An Access to Fully Substituted *β*-Iodo N-Arylated Enamines *via* Dehydrogenative Iodoarylation of Vinylogous Carbamates Using Phenyliodine(III) diacetate (PIDA)

A project report submitted as a part of requirements for the degree of

MASTER OF SCIENCE

By

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To The

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INDIAN INSTITUTE OF TECHNOLOGY, HYDERABAD
INDIA

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DECLARATION

I declare that this written submission represents my ideas in my own words, and where others ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

(Signature of the Supervisor)

Ajoy Chamuah

(Student's Signature)

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APROVAL SHEET

This thesis entitled **"An Access to Fully Substituted β-Iodo N-Arylated Enamines *via* Dehydrogenative Iodoarylation of Vinylogous Carbamates Using Phenyliodine(III) diacetate (PIDA)"** by **Ajoy Chamuah** is approved for the degree of Master of Science from IIT Hyderabad.

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Finally, I express respect to my parents and brothers for their love and encouragement for pursuing something extraordinary in my life.

Ajoy Chamuah

DEDICATED

TO

MY PARENTS AND BROTHERS

ABSTRACT

A novel and facile dehydrogenative iodoarylation of N-aryl vinylogous carbamates with hypervalent iodine (III) as the source of aryl and iodide has been developed. This protocol provides a valuable synthetic tool for the assembly of a wide range of β-iodo N-arylated enamines under mild conditions with functional group tolerance and scalability. This attractive route for the synthesis of β-iodo N-arylated enamines is of great importance due to the product versatile reactivity for further transformations.

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1.1 Introduction

a) Metal-Free transformations in organic synthesis

The contemporary synthetic world is now focusing on green chemistry to keep the environment green and healthy. Any synthetic works related to green chemistry are highly valued. In this regard, the development of a transition-metal-free approach for direct oxidative C-C or C-het bonds formation is certainly a topic of great interest in organic synthesis[1] since such transformations represent an attractive alternative to the traditional transition metal-catalyzed oxidative C-C or C-het coupling reactions.[2] Compounds of iodine having higher oxidation state are commonly known as hypervalent iodine compounds or reagents. In recent decades, hypervalent iodine reagents have emerged as a class of efficient and environmentally benign non-metal oxidants that can recognize the constructions of C-C or C-het bonds without the involvement of transition metals.[3]

b) Hypervalent Iodine reagents and literature Study

Among hypervalent iodine reagents, phenyliodine(III) diacetate(PIDA) **(Scheme 1**, eq. 1, 2, 5-7)[4], Phenyliodine(III) Bistrifluoroacetate(PIFA) (**Scheme 1**, eq. 3)[5] and iodosobenzene PhIO (Scheme1, eq. 4)[6] are widely used for elegant metal-free organic transformations, particularly, enamine derivatives as important precursors in organic transformations mediated by hypervalent reagents have been explored,[7] wherein iodobenzene is always formed as a by-product. For example as shown below.

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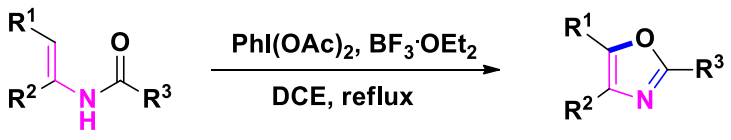

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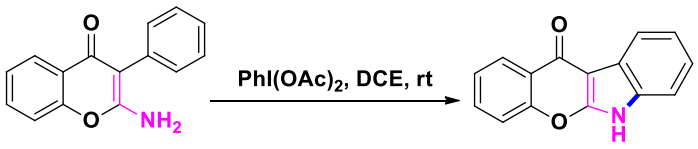

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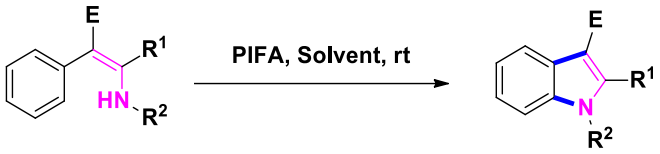

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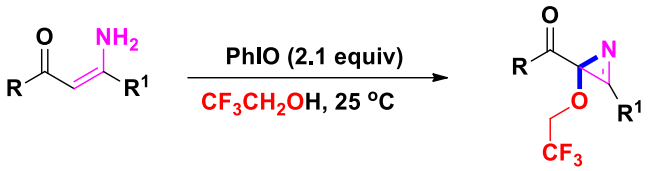

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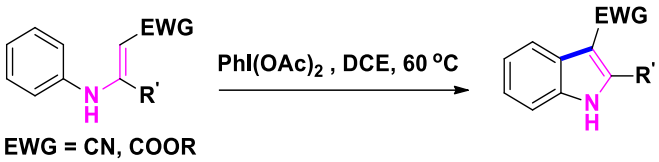

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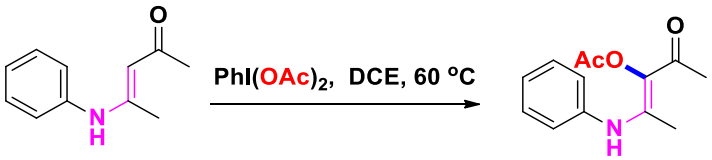

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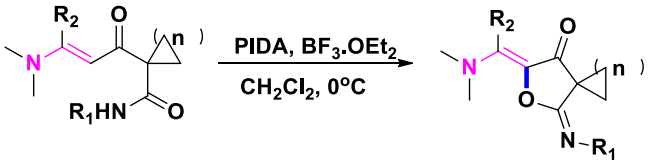
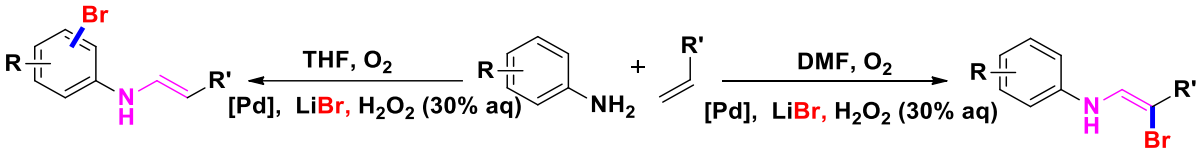


Scheme 1. Explorations of Enamine derivatives in organic transformations by hypervalent iodine reagents.

c) Importance of halogenated Enamines and literature methods

Halogenation and related reactions of unfunctionalized enamines are emerged as expedient tools, due to resulting products, particularly halogenated enamines are an important class of building blocks in both organic synthesis and medicinal chemistry.[8] The products can also be readily converted into numerous other valuable derivatives by replacing the halogen atoms through either intramolecular or intermolecular substitution reactions.[9] For example, iodinated enamine (**Scheme 3**, eq. 1)[10] used as a key precursor in the synthesis of central tryptophan core of **Celogentin C.** According to literature survey, a handful strategies also have been developed to incorporate iodide, arene group, and both arene as well as iodine into final products by using hypervalent iodine reagents. For example (i) α-iodination of β-cyclic enaminones using 1-[hydroxy(tosyloxy)iodo]-2,2,2-trifluoroethane (**Scheme 2**, eq. 5)[11] (ii) Copper-catalyzed direct arylation of cyclic enamides using diaryliodonium salts (**Scheme 2**, eq. 7),[12] (iii) Concurrent α-iodination and N-arylation of cyclic β-enaminones using PIDA (**Scheme 2,** eq. 8).[13]

1.



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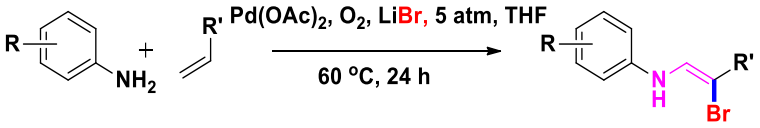

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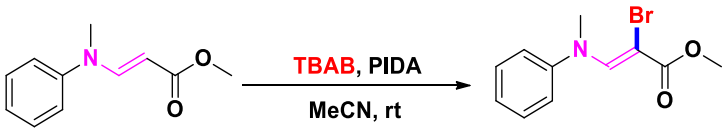

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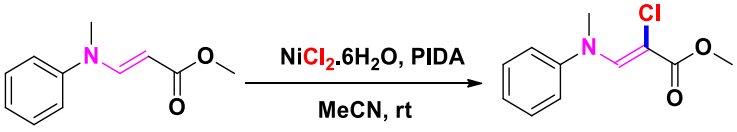

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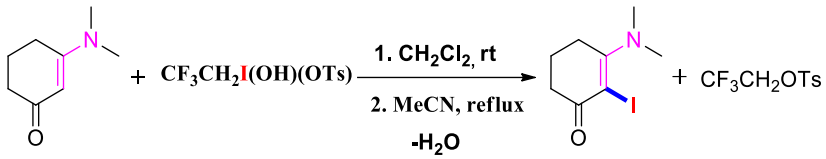

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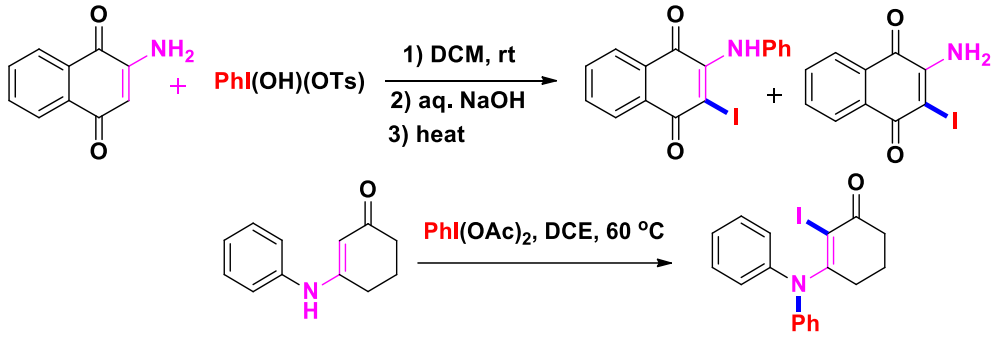

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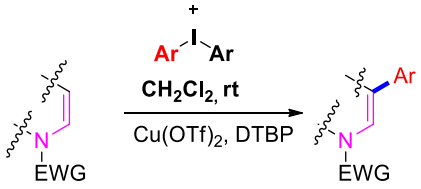
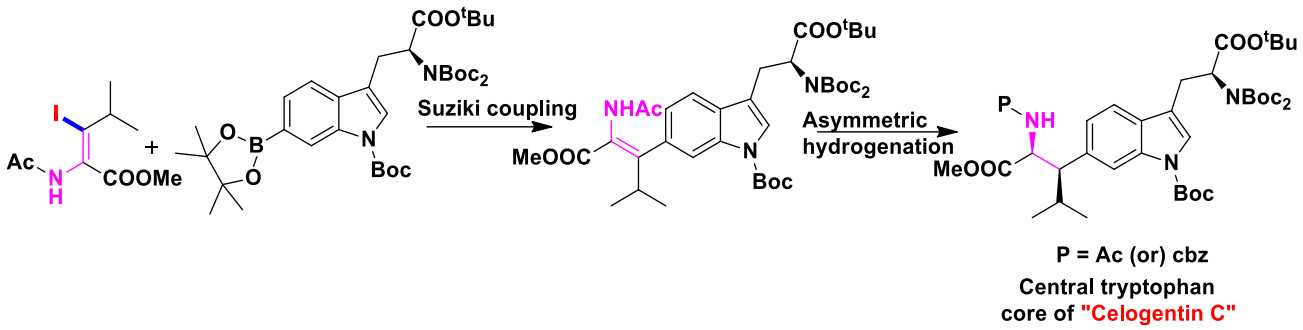


Scheme 2. Methods for synthesis of halogenated enamines.

Over the past decades, several attractive C−N bond forming methods have been developed using transition-metal catalysed or metal-free processes for the N-arylation of nitrogen-containing substrates with prefunctionalized compounds such as aryl halides and arylboronic acids.[14] However, the simultaneous construction of C–N and C–halogen bonds using hypervalent reagents as source of halogen and arene moiety in a tandem fashion is still challenging and desirable. Most recently, we have developed hypervalent iodine(III) promoted N-incorporation into N-aryl vinylogous carbamates to quinoxaline diesters using simple nitrogen sources under mild conditions.[15] As a continuation of our interest in the development of metal-free protocols[16] using hypervalent iodine reagents, herein we wish to report an efficient dehydrogenative iodoarylation of vinylogous carbamates using phenyliodine(III) diacetate (PIDA). To the best of our knowledge, the only example for the iodoarylation of cyclic *β*-enaminones using PIDA has been reported by Kang Zhao (**Scheme 2**, eq. 7).[11]

1.



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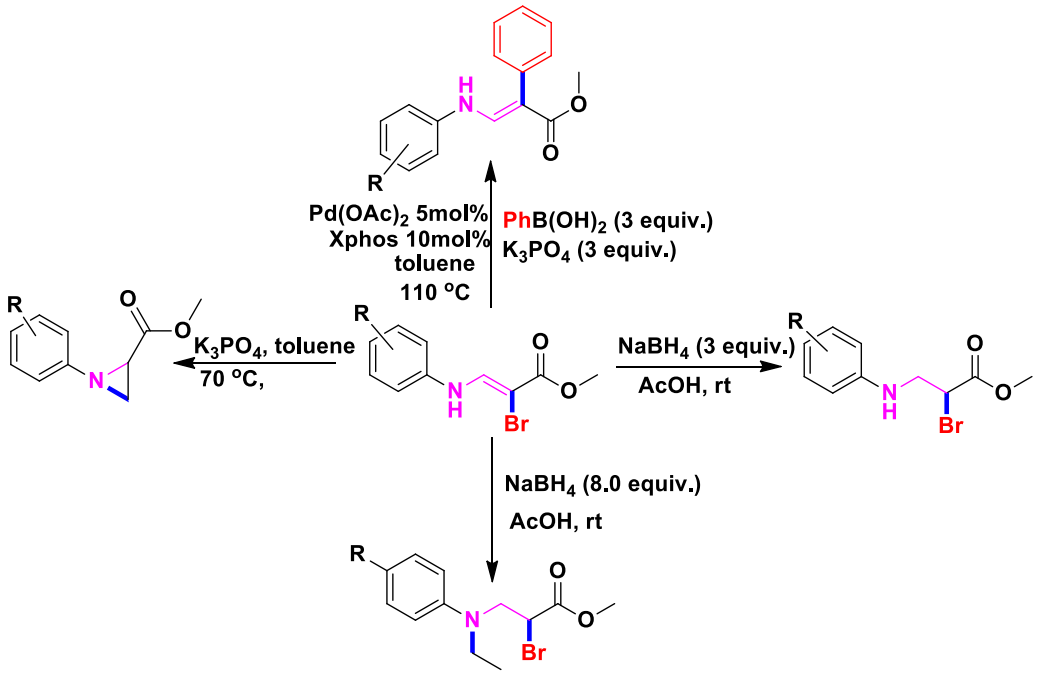
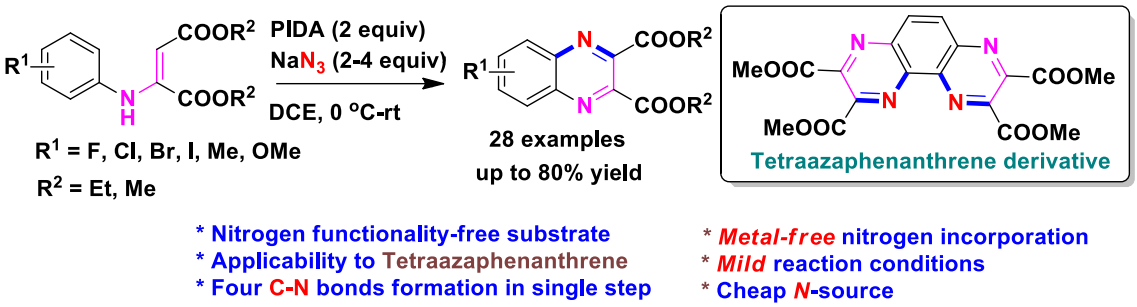


Scheme 3. Some important selected transformations of halogenated enamines

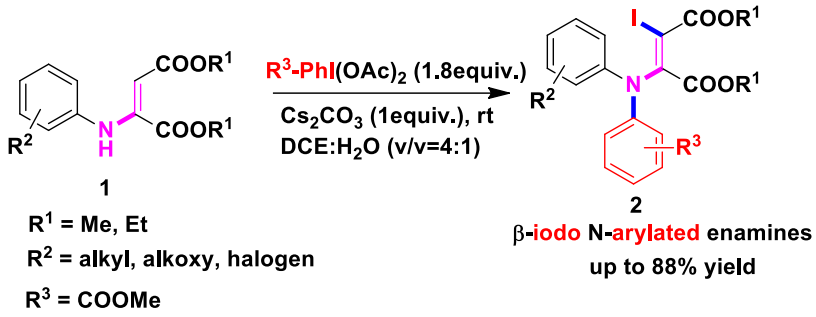
Our previous work:



* Nitrogen functionality-free substrate
* Applicability to Tetraazaphenanthrene
* Four C-N bonds formation in single step

* *Metal-free* nitrogen incorporation
* *Mild* reaction conditions
* Cheap *N*-source

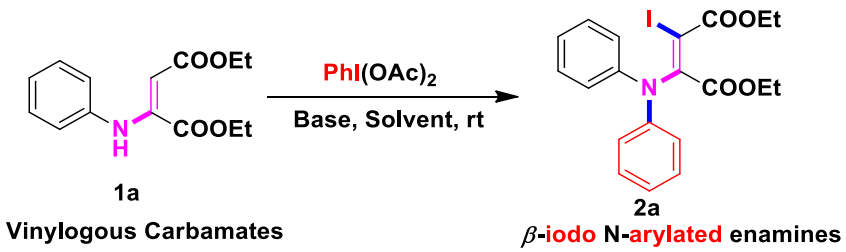
Our Present Work:



1.2 Results and Discussion

Initially, we investigated the reaction with readily prepared diethyl 2-(phenylamino)maleate (**1a**) under reported conditions[11] i.e. 1.5 equiv of PIDA, 60 ^{o} C, DCE (1,2 dichloroethane), unfortunately, the complex reaction mixture was formed rather desired *β*-iodo N-arylated enamine **2a**. Then we performed the reaction at rt (25 ^{o} C), afforded the expected product (**2a**) albeit in low yield (15%) (**Table 1**, entry 2). The structure of **2a** was confirmed by IR, NMR and HRMS. With this promising result in hand, we further optimized the reaction conditions. When the reaction was carried out in the presence of 4 equiv of Na_2SO_4 as additive, the product **2a** was yielded in 30 % after 18 h reaction time (**Table 1**, entry 3). No product was detected when the reaction performed with 2 equiv of TBAI (**Table 1**, entry 4). We then turned our attention to the bases screening to improve the reaction performance. When the reaction was performed with 1.3 equiv of Cs_2CO_3, to our delight, the product **2a** was obtained in 60% yield in 12 h (**Table 1**, entry 5). Other bases such as K_2CO_3, K_3PO_4, $NaHCO_3$, Na_2CO_3, and DABCO could not improve the yield of the product (**Table 1**, entry 6-10). We then screened the equivalents of PIDA and Cs_2CO_3, 1 equiv of Cs_2CO_3 and 1.8 equiv of PIDA were found to be the best conditions and afforded the product **2a** in 70 % yield in 12 h (**Table 1**, entry 13).

Table 1: Optimisation of *β*-Iodo and N-arylation of Vinylogous Carbamates*α*



1a
Vinylogous Carbamates

2a
β-iodo N-arylated enamines

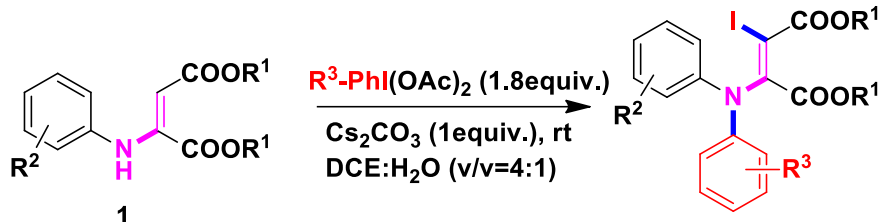
Entry	Iodide and aryl source (equiv.)	Base (equiv.)	Solvent	Time (h)	Yield (%)[a]
1	PIDA (1.5)	-----	DCE	12	0[b]
2	PIDA (1.5)	-----	DCE	14	15[c]
3	PIDA (1.5)	-----	DCE	18	30[d]
4	PIDA (1.5)	-----	DCE	24	0[e]
5	PIDA (1.5)	Cs_2CO_4 (1.3)	DCE	12	60
6	PIDA (1.5)	K_2CO_3 (1.3)	DCE	12	50
7	PIDA (1.5)	K_3PO_4 (1.3)	DCE	12	36
8	PIDA (1.5)	$NaHCO_3$ (1.3)	DCE	12	52
9	PIDA (1.5)	Na_2CO_3 (1.3)	DCE	12	46
10	PIDA (1.5)	DABCO (1.3)	DCE	12	ND
11	PIDA (1.3)	Cs_2CO_3 (1.3)	DCE	12	55
12	PIDA (2)	Cs_2CO_3 (1.3)	DCE	12	60
13	PIDA (1.8)	Cs_2CO_3 (1)	DCE	12	70
14	PIDA (1.8)	Cs_2CO_3 (1)	DCM	12	64
15	PIDA (1.8)	Cs_2CO_3 (1)	DCM	12	64
16	PIDA (1.8)	Cs_2CO_3 (1)	MeCN	12	61
17	PIDA (1.8)	Cs_2CO_3 (1)	THF	12	ND
18	PIDA (1.8)	Cs_2CO_3 (1)	H_2O	12	23
19	PIDA (1.8)	Cs_2CO_3 (1)	EtOAc	12	30
20	PIDA (1.8)	Cs_2CO_3 (1)	DCE: H_2O (v/v=5:1)	5	79
21	**PIDA (1.8)**	**Cs_2CO_3 (1)**	**DCE: H_2O (v/v=4:1)**	**4**	**88**
22	PIDA (1.8)	Cs_2CO_3 (1)	DCE: H_2O(v/v=3:2	4	80
23	PIDA (1.8)	Cs_2CO_3 (1)	DCE: H_2O (v/v=1:1)	4	75
24	PIDA (1.8)	Cs_2CO_3 (1)	MeCN: H_2O (v/v=4:1)	12	ND
25	PIDA (1.8)	Cs_2CO_3 (1)	DCM:H_2O (v/v=4:1)	4	83

Reaction conditions: **1a** (1 mmol), PIDA (1.8 mmol), Cs_2CO_3 (1 mmol), 3 mL DCE:H_2O (v/v=4:1), rt (27 °C) for 4 h; [a]isolated yield through silica column chromatography; [b]reaction was carried out at 60 °C; [c]reaction was carried out at 25 °C; [d]4 equivalent Na_2SO_4 was used; [e]2 equivalent TBAI was used; ND = not detected.

Among the solvents tested, DCE was found to be the best solvent choice (**Table1**, entries 13-19). Surprisingly, the experimental outcome showed that mixed solvent DCE/H_2O (v/v = 4:1) was found to be particularly effective to increase the yield of **2a** from 70 % to 88 % (**Table 1**, entry 21) in short reaction time (4 h). This is maybe due to hydrogen bonding between H_2O and ester functionalities, and some representative results are summarized in **Table 1**. Under the optimal reaction condition (**Table 1, entry 21**), the generality of the method was investigated.

In order to realise the versatility of this newly developed method, we anticipated to apply it to a series of enamines having different substituents *viz.* both weak electron withdrawing and electron donating groups on the phenyl ring of vinylogous carbamates. The results demonstrate that the substrates having weak electron- withd rawing substituents on the phenyl ring afforded the products (**Table 2**, **2c**, **2e**, **2i**, **2k** and **2o**) in good yield (73-86%), this may due to the stabilization of the intermediate **IV** by the weak electron withdrawing groups. The electron donating substituents (Me, OMe) destabilize the intermediate (**IV**) by giving electrons to the phenyl ring which results in relatively poor yield (**Table 2**, **2b**, **2h**, **2l**, **2n and 2p**). Presence of both weak electron withdrawing and electron donating groups on the same ring provided the products fairly in good yields (**Table 2**, **2d** and **2j**). Notably, unsubstituted vinylogous carbamates afforded the products in good yields (**Table 2**, **2a** and **2m**).

Table 2: Substrate Scope of *β*-Iodo and N-Arylated enamines



1

R^1 = Me, Et

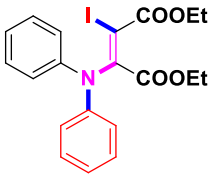
R^2 = alkyl, alkoxy, halogen

R^3 = COOMe

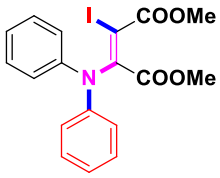
2

β-iodo N-arylated enamines

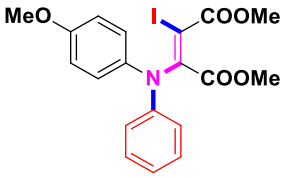
up to 88% yield



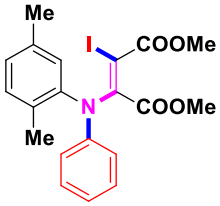
88%, 2a



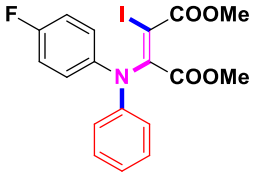
79%, 2b



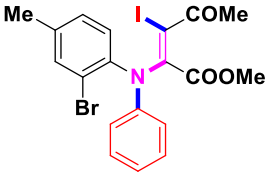
62%, 2c



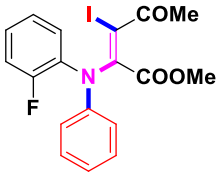
61%, 2d



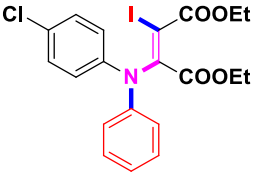
73%, 2n



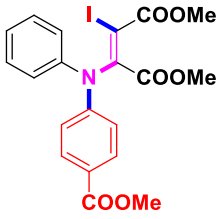
70%, 2f



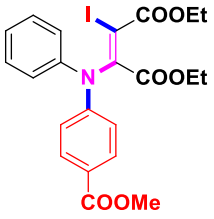
83%, 2g



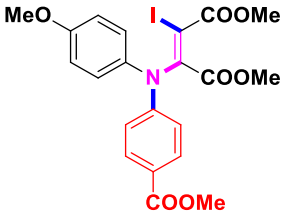
75%, 2h



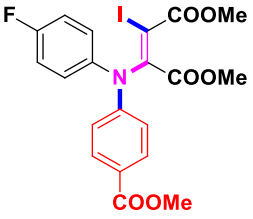
87%, 2i



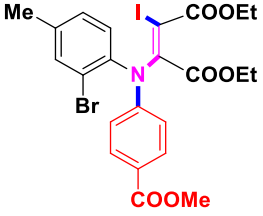
65%, 2j



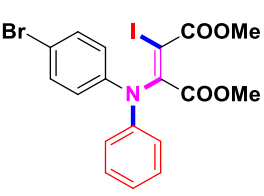
49%, 2k



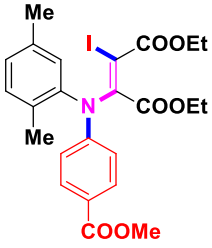
64%, 2l



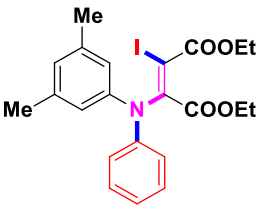
75%, 2m



73%, 2n



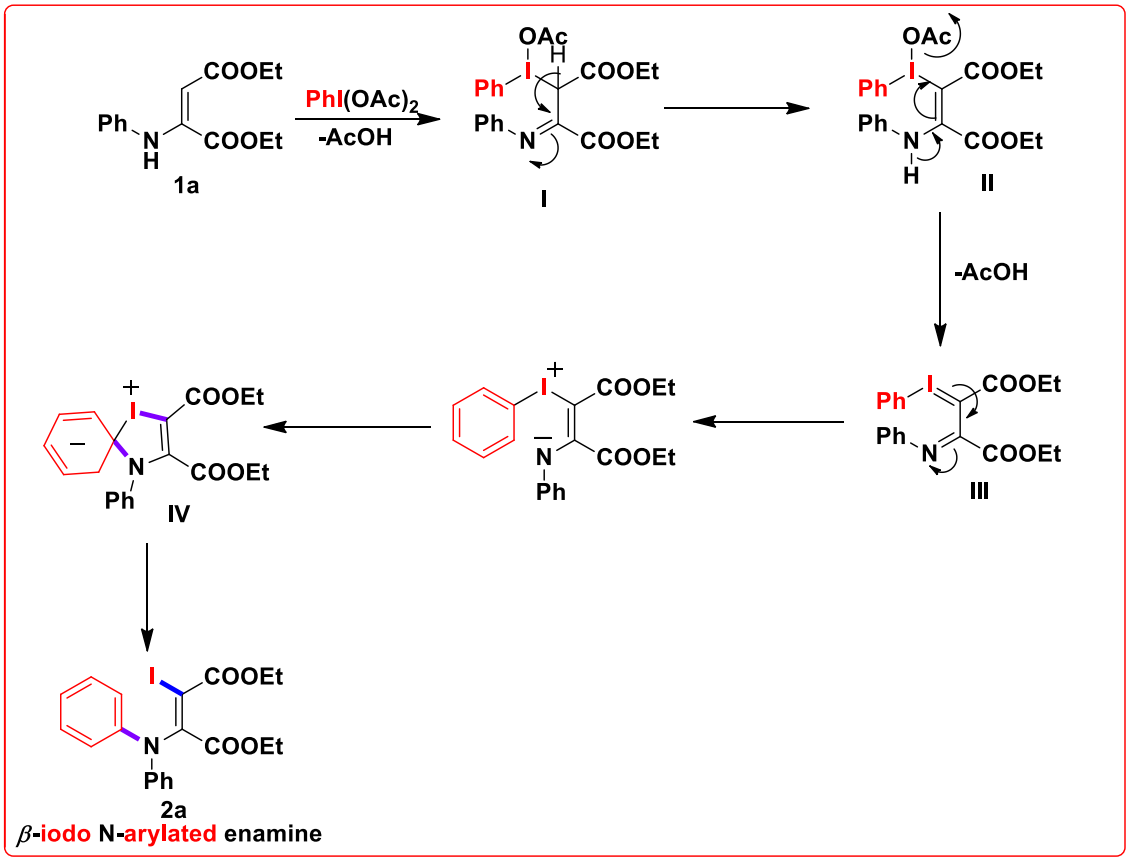
58%, 2o



60%, 2p

1.3 Mechanism

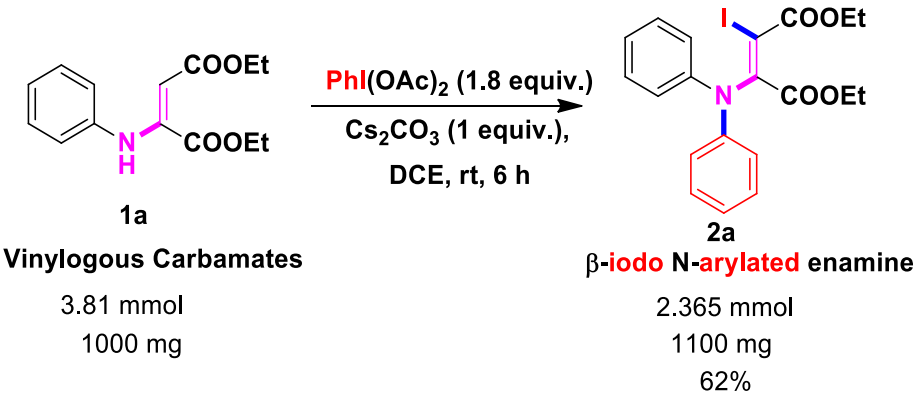
After successfully establishing the method, we looked forward to design the mechanistic pathway for this reaction. Based on the literature reports[17,11] we formulated the following plausible mechanism (**scheme 4**). In the first step the vinylogous carbamate is undergoing intermolecular reaction with $PhI(OAc)_2$ and forms an imine (**I**) having phenyliodo acetate moiety in the β-position. Further which transformed to intermediate (**III**) by the loss of AcOH. Deacetylation followed by subsequent rearrangement leads to the formation of a zweterion (**IV**) which is then transformed into the final product **2a**.



Scheme 4. Plausible mechanism

1.4. Large scale synthesis of *β*-iodo N-arylated enamine (2a)

After having successfully developed the syntheses of *β*-iodo N-arylated enamines (**2a-2p),** we have envisioned that these *β*-iodo N-arylated enamines could prove to be important starting materials for the synthesis of other complex molecules. Hence, we envisaged that it would be appropriate to check the scalability of our protocol for the synthesis of *β*-iodo N-arylated enamines. Accordingly, we performed the scaled-up reaction for the synthesis of *β*-iodo N-arylated enamines (**Scheme 5**), resulted in 62% yield.



Scheme 5. Large scale synthesis of 2a

1.5 Conclusion

We have developed a novel and facile approach for the synthesis of *β*-iodo N-arylated enamines by using Phenyliodine(III) diacetate as a source of iodide and aryl moiety. In this transformation, PIDA is not only facilitating the reaction but also incorporating into the product resulting the *β*-iodo N-arylated enamines. The significant feature of this reaction is the incorporation of iodide and aryl group concurrently in the same molecule. The advantages of this method are metal-free, mild reaction conditions and scalability. The synthesized *β*-iodo N-arylated compounds could prove important precursors in various organic transformations and our efforts in this direction are currently underway in lab.

1.6 Notes and References

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1.7 Experimental Sections

General Considerations

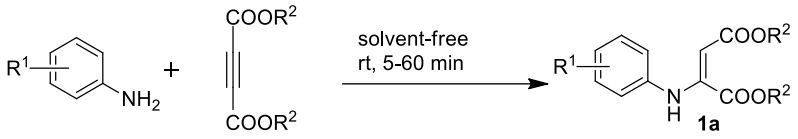
IR spectra were recorded on a FTIR spectrophotometer. ^{1}H NMR spectra were recorded on 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on 100 MHz spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{1}H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s. = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Q-TOF multimode source. Melting points (wherever required) were determined on an electrothermal melting point apparatus and are uncorrected. Hypervalent iodine reagent (PIDA) were purchased from Sigma Aldrich. All dry solvents used were dried over sodium metal and CH_3CN, DMF, DCE, DCM, HFIP, TFE which are commercial available were bought from sigma Aldrich.

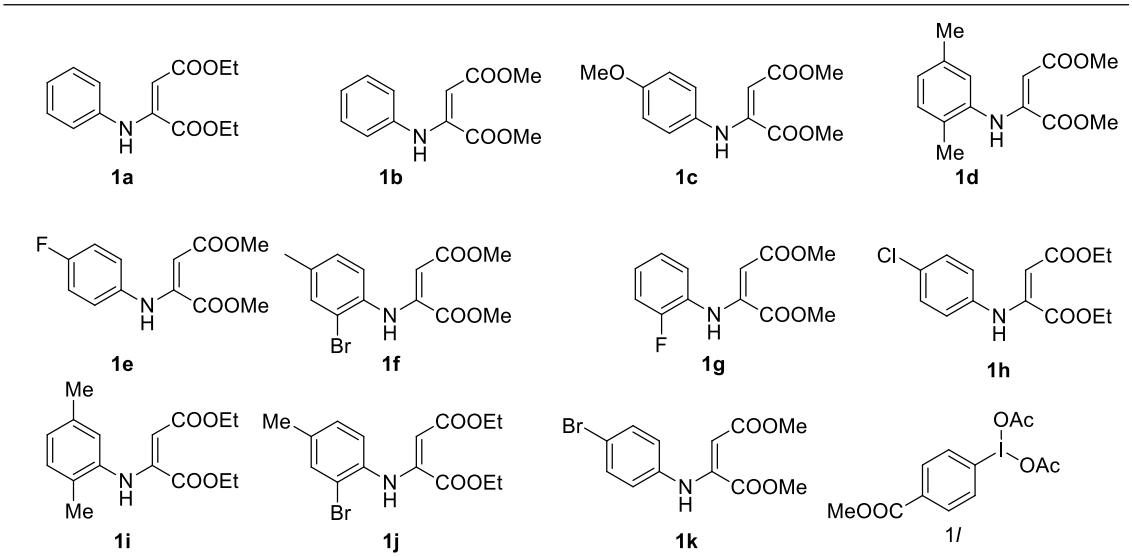
All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as eluents. Reactions were generally run in open air although only a few were run under argon or nitrogen atmosphere whichever necessary. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 ˚C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

I) General Procedure (GP-I) for the synthesis of (1a-1k)

Amine (1 mmol) was taken in a dried round bottom flask, and dialkyl acetylenedicarboxylate (1 mmol) was then added slowly with thorough mixing to form a homogeneous paste. Then the reaction mixture was stirred (if required) at room temperature for 5−60 min and then filtered through a short silica gel column using petroleum ether/ethyl acetate (9.8:0.2 to 9.6:0.4) as eluent to furnish the dialkyl-2-(phenylamino)maleate **1a-1k**. All the unknown compounds (**1d, 1i and 1j)** were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and HR-MS Spectral analyses. Compounds **1a-1c**, **1g, 1i-1k and 1*l*** were prepared using the reaction conditions reported in literature.

Following vinylogous carbamates were used as starting materials for the synthesis of iodinated enamines.





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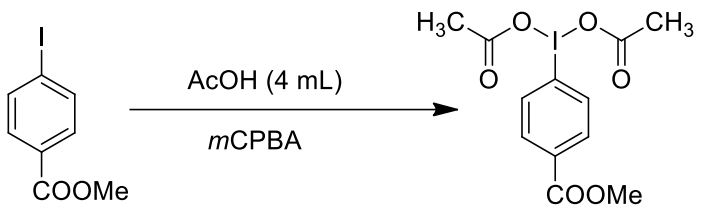
II) General procedure (GP-II) for the synthesis of 2a-2p

To a cold (0 °C), magnetically stirred solution of *N*-aryl vinylogous carbamates **1a-1k,** (0.19 mmol), Cs_2CO_3 (0.285 mmol) in DCE:H_2O in 3:1 ratio (3 mL), PIDA (0.38 mmol) was added portion wise for 10 minutes and the resulting mixture was stirred at room temperature (27 °C) for 2-3 h. Progress of the reaction was monitored by TLC until the reaction was completed. A distinct yellow coloured spot on TLC indicates the formation of the desired product. The reaction mixture was quenched by addition of aq. $Na_2S_2O_3$ (1.0 M, 5 mL) solution and extracted with EtOAc (3 × 10 mL). The organic layer was washed with saturated solution of $NaHCO_3$ and dried over Na_2SO_4, and concentrated in rotavapour. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate (9.7:0.3 to 9.3:0.7) as eluent furnished the iodinated enamine products **2a-2p**. All the compounds (**2a-2p**) were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and HR-MS Spectral analyses.

III) General procedure (GP-III) for the synthesis 4-Methoxycarbonyl [(Diacetoxy)iodo]benzene (1l)

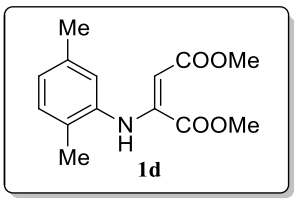
To a solution of methyl 4-iodobenzoate (1000 mg, 3.82 mmol) in AcOH (4 mL) was added MCPBA (ca. 65%, 757.46 mg, 4.39 mmol). The mixture was stirred at r.t. for 2 h. Then, H_2O (2 mL) was added to the reaction mixture and then it was extracted with $CHCl_3$ (3 × 20 mL). After being dried over Na_2SO_4, filtration, and removal of the solvent (residue ca. 3 mL), Et_2O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation. After filtration, the solids were washed with a mixture of Et_2O and hexane to provide product. 4-Methoxycarbonyl(diacetoxyiodo)benzene. Yield: 70%.



methyl 4-iodobenzoate

4-Methoxycarbonyl [(Diacetoxy)iodo]benzene

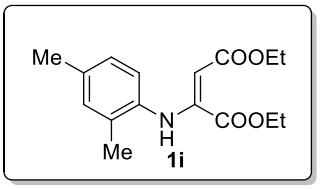
1.8 Spectral data of 1d, 1i, 1j and 2a-2p compounds



1d

Dimethyl 2-((2, 5-dimethylphenyl)amino)maleate (**1d**)

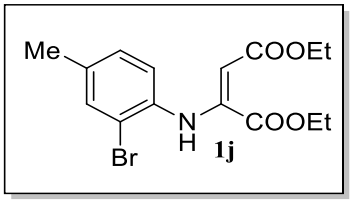
Yellow solid; (80%); mp 64−66 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3270, 2951, 1741, 1668, 1612, 1435, 1385, 1275, 1215, 1187, 1147, 1069, 1031, 798, 773; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.55 (br s, 1H), 7.00-6.93 (m, 2H), 6.63 (d, 1H, *J* = 7.3 Hz), 5.36 (s, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 2.3 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.3, 164.9, 149.4, 138.9, 137.8, 129.3, 126.8, 125.6, 119.7, 92.1, 52.7, 51.1, 20.5, 13.8; HR-MS (ESI+) m/z calculated for $[C_{14}H_{17}NNaO_4]^+$ = $[M+Na]^+$: 286.1050; found: 286.1061.



1i

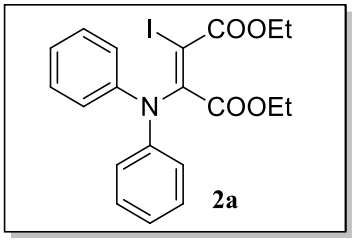
Diethyl 2-((2,4-dimethylphenyl)amino)maleate (**1i**)

Yellow viscous oil; (90%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3272, 2980, 1738, 1665, 1608, 1511, 1449, 1368, 1274, 1207, 1147, 1039, 813, 776; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.47 (br s, 1H), 6.99 (s, 1H), 6.88 (d, 1H, *J* = 8.3 Hz), 6.68 (d, 1H, *J* = 7.8 Hz), 5.33 (s, 1H), 4.19 (q, 2H, *J* = 7.3 Hz), 4.13 (q, 2H, *J* = 7.3 Hz), 2.3 (s, 3H), 2.27 (s, 3H), 1.30 (t, 3H, *J* = 7.1 Hz), 1.07 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.0, 164.4, 149.8, 136.5, 134.6, 131.3, 130.8, 126.9, 122.2, 91.8, 61.8, 59.8, 20.8, 17.8, 14.4, 13.6; HR-MS (ESI+) m/z calculated for $[C_{16}H_{21}NNaO_4]^+$ = $[M+Na]^+$: 314.1363; found: 314.1378.



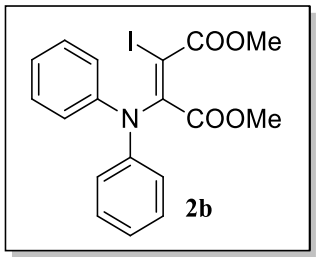
Diethyl 2-((2-bromo-4-methylphenyl)amino)maleate (1j)

Yellow viscous oil; (65%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3271, 2985, 2940, 1717, 1671, 1611, 1368, 1234, 1206, 1094, 1035, 856, 746, 673; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.65 (br s, 1H), 7.37 (s, 1H), 6.98 (d, 1H, *J* = 7.8 Hz), 6.7 (d, 1H, *J* = 8.3 Hz), 5.47 (s, 1H), 4.21 (q, 2H, *J* = 7.3 Hz), 4.16 (q, 2H, *J* = 7.24 Hz), 2.28 (s, 3H), 1.3 (t, 3H, *J* =7.1 Hz), 1.12 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.3, 164.0, 147.4, 136.3, 135.3, 133.3, 128.4, 121.7, 116.1, 95.0, 62.1, 60.1, 20.5, 14.4, 13.7; HR-MS (ESI+) m/z calculated for $[C_{15}H_{18}BrKNO_4]^+ = [M+K]^+$: 394.0051; found: 394.0052



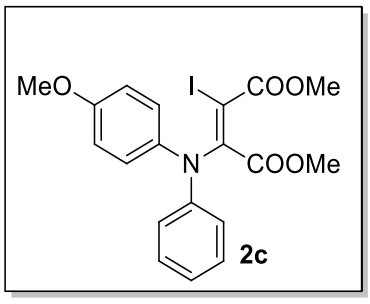
Diethyl 2-(diphenylamino)-3-iodomaleate (2a)

Yellow viscous oil; (88%, 31 mg); FT-IR (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 3034.9, 2980.5, 2936.4, 1729.9, 1491.7, 1288.1, 1219.4, 1041.4, 1027.6, 838.2, 756.9, 695.1; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.30 (m, 4H); 7.11 (m, 6H); 4.26 (m, 2H, J = 7.2 Hz); 4.02 (q, 2H, J = 6.8 Hz); 1.33 (t, 3H, J = 7.1 Hz); 0.96 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.3, 145.4, 144.5, 142.8, 141.8, 141.3, 133.3, 130.5, 102.6, 63.1, 14 .1; HR-MS (ESI+) m/z value calculated for $[C_{20}H_{20}INO_4]^+ = [M+H]^+$: 466.0510; found: 466.0498.



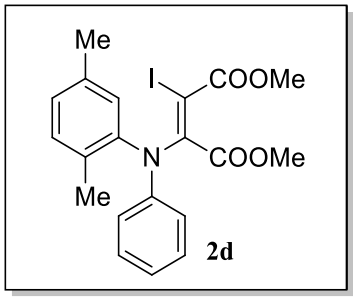
Dimethyl 2-(diphenylamino)-3-iodomaleate (2b)

Yellow gel; (79%, 29 mg); FT-IR: (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 3033.1, 3006.6, 2949.9, 2849.1, 1732.8, 1550.3, 1489.7, 1434.1, 1288.7, 1223.3, 1147.4, 1042.8, 988.8, 757.4, 695.2; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.30 (m, 4H); 7.1 (m, 6H); 3.80 (s, 3H); 3.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 166.2, 164.5, 149.5, 144.1, 129.3, 124.7, 124.0, 86.9, 53.5, 52.9; HR-MS (ESI+) m/z value calculated for $[C_{18}H_{16}INO_4]^+ = [M+K]^+$: 475.9756; found: 475.9749.



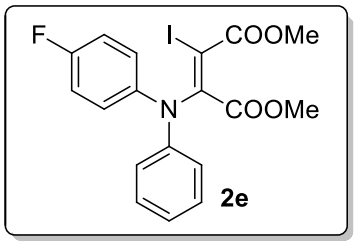
Dimethyl 2-iodo-3-((4-methoxyphenyl)(phenyl)amino)maleate (2c)

Yellowish gel; (61%, 22 mg); FT-IR: (MIR-ATR, 4000-600 cm^{-1}): 3002.0, 2950.2, 2837.7, 1731.2, 1546.9, 1505.4, 1433.7, 1242.1, 1220.0, 1145.9, 1031.6, 835.9, 758.7, 693.8; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.29 (m, 2H); 7.08 (m, 3H); 7.01 (d, 2H, J=7.8 Hz); 6.84 (d, 2H, J = 8.8 Hz); 3.80 (s, 6H); 3.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.0, 157.2, 154.5, 144.7, 137.0, 129.2, 126.7, 126.3, 124.2, 123.7, 123.4, 114.5, 83.5, 55.5, 53.5, 52.8; HR-MS (ESI+) m/z value calculated for $[C_{19}H_{18}INO_5]^+ = [M+H]^+$: 469.0335; found: 469.333.



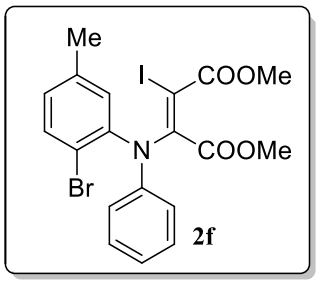
Dimethyl 2-((2, 5 dimethylphenyl)(phenyl)methyl)-3-iodomaleate (2d)

Yellowish gel; (61%, 22 mg); FT-IR: (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 2948.8, 1733.6, 1541.7, 1490.2, 1432.2, 1219.6, 1043.2, 988.7, 758.4, 718.8, 697.4: ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.24 (br s, 2H); 7.08 (m, 3H); 7.04 (m, 2H); 3.76 (s, 3H); 3.52 (s, 3H); 2.28 (s, 3H); 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.1, 164.8, 152.1, 144.9, 141.9, 138.5, 135.2, 129.1, 128.6, 126.3, 124.1, 123, 82.9, 53.5, 52.7, 20.6, 15.4; HR-MS (ESI+) m/z value calculated for $[C_{20}H_{20}INO_4]^+ = [M+H]^+$: 465.0437; found: 465.0431.



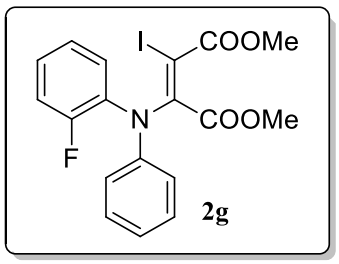
Dimethyl 2-((4-fluorophenyl)(phenyl)maleate)-3-iodomaleate (2e)

Yellow oil; (73%, 26 mg); FT-IR: (MIR-ATR, 400-600 cm^{-1}): ν_{max} = 2952.9, 2916.2, 2849.7, 1730.8, 1678.8, 1551.7, 1502.6, 1216.4, 1148.9, 616.8; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.29 (m, 2H); 7.09 (m, 3H); 7.02 (m, 4H); 3.80 (s, 3H); 3.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.1, 164.4, 161.1, 158.7, 149.6, 144.3 129.4 126.2, 124.6, 123.5, 116.3, 116.1, 86.5, 53.6, 53.9; HR-MS (ESI+) m/z value calculated for $[C_{18}H_{15}FINO_4]^+ = (M+NH_4)^+[-H_2O]$: 455.0262; found: 455.0255.



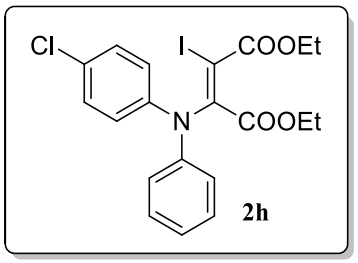
Dimethyl 2-((2-bromo-5-methylphenyl)(phenyl)amino)-3-iodomaleate (2f)

Yellow oil; (70%, 23 mg); FT-IT: : (MIR-ATR,4000-600 cm^{-1}): ν_{max} = 3002.8, 2928.4, 2890.4, 1720.6, 1555.7, 1429.7, 1420, 1230.6, 1078.9, 985.7, 760.5, 695.3; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.42 (s, 1H); 7.22 (d, 2H, J = 7.8 Hz); 7.12 (d, 3H, J = 8.3 Hz); 7.08 (s, 1H); 7.06 (s, 1H); 3.78 (s, 3H); 3.55 (s, 3H); 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.1, 164.5, 151.2, 144.3, 139.3, 138.3, 134.7, 129.7, 129.4, 129.1, 124.0, 123.1, 82.2, 53.5, 52.8, 20.8; HR-MS (ESI+) m/z value calculated for $[C_{19}H_{17}BrINO_4]^+ = [M+Na]^+$: 553.9260; found: 553.9271.



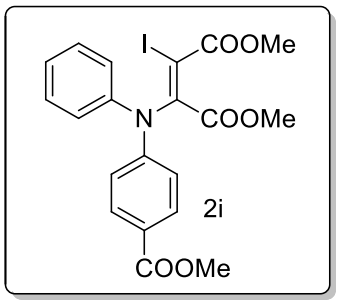
Dimethyl 2-((2-fluorophenyl)(phenyl)amino)-3-iodomaleate (2g)

Yellow oil; (83%, 30 mg); FT-IR: (MIR-ATR,4000-600 cm^{-1}): ν_{max} = 2951.5, 1990.1, 1731.9, 1590.7, 1497.3, 1434.2, 1299.9, 1230.6, 1043.2, 988.9, 757.4, 695.0: ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.27 (m, 4H); 7.12 (m, 3H); 6.97 (d, 2H, J = 7.8 Hz); 3.80 (s, 3H); 3.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.1, 164.1, 158.9, 156.4, 149.5, 136.4, 129.2, 124.95, 124.43, 121.77, 117.0, 116.8, 86.02, 53.56, 52.94; HR-MS(ESI+) m/z value calculated for $[C_{18}H_{15}FINO_4]^+ = [M+H]^+$: 456.0103; found: 456.0096.



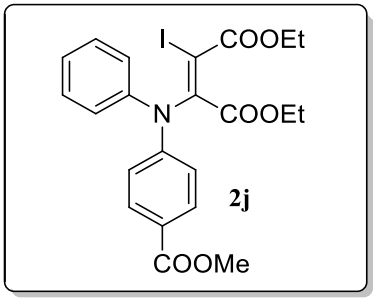
Diethyl 2-((4-chlorophenyl)(phenyl)amino)-3-iodomaleate (2h)

Yellow gel; (75%, 25); FT-IR: (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 2980.5, 2926.9, 2850.7, 1725.5, 1586.9, 1554.1, 1486.6, 1366.3, 1283.9, 1213.8, 1147.2, 1091.3, 1040.8, 823.6, 758.3, 695.5; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.29 (m, 4H); 7.11 (m, 3H); 7.04 (m, 2H); 4.27 (q, 2H, J = 7.3 Hz); 4.05 (q, 2H, J = 7 Hz); 1.33 (t, 3H, J = 7.1 Hz); 1.01(t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.7, 163.6, 148.6, 143.9, 142.9, 129.5, 129.4, 124.8, 123.8, 89.7, 62.8, 62.2, 13.9, 13.6; HR-MS (ESI+) m/z calculated for $[C_{20}H_{19}ClINO_4]^+$ = $[M+H]^+$: 499.0047; found: 499.0039.



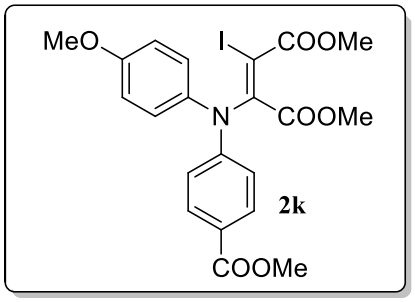
Dimethyl 2-iodo-3-((4-(methoxycarbonyl)phenyl)(phenyl)amino)maleate (2i)

Yellow gel; (87%, 36 mg); FR-IR: (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 3001.0, 2951.4, 2842.4, 1713.4, 1589.6, 1489.4, 1432.9, 1271.4, 1217.8, 1104.8, 1039.7, 800.8, 760.9, 695.6; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.96 (d, 2H, J = 8.8 Hz); 7.34 (m, 2H); 7.18 (d, 3H, J = 8.3 Hz); 7.05 (d, 2H, J = 8.8 Hz); 3.89 (s, 3H); 3.84 (s, 3H); 3.6 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.6, 166.1, 163.8, 148.3, 147.5, 142.9, 131.1, 129.6, 125.6, 124.9, 124.7, 121.2, 92.7, 53.6, 53.0, 52.0; HR-MS (ESI+) m/z value calculated for $[C_{20}H_{18}INO_6]^+$ = $(M+K)]^+[H_2O]$:515.9705; found : 515.9701.



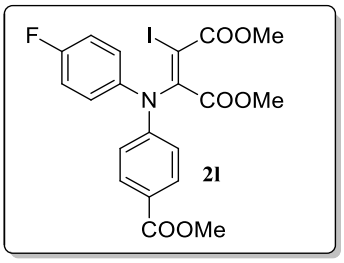
Diethyl 2-iodo-3-((4-(methoxycarbonyl)phenyl)(phenyl)amino)maleate (2j)

Yellow oil; (65%, 29 mg); FT-IR : (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 2982.2, 2952.2, 1714.8, 1590.5, 1506.7, 1489.8, 1434.6, 1366.6, 1271.9, 1216.4, 1175.6, 1106.7, 1039.5, 767.5, 695.5; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.96 (d, 2H, J = 8.8 Hz); 7.34 (m, 2H); 7.17 (m, 3H); 7.07 (d, 2H, J = 8.3 Hz); 4.29 (q, 2H, J = 7.2 Hz); 4.05 (q, 2H, J = 6.8 Hz); 3.89 (s, 3H); 1.35 (t, 3H, J = 7.3 Hz); 1.01 (t, 3H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.6, 165.7, 163.1, 148.5, 147.2, 143.1, 131.0, 129.5, 125.5, 124.8, 124.7, 121.2, 93.7, 62.8, 62.3, 52.0, 13.9, 13.6; HR-MS (ESI+) m/z value calculated for $[C_{22}H_{22}INO_6]^+ = [M+H]^+$: 523.0492; found: 523.0488.



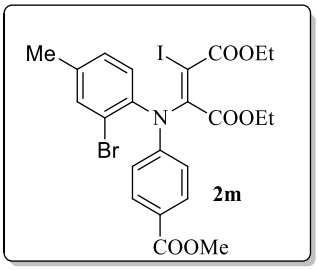
Dimethyl 2-iodo-3-((4-methoxycarbonyl)phenyl)(4-methoxyphenyl)aminomaleate (2k)

Yellow gel; (49%, 19 mg); FT-IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2952.1, 2924.2, 2851.7, 1719.9, 1605.7, 1506.6, 1434.1, 1277.0, 1245.4, 1176.7, 1109.6, 1035.7, 838.2, 769.1, 696.9; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.93 (d, 2H, J = 8.8 Hz); 7.14 (d, 2H, J = 8.8 Hz); 6.96 (d, 2H, J = 8.8 Hz); 6.88 (d, 2H, J = 8.8 Hz); 3.89 (s, 3H); 3.82 (s, 3H); 3.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.6, 166.0, 164.0, 157.8, 148.8, 148.1, 135.5, 131.0, 127.3, 124.4, 120.0, 114.7, 90.3, 55.5, 53.6, 53.0, 52.0; HR-MS (ESI+) m/z value calculated for $[C_{21}H_{22}INO_7]^+ = [M+H]^+$: 525.0284; found: 525.0280.



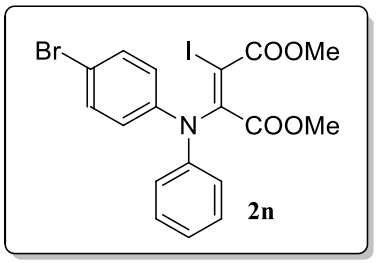
Dimethyl 2-((4-fluorophenyl)(4-(methoxycarbonyl)phenyl)amino)-3-iodomaleate (2l)

Yellow gel; (64%, 26 mg); FT-IR: (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 3001.7, 2952.1, 2848.0, 1714.2, 1600.42, 1502.6, 1433.3, 1275.2, 1212.6, 1104.1, 1039.8, 986.4, 839.6, 768, 696.6; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.95 (d, 2H, J = 8.8 Hz); 7.17 (m, 2H); 7.05 (m, 2H); 6.99 (d, 2H, J = 8.3 Hz); 3.89 (s, 3H); 3.84 (s, 3H); 3.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.5, 165.9, 163.7, 161.6, 148.4, 147.4, 138.9, 131.2 126.9, 124.9, 124.4, 120.6, 116.6, 116.4, 92.6, 53.7, 53.1, 53.0; HR-MS (ESI+) m/z value calculated for $[C_{20}H_{17}FINO_6]^+$ = $[M+H]^+$:513.0085; found: 513.0078.



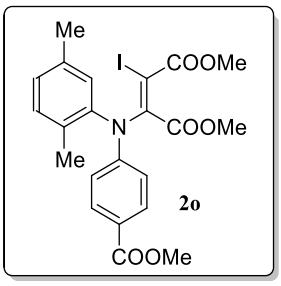
Diethyl 2-((3-bromo-5-methylphenyl(4-(methoxycarbonyl)phenyl)amino-3-iodomaleate (2m)

Yellow gel; (75%, 26 mg); FT-IR: (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 2981.3, 2951.9, 1714.3, 1606.8, 1565, 1486.9, 1434.4, 1275, 1215.6, 1104.8, 1014.3, 850.3, 768.5, 735.2, 696.5; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.93 (m, 2H); 7.45 (s, 1H); 7.24 (s, 1H); 7.18 (s, 1H); 6.95 (br s, 1H); 6.74 (br s, 1H); 4.25 (q, 2H, J = 7.3 Hz); 4.03 (q, 2H, J = 6.8 Hz); 3.88 (s, 3H); 2.36 (s, 3H); 1.32 (t, 3H, J = 7.1 Hz); 1.02 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.6, 165.6, 163.5, 149.0, 148.4, 138.7, 138.3, 134.8, 130.8, 129.7, 129.3, 124.8, 123.0, 89.3, 67.1, 62.8, 62.3, 52.0, 20.8, 13.9, 13.6; HR-MS (ESI+) m/z value calculated for $[C_{23}H_{23}BrINO_6]^+$ = $[M+H]^+$: 614.9753; found: 614.9749.



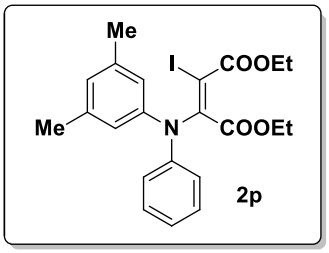
Dimethyl 2-((4-bromophenyl)(phenyl)amino)-3-iodomaleate (2n)

Yellow gel; (73%, 24 mg); FT-IR(MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 2951.6, 2923.2, 2851.3, 1729.9, 1552.4, 1485.4, 1433.2, 1219.9, 1146.6, 1043, 986.7, 816, 733, 695; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.40 (d, 2H, J = 8.8 Hz); 7.31 (m, 2H); 7.13 (s, 1H); 7.08 (d, 2H, J = 7.8 Hz); 6.96 (d, 2H, J = 8.8 Hz); 3.81 (s, 3H); 3.59 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.1, 164.1, 148.6, 143.7, 143.3, 132.4, 129.4, 125.1, 124.9, 123.9, 117.3, 88.9, 53.6, 53.0; HR-MS (ESI+) m/z value calculated for $[C_{18}H_{15}BrINO_4]^+ = [M+K]^+$: 514.9229; found: 514.9231.



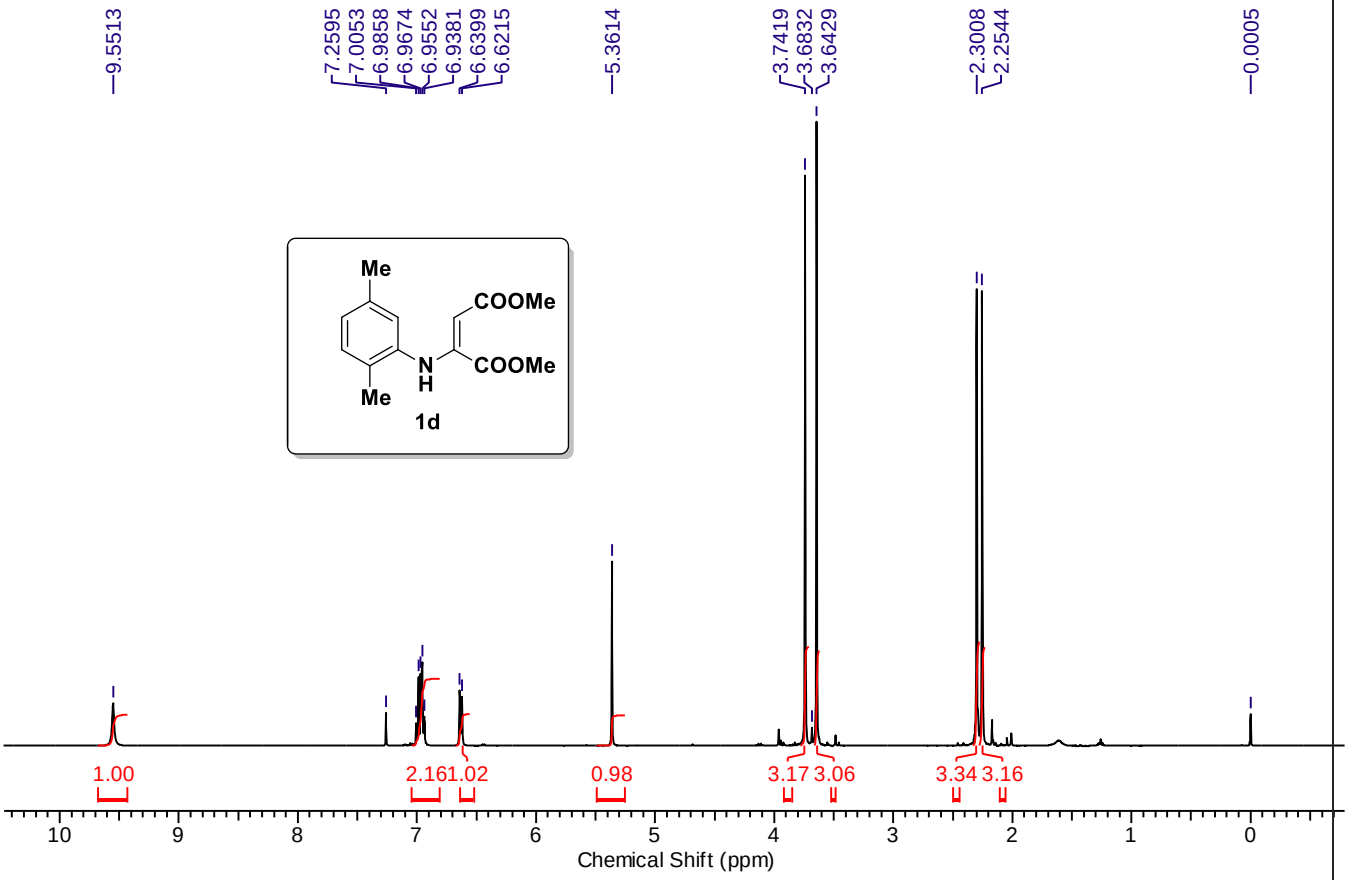
Dimethyl 2-((2, 5-dimethylphenyl)(4-methoxycarbonyl)phenylamino)-3-iodomaleate (2o)

Yellow oil; (58%, 22 mg); FT-IR: (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 2951.5, 2919.1, 2850.4, 1719, 1604.3, 1510.6, 1506.4, 1434.4, 1276.6, 1231.3, 1175.9, 1106.9, 1041.5, 770.3, 603.8; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.92 (br s, 2H); 7.11 (s, 1H); 7.03 (s, 1H); 6.99 (s, 1H); 6.9 (br s, 1H); 6.8 (br s, 1H); 3.88 (s, 3H); 3.81 (s, 3H); 3.56 (s, 3H); 2.30 (s, 3H); 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.6, 165.9, 164.3, 150.0, 148.5, 140.4, 137.2, 133.2, 131.6, 130.9, 128.5, 124.7, 121.0, 84.9, 53.6, 52.9, 52.0, 20.9, 18.7; HR-MS (ESI+) m/z value calculated for $[C_{22}H_{22}INO_6]^+ = [M+H]^+$: 523.3177; found: 523.3174.

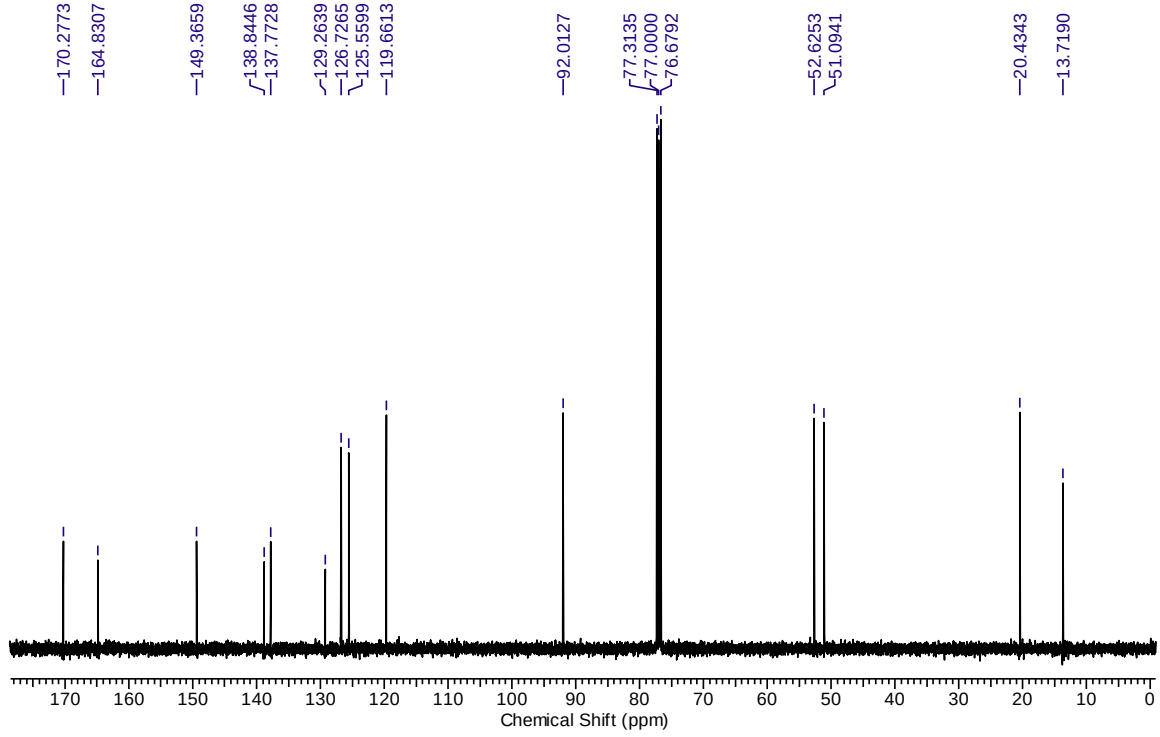


Diethyl 2-((3, 5-dimethylphenyl)(phenyl)amino)-3-iodomaleate (2p)

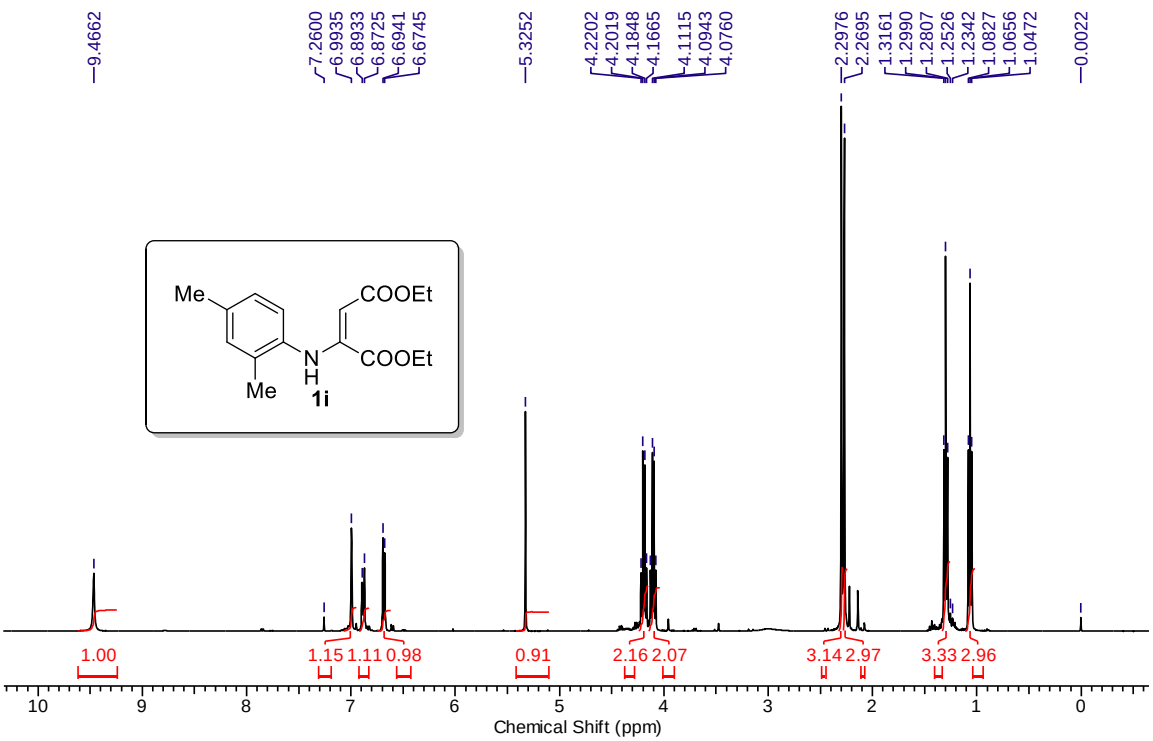
Yellow gel; (60%, 20 mg); FT-IR: (MIR-ATR, 4000-600 cm^{-1}): ν_{max} = 2998.4, 2945.1, 2818.4, 1718.9, 1600.3, 1500.6, 1498.4, 1419.3, 1216.5, 1200.8, 1143.4, 1100.8, 1032, 769.7, 693.2. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.23 (d, 2H, J = 6.4 Hz); 7.07, (m, 2H); 6.97 (m, 3H); 6.83 (br s, 1H); 4.21 (d, 2H, J = 7.3 Hz); 3.98 (d, 2H, J = 7.3 Hz); 2.28 (s, 3H); 2.04 (s, 3H); 0.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.8, 164.2, 151.7, 144.8, 141.2, 136.2, 133.7, 131.4, 129.0, 128.8, 127.7, 123.9, 123.2, 80.2, 62.5, 61.9, 21.7, 20.9, 18.8, 14, 13.5; HR-MS (ESI+) m/z value calculated for $[C_{22}H_{24}INO_4]^+ = [M+H]^+$: 493.0750; found: 493.0744.



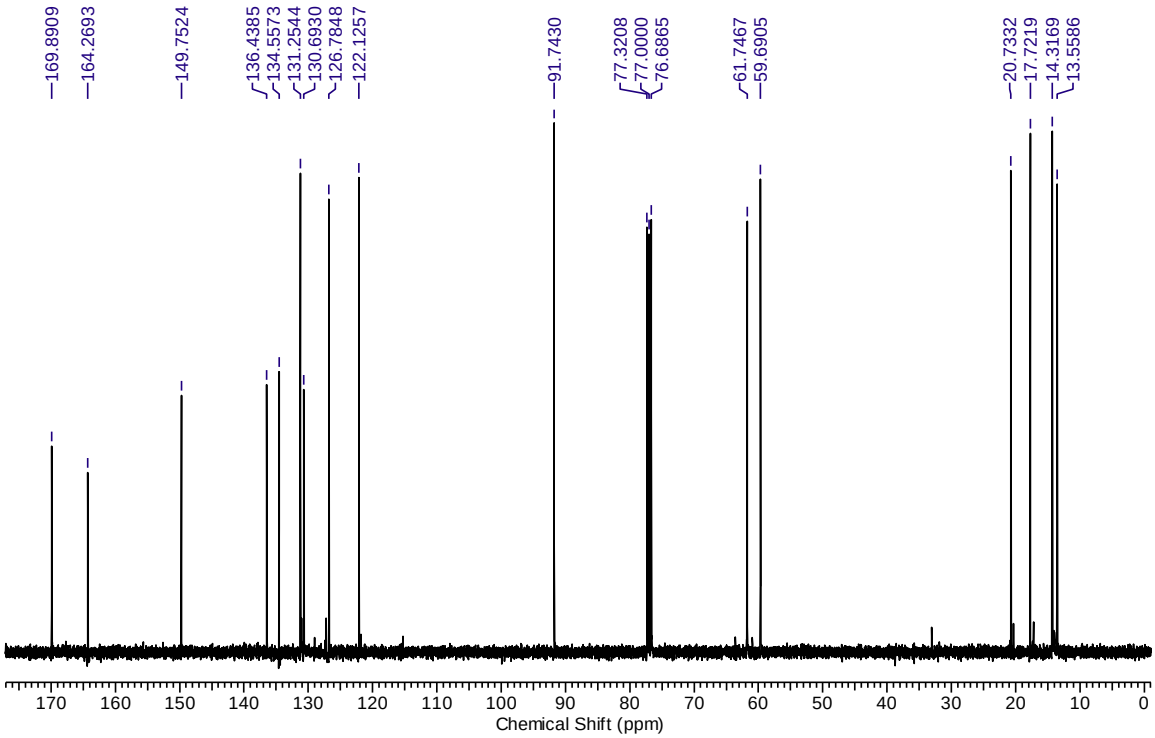
^{1}H NMR (400 MHz) spectrum of compound 1d in $CDCl_3$



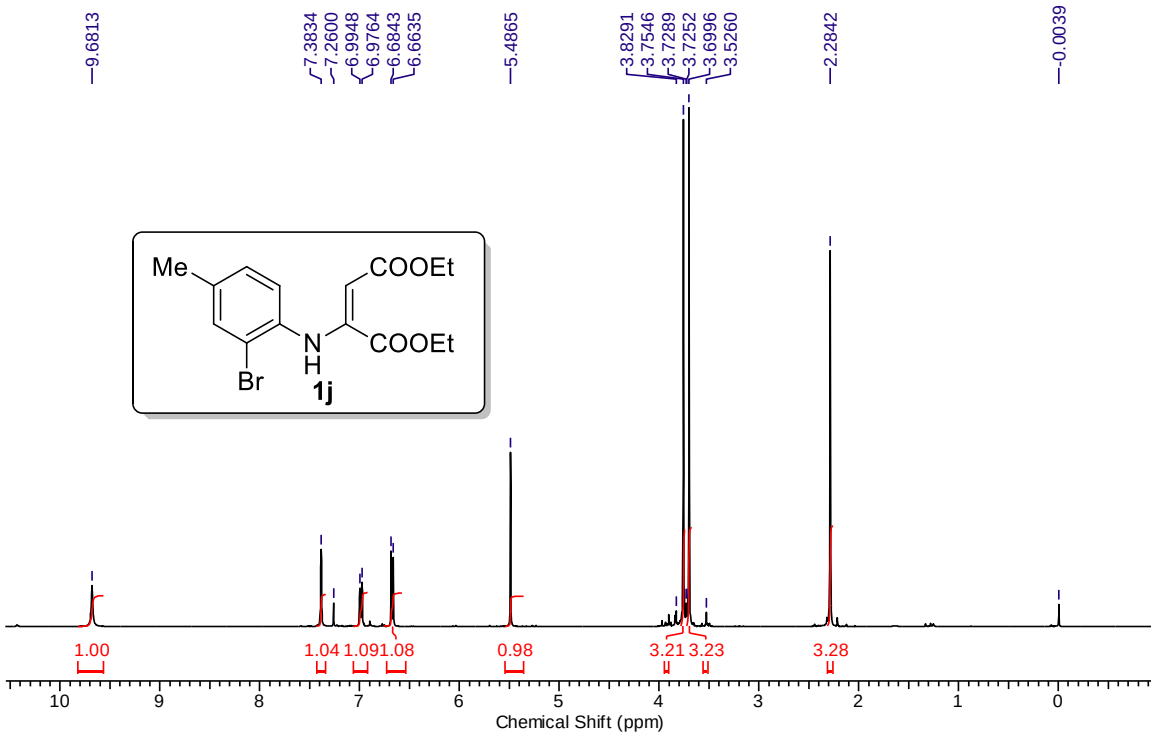
^{13}C NMR (100 MHz) spectrum of compound 1d in $CDCl_3$.



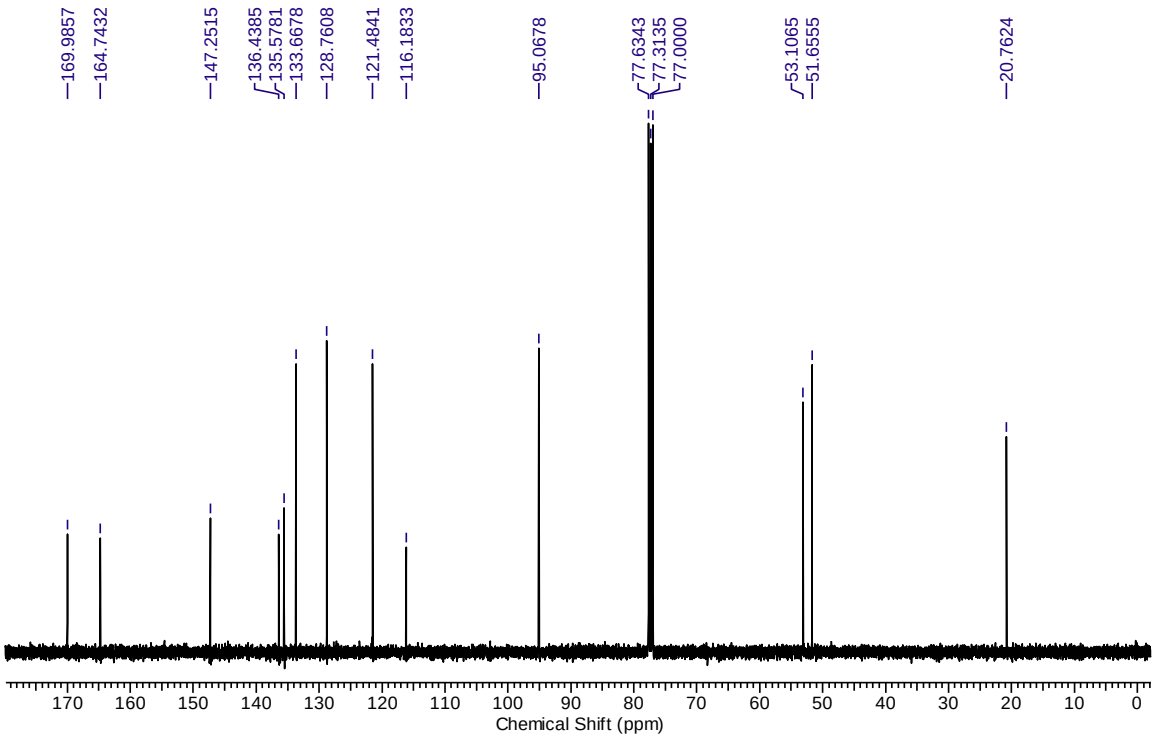
^{1}H NMR (400 MHz) spectrum of compound 1i in $CDCl_3$



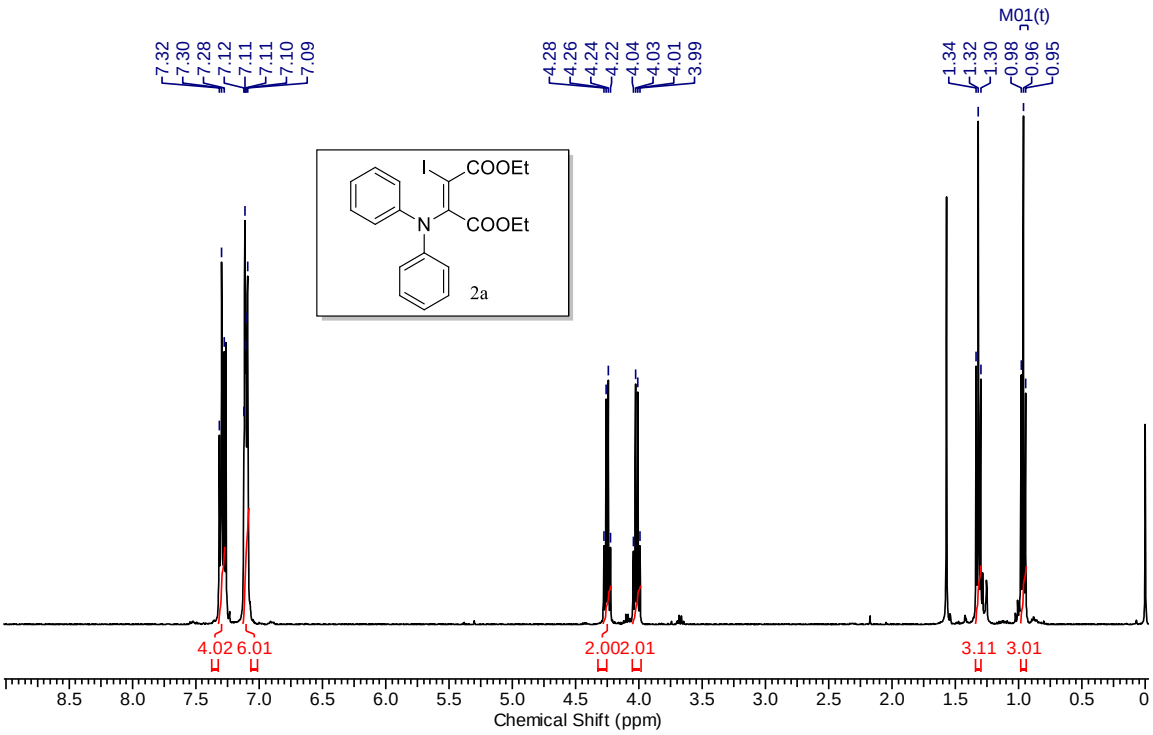
^{13}C NMR (100 MHz) spectrum of compound 1i in $CDCl_3$



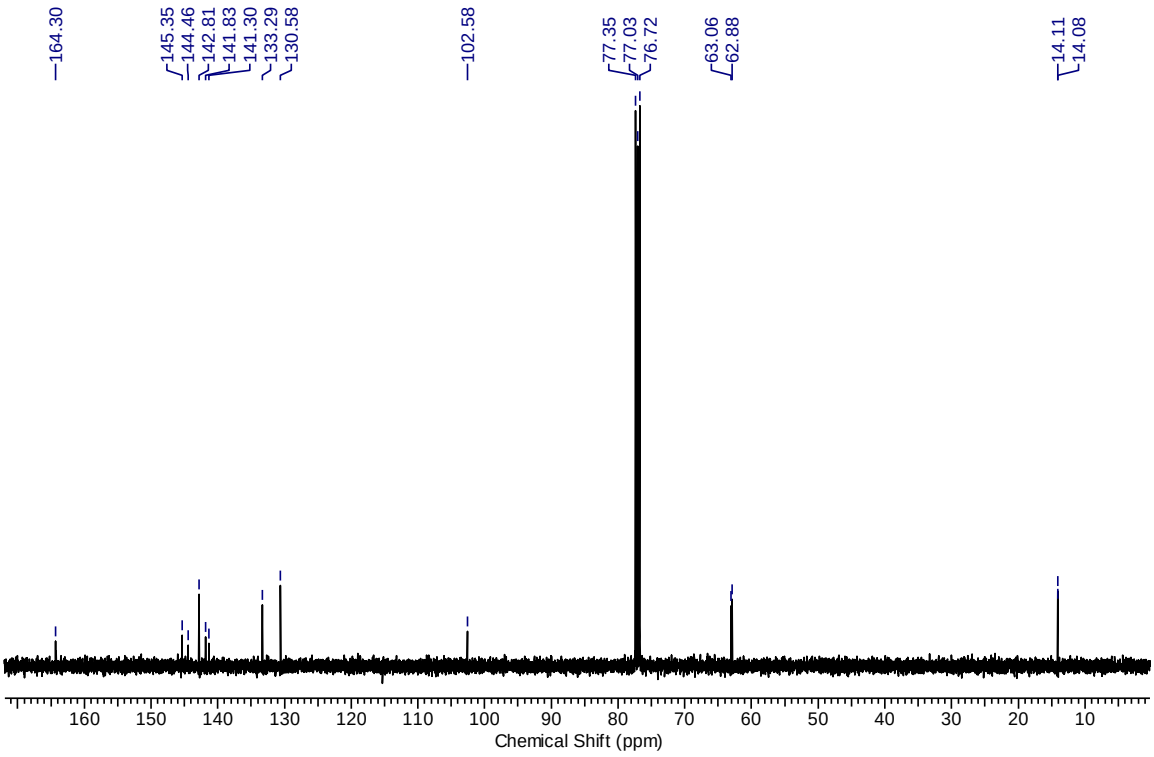
^{1}H NMR (400 MHz) spectrum of compound 1j in $CDCl_3$



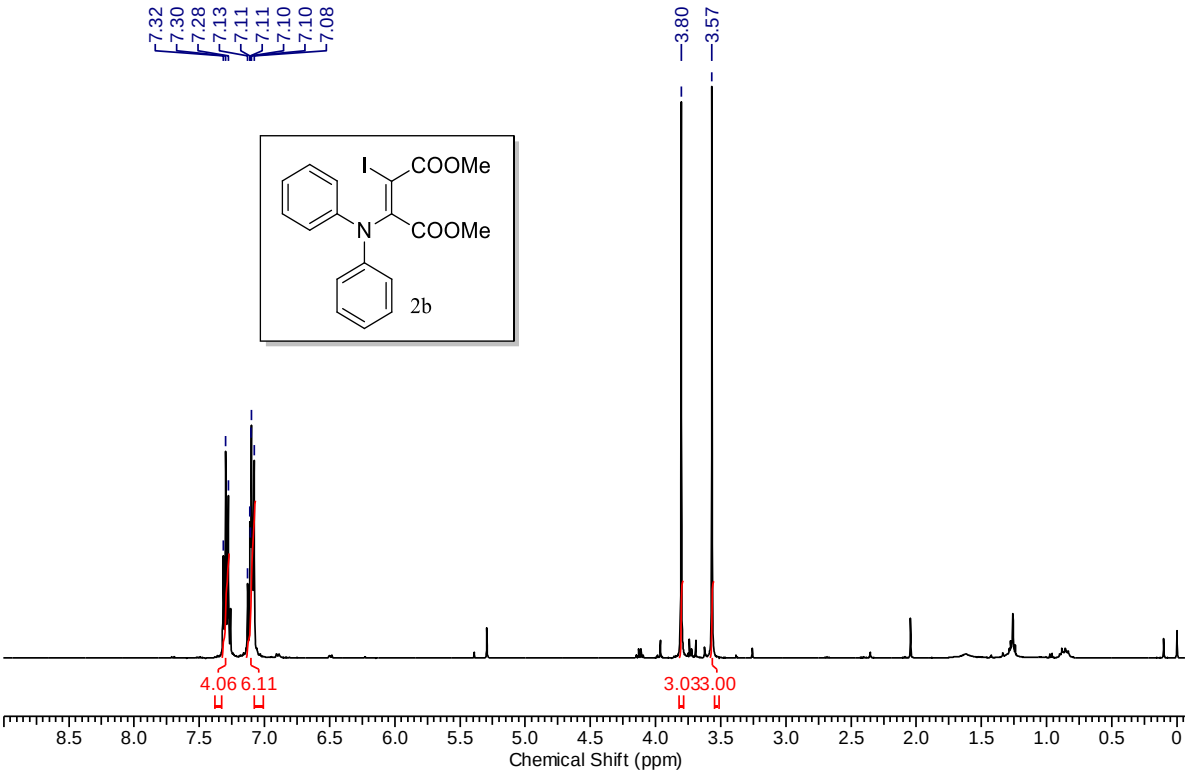
^{13}C NMR (100 MHz) spectrum of compound 1j in $CDCl_3$



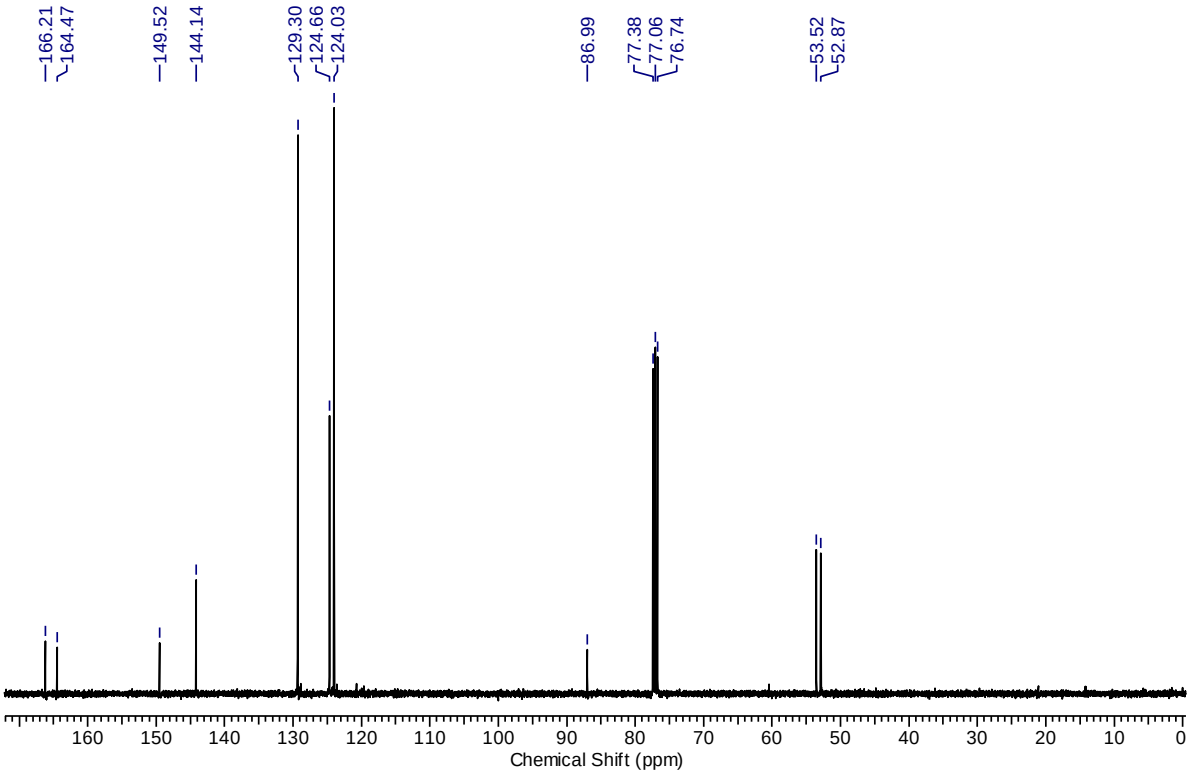
^{1}H NMR (400 MHz) spectrum of compound 2a in $CDCl_3$



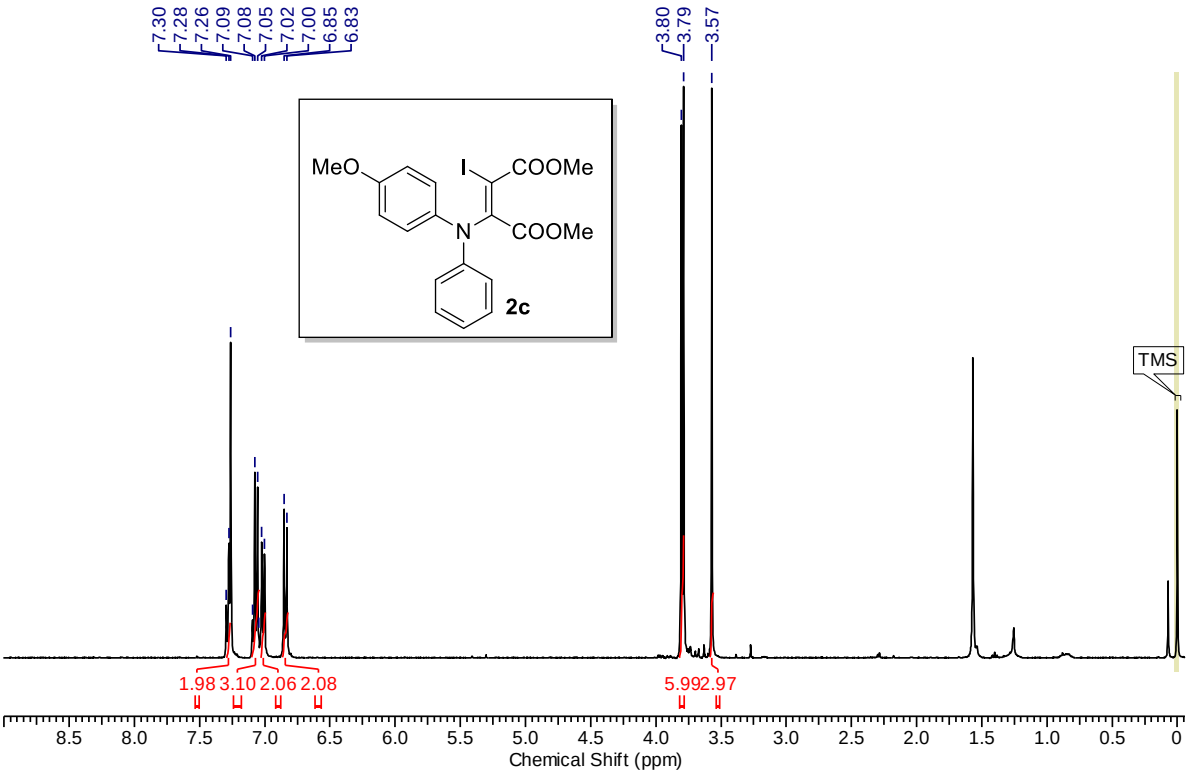
^{13}C NMR (100 MHz) spectrum of compound 2a in $CDCl_3$



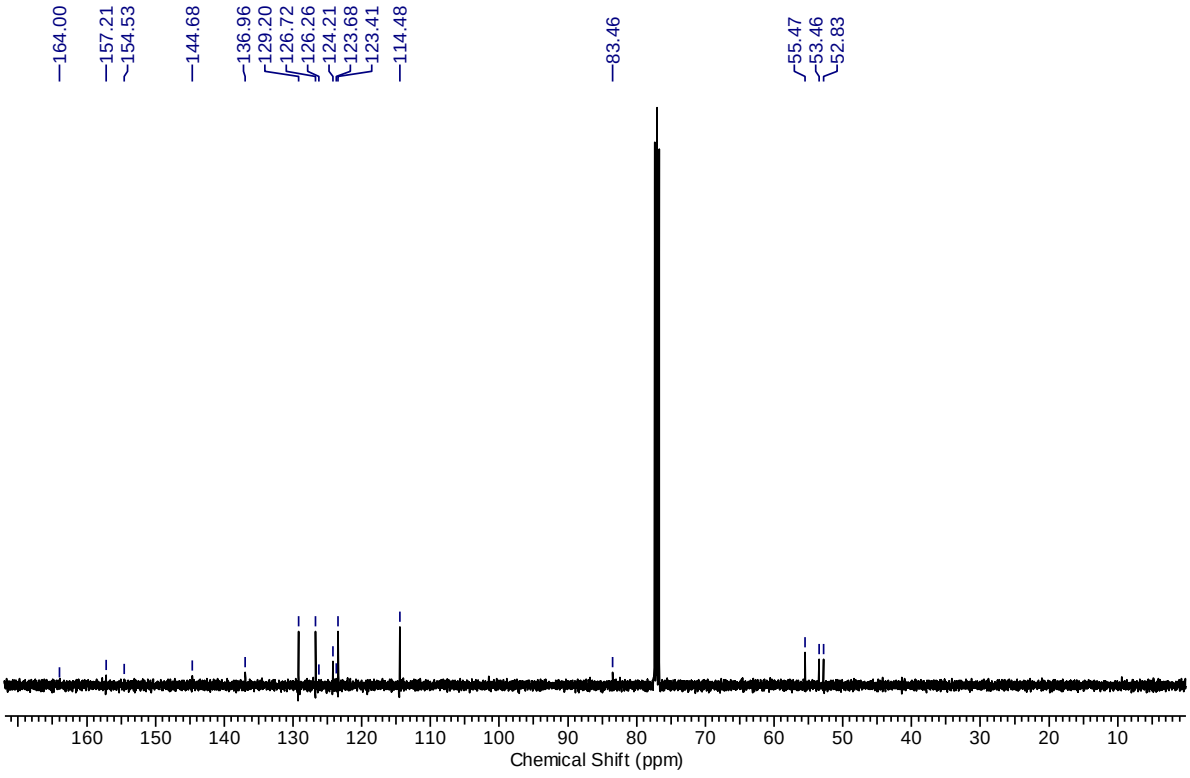
^{1}H NMR (400 MHz) spectrum of compound 2b in $CDCl_3$



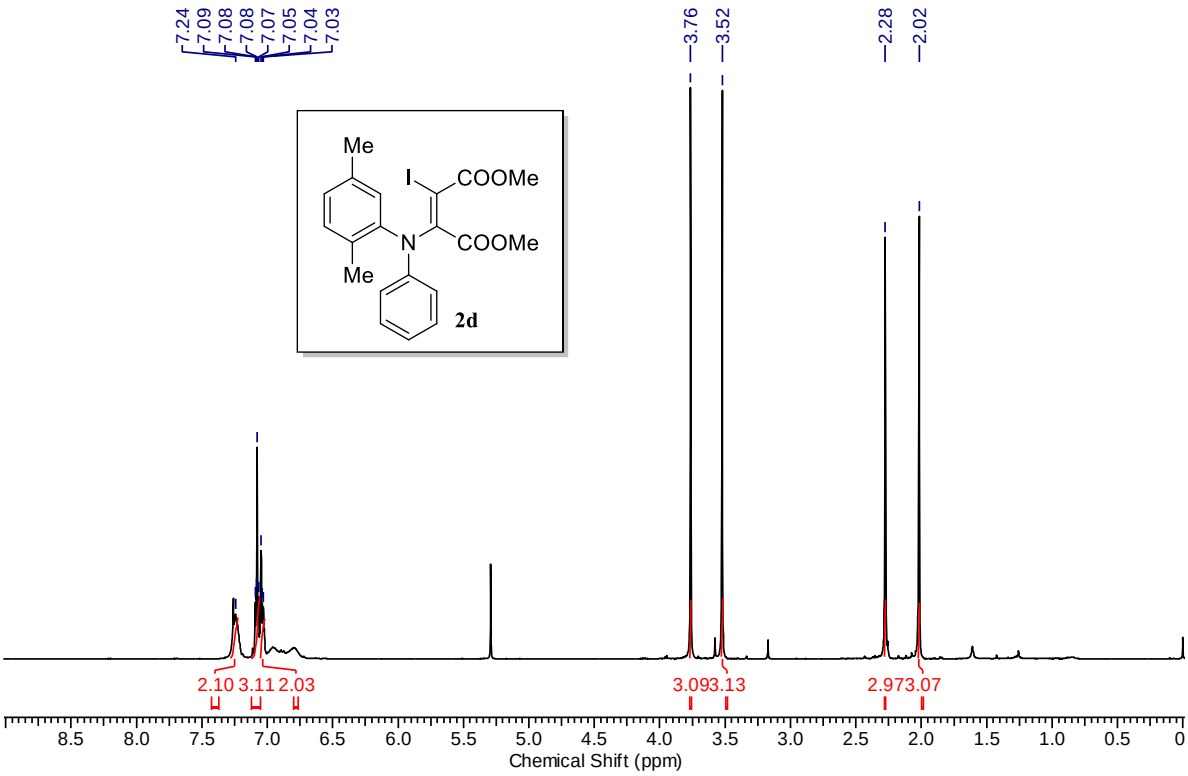
^{13}C NMR (100 MHz) spectrum of compound 2b in $CDCl_3$



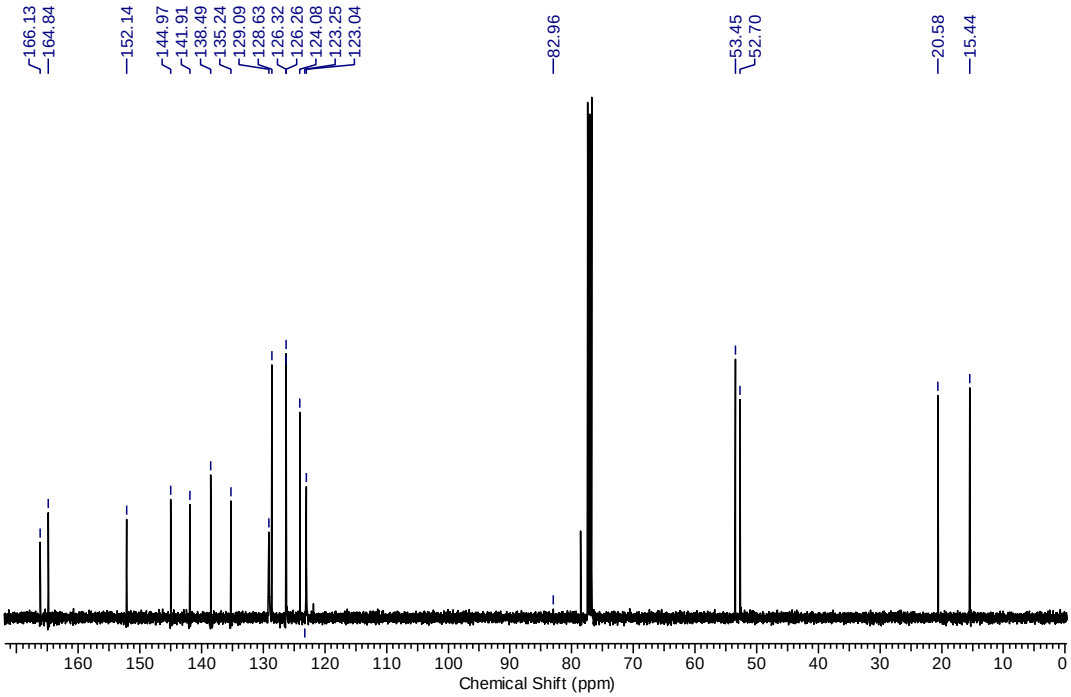
^{1}H NMR (400 MHz) spectrum of compound 2c in $CDCl_3$



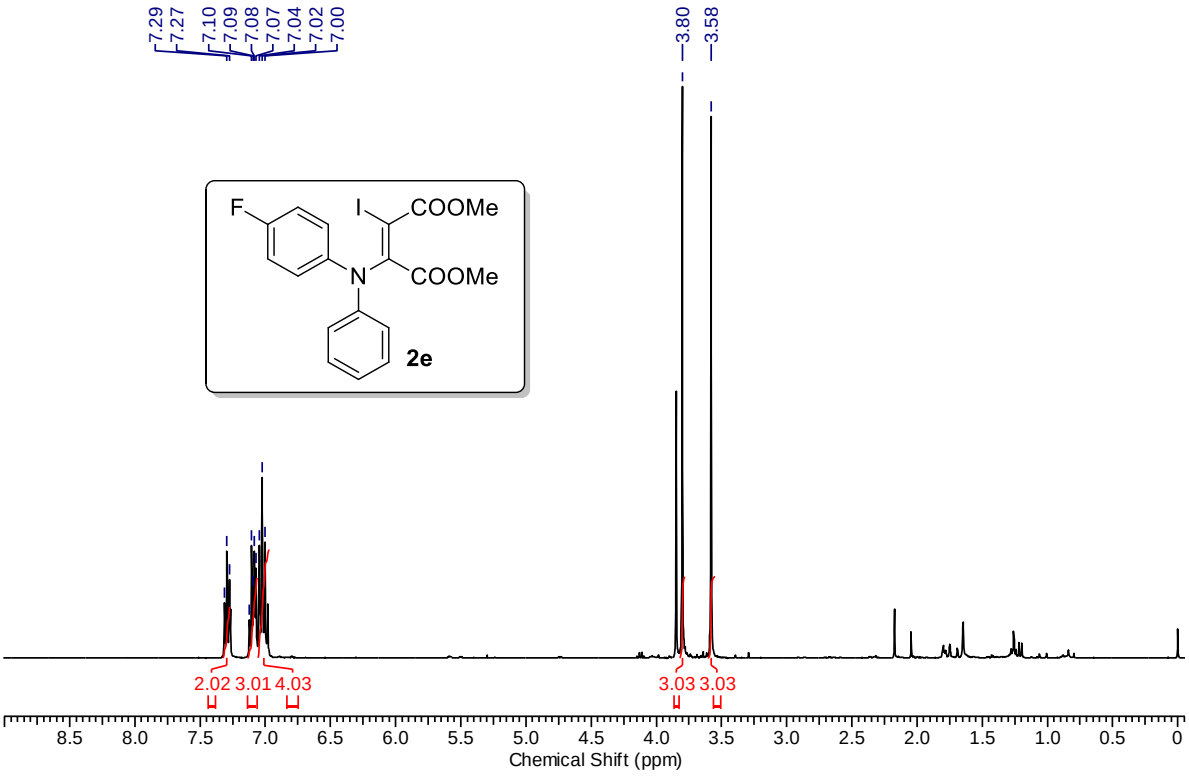
^{13}C NMR (100 MHz) spectrum of compound 2c in $CDCl_3$



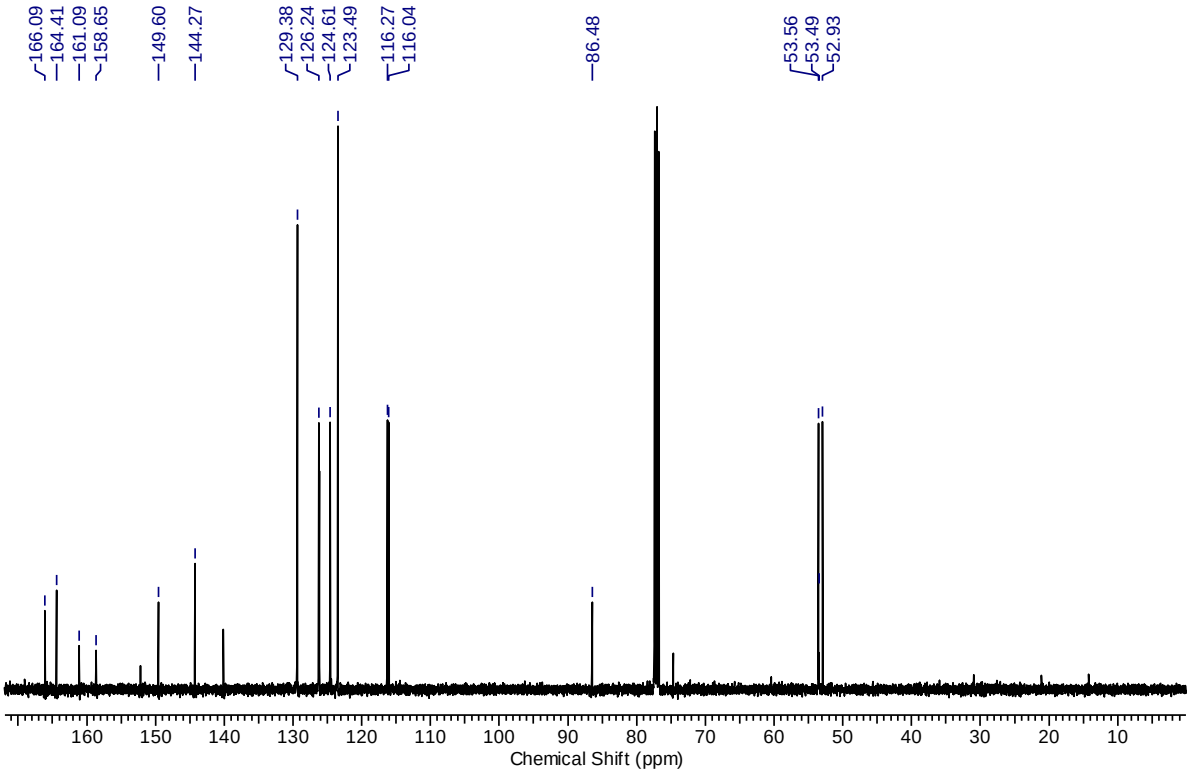
^{1}H NMR (400 MHz) spectrum of compound 2d in $CDCl_3$



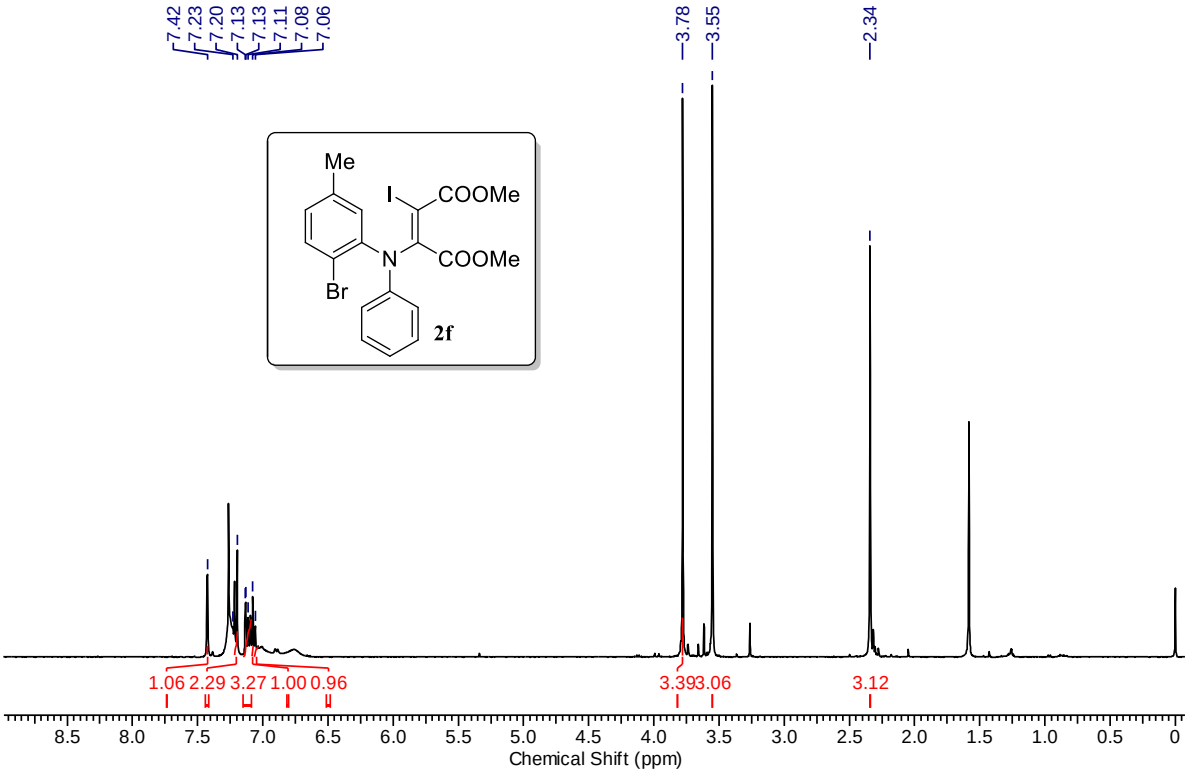
^{13}C NMR (100 MHz) spectrum of compound 2d in $CDCl_3$



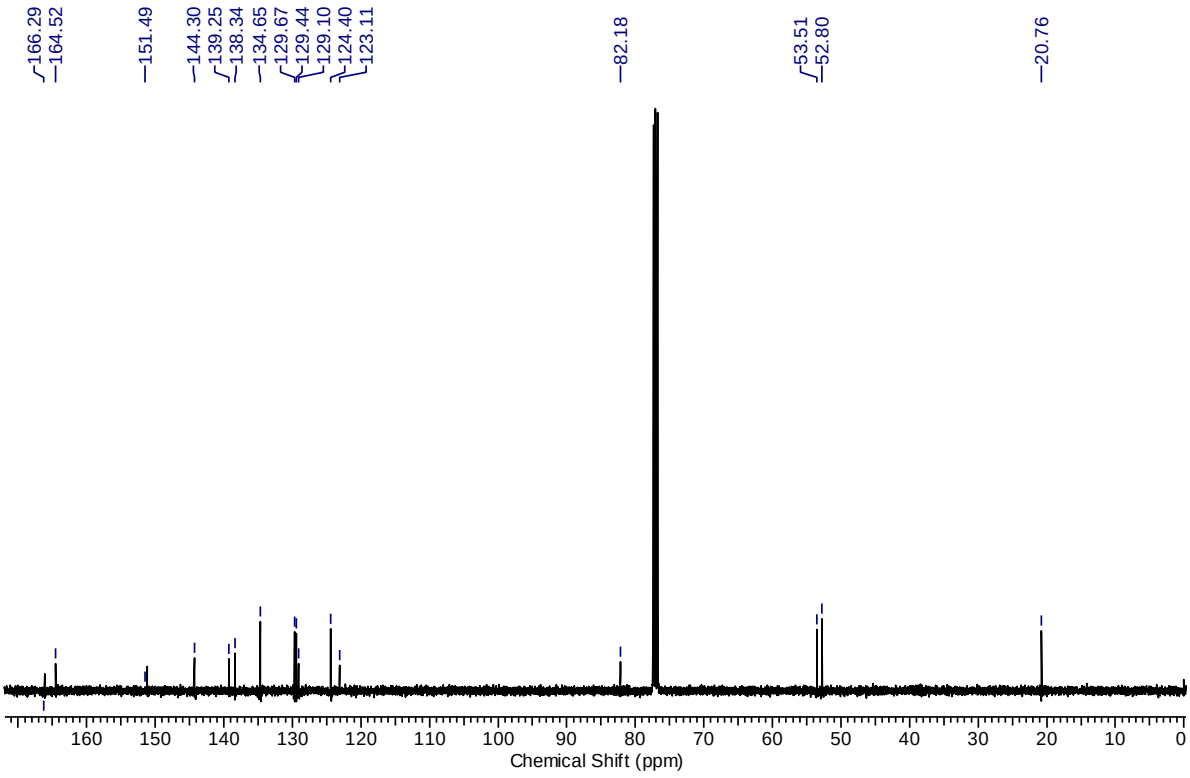
^{1}H NMR (400 MHz) spectrum of compound 2e in $CDCl_3$



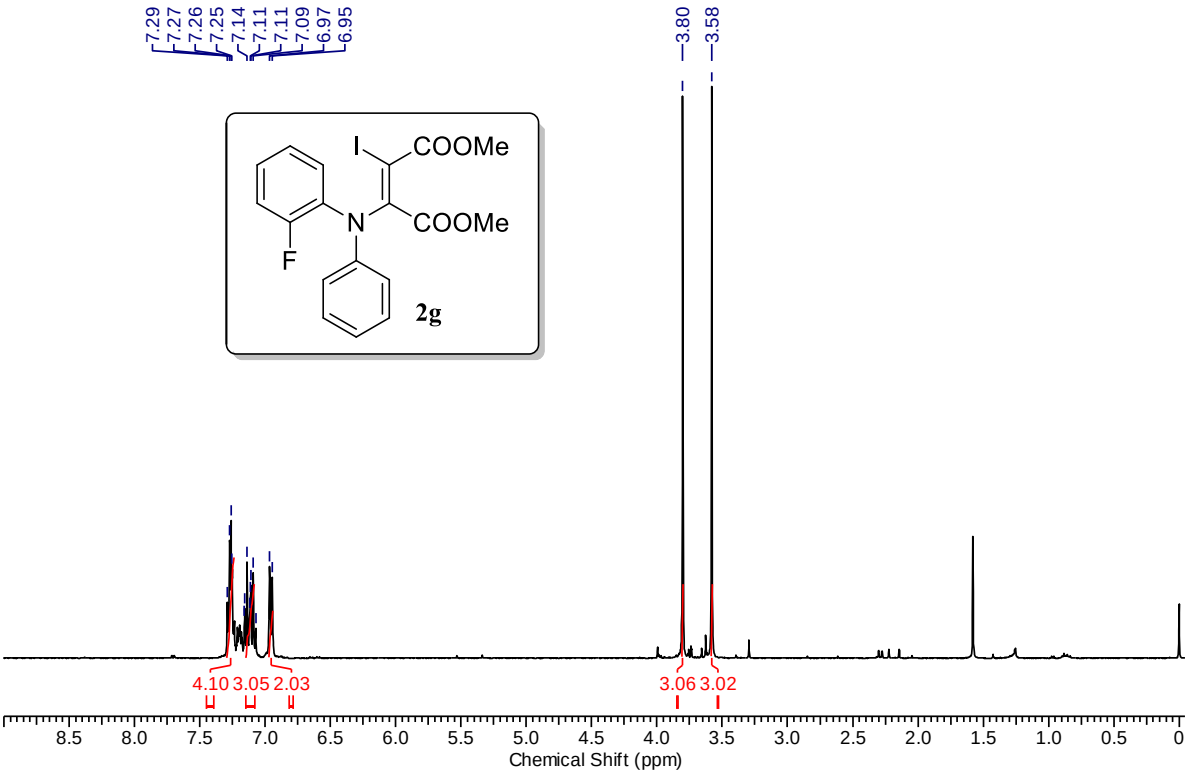
^{13}C NMR (100 MHz) spectrum of compound 2e in $CDCl_3$



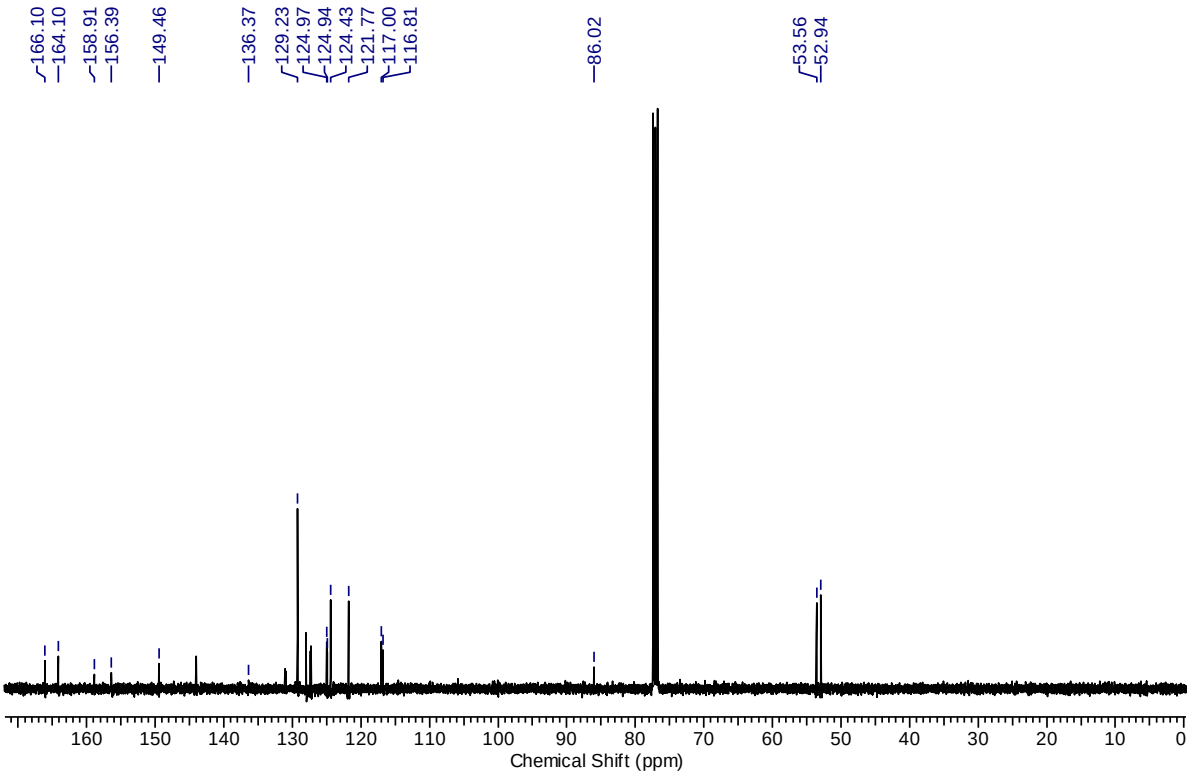
^{1}H NMR (400 MHz) spectrum of compound 2f in $CDCl_3$



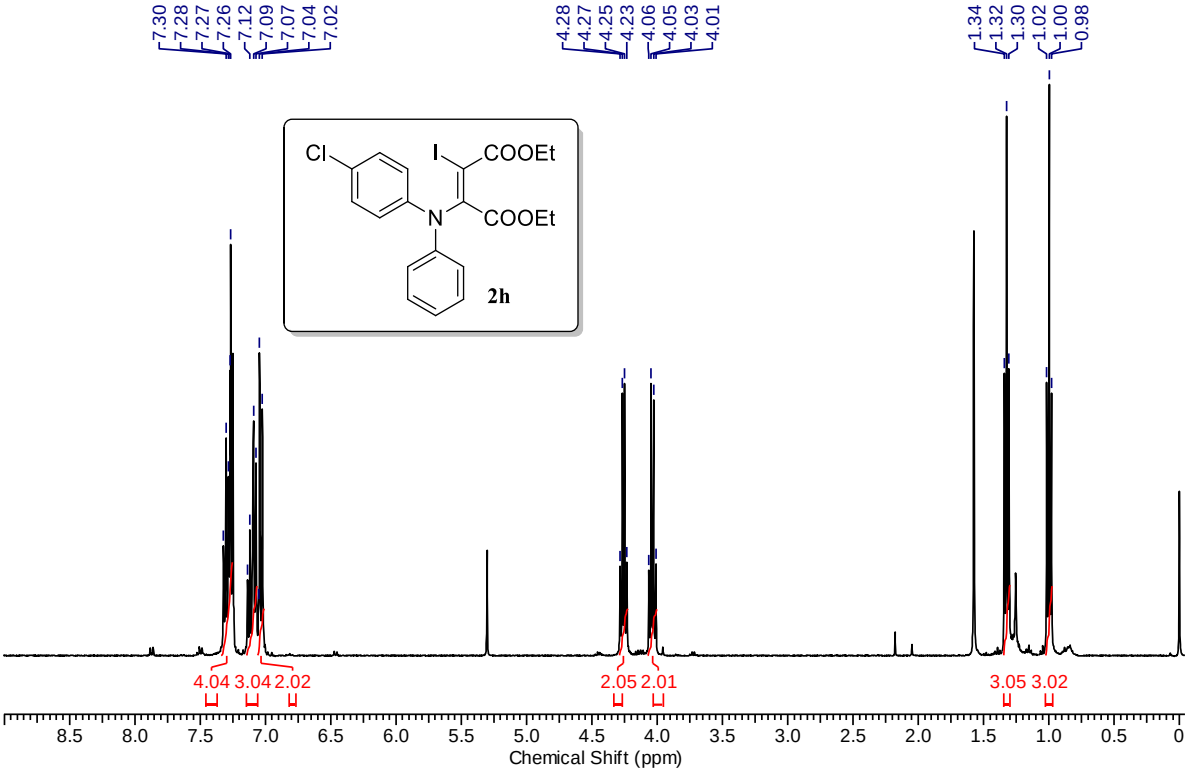
^{13}C NMR (100 MHz) spectrum of compound 2f in $CDCl_3$



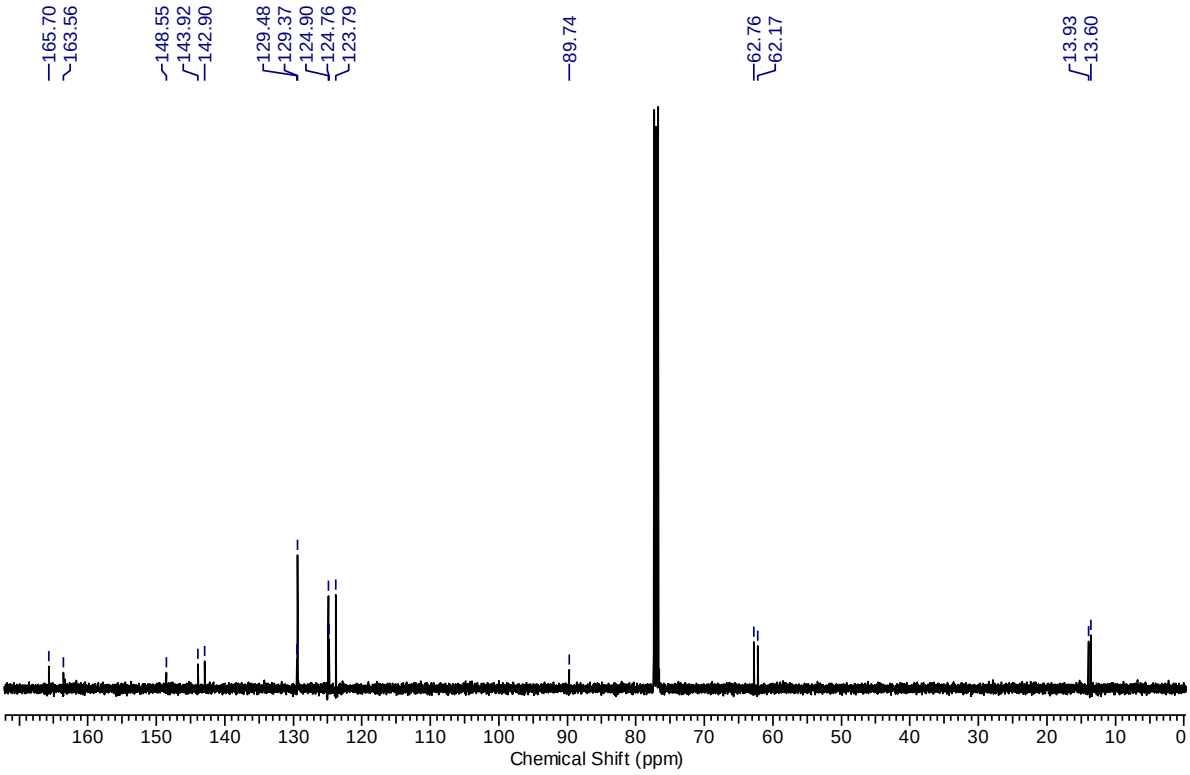
^{1}H NMR (400 MHz) spectrum of compound 2g in $CDCl_3$



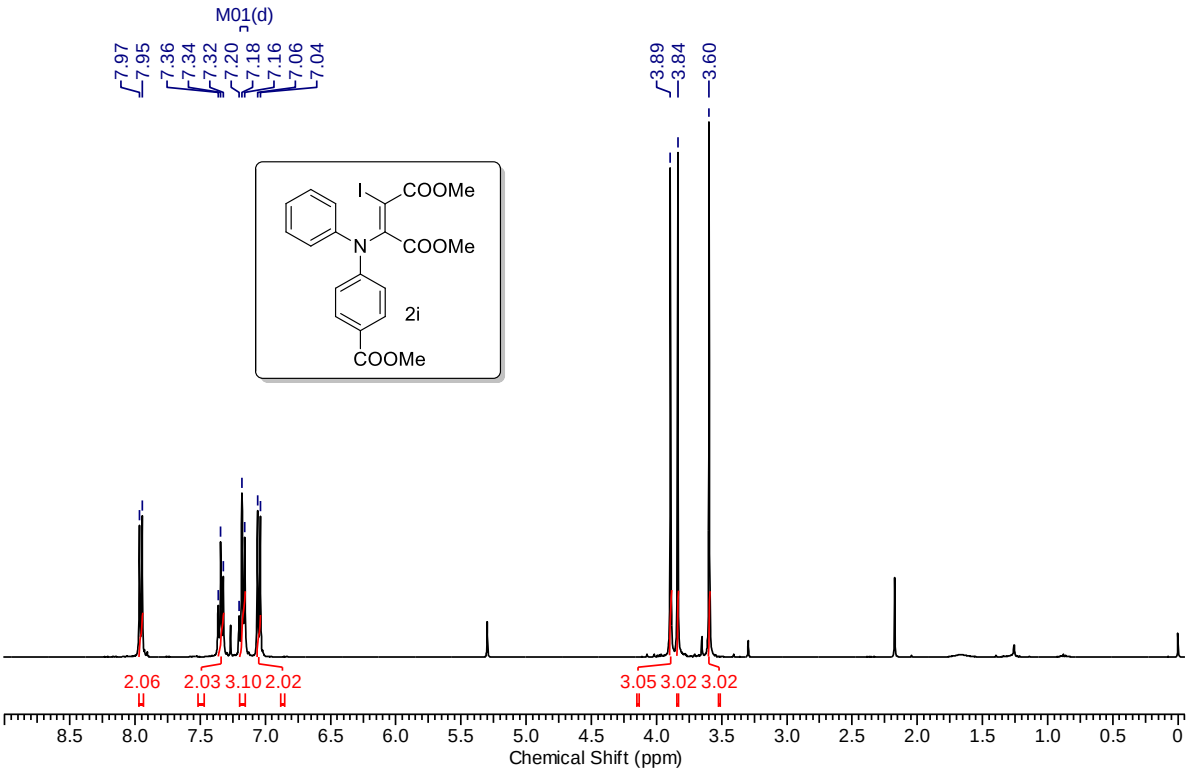
^{13}C NMR (100 MHz) spectrum of compound 2g in $CDCl_3$



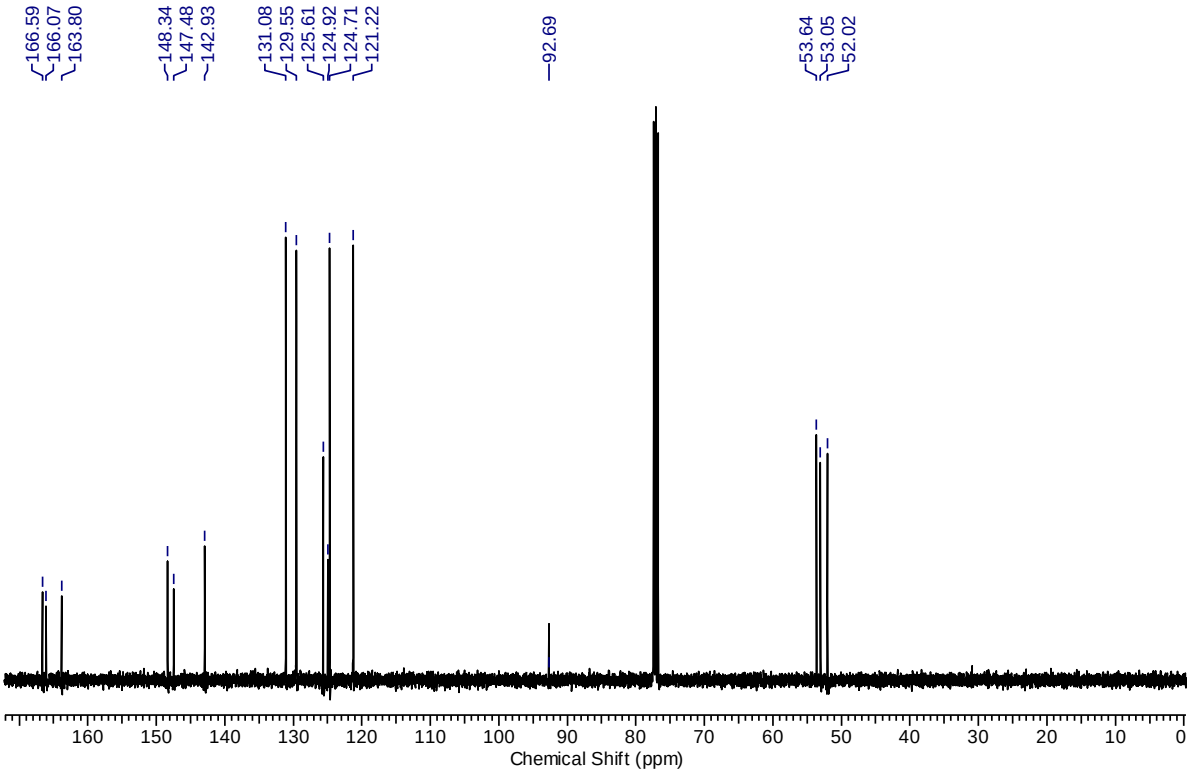
^{1}H NMR (400 MHz) spectrum of compound 2h in $CDCl_3$



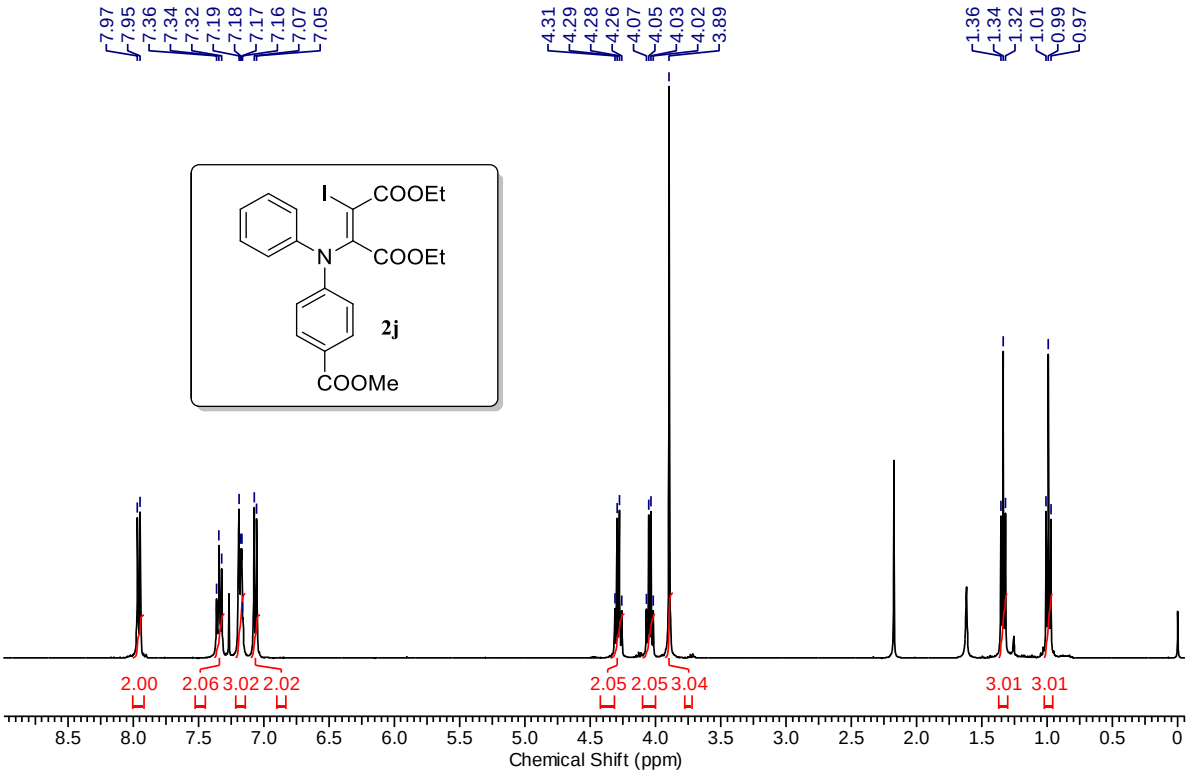
^{13}C NMR (100 MHz) spectrum of compound 2h in $CDCl_3$



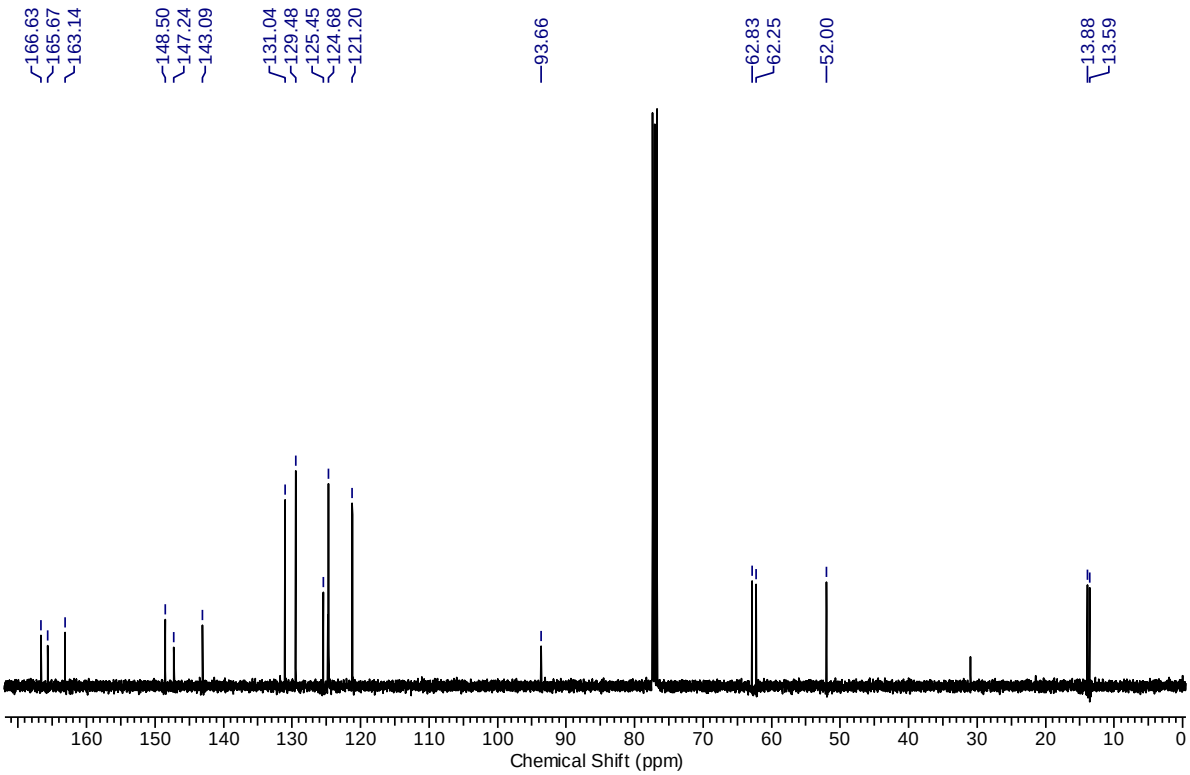
^{1}H NMR (400 MHz) spectrum of compound 2i in $CDCl_3$



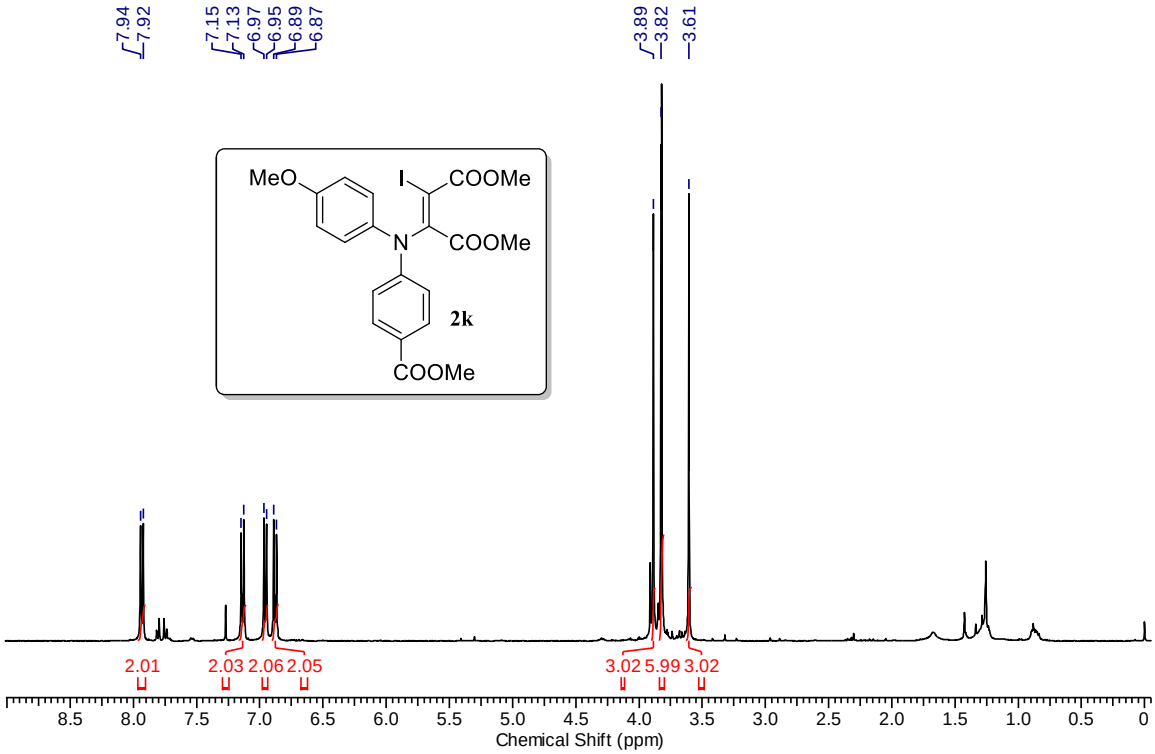
^{13}C NMR (100 MHz) spectrum of compound 2i in $CDCl_3$



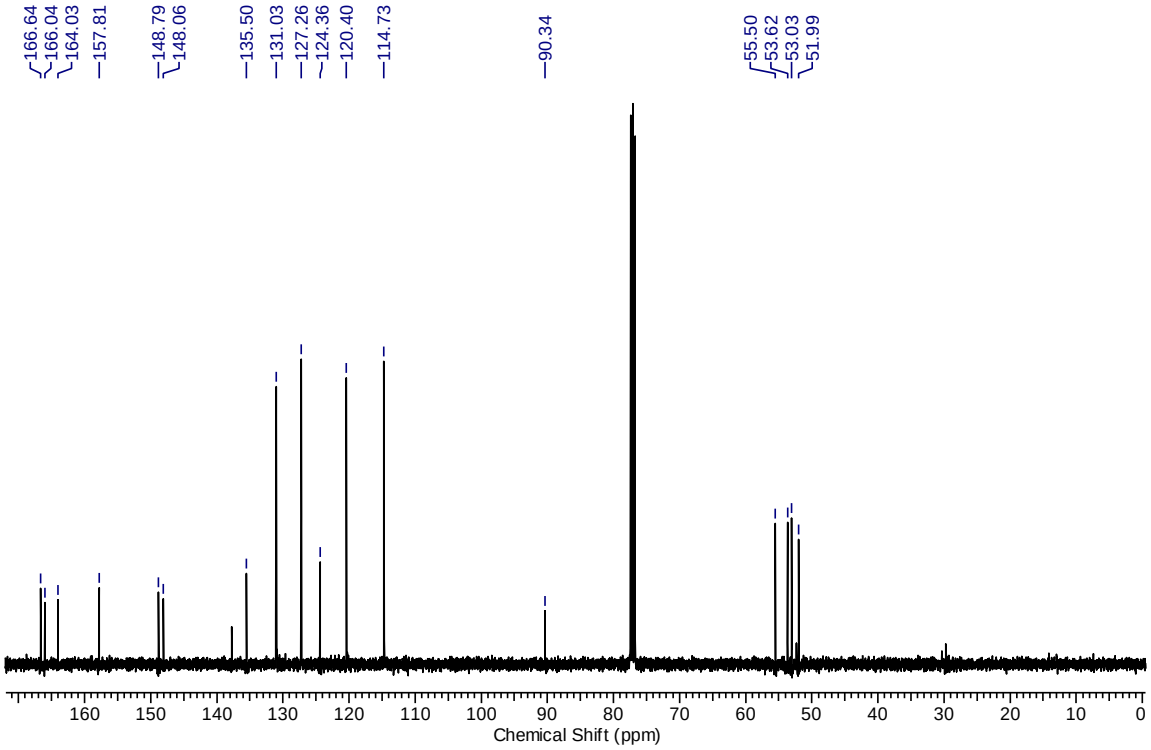
^{1}H NMR (400 MHz) spectrum of compound 2j in $CDCl_3$



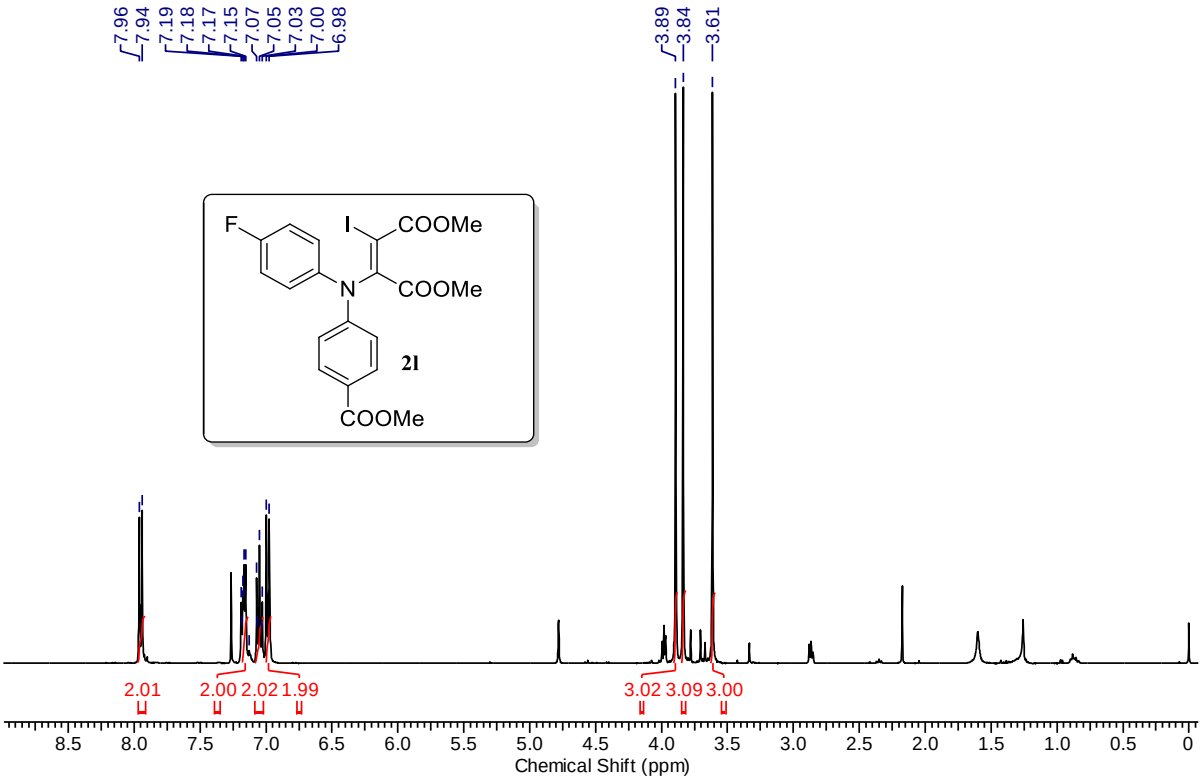
^{13}C NMR (100 MHz) spectrum of compound 2j in $CDCl_3$



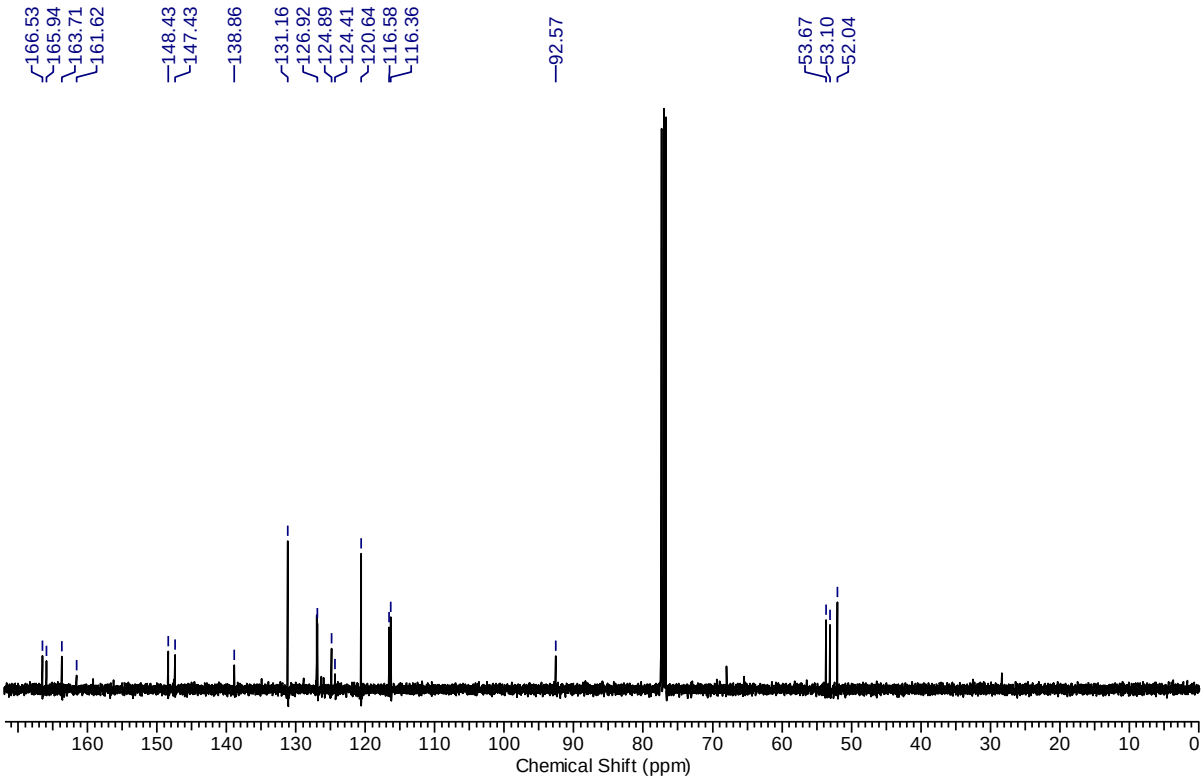
^{1}H NMR (400 MHz) spectrum of compound 2k in $CDCl_3$



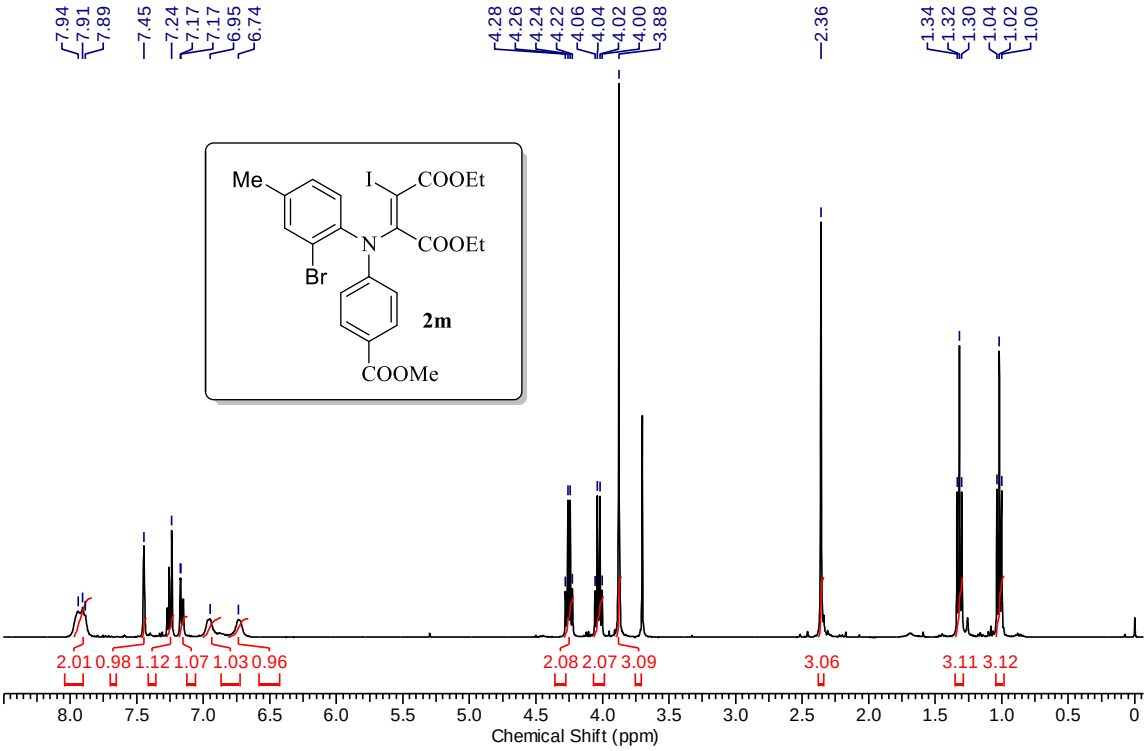
^{13}C NMR (100 MHz) spectrum of compound 2k in $CDCl_3$



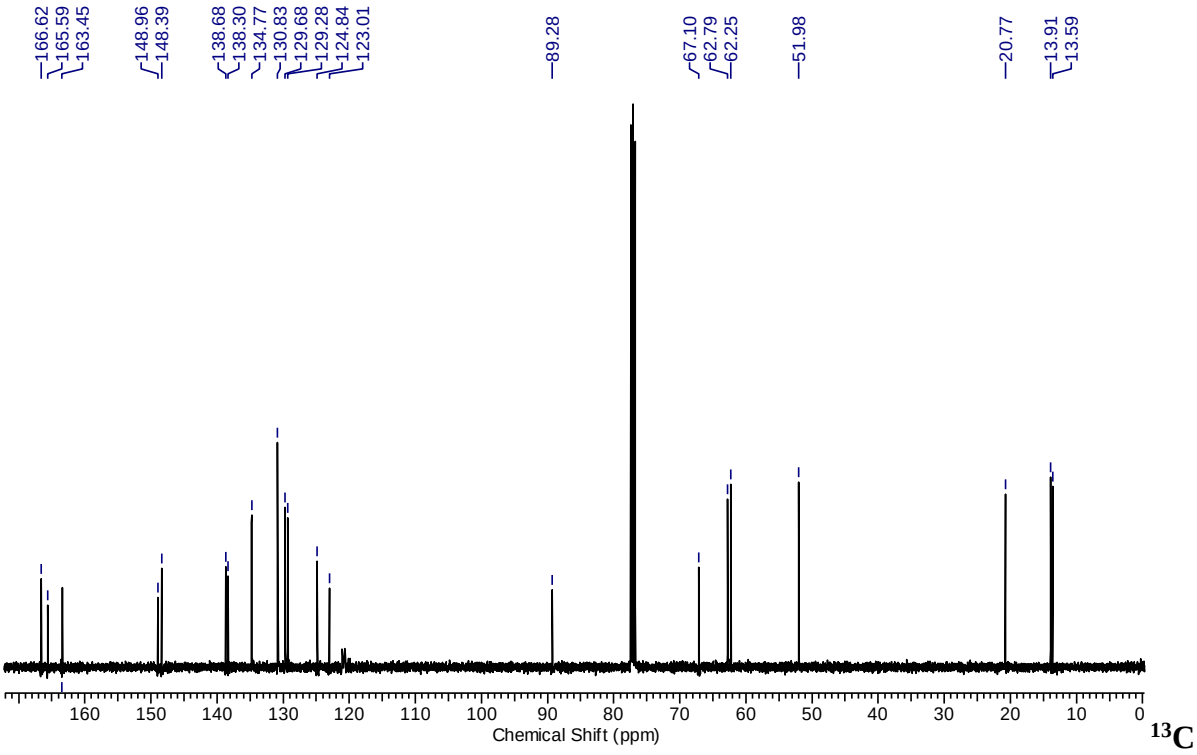
^{1}H NMR (400 MHz) spectrum of compound 2l in $CDCl_3$



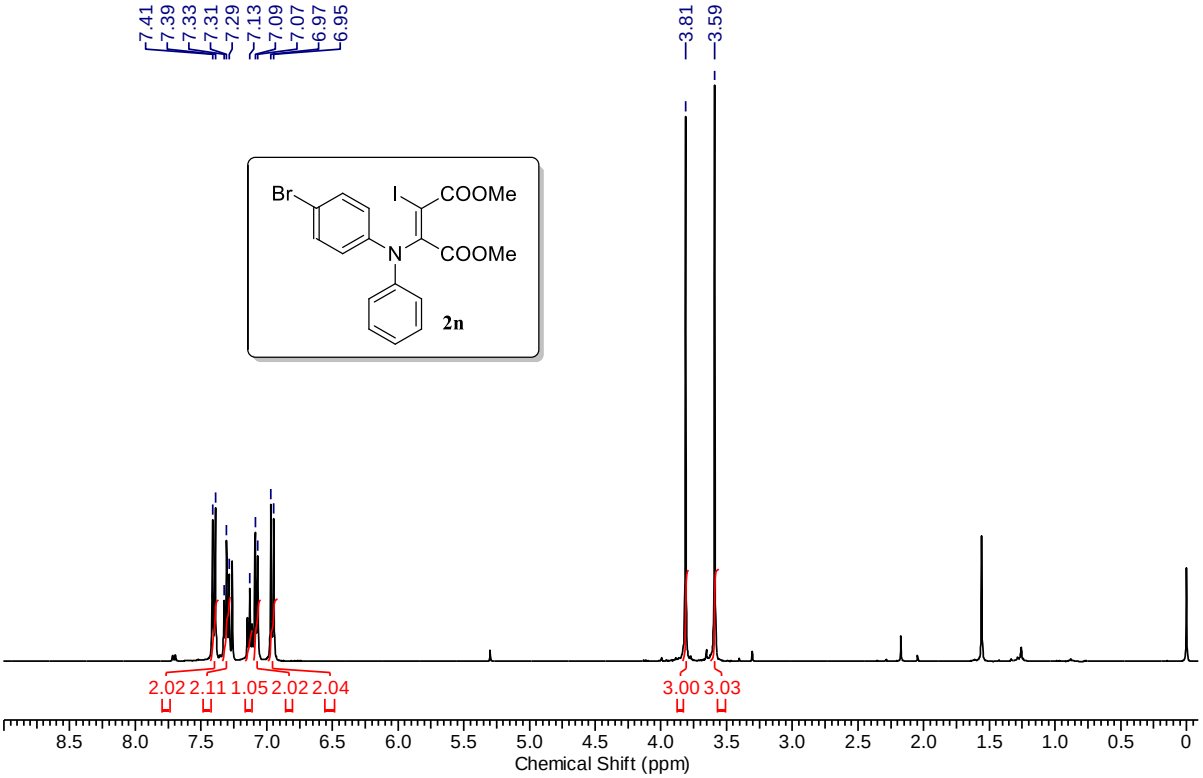
^{13}C NMR (100 MHz) spectrum of compound 2l in $CDCl_3$



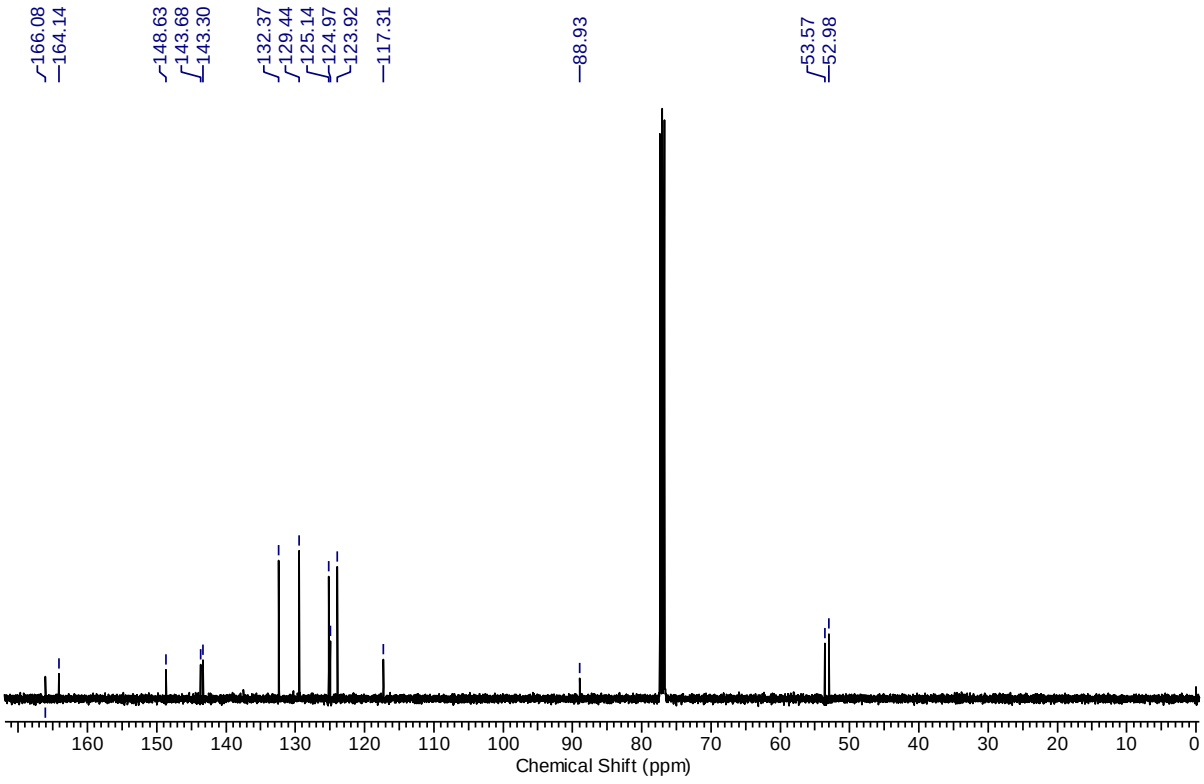
^{1}H NMR (400 MHz) spectrum of compound 2m in $CDCl_3$



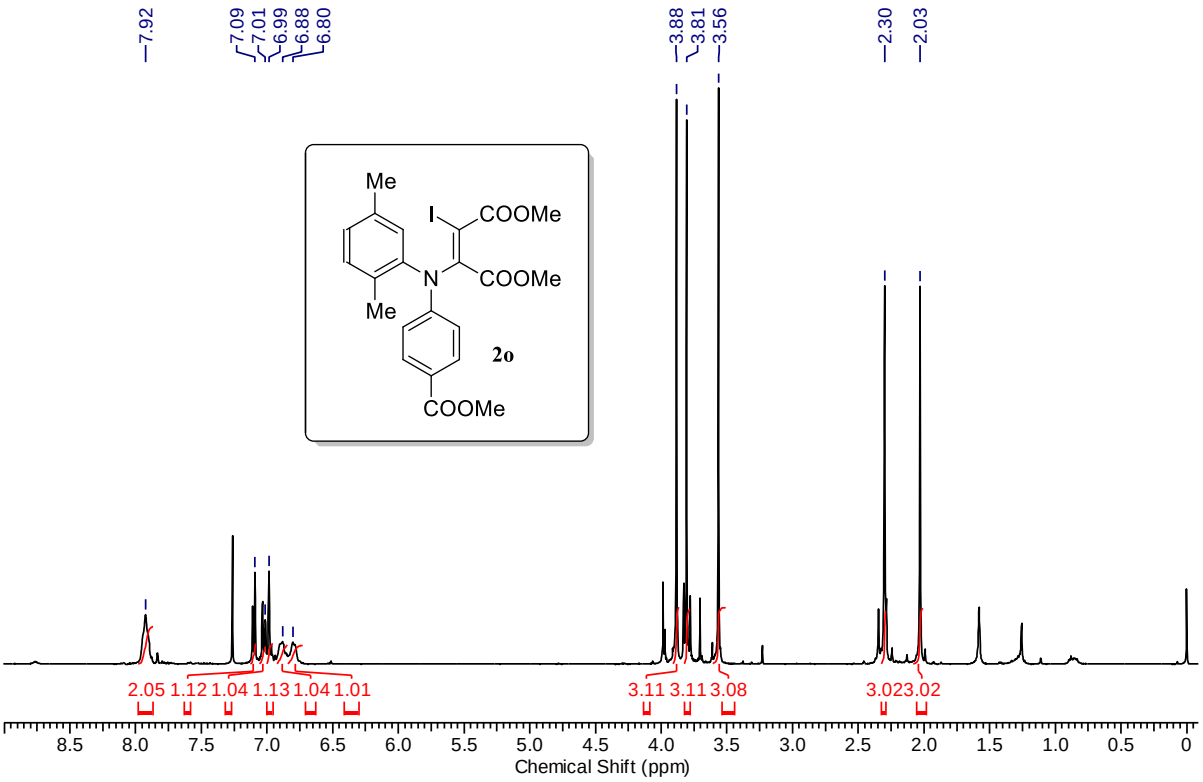
^{13}C NMR (100 MHz) spectrum of compound 2m in $CDCl_3$



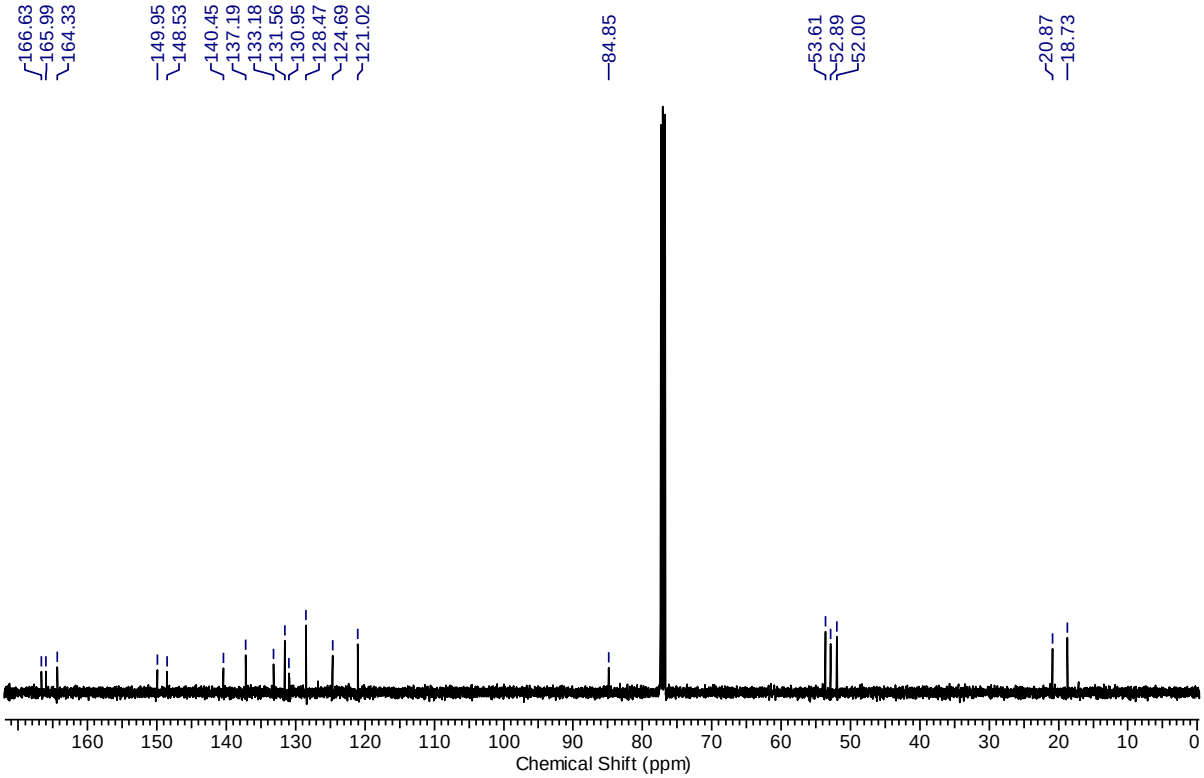
^{1}H NMR (400 MHz) spectrum of compound 2n in $CDCl_3$



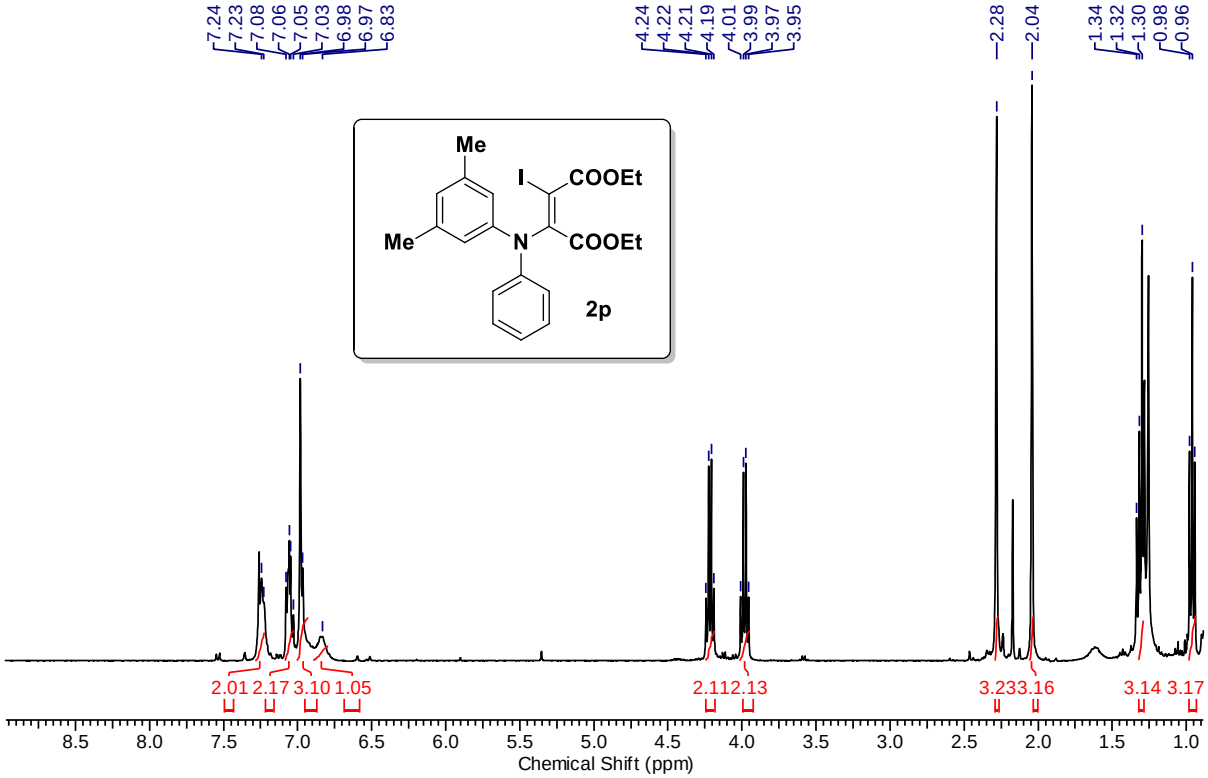
^{13}C NMR (100 MHz) spectrum of compound 2n in $CDCl_3$



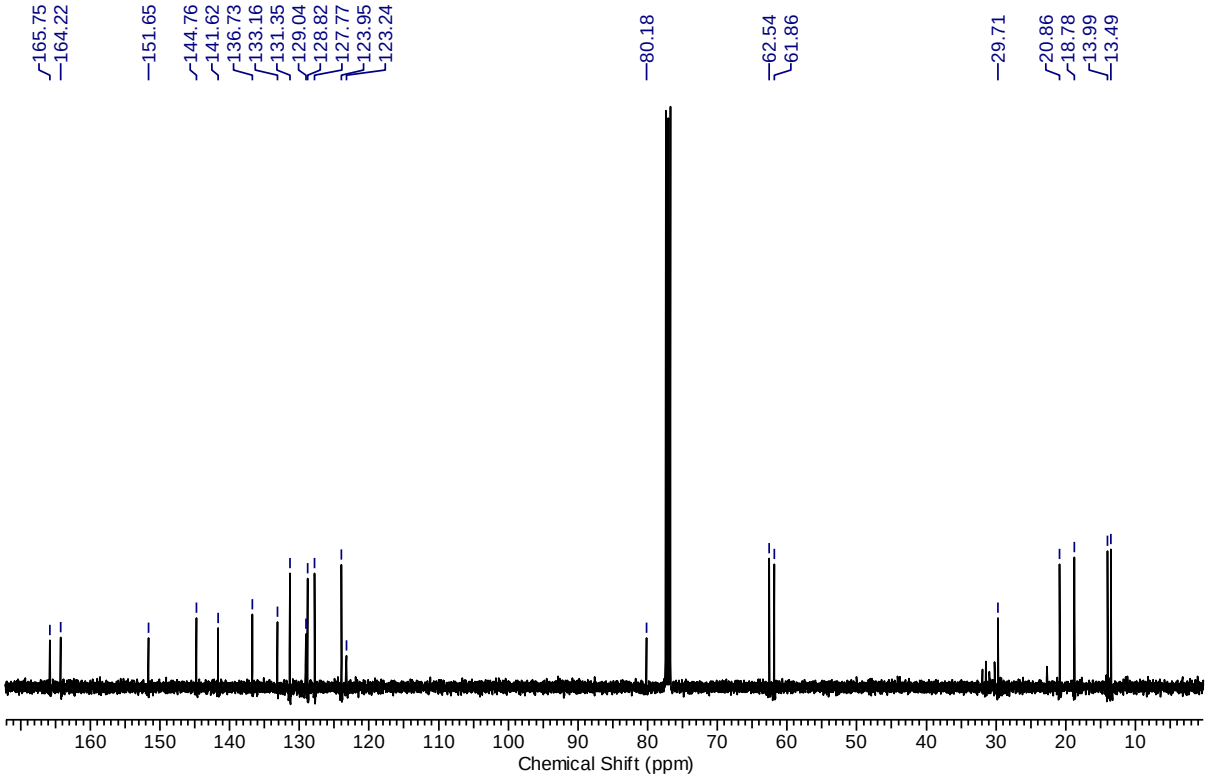
^{1}H NMR (400 MHz) spectrum of compound 2o in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound 2o in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of compound 2p in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound 2p in $CDCl_3$