), 873 (m), 786 (m), 709 (m), 653 (w). HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{16}H_{10}F_4^+$ 278.0713; Found 278.0720.

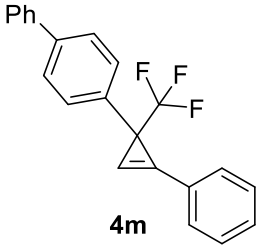
1-Bromo-4-(2-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (4l)



4l

Following the GP2, starting from 1-bromo-4-(1-diazo-2,2,2-trifluoroethyl)benzene (**26**) (362 mg, 1.36 mmol, 1.00 equiv) and phenylacetylene (418 mg, 4.10 mmol, 3.00 equiv), the title compound **4l** was obtained after purification by column chromatography(SiO_2, Pentane:EtOAc 95:5 to 80:20) as a colorless oil, which solidified upon storage at -20 ºC (264 mg, 778 µmol, 57% yield).
Rf=0.55 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H, Ar*H*), 7.51 – 7.40 (m, 5H, Ar*H*), 7.34 – 7.27 (m, 2H, Ar*H*), 7.14 (q, *J* = 1.5 Hz, 1H, C=C*H*).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 131.6, 130.7, 130.0, 129.4, 129.1, 126.5 (q, *J* = 277.7 Hz), 124.7, 121.3, 117.3 (q, *J* = 2.3 Hz), 98.5 (q, *J* = 2.9 Hz), 31.8 (q, *J* = 35.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0. IR (cm^{-1}): 3132(w), 1769(m), 1484(m), 1294(m), 1233(m), 1164(s), 1113(s), 1067(m), 1004(m), 974(m), 915(m), 823(m), 763(m), 744(m), 727(m), 699(s). HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{16}H_{10}{}^{79}BrF_3{}^+$ 337.9912; Found 337.9915.

4-(2-Phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl (4m)

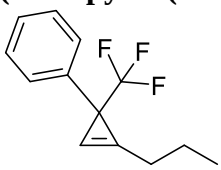


4m

Following the GP2, starting from 1-(1-diazo-2,2,2-trifluoroethyl)-4-phenylbenzene (**30**) (150 mg, 572 µmol, 1.00 equiv) and phenylacetylene (175 mg, 1.72 mmol, 3.00 equiv) the title compound **4m** was obtained after purification by column chromatography(SiO_2, Pentane) as a white solid (160 mg, 476 µmol, 83% yield).

Rf(pentane)=0.18. M.p. 119-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 2H, Ar*H*), 7.62 – 7.39 (m, 11H, Ar*H*), 7.39 – 7.30 (m, 1H, Ar*H)*, 7.20 (q, *J* = 1.6 Hz, 1H, C=C*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 140.1, 137.2, 130.5, 130.1, 129.1, 128.80, 128.11, 127.3, 127.2, 127.1, 126.7 (q, 278Hz), 125.0, 117.4, 98.8. 32.0 (q, *J* = 35.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.9. IR (ν_{max}, cm^{-1}) 3134 (w), 1487 (m), 1301 (m), 1243 (m), 1158 (s), 1119 (s), 922 (m), 844 (m), 768 (m), 708 (s) . HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{22}H_{15}F_3^+$ 336.1120; Found 336.1127.

(2-Propyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (4n)

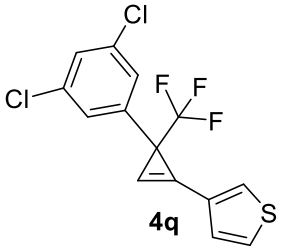


4n

Following the GP2, starting from (1-diazo-2,2,2-trifluoroethyl)benzene (**20**) (372 mg, 2.00 mmol, 1.00 equiv) and pent-1-yne (409 mg, 6.00 mmol, 3.00 equiv) the title compound **4n** was obtained after purification by column chromatography (SiO_2, Pentane) as a colorless oil (341 mg, 1.51 mmol, 75% yield).

Rf = 0.8 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.34 (m, 4H, Ar*H*), 7.34 – 7.26 (m, 1H, Ar*H*), 6.79 – 6.71 (m, 1H, C=C*H*), 2.57 (tt, *J* = 7.3, 1.6 Hz, 2H, C=C-CH_2), 1.80 – 1.60 (m, 2H, $CH_2CH_2CH_3$), 1.12 – 0.90 (m, 3H, CH_3). Spectral data of the obtained compound is corresponding to the reported values[11].

3-(3-(3,5-Dichlorophenyl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)thiophene (4q)



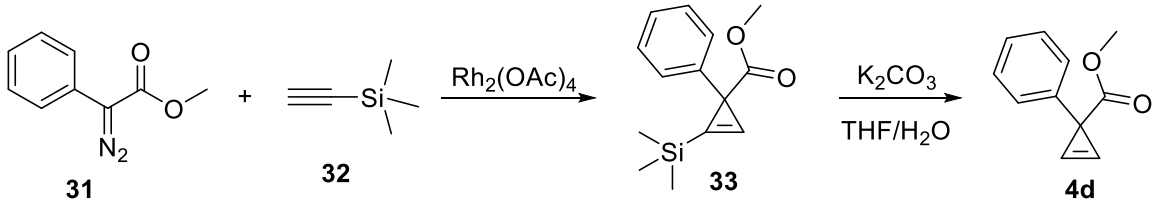
4q

Following the GP2, starting from 1,3-dichloro-5-(1-diazo-2,2,2-trifluoroethyl)benzene **(23)** (118 mg, 462 µmol, 1.00 equiv) and 3-ethynylthiophene (150 mg, 1.39 mmol, 3.00 equiv) the

[11] Tran, U. P.; Hommelsheim, R.; Yang, Z.; Empel, C.; Hock, K. J.; Nguyen, T. V.; Koenigs, R. M., *Chem. Eur. J.* **2020,** *26* (6), 1254-1257.

title compound **4q** was obtained after purification by column chromatography (SiO_2, Pentane) as a yellow oil (75.6 mg, 226 μmol, 49% yield).
Rf = 0.52 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 3.0, 1.2 Hz, 1H, Ar*H*), 7.33 (dd, *J* = 5.1, 2.9 Hz, 1H, Ar*H*), 7.24 (dd, *J* = 5.0, 1.2 Hz, 1H, Ar*H*), 7.22 – 7.14 (m, 3H, Ar*H*), 6.86 (q, *J* = 1.6 Hz, 1H, C=C*H*).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 135.1, 129.6, 128.0, 127.6, 127.4, 126.2 (q, *J* = 1.7 Hz), 126.1 (q, *J* = 277.6 Hz), 125.4, 111.5 (q, *J* = 2.3 Hz), 94.9 (q, *J* = 2.8 Hz), 31.6 (q, *J* = 36.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.1. HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{14}H_7Cl_2F_3S^+$ 333.9592; Found 333.9605.

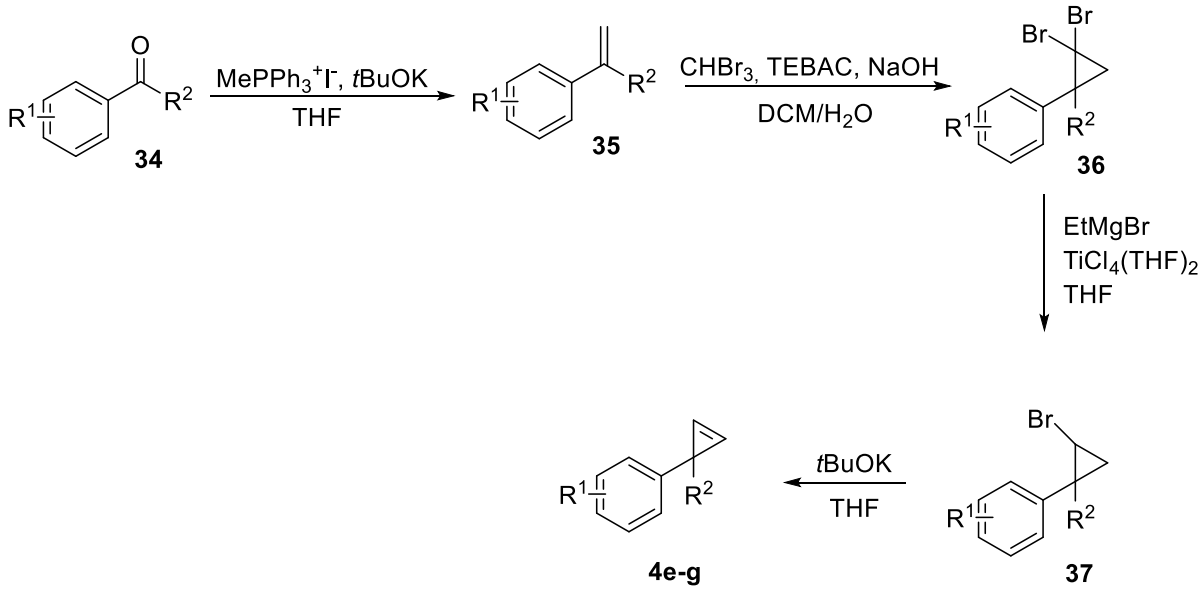
Methyl 1-phenylcycloprop-2-ene-1-carboxylate (4d)



Following a reported procedure[12], A solution of methyl diazophenylacetate (**31**) (2.95 g, 16.8 mmol) in trimethylsilylacetylene (**32**) (20 mL) was added via a syringe pump over 18 h to a stirred suspension of $Rh_2(OAc)_4$ (74 mg, 0.17 mmol, 1 mol%) in trimethylsilylacetylene (**32**) (15 mL) at 50 ºC under N_2 atmosphere. After the addition was complete, the reaction mixture was refluxed for an additional 2 h. The reaction mixture was concentrated under vacuum, diluted with DCM (20 mL), filtered through a small pad of silica gel(1cm). The sorbent was washed with DCM (50mL). The mother liquor was concentrated under vacuum to give methyl 1-phenyl-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**33**) (3.63 g, 90% purity, 13.3 mmol, 79% yield), which was used in the next step without further purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H, C=C*H*), 7.30 – 7.22 (m, 4H, Ar*H*), 7.19 – 7.14 (m, 1H, Ar*H*), 3.66 (s, 3H, OCH_3), 0.18 (s, 9H, Si(CH_3)$_3$). The spectral data of the obtained compound is corresponding to the reported values[12].
To a solution of **33** (3.63 g, 14.7 mmol, 1equiv) in THF (70 mL), cooled to 0 ºC, a solution of K_2CO_3 (3.00 g, 21.7 mmol, 1.5 equiv) was added dropwise. The reaction mixture was stirred at r.t for 2 h, then extracted with Et_2O (2x100 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product, which was purified by column chromatography (SiO_2, Pentane:EtOAc 90:10) to give methyl 1-phenylcycloprop-2-ene-1-carboxylate (**4d)** (1.55 g, 8.87 mmol, 53.2% yield over 2 steps) as a yellow oil.
Rf = 0.38 (Pentane:EtOAc 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.25 (m, 5H, Ar*H*), 7.23 (s, 2H, C=C*H*), 3.72 (m, 3H, CH_3); The spectral data of the obtained compound is corresponding to the reported values[12].

General procedure for the preparation of cyclopropenes via bromide elimination(GP3)

[12] Rubin, M.; Gevorgyan, V., *Synthesis* **2004,** *2004* (05), 796-800.



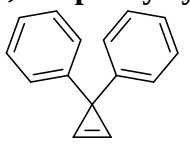
To a solution of methyltriphenylphosphonium iodide (1.36 equiv) in THF (0.25 M) *t*BuOK (1.3equiv) was added under nitrogen atmosphere. The reaction mixture was stirred for 1 h, then ketone **34** (1 equiv) was added. The mixture was stirred overnight. The reaction mixture was diluted with water and extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting crude was triturated with pentane. The mixture was stirred for 2 h to assure full dissolving of the alkene **35** product. The mixture was filtered, the precipitate was washed with pentane. The mother liquor was concentrated under vacuum to give crude **35**, which was used without further purification.

To a solution of crude alkene **35** (1equiv), $CHBr_3$ (2.5equiv) and triethylbenzylammonium chloride (0.1 equiv.) in DCM (1 M) a 50% NaOH solution (14.2 equiv) was added dropwise. The reaction mixture was stirred overnight at r.t. The reaction mixture was diluted with water and extracted with DCM (2x). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum to give dibromocyclopropane **36**, which was used without further purification.

To a solution of **36 (**1equiv) and $TiCl_4(THF)_2$ (0.025 equiv) in THF (0.25 M) EtMgBr (1.5equiv, 3.2 M in 2-MeTHF) was added dropwise over 10 min under N_2 atmosphere. The reaction mixture was stirred for another 10 min. Water was added. The organic solvent was concentrated under vacuum. The mixture was diluted with water and extracted with pentane(3x). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under vacuum to give crude bromide **37** which was used without further purification.

To a solution of *t*BuOK (2 equiv) in THF (0.5M), cooled to 0 ºC, a solution of **37** in THF (1 M) was added under N_2 atmosphere. The reaction mixture was stirred at r.t for 20-48 h. The reaction mixture was poured into ice/water, extracted with pentane (3x). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product. This crude was subjected to column chromatography (SiO_2, pentane) to give cyclopropene **4e-g**.

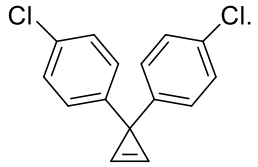
3,3-Diphenylcyclopropene (4e)



4e

Following the GP3, starting from benzophenone (1.16 g, 6.37 mmol) the title compound **4e** was obtained as a colorless oil (576 mg, 3.00 mmol, 47% yield over 4 steps).
Rf = 0.8 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 2H, C=C*H*), 7.32 – 7.23 (m, 4H, Ar*H*), 7.23 – 7.13 (m, 6H, Ar*H*). Spectral data of the obtained compound is corresponding to the reported values[13].

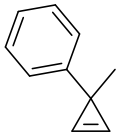
4,4'-(Cycloprop-2-ene-1,1-diyl)bis(chlorobenzene) (4f)



4f

Following the GP3, starting from 4,4'-dichlorobenzophenone(0.673 g, 2.68 mmol) the title compound **4f** was obtained as a white solid (273 mg, 1.04 mmol, 38.8% yield over 4 steps).
Rf = 0.68 (Pentane). ^{1}H NMR (400 MHz, $CDCl_3$) 7.05-7.08 (m, 4H, Ar*H*), 7.21-7.25 (m, 4H, Ar*H*), 7.45 (s, 2H, C=C*H*). Spectral data of the obtained compound is corresponding to the reported values[14].

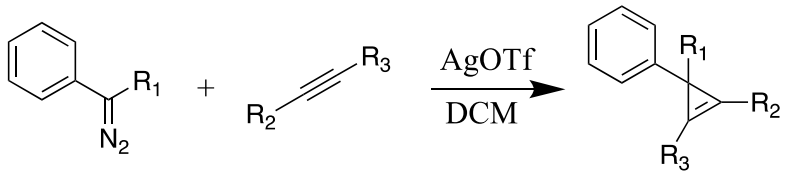
(1-Methylcycloprop-2-en-1-yl)benzene (4g)



4g

Following the GP3, starting from prop-1-en-2-ylbenzene (0.600 g, 5.00 mmol) the title compound **4g** was obtained as a light-yellow oil (310 mg, 2.38 mmol, 48% yield over 3 steps).
Rf = 0.7 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, *J* = 8.0 Hz, 2H, Ar*H*), 7.58-7.56 (m, 2H, Ar*H*), 7.53 (s, 2H, C=C*H*), 7.50 (t, *J* = 7.2 Hz, 1H, Ar*H*), 2.01 (s, 3H, CH_3). Spectral data of the obtained compound is corresponding to the reported values[15].

General procedure for Ag-catalyzed cyclopropenation of internal alkynes (GP4)



Following a modified reported procedure[16], a mixture of alkyne (4.0 mmol, 2 equiv.) and AgOTf (51 mg, 0.20 mmol, 0.10 equiv) was weighed in a 100-mL one-necked round bottom flask covered with aluminum foil to exclude light. The mixture was dissolved with 20 mL dichloromethane and stirred at room temperature under positive pressure of N_2. The diazo compound (2 mmol, 1 equiv) in 20 mL dichloromethane was then added via syringe pump over 1 h. After addition, the mixture was stirred for 1 hour. Then, the mixture was filtered through

[13] Nizovtsev, A. V., *Org. Prep. Proced. Int.* **2020,** *52* (6), 537-542.

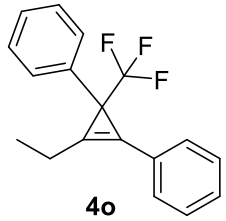
[14] Shintani, R.; Iino, R.; Nozaki, K., *J. Am. Chem. Soc.* **2014,** *136* (22), 7849-7852.

[15] Phan, D. H.; Kou, K. G.; Dong, V. M., *J. Am. Chem. Soc.* **2010,** *132* (46), 16354-16355.

[16] Briones, J. F.; Davies, H. M., *Org. Lett.* **2011,** *13* (15), 3984-3987.

a small pad of silica gel (1cm), the sorbent was washed with DCM; the mother liquor was concentrated in vacuo. The residue was purified on silica with the indicated solvents.

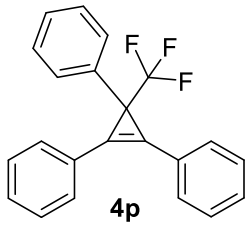
(3-Ethyl-1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (4o)



4o

Following the GP4, starting from (1-diazo-2,2,2-trifluoroethyl)benzene (**20**) (372 mg, 2.00 mmol, 1.00 equiv) and but-1-yn-1-ylbenzene (520 mg, 4.00 mmol, 2.00 equiv) the title compound **4o** was obtained after purification by column chromatography (SiO_2, Pentane) as a colorless oil (350 mg, 1.21 mmol, 61% yield).
Rf(pentane)=0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 2H, Ar*H*), 7.52 – 7.35 (m, 5H, Ar*H*), 7.36 – 7.21 (m, 3H, Ar*H*), 2.89 – 2.68 (m, 2H, C*H*$_2$), 1.40 (t, *J* = 7.5 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 129.5, 129.2, 128.9, 128.4, 127.6, 127,1(q, 277Hz), 126.8, 126.2, 114.6, 107.8, 33.7 (q, *J* = 34.6 Hz). 18.1, 12.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7. IR (ν_{max}, cm^{-1}) 3065 (w), 3033 (w), 2979 (w), 2935 (w), 2887 (w), 1496 (m), 1454 (m), 1300 (m), 1248 (m), 1157 (s), 1124 (s), 1078 (w), 919 (m), 761 (m), 699 (s), 654 (w). HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{18}H_{15}F_3^+$ 288.1120; Found 288.1126.

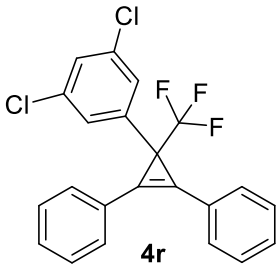
(3-(Trifluoromethyl)cycloprop-1-ene-1,2,3-triyl)tribenzene (4p)



4p

Following the GP4, starting from (1-diazo-2,2,2-trifluoroethyl)benzene (**20**) (372 mg, 2.00 mmol, 1.00 equiv) and 1,2-diphenylethyne (713 mg, 4.00 mmol, 2.00 equiv) the title compound **4p** was obtained after purification by column chromatography (SiO_2, Pentane) as a white solid (315 mg, 0.936 mmol, 47% yield).
Rf = 0.34 (Pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 4H, Ar*H*), 7.57 – 7.47 (m, 6H, Ar*H*), 7.47 – 7.39 (m, 2H, Ar*H*), 7.34 – 7.20 (m, 3H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 130.0, 129.8, 129.2, 128.5, 127.6, 127.1, 127.0 (q, *J* = 278.8 Hz), 126.2, 109.9, 33.7 (q, *J* = 34.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.0. IR (ν_{max}, cm^{-1}) 3064 (m), 3033 (w), 1957 (w), 1883 (w), 1834 (w), 1750 (w), 1602 (w), 1495 (m), 1450 (w), 1299 (m), 1251 (m), 1225 (m), 1159 (s), 1122 (s), 1078 (m), 1029 (w), 957 (w), 919 (m), 835 (w), 756 (s), 693 (s), 659 (w). HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{22}H_{15}F_3^+$ 336.1120; Found 336.1128. M.p. 110-112°C

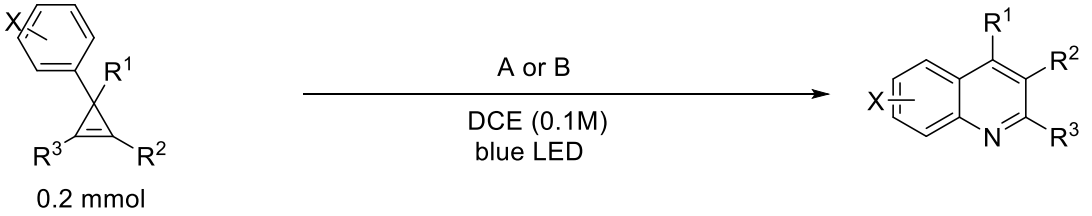
(3-(3,5-Dichlorophenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene (4r)



4r

Following the GP4, starting from (1-diazo-2,2,2-trifluoroethyl)benzene (**23**) (145 mg, 569 μmol, 1.00 equiv) and 1,2-diphenylethyne (203 mg, 1.14 mmol, 2.00 equiv) the title compound **4r** was obtained after purification by column chromatography (SiO_2 impregnated with $AgNO_3$,[17] Pentane) as a white solid (95.4 mg, 235 μmol, 41% yield).
Rf = 0.53 (Pentane). M.p. 118-120°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 4H, Ar*H*), 7.39 (dd, *J* = 8.2, 6.5 Hz, 4H, Ar*H*), 7.35 – 7.28 (m, 2H, Ar*H*), 7.26 (d, *J* = 1.9 Hz, 2H, Ar*H*), 7.12 (t, *J* = 1.9 Hz, 1H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 135.2, 130.3, 130.1, 129.4, 127.4, 126.5 (q, *J* = 276Hz), 125.9 (q, *J* = 1.9 Hz), 125.3, 108.8 (d, *J* = 2.5 Hz), 33.4 (q, *J* = 35.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.7. HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{22}H_{13}Cl_2F_3^+$ 404.0341; Found 404.0353.

3. Synthesis of quinolines



A: ABZ (1.4 equiv.), BIOAc (0.2 equiv.), Pyridine (2 equiv.), 14 h
B: ABZ (2 equiv.), BIOAc (0.2 equiv.), Pyridine (2 equiv.), 48 h

General procedure for quinoline synthesis: Method A (GP5)

DCE was degassed by bubbling Ar through it for 30 min. A 5 mL test tube, equipped with a stirring bar was charged with ABZ (**6**) (124 mg, 0.280 mmol, 1.40 equiv) and (3-oxo-1lambda3,2-benziodoxol-1-yl)acetate (**7**)[18] (12.2 mg, 0.0400 mmol, 0.200 equiv) and cyclopropene (**4)** (0.2 mmol, 1 equiv) (if it is solid). It was capped with the septum and evacuated-refilled with N_2 (3x). A solution of cyclopropene (**4)** (0.2 mmol, 1 equiv) (if oil) in DCE (2 mL) was added / 2mL of DCE was added to the reaction mixture, followed by pyridine (31.6 mg, 400 μmol, 2.00 equiv). The reaction mixture was stirred under blue LED irradiation for 14 h. Then, the reaction mixture was filtered through a small pad of silica (1cm), washing the sorbent with EtOAc. The resulting solution was concentrated under vacuum to give the crude product, which was purified by flash chromatography using the indicated solvents to give the quinoline product.

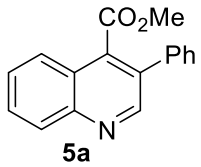
General procedure for quinoline synthesis: Method B (GP6)

[17] The sorbent was modified by mixing a solution of 5.5g of $AgNO_3$ in MeCN with 50g of silica gel, followed by evaporation and drying under vacuum.

[18] P. Caramenti, S. Nicolai, J. Waser, *Chem. Eur. J.*, **2017**, *23*, 14702

A procedure analogous to the method A was used, however 2 equiv of ABZ were used (177 mg, 0.400 mmol); the reaction time was extended to 48 h.

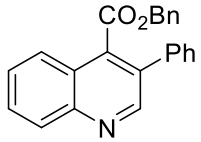
Methyl 3-phenylquinoline-4-carboxylate (5a)



5a

Following the GP5, starting from methyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (**4a**) (50.1 mg, 200 μmol, 1.00 equiv) the title compound **5a** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 10:90) as a yellow oil (20.0 mg, 76.0 μmol, 38% yield).
Rf=0.42 (Pentane:EtOAc 90:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H, Ar*H*), 8.19 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.92 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.78 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, Ar*H*), 7.65 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H, Ar*H*), 7.53 – 7.45 (m, 5H, Ar*H*), 3.78 (s, 3H, C*H*$_3$); Spectral data of the obtained compound is corresponding to the reported values.[4]

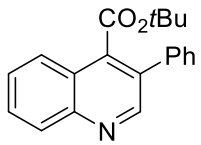
Benzyl 3-phenylquinoline-4-carboxylate (5b)



5b

Following the GP5, starting from benzyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (**4b**) (65.3 mg, 200 μmol, 1.00 equiv) the title compound **5b** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 10:90) as a yellow oil (29.0 mg, 85.4 μmol, 43% yield).
Rf=0.24 (EtOAc:pentane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H, Ar*H*), 8.10 (dt, *J* = 8.5, 0.9 Hz, 1H, Ar*H*), 7.84 (dd, *J* = 8.2, 1.4 Hz, 1H, Ar*H*), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, Ar*H*), 7.54 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H, Ar*H*), 7.43 – 7.30 (m, 5H, Ar*H*), 7.25 – 7.11 (m, 3H, Ar*H*), 7.00 – 6.90 (m, 2H, Ar*H*), 5.14 (s, 2H, C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 151.4, 147.2, 137.1, 136.8, 134.5, 131.8, 129.8, 128.9, 128.8, 128.6, 128.6, 128.5, 128.4, 128.1, 125.0, 123.8, 67.8.(one carbon is not resolved). IR (ν_{max}, cm^{-1}) 3061 (m), 3035 (m), 2953 (m), 2108 (m), 1959 (m), 1886 (m), 1814 (m), 1729 (s), 1576 (m), 1497 (m), 1454 (m), 1377 (m), 1321 (m), 1254 (s), 1212 (s), 1140 (m), 1088 (m), 1023 (m), 946 (m), 912 (m), 759 (s), 701 (s), 644 (m), 607 (m). HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{18}NO_2^+$ 340.1332; Found 340.1330.

***Tert*-butyl 3-phenylquinoline-4-carboxylate (5c)**

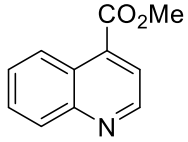


5c

Following the GP5, starting from *tert*-butyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (**4c**) (58.5 mg, 200 μmol, 1.00 equiv) the title compound **5c** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 10:90) as a yellow oil (23.0 mg, 75.3 μmol, 38% yield).

Rf=0.39 (EtOAc:Pentane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H, Ar*H*), 8.10 (ddd, *J* = 8.4, 1.3, 0.6 Hz, 1H, Ar*H*), 7.91 (ddd, *J* = 8.4, 1.4, 0.7 Hz, 1H Ar*H*), 7.69 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, Ar*H*), 7.56 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H, Ar*H*), 7.48 – 7.31 (m, 5H, Ar*H*), 1.29 (s, 9H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 151.4, 147.3, 138.4, 137.3, 131.3, 129.8, 129.6, 129.3, 128.6, 128.2, 127.9, 124.9, 123.8, 83.5, 27.8. IR (ν_{max}, cm^{-1}) 3061 (m), 2979 (m), 2935 (m), 1722 (s), 1608 (w), 1575 (w), 1494 (m), 1455 (m), 1375 (m), 1321 (m), 1263 (s), 1163 (s), 1096 (w), 1021 (m), 909 (m), 845 (m), 801 (m), 765 (s), 705 (m), 645 (w). HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}NO_2^+$ 306.1489; Found 306.1488.

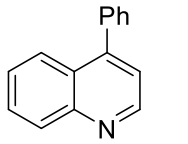
Methyl quinoline-4-carboxylate (5d)



5d

Following the GP6, starting from methyl 1-phenylcycloprop-2-ene-1-carboxylate (**4d**) (34.8 mg, 200 µmol, 1.00 equiv) the title compound **5d** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 10:90) as a yellow oil (15.0 mg, 80.1 µmol, 40% yield). Rf = 0.24 (EtOAc:Pentane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, *J* = 4.5 Hz, 1H, Ar*H*), δ 8.77 (dd, *J* = 8.5, 0.8 Hz, 1H, Ar*H*), 8.18 (dd, *J* = 8.5, 1.0 Hz, 1H, Ar*H*), 7.91 (d, *J* = 4.5 Hz, 1H, Ar*H*), 7.80−7.76 (m, 1H, Ar*H*), 7.68−7.65 (m, 1H, Ar*H*), 4.05 (s, 3H, C*H*$_3$). Spectral data of the obtained compound is corresponding to the reported values[19].

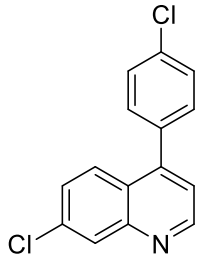
4-Phenylquinoline (5e)



5e

Following the GP5, starting from 3,3-diphenylcyclopropene (**4e**) (38.5 mg, 200 µmol, 1.00 equiv) the title compound **5e** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 5:95 to 20:80) as a white solid (28.1 mg, 137 µmol, 68% yield).
Rf=0.2 (Pentane:Et_2O 6:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 4.6 Hz, 1H, Ar*H*), 8.18 (dd, *J* = 8.5, 1.4 Hz, 1H, Ar*H*), 7.92 (dd, *J* = 8.5, 1.4 Hz, 1H, Ar*H*), 7.75 – 7.69 (m, 1H, Ar*H*), 7.56 – 7.45 (m, 6H, Ar*H*), 7.33 (d, *J* = 4.6 Hz, 1H, Ar*H*). Spectral data of the obtained compound is corresponding to the reported values[20].

7-Chloro-4-(4-chlorophenyl)quinoline (5f)



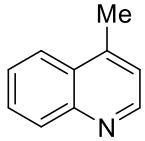
5f

[19] A. Chatterjee, B. König, *Angew. Chem. Int. Ed.* **2019**, *58*, 14289.

[20] Choy, P. Y.; Yuen, O. Y.; Leung, M. P.; Chow, W. K.; Kwong, F. Y., *Eur. J. Org. Chem.* **2020**.

Following the GP5, starting from 4,4'-(cycloprop-2-ene-1,1-diyl)bis(chlorobenzene) **(4f)** (52.2 mg, 200 µmol, 1.00 equiv) the title compound **5f** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 5:95 to 20:80) as a white solid (44.3 mg, 0.162 mmol, 81% yield).
Rf = 0.36 (EtOAc:Pentane 1:9). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.94 (d, *J* = 4.30 Hz, 1H, Ar*H*), 8.18 (s, 1H, Ar*H*), 7.80 (d, *J* = 9.04 Hz, 1H, Ar*H*), 7.52 (d, *J* = 8.10 Hz, 2H, Ar*H*), 7.46 (d, *J* = 9.04 Hz, 1H, Ar*H*), 7.42 (d, *J* = 8.10 Hz, 2H, Ar*H*), 7.31 (d, *J* = 4.30 Hz, 1H, Ar*H*). Spectral data of the obtained compound is corresponding to the reported values[21].

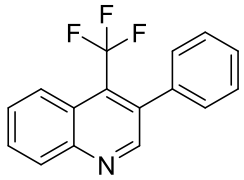
4-Methylquinoline (5g)



5g

Following the GP5, starting from (1-methylcycloprop-2-en-1-yl)benzene **(4g)** (26.0 mg, 200 µmol, 1.00 equiv) the title compound **5g** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 20:80) as a light-yellow oil (11.9 mg, 83.1 µmol, 42% yield).
Rf=0.40 (Pentane:EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.4 Hz, 1H, Ar*H*), 8.11 (d, *J* = 8.5 Hz, 1H, Ar*H*), 8.00 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar*H*), 7.71 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H, Ar*H*), 7.57 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H, Ar*H*), 7.23 (dd, *J* = 4.4, 1.2 Hz, 1H, Ar*H*), 2.71 (s, 3H, C*H*$_3$). Spectral data of the obtained compound is corresponding to the reported values[22].

3-Phenyl-4-(trifluoromethyl)quinoline (5h)



5h

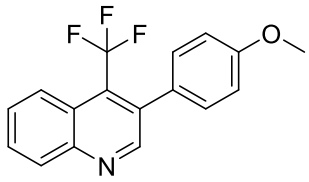
Following the GP5, starting from (1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (**4h**) (52.1 mg, 200 µmol, 1.00 equiv) the title compound **5h** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 5:95 to 20:80) as a yellow oil (32.0 mg, 117 µmol, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H, Ar*H*), 8.27 (d, *J* = 8.6 Hz, 1H, Ar*H*), 8.24 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.80-7.83 (m, 1H, Ar*H*), 7.70-7.73 (m, 1H, Ar*H*), 7.46-7.50 (m, 3H, Ar*H*), 7.38 (dd, *J* = 7.4, 1.7 Hz, 2H, Ar*H*). Spectral data of the obtained compound is corresponding to the reported values[23].

3-(4-Methoxyphenyl)-4-(trifluoromethyl)quinoline (5i)

[21] Jiang, H.; An, X.; Tong, K.; Zheng, T.; Zhang, Y.; Yu, S., *Angew. Chem. Int. Ed.* **2015,** *54* (13), 4055-4059.

[22] Sahoo, M. K.; Jaiswal, G.; Rana, J.; Balaraman, E., *Chem. Eur. J.* **2017,** *23* (57), 14167-14172.

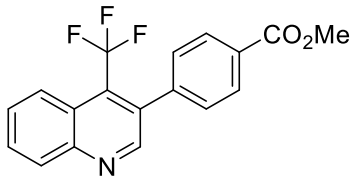
[23] Nagase, M.; Kuninobu, Y.; Kanai, M., *J. Am. Chem. Soc.* **2016,** *138* (19), 6103-6106.



5i

Following the GP5, starting from 1-methoxy-4-(3-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene **(5i)** (58.1 mg, 200 μmol, 1.00 equiv) the title compound **5i** was obtained after purification by column chromatography (SiO_2, Et_2O:Pentane 1:99 to 10:90) as a light-yellow oil (34.4 mg, 0.113 mmol, 59% yield).
Rf=0.22 (Pentane:Et_2O 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H, Ar*H*), 8.30 – 8.18 (m, 2H, Ar*H*), 7.80 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H, Ar*H*), 7.70 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, Ar*H*), 7.35 – 7.27 (m, 2H, Ar*H*), 7.06 – 6.97 (m, 2H, Ar*H*), 3.89 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 153.3, 147.9, 133.7 (q, *J* = 2.9 Hz), 130.7 (q, *J* = 29.6 Hz), 130.3, 130.2, 129.9, 129.7, 128.4, 124.9 (q, *J* = 3.9 Hz), 124.8 (q, *J* = 277.9 Hz) 123.4, 113.8, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.2. IR (ν_{max}, cm^{-1}) 3135 (w), 3059 (w), 2935 (w), 2851 (w), 1951 (w), 1765 (w), 1596 (w), 1503 (w), 1302 (m), 1249 (m), 1162 (s), 1126 (s), 1042 (w), 978 (w), 920 (m), 801 (m), 770 (m), 703 (m), 653 (m). HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{15}F_3N^+$ 350.1151; Found 350.1147.

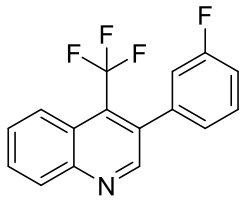
Methyl 4-(4-(trifluoromethyl)quinolin-3-yl)benzoate (5j)



5j

Following the GP5, starting from methyl 4-(3-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzoate **(5j)** (63.7 mg, 200 μmol, 1.00 equiv) the title compound **5j** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 5:95 to 20:80) as a yellow oil (42 mg, 0.12 mmol, 63% yield).
Rf=0.3(EtOAc:Pentane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H, Ar*H*), 8.25 (td, *J* = 8.9, 8.3, 1.7 Hz, 2H, Ar*H*), 8.19 – 8.08 (m, 2H, Ar*H*), 7.84 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H, Ar*H*), 7.73 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, Ar*H*), 7.49 – 7.40 (m, 2H, Ar*H*), 3.97 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 152.0, 148.3, 142.3, 132.7, 130.8 (q, *J* = 30.0 Hz), 130.4, 130.2, 130.1, 129.5, 129.1 (q, *J* = 1.9 Hz), 128.7, 124.9 (q, *J* = 3.7 Hz), 123.8 (q, 276Hz), 52.3.(one carbon is not resolved). ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.2. IR (ν_{max}, cm^{-1}) 3002 (w), 2953 (w), 2899 (w), 2846 (w), 2256 (w), 2113 (w), 1724 (s), 1612 (m), 1568 (w), 1502 (m), 1461 (m), 1437 (m), 1404 (m), 1386 (m), 1325 (m), 1277 (s), 1264 (s), 1227 (m), 1213 (m), 1174 (s), 1151 (m), 1129 (s), 1021 (m), 985 (m), 966 (w), 908 (s), 887 (m), 858 (m), 826 (w), 775 (m), 765 (m), 732 (s), 709 (s), 652 (s), 624 (w). HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}F_3NO_2^+$ 332.0893; Found 332.0903.

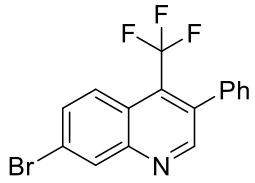
3-(3-Fluorophenyl)-4-(trifluoromethyl)quinoline (5k)



5k

Following the GP5, starting from 1-fluoro-3-(3-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene **(4k)** (55.7 mg, 200 μmol, 1.00 equiv) the title compound **5k** was obtained after purification by column chromatography (SiO_2, EtOAc:Pentane 5:95) as a light-yellow oil (34.5 mg, 118 μmol, 59% yield).
Rf=0.39 (pentane:EtOAc(19:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H, Ar*H*), 8.26 (td, *J* = 8.4, 1.7 Hz, 2H, Ar*H*), 7.84 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H, Ar*H*), 7.73 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, Ar*H*), 7.50 – 7.37 (m, 1H, Ar*H*), 7.22 – 7.05 (m, 3H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 247.5 Hz), 152.2, 148.3, 139.7 (d, *J* = 8.0 Hz), 132.4, 130.9 (q, *J* = 29.7 Hz), 130.4, 130.2, 129.9 (d, *J* = 8.4 Hz), 128.7, 125.0 – 124.7 (m)(2C), 123.8 (q, *J* = 278.0 Hz), 123.1, 116.1 (dq, *J* = 22.5, 1.8 Hz), 115.3 (d, *J* = 21.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.3, -112.8. IR (ν_{max}, cm^{-1}) 3073 (w), 1606 (w), 1587 (m), 1496 (m), 1441 (w), 1387 (w), 1328 (m), 1270 (m), 1227 (m), 1167 (s), 1130 (s), 997 (w), 930 (w), 876 (w), 830 (m), 768 (m), 696 (m), 638 (w). HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}F_4N^+$ 292.0744; Found 292.0745.

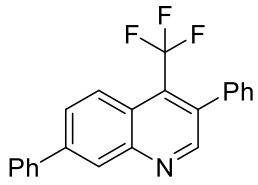
7-Bromo-3-phenyl-4-(trifluoromethyl)quinoline (5l)



5l

Following the GP5, starting from 1-bromo-4-(2-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene **(4l)** (33.9 mg, 100 μmol, 1.00 equiv) the title compound **5l** was obtained after purification by preparative TLC (SiO_2, Toluene:Pentane 50:50) as a light-yellow oil (19.1 mg, 54.2 μmol, 54% yield).
Rf (pentane:toluene(1:1)) = 0.13. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H, Ar*H*), 8.42 (d, *J* = 2.1 Hz, 1H, Ar*H*), 8.12 (dq, *J* = 9.2, 2.3 Hz, 1H, Ar*H*), 7.80 (dd, *J* = 9.2, 2.1 Hz, 1H, Ar*H*), 7.54 – 7.43 (m, 3H, Ar*H*), 7.41 – 7.32 (m, 2H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 148.7, 137.2, 134.1, 132.6, 132.0, 130.8 (q, *J* = 29Hz), 128.9, 128.5, 128.3, 126.3 (q, *J* = 4.1 Hz), 124.1, 123.7 (q, *J* = 276Hz), 122.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.2. IR (ν_{max}, cm^{-1}) 3061 (w), 3036 (w), 2952 (w), 2929 (w), 2857 (w), 1727 (w), 1602 (m), 1491 (m), 1445 (m), 1394 (m), 1319 (m), 1284 (m), 1259 (m), 1226 (m), 1200 (m), 1152 (s), 1128 (s), 1070 (m), 1031 (w), 984 (m), 940 (m), 888 (m), 911 (m), 853 (w), 828 (m), 783 (m), 763 (m), 736 (m), 700 (m), 659 (m), 626 (m). HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}{}^{79}BrF_3N^+$ 351.9943; Found 351.9960.

3,7-Diphenyl-4-(trifluoromethyl)quinoline (5m)

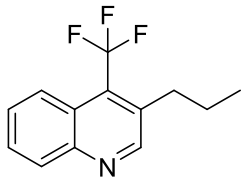


5m

Following the GP5, starting from methyl 4-(2-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl **(4m)** (67.3 mg, 200 μmol, 1.00 equiv) the title compound **5m** was obtained after purification by column chromatography (SiO_2, Et_2O:Pentane 5:95) as a white solid (47.0 mg, 0.135 mmol, 67% yield).

Rf =0.28 (Et_2O:pentane (1:19)). M.p. 95-97°C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H, Ar*H*), 8.46 (d, *J* = 2.0 Hz, 1H, Ar*H*), 8.34 (dq, *J* = 9.0, 2.5 Hz, 1H, Ar*H*), 8.01 (dd, *J* = 9.0, 2.0 Hz, 1H, Ar*H*), 7.81 (dd, *J* = 7.4, 1.8 Hz, 2H, Ar*H*), 7.59 – 7.34 (m, 8H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 148.5, 142.5, 139.4, 137.7, 133.6, 130.5 (q, *J* = 29.9 Hz), 129.2, 129.0, 128.4, 128.3, 128.0, 127.7, 127.5, 125.4 (q, *J* = 3.9 Hz), 124.0 (q, 276Hz), 122.3.(one carbon is not resolved). ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.2. IR (ν_{max}, cm^{-1}) 3058 (w), 3035 (w), 2955 (w), 2925 (w), 2857 (w), 2116 (w), 1956 (w), 1887 (w), 1804 (w), 1727 (w), 1682 (w), 1613 (w), 1492 (m), 1438 (w), 1395 (w), 1330 (m), 1276 (m), 1237 (m), 1190 (m), 1124 (s), 1082 (m), 1026 (w), 992 (w), 904 (m), 829 (w), 800 (w), 762 (s), 734 (m), 694 (s), 651 (w), 610 (w). HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{15}F_3N^+$ 350.1151; Found 350.1147.

3-Propyl-4-(trifluoromethyl)quinoline (5n)

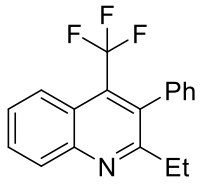


5n

Following the GP6, starting from (2-propyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene **(4n)** (45.3 mg, 200 μmol, 1.00 equiv) the title compound **5n** was obtained after purification by column chromatography (SiO_2, Et_2O:Pentane 1:99 to 10:90) as a yellow oil (16.5 mg, 0.0690 mmol, 34% yield).

Rf = 0.25 (Et_2O:Pentane 1:19). ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H, Ar*H*), 8.22 – 8.11 (m, 2H, Ar*H*), 7.73 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H, Ar*H*), 7.63 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, Ar*H*), 3.00 (ddq, *J* = 10.4, 4.8, 2.3 Hz, 2H, ArC*H*$_2$), 1.77 – 1.65 (m, 2H, $CH_2CH_2CH_3$), 1.04 (t, *J* = 7.3 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 147.5, 133.9, 130.6 (q, *J* = 29.7 Hz), 130.2, 129.1, 128.0, 124.9 (q, *J* = 278.0 Hz), 124.4 (q, *J* = 4.3 Hz), 123.7, 34.5 (q, *J* = 3.9 Hz), 25.5, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.7. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}F_3N^+$ 240.0995; Found 240.0994.

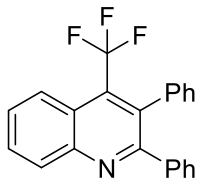
2-Ethyl-3-phenyl-4-(trifluoromethyl)quinoline (5o)



5o

Following the GP6, starting from **(**3-ethyl-1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene **(4o)** (57.7 mg, 200 μmol, 1.00 equiv) the title compound **5o** was obtained after purification by column chromatography (SiO_2, Et_2O:Pentane 1:99 to 10:90) as a white solid (27.4 mg, 0.0909 mmol, 45% yield).
Rf=0.91 (EtOAc:Pentane 10:90). M.p. 59-61°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (ddd, *J* = 9.9, 7.8, 1.7 Hz, 2H, Ar*H*), 7.69 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H, Ar*H*), 7.54 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, Ar*H*), 7.44 – 7.29 (m, 3H, Ar*H*), 7.19 – 7.12 (m, 2H, Ar*H*), 2.59 (q, *J* = 7.5 Hz, 2H, CH_2), 1.11 (t, *J* = 7.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 147.9, 137.4, 133.4, 131.3 (q, *J* = 28.6 Hz), 129.9, 129.6, 128.6, 128.2, 127.8, 127.4, 124.8 (q, *J* = 4.1 Hz), 124.1(q, 277Hz), 122.0, 30.3, 13.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.6. IR (ν_{max}, cm^{-1}) 3063 (w), 2979 (w), 2936 (w), 2877 (w), 1607 (w), 1570 (w), 1496 (w), 1452 (w), 1389 (m), 1329 (m), 1229 (s), 1174 (s), 1123 (s), 1076 (w), 913 (w), 859 (w), 762 (m), 708 (m), 639 (w). HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}F_3N^+$ 302.1151; Found 302.1158. The structure was confirmed by HMBC spectrum.

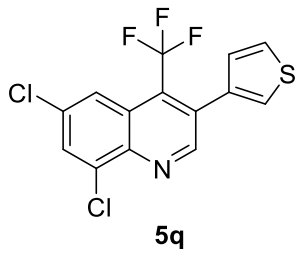
2,3-Diphenyl-4-(trifluoromethyl)quinoline (5p)



5p

Following the GP6, starting from (3-(trifluoromethyl)cycloprop-1-ene-1,2,3-triyl)tribenzene **(4p)** (67.3 mg, 200 μmol, 1.00 equiv) the title compound **5p** was obtained after purification by column chromatography (SiO_2, Et_2O:Pentane 1:99 to 10:90) as a white solid (49.1 mg, 0.141 mmol, 70% yield).
Rf=0.82(EtOAc:Pentane 10:90). M.p. 131-134°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 8.3, 1.5 Hz, 2H, Ar*H*), 7.83 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H, Ar*H*), 7.71 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, Ar*H*), 7.30 – 7.16 (m, 8H, Ar*H*), 7.15 – 7.09 (m, 2H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 147.8, 140.1, 137.2, 133.4, 132.1 (q, *J* = 29.1 Hz), 130.6, 130.0, 130.0, 129.6, 128.2, 127.8, 127.7, 127.6, 126.8(q, *J* = 277Hz), 124.9 (q, *J* = 4.3 Hz), 122.7.(one carbon is not resolved). ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.1. IR (ν_{max}, cm^{-1}) 3086 (w), 3060 (m), 3030 (w), 2112 (w), 1951 (w), 1882 (w), 1805 (w), 1719 (w), 1603 (w), 1580 (w), 1556 (m), 1496 (m), 1443 (m), 1399 (m), 1379 (m), 1343 (m), 1309 (m), 1278 (m), 1248 (m), 1227 (m), 1207 (s), 1171 (s), 1148 (s), 1119 (s), 1075 (m), 1032 (m), 989 (w), 909 (m), 855 (w), 761 (s), 730 (s), 697 (s), 645 (s). HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{15}F_3N^+$ 350.1151; Found 350.1149.

6,8-Dichloro-3-(thiophen-3-yl)-4-(trifluoromethyl)quinoline (5q)

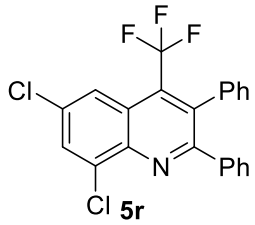


5q

Following the GP6, starting from 3-(3-(3,5-dichlorophenyl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)thiophene **(4q)** (67.0 mg, 200 μmol, 1.00 equiv) the title compound **5q** was obtained after purification by column chromatography (SiO_2, Et_2O:Pentane 1:99 to 10:90) as a white solid (32.6 mg, 93.6 μmol, 47% yield).

Rf=0.45 (Et_2O:Pentane 1:19). M.p. 152-153°C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H, Ar*H*), 8.15 (p, *J* = 2.1 Hz, 1H, Ar*H*), 7.92 (d, *J* = 2.1 Hz, 1H, Ar*H*), 7.47 (dd, *J* = 5.0, 3.0 Hz, 1H, Ar*H*), 7.40 (dd, *J* = 3.0, 1.4 Hz, 1H, Ar*H*), 7.17 (d, *J* = 4.9 Hz, 1H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 142.9, 136.2, 135.7, 134.2, 130.9 (q, *J* = 2.6 Hz), 130.8, 130.6 (q, *J* = 30.3 Hz), 128.7 (q, *J* = 2.2 Hz), 126.2, 125.2, 125.0 (q, *J* = 2.1 Hz), 123.4 (q, *J* = 278.0 Hz), 123.0 (q, *J* = 4.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.0. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_7Cl_2F_3NS^+$ 347.9623; Found 347.9622.

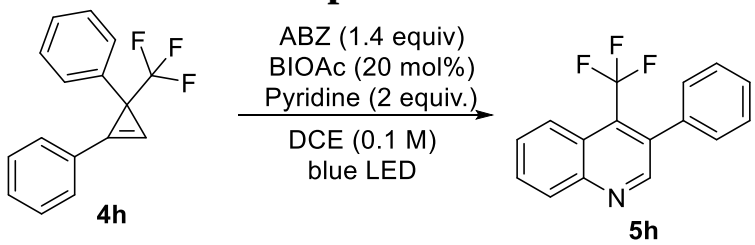
6,8-Dichloro-2,3-diphenyl-4-(trifluoromethyl)quinoline (5r)



5r

Following the GP6, starting from (3-(3,5-dichlorophenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene **(4r)** (81.0 mg, 200 μmol, 1.00 equiv) the title compound **5r** was obtained after purification by column chromatography (SiO_2, Et_2O:Pentane 1:99 to 10:90) as a white solid (44.9 mg, 107 μmol, 54% yield).
Rf=0.81 (Et_2O:Pentane 1:19). M.p. 113-115°C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.1 (p, *J* = 2.3 Hz, 1H, Ar*H*), 7.9 (d, *J* = 2.1 Hz, 1H, Ar*H*), 7.3 – 7.1 (m, 8H, Ar*H*), 7.0 (dd, *J* = 7.9, 1.7 Hz, 2H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 142.7, 139.3, 136.4, 136.1, 135.2 (q, *J* = 2.5 Hz), 133.5, 131.9 (q, *J* = 29.2 Hz), 130.8, 130.0, 129.8 (q, *J* = 2.2 Hz), 128.3, 128.1, 127.8, 127.6, 124.3, 123.6 (q, *J* = 278.7 Hz), 123.0 (q, *J* = 4.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.0. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{13}Cl_2F_3N^+$ 418.0372; Found 418.0378.

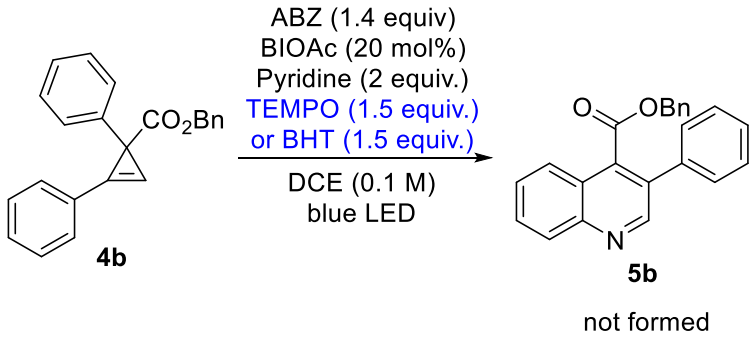
4. 1.5 mmol scale procedure



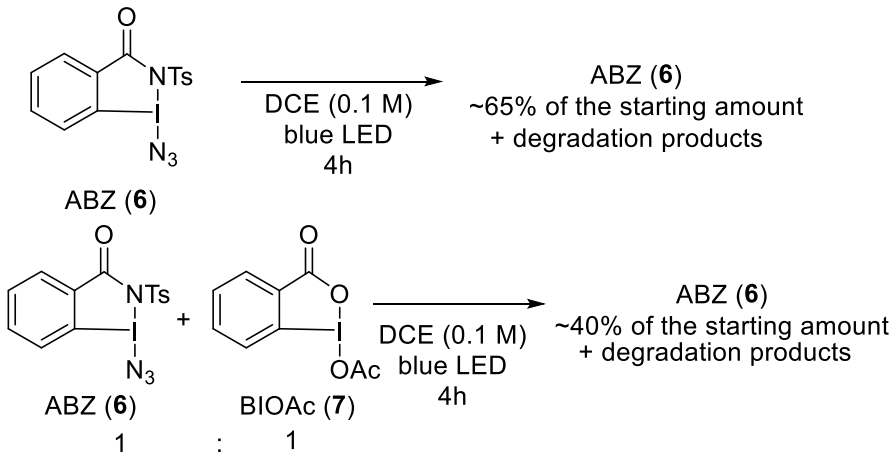
4h **5h**

DCE was degassed by bubbling Ar through it for 30 min. A 50 mL test tube, equipped with a stirring bar was charged with ABZ (**6**) (952 mg, 2.15 mmol, 1.40 equiv) and (3-oxo-1lambda3,2-benziodoxol-1-yl)acetate[18] (94.1 mg, 307 μmol, 0.200 equiv). It was capped with the septum and evacuated-refilled with N_2 (3x). A solution of (1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (**4h)** (400 mg, 1.54 mmol, 1.00 equiv) in DCE (15.4 ml) was added to the reaction mixture, followed by pyridine (243 mg, 3.07 mmol, 2.00 equiv). The reaction mixture was stirred under blue LED irradiation for 14 h. Then, the reaction mixture was filtered through a small pad of silica (3cm), washing the sorbent with EtOAc. The resulting solution was concentrated under vacuum to give crude product , which was purified by flash chromatography (SiO_2, EtOAc:Pentane 5:95 to 20:80) to give 3-phenyl-4-(trifluoromethyl)quinoline **(5h)** (263 mg, 963 μmol, 63% yield) as a yellow oil.

5. Control and mechanistic experiments

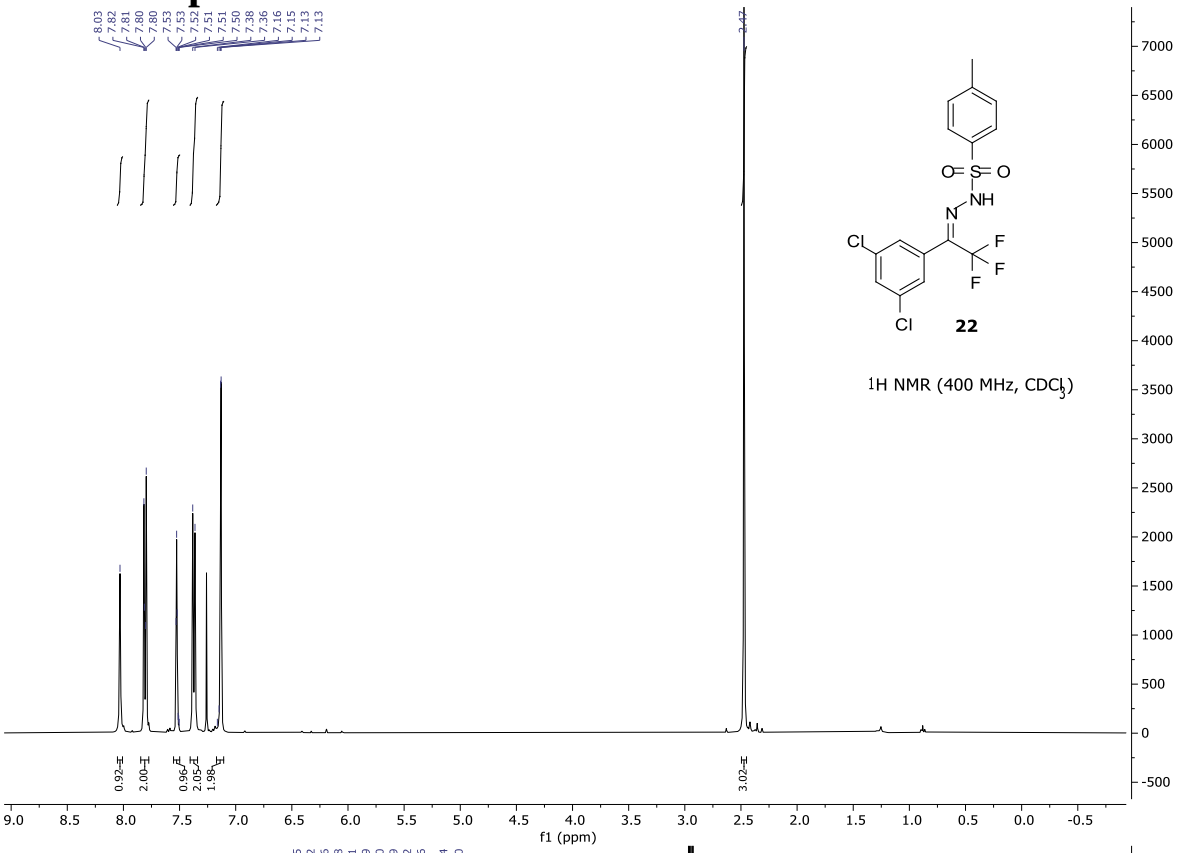


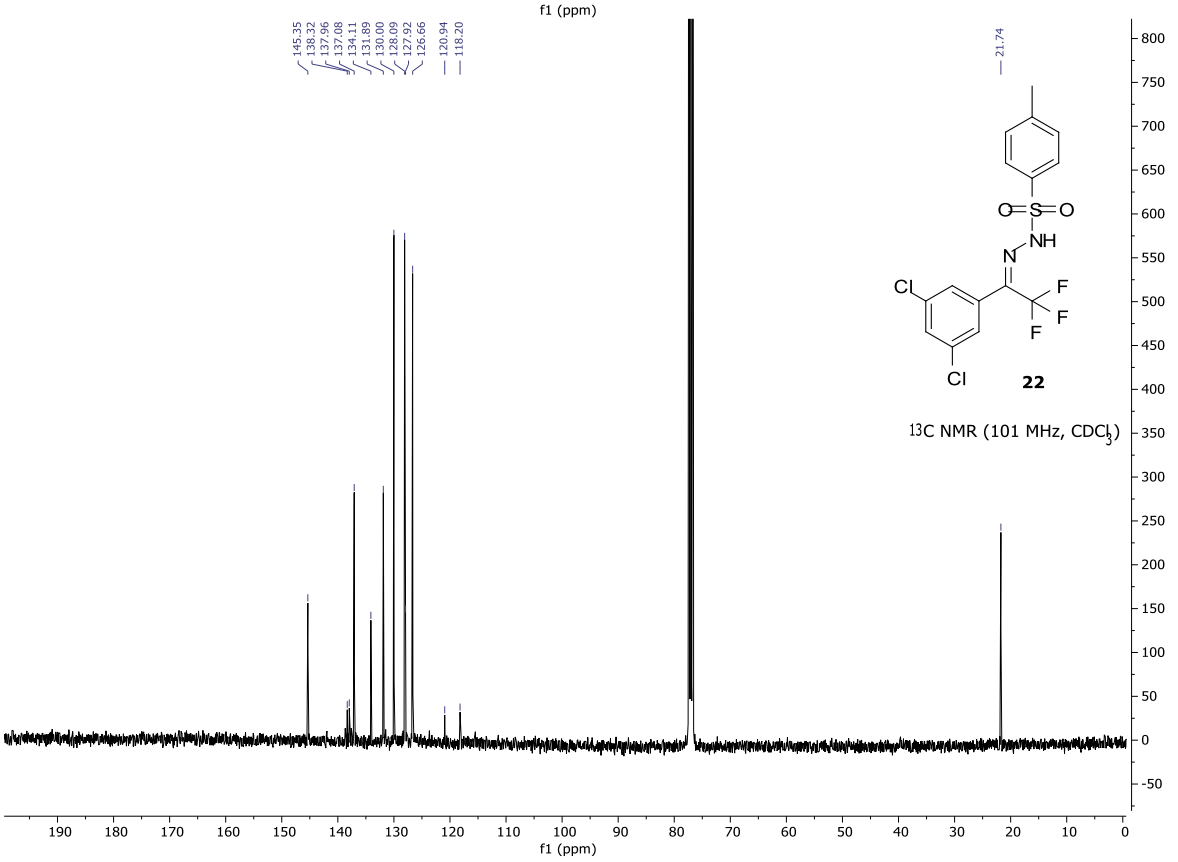
DCE was degassed by bubbling Ar through it for 30 min. A 5 mL test tube, equipped with a stirring bar was charged with ABZ (**6**) (124 mg, 0.280 mmol, 1.40 equiv), (3-oxo-1lambda3,2-benziodoxol-1-yl)acetate (**7**)[18] (12.2 mg, 0.0400 mmol, 0.200 equiv), radical scavenger (1.5 equiv.), and benzyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (**4b)** (65.3 mg, 200 μmol, 1.00 equiv). It was capped with the septum and evacuated-refilled with N_2 (3x). 2mL of DCE was added to the reaction mixture, followed by pyridine (31.6 mg, 400 μmol, 2.00 equiv). The reaction mixture was stirred under blue LED irradiation for 14 h. Then, the reaction mixture was filtered through a small pad of silica (1 cm), washing the sorbent with EtOAc. The resulting solution was concentrated under vacuum to give crude mixture, that does not contain the desired product **5b** as judged by ^{1}H NMR analysis.

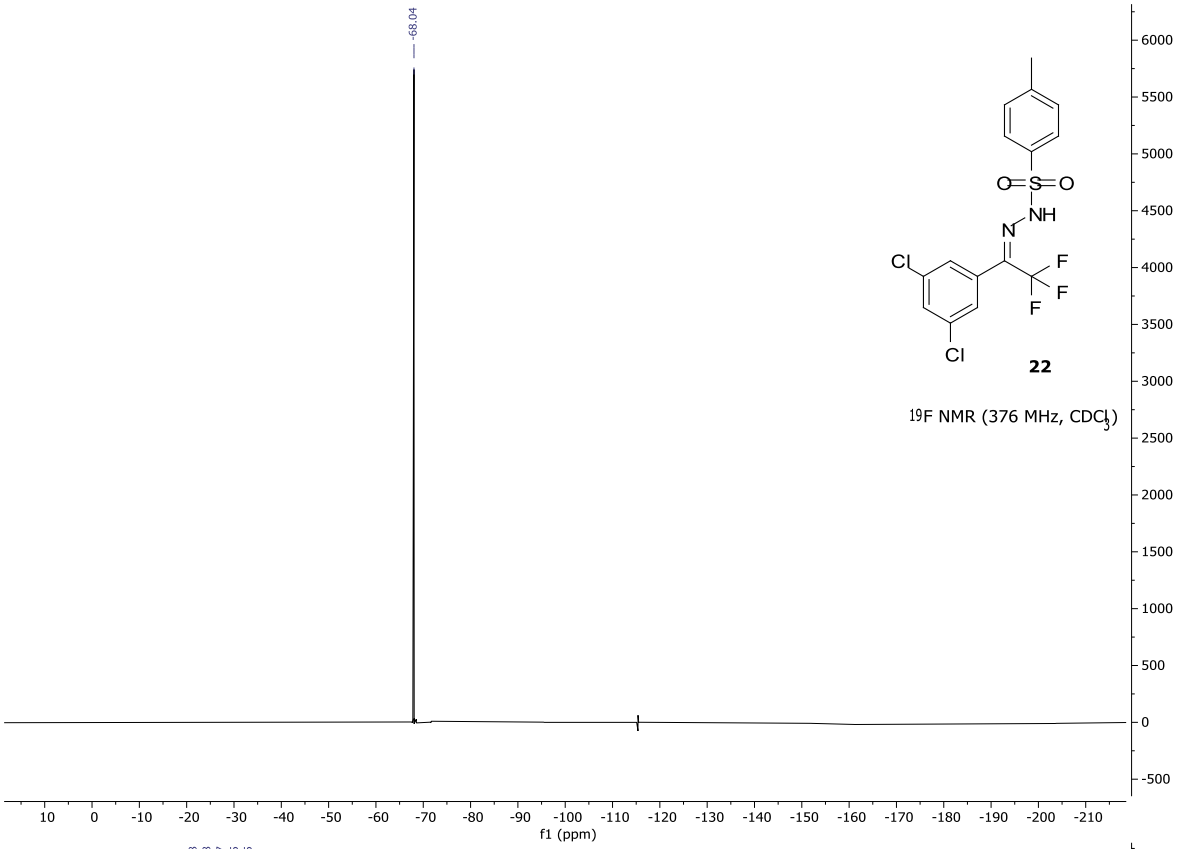


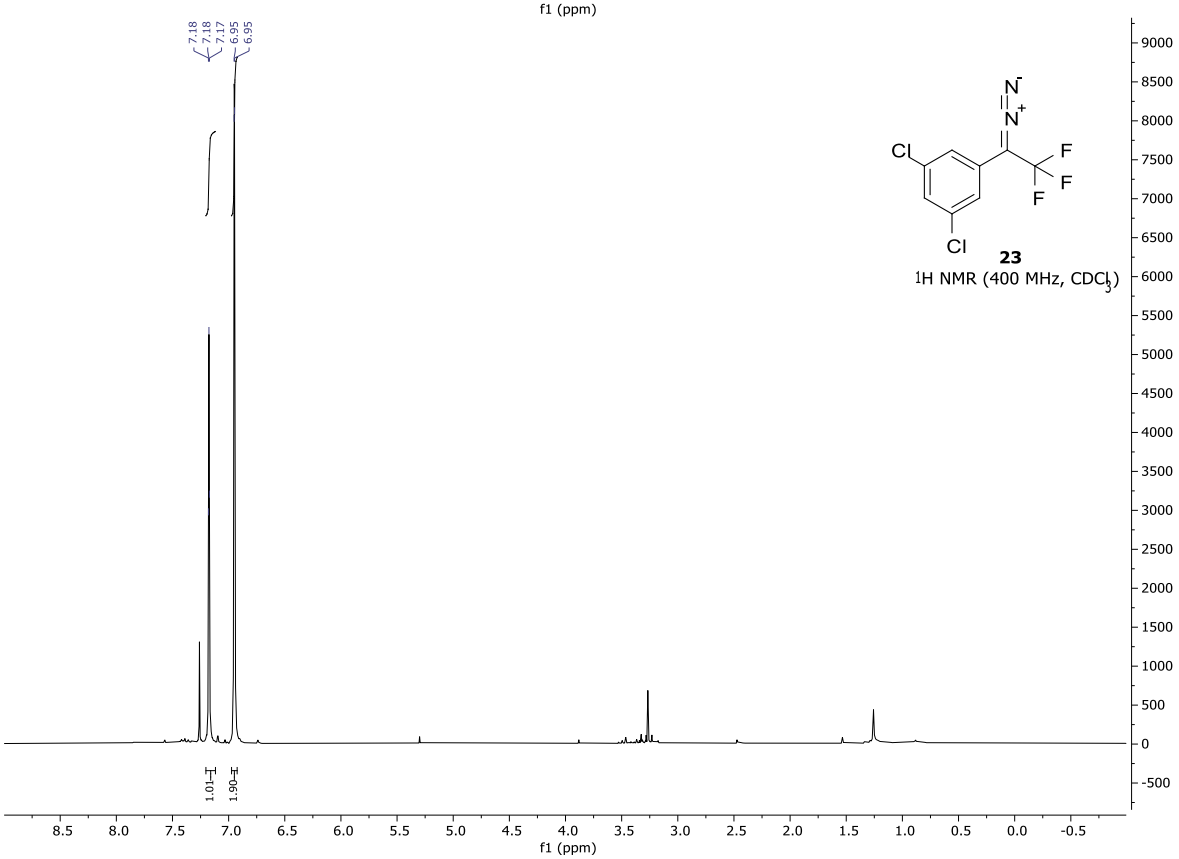
DCE was degassed by bubbling Ar through it for 30 min. A 5 mL test tube, equipped with a stirring bar was charged with corresponding reagents (0.1 mmol). 1mL of DCE was added to the reaction mixture. The reaction mixture was stirred under blue LED irradiation for 4 h. Then, the reaction mixture was concentrated under vacuum and analysed by ^{1}H NMR using CH_2Br_2 as an internal standard.

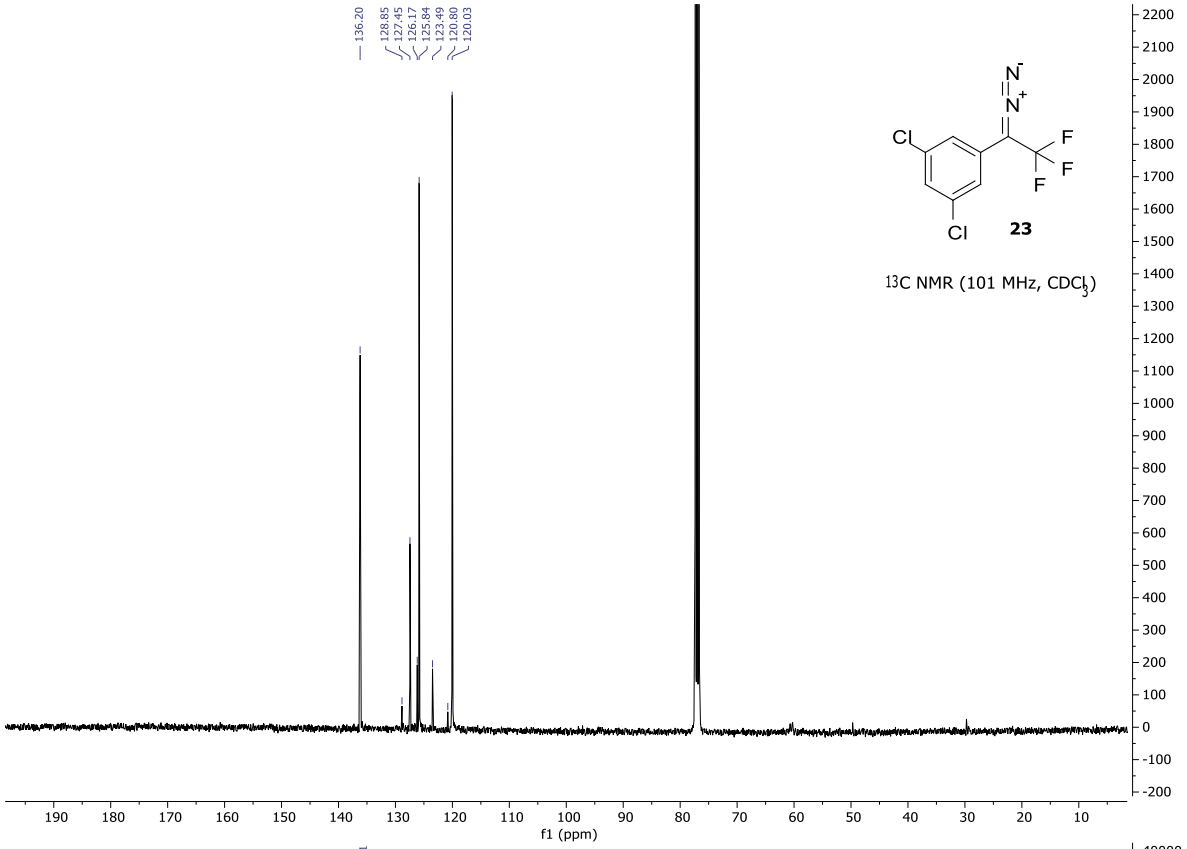
6. NMR Spectra





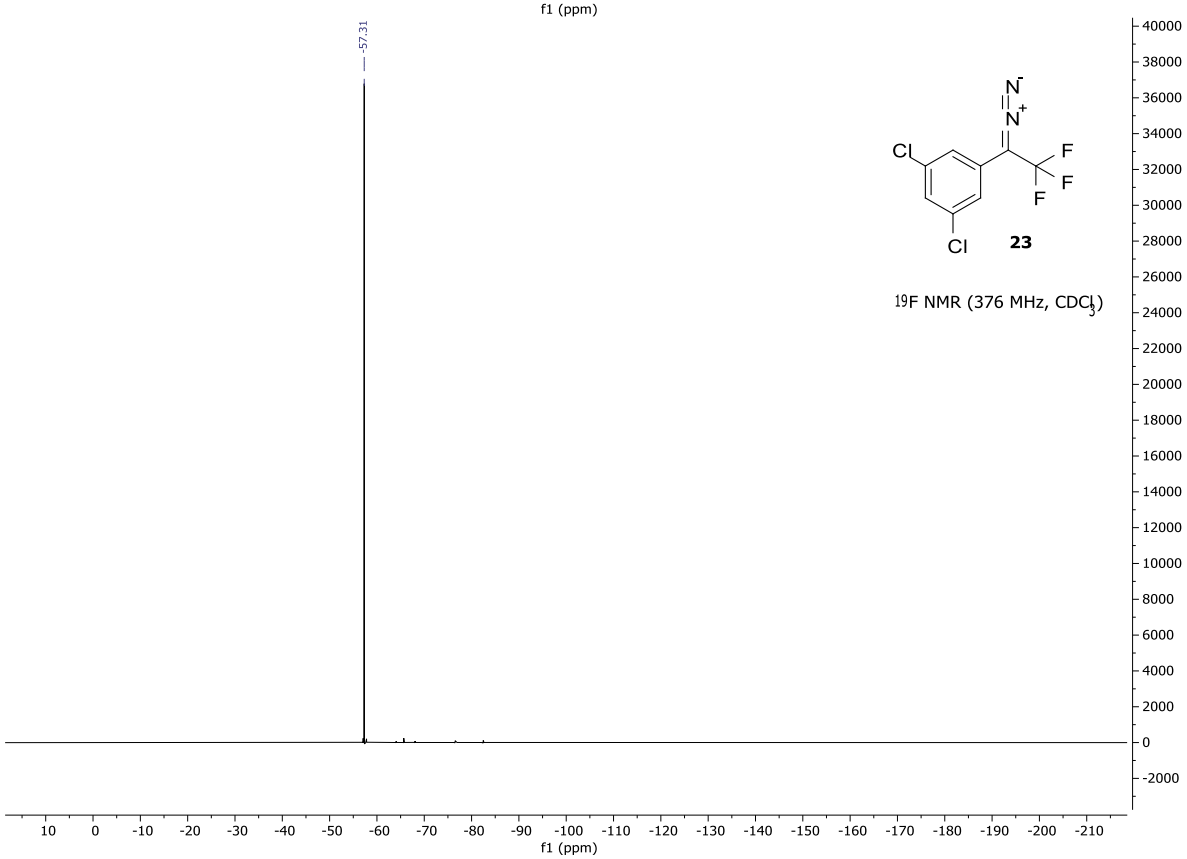

-68.04
Cl
F
F
F
Cl
NH
22
19F NMR (376 MHz, CDCl3)
f1 (ppm)


7.18
7.18
7.17
6.95
6.95
1.01
1.90
Cl
F
F
F
Cl
23
1H NMR (400 MHz, CDCl3)
f1 (ppm)



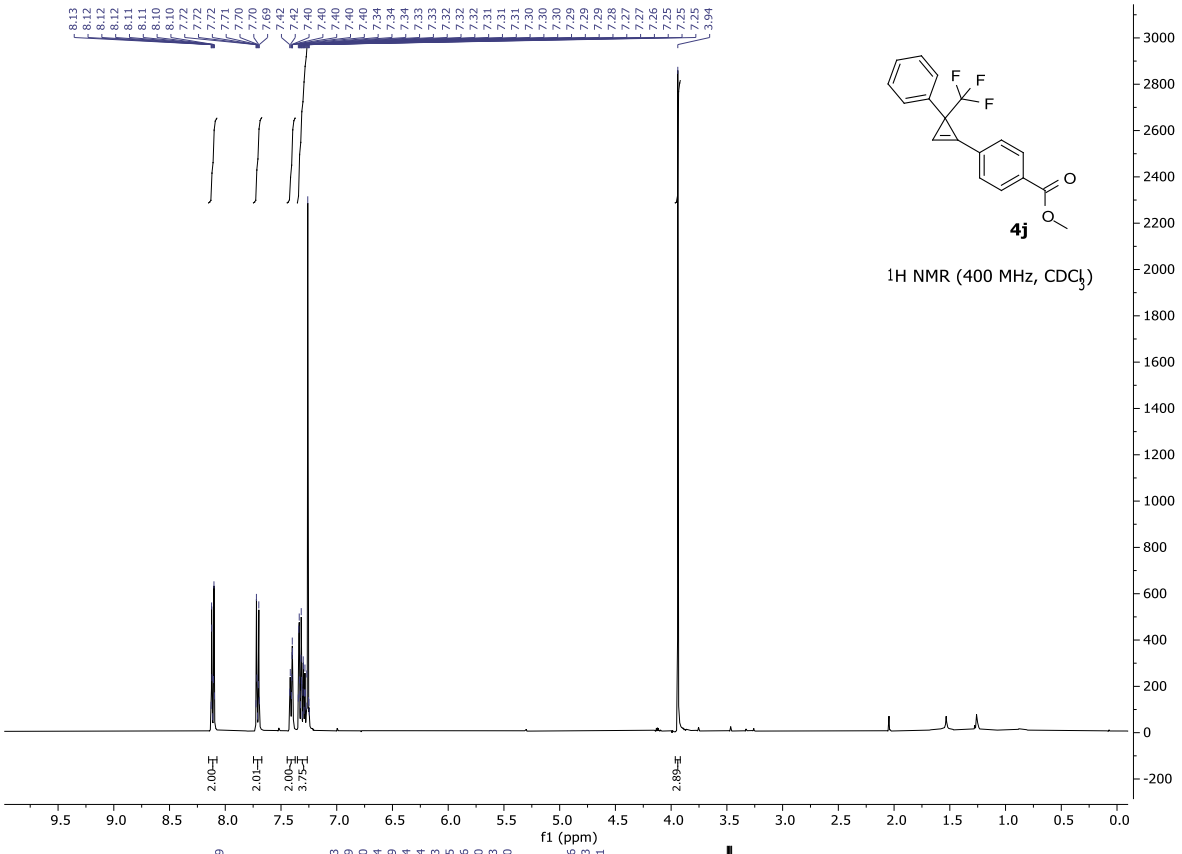
23

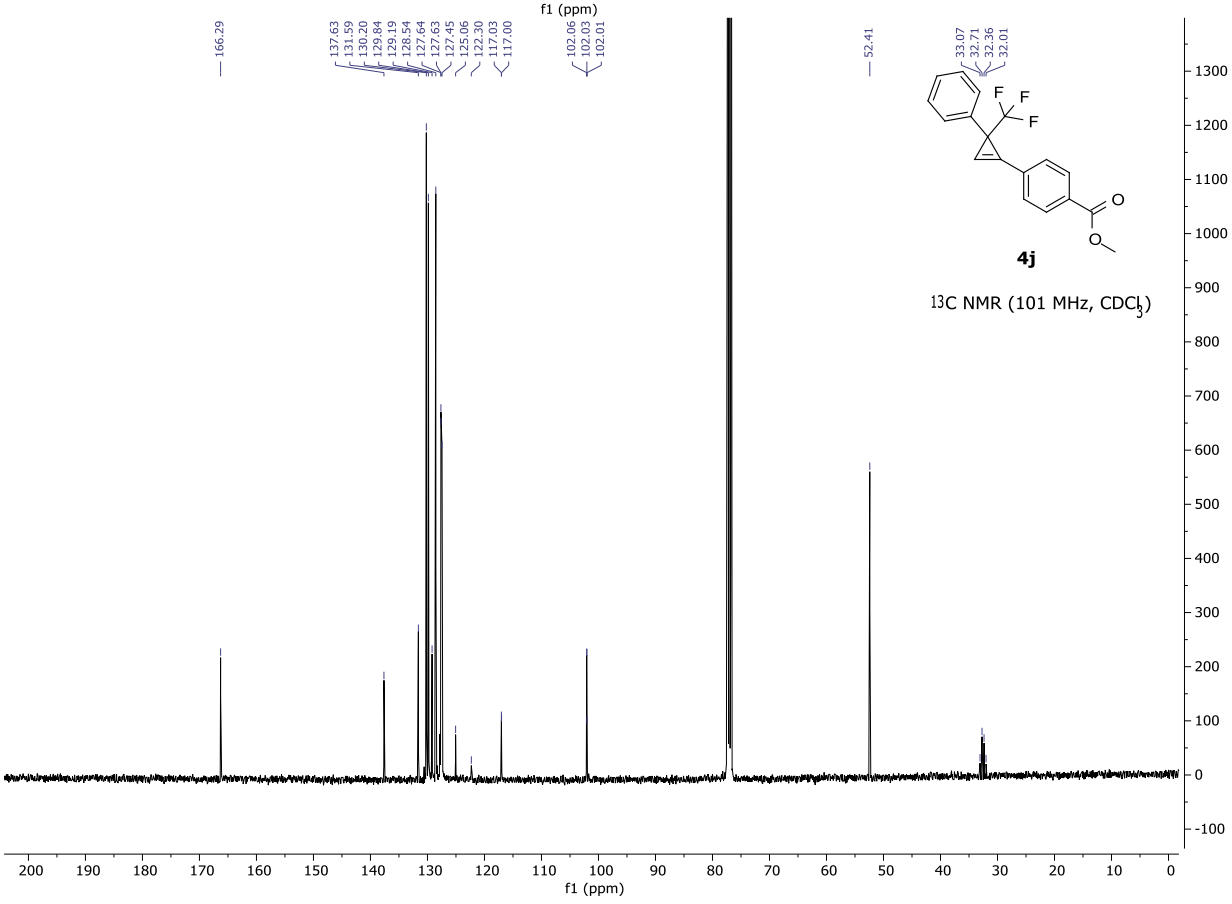
^{13}C NMR (101 MHz, $CDCl_3$)

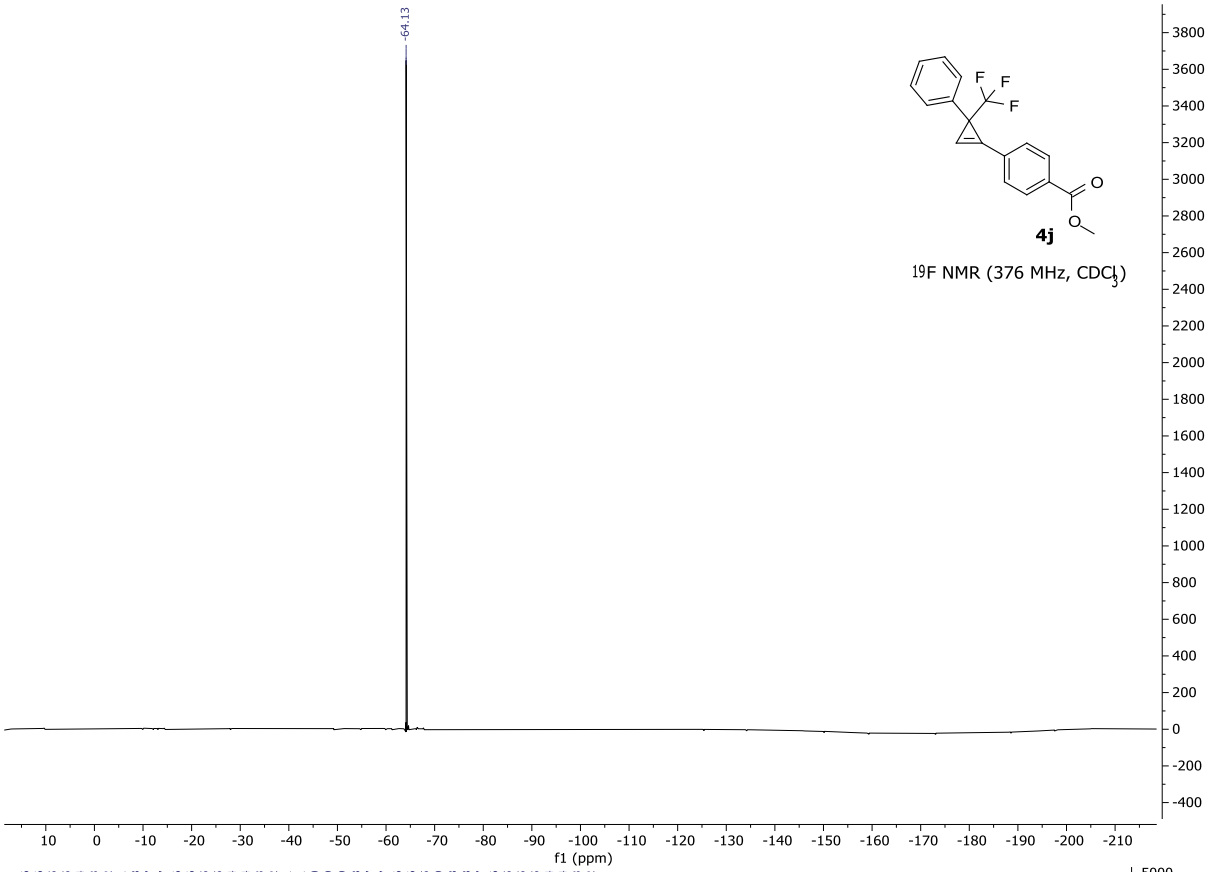


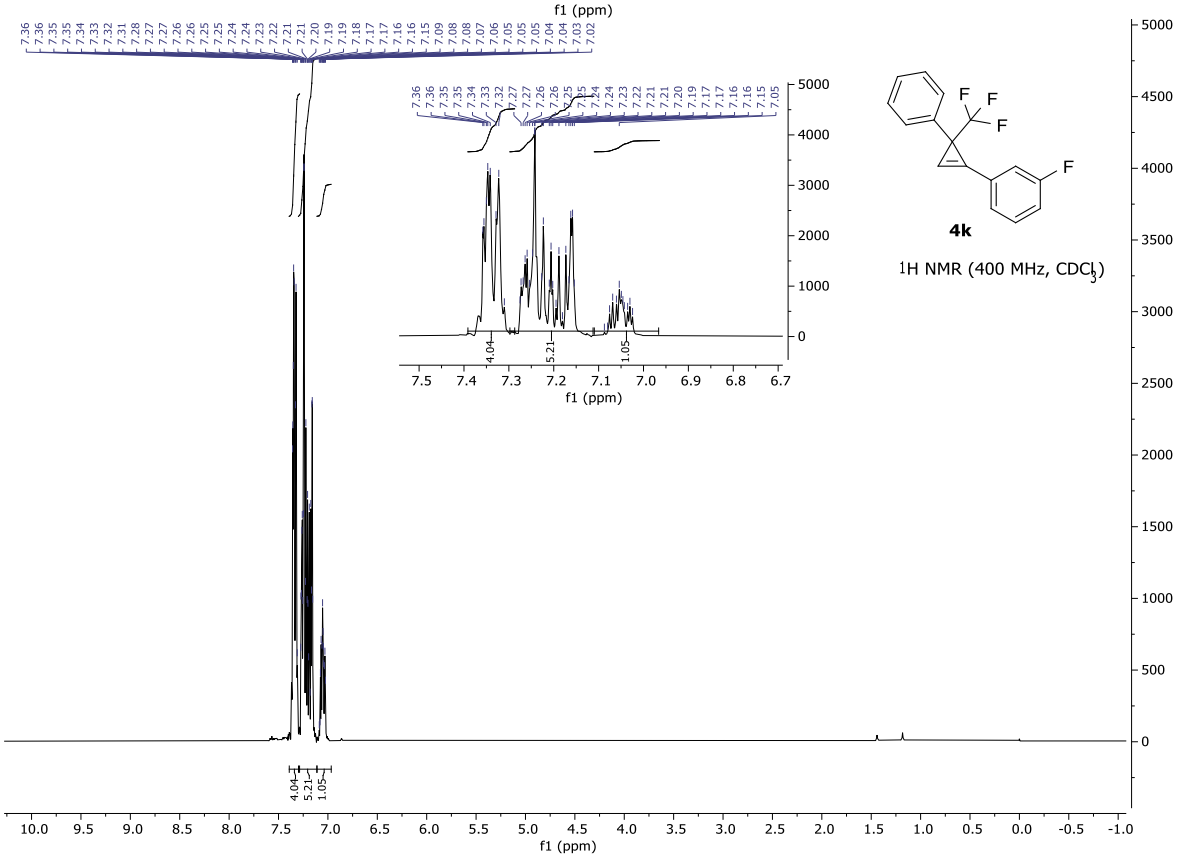
23

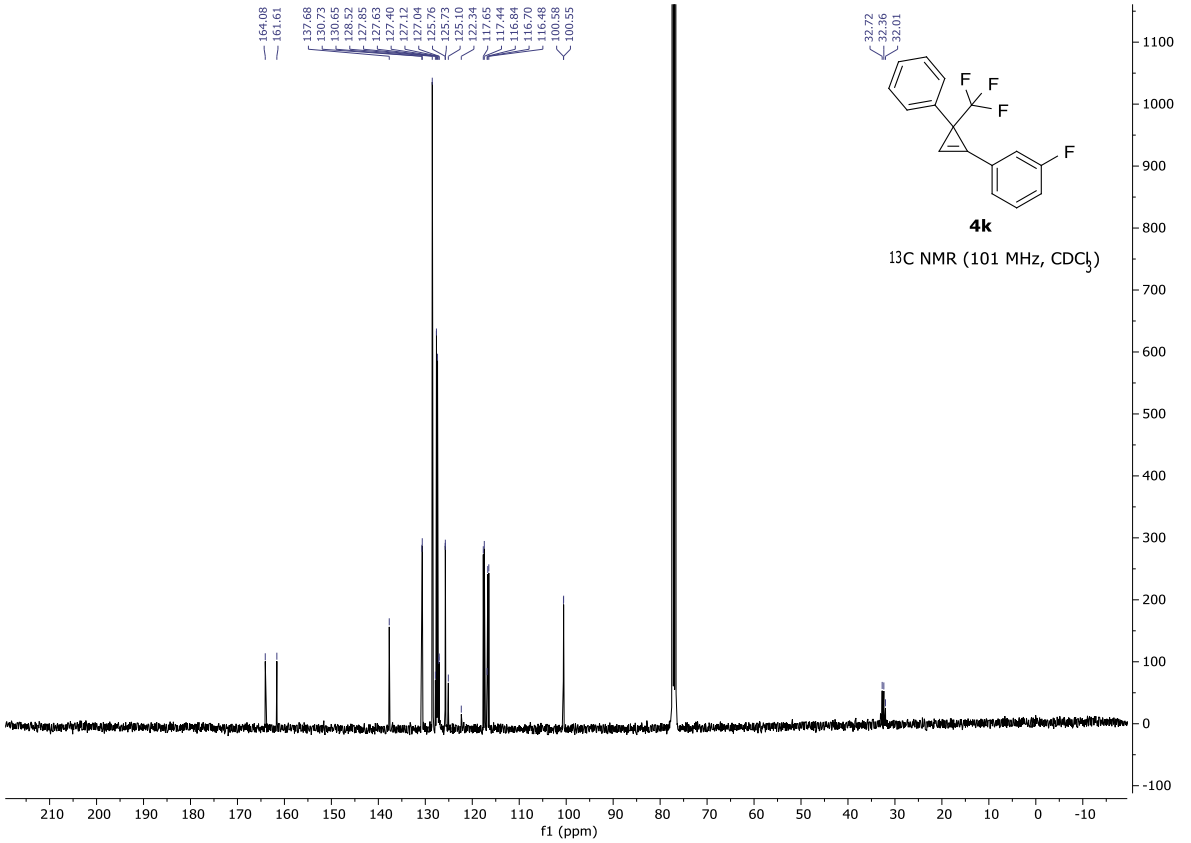
^{19}F NMR (376 MHz, $CDCl_3$)

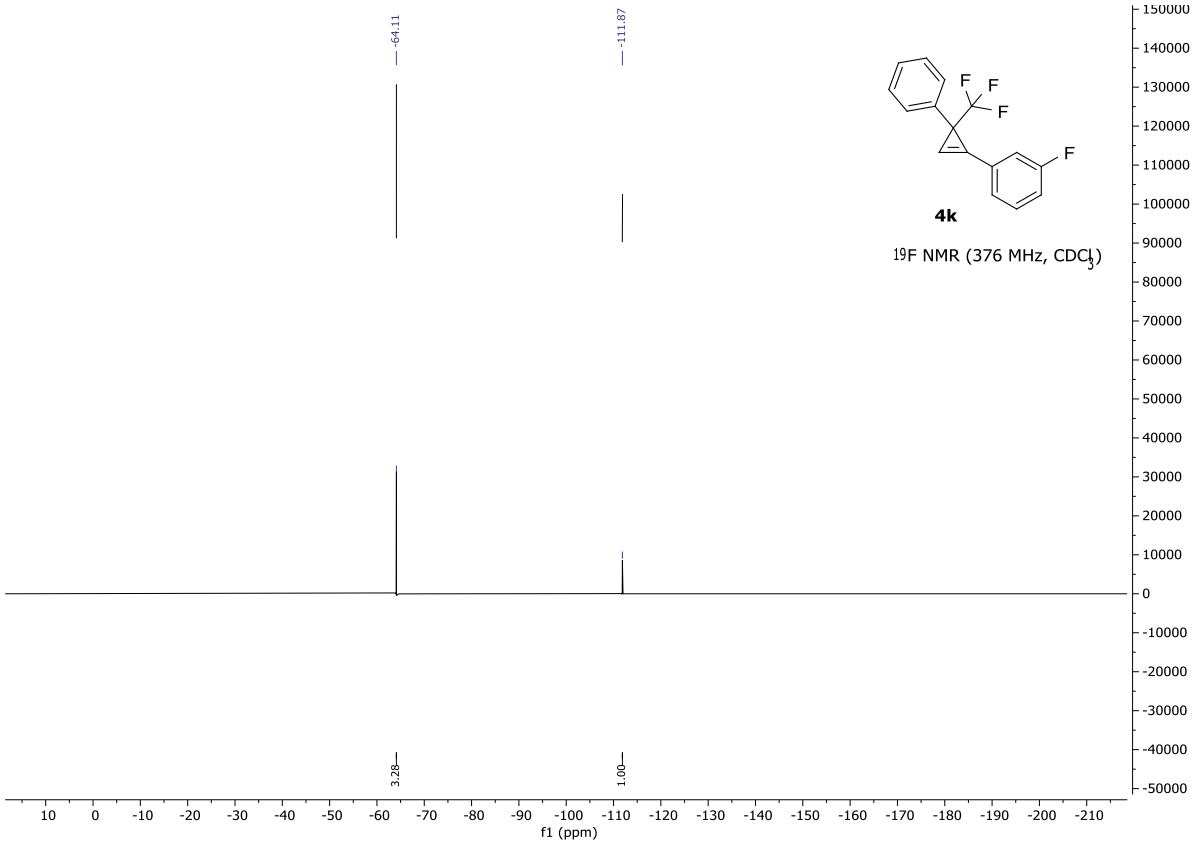

F F F
O
O
4j
1H NMR (400 MHz, CDCl3)
f1 (ppm)

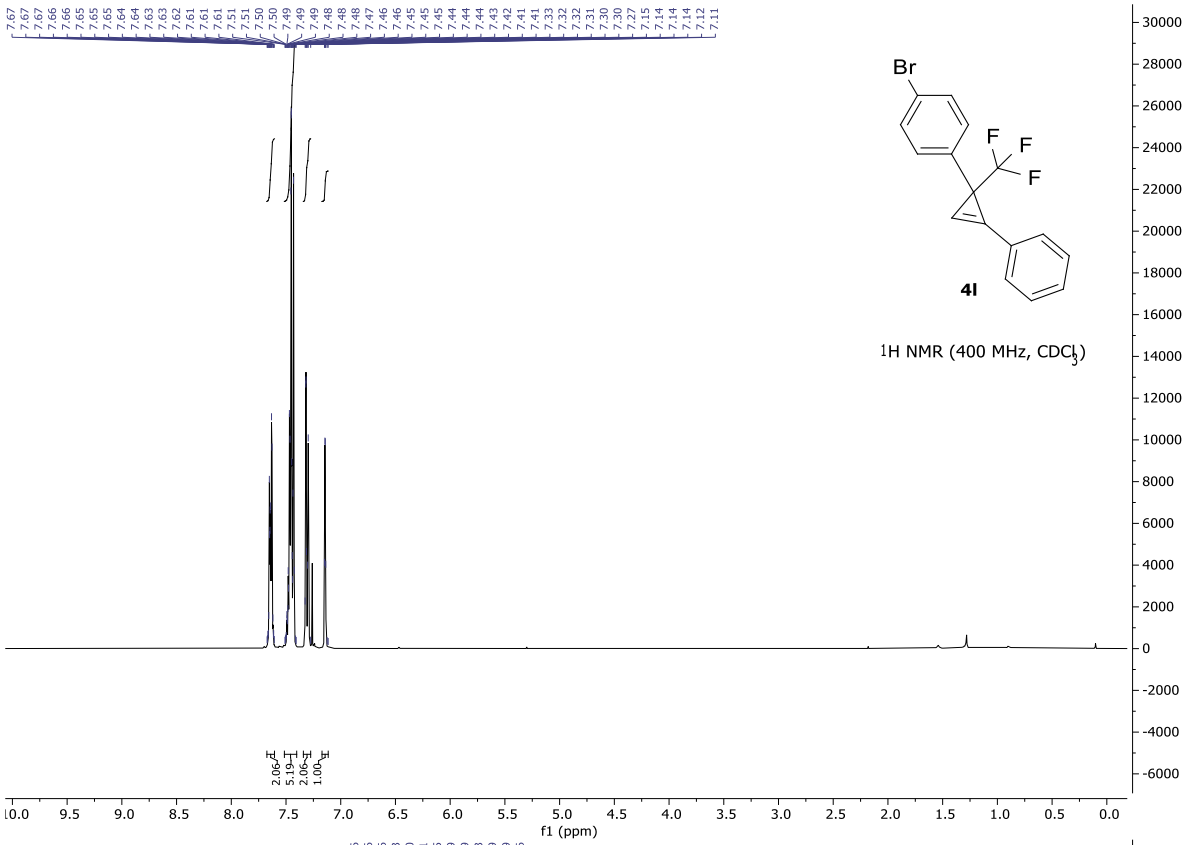

F F F
O
O
4j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

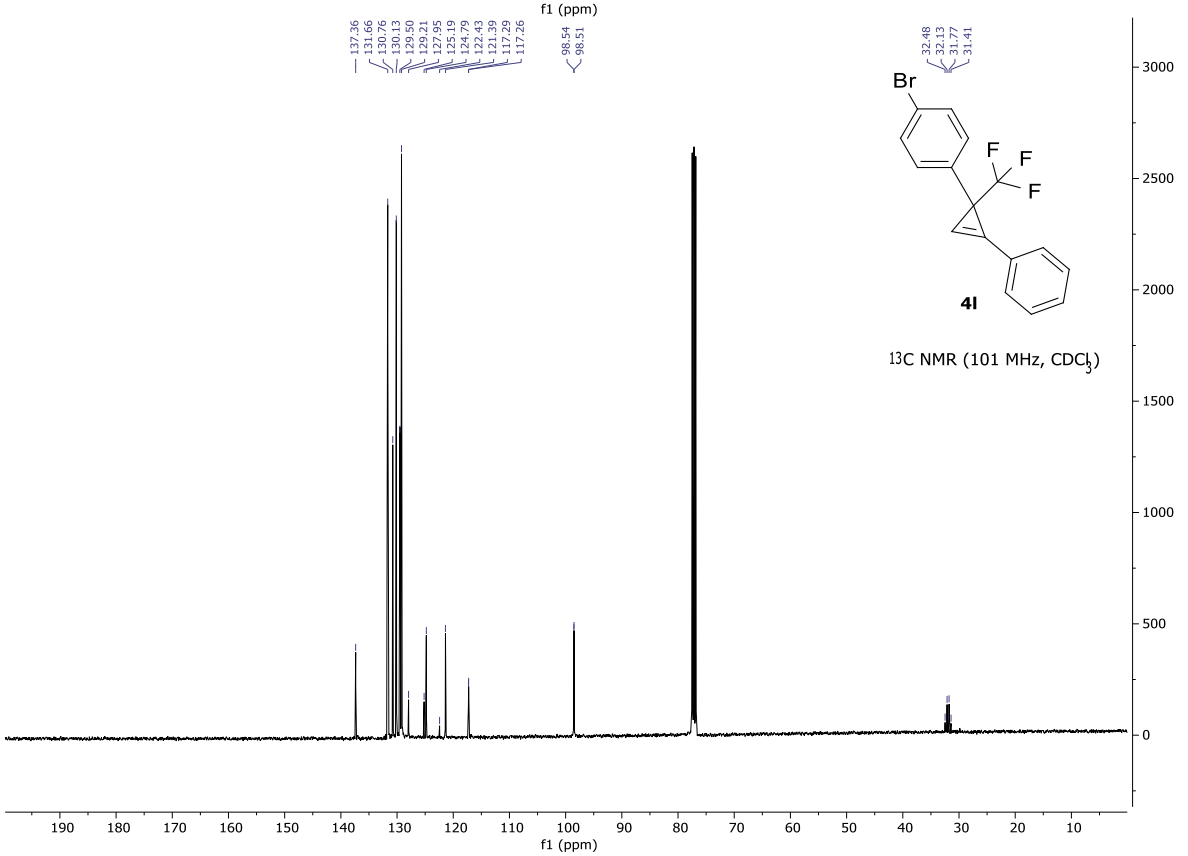

-64.13
F
F
F
O
O
4j
19F NMR (376 MHz, CDCl3)
f1 (ppm)


F
F
F
F
4k
1H NMR (400 MHz, CDCl3)
4.04
5.21
1.05
f1 (ppm)

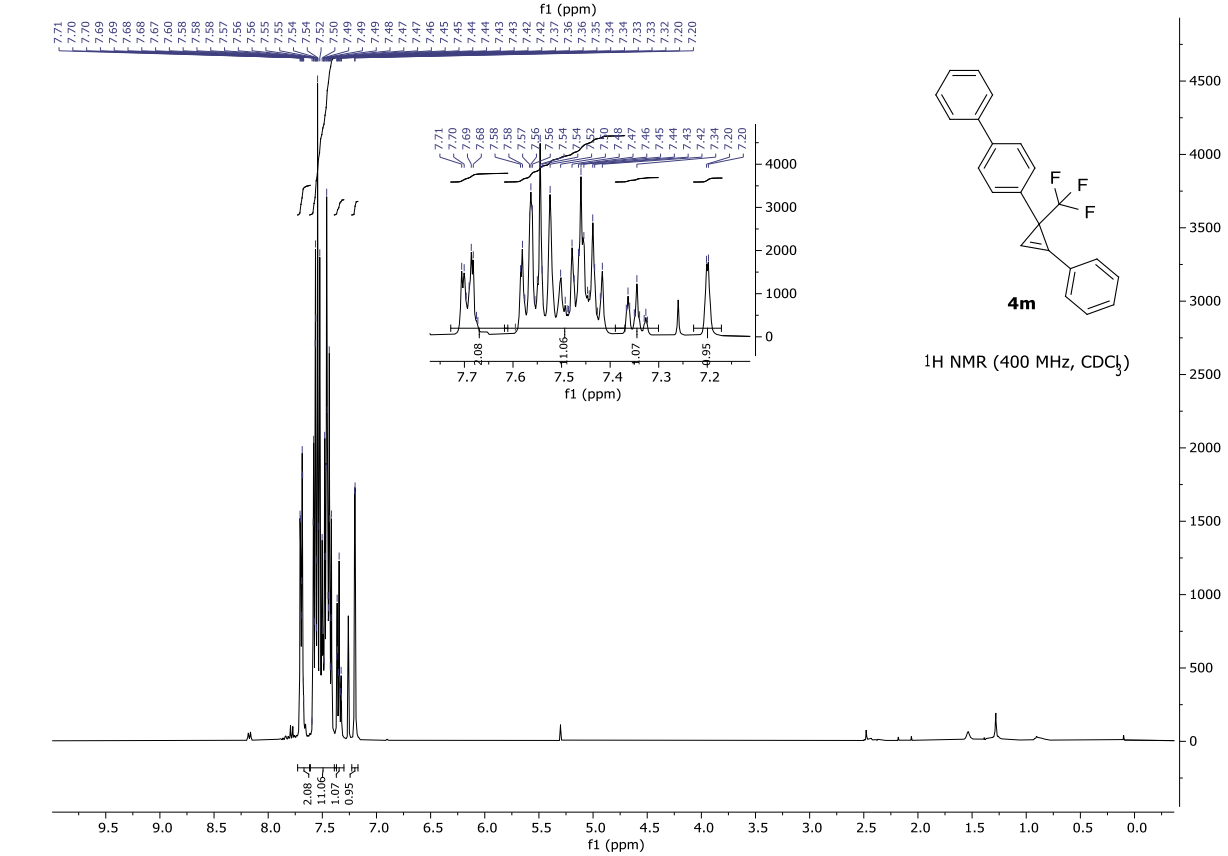

164.08
161.61
137.68
130.73
130.65
128.52
127.85
127.63
127.40
127.12
127.04
125.76
125.73
125.10
122.34
117.65
117.44
116.84
116.70
116.48
100.58
100.55
32.72
32.36
32.01
F
F
F
F
4k
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-64.11
-111.87
F
F
F
F
4k
19F NMR (376 MHz, CDCl3)
3.28
1.00
f1 (ppm)

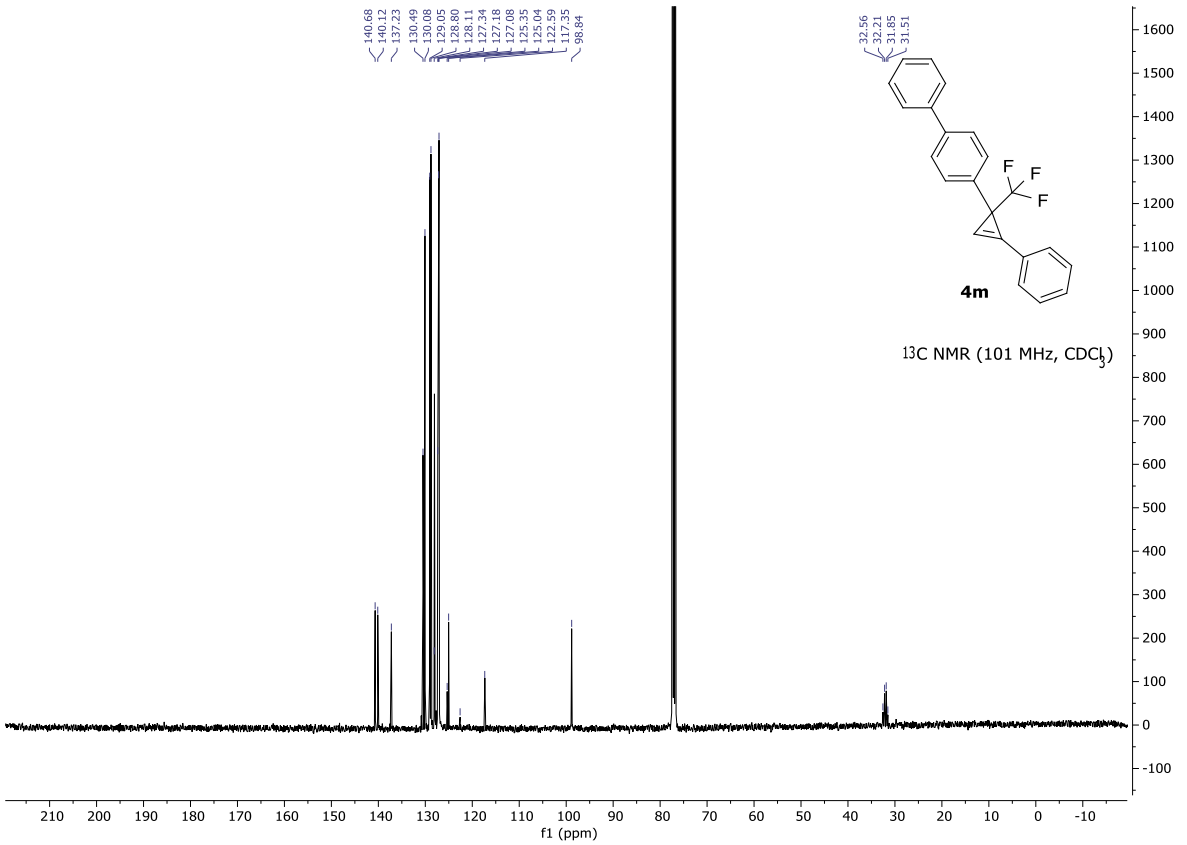

Br
F
F
F
4l
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Br
F
F
F
4l
13C NMR (101 MHz, CDCl3)
f1 (ppm)

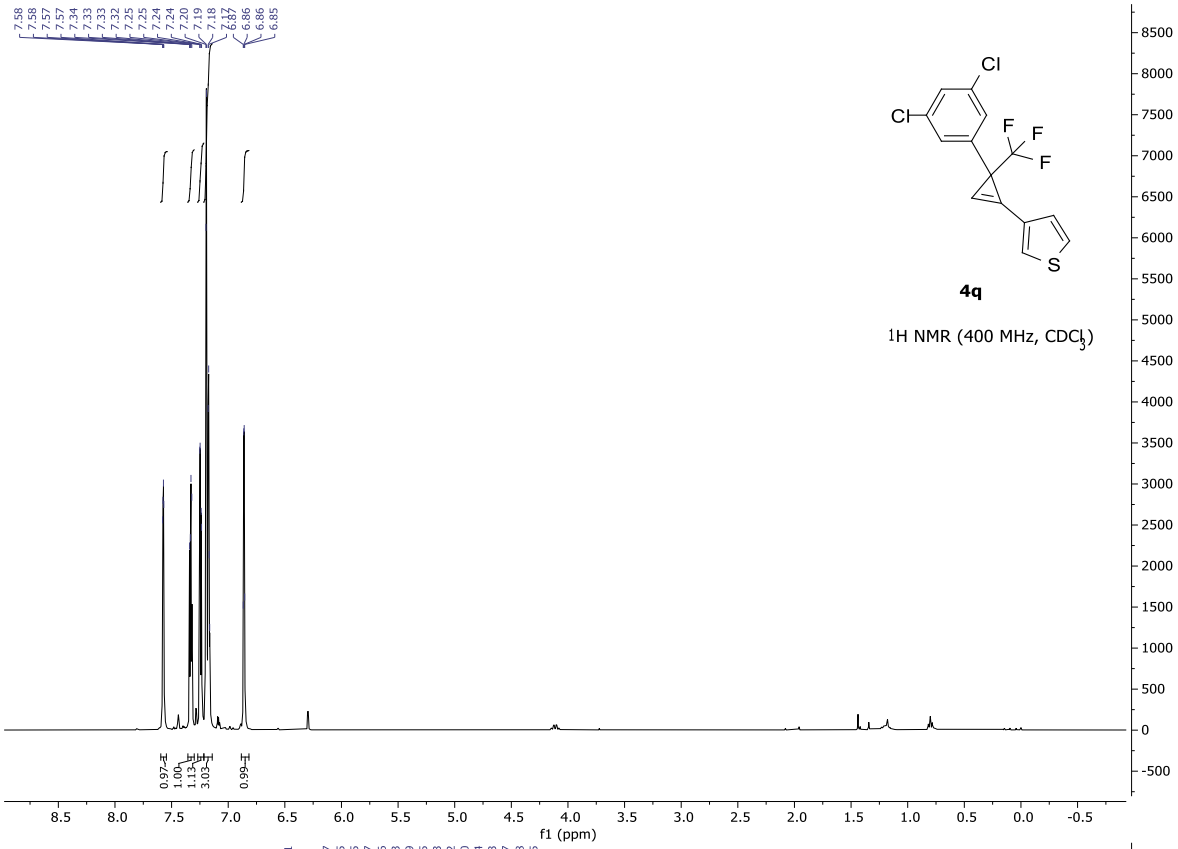
^{19}F NMR (376 MHz, $CDCl_3$)

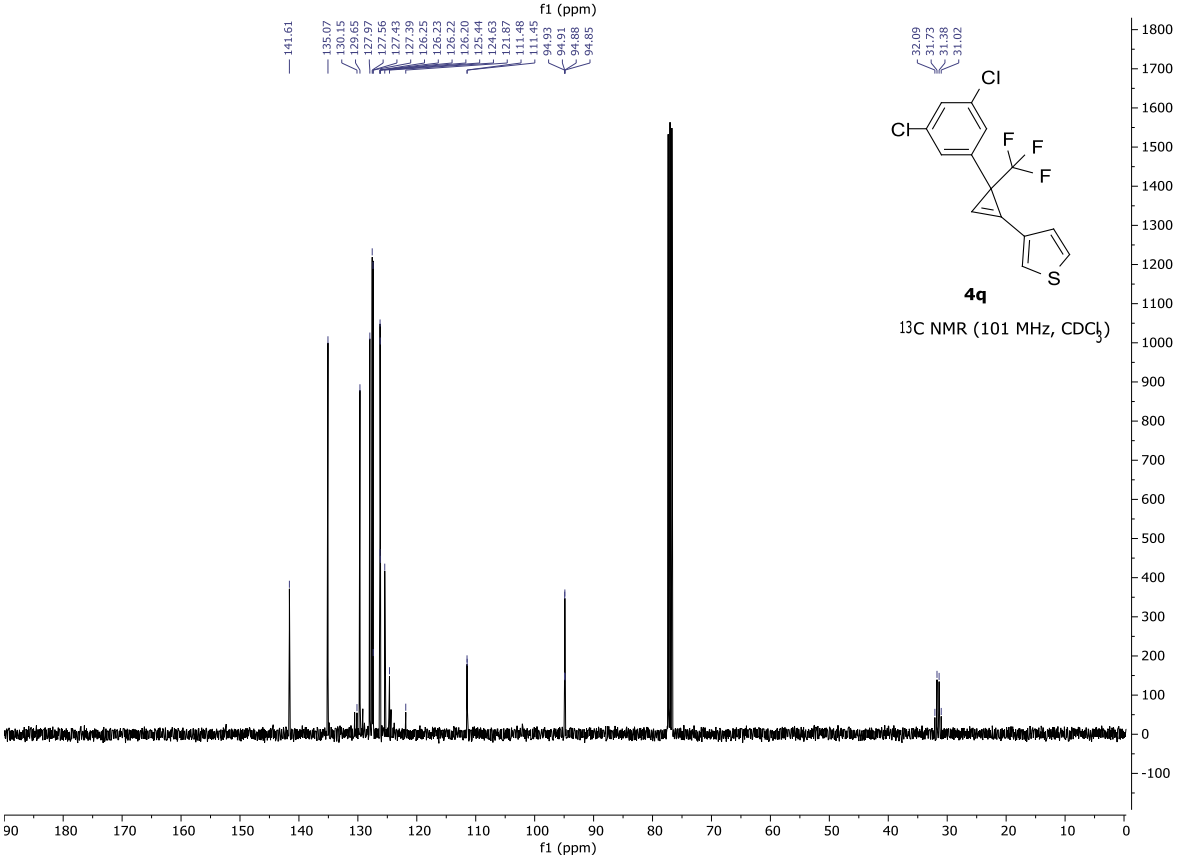


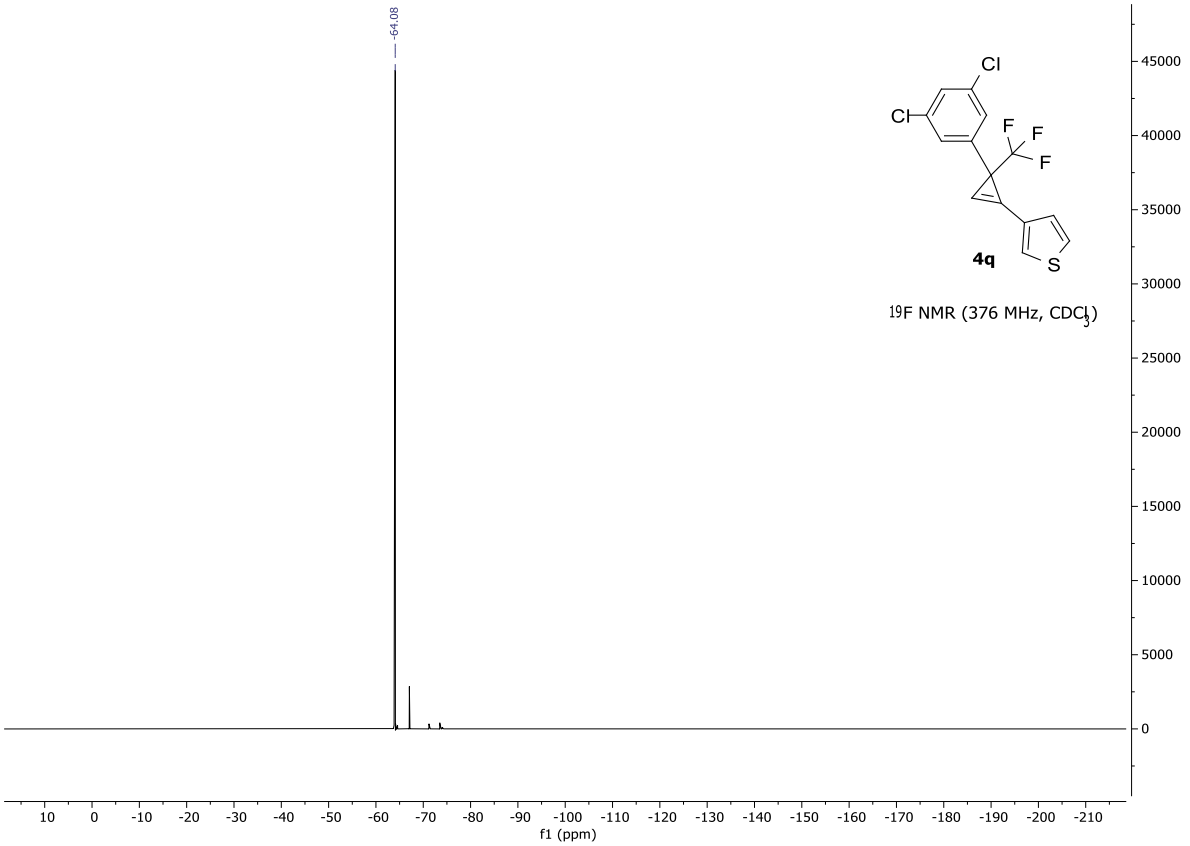
^{1}H NMR (400 MHz, $CDCl_3$)


140.68
140.12
137.23
130.49
130.08
129.05
128.80
128.11
127.34
127.18
127.08
125.35
125.04
122.59
117.35
98.84
32.56
32.21
31.85
31.51
F
F
F
4m
13C NMR (101 MHz, CDCl3)
f1 (ppm)

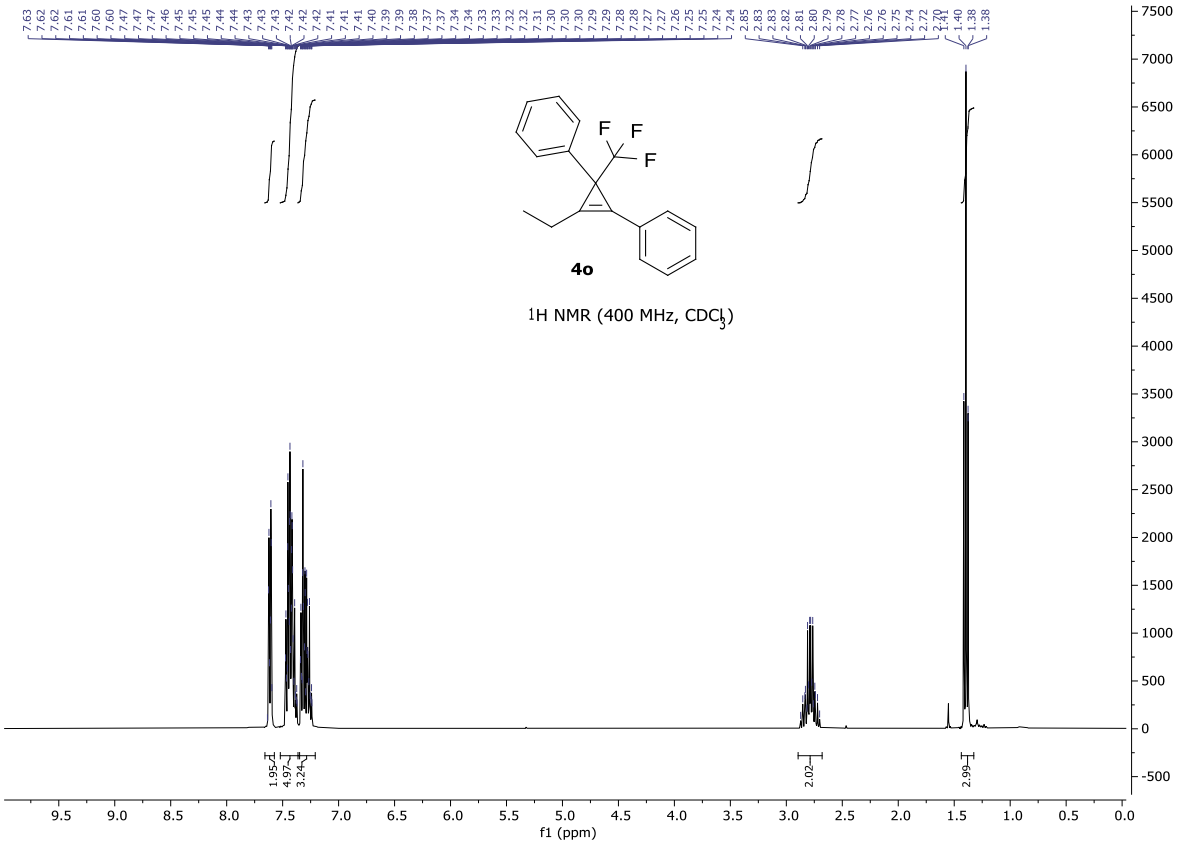

-63.90
F
F
F
4m
19F NMR (376 MHz, CDCl3)
f1 (ppm)


Cl
Cl
F
F
F
S
4q
1H NMR (400 MHz, CDCl3)
f1 (ppm)

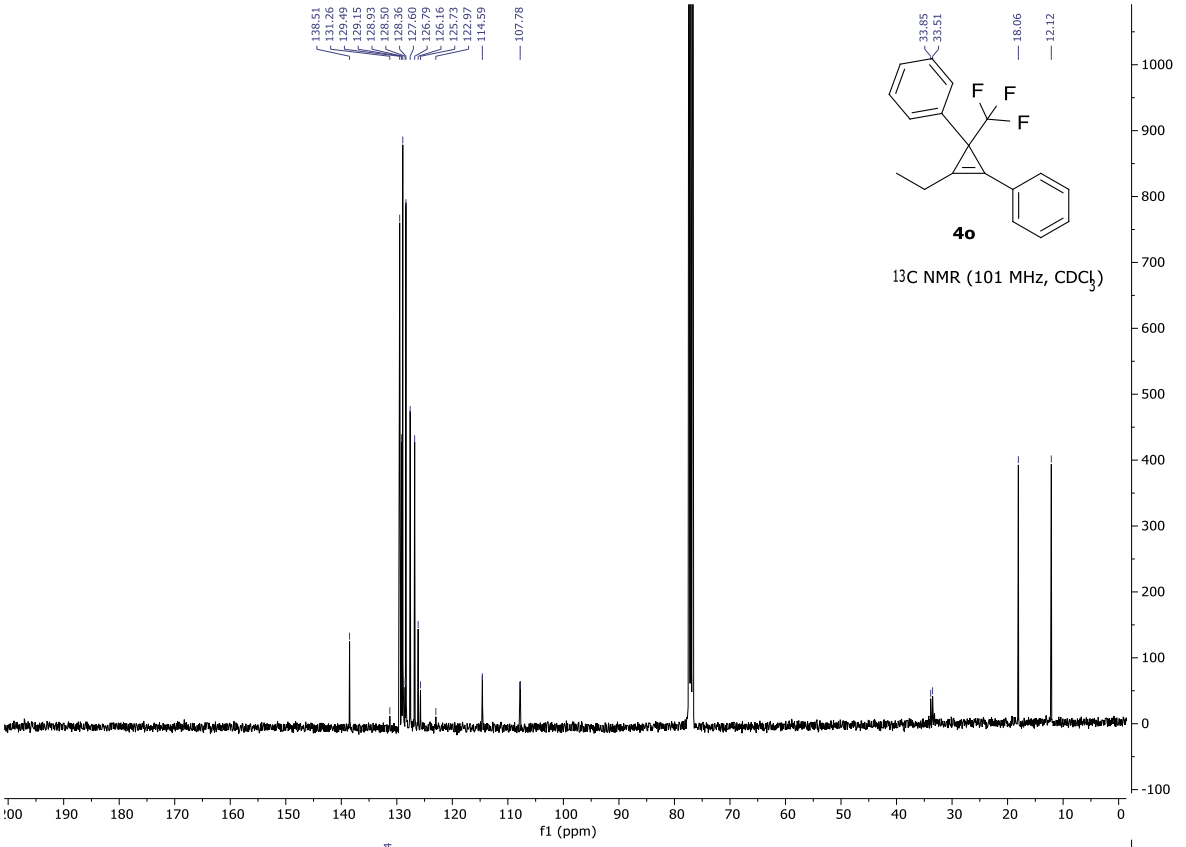

Cl
Cl
F
F
F
S
4q
13C NMR (101 MHz, CDCl3)
f1 (ppm)

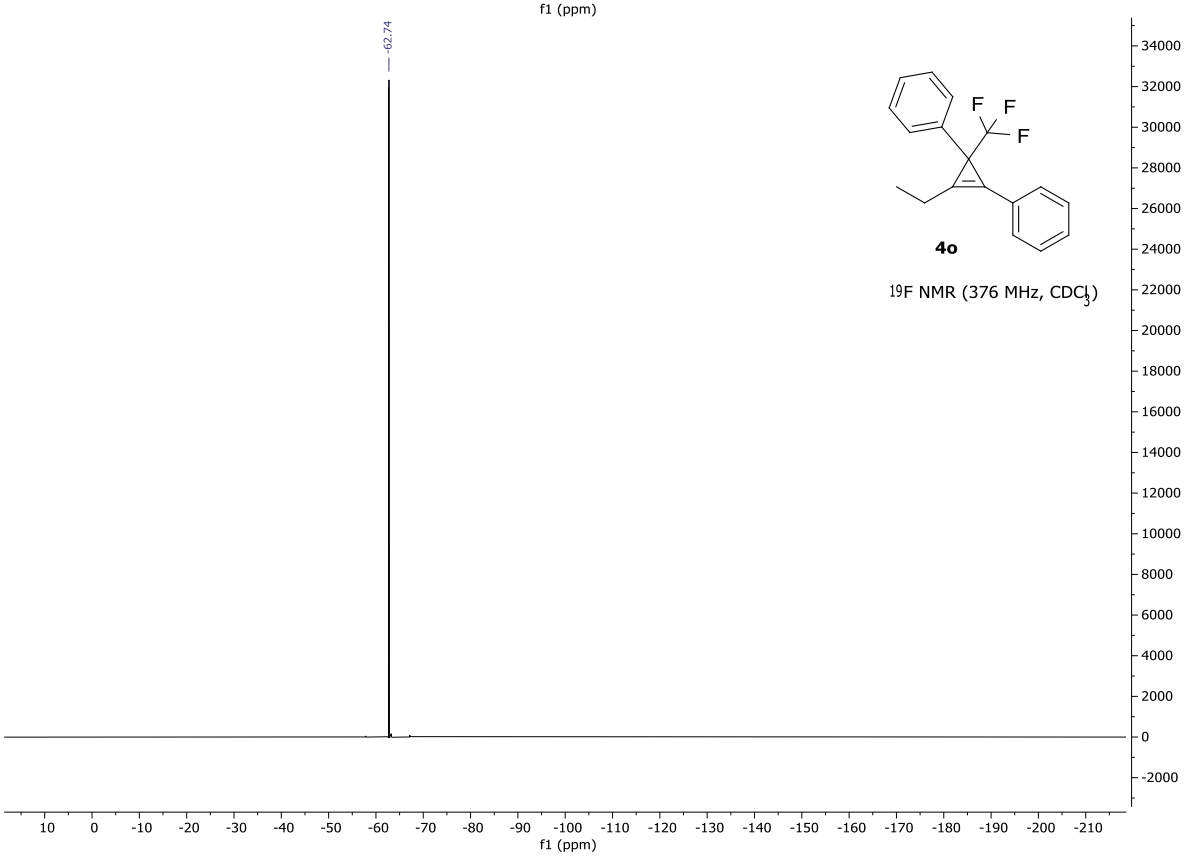


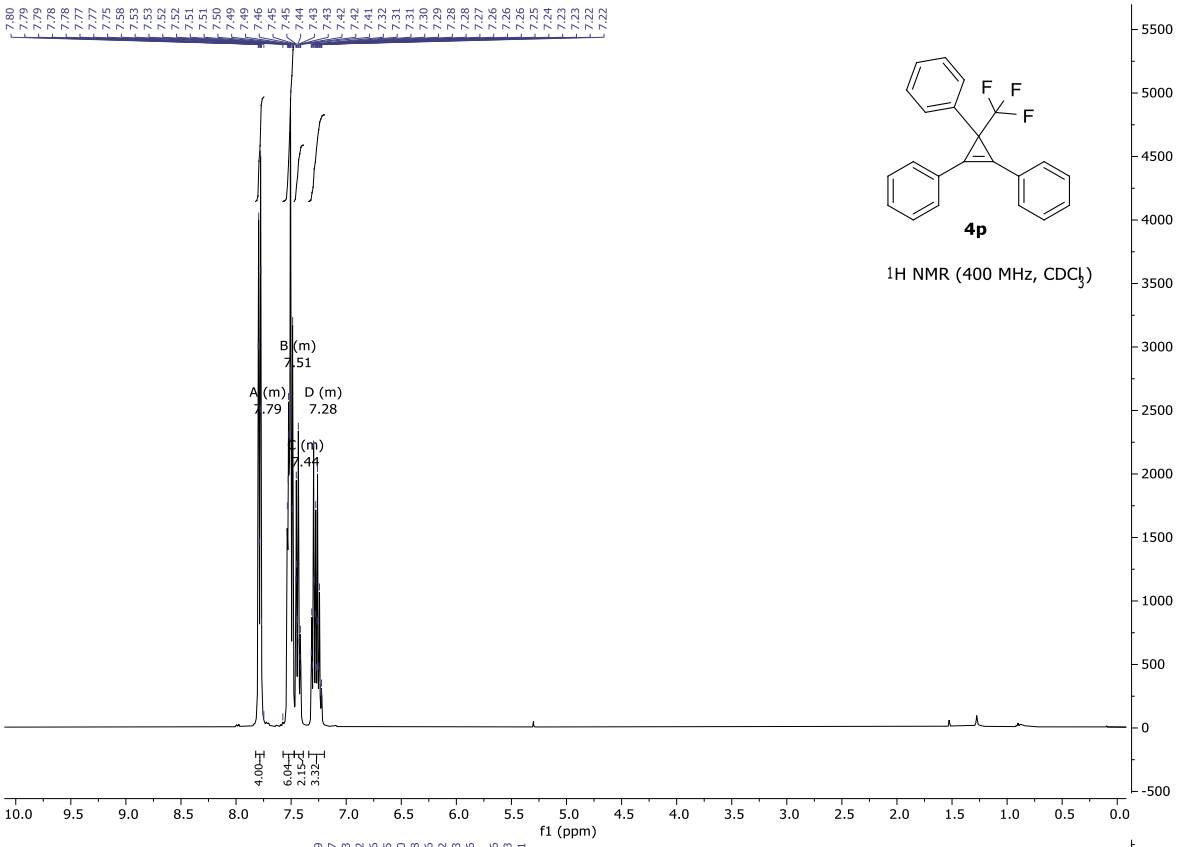
^{19}F NMR (376 MHz, $CDCl_3$)

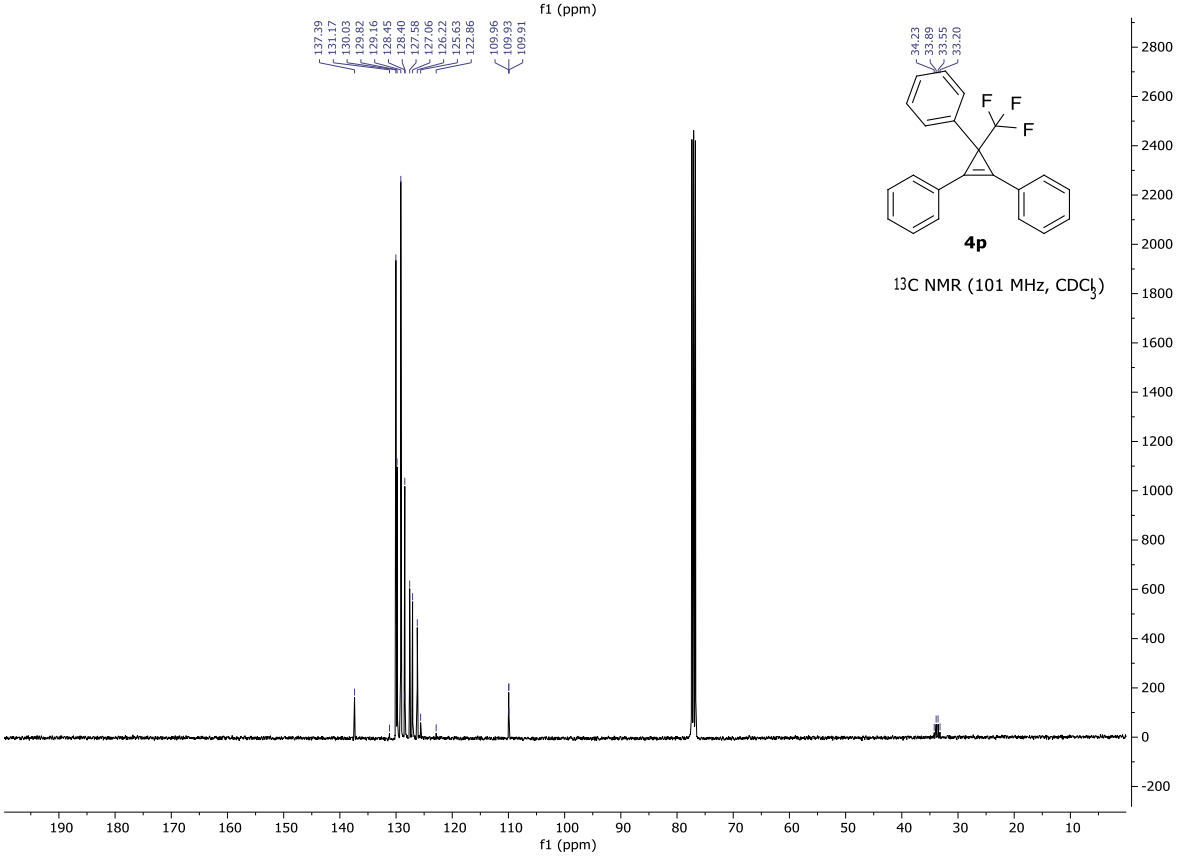


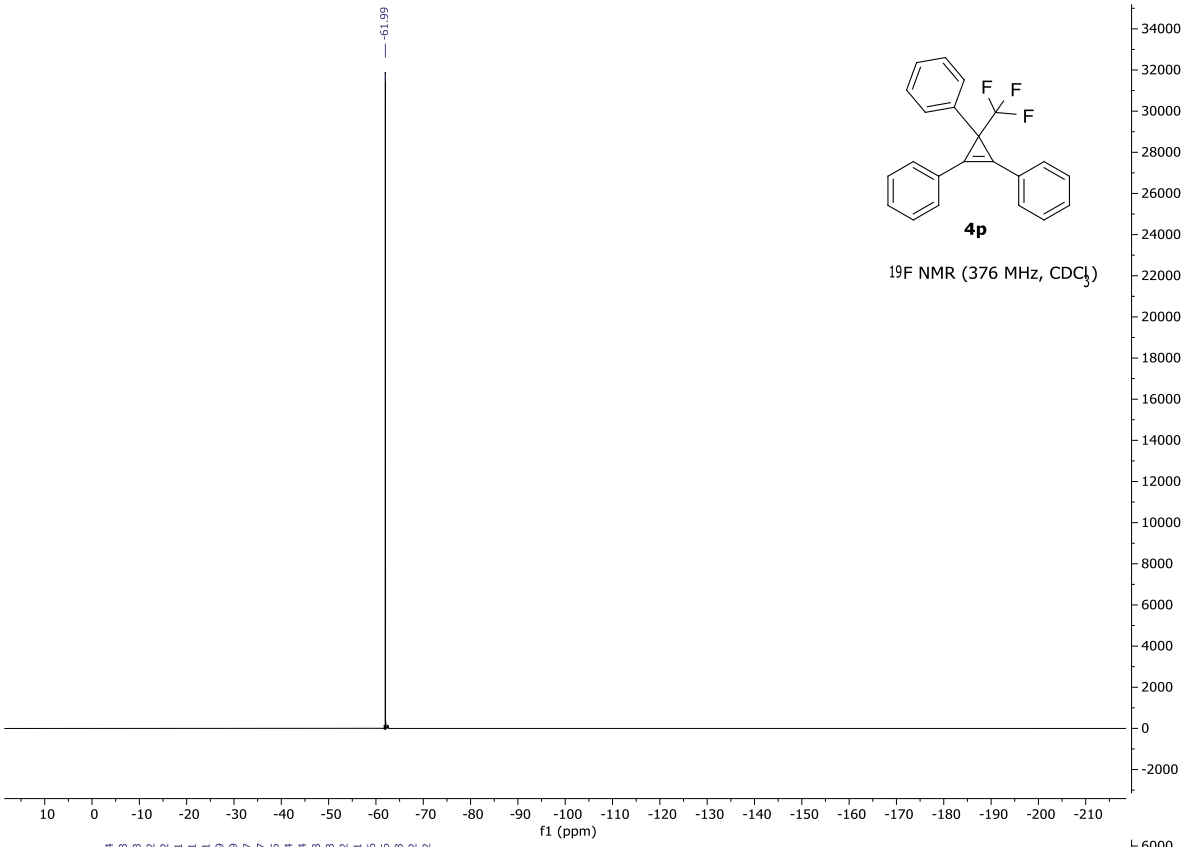
^{1}H NMR (400 MHz, $CDCl_3$)


138.51
131.26
129.49
129.15
128.93
128.50
128.36
127.60
126.79
126.16
125.73
122.97
114.59
107.78
33.85
33.51
18.06
12.12
F
F
F
4o
13C NMR (101 MHz, CDCl3)
f1 (ppm)

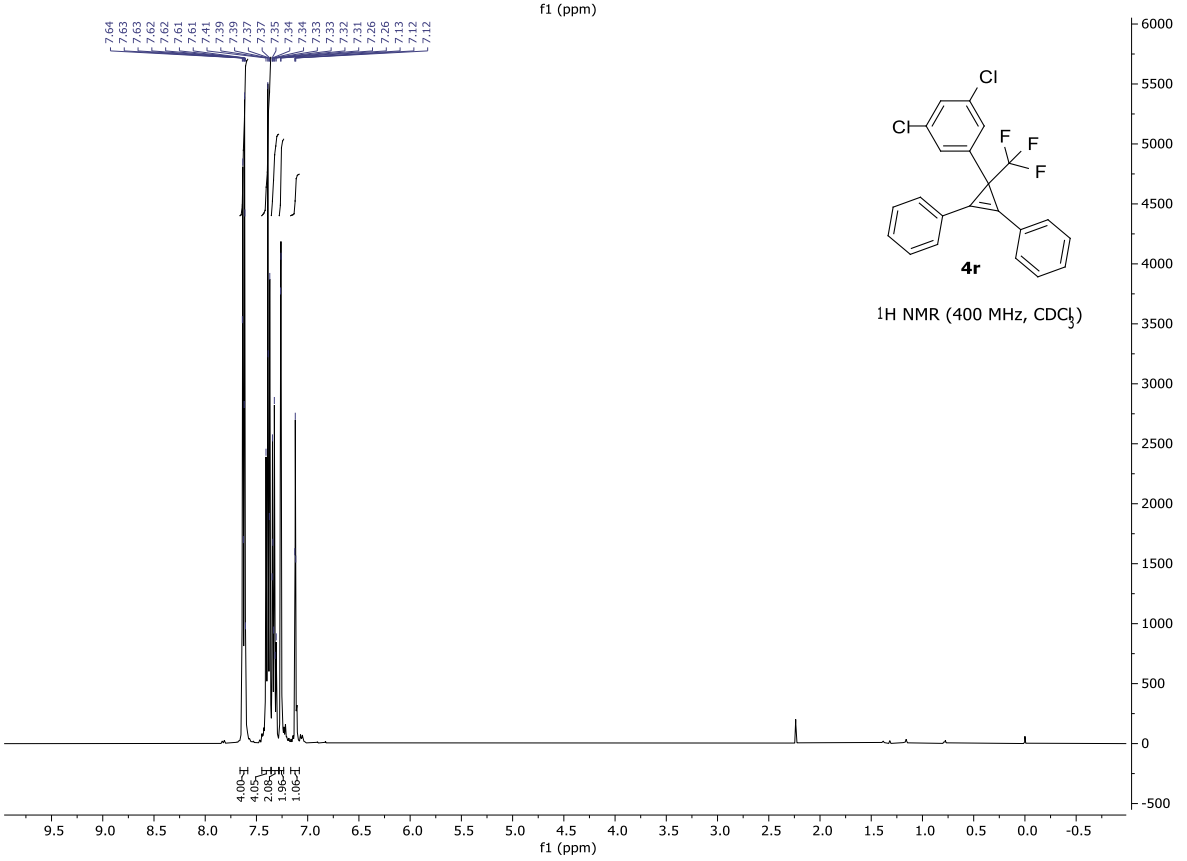

-62.74
F
F
F
4o
19F NMR (376 MHz, CDCl3)
f1 (ppm)


B (m)
7.51
A (m)
7.79
D (m)
7.28
C (m)
7.44
4.00
6.04
2.15
3.32
f1 (ppm)
F F
F
4p
1H NMR (400 MHz, CDCl3)

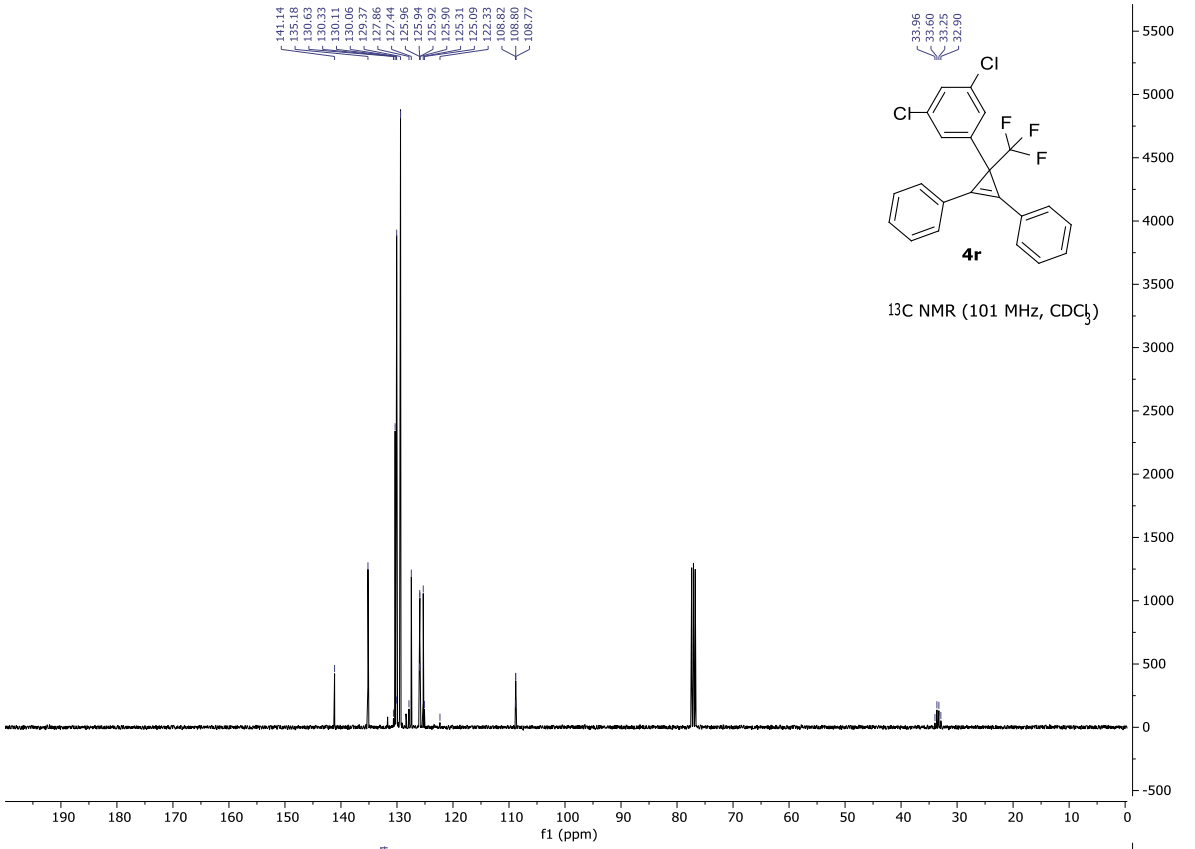

f1 (ppm)
F F
F
4p
13C NMR (101 MHz, CDCl3)

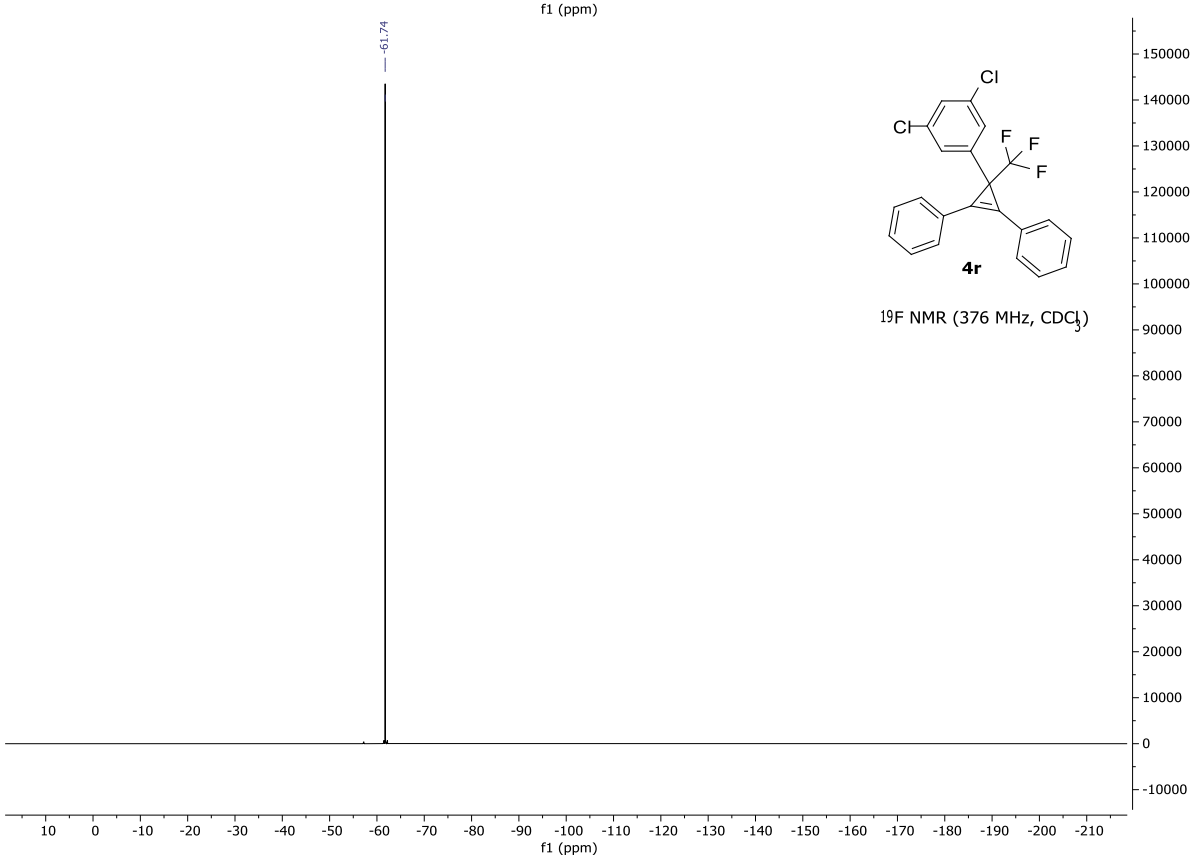


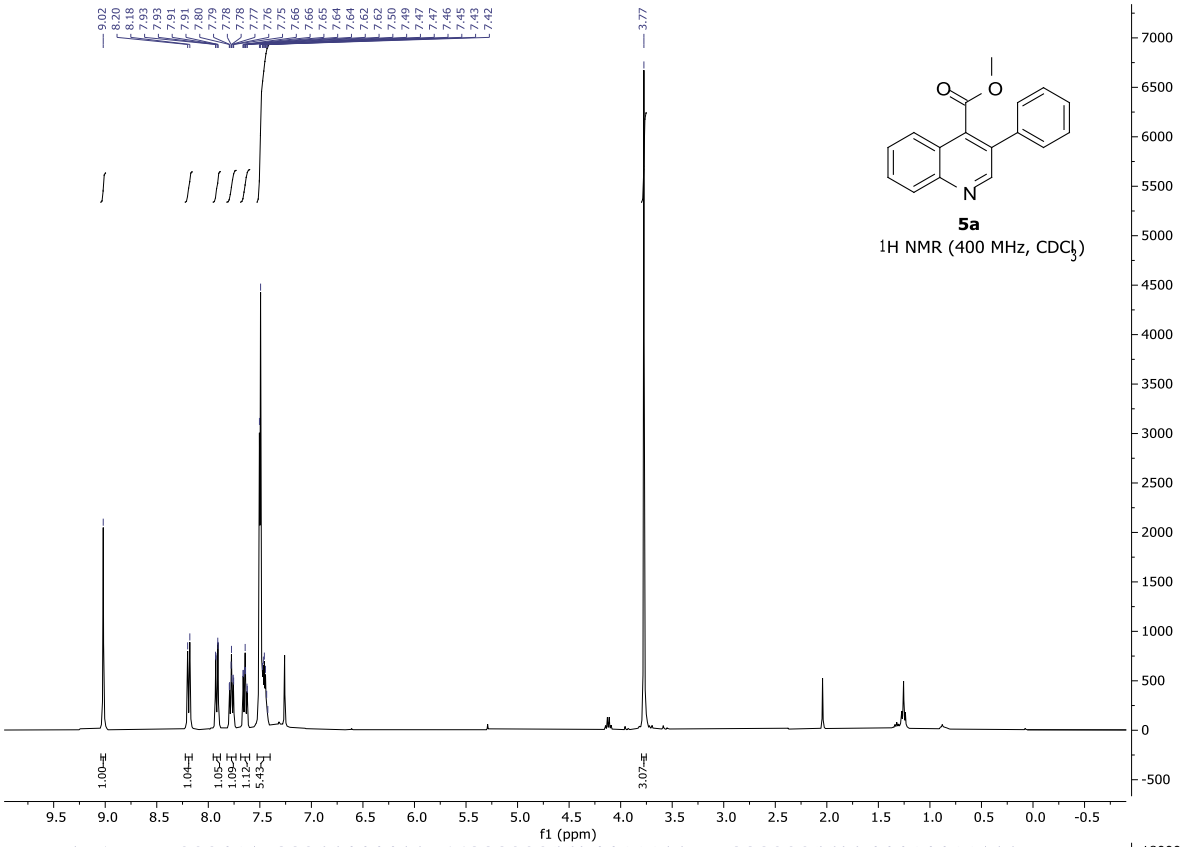
^{19}F NMR (376 MHz, $CDCl_3$)



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

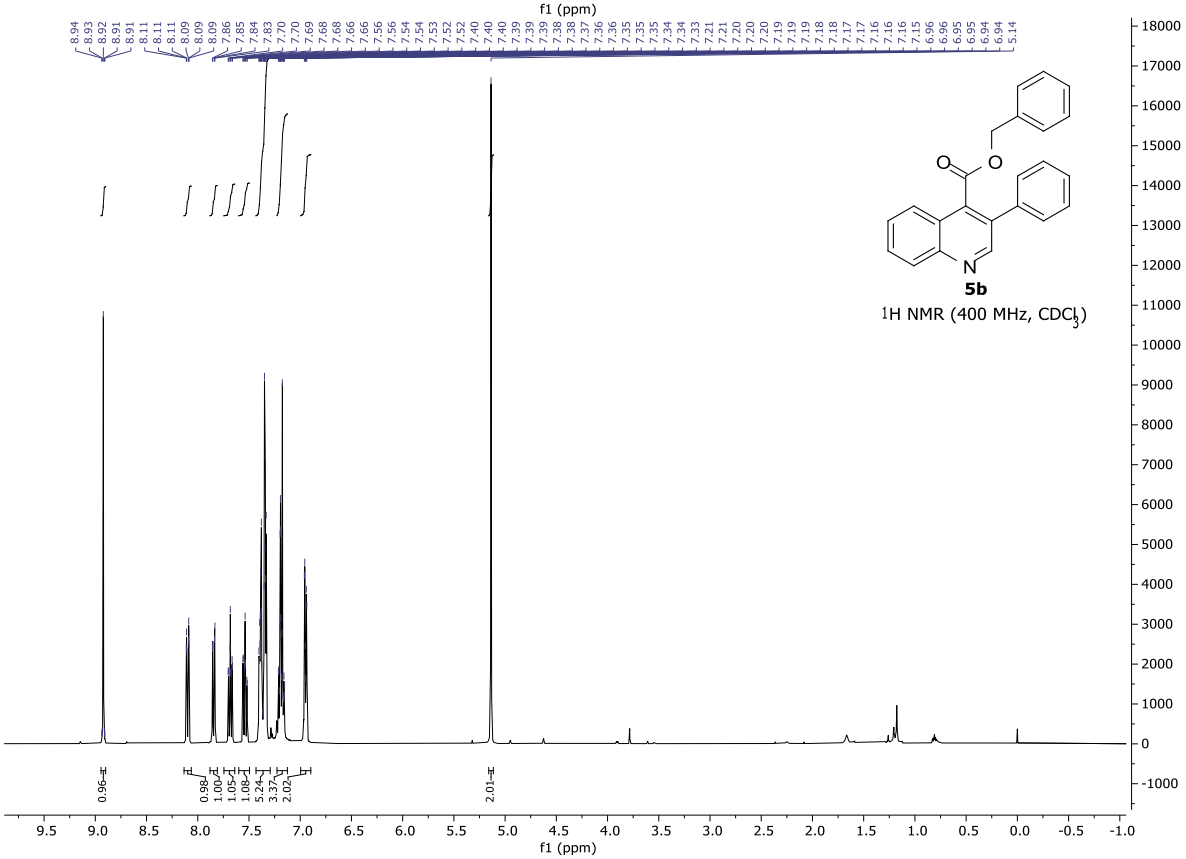

141.14
135.18
130.63
130.33
130.11
130.06
129.37
127.86
127.44
125.96
125.94
125.92
125.90
125.31
125.09
122.33
108.82
108.80
108.77
33.96
33.60
33.25
32.90
Cl
Cl
F
F
F
4r
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-61.74
Cl
Cl
F
F
F
4r
19F NMR (376 MHz, CDCl3)
f1 (ppm)



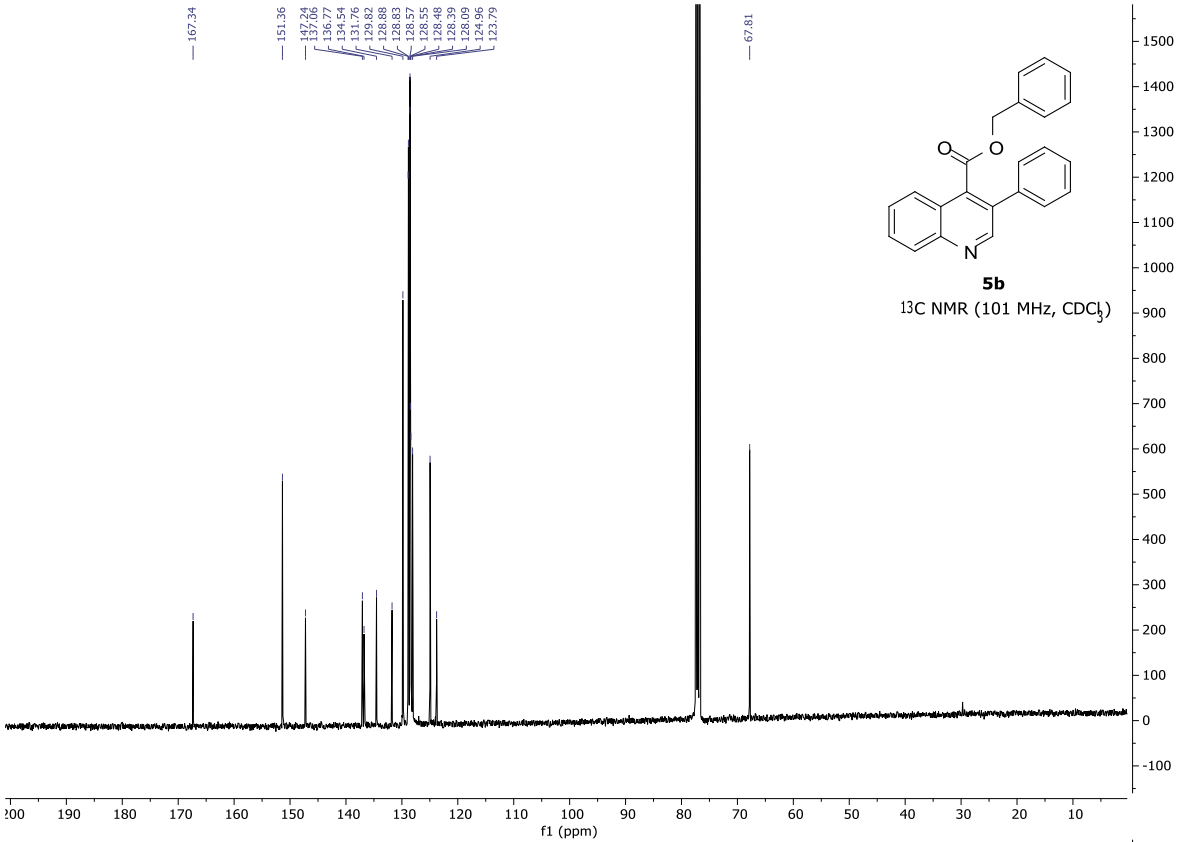
5a

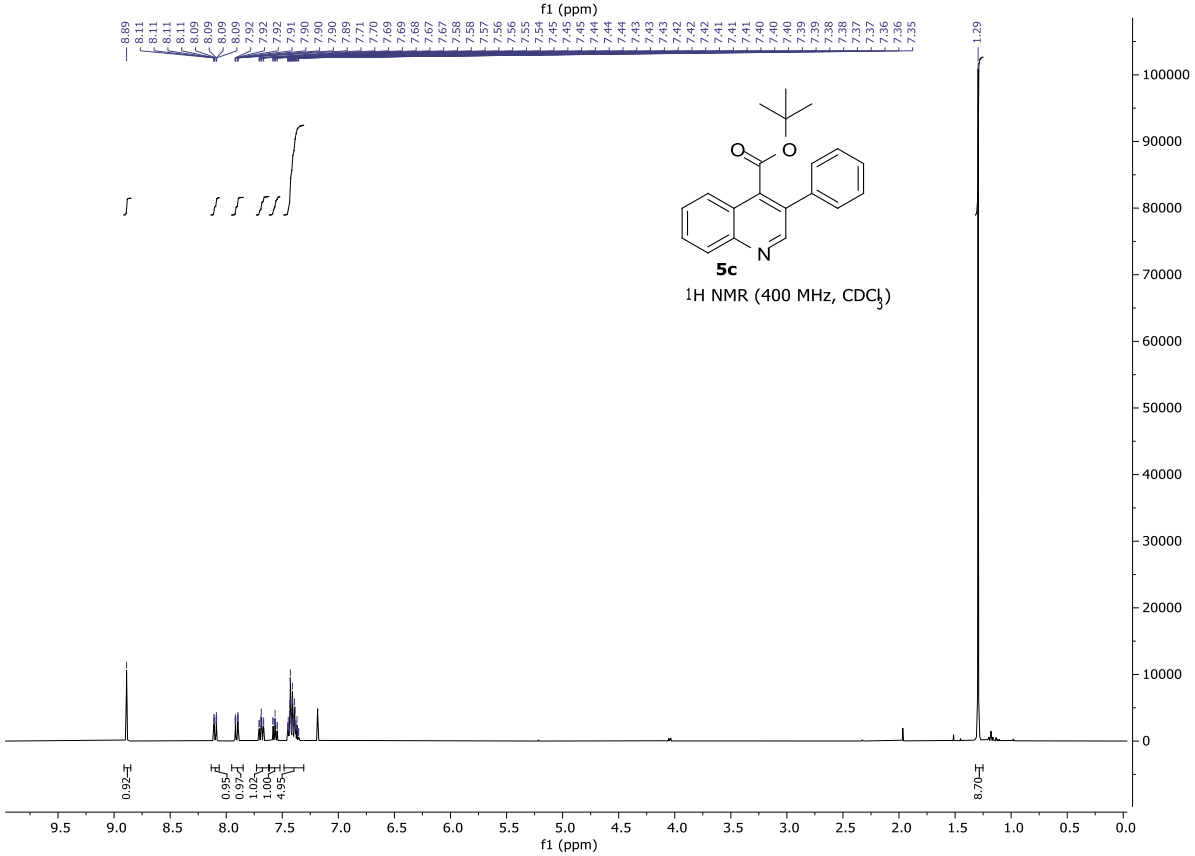
^{1}H NMR (400 MHz, $CDCl_3$)

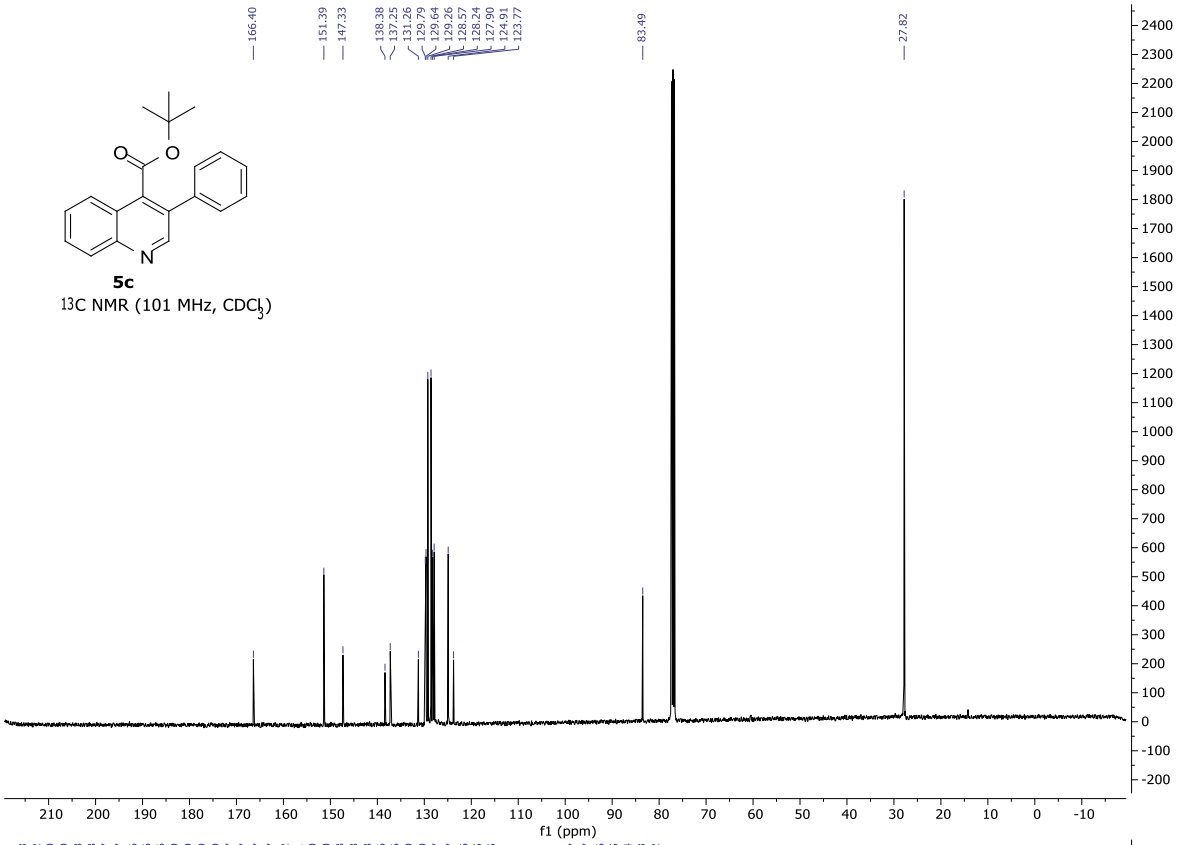


5b

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

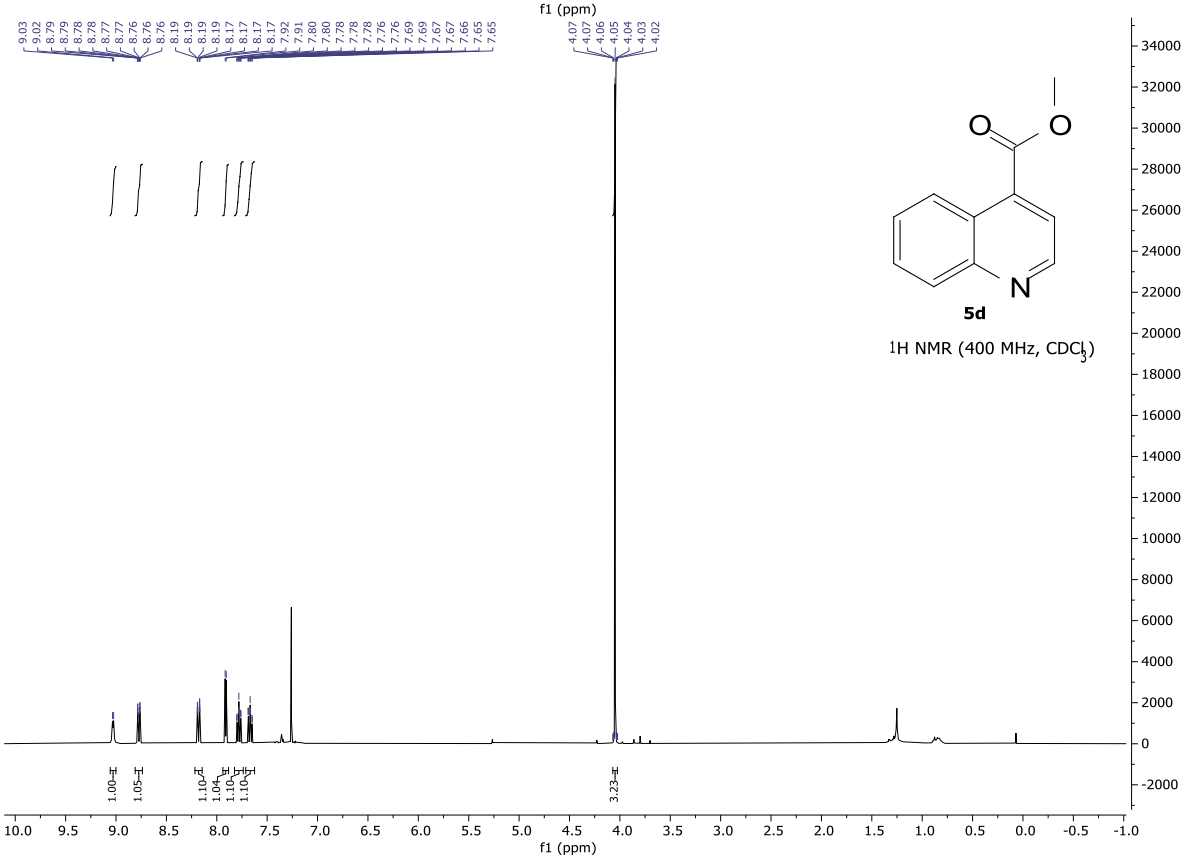

167.34
151.36
147.24
137.06
136.77
134.54
131.76
129.82
128.88
128.83
128.57
128.55
128.48
128.39
128.09
124.96
123.79
67.81
O
O
N
5b
13C NMR (101 MHz, CDCl3)
f1 (ppm)


8.89
8.11
8.11
8.11
8.09
8.09
8.09
8.09
7.92
7.92
7.92
7.91
7.90
7.90
7.90
7.90
7.89
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.58
7.58
7.57
7.56
7.56
7.55
7.54
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
1.29
O
O
N
5c
1H NMR (400 MHz, CDCl3)
0.92
0.95
0.97
1.02
1.00
4.95
8.70
f1 (ppm)



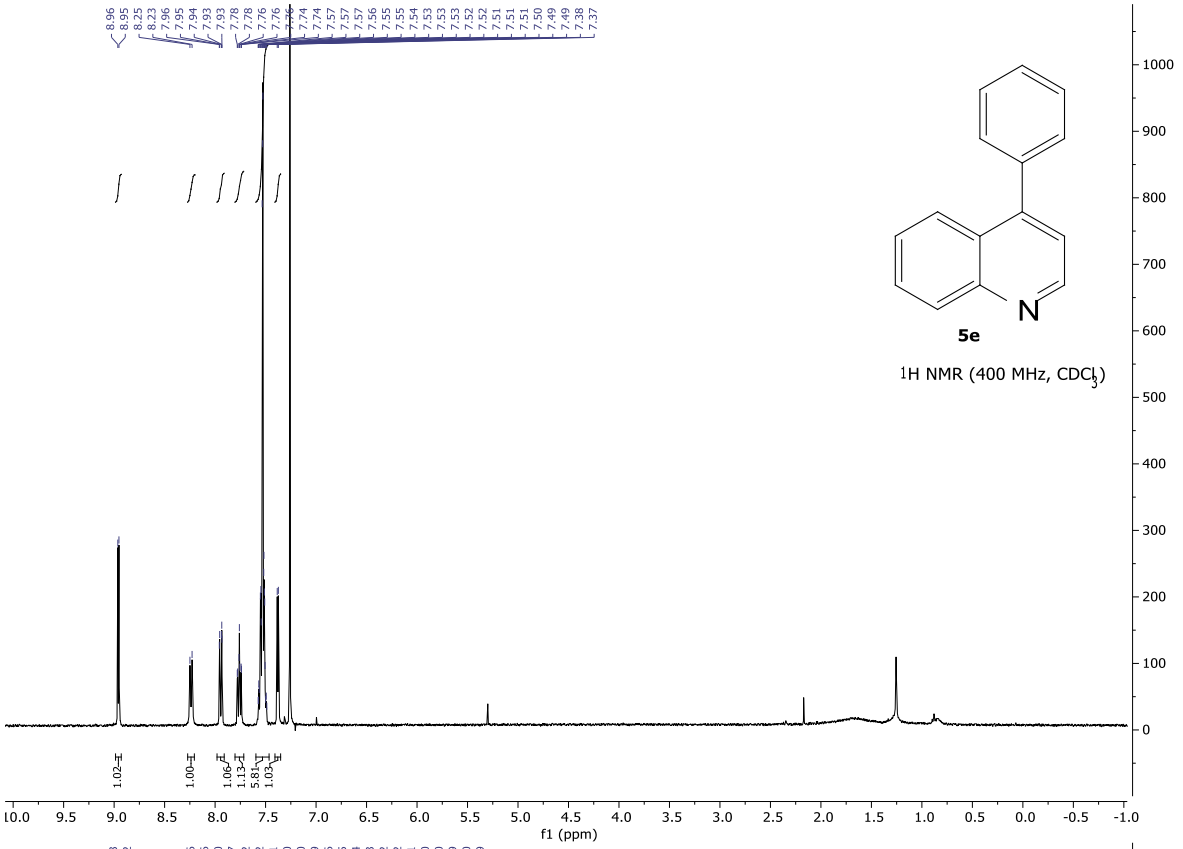
5c

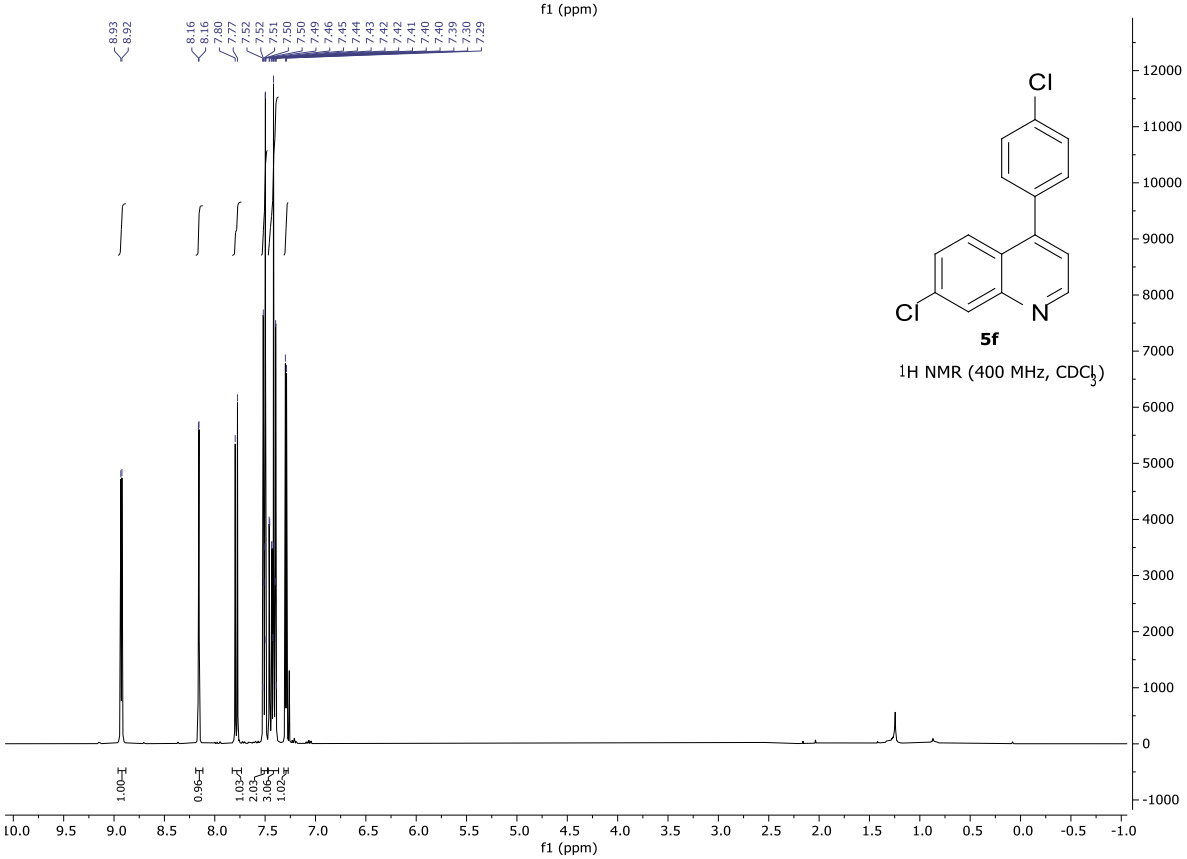
^{13}C NMR (101 MHz, $CDCl_3$)

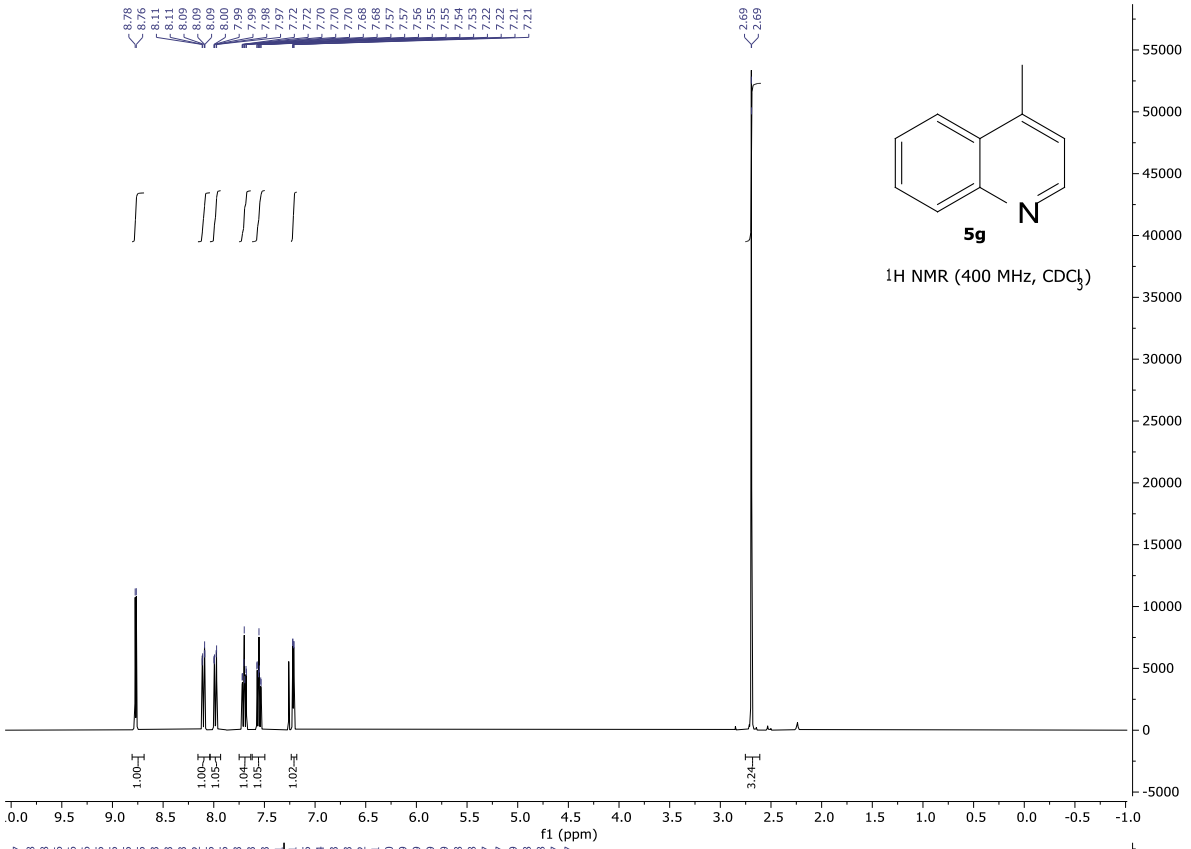


5d

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

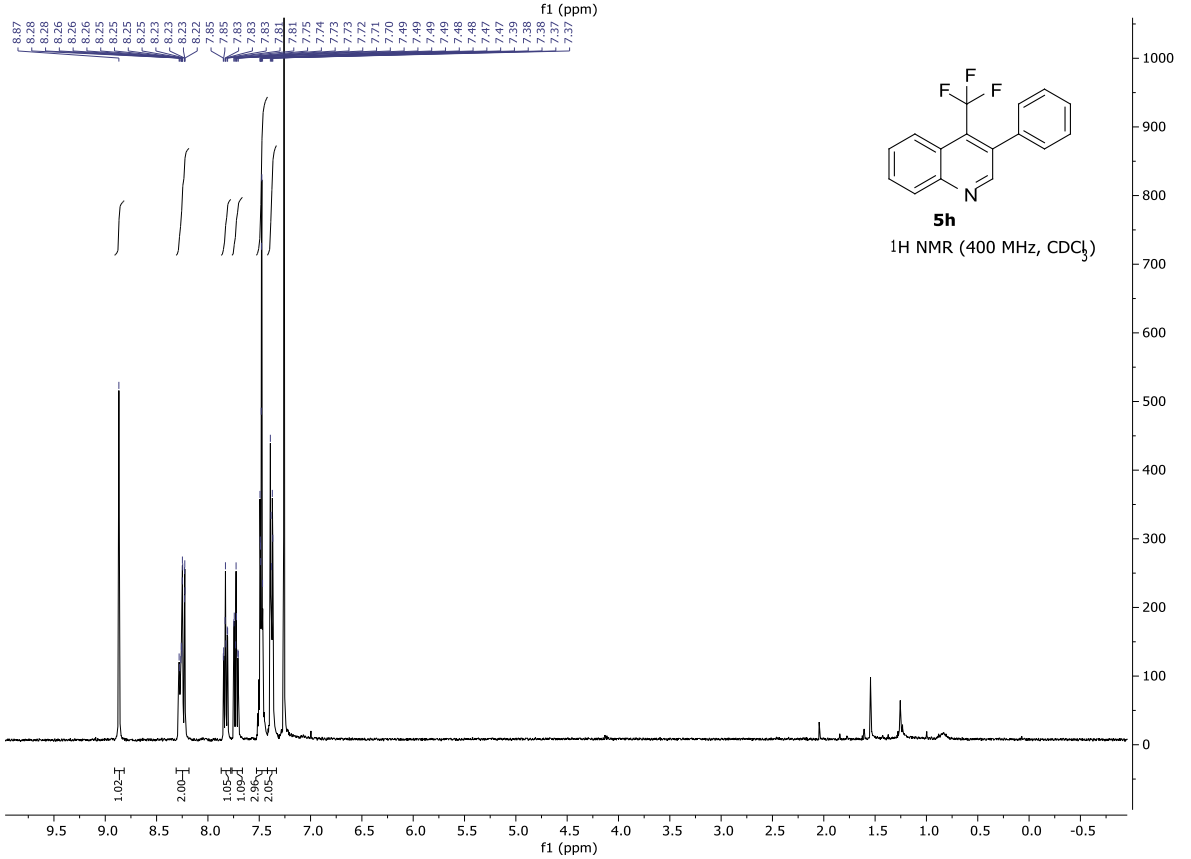

8.96
8.95
8.25
8.23
7.96
7.95
7.94
7.93
7.93
7.78
7.78
7.76
7.76
7.74
7.74
7.57
7.57
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.49
7.49
7.38
7.37
1.02
1.00
1.06
1.13
5.81
1.03
f1 (ppm)
5e
1H NMR (400 MHz, CDCl3)


8.93
8.92
8.16
8.16
7.80
7.77
7.52
7.52
7.51
7.50
7.50
7.49
7.46
7.45
7.44
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.30
7.29
1.00
0.96
1.03
2.03
3.06
1.02
f1 (ppm)
Cl
Cl
N
5f
1H NMR (400 MHz, CDCl3)



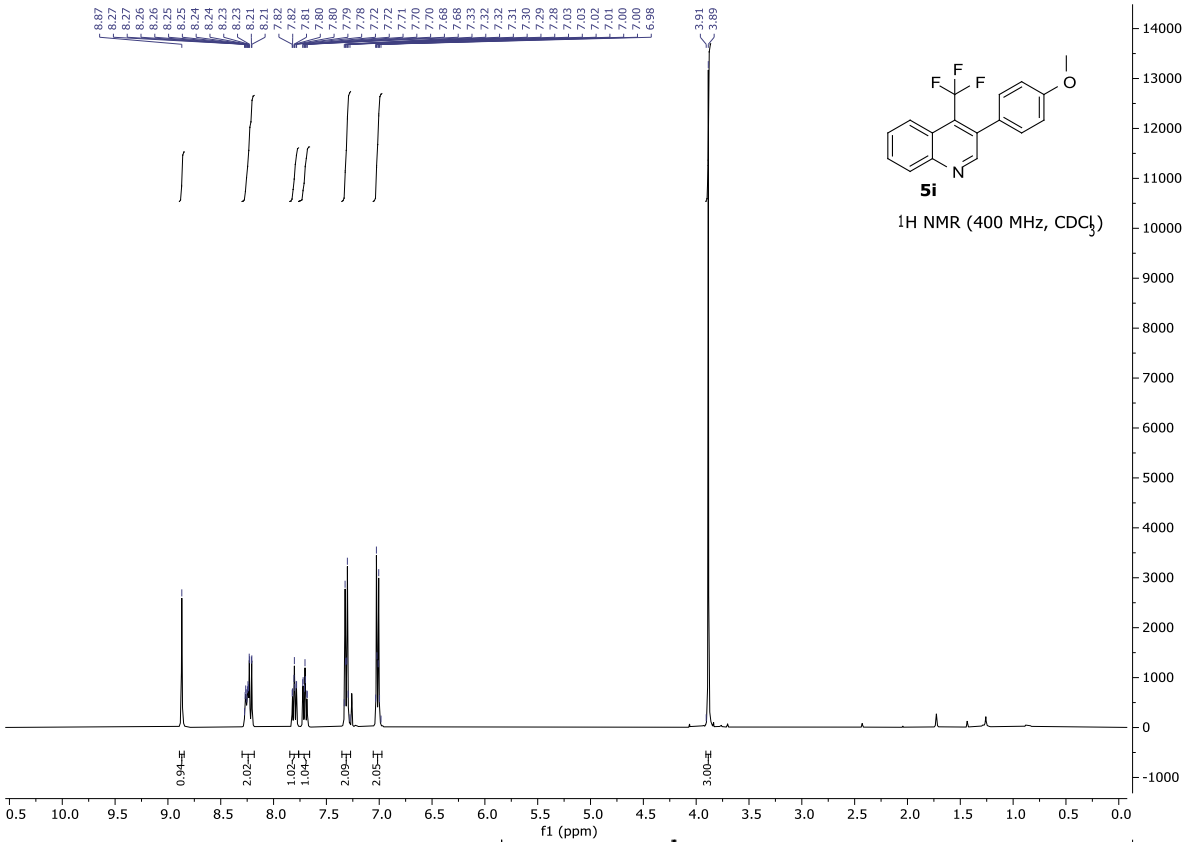
5g

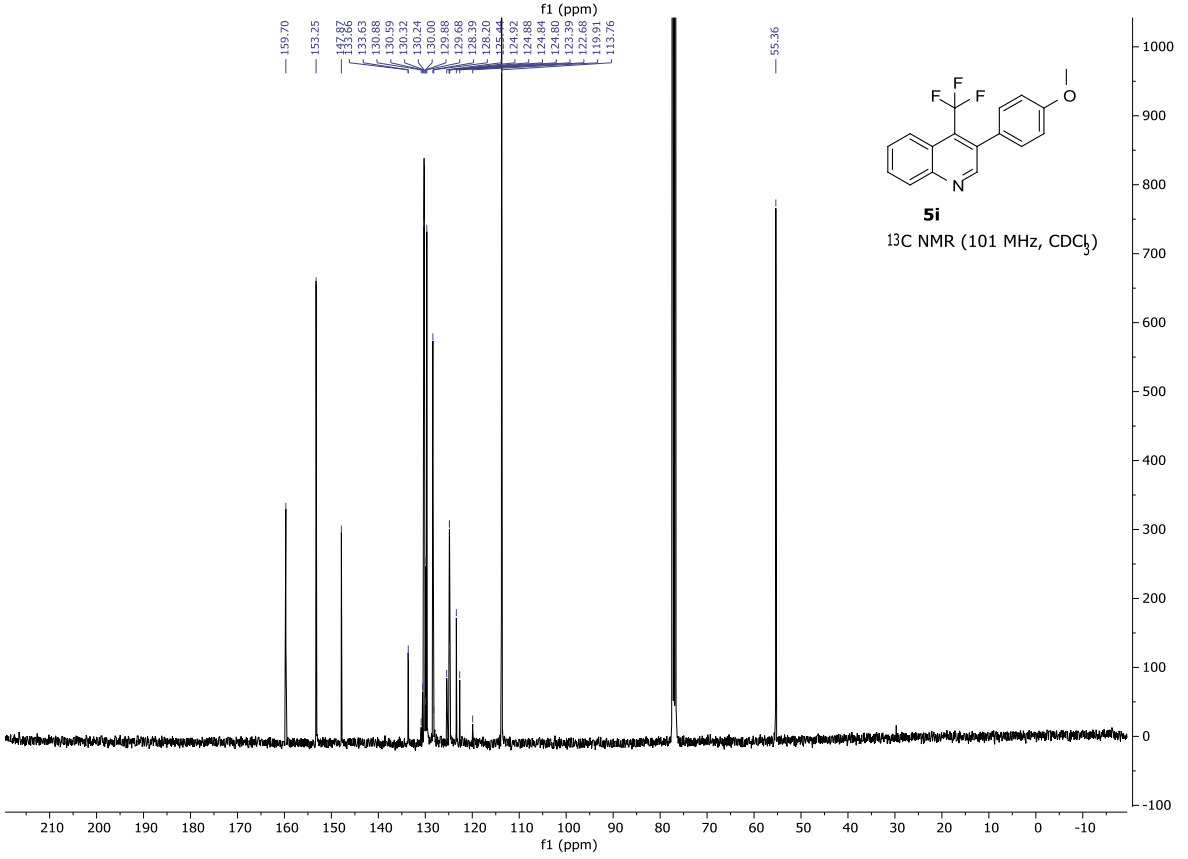
^{1}H NMR (400 MHz, $CDCl_3$)

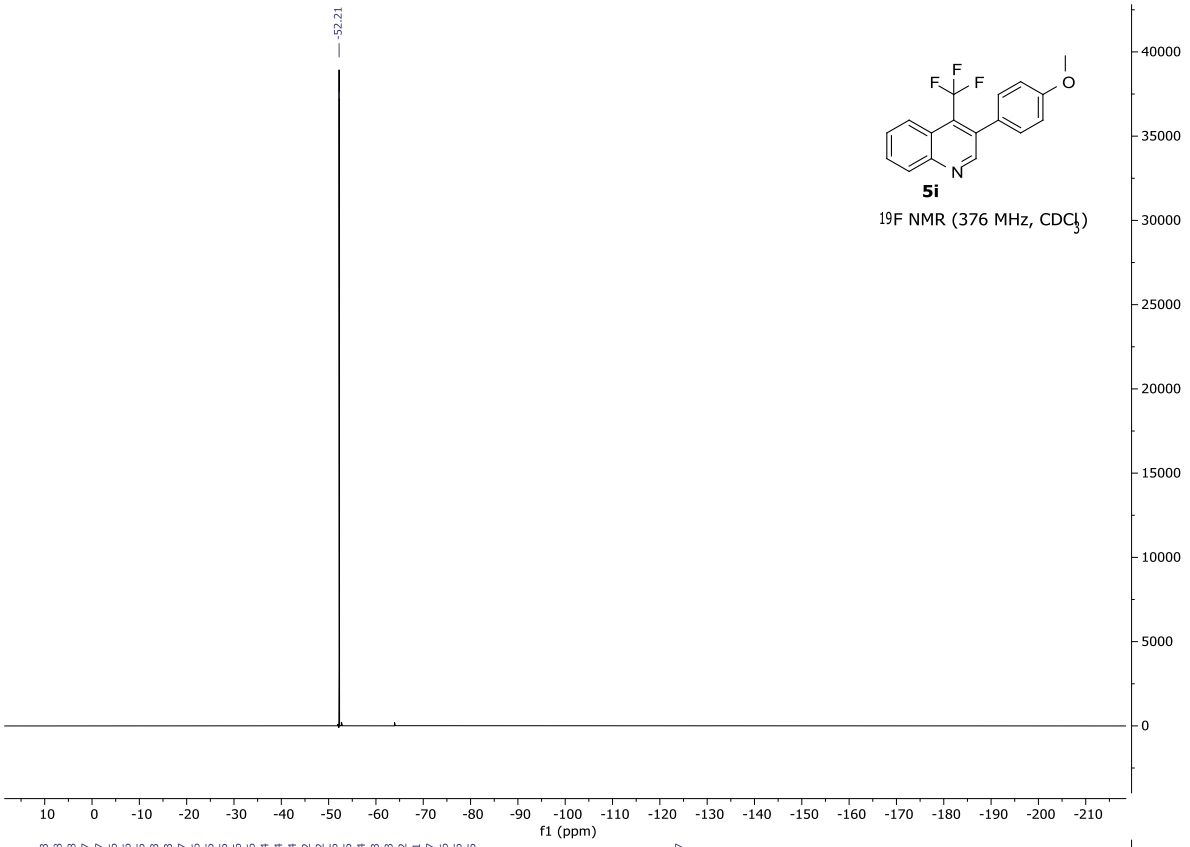


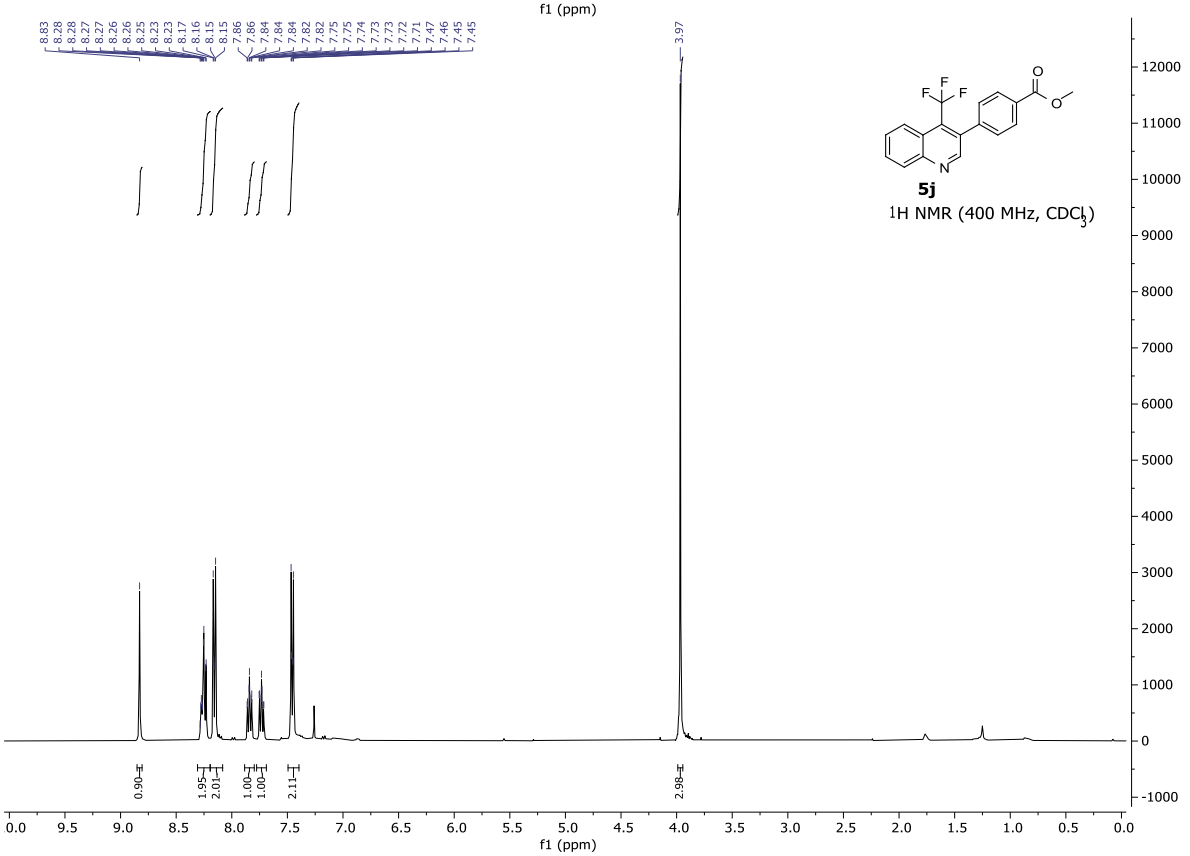
5h

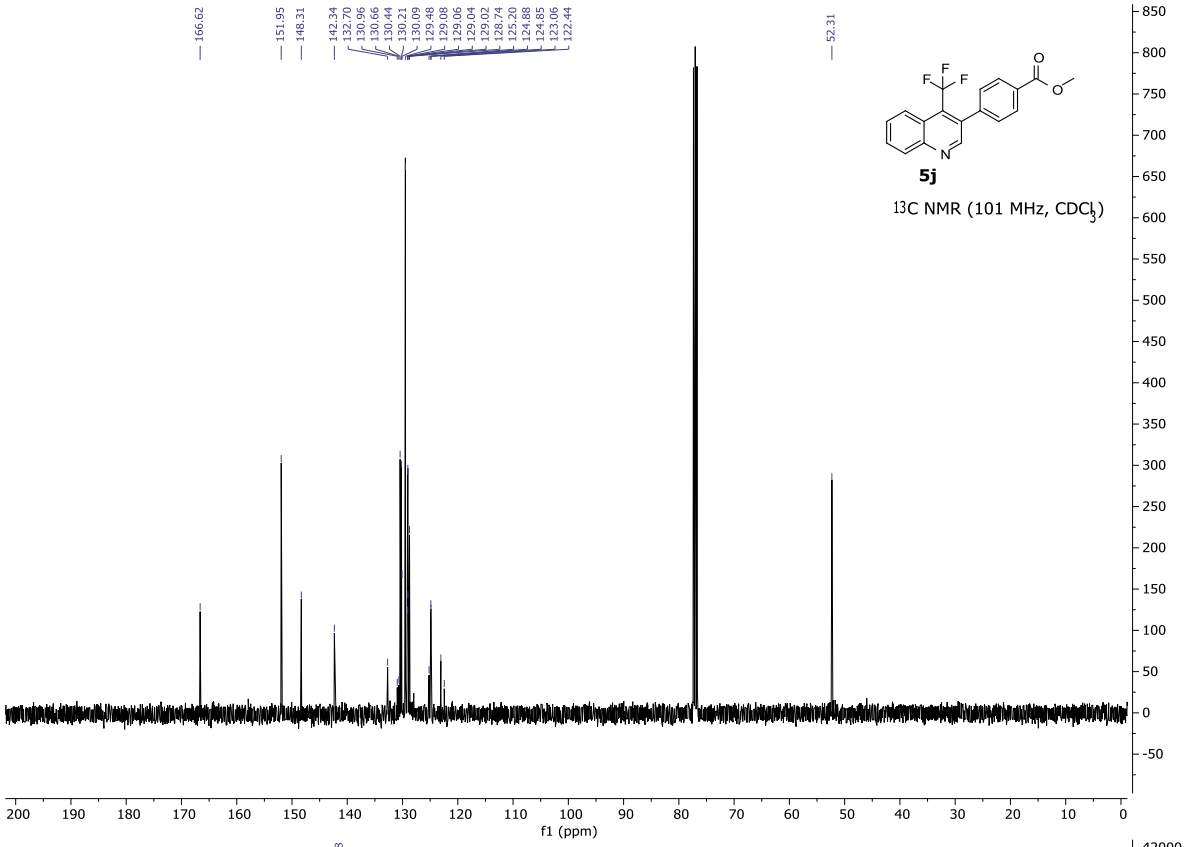
^{1}H NMR (400 MHz, $CDCl_3$)


8.87
8.27
8.27
8.26
8.26
8.25
8.25
8.24
8.24
8.23
8.23
8.21
8.21
7.82
7.82
7.81
7.80
7.80
7.79
7.78
7.72
7.72
7.71
7.70
7.70
7.68
7.68
7.33
7.32
7.31
7.30
7.29
7.28
7.03
7.02
7.01
7.00
7.00
6.98
3.91
3.89
F
F
F
O
N
5i
1H NMR (400 MHz, CDCl3)
0.94
2.02
1.02
1.04
2.09
2.05
3.00
f1 (ppm)


159.70
153.25
147.87
133.66
133.63
130.88
130.59
130.32
130.24
130.00
129.88
129.68
128.39
128.20
124.92
124.88
124.84
124.80
122.39
122.38
119.91
113.76
55.36
F
F
F
O
N
5i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

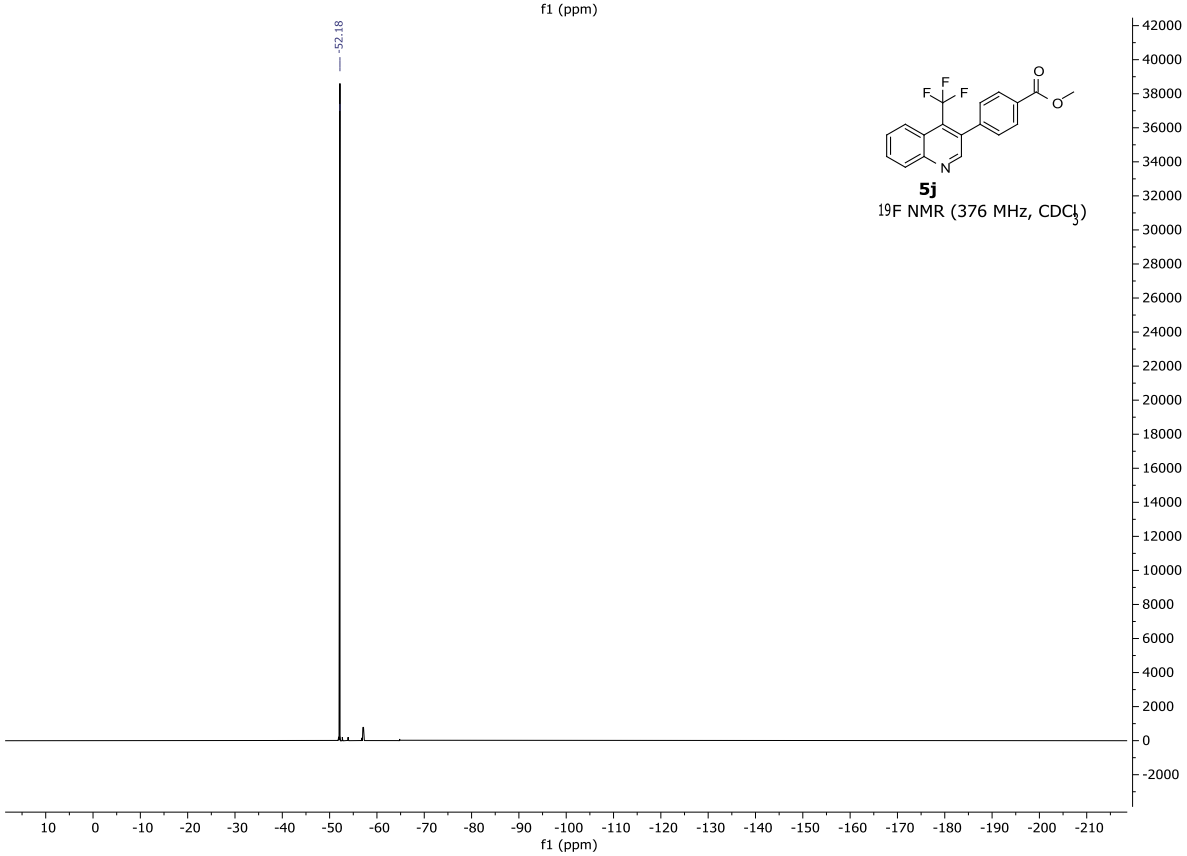

-52.21
F
F
F
O
N
5i
19F NMR (376 MHz, CDCl3)
f1 (ppm)


8.83
8.28
8.28
8.27
8.27
8.26
8.26
8.25
8.23
8.23
8.17
8.16
8.15
8.15
7.86
7.86
7.84
7.84
7.84
7.82
7.82
7.75
7.75
7.74
7.73
7.73
7.72
7.71
7.47
7.46
7.45
7.45
3.97
F
F
F
O
O
N
5j
1H NMR (400 MHz, CDCl3)
0.90
1.95
2.01
1.00
1.00
2.11
2.98
f1 (ppm)



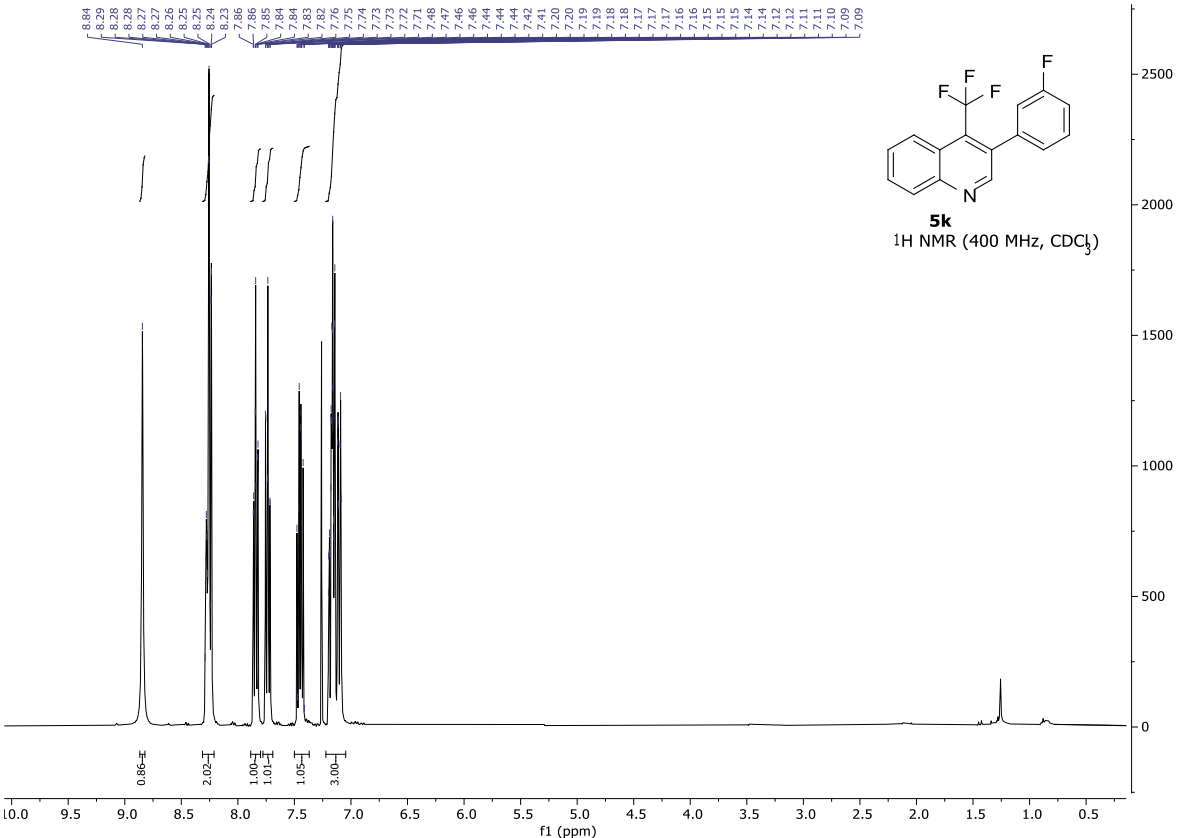
5j

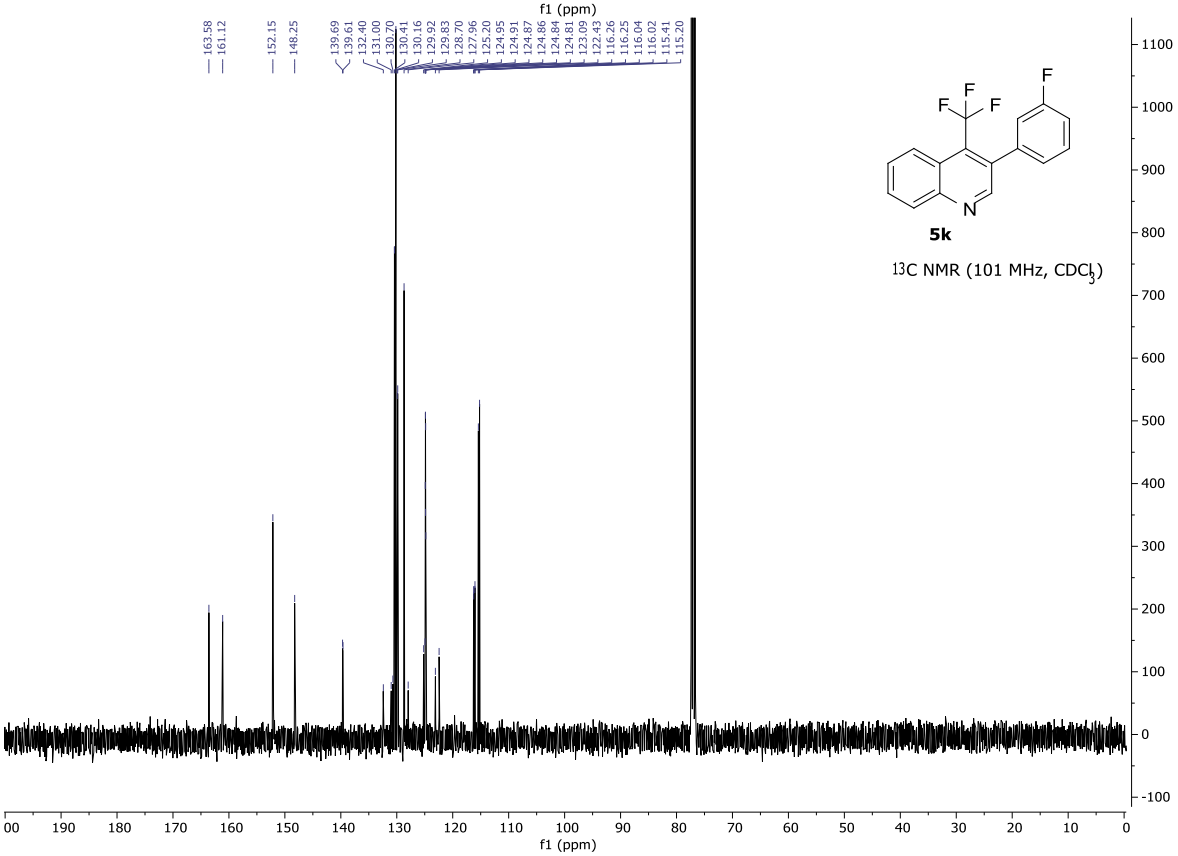
^{13}C NMR (101 MHz, $CDCl_3$)

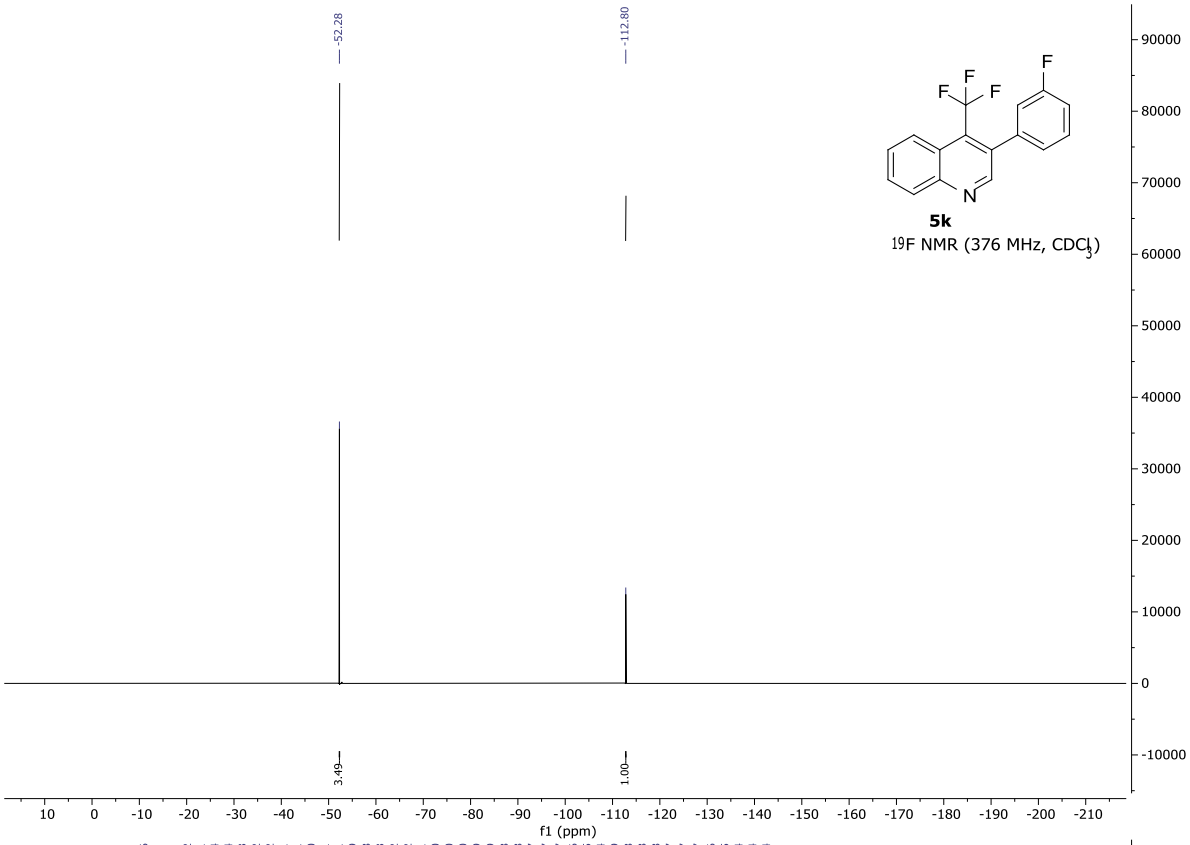


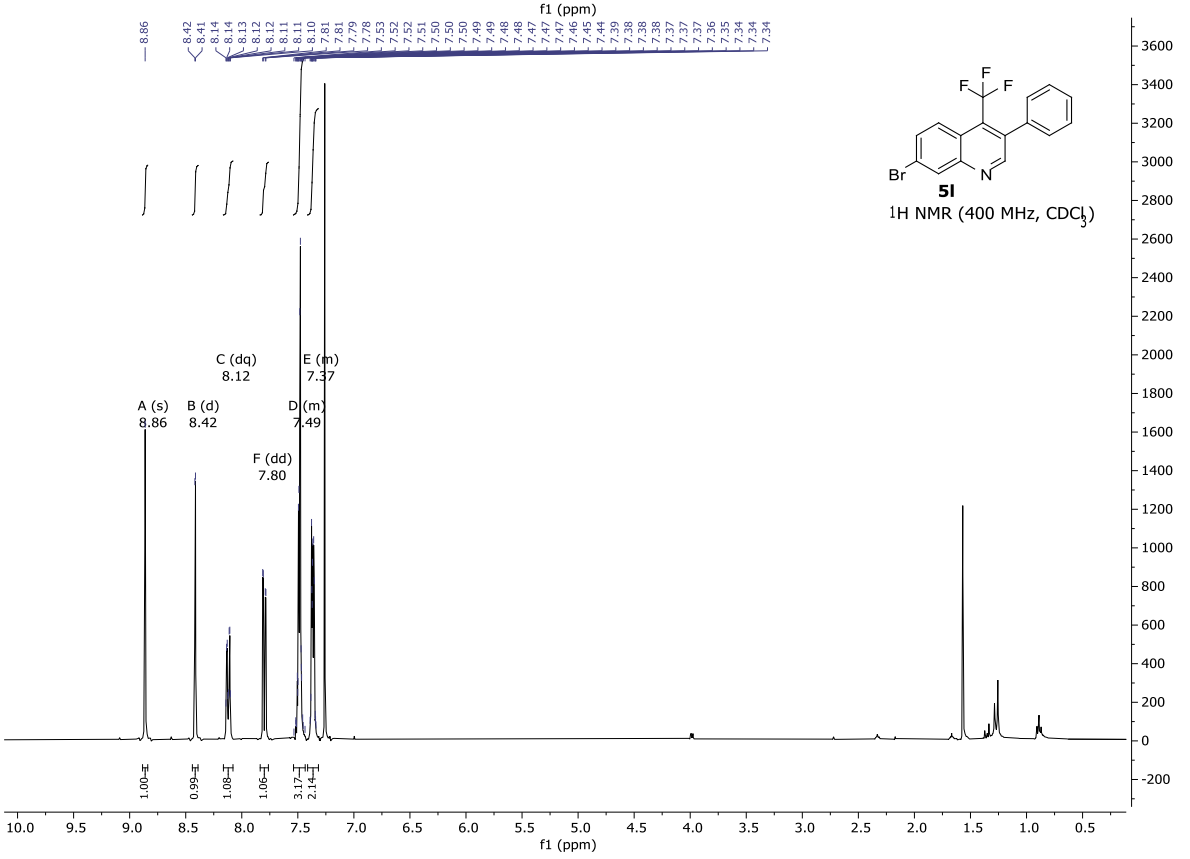
5j

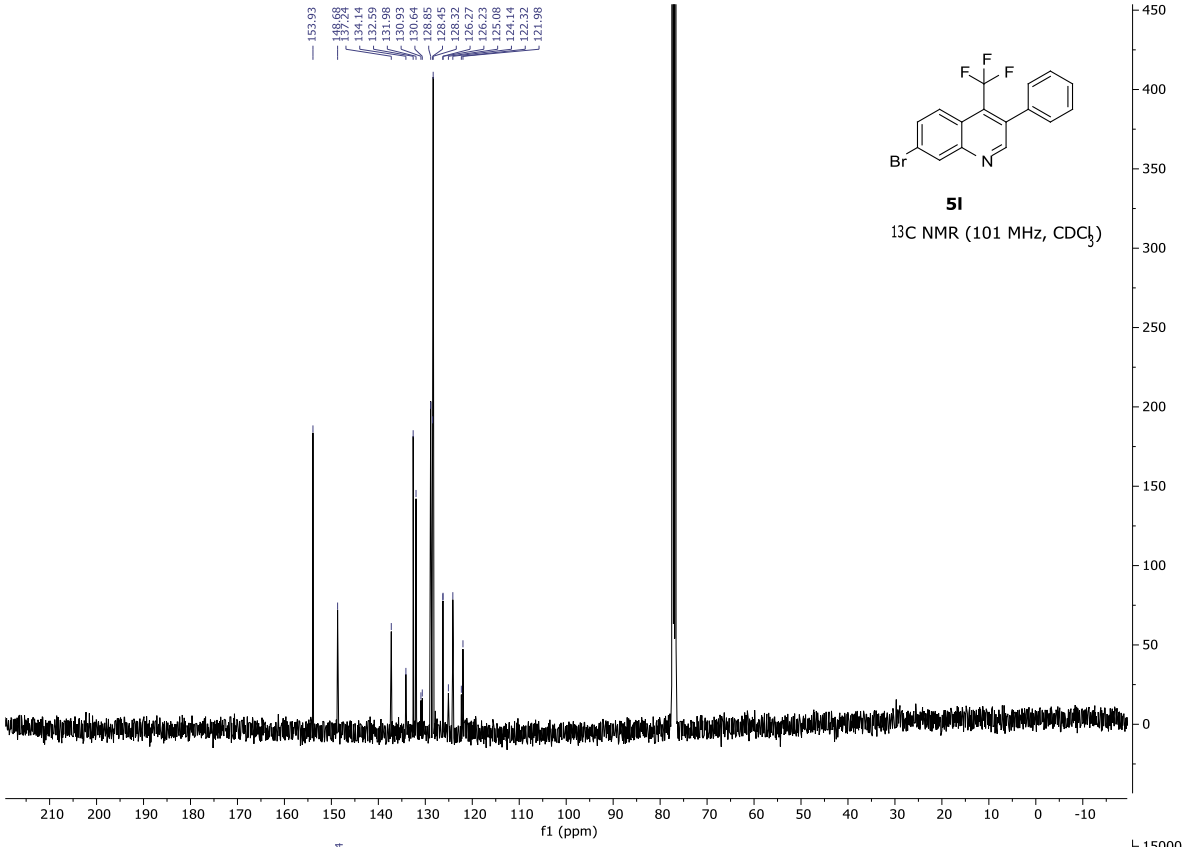
^{19}F NMR (376 MHz, $CDCl_3$)

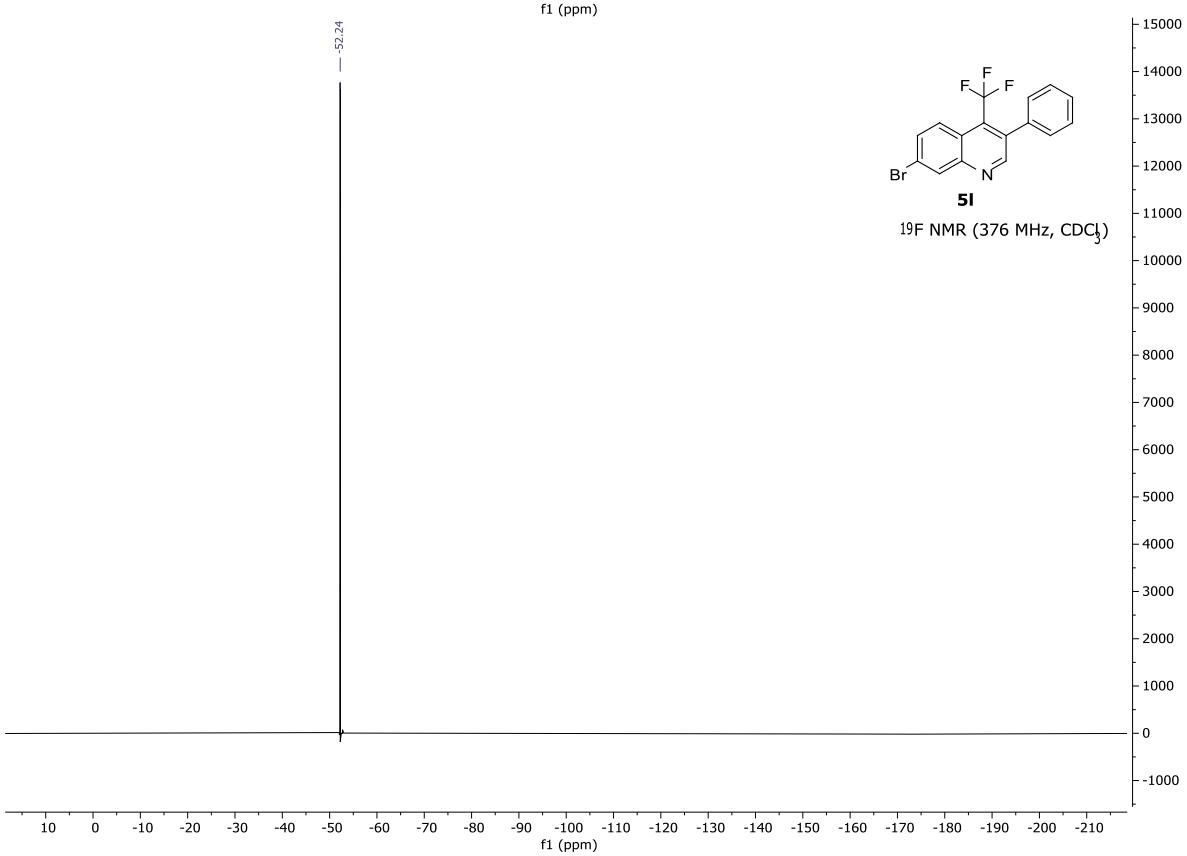

F
F F
F
N
5k
1H NMR (400 MHz, CDCl3)
f1 (ppm)

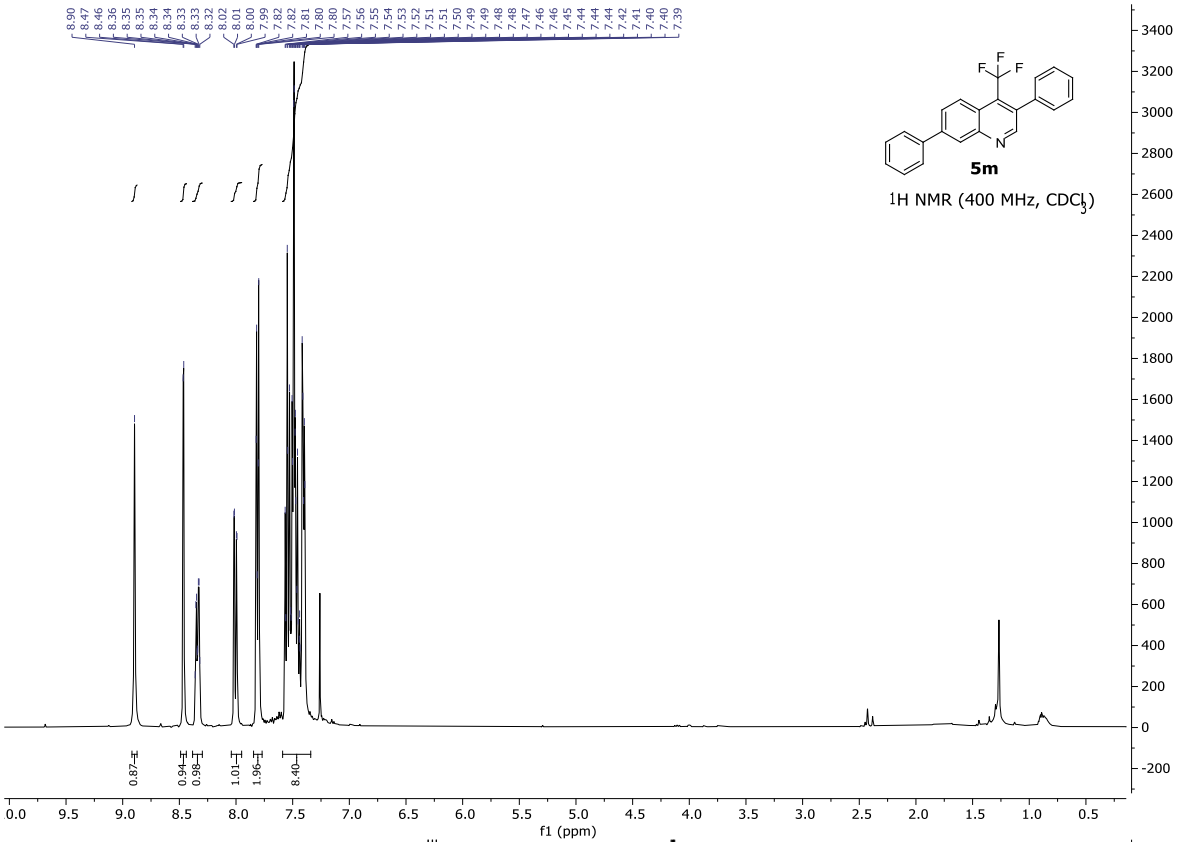

F
F F
F
N
5k
13C NMR (101 MHz, CDCl3)
f1 (ppm)

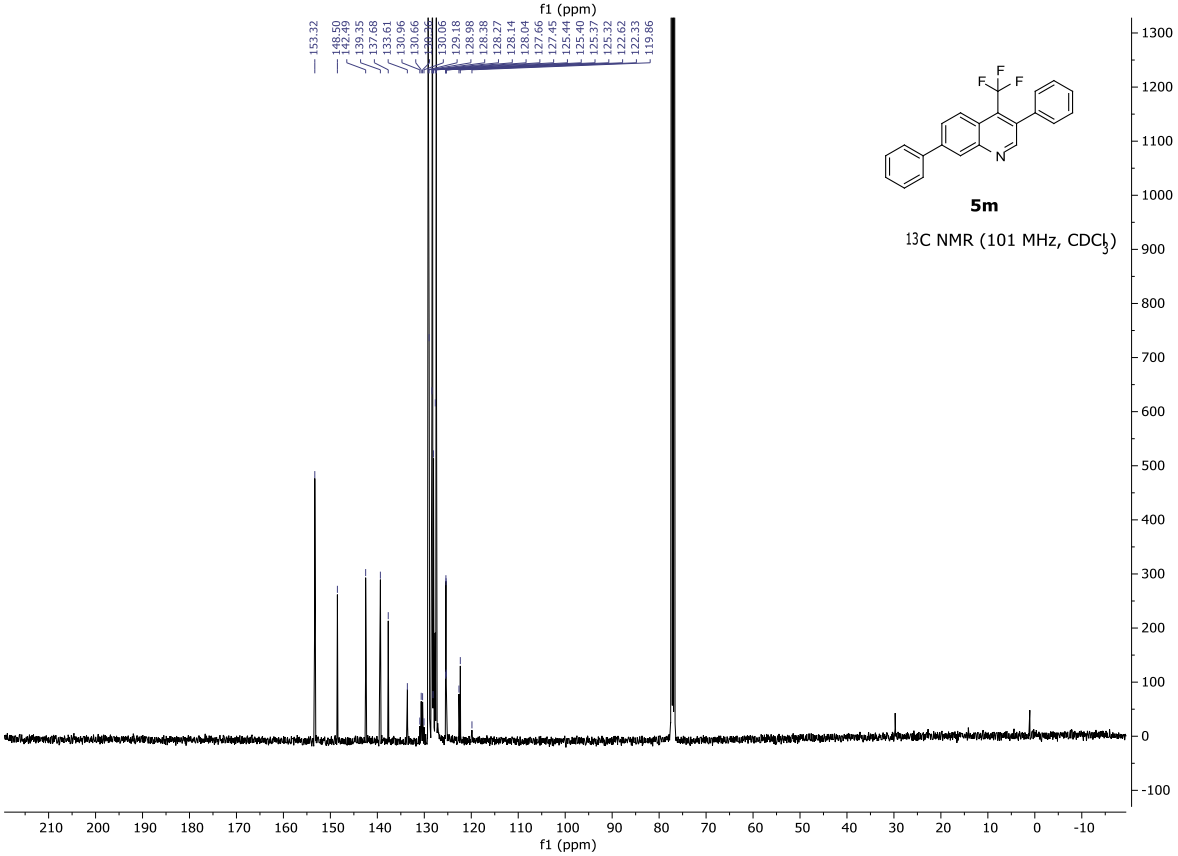

-52.28
-112.80
F
F
F
F
N
5k
19F NMR (376 MHz, CDCl3)
3.49
1.00
f1 (ppm)

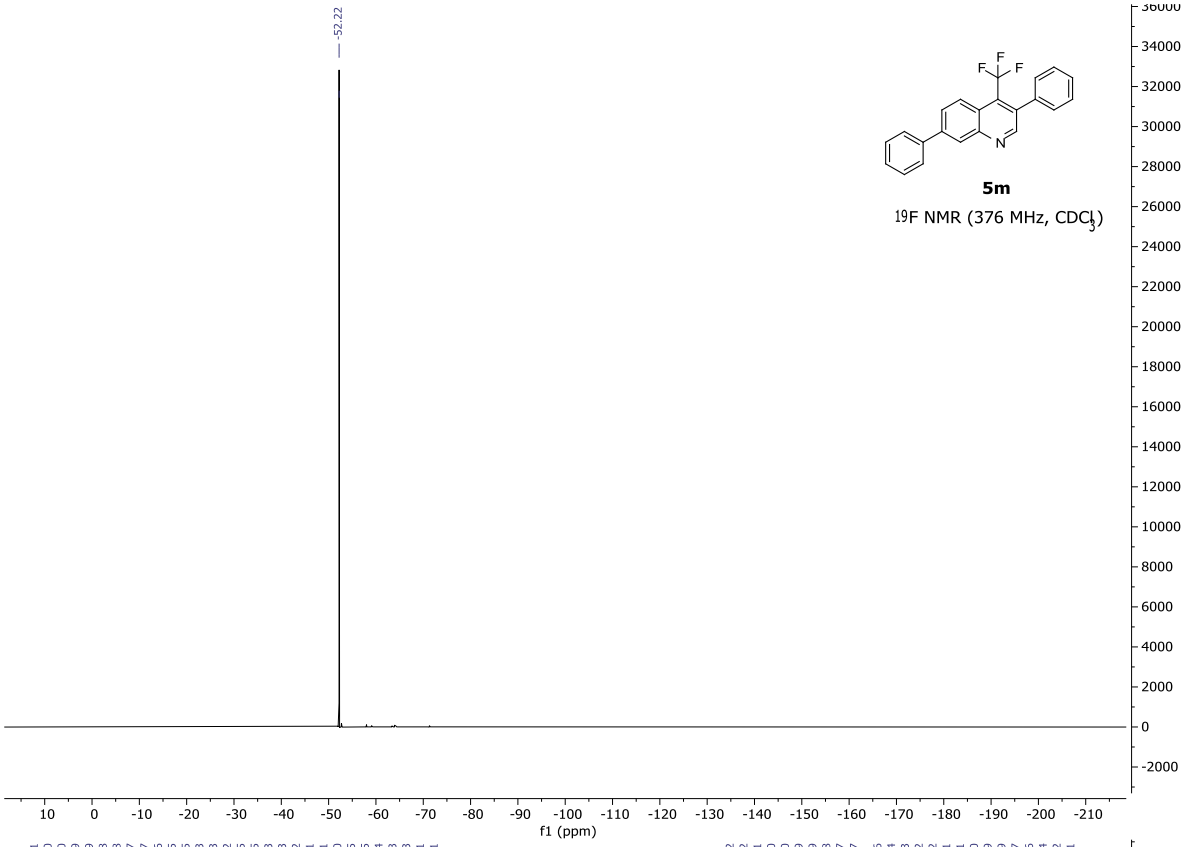

8.86
8.42
8.41
8.14
8.13
8.12
8.12
8.11
8.11
8.10
7.81
7.81
7.79
7.78
7.53
7.52
7.52
7.51
7.50
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.46
7.45
7.44
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.34
7.34
7.34
F
F
F
Br
N
5l
1H NMR (400 MHz, CDCl3)
A (s)
8.86
B (d)
8.42
C (dq)
8.12
D (m)
7.49
E (m)
7.37
F (dd)
7.80
1.00
0.99
1.08
1.06
3.17
2.14
f1 (ppm)


153.93
148.68
134.14
132.59
131.98
130.93
130.64
128.85
128.45
128.32
126.27
126.23
125.08
124.14
122.32
121.98
F
F
F
Br
N
5l
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-52.24
F
F
F
Br
N
5l
19F NMR (376 MHz, CDCl3)
f1 (ppm)

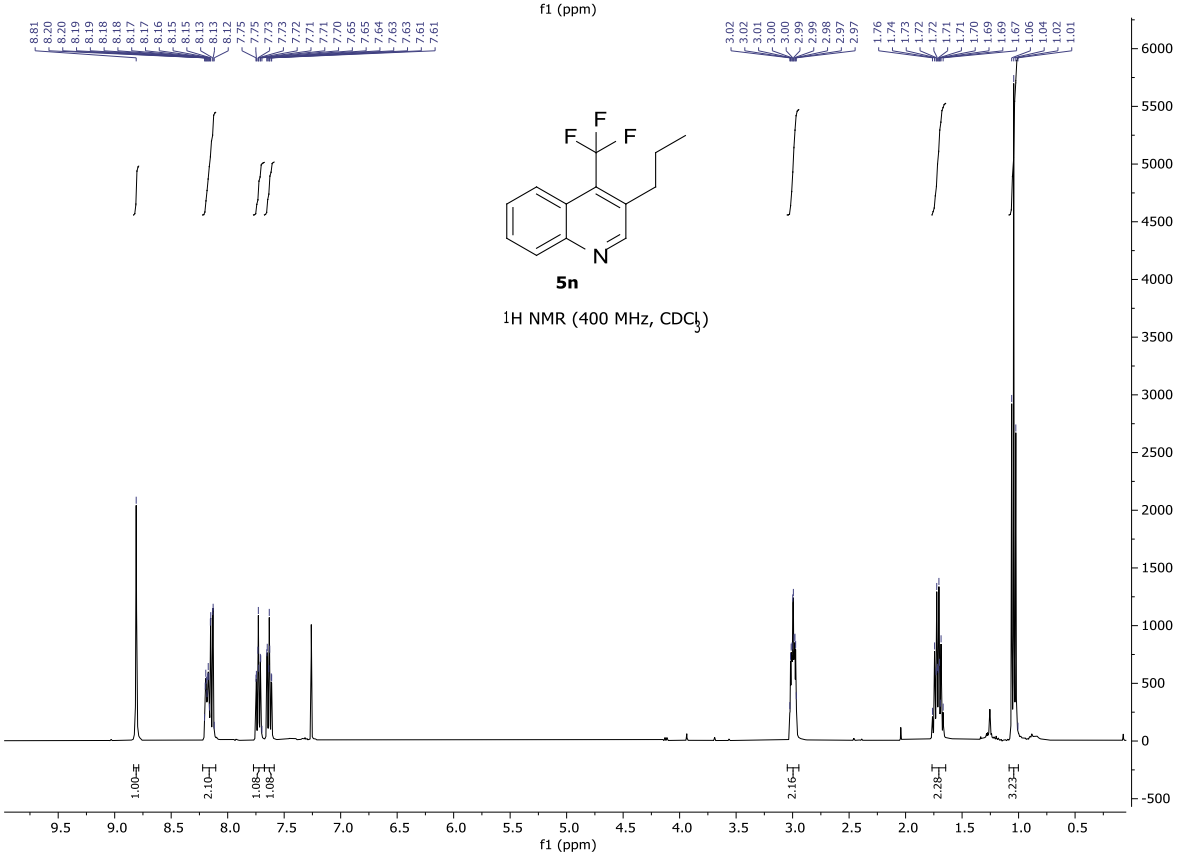

8.90 8.47 8.46 8.36 8.35 8.35 8.34 8.34 8.33 8.33 8.32 8.02 8.01 8.00 7.99 7.82 7.82 7.81 7.80 7.80 7.57 7.56 7.55 7.54 7.53 7.52 7.51 7.51 7.50 7.49 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.44 7.44 7.44 7.42 7.41 7.40 7.40 7.39
0.87 0.94 0.98 1.01 1.96 8.40
f1 (ppm)
5m
1H NMR (400 MHz, CDCl3)


153.32 148.50 142.49 139.35 137.68 133.61 130.96 130.66 130.06 129.18 128.98 128.39 128.27 128.14 128.04 127.66 127.45 125.44 125.40 125.37 125.32 122.62 122.33 119.86
f1 (ppm)
5m
13C NMR (101 MHz, CDCl3)



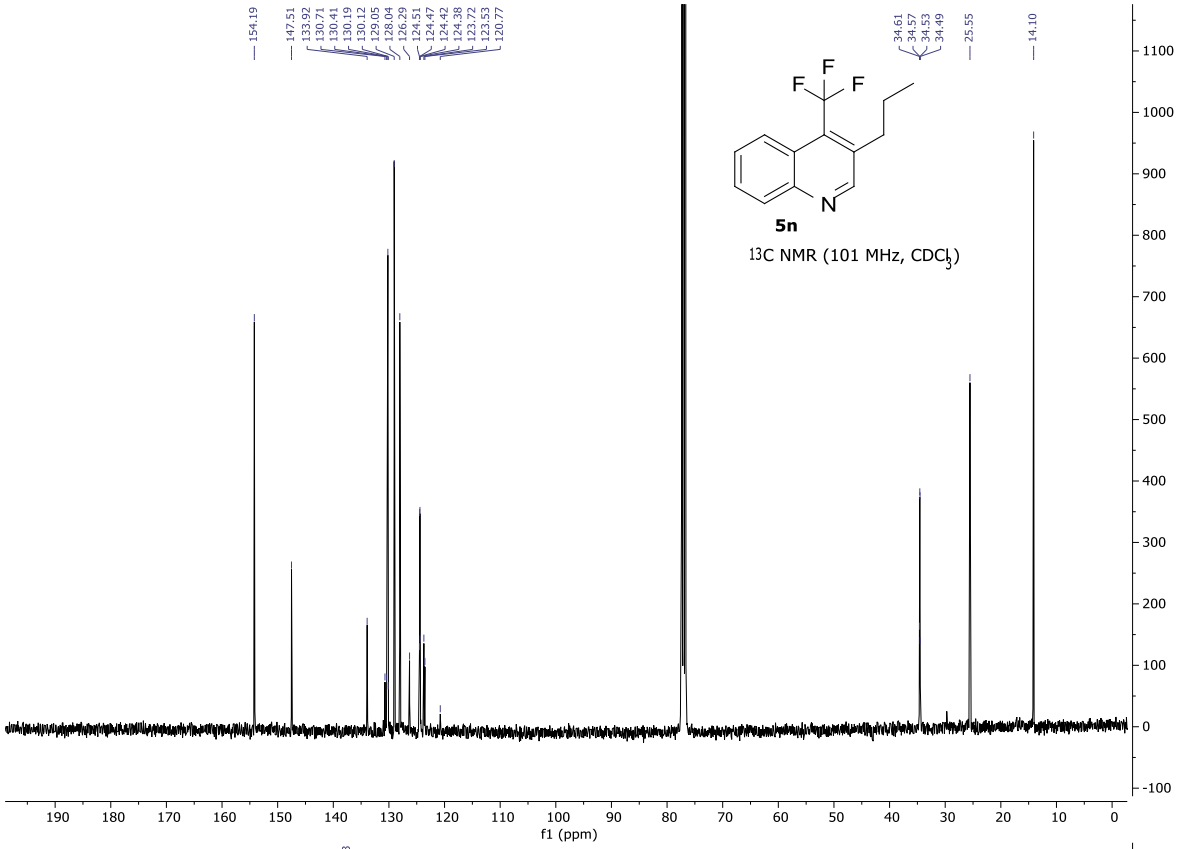
5m

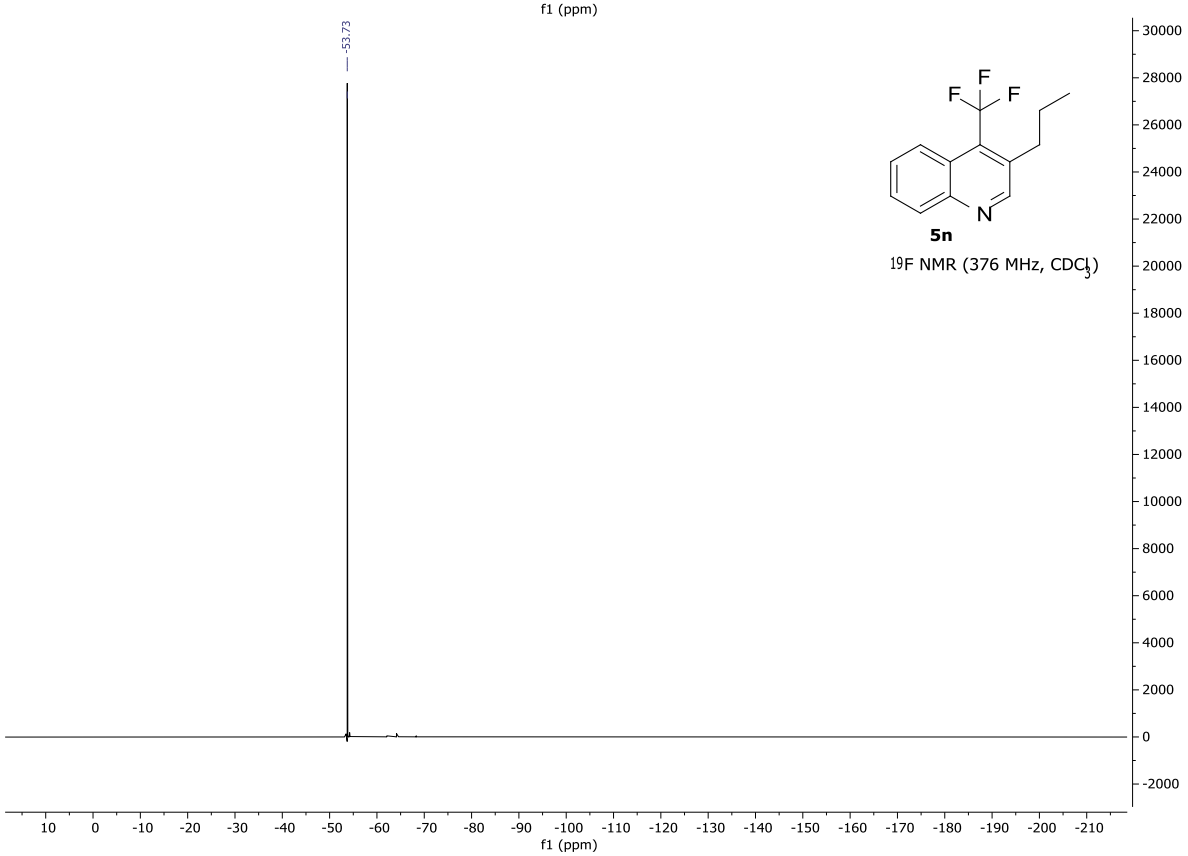
^{19}F NMR (376 MHz, $CDCl_3$)

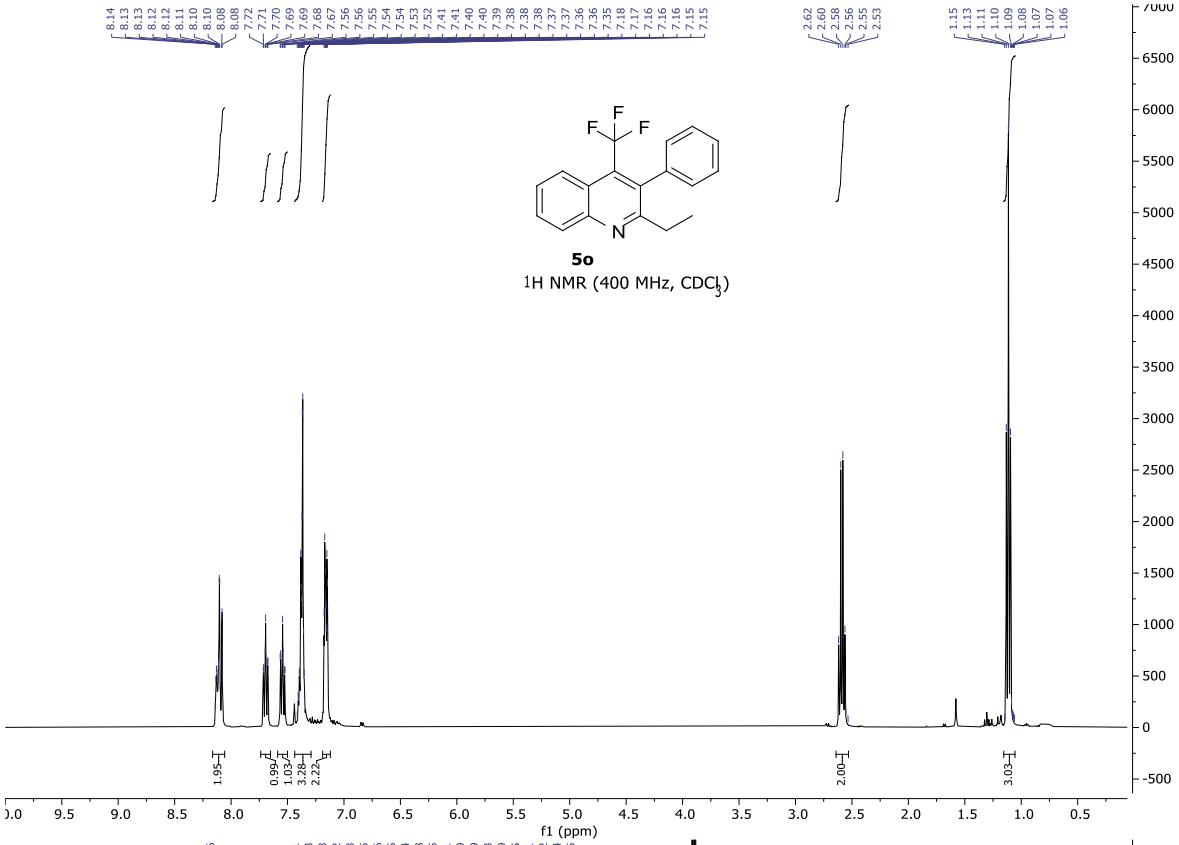


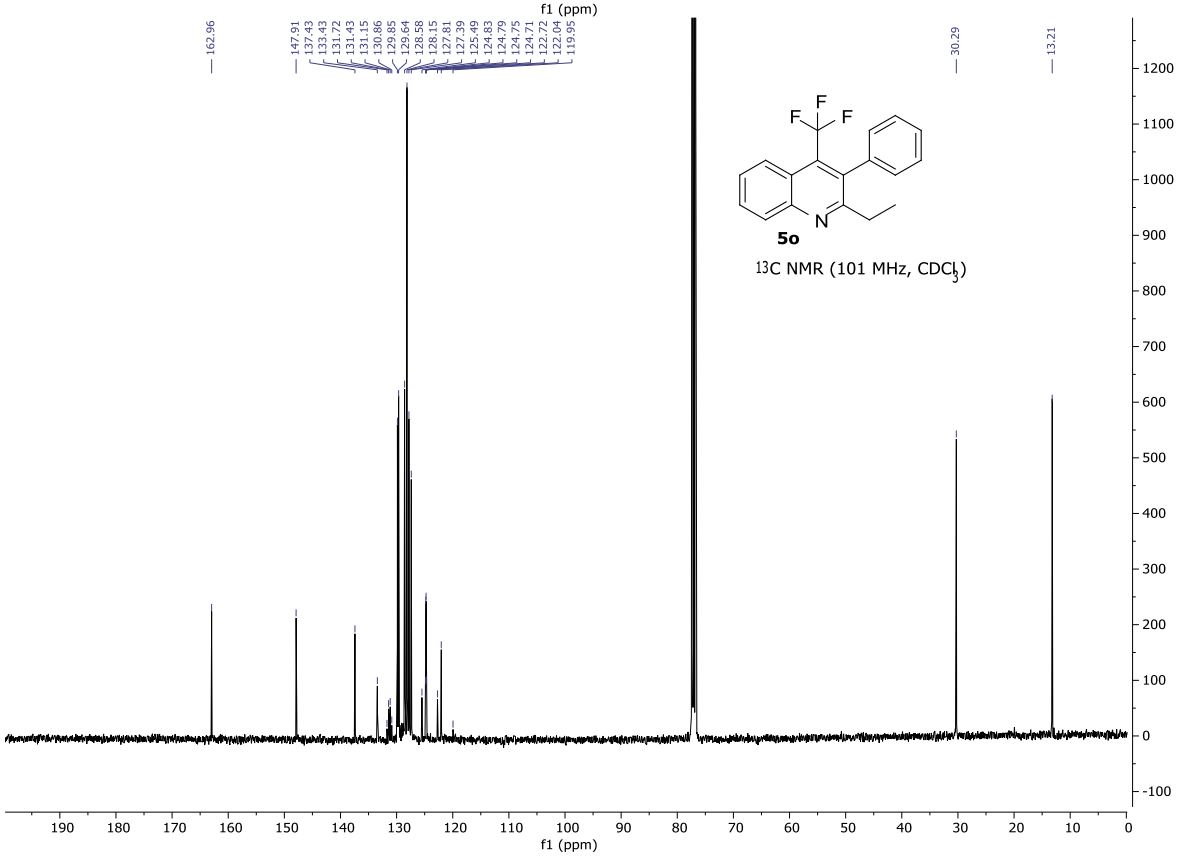
5n

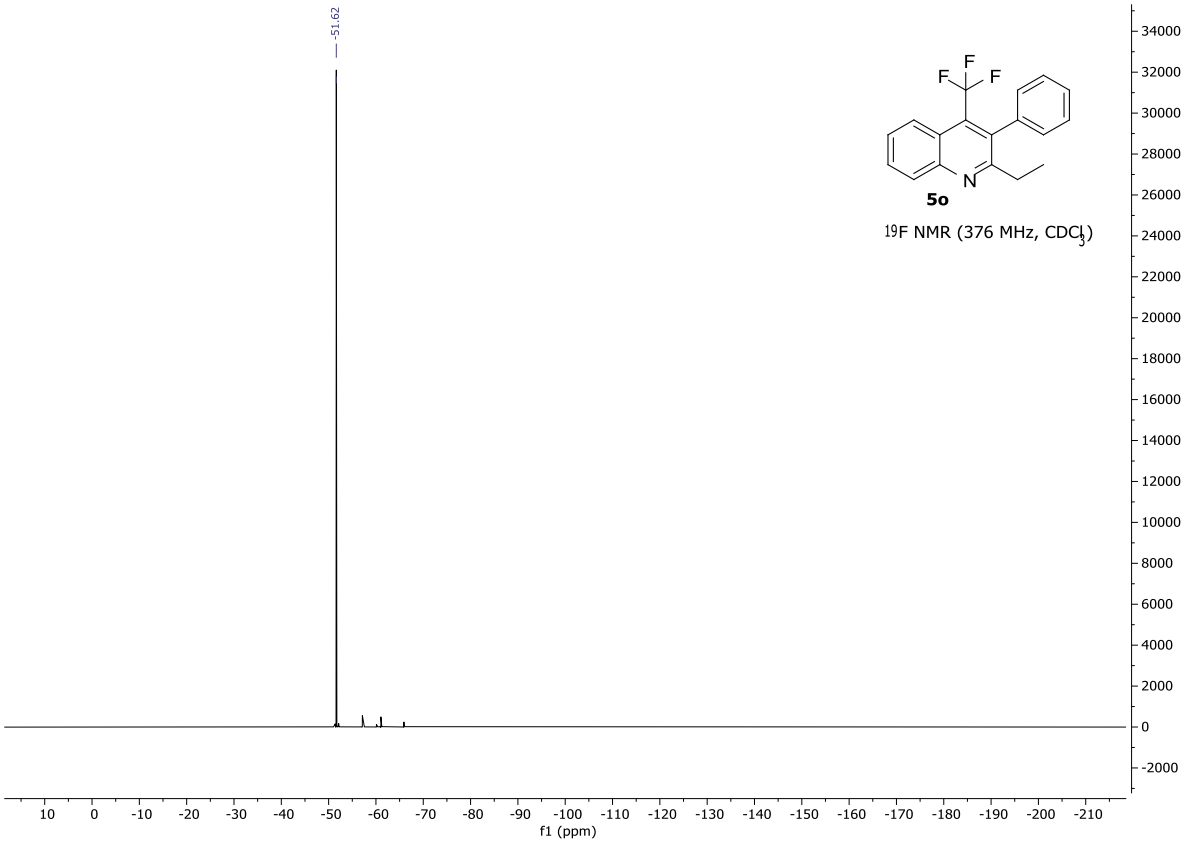
^{1}H NMR (400 MHz, $CDCl_3$)

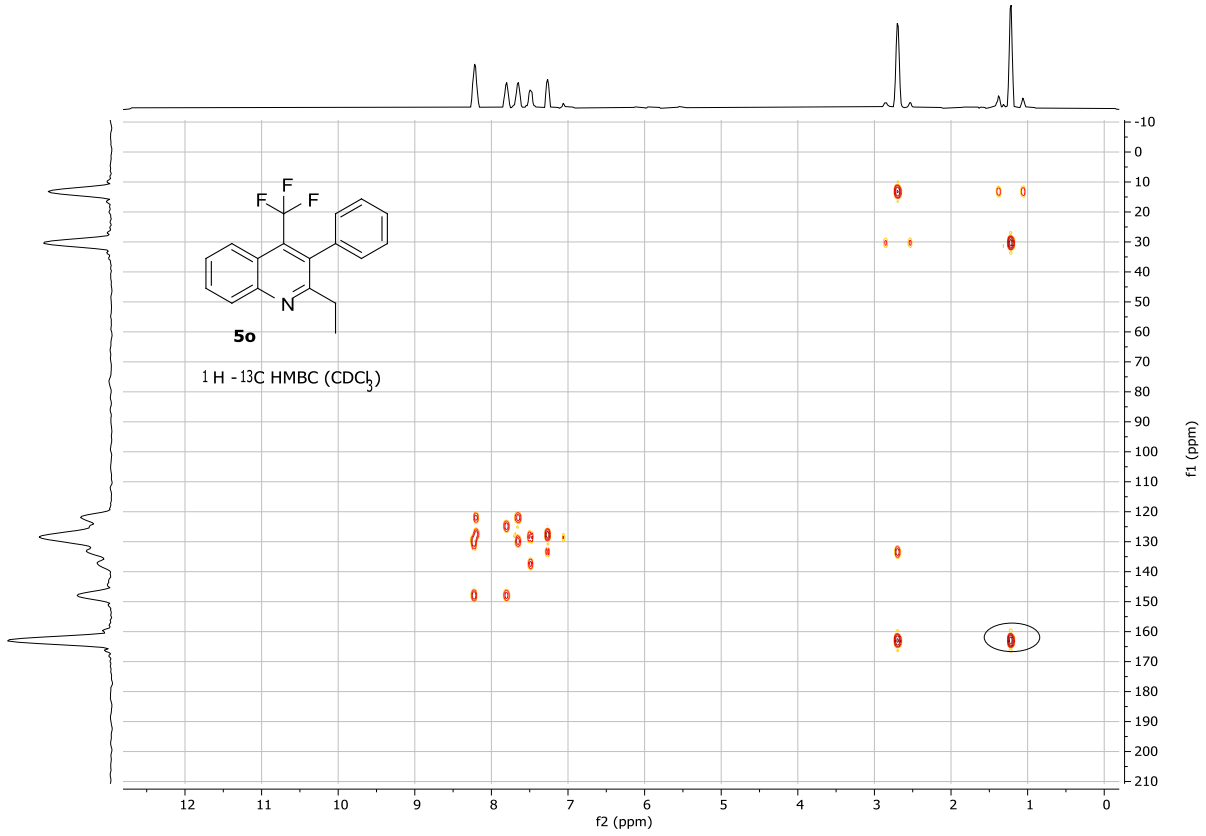

154.19
147.51
133.92
130.71
130.41
130.19
130.12
129.05
128.04
126.29
124.51
124.47
124.42
124.38
123.72
123.53
120.77
34.61
34.57
34.53
34.49
25.55
14.10
F
F
F
N
5n
13C NMR (101 MHz, CDCl3)
f1 (ppm)

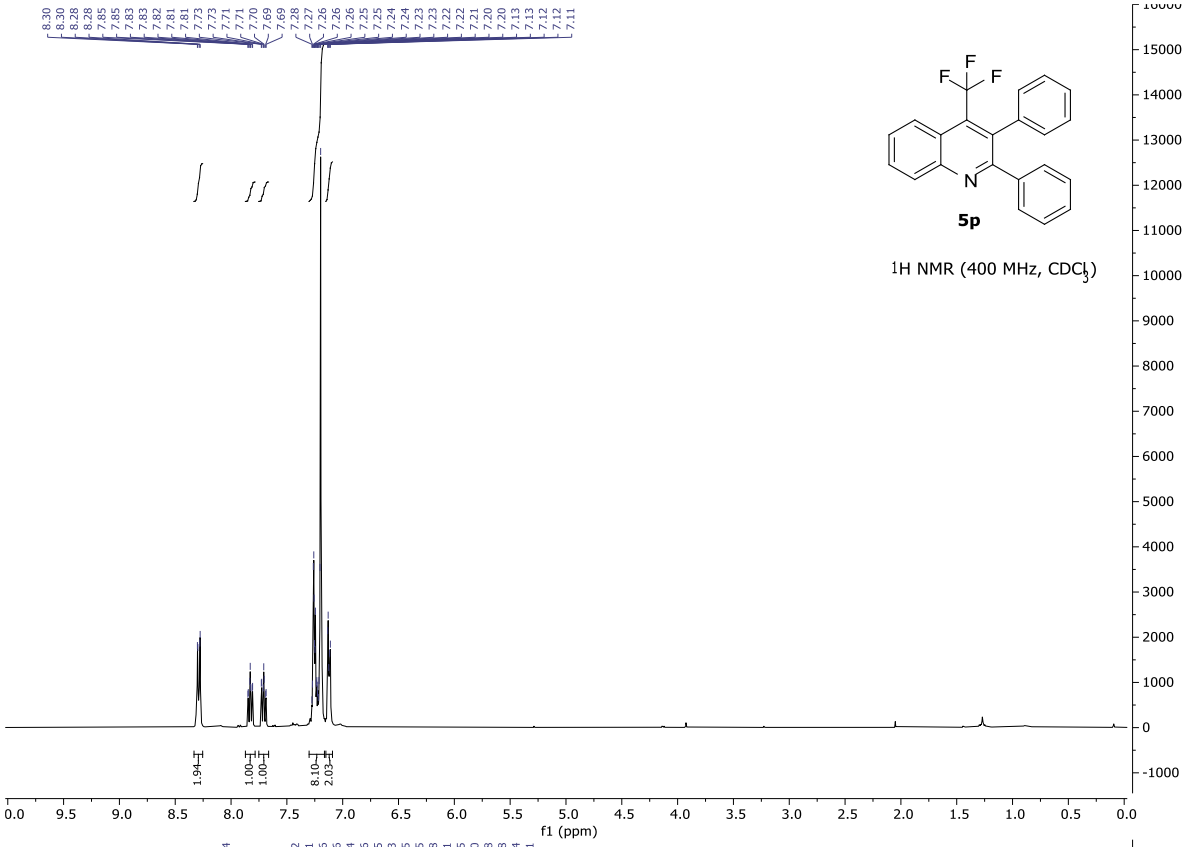

53.73
F
F
F
N
5n
19F NMR (376 MHz, CDCl3)
f1 (ppm)

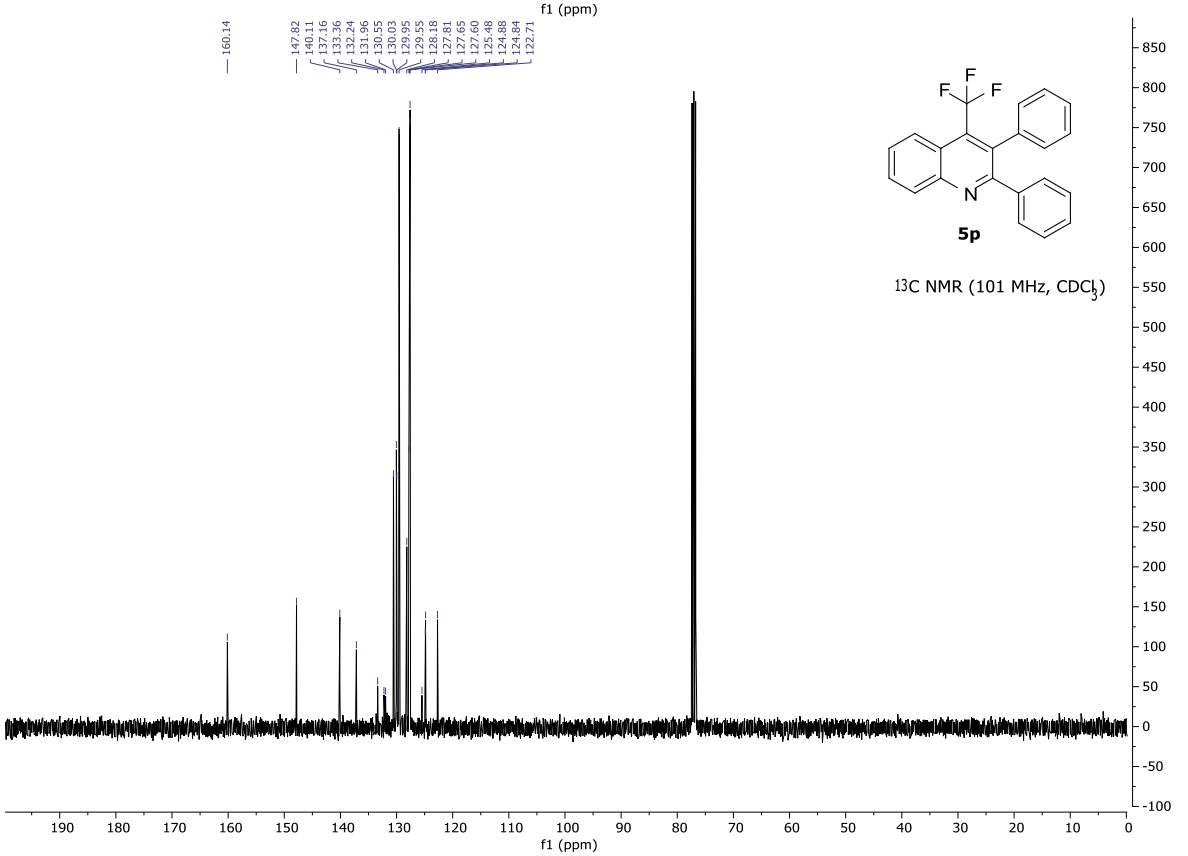

F
F F
N
5o
1H NMR (400 MHz, CDCl3)
f1 (ppm)

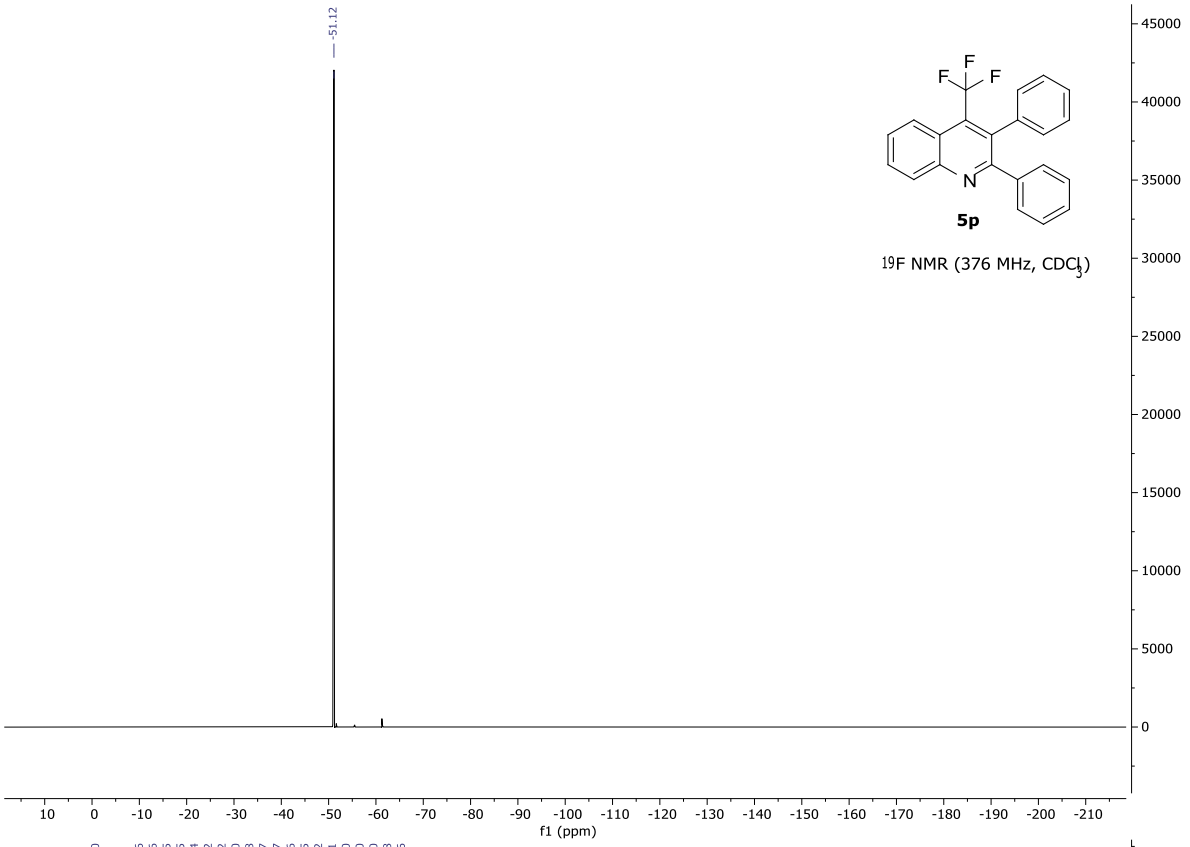

F
F F
N
5o
13C NMR (101 MHz, CDCl3)
f1 (ppm)

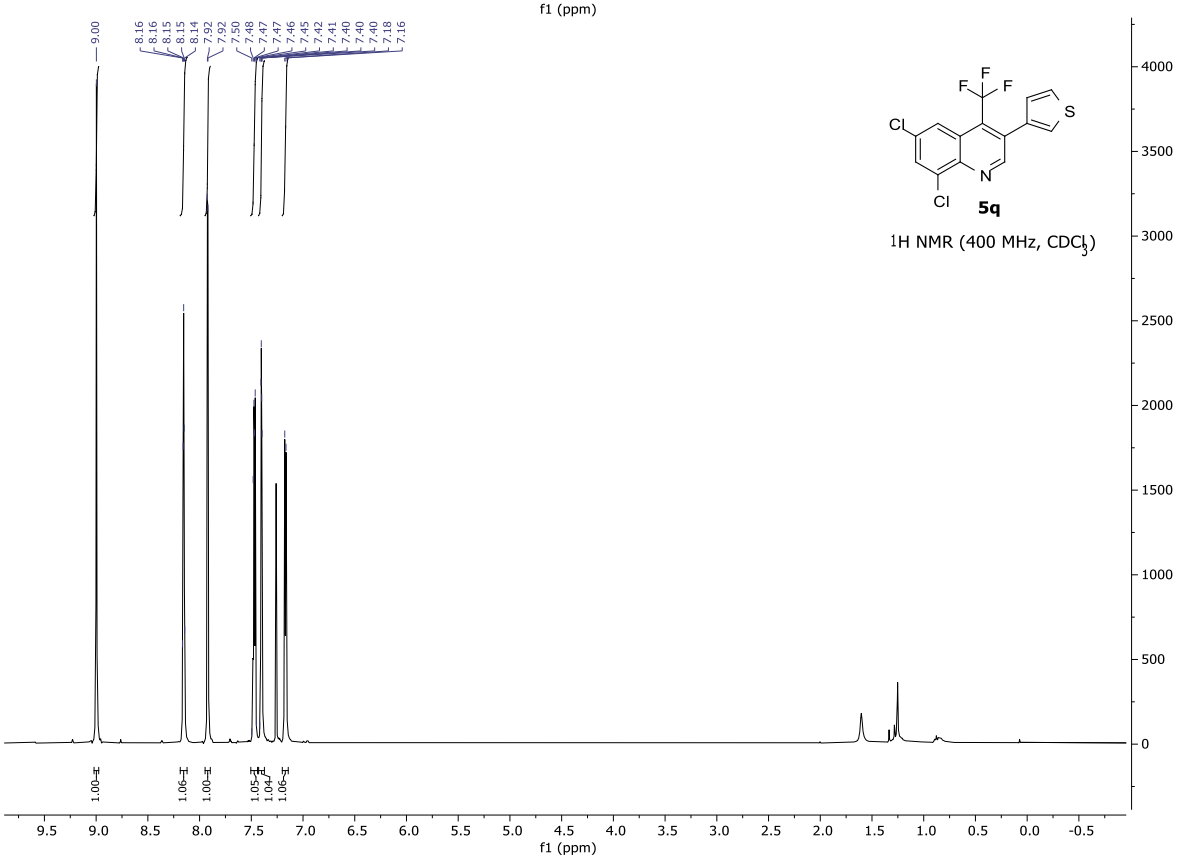

-51.62
F
F
F
N
5o
19F NMR (376 MHz, CDCl3)
f1 (ppm)

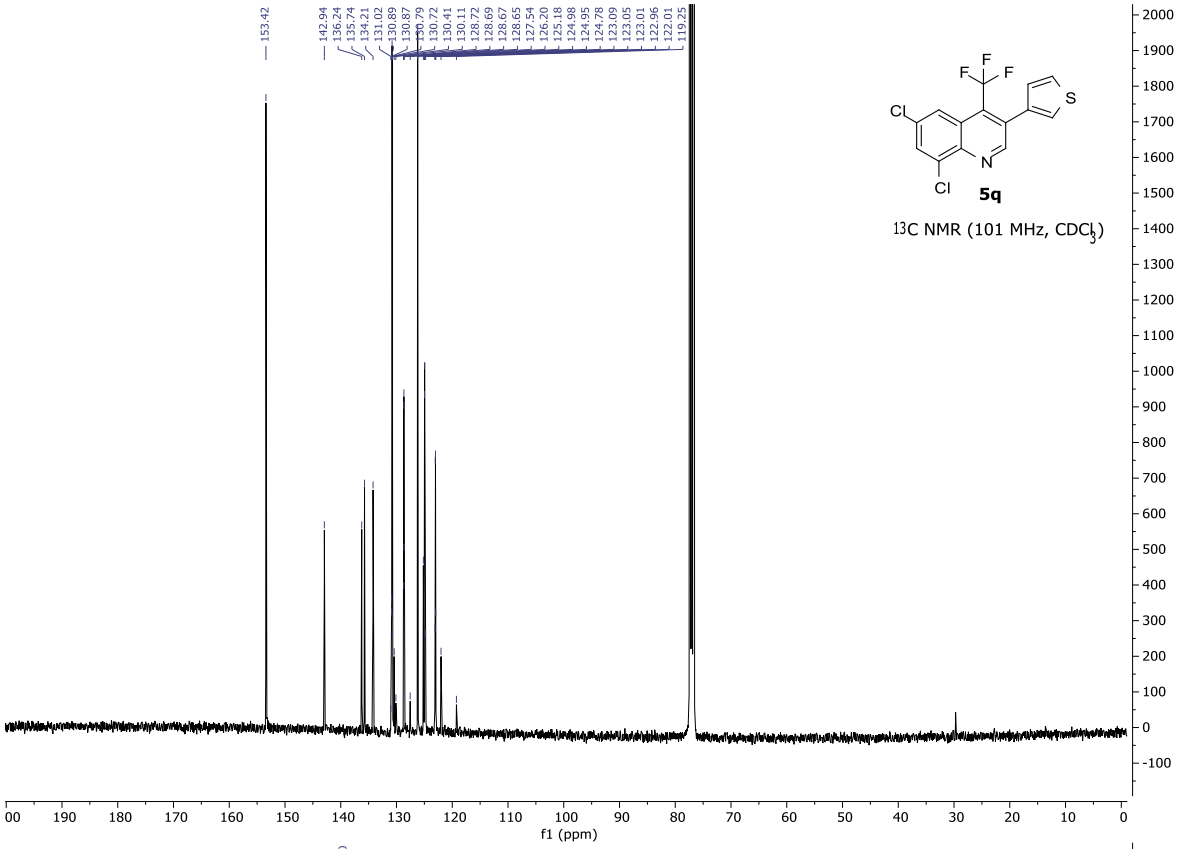

F
F
F
N
5o
1H -13C HMBC (CDCl3)
f2 (ppm)
f1 (ppm)


8.30
8.30
8.28
8.28
8.28
7.85
7.85
7.83
7.83
7.82
7.81
7.81
7.73
7.73
7.71
7.71
7.70
7.69
7.69
7.28
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.13
7.12
7.12
7.11
F
F
F
N
5p
1H NMR (400 MHz, CDCl3)
1.94
1.00
1.00
8.10
2.03
f1 (ppm)

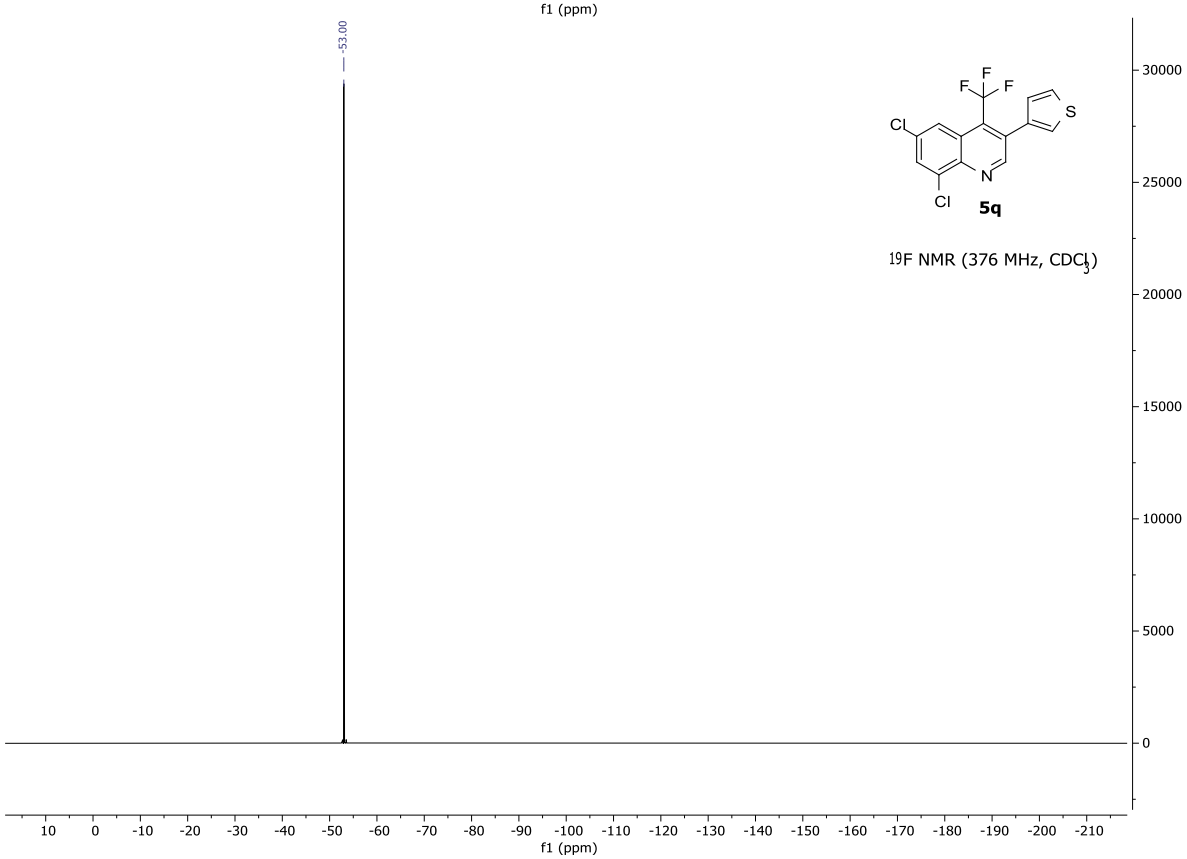

160.14
147.82
140.11
137.16
133.36
132.24
131.96
130.55
130.03
129.95
129.55
128.18
127.81
127.65
127.60
125.48
124.88
124.84
122.71
F
F
F
N
5p
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-51.12
F
F
F
N
5p
19F NMR (376 MHz, CDCl3)
f1 (ppm)

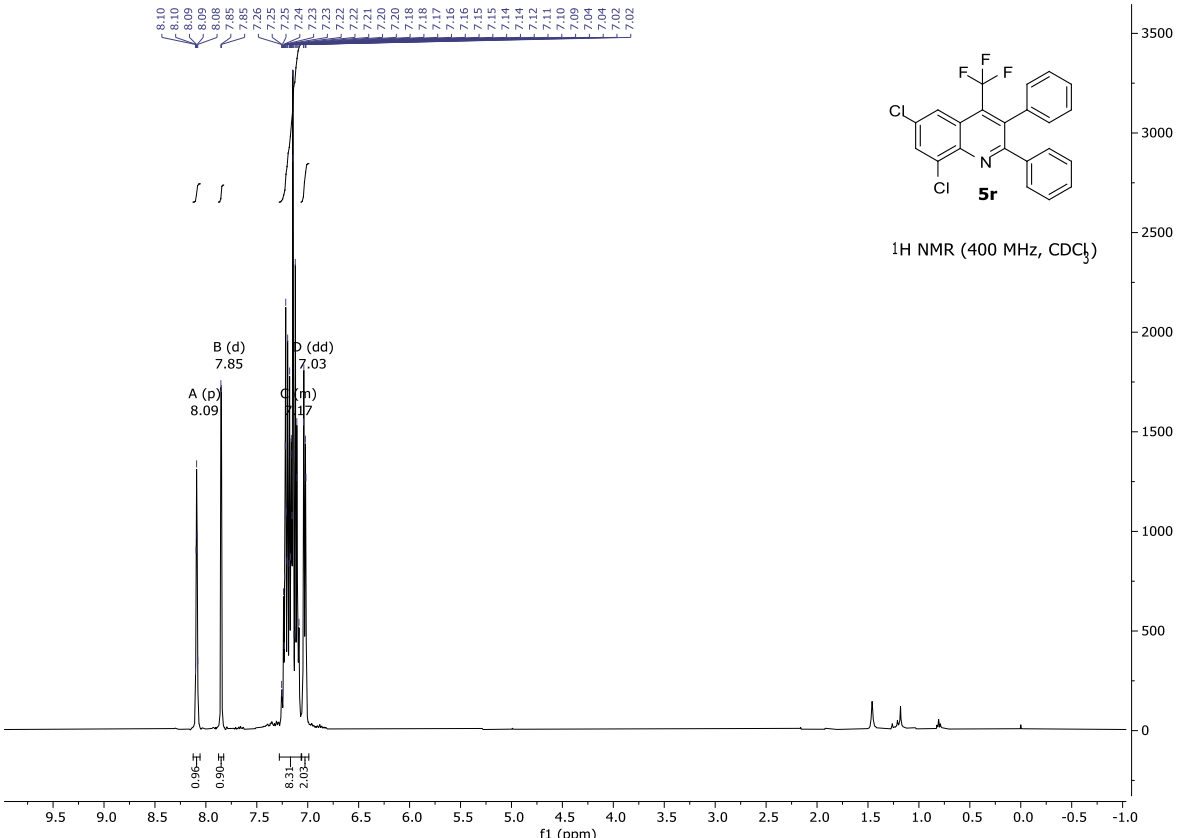

9.00
8.16
8.16
8.15
8.15
8.14
7.92
7.92
7.50
7.48
7.47
7.47
7.46
7.45
7.42
7.41
7.40
7.40
7.40
7.18
7.16
F
F
F
Cl
S
N
Cl
5q
1H NMR (400 MHz, CDCl3)
1.00
1.06
1.00
1.05
1.04
1.06
f1 (ppm)

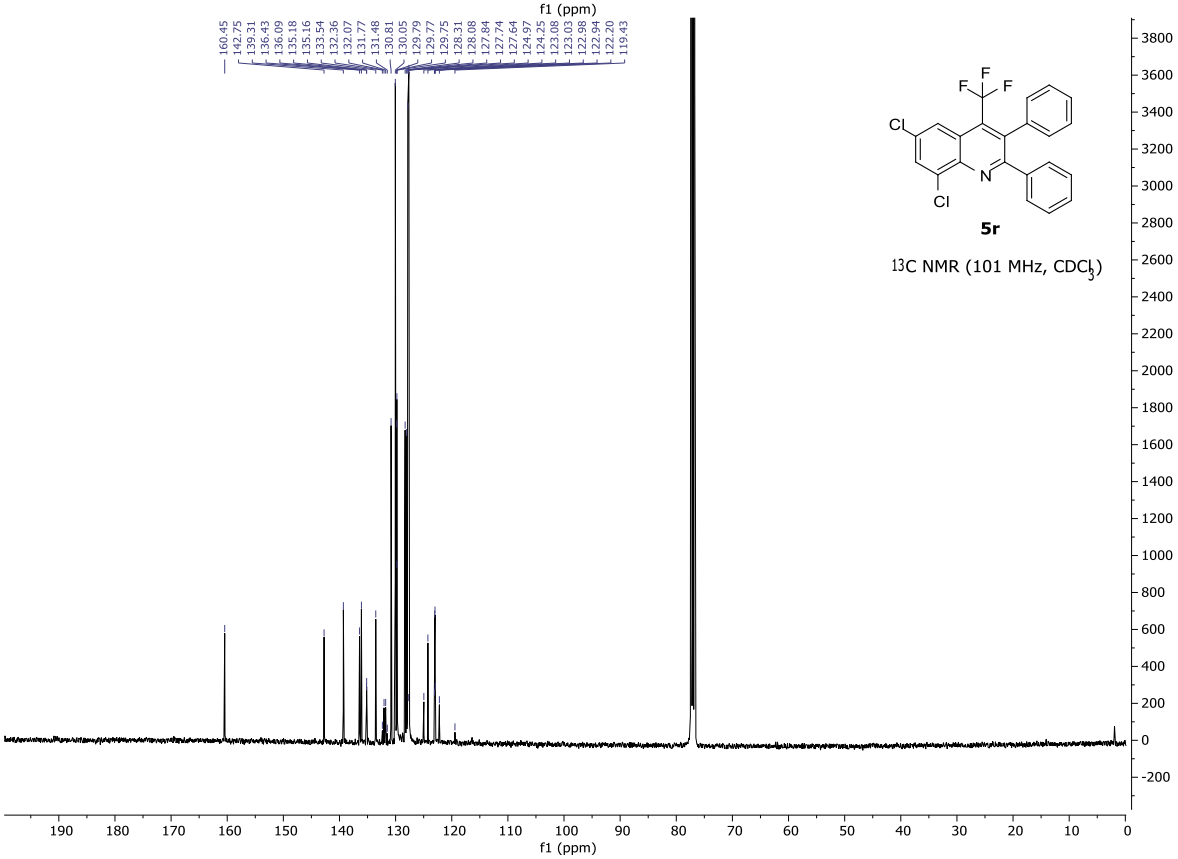


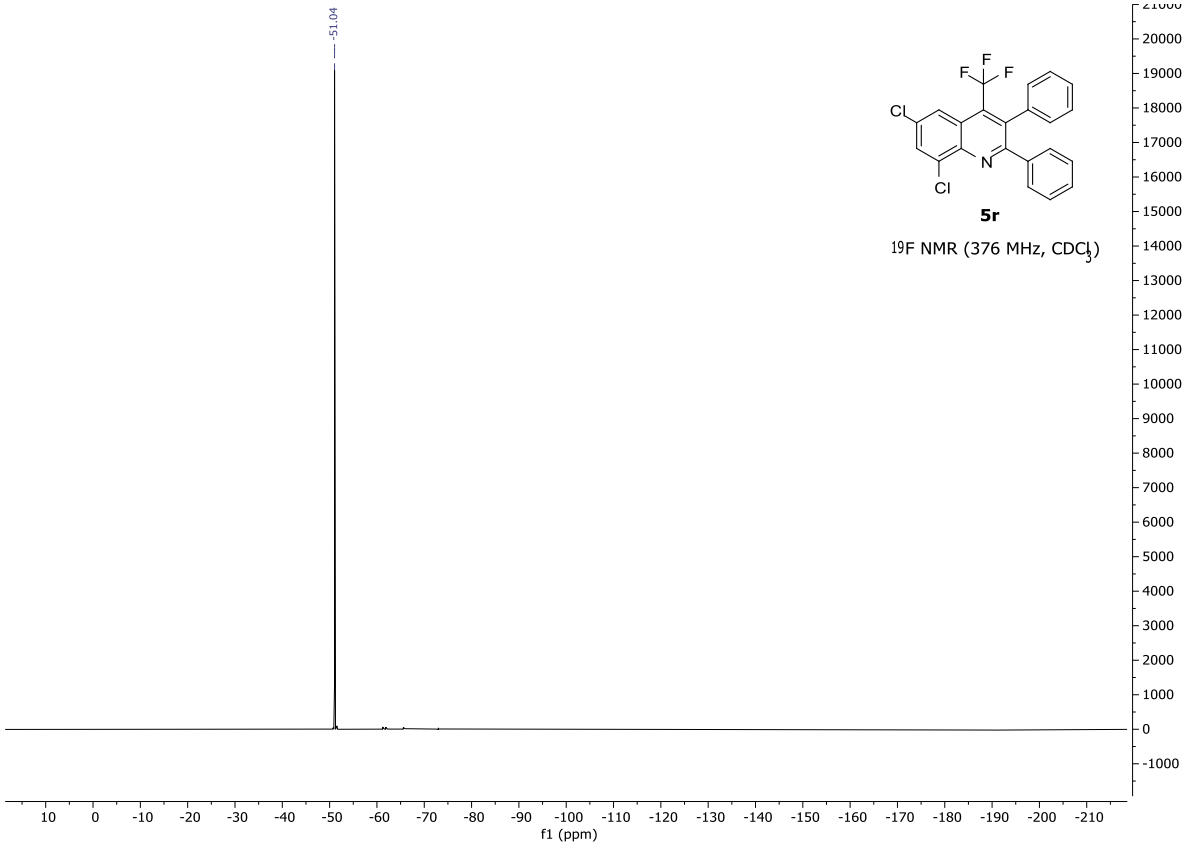
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)


A (p)
8.09
B (d)
7.85
D (dd)
7.03
0.96
0.90
8.31
2.03
f1 (ppm)
5r
1H NMR (400 MHz, CDCl3)


f1 (ppm)
5r
13C NMR (101 MHz, CDCl3)


-51.04
F
F
F
Cl
N
Cl
5r
19F NMR (376 MHz, CDCl3)
f1 (ppm)