Copper-Catalyzed Oxyvinylation of Diazo Compounds

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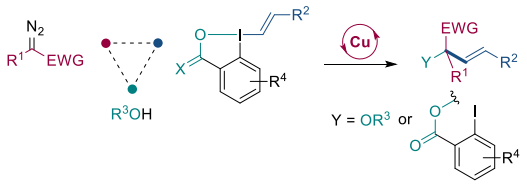
Supporting Information Placeholder



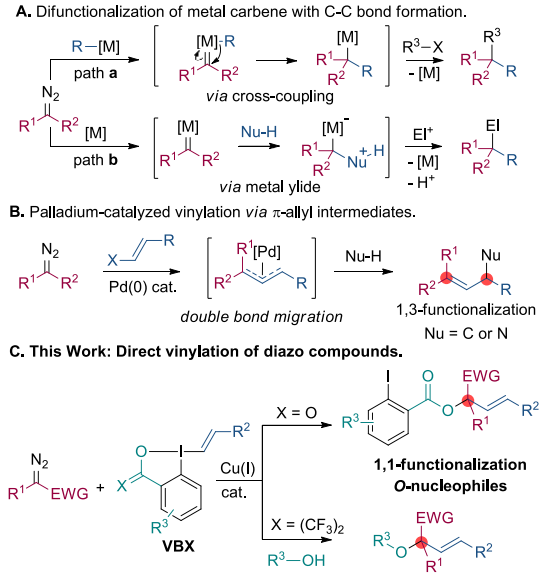
ABSTRACT: A copper(I)-catalyzed vinylation of diazo compounds with VinylBenziodoXolone reagents (VBX) as partners is reported. The transformation tolerates diverse functionalities on both reagents delivering polyfunctionalized vinylated products. The strategy was successfully extended to a three-component/intermolecular version with alcohols. The obtained products contain synthetically versatile functional groups, such as an aryl iodide, an ester and an allylic leaving group, enabling further modification.

Metal carbenes obtained from diazo compounds have been extensively used in synthetic chemistry[1] and their *gem*-difunctionalization is a powerful method to access complex products (Scheme 1A).[2] The formation of at least one new C-C bond in this process has been realized for alkylation, arylation and alkynylation reactions using palladium,[3] copper[4] and rhodium[5] catalysis. The most successful approaches involve cross-coupling through carbene migratory insertion (path **a**),[2b] or trapping of transient ylides with carbon electrophiles (path **b**).[2a]

The introduction of an olefin in such processes has been limited to the formation of a C-alkenyl and a C-H bond,[6] with the exception of a palladium-catalyzed cross-coupling combining vinylhalides and nucleophiles (Scheme 1B).[7] The reaction proceeds via a π-allyl palladium species, resulting in a 1,3 relationship between the nucleophile and the vinyl group. We considered a reverse approach to develop an unprecedented 1,1-oxyvinylation: Addition of an oxygen nucleophile first, followed by reaction with an electrophilic hypervalent iodine vinylation reagent (Scheme 1C). Our group established an efficient copper-catalyzed 1,1-oxyalkynylation of diazo compounds based on the use of electrophilic ethynylbenziodoxolone (EBX) hypervalent iodine reagents.[8,9] To develop the first direct vinylation of diazo compounds, we envisaged the use of the corresponding vinylbenziodoxolone (VBX) reagents recently reported by Olofsson and co-workers.[10]

In this work, we report a copper-catalyzed insertion of diazo compounds into VBX reagents proceeding with broad scope at room temperature. The transformation was successfully extended to the synthesis of allylic ethers using alcohols as external nucleophiles.

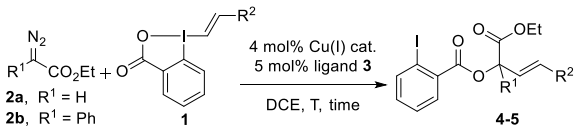
Scheme 1. General difunctionalization of metal carbenes (A) and vinylation of diazo compounds (B and C).



We started our optimization by reacting Ph-VBX (**1a**) with ethyl diazoacetate (**2a**) (Table 1; See Supporting Information for other tested conditions, Table S1). No desired product was isolated without copper catalyst or ligand (entries 1 and 2). Allylic ester **4a** was formed in 90% yield when $Cu(CH_3CN)_4BF_4$ (4 mol%) was used in combination with diimine **3a** (5 mol%) (entry 3).[8a] A lower yield was obtained with more electron-rich VBX **1c** (entry 4). No reaction occurred using the alkyl-substituted substrate **1j** even at a higher temperature (entry 5). We therefore investigated bisoxazoline (BOX) ligands, which had

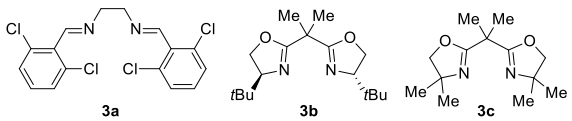
also been successful in our previous work.[8b] Using *t*Bu-BOX ligand **3b** the reaction could be performed in one hour at room temperature to give **4a** in 95% yield as a racemate (entry 6). The non-chiral ligand **3c** gave a similar result (entry 7). These conditions performed well with the more electron-rich and aliphatic substrates (entries 8 and 9), but were not successful for substituted diazo compound **2b** (entry 10). Product **5a** could be obtained in 80% yield using ligand **3a** (entry 11). In all reactions, only the *E*-olefin was obtained.

Table 1. Optimization of the insertion of diazo compounds 2a and 2b into VBX (1).[a]



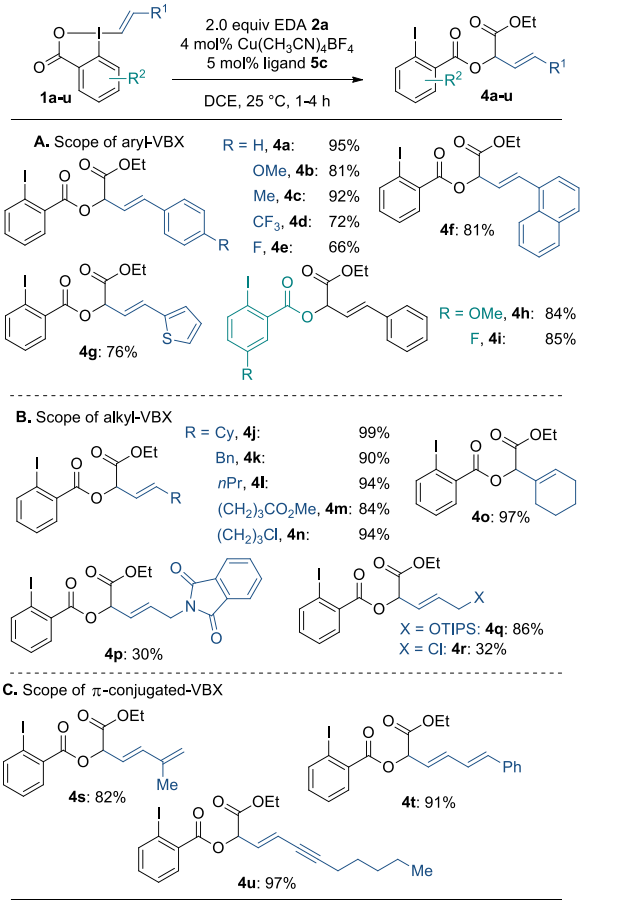
entry	ligand	diazo R^1 =	VBX R^2 =	product	temp	time	yield[b]
1[c]	**3a**	H (**2a**)	Ph (**1a**)	**4a**	40 °C	4 h	0%
2	none	H (**2a**)	Ph (**1a**)	**4a**	40 °C	4 h	< 5%
3	**3a**	H (**2a**)	Ph (**1a**)	**4a**	40 °C	4 h	90%
4	**3a**	H (**2a**)	PMP (**1c**)	**4b**	60 °C	24 h	50%
5	**3a**	H (**2a**)	Cy (**1j**)	**4j**	60 °C	24 h	< 5%
6	**3b**	H (**2a**)	Ph (**1a**)	**4a**	25 °C	1 h	95%
7[d]	**3c**	H (**2a**)	Ph (**1a**)	**4a**	25 °C	1 h	95%
8[d]	**3c**	H (**2a**)	PMP (**1c**)	**4b**	25 °C	4 h	81%
9[d]	**3c**	H (**2a**)	Cy (**1j**)	**4j**	25 °C	4 h	99%
10	**3c**	Ph (**2b**)	Ph (**1a**)	**5a**	40 °C	4 h	< 5%
11	**3a**	Ph (**2b**)	Ph (**1a**)	**5a**	40 °C	4 h	80%

[a]Reactions on 0.10 mmol scale with 2.0 equiv. of **2**, 4 mol% of $Cu(CH_3CN)_4BF_4$, 5 mol% of ligand in DCE (0.04 M). [b]Isolated yields. [c]Without $Cu(CH_3CN)_4BF_4$. [d]On 0.20 mmol scale. Ph = phenyl, Cy = cyclohexyl, PMP = *para*-methoxyphenyl.



Diverse aryl-substituted VBXs were then explored with ethyl diazoacetate (**2a**) (Scheme 2A).[11] Electron donating ether and alkyl groups on the arene afforded products **4b-c** in 81% and 92% yields. Fluorinated compounds **4d** and **4e** were obtained in 72% and 66% yield. A naphthyl-substituted VBX led to the formation of **4f** in 81% yield. A slightly diminished yield was obtained for thiophene-substituted **4g** (76% yield). Both electron-rich and -poor substituents on the benziodoxolone backbone were tolerated affording **4h** and **4i**. Next, we turned our attention to alkyl-substituted VBX reagents (Scheme 2B). VBXs bearing aliphatic chains (Cy, Bn and *n*Pr) provided allylic esters **4j-l** in 90-99% yield. The incorporation of an ester (**4m**) or a chloride (**4n**) group could also be achieved. Trisubstituted alkene **4o** was accessed in 97% yield. VBXs with amines, silyl ethers, and chlorides in allylic position delivered the corresponding products **4p-r**. A lower yield was obtained for **4p** and **4r**, maybe due to the low solubility of the corresponding VBX reagents in DCE. π-Conjugated systems were readily incorporated (Scheme 2C). An isoprene skeleton was introduced to give **4s** in 82% yield. Conjugated diene **4t** and enyne **4u** were also successfully synthesized.

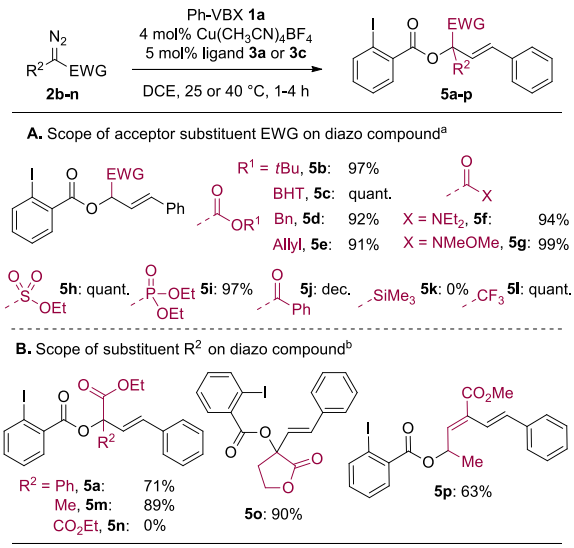
Scheme 2. Scope of VBX reagents.



Reactions using VBX **1** (0.2 mmol) and **2a** (0.4 mmol) in DCE (0.04 M).

We next investigated the scope of the acceptor substituent on the diazo compounds (Scheme 3A). Various esters such as *t*Bu or BHT were tolerated giving **5b** and **5c** in quantitative yield.[12] Product **5d** bearing a benzyl group was obtained in 92% yield and **5e** with an allyl group in 91%. 2-Diazo-*N*,*N*-diethylacetamide provided **5f** in 94% yield. Weinreb amide derivative **5g** was isolated in 99% yield. Sulfonate- and phosphonate-diazo compounds were efficient coupling partners, generating products **5h** and **5i** in quantitative yields.[13] Unfortunately, diazoketones underwent degradation through Wolff rearrangement (**5j**) and no conversion was obtained using trimethylsilyldiazomethane (**5k**, 0% yield). However, compound **5l** incorporating a trifluoromethyl group was isolated in quantitative yield. Organofluorine compounds are important for the pharmaceutical, agrochemical and materials industry.[14] Other less stable diazo compounds lacking an electron-withdrawing group were not yet investigated. Finally, the reaction of disubstituted diazo compounds was investigated using diimine ligand **3a** (Scheme 3B). Products **5a** and **5m** with tertiary allylic centers were formed in 71 and 89% yield. A second electron-withdrawing group suppressed the reactivity (**5n**, 0% yield). A cyclic diazo compound afforded the desired product **5o** in 90% yield. Diene product **5p** could be obtained in good yield when starting from a vinyl diazo precursor. Attack of the nucleophile at the vinylogous center was favored.[15]

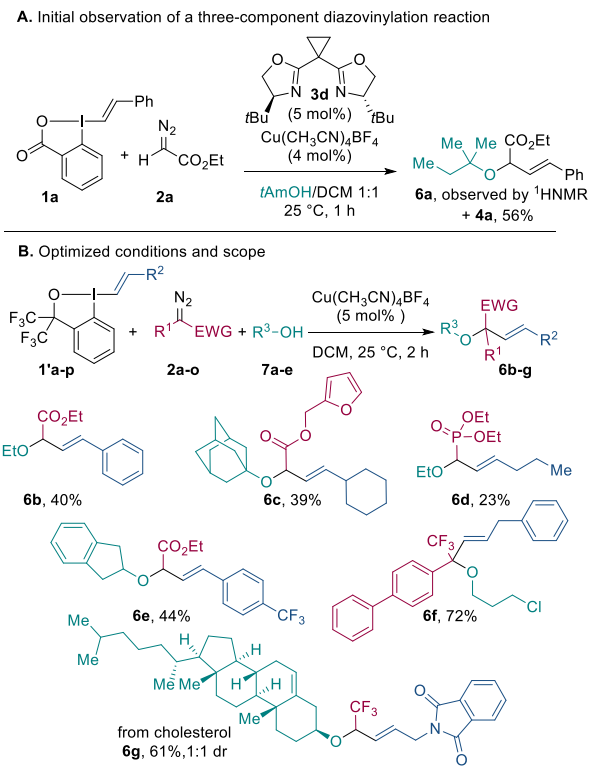
Scheme 3. **Scope of diazo compounds** 2.



Reactions using Ph-VBX (1a) (0.2 mmol) and 2 (0.4 mmol) in DCE (0.04 M). [a]3c as ligand at 25 °C. [b]3a as ligand at 40 °C.

We then investigated an enantioselective version of the reaction. Testing various substrates, chiral ligands and reaction conditions, we achieved a maximum of 75:25 er with ligand **3d** for the formation of **5c** (See Table S3 for details).[16] Interestingly, with *tert*-amyl alcohol as co-solvent, we observed ^{1}H NMR signals tentatively assigned to allylic ether product **6a** in the crude reaction mixture, in addition to expected **4a** for the reaction of VBX **1a** and **2a** (Scheme 4A).

Scheme 4. Extension to three-component reaction.

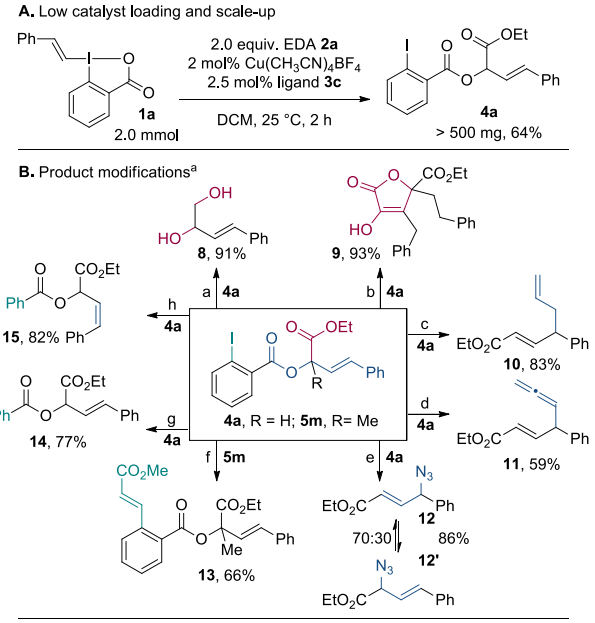


Reactions using VBX (**1v-z**) (0.3 mmol) and R^{3}OH (0.9 mmol) in DCM (0.075 M). Diazo **2** (0.6 mmol, 0.6 M in DCM) added via syringe pump over 1 h.

To favor the three-component reaction, we used less nucleophilic bis-trifluoromethyl benziodoxole VBX **1'** and removed the ligand (See Table S2 for details).[17] With 3 equivalents of alcohol, the three-component products were obtained in 23-72% yield (Scheme 4B). Primary, secondary and tertiary alcohols were combined with different VBXs and diazo compounds leading to functionalized allylic ethers bearing esters (**6b**, **6c** and **6e**), phosphonate (**6d**), chloride (**6f**), furan (**6c**), indanyl (**6e**), adamantyl (**6c**) or trifluoromethyl (**6e** and **6f**) groups. The vinylation of cholesterol was achieved in 61% yield affording **6g** with a trifluoromethyl and a phthalimide group.

Product **4a** was synthesized on 2.0 mmol scale using a lower catalyst loading at higher concentration (Scheme 5A). The esters groups in **4a** were readily reduced with $LiAlH_4$ to produce diol **8** (Scheme 5B). Butenolide **9** resulting from the formation of an α-keto ester followed by dimerization was formed under basic conditions. Treatment of **4a** with $TiCl_4$ and allyl-TMS led to the formation of conjugated ester **10**. Propargyl-TMS could also be used as nucleophile giving allene-containing product **11**. The introduction of an azide was accomplished using $TMSN_3$ to form **12**, which isomerizes spontaneously.[18] A Heck reaction between **5m** and methyl acrylate afforded **13** in 66% yield. Hydrogenolysis of the iodoarene was achieved with hydrogen and poisoned Pd/C to give product **14** in 77% yield. Visible light photoredox catalysis gave access to the deiodinated product **15** in 82% yield with *E* to *Z* isomerization of the olefin.

Scheme 5. Scale-up synthesis and product modifications.



[a]Reaction conditions: a) $LiAlH_4$ (3.00 equiv.), THF, 0 °C to rt, 1 h, 91%; b) DBU (10 equiv.), MeOH, 50 °C, 6 h, 93%; c) Allyl-TMS (1.5 equiv.), $TiCl_4$ (1.05 equiv.), DCM, 0° C, 15 min, 83%; d) Propargyl-TMS (2.0 equiv.), $TiCl_4$ (1.05 equiv.), DCM, -78 °C to 0 °C, 59%; e) $TMSN_3$ (1.5 equiv.), $TiCl_4$ (1.05 equiv.), DCM, -20 °C to 0 °C, **12**/**12'** 70:30, 86%; f) methyl acrylate (5.0 equiv.), $PdCl_2(PPh_3)_3$ (5 mol%), PPh_3 (5 mol%), Et_3N, 80 °C, 24 h, 66%; g) H_2, Pd/C (10 mol%, 10% w/w), DABCO (10 equiv.), MeOH, rt,

10 min, 77%; h) *fac*-Ir(ppy)$_3$ (2.5 mol%), NBu_3 (10 equiv.), HCO_2H (10 equiv.), blue LED, MeCN, 40 °C, 18 h, 82%.

Based on literature precedence and our work on the copper-catalyzed oxy-alkynylation reaction,[8a-c] a tentative reaction mechanism would involve an electrophilic copper-carbene generated from the diazo compound (See Scheme S1 in the Supporting Information). Nucleophilic attack of the carboxylate part of the VBX reagent or the alcohol nucleophile would generate an ylide intermediate, which is then vinylated.

In summary, we have developed a copper-catalyzed insertion of diazo compounds into vinylbenziodoxolone (VBX) reagents. The transformation provides access to a broad scope of functionalized allylic esters.[19] Extension of the strategy to a three-component reaction with alcohol nucleophiles allowed the synthesis of structurally diverse allylic ethers. The obtained products can be further modified to give important building blocks. Ongoing research is focused on the elucidation of the reaction mechanism and the development of the asymmetric version of the transformation based on our preliminary results.

ASSOCIATED CONTENT

Supporting Information

Supplementary tables and schemes, experimental procedures and characterization data (NMR, IR, MS, X-ray). The Supporting Information is available free of charge on the ACS Publications website. Raw NMR, IR and MS data is available at zenodo.org, DOI: 10.5281/zenodo.3764827.

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(9) (a) Ochiai, M.; Masaki, Y.; Shiro, M. Synthesis and Structure of 1-Alkynyl-1,2-Benziodoxol-3(1H)-ones. *J. Org. Chem.* **1991**, *56*, 5511. (b) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Simonsen, A. J. 1-(Organosulfonyloxy)-3(1H)-1,2-benziodoxoles: Preparation and reactions with alkynyltrimethylsilanes. *J. Org. Chem.* **1996**, *61*, 6547. (c) Zhdankin, V. Benziodoxole-Based Hypervalent Iodine Reagents in Organic Synthesis. *Curr. Org. Synth.* **2005**, *2*, 121. (d) Yoshimura, A.; Zhdankin, V. V. Advances in Synthetic Applications of Hypervalent Iodine Compounds. *Chem. Rev.* **2016**, *116*, 3328. (e) Li, Y.; Hari, D. P.; Vita, M. V.; Waser, J. Cyclic Hypervalent Iodine Reagents for Atom-Transfer Reactions: Beyond Trifluoromethylation. *Angew. Chem. Int. Ed.* **2016**, *55* , 4436. (f) Hari, D. P.; Caramenti, P.; Waser, J. Cyclic Hypervalent Iodine Reagents: Enabling Tools for Bond Disconnection via Reactivity Umpolung. *Acc. Chem. Res.* **2018**, *51*, 3212.

(10) (a) Stridfeldt, E.; Seemann, A.; Bouma, M. J.; Dey, C.; Ertan, A.; Olofsson, B. Synthesis, Characterization and Unusual Reactivity of Vinylbenziodoxolones–Novel Hypervalent Iodine Reagents. *Chem. Eur. J.* **2016**, *22*, 16066. For further applications of the reagents, see: (b) Boelke, A.; Caspers, L. D.; Nachtsheim, B. J. NH_2-Directed C–H Alkenylation of 2-Vinylanilines with Vinylbenziodoxolones. *Org. Lett.* **2017**, *19*, 5344. (c) Davies, J.; Sheikh, N. S.; Leonori, D. Photoredox Imino Functionalizations of Olefins. *Angew. Chem. Int. Ed.* **2017**, *56*, 13361; (d) Le Vaillant, F.; Garreau, M.; Nicolai, S.; Gryn'ova, G.; Corminboeuf, C.; Waser, J. Fine-Tuned Organic Photoredox Catalysts for Fragmentation-Alkynylation Cascades of Cyclic Oxime Ethers. *Chem. Sci.* **2018**, *9*, 5883.

(11) Aryl-VBX reagents were obtained in good yields using Olofsson's protocol (Ref. 10a). This method gave alkyl-VBX reagents in low yield only and a new method was developed to access this class of compounds. See Supporting Information for details.

(12) The structure of **5c** was confirmed by X-ray analysis. The data is available at the Cambridge Crystallographic Data Center (ccdc number 1897009).

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(14) *Organofluorine Chemistry*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Springer US: Boston, MA, 1994.

(15) Hansen, J. H.; Davies, H. M. L. Vinylogous Reactivity of Silver(I) Vinylcarbenoids. *Chem. Sci.* **2011**, *2*, 457.

(16) This result contrasts with the excellent e.r. obtained in the corresponding alkynylation using a very similar catalyst system. Nevertheless, this is not so surprising, considering that the geometry of the alkenyl and the alkynyl reagents, as well as in a lesser measure their reactivity, are very different, leading to different interactions with the ligands in the transition state. Obviously, another type of ligands will be needed to achieve high enantioinduction in this case.

(17) This approach was also successful for the development of the first three-component oxylalkynylation of diazo compounds (Ref. 8c).

(18) Sawama, Y.; Nagata, S.; Yabe, Y.; Morita, K.; Monguchi, Y.; Sajiki, H. Iron-Catalyzed Chemoselective Azidation of Benzylic Silyl Ethers. *Chem. Eur. J.* **2012**, *18*, 16608.

(19) This part of the work has previously appeared in a preprint: Pisella, G.; Gagnebin, A.; Waser, J. Copper-Catalyzed Insertion of Diazo Compounds into Vinyl Hypervalent Iodine Reagents to Generate Allylic Esters. *ChemRxiv*. **2019**, Preprint. https://doi.org/10.26434/chemrxiv.7892513.v1.

Copper-Catalyzed Oxyvinylation of Diazo Compounds

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Supporting Information

(159 pages)

Author contributions: G. P. performed and planned the experiments and prepared the manuscript and the experimental part, A. G. performed the experiments as a laboratory technician in formation under the supervision of G. P., J. W. supervised the project, prepared the manuscript and corrected the experimental part.

Table of Contents

1. General Methods

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. Heating was realized using heating blocks/mantles with external temperature control, unless indicated otherwise. For quantitative flash chromatography technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et_2O, CH_3CN, toluene, hexane and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 10 ppm, *Karl-Fischer* titration). The solvents were degassed by Freeze-Pump-Thaw method when mentioned. All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC aluminium plates and visualized with UV light, permanganate stain, CAN stain or Anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ^{1}H NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in $CDCl_3$, DMSO-d_6 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal methanol signal at 3.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation).^{13}C NMR spectra were recorded with ^{1}H-decoupling on a Brucker DPX-400 100 MHz spectrometer in $CDCl_3$, DMSO-d_6 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal methanol signal at 49.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm^{-1} (w = weak, m = medium, s = strong, br = broad). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API (Waters) or (APPI) LTQ Orbitrap ELITE ETD (Thermo Fisher). The raw data obtained from the Q-TOF Waters instrument does not take into account the mass of the electron for the ion, the obtained raw data has been therefore corrected by removing the mass of the electron (5 mDa). HPLC measurements were done on a Agilent 1260 Infinity autosampler using a CHIRALPAK IA, IB, IC or ID column from DAICEL Chemical. The diffraction data for crystal structures were collected at low temperature using Cu (323) or Mo (520) K_α radiation on a Rigaku SuperNova dual system in combination with Atlas type CCD detector. The data reduction and correction were carried out by *CrysAlis^{Pro}*.[1] The solutions and refinements were performed by *SHELXT*[2] and *SHELXL*[3], respectively. The crystal structures were refined using full-matrix least-squares based on F^2 with all non-H atoms defined in anisotropic manner. Hydrogen atoms were placed in calculated positions by means of the "riding" model. The blue LEDs were bought on www.conrad.ch/fr (Ruban LED avec câble à extrémités ouvertes Barthelme Y51516414 182405 24 V 502 cm bleu 1 pc(s)).

[1] *CrysAlis^{Pro}*, Rigaku Oxford Diffraction, release 1.171.40.68a, **2019**.

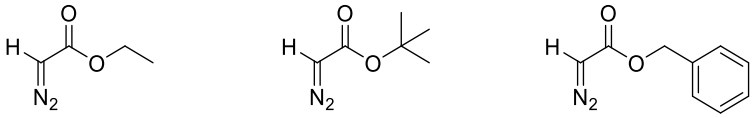
[2] *SHELXT* - Integrated space-group and crystal-structure determination¸ G. M. Sheldrick**,** *Acta Crystallogr.*, *Sect. A* **2015**, *71*, 3.

[3] *SHELXL* - Crystal structure refinement, G. M. Sheldrick**,** *Acta Crystallogr.*, *Sect. C* **2015**, *71*, 3.

2. Synthesis of diazo compounds

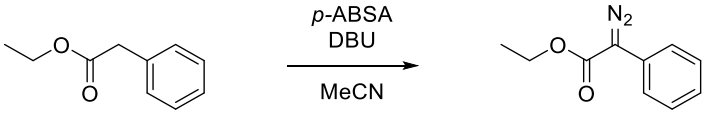
CAUTION: Diazo compounds are toxic and potentially explosive and should be handled with care in a well-ventilated hood.[4]

Ethyl 2-diazoacetate (**2a**), *tert*-butyl 2-diazoacetate (**2c**) and benzyl 2-diazoacetate (**2e**) were directly purchased from Sigma Aldrich.



2a **2c** **2e**

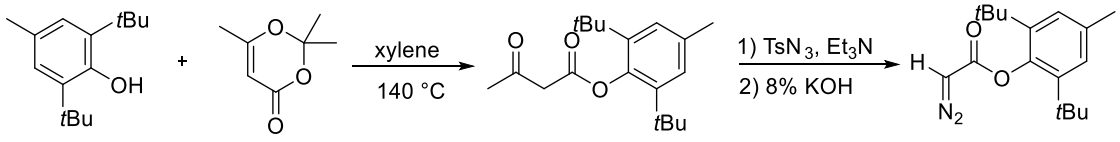
Ethyl 2-diazo-2-phenylacetate (4b)



16 **2b**

Following a reported procedure,[5] DBU (1.50 mL, 10.0 mmol, 2.00 equiv) was added slowly to a stirred solution of ethyl 2-phenylacetate (**16**) (0.80 mL, 5.0 mmol, 1.00 equiv) and *p*-ABSA (1.80 g, 7.50 mmol, 1.50 equiv) in dry MeCN (20 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 14 h, the reaction mixture was quenched with water (15 mL), and extracted with diethyl ether (3 x 15 mL). The organic layers were combined and washed with 10% NH_4Cl (20 mL), brine (20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 3:97 as mobile phase affording the corresponding ethyl 2-diazo-2-phenylacetate (**2b**) as a red oil (0.80 g, 4.2 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 - 7.45 (m, 2H, Ar*H*), 7.43 - 7.35 (m, 2H, Ar*H*), 7.22 - 7.14 (m, 1H, Ar*H*), 4.34 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 1.35 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.2, 128.8, 125.6, 125.6, 124.0, 61.1, 14.6. The values of the NMR spectra are in accordance with reported literature data.[6] One carbon was not resolved at 101 MHz.

2,6-Di-*tert*-butyl-4-methylphenyl 2-diazoacetate (2d)



16 **17** **18** **2d**

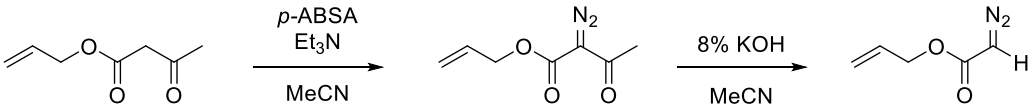
Following a reported procedure,[7] a mixture of 2,6-di-*tert*-butyl-4-methylphenol (**16**) (5.51 g, 25.0 mmol, 1.00 equiv), 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**17**) (3.32 mL, 25.0 mmol, 1.00 equiv), and xylene (5 mL) was stirred at 140 °C for 1.5 h. After cooling to room temperature, the reaction mixture was directly loaded on silica and was purified by column chromatography using EtOAc:pentane 2:98 as mobile phase to afford 2,6-di-*tert*-butyl-4-methylphenyl 3-oxobutanoate (**18**) as a white solid (5.77 g,

[4] S. P. Green, K. M. Wheelhouse, A. D. Payne, J. P. Hallett, P. W. Miller and J. A. Bull, *Org. Process Res. Dev.* **2020**, *24*, 67.
[5] O. A. Davis, R. A. Croft and J. A. Bull, *Chem. Commun.,* **2015**, *51*, 15446.
[6] H. Keipour and T. Ollevier, *Org. Lett.*, **2017**, *19*, 5736.
[7] P. Müller and P. Polleux, *Helv. Chim. Acta* **1994**, *77*, 645.

19.0 mmol, 76%). colorless thick oil (5.00 g, 19.1 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.08 (s, 0.22H, O*H* of enol form), 7.31 - 7.24 (m, 1H, Ar*H* of enol and keto form), 7.24 - 7.18 (m, 2H, Ar*H* of enol and keto form), 5.38 (s, 0.2H, vinyl *H* of enol form), 3.81 (s, 1.56H, CH_3COCH_2 of keto form), 3.03 (m, 2H, 2 x C*H*$(CH_3)_2$ of enol and keto form), 2.41 (s, 2.32H, CH_3COCH_2 of keto form), 2.08 (s, 0.6H, CH_3 of enol form), 1.28 - 1.21 (m, 12H, 2 x CH(CH_3)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$), Enol form: δ 177.7, 171.5, 144.5, 140.5, 126.5, 123.9, 88.7, 23.7, 22.7, 21.4; ^{13}C NMR (101 MHz, $CDCl_3$), Keto form: δ 199.9, 165.7, 145.1, 140.2, 126.8, 124.0, 49.6, 30.4, 27.4, 27.3. The values of the NMR spectra are in accordance with reported literature data.[8]

Following a reported procedure,[7] to a solution of 2,6-di-*tert*-butyl-4-methylphenyl 3-oxobutanoate (**18**) (5.48 g, 18.00 mmol, 1.00 equiv) in MeCN (22 mL) was added triethylamine (3.26 mL, 23.40 mmol, 1.30 equiv). The reaction mixture was cooled in an ice bath and a solution of tosyl azide (3.9 g, 19.8 mmol, 1.1 equiv) in MeCN (22 mL) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. 8% aqueous KOH solution (90 mL) was added and stirred vigorously for 4 h. The reaction mixture was diluted with water (50 mL), extracted with diethyl ether (3 x 100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography using Et_2O:pentane 2:98 as mobile phase to afford 2,6-di-*tert*-butyl-4-methylphenyl 2-diazoacetate (**2d**) as a yellow solid (4.80 g, 16.64 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (s, 2H, Ar*H*), 5.00 (s, 1H, C*H*N_2), 2.32 (s, 3H, ArCH_3), 1.36 (s, 18H, 2 x *t*Bu); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 145.1, 142.4, 134.8, 127.0, 47.3, 35.3, 31.5, 21.5. The values of the NMR spectra are in accordance with reported literature data.[9]

Allyl 2-diazoacetate (2f)



19 **20** **2f**

Following a reported procedure,[10] to a solution of allyl acetoacetate (**19**) (1.10 mL, 8.00 mmol, 1.00 equiv) and 4-acetamidobenzenesulfonyl azide (2.11 g, 8.80 mmol, 1.10 equiv) in MeCN (40 mL) at 0 °C was added dropwise Et_3N (2.23 mL, 16.0 mmol, 2.00 equiv). The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed under reduced pressure. The residue was suspended in diethyl ether (50 mL) and the solid removed by filtration. The solvent was removed under reduced pressure. . The crude product was purified by column chromatography using EtOAc:pentane 15:85 as mobile phase to afford) allyl 2-diazo-3-oxobutanoate (**20**) as a yellow oil (1.23 g, 7.34 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H, C*H*CH_2), 5.40 - 5.26 (m, 2H, CHCH_2), 4.73 (dt, *J* = 5.8, 1.3 Hz, 2H, CH_2O), 2.48 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.2, 161.2, 131.6, 119.3, 66.0, 28.4. One carbon was not resolved at 101 MHz. The values of the NMR spectra are in accordance with reported literature data.[10]

To a solution of allyl 2-diazo-3-oxobutanoate (**20**) (0.840 g, 5.00 mmol, 1.00 equiv) in MeCN (15 mL) was added 8% aqueous KOH solution (25 mL) and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with water (15 mL), extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 10:90 as

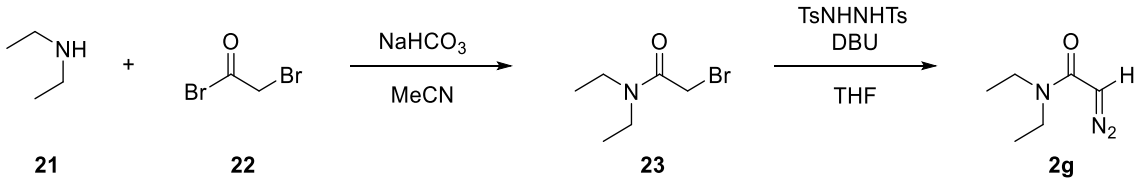
[8] D. P. Hari and J. Waser, *J. Am. Chem. Soc.*, 2017, **139**, 8420.

[9] M. P. Doyle, V. Bagheri, T. J. Wandless, N. K. Harn, D. A. Brinker, C. T. Eagle and K. L. Loh, *J. Am. Chem. Soc.* **1990**, *112*, 1906.

[10] P. Müller, Y. F. Allenbach and S. Grass, *Tetrahedron: Asymmetry*, 2005, **16**, 2007.

mobile phase to afford allyl 2-diazoacetate (**2f**) as a yellow oil (154 mg, 1.22 mmol, 24%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H, C*H*CH_2), 5.38 - 5.20 (m, 2H, CHC*H*$_2$), 4.77 (s, 1H, C*H*N_2), 4.65 (dt, *J* = 5.7, 1.5 Hz, 2H, C*H*$_2$O); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 132.4, 118.5, 65.2, 46.4. The values of the NMR spectra are in accordance with reported literature data.[11]

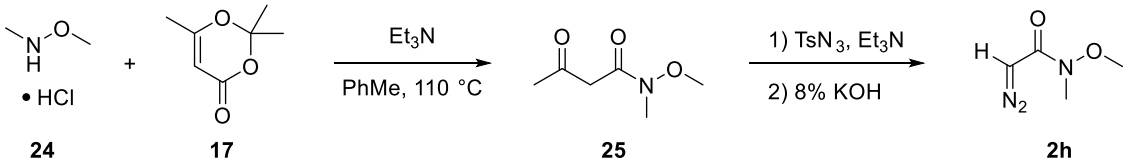
2-Diazo-*N*,*N*-diethylacetamide (2g)



21 **22** **23** **2g**

Following a reported procedure,[12] diethyl amine (**21**) (0.73 g, 10 mmol, 1.0 equiv) and $NaHCO_3$ (2.52 g, 30.0 mmol, 3.00 equiv) were dissolved in dry CH_2Cl_2 (20 mL) and bromoacetyl bromide (**22**) (1.75 mL, 20.0 mmol, 2.00 equiv) was added slowly at 0 °C and the reaction was stirred for 6 h at room temperature, quenched with 100 mL of H_2O and the solution was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with water (100 mL) and dried over $MgSO_4$, the solvent was evaporated and the residue was used in the next step without purification. The resulting 2-bromo-*N,N*-diethylacetamide (**23**) and *N,N'*-ditosylhydrazine (2.10 g, 6.08 mmol, 0.60 equiv) were dissolved in dry THF (20 mL) and cooled down to 0 ˚C, then DBU (2.30 mL, 15.2 mmol, 1.52 equiv) was added dropwise and stirred at room temperature for 1 h and then quenched with saturated solution of $NaHCO_3$ (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and purified by column chromatography using EtOAc:pentane 30:70 as mobile phase affording the corresponding 2-diazo-*N,N'*-diethylacetamide (**2g**) as a yellow oil (0.725 g, 5.14 mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.92 (s, 1H, C*H*N_2), 3.26 (br s, 4H, 2 x C*H*$_2$$CH_3$), 1.14 (t, *J* = 7.2 Hz, 6H, 2 x CH_2C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): 165.8, 46.4, 41.4, 13.9. The values of the NMR spectra are in accordance with reported literature data.[13]

2-Diazo-*N*-methoxy-*N*-methylacetamide (2h)



24 **17** **25** **2h**

Following a reported procedure,[14] a mixture of *N*,*O*-dimethylhydroxylamine hydrochloride (**24**) (2.44 g, 25.0 mmol, 1.00 equiv), 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**17**) (5.00 mL, 37.5 mmol, 1.50 equiv) and triethylamine (3.85 mL, 27.5 mmol, 1.10 equiv) was dissolved in toluene (75 mL) and refluxed for 2 h. The reaction mixture was cooled to room temperature and washed with aqueous hydrochloric acid (90 mL, 1.0 M) and the aqueous layer was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase to afford *N*-methoxy-*N*-methyl-3-oxobutanamide (**25**) as a yellow oil (2.40 g, 16.5 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.65 (s, 0.13H, O*H* of enol form), 5.32 (s, 0.13H, vinyl *H* of enol form) 3.60 (s, 3H, OC*H*$_3$), 3.50 (s, 1.74H, CH_3COC*H*$_2$ of keto form), 3.13 (s, 2.6H, *N*-C*H*$_3$ of keto form), 3.11 (s, 0.4H, enol

[11] M. Bolsønes, H. T. Bonge-Hansen and T. Bonge-Hansen, *Synlett*, 2014, **25**, 221.

[12] S. Chanthamath, S. Thongjareun, K. Shibatomi and S. Iwasa, *Tetrahedron Lett.* **2012**, *53*, 4862.

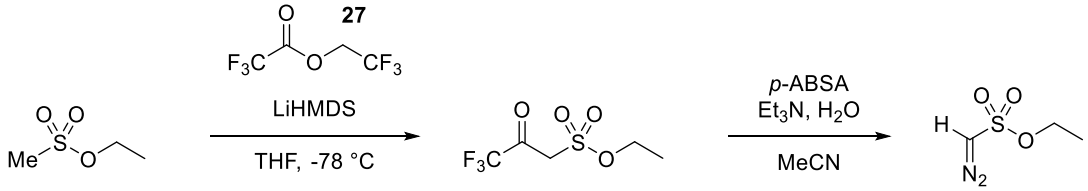
[13] D. Gauthier, R. H. Dodd and P. Dauban, *Tetrahedron* **2009**, *65*, 8542.

[14] S. Müller, F. Sasse and M. E. Maier, *Eur. J. Org. Chem.* **2014**, 1025.

form of *N*-C*H*$_3$), 2.17 (s, 2.6H, C*H*$_3$COCH$_2$ of keto form), 1.89 (s, 0.4H, enol form of C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.7, 167.8, 61.1, 48.3, 31.8, 30.0; Enol form, ^{13}C NMR (101 MHz, $CDCl_3$): δ 175.0, 172.2, 86.5, 21.6. Two carbons were not resolved at 101 MHz. The characterization data corresponded to the reported values.[14]

Following a reported procedure,[7] to a solution of *N*-methoxy-*N*-methyl-3-oxobutanamide (**25**) (0.73 g, 5.0 mmol, 1.0 equiv) in MeCN (6 mL) was added triethylamine (660 mg, 6.50 mmol, 1.30 equiv). The reaction mixture was cooled in an ice bath and a solution of tosyl azide (1.1 g, 5.5 mmol, 1.1 equiv) in MeCN (6 mL) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. 8% aqueous KOH solution (25 mL) was added and stirred vigorously for 4 h. The reaction mixture was diluted with water (15 mL), extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase to afford 2-diazo-*N*-methoxy-*N*-methylacetamide (**2h**) as a yellow oil (350 mg, 2.71 mmol, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.30 (s, 1H, C*H*N_2), 3.60 (s, 3H, OC*H*$_3$), 3.12 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 61.3, 46.1, 33.0. The values of the NMR spectra are in accordance with reported literature data.[15]

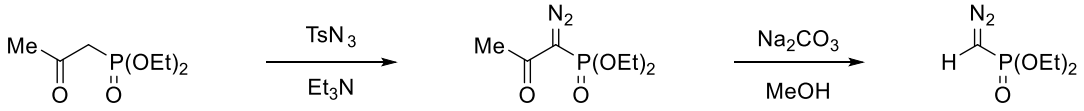
Ethyl diazomethanesulfonate (2i)



Following a reported procedure,[16] to a solution of ethyl methanesulfonate (**26**) (1.86 g, 15.0 mmol, 1.00 equiv) in dry THF (50 mL) was added a 1 M LiHMDS solution in hexane (18 mL, 18 mmol, 1.2 equiv) at -78 °C. After stirring the reaction mixture for 30 min at this temperature, 2,2,2-trifluoroethyl trifluoroacetate (**27**) (2.4 mL, 18 mmol, 1.2 equiv) was added rapidly in one portion *via* syringe. After 10 min, the reaction mixture was poured into a solution of diethyl ether (20 mL) and 5% HCl (50 mL). The mixture was extracted with diethyl ether (3 x 50 mL), washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a yellow oil. The resulting ethyl 3,3,3-trifluoro-2-oxopropane-1-sulfonate (**28**) was immediately dissolved in dry MeCN (30 mL). To this solution was added *p*-ABSA (4.32 g, 18.0 mmol, 1.20 equiv), Et_3N (2.5 mL, 18 mmol, 1.2 equiv), and water (0.27 mL, 15 mmol, 1.0 equiv). After stirring the reaction mixture overnight at room temperature, the solvent was removed under reduced pressure and the residue was filtered on short plug of silica gel and washed with a mixture of ethyl acetate (100 mL) and hexane (100 mL). The filtrate was concentrated under vacuum and the residue was purified by column chromatography using EtOAc:pentane 10:90 as mobile phase affording the corresponding ethyl diazomethanesulfonate (**2i**) as a yellow oil (0.9 g, 6 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25 (s, 1H, C*H*N_2), 4.26 (q, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_3$), 1.41 (t, *J* = 7.1 Hz, 3H, CH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 67.4, 52.4, 14.6. The values of the NMR spectra are in accordance with reported literature data.[16]

[15] H. Mao, A. Lin, Y. Shi, Z. Mao, X. Zhu, W. Li, H. Hu, Y. Cheng and C. Zhu, *Angew. Chem., Int. Ed.* **2013**, *52*, 6288.
[16] Ye T., Zhou C., *New J. Chem.* **2005**, *29*, 1159.

Diethyl (diazomethyl)phosphonate (2j)

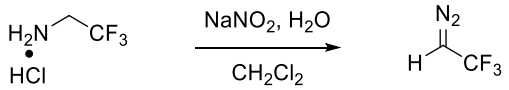


29 **30** **2j**

Following a reported procedure,[17] a mixture of diethyl (2-oxopropyl)phosphonate (**29**) (1.15 mL, 6.00 mmol, 1.00 equiv), tosyl azide (1.3 g, 6.6 mmol, 1.10 equiv) and triethylamine (6 mL) was stirred at room temperature for 18 h. After evaporation of the triethylamine under reduced pressure, the residue was dissolved in diethyl ether (50 mL). The precipitate was filtered off, the filtrate was evaporated and the residue was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase affording the corresponding diethyl (1-diazo-2- oxopropyl)phosphonate (**30**) as a yellow oil (0.810 g, 3.68 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 - 4.19 (m, 4H, 2 x C*H*$_2$CH$_3$) 2.19 (s, 3H, C*H*$_3$), 1.30 (t, *J* = 7.0 Hz, 6H, 2 x CH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.1 (d, *J* = 13.2 Hz), 63.4 (d, *J* = 5.6 Hz), 27.1, 16.0 (d, *J* = 6.8 Hz). The values of the NMR spectra are in accordance with reported literature data.[14]

Following a reported procedure,[8] to a solution of diethyl (1-diazo-2-oxopropyl)phosphonate (**30**) (694 mg, 3.15 mmol, 1.00 equiv) in MeOH (9.0 mL) was added Na_2CO_3 (401 mg, 3.78 mmol, 1.20 equiv). The mixture was stirred at room temperature for 15 min. The precipitate was filtered off, the filtrate was evaporated and the residue was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase affording the corresponding diethyl (diazomethyl)phosphonate (**2j**) as a yellow oil (533 mg, 2.99 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 - 4.08 (m, 4H, 2 x C*H*$_2$CH$_3$), 3.75 (d, *J* = 11.1 Hz, 1H, C*H*N$_2$), 1.34 (td, *J* = 7.1, 0.7 Hz, 6H, 2 x CH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 62.6 (d, *J* = 5.3 Hz), 16.1 (d, *J* = 6.9 Hz). The values of the NMR spectra are in accordance with reported literature data.[14] One carbon was not resolved at 101 MHz.

2,2,2-Trifluorodiazoethane (2k)



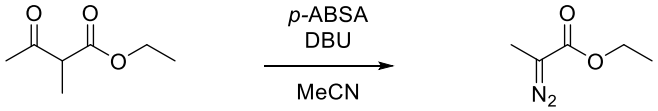
31 **2k**

Following a reported procedure,[18] under argon, 2,2,2-trifluoroethanamine hydrochloride (**31**) (0.678 g, 5.00 mmol, 1.00 equiv) and sodium nitrite (0.379 g, 5.50 mmol, 1.10 equiv) were dissolved in degassed CH_2Cl_2 (10 mL). Degassed water (1.00 mL, 55.5 mmol, 11.1 equiv) was added slowly at 0 °C. The solution was stirred for 2 h at 0 °C and 1 h at room temperature. The aqueous layer was frozen in the freezer overnight (-18 °C) and the organic layer was dried over a plug of potassium carbonate, transferred into a vial, sealed and stored at - 18 °C. The concentration of the obtained solution was determined to be 0.37 M by ^{19}F NMR analysis (according to an internal reference, $PhCF_3$). ^{19}F NMR (377 MHz, CH_2Cl_2) δ -55.56. The values of the NMR spectra are in accordance with reported literature data.[18]

[17] S. Chanthamath, S. Ozaki, K. Shibatomi and S. Iwasa, *Org. Lett.* **2014**, *16*, 3012.

[18] S. Hyde, J. Veliks, B. Liégault, D. Grassi, M. Taillefer and V. Gouverneur, *Angew. Chem. Int. Ed.,* 2016, **55**, 3785.

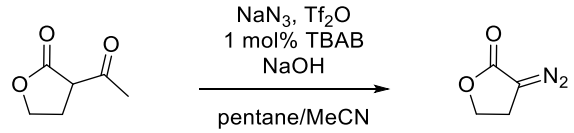
Ethyl 2-diazopropanoate (2l)



32 **2l**

Following a reported procedure,[19] DBU (1.8 mL, 12 mmol, 3.0 equiv) was added slowly to a stirred solution of ethyl 2-methylacetoacetate (**32**) (0.60 mL, 4.0 mmol, 1.0 equiv) and *p*-ABSA (1.4 g, 6.0 mmol, 1.5 equiv) in MeCN (80 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 12 h, the reaction mixture was quenched with 1 M HCl (8 mL), and extracted with hexane (3 x 40 mL). The organic layers were combined, washed with a saturated solution of $NaHCO_3$ (40 mL), brine (40 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using Et_2O:pentane 2:98 as mobile phase affording the corresponding ethyl 2-diazopropanoate (**2l**) as a yellow oil (241 mg, 1.88 mmol, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.20 (q, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_3$), 1.94 (s, 3H, N_2CC*H*$_3$), 1.25 (t, *J* = 7.1 Hz, 3H, CH_2C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9, 60.7, 14.5, 8.4. The values of the NMR spectra are in accordance with reported literature data.[20] One carbon was not resolved at 101 MHz.

3-Diazodihydrofuran-2(3*H*)-one (2m)

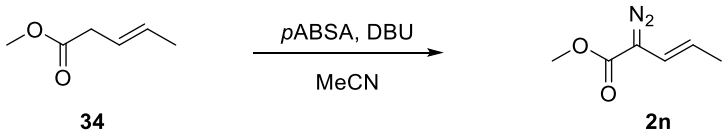


33 **2m**

Following a reported procedure,[21] sodium azide (2.42 g, 37.2 mmol, 4.00 equiv), sodium hydroxide (78 mL, 2 M in water), tetrabutylammonium bromide (30.0 mg, 0.09 mmol, 0.01 equiv) and pentane (40 mL) were mixed in a 250 mL round-bottom flask with magnetic stir bar open to the air and allowed to cool to 0 °C. With vigorous stirring, Tf_2O (3.10 mL, 18.6 mmol, 2.00 equiv) was added dropwise. After 10 min, a solution of 2-acetyl-butyrolactone (**33**) (1.00 mL, 9.30 mmol, 1.00 equiv) in MeCN (35 mL) was poured into the round-bottom flask through a funnel, followed by an additional MeCN (10 mL) to complete the transfer. The initially colorless reaction mixture immediately turned yellow. After allowing to stir for 30 min at 0 °C, the mixture was diluted with ice water (25 mL) and chilled EtOAc (25 mL) and transferred to a separatory funnel. After phase separation and removal of the organic layer, the aqueous layer was washed with cold EtOAc (2 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase affording the corresponding 3-diazodihydrofuran-2(3*H*)-one (**2m**) as a bright yellow crystalline solid (0.32 g, 2.8 mmol, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.38 (t, *J* = 8.0 Hz, 2H, C*H*$_2$), 3.36 (t, *J* = 8.0 Hz, 2H, C*H*$_2$); ^{13}C NMR (101 MHz, $CDCl_3$): 170.6, 65.3, 49.4, 23.1. The values of the NMR spectra are in accordance with reported literature data.[21]

[19] T. Hashimoto, Y. Naganawa and K. Maruoka, *J. Am. Chem. Soc.* **2011**, *133*, 8834.
[20] L. Huang and W. D. Wulff *J. Am. Chem. Soc.* **2011**, *133*, 8892.
[21] E. S. Sattely, S. J. Meek, S. J. Malcolmson, R. R. Schrock and A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, *131*, 943.

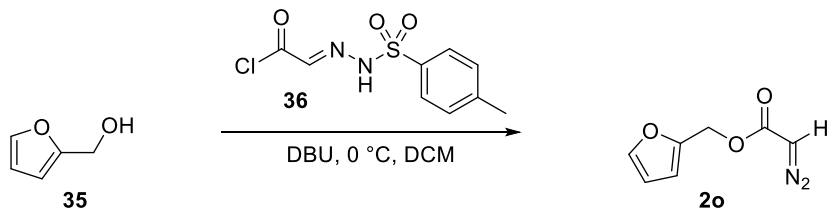
Methyl (*E*)-2-diazopent-3-enoate (2n)



34 **2n**

Following a reported procedure,[22] to a stirring solution of methyl trans-pent-3-enoate (**34**) (1.00 g, 8.76 mmol, 1.00 equiv) and *p*-ABSA (3.16 g, 13.1 mmol, 1.50 equiv) in dry MeCN (20 mL) at 0 °C, was added DBU (2.65 mL, 17.5 mmol, 2.00 equiv) slowly in 5 min. The reaction mixture was stirred at 0 °C for 1 h and then 12 h at room temperature. The reaction mixture was quenched with NH_4Cl (saturated solution, 20 mL). The aqueous layer was extracted with Et_2O (3 x 40 mL) and the combined organic layers were washed with brine (40 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using pentane as mobile phase affording the corresponding methyl (*E*)-2-diazopent-3-enoate (**2n**) as an orange oil (950 mg, 6.78 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 (dd, *J* = 15.8, 1.7 Hz, 1H, CH_3CHCH), 5.38 - 5.29 (m, 1H, CH_3CHCH), 3.79 (s, 3H, OCH_3), 1.84 (dd, *J* = 6.7, 1.7 Hz, 3H, CH_3CHCH); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 120.4, 112.6, 52.0, 18.2. The values of the NMR spectra are in accordance with reported literature data.[22] One carbon was not resolved at 101 MHz.

Furan-2-ylmethyl 2-diazoacetate (2o)

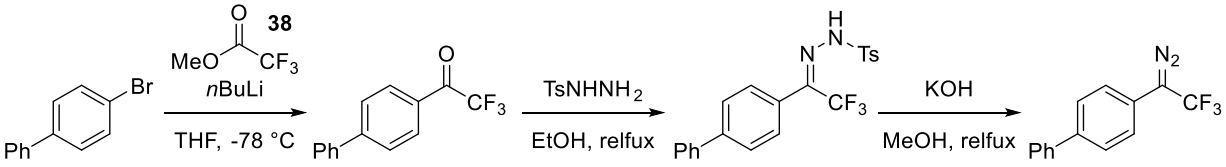


35 **2o**

Following a reported procedure,[23] to a solution of *p*-toluenesulfonylhydrazone of glyoxylic acid chloride (**36**) (1.30 g, 5.00 mmol, 1.00 equiv.) in CH_2Cl_2 (10 mL) were added furfuryl alcohol (**35**) (475 µL, 5.50 mmol, 1.10 equiv.) and then DBU (1.89 mL, 12.5 mmol, 2.50 equiv.) dropwise at 0 °C. After stirring for 2 h at the same temperature, the reaction was stirred 30 min at room temperature and then poured into saturated NH_4Cl solution (10 mL). The organic layer was then extracted with CH_2Cl_2 (3 x 10 mL), washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc/pentane 3:97 as eluent to afford furan-2-ylmethyl 2-diazoacetate (**2o**) as a yellow oil (534 mg, 3.21 mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 1.9, 0.9 Hz, 1H, Ar*H*), 6.42 (dd, *J* = 3.3, 0.8 Hz, 1H, Ar*H*), 6.36 (dd, *J* = 3.3, 1.8 Hz, 1H, Ar*H*), 5.14 (s, 2H, CH_2O), 4.78 (br s, 1H, CN_2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 149.5, 143.5, 111.0, 110.7, 58.3, 46.5. The values of the NMR spectra are in accordance with reported literature data.[24]

[22] H. M. L. Davies and A. M. Walji, *Angew. Chem., Int. Ed.* **2005**, *44*, 1733.
[23] T. Hashimoto, N. Uchiyama and K. Maruoka, *J. Am. Chem. Soc.* **2008**, *130*, 14380.
[24] S. Bew, P.-A. Ashford and D. Bachera, *Synthesis* **2013**, *45*, 903.

4-(1-Diazo-2,2,2-trifluoroethyl)-1,1'-biphenyl (2p)



Following a reported synthesis,[25] a solution of 4-bromo-biphenyl (**37**) (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 (**38**) (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 $MgSO_4$, 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 (**39**) as a slight 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 -71.3. The values of the NMR spectra are in accordance with reported literature data.[26]

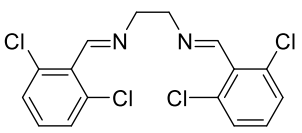
Following a reported procedure,[26] 1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethanone (**39**) (3.36 g, 13.5 mmol, 1.05 equiv.) was added to EtOH (9 mL) at room temperature followed by *p*-toluenesulfonylhydrazide (2.40 g, 12.9 mmol, 1.00 equiv.) in one portion. A condenser was then attached and the contents 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,[26] *N*'-(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (**40**) was disolved 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 $MgSO_4$, 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 (**2p**) as a red solid (1.42 g, 5.44 mmol, 50%). The compound was kept at -18 °C. R_f = 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 -57.3. One carbon was not resolved at 101 MHz. The values of the NMR spectra are in accordance with reported literature data.[26]

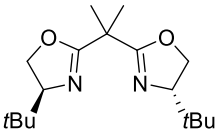
[25] A. S. Golubev, A. F. Shidlovskii, A. S. Peregudov and N. D. Kagramanov, *Russ Chem Bull.* **2014**, *63*, 2264.
[26] E. Emer, J. Twilton, M. Tredwell, S. Calderwood, T. L. Collier, B. Liégault, M. Taillefer and V. Gouverneur, *Org. Lett.* **2014**, *16*, 6004.

3. Synthesis of ligands

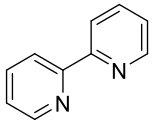
Ligand **3a** was synthesized using a simple reported procedure.[27] **3b** was purchased directly from TCI. **3f** was purchased directly from Sigma-Aldrich.



3a

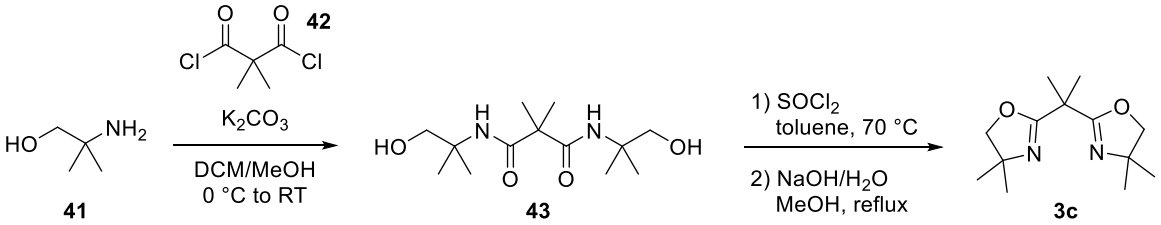


3b



3f

2,2'-(propane-2,2-diyl)bis(4,4-dimethyl-4,5-dihydrooxazole) (3c)

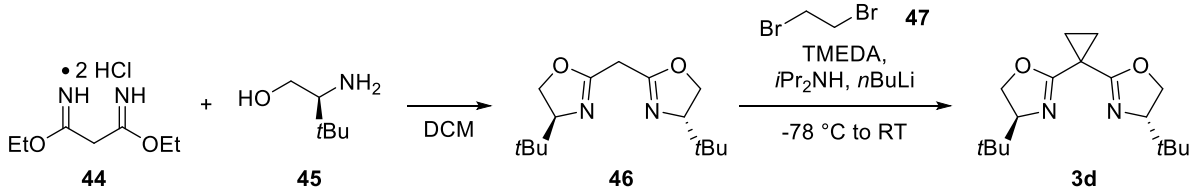


Following a reported procedure,[28] 2-amino-2-methylpropan-1-ol (**41**) (0.952 mL, 10.5 mmol, 2.1 equiv) was added to a suspension of K_2CO_3 (2.76 g, 20.0 mmol, 4.0 equiv) DCM (50 mL) at 0 °C under argon. A solution of dimethylmalonyl dichloride (**42**) (0.660 mL, 5.00 mmol, 1.0 equiv) in DCM (10 mL) was added dropwise to the cold mixture. The mixture was allowed to warm to room temperature and stirred for 16 h. MeOH (50 mL) was added and the mixture was stirred for 2 h. The whole reaction mixture was filtered through Celite (5 g) and rinsed twice with MeOH (2 × 10 mL). The solvent was removed under reduce pressure. The crude *N*1,*N*3-bis(1-hydroxy-2-methylpropan-2-yl)-2,2-dimethylmalonamide (**43**) was obtained as a white residue (1.42 g) and was used directly into the next step without further purification.

The crude bisamide (**43**) was dissolved in toluene (30 mL) and heated to 70 °C under argon. Thionyl chloride (1.50 mL, 20.0 mmol, 4.0 equiv) was added in one portion and the resulting mixture was stirred at 70 °C for 5 h. The reaction was cooled to 0 °C and quenched with a saturated $NaHCO_3$ solution (15 mL). The mixture was extracted with DCM (5 × 30 mL) and the combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to furnish a pale yellow oil. The residue was dissolved in 17.0 mL of a 5% methanolic NaOH solution (0.830 g of NaOH was completely dissolved in 0.850 mL H_2O and then diluted with 16.1 mL MeOH) and heated to reflux for 2 h under argon. The solvent was removed under reduced pressure and the resulting residue was partitioned between DCM (10 mL) and H_2O (10 mL). The aqueous layer was extracted with DCM (5 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to furnish afford 2,2'-(propane-2,2-diyl)bis(4,4-dimethyl-4,5-dihydrooxazole) (**3c**) as a pale yellow wax (471 mg, 2.00 mmol, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 4H, 2 x CH_2O), 1.49 (s, 6H, 2 x CH_3), 1.27 (s, 12H, 4 x CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 79.4, 67.0, 38.2, 28.0, 25.4. The values of the NMR spectra are in accordance with reported literature data.[29]

[27] H. Liu, H.-L. Zhang, S.-J. Wang, A.-Q. Mi, Y.-Z. Jiang and L.-Z. Gong, *Tetrahedron-Asymmetry*, **2005**, *16*, 2901.
[28] M. C. Paderes and S. R. Chemler, *Eur. J. Org. Chem.,* **2011**, *2011*, 3679.
[29] K. M. Partridge, I. A. Guzei and T. P. Yoon, *Angew. Chem. Int. Ed.*, **2010**, *49*, 930.

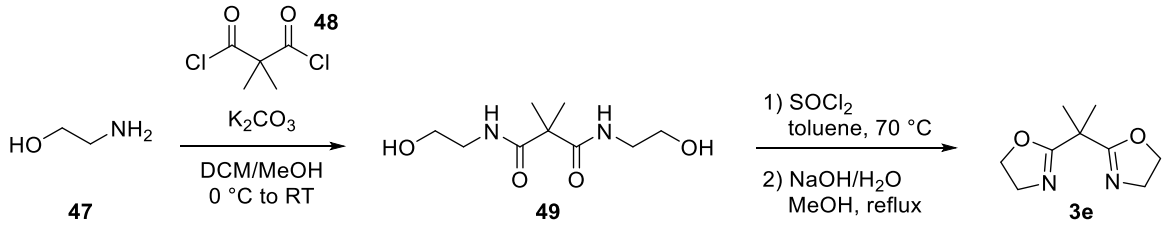
(4*S*,4'*S*)-2,2'-(Cyclopropane-1,1-diyl)bis(4-(tert-butyl)-4,5-dihydrooxazole) (3d)



Following a reported procedure,[30] to a solution of (*S*)-*tert*-leucinol (**45**) (0.94 g, 8.0 mmol, 2.0 equiv) in DCM (40 mL) was added diethyl malonimidate dihydrochloride (**44**) (0.93 g, 4.0 mmol, 1.0 equiv). The resulting cloudy solution was stirred at room temperature for 36 h. The reaction mixture was diluted with water (8 mL) and extracted with DCM (3 x 20 mL). The combined organic layers were washed with brine (40 mL), dried over $MgSO_4$, and concentrated. The resulting oily residue was distilled bulb-to-bulb (Kugelrohr distillation, 150 °C at 0.2 mbar) to afford bis((*S*)-4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)methane (**46**) as a white solid (0.600 g, 2.84 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (dd, *J* = 10.1, 8.7 Hz, 2H, 2 x OC*H*$_a$), 4.02 (dd, *J* = 8.7, 7.7 Hz, 2H, 2 x C(CH$_3$)$_3$C*H*), 3.81 (ddt, *J* = 10.1, 7.8, 1.1 Hz, 2H, 2 x OC*H*$_b$), 3.27 (t, *J* = 1.2 Hz, 2H, O(C=N)C*H*$_2$), 0.82 (s, 18H, 2 x C(C*H*$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 76.0, 69.1, 34.0, 28.4, 26.0. The values of the NMR spectra are in accordance with reported literature data.[30]

Following a reported procedure,[30] to a solution of bis((*S*)-4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)methane (**46**) (75 mg, 0.28 mmol, 1.0 equiv) in THF (5 mL) in a 20 mL microwave vial, was added TMEDA (85 µL, 0.56 mmol, 2.0 equiv) and *i*-Pr$_2$NH (40 mL, 0.28 mmol, 1.0 equiv). The solution was cooled to -78 °C and *n*-BuLi (0.38 mL, 1.5 M in hexane, 0.56 mmol, 2.0 equiv) was added. The reaction mixture was warmed to -20 °C and stirred at that temperature for 30 minutes. The solution was cooled back to -78 °C and 1,2-dibromoethane (**47**) (25 µL, 0.28 mmol, 2.0 equiv) was added. After the addition, the cold bath was removed and the reaction mixture was allowed to stir at room temperature for an additional 16 h. The reaction mixture was quenched by the addition of sat. aq. NH_4Cl (2.5 mL) and diluted with water (2 mL) to dissolve the resulting salts. The mixture was extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated. The resulting oily residue was purified by column chromatography using EtOAc/pentane 1:2 to 1:1 as mobile phase to afford (4*S*,4'*S*)-2,2'-(cyclopropane-1,1-diyl)bis(4-(*tert*-butyl)-4,5-dihydrooxazole) (**3d**) as a white solid (42 mg, 0.14 mmol, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.18 (dd, *J* = 10.0, 8.6 Hz, 2H, 2 x OC*H*$_a$), 4.10 (dd, *J* = 8.7, 7.3 Hz, 2H, 2 x C(CH$_3$)$_3$C*H*), 3.82 (dd, *J* = 10.0, 7.2 Hz, 2H, 2 x OC*H*$_b$), 1.52 - 1.47 (m, 2H, 2 x C*H*$_a$ of CyP), 1.30 - 1.24 (m, 2H, 2 x C*H*$_b$ of CyP), 0.86 (s, 18H, 2 x C(C*H*$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 75.2, 69.1, 33.8, 25.7, 18.2, 15.1. The values of the NMR spectra are in accordance with reported literature data.[30]

2,2'-(Propane-2,2-diyl)bis(4,5-dihydrooxazole) (3e)



Following a reported procedure,[31] K_2CO_3 (2.76 g, 20.0 mmol, 4.0 equiv) was suspended in DCM (50 mL) at 0 °C under argon and then ethanolamine (**47**) (0.63 mL, 10.5 mmol, 2.1 equiv) was added. A solution

[30] S. E. Denmark and C. M. Stiff, *J. Org. Chem.*, **2000**, *65*, 5875.

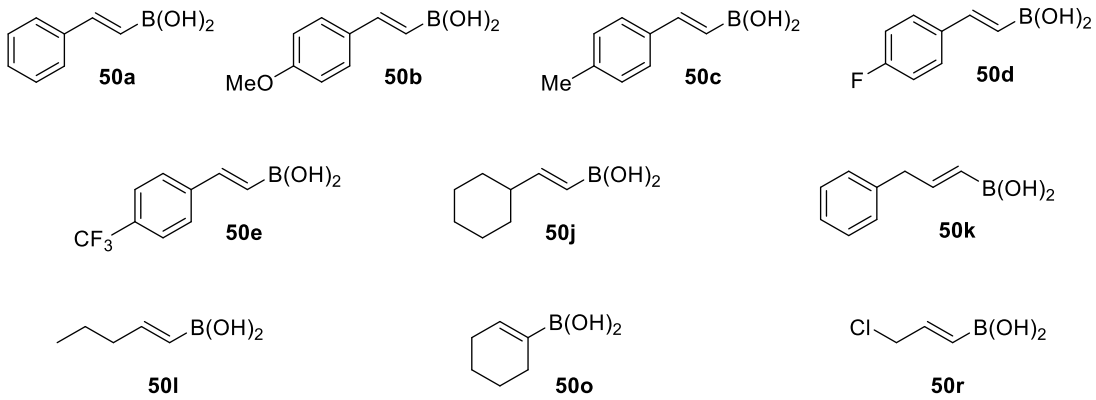
[31] L. Miao, I. Haque, M. R. Manzoni, W. S. Tham and S. R. Chemler, *Org. Lett.*, **2010**, *12*, 4739.

of dimethylmalonyl dichloride (**48**) (0.660 mL, 5.00 mmol, 1.0 equiv) in DCM (10 mL) was added dropwise to the cold mixture. The mixture was allowed to warm to room temperature and stirred for 16 h. MeOH (50 mL) was added and the mixture was stirred for 2 h. The whole reaction mixture was filtered through Celite (5 g) and rinsed twice with MeOH (2 × 10 mL). The solvent was removed under reduce pressure. The crude N^1,N^3-bis(2-hydroxyethyl)-2,2-dimethylmalonamide (**49**) was obtained as a white residue (1.12 g) and was used directly into the next step without further purification.

The crude bisamide (**49**) was dissolved in toluene (30 mL) and heated to 70 °C under argon. Thionyl chloride (1.46 mL, 20.0 mmol, 4.0 equiv) was added in one portion and the resulting mixture was stirred at 70 °C for 5 h. The reaction was cooled to 0 °C and quenched with a saturated $NaHCO_3$ solution (15 mL). The mixture was extracted with DCM (5 × 30 mL) and the combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to furnish a pale yellow oil. The residue was dissolved in 17.0 mL of a 5% methanolic NaOH solution (0.830 g of NaOH was completely dissolved in 0.850 mL H_2O and then diluted with 16.1 mL MeOH) and heated to reflux for 2 h under argon. The solvent was removed under reduced pressure and the resulting residue was partitioned between DCM (10 mL) and H_2O (10 mL). The aqueous phase was extracted with DCM (5 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to furnish afford 2,2'-(propane-2,2-diyl)bis(4,5-dihydrooxazole) (**3e**) as a pale yellow wax (412 mg, 2.26 mmol, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ δ 4.28 (t, *J* = 9.5 Hz, 4H, 2 x CH_2O), 3.87 (t, *J* = 9.5 Hz, 4H, 2 x CH_2N), 1.51 (s, 6H, 2 x CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 68.2, 54.5, 38.8, 24.4. The values of the NMR spectra are in accordance with reported literature data.[31]

4. Preparation of VBX reagents

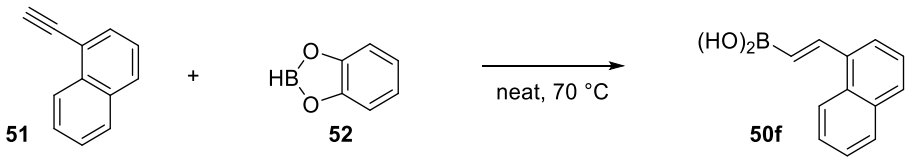
trans-2-Phenylvinylboronic acid (**50a**), *trans*-2-(4-Methoxyphenyl)vinylboronic acid (**50b**), *trans*-2-(4-Methylphenyl)vinylboronic acid (**50c**), *trans*-2-(4-Fluorophenyl)vinylboronic acid (**50d**), *trans*-2-[4-(Trifluoromethyl)phenyl]vinylboronic acid (**50e**), 2-Cyclohexylvinylboronic acid (**50j**), *trans*-3-Phenyl-1-propen-1-ylboronic acid (**50k**), 1-Penten-1-ylboronic acid (**50l**), 1-Cyclohexenylboronic acid (**50o**), and *trans*-2-Chloromethylvinylboronic acid (**50r**) were directly purchased from Sigma Aldrich.



The ^{13}C NMR signal for carbons attached to boron was broad or did not appear in the collected spectra due to the quadrupolar splitting of ^{11}B.[32]

All boronic acids analyzed under electrospray ionization-MS analysis gave complex ionization pathways.[33] Faint signals could be obtained using APPI-MS.

(*E*)-(2-(Naphthalen-1-yl)vinyl)boronic acid (50f)



Following a reported procedure,[34] catecholborane (**52**) (640 µl, 6.00 mmol, 1.20 equiv) was added dropwise to stirring neat 1-ethynylnaphthalene (**51**) (711 µl, 5.00 mmol, 1.00 equiv) at 0 °C under inert atmosphere. The reaction mixture was stirred at room temperature until the gas evolution had ceased and, then was heated to 70 °C and stirred for 3 h. The resulting thick oil was dissolved in THF (8 mL) and then slowly added to an ice-cold mixture of 1:1 Et_2O/water (25 mL) and stirred for an additional 30 minutes. The two layers were separated and the aqueous layer was extracted with Et_2O (2 x 15 mL). The combined organic layers were washed with water (5 x 15 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The resulting crude residue was dissolved in boiling water (70 mL). The insoluble materials were discarded by hot filtration and the aqueous filtrate was allowed to cool to room temperature. The precipitate was collected by filtration to give (*E*)-(2-(naphthalen-1-yl)vinyl)boronic acid (**50f**) as a white solid (324 mg, 1.60 mmol, 33%). ^1H NMR (400 MHz, DMSO-d_6/D_2O 9:1) δ 8.21 (d, *J* = 8.3 Hz, 1H, Ar*H*), 8.09 (d, *J* = 18.2 Hz, 1H, BCHC*H*), 7.93 - 7.82 (m, 2H, Ar*H*), 7.73 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.62 - 7.44 (m, 3H, Ar*H*), 6.20 (d, *J* = 18.2 Hz, 1H, BC*H*CH); ^{13}C NMR (101 MHz, DMSO-d_6/D_2O 9:1) δ 143.5, 135.6, 134.0, 131.3, 129.4, 129.3, 127.3, 126.9, 126.6, 124.2, 124.0; ^{11}B NMR (128 MHz, DMSO-d_6/D_2O 9:1) δ 29.0. The ^{13}C NMR signal for the carbon attached to

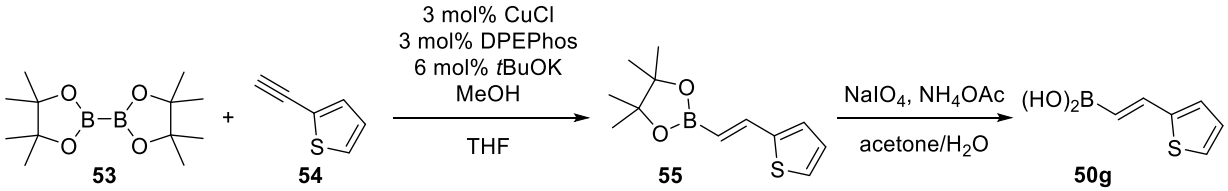
[32] B. Wrackmeyer, *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *12*, 227.

[33] L. Wang, C. Dai, S. K. Burroughs, S. L. Wang and B. Wang, *Chem. Eur. J.*, **2013**, *19*, 7587.

[34] T. Haddad, R. Gershman, R. Dilis, D. Labaree, R. B. Hochberg and R. N. Hanson, *Bioorg. Med. Chem. Lett.*, **2012**, *22*, 5999.

boron did not appear due to the quadrupolar splitting of ^{11}B. The values of the NMR spectra are in accordance with reported literature data.[34]

(*E*)-(2-(Thiophen-2-yl)vinyl)boronic acid (50g)

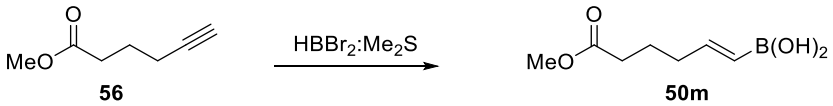


Following a reported procedure,[35] CuCl (15.0 mg, 0.150 mmol, 0.03 equiv), NaO*t*Bu (29.0 mg, 0.300 mmol, 0.06 equiv) and DPEPhos (81.0 mg, 0.150 mmol, 0.03 equiv) were dissolved in THF (5 mL) under argon. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron (**53**) (1.40 g, 5.50 mmol, 1.10 equiv) and THF (2.5 mL) were added and the reaction mixture was stirred for another 10 min and then 2-ethynylthiophene (**54**) (0.475 mL, 5.00 mmol, 1.00 equiv) was added, followed by MeOH (0.405 mL, 10.0 mmol, 2.00 equiv). The reactor wall was washed with THF (1.5 mL), sealed, and stirred for 4 h. The reaction mixture was filtered through a pad of Celite, washed with EtOAc and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography using EtOAc/pentane 5:95 as mobile phase affording (*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (**55**) as a clear yellow oil (1.07 g, 4.53 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 18.1 Hz, 1H, CHC*H*B), 7.24 (d, *J* = 5.1, 1H, Ar*H*), 7.11 - 7.05 (m, 1H, Ar*H*), 6.99 (dd, *J* = 5.1, 3.6 Hz, 1H, Ar*H*), 5.91 (d, *J* = 18.1 Hz, 1H, CHC*H*B), 1.30 (s, 12H, 4 x C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 141.9, 127.8, 127.8, 126.4, 83.5, 24.9. The ^{13}C NMR signal for the carbon attached to boron did not appear due to the quadrupolar splitting of ^{11}B. The values of the NMR spectra are in accordance with reported literature data.[35]

Following a reported procedure,[35] (*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (**55**) (1.00 g, 4.23 mmol, 1.00 equiv), NH_4OAc (1.63 g, 21.2 mmol, 5.00 equiv), $NaIO_4$ (4.53 g, 21.2 mmol, 5.00 equiv) were suspended in a mixture 1:1 acetone/water (42 mL). The resulting slurry was stirred at room temperature for 16 h. It was then diluted with EtOAc (30 mL), washed successively with water (2 x 20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude yellow oil was dissolved with diethyl ether (20 mL) then shaken 5 min with a basic aqueous solution of sorbitol (25 mL, 1 M sorbitol, 1 M Na_2CO_3), the aqueous layer was re-acidified with 4 M HCl (25 mL, pH = 2) and extracted with diethyl ether (35 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure affording (*E*)-(2-(thiophen-2-yl)vinyl)boronic acid (**50g**) as a clear yellow solid (0.416 g, 2.70 mmol, 64%). M.p. 118-120 °C; ^{1}H NMR (400 MHz, DMSO-d_6/D_2O 9:1) δ 7.47 (d, *J* = 5.1 Hz, 1H, Ar*H*), 7.36 (d, *J* = 18.1 Hz, 1H, C*H*CHB), 7.14 (m, 1H, Ar*H*), 7.04 (dd, *J* = 5.1, 3.5 Hz, 1H, Ar*H*), 5.80 (d, *J* = 18.1 Hz, 1H, CHC*H*B); ^{13}C NMR (101 MHz, DMSO-d_6/D_2O 9:1) δ 144.0, 138.8, 128.2, 127.6, 126.4, 122.6 (br); ^{11}B NMR (128 MHz, DMSO-d_6/D_2O 9:1) δ 28.5. The ^{13}C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ^{11}B. The values of the NMR spectra are in accordance with reported literature data.[36]

(*E*)-(6-Methoxy-6-oxohex-1-en-1-yl)boronic acid (50m)

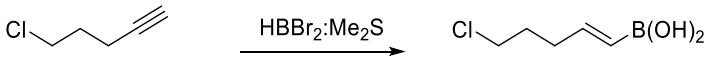
[35] C. Feng, H. Wang, L. Xua and P. Li, *Org. Biomol. Chem.*, **2015**, *13*, 7136.
[36] S. Liu and L. S. Liebeskind, *J. Am. Chem. Soc.*, **2008**, *130*, 6918.



56 **50m**

Following a reported procedure,[37] a solution of 1 M dibromoborane dimethyl sulfide complex in DCM (6.00 mL, 6.00 mmol, 1.2 equiv) was added dropwise to neat methyl hex-5-ynoate (**56**) (631 mg, 5.00 mmol, 1.00 equiv) at 0 °C. The resulting solution was allowed to warm to room temperature. After stirring for 4 h, the solution was transferred slowly to an ice-cooled mixture of 2:1 diethyl ether/water (18 mL) and stirred vigorously for 15 min. The mixture was diluted with diethyl ether (20 mL) and extracted with water (2 x 10 mL). The organic layer was then shaken 5 min with a basic aqueous solution of sorbitol (25 mL, 1 M sorbitol, 1 M Na_2CO_3), the aqueous layer was re-acidified with 4 M HCl (25 mL, pH = 2) and extracted with diethyl ether (35 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure affording (*E*)-(6-methoxy-6-oxohex-1-en-1-yl)boronic acid (**50m**) as a light brown oil (517 mg, 3.01 mmol, 60 %). ^{1}H NMR (400 MHz, DMSO-d_6/D_2O 9:1) δ 6.38 (dt, *J* = 17.9, 6.4 Hz, 1H, CHC*H*CH_2), 5.30 (dt, *J* = 17.9, 1.6 Hz, 1H, BC*H*CH), 3.55 (s, 3H, OCH_3), 2.26 (t, *J* = 7.4 Hz, 2H, CH_2CO_2Me), 2.10 - 2.00 (m, 2H, CH_2BCC), 1.59 (p, *J* = 7.4 Hz, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (101 MHz, DMSO-d_6/D_2O 9:1) δ 174.4, 150.1, 125.2 (br), 51.8, 34.5, 33.0, 23.6. The ^{13}C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ^{11}B. The values of the NMR spectra are in accordance with reported literature data.[37]

(*E*)-(5-Chloropent-1-en-1-yl)boronic acid (50n)

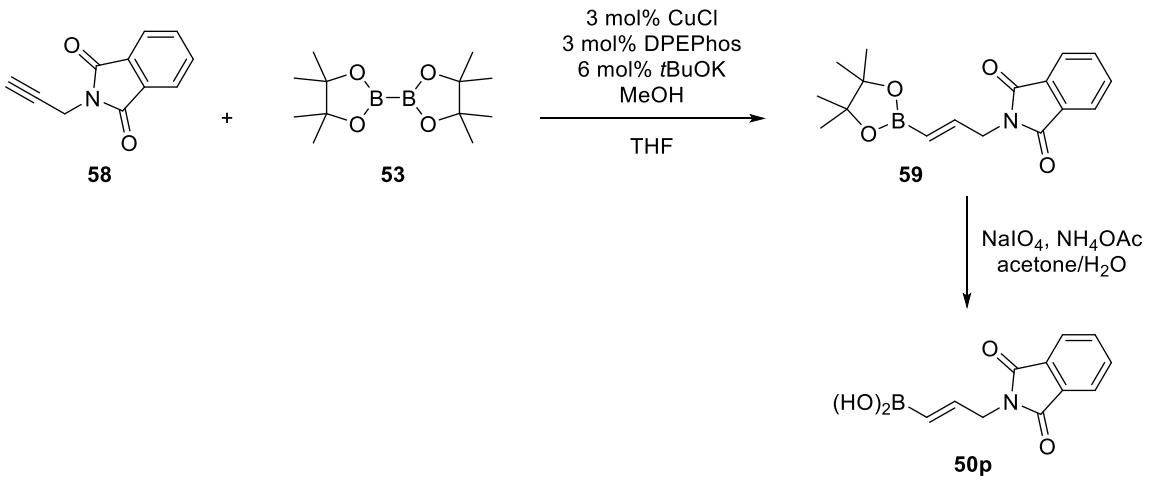


57 **50n**

A solution of 1 M dibromoborane dimethyl sulfide complex in DCM (6.00 mL, 6.00 mmol, 1.2 equiv) was added dropwise to neat 5-chloropent-1-yne (**57**) (0.523 mL, 5.00 mmol, 1.0 equiv) at 0 °C. The resulting solution was allowed to warm to room temperature. After stirring for 4 h, the solution was transferred slowly to an ice-cooled mixture of 2:1 diethyl ether/water (18 mL) and stirred vigorously for 15 min. The mixture was diluted with diethyl ether (20 mL) and extracted with water (2 x 10 mL). The organic layer was then shaken 5 min with a basic aqueous solution of sorbitol (25 mL, 1 M sorbitol, 1 M Na_2CO_3), the aqueous layer was re-acidified with 4 M HCl (25 mL, pH = 2) and extracted with diethyl ether (35 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure affording (*E*)-(5-chloropent-1-en-1-yl)boronic acid (**50n**) as a light yellow oil (461 mg, 3.11 mmol, 62 %). ^{1}H NMR (400 MHz, DMSO-d_6/D_2O 9:1) δ 6.40 (dt, *J* = 17.9, 6.5 Hz, 1H, CHC*H*CH_2), 5.35 (dt, *J* = 17.9, 1.5 Hz, 1H, BC*H*CH), 3.60 (t, *J* = 6.5 Hz, 2H, CH_2Cl), 2.19 (dtd, *J* = 7.8, 6.6, 1.6 Hz, 2H, CHCH_2CH_2), 1.79 (dq, *J* = 8.4, 6.6 Hz, 2H, CH_2CH_2Cl); ^{13}C NMR (101 MHz, DMSO-d_6/D_2O 9:1) δ 149.0, 125.8 (br), 45.3, 32.4, 31.3; ^{11}B NMR (128 MHz, DMSO-d_6/D_2O 9:1) δ 27.3; IR (ν_{max}, cm^{-1}) 2961 (m), 2922 (w), 1634 (m), 1347 (s), 1305 (m), 1225 (m), 1051 (w), 998 (m), 691 (m), 652 (m); HRMS (APPI/LTQ-Orbitrap) calcd for $C_5H_9BClO_2^-$ [M^-] 147.0390; found 147.0394. The ^{13}C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ^{11}B.

[37] D. Kontokosta, D. S. Mueller, H.-Y. Wang and L. L. Anderson, *Org. Lett.*, **2013**, *15*, 4830.

(*E*)-(3-(1,3-Dioxoisoindolin-2-yl)prop-1-en-1-yl)boronic acid (50p)

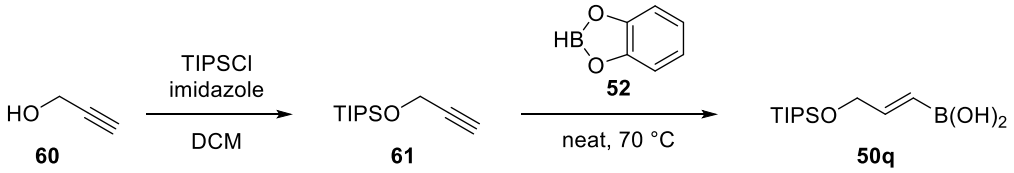


58 **53** **59** **50p**

Following a reported procedure,[35] CuCl (15.0 mg, 0.150 mmol, 0.03 equiv), NaO*t*Bu (29.0 mg, 0.300 mmol, 0.06 equiv) and DPEPhos (81.0 mg, 0.150 mmol, 0.03 equiv) were dissolved in THF (5 mL) under argon. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron (**53**) (1.40 g, 5.50 mmol, 1.10 equiv) and THF (2.5 mL) were added and the reaction mixture was stirred for another 10 min and then *N*-propargylphtalimide (**58**) (0.926 g, 5.00 mmol, 1.00 equiv) was added, followed by MeOH (0.405 mL, 10.0 mmol, 2.00 equiv). The reactor wall was washed with THF (1.5 mL), sealed, and stirred for 4 h. The reaction mixture was filtered through a pad of Celite, washed with EtOAc and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography using EtOAc/pentane 15:85 as mobile phase affording (*E*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)isoindoline-1,3-dione (**59**) as a white solid (1.49 g, 4.75 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H, Ar*H*), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H, Ar*H*), 6.59 (dt, *J* = 18.0, 4.5 Hz, 1H, C*H*CHB), 5.48 (dt, *J* = 18.0, 1.9 Hz, 1H, CHC*H*B), 4.38 (dd, *J* = 4.6, 1.8 Hz, 2H, C*H*$_2$N), 1.22 (s, 12H, 4 x C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 145.4, 134.2, 132.2, 123.5, 83.5, 41.1, 24.9. The ^{13}C NMR signal for the carbon attached to boron did not appear due to the quadrupolar splitting of ^{11}B. The values of the NMR spectra are in accordance with reported literature data.[35]

Following a reported procedure,[35] (*E*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)isoindoline-1,3-dione (**59**) (1.49 g, 4.75 mmol), NH_4OAc (1.83 g, 23.7 mmol, 5.00 equiv), $NaIO_4$ (5.08 g, 23.7 mmol, 5.00 equiv) were suspended in a mixture 1:1 acetone/water (46 mL). The resulting slurry was stirred at room temperature for 16 h. It was then diluted with EtOAc (30 mL), washed successively with water (2 x 20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure affording (*E*)-(3-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl)boronic acid (**50p**) as a white solid (0.805 g, 3.48 mmol, 73%). M.p. 145-147 °C; ^{1}H NMR (400 MHz, DMSO-d_6/D_2O 9:1) δ 7.95 - 7.77 (m, 4H, Ar*H*), 6.41 (dt, *J* = 18.0, 4.3 Hz, 1H, C*H*CHB), 5.24 (dt, *J* = 18.0, 1.9 Hz, 1H, CHC*H*B), 4.22 (dd, *J* = 4.3, 1.9 Hz, 2H, C*H*$_2$N); ^{13}C NMR (101 MHz, DMSO-d_6/D_2O 9:1) δ 168.2, 143.2, 135.2, 131.9, 124.4 (br), 123.7, 41.0; ^{11}B NMR (128 MHz, DMSO-d_6/D_2O 9:1) δ 26.8; IR (ν_{max}, cm^{-1}) 2985 (m), 2904 (m), 1773 (m), 1716 (s), 1427 (m), 1395 (s), 1343 (m), 1071 (s), 1055 (s), 726 (m); HRMS (APPI/LTQ-Orbitrap) calcd for $C_{11}H_{11}BNO_4^+$ $[M+H]^+$ 232.0776; found 232.0775. The ^{13}C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ^{11}B.

(*E*)-(3-((Triisopropylsilyl)oxy)prop-1-en-1-yl)boronic acid (50q)

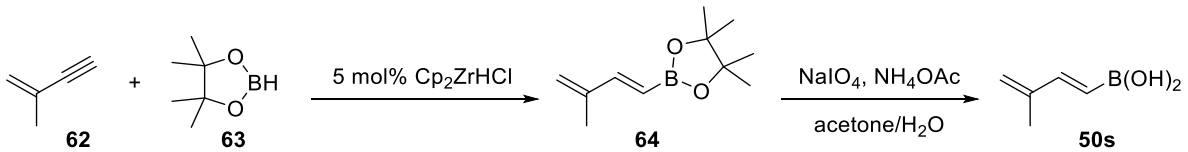


60 61 50q

Following a reported procedure,[38] a solution of propargyl alcohol (**60**) (1.04 mL, 17.8 mmol, 1.00 equiv), imidazole (3.04 g, 44.7 mmol, 2.50 equiv), and triisopropylchlorosilane (5.73 mL, 26.8 mmol, 1.50 equiv) in DCM (30 mL) was stirred at room teperature for 16 h. The reaction mixture was diluted with DCM (30 mL) and quenched with water (10 mL). The aqueous layer was separated and extracted with DCM (2 × 15 mL). The combined organic layers were washed successively with water (2 × 15 mL) and brine (15 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using pentane as mobile phase providing triisopropyl(prop-2-yn-1-yloxy)silane (**61**) as a colorless oil (3.23 g, 15.2 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 (d, *J* = 2.4 Hz, 2H, C*H*$_2$O), 2.39 (t, *J* = 2.4 Hz, 1H, CC*H*), 1.26 - 0.99 (m, 21H, TIPS); ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.5, 72.7, 51.7, 17.8, 12.0. The values of the NMR spectra are in accordance with reported literature data.[38]

Catecholborane (**52**) (1.71 mL, 16.0 mmol, 1.05 equiv) was added dropwise to stirring neat triisopropyl(prop-2-yn-1-yloxy)silane (**61**) (3.23 g, 15.2 mmol, 1.00 equiv) at 0 °C under inert atmosphere. The reaction mixture was stirred at room temperature until the gas evolution had ceased and, then was heated to 70 °C and stirred for 4 h. After cooling to room temperature, the reaction mixture was diluted in Et_2O (150 mL) and 1 N NaOH (45 mL, 45 mmol) was added. After vigorous stirring for 10 min, the mixture was transferred to a separatory funnel and the layers were separated. The organic layer was washed with 1 N NaOH (60 mL), water (3 x 60 mL) and 1:1 water/brine (60 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using Et_2O/pentane 50:50 as mobile phase affording (*E*)-(3-((triisopropylsilyl)oxy)prop-1-en-1-yl)boronic acid (**50q**) as a colorless oil (2.12 g, 8.21 mmol, 54%).TLC (Et_2O/pentane, 50:50): Rf = 0.37, KMnO4; ^{1}H NMR (400 MHz, DMSO-d_6/D_2O 9:1) δ 6.46 (dt, *J* = 17.9, 3.7 Hz, 1H, C*H*CHB), 5.59 (dt, *J* = 17.9, 2.0 Hz, 1H, CHC*H*B), 4.22 (dd, *J* = 3.7, 2.0 Hz, 2H, C*H*$_2$O), 1.05 - 0.94 (m, 21H, TIPS); ^{13}C NMR (101 MHz, DMSO-d_6/D_2O 9:1) δ 149.6, 122.0 (br), 65.1, 18.5, 12.1; ^{11}B (128 MHz, DMSO-d_6/D_2O 9:1) δ 26.1; IR (ν_{max}, cm^{-1}) 2942 (m), 2895 (m), 2867 (m), 1638 (m), 1462 (m), 1372 (s), 1344 (s), 1291 (s), 1258 (m), 1131 (s), 1107 (s), 1055 (m), 1017 (m), 994 (m), 953 (m), 882 (s), 771 (m), 681 (s), 663 (s), 653 (s); HRMS (APPI/LTQ-Orbitrap) calcd for $C_{12}H_{26}BO_3Si^-$ [M^-] 257.1750; found 257.1749. The ^{13}C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ^{11}B.

(*E*)-(3-Methylbuta-1,3-dien-1-yl)boronic acid (50s)



62 63 64 50s

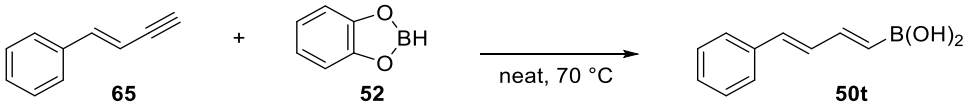
Following a reported procedure,[39] to a flask containing Cp_2ZrHCl (64.0 mg, 0.250 mmol, 0.05 equiv) at 0 °C under argon atmosphere was added pinacolborane (**63**) (0.798 mL, 5.50 mmol, 1.10 equiv) then dropwise 2-methylbut-1-en-3-yne (**62**) (0.485 mL, 5.00 mmol, 1.00 equiv). The resulting mixture was

[38] M. S. Oderinde, H. N. Hunter and M. G. Organ, *Chem. Eur. J.*, **2012**, 18, 10817.
[39] A. Cannillo, S. Norsikian, P. Retailleau, M.-E. T. H. Dau, B. I. Iorga and J.-M. Beau, *Chem. Eur. J.*, **2013**, *19*, 9127.

stirred at 0 °C for 30 min and then at room temperature for 24 h. The crude reaction was directly purified by column chromatography using EtOAc/pentane 2:98 as mobile phase affording 4,4,5,5-tetramethyl-2-[(1*E*)-3-methylbuta-1,3-dien-1-yl]-1,3,2-dioxaborolane (**64**) as a colorless oil (789 mg, 4.05 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 18.2 Hz, 1H, C*H*CHB), 5.56 (d, *J* = 18.2 Hz, 1H, CHC*H*B), 5.21 - 5.13 (m, 2H, CCH_2), 1.85 (t, *J* = 1.1 Hz, 3H, CCH_3), 1.28 (s, 12H, 4 x CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 143.2, 120.3, 116.7 (br), 83.4, 24.9, 17.9. The ^{13}C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ^{11}B. The values of the NMR spectra are in accordance with reported literature data.[39]

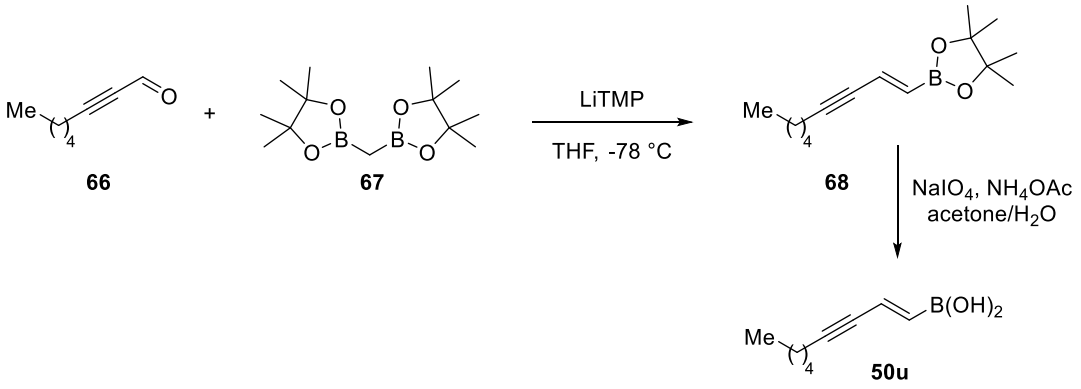
Following a reported procedure,[39] to a stirred solution of 4,4,5,5-tetramethyl-2-[(1*E*)-3-methylbuta-1,3-dien-1-yl]-1,3,2-dioxaborolane (**64**) (772 mg, 3.98 mmol, 1.00 equiv) in acetone (125 mL) were added an aqueous solution of NH_4OAc (79 mL, 0.1 M, 1.50 equiv) and $NaIO_4$ (2.55 g, 11.9 mmol, 3.0 equiv). The cloudy mixture was stirred at room temperature for 24 h. After cautious acidification with aqueous 2 M HCl (pH = 2), the aqueous layer was extracted with AcOEt (2 x 80 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure affording (*E*)-(3-methylbuta-1,3-dien-1-yl)boronic acid (**50s**) as a light yellow solid (200 mg, 1.79 mmol, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 17.8 Hz, 1H, C*H*CHB), 5.68 (d, *J* = 17.9 Hz, 1H, CHC*H*B), 5.29 (s, 1H, CCH_2), 5.27 (s, 1H, CCH_2), 1.92 (s, 3H, CCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 143.2, 121.6, 120.0 (br), 18.1; ^{11}B NMR (128 MHz, DMSO-d_6/D_2O 9:1) δ 19.38. The ^{13}C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ^{11}B. The values of the NMR spectra are in accordance with reported data.[39]

((1*E*,3*E*)-4-Phenylbuta-1,3-dien-1-yl)boronic acid (50t)



Catecholborane (**52**) (533 µl, 5.00 mmol, 1.00 equiv) was added dropwise to stirring neat (*E*)-but-1-en-3-yn-1-ylbenzene (**65**) (641 mg, 5.00 mmol, 1.00 equiv) at 0 °C under inert atmosphere. The reaction mixture was stirred at room temperature until the gas evolution had ceased and, then was heated to 70 °C and stirred for 1 h. The reaction was cooled to 0 °C and quenched by dropwise addition of water (3 mL). The solid was suspended in water (20 mL) and vigorously stirred at room temperature for 18 h. The mixture was extracted with diethyl ether (2 x 20 mL) and washed with water (5 x 20 mL). The organic layer was then shaken 5 min with a basic aqueous solution of sorbitol (25 mL, 1 M sorbitol, 1 M Na_2CO_3), the aqueous layer was re-acidified with 4 M HCl (25 mL, pH = 2) and extracted with diethyl ether (35 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure affording ((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)boronic acid (**50t**) as a off-white solid (461 mg, 3.11 mmol, 62 %). M.p. 110-112 °C; ^{1}H NMR (400 MHz, DMSO-d_6/D_2O 9:1) δ 7.54 - 7.48 (m, 2H), 7.38 - 7.30 (m, 2H), 7.30 - 7.22 (m, 1H), 7.08 - 6.87 (m, 2H), 6.69 (d, *J* = 15.4 Hz, 1H), 5.65 (d, *J* = 17.3 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6/D_2O 9:1) δ 146.9, 137.0, 134.7, 131.4, 129.1, 128.6 (br), 128.4, 127.0; ^{11}B NMR (128 MHz, DMSO-d_6/D_2O 9:1) δ 29.2; IR (ν_{max}, cm^{-1}) 2967 (m), 2912 (m), 1622 (m), 1427 (m), 1456 (s), 1082 (s), 1021 (s); HRMS (APPI/LTQ-Orbitrap) calcd for $C_{10}H_{11}BO_2^+$ [M^+] 174.0847; found 174.0847. The ^{13}C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ^{11}B.

(*E*)-Non-1-en-3-yn-1-ylboronic acid (50u)

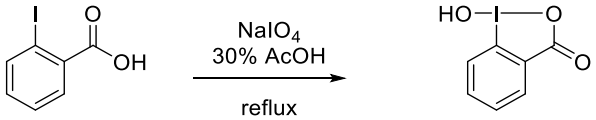


Following a reported procedure,[40] a 100 mL flask was charged with LiTMP (883 mg, 6.00 mmol, 1.20 equiv), sealed with a septum cap, and removed from the glovebox. The reaction flask was cooled to 0 °C, and dry THF (6 mL), followed by a solution of bis[(pinacolato)boryl]methane (**67**) (1.60 g, 6.00 mmo, 1.20 equiv) in THF (12 mL) were added. The reaction was stirred for 5 minutes at 0 °C and then was cooled to -78 °C, and a solution of oct-2-ynal (**66**) (0.735 mL, 5.00 mmol, 1.00 equiv) in THF (6.00 mL) was added slowly. The reaction was stirred at -78 °C for 4 h and the solvent was removed under reduced pressure. The crude reaction mixture was purified by column chromatography using EtOAc/pentane 2:98 as mobile phase affording (E)-4,4,5,5-tetramethyl-2-(non-1-en-3-yn-1-yl)-1,3,2-dioxaborolane (**68**) as a clear yellow oil (805 mg, 3.24 mmol, 65 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (dt, *J* = 18.3, 2.1 Hz, 1H, C*H*CHB), 5.92 (dd, *J* = 18.3, 0.6 Hz, 1H, CHC*H*B), 2.32 (tdd, *J* = 7.2, 2.2, 0.6 Hz, 2H, CCH_2), 1.56 - 1.48 (m, 2H, CH_2), 1.42 - 1.27 (m, 4H, 2 x CH_2), 1.26 (s, 12H, 4 x CH_3 pinacol), 0.89 (t, *J* = 7.1 Hz, 3H, CH_2CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.5, 95.4, 83.6, 81.0, 31.2, 28.4, 24.9, 22.3, 19.7, 14.1. The ^{13}C NMR signal for the carbon attached to boron did not appear due to the quadrupolar splitting of ^{11}B. The values of the NMR spectra are in accordance with reported literature data.[40]

(*E*)-4,4,5,5-Tetramethyl-2-(non-1-en-3-yn-1-yl)-1,3,2-dioxaborolane (**68**) (0.805 g, 3.24 mmol, 1.00 equiv), NH_4OAc (1.250 g, 16.22 mmol, 5.00 equiv) and $NaIO_4$ (3.470 g, 16.22 mmol, 5.00 equiv) were suspended in a mixture 1:1 acetone/water (30 mL). The resulting slurry was stirred at room temperature for 16 h. It was then diluted with EtOAc (30 mL), washed successively with water (2 x 20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting yellow oil was dissolved in diethyl ether (20 mL) then shaken 5 min with a basic aqueous solution of sorbitol (25 mL, 1 M sorbitol, 1 M Na_2CO_3), the aqueous layer was re-acidified with 4 M HCl (25 mL, pH = 2) and extracted with diethyl ether (35 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure affording (*E*)-non-1-en-3-yn-1-ylboronic acid (**50u**) as a yellow oil (0.365 g, 2.20 mmol, 68%). ^{1}H NMR (400 MHz, DMSO-d_6/D_2O 9:1) δ 6.27 (dt, *J* = 18.3, 2.1 Hz, 1H, C*H*CHB), 5.83 (d, *J* = 18.4 Hz, 1H, CHC*H*B), 2.32 (td, *J* = 7.0, 2.2 Hz, 2H, CCH_2), 1.46 (m, 2H, CH_2), 1.38 - 1.23 (m, 4H, 2 x CH_2), 0.86 (t, *J* = 7.0 Hz, 3H, CH_2CH_3); ^{13}C NMR (101 MHz, DMSO-d_6/D_2O 9:1) δ 136.6 (br), 126.6, 93.7, 81.2, 30.6, 27.9, 21.7, 18.7, 14.0; ^{11}B NMR (128 MHz, DMSO-d_6/D_2O 9:1) δ 27.2; IR (ν_{max}, cm^{-1}) 2985 (m), 2904 (m), 1773 (m), 1716 (s), 1427 (m), 1395 (s), 1343 (m), 1071 (s), 1055 (s), 726 (m); HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_9H_{15}BO_2^+$ 166.1160; found 166.1161. The ^{13}C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ^{11}B.

[40] J. R. Coombs, L. Zhang and J. P. Morken, *Org. Lett.*, **2015**, 17, 1708.

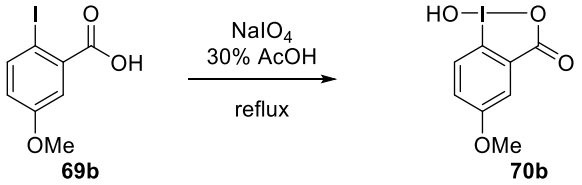
2-Iodosylbenzoic acid (70a)



69a **70a**

Following a reported procedure,[41] $NaIO_4$ (18.1 g, 85.0 mmol, 1.05 equiv) and 2-iodobenzoic acid (**69a**) (20.0 g, 81.0 mmol, 1.00 equiv) were suspended in 30% (v/v) aq. AcOH (160 mL). The mixture was vigorously stirred under reflux for 4 h and allowed to cool to room temperature. The precipitate was collected by filtration, washed on the filter with ice water (3 x 40 mL) and acetone (45 mL), and air-dried in the dark to give 2-iodosylbenzoic acid (**70a**) as a white solid (20.8 g, 79.0 mmol, 98%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.02 (dd, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.97 (m, 1H, Ar*H*), 7.85 (dd, *J* = 8.2, 0.7 Hz, 1H, Ar*H*), 7.71 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4. The values of the NMR spectra are in accordance with reported literature data.[41]

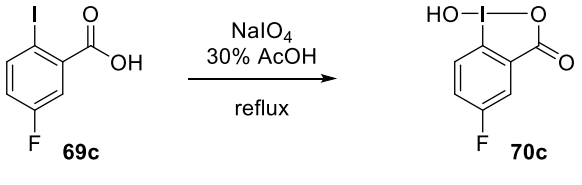
1-Hydroxy-5-methoxy-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (70b)



69b **70b**

Following a reported procedure,[42] $NaIO_4$ (2.25 g, 10.5 mmol, 1.05 equiv) and 2-iodo-5-methoxybenzoic acid (**69b**) (2.78 g, 10.0 mmol, 1.00 equiv) were suspended in 30% (v/v) aq. AcOH (27 mL). The mixture was vigorously stirred under reflux for 4 h and allowed to cool to room temperature. The precipitate was collected by filtration, washed on the filter with ice water (3 x 8 mL) and acetone (3 x 6 mL), and air-dried in the dark to give 1-hydroxy-5-methoxy-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**70b**) as a white solid (2.31 g, 7.90 mmol, 79%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (s, 1H, Ar*H*), 7.72 - 7.61 (m, 1H, Ar*H*), 7.59 - 7.47 (m, 1H, Ar*H*), 3.88 (s, 3H, OCH_3); ^{13}C NMR (101MHz, DMSO-d_6) δ 167.9, 162.0, 133.5, 127.6, 122.0, 115.4, 109.5, 56.4. The values of the NMR spectra are in accordance with reported literature data.[42]

5-Fluoro-1-hydroxy-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (70c)



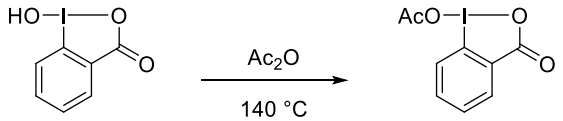
69c **70c**

Following a reported procedure,[42] $NaIO_4$ (2.25 g, 10.5 mmol, 1.05 equiv) and 5-fluoro-2-iodobenzoic acid (**69c**) (2.70 g, 10.0 mmol, 1.00 equiv) were suspended in 30% (v/v) aq. AcOH (27 mL). The mixture was vigorously stirred under reflux for 4 h and allowed to cool to room temperature. The precipitate was collected by filtration, washed on the filter with ice water (3 x 8 mL) and acetone (3 x 6 mL), and air-dried in the dark to give 5-fluoro-1-hydroxy-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**70c**) as a white solid (2.62 g, 9.30 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (s, 1H, Ar*H*), 7.89 - 7.78 (m, 2H,

[41] L. Kraszkiewicz and L. Skulski, *Arkivoc.* **2003**, *6*, 120.
[42] S. Bertho, R. Rey-Rodriguez, C. Colas, P. Retailleau and I. Gillaizeau, *Chem. Eur. J.*, **2017**, *23*, 17674.

Ar*H*), 7.78 - 7.72 (m, 1H, Ar*H*); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.5, 164.0 (d, *J* = 248.3 Hz), 134.2 (d, *J* = 7.3 Hz), 128.4 (d, *J* = 8.6 Hz), 121.8 (d, *J* = 24.0 Hz), 117.5 (d, J = 23.5 Hz), 114.3; ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.7. The values of the NMR spectra are in accordance with reported literature data.[42]

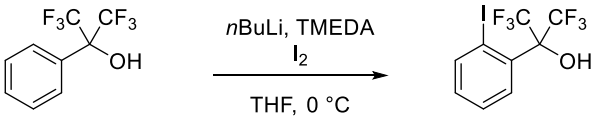
1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one (71)



70a **71**

Following a reported procedure,[43] 2-iodosylbenzoic acid (**70a**) (20.8 g, 79.0 mmol, 1.00 equiv) was suspended in acetic anhydride (75.0 mL, 788 mmol, 10.0 equiv) and heated to reflux (140 °C) until complete dissolution (about 15 min). The resulting clear solution was allowed to cool to room temperature and then cooled to 5 °C overnight. The white crystals were filtered, washed with pentane (3 x 30 mL) and dried under reduced pressure to afford 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) as a white solid (22.3 g, 73.0 mmol, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar*H*), 8.00 (dd, *J* = 8.3, 1.0 Hz, 1H, Ar*H*), 7.92 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H, Ar*H*), 7.71 (td, *J* = 7.3, 1.1 Hz, 1H, Ar*H*), 2.25 (s, 3 H, COCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.5, 168.2, 136.2, 133.3, 131.4, 129.4, 129.1, 118.4, 20.4. The values of the NMR spectra are in accordance with reported literature data.[44]

1,1,1,3,3,3-Hexafluoro-2-(2-iodophenyl)propan-2-ol (69')

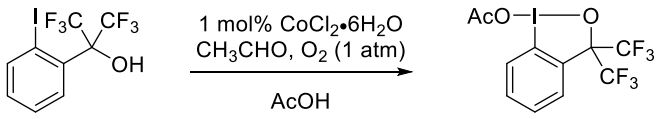


72 **69'**

Following a reported procedure,[45] TMEDA (1.27 mL, 8.40 mmol, 0.20 equiv.) was added to a solution of *n*-BuLi (37.0 mL, 92.0 mmol, 2.20 equiv., 2.5 M in hexanes). After 15 min, the cloudy solution was cooled to 0 °C and 1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-ol (**72**) (7.07 mL, 42.0 mmol, 1.00 equiv.) in THF (6.0 mL) was added dropwise. The reaction was stirred 30 min at 0 °C and then 18 h at room temperature. Then, THF (30.0 mL) was added, followed by the portionwise addition of I_2 (11.3 g, 44.5 mmol, 1.05 equiv.) at 0 °C and the mixture was stirred at 0 °C for 30 min and 4 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (50 mL) and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with water, brine, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using EtOAc/pentane 3:97 as eluent to afford 1,1,1,3,3,3-hexafluoro-2-(2-iodophenyl)propan-2-ol (**69'**) as a colorless oil (13.9 g, 37.5 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.9, 1.4 Hz, 1H, Ar*H*), 7.63 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.43 (dt, *J* = 8.4, 1.4 Hz, 1H, Ar*H*), 7.11 (dt, *J* = 8.0, 1.5 Hz, 1H, Ar*H*), 4.23 (s, 1H, O*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 131.4, 130.0, 129.7, 128.0, 122.6 (q, *J* = 291.4 Hz), 90.6, 78.9 (q, *J* = 32.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.4. The values of the NMR spectra are in accordance with reported literature data.[45]

[43] P. Caramenti, S. Nicolai and J. Waser, *Chem. Eur. J.,* **2017**, *23*, 14702.
[44] P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.*, **2006**, *12*, 2579.
[45] J. Cvengroš, D. Stolz and A. Togni, *Synthesis* **2009**, 2818.

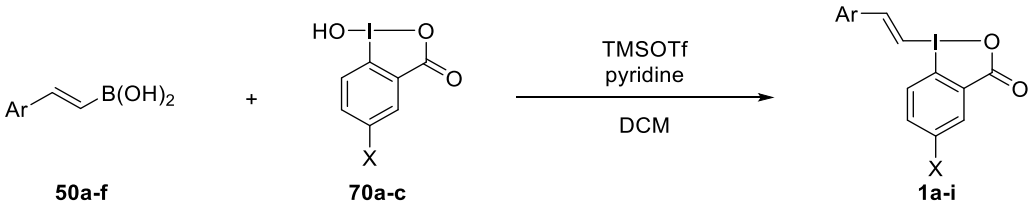
3,3-Bis(trifluoromethyl)-1λ³-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (71')



69' **71'**

Following a reported procedure,[46] a 500 mL flask was charged with glacial acetic acid (188 mL), 1,1,1,3,3,3-hexafluoro-2-(2-iodophenyl)propan-2-ol (**69'**) (13.9 g, 37.5 mmol, 1.00 equiv.) and cobalt(II) chloride hexahydrate (89.0 g, 0.375 mmol, 0.01 equiv.). The reaction vessel was purged with O_2 for 5 min before acetaldehyde (21.4 mL, 379 mmol, 10.0 equiv.) was added in one portion. The reaction mixture was stirred under 1 atm of O_2, delivered by inflated balloon, at room temperature for 12 h. Acetaldehyde (21.4 mL, 379 mmol, 10.0 equiv.) was added and the reaction continued for 6 h. The solvent was removed under reduced pressure and the residue was dissolved in DCM. The organic layer was washed with distilled water (50 mL) and extracted with DCM (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The obtained residue was triturated in pentane for 0.5 h, filtered and washed with pentane (operation repeated 2 times) to afford 3,3-bis(trifluoromethyl)-1λ³-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**71'**) as a white solid (9.91 g, 23.2 mmol, 62%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (ddd, *J* = 8.4, 7.1, 1.6 Hz, 1H, Ar*H*), 7.85 – 7.69 (m, 3H, Ar*H*), 2.19 (s, 3H, (O)CC*H*$_3$); ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.4, 134.2, 131.4, 131.0, 130.8, 129.5 – 129.0 (m), 123.1 (q, *J* = 289.5 Hz), 116.1, 84.5 – 83.7 (m), 20.0; ^{19}F NMR (376 MHz, DMSO-d_6) δ -75.1. The values of the NMR spectra are in accordance with reported literature data.[47]

General procedure A: Synthesis of VBX reagents:



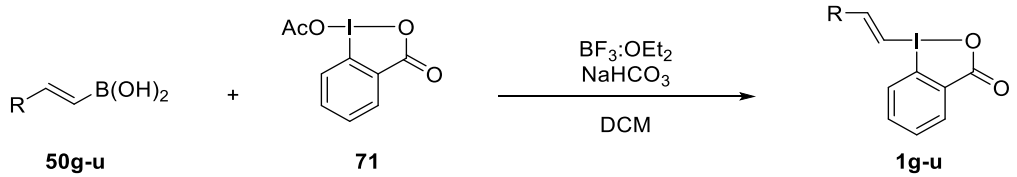
50a-f **70a-c** **1a-i**

To a suspension of 2-iodosylbenzoic acid (**70a-c**) (1.30 mmol, 1.00 equiv) in dry DCM (13 mL) was added TMSOTf (0.270 mL, 1.50 mmol, 1.15 equiv) dropwise over 10 min and stirred for 30 min at room temperature. Afterwards, the corresponding vinyl boronic acid (**50a-i**) (1.50 mmol, 1.15 equiv) was added and the reaction mixture was stirred until the reaction was completed (1 to 8 h, monitored by TLC, MeOH/DCM 5:95). Pyridine (0.121 mL, 1.50 mmol, 1.15 equiv) was added and after further stirring for 10 min at room temperature, the solvent was removed under reduced pressure. The resulting solid was dissolved in DCM (20 mL) and washed with 1 M HCl (10 mL). The aqueous layer was extracted with DCM (3 x 20 mL). The organic layers were combined, washed successively with a saturated solution of $NaHCO_3$ (40 mL) and water (3 x 20 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting solid was dissolved again in DCM (minimum amount until dissolution) and precipitated in Et_2O (ca. 150 mL). After precipitation at 4 °C for 2 h, the solid was filtered and washed with Et_2O to afford the corresponding VBX reagent.

[46] A. Maity, S.-M. Hyun and D. C. Powers, *Nat. Chem.* **2018**, *10*, 200.

[47] P. Eisenberger, S. Gischig and A. Togni, *Chem. Eur J.* **2006**, *12*, 2579.

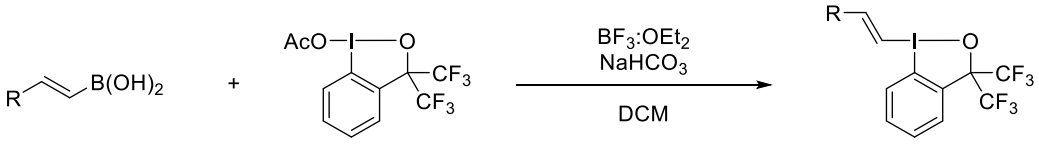
General procedure B: Synthesis of VBX reagents:



50g-u **71** **1g-u**

To a solution of the corresponding vinyl boronic acid (**50g-u**) (1.30 mmol, 1.00 equiv) in dry DCM (13 mL) was added BF_3:OEt_2 (0.198 mL, 1.56 mmol, 1.20 equiv) dropwise at 0 °C. After 15 minutes, 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol, 1.20 equiv) was added in one portion at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred until the reaction was completed (4 to 24 h, monitored by TLC using MeOH/DCM 5:95). The reaction was then quenched with a saturated solution of $NaHCO_3$ (13 mL) and stirred vigorously for 1 h. The resulting suspension was filtered and the filtrate was extracted with DCM (3 x 20 mL). The combined organic layers were washed with water (3 x 20 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting solid was dissolved in DCM (minimum amount until dissolution) and precipitated in Et_2O (ca. 150 mL). After precipitation at 4 °C for 2 h, the solid was filtered and washed with Et_2O to afford the corresponding VBX reagent.

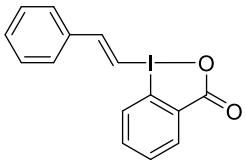
General procedure C: Synthesis of VBX reagents:



50a-p **71'** **1'a-p**

To a solution of the corresponding vinyl boronic acid (**50a – 50p**) (1.00 mmol, 1.00 equiv) in dry DCM (10 mL) was added BF_3:OEt_2 (0.152 mL, 1.20 mmol, 1.20 equiv) dropwise at 0 °C. After 15 minutes, 3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**71'**) (514 mg, 1.20 mmol, 1.20 equiv.) was added in one portion at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 1 h. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ solution and extracted with dichloromethane (3 times). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using EtOAc/pentane as eluent to give the corresponding VBX reagent.

(*E*)-1-Styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1a)



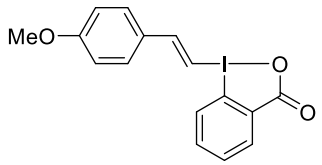
1a

Following general procedure A, starting from *trans*-2-phenylvinylboronic acid (**50a**) (221 mg, 1.50 mmol) and 2-iodosylbenzoic acid (**70a**) (343 mg, 1.30 mmol), afforded (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) as a white solid (351 mg, 1.00 mmol, 77%). ^{1}H NMR (400 MHz, MeOD) δ 8.32 - 8.25 (m, 1H, Ar*H*), 7.97 (d, *J* = 15.5 Hz, 1H, ICHC*H*Ph), 7.77 - 7.63 (m, 6H, Ar*H* and IC*H*CHPh), 7.54 - 7.45 (m, 3H, Ar*H*). ^{13}C NMR (101 MHz, MeOD) δ 170.1, 155.8, 136.7, 135.3, 134.5,

133.3, 132.1, 131.8, 130.2, 129.0, 129.0, 115.5, 100.0. The values of the NMR spectra are in accordance with reported literature data.[48]

The reaction was scaled up to *trans*-2-phenylvinylboronic acid (**50a**) (1.48 g, 10.0 mmol) and 2-iodosylbenzoic acid (**70a**) (2.30 g, 8.70 mmol) affording (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (2.20 g, 6.30 mmol, 72%).

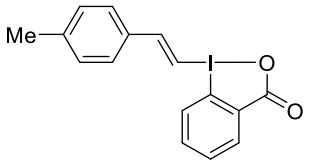
(*E*)-1-(4-Methoxystyryl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1b)



1b

Following general procedure A, starting from *trans*-2-(4-methoxyphenyl)vinylboronic acid (**50c**) (266 mg, 1.50 mmol) and 2-iodosylbenzoic acid (**70a**) (343 mg, 1.30 mmol), afforded (*E*)-1-(4-methoxystyryl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1b**) as a white solid (306 mg, 0.805 mmol, 62%). ^{1}H NMR (400 MHz, MeOD) δ 8.29 (dt, *J* = 5.8, 3.5 Hz, 1H, Ar*H*), 7.89 (d, *J* = 15.3 Hz, 1H, ICHC*H*Ph), 7.78 - 7.60 (m, 5H, Ar*H*), 7.45 (d, *J* = 15.4 Hz, 1H, IC*H*CHPh), 7.12 - 6.95 (m, 2H, Ar*H*), 3.87 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, MeOD) δ 170.1, 163.7, 155.8, 135.2, 134.5, 133.3, 131.8, 130.8, 129.4, 128.9, 115.6, 115.5, 95.9, 56.0. The values of the NMR spectra are in accordance with reported literature data.[48]

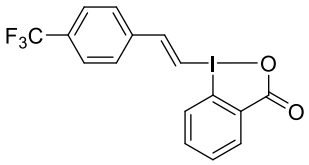
(*E*)-1-(4-Methylstyryl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1c)



1c

Following general procedure A, starting from *trans*-2-(4-methylphenyl)vinylboronic acid (**50b**) (242 mg, 1.50 mmol) and 2-iodosylbenzoic acid (**70a**) (343 mg, 1.30 mmol), afforded (*E*)-1-(4-methylstyryl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1c**) as a white solid (335 mg, 0.920 mmol, 71%). ^{1}H NMR (400 MHz, MeOD) δ 8.32 - 8.25 (m, 1H, Ar*H*), 7.92 (d, *J* = 15.4 Hz, 1H,ICHC*H*Ph), 7.76 - 7.64 (m, 3H, Ar*H*), 7.62 - 7.54 (m, 3H, Ar*H* and IC*H*CHPh), 7.31 (d, *J* = 7.9 Hz, 2H, Ar*H*), 2.42 (s, 3H, CH_3); ^{13}C NMR (101 MHz, MeOD) δ 169.9, 155.7, 142.8, 135.0, 134.3, 133.8, 133.1, 131.6, 130.6, 128.8, 128.7, 115.3, 98.1, 21.3. The values of the NMR spectra are in accordance with reported literature data.[48]

(*E*)-1-(4-(Trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1d)



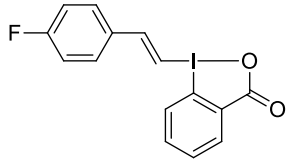
1d

Following general procedure A, starting from *trans*-2-[4-(trifluoromethyl)phenylvinylboronic acid (**50d**) (323 mg, 1.50 mmol) and 2-iodosylbenzoic acid (**70a**) (343 mg, 1.30 mmol), afforded (*E*)-1-(4-(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1d**) as a white solid (275 mg, 0.658 mmol,

[48] E. Stridfeldt, A. Seemann, M. J. Bouma, C. Dey, A. Ertan and B. Olofsson, *Chem. Eur. J.*, **2016**, *22*, 16066.

51%). ^{1}H NMR (400 MHz, MeOD) δ 8.30 (m, 1H, Ar*H*), 8.05 (d, *J* = 15.5 Hz, 1H, ICHC*H*Ph), 7.93 - 7.84 (m, 3H, Ar*H* and IC*H*CHPh), 7.81 (m, 2H, Ar*H*), 7.74 (m, 3H, Ar*H*); ^{13}C NMR (101 MHz, MeOD) δ 170.6, 154.1, 140.6, 136.0, 134.4, 133.8, 133.7 (q, *J* = 37.7 Hz), 132.4, 129.9, 129.7, 127.5 (q, *J* = 3.8 Hz), 125.8 (q, *J* = 271.5 Hz) 115.9, 104.1; ^{19}F NMR (376 MHz, MeOD) δ -64.4. The values of the NMR spectra are in accordance with reported literature data.[48]

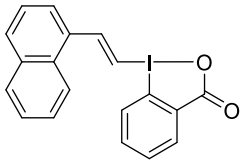
(*E*)-1-(4-Fluorostyryl)-1λ^{3}-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1e)



1e

Following general procedure A, starting from *trans*-2-(4-fluorophenyl)vinylboronic acid (**50e**) (248 mg, 1.50 mmol) and 2-iodosylbenzoic acid (**70a**) (343 mg, 1.30 mmol), afforded (*E*)-1-(4-fluoroystyryl)-1λ^{3}-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1e**) as a white solid (424 mg, 1.152 mmol, 89%). M.p. 146-148 °C; R_f = 0.11 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.38 - 8.31 (m, 1H, Ar*H*), 8.02 (d, *J* = 15.2 Hz, 1H, ICHC*H*Ph), 7.85 - 7.71 (m, 5H, Ar*H*), 7.66 (d, *J* = 15.3, 1H, IC*H*CHPh), 7.30 - 7.22 (m, 2H, Ar*H*); ^{13}C NMR (101 MHz, MeOD) δ 170.9, 166.4 (d, *J* = 251.2 Hz), 155.9, 137.0, 134.2, 133.3 (d, *J* = 3.0 Hz), 132.6, 132.2, 131.9 (d, *J* = 8.7 Hz), 130.4, 117.7 (d, *J* = 22.3 Hz), 115.7, 98.2; ^{19}F NMR (376 MHz, MeOD) δ -110.9; IR (ν_{max}, cm^{-1}) 3018 (s), 2946 (s), 2858 (m), 1750 (s), 1731 (s), 1542 (s), 1512 (s), 1319 (s), 1271 (s), 1243 (s), 1200 (s), 1165 (s), 1124 (s), 968 (s), 838 (m); HRMS (ESI) calcd for $C_{15}H_{11}FIO_2^+$ $[M+H]^+$ 368.9782; found 368.9785.

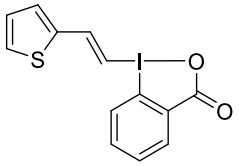
(*E*)-1-(2-(Naphthalen-1-yl)-1λ^{3}-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1f)



1f

Following general procedure A, starting from (*E*)-(2-(naphthalen-1-yl)vinyl)boronic acid (**50f**) (296 mg, 1.50 mmol) and 2-iodosylbenzoic acid (**70a**) (343 mg, 1.30 mmol), afforded (*E*)-1-(2-(naphthalen-1-yl)-1λ^{3}-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1f**) as a white solid (316 mg, 0.790 mmol, 61%). M.p. 164-166 °C; R_f = 0.20 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.79 (d, *J* = 15.1 Hz, 1H, ICHC*H*Ph), 8.33 - 8.28 (m, 1H, Ar*H*), 8.27 - 8.23 (m, 1H, Ar*H*), 8.05 - 7.89 (m, 3H, Ar*H*), 7.85 - 7.79 (m, 1H, Ar*H*), 7.74 - 7.66 (m, 3H, Ar*H* and IC*H*CHPh), 7.65 - 7.55 (m, 3H, Ar*H*); ^{13}C NMR (101 MHz, MeOD) δ 168.7, 151.7, 133.9, 133.8, 133.1, 132.6, 131.9, 131.0, 130.8, 130.4, 128.5, 127.7, 127.0, 126.2, 125.2, 122.8, 114.3, 101.2, 78.1; IR (ν_{max}, cm^{-1}) 2985 (s), 2906 (s), 1390 (m), 1247 (m), 1227 (m), 1065 (s), 1051 (s), 896 (m), 867 (m); HRMS (ESI) calcd for $C_{19}H_{13}INaO_2^+$ $[M+Na]^+$ 422.9852; found 422.9851.

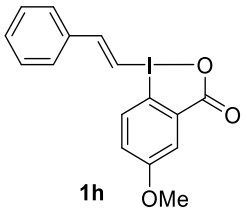
(*E*)-1-(2-(Thiophen-2-yl)vinyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1g)



1g

Following general procedure B, with a final purification by column chromatography using MeOH/DCM 5:95 as mobile phase to obtain the titled compound in pure form. Starting from (*E*)-(2-(thiophen-2-yl)vinyl)boronic acid (**50g**) (169 mg, 1.10 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(non-1-en-3-yn-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1g**) as a beige solid (145 mg, 0.407 mmol, 37%). M.p. (dec.) 201-205 °C; R_f = 0.13 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD/CD_2Cl_2 9:1) δ 8.32 - 8.25 (m, 1H, Ar*H*), 8.04 (d, *J* = 15.3 Hz, 1H, ICHC*H*), 7.74 - 7.65 (m, 3H, Ar*H*), 7.62 (dt, *J* = 5.0, 0.9 Hz, 1H, Ar*H*), 7.43 (dd, *J* = 3.7, 1.1 Hz, 1H, Ar*H*), 7.29 (d, *J* = 15.3 Hz, 1H, IC*H*CH), 7.18 (dd, *J* = 5.1, 3.7 Hz, 1H, Ar*H*); ^{13}C NMR (101 MHz, MeOD/CD_2Cl_2 9:1) δ 169.8, 148.0, 140.9, 135.1, 134.2, 133.2, 132.3, 131.7, 130.7, 129.1, 128.5, 115.7, 96.3; IR (ν_{max}, cm^{-1}) 2987 (s), 2967 (s), 2907 (m), 1750 (m), 1735 (m), 1649 (m), 1573 (m), 1557 (m), 1540 (m), 1512 (m), 1452 (w), 1393 (m), 1251 (m), 1101 (w), 1068 (s), 1054 (s), 869 (m), 765 (m), 734 (m), 687 (m), 629 (s), 611 (s); HRMS (ESI/QTOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{10}IO_2S^+$ 356.9441; found 356.9442.

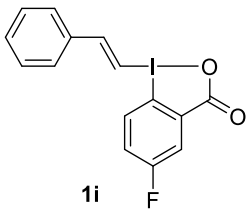
(*E*)-5-Methoxy-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1h)



1h

Following general procedure A, starting from (*E*)-styrylboronic acid (**50a**) (221 mg, 1.50 mmol) and 5-methoxy-1-hydroxy-1,2-benziodoxol-3-(1H)-one (**70b**) (382 mg, 1.30 mmol), afforded (*E*)-5-methoxy-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1h**) as a white solid (422 mg, 1.11 mmol, 85%). M.p. 167-168 °C; R_f = 0.13 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 7.95 (d, *J* = 15.4 Hz, 1H, ICHC*H*Ph), 7.82 (d, *J* = 3.0 Hz, 1H, Ar*H*), 7.74 - 7.61 (m, 3H, Ar*H* and IC*H*CHPh), 7.55 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.52 - 7.44 (m, 3H, Ar*H*), 7.25 (dd, *J* = 9.0, 3.1 Hz, 1H, Ar*H*), 3.88 (s, 3H, OC*H*$_3$); ^{13}C NMR (101 MHz, MeOD) δ 169.9, 163.7, 155.6, 136.7, 135.9, 132.1, 130.2, 129.7, 129.0, 121.7, 117.8, 103.6, 99.6, 56.4; IR (ν_{max}, cm^{-1}) 2977 (s), 2903 (m), 1617 (w), 1580 (w), 1411 (s), 1379 (s), 1259 (m), 1052 (s), 811 (m), 881 (m); HRMS (ESI/QTOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}IO_3^+$ 380.9982; found 380.9980.

(*E*)-5-Fluoro-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1i)

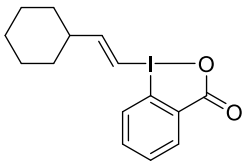


1i

Following general procedure A, starting from (*E*)-styrylboronic acid (**50a**) (221 mg, 1.50 mmol) and 1-hydroxy-5-fluoro-1,2-benziodoxol-3(1H)-one (**70c**) (367 mg, 1.30 mmol), afforded (*E*)-5-fluoro-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1i**) as a white solid (278 mg, 0.760 mmol, 58%). M.p. 174-176 °C;

R_f = 0.15 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.03 - 7.94 (m, 2H, Ar*H* and ICHC*H*Ph), 7.77 - 7.64 (m, 4H, Ar*H* and IC*H*CHPh), 7.55 - 7.44 (m, 4H, Ar*H*); ^{13}C NMR (101 MHz, MeOD) δ 168.7, 166.1 (d, *J* = 250.5 Hz), 156.1, 137.3, 136.6, 132.2, 131.0 (d, *J* = 8.4 Hz), 130.2, 129.0, 122.3 (d, *J* = 24.0 Hz), 119.8 (d, *J* = 23.9 Hz), 108.5, 99.7; ^{19}F NMR (376 MHz, MeOD) δ -113.5; IR (ν_{max}, cm^{-1}) 2987 (s), 2973 (s), 2905 (s), 1748 (m), 1737 (m), 1649 (m), 1559 (m), 1540 (m), 1512 (m), 1395 (m), 1255 (m), 1079 (s), 1054 (s), 863 (m); HRMS (ESI/QTOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{10}FINaO_2^+$ 390.9602; Found 390.9595.

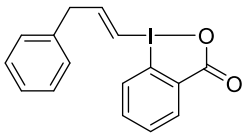
(*E*)-1-(2-Cyclohexylvinyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1j)



1j

Following general procedure B, starting from *trans*-2-cyclohexylvinyl)boronic acid (**50j**) (200 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(2-cyclohexylvinyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1j**) as a white solid (274 mg, 0.769 mmol, 59%). M.p. 136-138 °C; R_f = 0.19 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.31 - 8.24 (m, 1H, Ar*H*), 7.75 - 7.65 (m, 3H, Ar*H*), 7.13 (dd, *J* = 15.1, 7.0 Hz, 1H, ICHC*H*cy), 6.84 (dd, *J* = 15.1, 1.2 Hz, 1H, IC*H*CHcy), 2.54 - 2.41 (m, 1H, cy-*H*), 1.99 - 1.90 (m, 2H, cy-*H*), 1.89 - 1.79 (m, 2H, cy-*H*), 1.78 - 1.69 (m, 1H, cy-*H*), 1.50 - 1.21 (m, 5H, cy-*H*); ^{13}C NMR (101 MHz, MeOD) δ 170.4, 166.0, 135.6, 134.9, 133.8, 132.2, 129.2, 115.2, 99.4, 46.2, 33.2, 27.3, 27.2. The values of the NMR spectra are in accordance with reported literature data.[48]

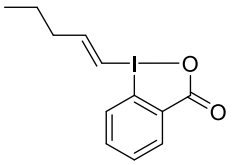
(*E*)-1-(3-Phenylprop-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1k)



1k

Following general procedure B, starting from *trans*-3-Phenyl-1-propen-1-ylboronic acid (**50k**) (211 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(3-phenylprop-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1l**) as a white solid (332 mg, 0.912 mmol, 70%). M.p. 144-145 °C; R_f = 0.18 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.30 - 8.23 (m, 1H, Ar*H*), 7.72 - 7.64 (m, 3H, Ar*H*), 7.41 - 7.23 (m, 6H, Ar*H* and ICHC*H*Bn), 6.88 (dt, *J* = 14.9, 1.5 Hz, 1H, IC*H*CHPh), 3.83 (dd, *J* = 6.9, 1.4 Hz, 2H, C*H*$_2$Ph); ^{13}C NMR (101 MHz, MeOD) δ 170.0, 159.0, 138.4, 135.2, 134.2, 133.4, 131.8, 130.0, 130.0, 129.0, 128.1, 115.0, 101.2, 42.7; IR (ν_{max}, cm^{-1}) 2987 (s), 2973 (s), 2905 (s), 1748 (m), 1737 (m), 1649 (m), 1559 (m), 1540 (m), 1512 (m), 1395 (m), 1255 (m), 1079 (s), 1054 (s), 863 (m); HRMS (ESI) calcd for $C_{16}H_{14}IO_2^+$ $[M+H]^+$ 365.0033; found 365.0033.

(*E*)-1-(Pent-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1l)

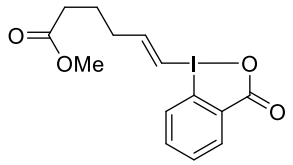


1l

Following general procedure B, starting from *trans*-1-penten-1-yboronic acid (**50l**) (148 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(pent-1-en-1-yl)-

1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1l**) as a white solid (115 mg, 0.364 mmol, 28%). M.p. (dec.) 154-160 °C; R_f = 0.15 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.34 - 8.22 (m, 1H, Ar*H*), 7.80 - 7.63 (m, 3H, Ar*H*), 7.16 (dt, *J* = 14.9, 7.0 Hz, 1H, ICHC*H*CH$_2$), 6.87 (dt, *J* = 15.0, 1.4 Hz, 1H, IC*H*CHCH$_2$), 2.49 (qd, *J* = 7.2, 1.5 Hz, 2H, CHC*H*$_2$CH$_2$), 1.65 (h, *J* = 7.4 Hz, 2H, CH$_2$C*H*$_2$CH$_3$), 1.05 (t, *J* = 7.4 Hz, 3H, CH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, MeOD) δ 169.7, 160.4, 134.9, 133.1, 131.6, 128.7, 114.7, 100.1, 38.6, 22.2, 13.7; IR (ν_{max}, cm^{-1}) 2987 (s), 2973 (s), 2905 (s), 1748 (m), 1737 (m), 1649 (m), 1559 (m), 1540 (m), 1512 (m), 1395 (m), 1255 (m), 1079 (s), 1054 (s), 863 (m); HRMS (ESI) calcd for $C_{12}H_{14}IO_2^+$ [M+H]$^+$ 317.0033; found 317.0033.

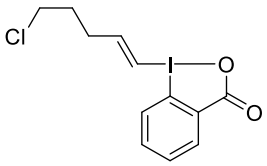
Methyl (*E*)-6-(3-oxo-1λ^3-benzo[*d*][1,2]iodaoxol-1(*3H*))-yl)hex-5-enoate (1m)



1m

Following general procedure B, starting from (E)-(6-methoxy-6-oxohex-1-en-1-yl)boronic acid (**50m**) (224 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded methyl (*E*)-6-(3-oxo-1λ^3-benzo[*d*][1,2]iodaoxol-1(*3H*))-yl)hex-5-enoate (**1m**) (210 mg, 0.561 mmol, 43%) as an off-white solid. M.p. 147-149 °C; R_f = 0.07 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.31 - 8.23 (m, 1H, Ar*H*), 7.78 - 7.64 (m, 3H, Ar*H*), 7.15 (dt, *J* = 15.0, 6.9 Hz, 1H, ICHC*H*), 6.90 (dt, *J* = 14.9, 1.4 Hz, 1H, IC*H*CH), 3.68 (s, 3H, OC*H*$_3$), 2.61 - 2.50 (m, 2H, C*H*$_2$CC), 2.46 (t, *J* = 7.3 Hz, 2H, C*H*$_2$CO$_2$Me), 1.91 (p, *J* = 7.4 Hz, 2H, CH$_2$C*H*$_2$CH$_2$); ^{13}C NMR (101 MHz, MeOD) δ 175.2, 170.0, 159.4, 135.2, 134.6, 133.3, 131.8, 129.0, 114.9, 101.1, 52.1, 35.9, 33.8, 24.3; IR (ν_{max}, cm^{-1}) 3443 (w), 3047 (w), 2958 (w), 2922 (w), 1731 (m), 1606 (s), 1557 (m), 1440 (m), 1363 (m), 1342 (m), 1294 (w), 1205 (m), 1184 (m), 1151 (m), 1005 (m), 961 (m), 830 (m); HRMS (ESI) calcd for $C_{14}H_{16}IO_4^+$ [M+H]$^+$ 375.0088; found 375.0091.

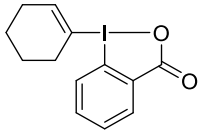
(*E*)-1-(5-Chloropent-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1n)



1n

Following general procedure B, starting from (*E*)-(5-chloropent-1-en-1-yl)boronic acid (**50n**) (193 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(5-chloropent-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1n**) as a white solid (201 mg, 0.573 mmol, 44%). M.p. 133-135 °C; R_f = 0.19 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.34 - 8.24 (m, 1H, Ar*H*), 7.83 - 7.66 (m, 3H, Ar*H*), 7.19 (dt, *J* = 15.0, 6.9 Hz, 1H, ICHC*H*CH$_2$), 6.97 (dt, *J* = 15.0, 1.5 Hz, 1H, IC*H*CHCH$_2$), 3.70 (t, *J* = 6.4 Hz, 2H, C*H*$_2$Cl), 2.76 - 2.62 (m, 2H, CH$_2$C*H*$_2$CH), 2.09 (p, *J* = 6.7 Hz, 2H, C*H*$_2$CH$_2$Cl); ^{13}C NMR (101 MHz, MeOD) δ 168.6, 157.4, 133.8, 133.1, 131.9, 130.4, 127.6, 113.5, 100.1, 43.4, 32.5, 30.4; IR (ν_{max}, cm^{-1}) 2968 (m), 2897 (m), 1719 (w), 1596 (m), 1557 (m), 1346 (m), 1276 (m), 1261 (m), 1056 (m), 961 (m), 830 (m), 751 (s); HRMS (ESI) calcd for $C_{12}H_{13}ClIO_2^+$ [M+H]$^+$ 350.9643; found 350.9645.

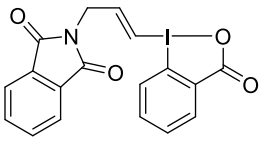
(*E*)-1-(Cyclohex-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1o)



1o

Following general procedure B, starting from 1-cyclohexenylboronic acid (**50o**) (164 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(cyclohex-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1o**) as a white solid (213 mg, 0.649 mmol, 50%). M.p. 116-118 °C; R_f = 0.15 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.28 (dt, *J* = 7.2, 1.3 Hz, 1H, Ar*H*), 7.78 - 7.66 (m, 3H, Ar*H*), 7.07 (tt, *J* = 3.9, 1.8 Hz, 1H, ICC*H*), 2.73-2.68 (m, 2H, cy-*H*), 2.53 (tq, *J* = 6.0, 3.0 Hz, 2H, cy-*H*), 1.94 (pd, *J* = 6.0, 3.6 Hz, 2H, cy-*H*), 1.88 - 1.80 (m, 2H, cy-*H*); ^{13}C NMR (101 MHz, MeOD) δ 170.0, 152.3, 135.8, 133.8, 132.0, 129.0, 118.6, 113.5, 35.2, 30.1, 25.7, 21.5; IR (ν_{max}, cm^{-1}) 2976 (w), 2934 (w), 2906 (w), 1651 (m), 1600 (s), 1558 (m), 1435 (m), 1377 (m), 1346 (m), 1332 (m), 1107 (s), 905 (s), 853 (m), 826 (m), 748 (s); HRMS (ESI) calcd for $C_{13}H_{14}IO_2^+$ $[M+H]^+$ 329.0033; found 329.0031. One carbone was not resolved at 101 MHz.

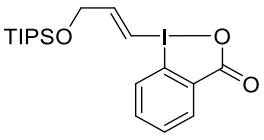
(*E*)-2-(3-(3-Oxo-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)allyl)isoindoline-1,3-dione (1p)



1p

Following general procedure B, with the addition of 2,2,2-trifluoroethanol (1.3 mL) after 3 h of reaction to dissolve the insoluble material. Starting from (*E*)-(3-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl)boronic acid (**50p**) (300 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-2-(3-(3-oxo-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)allyl)isoindoline-1,3-dione (**1p**) as a white solid (417 mg, 0.963 mmol, 74%). M.p. (dec.) 163-167 °C; R_f = 0.12 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.40 - 8.34 (m, 1H, Ar*H*), 7.98 - 7.77 (m, 7H, Ar*H*), 7.35 (dt, *J* = 14.8, 4.8 Hz, 1H, ICHC*H*), 7.21 (dt, *J* = 14.8, 1.6 Hz, 1H, IC*H*CH), 4.75 (dd, *J* = 4.8, 1.6 Hz, 2H, CH_2N); ^{13}C NMR (101 MHz, MeOD) δ 171.0, 169.2, 154.8, 137.6, 135.7, 134.1, 133.4, 132.5, 131.1, 129.1, 124.5, 114.8, 100.4, 42.0; IR (ν_{max}, cm^{-1}) 2977 (s), 2917 (s), 1722 (m), 1483 (m), 1407 (s), 1374 (m), 1261 (m), 1329 (m), 1056 (s), 875 (w); HRMS (ESI) calcd for $C_{18}H_{12}INNaO_4^+$ $[M+Na]^+$ 455.9703; found 455.9702.

(*E*)-1-(3-((Triisopropylsilyl)oxy)prop-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (1q)

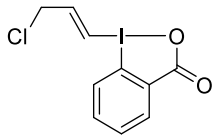


1q

Following general procedure B, starting from (*E*)-(3-((triisopropylsilyl)oxy)prop-1-en-1-yl)boronic acid (**50q**) (336 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(3-((triisopropylsilyl)oxy)prop-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (**1q**) (370 mg, 0.804 mmol, 62%) as a white solid. M.p. 157-159 °C; R_f = 0.20 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.36 - 8.26 (m, 1H, Ar*H*), 7.73 (m, 3H, Ar*H*), 7.34 (dt, *J* = 14.7, 3.2 Hz, 1H, ICHC*H*), 7.08 (dt, *J* = 14.7, 2.2 Hz, 1H, IC*H*CH), 4.71 (dd, *J* = 3.2, 2.1 Hz, 2H, CH_2O), 1.31 - 1.10 (m, 21H, TIPS); ^{13}C NMR

(101 MHz, MeOD) δ 170.3, 159.7, 135.7, 133.6, 132.9, 132.0, 129.3, 114.9, 98.7, 66.2, 18.5, 13.2; IR (ν_{max}, cm^{-1}) 3057 (w), 2944 (w), 2863 (w), 1644 (w), 1607 (w), 1264 (m), 1129 (w), 1014 (w), 943 (w), 914 (w), 734 (s), 701 (s); HRMS (ESI) calcd for $C_{19}H_{30}IO_3Si^+$ $[M+H]^+$ 461.1003; found 461.1015.

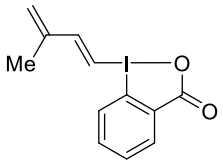
(*E*)-1-(3-Chloroprop-1-en-1-yl)-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1r)



1r

Following general procedure B, with the addition of 2,2,2-trifluoroethanol (1.3 mL) after 3 h of reaction to dissolve the insoluble material. Starting from *trans*-2-chloromethylvinylboronic acid (**50r**) (156 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(3-chloroprop-1-en-1-yl)-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1r**) as a white solid (137 mg, 0.425 mmol, 46%). M.p. (dec.) 166-170 °C; R_f = 0.10 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.37 - 8.27 (m, 1H, Ar*H*), 7.84 - 7.70 (m, 3H, Ar*H* and IC*H*C*H*CH_2), 7.33 - 7.28 (m, 2H, Ar*H*), 4.53 - 4.46 (m, 2H, CH_2Cl); ^{13}C NMR (101 MHz, MeOD) δ 170.3, 153.6, 136.0, 133.6, 132.9, 132.1, 129.6, 115.0, 104.3, 45.2; IR (ν_{max}, cm^{-1}) 2987 (s), 2973 (s), 2905 (s), 1748 (m), 1737 (m), 1649 (m), 1559 (m), 1540 (m), 1512 (m), 1395 (m), 1255 (m), 1079 (s), 1054 (s), 863 (m); HRMS (ESI) calcd for $C_{10}H_9ClIO_2^+$ $[M+H]^+$ 322.9330; found 322.9332.

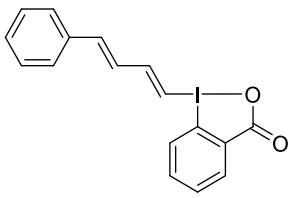
(*E*)-1-(3-Methylbuta-1,3-dien-1-yl)-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1s)



1s

Following general procedure B, starting from (*E*)-(3-methylbuta-1,3-dien-1-yl)boronic acid (**50s**) (146 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(3-methylbuta-1,3-dien-1-yl)-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1s**) as a beige solid (225 mg, 0.716 mmol, 55%). M.p. (dec.) 70-72 °C; R_f = 0.11 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.31 - 8.26 (m, 1H, Ar*H*), 7.78 - 7.61 (m, 4H, Ar*H* and ICHC*H*C), 7.09 (d, *J* = 15.2 Hz, 1H, IC*H*CHC), 5.53 - 5.42 (m, 2H, CCH_2), 2.05 (t, *J* = 1.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, MeOD) δ 170.6, 158.7, 143.6, 135.9, 134.3, 133.8, 132.3, 129.5, 126.2, 115.5, 100.5, 18.3; IR (ν_{max}, cm^{-1}) 2987 (s), 2896 (m), 1632 (w), 1584 (m), 1570 (m), 1407 (m), 1381 (m), 1261 (m), 1230 (m), 1054 (s), 873 (m), 813 (m); HRMS (ESI) calcd for $C_{12}H_{11}INaO_2^+$ $[M+Na]^+$ 336.9696; found 336.9695.

(*E*)-1-((1*E*,3*E*)-4-Phenylbuta-1,3-dien-1-yl)-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1t)

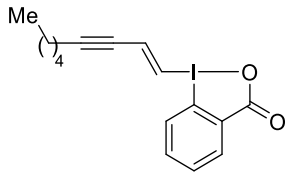


1t

Following general procedure B, starting from ((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)boronic acid (**50t**) (226 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded

(*E*)-1-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1t**) as a beige solid (196 mg, 0.520 mmol, 40%). M.p. (dec.) 169-173 °C; R_f = 0.17 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.35 - 8.27 (m, 1H, Ar*H*), 7.82 - 7.68 (m, 4H, Ar*H* and ICHC*H*), 7.62 - 7.56 (m, 2H, Ar*H*), 7.45 - 7.32 (m, 3H, Ar*H*), 7.22 (dd, *J* = 15.6, 10.6 Hz, 1H, C*H*CHPh), 7.13 (d, *J* = 14.7 Hz, 1H, IC*H*CH), 7.05 (d, *J* = 15.6 Hz, 1H, CHC*H*Ph); ^{13}C NMR (101 MHz, MeOD) δ 170.4, 156.9, 143.1, 137.2, 136.0, 133.7, 133.5, 132.2, 131.0, 130.2, 129.5, 128.9, 127.8, 115.7, 100.0; IR (ν_{max}, cm^{-1}) 2975 (s), 2911 (m), 1720 (m), 1448 (m), 1409 (s), 1381 (m), 1259 (m), 1056 (s), 873 (m), 809 (m), 782 (m); HRMS (ESI) calcd for $C_{17}H_{13}INaO_2^+$ $[M+Na]^+$ 398.9852; found 398.9852.

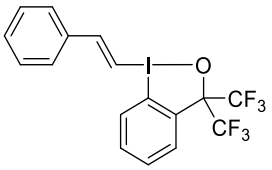
(*E*)-1-(Non-1-en-3-yn-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (1u)



1u

Following general procedure B, starting from (*E*)-non-1-en-3-yn-1-ylboronic acid (**50u**) (216 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**71**) (477 mg, 1.56 mmol), afforded (*E*)-1-(non-1-en-3-yn-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1u**) as a white solid (376 mg, 1.02 mmol, 79%). M.p. 139-141 °C; R_f = 0.26 (MeOH/DCM 5:95); ^{1}H NMR (400 MHz, MeOD) δ 8.30 - 8.22 (m, 1H, Ar*H*), 7.77 - 7.62 (m, 3H, Ar*H*), 7.33 (d, *J* = 15.5 Hz, 1H, ICHC*H*), 7.06 (dt, *J* = 15.5, 2.3 Hz, 1H, IC*H*CH), 2.47 (td, *J* = 7.0, 2.2 Hz, 2H, CCH_2CH$_2$), 1.66 - 1.56 (m, 2H, CCH$_2$CH_2), 1.51 - 1.31 (m, 4H, 2 x CH_2), 0.94 (t, *J* = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C NMR (101 MHz, MeOD) δ 170.0, 136.3, 135.4, 134.3, 133.3, 131.9, 129.1, 115.5, 111.8, 101.4, 79.2, 32.2, 29.1, 23.2, 20.2, 14.3; IR (ν_{max}, cm^{-1}) 2975 (s), 2911 (m), 1720 (m), 1448 (m), 1409 (s), 1381 (m), 1259 (m), 1056 (s), 873 (m), 809 (m), 782 (m); HRMS (ESI) calcd for $C_{16}H_{18}IO_2^+$ $[M+H]^+$ 369.0346; found 369.0340.

(*E*)-1-Styryl-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (1'a)

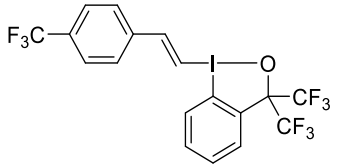


1'a

Following general procedure C, starting from *trans*-2-phenylvinylboronic acid (**50a**) (148 mg, 1.00 mmol) and 3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**71'**) (514 mg, 1.20 mmol), afforded (*E*)-1-styryl-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (**1'a**) as a white solid (450 mg, 0.950 mmol, 95%). M.p. 167-168 °C; R_f = 0.57 (EtOAc/pentane 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 1H, Ar*H*), 7.66 – 7.57 (m, 2H, Ar*H* and ICHC*H*Ph), 7.57 – 7.42 (m, 7H, Ar*H*), 7.22 (d, *J* = 16.1 Hz, 1H, IC*H*CHPh); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 135.5, 132.2, 131.1, 130.8, 130.6, 130.6, 129.3, 127.5, 127.4, 124.2 (q, *J* = 291.4 Hz), 111.3, 104.8, 81.4 (p, *J* = 29.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1; IR (ν_{max}, cm^{-1}) 3675 (w), 2987 (s), 2900 (s), 1407 (m), 1394 (m), 1260 (s), 1174 (s), 1147 (s), 1050 (s), 959 (m), 939 (s), 741 (s), 729 (s), 691 (s); HRMS (APPI/LTQ-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{17}H_{12}F_6IO^+$ 472.9832; Found 472.9827; The structure of **1'a** was confirmed by X-ray analysis. Crystals were grown by dissolving 10 mg of pure **1'a** in $CDCl_3$ (500 µL) at room temperature. Slow evaporation over one week provided suitable crystals. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (CCDC 1993681) and can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/

The reaction was scaled up to *trans*-2-phenylvinylboronic acid (**50a**) (0.740 g, 5.00 mmol) and 3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**71'**) (2.57 g, 6.00 mmol), affording (*E*)-1-styryl-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (**1'a**) (2.20 g, 4.65 mmol, 93%).

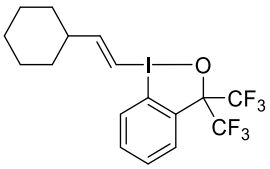
(*E*)-3,3-Bis(trifluoromethyl)-1-(4-(trifluoromethyl)styryl)-1,3-dihydro-benzo[*d*][1,2]iodaoxole (1'd)



1'd

Following general procedure C, starting from *trans*-2-[4-(trifluoromethyl)phenylvinylboronic acid (**50d**) (216 mg, 1.00 mmol) and 3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**71'**) (514 mg, 1.20 mmol), afforded (*E*)-3,3-bis(trifluoromethyl)-1-(4-(trifluoromethyl)styryl)-1,3-dihydro-benzo[*d*][1,2]iodaoxole (**1'd**) as a white solid (455 mg, 0.840 mmol, 84%). M.p. 188-187 °C; R_f = 0.73 (EtOAc/pentane 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 1H, Ar*H*), 7.76 – 7.59 (m, 6H, Ar*H* and ICHC*H*Ph), 7.59 – 7.51 (m, 1H, Ar*H*), 7.51 – 7.45 (m, 1H, Ar*H*), 7.38 (d, *J* = 16.2 Hz, 1H, IC*H*CHPh); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 138.7, 132.3, 132.3 (q, *J* = 32.8 Hz), 131.0, 130.8, 130.9 - 130.6 (m), 127.7, 127.4, 126.3 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 291.6 Hz), 123.8 (q, *J* = 272.2 Hz), 111.2, 108.7, 81.4 (p, *J* = 28.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9, -76.1; IR (ν_{max}, cm^{-1}) 2987 (m), 2900 (m), 1323 (m), 1261 (s), 1183 (s), 1152 (s), 1119 (s), 1065 (s), 945 (s), 763 (s), 731 (s), 692 (m); HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{11}F_9IO^+$ 540.9705; Found 540.9708.

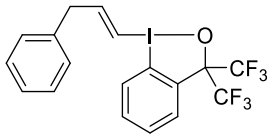
(*E*)-1-(2-Cyclohexylvinyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzobenzo[*d*][1,2]iodaoxole (1'j)



1'j

Following general procedure C, starting from *trans*-2-cyclohexylvinyl)boronic acid (**50j**) (154 mg, 1.00 mmol) and 3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**71'**) (514 mg, 1.20 mmol), afforded (*E*)-1-(2-cyclohexylvinyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzobenzo[*d*][1,2]iodaoxole (**1'j**) as a white solid (263 mg, 0.550 mmol, 55%). M.p. 170 °C; R_f = 0.55 (EtOAc/pentane 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dq, *J* = 7.7, 1.5 Hz, 1H, Ar*H*), 7.65 – 7.44 (m, 3H, Ar*H*), 6.80 (dd, *J* = 15.7, 6.7 Hz, 1H, CH=C*H*CH), 6.44 (dd, *J* = 15.7, 1.3 Hz, 1H, IC*H*=CH), 2.36 – 2.22 (m, 1H, C*H*$_{\text{-cyclohexyl}}$), 1.92 – 1.76 (m, 4H, C*H*$_{\text{-cyclohexyl}}$), 1.76 – 1.64 (m, 1H, C*H*$_{\text{-cyclohexyl}}$), 1.45 – 1.13 (m, 5H, C*H*$_{\text{-cyclohexyl}}$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 131.9, 131.2, 130.6 – 130.5 (m), 130.4, 127.1, 124.3 (q, *J* = 292.1 Hz), 110.9, 103.1, 81.4 (p, *J* = 28.7 Hz), 44.4, 32.0, 25.9, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.14; IR (ν_{max}, cm^{-1}) 2925 (w), 1256 (m), 1178 (s), 1149 (s), 1126 (m), 960 (m), 943 (s), 761 (s), 730 (s), 692 (m); HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}F_6IO^+$ 479.0301; Found 479.0309.

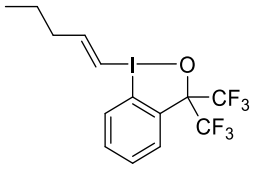
(*E*)-1-(3-Phenylprop-1-en-1-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzobenzo[*d*][1,2]iodaoxole (1'k)



1'k

Following general procedure C, starting from *trans*-3-Phenyl-1-propen-1-ylboronic acid (**50k**) (162 mg, 1.00 mmol) and 3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**71'**) (514 mg, 1.20 mmol), afforded (*E*)-1-(3-phenylprop-1-en-1-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzobenzo[*d*][1,2]iodaoxole (**1'k**) as a white solid (416 mg, 0.860 mmol, 86%). M.p. 125-126 °C; R_f = 0.36 (EtOAc/pentane 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 1H, Ar*H*), 7.58 (td, *J* = 7.4, 1.3 Hz, 1H, Ar*H*), 7.52 (ddd, *J* = 8.6, 7.0, 1.6 Hz, 1H, Ar*H*), 7.44 (dd, *J* = 8.2, 1.2 Hz, 1H, Ar*H*), 7.41 – 7.34 (m, 2H, Ar*H*), 7.33 – 7.27 (m, 1H, Ar*H*), 7.25 – 7.20 (m, 2H, Ar*H*), 7.01 (dt, *J* = 15.6, 6.5 Hz, 1H, CH_2CH=CH), 6.50 (dt, *J* = 15.6, 1.5 Hz, 1H, IC*H*=CH), 3.69 (dd, *J* = 6.5, 1.5 Hz, 2H, CH_2Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 136.9, 132.0, 131.1, 130.6 – 130.4 (m), 130.5, 129.2, 128.8, 127.3, 127.28, 124.2 (q, *J* = 291.9 Hz), 111.0, 106.8, 81.3 (p, *J* = 28.9 Hz), 42.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1; IR (ν_{max}, cm^{-1}) 3674 (m), 2972 (s), 2901 (s), 1394 (m), 1258 (s), 1212 (m), 1173 (s), 1144 (s), 1121 (m), 1049 (s), 961 (m), 942 (s), 767 (s), 750 (s), 707 (s), 693 (s), 679 (m); HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}F_6IO^+$ 486.9988; Found 486.9994.

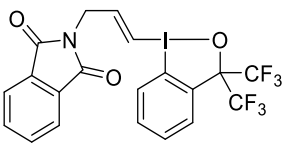
(*E*)-1-(Pent-1-en-1-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzobenzo[*d*][1,2]iodaoxole (1'l)



1'l

Following general procedure C, starting from *trans*-1-penten-1-yboronic acid (**50l**) (114 mg, 1.00 mmol) and 3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**71**) (514 mg, 1.20 mmol), afforded (*E*)-1-(pent-1-en-1-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzobenzo[*d*][1,2]iodaoxole (**1'l**) as a white solid (350 mg, 0.800 mmol, 80%). M.p. 150-151 °C; R_f = 0.39 (EtOAc/pentane 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.64 – 7.49 (m, 3H, Ar*H*), 6.87 (dt, *J* = 15.4, 6.7 Hz, 1H, CH=C*H*CH_2), 6.52 (d, *J* = 15.4 Hz, 1H, IC*H*=CH), 2.37 (q, *J* = 7.1 Hz, 2H, CHCH_2), 1.59 (h, *J* = 7.4 Hz, 2H, $CH_2CH_2CH_3$), 1.02 (t, *J* = 7.3 Hz, 3H, CH_2CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 132.0, 131.3, 130.6, 130.5, 127.3, 124.3 (q, *J* = 291.9 Hz), 111.0, 105.1, 82.5 – 80.7 (m), 38.1, 21.6, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1; IR (ν_{max}, cm^{-1}) 3669 (w), 2987 (s), 2972 (s), 2908 (s), 2851 (m), 1755 (m), 1734 (m), 1450 (m), 1250 (m), 1153 (m), 1104 (m), 1078 (s), 1057 (s), 966 (m), 739 (m); HRMS (APPI/LTQ-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}F_6IO^+$ 438.9988; Found 438.9992.

(*E*)-2-(3-(3,3-Bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)allyl)isoindoline-1,3-dione (1'p)



1'p

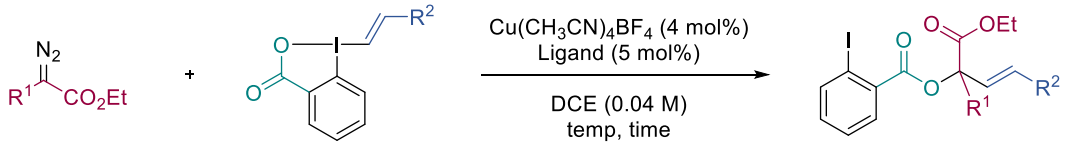
Following general procedure C, starting from (*E*)-(3-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl)boronic acid (**50p**) (231 mg, 1.00 mmol) and 3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**71'**) (514 mg, 1.20 mmol), afforded (*E*)-2-(3-(3,3-bis(trifluoromethyl)-1λ^3-

benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)allyl)isoindoline-1,3-dione (**1'p**) as a white solid (422 mg, 0.760 mmol, 76%). M.p. 179-180 °C; R_f = 0.18 (EtOAc/pentane 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.5, 3.0 Hz, 2H, Ar*H*), 7.86 – 7.74 (m, 3H, Ar*H*), 7.64 – 7.56 (m, 2H, Ar*H*), 7.56 – 7.48 (m, 1H, Ar*H*), 6.83 (dt, *J* = 15.8, 5.0 Hz, 1H, CH_2C*H*=CH), 6.72 (dt, *J* = 15.8, 1.4 Hz, 1H, CH=C*H*I), 4.56 (dd, *J* = 5.0, 1.4 Hz, 2H, NCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 146.9, 134.7, 132.5, 131.9, 130.8, 130.6, 130.6 – 130.4 (m), 127.9, 124.1 (q, *J* = 291.5 Hz), 123.9, 111.1, 109.3, 81.2 (*p*, *J* = 29.2 Hz), 41.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1; IR (ν_{max}, cm^{-1}) 3674 (m), 2973 (s), 2900 (s), 1771 (m), 1720 (s), 1421 (m), 1392 (s), 1260 (s), 1211 (m), 1173 (s), 1156 (s), 1048 (s), 978 (w), 962 (m), 944 (s), 930 (s), 761 (m), 718 (s), 693 (m); HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{13}F_6INO_3^+$ 555.9839; Found 555.9839.

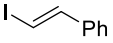
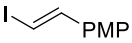
5. Optimization of the reaction

a) Table S1 - Intramolecular reaction

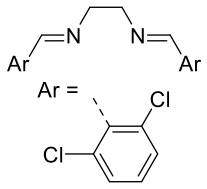
Under inert atmosphere, a solution of catalyst was prepared by mixing $Cu(CH_3CN)_4BF_4$ (12.6 mg, 40.0 µmol) and ligand (**3a-f**) (50.0 µmol) in DCE (5.0 mL) at 25 °C for 1 h. Then, 0.5 mL of the catalytic solution was then added to a stirring suspension of VBX (0.10 mmol, 1.00 equiv) and diazo compound (0.200 mmol, 1.00 equiv) in DCE (2.0 mL). After completion of the reaction, the solvent was removed under reduced pressure and the resulting crude oil was purified by column chromatography (EtOAc/pentane) directly without further work-up to afford the corresponding product.



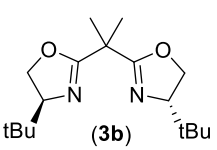
(2 equiv.) (1 equiv.)

entry	Ligand	diazo R^1 =	VBX R^2 =	temp.	time	yield[a]	by-product
1	**3a**, no Cu	H, **2a**	Ph,**1a**	40 °C	4 h	0%	
2	none	H, **2a**	Ph,**1a**	40 °C	4 h	< 5%	
3	**3a**	H, **2a**	Ph,**1a**	40 °C	4 h	90%	
4	**3a**	**Ph, 2b**	**Ph,1a**	**40 °C**	**4 h**	**80%**	 (< 10%)
5	**3a**	H, **2a**	PMP, **1c**	60 °C	24 h	50%	 (27%)
6	**3a**	H, **2a**	Cy, **1j**	60 °C	24 h	< 5%	
7	**3b**	H, **2a**	Ph,**1a**	25 °C	1 h	95%	
8	**3e**	H, **2a**	Ph,**1a**	25 °C	24 h	< 5%	
9[b]	**3c**	**H,2a**	**Ph, 1a**	**25 °C**	**1 h**	**95%**	
10[b]	**3c**	H, **2a**	PMP, **1c**	25 °C	4 h	81%	
11[b]	**3c**	H, **2a**	Cy, **1j**	25 °C	4 h	99%	
12	**3c**	Ph, **2b**	Ph,**1a**	25 °C	4 h	< 5%	
13	**3f**	H, **2a**	Ph,**1a**	25 °C	24 h	< 5%	

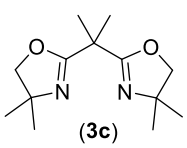
[a] Isolated yield. [b] On 0.20 mmol scale. Ph = phenyl, Cy = cyclohexyl, PMP = para-methoxyphenyl.



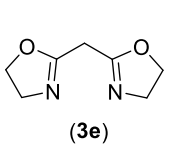
(**3a**)



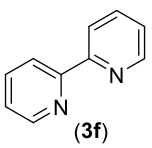
(**3b**)



(**3c**)



(**3e**)



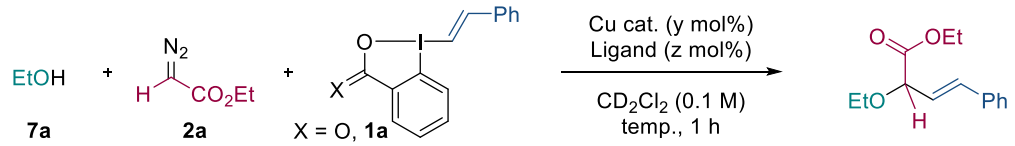
(**3f**)

Two sets of reactions conditions were identified:

- For non-substituted diazo (R^1 = H): $Cu(CH_3CN)_4BF_4$ (4 mol%) + **3c** (5 mol%) in DCE at 25 °C.
- For substituted diazo (R1 ≠ H): $Cu(CH_3CN)_4BF_4$ (4 mol%) + **3a** (5 mol%) in DCE at 40 °C.

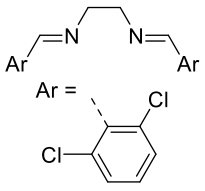
b) Table S2 - Intermolecular/3-component reaction

Under inert atmosphere, ethyl diazoacetate (**2a**) (19.0 µL, 0.16 mmol, 2.00 equiv., 87%wt in DCM) was added to a stirred solution of Ph-VBX (**1'a**) (38 mg, 80 µmol, 1.00 equiv.), EtOH (**7a**) (x equiv.) and Cu cat. (y mol%) in CD_2Cl_2 (0.8 mL). The resulting reaction mixture was stirred at 25 °C for 1 h. After this time, CH_2Br_2 (100 µL, 0.8 M in CD_2Cl_2, 0.08 mmol, 1.00 equiv.) was added as internal standard and the ^{1}H NMR spectrum of the reaction mixture was recorded.
When a ligand was used, the corresponding catalytic solution (Cu cat. + Ligand) was premixed for 1 h in CD_2Cl_2 before addition of Ph-VBX (**1'a**), EtOH (**7a**) and ethyl diazoacetate (**2a**).

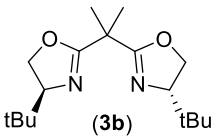


entry	EBX X =	EtOH (x equiv.)	Cu cat. (y mol%)	ligand (z mol%)	temp.	yield[a]
1	O, **1a**	as solvent	$Cu(CH_3CN)_4BF_4$ (4 mol%)	**3b** (5 mol%)	25 °C	30%
2	$(CF_3)_2$, **1'a**	4.00	$Cu(CH_3CN)_4PF_6$ (10 mol%)	-	25 °C	43%
3	$(CF_3)_2$, **1'a**	4.00	$Cu(CH_3CN)_4PF_6$ (5 mol%)	-	25 °C	45%
4	$(CF_3)_2$, **1'a**	4.00	$Cu(CH_3CN)_4PF_6$ (5 mol%)	**3a** (5 mol%)	25 °C	28%
5	$(CF_3)_2$, **1'a**	4.00	$Cu(CH_3CN)_4PF_6$ (5 mol%)	**3c** (5 mol%)	25 °C	14%
6	$(CF_3)_2$, **1'a**	10.0	$Cu(CH_3CN)_4PF_6$ (5 mol%)	-	25°C	18%
7	$(CF_3)_2$, **1'a**	2.00	$Cu(CH_3CN)_4PF_6$ (5 mol%)	-	25 °C	38%
8	$(CF_3)_2$, **1'a**	3.00	$Cu(CH_3CN)_4PF_6$ (5 mol%)	-	25 °C	51%
9	$(CF_3)_2$, **1'a**	3.00	$Cu(CH_3CN)_4BF_4$ (5 mol%)	-	25 °C	54%
10	$(CF_3)_2$, **1'a**	3.00	CuOTf toluene (5 mol%)	-	25 °C	<5%
11	$(CF_3)_2$, **1'a**	3.00	CuTC (5 mol%)	-	25 °C	13%
12	$(CF_3)_2$, **1'a**	3.00	CuCl (5 mol%)	-	25 °C	14%
13	$(CF_3)_2$, **1'a**	3.00	$CuCl_2$ (5 mol%)	-	25 °C	18%
14[b]	**$(CF_3)_2$, 1'a**	**3.00**	**$Cu(CH_3CN)_4BF_4$ (5 mol%)**	**-**	**25 °C**	**59%**
15[b]	$(CF_3)_2$, **1'a**	3.00	$Cu(CH_3CN)_4BF_4$ (5 mol%)	-	0 °C	< 5%
16[b]	$(CF_3)_2$, **1'a**	3.00	$Cu(CH_3CN)_4BF_4$ (5 mol%)	-	40 °C	49%

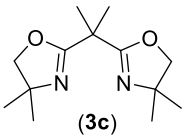
[a] Determined by ^1H NMR analysis. [b] **2a** was slowly added in 1 h as a 0.6 M solution in CD_2Cl_2 using a seringe pump.



(**3a**)



(**3b**)



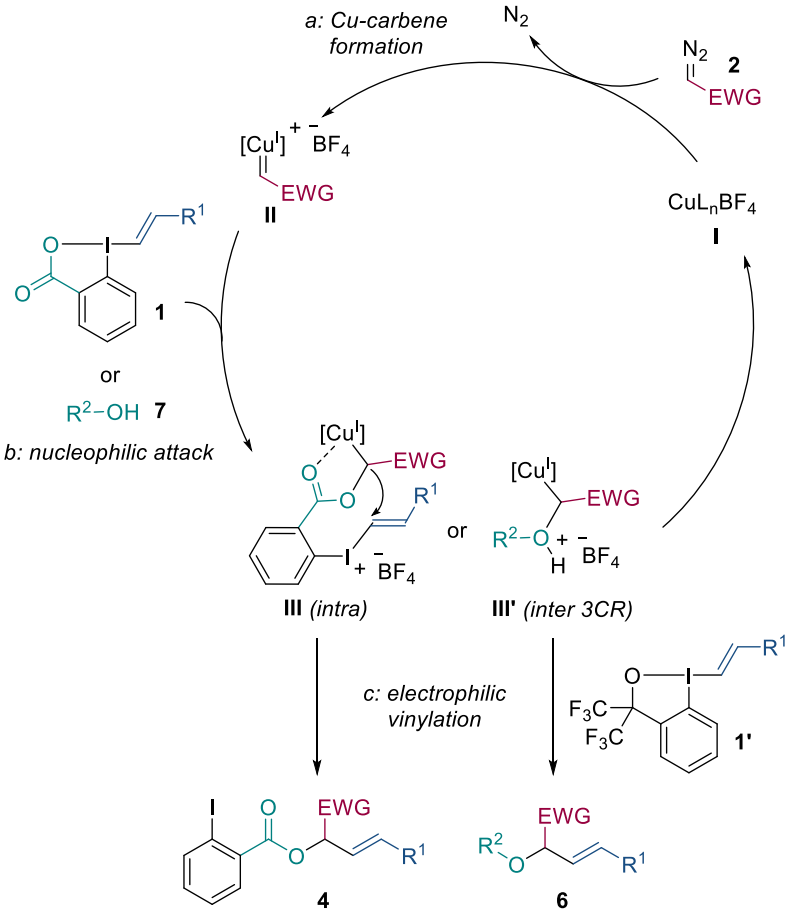
(**3c**)

In line with our previous work,[49] no competitive intramolecular reaction was observed with non-nucleophilic Ph-VBX **1'a**. The reaction perfomed better without additional ligand. $Cu(CH_3CN)_4BF_4$ (5 mol%) was the optimal catalyst found.

[49] G. Pisella, A. Gagnebin, and J. Waser, *Chem. Eur. J.* **2020**, DOI: 10.1002/chem.202001317.

6. Reaction mechanism

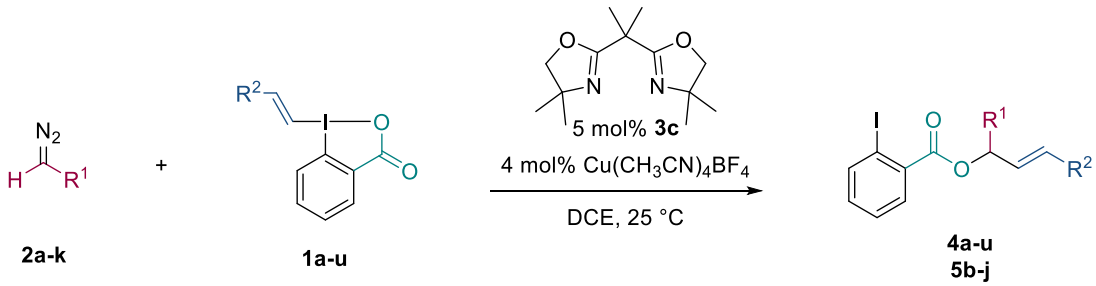
Scheme S1 – Proposed reaction mechanism



Starting with Cu(I) catalyst **I**, decomposition of diazo compound **2** would generate electrophilic copper-carbene **II**. At this stage, nucleophilic attack of the carboxylate part of the VBX reagent **1** forms copper-iodonium intermediate **III**. Direct intramolecular electrophilic vinylation leads to product **4** and regenerates catalyst **I**; With bis-trifluoromethyl reagents **1'**, the oxygen atom of the benziodoxole is not nucleophilic enough, and attack of the external alcohol **7** forms oxonium-ylide intermediate **III'**. Intermolecular alkenylation by VBX reagent **1'** with simultaneous deprotonation then generates the 3-component product **6** and release the copper catalyst **I**.

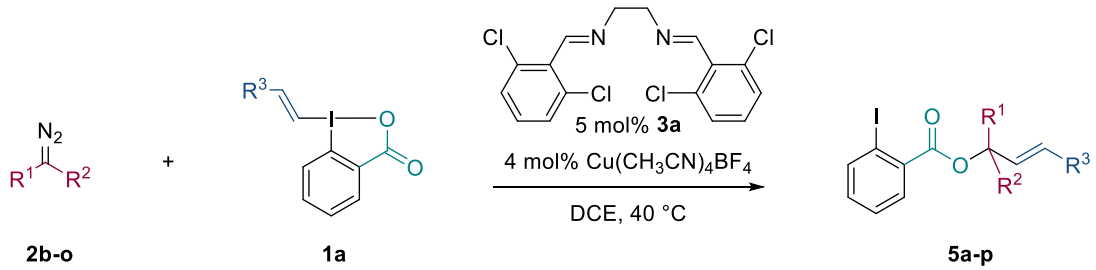
7. Oxy-vinylation reaction with VBX reagents

General procedure D: Oxy-vinylation of unsubstituted diazo compound:



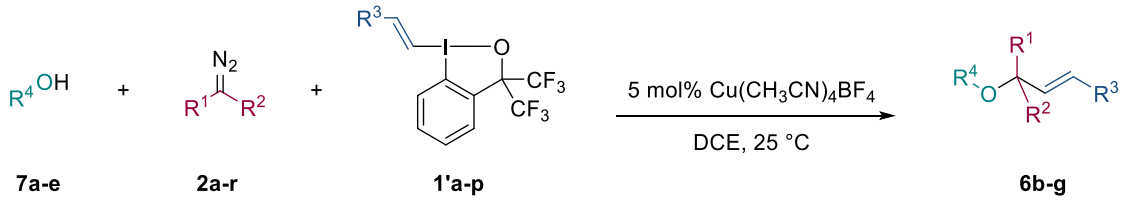
Under inert atmosphere, a catalytic solution was prepared by mixing $Cu(CH_3CN)_4BF_4$ (12.6 mg, 40.0 µmol) and 2,2'-(propane-2,2-diyl)bis(4,4-dimethyl-4,5-dihydrooxazole) (**3c**) (11.9 mg, 50.0 µmol) in DCE (5.0 mL) at 25 °C for 1 h.
1.0 mL of the catalytic solution was then added to a suspension of VBX (**1a-u**) (0.200 mmol, 1.00 equiv) and diazo compound (**2a-k**) (0.400 mmol, 2.00 equiv) in DCE (4.0 mL).
The reaction mixture was stirred at 25 °C. After the reaction was completed (monitored by TLC, EtOAc/pentane 5:95 and MeOH/DCM 5:95), the solvent was removed under reduced pressure and the resulting crude oil was purified by column chromatography (EtOAc/pentane) directly without further work-up to afford the corresponding product (**4a-u; 5b-j**).

General procedure E: Oxy-vinylation of substituted diazo compound:



Under inert atmosphere, a catalytic solution was prepared by mixing $Cu(CH_3CN)_4BF_4$ (12.6 mg, 40.0 µmol) and (1*E*,1'*E*)-*N*,*N*'-(ethane-1,2-diyl)bis(1-(2,6-dichlorophenyl)methanimine) (**3a**) (18.7 mg, 50.0 µmol) in DCE (5.0 mL) at 25 °C for 1 h.
1.0 mL of the catalytic solution was then added to a suspension of Ph-VBX (**1a**) (0.200 mmol, 1.00 equiv) and diazo compound (**2b-o**) (0.400 mmol, 2.00 equiv) in DCE (4.0 mL).
The reaction mixture was stirred at 40 °C. After the reaction was completed (monitored by TLC, EtOAc/pentane 5:95 and MeOH/DCM 5:95), the solvent was removed under reduced pressure and the resulting crude oil was purified by column chromatography (EtOAc/pentane, ratio indicated in the R_f measurement) directly without further work-up to afford the corresponding product (**5a-p**).

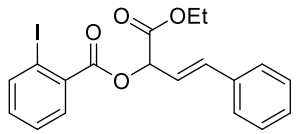
General procedure F: Oxy-vinylation of diazo compound, three-component reaction:



An oven-dried 10 mL microwave vial was charged with $Cu(CH_3CN)_4BF_4$ (4.72 mg, 15.0 µmol, 0.05 equiv.), VBX reagent (**1'a-p**) (0.30 mmol, 1.00 equiv.) and alcohol (**7a-e**) (0.90 mmol, 3.00 equiv.), if

solid. The vial was capped, removed from the glovebox and dry DCM (3.0 mL) was added. The alcohol was added at this point if liquid. To the resulting solution was added a 0.6 M solution of diazo compound (**2a-r**) (0.60 mmol, 2.00 equiv.) in dry DCM (1.0 mL) in 1 h *via* seringe pump at 25 °C. At the end of the addition, the reaction was continued for 1 h at the same temperature. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography using EtOAc/pentane as eluent (the solvent ratio indicated in the Rf measurement was used), directly without further work-up to afford the corresponding product (**6b-g**).

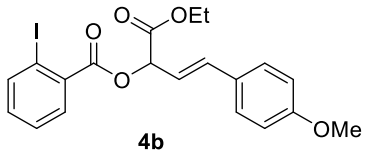
(*E*)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (4a)



4a

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**4a**) as a colorless oil (83 mg, 0.19 mmol, 95%). R_f = 0.24 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (ddd, *J* = 10.8, 7.9, 1.4 Hz, 2H, Ar*H*), 7.49 - 7.41 (m, 3H, Ar*H*), 7.38 - 7.27 (m, 3H, Ar*H*), 7.19 (ddd, *J* = 7.9, 7.4, 1.7 Hz, 1H, Ar*H*), 6.93 (dd, *J* = 15.9, 1.2 Hz, 1H, CHC*H*Ph), 6.38 (dd, *J* = 15.9, 7.1 Hz, 1H, C*H*CHPh), 5.87 (dd, *J* = 7.1, 1.3 Hz, 1H, OC*H*CC), 4.29 (qd, *J* = 7.1, 2.4 Hz, 2H, OC*H*$_2$CH$_3$), 1.32 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 165.6, 141.6, 135.8, 135.7, 134.2, 133.2, 131.7, 128.8, 128.8, 128.1, 127.0, 120.7, 94.6, 74.3, 62.2, 14.3; IR (ν_{max}, cm^{-1}) 2978 (m), 2902 (m), 1735 (s), 1582 (w), 1451 (m), 1395 (m), 1369 (m), 1278 (s), 1258 (s), 1199 (m), 1129 (m), 1098 (s), 1044 (s), 1016 (s), 966 (m), 863 (m), 764 (s), 750 (s); HRMS (ESI) calcd for $C_{19}H_{17}INaO_4^+$ [M+Na]$^+$ 459.0064; found 459.0070.

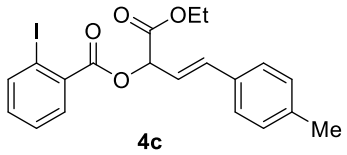
(*E*)-1-Ethoxy-4-(4-methoxyphenyl)-1-oxobut-3-en-2-yl 2-iodobenzoate (4b)



4b

Following general procedure D, starting from (*E*)-1-(4-methoxystyryl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1b**) (76.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-4-(4-methoxyphenyl)-1-oxobut-3-en-2-yl 2-iodobenzoate (**4b**) as a colorless oil (76 mg, 0.16 mmol, 81%). R_f = 0.12 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 - 7.95 (m, 2H, Ar*H*), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.40 - 7.34 (m, 2H, Ar*H*), 7.18 (ddd, *J* = 7.9, 7.4, 1.7 Hz, 1H, Ar*H*), 6.90 - 6.82 (m, 3H, Ar*H* and CHC*H*Ph), 6.23 (dd, *J* = 15.9, 7.4 Hz, 1H, C*H*CHPh), 5.83 (dd, *J* = 7.4, 1.2 Hz, 1H, OC*H*CC), 4.28 (qd, *J* = 7.1, 3.0 Hz, 2H, OC*H*$_2$CH$_3$), 3.81 (s, 3H, ArOC*H*$_3$), 1.31 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 165.7, 160.1, 141.6, 135.6, 134.2, 133.2, 131.7, 128.4, 128.3, 128.1, 118.3, 114.2, 94.5, 74.6, 62.1, 55.5, 14.3; IR (ν_{max}, cm^{-1}) 2933 (m), 2862 (w), 2091 (w), 1731 (s), 1607 (m), 1582 (w), 1511 (s), 1465 (m), 1288 (m), 1248 (s), 1194 (m), 1175 (s), 1128 (m), 1096 (s), 1015 (s), 969 (m), 824 (m); HRMS (ESI) calcd for $C_{20}H_{19}INaO_5^+$ [M+Na]$^+$ 489.0169; found 489.0169.

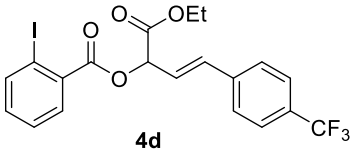
(*E*)-1-Ethoxy-1-oxo-4-(*p*-tolyl)but-3-en-2-yl 2-iodobenzoate (4c)



4c

Following general procedure D, starting from (*E*)-1-(4-methylstyryl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1c**) (72.8 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-4-(*p*-tolyl)but-3-en-2-yl 2-iodobenzoate (**4c**) as a colorless oil (83 mg, 0.18 mmol, 92%). R_f = 0.26 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (ddd, *J* = 9.7, 7.9, 1.4 Hz, 2H, Ar*H*), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.37 - 7.29 (m, 2H, Ar*H*), 7.23 - 7.12 (m, 3H, Ar*H*), 6.93 - 6.85 (m, 1H, CHC*H*Ph), 6.32 (dd, *J* = 15.9, 7.2 Hz, 1H, C*H*CHPh), 5.85 (dd, *J* = 7.2, 1.3 Hz, 1H, OC*H*CC), 4.28 (qd, *J* = 7.1, 2.2 Hz, 2H, OCH_2CH$_3$), 2.35 (s, 3H, ArCH_3), 1.31 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 165.6, 141.6, 138.8, 135.8, 134.2, 133.2, 132.9, 131.7, 129.5, 128.1, 126.9, 119.6, 94.5, 74.5, 62.1, 21.4, 14.3; IR (ν_{max}, cm^{-1}) 2979 (m), 2906 (m), 1732 (s), 1462 (m), 1429 (m), 1372 (m), 1294 (s), 1239 (s), 1198 (s), 1127 (s), 1098 (s), 1041 (s), 1014 (s), 965 (s), 855 (m), 810 (m), 740 (s); HRMS (ESI) calcd for $C_{20}H_{19}INaO_4^+$ $[M+Na]^+$ 473.0220; found 473.0220.

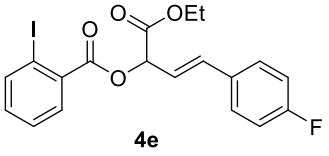
(*E*)-1-Ethoxy-1-oxo-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl 2-iodobenzoate (4d)



4d

Following general procedure D, starting from (*E*)-1-(4-(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1d**) (84.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl 2-iodobenzoate (**4d**) as a colorless oil (73 mg, 0.15 mmol, 72%). R_f = 0.22 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (ddd, *J* = 15.1, 7.9, 1.4 Hz, 2H, Ar*H*), 7.60 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.53 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.46 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.24 - 7.17 (m, 1H, Ar*H*), 6.96 (dd, *J* = 16.0, 1.4 Hz, 1H, CHC*H*Ph), 6.48 (dd, *J* = 16.0, 6.6 Hz, 1H, C*H*CHPh), 5.91 (dd, *J* = 6.7, 1.4 Hz, 1H, OC*H*CC), 4.30 (qd, *J* = 7.1, 2.3 Hz, 2H, OCH_2CH$_3$), 1.33 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 165.5, 141.7, 139.2, 134.0, 133.9, 133.4, 131.7, 130.5 (q, *J* = 32.6 Hz), 128.2, 127.2, 125.8 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 272.0 Hz), 123.5, 94.6, 73.8, 62.4, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; IR (ν_{max}, cm^{-1}) 2979 (m), 2914 (m), 1732 (m), 1466 (w), 1415 (m), 1374 (w), 1325 (s), 1243 (s), 1196 (m), 1166 (m), 1108 (s), 1067 (s), 1047 (s), 1014 (s), 969 (m), 857 (m), 822 (m), 742 (s); HRMS (ESI) calcd for $C_{20}H_{16}F_3INaO_4^+$ $[M+Na]^+$ 526.9938; found 526.9951.

(*E*)-1-Ethoxy-4-(4-fluorophenyl)-1-oxobut-3-en-2-yl 2-iodobenzoate (4e)

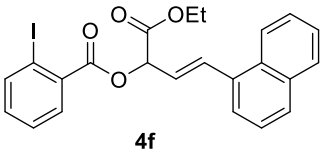


4e

Following general procedure D, starting from (*E*)-1-(4-fluorostyryl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1e**) (73.6 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-4-(4-fluorophenyl)-1-oxobut-3-en-2-yl 2-iodobenzoate (**4e**) as a colorless oil (60 mg, 0.13 mmol, 66%). R_f = 0.22 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.9, 1.2 Hz, 1H, Ar*H*), 7.99 (dd, *J* = 7.8, 1.8 Hz, 1H, Ar*H*), 7.50 - 7.36 (m, 3H, Ar*H*), 7.19 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.08 - 6.99 (m, 2H, Ar*H*), 6.93 - 6.84 (m, 1H, CHC*H*Ph), 6.30 (dd, *J* = 15.9, 7.1 Hz, 1H, C*H*CHPh),

5.85 (dd, *J* = 7.1, 1.3 Hz, 1H, OC*H*CC), 4.28 (qd, *J* = 7.1, 3.2 Hz, 2H, OC*H*$_2$CH$_3$), 1.32 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 165.6, 163.0 (d, *J* = 248.5 Hz), 141.6, 134.6, 134.1, 133.3, 131.9 (d, *J* = 3.3 Hz), 131.7, 128.7 (d, *J* = 8.2 Hz), 128.2, 120.5 (d, *J* = 2.2 Hz), 115.8 (d, *J* = 21.7 Hz), 94.5, 74.2, 62.2, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.7; IR (ν_{max}, cm^{-1}) 2981 (m), 2932 (w), 1734 (s), 1601 (m), 1585 (m), 1509 (s), 1466 (m), 1423 (m), 1376 (m), 1290 (s), 1211 (s), 1131 (s), 1104 (s), 1016 (s), 967 (m), 859 (m), 826 (m), 740 (s), 716 (m); HRMS (ESI) calcd for $C_{19}H_{16}FINaO_4^+$ $[M+Na]^+$ 476.9970; found 476.9971.

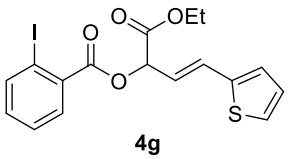
(*E*)-1-Ethoxy-4-(naphthalen-1-yl)-1-oxobut-3-en-2-yl 2-iodobenzoate (4f)



4f

Following general procedure D, starting from (*E*)-1-(2-(naphthalen-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1f**) (80.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-4-(naphthalen-1-yl)-1-oxobut-3-en-2-yl 2-iodobenzoate (**4f**) as a white solid (79 mg, 0.16 mmol, 81%). M.p. 59-61 °C; R_f = 0.18 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 - 8.09 (m, 1H, Ar*H*), 8.04 (dt, *J* = 7.8, 1.4 Hz, 2H, Ar*H*), 7.91 - 7.78 (m, 2H, Ar*H*), 7.71 (d, *J* = 15.7 Hz, 1H, CHC*H*Ph), 7.64 (dt, *J* = 7.2, 1.0 Hz, 1H, Ar*H*), 7.58 - 7.42 (m, 4H, Ar*H*), 7.20 (ddd, *J* = 7.9, 7.4, 1.7 Hz, 1H, Ar*H*), 6.44 (dd, *J* = 15.7, 6.9 Hz, 1H, C*H*CHPh), 6.01 (dd, *J* = 6.9, 1.4 Hz, 1H, OC*H*CC), 4.33 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 1.35 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 165.7, 141.6, 134.2, 133.7, 133.5, 133.3, 133.1, 131.7, 131.2, 129.0, 128.7, 128.2, 126.5, 126.1, 125.7, 124.5, 123.9, 123.8, 94.5, 74.4, 62.2, 14.3; IR (ν_{max}, cm^{-1}) 3057 (w), 2985 (m), 2904 (m), 1732 (s), 1583 (m), 1464 (m), 1429 (m), 1395 (m), 1370 (m), 1335 (m), 1284 (s), 1241 (s), 1192 (s), 1131 (s), 1094 (s), 1016 (s), 967 (s), 859 (m), 775 (s), 736 (s); HRMS (ESI) calcd for $C_{23}H_{19}INaO_4^+$ $[M+Na]^+$ 509.0220; found 509.0233.

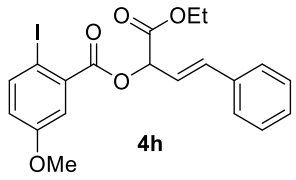
(*E*)-1-Ethoxy-1-oxo-4-(thiophen-2-yl)but-3-en-2-yl 2-iodobenzoate (4g)



4g

Following general procedure D, starting from (*E*)-1-(2-(thiophen-2-yl)vinyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1g**) (71.2 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 mL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-4-(thiophen-2-yl)but-3-en-2-yl 2-iodobenzoate (**4g**) as a clear yellow oil (67 mg, 0.15 mmol, 76%). R_f = 0.24 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 - 7.95 (m, 2H, Ar*H*), 7.45 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.24 (dt, *J* = 5.0, 0.9 Hz, 1H, Ar*H*), 7.19 (ddd, *J* = 7.9, 7.4, 1.7 Hz, 1H, Ar*H*), 7.08 - 7.00 (m, 2H, Ar*H* and CHC*H*Ph), 6.99 (dd, *J* = 5.1, 3.6 Hz, 1H, Ar*H*), 6.20 (dd, *J* = 15.7, 7.2 Hz, 1H, C*H*CHPh), 5.82 (dd, *J* = 7.2, 1.3 Hz, 1H, OC*H*CC), 4.28 (qq, *J* = 7.1, 3.6 Hz, 2H, OC*H*$_2$CH$_3$), 1.32 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 165.6, 141.6, 140.6, 134.1, 133.3, 131.7, 128.9, 128.2, 127.7, 127.6, 125.8, 119.9, 94.6, 74.1, 62.2, 14.3; IR (ν_{max}, cm^{-1}) 3057 (w), 2985 (m), 2904 (m), 1732 (s), 1583 (m), 1464 (m), 1429 (m), 1395 (m), 1370 (m), 1335 (m), 1284 (s), 1241 (s), 1192 (s), 1131 (s), 1094 (s), 1016 (s), 967 (s), 859 (m), 775 (s), 736 (s); HRMS (ESI) calcd for $C_{17}H_{15}IO_4S$ $[M^+]$ 441.9730; found 441.9733.

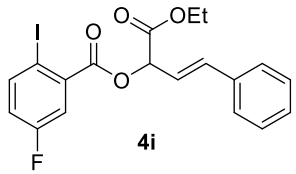
(*E*)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodo-5-methoxybenzoate (4h)



4h

Following general procedure D, starting from (*E*)-5-methoxy-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1h**) (76.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodo-5-methoxybenzoate (**4h**) as a colorless oil (78 mg, 0.17 mmol, 84%). R_f = 0.14 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.52 (d, *J* = 3.1 Hz, 1H, Ar*H*), 7.48 - 7.41 (m, 2H, Ar*H*), 7.39 - 7.27 (m, 3H, Ar*H*), 6.93 (dd, *J* = 16.0, 1.2 Hz, 1H, CHC*H*Ph), 6.79 (dd, *J* = 8.7, 3.1 Hz, 1H, Ar*H*), 6.38 (dd, *J* = 15.9, 7.1 Hz, 1H, C*H*CHPh), 5.85 (dd, *J* = 7.1, 1.3 Hz, 1H, OC*H*CC), 4.29 (qd, *J* = 7.1, 2.8 Hz, 2H, OC*H*$_2$CH$_3$), 3.84 (s, 3H, ArOC*H*$_3$), 1.32 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 165.5, 159.7, 142.1, 135.8, 135.7, 135.0, 128.8, 128.8, 127.0, 120.7, 119.8, 117.2, 82.8, 74.4, 62.1, 55.7, 14.3; IR (ν_{max}, cm^{-1}) 2986 (w), 2937 (w), 1736 (s), 1590 (m), 1565 (m), 1469 (m), 1449 (m), 1394 (m), 1368 (m), 1313 (m), 1284 (s), 1241 (s), 1213 (s), 1184 (s), 1092 (s), 1046 (s), 1029 (s), 1009 (s), 966 (s), 911 (m), 811 (m), 777 (m), 732 (s), 693 (s); HRMS (ESI) calcd for $C_{20}H_{19}IO_5$ [M$^+$] 466.0272; found 466.0276.

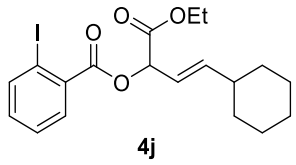
(*E*)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl 5-fluoro-2-iodobenzoate (4i)



4i

Following general procedure D, starting from (*E*)-5-fluoro-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1i**) (73.6 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 5-fluoro-2-iodobenzoate (**4i**) as a colorless oil (77 mg, 0.17 mmol, 85%). R_f = 0.34 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.7, 5.3 Hz, 1H, Ar*H*), 7.73 (dd, *J* = 8.9, 3.1 Hz, 1H, Ar*H*), 7.48 - 7.41 (m, 2H, Ar*H*), 7.39 - 7.28 (m, 3H, Ar*H*), 7.01 - 6.88 (m, 2H, Ar*H* and CHC*H*Ph), 6.37 (dd, *J* = 15.9, 7.2 Hz, 1H, C*H*CHPh), 5.85 (dd, *J* = 7.2, 1.3 Hz, 1H, OC*H*CC), 4.29 (qd, *J* = 7.1, 3.3 Hz, 2H, OC*H*$_2$CH$_3$), 1.32 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 164.5 (d, *J* = 2.6 Hz), 162.5 (d, *J* = 249.7 Hz), 143.0 (d, *J* = 7.3 Hz), 136.1, 135.6 (d, *J* = 7.3 Hz), 135.6, 128.9, 127.0, 120.9 (d, *J* = 21.4 Hz), 120.4, 119.2 (d, *J* = 24.2 Hz), 87.6 (d, *J* = 3.6 Hz), 74.6, 62.3, 14.3; ^{19}F NMR (376 MHz, CDCl3) δ -113.0; IR (ν_{max}, cm^{-1}) 1736 (s), 1575 (m), 1465 (m), 1449 (m), 1394 (m), 1370 (m), 1296 (m), 1264 (s), 1241 (s), 1188 (s), 1127 (m), 1084 (m), 1017 (s), 964 (m), 819 (m), 777 (m), 734 (s), 691 (m); HRMS (ESI) calcd for $C_{19}H_{16}FIO_4$ [M$^+$] 454.0072; found 454.0074. One carbon was not resolved at 101 MHz.

(*E*)-4-Cyclohexyl-1-ethoxy-1-oxobut-3-en-2-yl 2-iodobenzoate (4j)

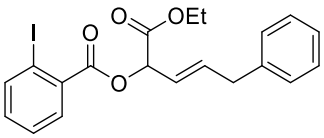


4j

Following general procedure D, starting from (*E*)-1-(2-cyclohexylvinyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1j**) (71.2 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-5-phenylpent-3-en-2-yl 2-iodobenzoate (**4j**) as a colorless oil (88 mg, 0.20 mmol, 99%). R_f = 0.37 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.2

Hz, 1H, Ar*H*), 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.17 (ddd, *J* = 7.9, 7.4, 1.7 Hz, 1H, Ar*H*), 6.04 - 5.94 (m, 1H, CHC*H*cy), 5.66 - 5.57 (m, 2H, C*H*CHy and OC*H*CC), 4.24 (qd, *J* = 7.1, 2.7 Hz, 2H, OC*H*$_2$CH$_3$), 2.98 (m, 1H, cy-*H*), 1.80 - 1.69 (m, 4H, cy-*H*), 1.69 - 1.61 (m, 1H, cy-*H*), 1.34 - 1.03 (m, 8H, cy-*H* and OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 165.7, 143.9, 141.5, 134.3, 133.1, 131.7, 128.1, 119.4, 94.5, 74.6, 61.8, 40.6, 32.5 – 32.3 (2 s, rotamer), 32.5, 32.4, 26.2, 26.0, 14.3; IR (ν_{max}, cm^{-1}) 2977 (m), 2920 (m), 2848 (m), 1736 (s), 1579 (m), 1450 (m), 1286 (s), 1239 (s), 1190 (s), 1133 (s), 1100 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for $C_{19}H_{23}INaO_4^+$ $[M+Na]^+$ 465.0533; found 465.0542.

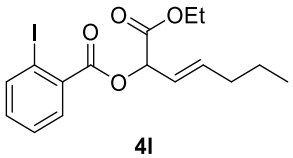
(*E*)-1-Ethoxy-1-oxo-5-phenylpent-3-en-2-yl 2-iodobenzoate (4k)



4k

Following general procedure D, starting from (*E*)-1-(3-phenylprop-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1k**) (72.8 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-5-phenylpent-3-en-2-yl 2-iodobenzoate (**4k**) as a colorless oil (81 mg, 0.18 mmol, 90%). R_f = 0.26 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar*H*), 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.35 - 7.27 (m, 2H, Ar*H*), 7.25 - 7.13 (m, 4H, Ar*H*), 6.22 (dtd, *J* = 14.7, 6.8, 0.8 Hz, 1H, CHC*H*Bn), 5.80 - 5.66 (m, 2H, C*H*CHBn and OC*H*CC), 4.26 (qd, *J* = 7.1, 2.4 Hz, 2H, OC*H*$_2$CH$_3$), 3.50 - 3.43 (m, 2H, CHC*H*$_2$Ph), 1.29 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 165.5, 141.4, 138.9, 136.3, 134.1, 133.0, 131.5, 128.6, 128.6, 128.0, 126.4, 123.1, 94.4, 74.0, 61.8, 38.6, 14.2; IR (ν_{max}, cm^{-1}) 2981 (w), 2918 (m), 1732 (s), 1456 (m), 1429 (m), 1288 (s), 1237 (s), 1200 (s), 1129 (s), 1098 (s), 1016 (s), 973 (s), 742 (s), 699 (s); HRMS (ESI) calcd for $C_{20}H_{19}INaO_4^+$ $[M+Na]^+$ 473.0220; found 473.0223.

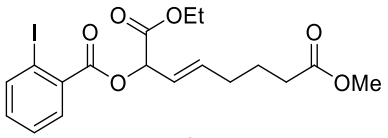
(*E*)-1-Ethoxy-1-oxohept-3-en-2-yl 2-iodobenzoate (4l)



4l

Following general procedure D, starting from (*E*)-1-(1-(pent-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1l**) (63.2 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxohept-3-en-2-yl 2-iodobenzoate (**4l**) as a colorless oil (76 mg, 0.19 mmol, 94%). R_f = 0.37 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar*H*), 7.95 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.21 - 7.12 (m, 1H, Ar*H*), 6.10 - 5.99 (m, 1H, CHC*H*CH$_2$), 5.72 - 5.60 (m, 2H, C*H*CHCH$_2$ and OC*H*CC), 4.25 (td, *J* = 7.2, 6.7 Hz, 2H, OC*H*$_2$CH$_3$), 2.15 - 2.05 (m, 2H, CHC*H*$_2$CH$_2$), 1.45 (h, *J* = 7.3 Hz, 2H, CH$_2$C*H*$_2$CH$_3$), 1.29 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 0.91 (t, *J* = 7.4 Hz, 3H, CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 165.7, 141.6, 138.4, 134.3, 133.1, 131.7, 128.1, 121.9, 94.5, 74.5, 61.8, 34.5, 21.9, 14.3, 13.7; IR (ν_{max}, cm^{-1}) 2959 (m), 2928 (m), 2867 (m), 1732 (s), 1591 (m), 1464 (m), 1431 (m), 1368 (m), 1284 (s), 1239 (s), 1192 (s), 1131 (s), 1096 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for $C_{16}H_{19}INaO_4^+$ $[M+Na]^+$ 425.0220; found 425.0232.

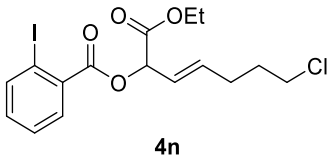
(*E*)-1-Ethyl 8-methyl 2-((2-iodobenzoyl)oxy)oct-3-enedioate (4m)



4m

Following general procedure D, starting from methyl (*E*)-6-(3-oxo-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-one (**1m**) (74.8 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethyl 8-methyl 2-((2-iodobenzoyl)oxy)oct-3-enedioate (**4m**) as a colorless oil (77 mg, 0.17 mmol, 84%). R_f = 0.13 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar*H*), 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.21 - 7.14 (m, 1H, Ar*H*), 6.01 (dtd, *J* = 14.8, 6.8, 0.8 Hz, 1H, CHC*H*CH$_2$), 5.75 - 5.60 (m, 2H, OC*H*CC and *CH*CHCH$_2$), 4.24 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 3.66 (s, 3H, OC*H*$_3$), 2.32 (t, *J* = 7.5 Hz, 2H, C*H*$_2$CO$_2$Me), 2.21 - 2.12 (m, 2H, CHC*H*$_2$CH$_2$), 1.76 (p, *J* = 7.3 Hz, 2H, CH$_2$C*H*$_2$CH$_2$), 1.29 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 168.7, 165.6, 141.5, 136.9, 134.2, 133.1, 131.6, 128.1, 122.8, 94.5, 74.2, 61.9, 51.7, 33.3, 31.7, 23.9, 14.3; IR (ν_{max}, cm^{-1}) 2956 (w), 1735 (s), 1606 (s), 1436 (m), 1367 (w), 1344 (m), 1292 (m), 1238 (m), 1209 (m), 1157 (m), 1096 (m), 1017 (s), 965 (m), 834 (m); HRMS (ESI) calcd for $C_{18}H_{21}INaO_6^+$ $[M+Na]^+$ 483.0275; found 483.0280.

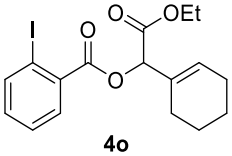
(*E*)-7-Chloro-1-ethoxy-1-oxohept-3-en-2-yl 2-iodobenzoate (4n)



4n

Following general procedure D, starting from (*E*)-1-(5-chloropent-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1n**) (70.1 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-7-chloro-1-ethoxy-1-oxohept-3-en-2-yl 2-iodobenzoate (**4n**) as a colorless oil (82 mg, 0.19 mmol, 94%). R_f = 0.20 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.1 Hz, 1H, Ar*H*), 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.02 (dtd, *J* = 15.1, 6.9, 1.1 Hz, 1H, CHC*H*CH$_2$), 5.75 (ddt, *J* = 15.3, 7.1, 1.4 Hz, 1H, C*H*CHCH$_2$), 5.66 (dd, *J* = 7.1, 1.0 Hz, 1H, OC*H*CC), 4.25 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 3.54 (t, *J* = 6.5 Hz, 2H, CH$_2$C*H*$_2$Cl), 2.35 - 2.24 (m, 2H, CHC*H*$_2$CH$_2$), 1.96 - 1.85 (m, 2H, CH$_2$C*H*$_2$CH$_2$Cl), 1.30 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 165.6, 141.6, 136.1, 134.2, 133.2, 131.6, 128.1, 123.3, 94.5, 74.1, 62.0, 44.2, 31.4, 29.5, 14.3; IR (ν_{max}, cm^{-1}) 2977 (m), 2920 (m), 2848 (m), 1736 (s), 1579 (m), 1450 (m), 1286 (s), 1239 (s), 1190 (s), 1133 (s), 1100 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for $C_{16}H_{18}ClINaO_4^+$ $[M+Na]^+$ 458.9831; found 458.9835.

1-(Cyclohex-1-en-1-yl)-2-ethoxy-2-oxoethyl 2-iodobenzoate (4o)

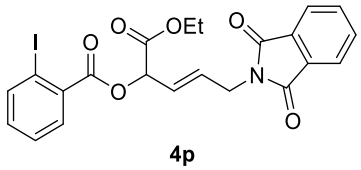


4o

Following general procedure D, starting from (*E*)-1-(cyclohex-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1o**) (65.6 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded 1-(cyclohex-1-en-1-yl)-2-ethoxy-2-oxoethyl 2-iodobenzoate (**4o**) as a colorless oil (80 mg, 0.19 mmol, 97%). R_f = 0.36 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar*H*), 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.20 - 7.14 (m, 1H, Ar*H*), 6.04 - 5.99 (m, 1H, CC*H*CH$_2$), 5.55 (d, *J* = 1.0 Hz, 1H, OC*H*CC), 4.25 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$),

2.30 - 1.18 (m, 1H, cy-*H*), 2.16 - 1.96 (m, 3H, cy-*H*), 1.74 - 1.58 (m, 4H, cy-*H*), 1.29 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 165.9, 141.6, 134.4, 133.1, 131.7, 131.1, 130.5, 128.1, 94.5, 78.1, 61.7, 25.4, 24.9, 22.4, 22.0, 14.3; IR (ν_{max}, cm^{-1}) 2959 (m), 2928 (m), 2867 (m), 1732 (s), 1591 (m), 1464 (m), 1431 (m), 1368 (m), 1284 (s), 1239 (s), 1192 (s), 1131 (s), 1096 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for $C_{17}H_{19}INaO_4^+$ $[M+Na]^+$ 437.0220; found 437.0225.

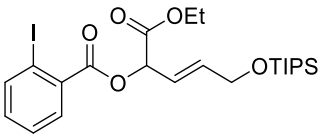
(*E*)-5-(1,3-Dioxoisoindolin-2-yl)-1-ethoxy-1-oxopent-3-en-2-yl 2-iodobenzoate (4p)



4p

Following general procedure D, starting from (*E*)-2-(3-(3-oxo-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)allyl)isoindoline-1,3-dione (**1p**) (87.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-5-(1,3-dioxoisoindolin-2-yl)-1-ethoxy-1-oxopent-3-en-2-yl 2-iodobenzoate (**4p**) as a white sticky solid (31.0 mg, 0.06 mmol, 30%). M.p. 77-78 °C; R_f = 0.31 (EtOAc/pentane 25:75); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar*H*), 7.93 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.89 – 7.81 (m, 2H, Ar*H*), 7.77 – 7.69 (m, 2H, Ar*H*), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.12 (dtd, *J* = 15.5, 5.9, 1.4 Hz, 1H, CHC*H*CH_2N), 5.96 (ddt, *J* = 15.5, 6.0, 1.4 Hz, 1H, C*H*CHCH$_2$N), 5.71 (dd, *J* = 6.0, 1.3 Hz, 1H, OC*H*CC), 4.36 (dt, *J* = 5.9, 1.2 Hz, 2H, CH_2NPhth), 4.24 (qd, *J* = 7.1, 0.9 Hz, 2H, OCH_2CH_3), 1.28 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 167.9, 165.4, 141.6, 134.3, 133.9, 133.2, 132.2, 131.7, 129.3, 128.1, 125.7, 123.6, 94.5, 73.1, 62.2, 38.9, 14.2; IR (ν_{max}, cm^{-1}) 3463 (w), 3053 (w), 2985 (w), 2922 (m), 2854 (w), 1733 (m), 1709 (s), 1582 (w), 1467 (m), 1430 (m), 1392 (s), 1288 (m), 1244 (m), 1200 (m), 1130 (m), 1101 (m), 1046 (m), 1017 (s), 944 (m); HRMS (ESI) calcd for $C_{22}H_{18}INNaO_6^+$ $[M+Na]^+$ 542.0071; found 542.0082.

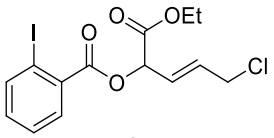
(*E*)-1-Ethoxy-1-oxo-5-((triisopropylsilyl)oxy)pent-3-en-2-yl 2-iodobenzoate (4q)



4q

Following general procedure D, starting from (*E*)-1-(3-((triisopropylsilyl)oxy)prop-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1q**) (92.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-5-((triisopropylsilyl)oxy)pent-3-en-2-yl 2-iodobenzoate (**4q**) as a colorless oil (94 mg, 0.17 mmol, 86%). R_f = 0.54 (EtOAc/pentane 5:95); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar*H*), 7.96 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.14 (dtd, *J* = 15.4, 3.7, 1.2 Hz, 1H, CHC*H*CH_2O), 6.02 (ddt, *J* = 15.4, 6.5, 2.0 Hz, 1H, C*H*CHCH$_2$O), 5.74 (dq, *J* = 6.5, 1.3 Hz, 1H, OC*H*CC), 4.33 (dt, *J* = 3.6, 1.7 Hz, 2H, CH_2OTIPS), 4.25 (qd, *J* = 7.1, 1.2 Hz, 2H, OCH_2CH_3), 1.29 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.17 - 1.02 (m, 21H, TIPS); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 165.6, 141.6, 136.0, 134.2, 133.2, 131.7, 128.1, 120.8, 94.5, 73.8, 62.8, 61.9, 18.1, 14.3, 12.1; IR (ν_{max}, cm^{-1}) 2960 (m), 2941 (s), 2866 (s), 2727 (w), 1736 (s), 1463 (m), 1378 (w), 1284 (m), 1248 (s), 1200 (m), 1124 (s), 1044 (s), 1017 (s), 967 (m), 880 (s); HRMS (ESI) calcd for $C_{23}H_{35}INaO_5Si^+$ $[M+Na]^+$ 569.1191; found 569.1197.

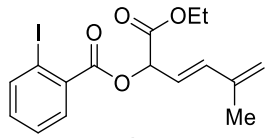
(*E*)-5-Chloro-1-ethoxy-1-oxopent-3-en-2-yl 2-iodobenzoate (4r)



4r

Following general procedure D, starting from (*E*)-1-(3-chloroprop-1-en-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1r**) (64.5 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-5-chloro-1-ethoxy-1-oxopent-3-en-2-yl 2-iodobenzoate (**4r**) as a colorless oil (26.0 mg, 0.06 mmol, 32%). R_f = 0.19 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar*H*), 7.96 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.20 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H, Ar*H*), 6.20 (dtd, *J* = 15.3, 6.4, 1.4 Hz, 1H, CHC*H*CH$_2$Cl), 6.04 (ddt, *J* = 15.3, 6.0, 1.3 Hz, 1H, C*H*CHCH$_2$Cl), 5.76 (dq, *J* = 5.9, 1.1 Hz, 1H, OC*H*CC), 4.27 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 4.11 (dt, *J* = 6.4, 1.1 Hz, 2H, C*H*$_2$Cl), 1.31 (t, *J* = 7.2 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 165.4, 141.7, 133.9, 133.3, 131.7, 131.3, 128.2, 126.0, 94.6, 72.9, 62.3, 43.6, 14.3; IR (ν_{max}, cm^{-1}) 2959 (m), 2928 (m), 2867 (m), 1732 (s), 1591 (m), 1464 (m), 1431 (m), 1368 (m), 1284 (s), 1239 (s), 1192 (s), 1131 (s), 1096 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for $C_{14}H_{14}ClINaO_4^+$ $[M+Na]^+$ 430.9518; found 430.9521.

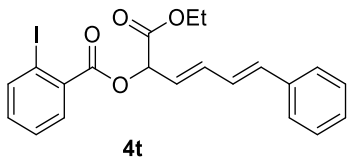
(*E*)-1-Ethoxy-5-methyl-1-oxohexa-3,5-dien-2-yl 2-iodobenzoate (4s)



4s

Following general procedure D, starting from (*E*)-1-(3-methylbuta-1,3-dien-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1s**) (62.8 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-5-methyl-1-oxohexa-3,5-dien-2-yl 2-iodobenzoate (**4s**) as a colorless oil (66 mg, 0.17 mmol, 82%). R_f = 0.33 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.2 Hz, 1H, Ar*H*), 7.97 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.18 (ddd, *J* = 8.0, 7.5, 1.7 Hz, 1H, Ar*H*), 6.63 (d, *J* = 15.3 Hz, 1H, CHC*H*C), 5.85 - 5.73 (m, 2H, C*H*CHC and OC*H*CC), 5.14 - 5.09 (m, 2H, CC*H*$_2$), 4.27 (qd, *J* = 7.1, 1.7 Hz, 2H, OC*H*$_2$CH$_3$), 1.88 (t, *J* = 1.0 Hz, 3H, CC*H*$_3$), 1.31 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 165.6, 141.6, 140.8, 138.5, 134.2, 133.2, 131.7, 128.1, 120.7, 119.6, 94.5, 74.3, 62.1, 18.5, 14.3; IR (ν_{max}, cm^{-1}) 2959 (m), 2928 (m), 2867 (m), 1732 (s), 1591 (m), 1464 (m), 1431 (m), 1368 (m), 1284 (s), 1239 (s), 1192 (s), 1131 (s), 1096 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for $C_{16}H_{17}INaO_4^+$ $[M+Na]^+$ 423.0064; found 423.0065.

(3*E*,5*E*)-1-Ethoxy-1-oxo-6-phenylhexa-3,5-dien-2-yl 2-iodobenzoate (4t)

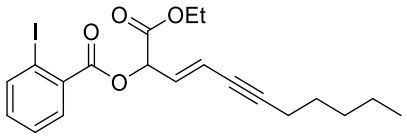


4t

Following general procedure D, starting from (*E*)-1-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1t**) (75.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (3*E*,5*E*)-1-ethoxy-1-oxo-6-phenylhexa-3,5-dien-2-yl 2-iodobenzoate (**4t**) as a colorless oil (84 mg, 0.18 mmol, 91%). R_f = 0.23 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.9, 1.1 Hz, 1H, Ar*H*), 7.98 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.49 - 7.38 (m,

3H, Ar*H*), 7.37 - 7.30 (m, 2H, Ar*H*), 7.29 - 7.22 (m, 1H, Ar*H*), 7.19 (td, *J* = 7.7, 1.8 Hz, 1H, Ar*H*), 6.80 (dd, *J* = 15.4, 10.3 Hz, 1H, CHCHC*H*CHPh), 6.75 - 6.64 (m, 2H, CHC*H*CHC*H*Ph), 6.01 - 5.93 (m, 1H, C*H*CHCHCHPh), 5.79 (dd, *J* = 7.0, 1.1 Hz, 1H, OC*H*CC), 4.28 (qd, *J* = 7.1, 0.9 Hz, 2H, OC*H*$_2$CH$_3$), 1.32 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 165.6, 141.6, 136.8, 136.0, 135.5, 134.1, 133.2, 131.7, 128.8, 128.3, 128.1, 127.2, 126.8, 124.0, 94.6, 74.1, 62.1, 14.3; IR (ν_{max}, cm^{-1}) 2985 (w), 2918 (w), 1732 (s), 1583 (w), 1466 (w), 1284 (m), 1243 (s), 1129 (m), 1100 (m), 1014 (s), 988 (m), 738 (s), 689 (s); HRMS (ESI) calcd for $C_{21}H_{19}INaO_4^+$ $[M+Na]^+$ 485.0220; found 485.0216.

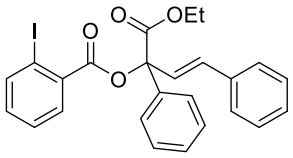
(*E*)-1-Ethoxy-1-oxoundec-3-en-5-yn-2-yl 2-iodobenzoate (4u)



4u

Following general procedure D, starting from (*E*)-1-(non-1-en-3-yn-1-yl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1u**) (73.6 mg, 0.200 mmol) and ethyl 2-diazoacetate (**2a**) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxoundec-3-en-5-yn-2-yl 2-iodobenzoate (**4u**) as a colorless oil (88 mg, 0.19 mmol, 97%). R_f = 0.40 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.1 Hz, 1H, Ar*H*), 7.95 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.18 (ddd, *J* = 7.9, 7.4, 1.7 Hz, 1H, Ar*H*), 6.17 (ddt, *J* = 15.8, 6.5, 0.7 Hz, 1H, C*H*CHCC), 6.02 (dtd, *J* = 15.8, 2.1, 1.4 Hz, 1H, CHC*H*CC), 5.72 (dd, *J* = 6.6, 1.4 Hz, 1H, OC*H*CC), 4.25 (qd, *J* = 7.1, 2.2 Hz, 2H, OC*H*$_2$CH$_3$), 2.31 (td, *J* = 7.1, 2.2 Hz, 2H, CC*H*$_2$CH$_2$), 1.57 - 1.48 (m, 2H, CCH$_2$C*H*$_2$), 1.42 - 1.21 (m, 7H, pentyl-*H* and OCH$_2$C*H*$_3$), 0.90 (t, *J* = 7.1 Hz, 3H, CH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 165.2, 141.5, 133.7, 133.2, 131.8, 131.6, 128.0 116.1, 94.5, 94.2, 77.5, 73.4, 62.1, 31.1, 28.2, 22.2, 19.4, 14.1, 14.0; IR (ν_{max}, cm^{-1}) 2957 (m), 2935 (m), 2859 (w), 2219 (w), 1738 (s), 1584 (m), 1465 (m), 1429 (m), 1370 (m), 1284 (m), 1241 (s), 1196 (s), 1131 (s), 1096 (s), 1043 (m), 1027 (s), 1017 (s), 954 (s), 738 (s); HRMS (ESI) calcd for $C_{20}H_{24}IO_4^+$ $[M+H]^+$ 455.0714; found 455.0720.

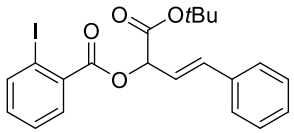
(*E*)-1-Ethoxy-1-oxo-2,4-diphenylbut-3-en-2-yl 2-iodobenzoate (5a)



5a

Following general procedure E, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and ethyl 2-diazo-2-phenylacetate (**2b**) (76.0 mg, 0.400 mmol), afforded (*E*)-1-ethoxy-1-oxo-2,4-diphenylbut-3-en-2-yl 2-iodobenzoate (**5a**) as a colorless oil (73 mg, 0.14 mmol, 71%). R_f = 0.40 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.95 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.76 - 7.64 (m, 2H, Ar*H*), 7.52 - 7.14 (m, 11H, Ar*H* and CHC*H*Ph), 6.53 (d, *J* = 16.3 Hz, 1H, C*H*CHPh), 4.41 - 4.15 (m, 2H, OC*H*$_2$CH$_3$), 1.26 (t, *J* = 7.2 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 165.2, 141.5, 138.2, 136.2, 135.2, 133.9, 133.0, 131.2, 128.7, 128.6, 128.6, 128.4, 128.2, 127.1, 126.6, 94.1, 84.2, 62.4, 14.2; IR (ν_{max}, cm^{-1}) 2974 (m), 2900 (m), 1735 (s), 1495 (m), 1449 (m), 1431 (m), 1276 (s), 1256 (s), 1092 (s), 1042 (s), 1016 (s), 974 (m), 764 (s), 750 (s); HRMS (ESI) calcd for $C_{24}H_{19}INaO_4^+$ $[M+Na]^+$ 521.0220; found 521.0227. One carbon was not resolved at 101 MHz.

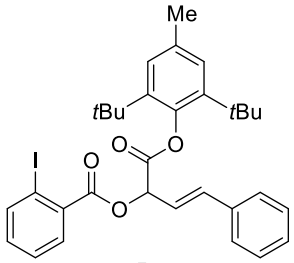
(*E*)-1-(*tert*-Butoxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (5b)



5b

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and *tert*-butyl 2-diazoacetate (**2c**) (65.0 µL, 85% wt in DCM, 0.400 mmol), afforded (*E*)-1-(*tert*-butoxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**5b**) as a white solid (90 mg, 0.19 mmol, 97%). M.p. 62-64 °C; R_f = 0.36 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (td, *J* = 7.9, 1.4 Hz, 2H, Ar*H*), 7.47 - 7.40 (m, 3H, Ar*H*), 7.38 - 7.32 (m, 2H, Ar*H*), 7.32 - 7.27 (m, 1H, Ar*H*), 7.19 (ddd, *J* = 7.9, 7.4, 1.8 Hz, 1H, Ar*H*), 6.90 (dd, *J* = 15.9, 1.4 Hz, 1H, CHC*H*Ph), 6.37 (dd, *J* = 16.0, 6.9 Hz, 1H, C*H*CHPh), 5.75 (dd, *J* = 6.9, 1.4 Hz, 1H, OC*H*CC), 1.51 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 165.7, 141.6, 135.9, 135.2, 134.4, 133.1, 131.7, 128.8, 128.6, 128.1, 127.0, 121.2, 94.5, 83.1, 74.8, 28.2; IR (ν_{max}, cm^{-1}) 2978 (m), 2902 (m), 1735 (s), 1582 (w), 1451 (m), 1395 (m), 1369 (m), 1278 (s), 1258 (s), 1199 (m), 1129 (m), 1098 (s), 1044 (s), 1016 (s), 966 (m), 863 (m), 764 (s), 750 (s); HRMS (ESI) calcd for $C_{21}H_{21}INaO_4^+$ $[M+Na]^+$ 487.0377; found 487.0382.

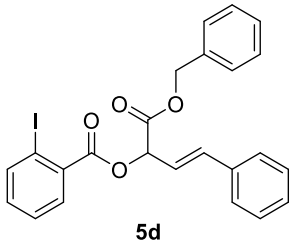
(*E*)-1-(2,6-di-*tert*-Butyl-4-methylphenoxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (5c)



5c

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and 2,6-di-*tert*-butyl-4-methylphenyl 2-diazoacetate (**2d**) (115 mg, 0.400 mmol), afforded (*E*)-1-(2,6-di-*tert*-butyl-4-methylphenoxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**5c**) as a white solid (123 mg, 0.200 mmol, 100%). R_f = 0.45 (EtOAc/pentane 5:95); M.p. 151-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (ddd, *J* = 7.8, 4.5, 1.4 Hz, 2H, Ar*H*), 7.51 - 7.45 (m, 2H, Ar*H*), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.40 - 7.29 (m, 3H, Ar*H*), 7.23 - 7.16 (m, 1H, Ar*H*), 7.16 - 7.10 (m, 2H, Ar*H*), 7.02 (d, *J* = 14.9 Hz, 1H, CHC*H*Ph), 6.62 - 6.52 (m, 2H, C*H*CHPh and OC*H*CC), 2.32 (s, 3H, ArC*H*$_3$), 1.38 (s, 9H, C(C*H*$_3$)$_3$), 1.31 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 165.0, 145.8, 142.2, 142.1, 141.6, 136.2, 135.7, 135.2, 134.4, 133.2, 131.6, 128.9, 128.8, 128.1, 127.5, 127.2, 127.0, 120.7, 94.6, 74.1, 35.5, 35.5, 31.8, 31.4, 21.6; IR (ν_{max}, cm^{-1}) 2961 (m), 2922 (m), 1769 (s), 1742 (s), 1468 (m), 1425 (m), 1270 (s), 1247 (s), 1196 (s), 1180 (s), 1129 (s), 1100 (s), 1016 (s), 969 (m), 742 (s); HRMS (ESI) calcd for $C_{32}H_{35}INaO_4^+$ $[M+Na]^+$ 633.1472; found 633.1474; The structure of **5c** was confirmed by X-ray analysis. Crystals were grown by dissolving 10 mg of pure **5c** in a minimum amount of benzene (100 µL) at room temperature. Slow evaporation over one week provided suitable crystals. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (CCDC 1897009) and can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/

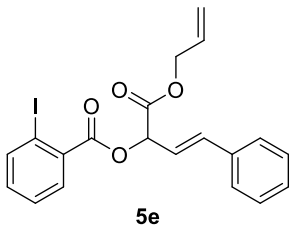
(*E*)-1-(Benzyloxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (5d)



5d

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and benzyl 2-diazoacetate (**2e**) (88.0 µL, 90% wt in DCM, 0.400 mmol), afforded (*E*)-1-(Benzyloxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**5d**) as a colorless oil (92.0 mg, 0.19 mmol, 92%). R_f = 0.26 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar*H*), 7.96 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.46 - 7.27 (m, 11H, Ar*H*), 7.19 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.90 (dd, *J* = 16.0, 1.3 Hz, 1H, CHC*H*Ph), 6.37 (dd, *J* = 15.9, 7.1 Hz, 1H, C*H*CHPh), 5.93 (dd, *J* = 7.1, 1.3 Hz, 1H, OC*H*CC), 5.26 (s, 2H, OCH_2Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 165.6, 141.6, 136.0, 135.7, 135.3, 134.1, 133.3, 131.7, 128.8, 128.8, 128.8, 128.6, 128.4, 128.1, 127.0, 120.5, 94.5, 74.3, 67.7; IR (ν_{max}, cm^{-1}) 2978 (m), 2902 (m), 1735 (s), 1582 (w), 1451 (m), 1395 (m), 1369 (m), 1278 (s), 1258 (s), 1199 (m), 1129 (m), 1098 (s), 1044 (s), 1016 (s), 966 (m), 863 (m), 764 (s), 750 (s); HRMS (ESI) calcd for $C_{24}H_{19}INaO_4^+$ $[M+Na]^+$ 521.0220; found 521.0235.

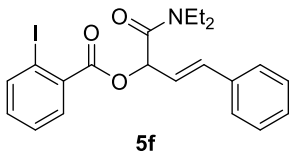
(*E*)-1-(Allyloxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (5e)



5e

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and allyl 2-diazoacetate (**2f**) (50.4 mg, 0.400 mmol), afforded (*E*)-1-(allyloxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**5e**) as a colorless oil (82 mg, 0.18 mmol, 91%). R_f = 0.24 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (ddd, *J* = 10.7, 7.9, 1.4 Hz, 2H, Ar*H*), 7.45 (td, *J* = 7.6, 1.2 Hz, 3H, Ar*H*), 7.39 - 7.27 (m, 3H, Ar*H*), 7.19 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.94 (dd, *J* = 16.0, 1.2 Hz, 1H, CHC*H*Ph), 6.39 (dd, *J* = 15.9, 7.1 Hz, 1H, C*H*CHPh), 6.00 - 5.87 (m, 2H, OC*H*CC and OCH_2CHCH_2), 5.36 (dq, *J* = 17.2, 1.5 Hz, 1H, CHCH_2), 5.26 (dq, *J* = 10.5, 1.3 Hz, 1H, CHCH_2), 4.72 (dt, *J* = 5.8, 1.4 Hz, 2H, OCH_2CHCH$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 165.6, 141.6, 136.0, 135.7, 134.1, 133.3, 131.7, 131.5, 128.9, 128.8, 128.1, 127.0, 120.6, 119.1, 94.6, 74.3, 66.5; IR (ν_{max}, cm^{-1}) 3063 (w), 3026 (w), 2946 (w), 1736 (s), 1585 (m), 1427 (w), 1290 (m), 1239 (s), 1188 (s), 1133 (s), 1096 (s), 1043 (m), 1014 (s), 963 (s), 937 (m), 742 (s), 689 (s); HRMS (ESI) calcd for $C_{20}H_{17}INaO_4^+$ $[M+Na]^+$ 471.0064; found 471.0063.

(*E*)-1-(Diethylamino)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (5f)

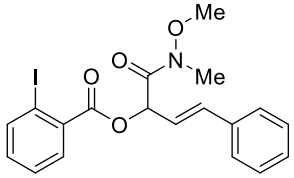


5f

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and 2-diazo-*N*,*N*-diethylacetamide (**2g**) (56.5 mg, 0.400 mmol), afforded (*E*)-1-(diethylamino)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**5f**) as a white solid (87 mg, 0.19 mmol,

94%). R_f = 0.24 (EtOAc/pentane 20:80); M.p. 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.98 (dd, *J* = 7.9, 1.1 Hz, 1H, Ar*H*), 7.46 - 7.38 (m, 3H, Ar*H*), 7.38 - 7.27 (m, 3H, Ar*H*), 7.15 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.88 (d, *J* = 16.0 Hz, 1H, CHC*H*Ph), 6.43 (dd, *J* = 16.0, 7.9 Hz, 1H, C*H*CHPh), 6.12 (dd, *J* = 7.9, 0.9 Hz, 1H, OC*H*CC), 3.59 - 3.30 (m, 4H, N(CH_2CH_3)$_2$), 1.31 (t, *J* = 7.2 Hz, 3H, N(CH_2CH_3)$_2$), 1.17 (t, *J* = 7.1 Hz, 3H, N(CH_2CH_3)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 166.1, 141.3, 136.9, 135.7, 134.5, 133.0, 132.1, 128.9 (2 C), 128.1, 127.1, 122.0, 94.4, 72.9, 41.9, 41.0, 14.5, 13.0; IR (ν_{max}, cm^{-1}) 3063 (w), 3026 (w), 2946 (w), 1736 (s), 1585 (m), 1427 (w), 1290 (m), 1239 (s), 1188 (s), 1133 (s), 1096 (s), 1043 (m), 1014 (s), 963 (s), 937 (m), 742 (s), 689 (s); HRMS (ESI) calcd for $C_{21}H_{22}INNaO_3^+$ $[M+Na]^+$ 486.0537; found 486.0535.

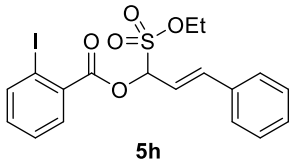
(*E*)-1-(Methoxy(methyl)amino)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (5g)



5g

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and 2-diazo-*N*-methoxy-*N*-methylacetamide (**2h**) (51.6 mg, 0.400 mmol), afforded (*E*)-1-(methoxy(methyl)amino)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**5g**) as a white solid (89 mg, 0.20 mmol, 99%). R_f = 0.27 (EtOAc/pentane 20:80); M.p. 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 8.00 (dd, *J* = 7.9, 1.1 Hz, 1H, Ar*H*), 7.45 - 7.40 (m, 3H, Ar*H*), 7.37 - 7.26 (m, 3H, Ar*H*), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.93 (d, *J* = 15.9 Hz, 1H, CHC*H*Ph), 6.41 (dd, *J* = 15.9, 7.5 Hz, 1H, C*H*CHPh), 6.27 (d, *J* = 7.5 Hz, 1H, OC*H*CC), 3.87 (s, 3H, OCH_3), 3.27 (s, 3H, NCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 166.0, 141.4, 136.0, 136.0, 134.4, 133.1, 132.0, 128.8, 128.7, 128.1, 127.0, 121.0, 94.4, 72.9, 61.7, 32.5; IR (ν_{max}, cm^{-1}) 3055 (w), 3020 (w), 2973 (w), 2942 (w), 1728 (s), 1681 (s), 1466 (m), 1431 (m), 1284 (m), 1251 (s), 1133 (s), 1102 (s), 1016 (m), 969 (s), 738 (s); HRMS (ESI) calcd for $C_{19}H_{18}INNaO_4^+$ $[M+Na]^+$ 474.0173; found 474.0175.

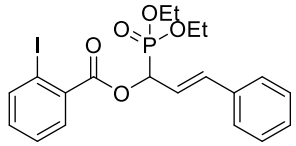
(*E*)-1-(Ethoxysulfonyl)-3-phenylallyl 2-iodobenzoate (5h)



5h

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and ethyl diazomethanesulfonate (**2i**) (60.1 mg, 0.400 mmol), afforded (*E*)-1-(ethoxysulfonyl)-3-phenylallyl 2-iodobenzoate (**5h**) as a colorless oil (96 mg, 0.20 mmol, 100%). R_f = 0.12 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar*H*), 8.01 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.51 - 7.44 (m, 3H, Ar*H*), 7.40 - 7.30 (m, 3H, Ar*H*), 7.27 - 7.21 (m, 1H, Ar*H*), 7.12 - 7.03 (m, 1H, CHC*H*Ph), 6.70 (dd, *J* = 7.5, 1.1 Hz, 1H, OC*H*CC), 6.40 (dd, *J* = 15.9, 7.5 Hz, 1H, C*H*CHPh), 4.43 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 1.40 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 142.1, 140.0, 134.8, 134.0, 132.6, 132.0, 129.6, 129.0, 128.4, 127.4, 116.0, 95.1, 84.1 69.8, 15.5; IR (ν_{max}, cm^{-1}) 2975 (w), 2924 (w), 1742 (m), 1675 (s), 1624 (m), 1581 (m), 1364 (m), 1291 (m), 1237 (s), 1174 (s), 1129 (s), 1088 (s), 1015 (s), 968 (s), 919 (s), 739 (s), 688 (s); HRMS (ESI) calcd for $C_{18}H_{17}INaO_5S^+$ $[M+Na]^+$ 494.9734; found 494.9730.

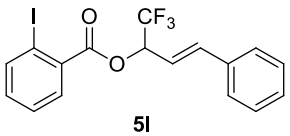
(*E*)-1-(Diethoxyphosphoryl)-3-phenylallyl 2-iodobenzoate (5i)



5i

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and diethyl (diazomethyl)phosphonate (**2j**) (71.3 mg, 0.400 mmol), afforded (*E*)-1-(diethoxyphosphoryl)-3-phenylallyl 2-iodobenzoate (**5i**) as a colorless oil (97 mg, 0.19 mmol, 97%). R_f = 0.28 (EtOAc/pentane 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.2 Hz, 1H, Ar*H*), 7.93 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.47 - 7.40 (m, 3H, Ar*H*), 7.36 - 7.27 (m, 3H, Ar*H*), 7.22 - 7.16 (m, 1H, Ar*H*), 6.91 - 6.83 (m, 1H, CHC*H*Ph), 6.37 (ddd, *J* = 15.9, 7.6, 5.8 Hz, 1H, C*H*CHPh), 6.09 (ddd, *J* = 13.5, 7.6, 1.3 Hz, 1H, OC*H*CC), 4.27 - 4.16 (m, 4H, (O)P(OCH_2CH$_3$)$_2$), 1.33 (t, *J* = 7.1 Hz, 6H, (O)P(OCH$_2$CH_3)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9 (d, *J* = 7.9 Hz), 141.7, 136.0, 135.9 (d, *J* = 3.1 Hz), 134.1, 133.3, 131.5, 128.8, 128.6, 128.2, 127.0, 120.0 (d, *J* = 4.5 Hz), 94.7, 70.6 (d, *J* = 170.7 Hz), 63.6 (dd, *J* = 9.0, 6.8 Hz), 16.7 (t, *J* = 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.4; IR (ν_{max}, cm^{-1}) 3057 (w), 2981 (w), 2930 (w), 2901 (w), 1734 (m), 1288 (m), 1241 (s), 1131 (m), 1096 (m), 1014 (s), 967 (s), 793 (m), 738 (s), 691 (m); HRMS (ESI) calcd for $C_{20}H_{22}INaO_5P^+$ $[M+Na]^+$ 523.0142; found 523.0154.

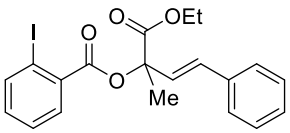
(*E*)-1,1,1-Trifluoro-4-phenylbut-3-en-2-yl 2-iodobenzoate (5l)



5l

Following general procedure D, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and 2-diazo-1,1,1-trifluoroethane (**2k**) (1.08 mL, 0.37 M in DCM, 0.400 mmol), afforded (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl 2-iodobenzoate (**5l**) as a colorless oil (88 mg, 0.20 mmol, 100%). R_f = 0.52 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar*H*), 7.93 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.45 (dtd, *J* = 7.7, 4.1, 1.9 Hz, 3H, Ar*H*), 7.40 - 7.29 (m, 3H, Ar*H*), 7.21 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.00 (d, *J* = 15.9 Hz, 1H, CHC*H*Ph), 6.24 (dd, *J* = 15.9, 7.9 Hz, 1H, C*H*CHPh), 6.12 - 6.02 (m, 1H, OC*H*CC); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 141.9, 139.6, 135.1, 133.6, 133.3, 131.6, 129.3, 128.9, 128.2, 127.2, 123.3 (q, *J* = 280.6 Hz), 117.0 (d, *J* = 1.7 Hz), 94.8, 72.4 (q, *J* = 33.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.9; HRMS (ESI) calcd for $C_{17}H_{12}F_3IO_2$ $[M^+]$ 431.9829; found 431.9846.

(*E*)-1-Ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (5m)

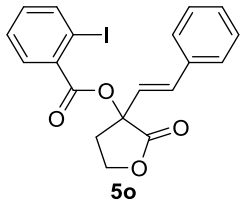


5m

Following general procedure E, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and ethyl 2-diazopropanoate (**2l**) (51.3 mg, 0.400 mmol), afforded (*E*)-1-ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**5m**) as a colorless oil (80 mg, 0.18 mmol, 89%). R_f = 0.26 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar*H*), 7.85 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.45 - 7.39 (m, 3H, Ar*H*), 7.35 - 7.29 (m, 2H, Ar*H*), 7.28 - 7.23 (m, 1H, Ar*H*), 7.16 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H, Ar*H*), 6.80 (d, *J* = 16.3 Hz, 1H, CHC*H*Ph), 6.62 (d, *J* = 16.2 Hz, 1H, C*H*CHPh), 4.27 (qd, *J* = 7.1, 2.6 Hz, 2H, OCH_2CH$_3$), 1.92 (s, 3H, CCH_3), 1.29 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 165.4, 141.4, 136.1, 135.3, 132.9, 131.4, 131.2, 128.8, 128.4, 128.1, 127.8,

126.9, 94.0, 81.4, 62.1, 23.2, 14.2; IR (ν_{max}, cm^{-1}) 2963 (w), 2920 (m), 2856 (w), 1744 (m), 1345 (w), 1274 (m), 1241 (s), 1180 (s), 1131 (s), 1092 (s), 1043 (m), 1016 (s), 965 (m), 914 (m), 736 (s), 691 (s); HRMS (ESI) calcd for $C_{20}H_{19}INaO_4^+$ $[M+Na]^+$ 473.0220; found 473.0213.

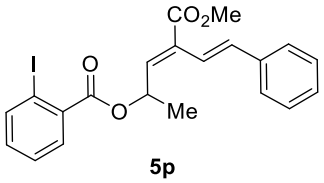
(*E*)-2-Oxo-3-styryltetrahydrofuran-3-yl 2-iodobenzoate (5o)



5o

Following general procedure E, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and 3-diazodihydrofuran-2(3*H*)-one (**2m**) (44.8 mg, 0.400 mmol), afforded (*E*)-2-oxo-3-styryltetrahydrofuran-3-yl 2-iodobenzoate (**5o**) as a thick colorless oil (78 mg, 0.18 mmol, 90%). R_f = 0.31 (EtOAc/pentane 20:80); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.1 Hz, 1H, Ar*H*), 7.91 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.50 - 7.39 (m, 3H, Ar*H*), 7.39 - 7.28 (m, 3H, Ar*H*), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.95 (d, *J* = 16.2 Hz, 1H, CHC*H*Ph), 6.48 (d, *J* = 16.2 Hz, 1H, C*H*CHPh), 4.65 (td, *J* = 9.2, 2.4 Hz, 1H, OCH_2^1), 4.36 (td, *J* = 9.4, 7.0 Hz, 1H, OCH_2^2), 3.10 (dt, *J* = 13.4, 9.4 Hz, 1H, CCH_2^1), 2.90 (ddd, *J* = 13.4, 7.0, 2.5 Hz, 1H, CCH_2^2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 165.2, 141.6, 135.1, 134.6, 133.9, 133.4, 131.6, 129.1, 128.9, 128.2, 127.2, 123.1, 94.3, 80.4, 65.0, 33.4; IR (ν_{max}, cm^{-1}) 2974 (m), 2900 (m), 1735 (s), 1495 (m), 1449 (m), 1431 (m), 1276 (s), 1256 (s), 1092 (s), 1127 (m), 1042 (s), 1016 (s), 974 (m), 764 (s), 750 (s); HRMS (ESI) calcd for $C_{19}H_{15}INaO_4^+$ $[M+Na]^+$ 456.9907; found 456.9906.

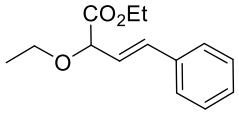
(3*E*,5*E*)-4-(Methoxycarbonyl)-6-phenylhexa-3,5-dien-2-yl 2-iodobenzoate (5p)



5p

Following general procedure E, starting from (*E*)-1-styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**1a**) (70.0 mg, 0.200 mmol) and (*E*)-methyl 2-diazopent-3-enoate (**2n**) (0.400 mL, 1.0 M in pentane, 0.400 mmol), afforded (3*E*,5*E*)-4-(methoxycarbonyl)-6-phenylhexa-3,5-dien-2-yl 2-iodobenzoate (**5p**) as a colorless oil (58 mg, 0.13 mmol, 63%). R_f = 0.22 (EtOAc/pentane 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar*H*), 7.79 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.53 - 7.46 (m, 2H, Ar*H*), 7.43 - 7.31 (m, 3H, Ar*H*), 7.31 - 7.27 (m, 1H, Ar*H*), 7.15 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.09 (d, *J* = 16.3 Hz, 1H, CHC*H*Ph), 6.97 (d, *J* = 16.0 Hz, 1H, C*H*CHPh), 6.71 (d, *J* = 8.7 Hz, 1H, CH_3CHC*H*), 6.15 (dq, *J* = 8.3, 6.5 Hz, 1H, OC*H*CH_3), 3.83 (s, 3H, OCH_3), 1.59 (d, *J* = 6.5 Hz, 3H, OCHCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 165.9, 141.5, 139.3, 136.9, 135.7, 135.2, 132.8, 131.7, 131.1, 128.8, 128.5, 128.1, 127.1, 120.2, 94.2, 68.9, 52.4, 20.5; IR (ν_{max}, cm^{-1}) 2948 (w), 2995 (w), 2844 (w), 1789 (w), 1718 (s), 1583 (m), 1436 (m), 1282 (m), 1241 (s), 1156 (m), 1129 (s), 1098 (s), 1039 (s), 1015 (s), 968 (m), 739 (s), 694 (s); HRMS (ESI) calcd for $C_{21}H_{19}INaO_4^+$ $[M+Na]^+$ 485.0220; found 485.0219.

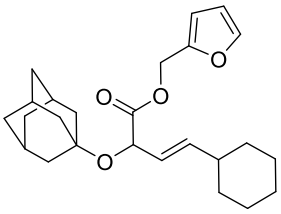
(*E*)-Ethyl 2-ethoxy-4-phenylbut-3-enoate (6b)



6b

Following general procedure F, starting from ethanol (**7a**) (52.5 µL, 0.900 mmol), (*E*)-1-styryl-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (**1'a**) (142 mg, 0.300 mmol) and ethyl 2-diazoacetate (**2a**) (1.0 mL, 0.60 mmol, 0.6 M in DCM), afforded (*E*)-ethyl 2-ethoxy-4-phenylbut-3-enoate (**6b**) as a colorless oil (28 mg, 0.12 mmol, 40%). R_f = 0.26 (EtOAc/pentane 3:97), *p*-anisaldehyde; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H, Ar*H*), 7.35 – 7.29 (m, 2H, Ar*H*), 7.29 – 7.23 (m, 1H, Ar*H*), 6.77 (dd, *J* = 16.0, 1.3 Hz, 1H, HC=C*H*Ph), 6.23 (dd, *J* = 15.9, 6.8 Hz, 1H, *H*C=CHPh), 4.51 (dd, *J* = 6.8, 1.4 Hz, 1H, OC*H*C), 4.31 – 4.18 (m, 2H, C(O)OC*H*$_2$CH$_3$), 3.61 (qq, *J* = 9.1, 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 1.30 (t, *J* = 7.1 Hz, 6H, 2 x OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 136.2, 134.0, 128.7, 128.3, 126.9, 124.3, 79.9, 65.5, 61.4, 15.3, 14.4; IR (ν_{max}, cm^{-1}) 2980 (m), 2937 (w), 1738 (s), 1636 (m), 1451 (m), 1371 (m), 1313 (s), 1268 (s), 1189 (s), 1159 (s), 1091 (s), 1023 (s), 699 (s); HRMS (ESI) calcd for $C_{14}H_{18}NaO_3^+$ $[M+Na]^+$ 257.1148; found 257.1146.

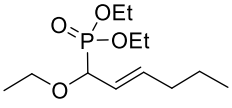
(*E*)-Furan-2-ylmethyl 2-adamantan-1-yloxy)-4-cyclohexylbut-3-enoate (6c)



6c

Following general procedure F, starting from 1-adamantanol (**7b**) (161 mg, 0.90 mmol), (*E*)-1-(2-cyclohexylvinyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzobenzo[*d*][1,2]iodaoxole (**1'j**) (143 mg, 0.300 mmol) and furan-2-ylmethyl 2-diazoacetate (**2o**) (1.0 mL, 0.60 mmol, 0.6 M in DCM), afforded (*E*)-furan-2-ylmethyl 2-adamantan-1-yloxy)-4-cyclohexylbut-3-enoate (**6c**) as a colorless oil (47 mg, 0.12 mmol, 39%). R_f = 0.21 (EtOAc/pentane 2:98), *p*-anisaldehyde; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 1H, Ar*H*), 6.40 (d, *J* = 3.2 Hz, 1H, Ar*H*), 6.34 (dd, *J* = 3.3, 1.8 Hz, 1H, Ar*H*), 5.72 (ddd, *J* = 15.6, 6.6, 1.4 Hz, 1H, HC=C*H*-cHex), 5.43 (ddd, *J* = 15.6, 5.9, 1.4 Hz, 1H, *H*C=CH-cHex), 5.12 (q, *J* = 13.1 Hz, 2H, C*H*$_2$Ar), 4.65 (dt, *J* = 5.9, 1.1 Hz, 1H, OC*H*C), 2.10 (p, *J* = 3.3 Hz, 3H,C*H*-$_{aliphatic}$), 1.93 (dtd, *J* = 11.1, 7.4, 3.2 Hz, 1H, C*H*-$_{aliphatic}$), 1.80 – 1.50 (m, 17H,C*H*-$_{aliphatic}$), 1.33 – 0.95 (m, 5H,C*H*-$_{aliphatic}$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 149.5, 143.2, 139.8, 124.1, 111.0, 110.7, 74.7, 70.8, 58.3, 41.8, 40.4, 36.4, 32.6, 32.5, 30.7, 26.3, 26.1; IR (ν_{max}, cm^{-1}) 3669 (w), 2972 (s), 2908 (s), 2851 (m), 1755 (m), 1734 (m), 1450 (m), 1250 (m), 1153 (m), 1104 (m), 1078 (s), 966 (m), 739 (m); HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{35}O_4^+$ 399.2530; Found 399.2536.

(*E*)-Diethyl (1-ethoxyhex-2-en-1-yl)phosphonate (6d)

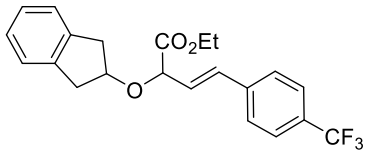


6d

Following general procedure F, starting from ethanol (**7a**) (52.5 µL, 0.900 mmol), (*E*)-1-(pent-1-en-1-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzobenzo[*d*][1,2]iodaoxole (**1'l**) (131 mg, 0.300 mmol) and diethyl (diazomethyl)phosphonate (**2j**) (1.0 mL, 0.60 mmol, 0.6 M in DCM), afforded (*E*)-diethyl (1-

ethoxyhex-2-en-1-yl)phosphonate (**6d**) as a colorless oil (18 mg, 70 µmol, 23%). R_f = 0.22 (EtOAc/pentane 50:50), *p*-anisaldehyde; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 – 5.75 (m, 1H, HC=C*H*-*n*Pr), 5.49 (dddt, *J* = 15.5, 7.8, 4.8, 1.5 Hz, 1H, *H*C=CH-*n*Pr), 4.22 – 4.11 (m, 4H, 2 x P(O)OC*H*$_2$CH$_3$), 4.05 (ddd, *J* = 14.7, 7.8, 1.0 Hz, 1H, OC*H*C), 3.66 (dq, *J* = 9.3, 7.0 Hz, 1H, OC*H*$_2$CH$_3$), 3.49 (dq, *J* = 9.3, 6.9 Hz, 1H, OC*H*$_2$CH$_3$), 2.13 – 2.02 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 1.43 (h, *J* = 7.3 Hz, 2H, CH$_2$C*H*$_2$CH$_3$), 1.32 (td, *J* = 7.1, 1.2 Hz, 6H, 2 x P(O)OCH$_2$C*H*$_3$), 1.21 (t, *J* = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 0.91 (t, *J* = 7.4 Hz, 3H, CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0 (d, *J* = 13.5 Hz), 123.6 (d, *J* = 3.6 Hz), 77.3 (d, *J* = 169.8 Hz), 66.0 (d, *J* = 12.6 Hz), 62.9 (dd, *J* = 25.4, 6.9 Hz), 34.6, 22.3 (d, *J* = 2.9 Hz), 16.7 (t, *J* = 5.0 Hz), 15.3, 13.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.49; IR (ν_{max}, cm^{-1}) 2968 (m), 2930 (m), 2872 (w), 1393 (w), 1251 (m), 1099 (m), 1051 (s), 1024 (s), 967 (s), 790 (m); HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{25}NaO_4P^+$ 287.1383; Found 287.1391.

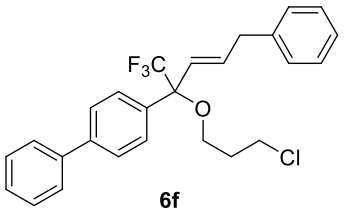
(*E*)-Ethyl 2-((2,3-dihydro-1*H*-inden-2-yl)oxy)-4-(4-(trifluoromethyl)phenyl)but-3-enoate (6e)



6e

Following general procedure F, starting from 2-indanol (**7c**) (161 mg, 0.900 mmol), (*E*)-3,3-bis(trifluoromethyl)-1-(4-(trifluoromethyl)styryl)-1,3-dihydro-benzo[*d*][1,2]iodaoxole (**1'd**) (162 mg, 0.300 mmol) and ethyl 2-diazoacetate (**2a**) (1.0 mL, 0.60 mmol, 0.6 M in DCM), afforded (*E*)-ethyl 2-((2,3-dihydro-1*H*-inden-2-yl)oxy)-4-(4-(trifluoromethyl)phenyl)but-3-enoate (**6e**) as a colorless oil (52 mg, 0.13 mmol, 44%). R_f = 0.12 (EtOAc/pentane 3:97), *p*-anisaldehyde; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.46 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.25 – 7.12 (m, 4H, Ar*H*), 6.78 (dd, *J* = 16.0, 1.5 Hz, 1H, HC=C*H*Ar), 6.37 (dd, *J* = 15.9, 6.0 Hz, 1H, *H*C=CHAr), 4.70 (dd, *J* = 6.1, 1.5 Hz, 1H, OC*H*C), 4.54 (tt, *J* = 6.6, 5.1 Hz, 1H, OC*H*(CH$_2$)$_2$), 4.27 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 3.29 – 3.03 (m, 4H, 2 x C*H*$_2$Ar), 1.32 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 140.7, 140.4, 139.7, 132.0, 130.0 (q, *J* = 32.6 Hz), 127.2, 127.0, 126.9, 126.8, 125.7 (q, *J* = 3.8 Hz), 124.8, 124.2 (q, *J* = 272.1 Hz), 80.3, 78.3, 61.7, 39.7, 39.3, 14.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; IR (ν_{max}, cm^{-1}) 2932 (w), 2359 (w), 1743 (m), 1614 (w), 1324 (s), 1261 (m), 1168 (s), 1116 (s), 1067 (s), 1024 (m), 972 (m), 831 (m), 742 (m); HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{21}F_3NaO_3^+$ 413.1335; Found 413.1342.

(*E*)-4-(2-(3-Chloropropoxy)-1,1,1-trifluoro-5-phenylpent-3-en-2-yl)-1,1'-biphenyl (6f)

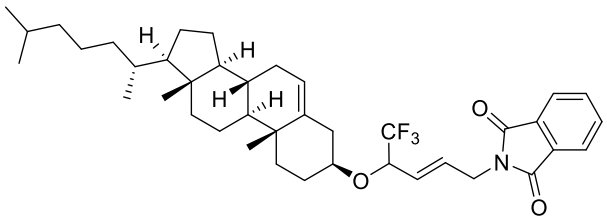


6f

Following general procedure F, starting from 3-chloro-1-propanol, (**7d**) (75 µL, 0.90 mmol), (*E*)-1-(3-phenylprop-1-en-1-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzobenzo[*d*][1,2]iodaoxole (**1'k**) (146 mg, 0.300 mmol) and 4-(1-diazo-2,2,2-trifluoroethyl)-1,1'-biphenyl (**2p**) (1.0 mL, 0.60 mmol, 0.60 M in DCM), afforded (*E*)-4-(2-(3-chloropropoxy)-1,1,1-trifluoro-5-phenylpent-3-en-2-yl)-1,1'-biphenyl (**6f**) as a colorless oil (96 mg, 0.22 mmol, 72%). R_f = 0.45 (EtOAc/pentane 2:98); ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 6H, Ar*H*), 7.53 – 7.43 (m, 2H, Ar*H*), 7.43 – 7.31 (m, 3H, Ar*H*), 7.30 – 7.20 (m, 3H, Ar*H*), 6.21 (dt, *J* = 15.9, 6.8 Hz, 1H, HC=C*H*-CH$_2$Ph), 5.95 – 5.82 (m, 1H, *H*C=CH-CH$_2$Ph), 3.72 (t, *J* = 6.4 Hz, 2H, C*H*$_2$Cl), 3.66 (t, *J* = 5.9 Hz, 2H, C*H*$_2$O), 3.59 (dd, *J* = 6.9, 1.5 Hz, 2H, C*H*$_2$Ph), 2.10 (p, *J* = 6.1 Hz, 2H, C*H*$_2$CH$_2$Cl); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 140.5, 139.1, 137.6, 134.5, 129.0, 129.0, 128.8, 128.7, 127.7, 127.3, 127.0, 126.6, 125.9, 125.0 (q, *J* = 287.5 Hz), 81.9 (q, *J* = 27.4

Hz), 61.2, 41.8, 39.3, 33.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.9; IR (ν_{max}, cm^{-1}) 3668 (w), 2987 (m), 2971 (m), 2910 (m), 1487 (w), 1262 (m), 1163 (s), 1075 (s), 840 (m), 766 (m), 737 (s), 696 (s); HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{24}ClF_3NaO^+$ 467.1360; Found 467.1366.

2-((*E*)-4-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)-5,5,5-trifluoropent-2-en-1-yl)isoindoline-1,3-dione (6g)

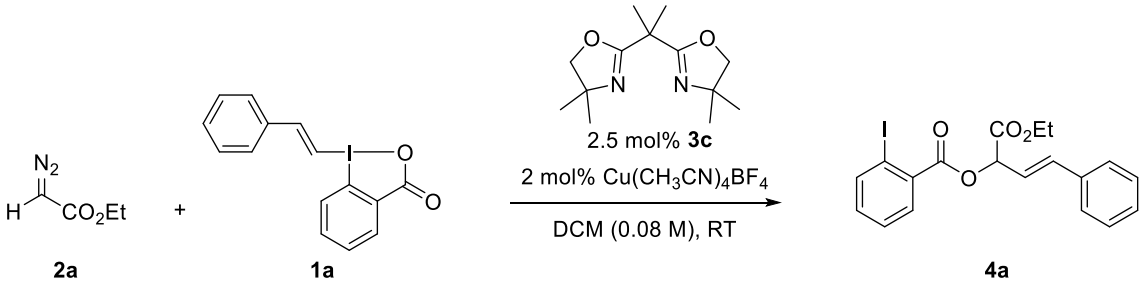


6g

Following general procedure F, starting from cholesterol (**7e**) (348 mg, 0.900 mmol), (*E*)-2-(3-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)allyl)isoindoline-1,3-dione (**1'p**) (167 mg, 0.300 mmol) and 2-diazo-1,1,1-trifluoroethane (**2k**) (1.67 mL, 0.600 mmol, 0.36 M in DCM), afforded 2-((*E*)-4-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)-5,5,5-trifluoropent-2-en-1-yl)isoindoline-1,3-dione (**6g**) (55:45 *dr* in the crude ^{19}F NMR) as a white solid (120 mg, 0.180 mmol, 61%). M.p. 158 °C; R_f = 0.23 (EtOAc/pentane 5:95), *p*-anisaldehyde; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.82 (m, 2H, Ar*H*), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H, Ar*H*), 6.08 - 5.96 (m, 1H, HC=C*H*-CH_2N), 5.75 - 5.63 (m, 1H, *H*C=CH-CH_2N), 5.34 - 5.26 (m, 1H, *H*C=C$(C)_2$), 4.34 (dt, *J* = 6.0, 1.8 Hz, 2H, C*H*$_2$N), 4.24 - 4.15 (m, 1H, C*H*CF_3), 3.36 - 3.23 (m, 1H, C*H*O), 2.36 - 2.19 (m, 2H, C*H*-$_{aliphatic}$), 2.03 - 1.73 (m, 5H, C*H*-$_{aliphatic}$), 1.62 - 0.79 (m, 33H, C*H*-$_{aliphatic}$), 0.66 (s, 3H, C*H*-$_{aliphatic}$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 140.4, 140.3, 134.2, 132.2, 130.5, 130.5, 126.0, 125.9, 124.0 (q, *J* = 281.9 Hz), 124.0 (q, *J* = 281.9 Hz), 123.6, 122.3, 122.3, 80.0, 79.9, 75.5 (q, *J* = 31.1 Hz), 75.5 (q, *J* = 31.1 Hz), 56.9, 56.3, 50.2, 42.4, 39.9, 39.7, 39.5, 38.9, 38.8, 37.2, 37.1, 36.8, 36.8, 36.3, 35.9, 32.0, 32.0, 29.0, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0;[50] ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.26, -77.28; IR (ν_{max}, cm^{-1}) 2949 (m), 1775 (w), 1711 (s), 1468 (w), 1429 (m), 1399 (m), 1275 (m), 1181 (m), 1150 (m), 1121 (s), 1078 (m), 944 (m), 727 (s), 714 (m); HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{40}H_{54}F_3NNaO_3^+$ 676.3948; Found 676.3954.

[50] All ^{13}C signals of the diastereoisomeric mixture were not resolved.

Scale-up synthesis of 4a using DCM as solvent and using a lower catalyst loading



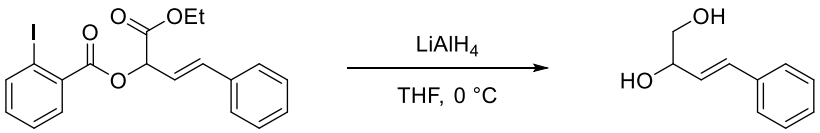
A catalytic solution was prepared by mixing $Cu(CH_3CN)_4BF_4$ (12.6 mg, 40.0 µmol) and 2,2'-(propane-2,2-diyl)bis(4,4-dimethyl-4,5-dihydrooxazole) (**3c**) (11.9 mg, 50.0 µmol) in DCM (5.0 mL) at 25 °C for 1 h.

The catalyst solution was then added to a stirring suspension of Ph-VBX (**1a**) (700 mg, 2.00 mmol, 1.00 equiv) and ethyl 2-diazoacetate (**2a**) (0.484 mL, 4.00 mmol, 2.00 equiv) in DCM (20.0 mL).

The reaction mixture was stirred at 25 °C for 2 h, then the solvent was removed under reduced pressure and the resulting crude oil was purified by column chromatography using EtOAc/pentane 5:95 as mobile phase to afford (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**4a**) as a colorless oil (562 mg, 1.29 mmol, 64%).

8. Product modifications

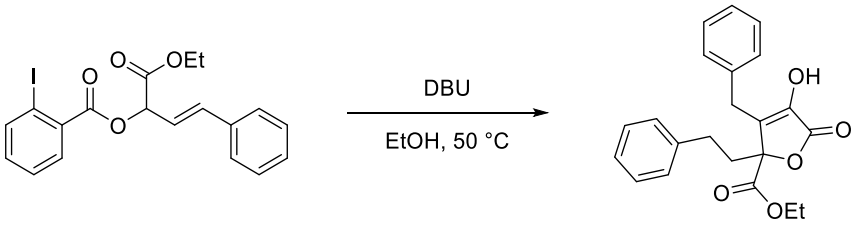
(*E*)-4-Phenylbut-3-ene-1,2-diol (8)



4a **8**

Following a reported procedure,[8] (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**4a**) (87.2 mg, 0.200 mmol, 1.00 equiv) was dissolved in anhydrous THF (2.00 mL) under N_2 in a 5 mL microwave vial. Then $LiAlH_4$ (2.4 M in THF, 0.300 mL, 0.600 mmol, 3.00 equiv) was added at 0 °C and stirred for 1 h. The resulting solution was quenched by the addition of saturated aqueous potassium sodium tartrate (2.00 mL) and the biphasic mixture was stirred for 1 h at room temperature. Then the reaction mixture was diluted with water (2.0 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography using EtOAc/pentane 50:50 as mobile phase affording (*E*)-4-phenylbut-3-ene-1,2-diol (**8**) as a white solid (30.0 mg, 0.183 mmol, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.18 (m, 5H, Ar*H*), 6.70 (dd, *J* = 16.0, 1.3 Hz, 1H, CHC*H*Ph), 6.21 (dd, *J* = 16.0, 6.3 Hz, 1H, C*H*CHPh), 4.44 (m, 1H, HOC*H*CC), 3.76 (dd, *J* = 11.2, 3.6 Hz, 1H, CH_2OH), 3.61 (dd, *J* = 11.2, 7.3 Hz, 1H, CH_2OH), 2.09 (br s, 2H, 2 x O*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 132.4, 128.8, 128.1, 127.8, 126.7, 73.3, 66.6. The values of the NMR spectra are in accordance with reported literature data.[51]

Ethyl 3-benzyl-4-hydroxy-5-oxo-2-phenethyl-2,5-dihydrofuran-2-carboxylate (9)

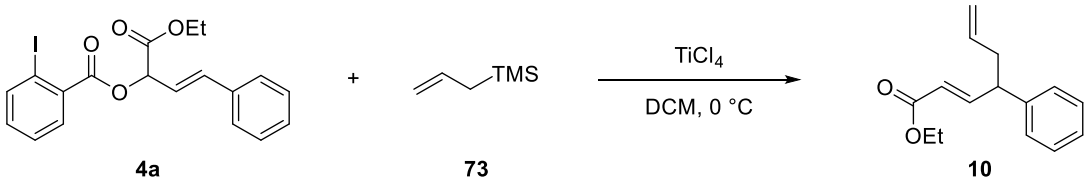


4a **9**

DBU (0.151 mL, 1.00 mmol, 10.0 equiv) was added to a solution of (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**4a**) (43.6 mg, 0.100 mmol, 1.00 equiv) in ethanol (1 mL). The resulting solution was stirred 6 h at 50 °C. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography using MeOH/DCM 2:98 as mobile phase affording ethyl 3-benzyl-4-hydroxy-5-oxo-2-phenethyl-2,5-dihydrofuran-2-carboxylate (**9**) as a white solid (17 mg, 0.046 mmol, 93%). M.p. 111-113 °C; R_f = 0.55 (MeOH/DCM 3:97); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 2H, Ar*H*), 7.27 - 7.21 (m, 5H, Ar*H*), 7.20 - 7.14 (m, 1H, Ar*H*), 7.01 - 6.94 (m, 2H, Ar*H*), 5.78 (br s, 1H, O*H*), 3.95 (q, *J* = 7.1 Hz, 2H, OCH_2CH$_3$), 3.67 (s, 2H, CCH_2Ph), 2.55 - 2.32 (m, 3H, CH_2), 2.19 - 2.05 (m, 1H, CH_2), 1.15 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 168.0, 140.4, 139.1, 136.2, 130.9, 129.1, 128.9, 128.6, 128.5, 127.2, 126.4, 87.2, 62.6, 36.0, 30.2, 29.3, 14.0; IR (ν_{max}, cm^{-1}) 2919 (w), 1739 (s), 1292 (m), 1249 (m), 1218 (m), 1136 (m), 1105 (m), 1017 (m), 748 (s), 691 (m), 668 (s); HRMS (ESI) calcd for $C_{22f}H_{23}O_5^+$ $[M+H]^+$ 367.1540; found $[M+H]^+$ 367.1549.

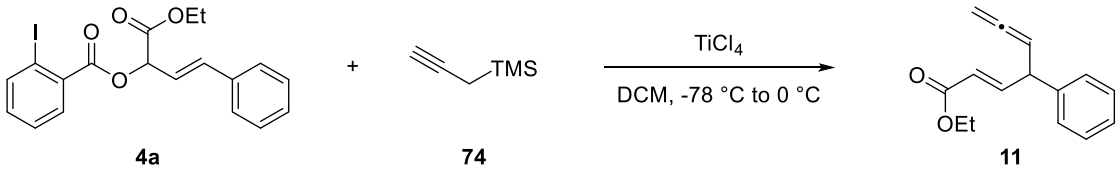
[51] T. Saravanan, R. Selvakumar, M. Doble and A. Chadha, *Tetrahedron: Asymmetry*, **2012**, *23*, 1360.

(*E*)-ethyl 4-phenylhepta-2,6-dienoate (10)



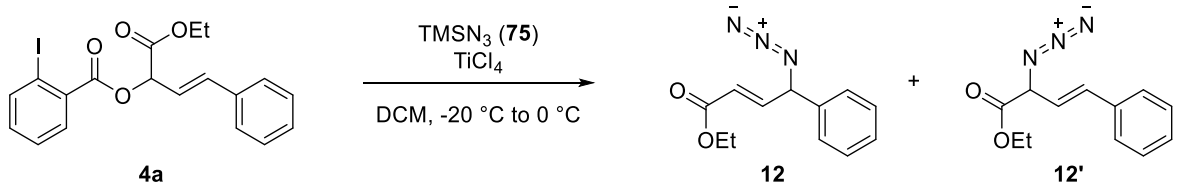
To a solution of (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**4a**) (87.2 mg, 0.200 mmol, 1.00 equiv) and allyltrimethylsilane (**73**) (48.0 µL, 0.300 mmol, 1.50 equiv) in dry DCM (2.0 mL) was added $TiCl_4$ (23.0 µL, 0.210 mmol, 1.05 equiv) dropwise at 0 °C under N_2. The reaction was stirred 15 minutes at 0 °C and then quenched with a saturated solution of $NaHCO_3$ (2.0 mL). The layers were separated and the aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using DCM/pentane 10:90 as mobile phase affording (*E*)-ethyl 4-phenylhepta-2,6-dienoate (**10**) as a colorless oil (38.0 mg, 0.165 mmol, 83 %). R_f = 0.50 (DCM/pentane 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.28 (m, 2H, Ar*H*), 7.27 - 7.15 (m, 3H, Ar*H*), 7.09 (dd, *J* = 15.7, 7.5 Hz, 1H, C*H*CHCO$_2$Et), 5.78 (dd, *J* = 15.7, 1.4 Hz, 1H, CHC*H*CO$_2$Et), 5.69 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1H, CHC*H$_2$*), 5.10 - 4.96 (m, 2H, C*HCH$_2$*), 4.17 (q, *J* = 7.2 Hz, 2H, OC*H$_2$*CH$_3$), 3.50 (qd, *J* = 7.5, 1.3 Hz, 1H, PhC*H*CH$_2$), 2.56 (tt, *J* = 7.1, 1.3 Hz, 2H, PhCHC*H$_2$*), 1.27 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H$_3$*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 151.0, 141.7, 135.7, 128.8, 128.0, 127.0, 121.3, 117.2, 60.5, 48.4, 39.3, 14.4; IR (ν_{max}, cm^{-1}) 2975 (m), 2924 (m), 1718 (s), 1650 (m), 1456 (w), 1368 (m), 1311 (m), 1270 (m), 1233 (m), 1168 (s), 1045 (m), 981 (m), 916 (m), 759 (m), 699 (s); HRMS (ESI) calcd for $C_{15}H_{19}O_2^+$ $[M+H]^+$ 231.1380; found 231.1377.

(*E*)-Ethyl 4-phenylhepta-2,5,6-trienoate (11)



To a solution of (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**4a**) (87.2 mg, 0.200 mmol, 1.00 equiv) and propargyltrimethylsilane (**74**) (60.0 µL, 0.400 mmol, 2.00 equiv) in dry DCM (2.0 mL) was added $TiCl_4$ (23.0 µL, 0.210 mmol, 1.05 equiv) dropwise at -78 °C under N_2. The reaction was allowed to warm slowly to 0 °C and then quenched with a saturated solution of $NaHCO_3$ (2.0 mL). The layers were separated and the aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using EtOAc/pentane 2:98 as mobile phase affording afford (*E*)-ethyl 4-phenylhepta-2,5,6-trienoate (**11**) as a colorless oil (27.0 mg, 0.118 mmol, 59 %). R_f = 0.54 (DCM/pentane 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.31 (m, 2H, Ar*H*), 7.29 - 7.20 (m, 3H, Ar*H*), 7.13 (dd, *J* = 15.6, 7.0 Hz, 1H, C*H*CHCO$_2$Et), 5.84 (dd, *J* = 15.6, 1.5 Hz, 1H, CHC*H*CO$_2$Et), 5.37 (q, *J* = 6.8 Hz, 1H, C*H*CCH$_2$), 4.82 (dd, *J* = 6.6, 2.7 Hz, 2H, CHCC*H$_2$*), 4.18 (q, *J* = 7.1 Hz, 3H, PhC*H* and OC*H$_2$*CH$_3$), 1.28 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H$_3$*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6, 166.6, 149.4, 140.9, 128.9, 128.1, 127.3, 121.9, 91.9, 77.2, 60.5, 47.4, 14.4; IR (ν_{max}, cm^{-1}) 2982 (m), 2924 (m), 2853 (w), 1958 (w), 1715 (s), 1650 (m), 1454 (m), 1367 (m), 1307 (m), 1269 (m), 1232 (m), 1169 (s), 1071 (m), 1040 (s), 982 (m), 853 (m); HRMS (ESI) calcd for $C_{15}H_{17}O_2^+$ $[M+H]^+$ 229.1223; found 229.1220.

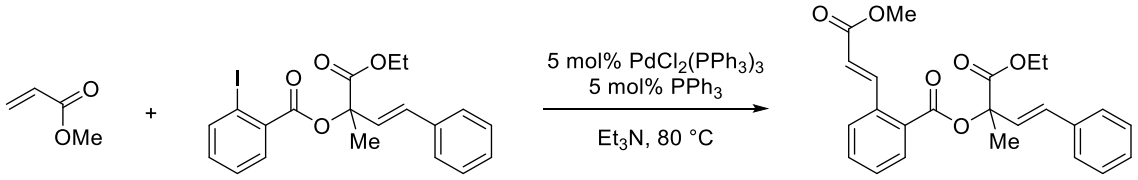
(*E*)-Ethyl 4-azido-4-phenylbut-2-enoate (12) and (*E*)-Ethyl 2-azido-4-phenylbut-3-enoate (12')



4a 12 12'

To a solution of (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**4a**) (87.2 mg, 0.200 mmol, 1.00 equiv) and azidotrimethylsilane (**75**) (40.0 µL, 0.300 mmol, 1.50 equiv) in dry DCM (2.0 mL) was added $TiCl_4$ (23.0 µL, 0.210 mmol, 1.05 equiv) dropwise at -20 °C under N_2. The reaction was allowed to warm to room temperature and then quenched with a saturated solution of $NaHCO_3$ (2.0 mL). The layers were separated and the aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using DCM/pentane 10:90 as mobile phase affording an isomeric mixture of (*E*)-ethyl 4-azido-4-phenylbut-2-enoate (**12**) and (*E*)-ethyl 2-azido-4-phenylbut-3-enoate **(12')** as a colorless oil, 70:30 mixture of **12** and **12'** (40 mg, 0.17 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.28 (m, 5H, Ar*H*), 6.94 (dd, *J* = 15.5, 5.7 Hz, 1H, C*H*CHCO$_2$Et), 6.14 (dd, *J* = 15.5, 1.6 Hz, 1H, CHC*H*CO$_2$Et), 5.18 (dd, *J* = 5.7, 1.6 Hz, 1H, N$_3$C*H*CC), 4.33 - 4.18 (m, 2H, OC*H*$_2$CH$_3$), 1.34 - 1.28 (m, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 144.0, 129.3, 129.1, 127.6, 127.0, 123.0, 65.6, 60.9, 14.4 for γ-azidated ester (**12**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.28 (m, 5H, Ar*H*), 6.77 (dd, *J* = 15.8 Hz, 1.2 Hz, 1H, PhC*H*CH), 6.27 (dd, *J* = 15.8, 7.5 Hz, 1H, PhCHC*H*), 4.54 (dd, *J* = 7.5, 1.3 Hz, 1H, N$_3$C*H*CO$_2$Et), 4.33 - 4.18 (m, 2H, OC*H*$_2$CH$_3$), 1.34 - 1.28 (m, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 136.6, 136.0, 135.5, 128.9, 128.9, 120.8, 63.9, 62.4, 14.3 for α-azidated ester (**12'**). The values of the NMR spectra are in accordance with reported literature data.[52]

(*E*)-1-Ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)benzoate (13)



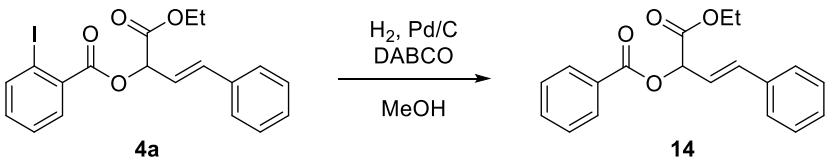
76 5m 13

A flame dried 8 mL microwave vial was charged with (*E*)-1-ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**5m**) (45.0 mg, 0.100 mmol, 1.00 equiv), bis(triphenylphosphine)palladium (II) chloride (3.51 mg, 5.00 µmol, 0.05 equiv), triphenylphosphine (1.31 mg, 5.00 µmol, 0.05 equiv) and trimethylamine (0.5 mL). The resulting reaction mixture was degassed by "pump-freeze-thaw" cycles (3 times) *via* a syringe needle and then methyl acrylate (**76**) (45.0 µL, 0.500 mmol, 5.00 equiv) was added by syringe and the reaction mixture was stirred at 80 °C for 24 h. The solvent was removed under reduced pressure and the product was purified by column chromatography using EtOAc/pentane 15:85 as mobile phase affording (*E*)-1-ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)benzoate (**13**) as a thick colorless oil (27.0 mg, 66.1 µmol, 66%). R_f = 0.32 (EtOAc/pentane 15:85); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 15.9 Hz, 1H, ArC*H*CHCO$_2$Me), 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar*H*), 7.66 – 7.59 (m, 1H, Ar*H*), 7.59 – 7.54 (m, 1H, Ar*H*), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 7.44 – 7.39 (m, 2H, Ar*H*), 7.37 – 7.30 (m, 2H, Ar*H*), 7.29 – 7.22 (m, 1H, Ar*H*), 6.77 (d, *J* = 16.2 Hz, 1H, CHC*H*Ph), 6.65 (d, *J* = 16.2 Hz, 1H, C*H*CHPh), 6.34 (d, *J* = 15.9 Hz, 1H, ArCHC*H*CO$_2$Me), 4.28 (qd, *J* = 7.1, 1.9 Hz, 2H, OC*H*$_2$CH$_3$), 3.74 (s, 3H, OC*H*$_3$), 1.93 (s, 3H, CC*H*$_3$), 1.29 (t, *J* = 7.1 Hz, 3H,

[52] Y. Sawama, S. Nagata, Y. Yabe, K. Morita, Y. Monguchi and H. Sajiki, *Chem. Eur. J.*, **2012**, *18*, 16608.

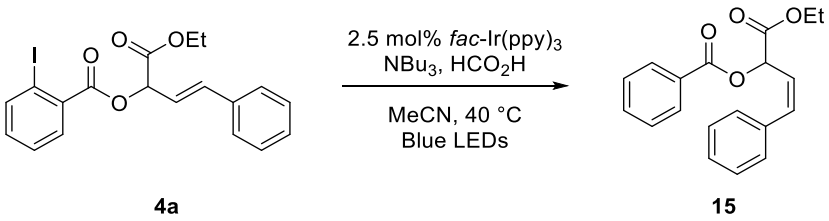
OCH_2CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 167.0, 165.8, 144.0, 136.3, 136.1, 132.7, 131.4, 131.0, 130.3, 129.6, 128.8, 128.4, 128.0, 127.9, 127.0, 120.8, 81.3, 62.1, 51.9, 23.2, 14.2; IR (ν_{max}, cm^{-1}) 2991 (m), 2956 (m), 2926 (m), 1715 (s), 1636 (w), 1479 (w), 1448 (m), 1377 (w), 1315 (m), 1269 (s), 1196 (m), 1173 (m), 1121 (m), 1071 (s), 1044 (m), 1021 (m), 972 (m), 865 (m); HRMS (ESI) calcd for $C_{24}H_{24}NaO_6^+$ $[M+Na]^+$ 431.1465; found 431.1472.

(*E*)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate (14)



Following a reported procedure,[53] in a 20 mL Schlenk flask, (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**4a**) (43.6 mg, 0.100 mmol, 1.00 equiv), DABCO (112 mg, 1.00 mmol, 10.0 equiv) and Pd/C (5.0 mg) were suspended in MeOH (10 mL). The reaction flask was evacuated and backfilled with argon (3 times) before being evacuated and backfilled with H_2 (1 atm). The reaction was stirred 10 min at room temperature, then the hydrogen was evacuated and replaced with argon. The reaction mixture was filtered through a pad of celite and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography using EtOAc/pentane 95:5 as mobile phase affording (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate (**14**) as a colorless oil (24.0 mg, 77.0 µmol, 77 %). R_f = 0.29 (EtOAc/pentane 5:95); ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 - 8.10 (m, 2H, Ar*H*), 7.65 - 7.55 (m, 1H, Ar*H*), 7.53 - 7.41 (m, 4H, Ar*H*), 7.40 - 7.27 (m, 3H, Ar*H*), 6.92 (dd, *J* = 16.0, 1.3 Hz, 1H, CHC*H*Ph), 6.41 (dd, *J* = 15.9, 7.0 Hz, 1H, C*H*CHPh), 5.85 (dd, *J* = 7.0, 1.3 Hz, 1H, OC*H*CC), 4.27 (qd, *J* = 7.1, 5.1 Hz, 2H, OCH_2CH_3), 1.30 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 165.9, 135.8, 135.4, 133.6, 130.1, 129.5, 128.8, 128.7, 128.6, 127.0, 121.2, 73.8, 62.0, 14.3; IR (ν_{max}, cm^{-1}) 3057 (w), 3030 (w), 1748 (m), 1724 (s), 1452 (m), 1315 (w), 1272 (s), 1251 (m), 1196 (m), 1106 (s), 1069 (m), 1024 (m), 965 (m), 738 (m), 712 (s), 689 (s); HRMS (ESI) calcd for $C_{19}H_{18}NaO_4^+$ $[M+Na]^+$ 333.1097; found 333.1099.

(*Z*)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate (15)



Following a reported procedure,[54] a flame dried 8 mL microwave vial with a rubber septum and magnetic stirring bar was charged with (*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (**4a**) (43.6 mg, 0.100 mmol, 1.00 equiv), MeCN (1.0 mL), tributylamine (240 µL, 1.00 mmol, 10.0 equiv), formic acid (38 µL, 1.00 mmol, 10.0 equiv) and *fac*-Ir(ppy)$_3$ (1.64 mg, 2.50 µmol, 0.025 equiv). The resulting reaction mixture was degassed by "pump-freeze-thaw" cycles (3 times) *via* a syringe needle and placed in a 250 mL beaker with blue LEDs wrapped inside. The reaction mixture was stirred at 40 °C for 18 h. The solvent was removed under reduced pressure and the product was purified by column chromatography using DCM/pentane 50:50 as mobile phase affording (*Z*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate (**15**) as a white solid (25.2 mg, 82.0 µmol, 82%). M.p. 76-78 °C; R_f = (DCM/pentane 50:50); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 - 8.03 (m, 2H, Ar*H*), 8.60 - 7.54 (m, 1H, Ar*H*),

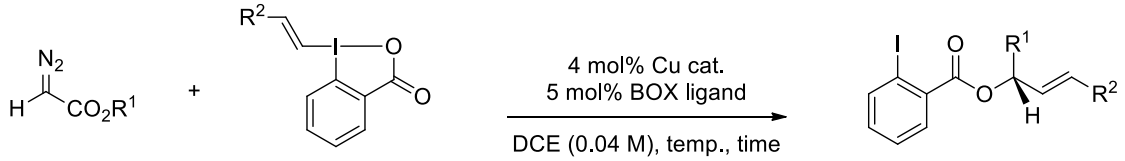
[53] N. Faucher, Y. Ambroise, J.-C. Cintrat, E. Doris, F. Pillon and B. Rousseau, *J. Org. Chem.*, **2002**, *67*, 932.
[54] J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam and C. R. J. Stephenson, *Nat. Chem.*, **2012**, *4*, 854.

7.51 - 7.28 (m, 7H, Ar*H*), 6.94 (d, *J* = 11.4 Hz, 1H, CHC*H*Ph), 6.05 (dd, *J* = 9.8, 0.9 Hz, 1H, OC*H*CC), 5.91 (dd, *J* = 11.4, 9.9 Hz, 1H, C*H*CHPh), 4.28 (q, *J* = 7.1 Hz, 2H, OC$H_2$$CH_3$), 1.30 (t, *J* = 7.1 Hz, 3H, OCH_2C*H_3*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 165.8, 136.8, 135.4, 133.5, 130.1, 129.5, 129.0, 128.7, 128.5, 128.3, 123.0, 70.3, 62.0, 14.2; IR (ν_{max}, cm^{-1}) 3065 (w), 3024 (w), 2981 (w), 1750 (s), 1722 (s), 1452 (m), 1370 (w), 1333 (w), 1315 (m), 1278 (s), 1258 (s), 1194 (m), 1100 (s), 1069 (s), 1026 (s), 814 (m), 773 (m), 710 (s); HRMS (ESI) calcd for $C_{19}H_{18}NaO_4^+$ $[M+Na]^+$ 333.1097; found 333.1106.

9. Enantioselective transformation

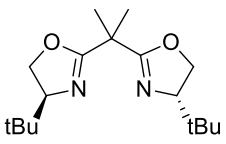
Table S3: Preliminary results for the enantioselective transformation

Under inert atmosphere, a catalytic solution was prepared by mixing Cu cat. (4.00 µmol, 0.08 equiv), and BOX ligand (**3b-d**) (5.00 µmol, 0.10 equiv) in DCE (0.500 mL) at 25 °C for 1 h.
0.250 mL of the catalytic solution was then added to a stirring suspension of VBX (0.05 mmol, 1.00 equiv) and diazo compound (0.10 mmol, 2.00 equiv) in DCE (1.0 mL).
The reaction mixture was stirred at the indicated temperature and time (monitored by TLC (EtOAc/pentane 5:95 and MeOH/DCM 5:95)) and the solvent was removed under reduced pressure. The resulting crude oil was purified by PTLC (EtOAc/pentane) directly without further work-up to afford the corresponding allylic ester product.

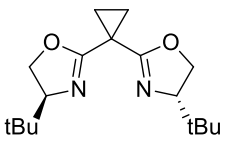


entry	diazo R^1 =	VBX R^2 =	Cu cat.	ligand	temp.	time	yield[a]	ee[b]
1	Et	Ph	$Cu(CH_3CN)_4BF_4$	**3b**	25 °C	2 h	> 90%	14%
2	Et	Ph	$Cu(OTf)_2$	**3b**	25 °C	2 h	> 90%	13%
3	Et	Ph	$Cu(CH_3CN)_4BF_4$	**3d**	25 °C	2 h	> 90%	33%
4	Et	Ph	$Cu(CH_3CN)_4BF_4$	**3d**	0 °C	8 h	50%	20%
5[c]	Et	Ph	$Cu(CH_3CN)_4BF_4$	**3d**	25 °C	2 h	> 90%	40%
6[d]	Et	Ph	$Cu(CH_3CN)_4BF_4$	**3d**	25 °C	2 h	56%	30%
7	Et	Ph	$Cu(OTf)_2$	**3d**	25 °C	2 h	> 90%	30%
8[e]	Et	Ph	$Cu(CH_3CN)_4BF_4$	**3d**	25 °C	2 h	> 90%	23%
9	Et	Cy	$Cu(CH_3CN)_4BF_4$	**3d**	25 °C	< 1h	> 90%	30%
10	BHT	Ph	$Cu(CH_3CN)_4BF_4$	**3d**	25 °C	< 1h	> 90%	50%

[a] Crude ^1H NMR yield using CH_2Br_2 as internal standard. [b] Obtained by chiral HPLC. [c] Using DCE/acetone 1:1 as solvent. [d] Using DCE/*t*AmOH 1:1 as solvent. In this case, the three-component product **6a** was also observed (19%). [e] Dropwise addition of the diazo in 1 h (0.6 M solution in DCE). Et = ethyl, Ph = phenyl, Cy = cyclohexyl, BHT = 2,6-di-*tert*-butyl-4-methylphenyl.

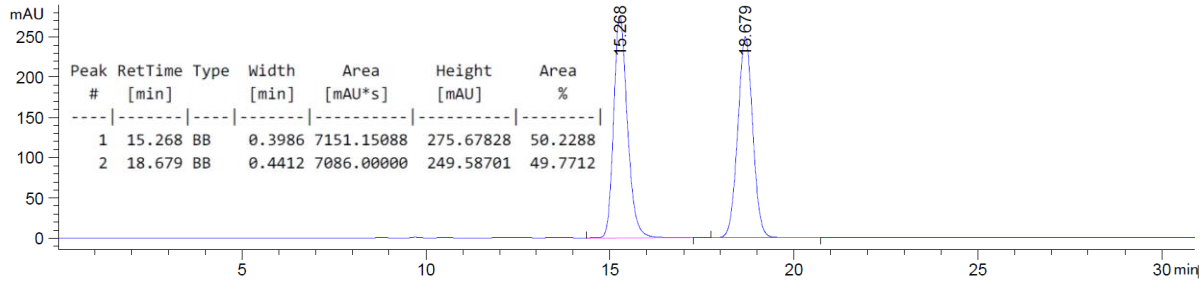


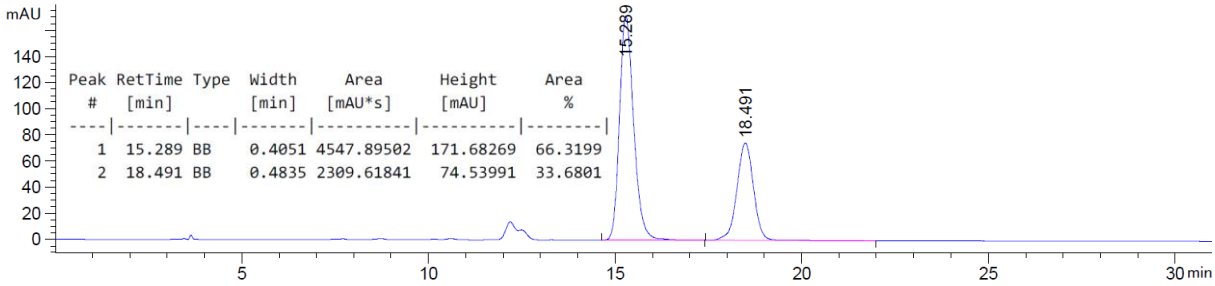
3b



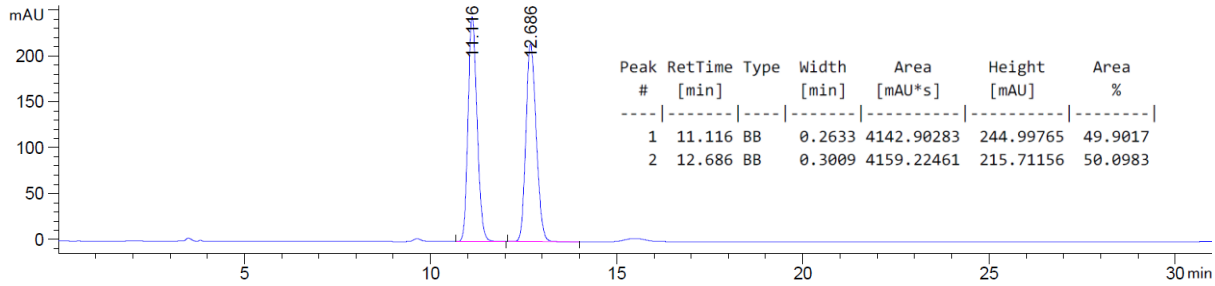
3d

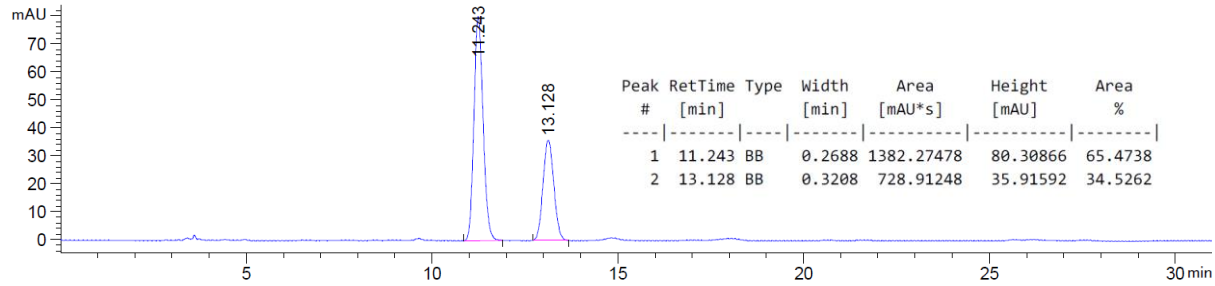
HPLC of compound **4a** (entry 3)



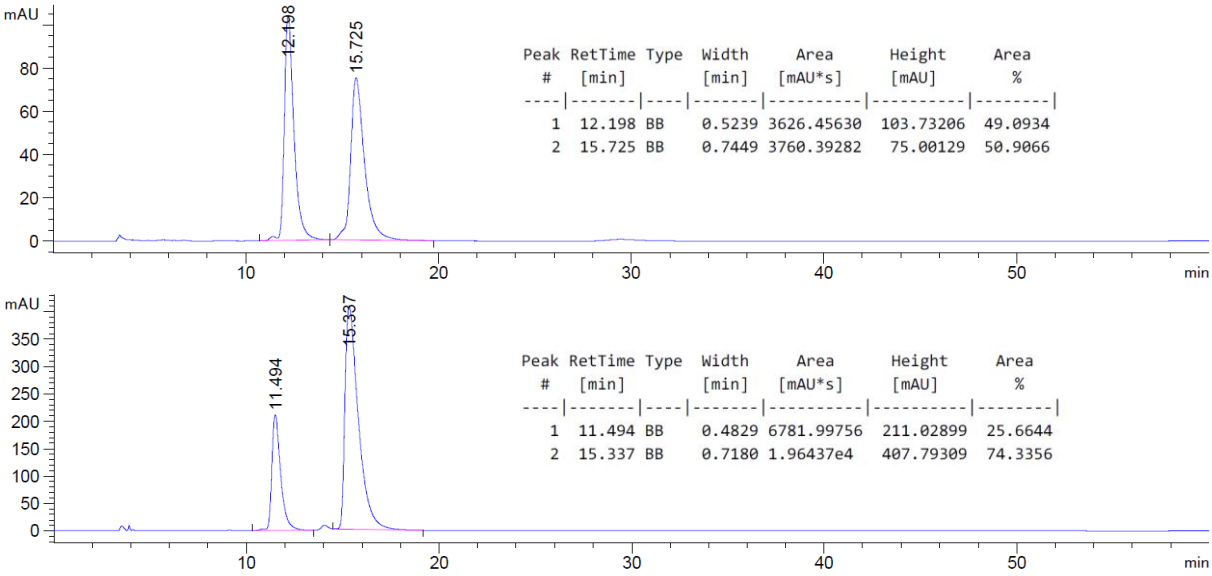


HPLC of compound **4j** (entry 9)





HPLC of compound **5c** (entry 10)

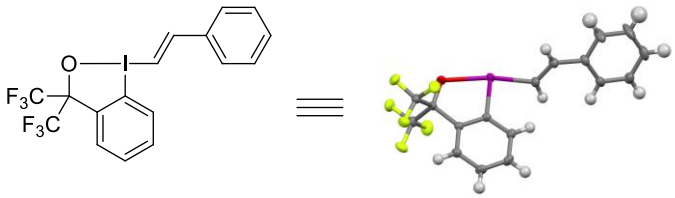


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.198	BB	0.5239	3626.45630	103.73206	49.0934
2	15.725	BB	0.7449	3760.39282	75.00129	50.9066

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.494	BB	0.4829	6781.99756	211.02899	25.6644
2	15.337	BB	0.7180	1.96437e4	407.79309	74.3356

10. Crystals data

Compound 1'a. CCDC number 1993681.

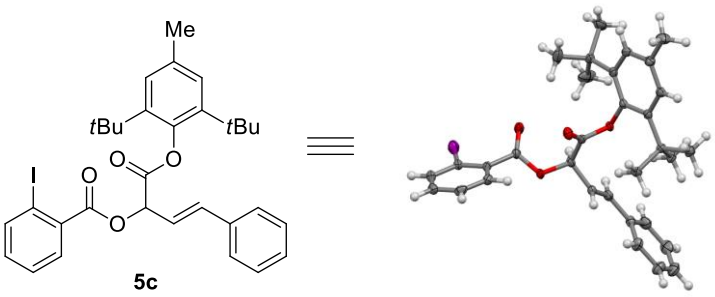


1'a

The ORTEP picture has been obtained by using a probability level of 50% for the ellipsoid display.

Empirical formula	$C_{17}H_{11}F_6IO$	
Formula weight	472.16	
Temperature	100.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.1353(5) Å	α = 90°.
	b = 15.0180(6) Å	β= 106.691(5)°.
	c = 10.6385(5) Å	γ = 90°.
Volume	1704.12(14) $Å^3$	
Z	4	
Density (calculated)	1.840 Mg/m^3	
Absorption coefficient	1.942 mm^{-1}	
F(000)	912	
Crystal size	0.514 x 0.114 x 0.098 mm^3	
Theta range for data collection	2.415 to 33.022°.	
Index ranges	-16 ≤ h ≤ 16, -22 ≤ k ≤ 21, -16 ≤ l ≤ 15	
Reflections collected	7694	
Independent reflections	7694	
Completeness to q = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.696	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7694 / 0 / 227	
Goodness-of-fit on F^2	0.914	
Final R indices [I > 2sigma(I)]	R_1 = 0.0264, wR_2 = 0.0545	
R indices (all data)	R_1 = 0.0419, wR_2 = 0.0568	
Largest diff. peak and hole	1.621 and -0.734 e.$Å^{-3}$	

Compound 5c. CCDC number 1897009.



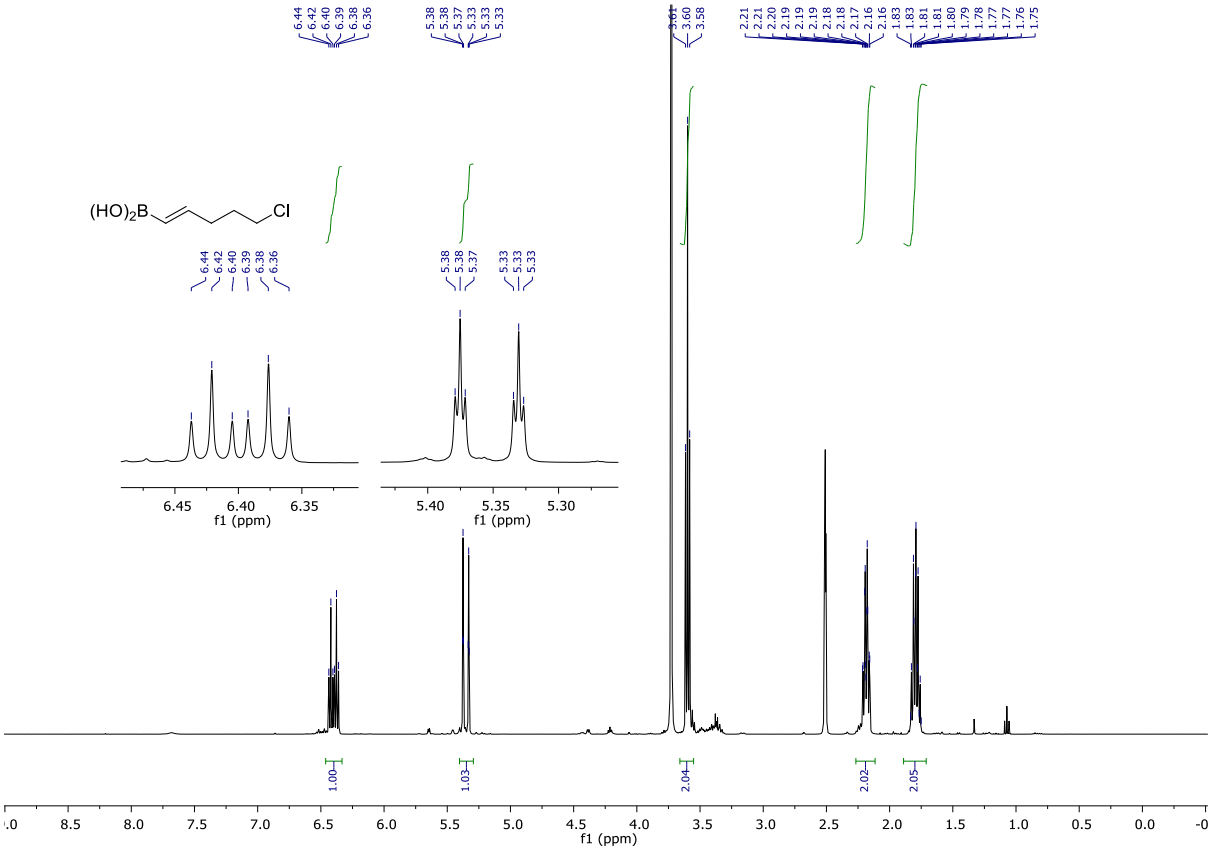
5c

The ORTEP picture has been obtained by using a probability level of 50% for the ellipsoid display.

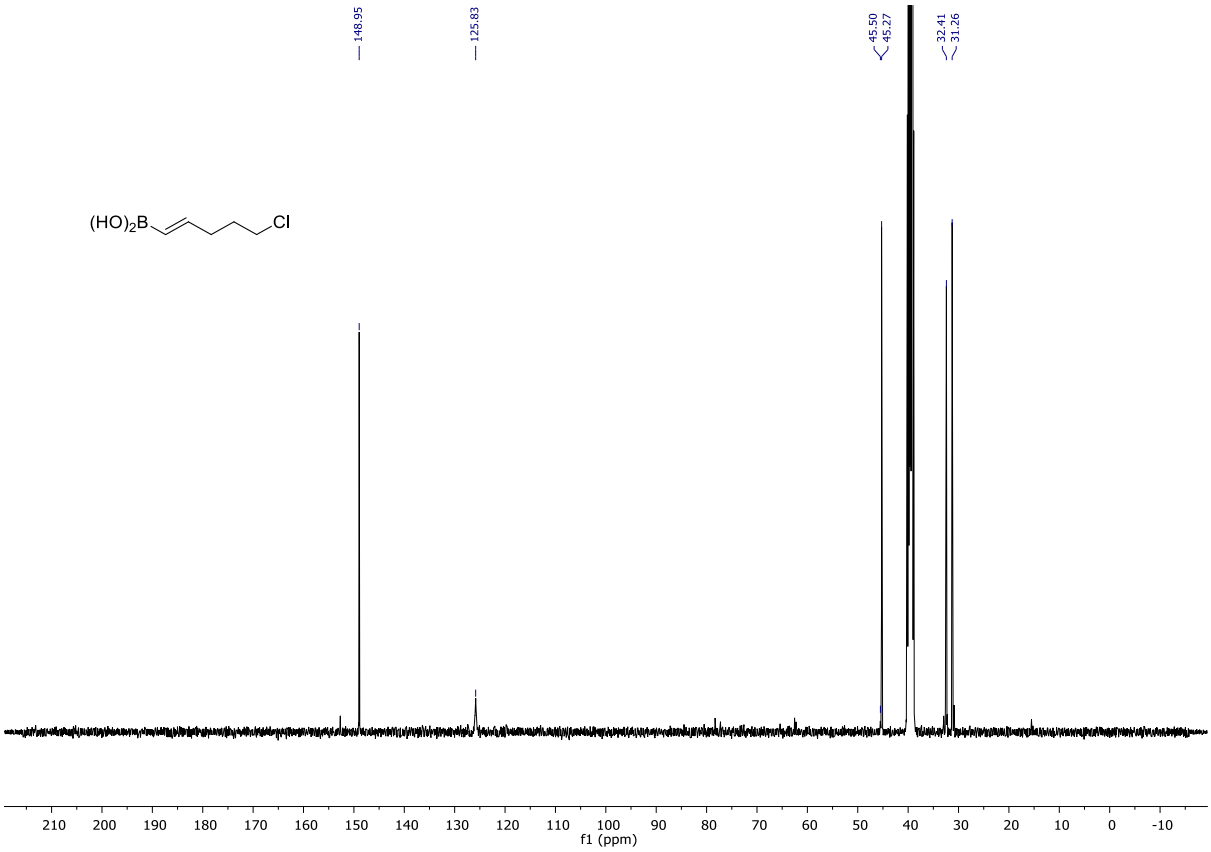
Empirical formula	$C_{32}H_{35}IO_4$	
Formula weight	610.50	
Temperature	101(1) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.8114(6) Å	α = 81.599(4)°.
	b = 10.9975(5) Å	β = 82.906(5)°.
	c = 12.6115(7) Å	γ = 78.119(4)°.
Volume	1444.84(13) $Å^3$	
Z	2	
Density (calculated)	1.403 Mg/m^3	
Absorption coefficient	8.972 mm^{-1}	
F(000)	624	
Crystal size	0.635 x 0.181 x 0.049 mm^3	
Theta range for data collection	3.559 to 75.162°.	
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 10, -15 ≤ l ≤ 15	
Reflections collected	10366	
Independent reflections	5771 [R_{int} = 0.0382]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.675 and 0.116	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5771 / 0 / 341	
Goodness-of-fit on F^2	1.039	
Final R indices [I > 2sigma(I)]	R_1 = 0.0400, wR_2 = 0.1027	
R indices (all data)	R_1 = 0.0464, wR_2 = 0.1072	
Largest diff. peak and hole	0.919 and -1.211 e.$Å^{-3}$	

11. Spectra of new compounds

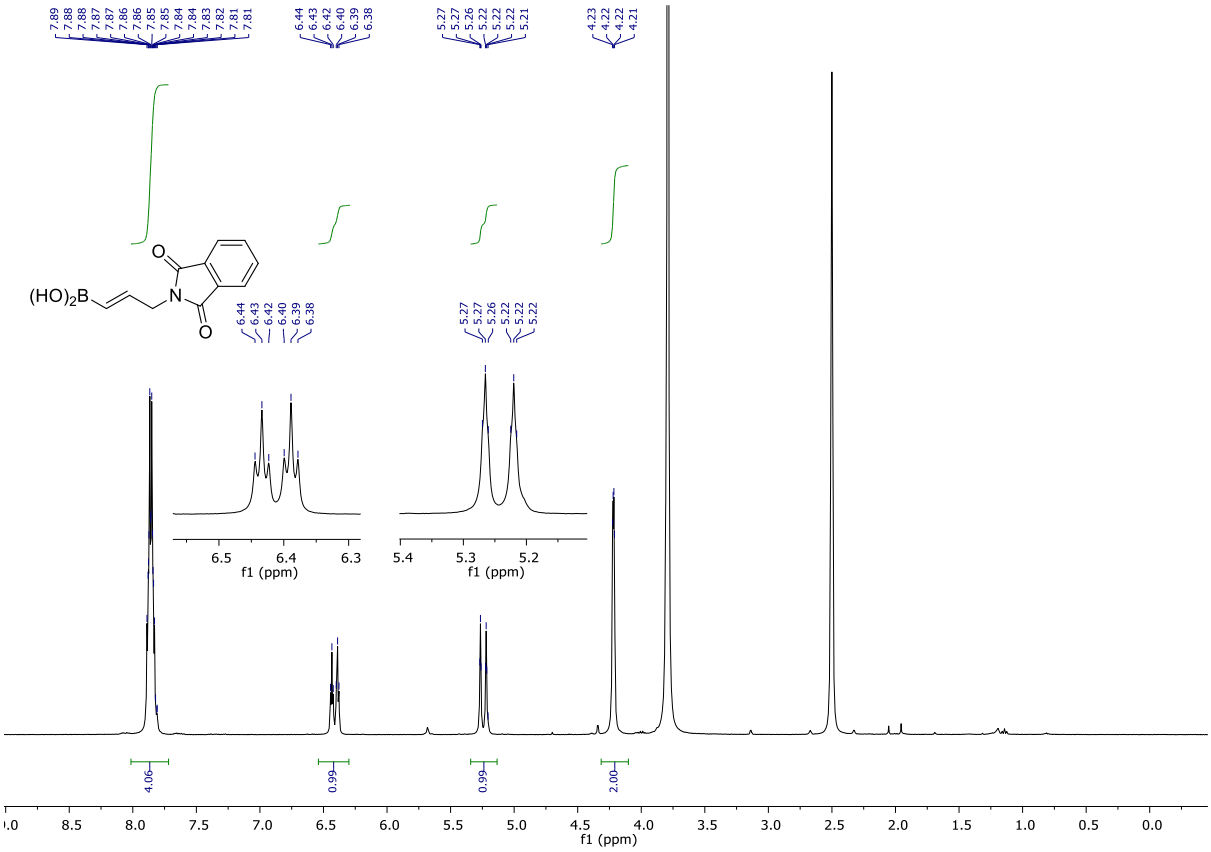
^{1}H-NMR (400 MHz, DMSO-d_6/D_2O 9:1) of compound **50n**



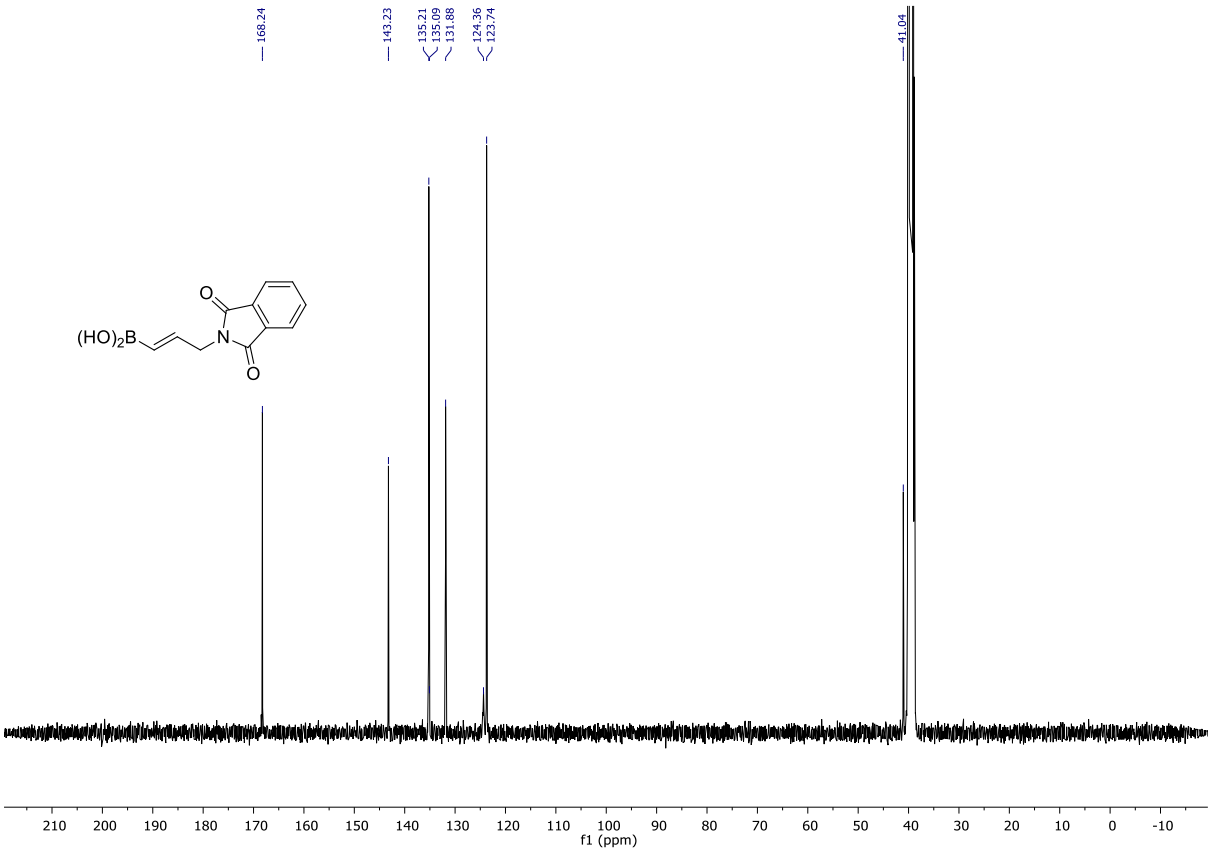
^{13}C-NMR (101 MHz, DMSO-d_6/D_2O 9:1) of compound **50n**



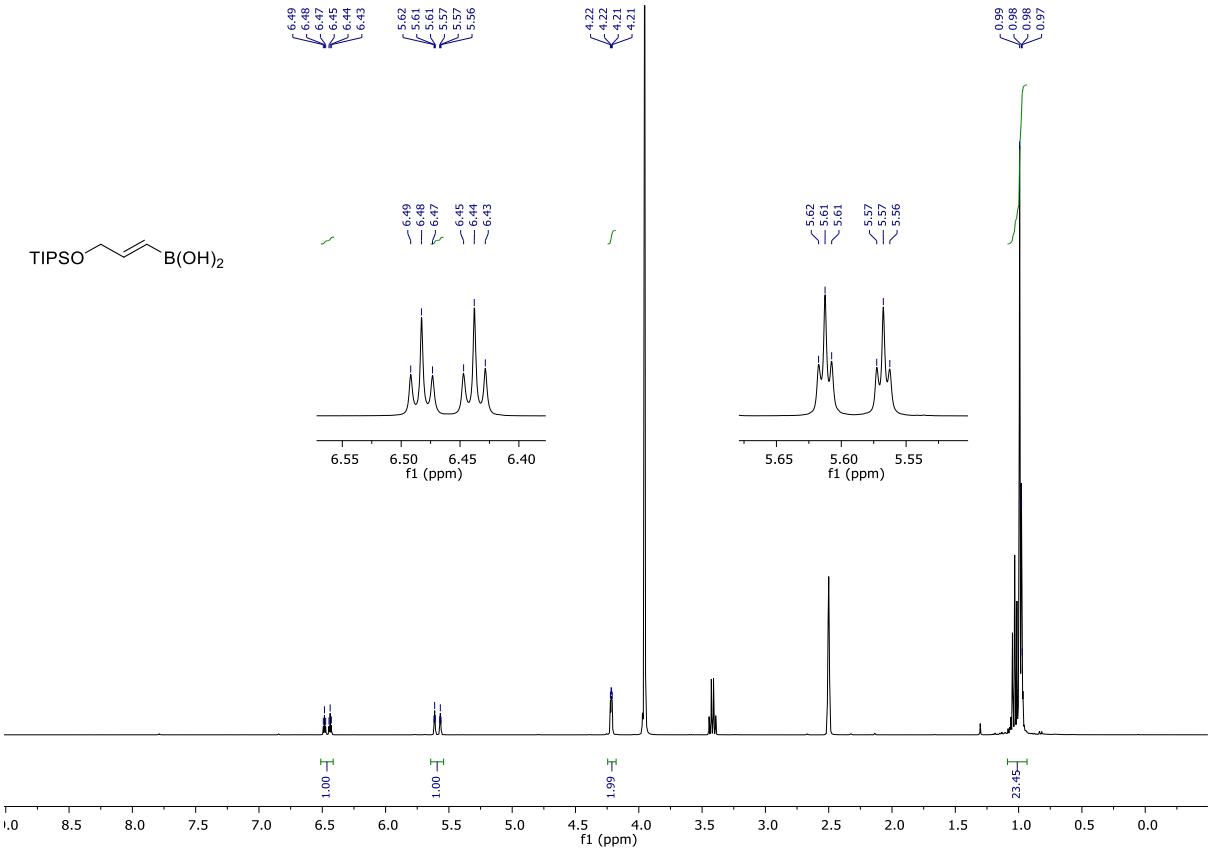
^{1}H-NMR (400 MHz, DMSO-d_6/D_2O 9:1) of compound **50p**



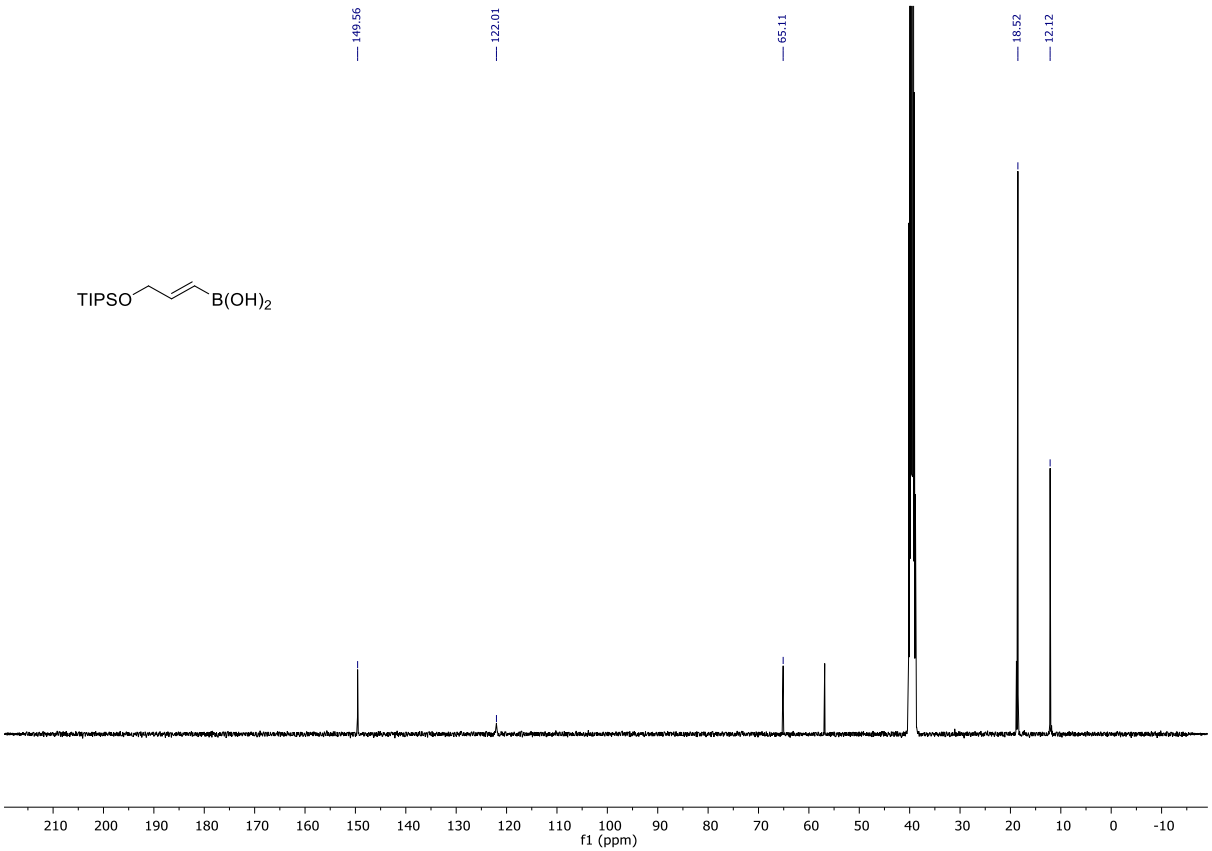
^{13}C-NMR (101 MHz, DMSO-d_6/D_2O 9:1) of compound **50p**



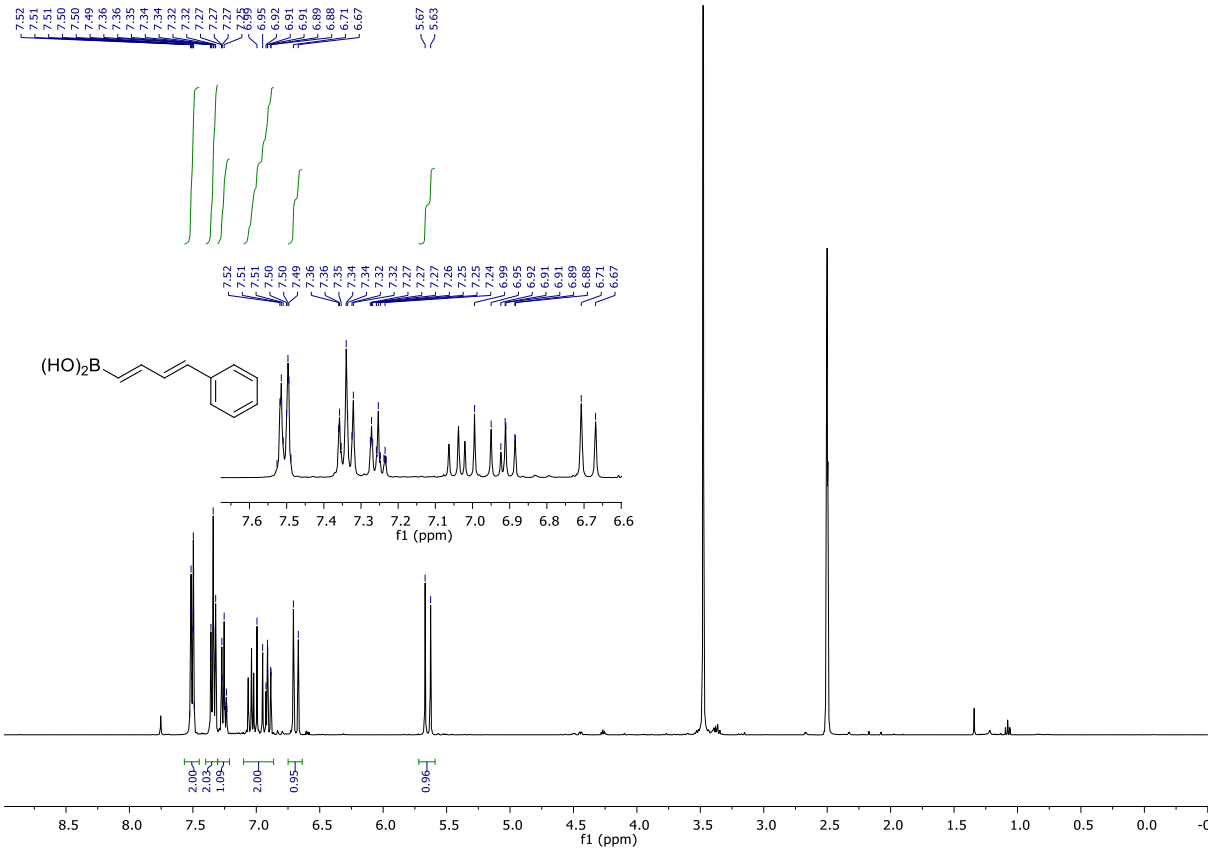
^{1}H-NMR (400 MHz, DMSO-d_6/D_2O 9:1) of compound **50q**



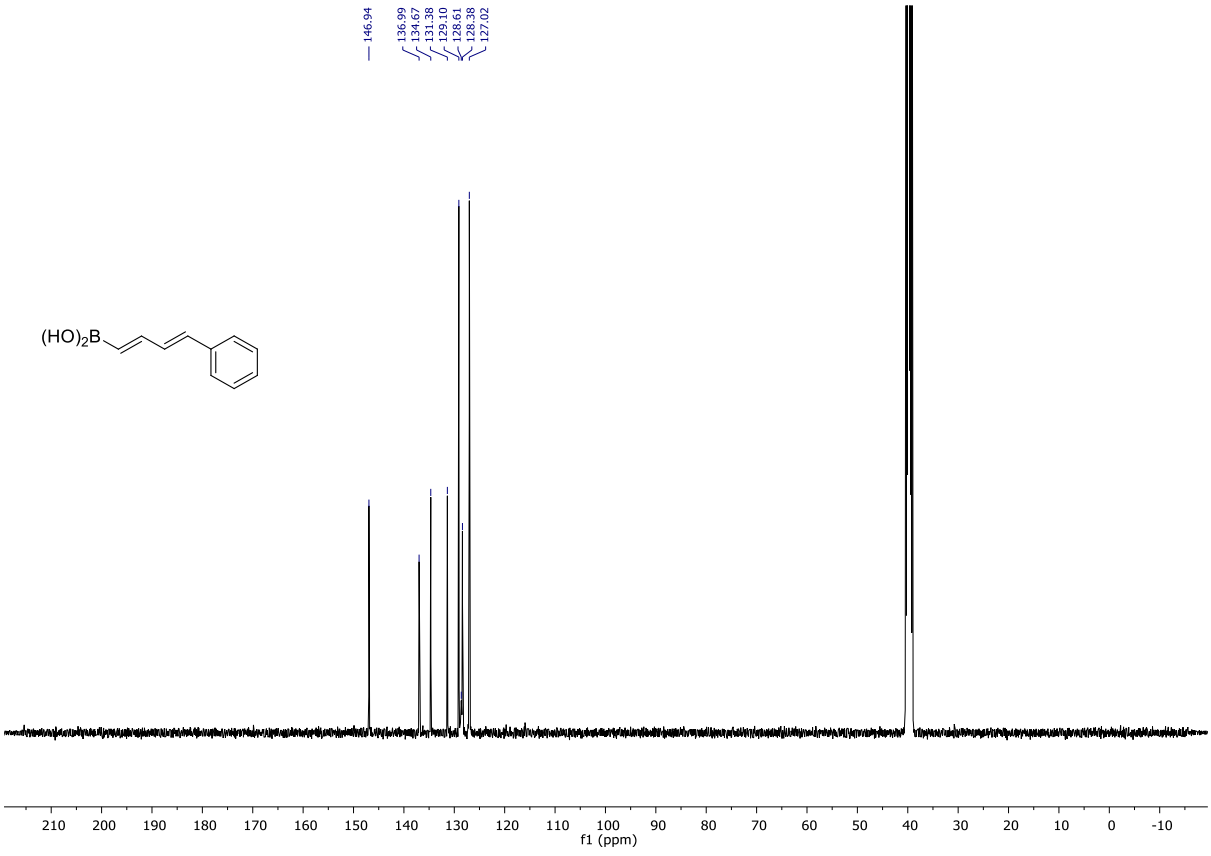
^{13}C-NMR (101 MHz, DMSO-d_6/D_2O 9:1) of compound **50q**



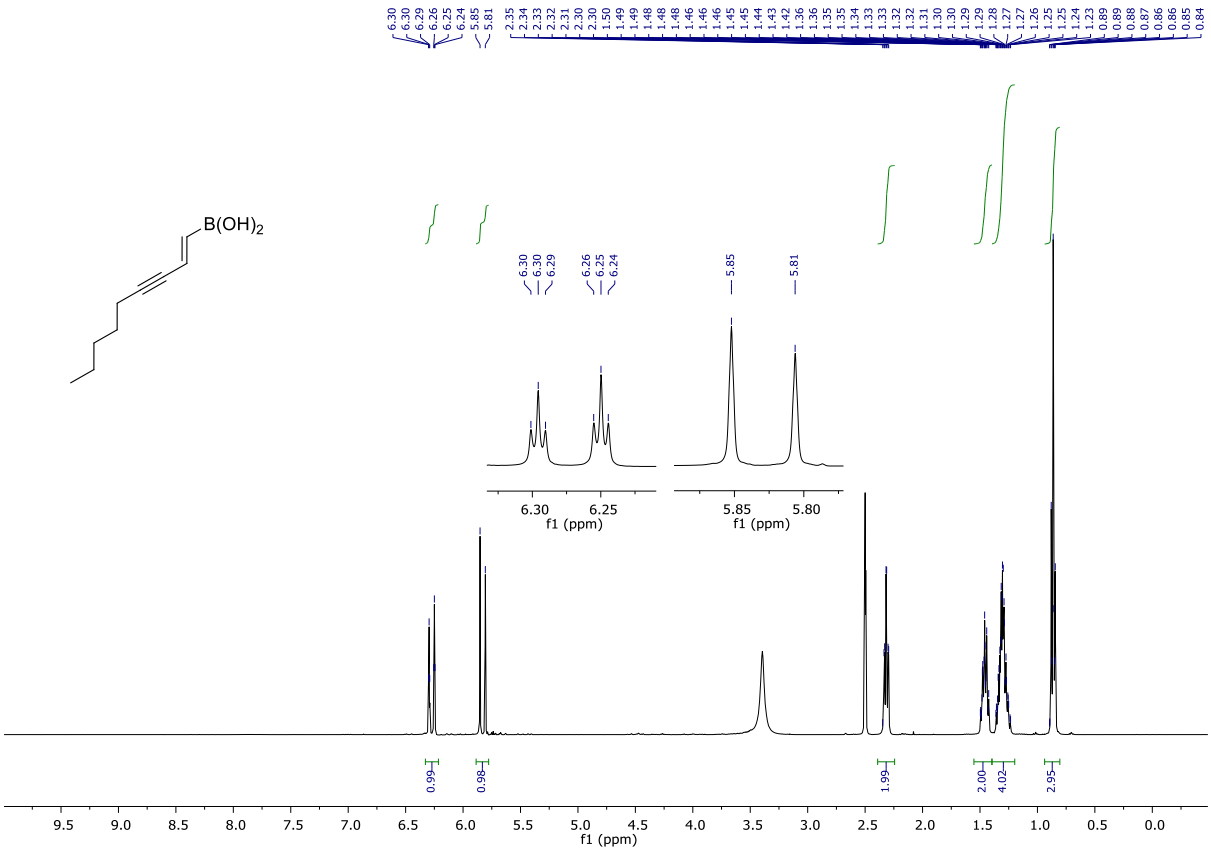
^{1}H-NMR (400 MHz, DMSO-d_6/D_2O 9:1) of compound **50t**



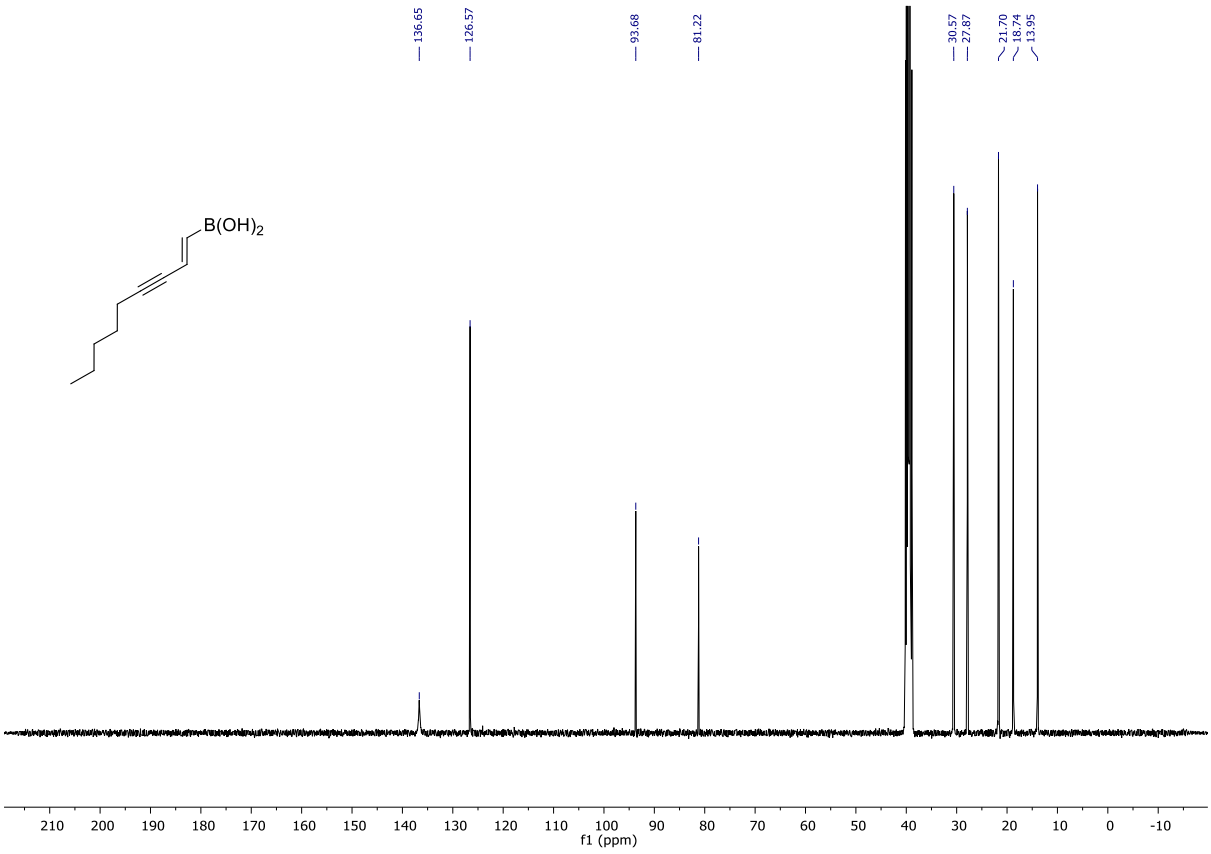
^{13}C-NMR (101 MHz, DMSO-d_6/D_2O 9:1) of compound **50t**



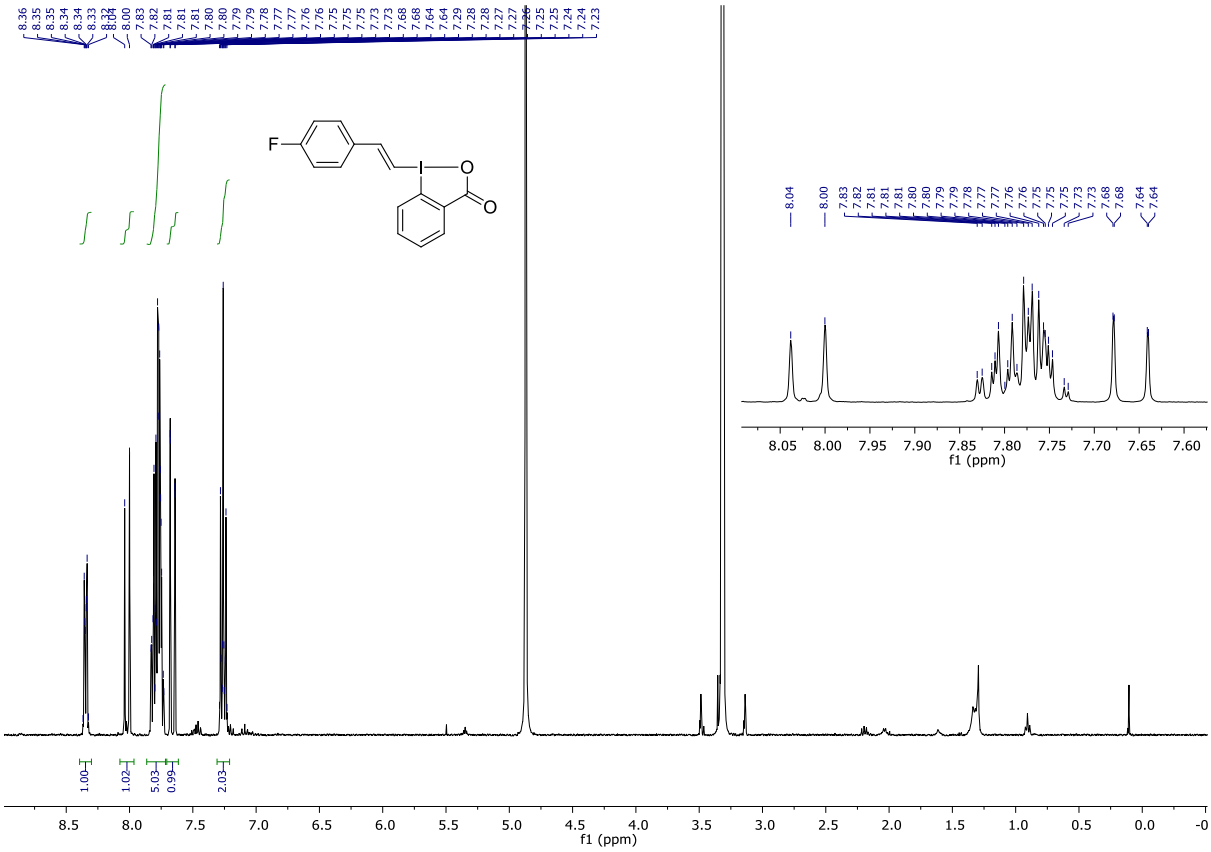
^{1}H-NMR (400 MHz, DMSO-d_6/D_2O 9:1) of compound **50u**



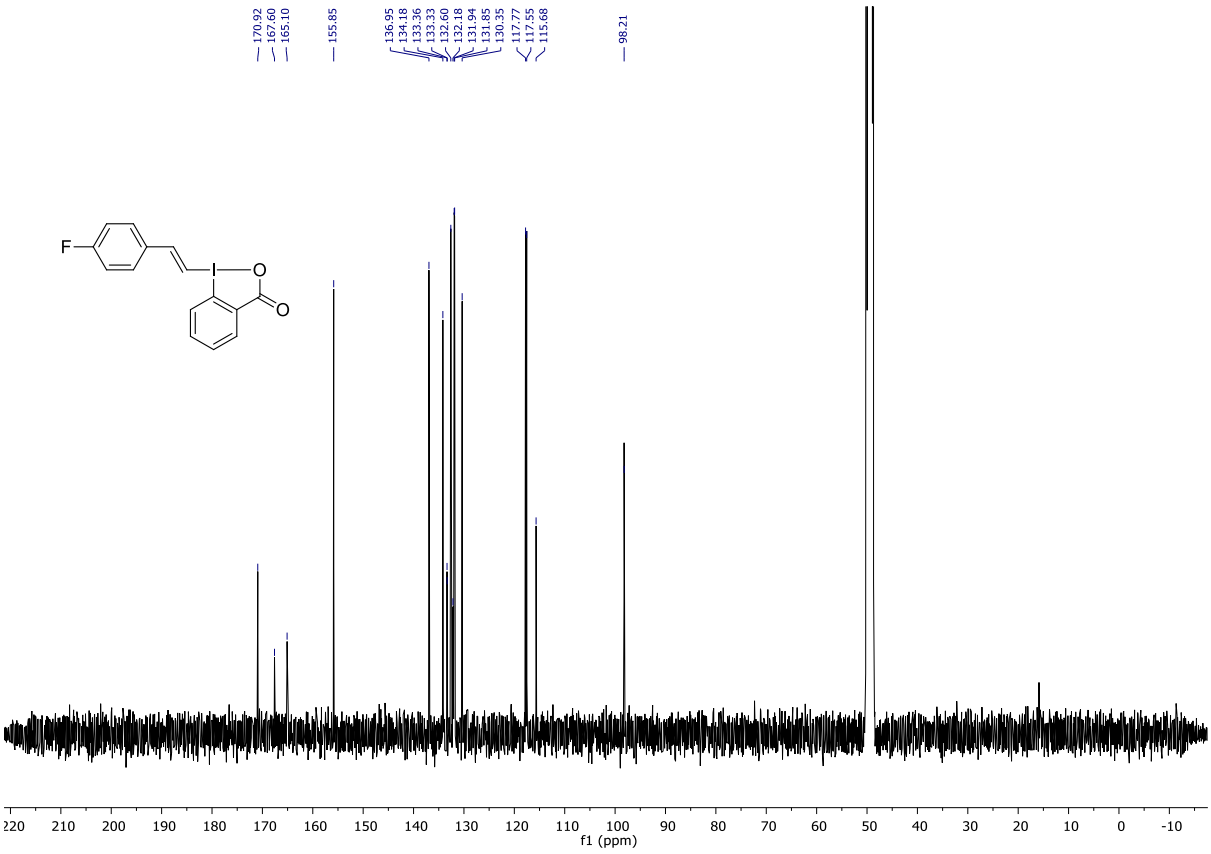
^{13}C-NMR (101 MHz, DMSO-d_6/D_2O 9:1) of compound **50u**



^{1}H-NMR (400 MHz, CD_3OD) of compound **1e**

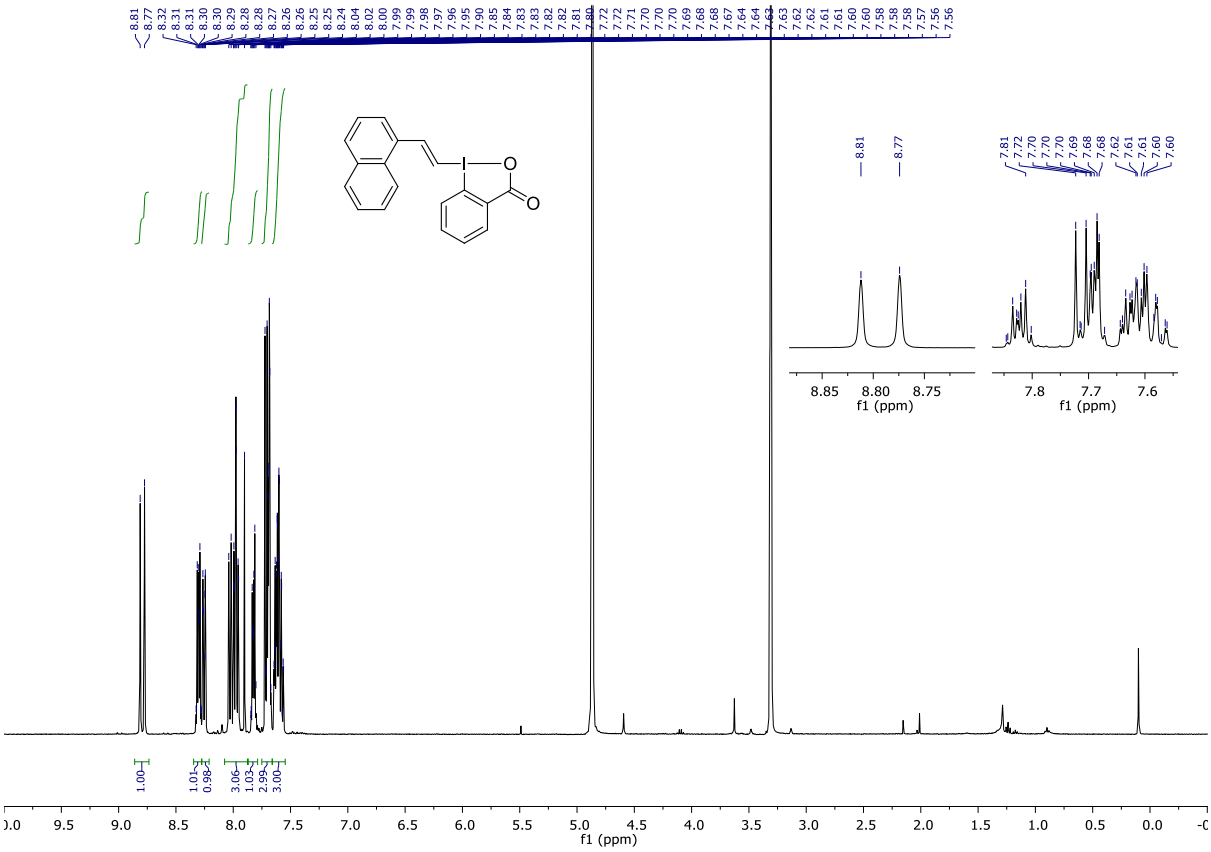


^{13}C-NMR (101 MHz, CD_3OD) of compound **1e**

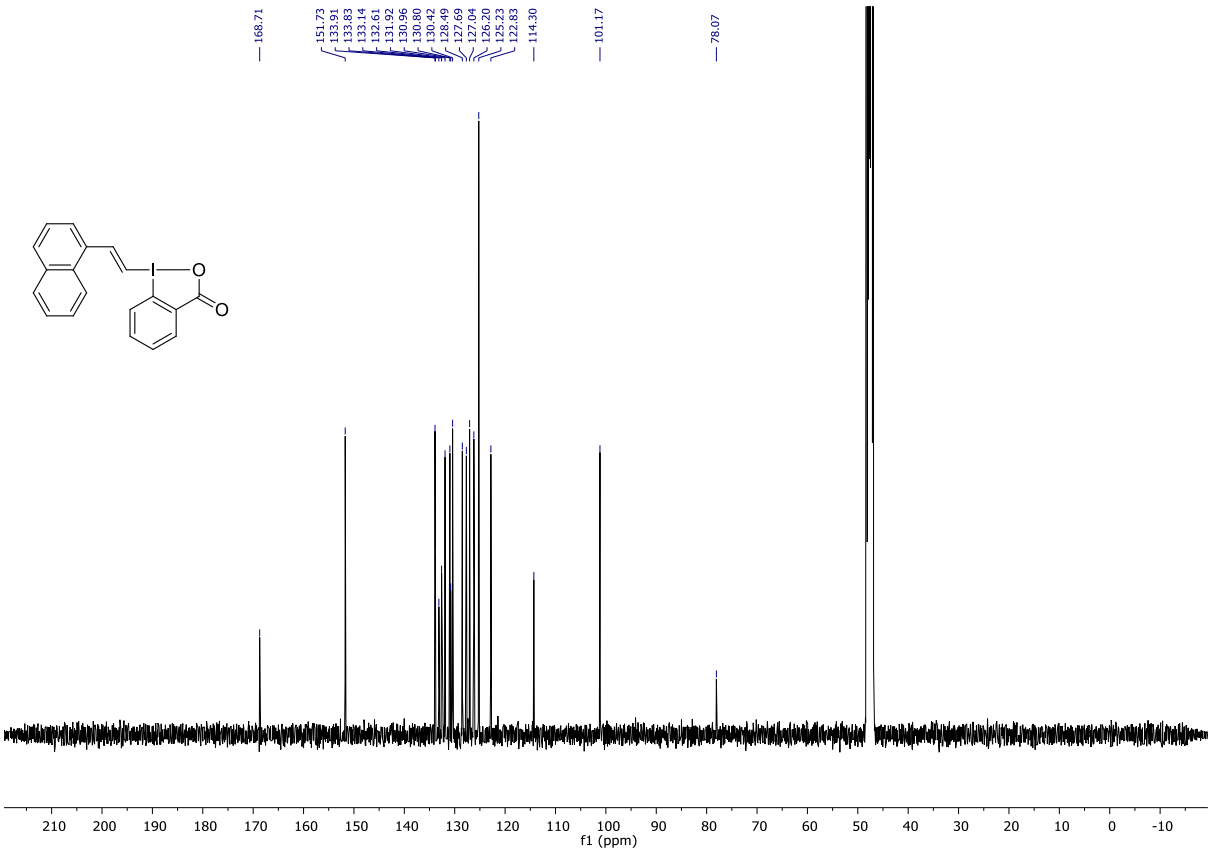


^{19}F-NMR (376 MHz, CD_3OD) of compound **1e**

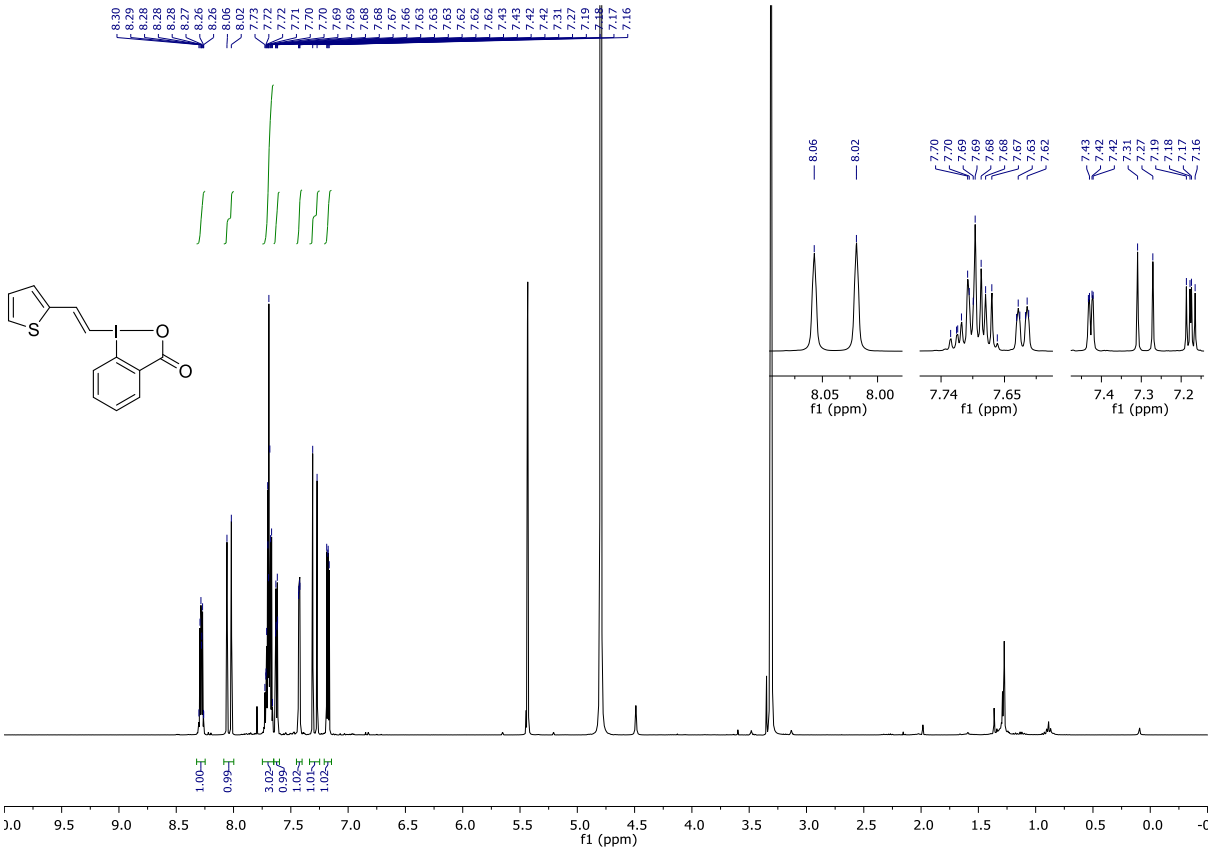
^{1}H-NMR (400 MHz, CD_3OD) of compound **1f**



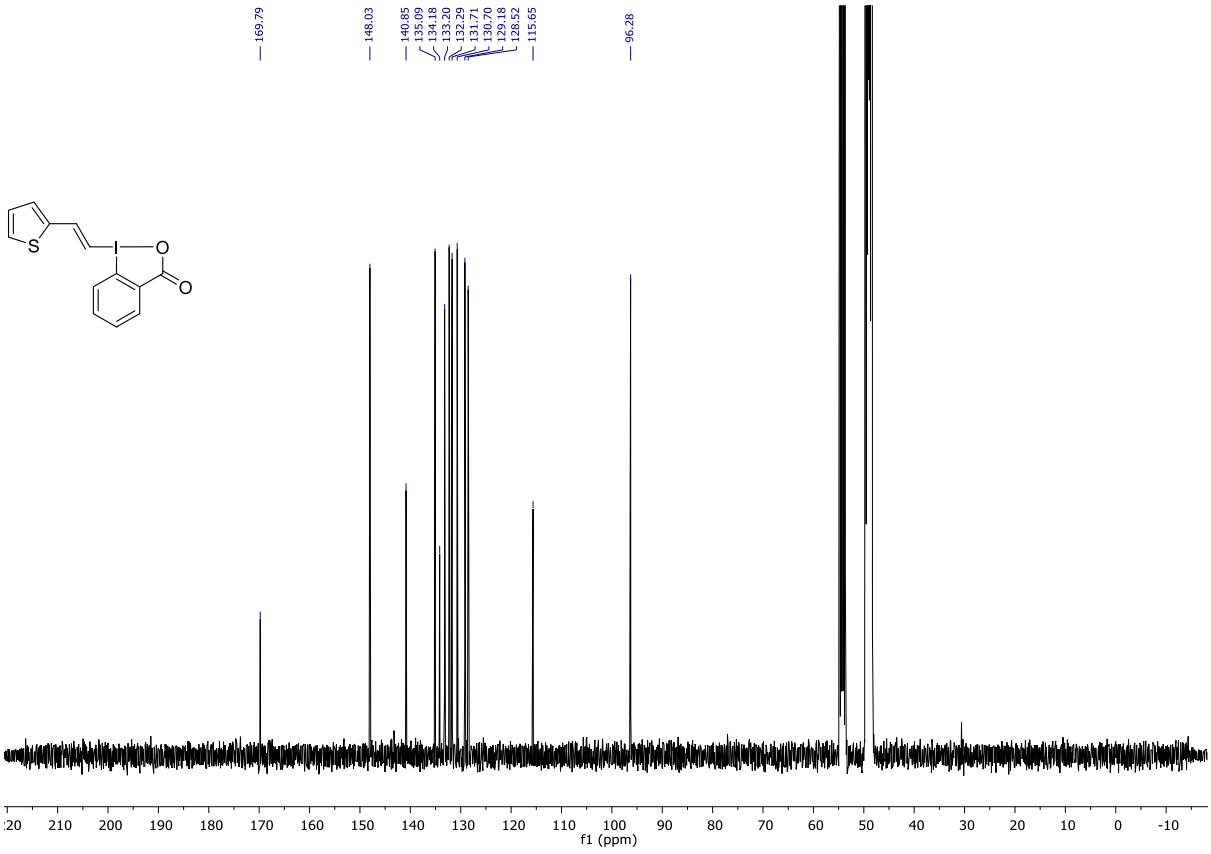
^{13}C-NMR (101 MHz, CD_3OD) of compound **1f**



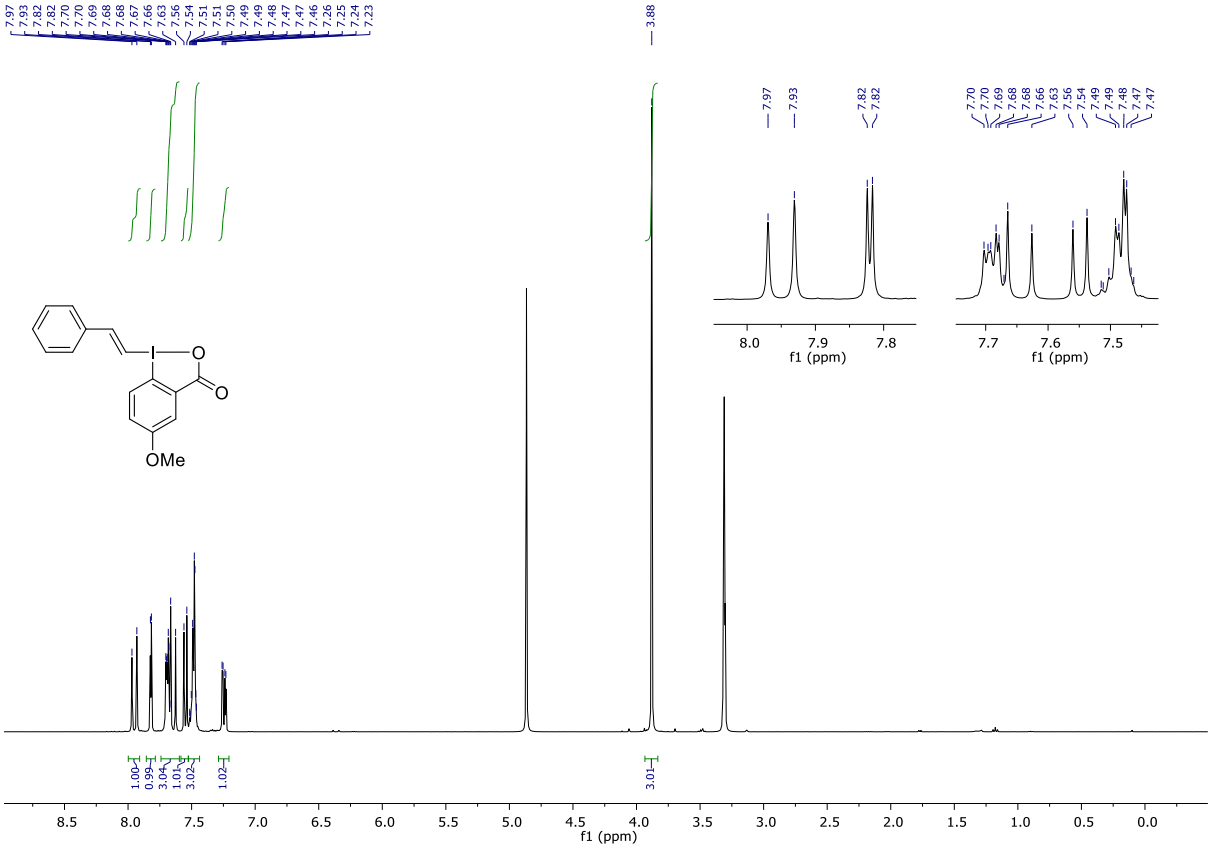
^{1}H-NMR (400 MHz, CD_3OD/CD_2Cl_2 9:1) of compound **1g**



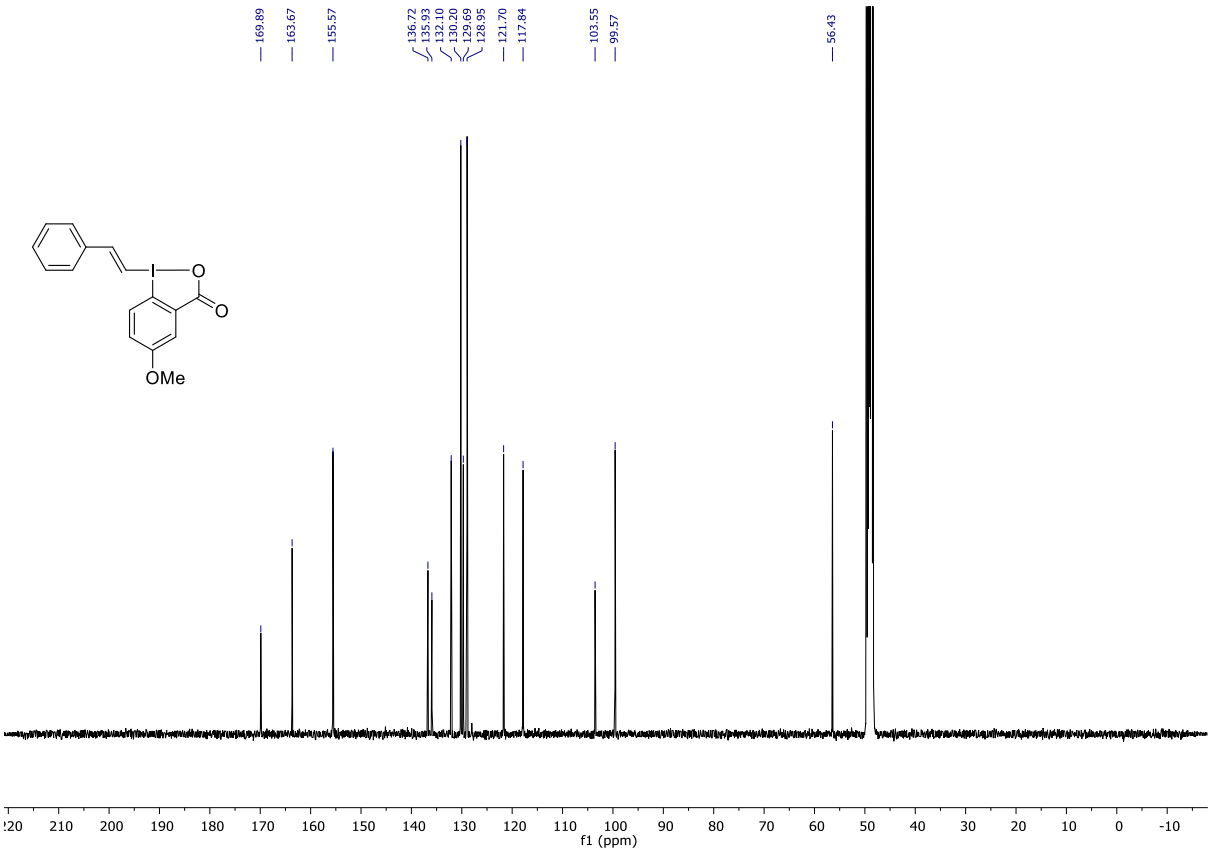
^{13}C-NMR (101 MHz, CD_3OD/CD_2Cl_2 9:1) of compound **1g**



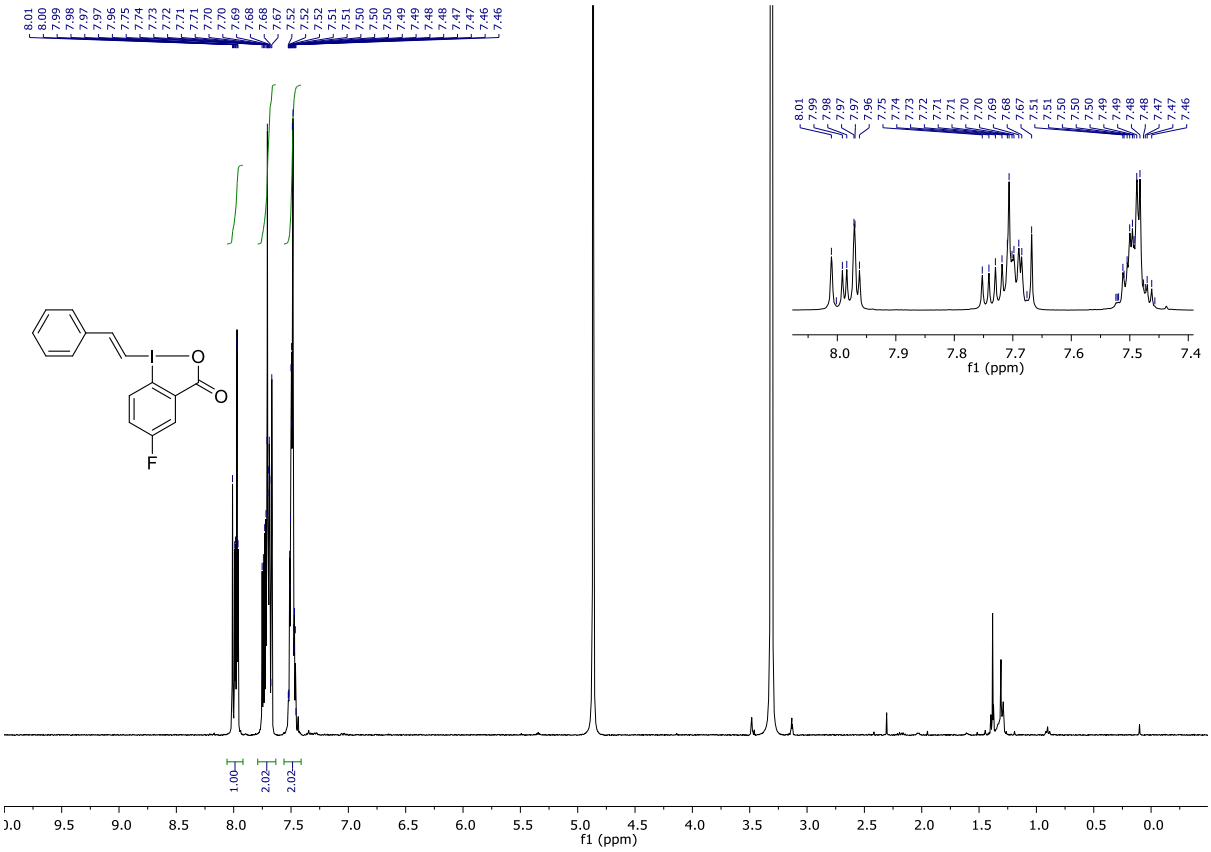
^{1}H-NMR (400 MHz, CD_3OD) of compound **1h**



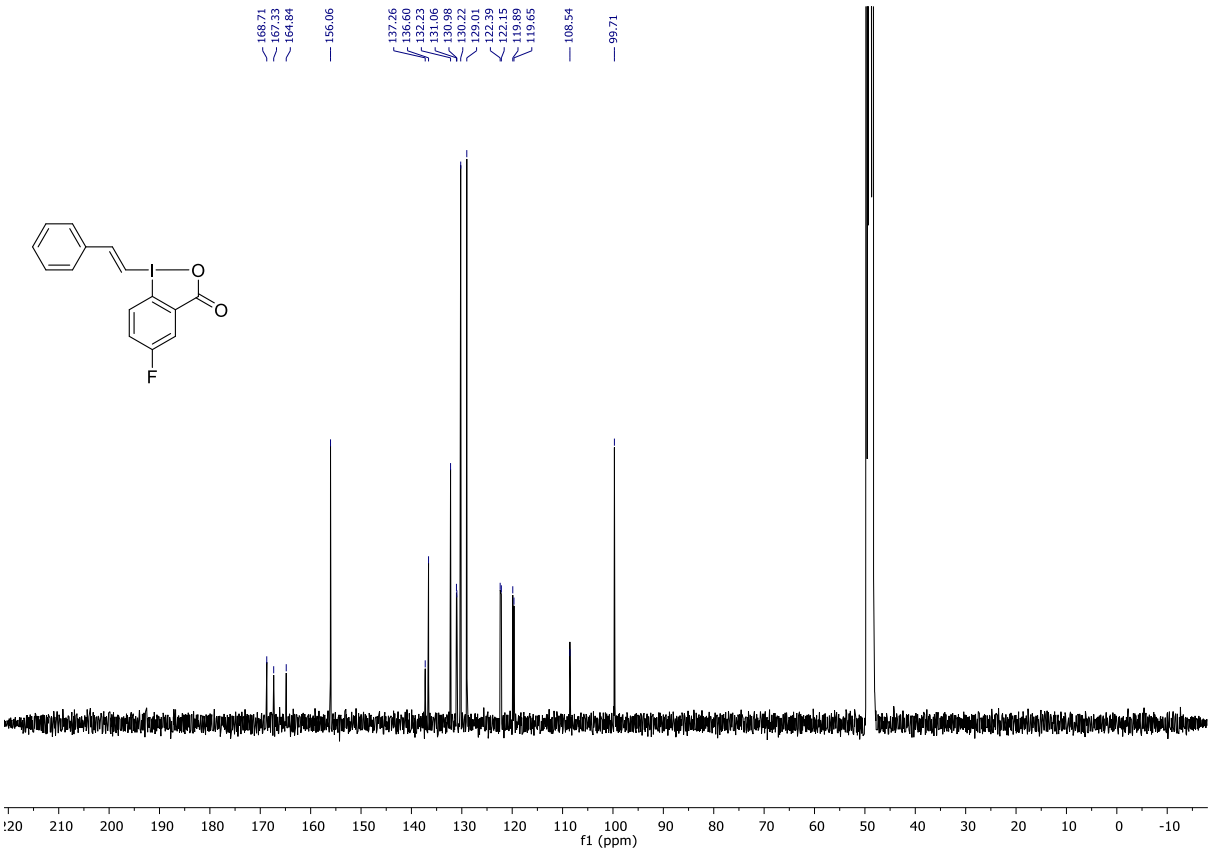
^{13}C-NMR (101 MHz, CD_3OD) of compound **1h**



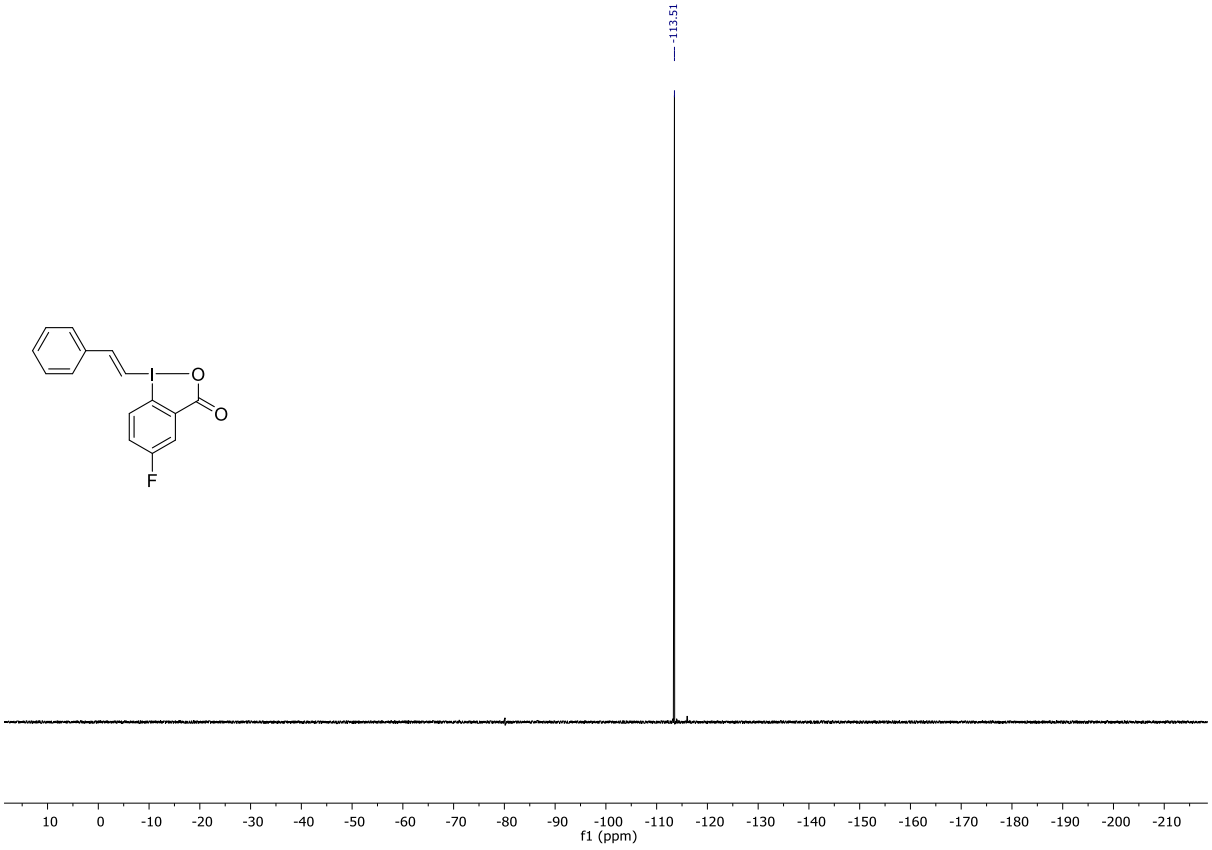
^{1}H-NMR (400 MHz, CD_3OD) of compound **1i**



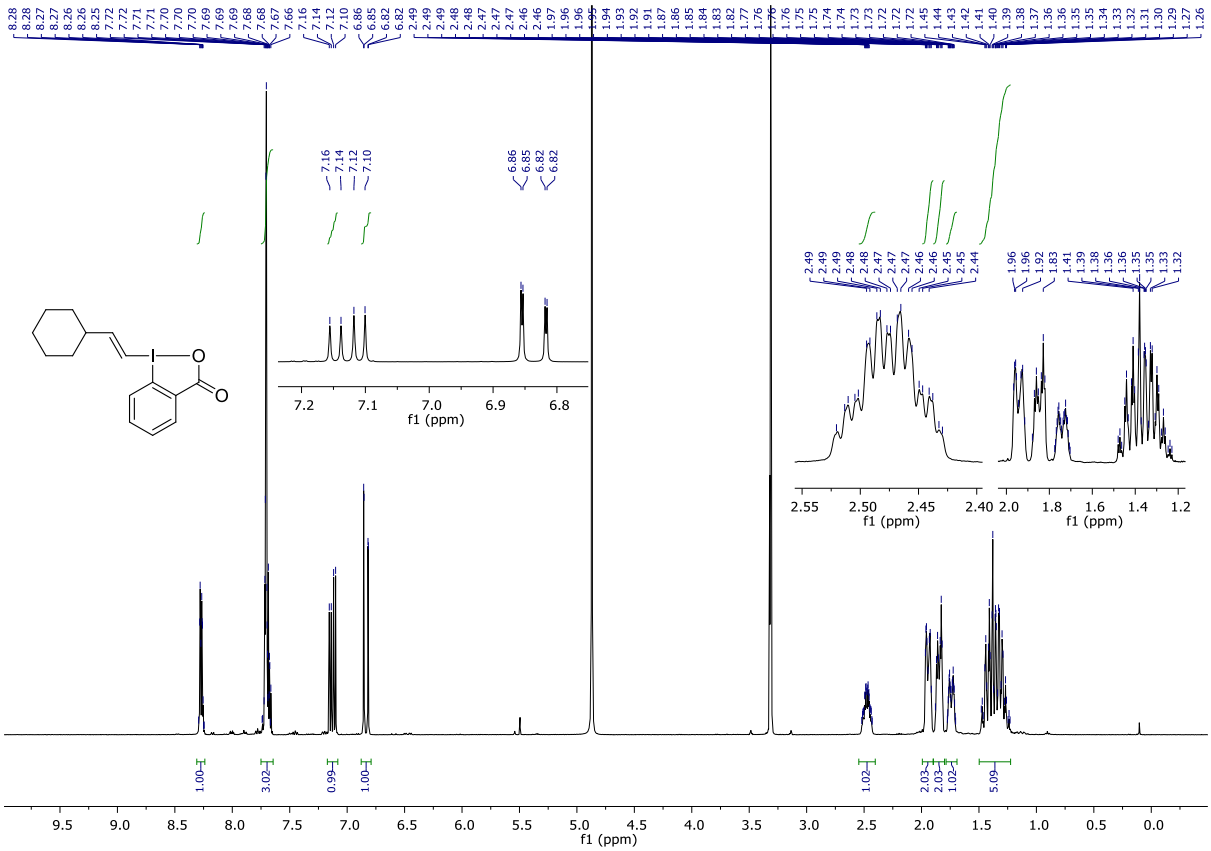
^{13}C-NMR (101 MHz, CD_3OD) of compound **1i**



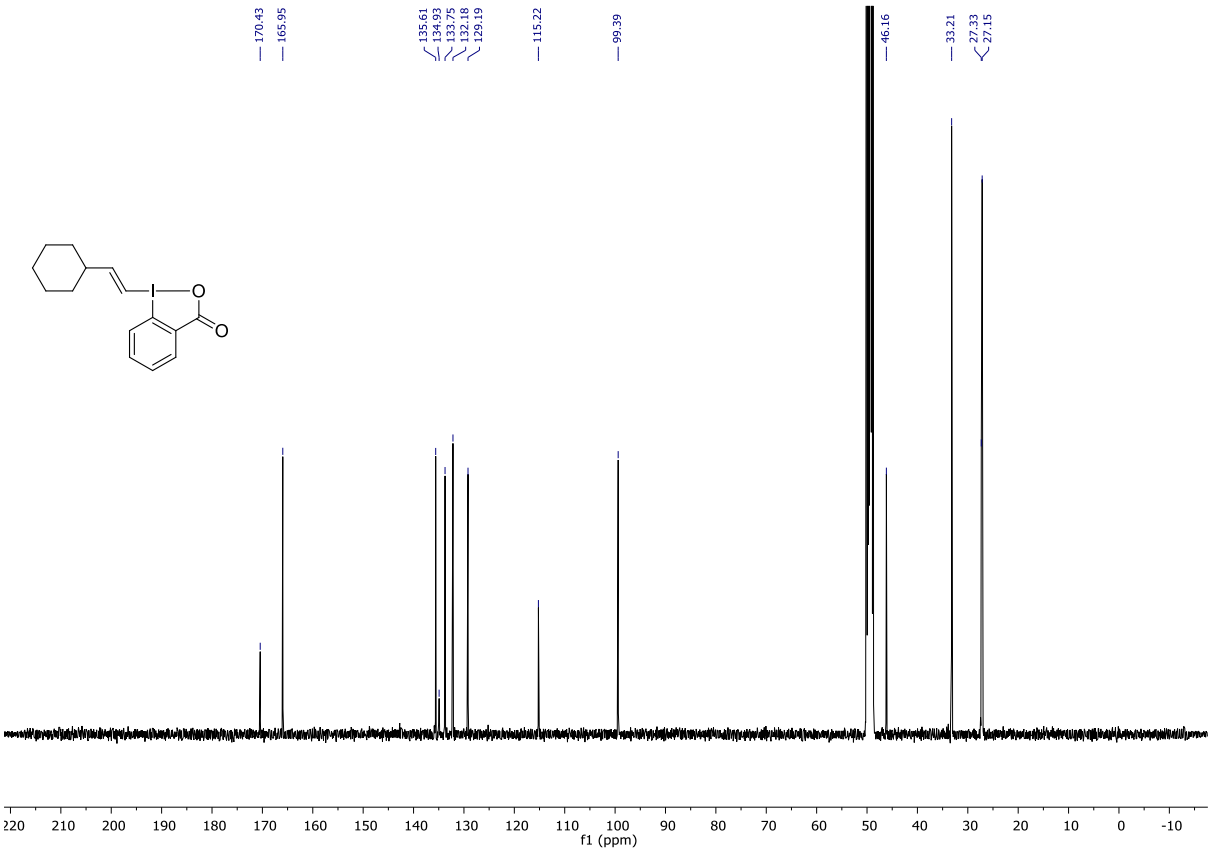
^{19}F-NMR (376 MHz, CD_3OD) of compound **1i**



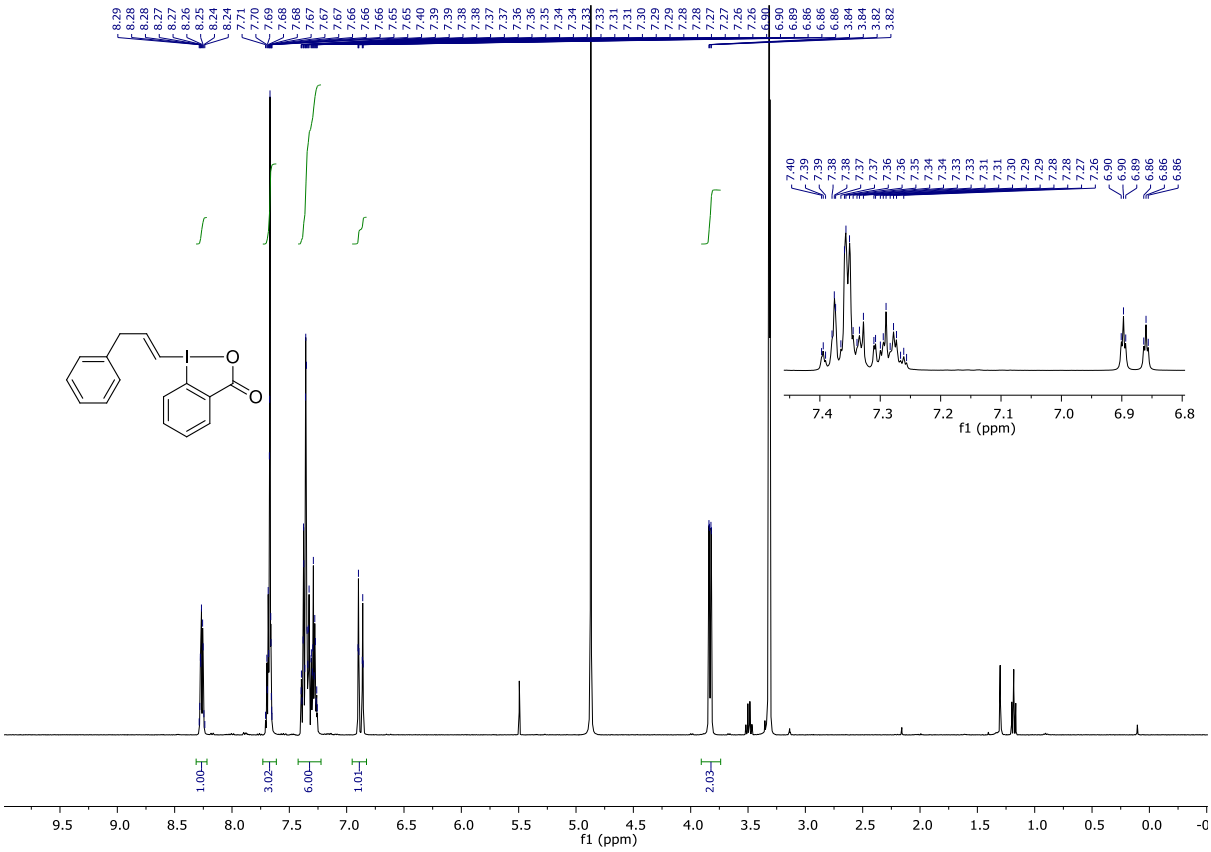
^{1}H-NMR (400 MHz, CD_3OD) of compound **1j**



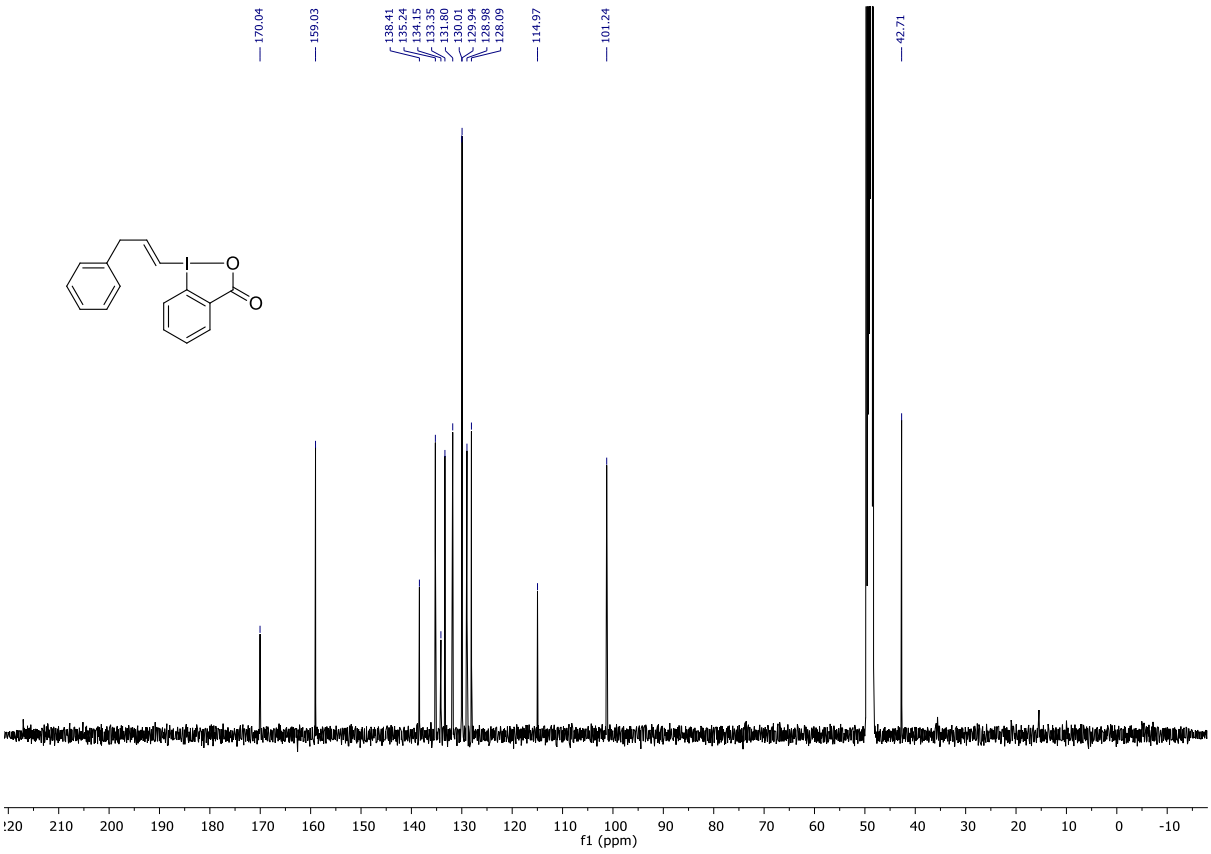
^{13}C-NMR (101 MHz, CD_3OD) of compound **1j**



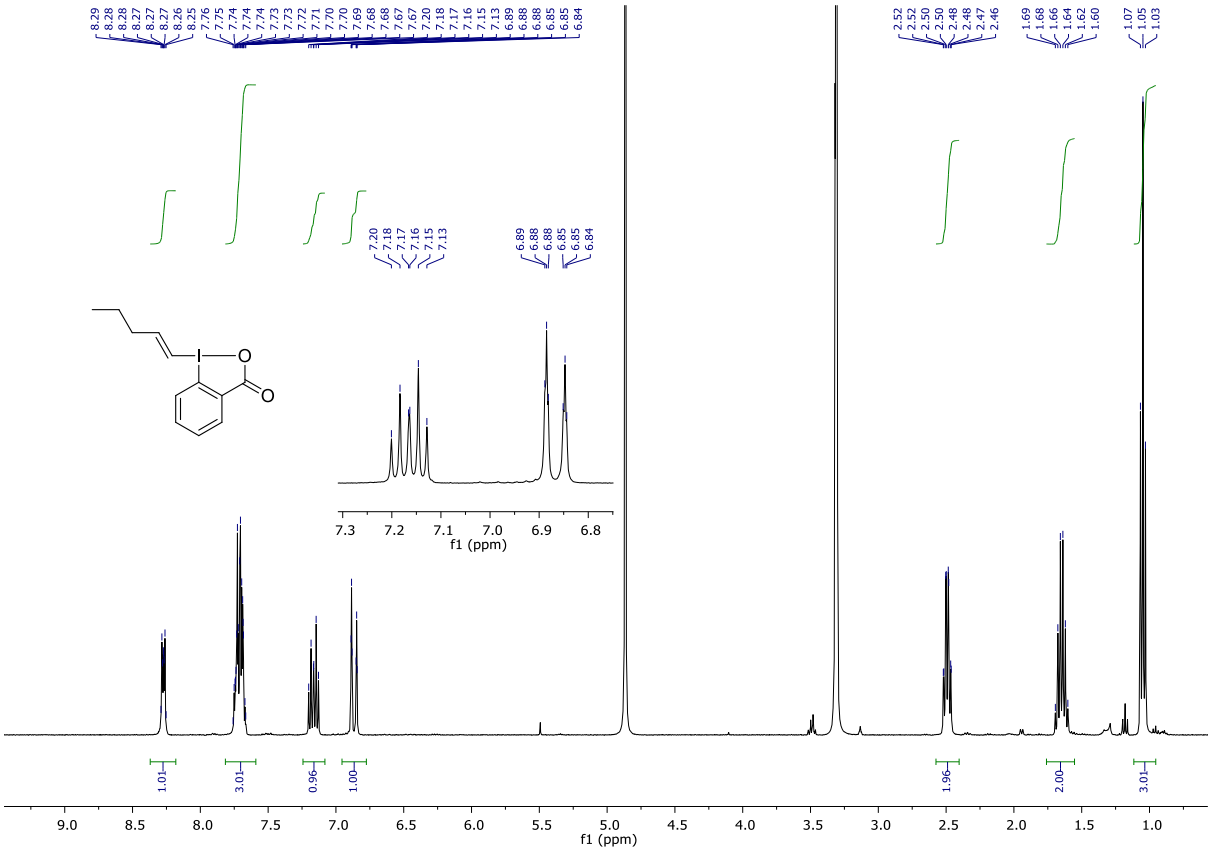
^{1}H-NMR (400 MHz, CD_3OD) of compound **1k**



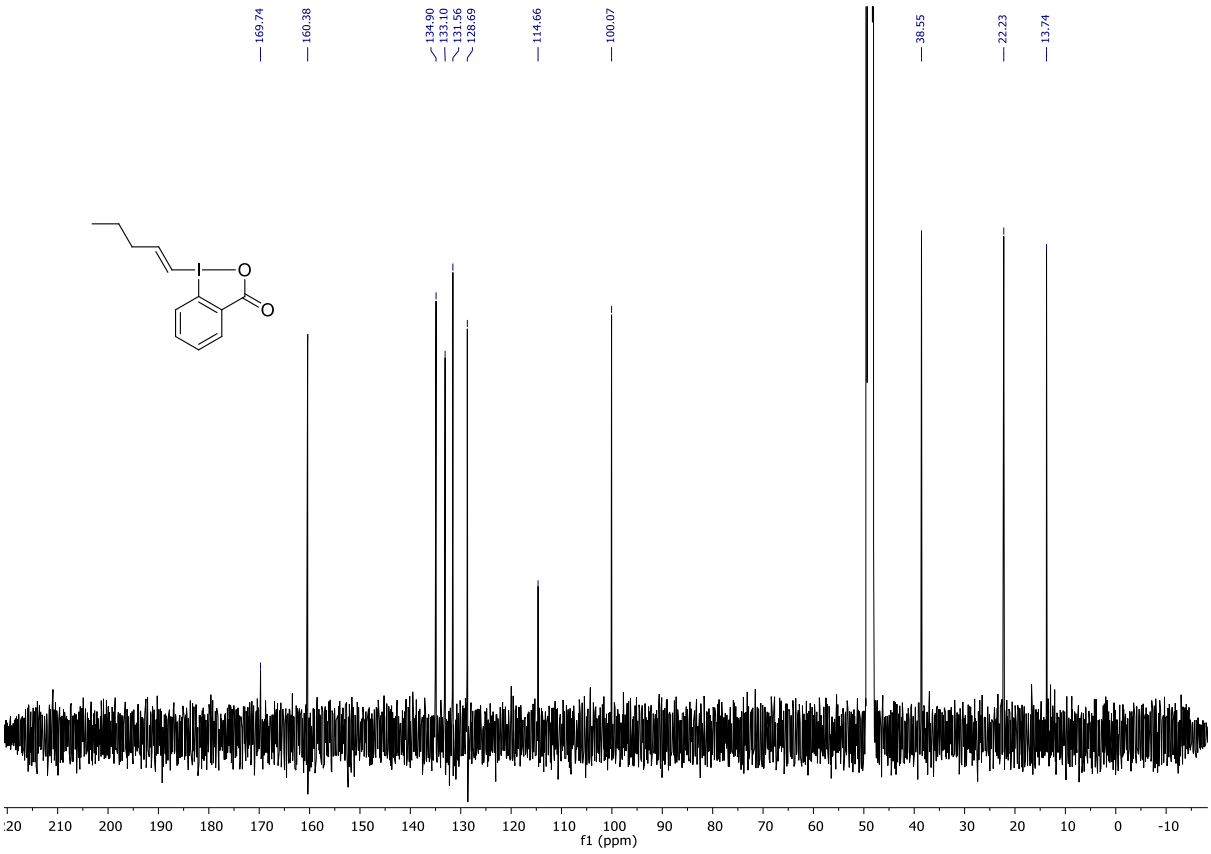
^{13}C-NMR (101 MHz, CD_3OD) of compound **1k**



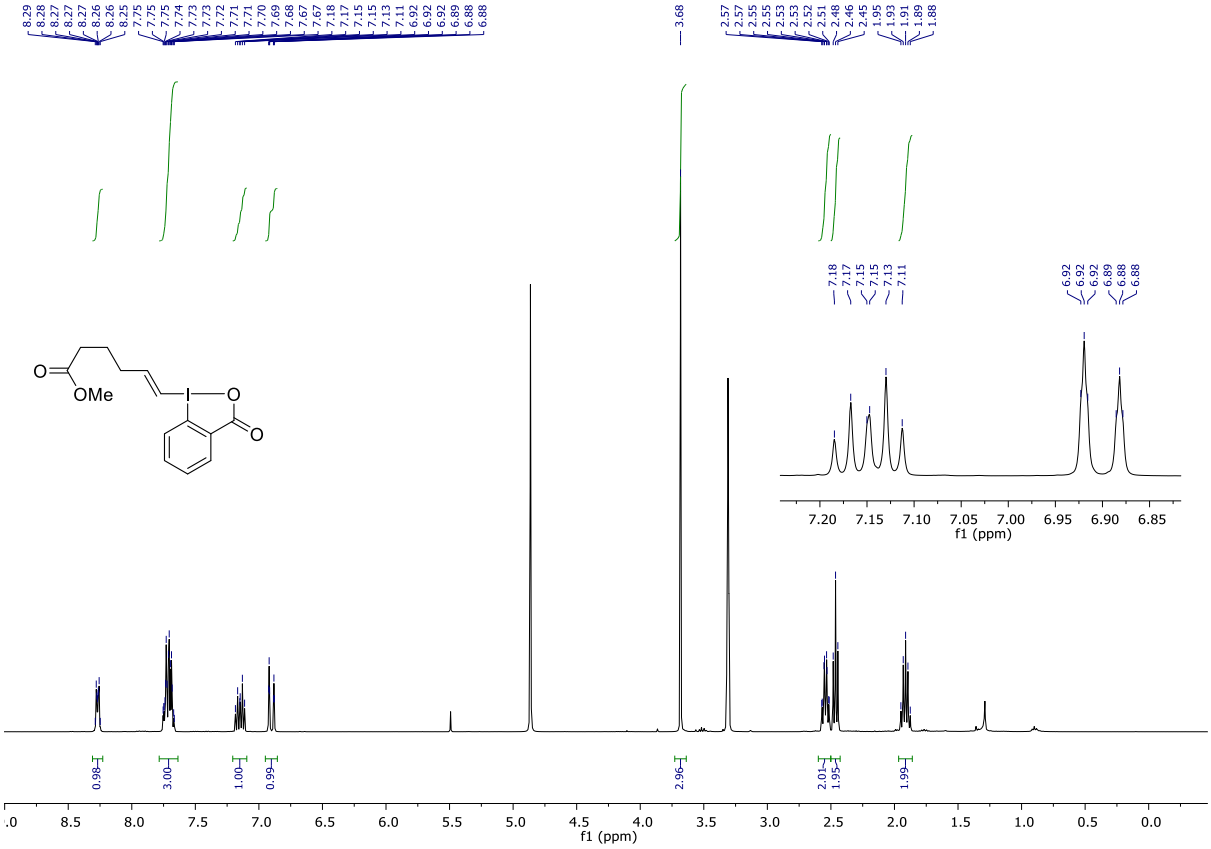
^{1}H-NMR (400 MHz, CD_3OD) of compound **1l**



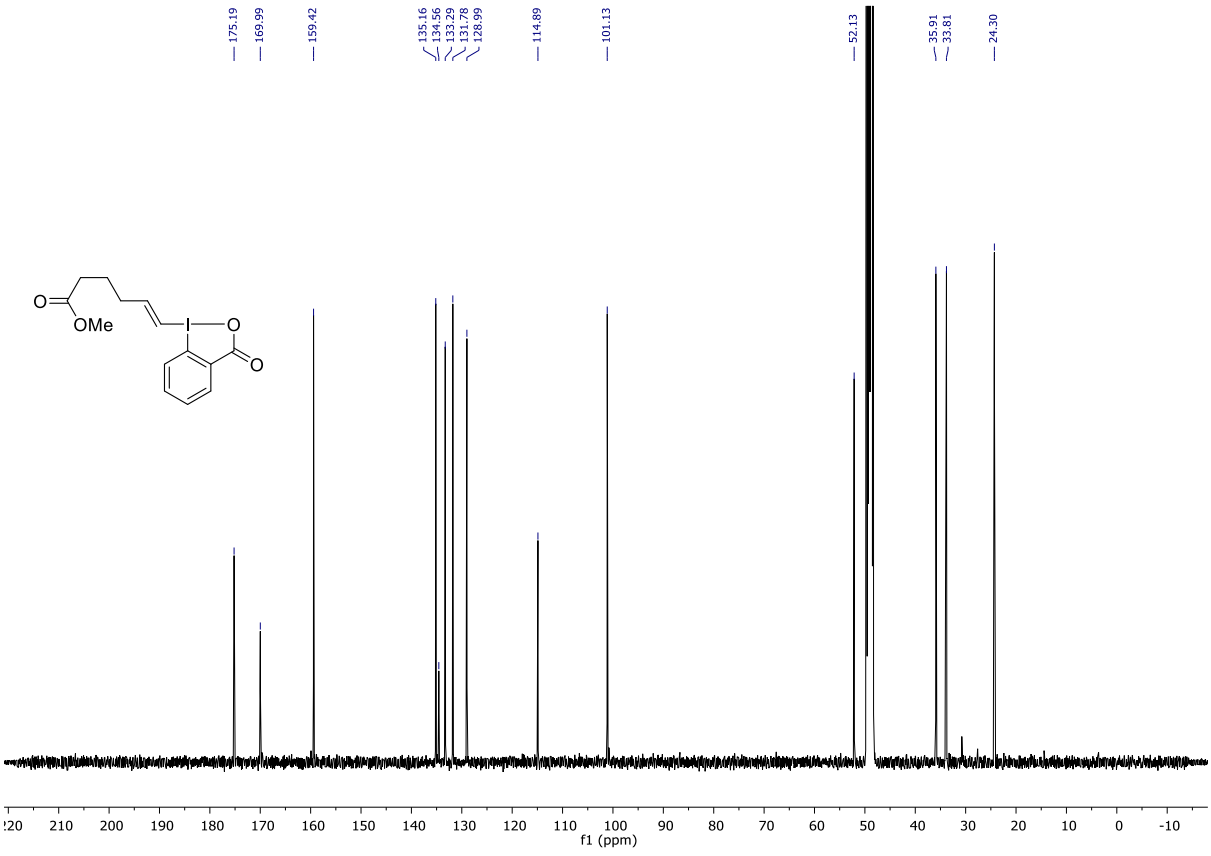
^{13}C-NMR (101 MHz, CD_3OD) of compound **1l**



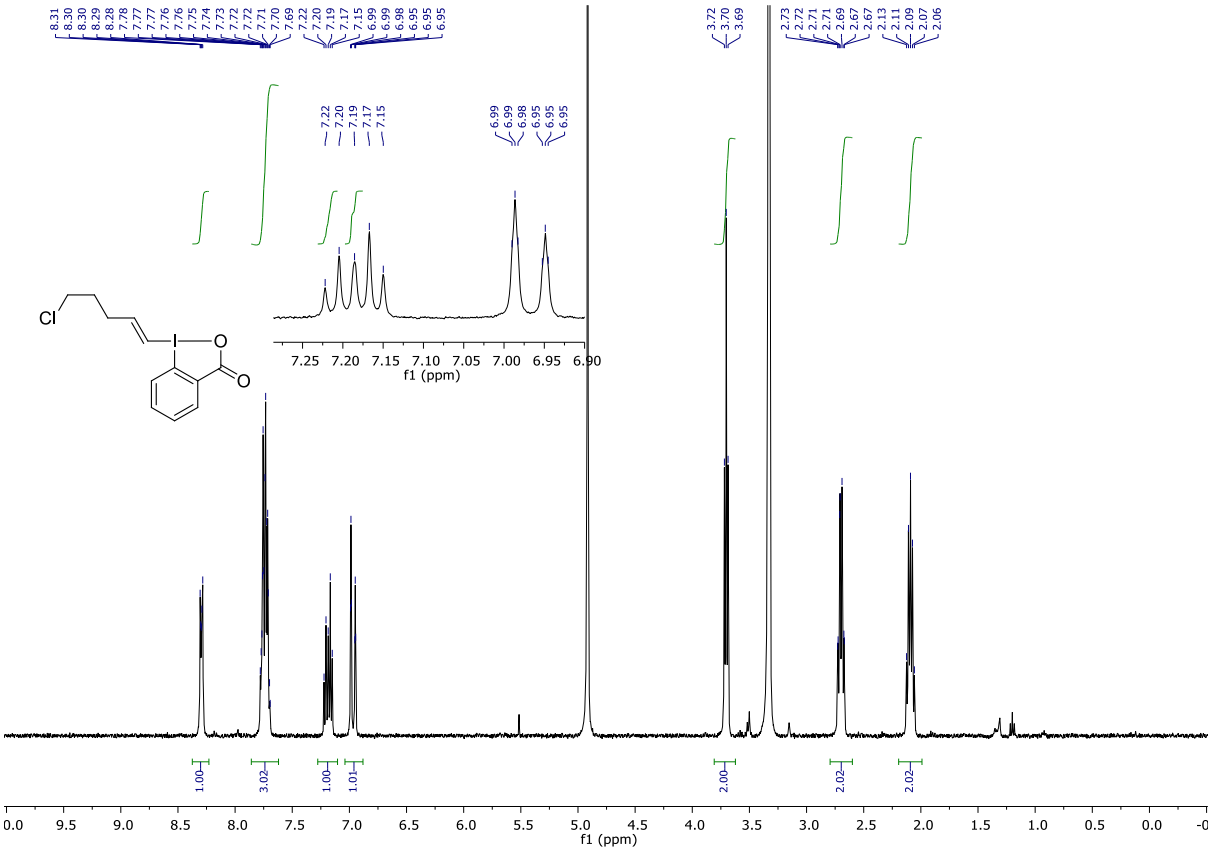
^{1}H-NMR (400 MHz, CD_3OD) of compound **1m**



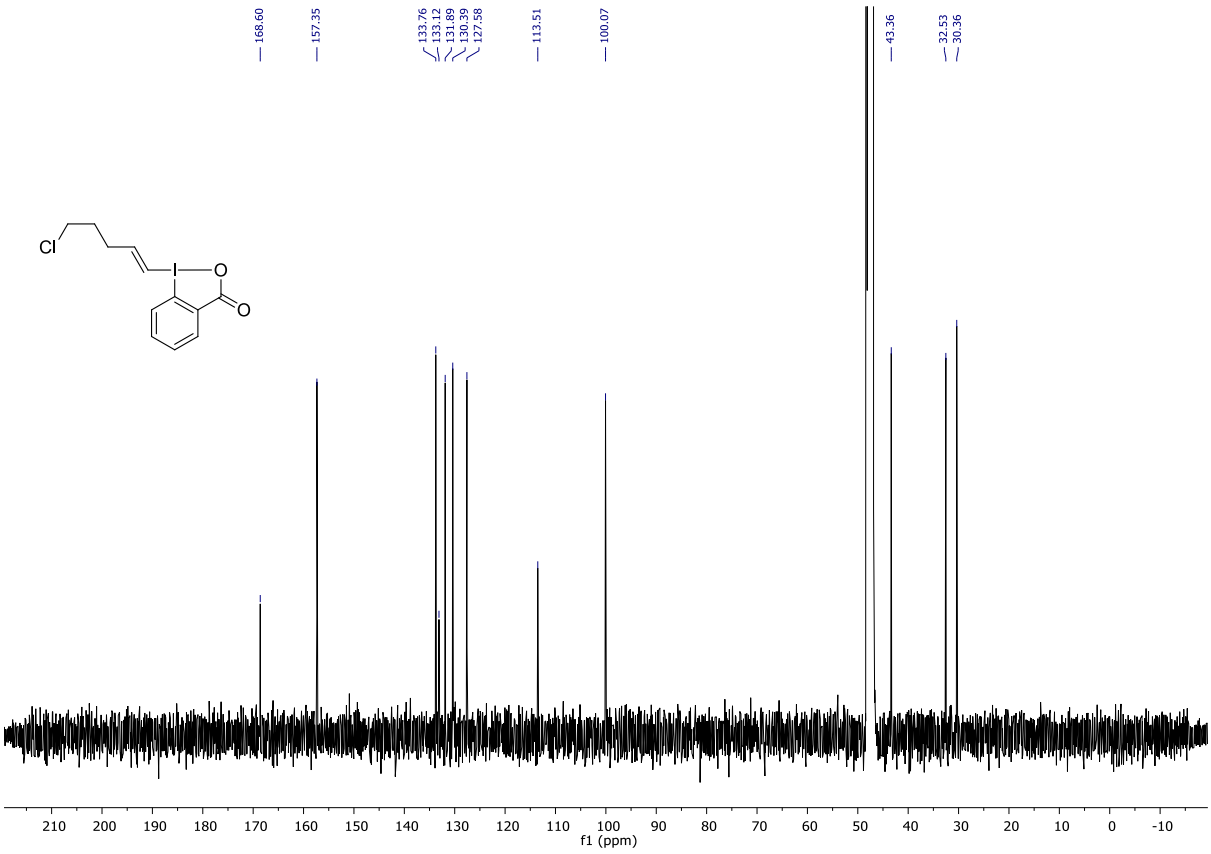
^{13}C-NMR (101 MHz, CD_3OD) of compound **1m**



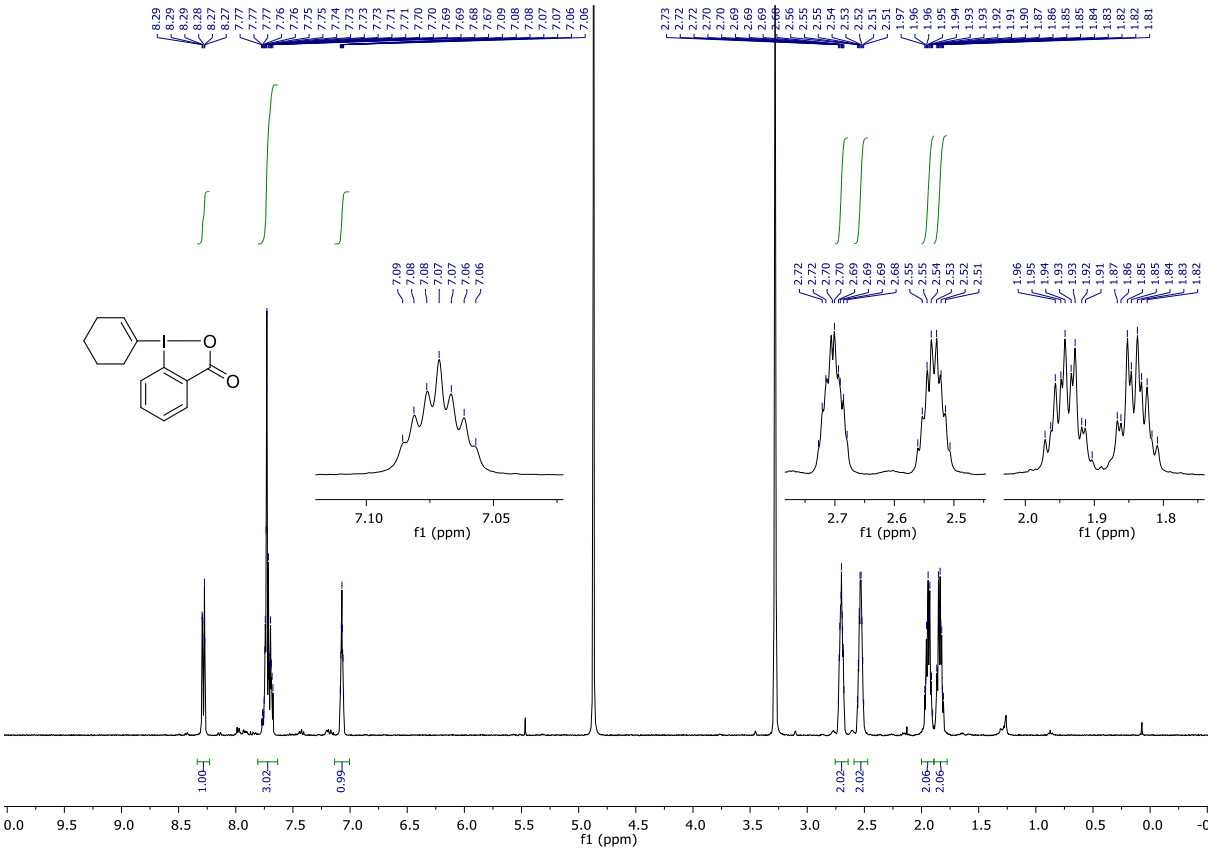
^{1}H-NMR (400 MHz, CD_3OD) of compound **1n**



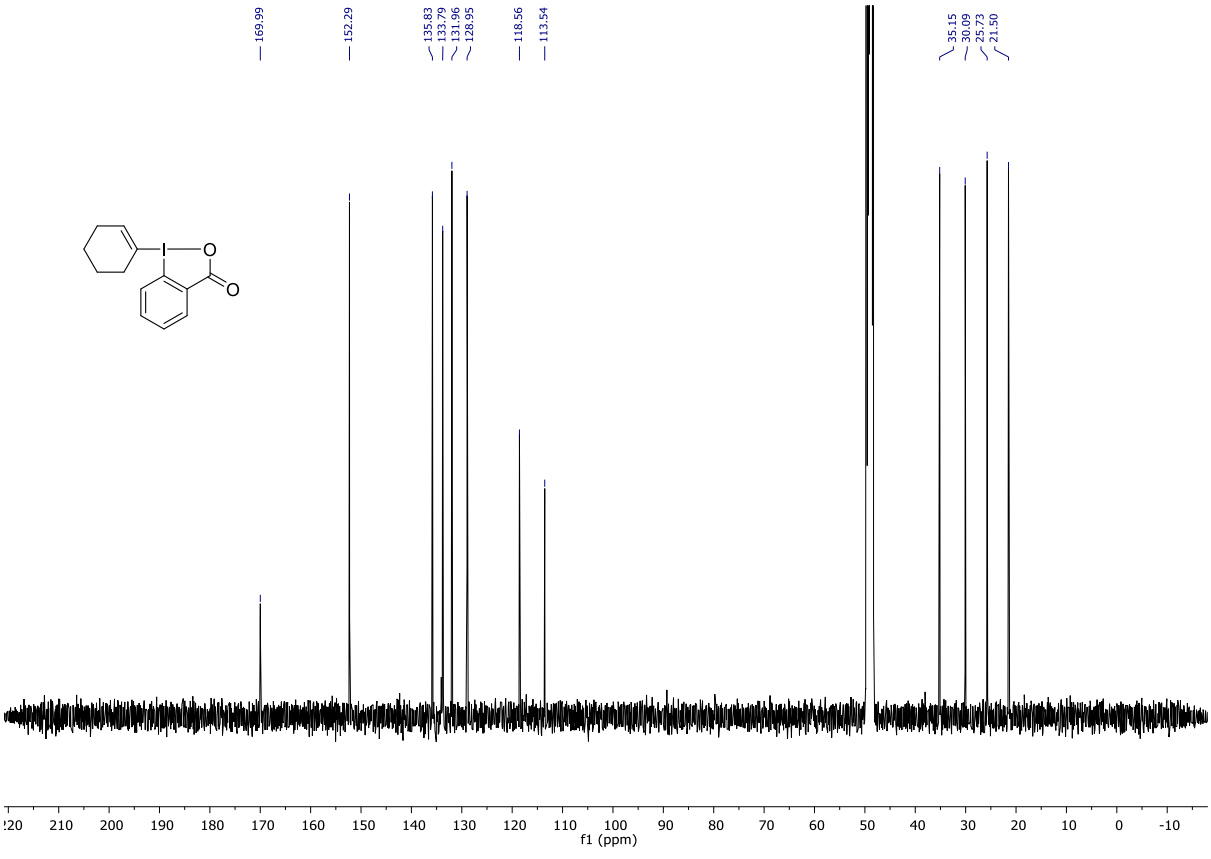
^{13}C-NMR (101 MHz, CD_3OD) of compound **1n**



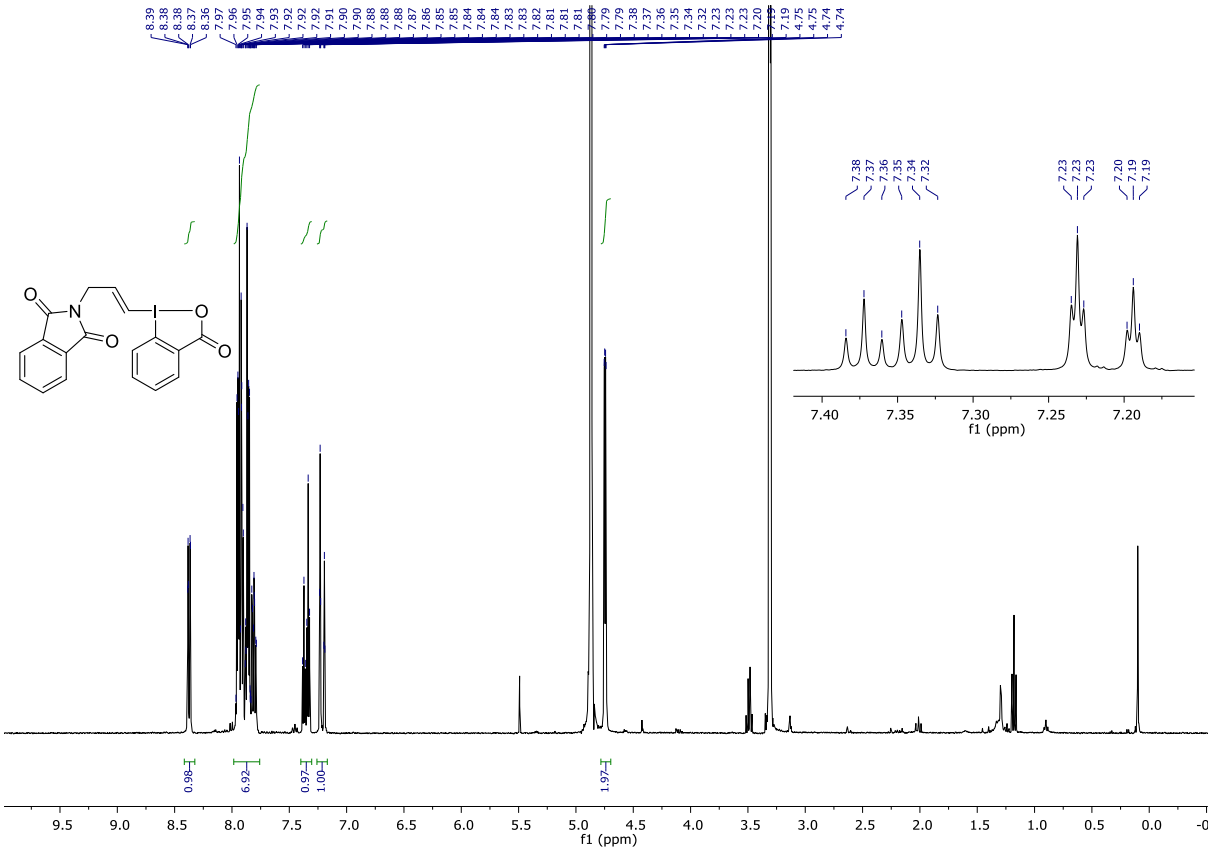
^{1}H-NMR (400 MHz, CD_3OD) of compound **1o**



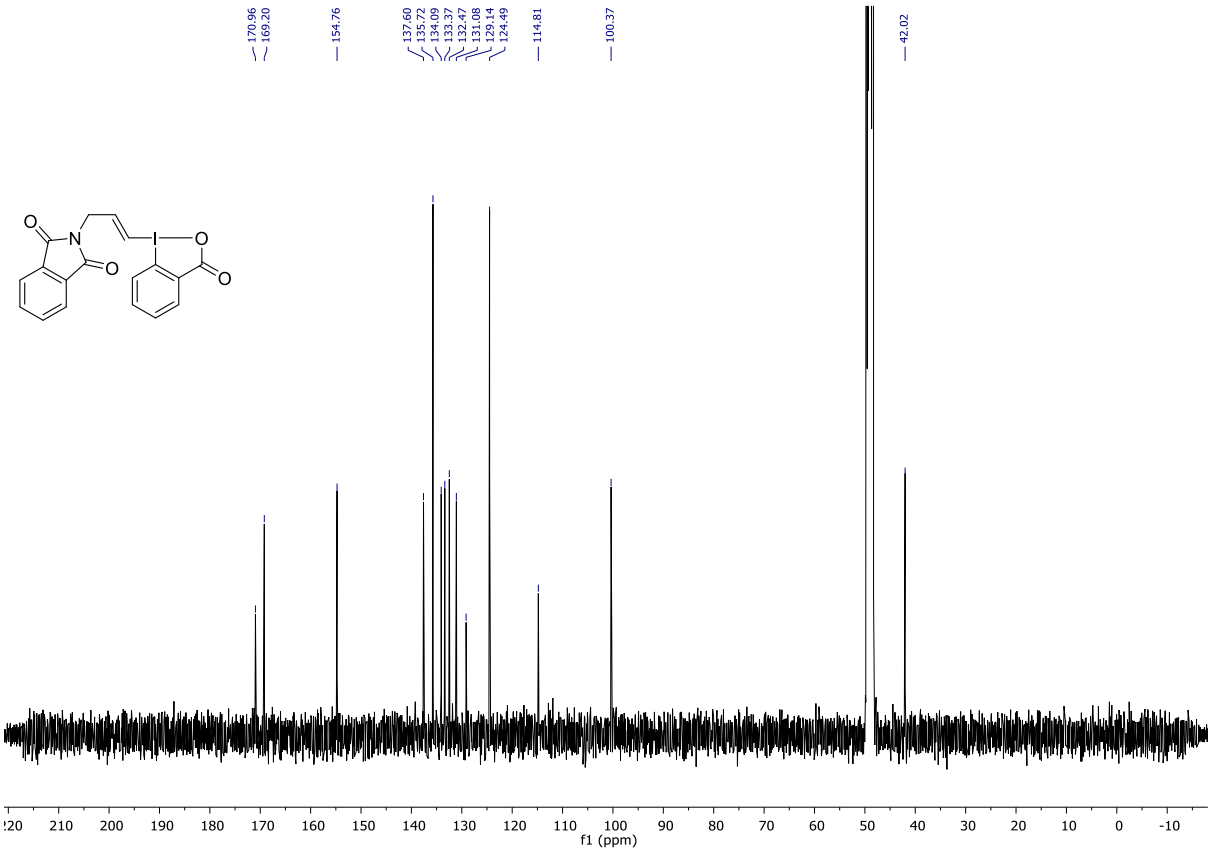
^{13}C-NMR (101 MHz, CD_3OD) of compound **1o**



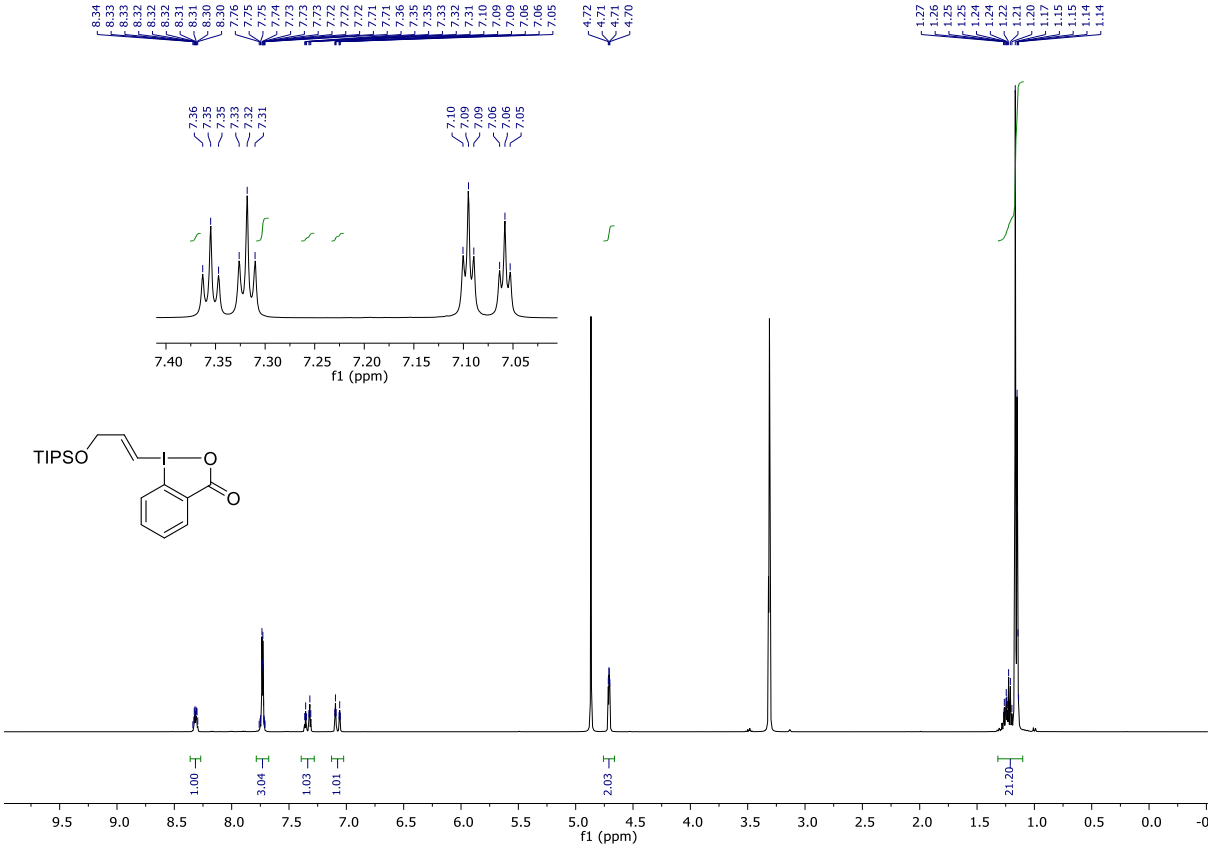
^{1}H-NMR (400 MHz, CD_3OD) of compound **1p**



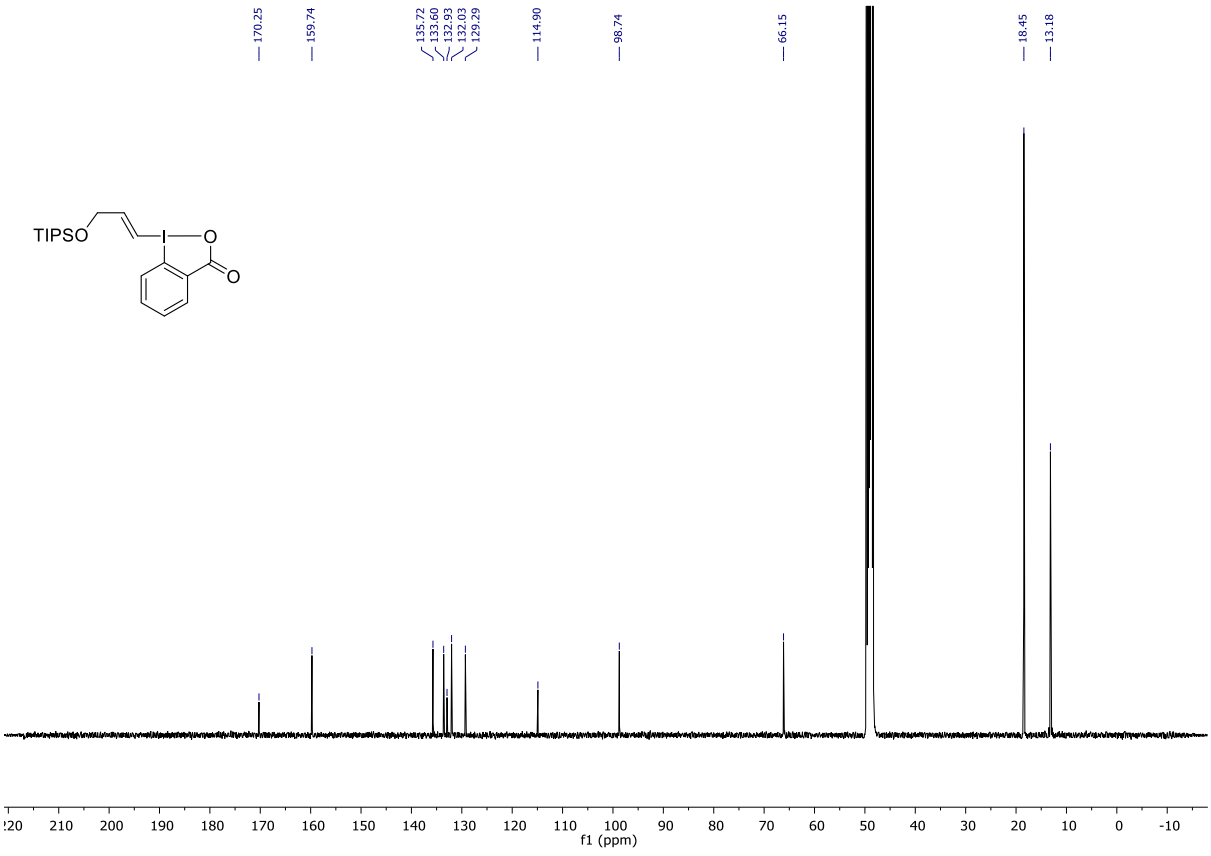
^{13}C-NMR (101 MHz, CD_3OD) of compound **1p**



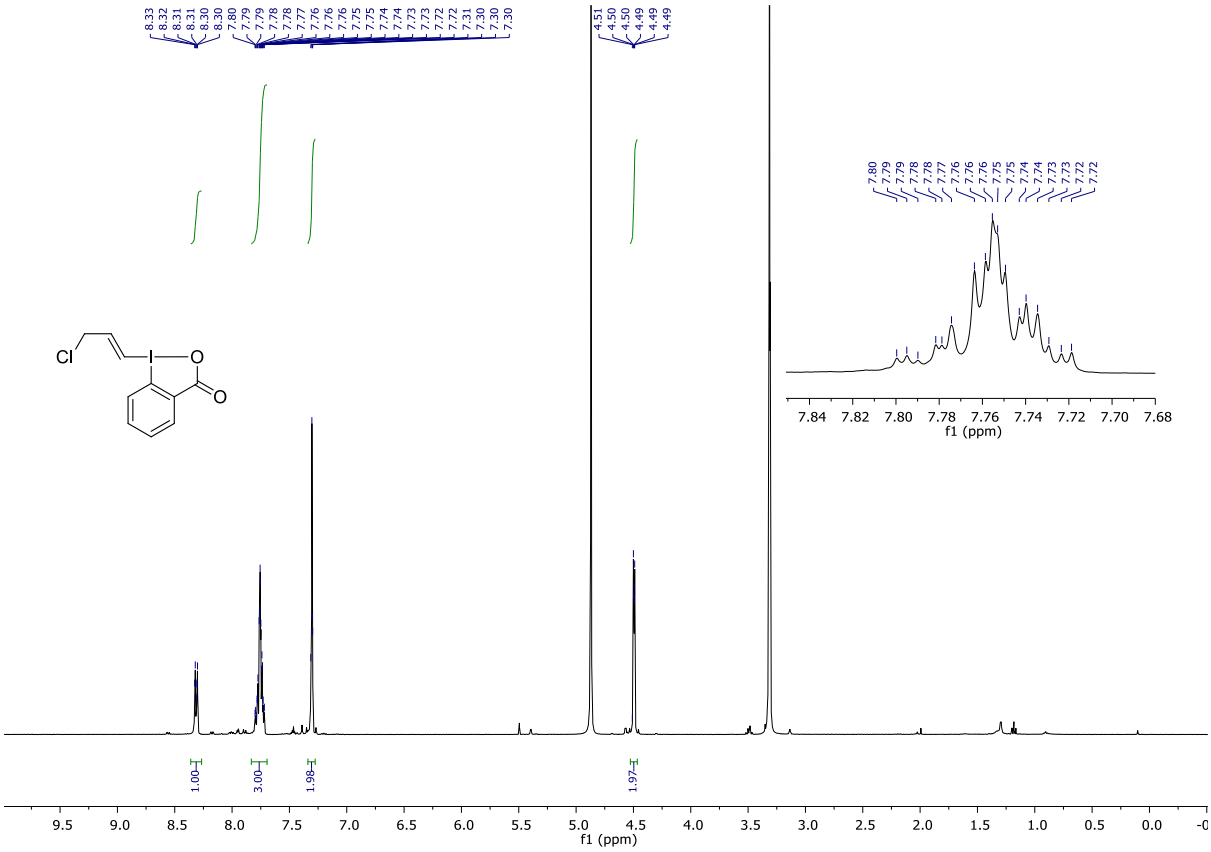
^{1}H-NMR (400 MHz, CD_3OD) of compound **1q**



^{13}C-NMR (101 MHz, CD_3OD) of compound **1q**



^{1}H-NMR (400 MHz, CD_3OD) of compound **1r**



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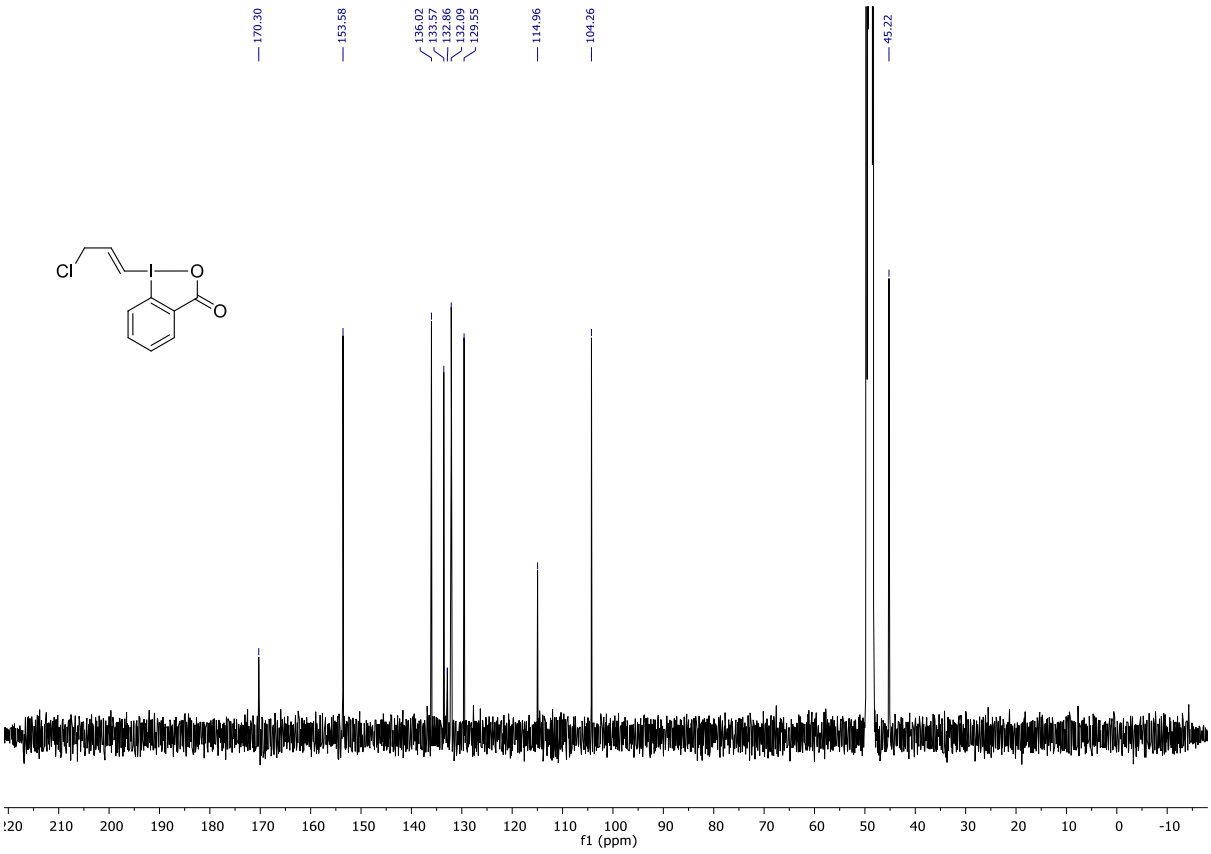
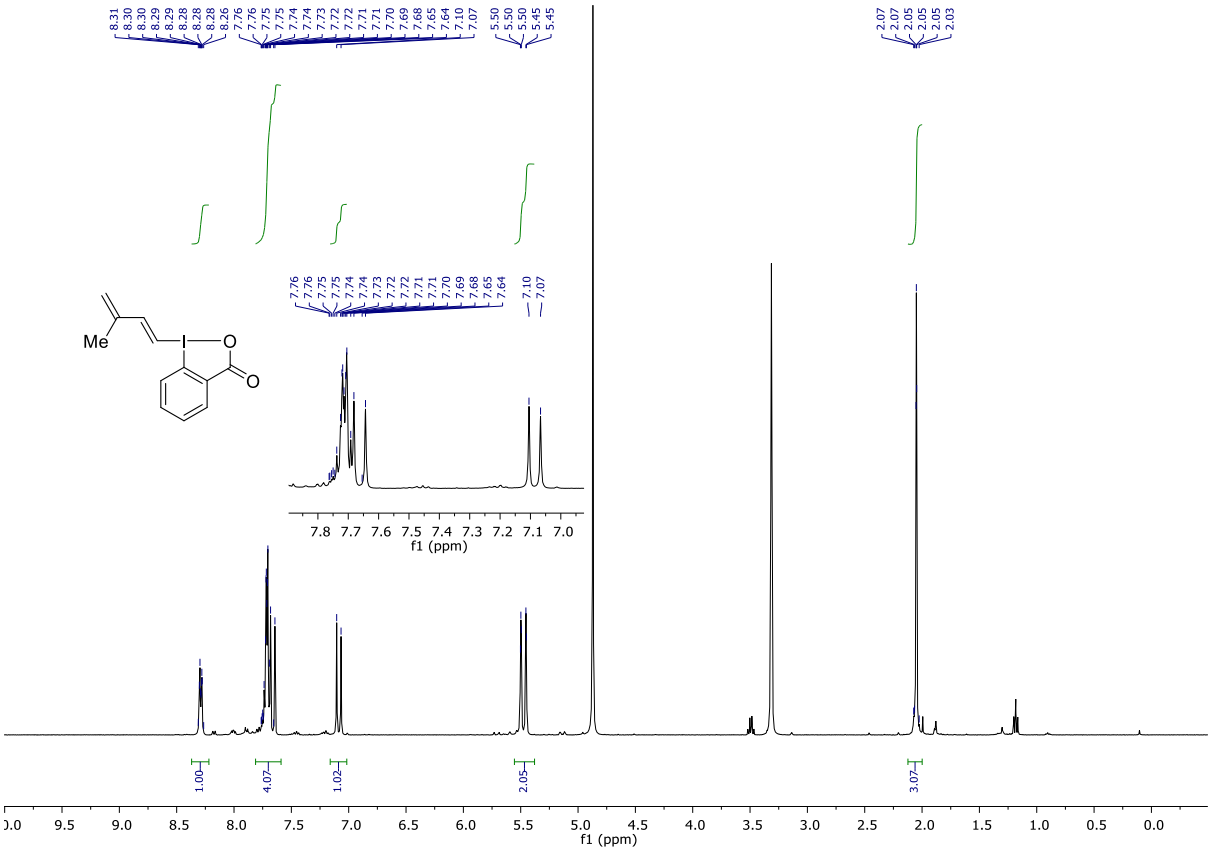
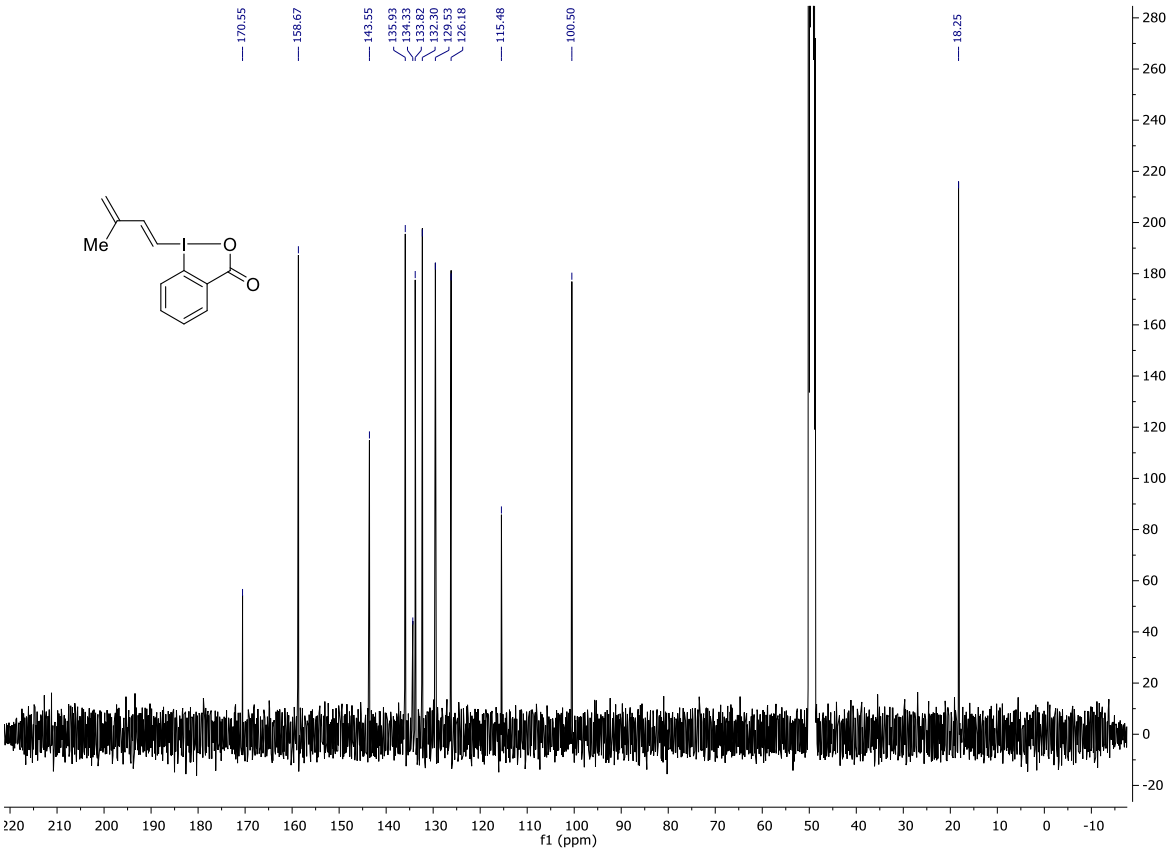


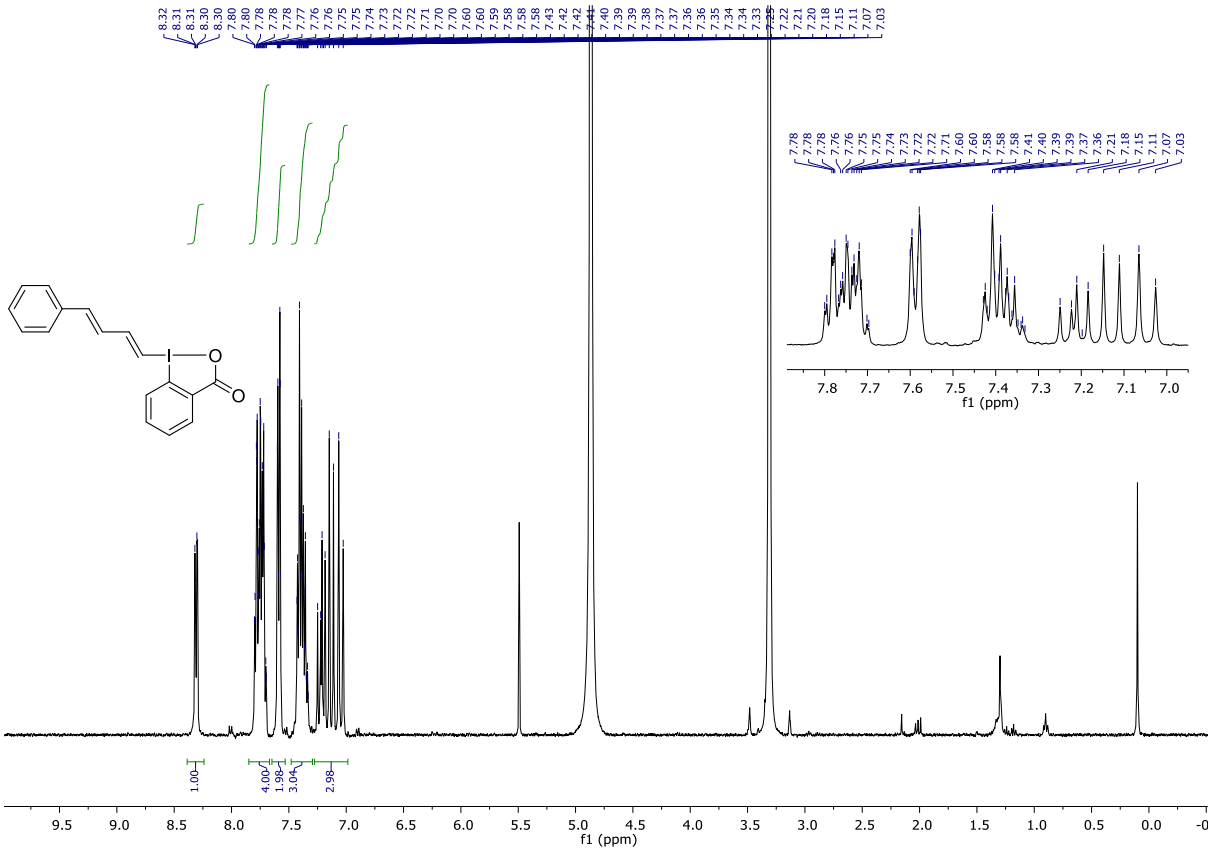
^{1}H-NMR (400 MHz, CD_3OD) of compound **1s**



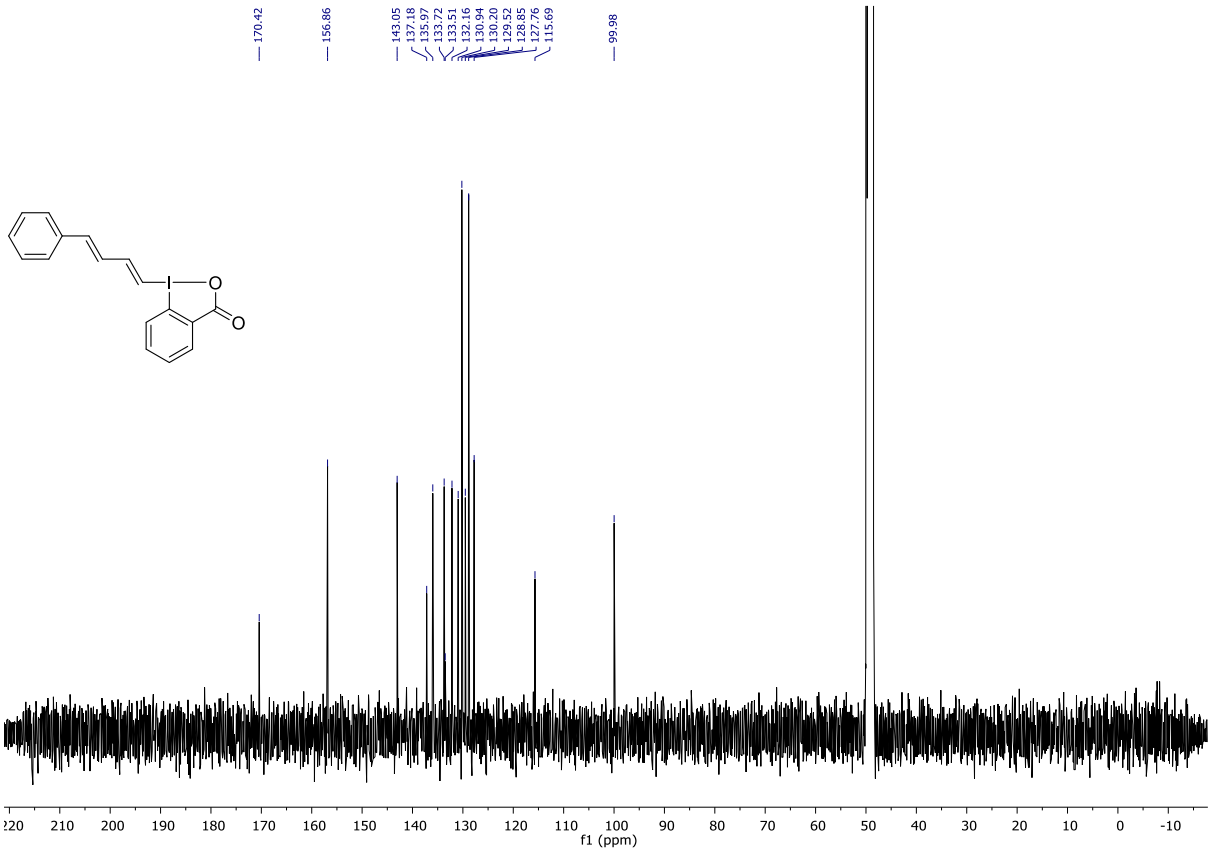
^{13}C-NMR (101 MHz, CD_3OD) of compound **1s**



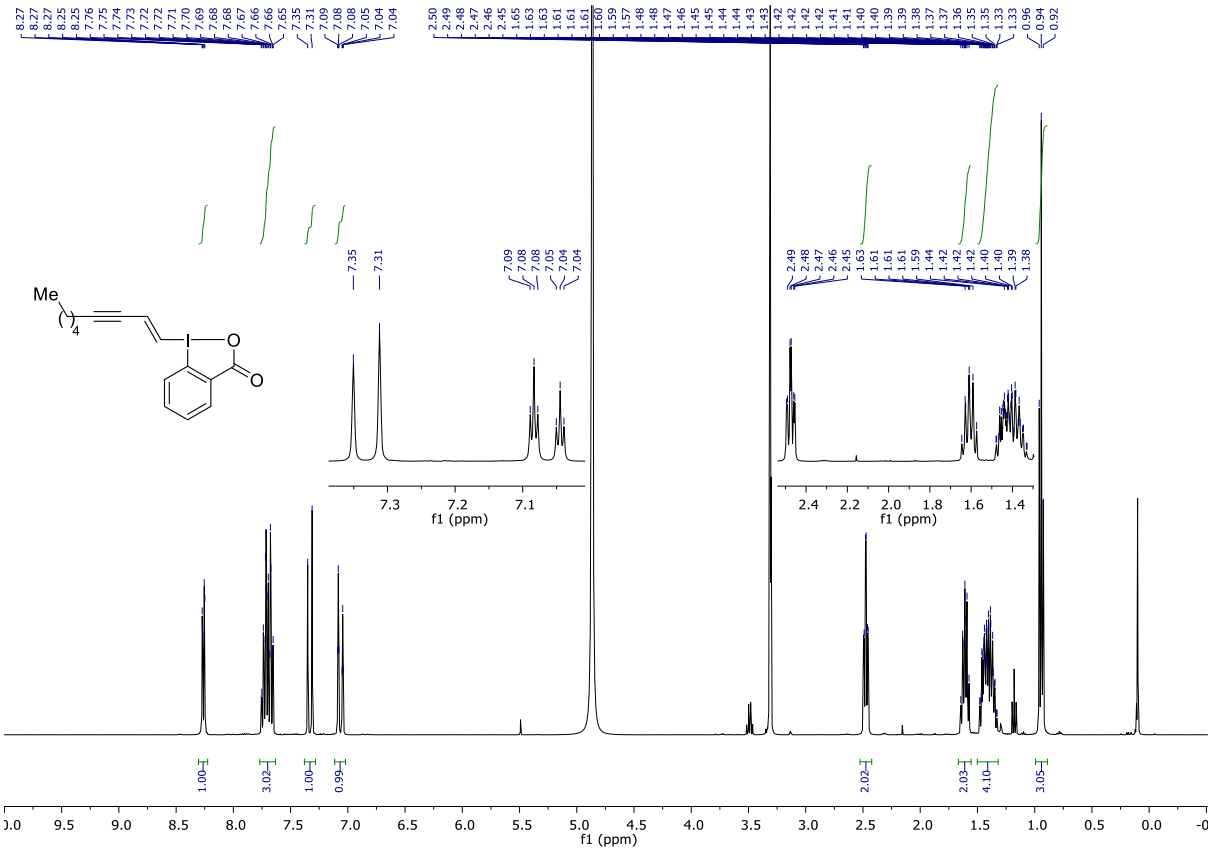
^{1}H-NMR (400 MHz, CD_3OD) of compound **1t**



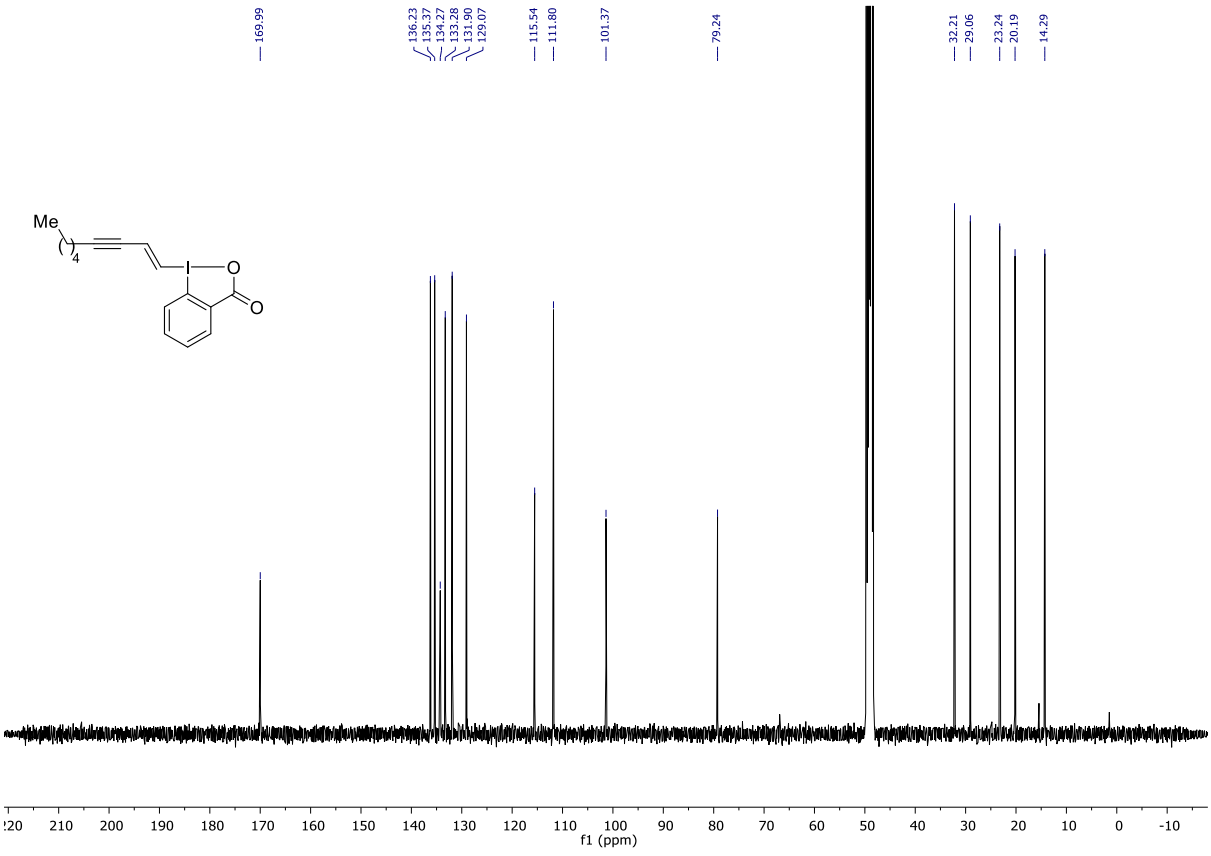
^{13}C-NMR (101 MHz, CD_3OD) of compound **1t**



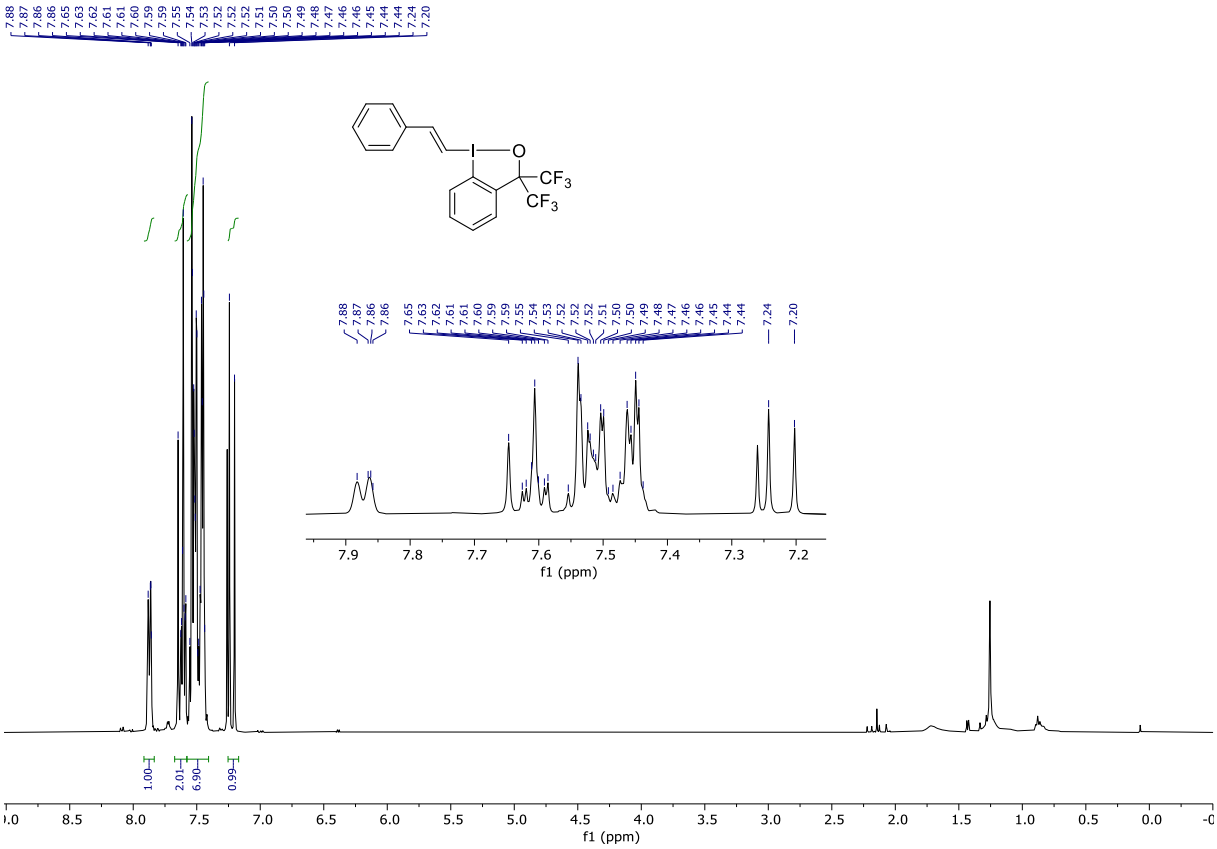
^{1}H-NMR (400 MHz, CD_3OD) of compound **1u**



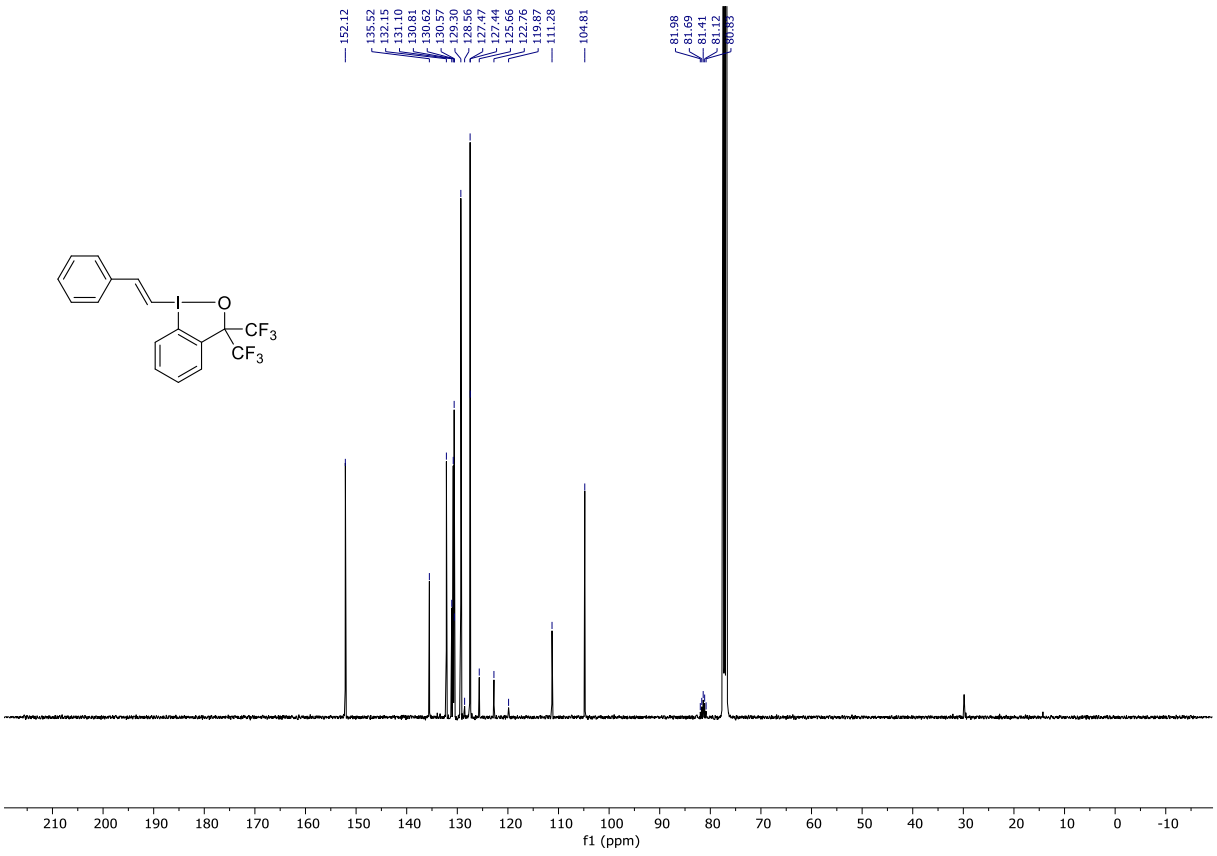
^{13}C-NMR (101 MHz, CD_3OD) of compound **1u**



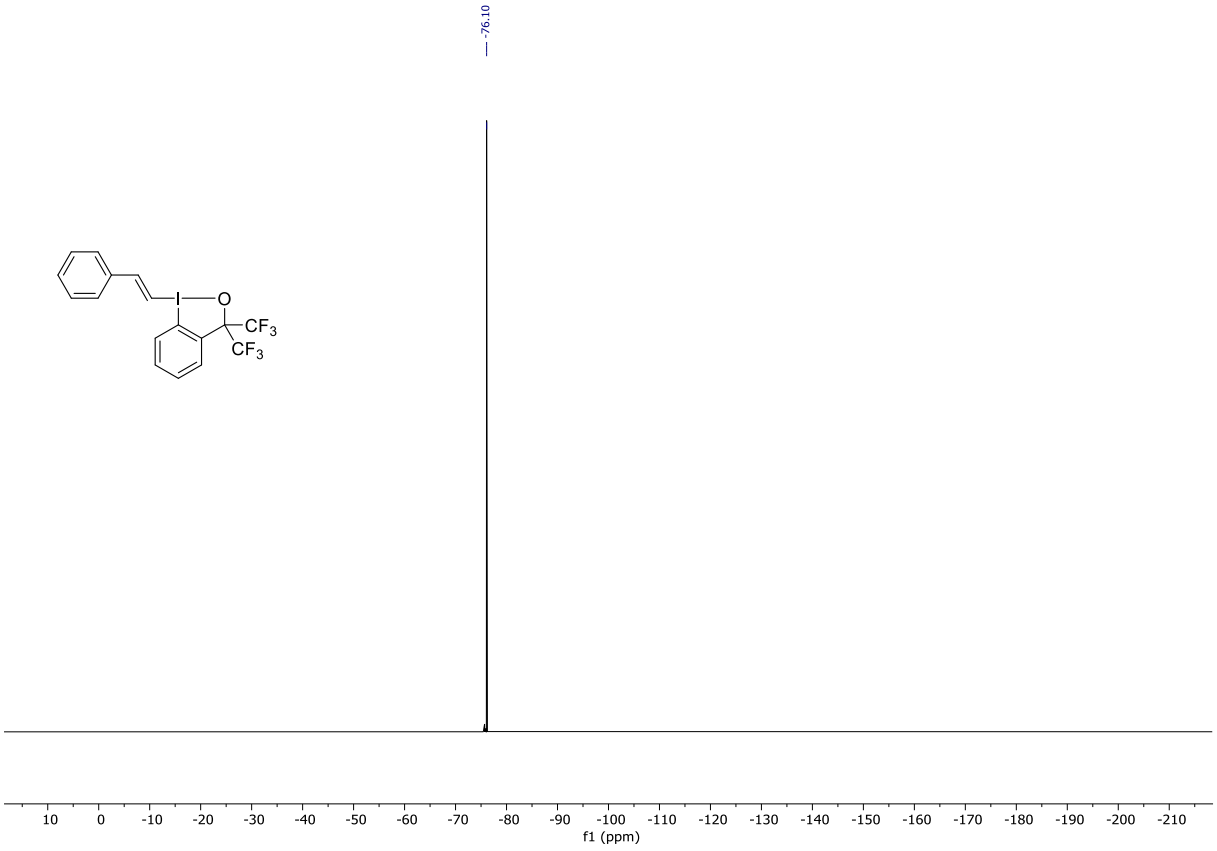
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **1'a**



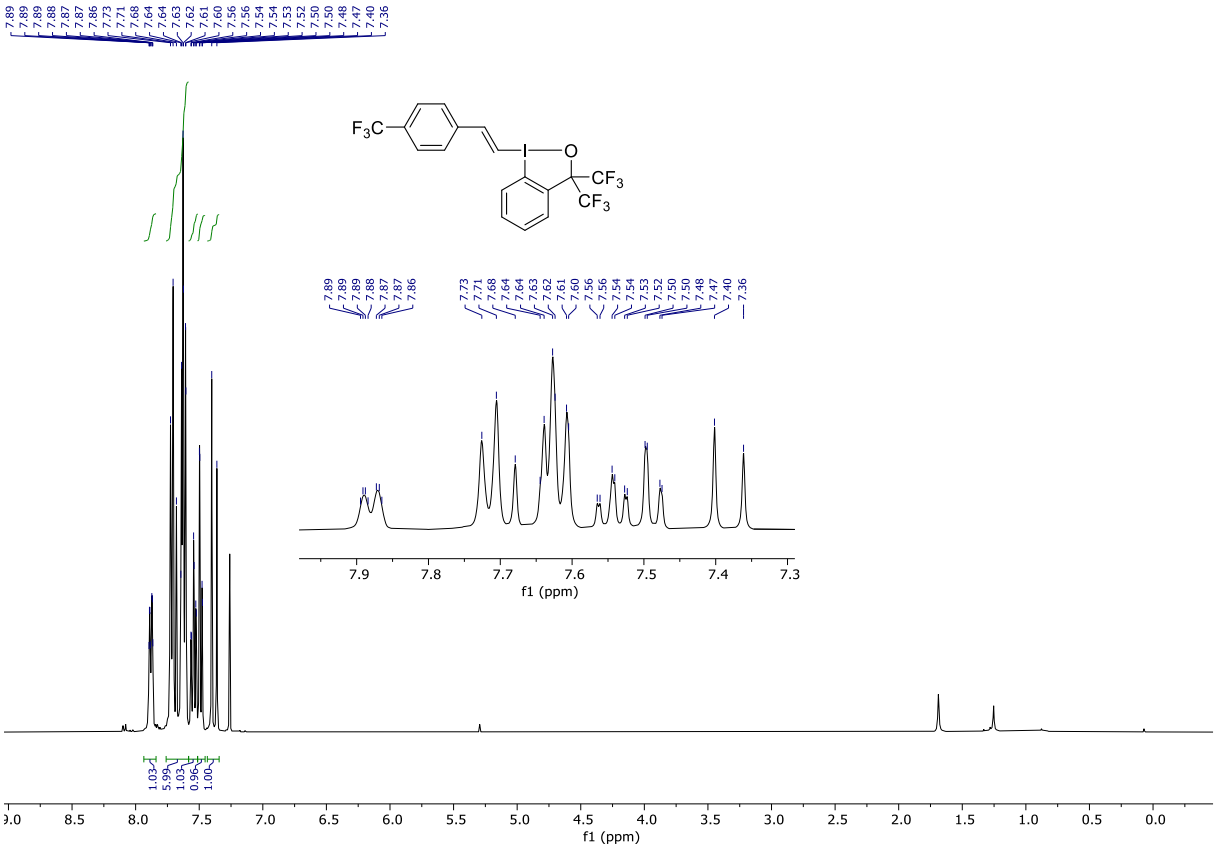
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **1'a**



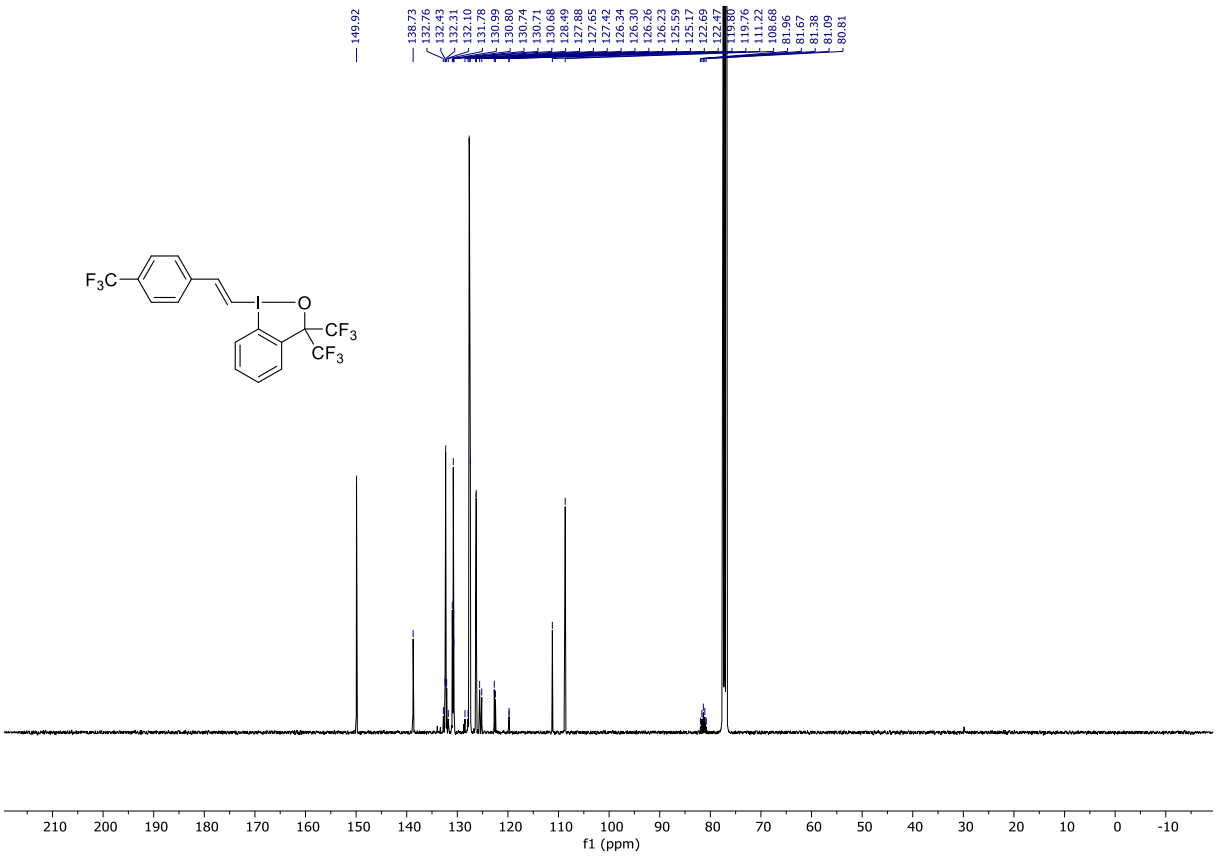
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **1'a**



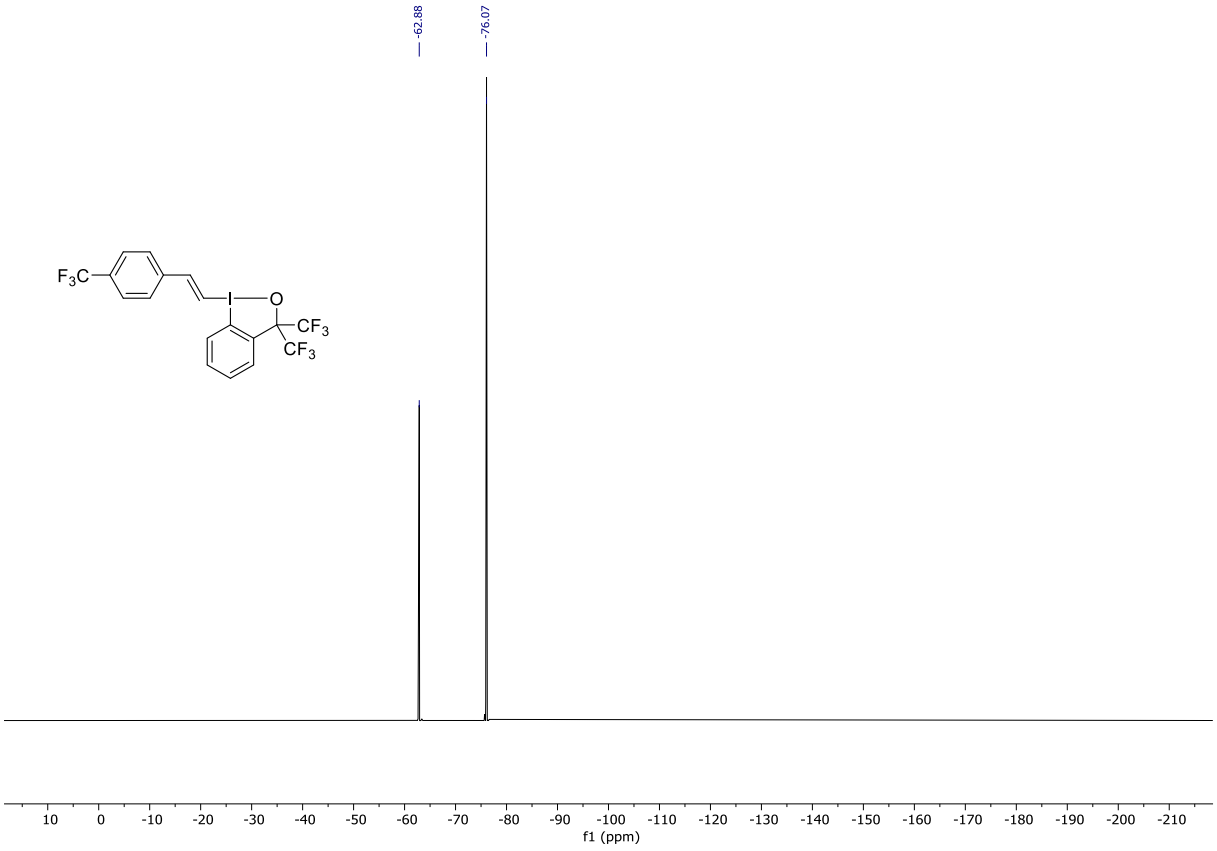
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **1'd**



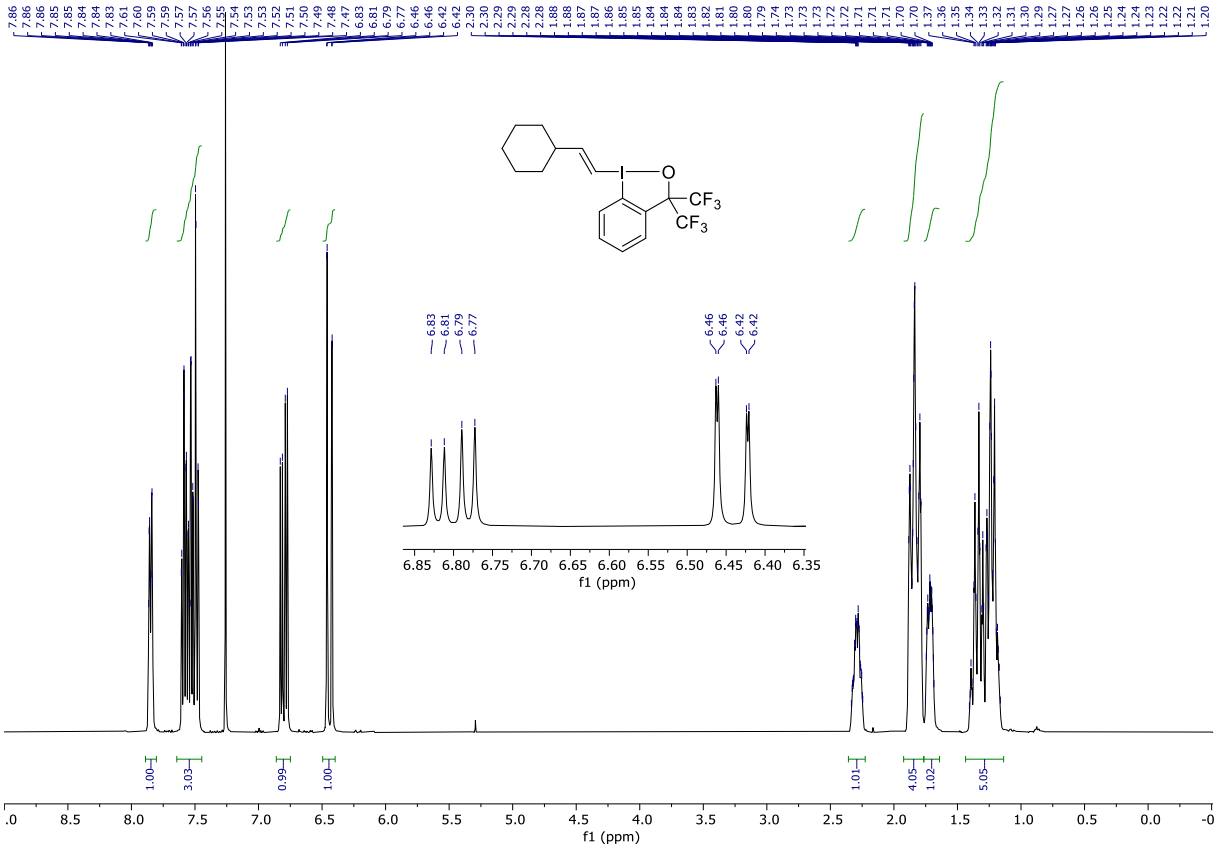
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **1'd**



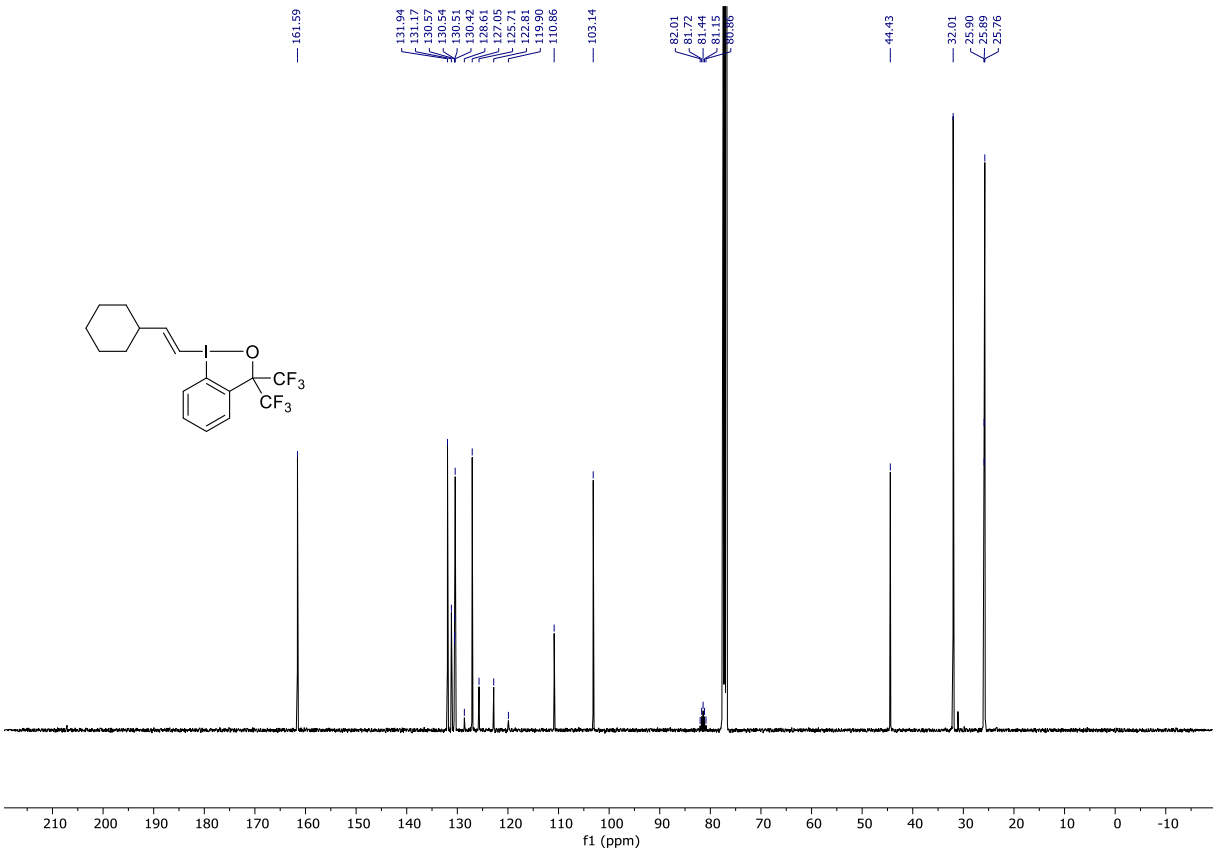
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **1'd**



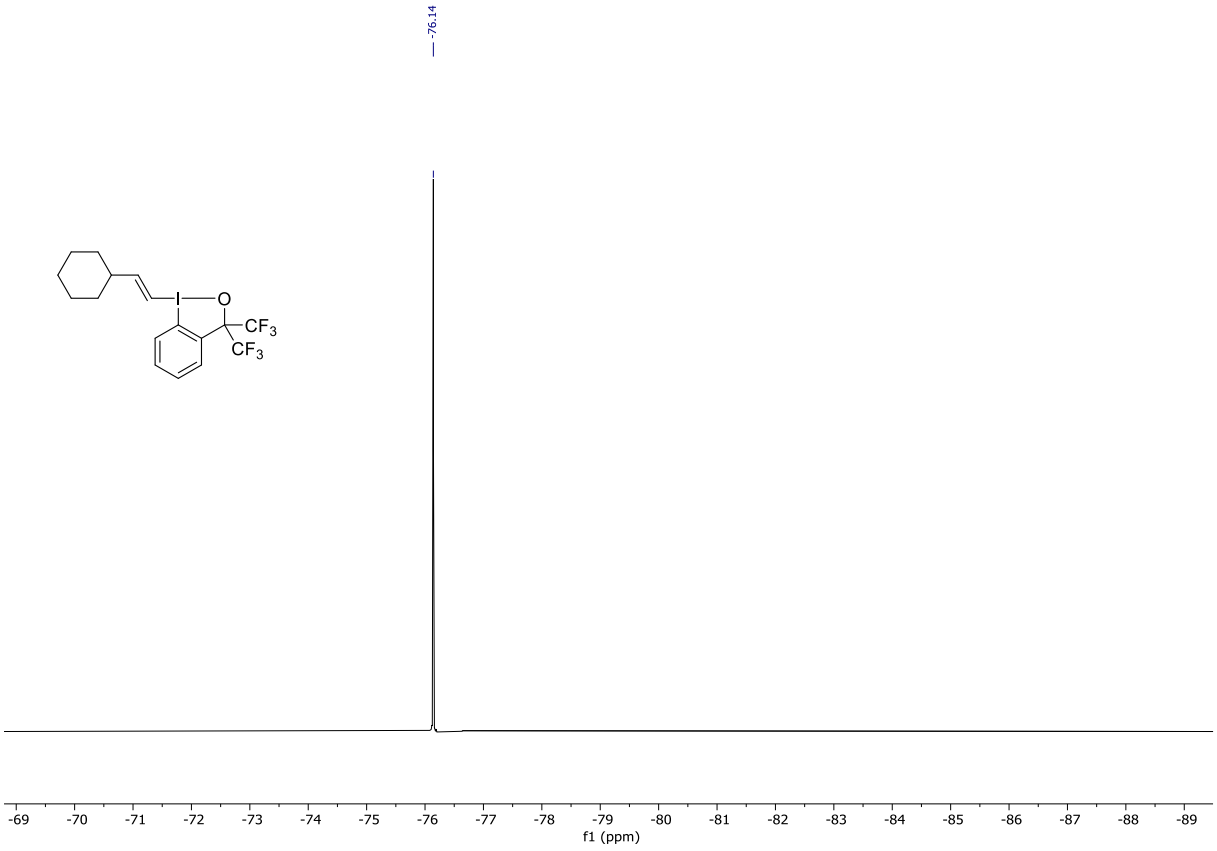
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **1'j**



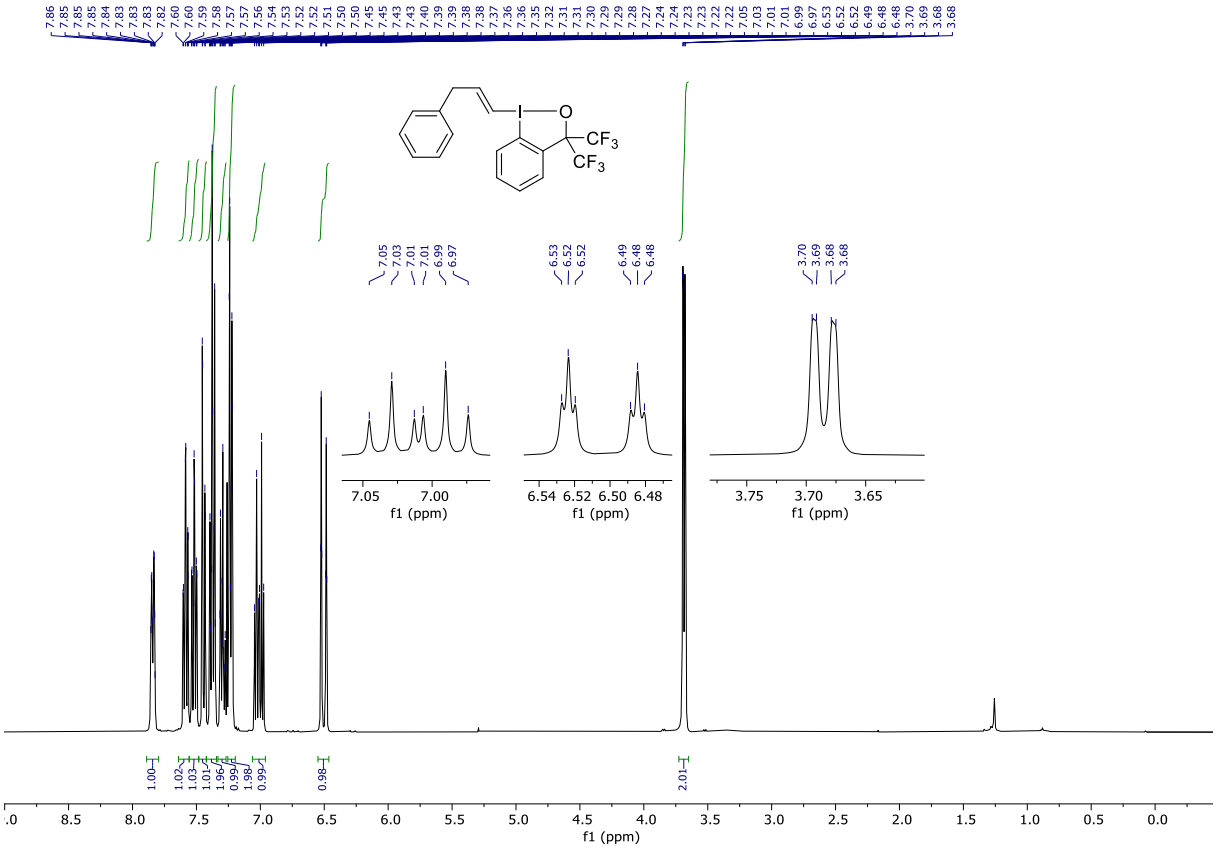
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **1'j**



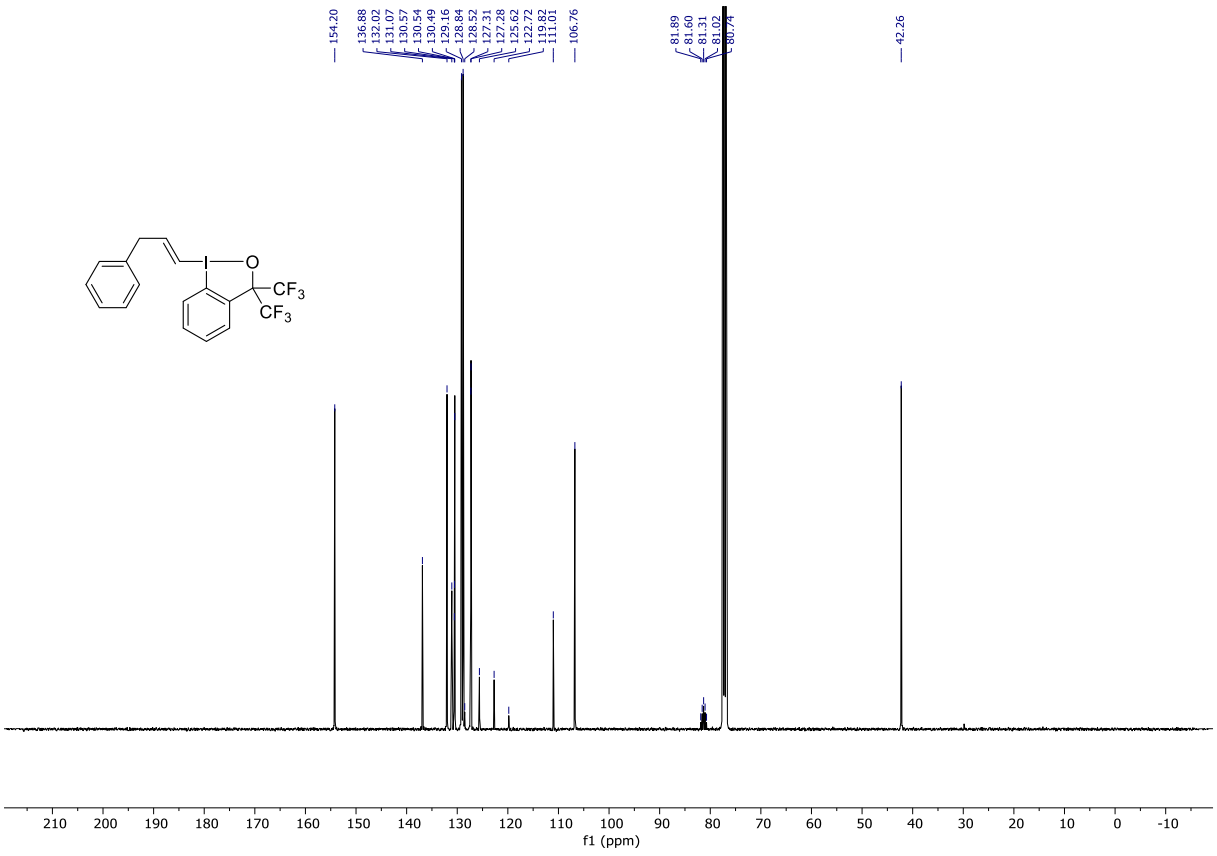
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **1'j**



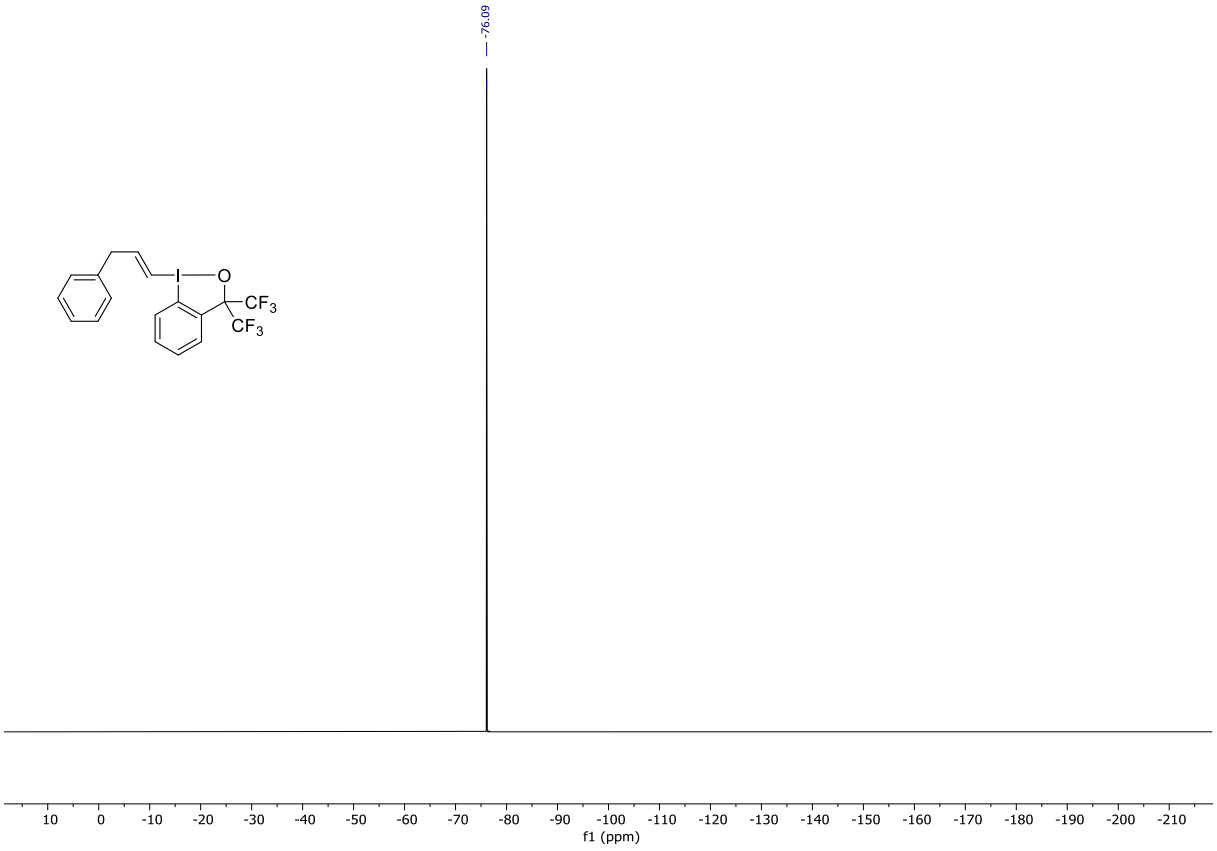
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **1'k**



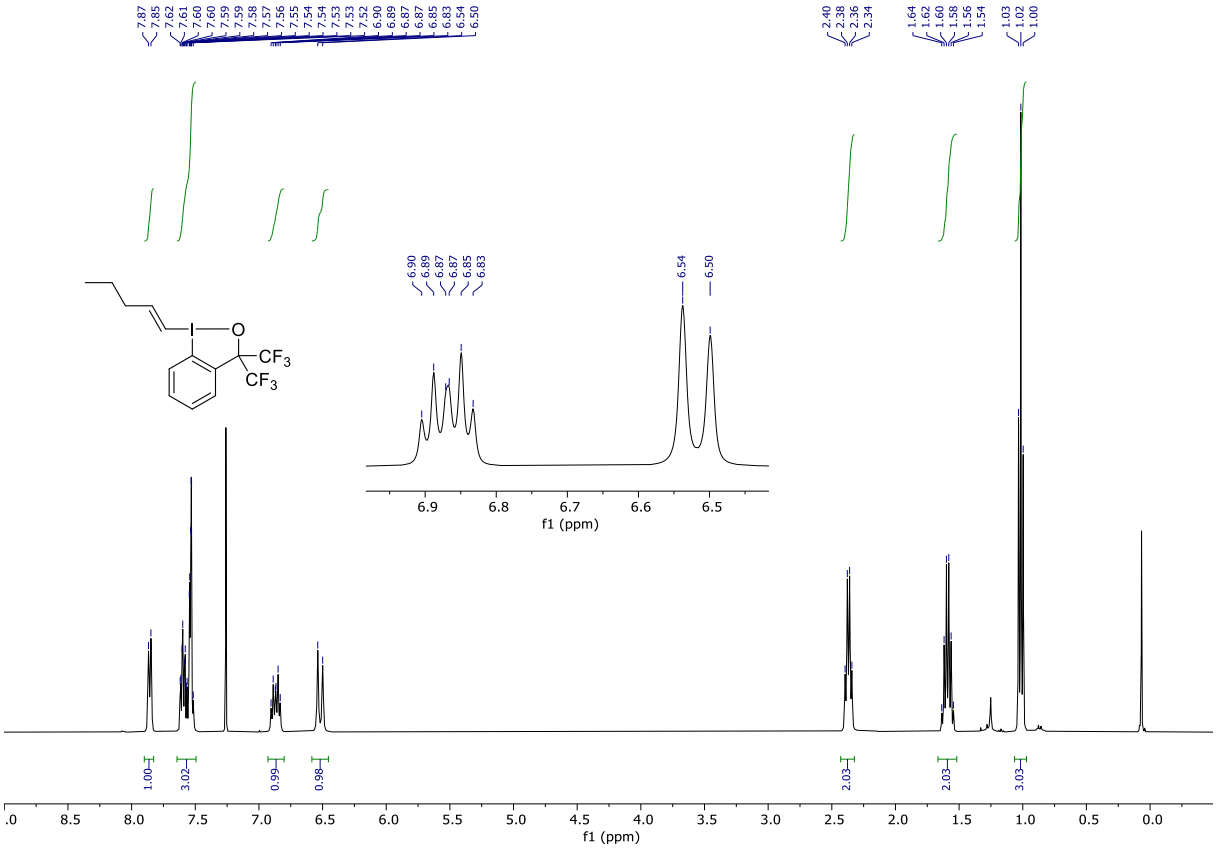
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **1'k**



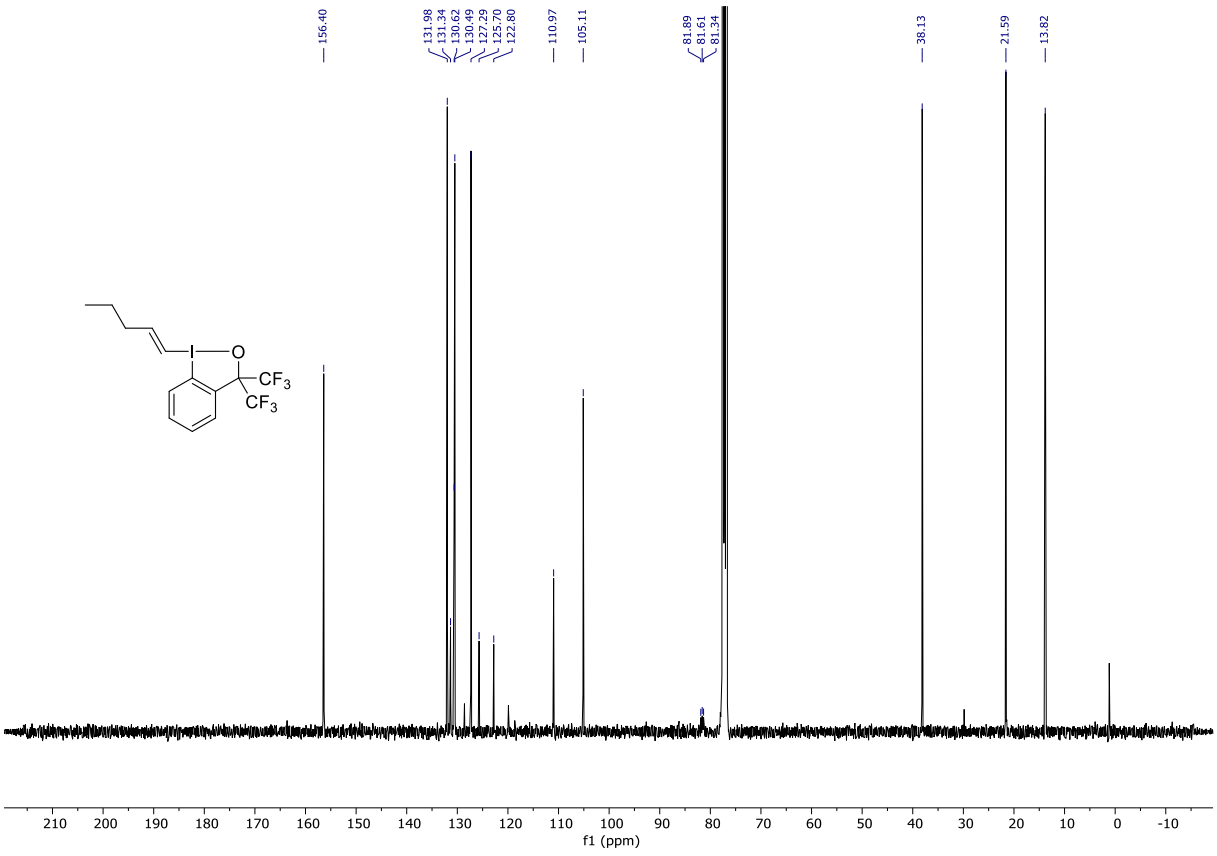
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **1'k**



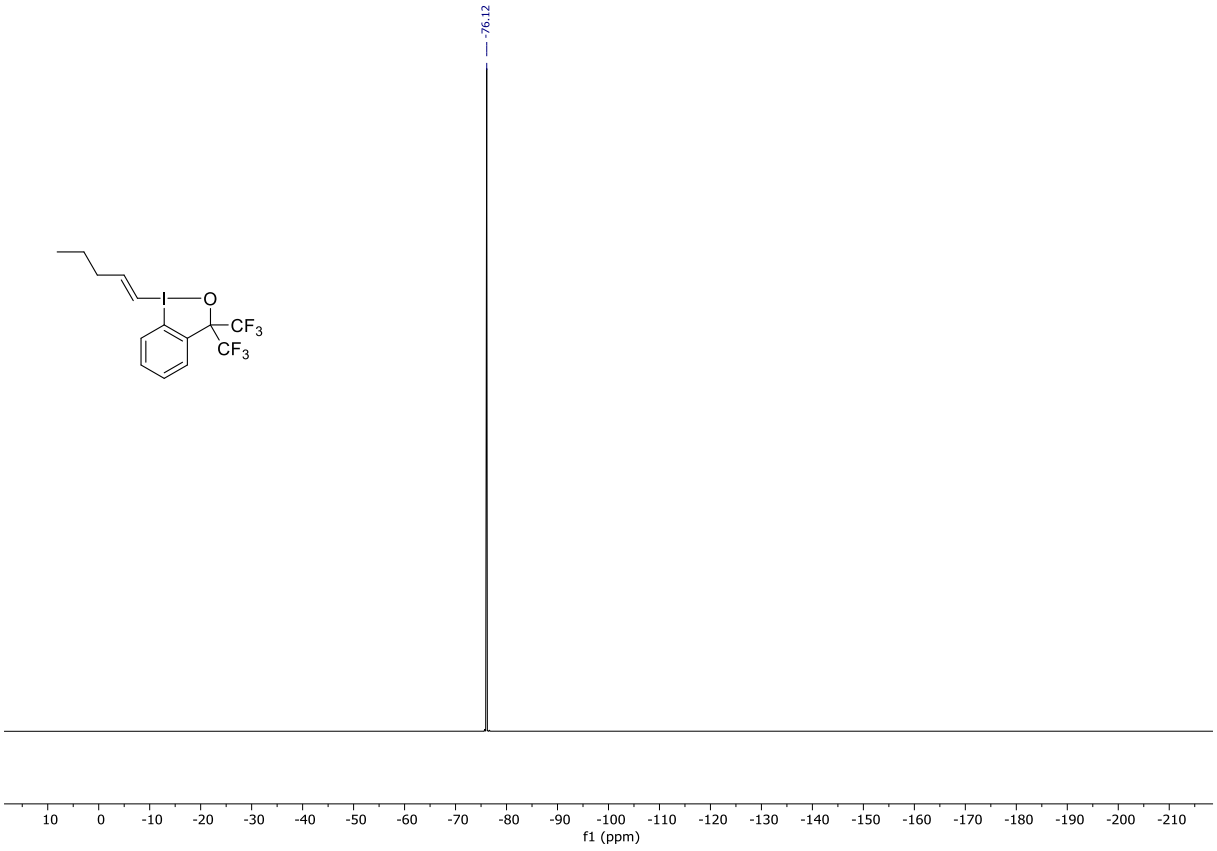
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **1'l**



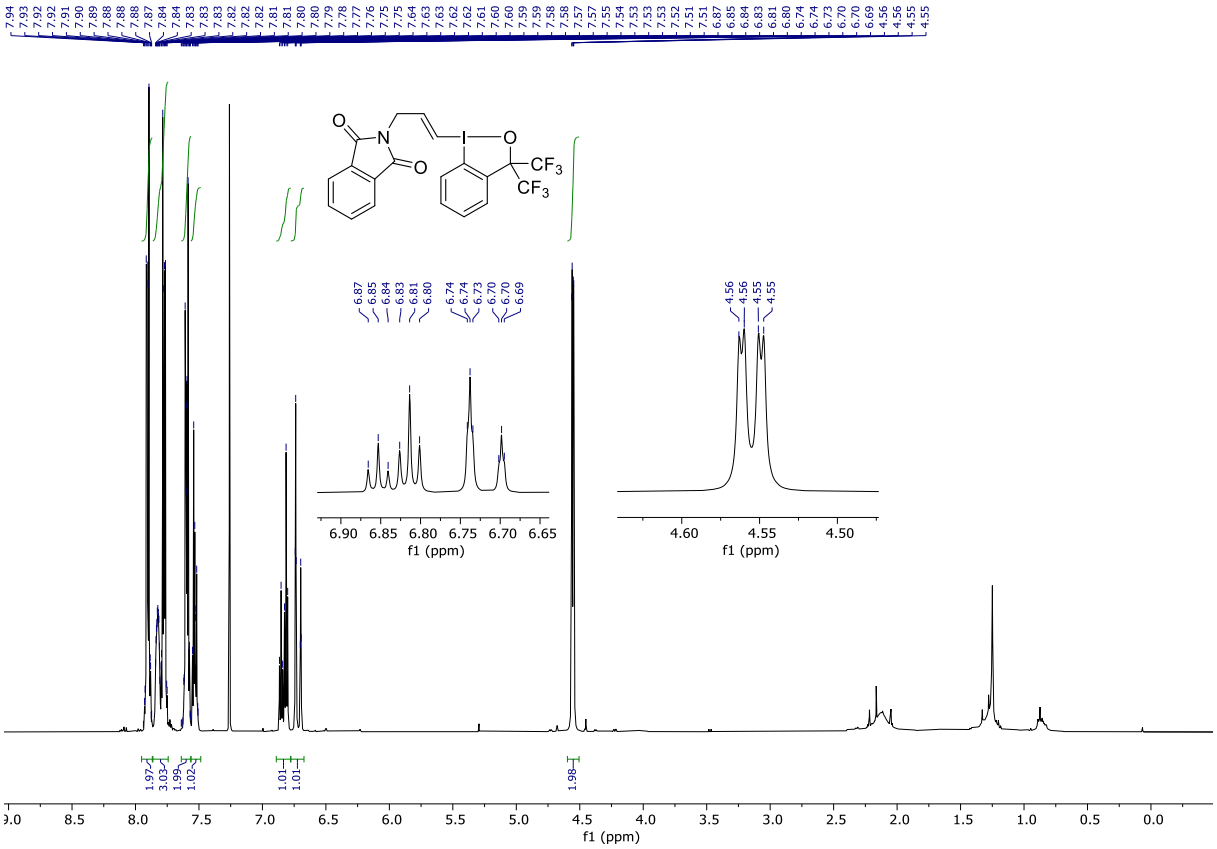
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **1'l**



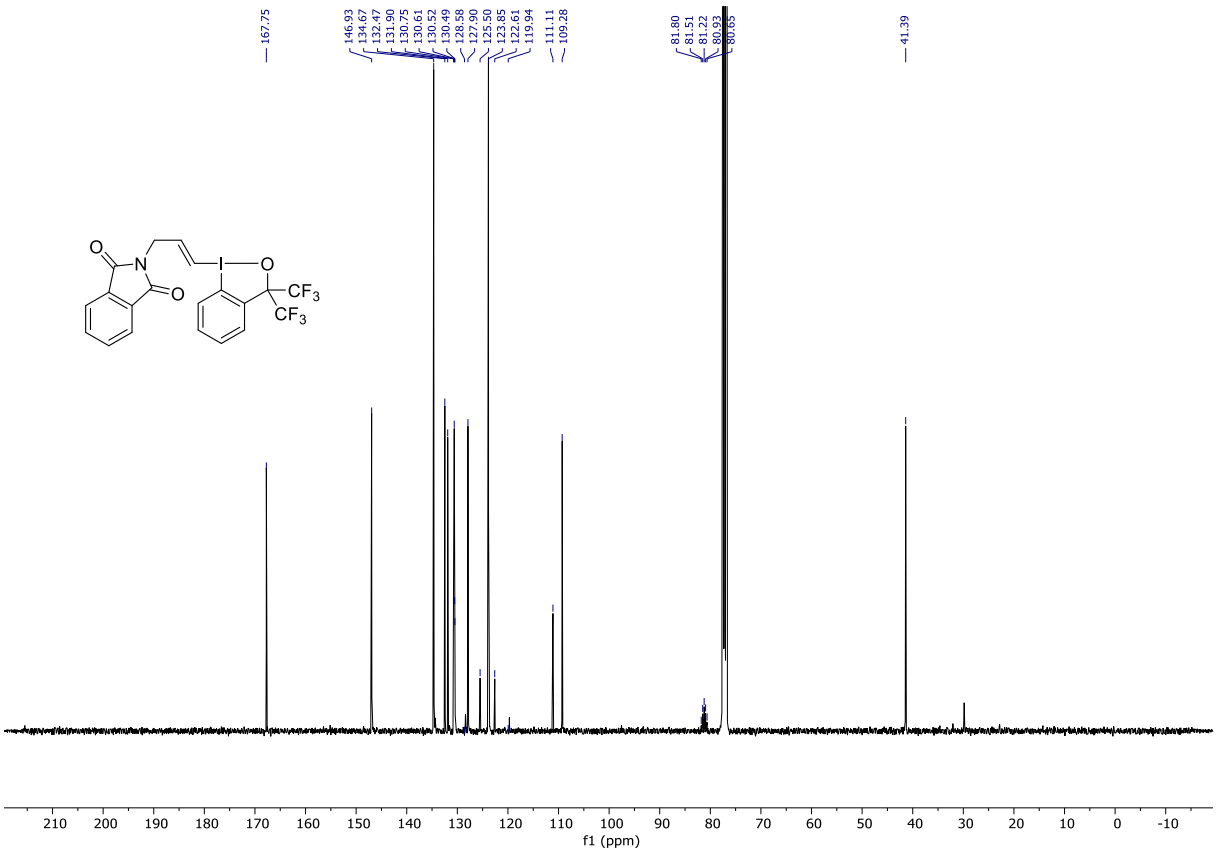
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **1'l**



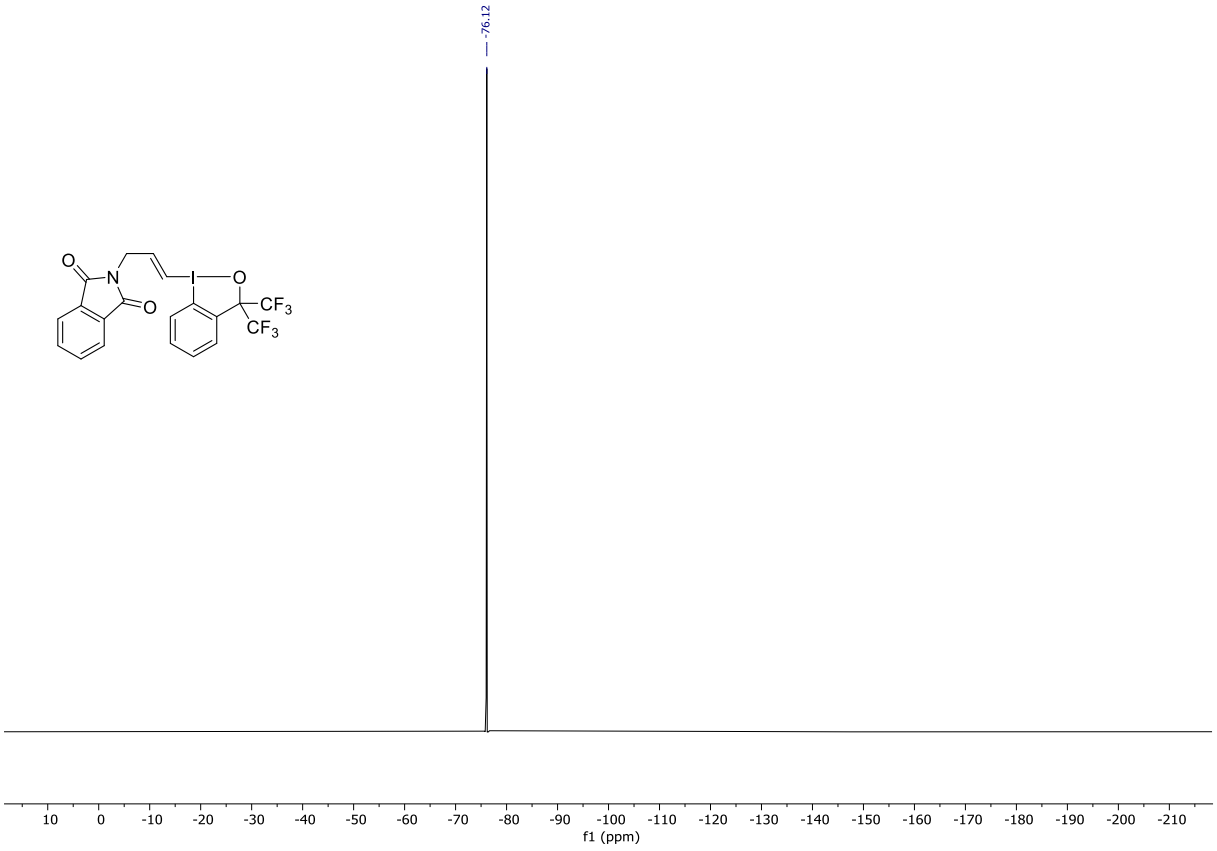
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **1'p**



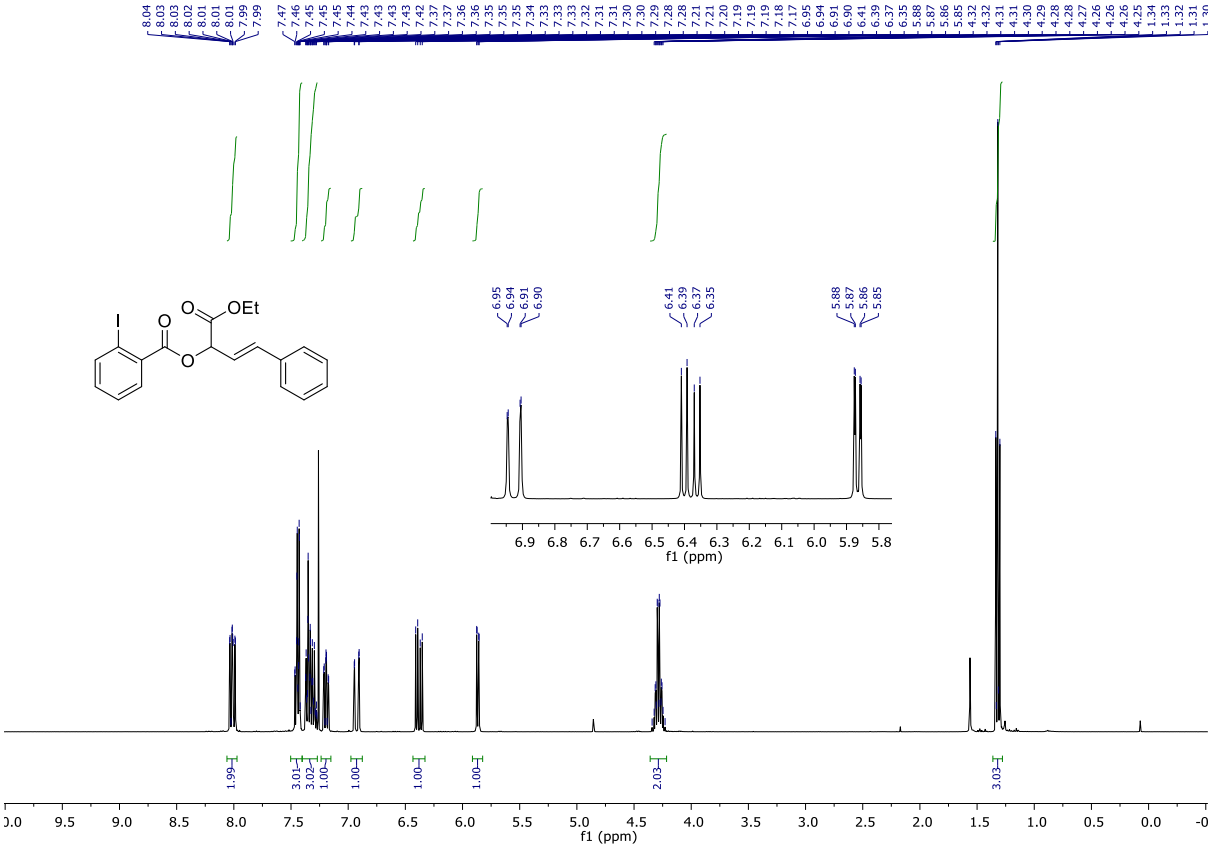
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **1'p**



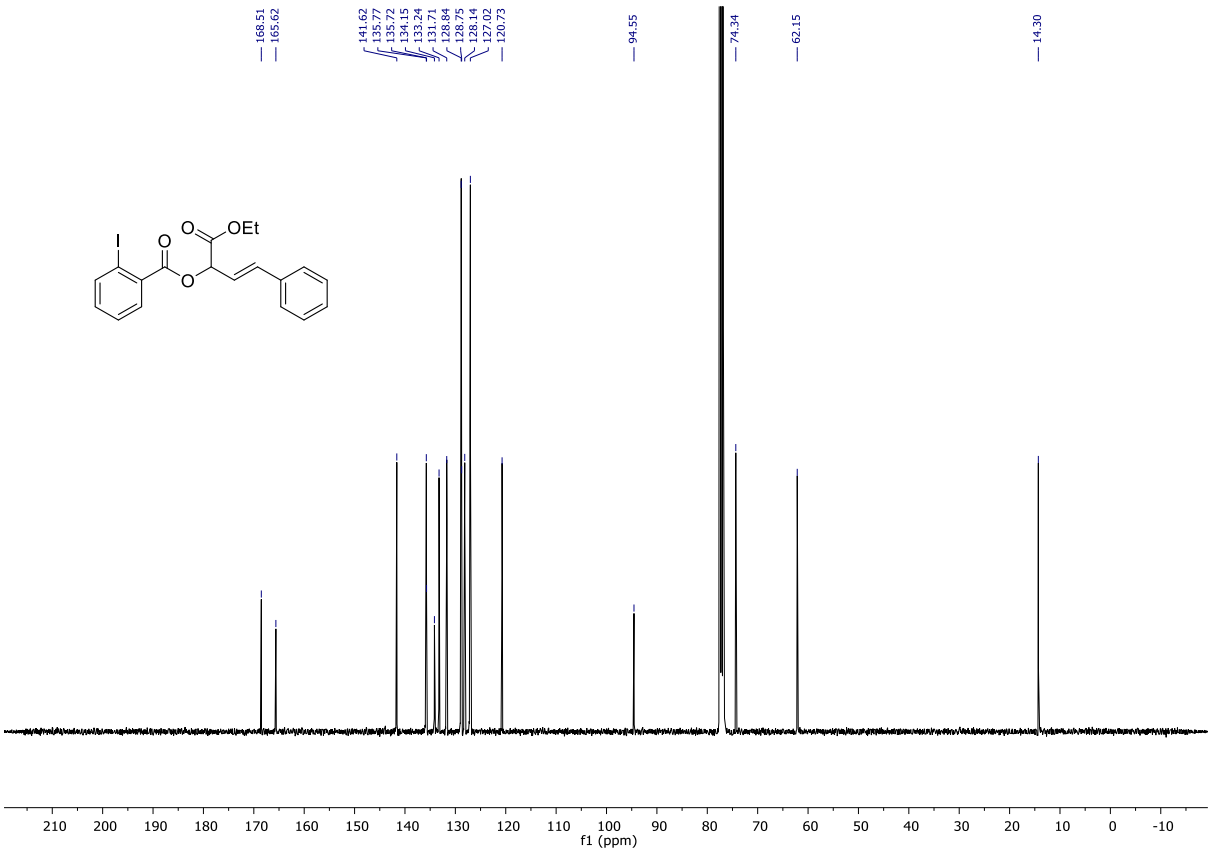
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **1'p**



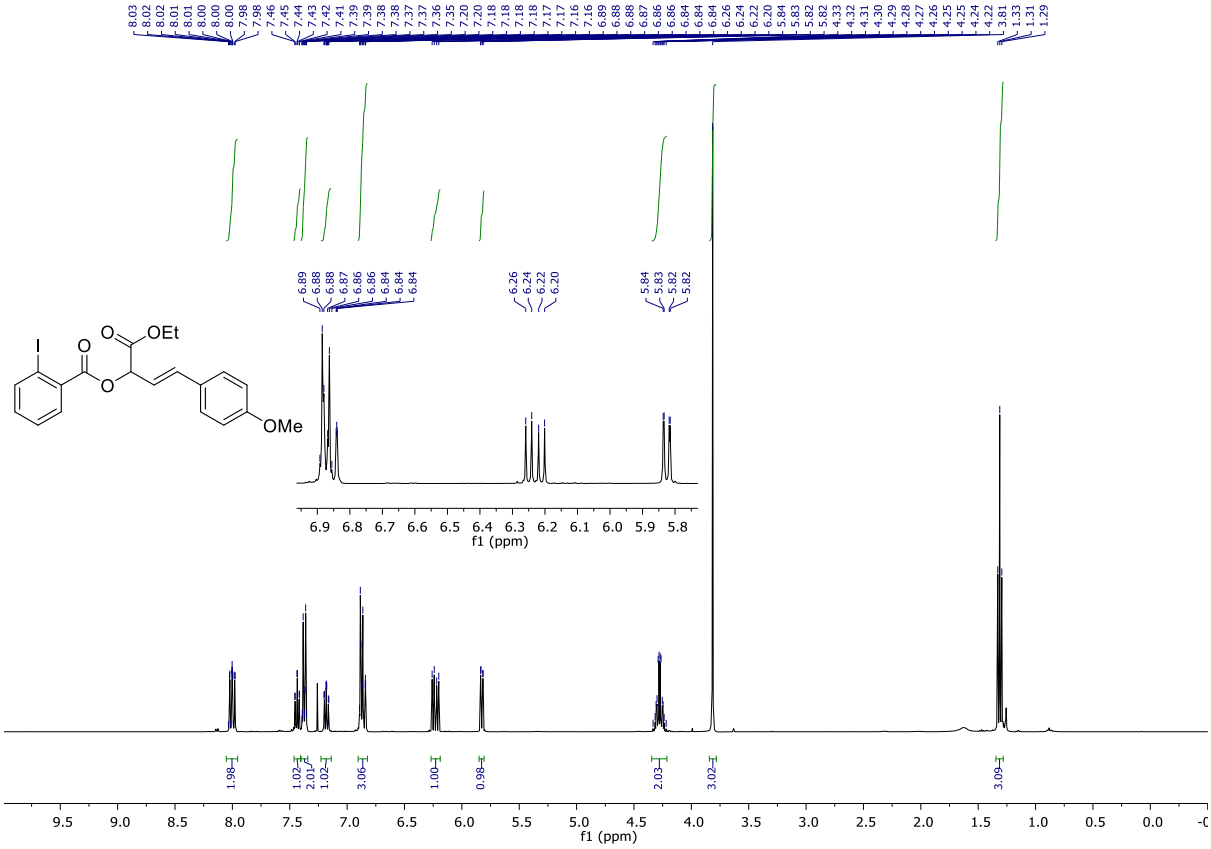
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4a**



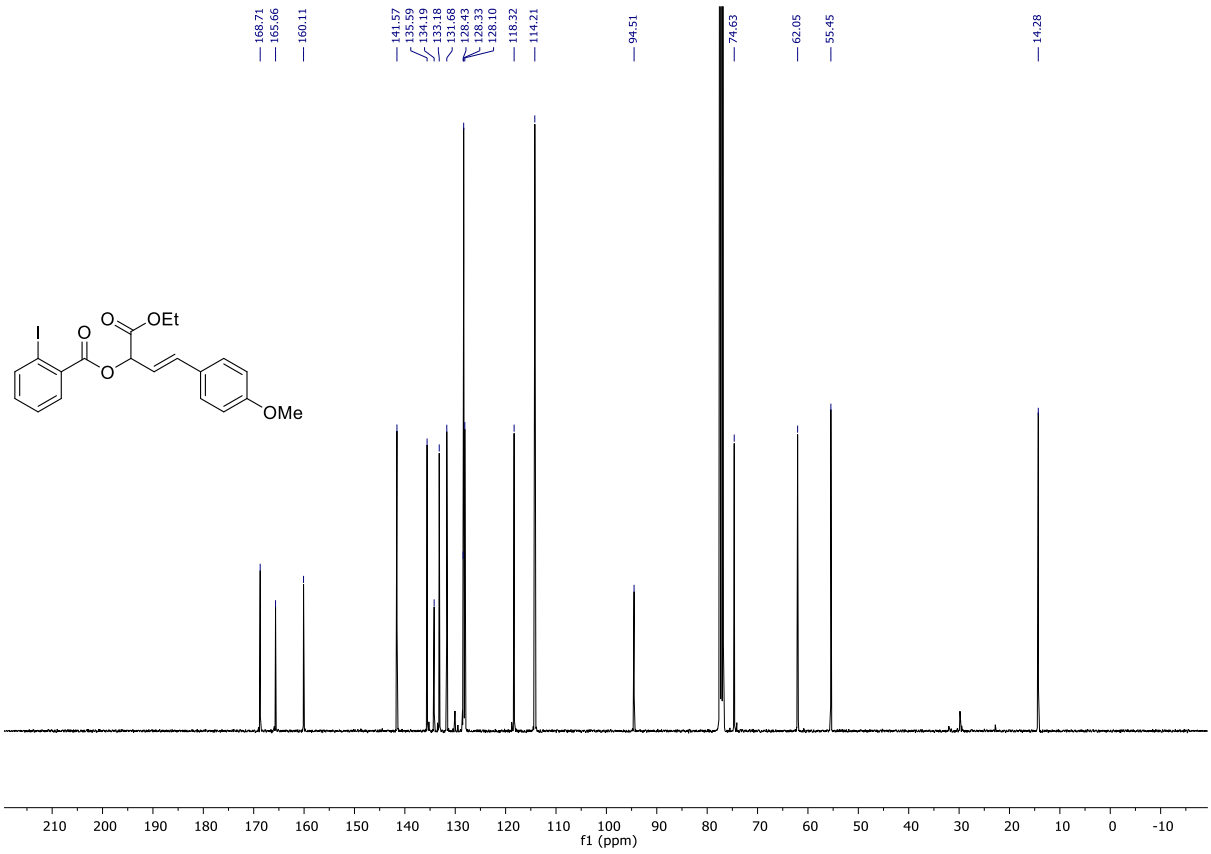
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4a**



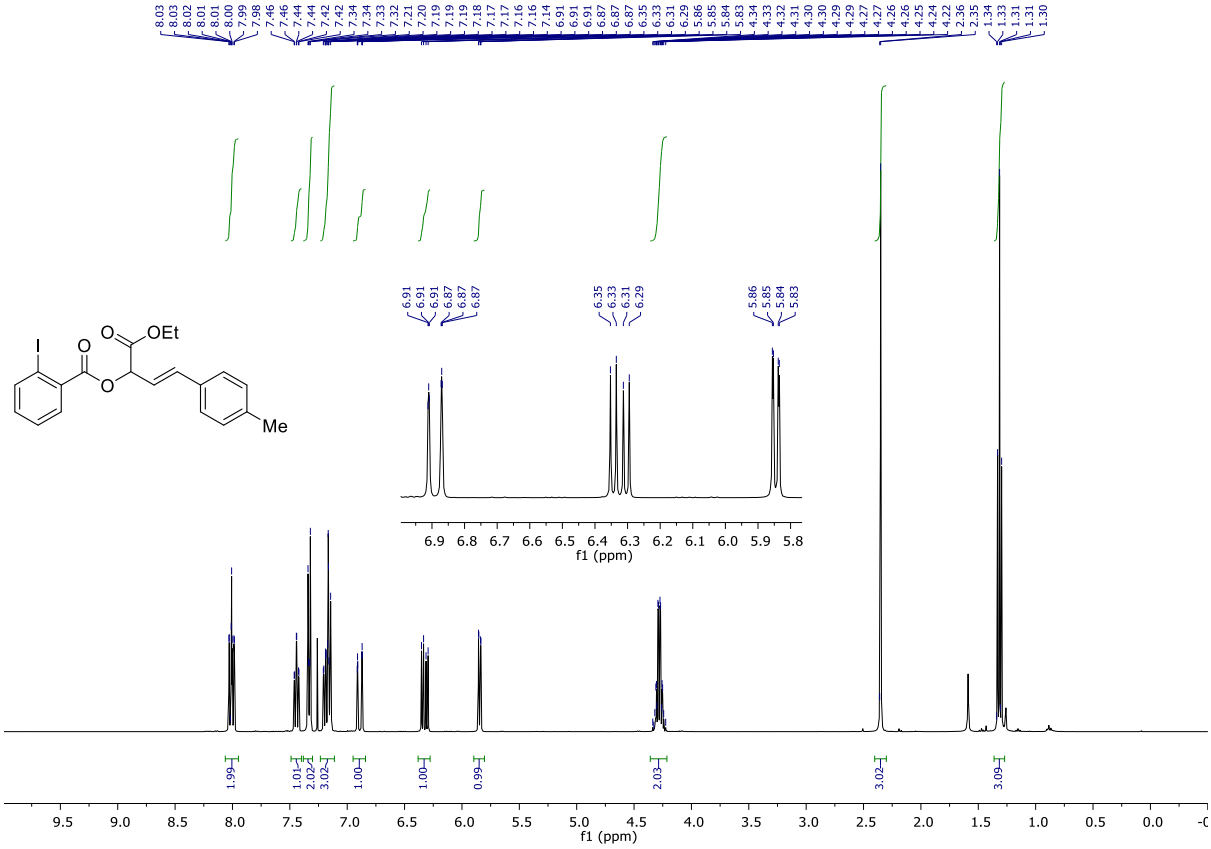
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4b**



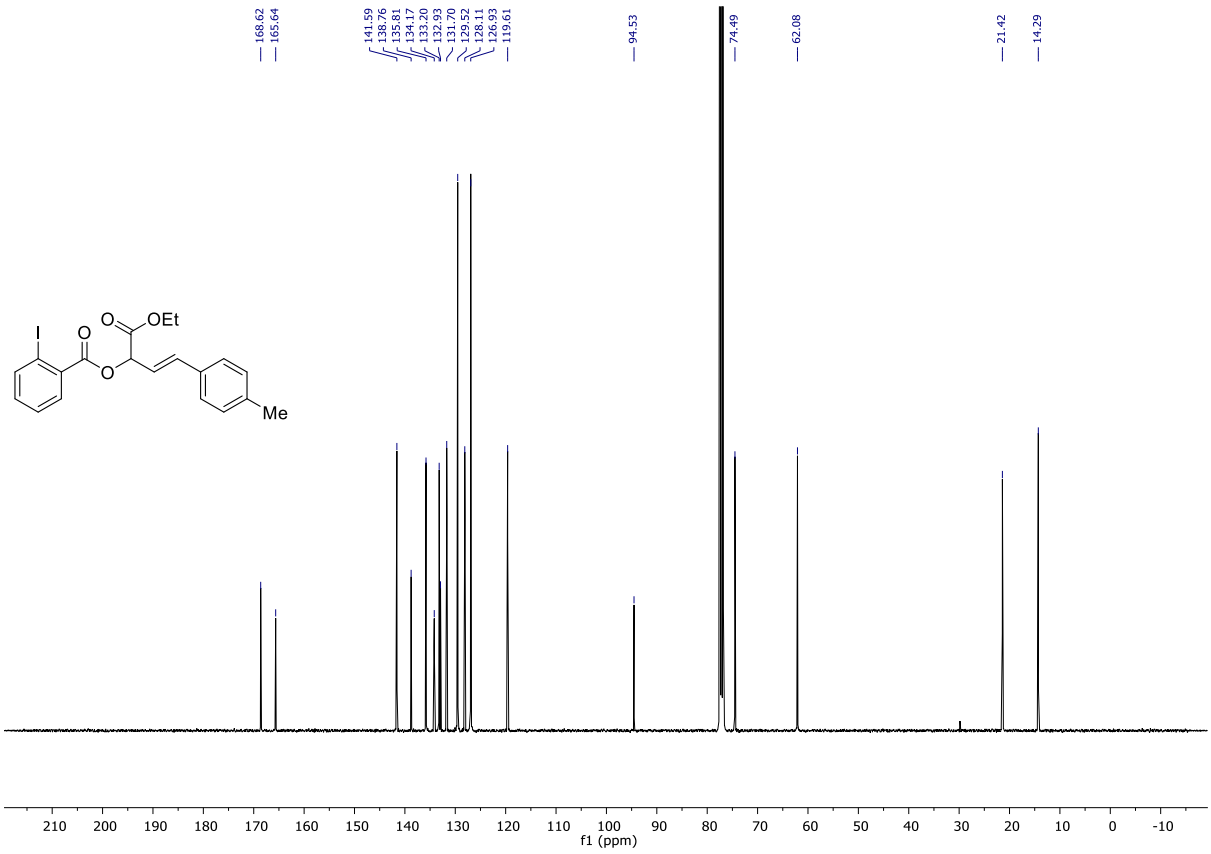
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4b**



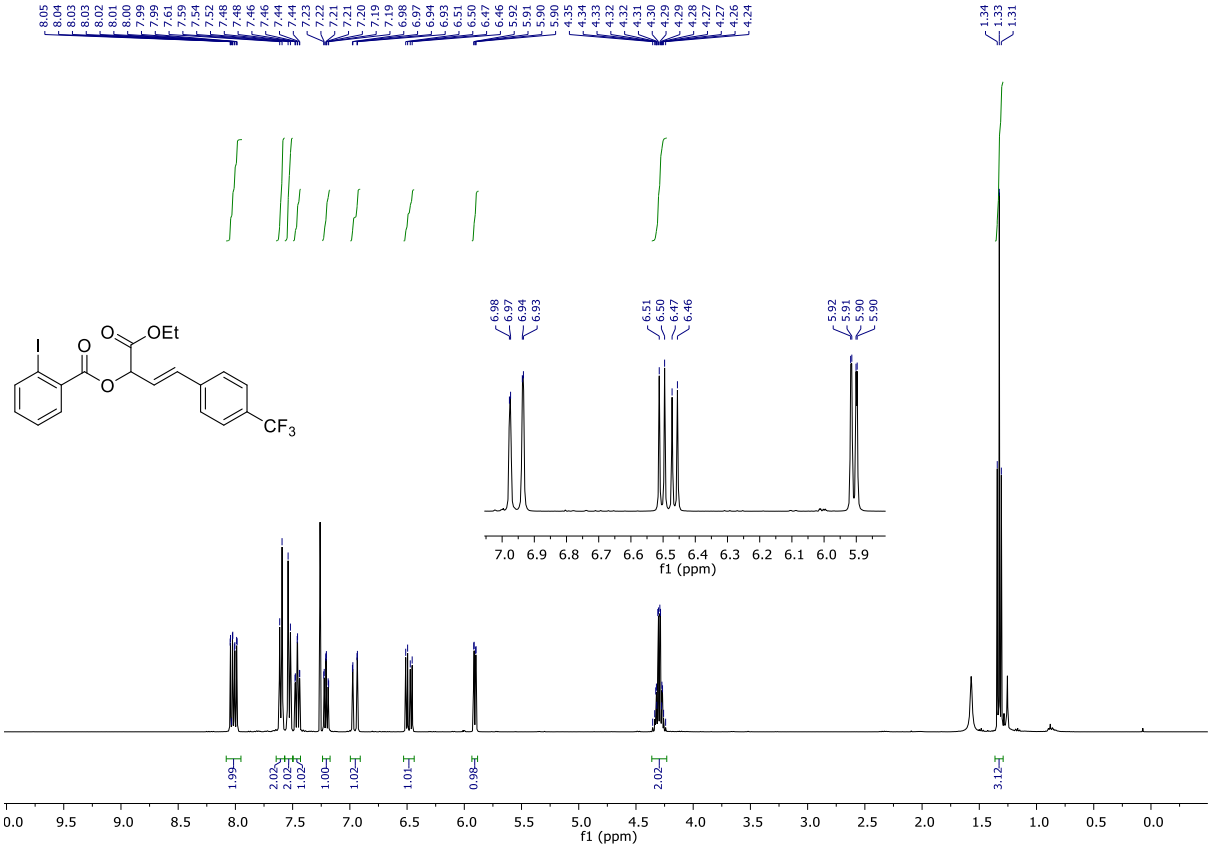
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4c**



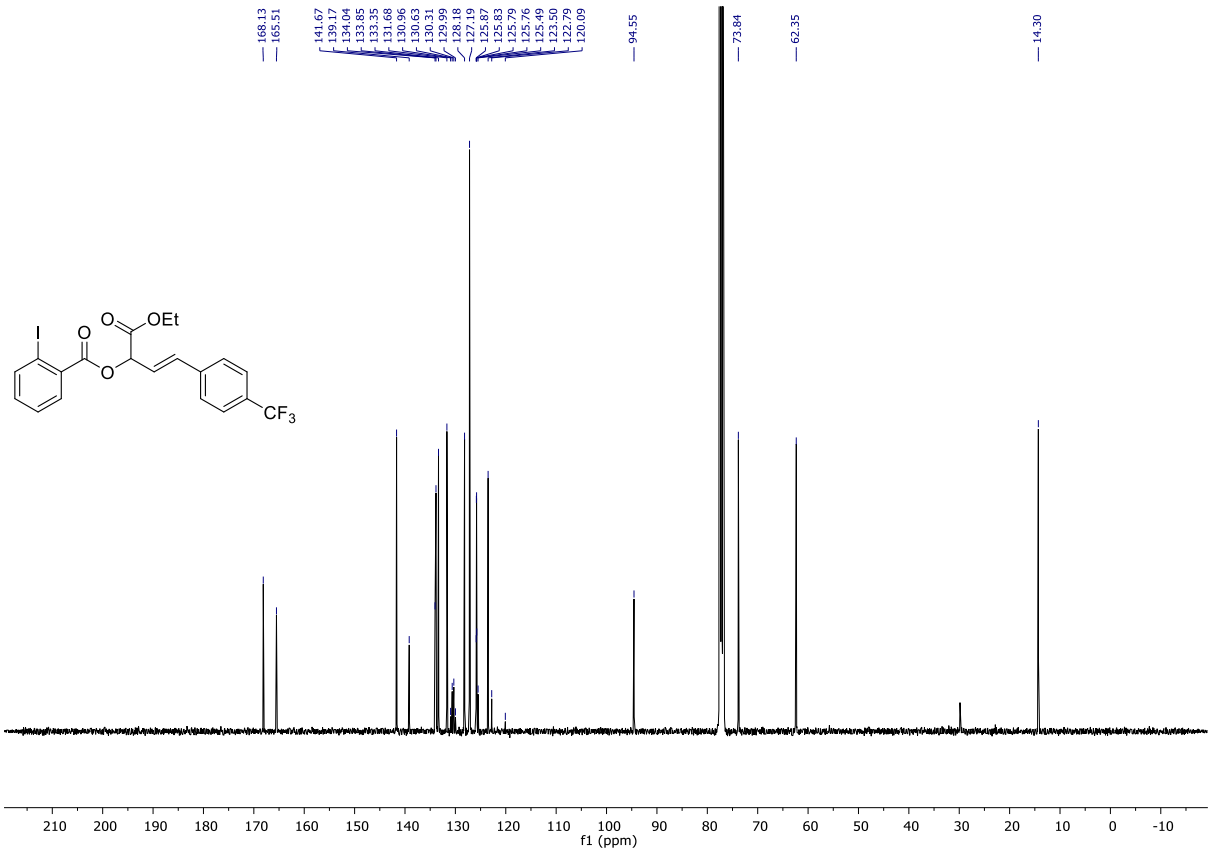
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4c**



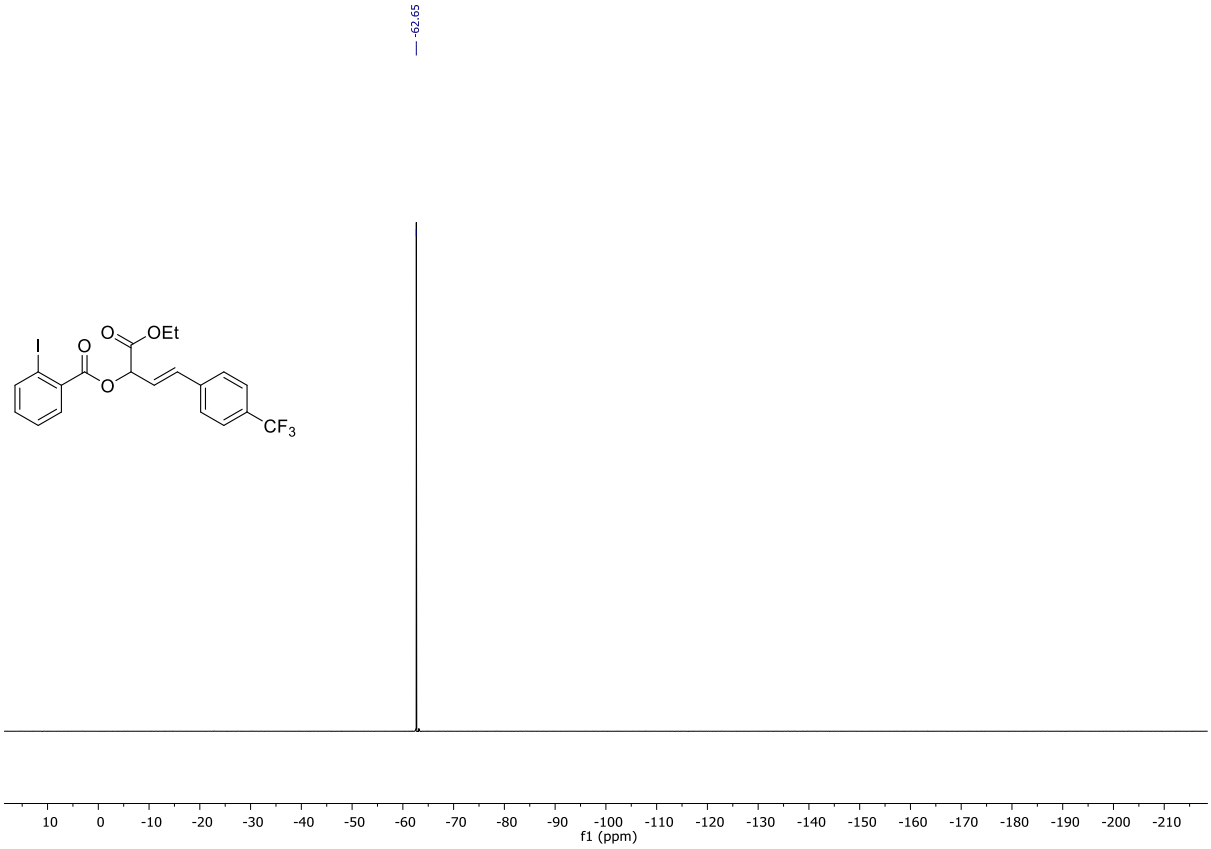
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4d**



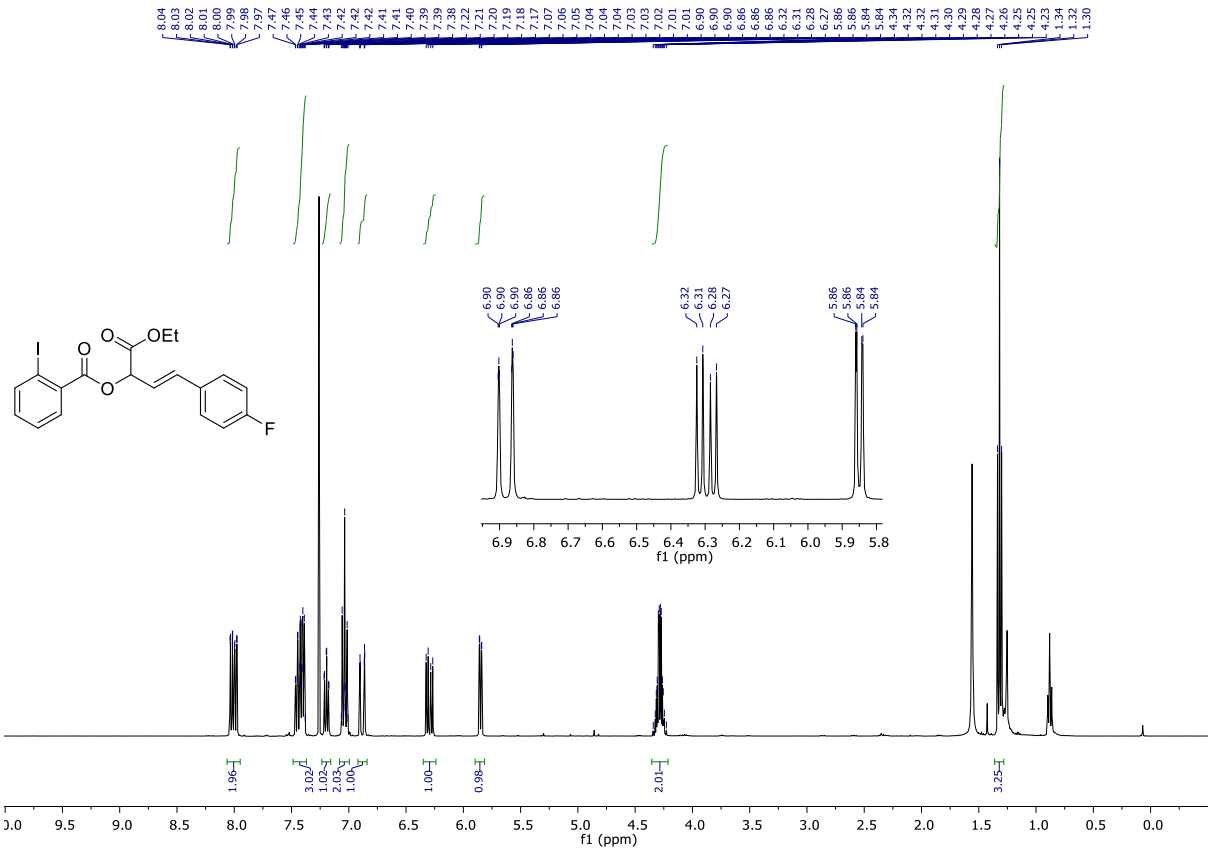
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4d**



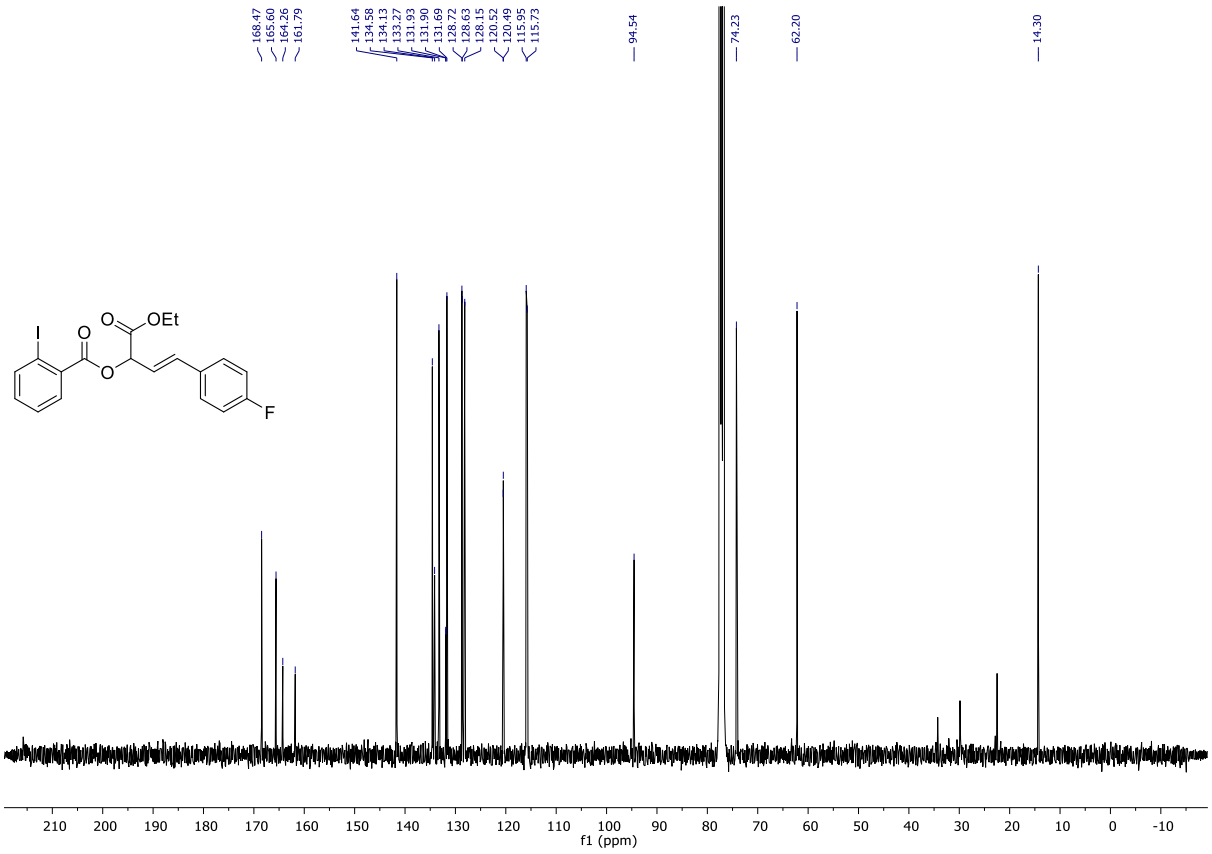
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **4d**



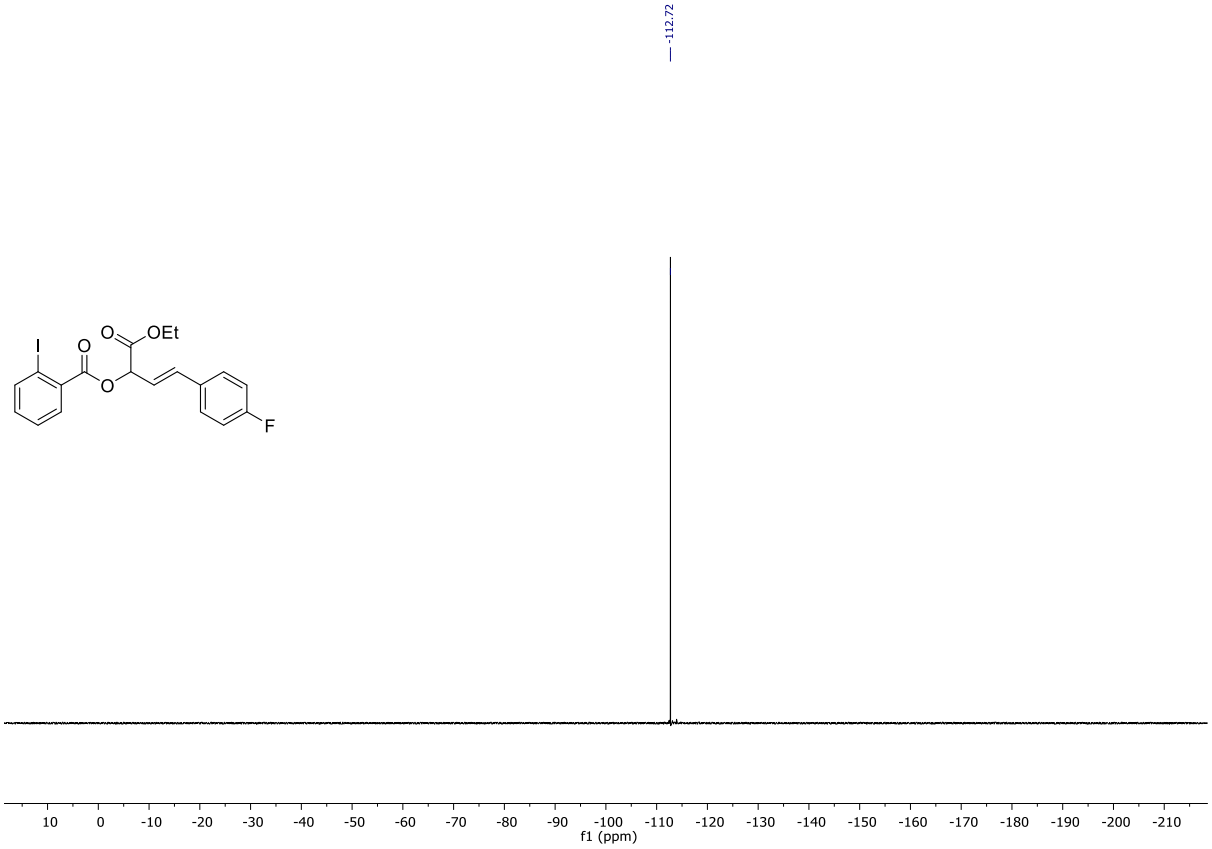
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4e**



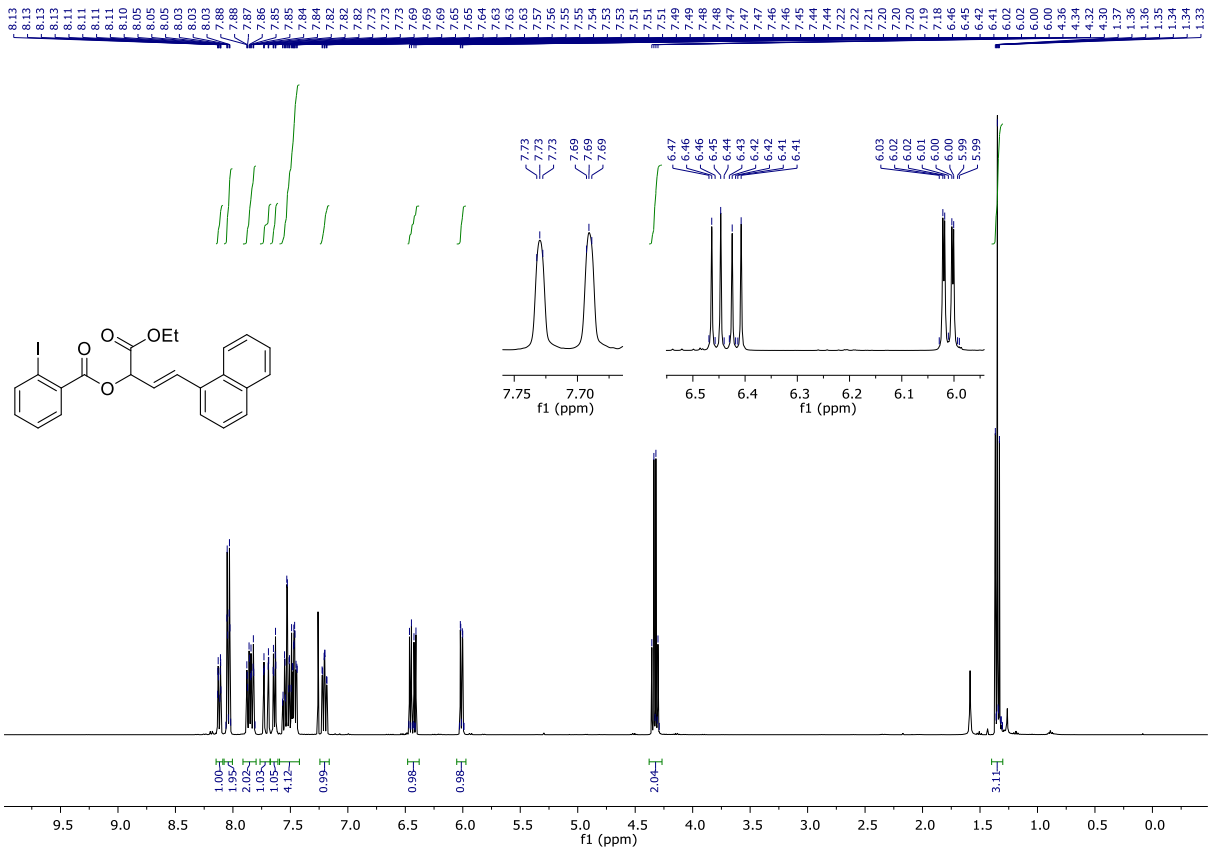
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4e**



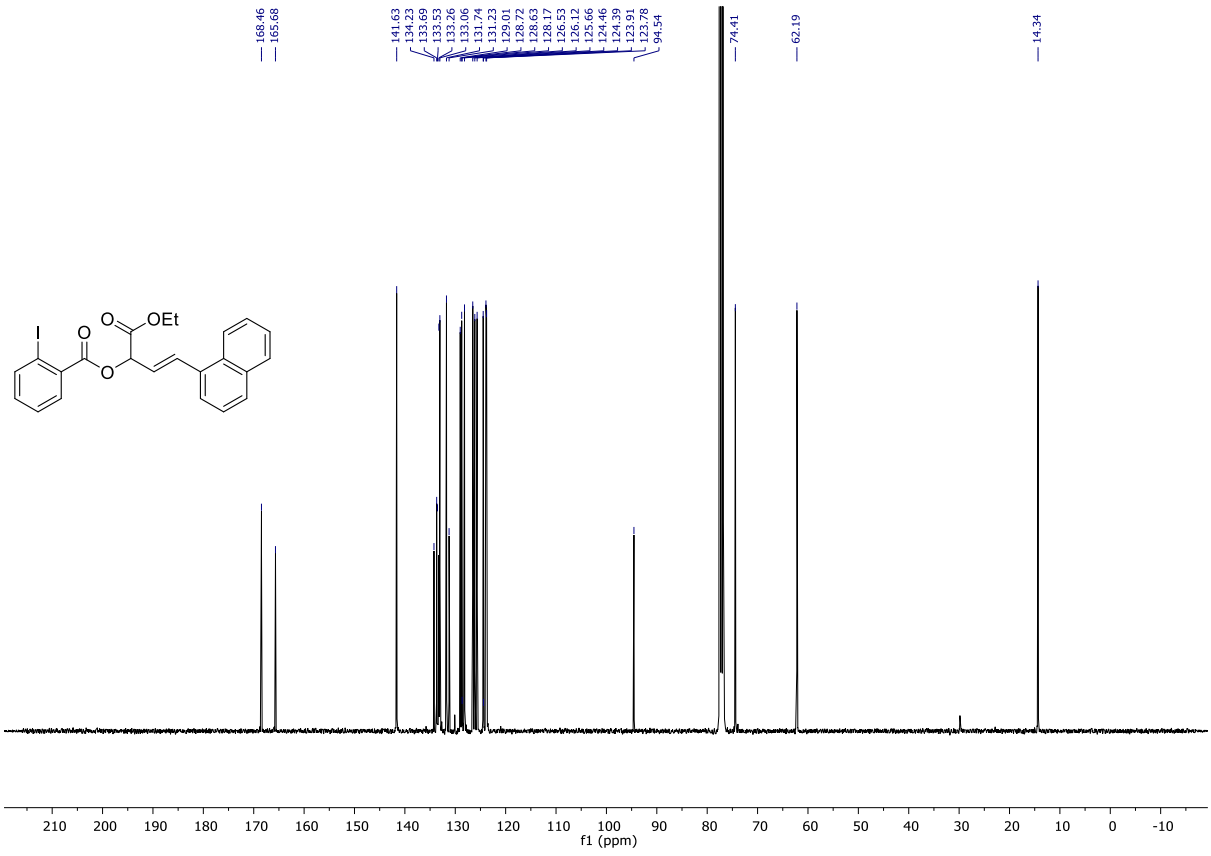
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **4e**



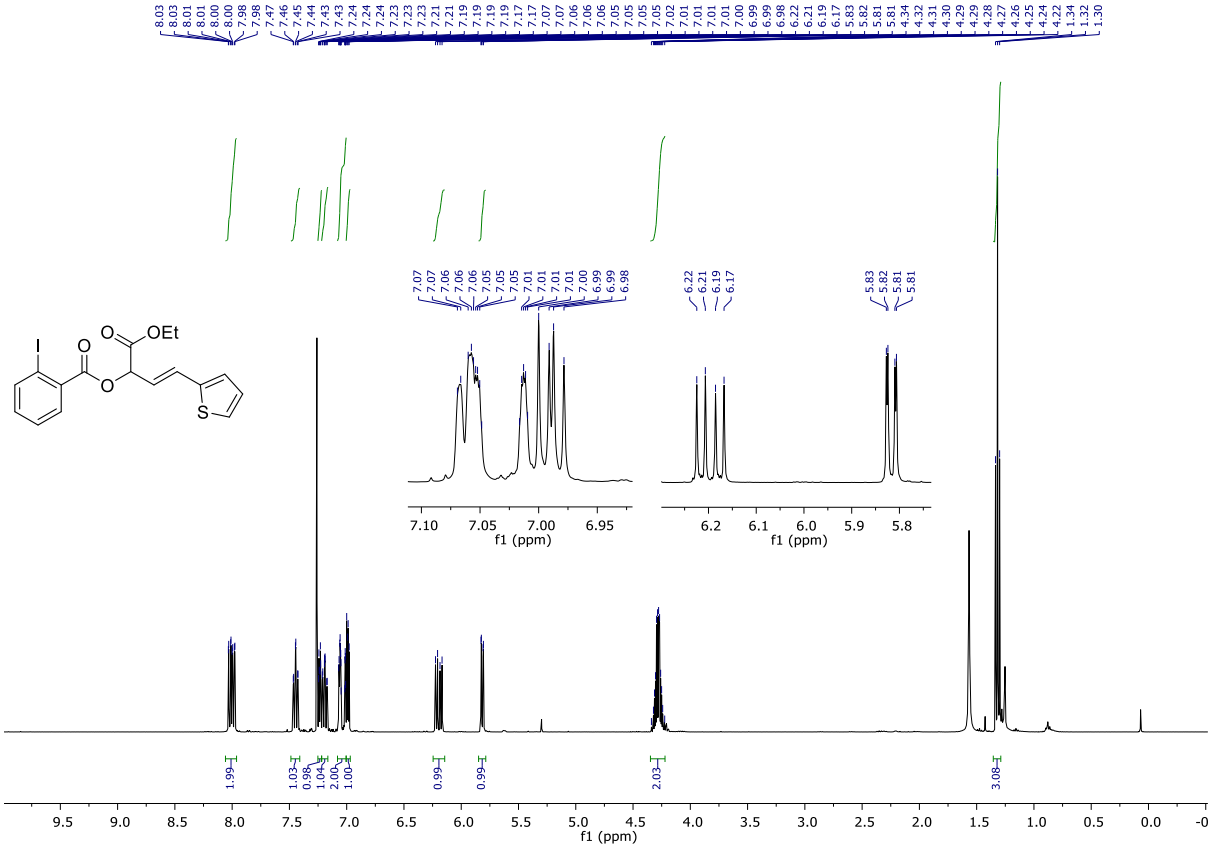
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4f**



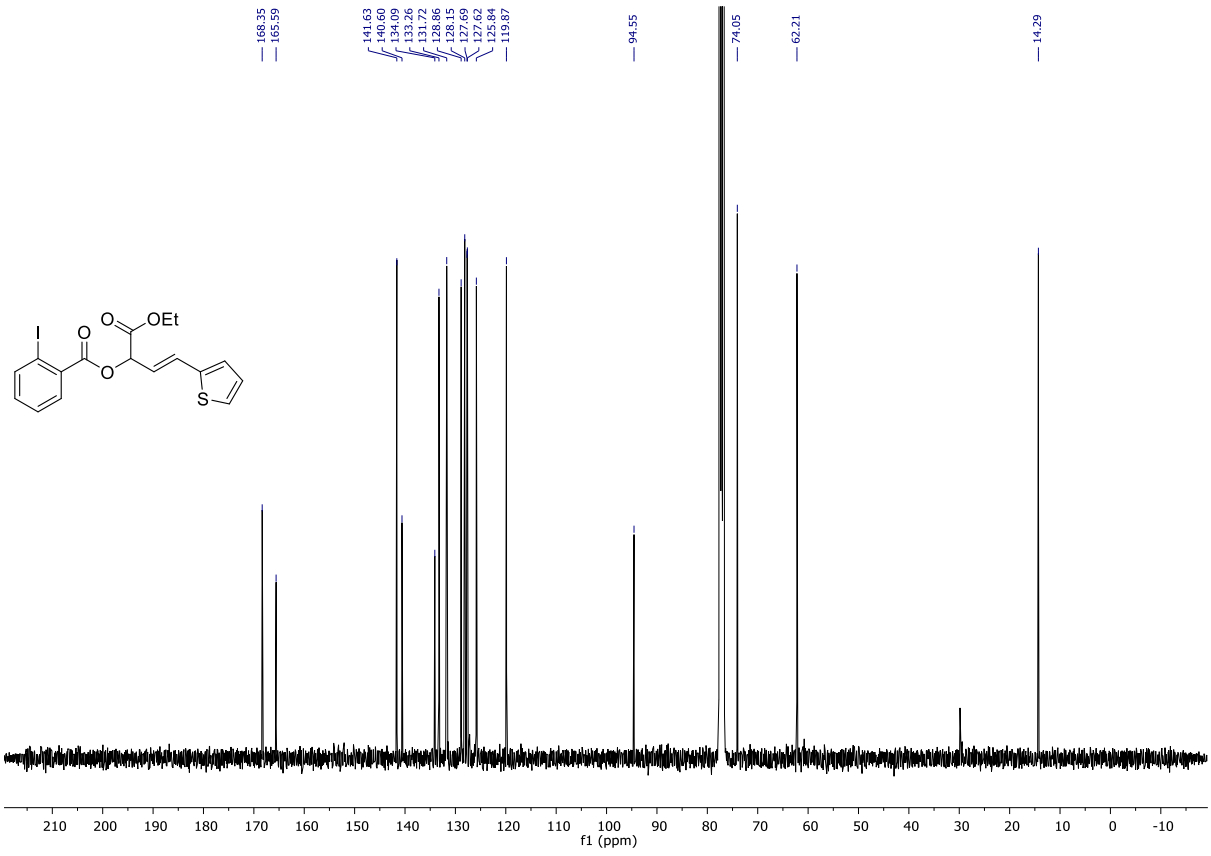
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4f**



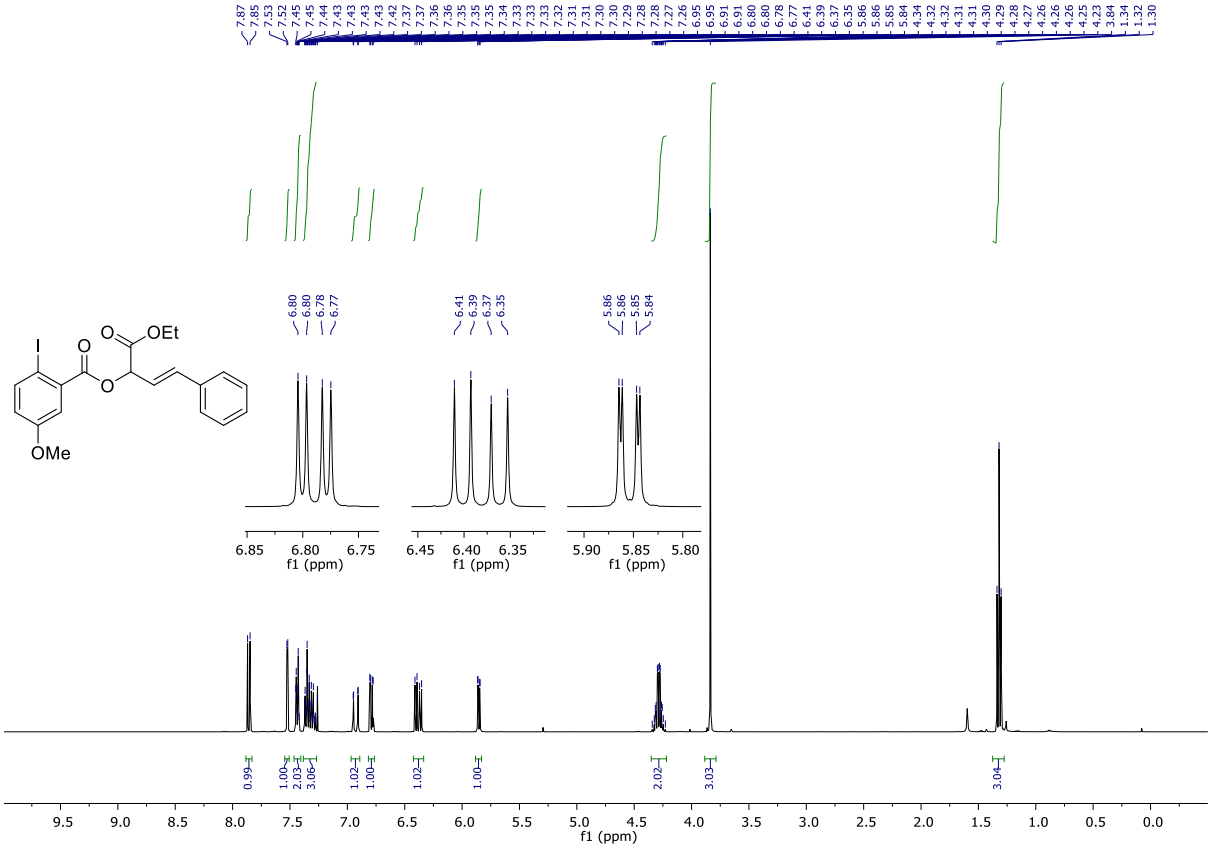
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4g**



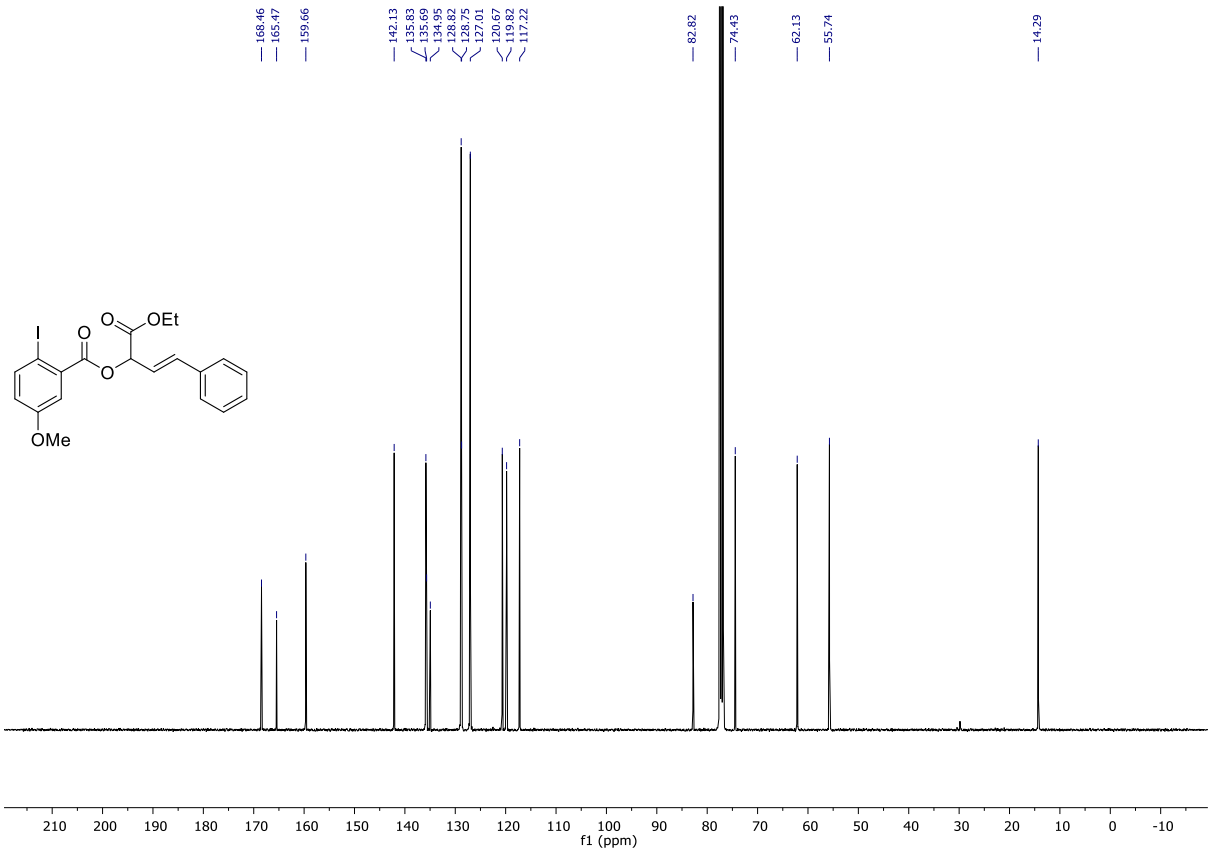
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4g**



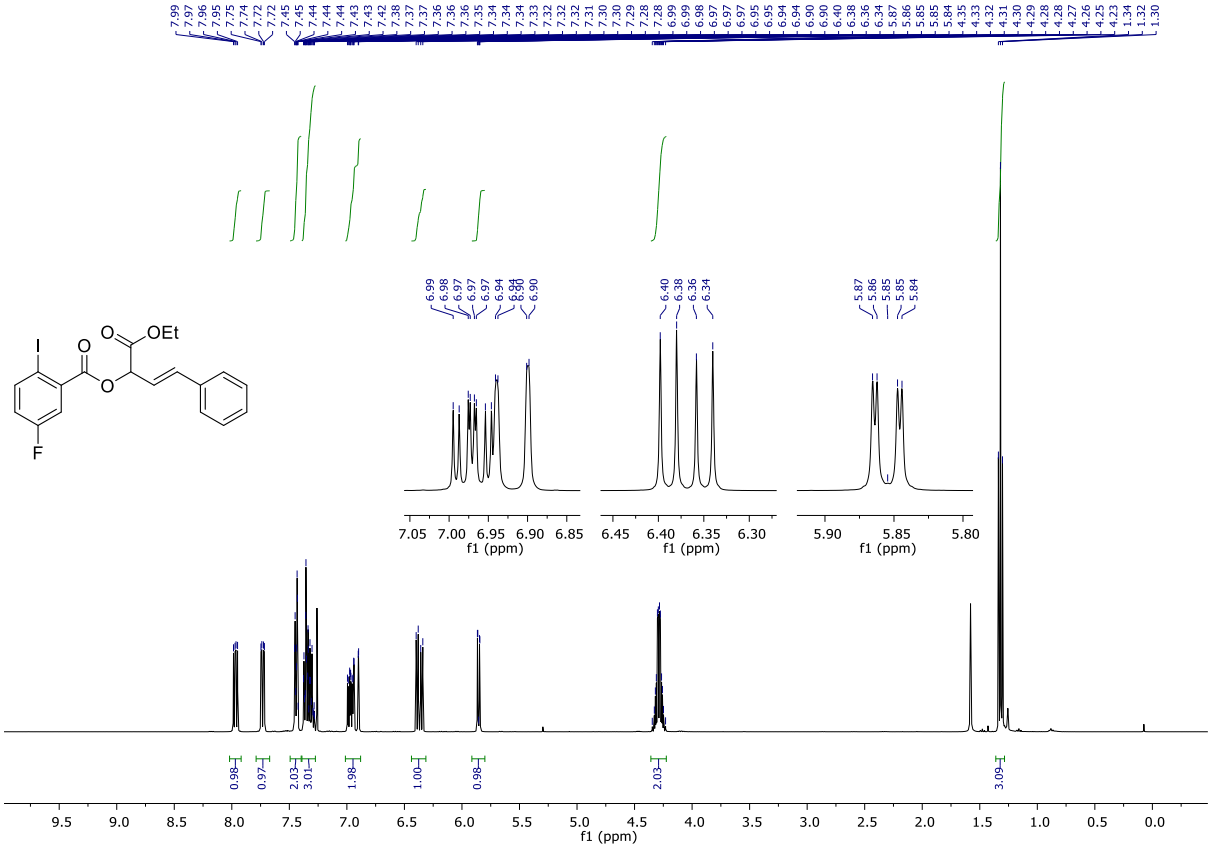
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4h**



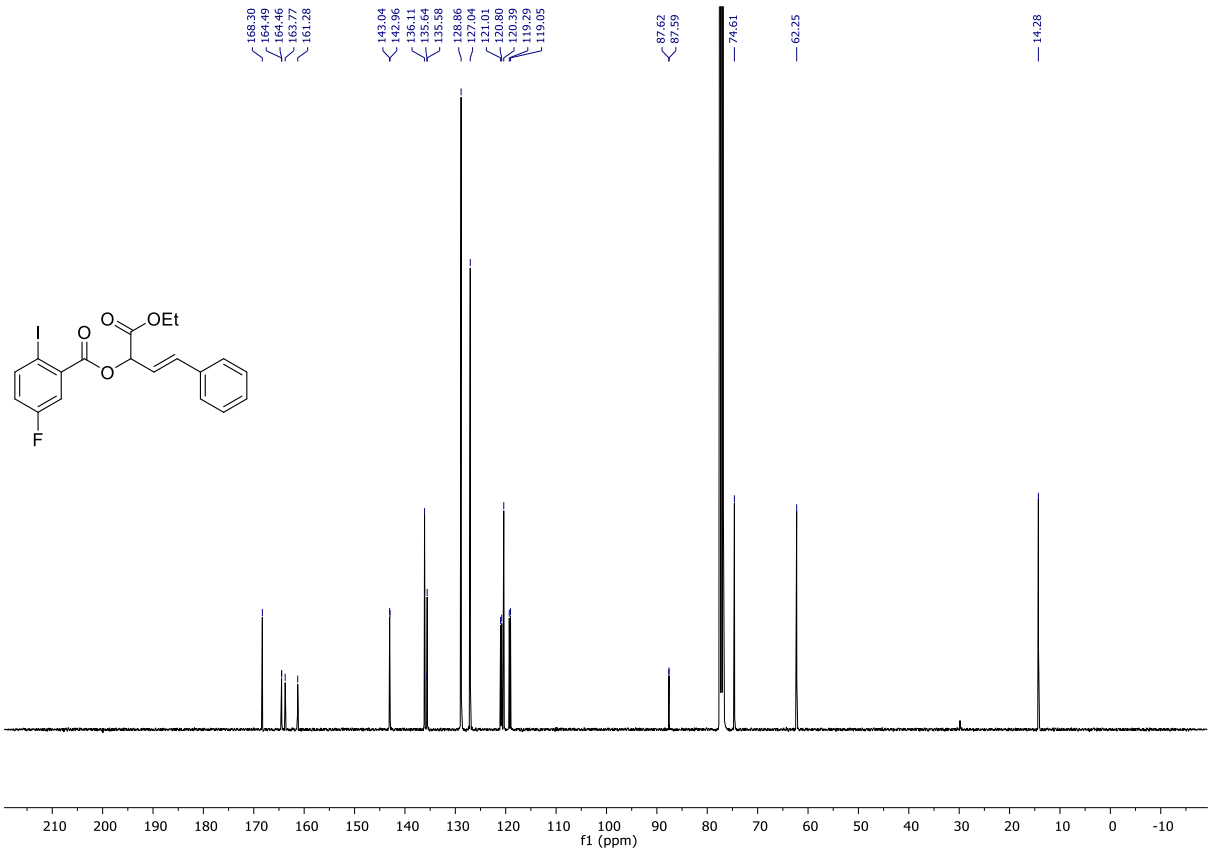
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4h**



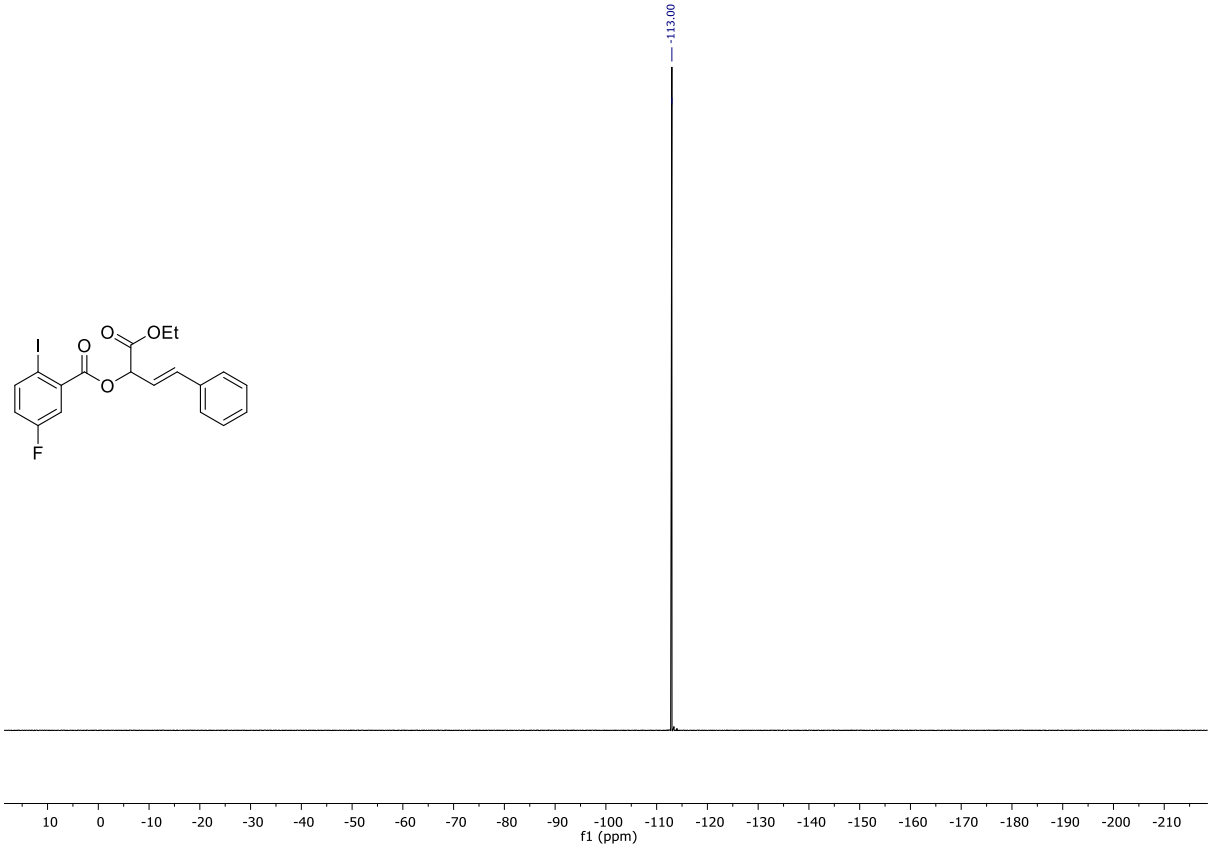
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4i**



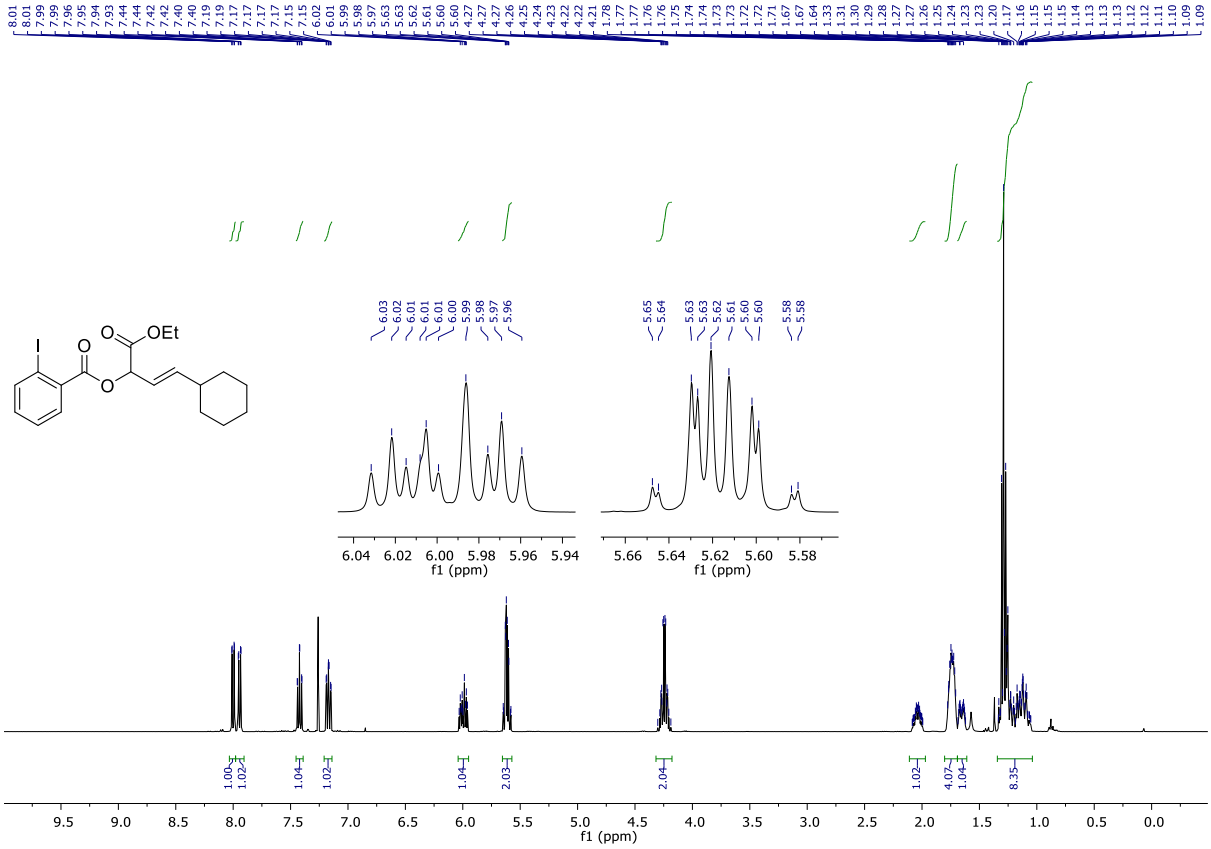
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4i**



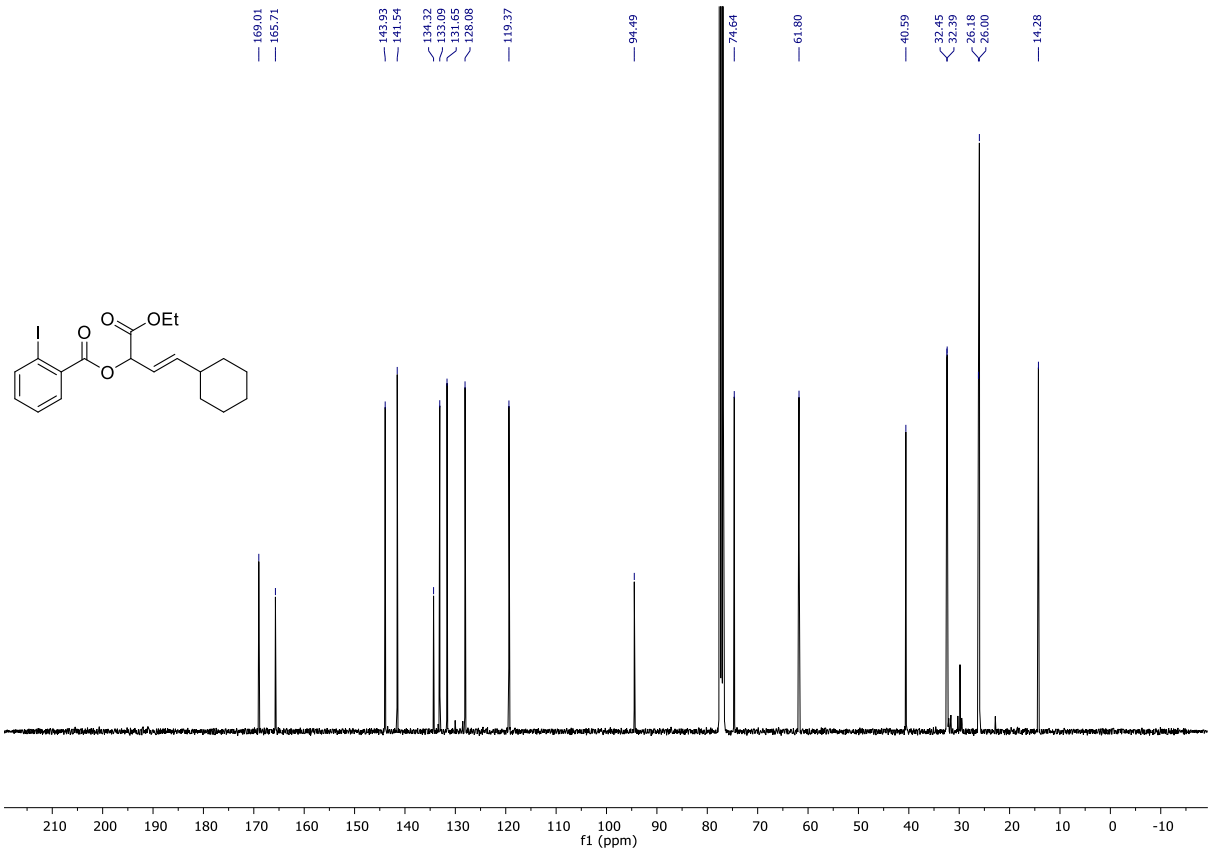
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **4i**



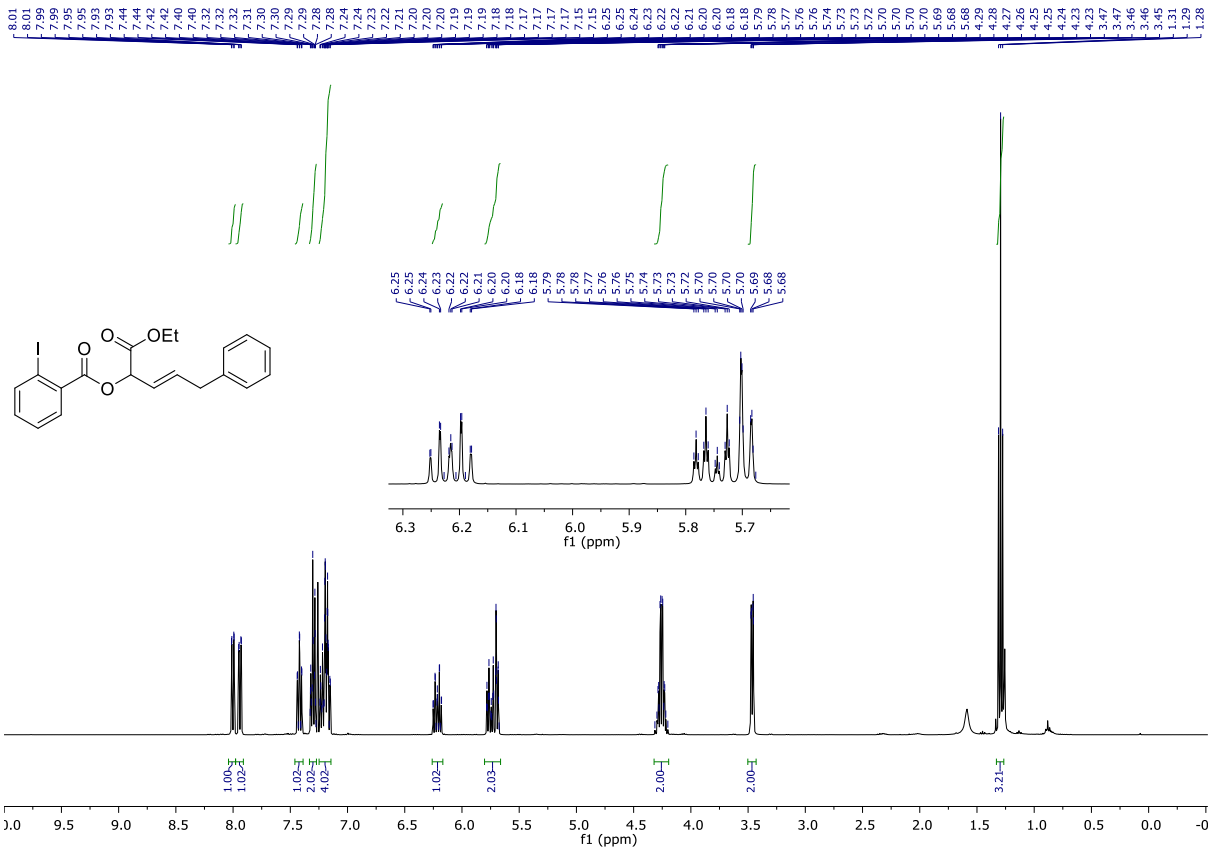
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4j**



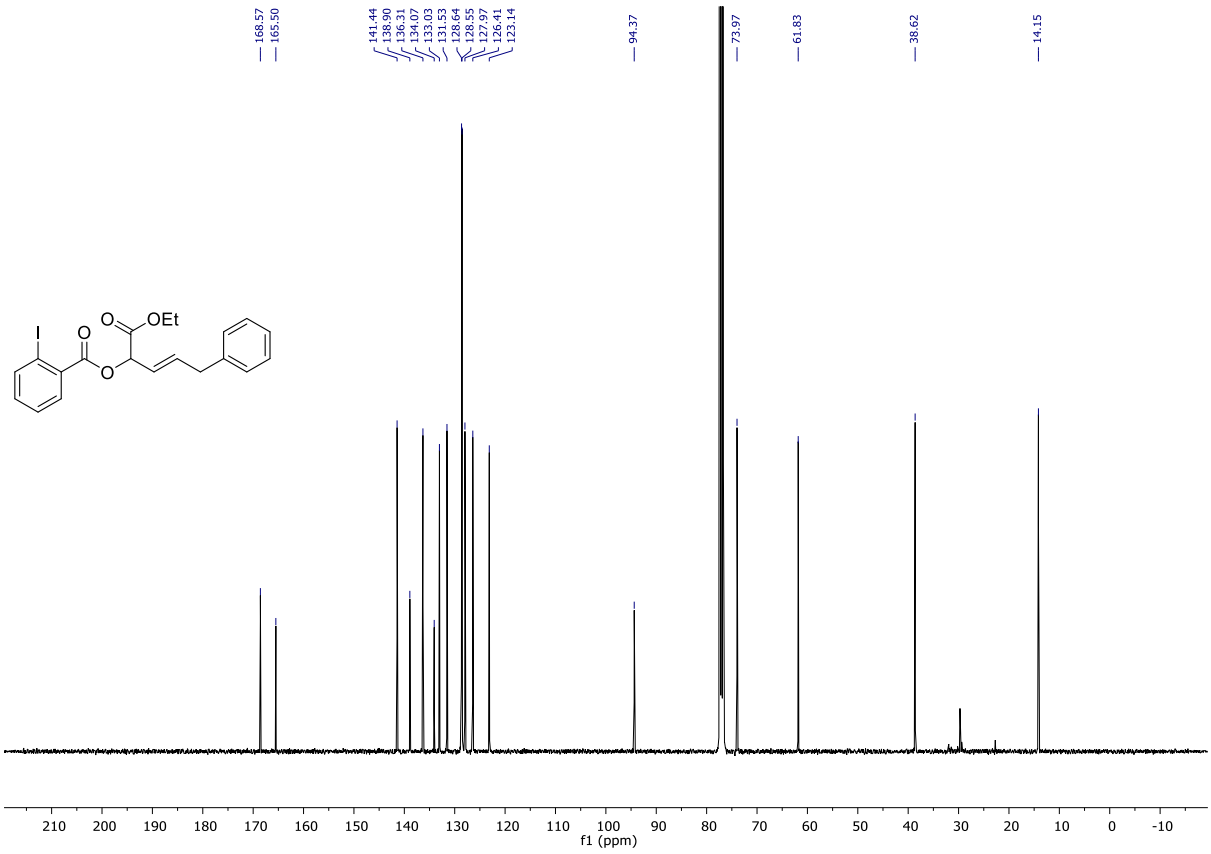
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4j**



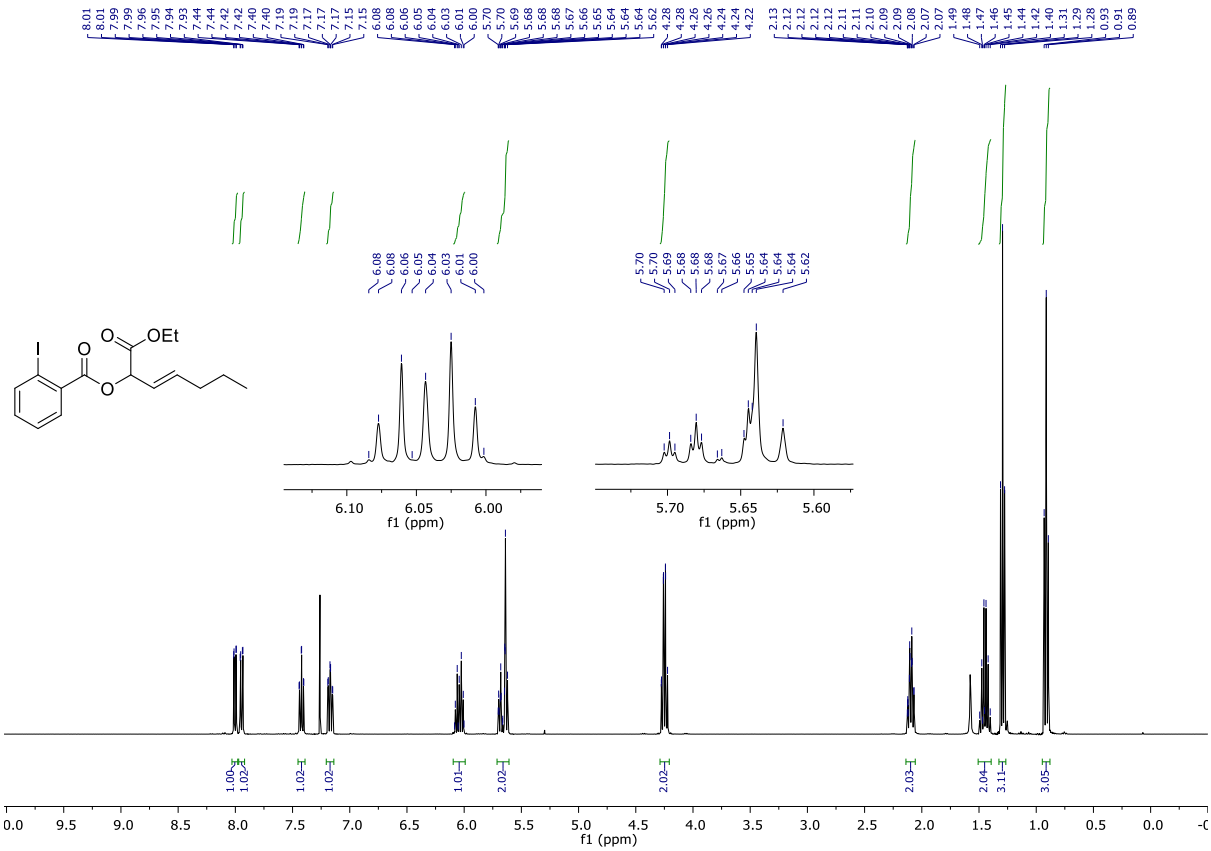
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4k**



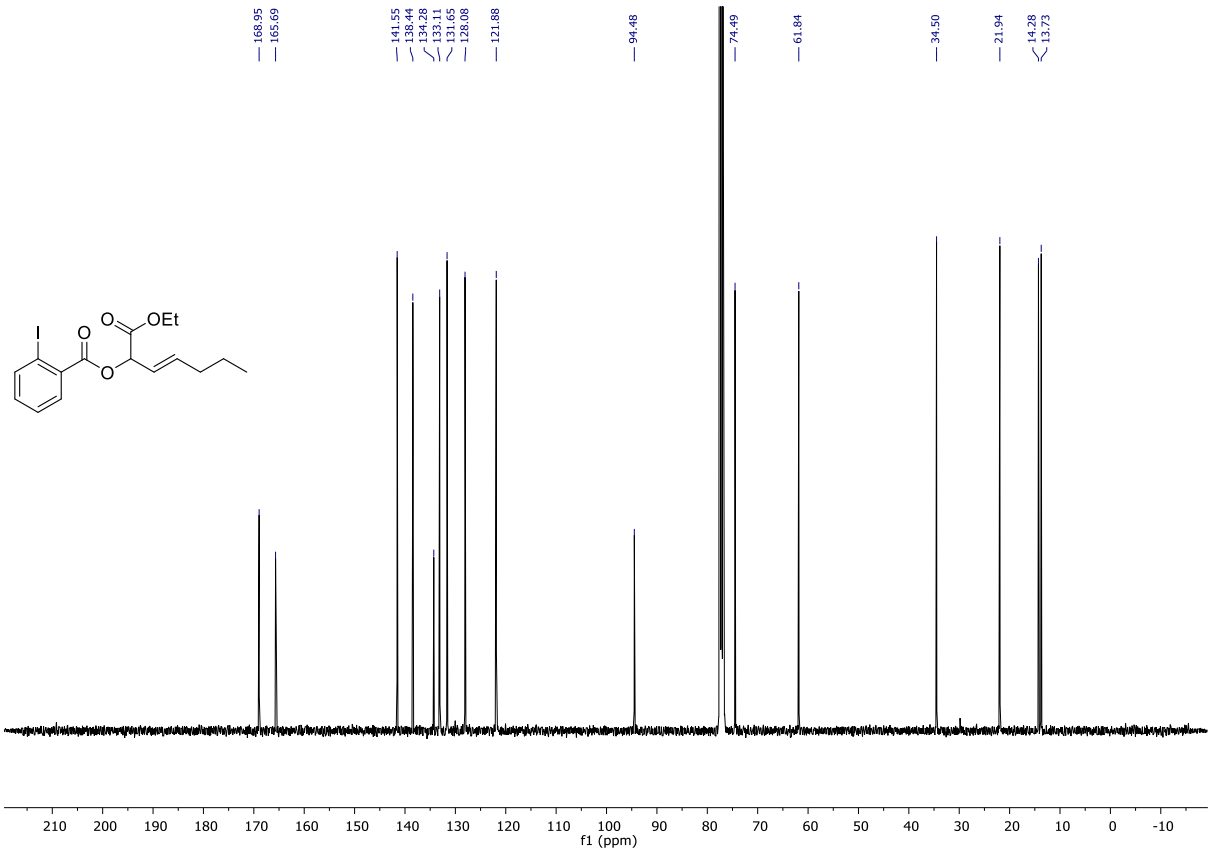
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4k**



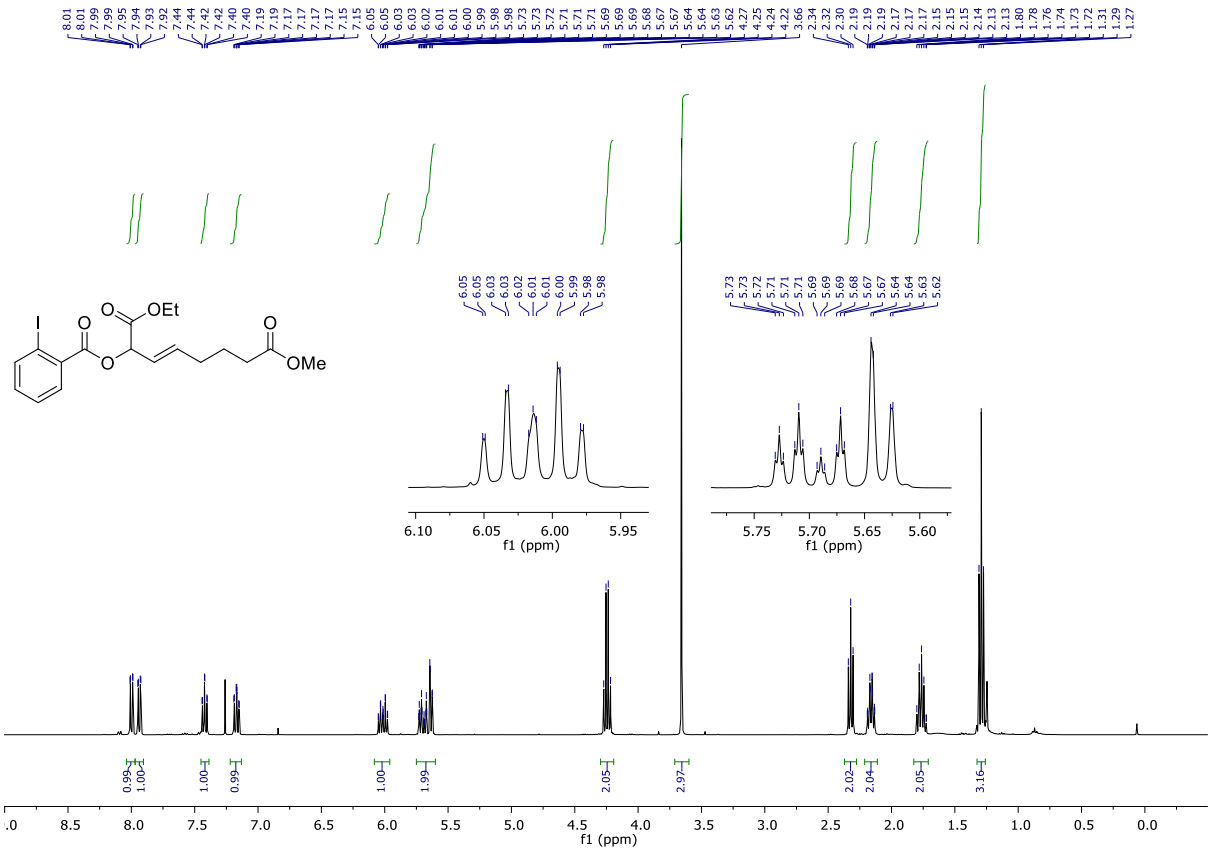
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4l**



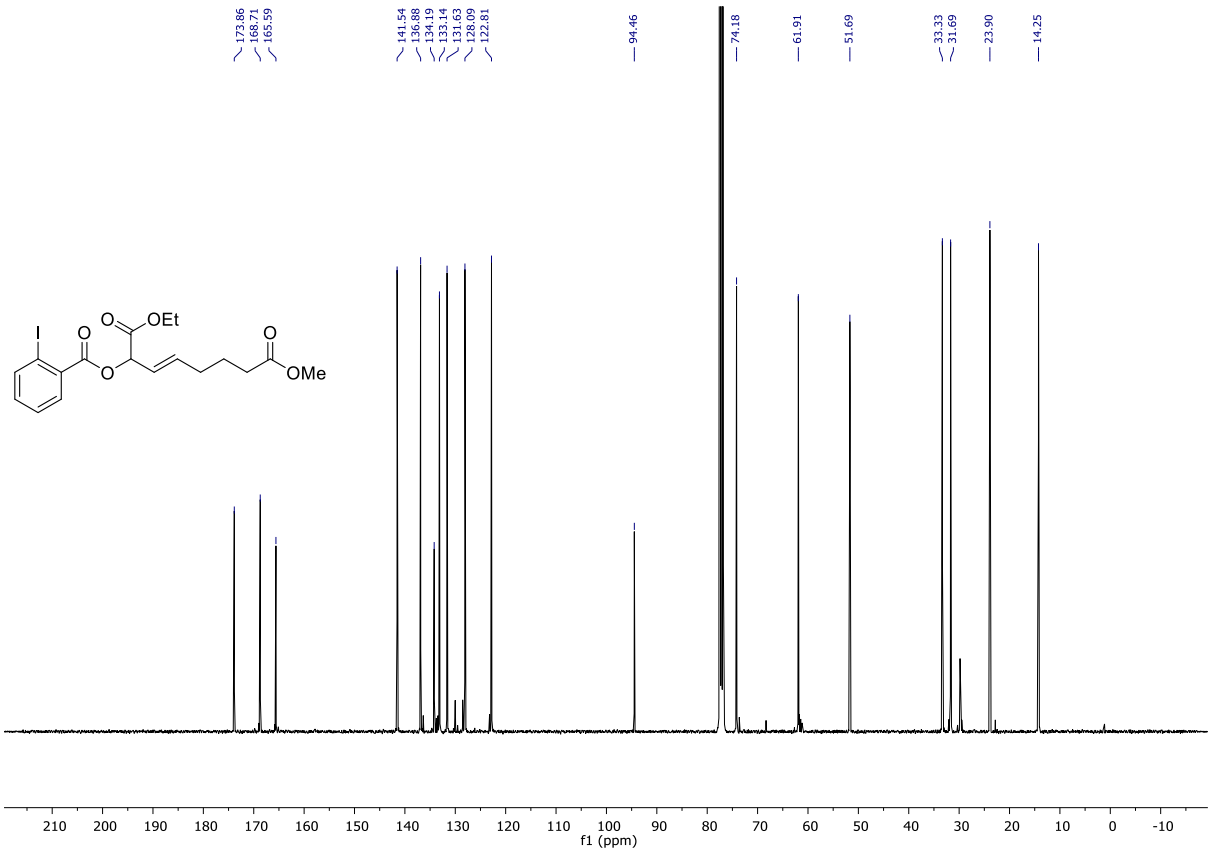
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4l**



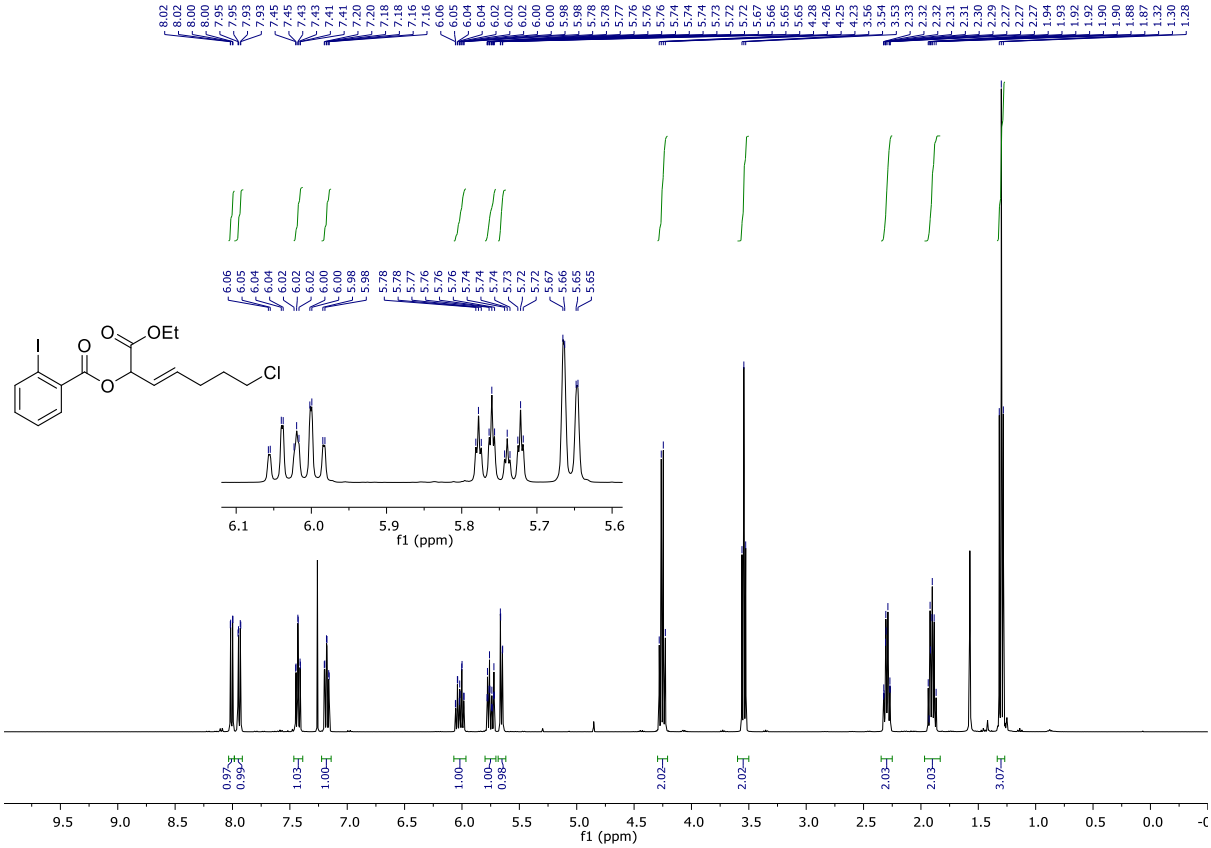
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4m**



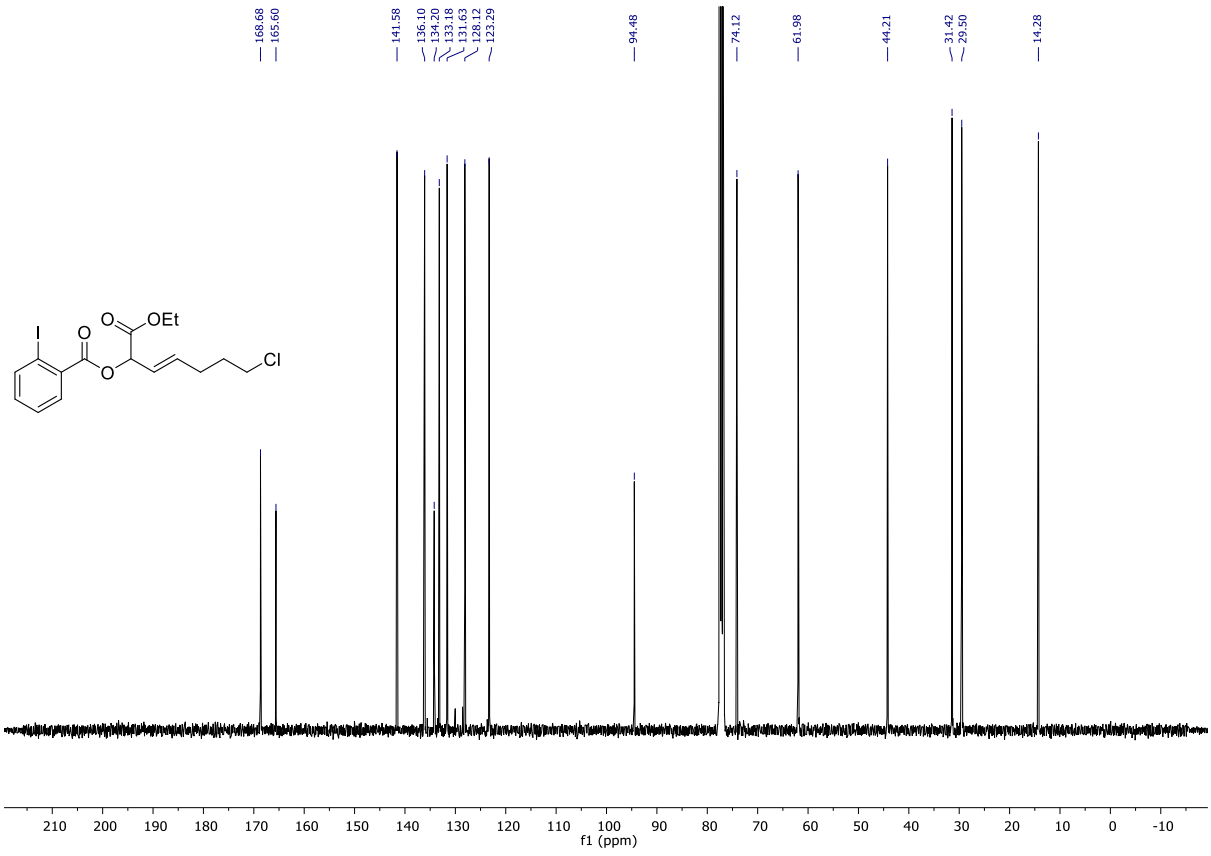
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4m**



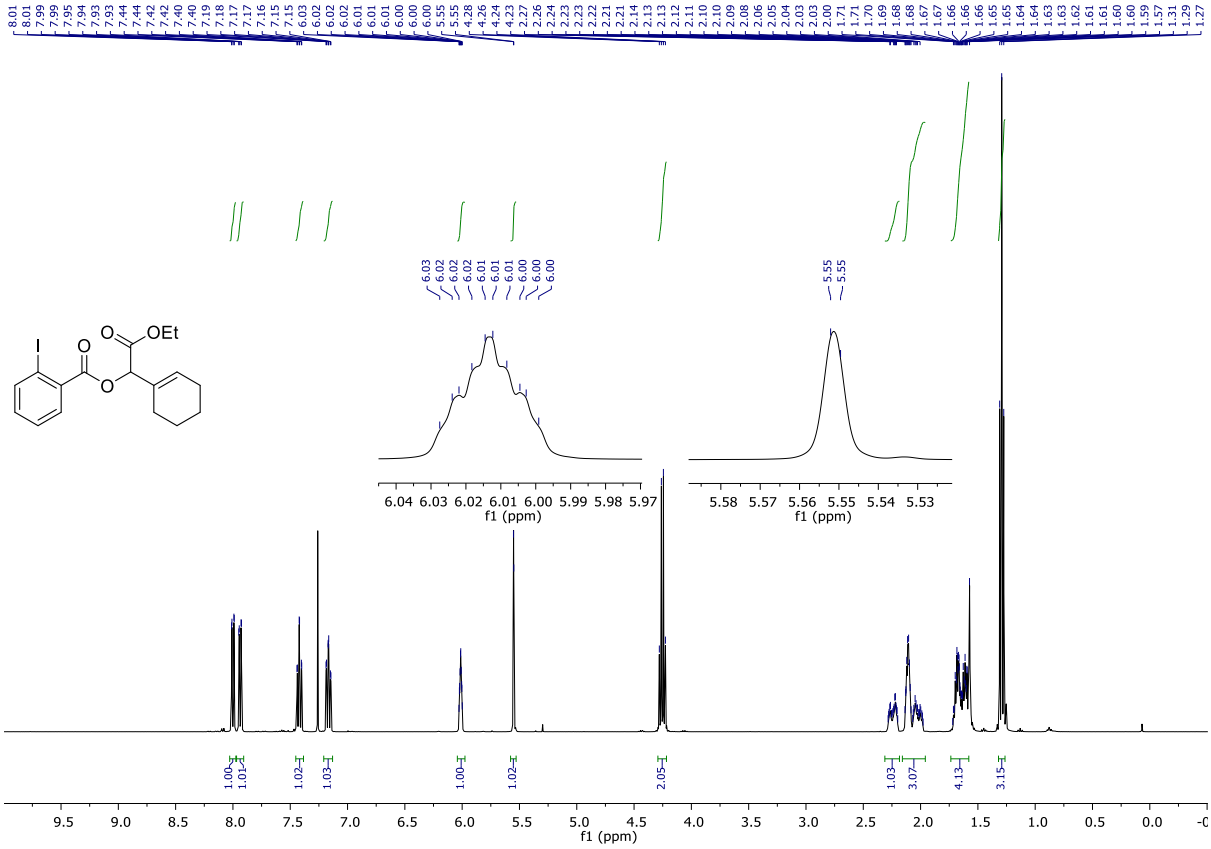
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4n**



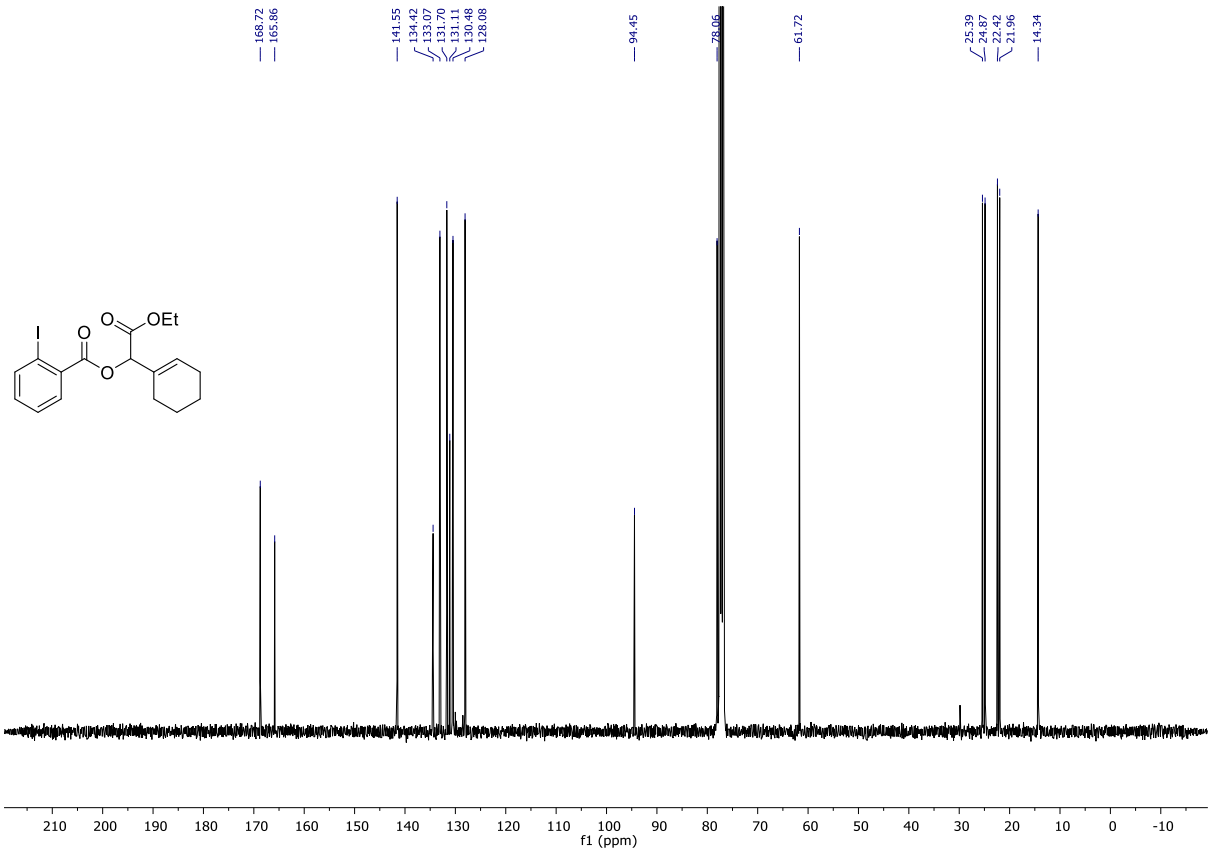
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4n**



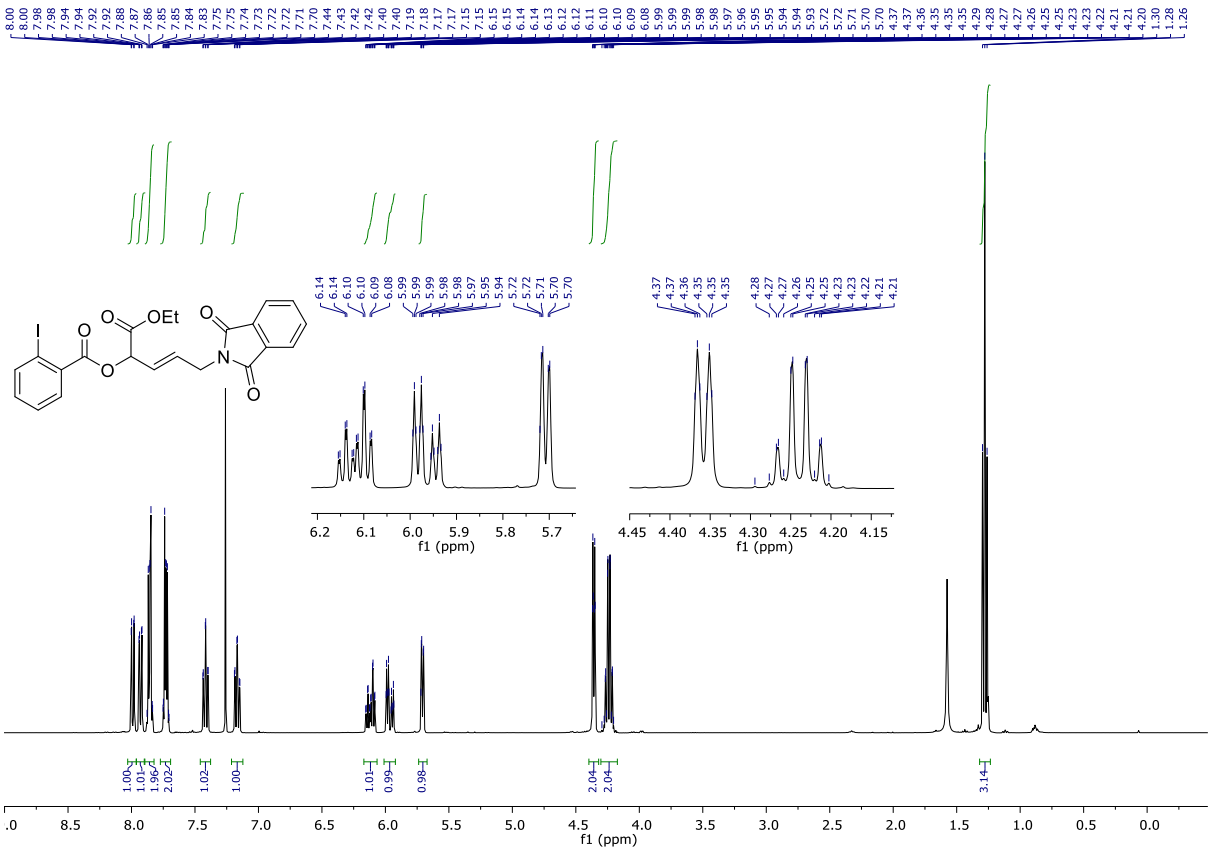
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4o**



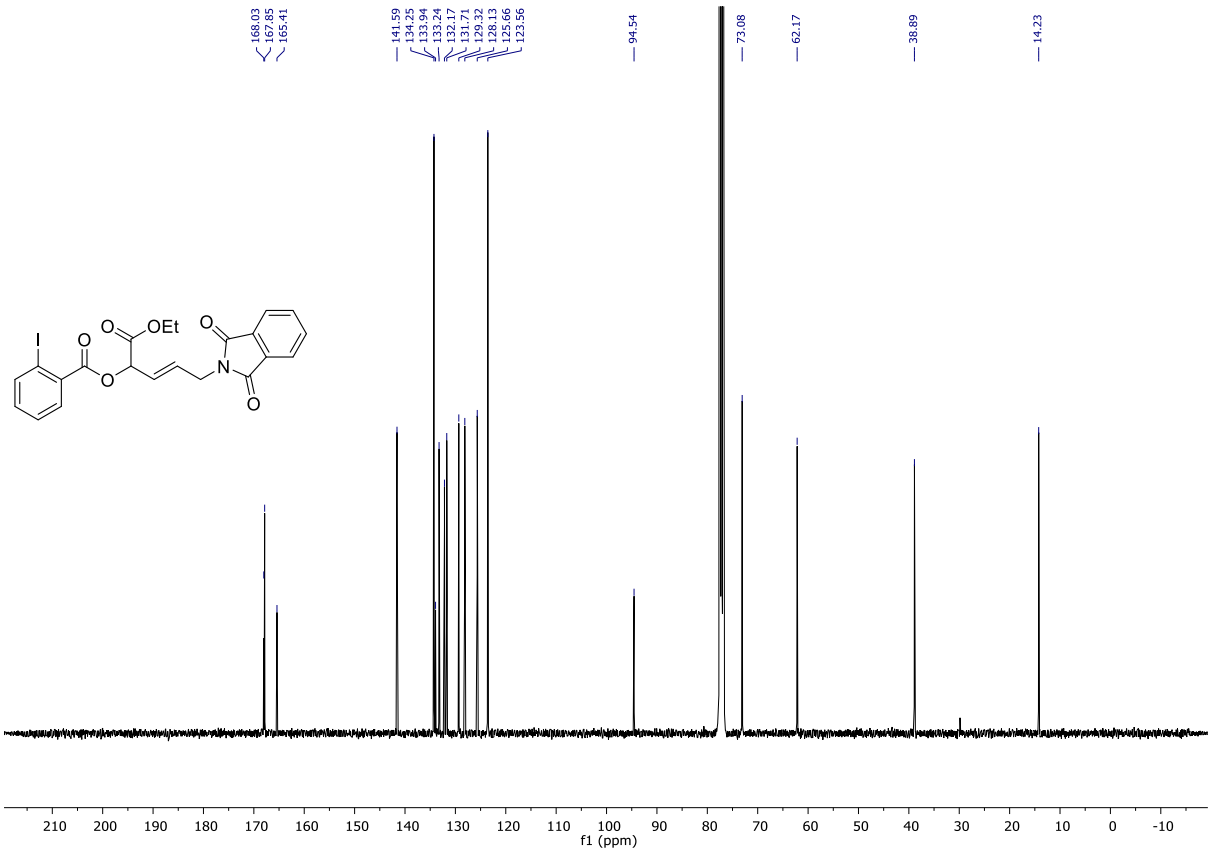
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4o**



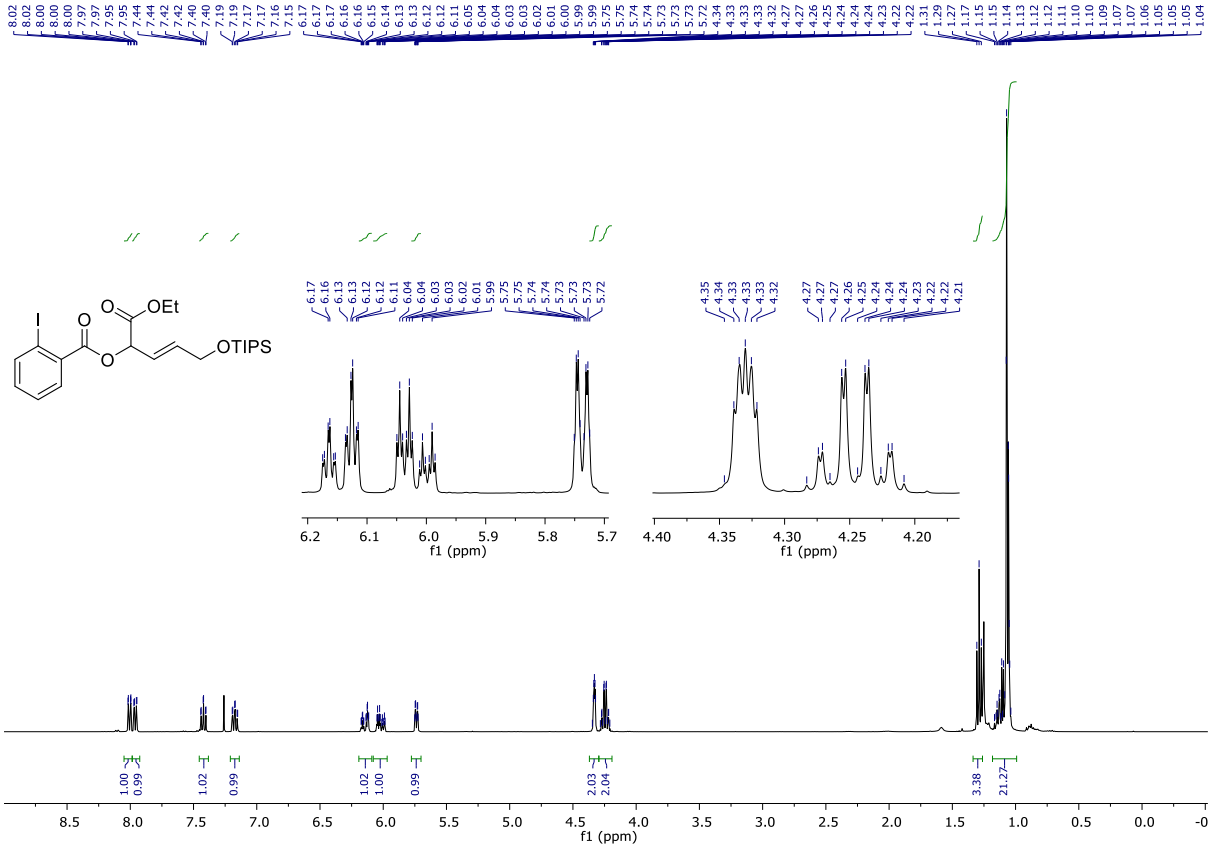
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4p**



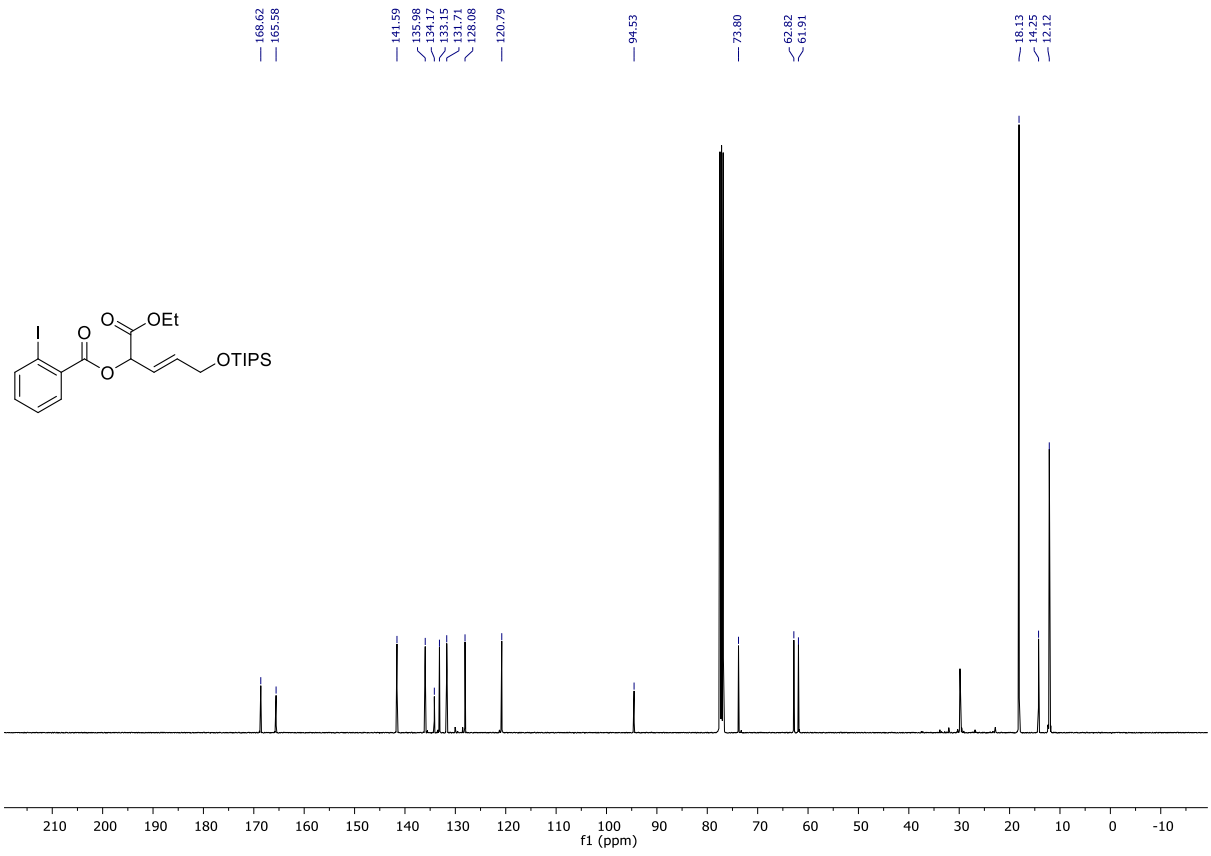
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4p**



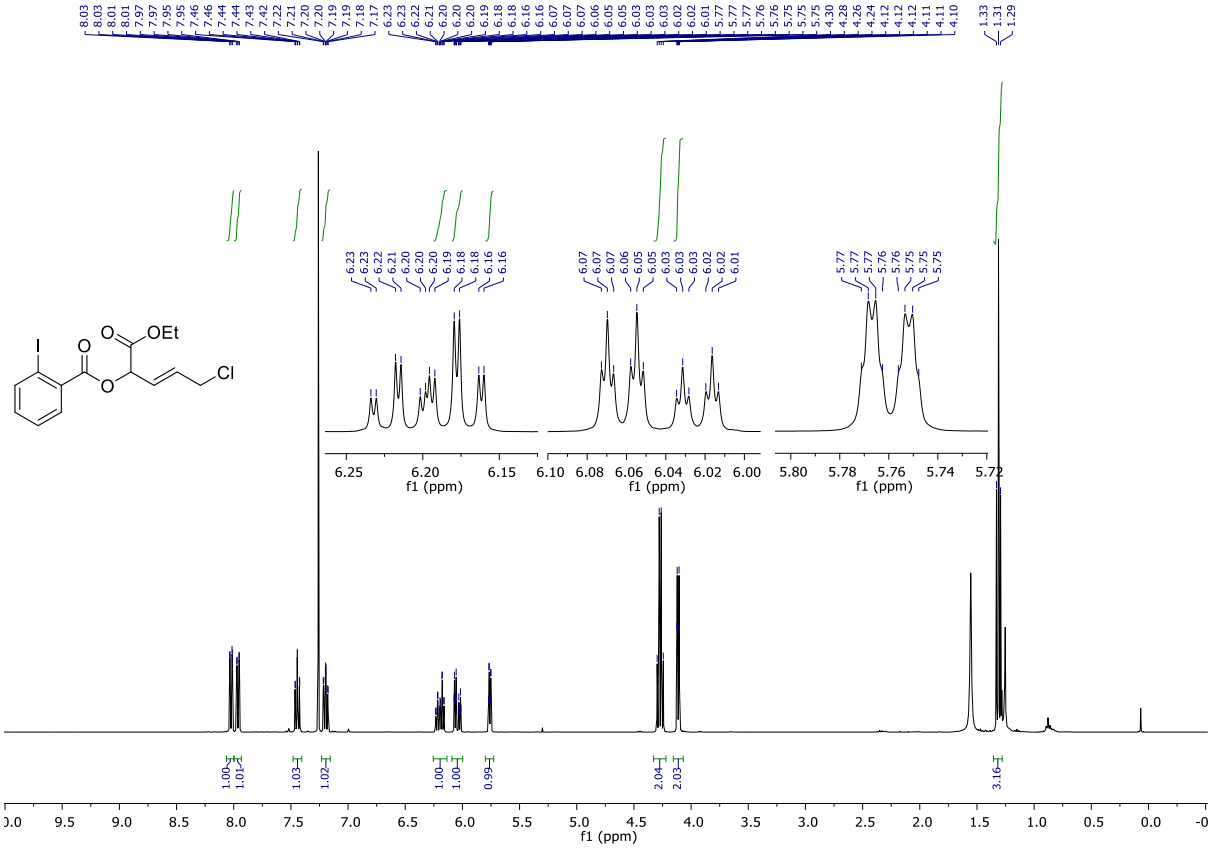
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4q**



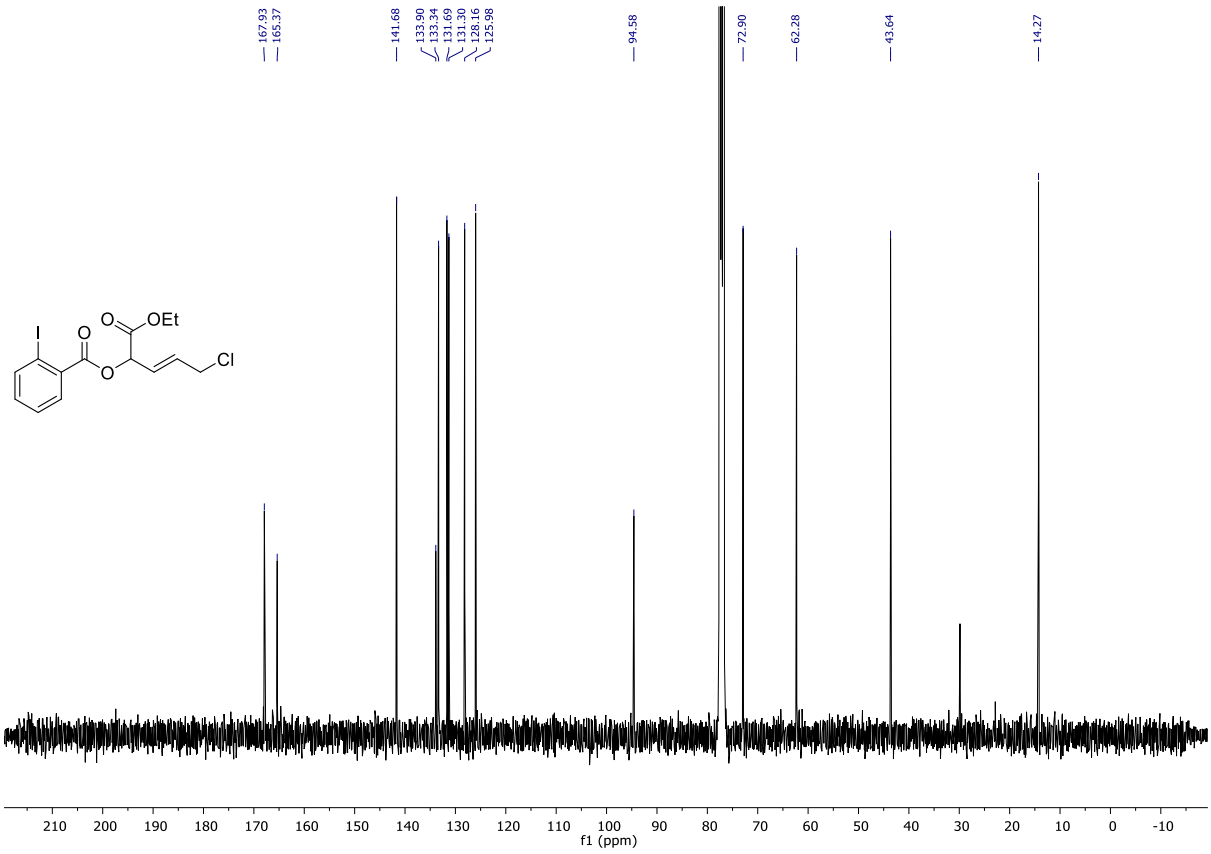
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4q**



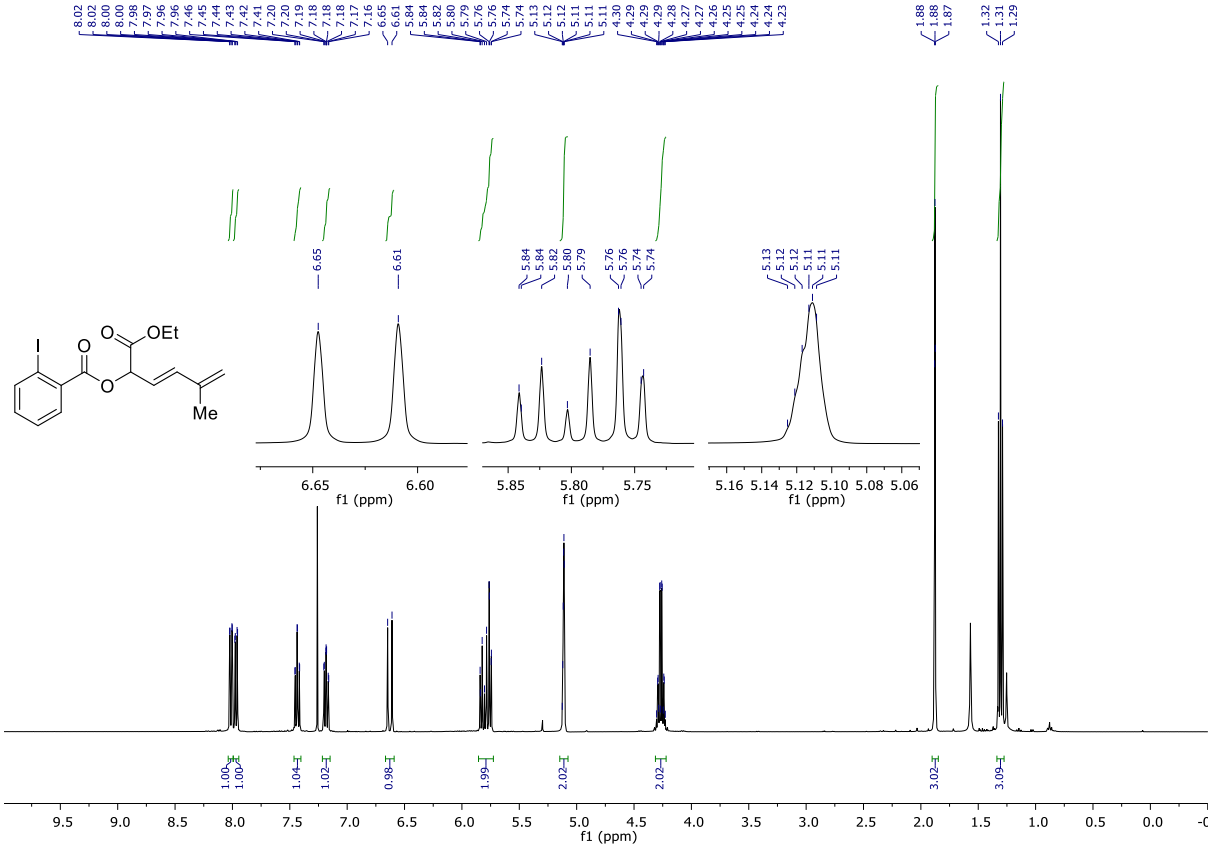
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4r**



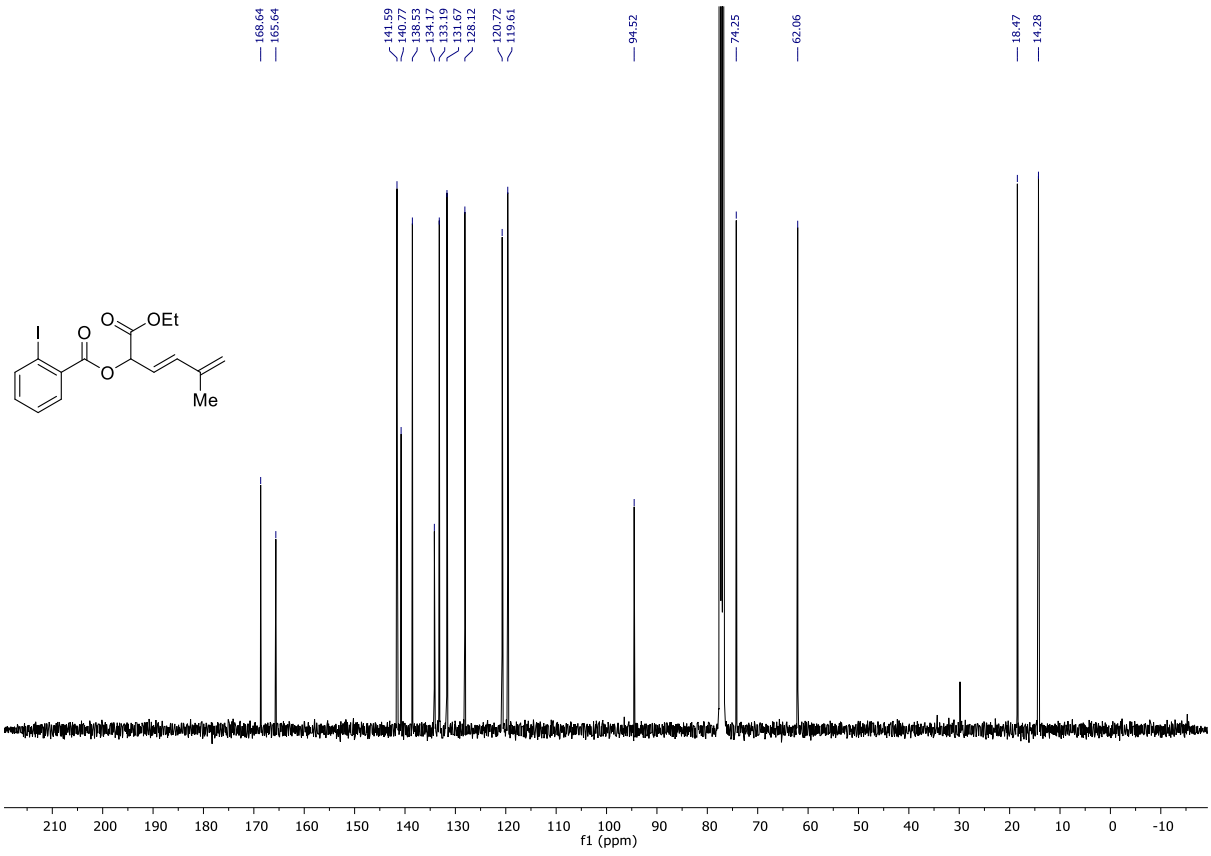
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4r**



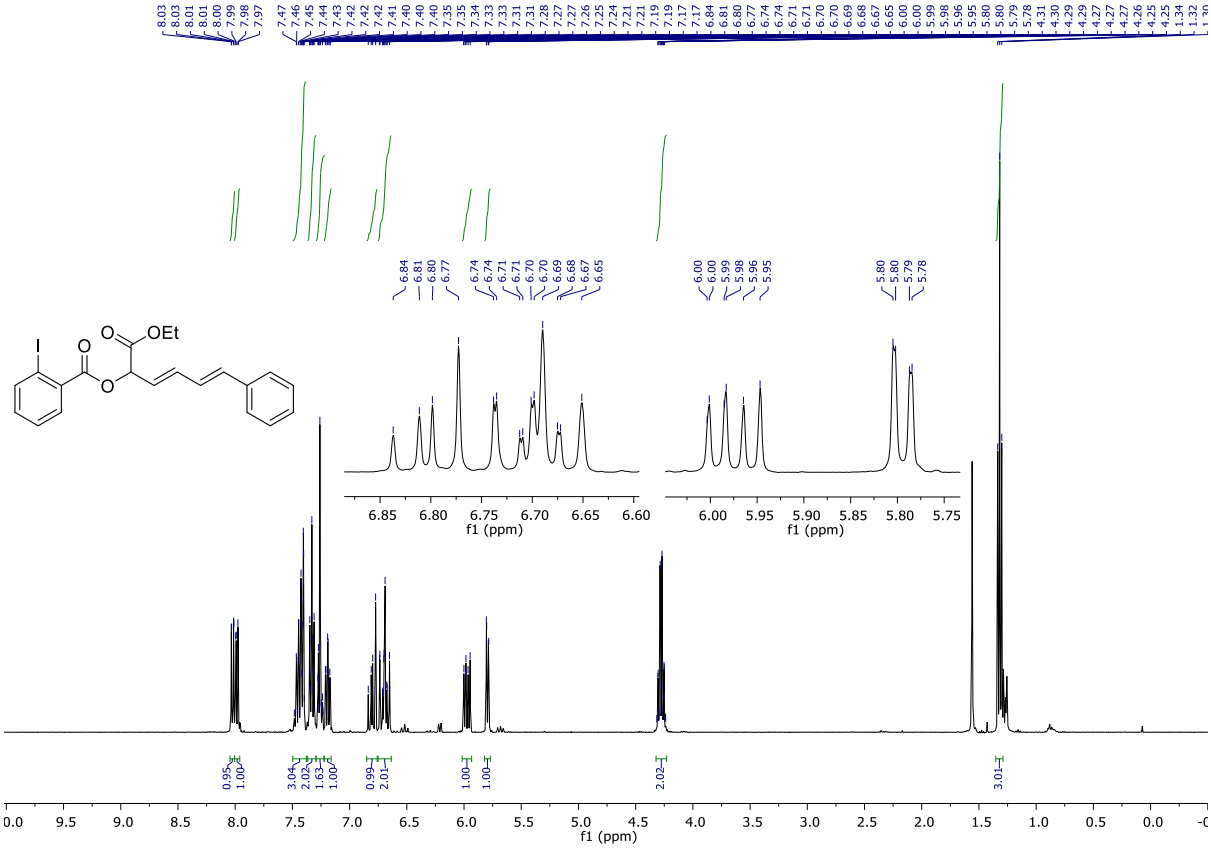
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4s**



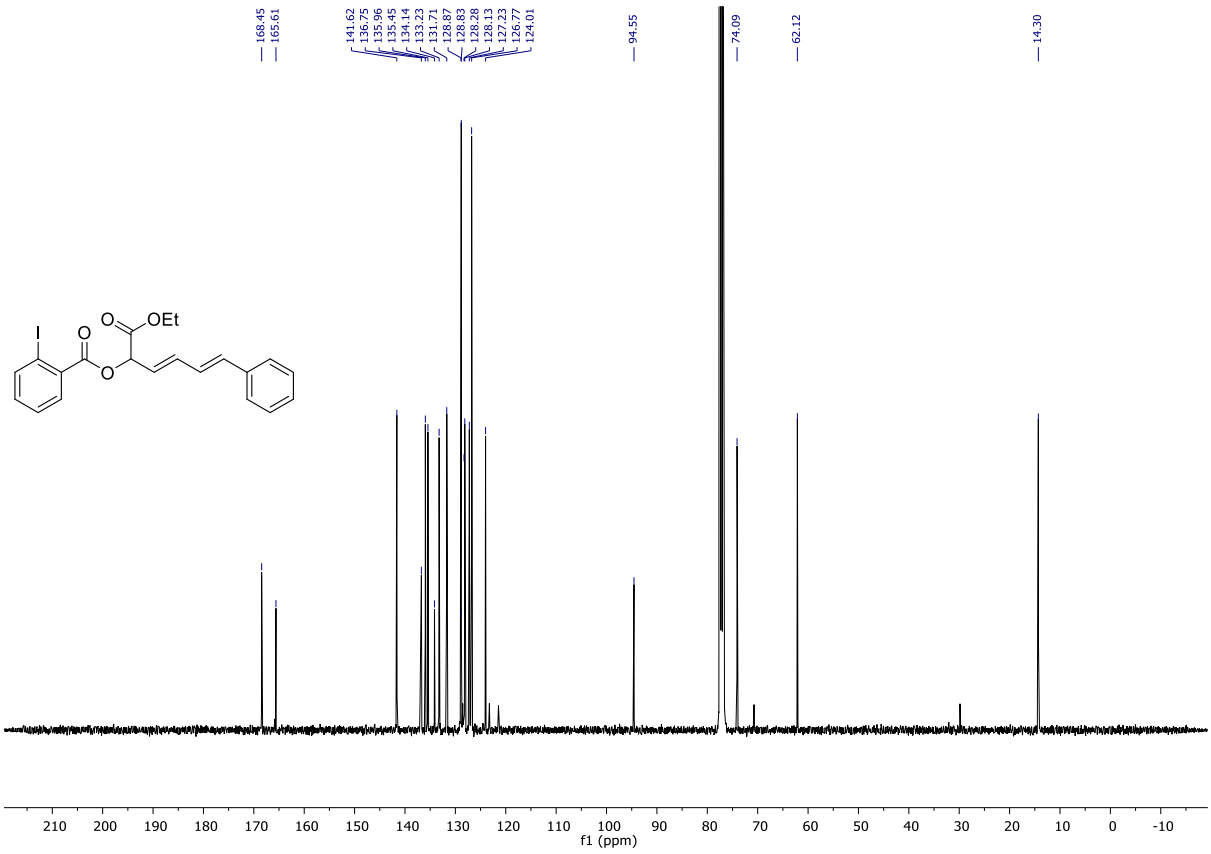
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4s**



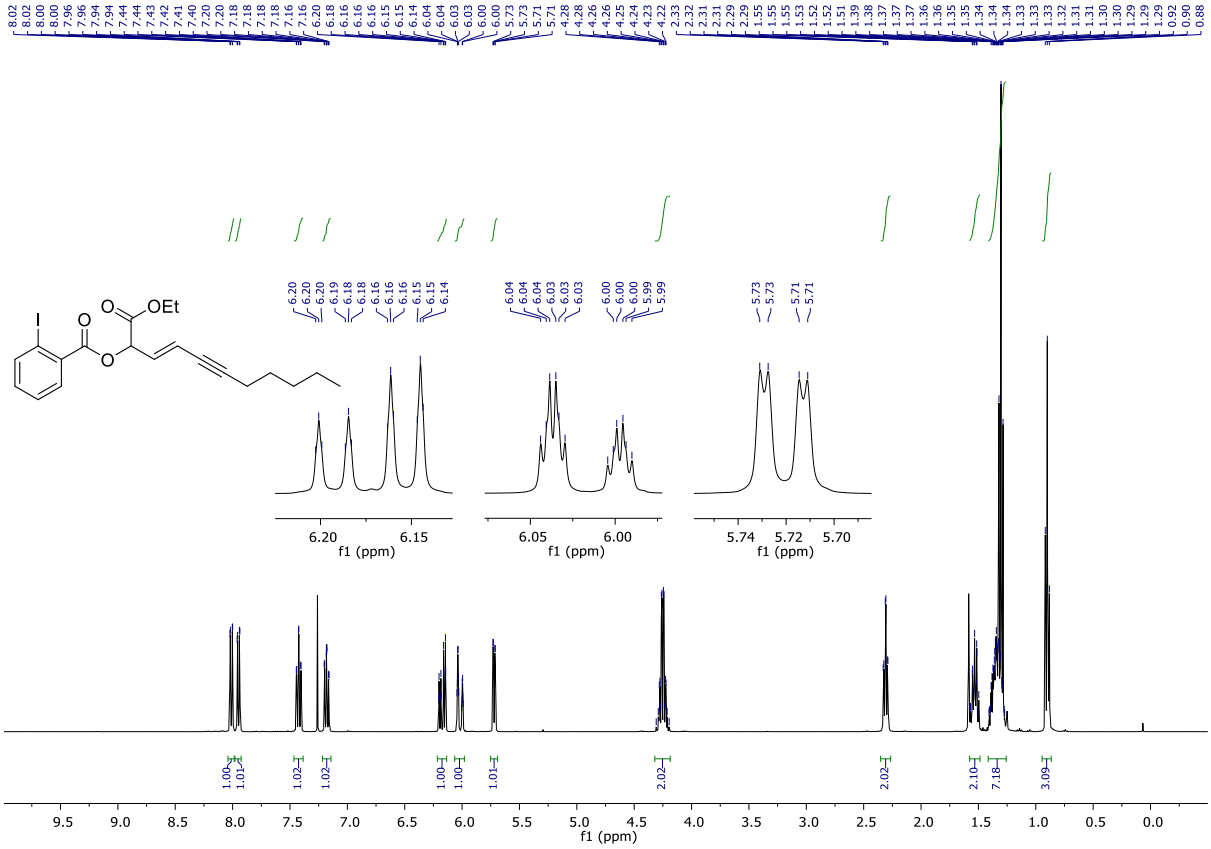
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4t**



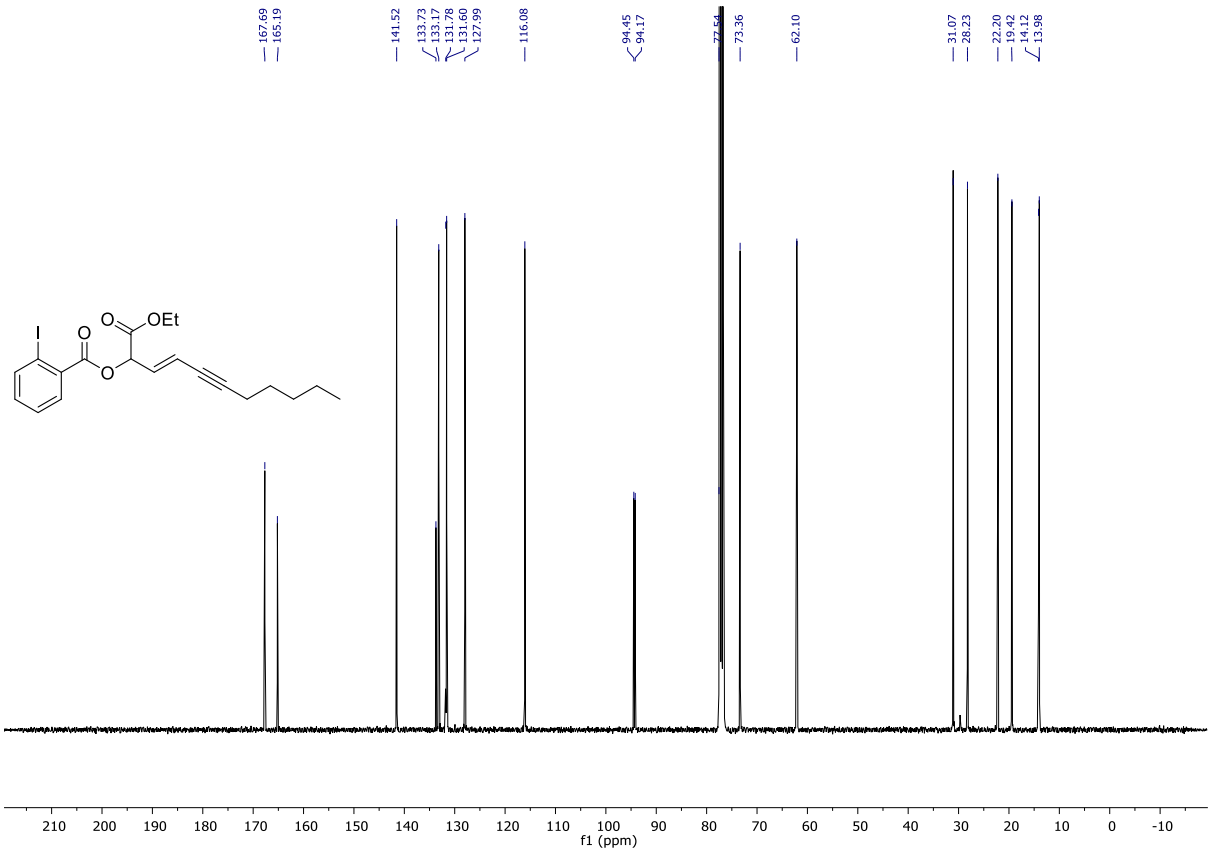
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4t**



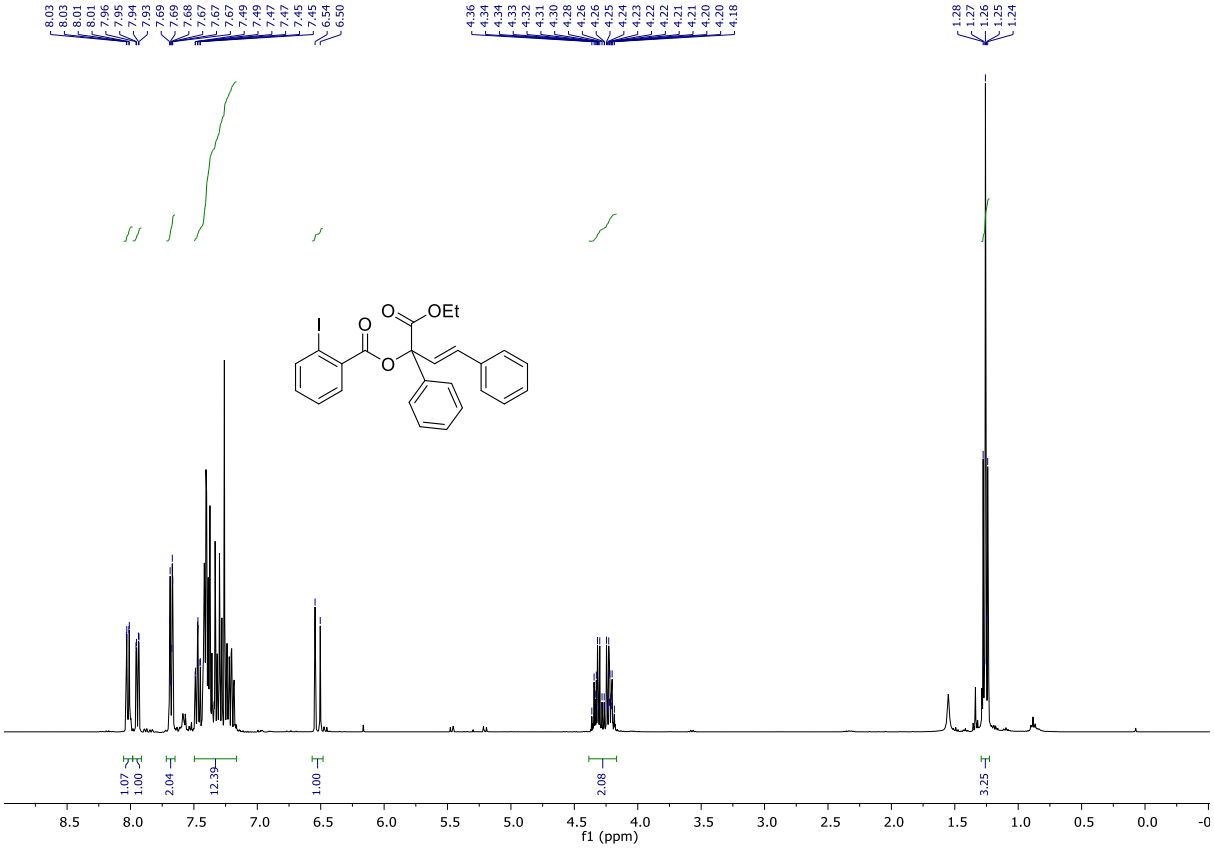
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4u**



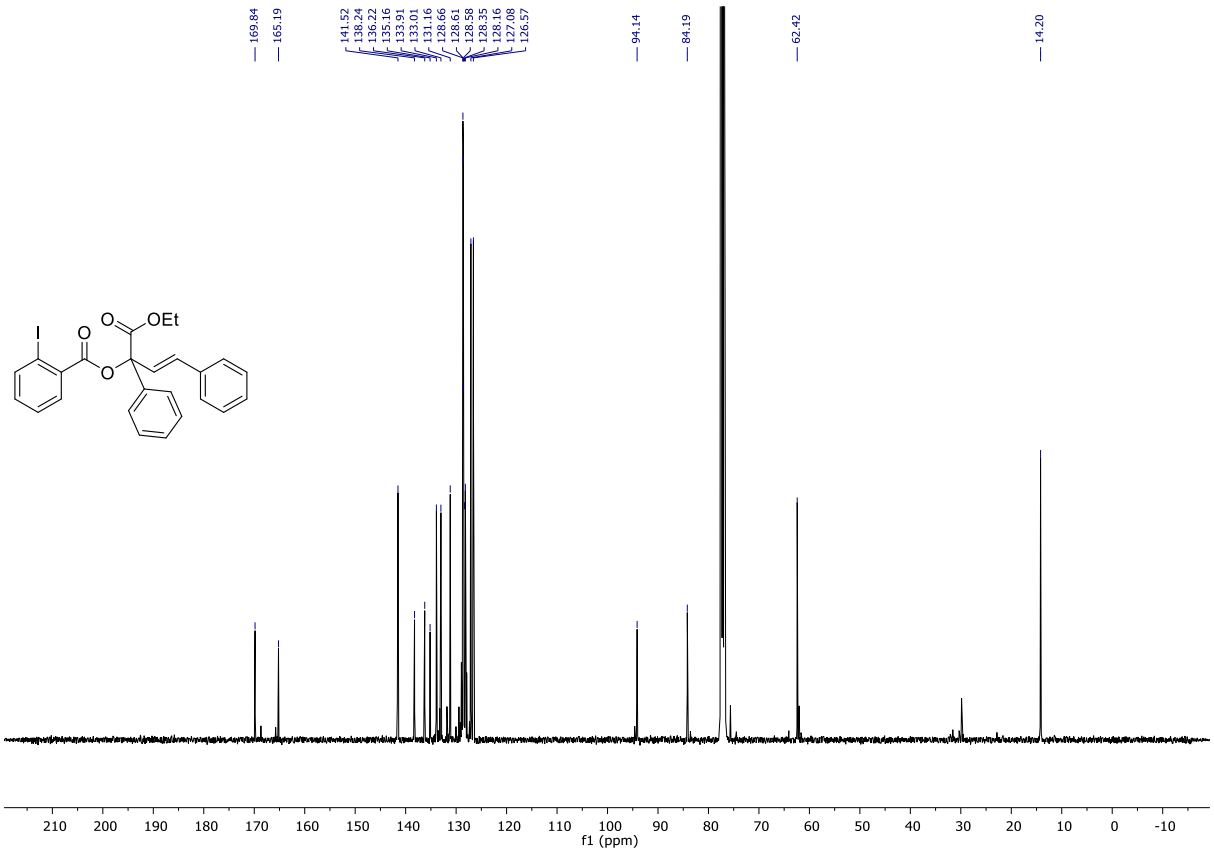
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4u**



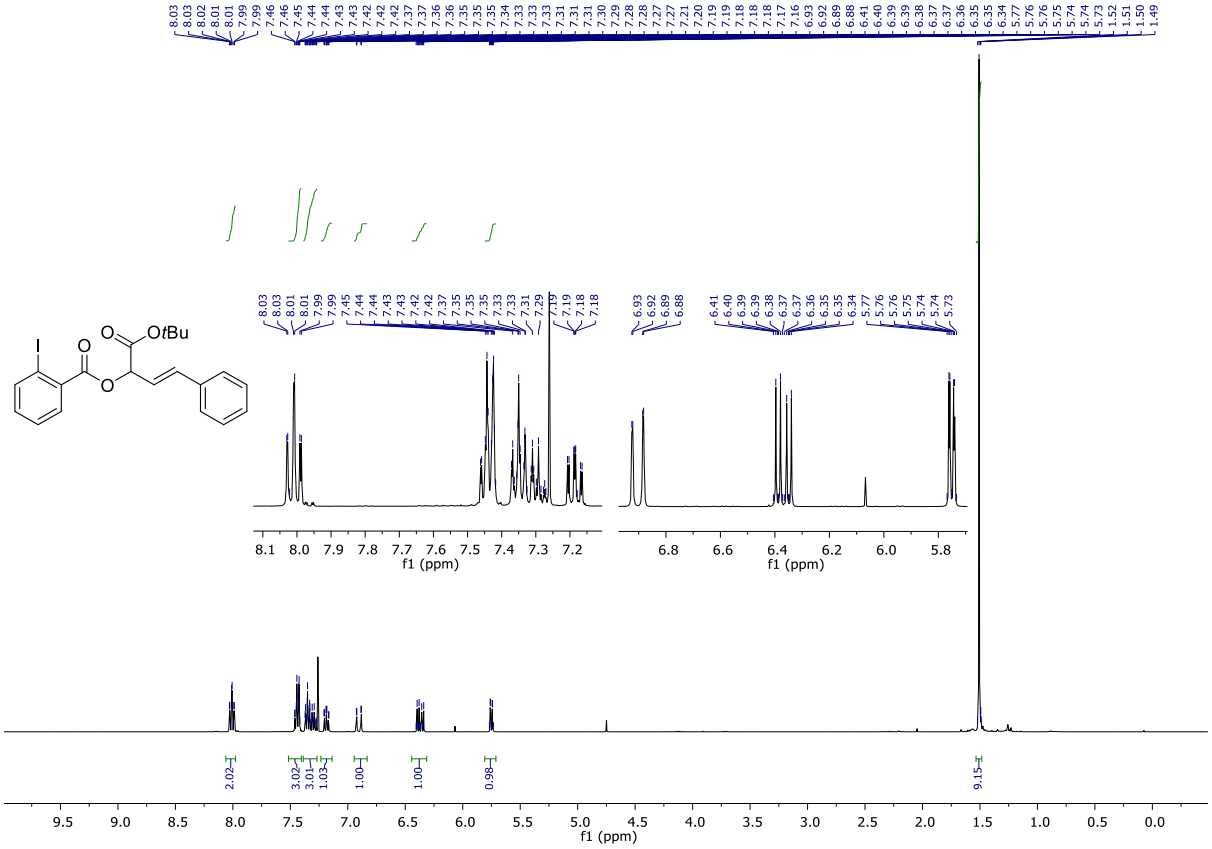
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5a**



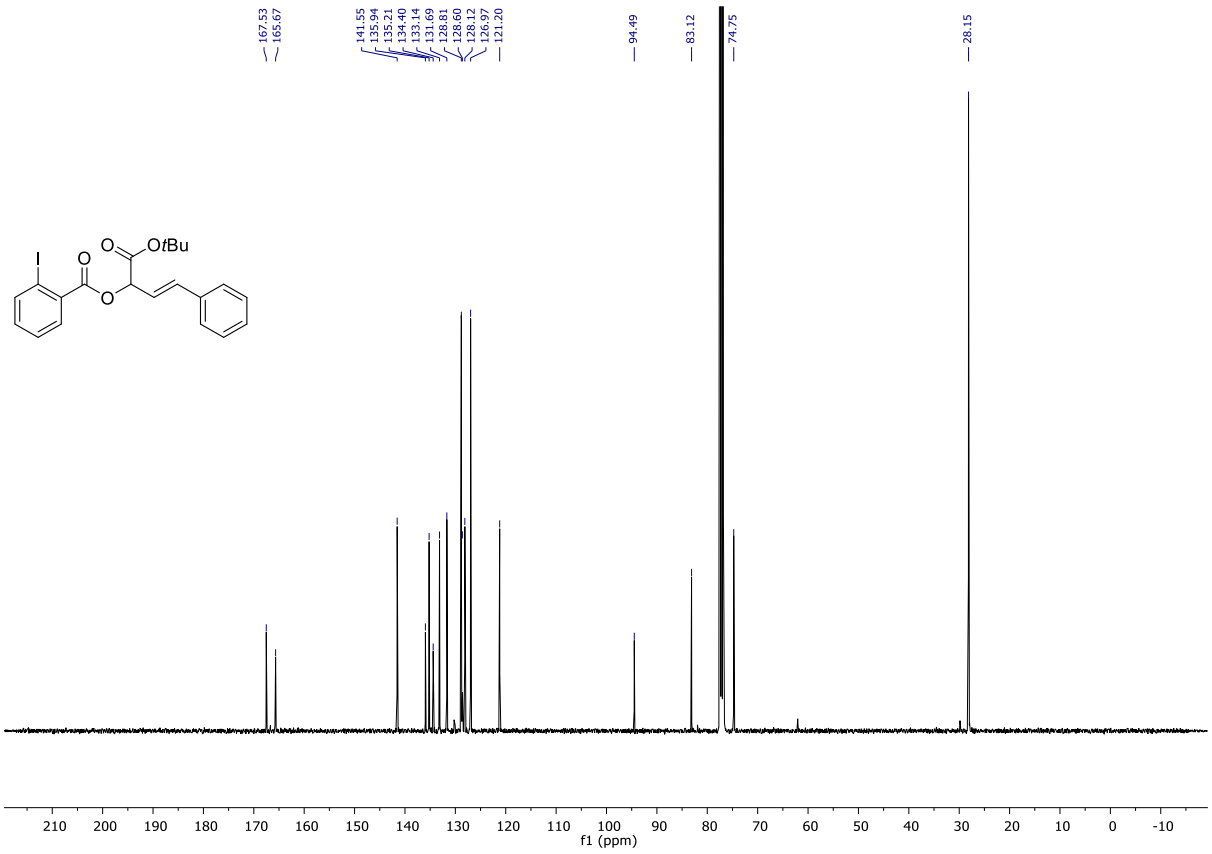
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5a**



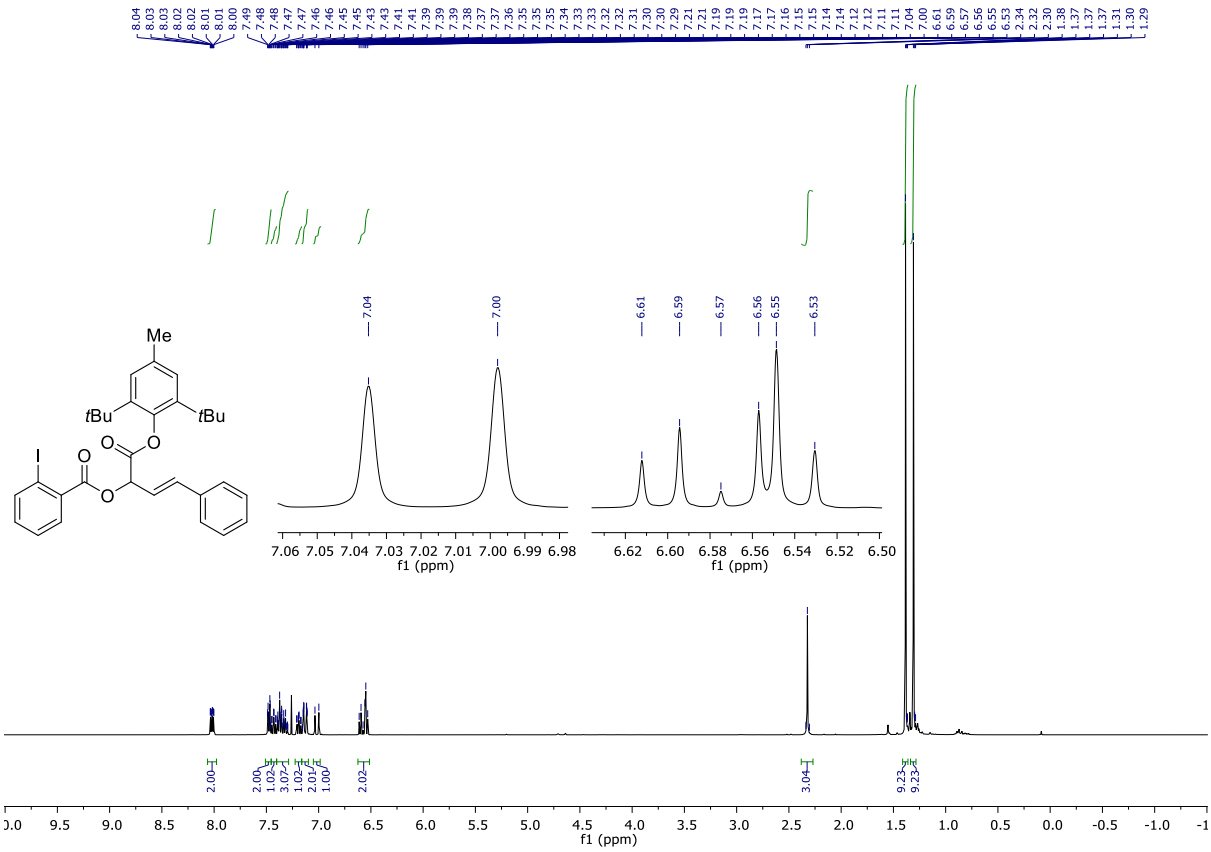
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5b**



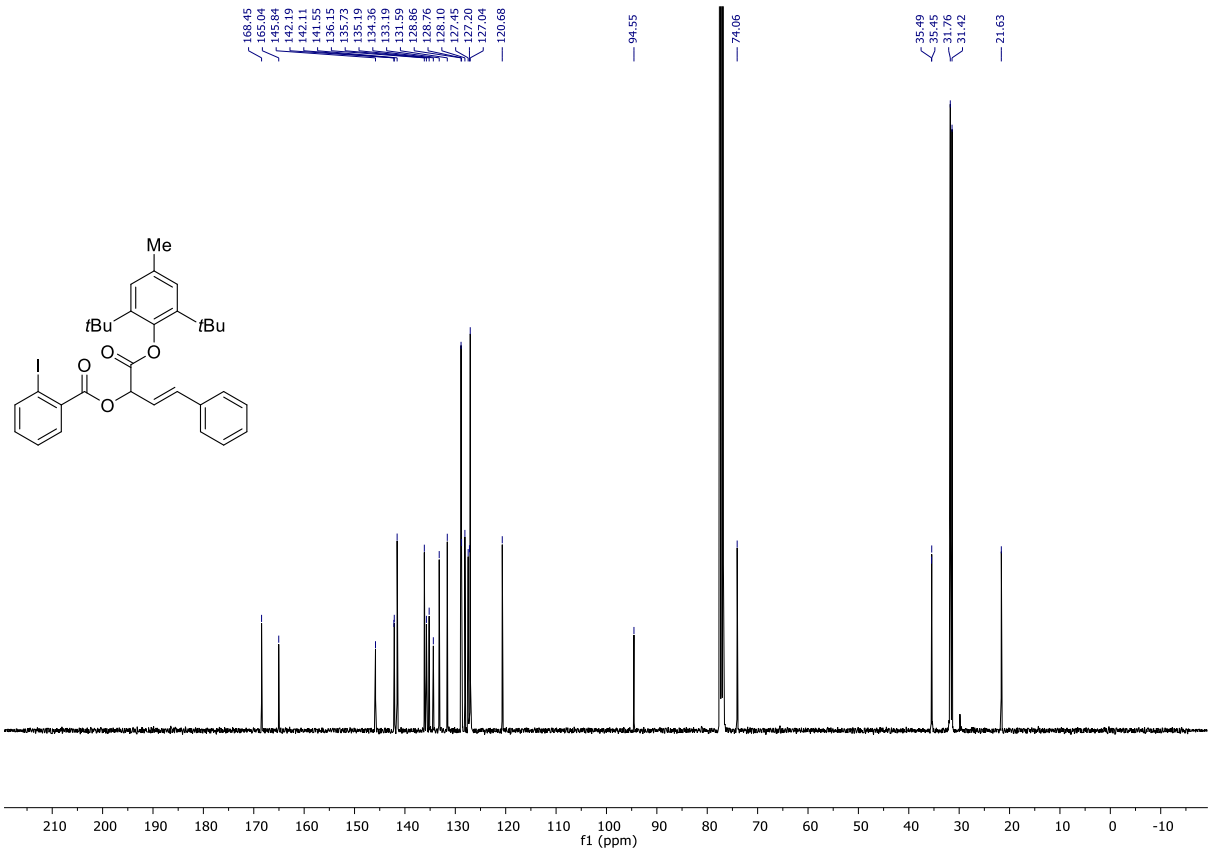
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5b**



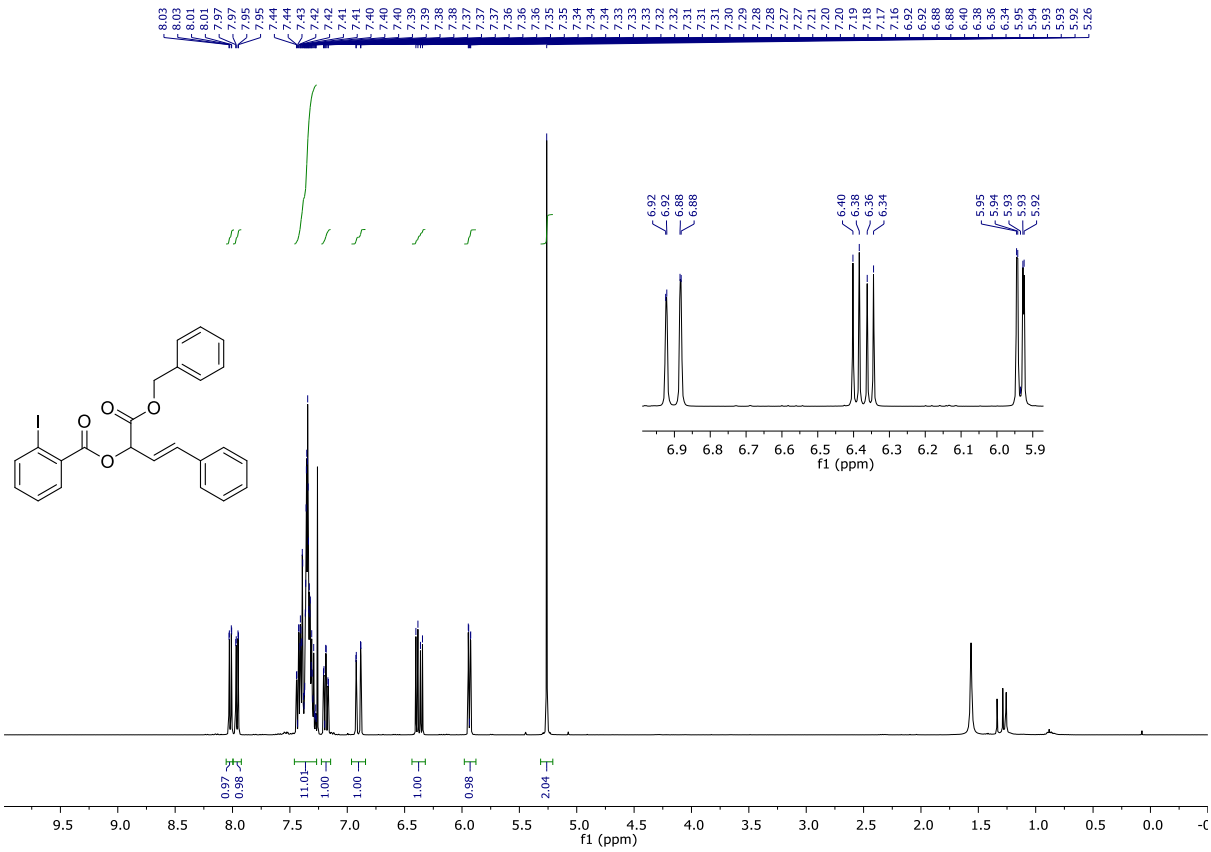
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5c**



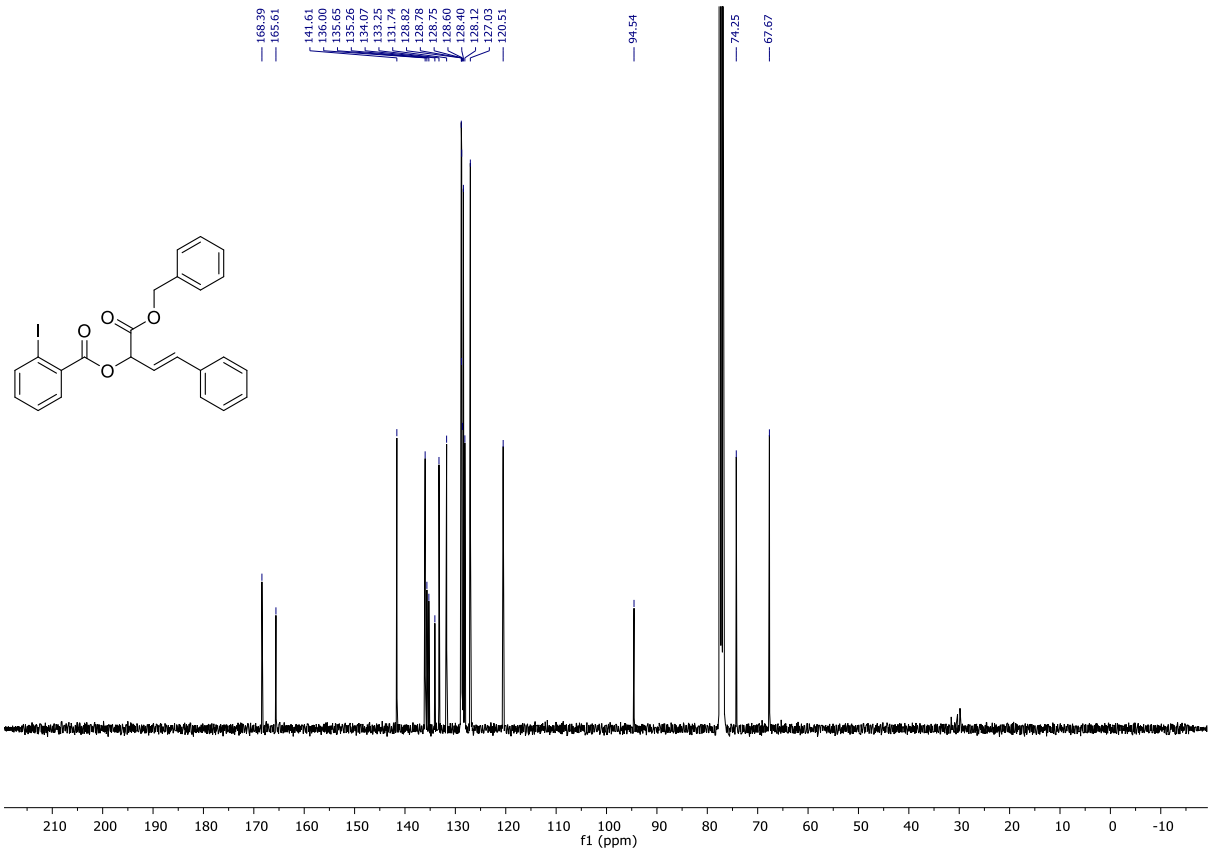
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5c**



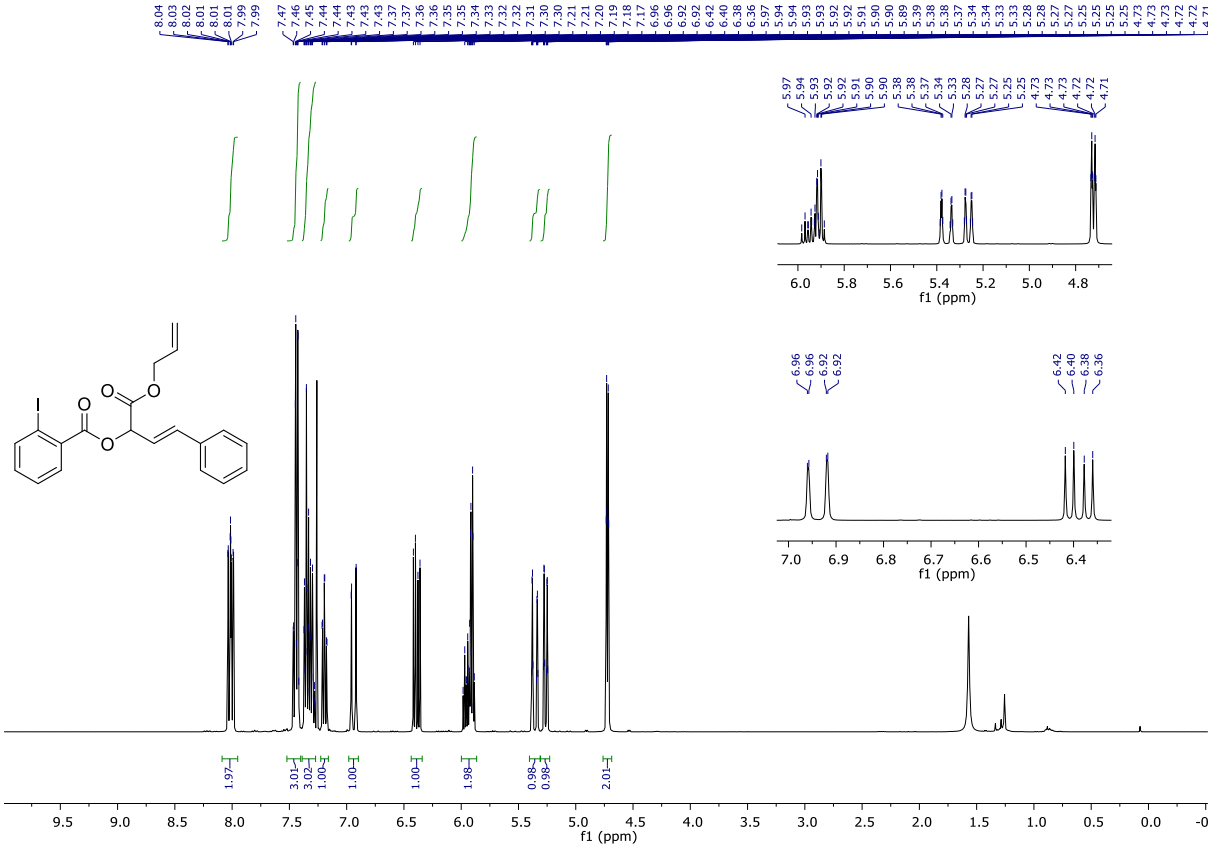
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5d**



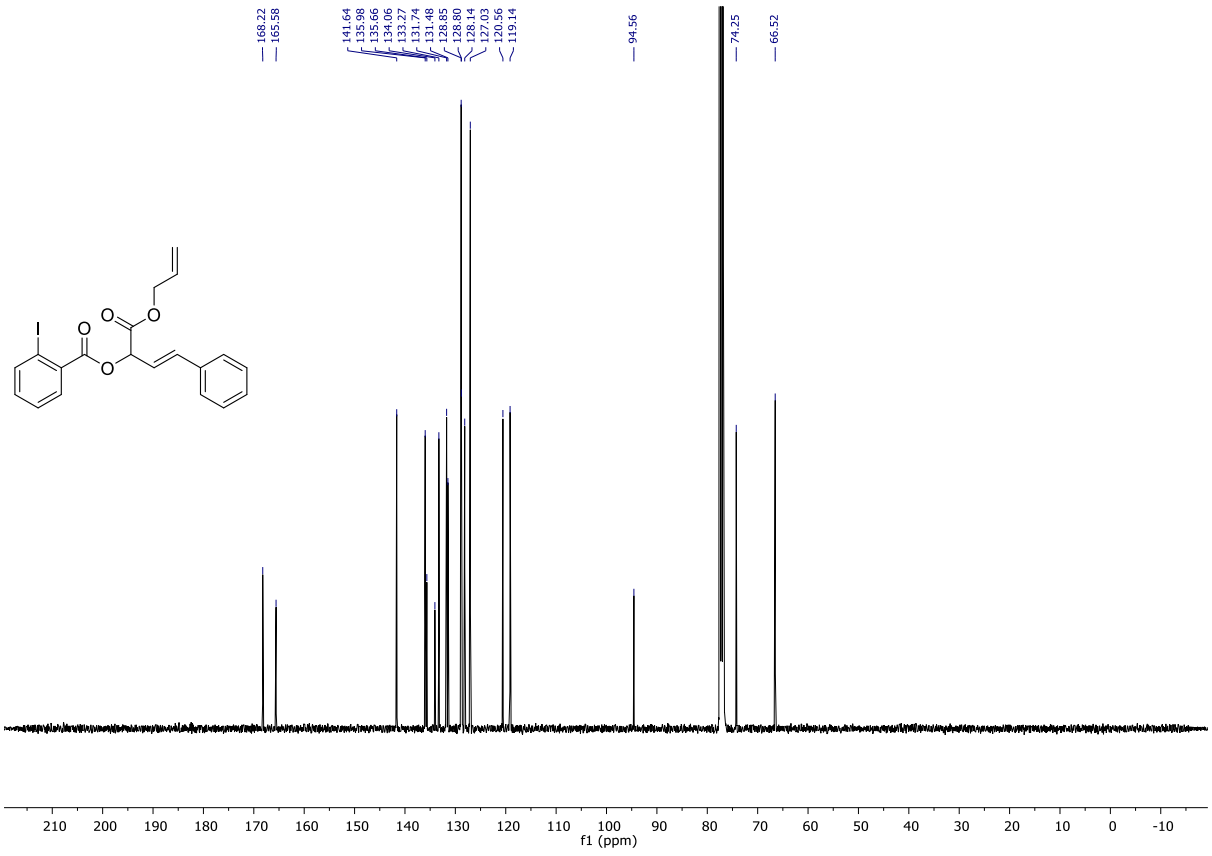
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5d**



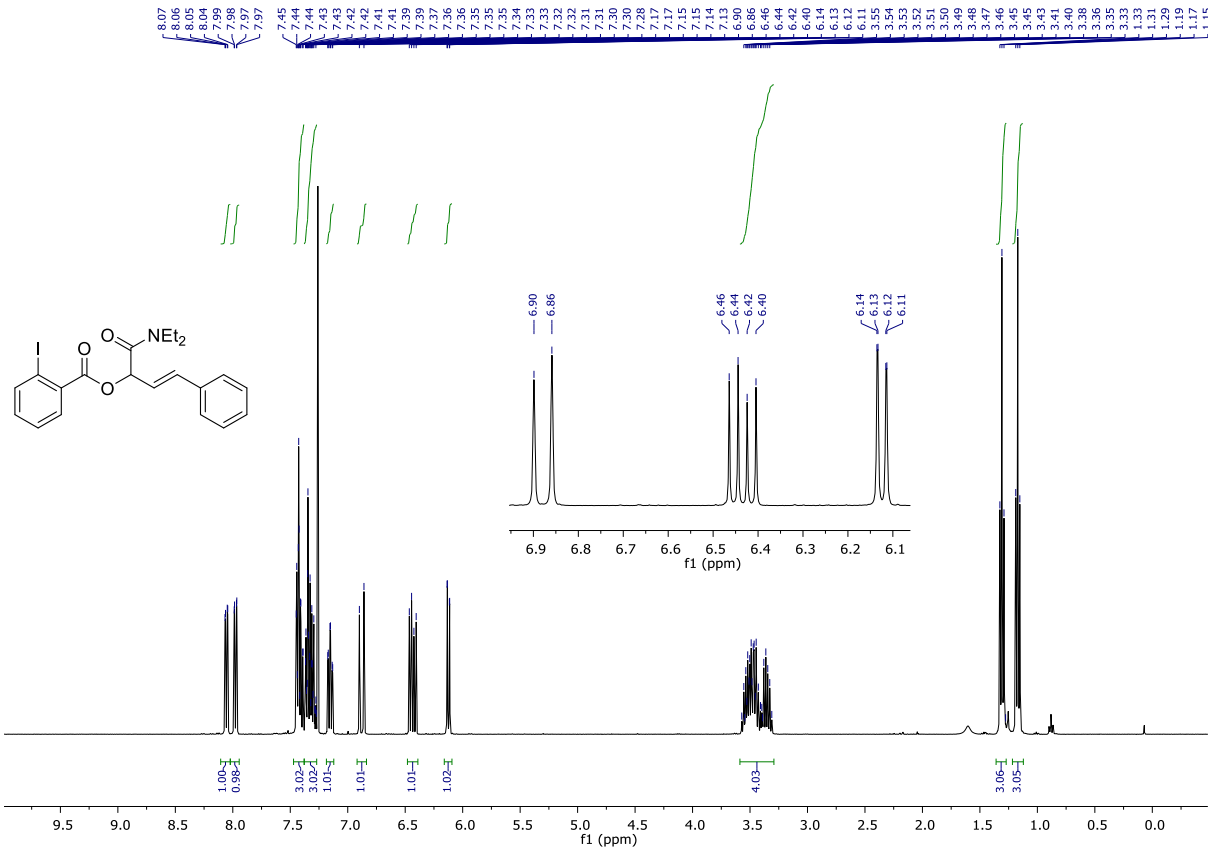
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5e**



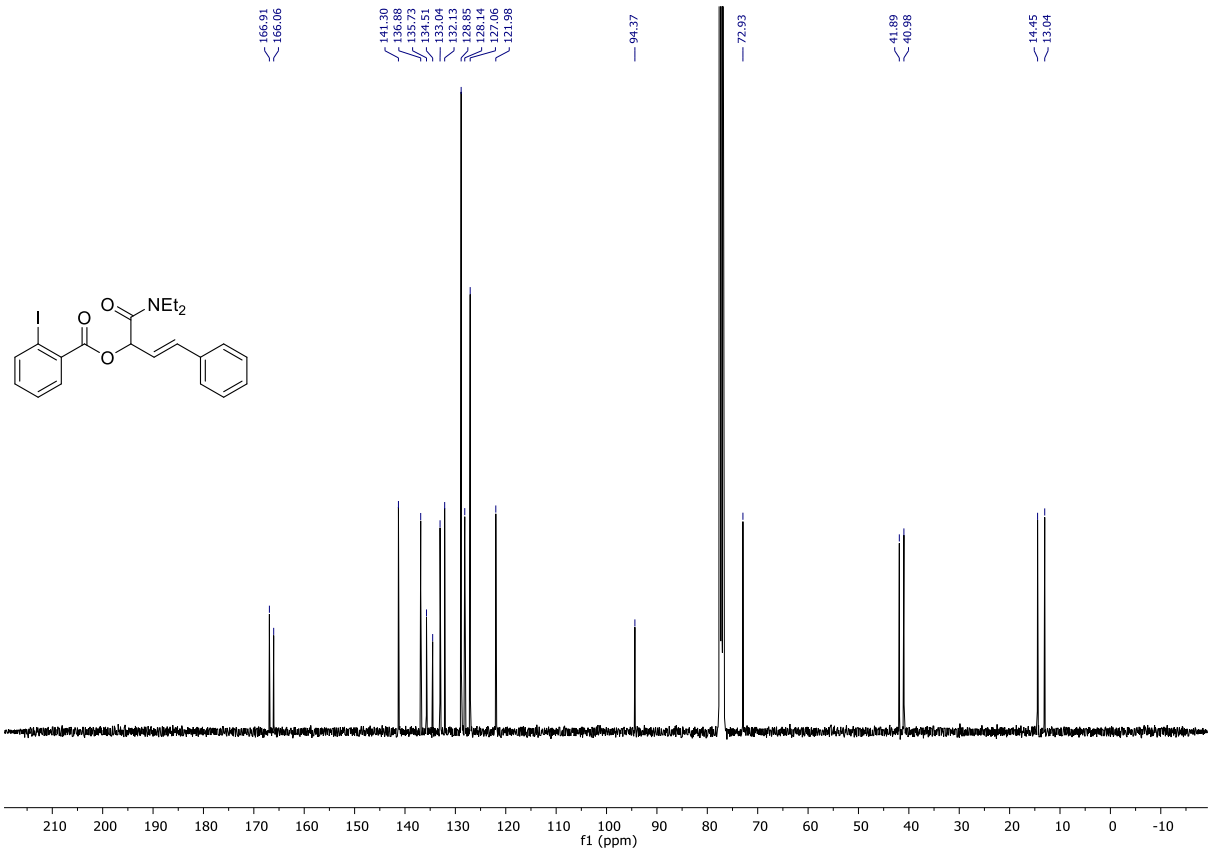
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5e**



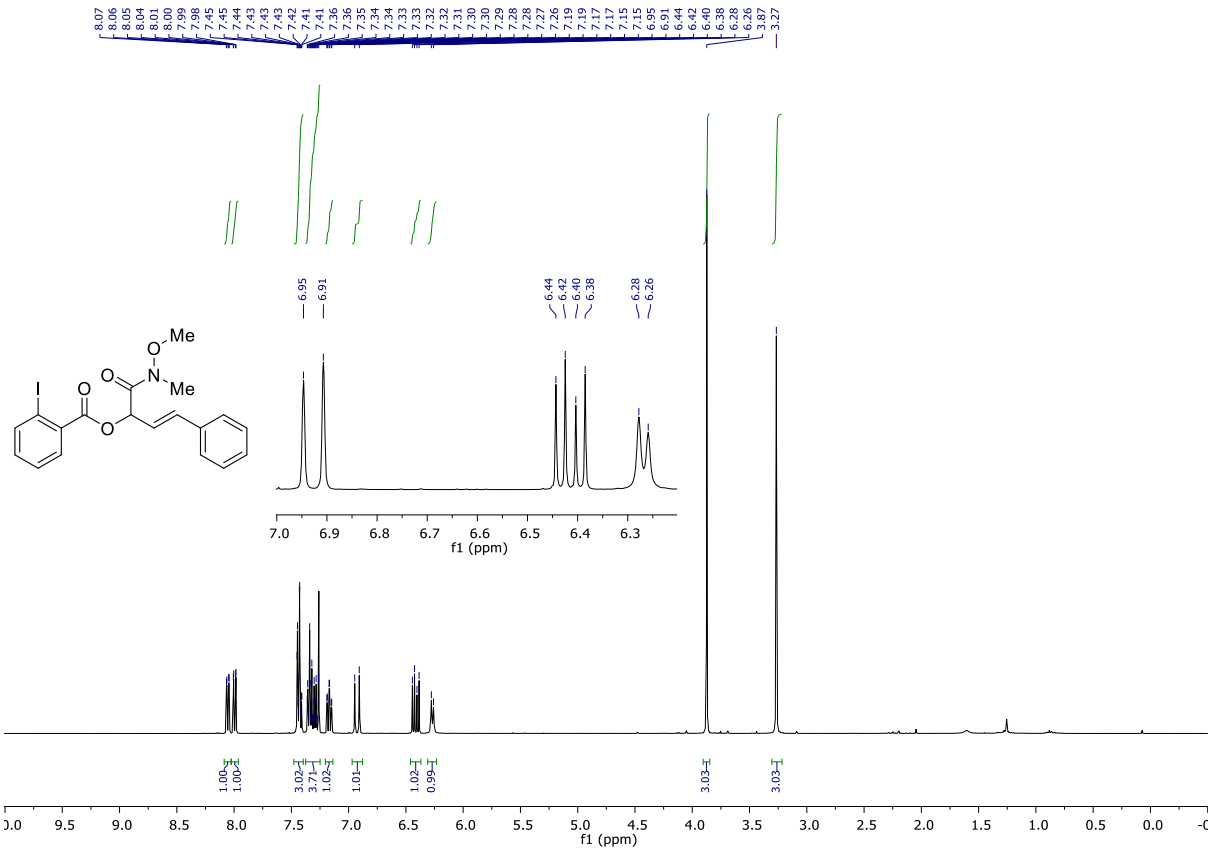
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5f**



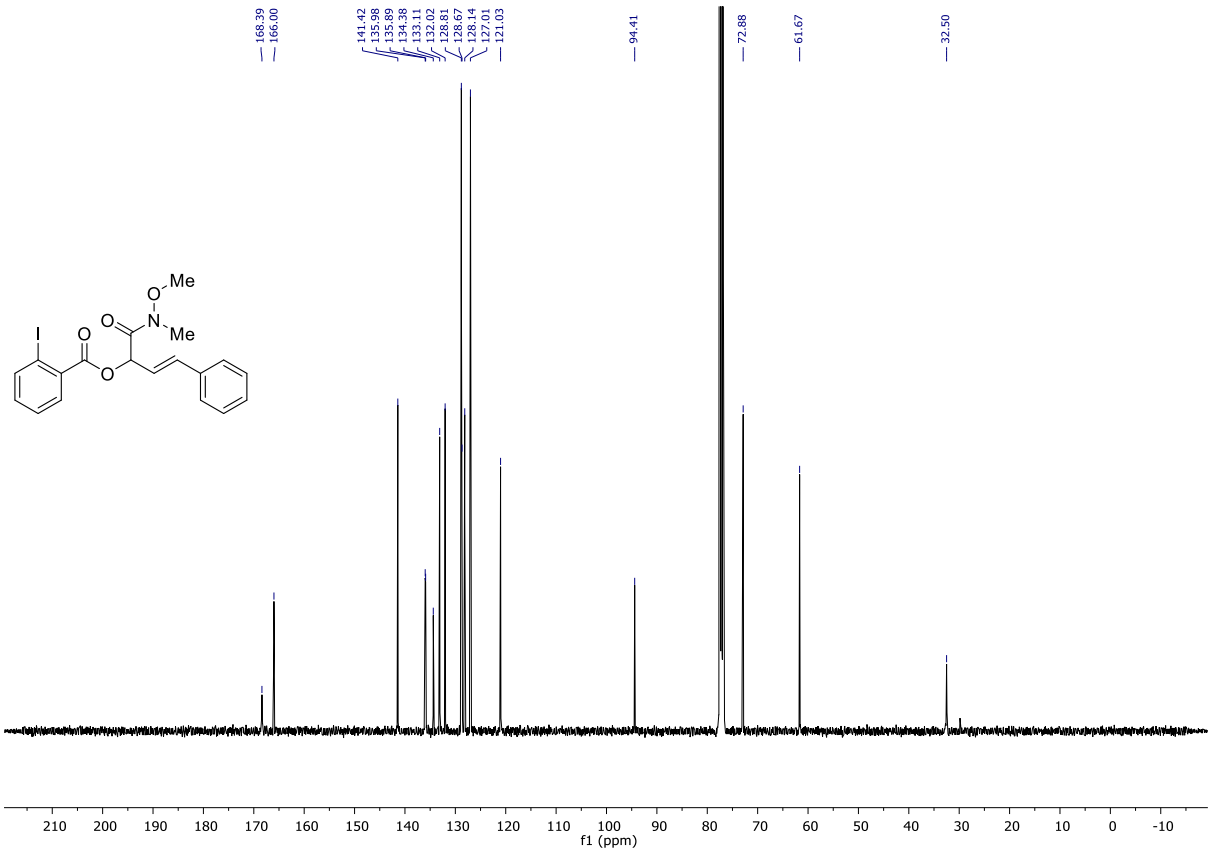
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5f**



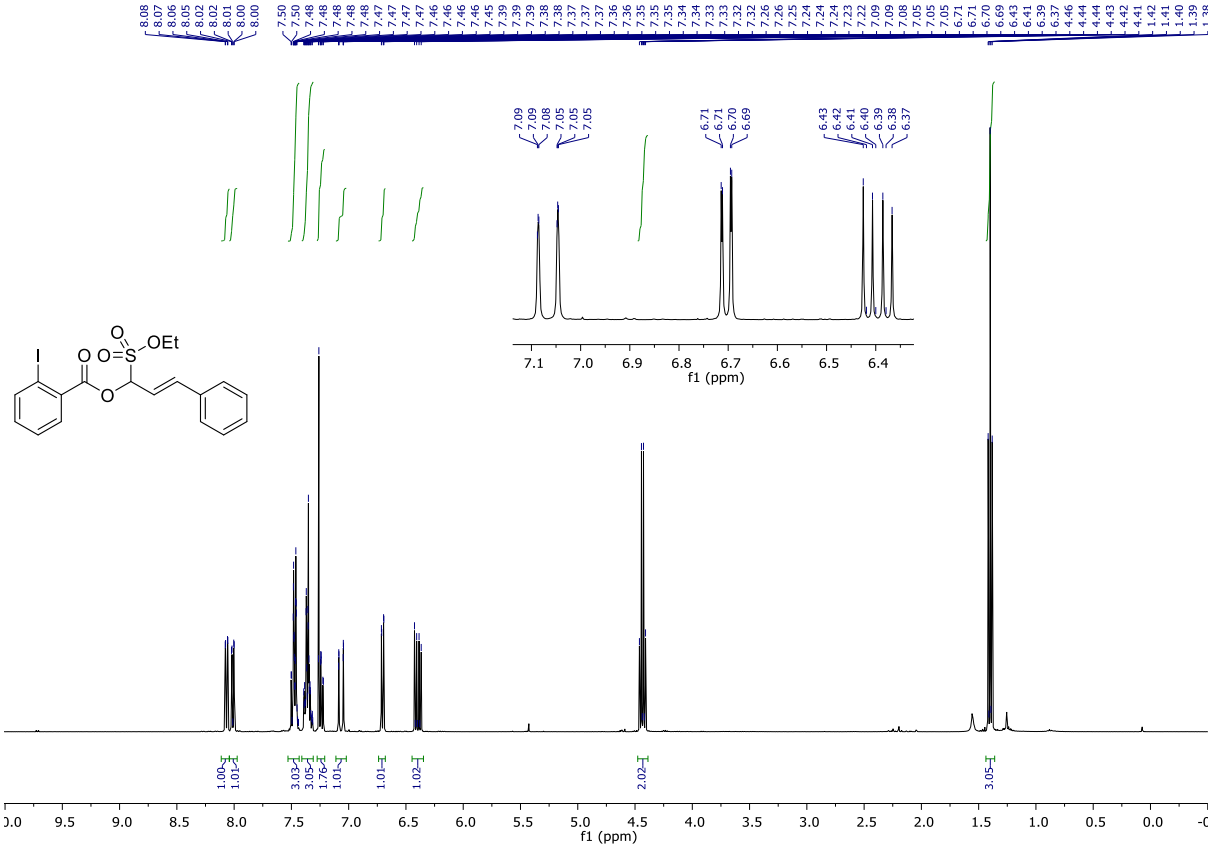
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5g**



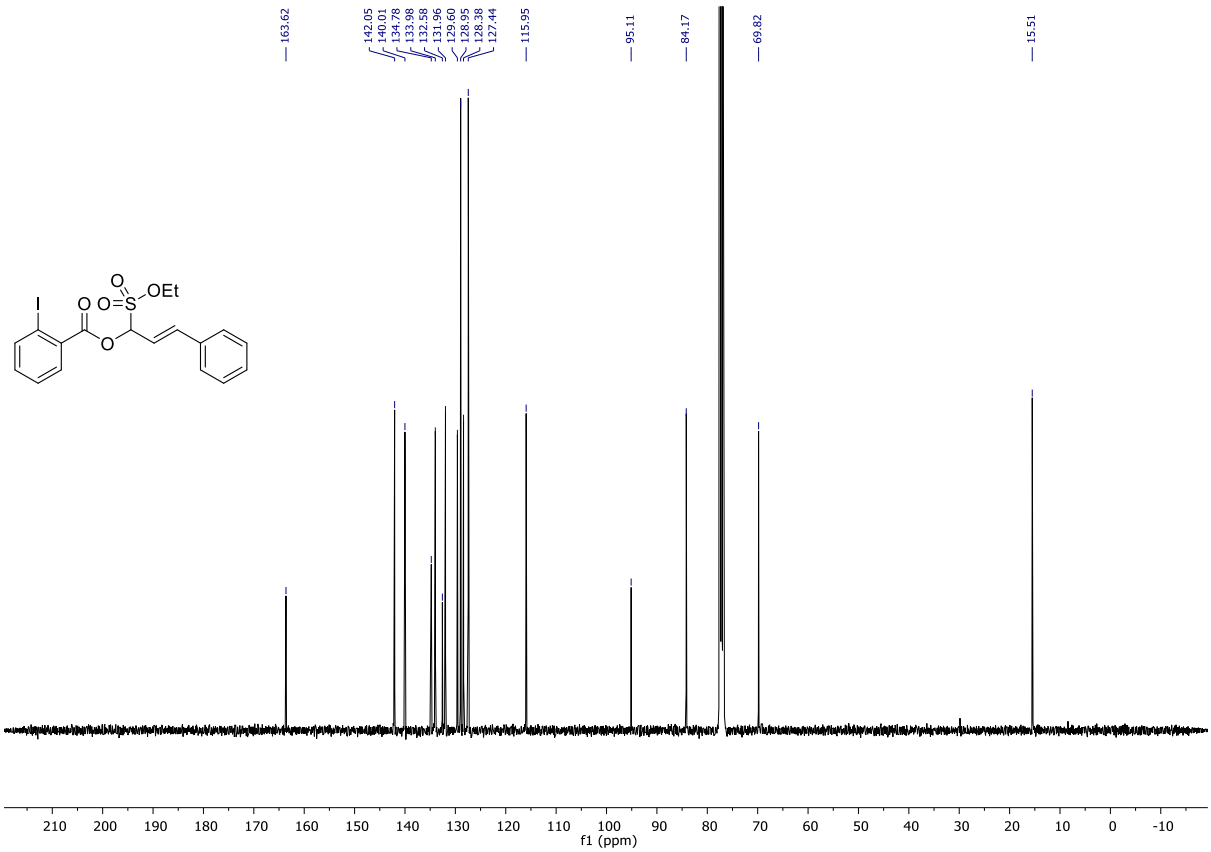
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5g**



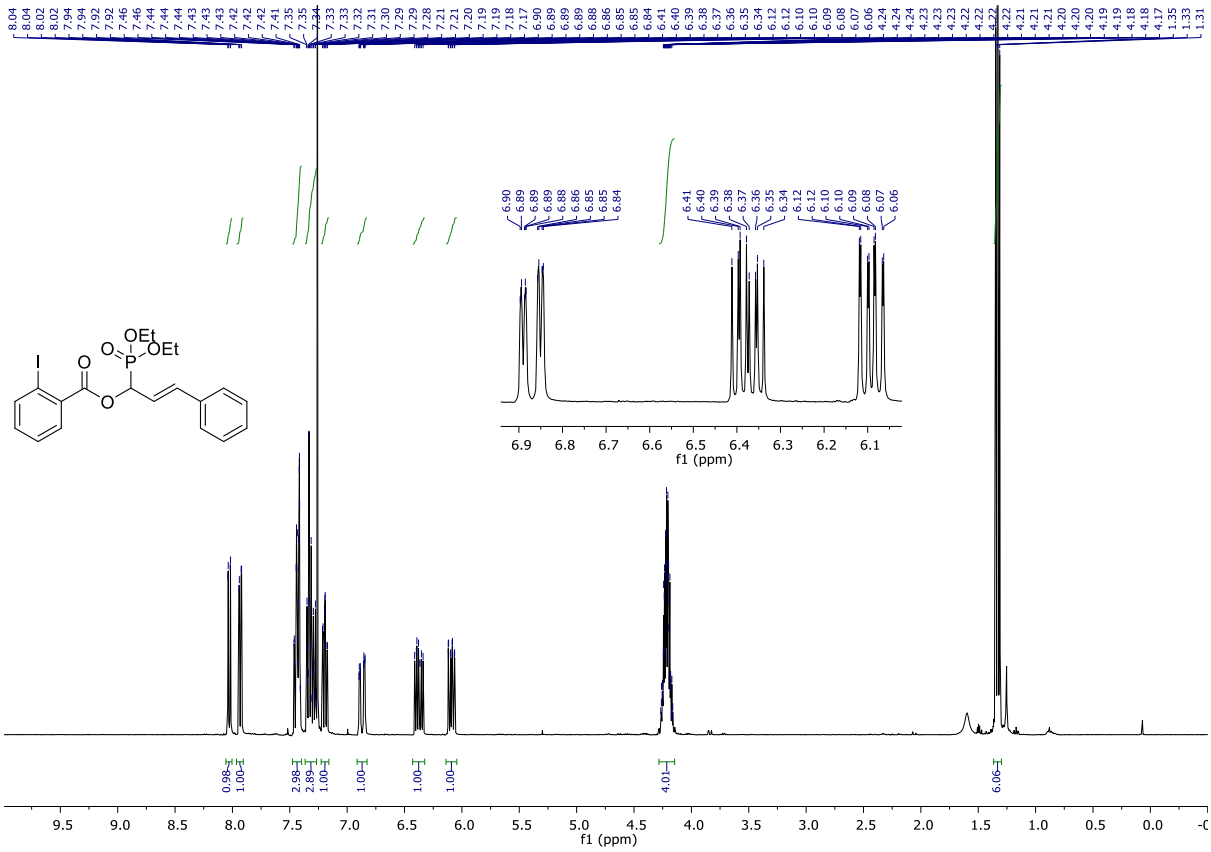
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5h**



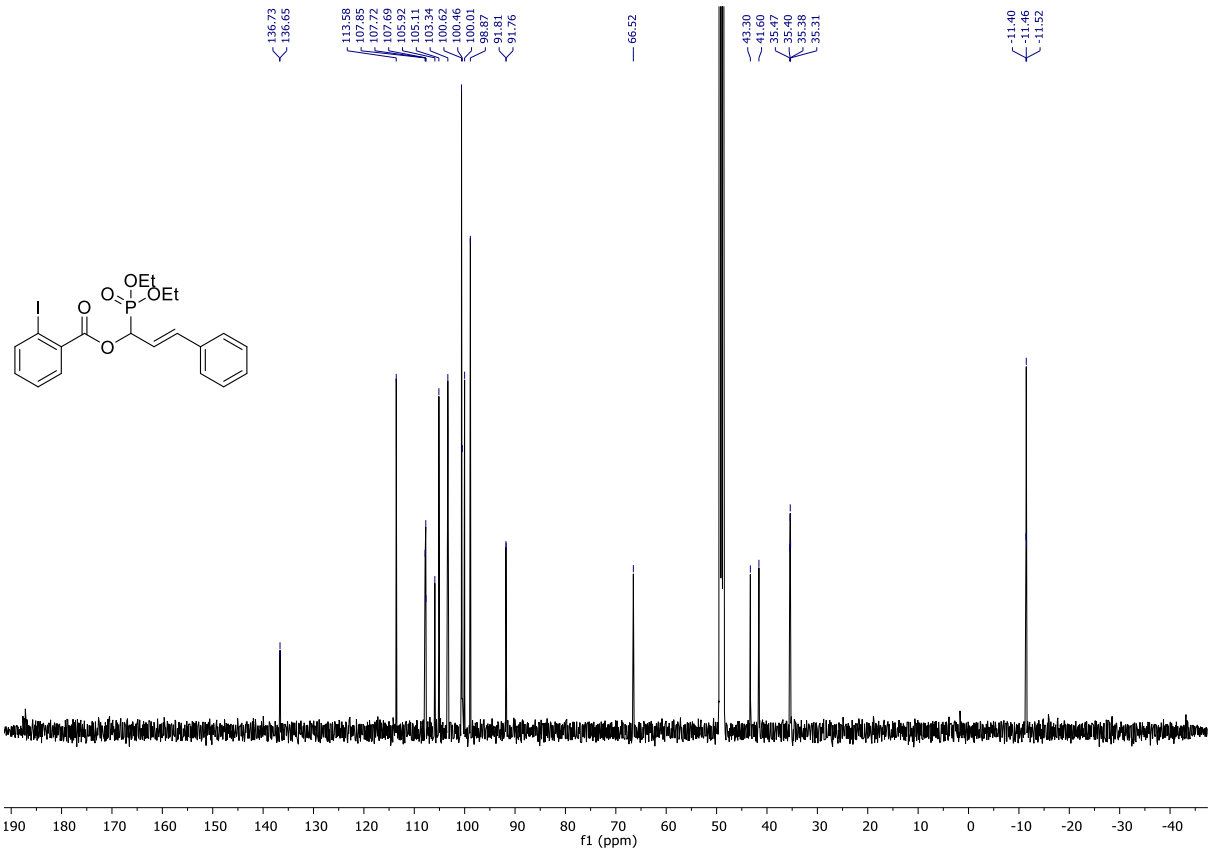
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5h**



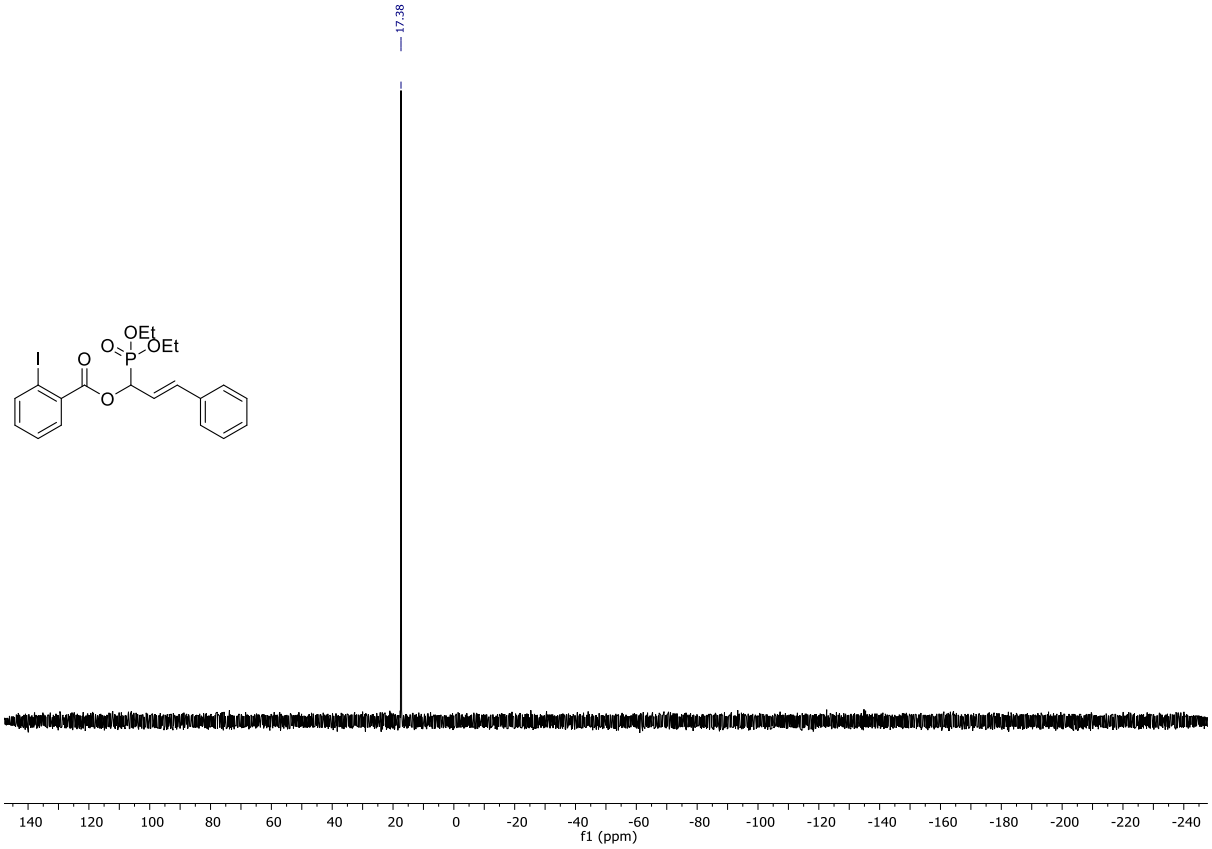
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5i**



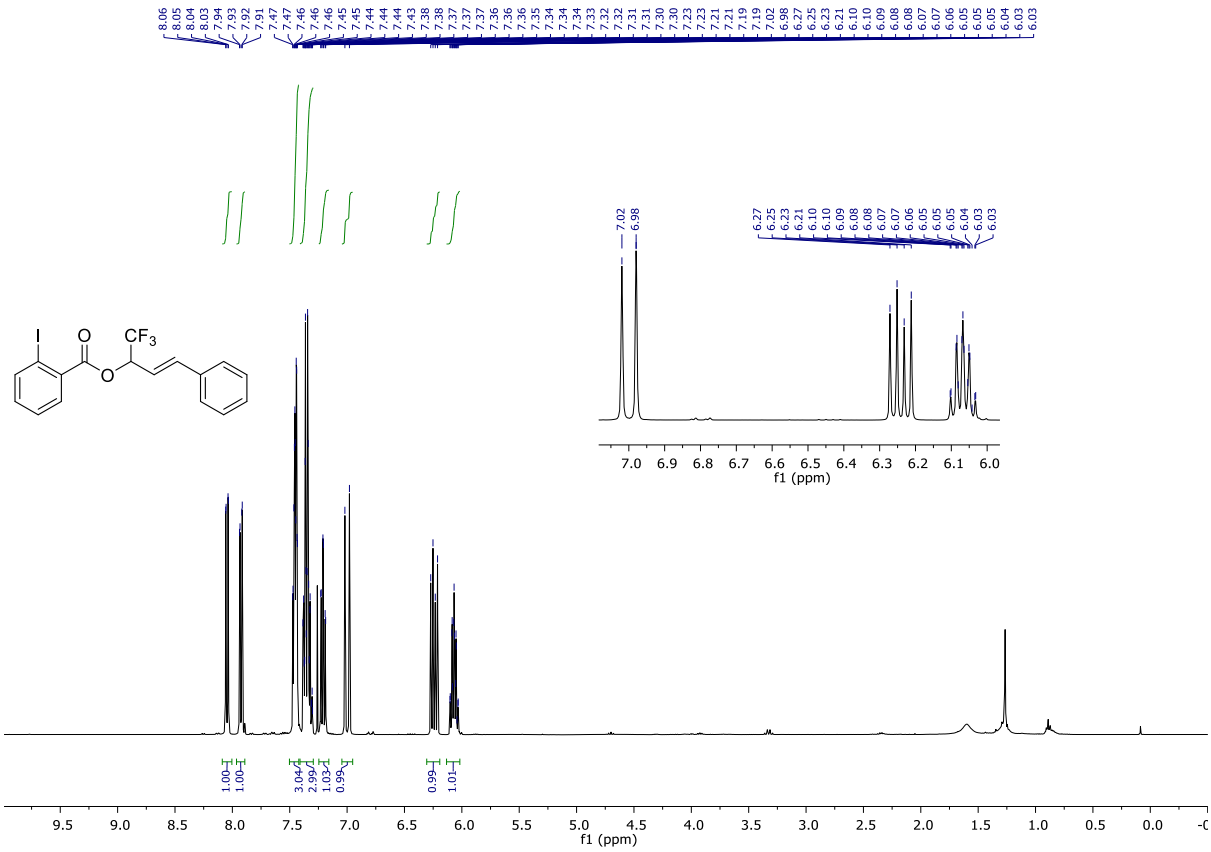
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5i**



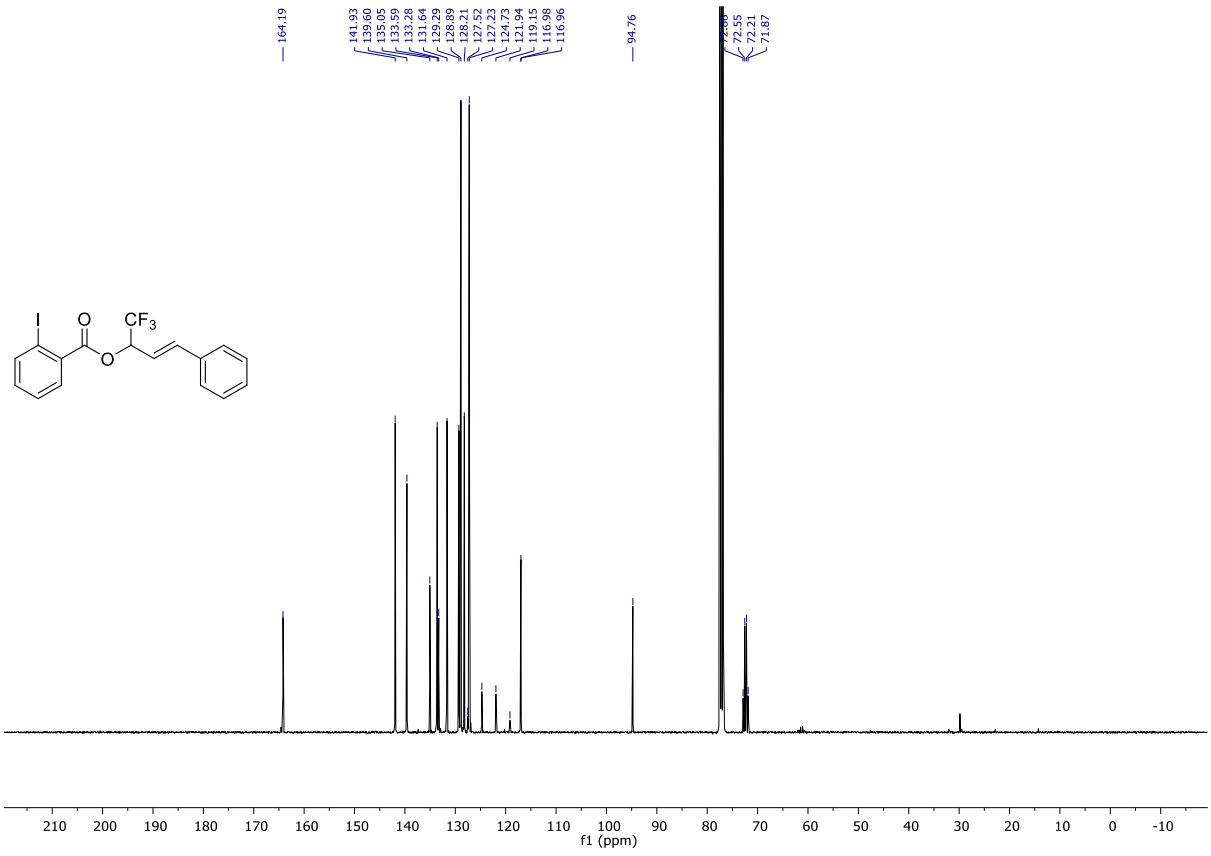
^{31}P-NMR (126 MHz, $CDCl_3$) of compound **5i**



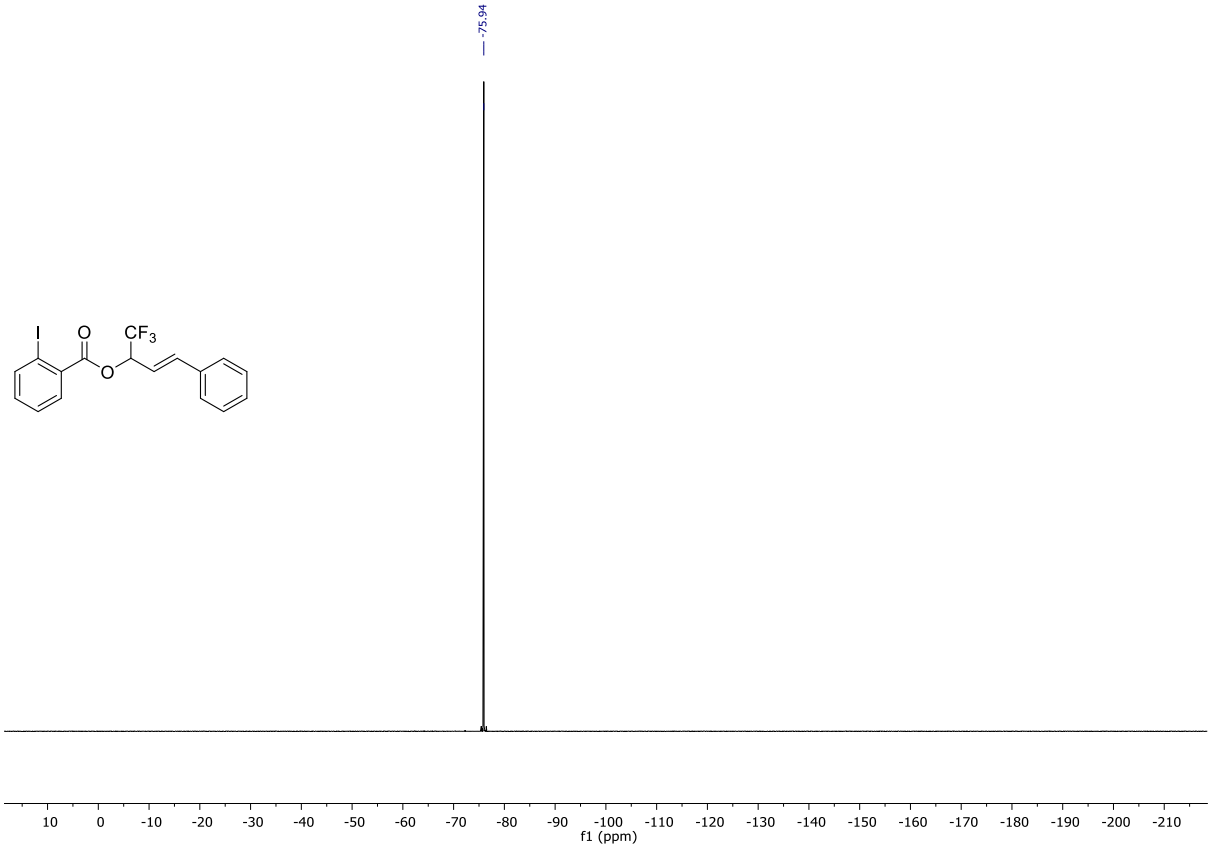
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5l**



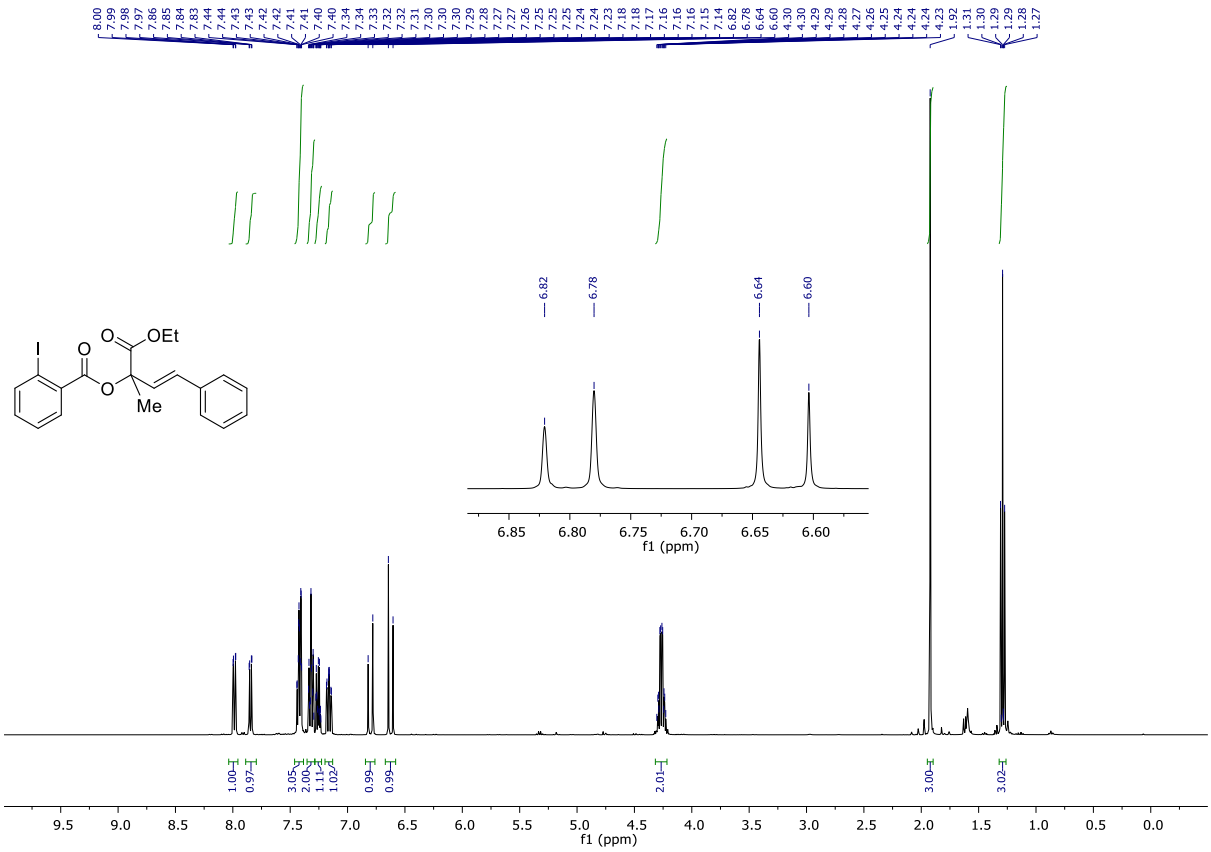
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5l**



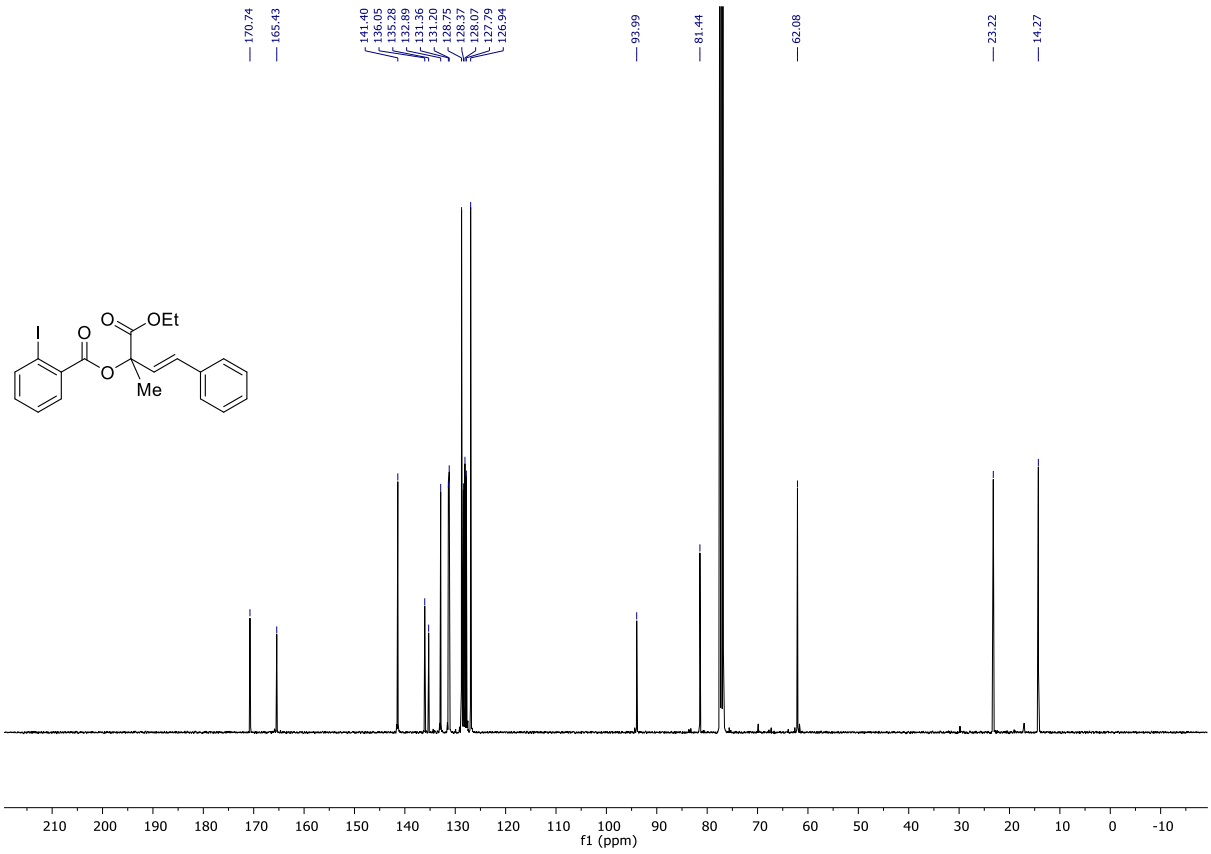
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **5l**



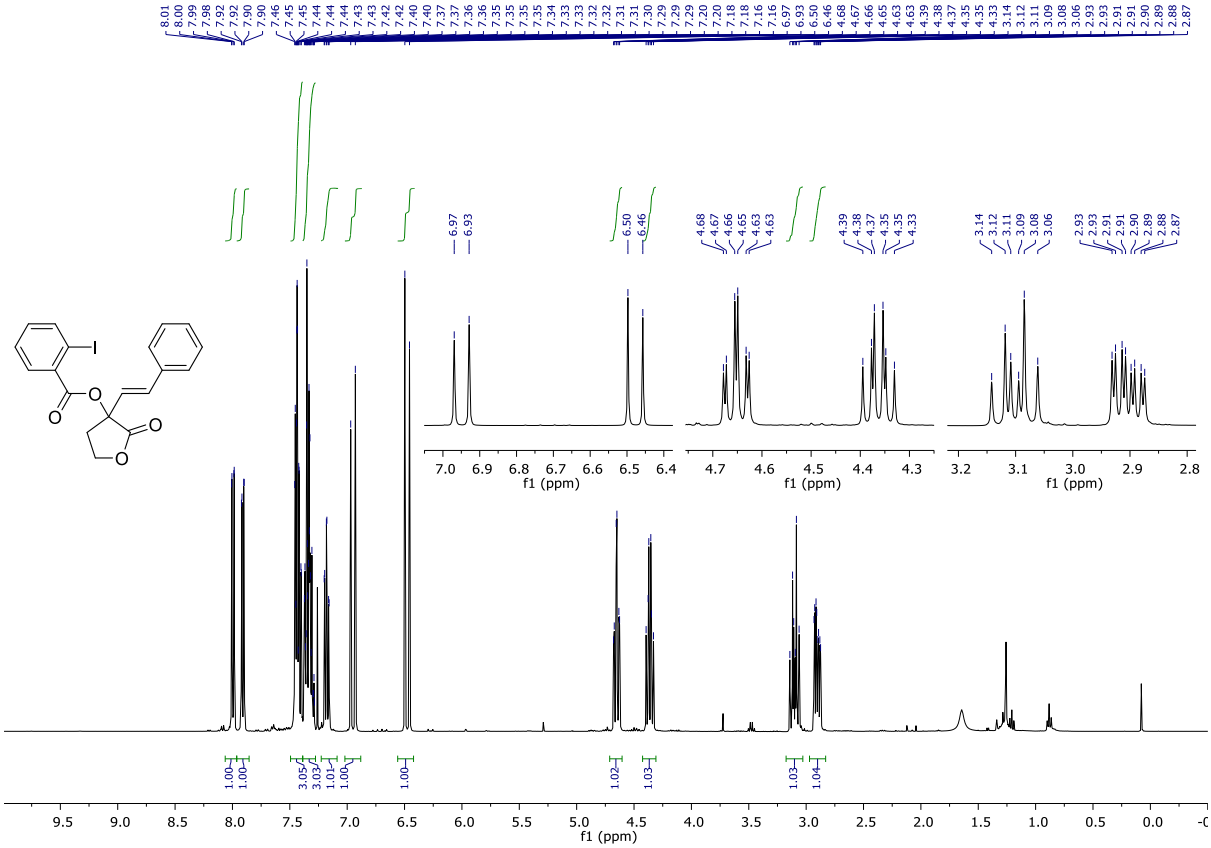
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5m**



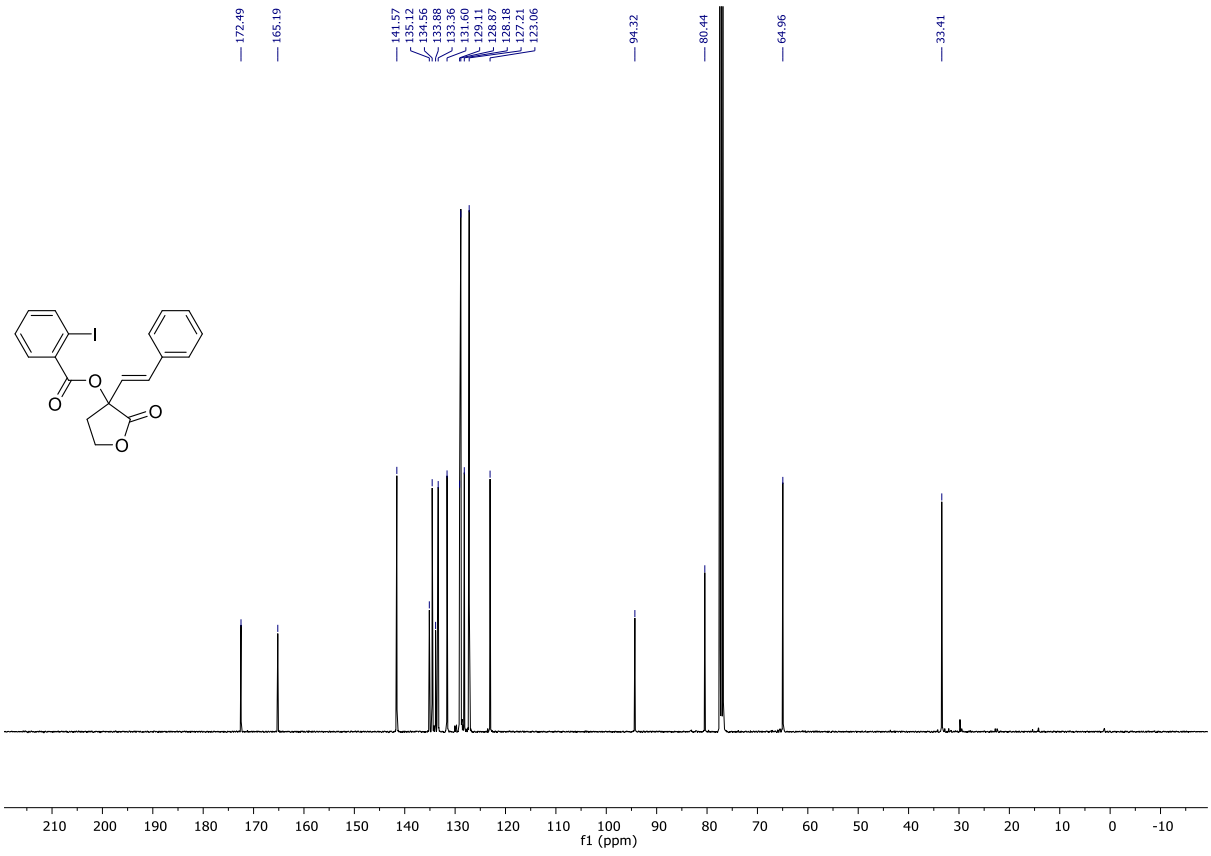
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5m**



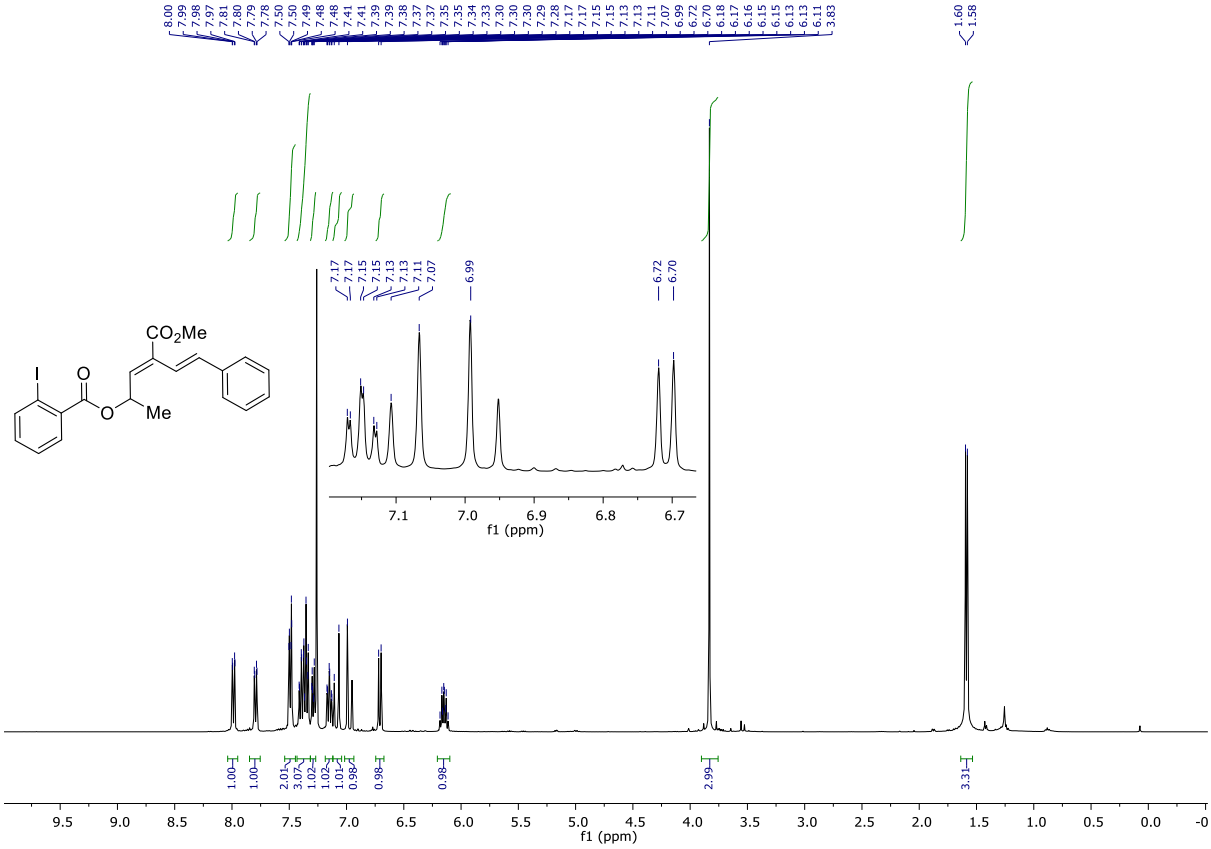
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5o**



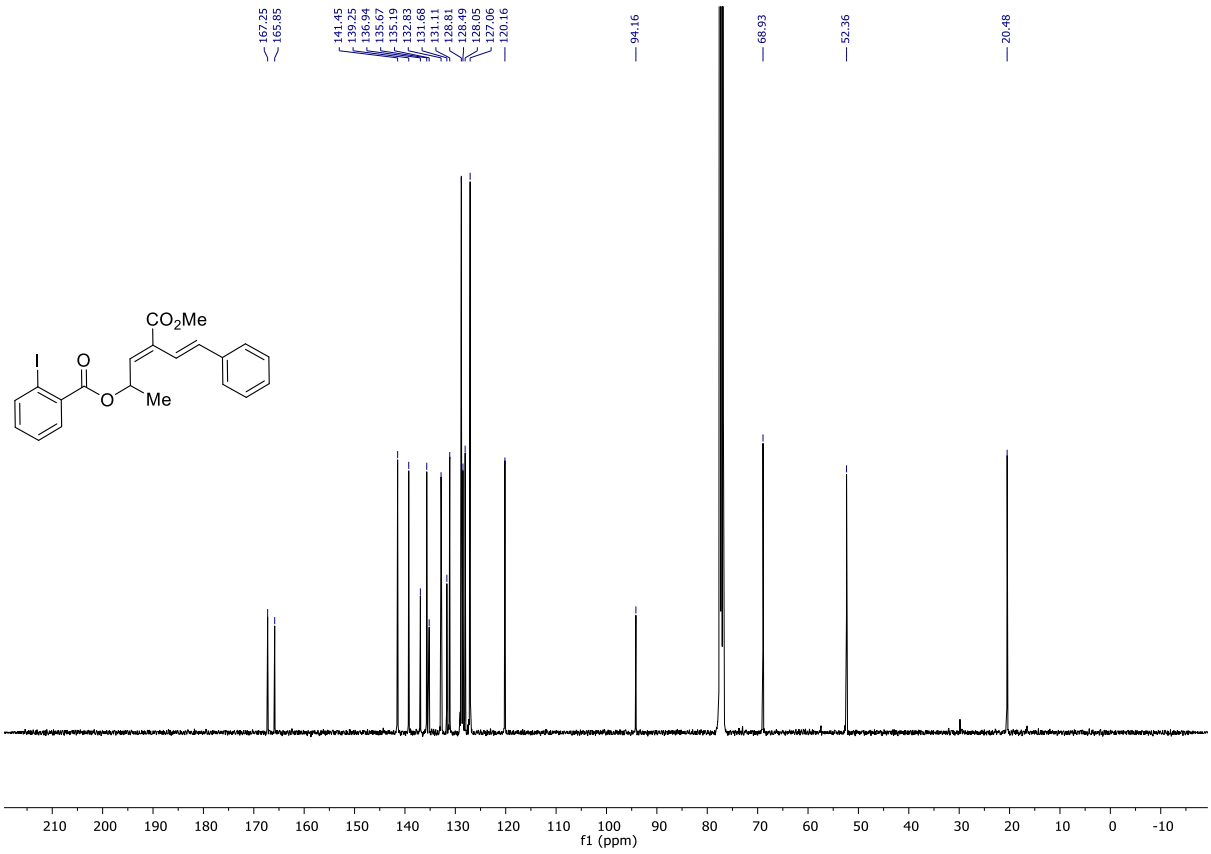
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5o**



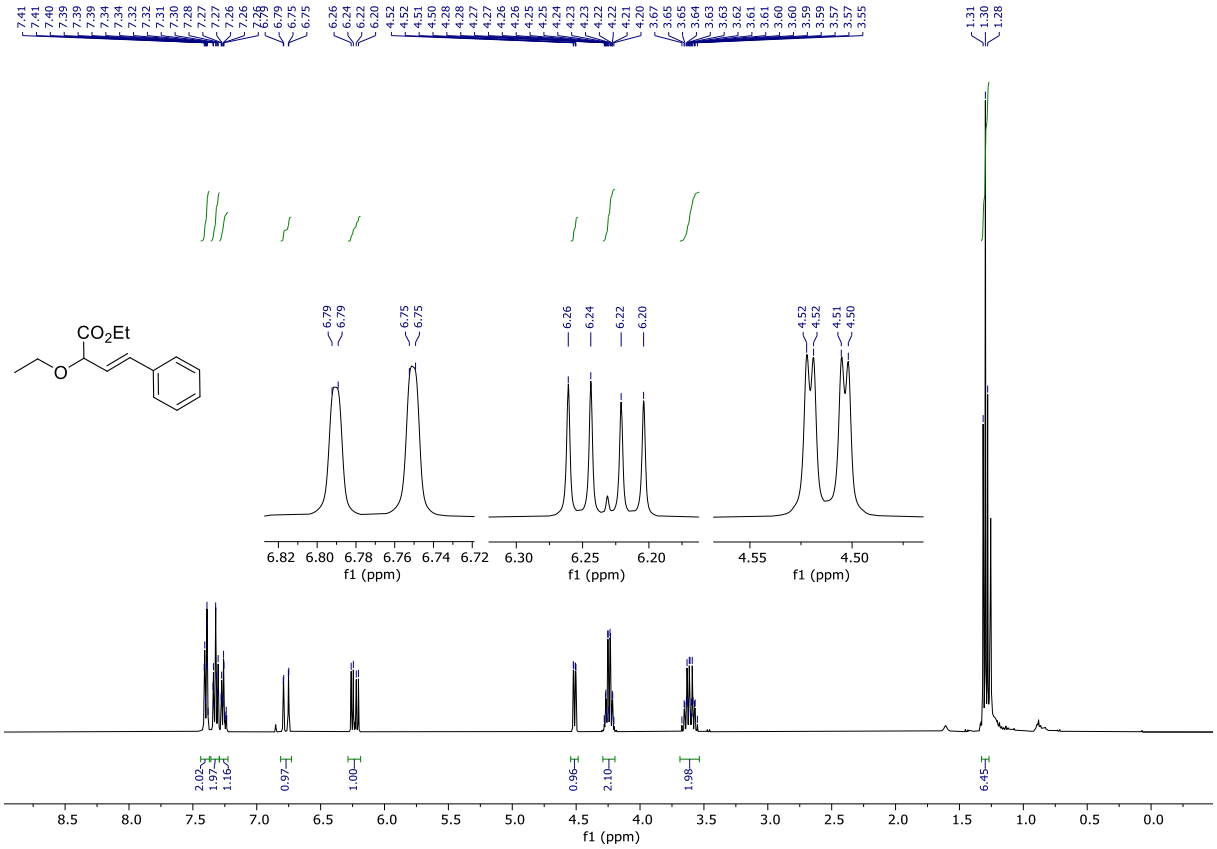
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5p**



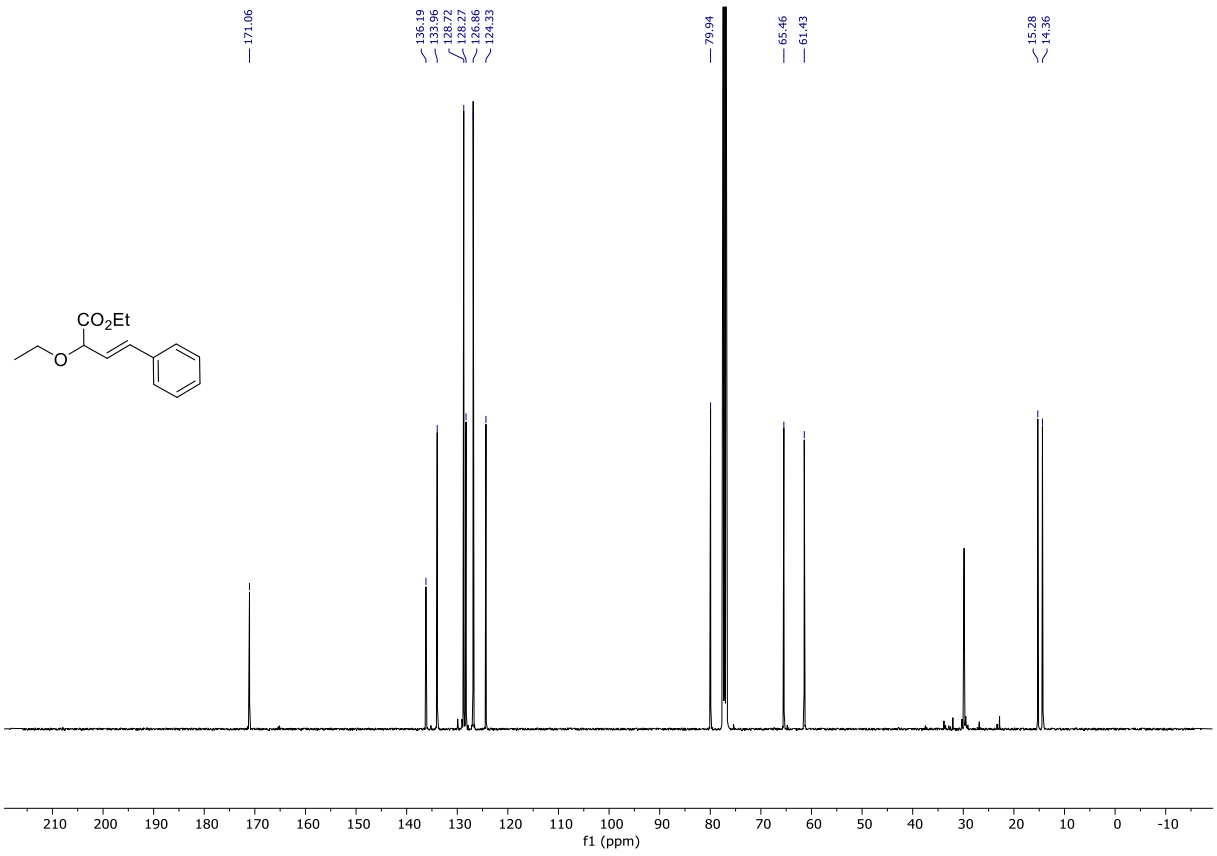
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5p**



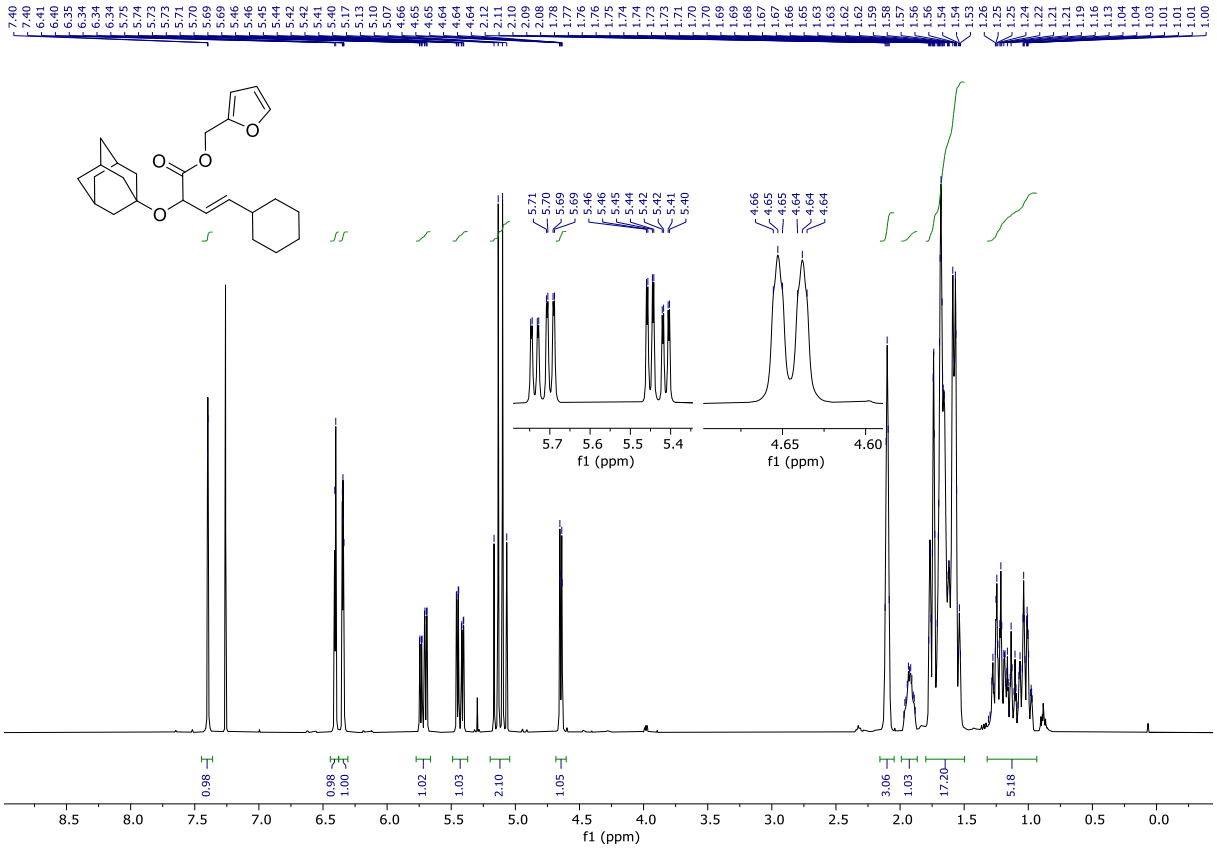
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6b**



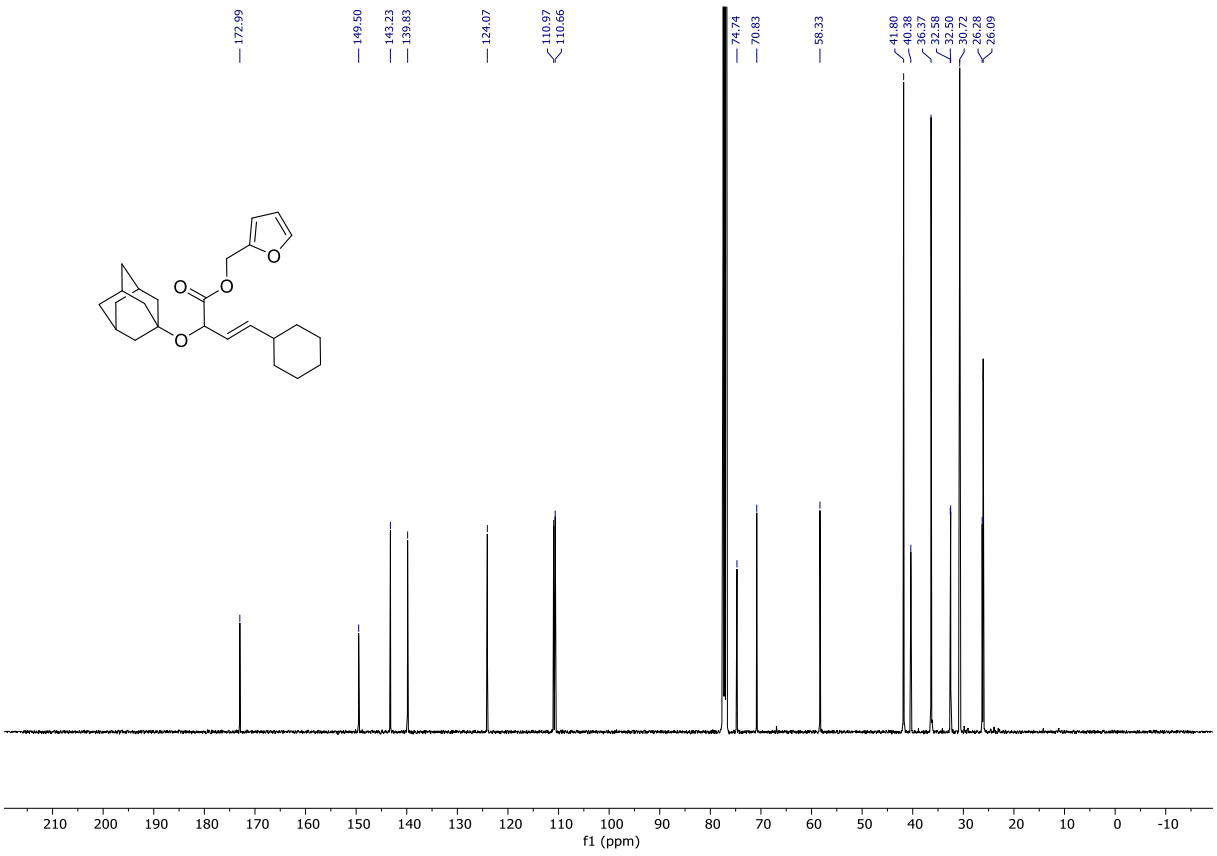
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6b**



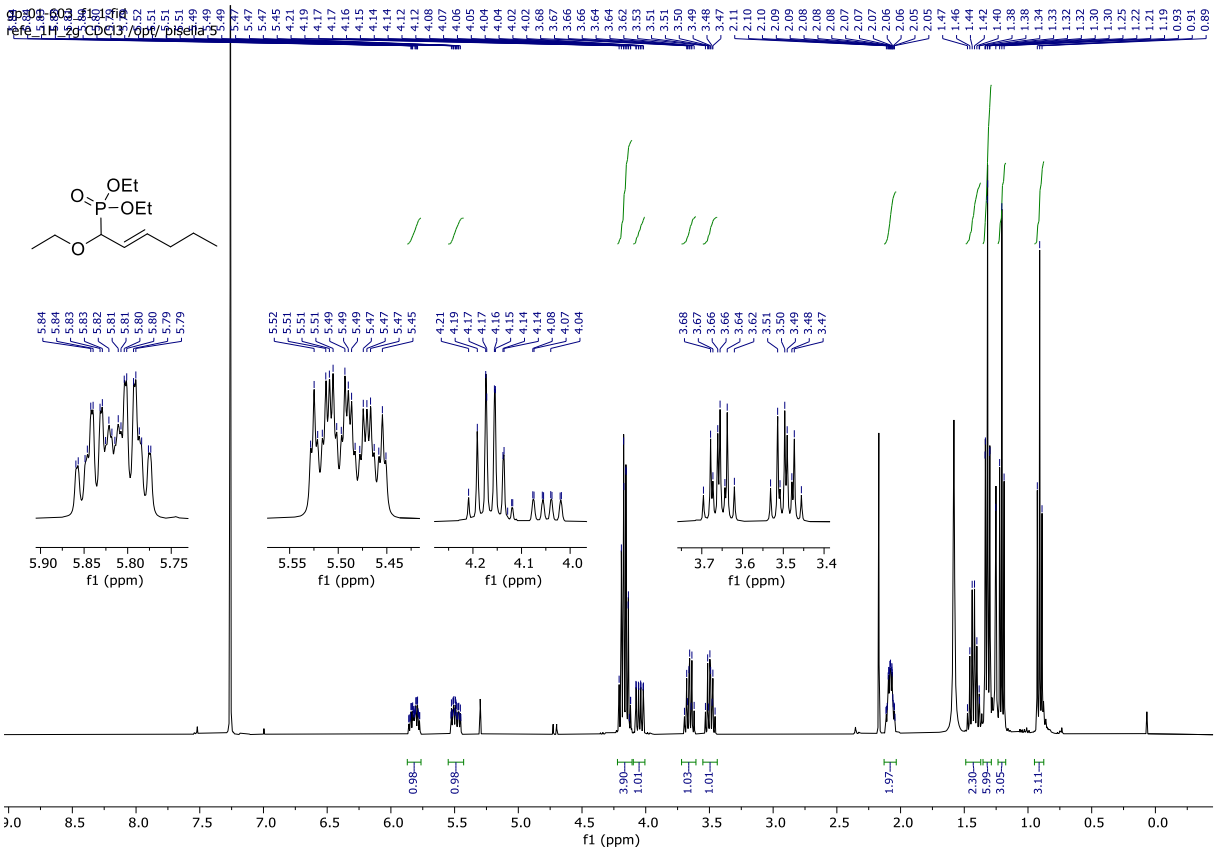
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6c**



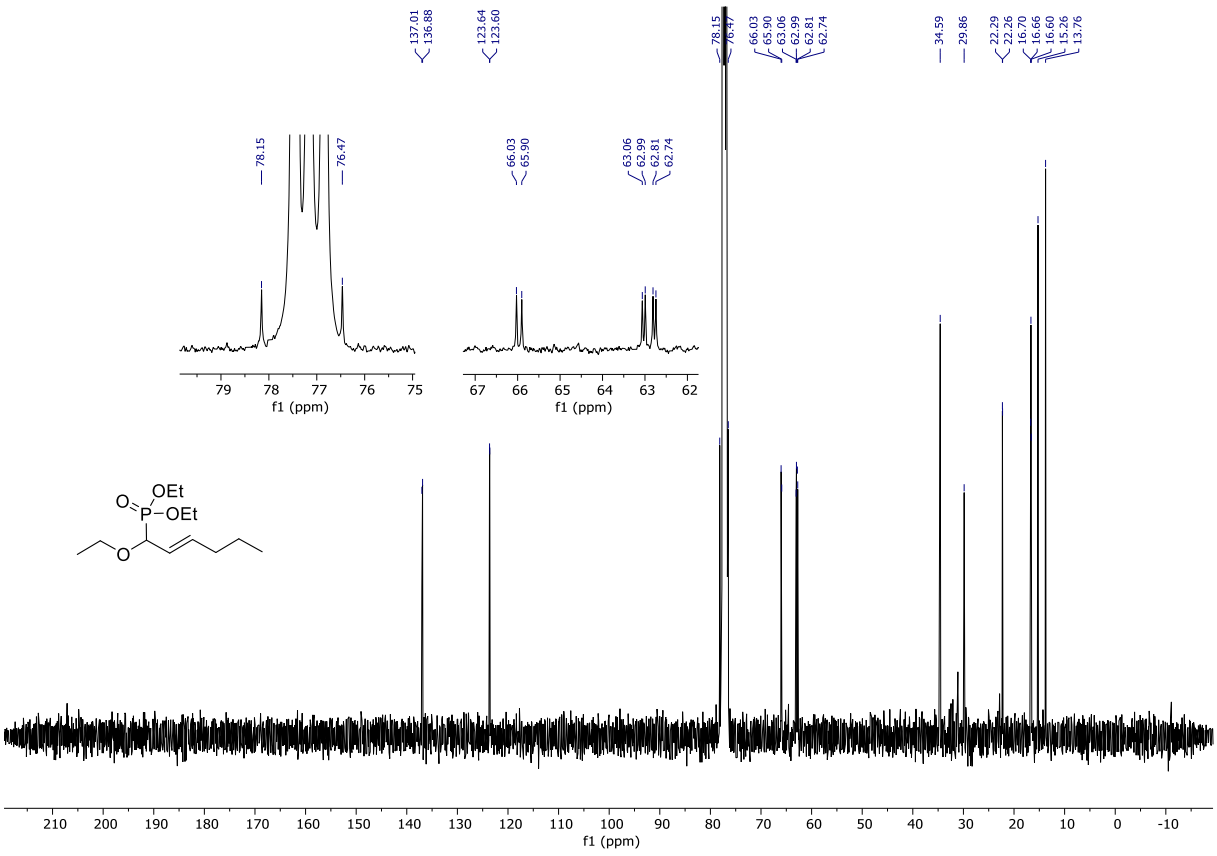
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6c**



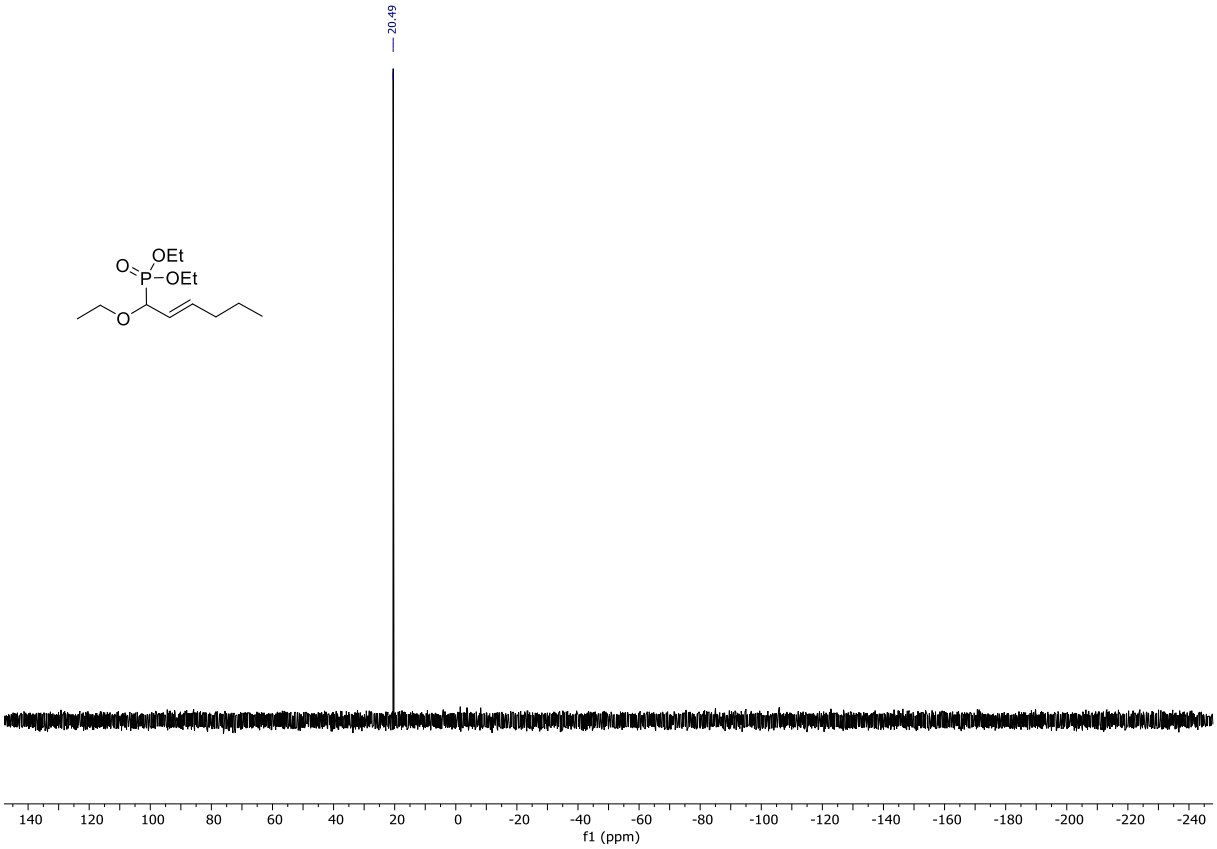
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6d**



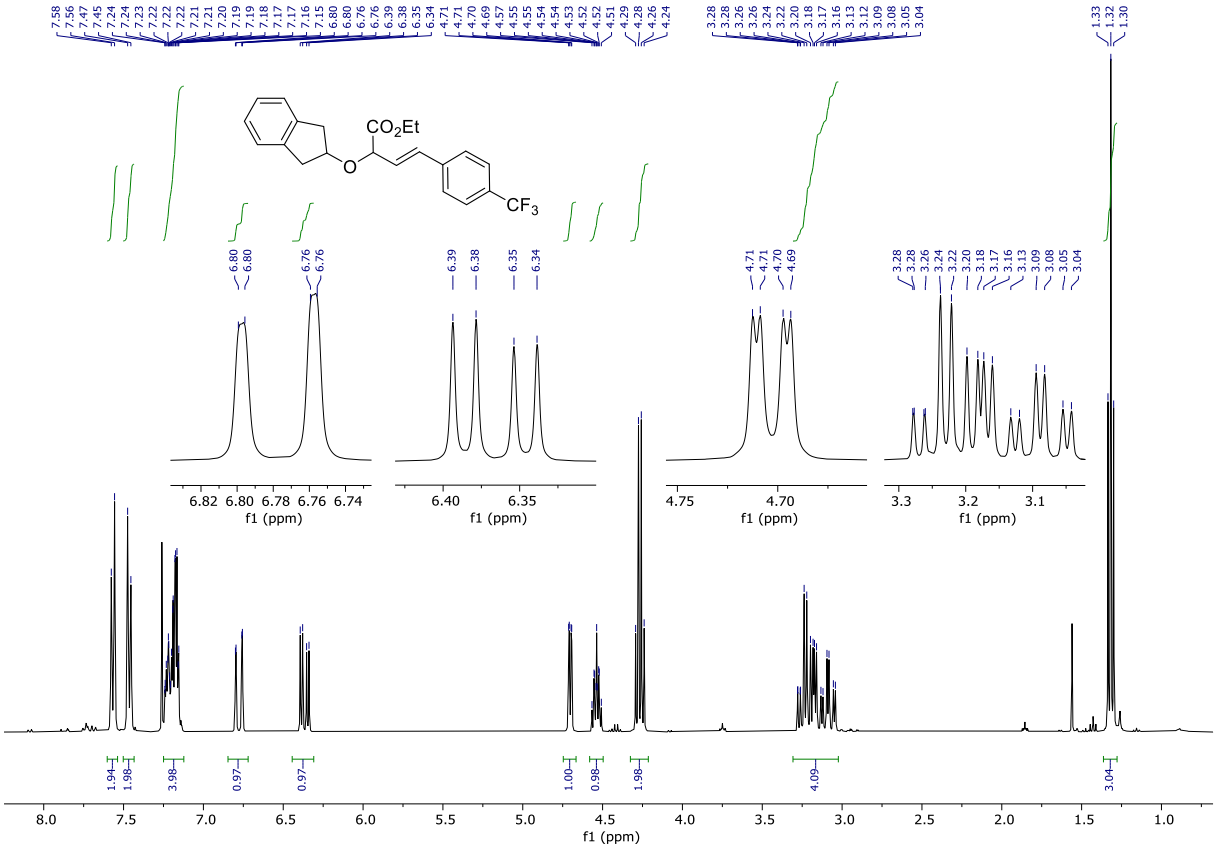
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6d**



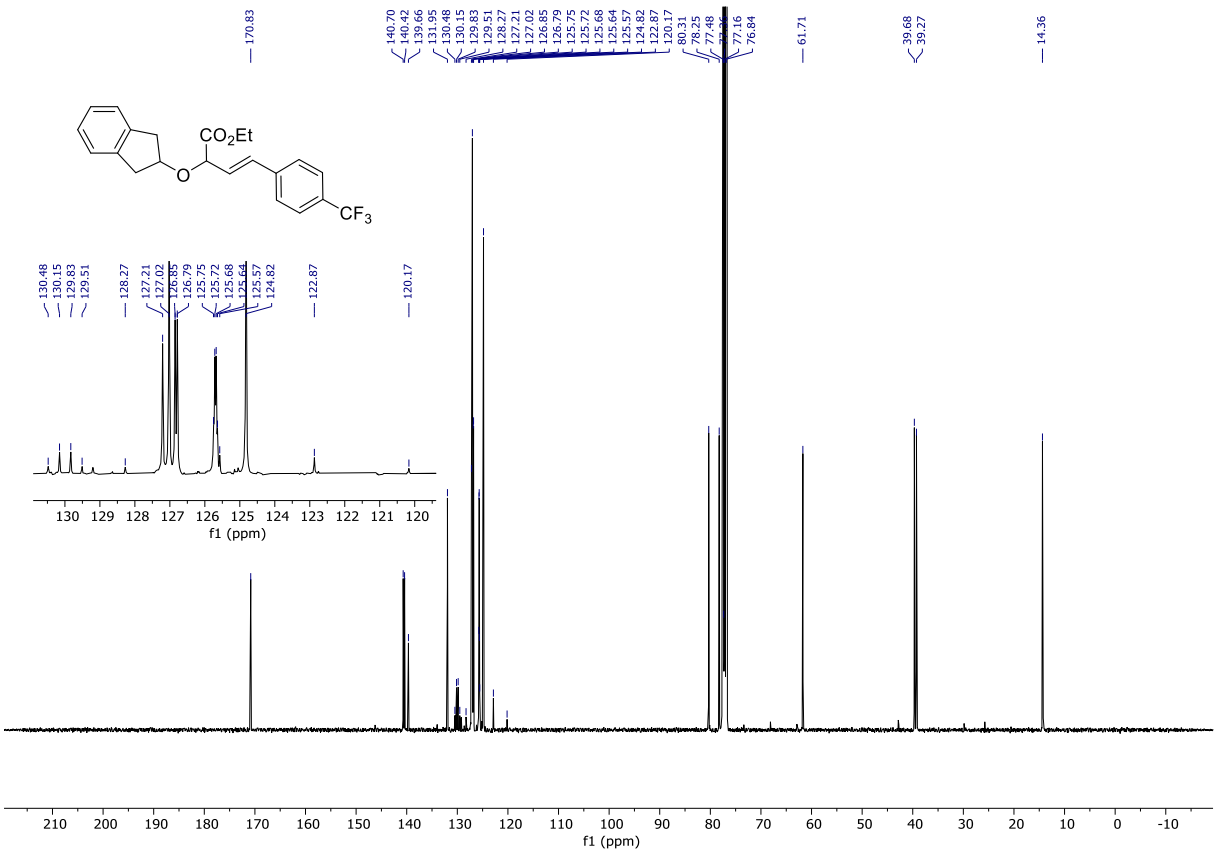
^{31}P-NMR (162 MHz, $CDCl_3$) of compound **6d**



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

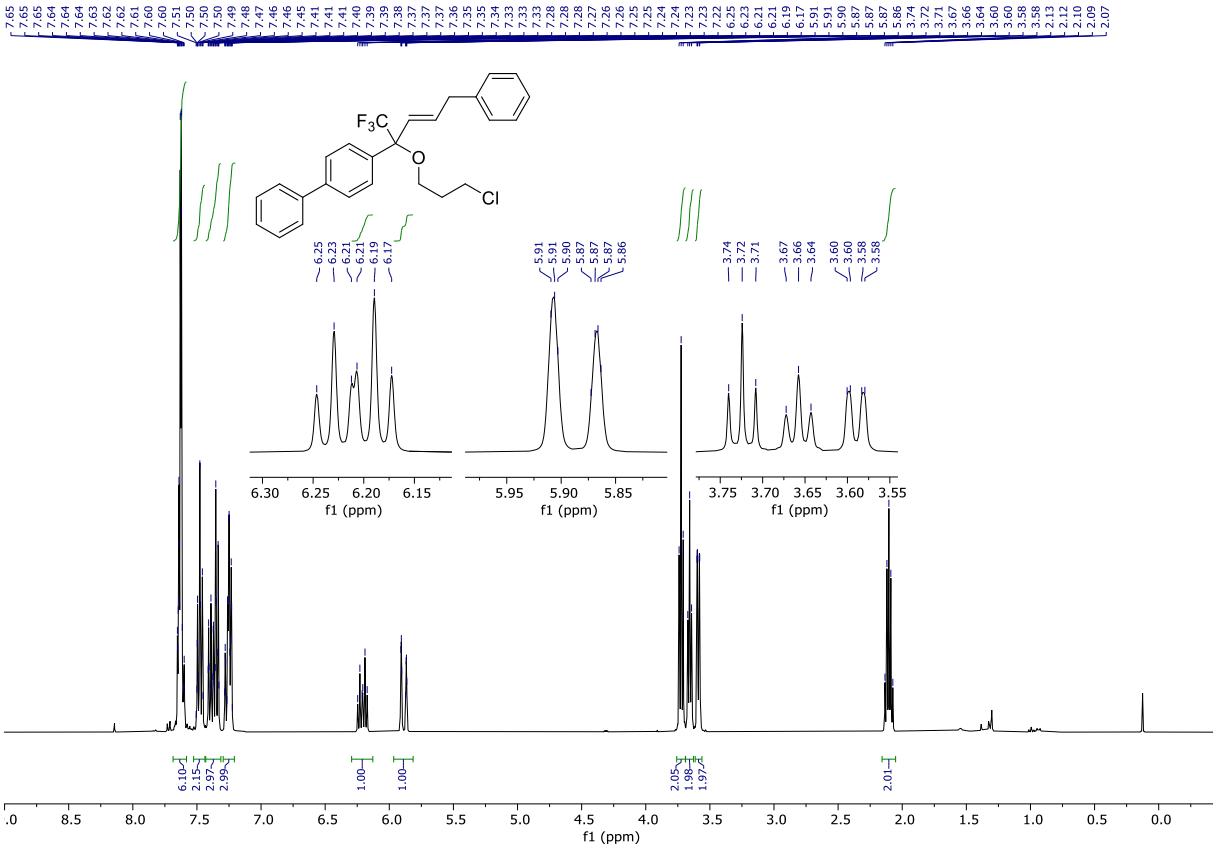


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6e**

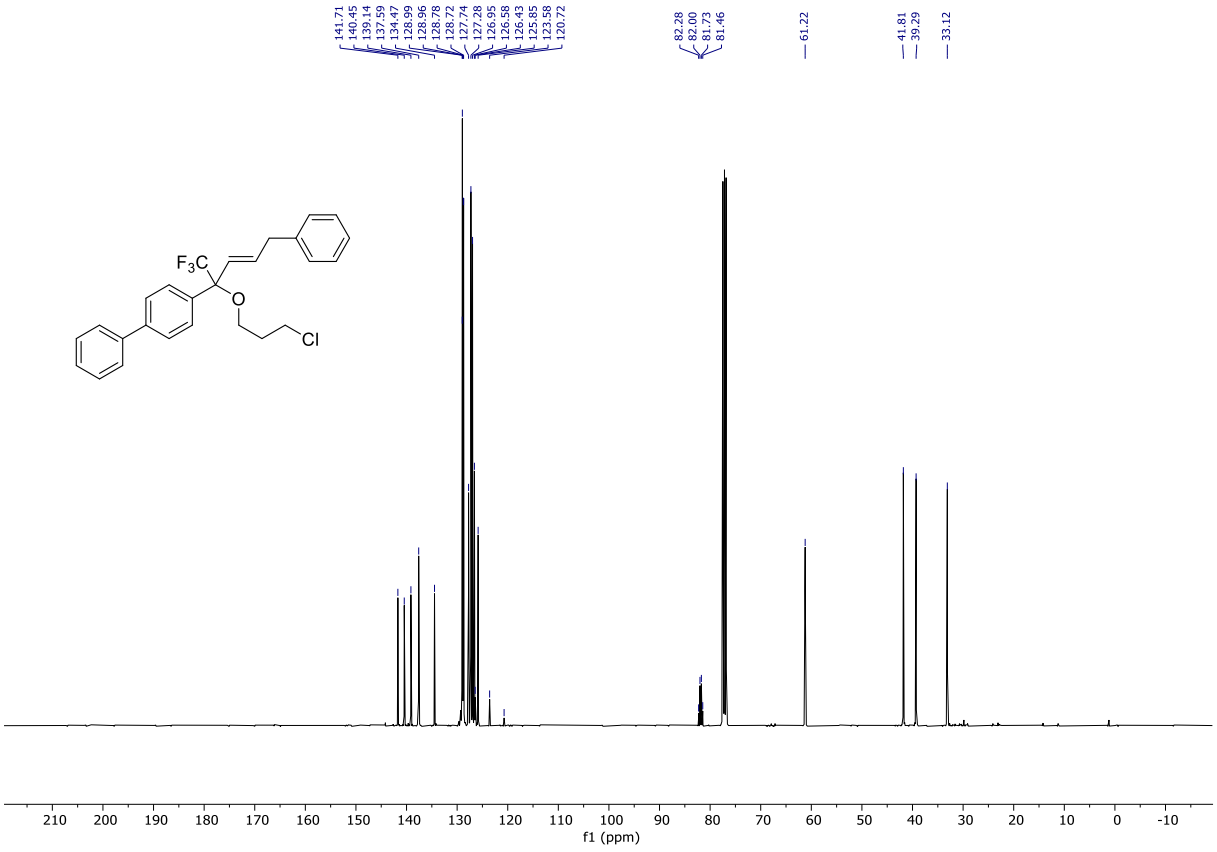


^{19}F-NMR (376 MHz, $CDCl_3$) of compound **6e**

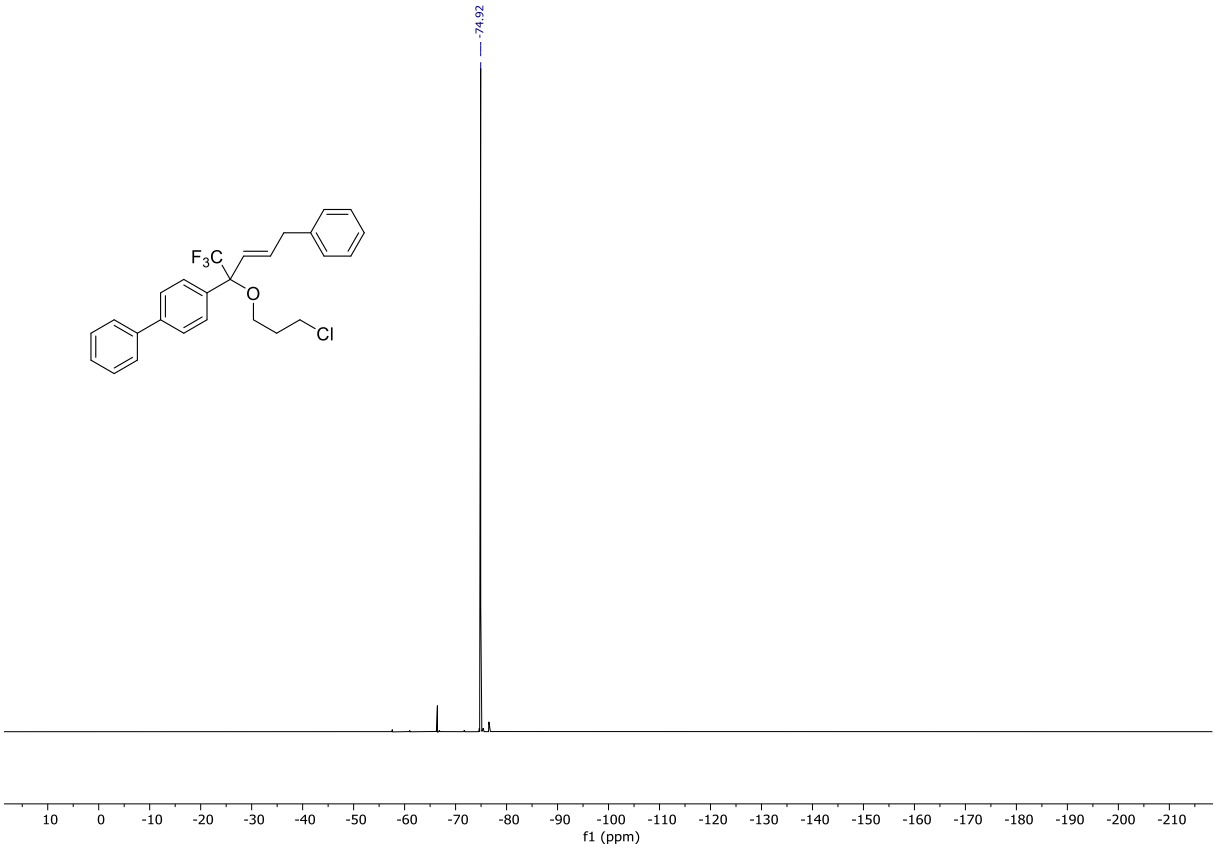
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6f**



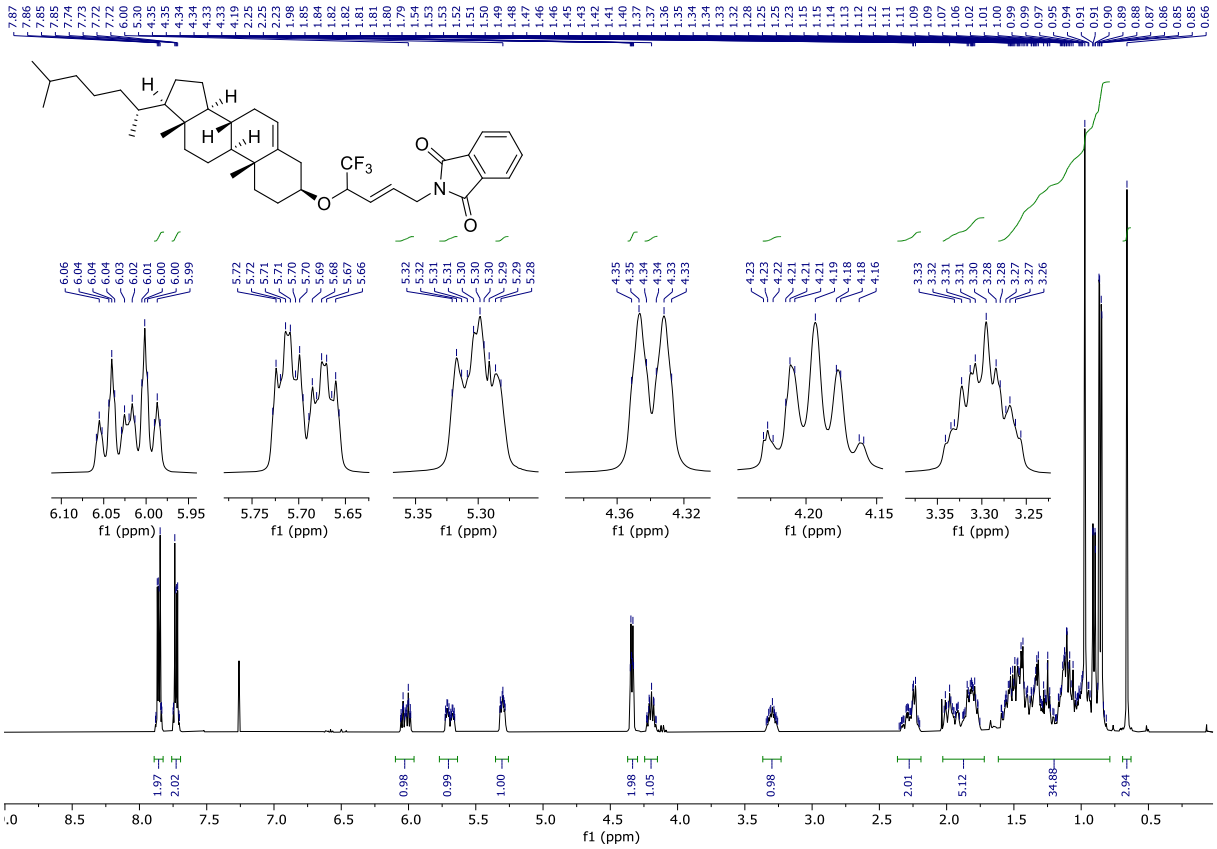
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6f**



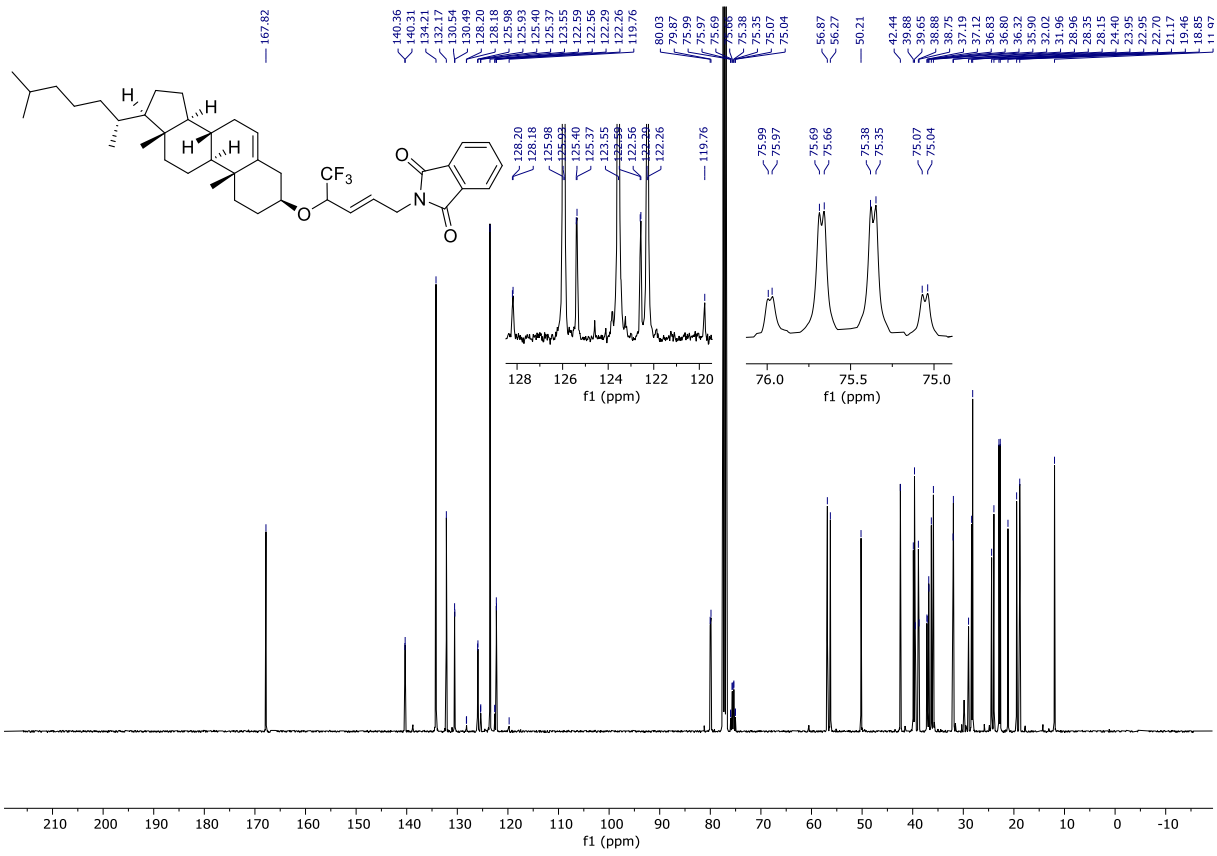
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **6f**



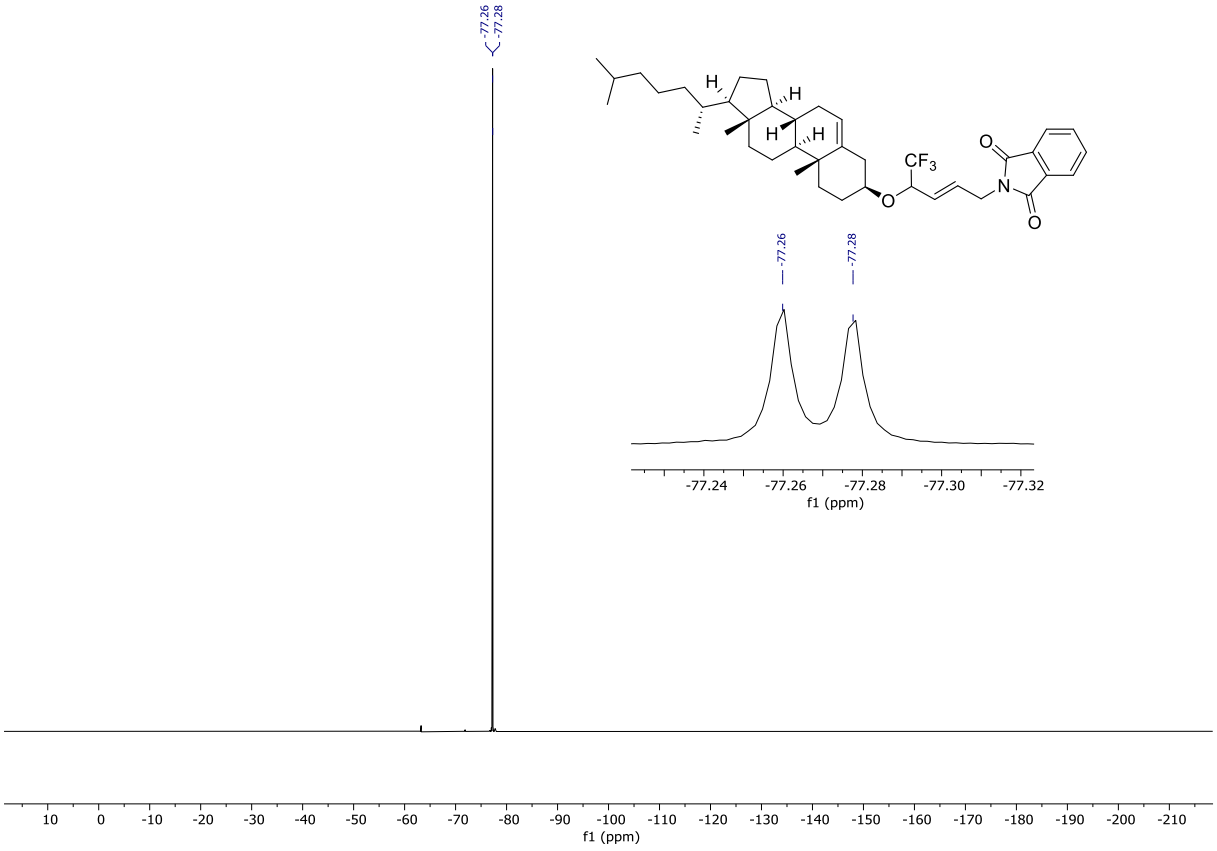
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6g**



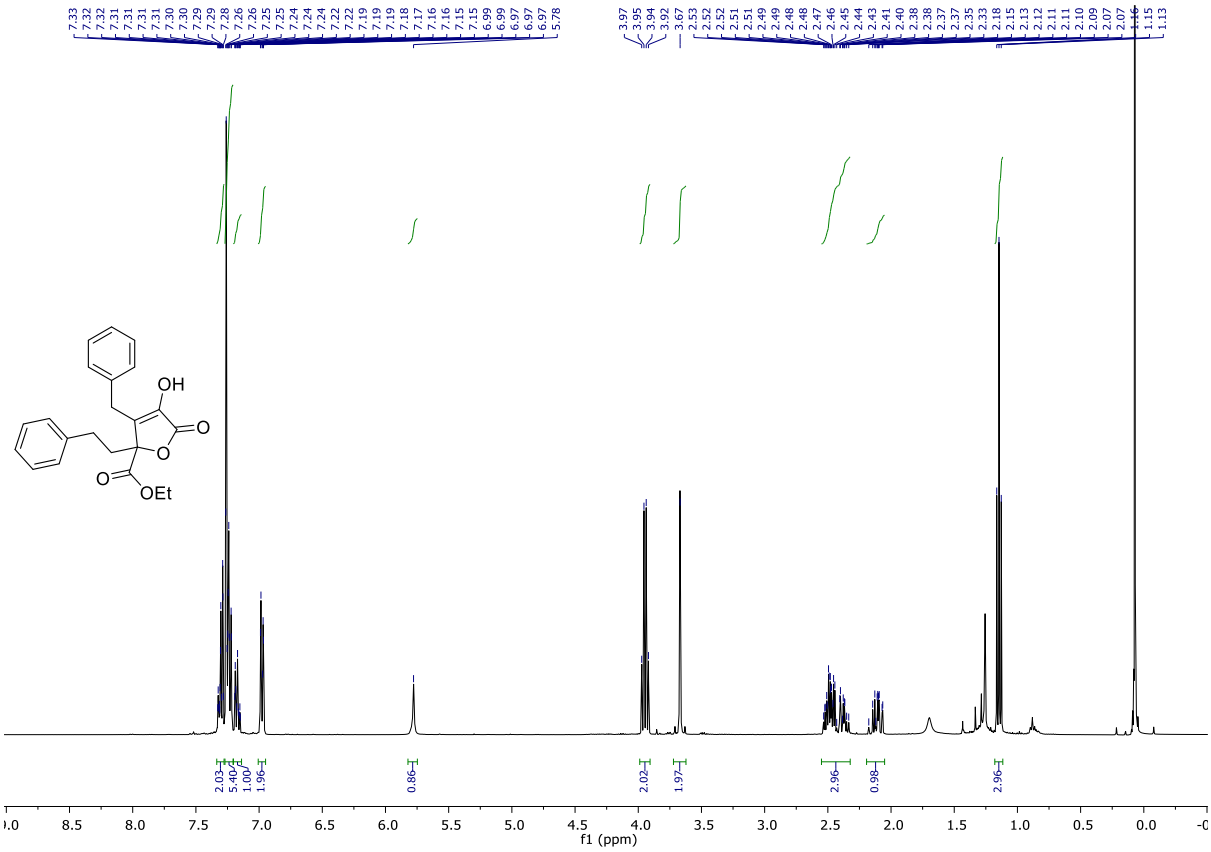
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6g**



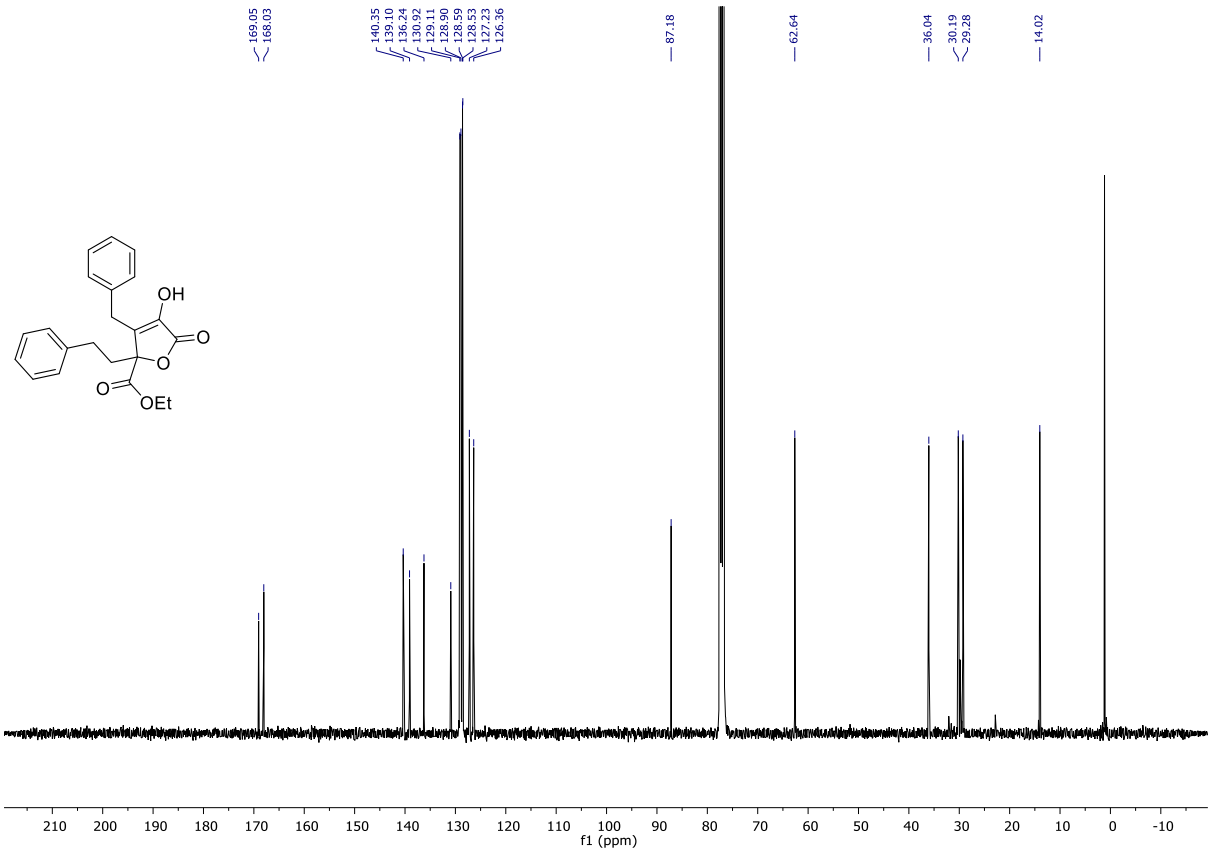
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **6g**



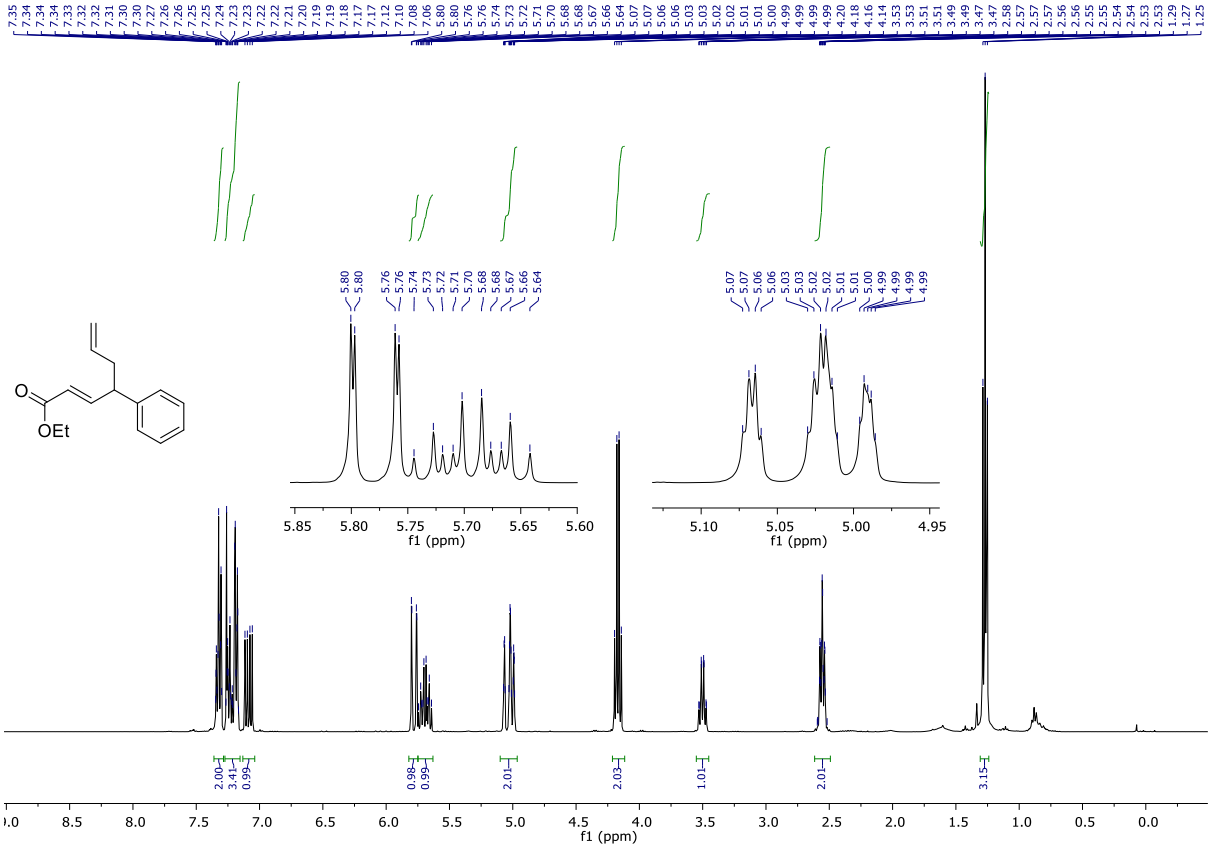
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9**



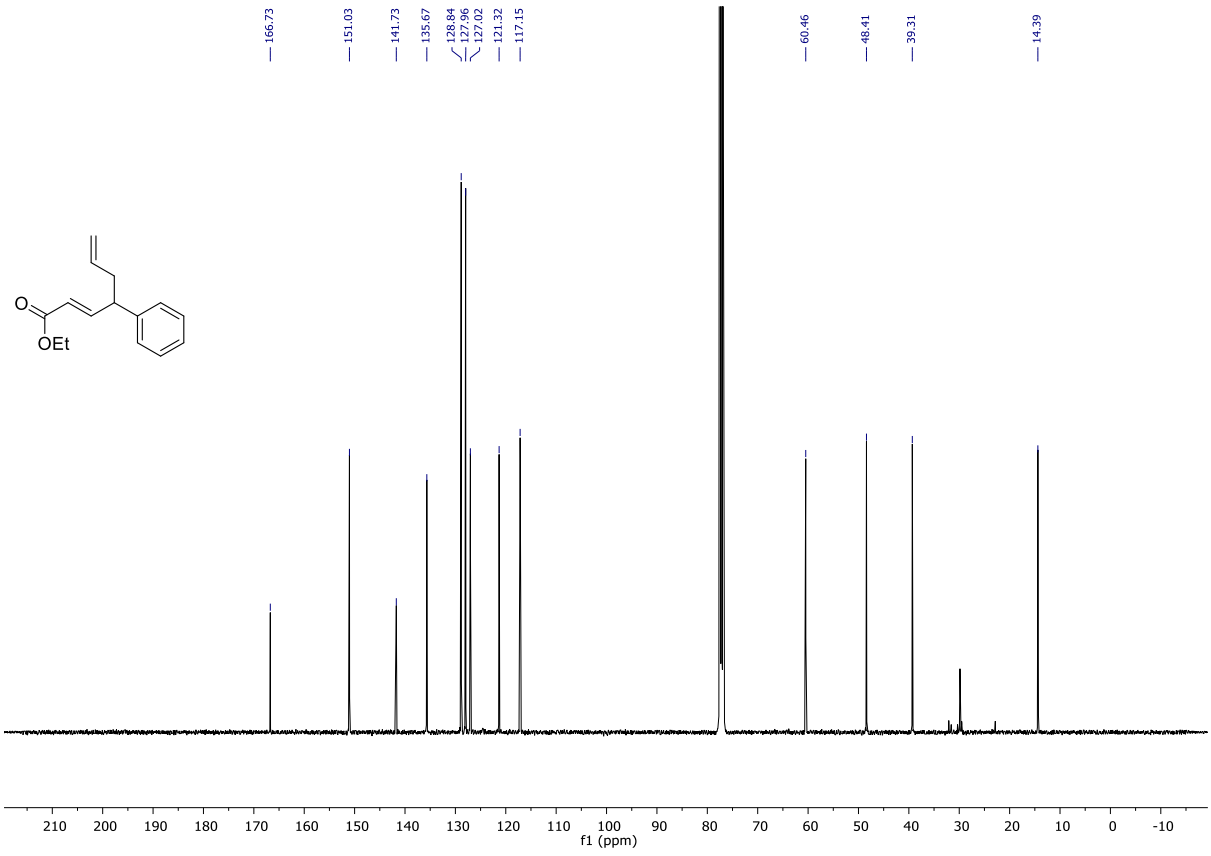
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9**



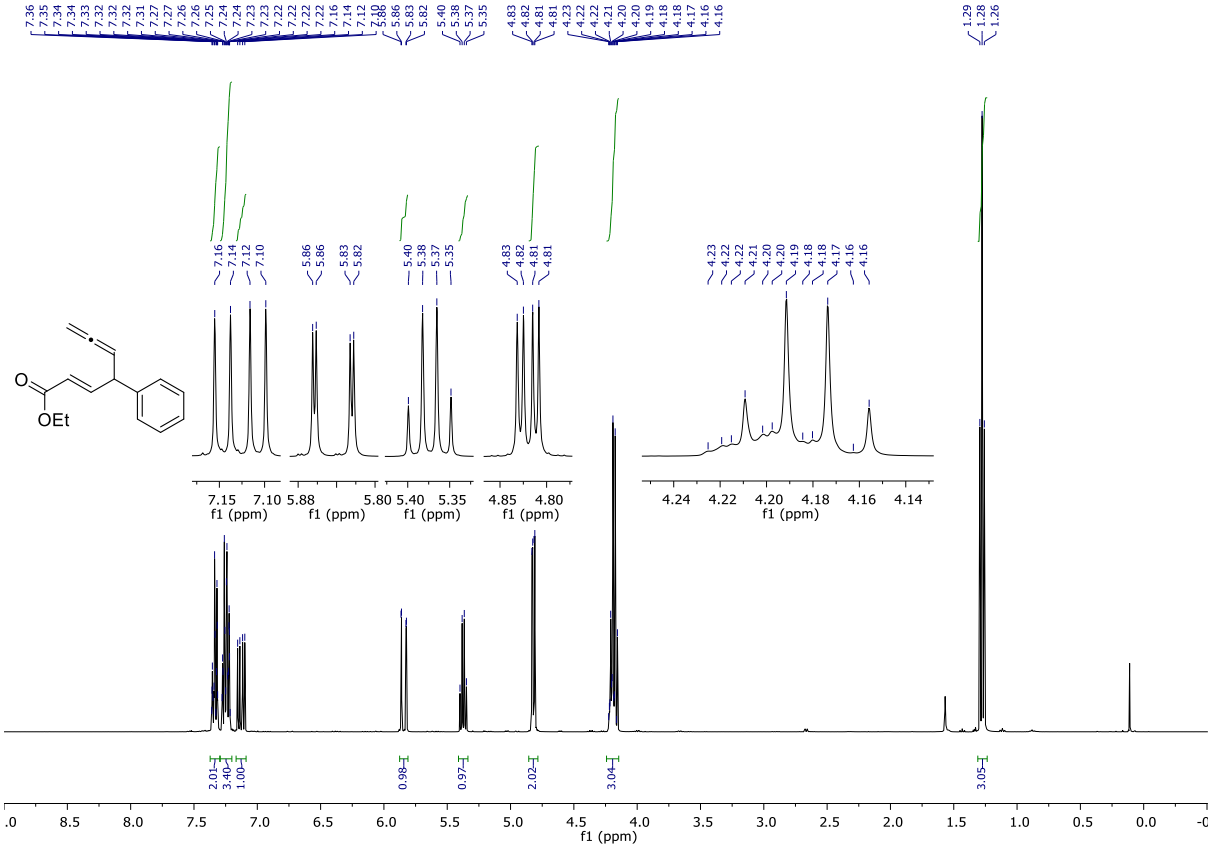
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **10**



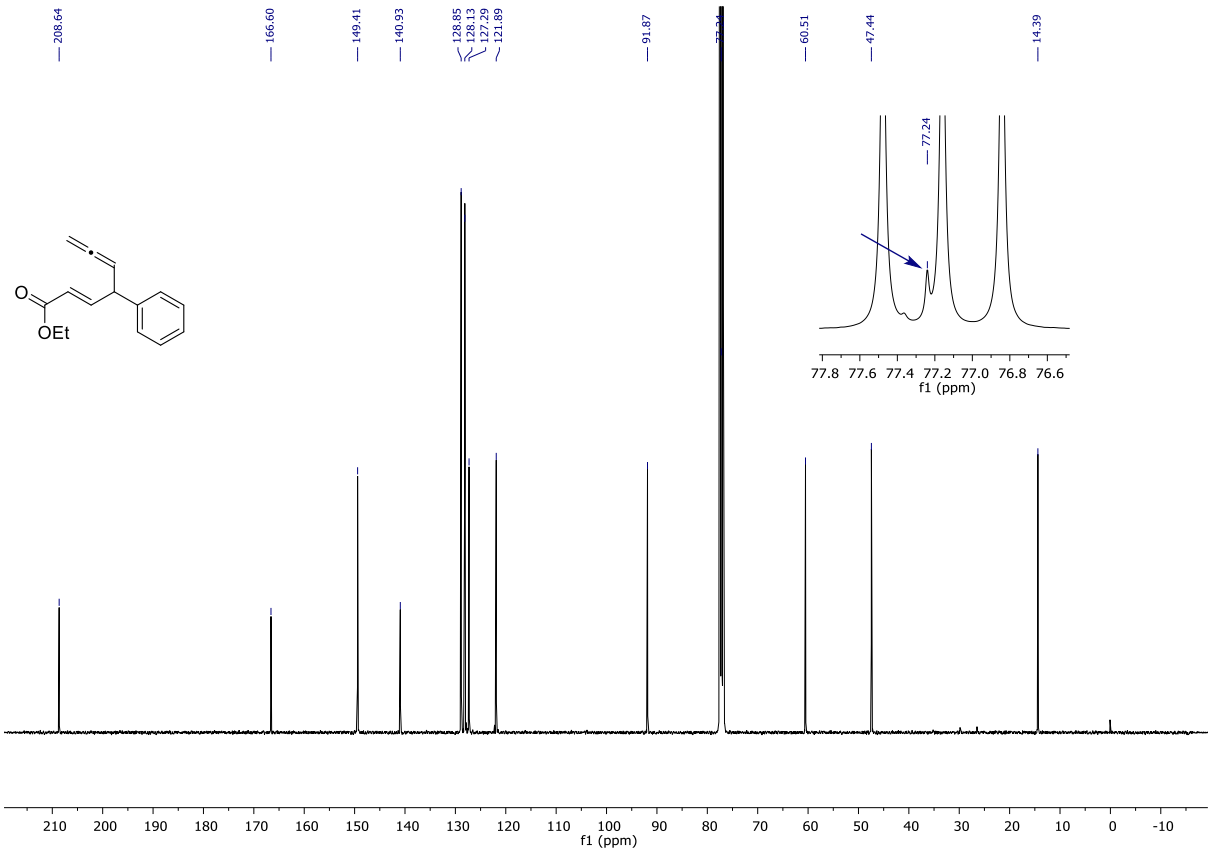
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **10**



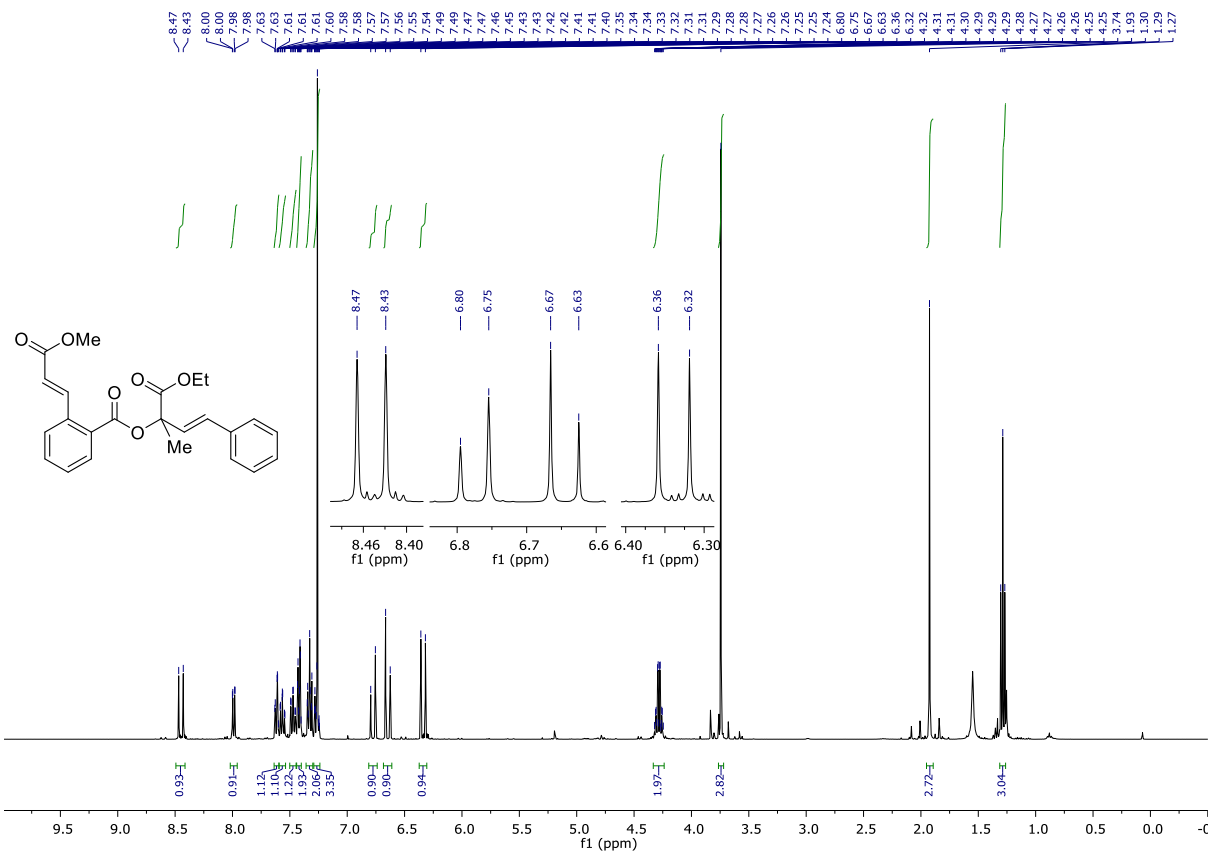
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **11**



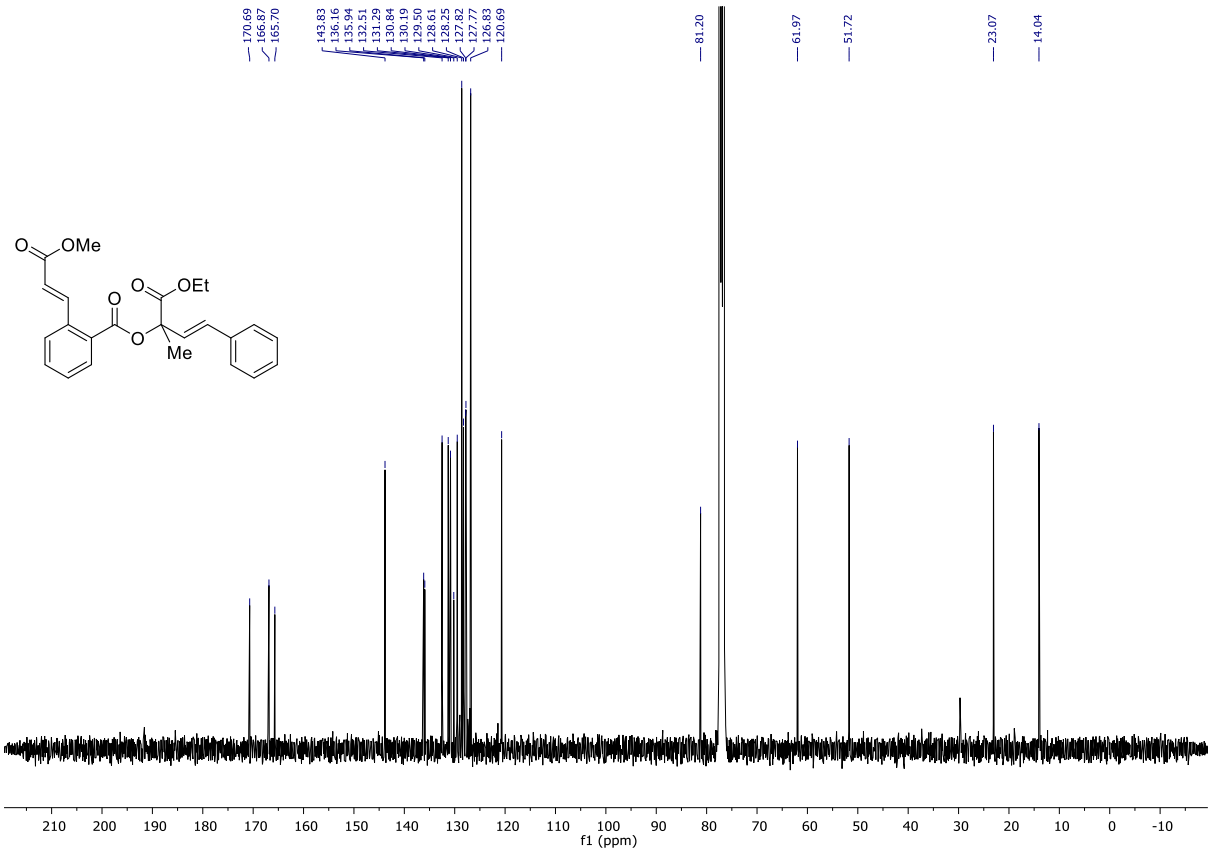
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **11**



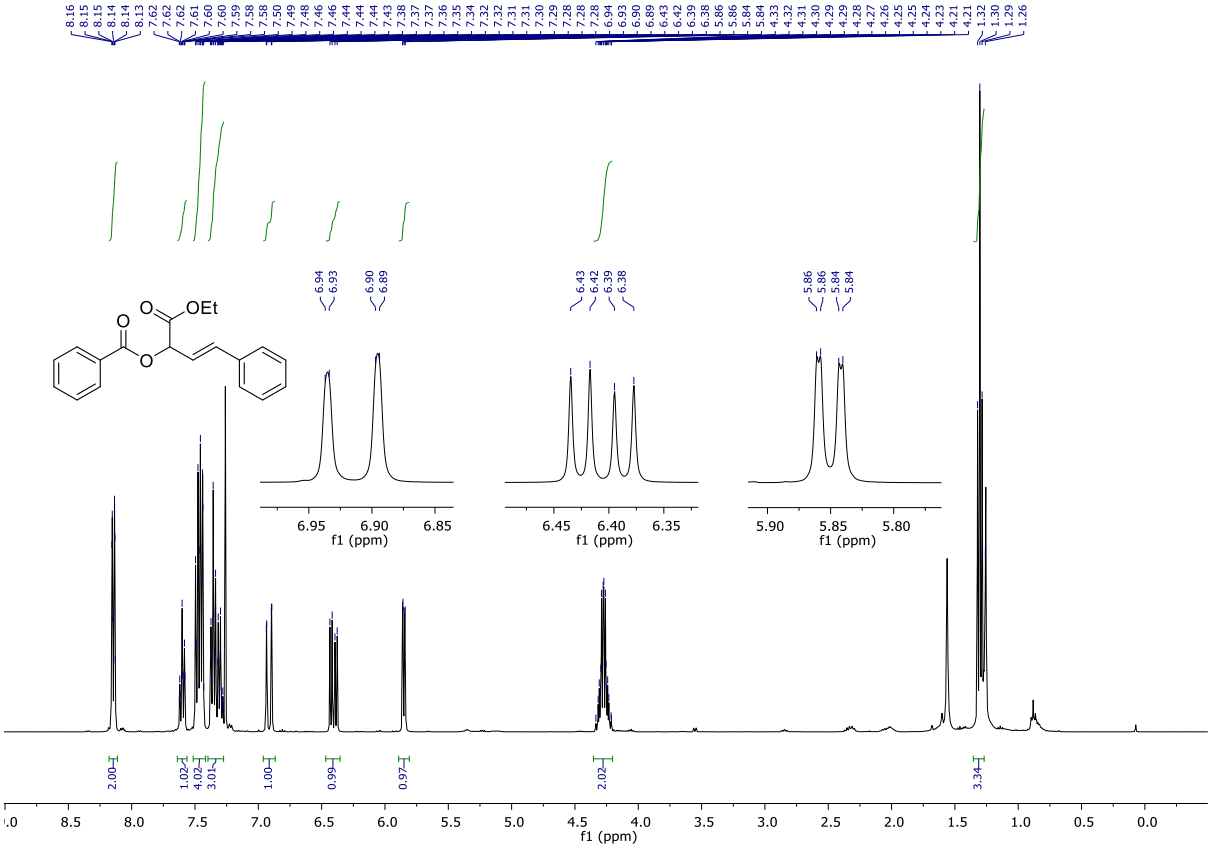
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **13**



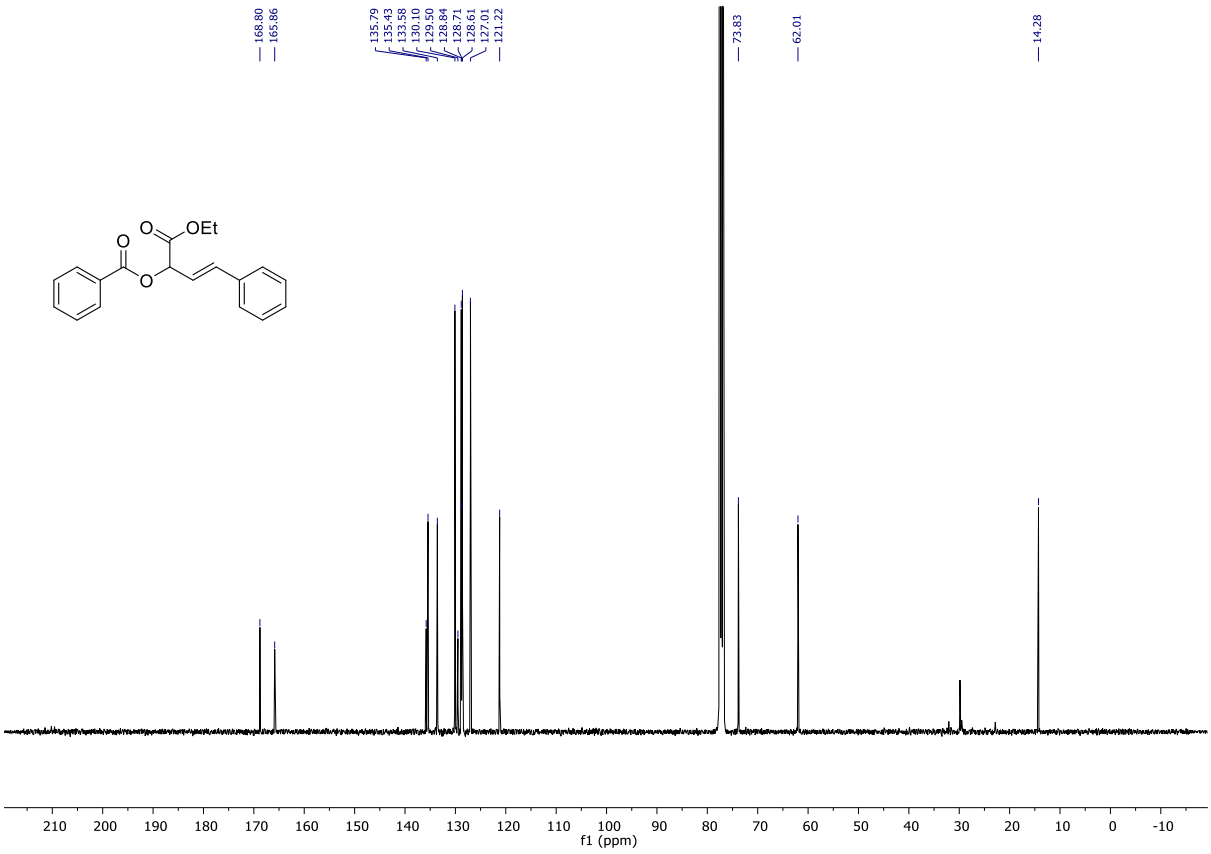
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **13**



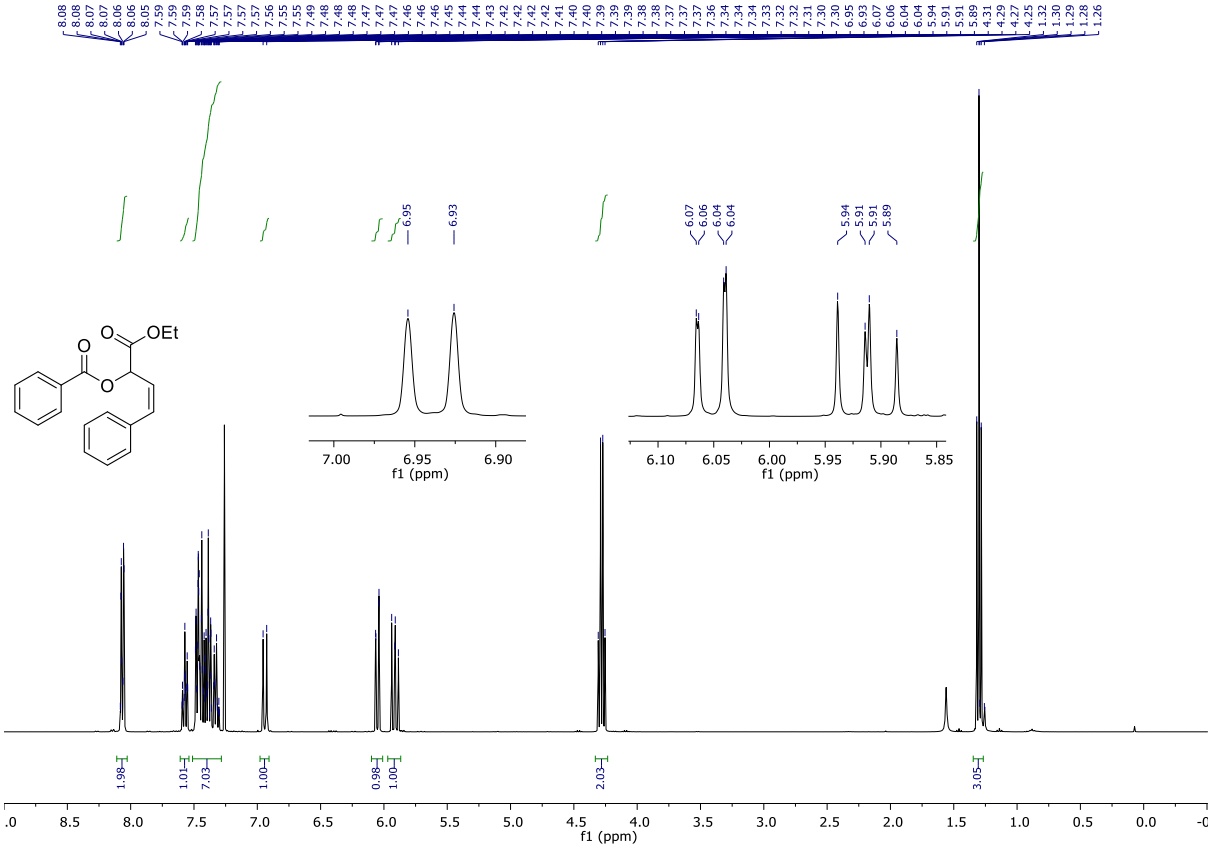
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **14**



^{13}C-NMR (101 MHz, $CDCl_3$) of compound **14**



^{1}H-NMR (400 MHz, $CDCl_3$) of compound **15**



^{13}C-NMR (101 MHz, $CDCl_3$) of compound **15**