

Pseudocyclic Bis-N-Heterocycle-Stabilized Iodanes – Synthesis, Characterization and Applications

Andreas Boelke, Soleicha Sadat, Enno Lork, **Boris Nachtsheim**

Submitted date: 09/06/2021 • Posted date: 10/06/2021

Licence: CC BY-NC-ND 4.0

Citation information: Boelke, Andreas; Sadat, Soleicha; Lork, Enno; Nachtsheim, Boris (2021): Pseudocyclic Bis-N-Heterocycle-Stabilized Iodanes – Synthesis, Characterization and Applications. ChemRxiv. Preprint.

<https://doi.org/10.26434/chemrxiv.14754525.v1>

In this manuscript we describe novel bicationic iodonium salts which are stabilized by covalently connected N-heterocycles (Bis-N-Heterocycle-stabilized Iodanes BNHIs). We provide structural data, their synthesis as well as their application in benchmark oxidative transformations.

File list (3)

BNHIs-ChemRXIV.pdf (430.57 KiB)

[view on ChemRxiv](#) • [download file](#)

Graphical Abstract.jpg (337.25 KiB)

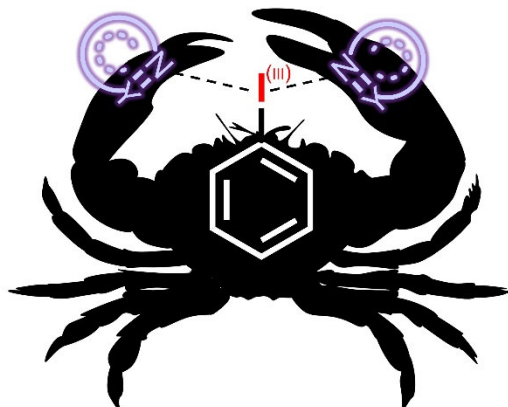
[view on ChemRxiv](#) • [download file](#)

Supporting Information-ChemRxiv.pdf (1.90 MiB)

[view on ChemRxiv](#) • [download file](#)

Pseudocyclic Bis-*N*-Heterocycle-stabilized Iodanes – Synthesis, Characterization and Applications

Andreas Boelke,^a Soleicha Sadat,^a Enno Lork^b and Boris J. Nachtsheim^{*a}



Bis-*N*-heterocycle-stabilized λ^3 -iodanes (BNHIs) based on azoles are introduced as novel structural motifs in hypervalent iodine chemistry. A performance test in a variety of benchmark reactions including sulfoxidations and phenol dearomatizations revealed a bis-*N*-bound pyrazole substituted BNHI as the most reactive derivative. Its solid-state structure was characterized via X-ray analysis implying strong intramolecular interactions between the pyrazole nitrogen atoms and the hypervalent iodine centre.

Over the last three decades, hypervalent iodine compounds have received increasing interest and their chemistry witnessed an unprecedented growth. By now, they have been established as easy to handle, readily available, diverse, and environmentally benign reagents for a plethora of oxidative transformations.^{1–9}

Despite a convenient reactivity as mild oxidants, the most puristic examples (iodoso- and iodylbenzene) suffer from unfavourable features such as poor solubility and thermal lability. Therefore, strategies to overcome these drawbacks came into focus recently. Due to the electrophilic nature of the hypervalent iodine centre, heteroatoms in its vicinity should alter the structure, reactivity, and selectivity of these reagents through beneficial non-covalent intramolecular interactions.^{10,11} Historically, the so formed pseudocyclic compounds included oxygen-containing stabilizing units, such as sulfonyl-groups, carboxylic acids, ethers or carbonyls.^{12–20} *N*-heterocycles as stabilizing functional groups have been widely neglected, despite their high synthetic versatility. Recent years showed growing interest in the investigation of λ^3 -iodanes containing heterocycles, not only as free ligands, as in the bispyridinium derivatives,^{21–23} but even more important as an

intramolecular anchored stabilizing moiety.^{24–29} The first confirmation about a direct intramolecular N-I interaction in hydroxy- λ^3 -iodanes was presented in 2017 by Muñiz and co-workers for a 2-pyridinyl-substituted reagent which showed an improved reactivity in the catalytic diacetoxylation of alkenes.³⁰ Our group systematically investigates related *N*-heterocycle-stabilized iodanes (**NHIs**, Figure 1) based on azoles.^{31–34}

Although 2,6-bis-heterocyclic systems are long known as pincer-ligands (so-called phebox) in transition metal complexes,^{35,36} their effective transfer to the chemistry of hypervalent iodine has not been described so far. Only in one initial investigation by Legault and co-workers a 2,6-bisoxazoline-substituted iodoarene was tested as a catalyst in the α -oxytosylation of ketones but was found to be inefficient.²⁷

Herein, we want to present the first systematic investigations of bis-*N*-heterocycle-stabilized iodanes (**BNHIs**) by describing their synthesis, characterization and finally their application as highly potent oxidants.

Starting with the preparation of the corresponding iodoarenes, two different strategies divided into *N*- and *C*-bound derivatives were chosen. First, 2,6-difluoronitrobenzene (**1**), which is either commercially available or easily prepared on a decagram-scale (see ESI), was reacted with pyrazole or 1,2,4-triazole via S_NAr to **2** and **3**. A subsequent Sandmeyer-sequence gave the bis-pyrazole **4** (X=CH) and the bis 1,2,4-triazole **5** (X=N) in 77% and 40% yield over three steps on a multigram scale, without the need for column chromatography (Scheme 1, a). *C*-bound derivatives were obtained starting from 2-iodoisophthalonitrile (**6**) which was transformed into the corresponding aldehyde **7** via an iodination- and reduction

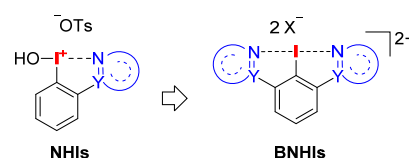


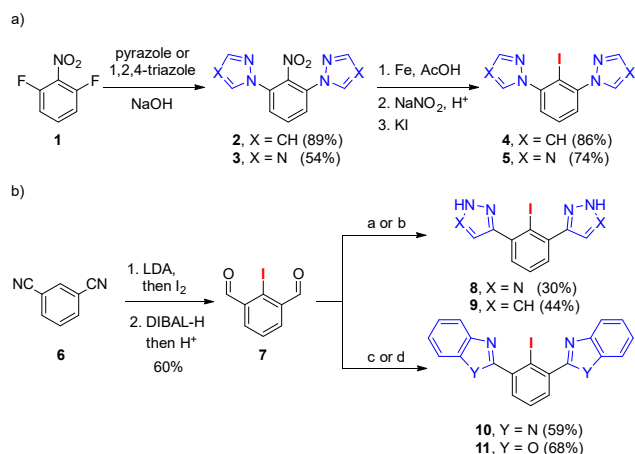
Figure 1 General structures of mono- and bis-*N*-heterocycle-stabilized λ^3 -iodanes.

^a Institute for Organic and Analytical Chemistry, University of Bremen, 28359 Bremen, Germany. E-mail: nachtsheim@uni-bremen.de

^b Institute for Inorganic Chemistry and Crystallography, University of Bremen, 28359 Bremen, Germany.

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: Synthesis details, NMR spectra, and X-ray data. CCDC 2086526. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

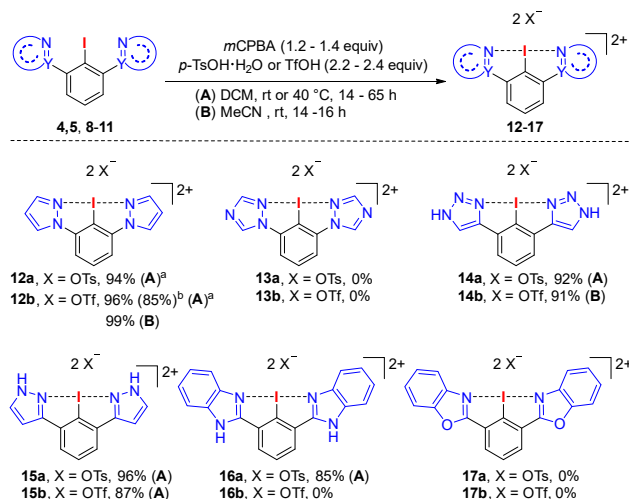


Scheme 1 Synthesis of heterocyclic bis-*N*-bound (a) and *C*-bound (b) iodoarenes. a: 1. MeNO₂, NaOH, then H⁺; 2. NaN₃, *p*-TsOH; b: 1. TsNHNH₂, 2. NaOEt, then TMS-acetylene, then TBAF; c: *o*-phenylenediamine, then NaOH, I₂; d: 2-aminophenol, then DDQ.

sequence in 60% overall yield. A final two-step sequence gave bis-*NH*-triazole **8** and bis-*NH*-pyrazole **9** in 30–44% yield. Benzimidazole **10** and benzoxazole **11** were obtained in 59% and 68% yield, in one step (Scheme 1, b).

With these six structurally diverse iodoarenes in hand the oxidation to the corresponding hypervalent iodine compounds was investigated using *meta*-chloroperbenzoic acid as the oxidant in the presence of *p*-toluenesulfonic acid or triflic acid (Scheme 2). Bis-Pyr-I-OTs **12a** was obtained using DCM as the solvent in 94% (2.0 mmol scale). Under similar conditions Bis-Pyr-I-OTf **12b** was synthesized in 96% yield (85% after recrystallization from MeOH/Et₂O) on a multigram-scale. For this compound, a solvent exchange for MeCN proved to be highly beneficial, cutting the reaction time to only 16 h at rt and giving **12b** in near quantitative yield. In contrast, bis-1,2,4-triazole **5** could either not be oxidized – even under harsh conditions (65 h at 75 °C) – or not be isolated in its oxidized form **13**. In contrast, *C*-bound 1,2,3-triazole **8**, was oxidized smoothly giving bis-NH-Tria-I-OTs **14a** and bis-NH-Tria-I-OTf **14b** in 92% and 91% yield, respectively, after 14 h. Bis-NH-Pyr-I-OTs **15a** and Bis-NH-Pyr-I-OTf **15b** were obtained in 87–96% – even though after elongated reaction times (24–42 h). Benzimidazole **10** was also suitable for the oxidation employing *p*-toluenesulfonic acid (85% yield of **16a**), but mainly decomposition was observed using triflic acid. The oxidized bis-benzoxazole **17** appeared to be unstable under any tested condition. In contrast, isolated **BNHIs** (**12**, **14**, **15** and **16**) were throughout shelf-stable for at least several months without any signs of decomposition.

The solid-state structure of the recrystallized Bis-Pyr-I-OTf **12b** was investigated by X-ray crystallography, which confirmed the expected T-shaped pseudo-bicyclic benziodazole structure with two short dative bonds between the iodine atom and the coordinating pyrazole-nitrogens (I1-N1 = 2.2301(12) Å; I1-N3: 2.1944(12) Å) with a N1-I1-N3 bond angle of 150.93(5)° (Figure 2). In comparison, these coordinative bonds are only slightly longer than the reported covalent bonds in bicyclic



Scheme 2 Oxidation of bis-*N*-heterocycle-substituted iodoarenes into iodonanes **12–17**. ^aat 40 °C. ^bafter recrystallization from MeOH/Et₂O, 8.0 mmol scale.

benziodoxoles and benziodazoles, while the distorted T-shaped geometry appears to be the most bent among bicyclic hypervalent iodine compounds.^{37–40} Furthermore, the coordination of one MeOH molecule (2.712 Å) and a weak interaction of the two expected triflate counterions (2.808 Å and 3.206 Å) with the iodine atom were observed.

Finally, we investigated the reactivity of these hypervalent iodine compounds. As a model reaction the oxidation of thioanisole (**18**) to sulfoxide **19** was chosen (Figure 3). In MeOH/H₂O (conditions **A**) Bis-Pyr-I-OTs **12a** showed remarkably high reactivity with a full conversion of **18** almost instantly (>30 sec, 95%) at 0 °C, but was inefficient in MeCN (conditions **B**). In comparison, the triflate salt **12b** showed an outstanding performance giving **19** instantly (<30 sec) in near quantitative

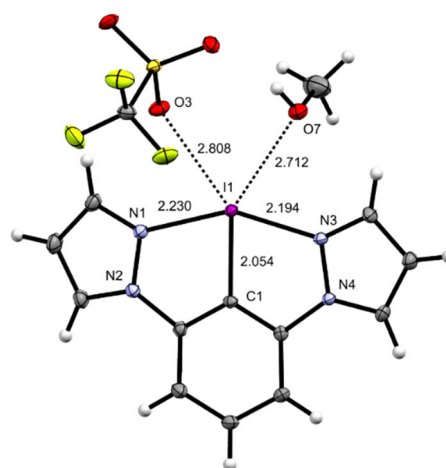


Figure 2 Crystal structure (ORTEP drawing) of **12b** (CCDC 2086526) with coordination of MeOH. Second triflate counterion omitted for clarity (see ESI). Thermal ellipsoids displayed with 50% probability. Selected bond length: I1-C1: 2.0533 (13) Å; I1-N1: 2.2301(12) Å; I1-N3: 2.1944(12) Å; I1-O3: 2.808 Å, I1-O7: 2.712 Å, I1-O6: 3.206 Å (second triflate). Selected bond angles: N1-I1-N3: 150.93(4)°; C1-I1-N1: 75.05(5)°; C1-I1-N3: 75.89(5)°.

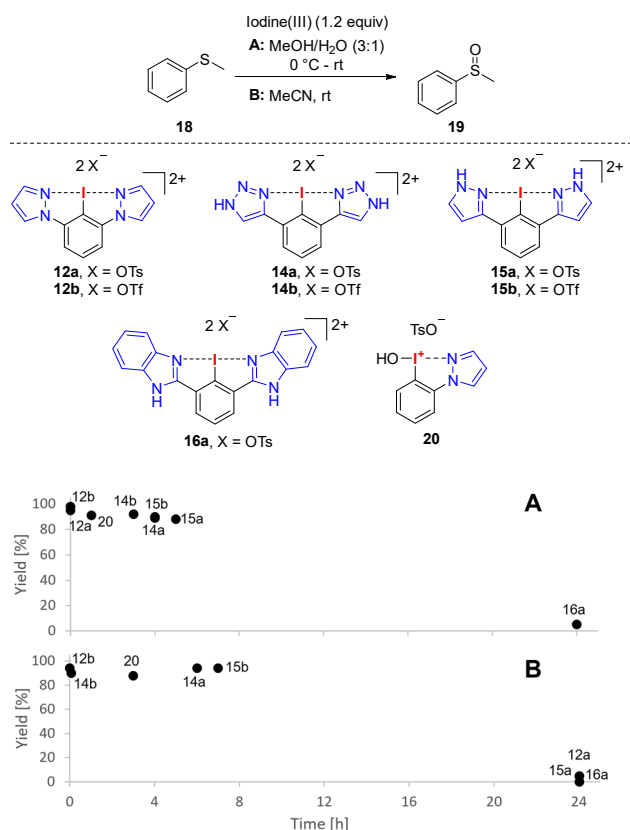
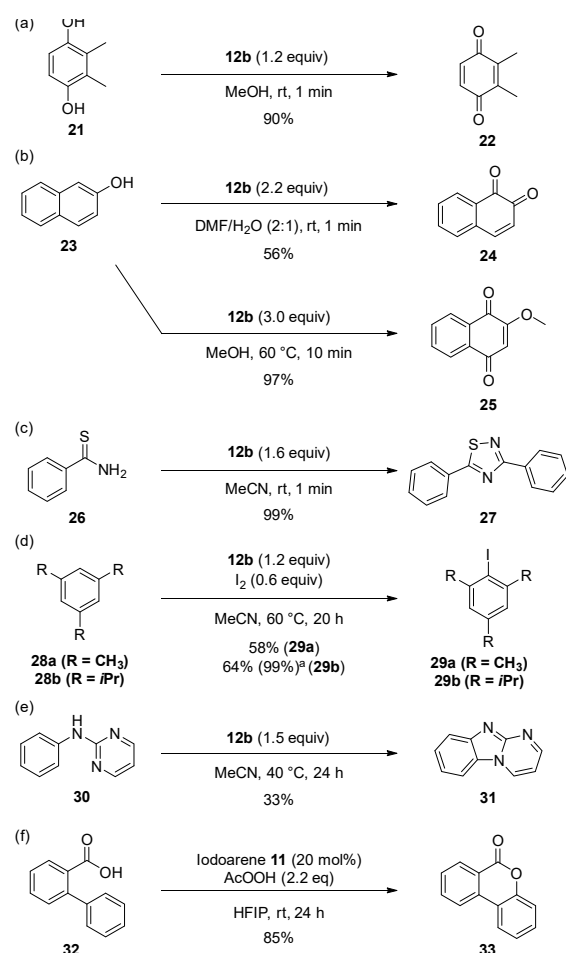


Figure 3 Oxidation of thioanisole (**18**) to sulfoxide **19** and the yield-vs.-time profile for the investigated iodonanes in MeOH/H₂O (**A**) or MeCN (**B**).

yields in both chosen solvent systems. Both triazole-substituted **BNHIs** **14a** and **14b** showed a significantly lower reactivity under both conditions (5 min – 6 h, 89–94%). As expected from the previous results for the **NHIs**,³³ bis-NH-pyrazoles **15a** and **15b** were less reactive than the triazole derivatives (4–7 h, 88–94%), with **15a** being inefficient in MeCN. Bis-benzimidazole-substituted **BNHI** **16a** proved to be nearly unreactive in both solvents. These results were compared to the previously introduced mono-pyrazole stabilized iodonane **20**.³³ In comparison to bis-pyrazole **12a**, **20** showed a much slower conversion in MeOH/H₂O (1 h, 91%), but an enhanced reactivity in MeCN (3 h, 88%). However, in both reaction media **20** was drastically outperformed by the triflate derivative **12b**.

With its high reactivity, **BNHI** **12b** appears to be among the most potent pseudocyclic λ^3 -iodanes reported so far for this oxidation.^{12–14,20,31,33} Due to these promising results, we were eager to investigate the versatility and potency of **12b** in a variety of other oxidative transformations (Scheme 3, a–f). 2,3-Dimethylhydroquinone (**21**) was efficiently oxidized to *p*-quinone **22** in 90% yield in only one minute.⁴¹ Similarly, the reaction of 2-naphthol (**23**) with 2.2 equivalents of Bis-Pyr-I-OTf **12b** gave *o*-dione **24** in 56%.⁴² When the same reaction was performed with 3.0 equivalents of **12b** in MeOH under elevated temperature, 2-methoxynaphthalene-1,4-dione **25** was directly obtained in one step from 2-naphthol. This is the first example for this reaction with quantitative results (97%). Furthermore, for the oxidative cyclization of thiobenzamide (**26**) again



Scheme 2 Further applications of Bis-Pyr-I-OTf **12b** and the catalytic application of bis-benzoxazole **11**. ^a1.5 equiv of **12b** and I₂ for 16 h.

outstanding reactivity was observed, yielding thiadiazole **27** in 99% after only one minute.^{12,14,20,31} In the iodination of arenes (Scheme 3, d), iodomesitylene (**29a**) and 1-iodo-2,4,6-triisopropylbenzene (**29b**) were obtained in 58–64% from the corresponding arenes. However, with increased equivalents of Bis-Pyr-I-OTf **12b** and iodine the triisopropyl derivative **29b** was obtained in quantitative yield.^{43,44} In contrast, Bis-Pyr-I-OTf **12b** showed only a moderate performance in the oxidative cyclization of aminopyrimidine **30**, yielding imidazopyrimidine **31** in 33%.⁴⁵ As expected, similarly to the report of Legault and co-workers, **12b** was found to be inefficient in the α -functionalization of ketones, most probably due to its highly stabilized and planar structure.²⁷

In addition, although bis-benzoxazole **11** did not form a stable hypervalent iodine species, it was found to be an efficient catalyst for the lactonization of biphenylcarboxylic acid **32**, giving chromenone **33** in 85% yield (Scheme 3, f).⁴⁶

In conclusion, we synthesized seven pseudocyclic bis-*N*-heterocycle stabilized iodonanes (**BNHIs**) and elucidated the solid-state structure of the bis-pyrazole derivative **12b**. The X-ray analysis revealed a highly bent T-shaped structure and strong intramolecular interactions between the iodine and pyrazole-nitrogen atoms (2.2301 Å and 2.1944 Å). Furthermore, **12b** is easily prepared in four steps from commercially available

starting materials in 76% overall yield and was found to be the most potent reagent in the oxidation of thioanisole among these novel λ^3 -iodanes. Beside the oxidation of sulfides, **12b** was demonstrated to be an efficient reagent in further oxidative transformations, like the oxidation of phenols.

Funding by the Fonds der Chemischen Industrie (PhD scholarship to AB) is gratefully acknowledged.

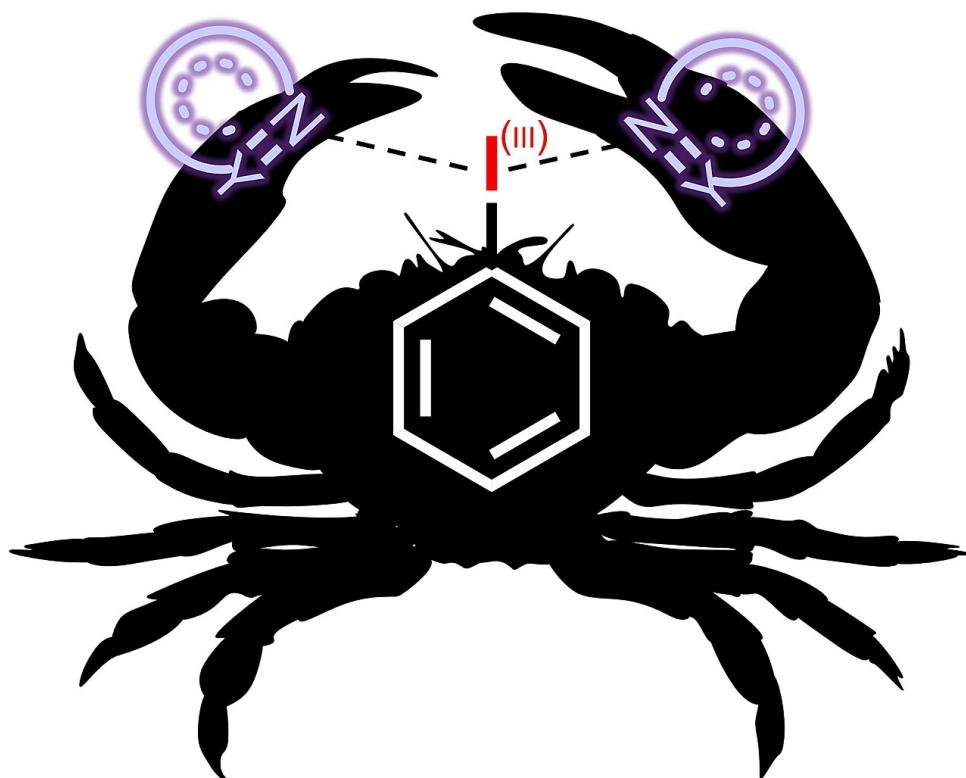
There are no conflicts to declare.

Notes and references

- 1 I. F. D. Hyatt, L. Dave, N. David, K. Kaur, M. Medard and C. Mowdawalla, *Org. Biomol. Chem.*, 2019, **17**, 7822–7848.
- 2 M. Ghosh, A. Rajkiewicz and M. Kalek, *Synthesis*, 2019, **51**, 359–370.
- 3 G. Grelier, B. Darses and P. Dauban, *Beilstein. J. Org. Chem.*, 2018, **14**, 1508–1528.
- 4 A. Boelke, P. Finkbeiner and B. J. Nachtsheim, *Beilstein. J. Org. Chem.*, 2018, **14**, 1263–1280.
- 5 N. Chatterjee and A. Goswami, *Eur. J. Org. Chem.*, 2017, 3023–3032.
- 6 A. Yoshimura and V. V. Zhdankin, *Chem. Rev.*, 2016, **116**, 3328–3435.
- 7 E. A. Merritt and B. Olofsson, *Angew. Chem. Int. Ed.*, 2009, **48**, 9052–9070.
- 8 V. V. Zhdankin, *Hypervalent Iodine Chemistry*, John Wiley & Sons Ltd, Chichester, UK, 2013.
- 9 T. Wirth, *Hypervalent Iodine Chemistry*, Springer International Publishing, Cham, 2016.
- 10 A. Yoshimura, M. S. Yusubov and V. V. Zhdankin, *Org. Biomol. Chem.*, 2016, **14**, 4771–4781.
- 11 V. V. Zhdankin and J. D. Protasiewicz, *Coord. Chem. Rev.*, 2014, **275**, 54–62.
- 12 M. Yudasaka, T. Maruyama, E. Yamaguchi, N. Tada and A. Itoh, *Eur. J. Org. Chem.*, 2018, 550–556.
- 13 A. Yoshimura, S. C. Klasen, M. T. Shea, K. C. Nguyen, G. T. Rohde, A. Saito, P. S. Postnikov, M. S. Yusubov, V. N. Nemykin and V. V. Zhdankin, *Chem. Eur. J.*, 2017, **23**, 691–695.
- 14 A. Yoshimura, K. C. Nguyen, S. C. Klasen, A. Saito, V. N. Nemykin and V. V. Zhdankin, *Chem. Commun.*, 2015, **51**, 7835–7838.
- 15 A.-A. Guibault and C. Y. Legault, *ACS Catal.*, 2012, **2**, 219–222.
- 16 U. H. Hirt, M. F. H. Schuster, A. N. French, O. G. Wiest and T. Wirth, *Eur. J. Org. Chem.*, 2001, 1569–1579.
- 17 D. Macikenas, E. Skrzypczak-Jankun and J. D. Protasiewicz, *Angew. Chem. Int. Ed.*, 2000, **39**, 2007–2010.
- 18 D. Macikenas, E. Skrzypczak-Jankun and J. D. Protasiewicz, *J. Am. Chem. Soc.*, 1999, **121**, 7164–7165.
- 19 T. Wirth and U. H. Hirt, *Tetrahedron: Asymmetry*, 1997, **8**, 23–26.
- 20 J. Qurban, M. Elsherbini, H. Alharbi and T. Wirth, *Chem. Commun.*, 2019, **55**, 7998–8000.
- 21 M. Mikhael, S. A. Adler and S. E. Wengryniuk, *Org. Lett.*, 2019, **21**, 5889–5893.
- 22 J. C. Walters, A. F. Tierno, A. H. Dubin and S. E. Wengryniuk, *Eur. J. Org. Chem.*, 2018, 1460–1464.
- 23 R. Weiss and J. Seubert, *Angew. Chem. Int. Ed.*, 1994, **33**, 891–893.
- 24 Y. A. Vlasenko, M. S. Yusubov, A. Shafir and P. S. Postnikov, *Chem. Heterocycl. Comp.*, 2020, **56**, 854–866.
- 25 A. H. Abazid and B. J. Nachtsheim, *Angew. Chem. Int. Ed.*, 2020, **59**, 1479–1484.
- 26 A. Boelke and B. J. Nachtsheim, *Adv. Synth. Catal.*, 2020, **362**, 184–191.
- 27 A.-A. Guibault, B. Basdevant, V. Wanie and C. Y. Legault, *J. Org. Chem.*, 2012, **77**, 11283–11295.
- 28 C. Hempel, C. Maichle-Mössmer, M. A. Pericàs and B. J. Nachtsheim, *Adv. Synth. Catal.*, 2017, **359**, 2931–2941.
- 29 P. Mizar, A. Laverny, M. El-Sherbini, U. Farid, M. Brown, F. Malmedy and T. Wirth, *Chem. Eur. J.*, 2014, **20**, 9910–9913.
- 30 K. Aertker, R. J. Rama, J. Opalach and K. Muñiz, *Adv. Synth. Catal.*, 2017, **359**, 1290–1294.
- 31 A. Vaish, K. D. Sayala and N. V. Tsarevsky, *Tetrahedron Letters*, 2019, **60**, 150995.
- 32 A. Boelke, Y. A. Vlasenko, M. S. Yusubov, B. J. Nachtsheim and P. S. Postnikov, *Beilstein. J. Org. Chem.*, 2019, **15**, 2311–2318.
- 33 A. Boelke, E. Lork and B. J. Nachtsheim, *Chem. Eur. J.*, 2018, **24**, 18653–18657.
- 34 Y. A. Vlasenko, P. S. Postnikov, M. E. Trusova, A. Shafir, V. V. Zhdankin, A. Yoshimura and M. S. Yusubov, *J. Org. Chem.*, 2018, **83**, 12056–12070.
- 35 Ł. Woźniak, J.-F. Tan, Q.-H. Nguyen, A. Du Madron Vigné, V. Smal, Y.-X. Cao and N. Cramer, *Chem. Rev.*, 2020, **120**, 10516–10543.
- 36 H. Nishiyama, *Chem. Soc. Rev.*, 2007, **36**, 1133–1141.
- 37 A. Yoshimura, M. T. Shea, C. L. Makitalo, M. E. Jarvi, G. T. Rohde, A. Saito, M. S. Yusubov and V. V. Zhdankin, *Beilstein. J. Org. Chem.*, 2018, **14**, 1016–1020.
- 38 W.-C. Gao and C. Zhang, *Tetrahedron Letters*, 2014, **55**, 2687–2690.
- 39 J. Tian, W.-C. Gao, D.-M. Zhou and C. Zhang, *Org. Lett.*, 2012, **14**, 3020–3023.
- 40 T. T. Nguyen, S. R. Wilson and J. C. Martin, *J. Am. Chem. Soc.*, 1986, **108**, 3803–3811.
- 41 S. Ficht, M. Mülbaier and A. Giannis, *Tetrahedron*, 2001, **57**, 4863–4866.
- 42 T. Dohi, T. Nakae, N. Takenaga, T. Uchiyama, K.-i. Fukushima, H. Fujioka and Y. Kita, *Synthesis*, 2012, **44**, 1183–1189.
- 43 T. Muraki, H. Togo and M. Yokoyama, *J. Org. Chem.*, 1999, **64**, 2883–2889.
- 44 Togo, Nabana and Yamaguchi, *J. Org. Chem.*, 2000, **65**, 8391–8394.
- 45 G. Qian, B. Liu, Q. Tan, S. Zhang and B. Xu, *Eur. J. Org. Chem.*, 2014, 4837–4843.
- 46 X. Wang, J. Gallardo-Donaire and R. Martin, *Angew. Chem. Int. Ed.*, 2014, **53**, 11084–11087.

BNHIs-ChemRXIV.pdf (430.57 KiB)

[view on ChemRxiv](#) • [download file](#)



Graphical Abstract.jpg (337.25 KiB)

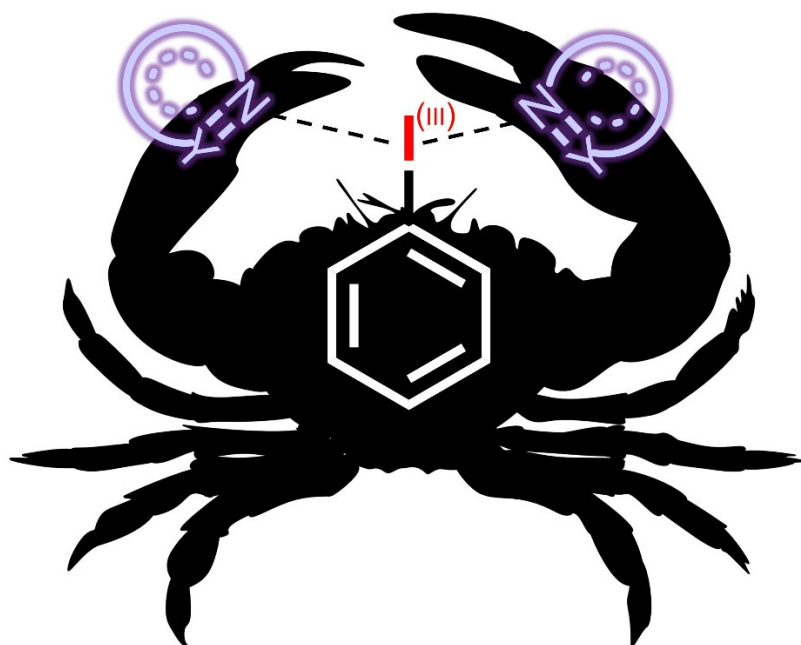
[view on ChemRxiv](#) • [download file](#)

Supporting Information

for

Pseudocyclic Bis-*N*-Heterocycle-stabilized Iodanes – Synthesis, Characterization and Applications

Andreas Boelke^[a], Soleicha Sadat^[a], Enno Lork^[b] and Boris J. Nachtsheim^{*[a]}



[a] Institute for Organic und Analytical Chemistry
University of Bremen, 28359 Bremen, Germany

[b] Institute for Inorganic Chemistry und Crystallography
University of Bremen, 28359 Bremen, Germany

Table of Contents

1. General Information.....	3
2. Preparation of <i>N</i> -bound Bis-(<i>N</i> -HetAr)-aryl iodides	5
3. Preparation of λ^3 -Iodanes	13
4. Applications.....	17
5. Crystallographic data.....	23
6. References	29
7. NMR spectra	30

1. General Information

Unless otherwise stated, all reactions with moisture- or oxygen-sensitive reagents were performed using standard Schlenk techniques under a nitrogen or argon atmosphere. Reagents were used as received from their commercial supplier (abcr, Acros Organics, Alfa Aesar, Apollo Scientific, Carbolution Chemicals, Sigma Aldrich, TCI). Anhydrous dichloromethane (DCM), tetrahydrofuran (THF) and toluene were obtained from an *inert* PS-MD-6 solvent purification system. All other solvents were dried using standard methods.^[1] Unless otherwise stated, all yields refer to isolated yields of compounds estimated to be >95% pure as determined by ¹H-NMR spectroscopy.

Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (*Macherey-Nagel*, ALUGRAM Xtra SIL G/UV₂₅₄) and visualized by UV light (254 nm/366 nm). Flash column chromatography was performed on silica gel (0.040 – 0.063 mm) with the solvents given in the procedures.

¹H-, ¹³C- and ¹⁹F-NMR spectra were recorded on *Bruker Avance Neo* 600-spectrometers. Chemical shifts for ¹H-NMR spectra were reported as δ (parts per million) relative to the residual signal of CHCl₃ at 7.26 ppm (s), *d*₃-MeCN at 1.94 ppm (quin.), *d*₄-MeOH at 3.31 ppm (quin.) or *d*₆-DMSO at 2.50 ppm (quin.). Chemical shifts for ¹³C-NMR spectra were reported as δ (parts per million) relative to the signal of CDCl₃ at 77.0 ppm (t), *d*₃-MeCN at 1.3 ppm (sept.), *d*₄-MeOH at 49.0 ppm (sept.) or *d*₆-DMSO at 39.5 ppm (sept.). ¹⁹F-NMR spectra were reported as δ (parts per million) relative to CFCl₃ at 0.00 ppm as external standard. The following abbreviations were used to describe splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext. = sextet, sept = septet, m = multiplet. Coupling constants *J* are given in Hertz.

High resolution (HR) EI mass spectra were recorded on the double focussing mass spectrometer ThermoQuest MAT 95 XL from *Finnigan MAT*. HR-ESI mass spectra were recorded on a Bruker impact II. APCI mass spectra were recorded on an *Advion* Expression CMS^L via ASAP probe or direct inlet. EI mass spectra were obtained from an Agilent 7890B GC System with an Agilent 5977A MSD mass spectrometer. All signals were reported with the quotient from mass to charge *m/z*.

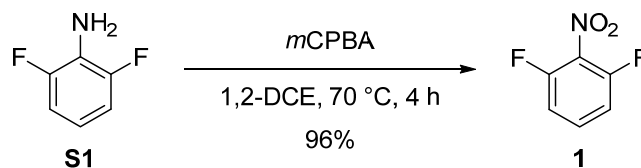
IR spectra were recorded on a *Nicolet* Thermo iS10 scientific spectrometer with a diamond ATR unit. The absorption bands were reported in cm⁻¹.

Melting points were determined on a *Büchi* M-5600 Melting Pint apparatus with a heating rate of 5 °C/min. The melting points were reported in °C. Most of the hypervalent iodine compounds underwent changes in appearance (e.g. softening) before final melting/decomposition.

Single crystals were grown from MeOH-solution by slow Et₂O diffusion. A suitable crystal was selected and measured on a Bruker D8 Venture diffractometer. The crystal was kept at 100 K during data collection. Using Olex2,^[2] the structure was solved with the ShelXT^[3] structure solution program using Intrinsic Phasing and refined with the XL^[4] refinement package using Least Squares minimization. The ORTEP drawings were made using the program Mercury from the CCDC.

2. Preparation of Bis-(*N*-HetAr)-aryl iodides

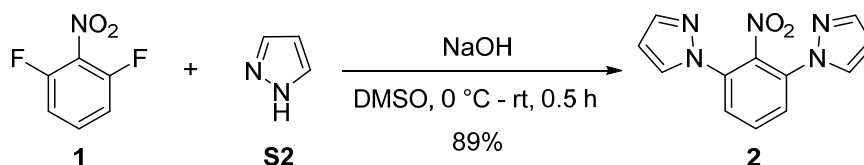
1,3-Difluoro-2-nitrobenzene (**1**)



A modified literature procedure was used.^[5] To a solution of 2,6-difluoroaniline (**S1**, 25.8 g, 200 mmol, 1.0 equiv) in 1,2-dichloroethane (400 mL) was added *m*CPBA (75 %, 197 g, 800 mmol, 4.0 equiv). The reaction mixture was stirred for 4 h at 70 °C (mechanical stirring is highly recommended). Afterwards the mixture was diluted with DCM (400 mL) and the formed precipitate (*m*CBA) was filtered off and extracted with further DCM (2 x 100 mL). The filtrate was washed with 1 M aq. KOH solution (4 x 500 mL) and brine (200 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give 1,3-difluoro-2-nitrobenzene (**1**, 30.5 g, 192 mmol, 96 %) as an orange liquid.

¹H-NMR (CDCl₃, 601 MHz): δ (ppm) 7.53 (tt, *J* = 8.6, 5.9 Hz, 1H), 7.14 – 7.09 (m, 2H). ¹³C-NMR (CDCl₃, 151 MHz) δ (ppm) 154.7 (d, *J* = 261.5 Hz), 132.9 (d, *J* = 19.3 Hz), 132.9, 112.9 (dd, *J* = 19.4, 3.9 Hz). IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3105, 1534, 1357, 1025, 788. MS (EI) *m/z* = 159.08 [M]⁺. Analytical data is in accordance with literature data.^[5]

1,1'-(2-Nitro-1,3-phenylene)bis(1*H*-pyrazole) (**2**)

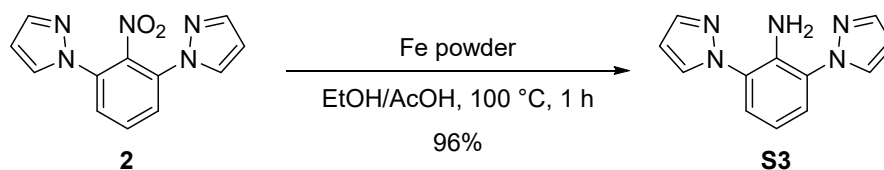


A modified literature procedure was used.^[6] 1,3-Difluoro-2-nitrobenzene (**1**, 3.18 g, 20.0 mmol, 1.00 equiv) and 1*H*-pyrazole (**S2**, 3.06 g, 45.0 mmol, 2.25 equiv) were dissolved in DMSO (7.5 mL) and powdered NaOH (freshly ground pellets, 2.70 g, 67.5 mmol, 3.38 mmol) was slowly added while the mixture was cooled with an ice-bath (strong exothermic reaction!). Afterwards the mixture was vigorously stirred for 0.5 h without cooling and was then diluted with H₂O (80 mL) and stirring continued for 5 min. The reaction mixture was stored at 4 °C for 0.5 h and the formed precipitate was filtered off and washed with water (3 x 50 mL). Drying *in vacuo* afforded 1,1'-(2-nitro-1,3-phenylene)bis(1*H*-pyrazole) (**2**, 4.56 g, 17.9 mmol, 89%) as a beige solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 7.78 (d, *J* = 2.5 Hz, 2H), 7.76 (d, *J* = 1.8 Hz, 2H), 7.68 (dd, *J* = 8.8, 7.4 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 6.50 (dd, *J* = 2.5, 1.8 Hz, 2H). ¹³C-NMR (CDCl₃, 151 MHz) δ (ppm): 142.7, 139.6, 133.7, 131.2, 130.0, 124.6, 108.5. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3143,

1602, 1591, 1493, 1482, 754. HR-MS (ESI) Calculated for $C_{12}H_9N_5NaO_2^+$ $[M+Na]^+$: m/z 278.06485, found 278.06483. Mp. 159–161 °C.

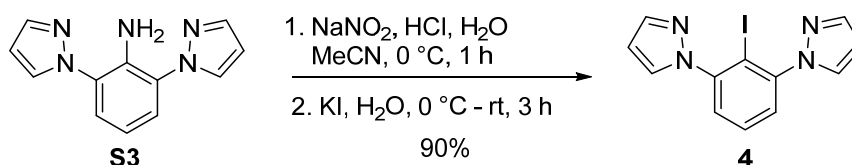
2,6-Di(1*H*-pyrazol-1-yl)aniline (**S3**)



A modified literature procedure was used.^[7] 1,1'-(2-Nitro-1,3-phenylene)bis(1*H*-pyrazole) (**2**, 4.47 g, 17.5 mmol, 1.0 equiv) was suspended in EtOH/AcOH (1:1, 100 mL), iron powder (2.93 g, 53.5 mmol, 3.0 equiv) was added and the mixture was stirred at 100 °C for 1 h. After cooling to room temperature, the mixture was neutralized with sat. $NaHCO_3$ -solution and extracted with EtOAc (4 x 300 mL). The combined organic phases were washed with brine (300 mL), dried over Na_2SO_4 , filtered and concentrated *in vacuo* to give 2,6-di(1*H*-pyrazol-1-yl)aniline (**S3**, 3.78 g, 16.8 mmol, 96%) as a beige solid.

1H -NMR ($CDCl_3$, 601 MHz) δ (ppm) 7.78 (dd, J = 1.9, 0.7 Hz, 2H), 7.74 (dd, J = 2.4, 0.8 Hz, 2H), 7.22 (dd, J = 8.0, 0.9 Hz, 2H), 6.82 (dd, J = 8.8, 7.1 Hz, 1H), 6.48 (dd, J = 2.4, 1.9 Hz, 2H), 5.35 (s, 2H). ^{13}C -NMR ($CDCl_3$, 151 MHz) δ (ppm) 140.9, 137.1, 130.3, 127.8, 123.8, 116.4, 106.7. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3478, 3367, 3130, 1614, 1575, 1516, 1507, 1307, 1050, 778. HR-MS (ESI) Calculated for $C_{12}H_{12}N_5^+$ $[M+H]^+$: m/z 226.10872, found 226.10865. Mp. 107–109 °C.

1,1'-(2-Iodo-1,3-phenylene)bis(1*H*-pyrazole) (**4**)

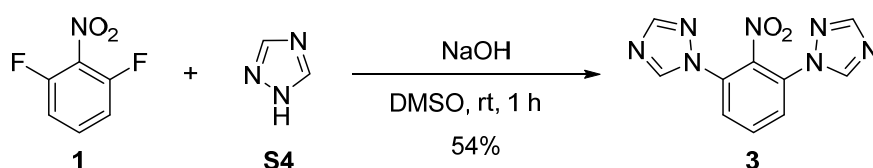


A modified literature procedure was used.^[8] 2,6-Di(1*H*-pyrazol-1-yl)aniline (**S3**, 3.72 g, 16.5 mmol, 1.00 equiv) was dissolved in MeCN (50 mL) and aqueous 6 M HCl (50 mL) was added. The mixture was cooled to 0 °C and a solution of $NaNO_2$ (1.32 g, 19.0 mmol, 1.15 equiv) in H_2O (15 mL) was added dropwise over the course of 5 min. The reaction mixture was stirred for 1 h at 0 °C, before a solution of KI (8.22 g, 49.5 mmol, 3.00 equiv) in H_2O (15 mL) was added dropwise over the course of 5 min. After further 5 min at 0 °C, the ice-bath was removed, and the reaction mixture was stirred for 3 h at room temperature. Afterwards H_2O (250 mL) was added, and the mixture was extracted with EtOAc (3 x 250 mL). The combined organic phases were washed with sat. $Na_2S_2O_3$ -solution (200 mL) and brine (200 mL), dried over Na_2SO_4 , filtered and concentrated *in vacuo* to give 1,1'-(2-iodo-1,3-phenylene)bis(1*H*-pyrazole) (**4**, 5.40 g, 16.1 mmol, 97%) as a yellow solid. Recrystallization

from *i*-PrOH provided analytical pure **4** (5.00 g, 14.9 mmol, 90%) as a colourless to off-white solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 7.77 (dd, *J* = 1.8, 0.6 Hz, 2H), 7.73 (dd, *J* = 2.4, 0.6 Hz, 2H), 7.54 (dd, *J* = 8.7, 6.9 Hz, 1H), 7.48 (d, *J* = 0.6 Hz, 1H), 7.47 (d, *J* = 1.2 Hz, 1H), 6.49 (dd, *J* = 2.4, 1.9 Hz, 2H). ¹³C-NMR (CDCl₃, 151 MHz) δ (ppm) 145.1, 141.0, 131.3, 129.4, 128.4, 106.9, 97.3. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3112, 1474, 1321, 1079, 1048, 746. HR-MS (ESI) Calculated for C₁₂H₁₀IN₄⁺ [M+H]⁺: *m/z* 336.99447, found 336.99427. Mp. 147–149 °C.

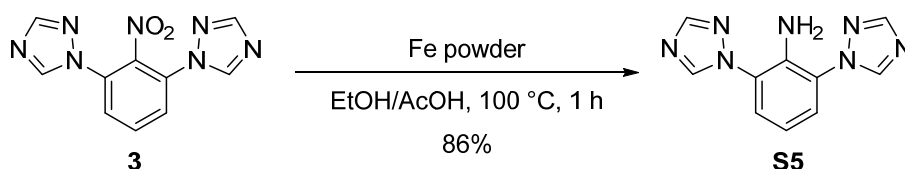
1,1'-(2-Nitro-1,3-phenylene)bis(1*H*-1,2,4-triazole) (**3**)



A slightly modified literature procedure was used.^[6] 1,3-Difluoro-2-nitrobenzene (**1**, 3.18 g, 20.0 mmol, 1.00 equiv) and 1*H*-1,2,4-triazole (**S4**, 3.11 g, 45.0 mmol, 2.25 equiv) were dissolved in DMSO (7.5 mL) and powdered NaOH (freshly ground pellets, 2.70 g, 67.5 mmol, 3.38 mmol) was slowly added (strong exothermic reaction!). Afterwards the mixture was vigorously stirred for 1 h, was then diluted with H₂O (100 mL) and extracted with EtOAc (3 x 150 mL). The combined organic phases were washed with brine (100 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was recrystallized from MeOH to give 1,1'-(2-nitro-1,3-phenylene)bis(1*H*-1,2,4-triazole) (**3**, 2.76 g, 10.7 mmol, 54%) as a beige solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 8.48 (s, 2H), 8.15 (s, 2H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H). ¹³C-NMR (CDCl₃, 151 MHz) δ (ppm) 153.8, 143.7, 139.9, 132.2, 130.6, 126.5. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3116, 1607, 1593, 1540, 1507, 1360, 1012, 809. HR-MS (ESI) Calculated for C₁₀H₈N₇O₂⁺ [M+H]⁺: *m/z* 258.07340, found 258.07342. Mp. 209–211 °C.

2,6-Di(1*H*-1,2,4-triazol-1-yl)aniline (**S5**)

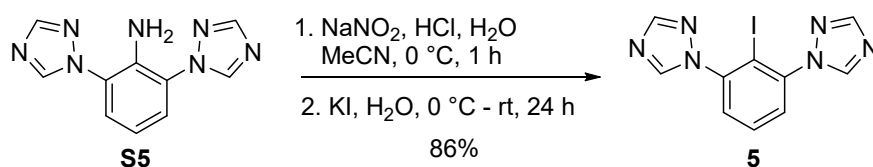


A slightly modified literature procedure was used.^[7] 1,1'-(2-Nitro-1,3-phenylene)bis(1*H*-1,2,4-triazole) (**3**, 2.75 g, 10.7 mmol, 1.0 equiv) was suspended in EtOH/AcOH (1:1, 60 mL), iron powder (1.79 g, 32.1 mmol, 3.0 equiv) was added and the mixture was stirred at 100 °C for 1 h. After cooling to room temperature, the mixture was neutralized with sat. NaHCO₃-solution and the formed precipitate was filtered off, washed with H₂O (200 mL) and extracted with

EtOAc (500 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 x 400 mL). The combined organic phases were washed with brine (400 mL), dried over Na₂SO₄, filtered and concentrated *in vacuo* to give 2,6-di(1*H*-1,2,4-triazol-1-yl)aniline (**S5**, 2.09 g, 9.20 mmol, 86%) as a colourless solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 8.41 (s, 2H), 8.21 (s, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 8.0 Hz, 1H), 5.47 (s, 2H). ¹³C-NMR (CDCl₃, 151 MHz) δ (ppm) 152.9, 143.8, 136.8, 125.1, 124.2, 116.9. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3457, 3365, 3086, 1508, 1495, 1278, 788. HR-MS (ESI) Calculated for C₁₀H₉N₇Na⁺ [M+Na]⁺: *m/z* 250.08116, found 250.08117. Mp. 180–182 °C.

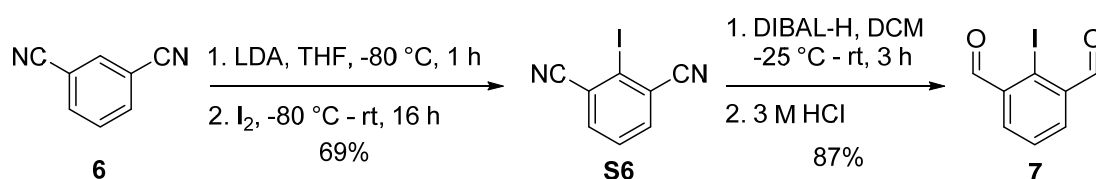
1,1'-(2-Iodo-1,3-phenylene)bis(1*H*-1,2,4-triazole) (**5**)



A modified literature procedure was used.^[8] 2,6-Di(1*H*-1,2,4-triazol-1-yl)aniline (**S5**, 2.09 g, 9.20 mmol, 1.00 equiv) was dissolved in MeCN (30 mL) and aqueous 6 M HCl (30 mL) was added. The mixture was cooled to 0 °C and a solution of NaNO₂ (0.730 g, 10.6 mmol, 1.15 equiv) in H₂O (10 mL) was added dropwise over the course of 5 min. The reaction mixture was stirred for 1 h at 0 °C, before a solution of KI (4.58 g, 27.6 mmol, 3.00 equiv) in H₂O (10 mL) was added dropwise over the course of 5 min. After further 5 min at 0 °C, the ice-bath was removed, and the reaction mixture was stirred for 24 h at room temperature. Afterwards H₂O (200 mL) was added, and the mixture was extracted with EtOAc (4 x 300 mL). The combined organic phases were washed with sat. Na₂S₂O₃-solution (300 mL) and brine (300 mL), dried over Na₂SO₄, filtered and concentrated *in vacuo* to give 1,1'-(2-iodo-1,3-phenylene)bis(1*H*-1,2,4-triazole) (**5**, 2.69 g, 7.96 mmol, 86%) as a beige solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 8.43 (d, *J* = 2.0 Hz, 2H), 8.17 (s, 2H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.1, 2.3 Hz, 2H). ¹³C-NMR (CDCl₃, 151 MHz) δ (ppm) 152.7, 144.3, 141.9, 130.1, 129.3, 97.6. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3105, 1585, 1470, 1180, 1119, 1025, 994. HR-MS (ESI) Calculated for C₁₀H₈IN₆⁺ [M+H]⁺: *m/z* 338.98497, found 338.98471. Mp. 170–172 °C.

2-Iodoisophthalaldehyde (**7**)



A slightly modified literature procedure was used.^[9] A solution of isophthalonitrile (**6**, 6.41 g, 50.0 mmol, 1.0 equiv) in dry THF (100 mL) was added dropwise to a 0.3 M LDA solution in dry

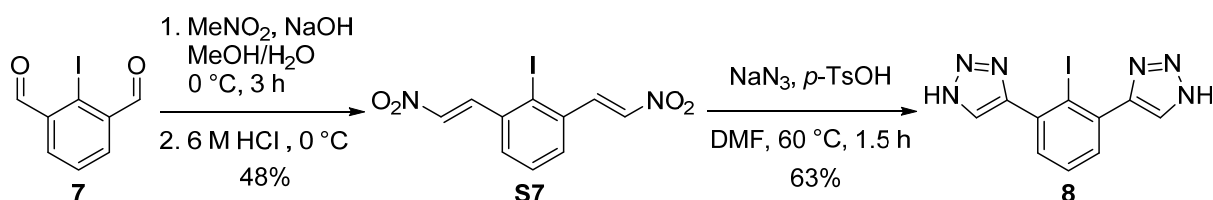
THF (200 mL, 60.0 mmol, 1.2 equiv) over the course of 0.5 h at $-80\text{ }^{\circ}\text{C}$. After stirring at this temperature for 1 h, iodine (15.2 g, 60.0 mmol, 1.2 equiv) was added portionwise and stirring continued at $-80\text{ }^{\circ}\text{C}$ for 0.5 h before the mixture was slowly warmed up to room temperature (in total 16 h). The reaction was quenched with sat. $\text{Na}_2\text{S}_2\text{O}_3$ -solution (40 mL) and H_2O (100 mL) was added. The mixture was extracted with EtOAc (3 x 150 mL) and the combined organic phases were washed with brine (150 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (cyclohexane/EtOAc 3:1) and subsequent recrystallization from cyclohexane/EtOAc to give 2-iodoisophthalonitrile (**S6**, 8.76 g, 34.5 mmol, 69%) as a colourless solid.

$^1\text{H-NMR}$ (CDCl_3 , 601 MHz) δ (ppm) 7.79 (d, $J = 7.8\text{ Hz}$, 2H), 7.62 (t, $J = 7.8\text{ Hz}$, 1H). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz) δ (ppm) 137.2, 129.1, 123.4, 118.1, 103.7. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3064, 2231, 1403, 1023, 804. MS (EI) $m/z = 253.99\text{ [M]}^{+}$. Mp. 208–210 $^{\circ}\text{C}$. Analytical data is in accordance with literature data.^[10]

A modified literature procedure was used.^[10] To a solution of 2-iodoisophthalonitrile (**S6**, 5.08 g, 20.0 mmol, 1.0 equiv) in dry DCM (80 mL) was added DIBAL-H (1.1 M in cyclohexane, 40 mL, 44.0 mmol, 2.2 equiv) dropwise over the course of 20 min at $-25\text{ }^{\circ}\text{C}$. Afterwards the reaction mixture was slowly warmed up to room temperature over the course of 3 h and was then quenched with aqueous 3 M HCl (40 mL). H_2O (50 mL) was added and the mixture was extracted with DCM (3 x 60 mL). The combined organic phases were washed with brine (60 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was recrystallized from cyclohexane to give 2-iodoisophthalaldehyd (**7**, 4.51 g, 17.3 mmol, 87%) as yellow needles.

$^1\text{H-NMR}$ (CDCl_3 , 601 MHz) δ (ppm) 10.31 (s, 2H), 8.08 (d, $J = 7.6\text{ Hz}$, 2H), 7.55 (t, $J = 7.9$, 6.9 Hz, 1H). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz) δ (ppm) 195.0, 136.0, 135.6, 129.0, 106.1. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3051, 1700, 1675, 1054, 791. MS (EI) $m/z = 259.98\text{ [M]}^{+}$. Mp. 132–134 $^{\circ}\text{C}$. Analytical data is in accordance with literature data.^[10]

4,4'-(2-Iodo-1,3-phenylene)bis(1H-1,2,3-triazole) (**8**)



A slightly modified literature procedure was used.^[11] 2-Iodoisophthalaldehyd (**7**, 2.60 g, 10.0 mmol, 1.0 equiv) and nitromethane (2.64 mL, 50.0 mmol, 5.0 equiv) were dissolved in MeOH (50 mL) and aqueous 10% NaOH (18 mL, 50.0 mmol, 5.0 equiv) was added dropwise over the course of 3 min at $0\text{ }^{\circ}\text{C}$. After stirring at $0\text{ }^{\circ}\text{C}$ for 3 h, the reaction mixture was slowly

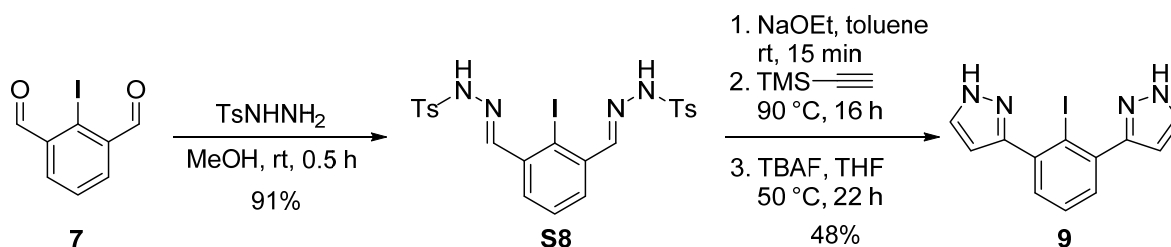
transferred to vigorously stirred aqueous 6 M HCl (75 mL) at 0 °C. The formed precipitate was filtered off and washed with H₂O. After drying *in vacuo*, the solid was recrystallized from EtOH to give 2-iodo-1,3-bis((*E*)-2-nitrovinyl)benzene (**S7**, 1.67 g, 4.83 mmol, 48%) as a yellowish solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 8.36 (d, *J* = 13.5 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.50 (dd, *J* = 8.4, 7.0 Hz, 1H), 7.42 (d, *J* = 13.4 Hz, 2H). ¹³C-NMR (CDCl₃, 151 MHz) δ (ppm) 142.0, 139.8, 136.6, 130.2, 129.3, 108.2. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3107, 1626, 1500, 1393, 1333, 1260, 950. HR-MS (EI) Calculated for C₁₀H₇IN₂O₄⁺ [M]⁺: *m/z* 345.94451, found 345.94392. Mp. 196–199 °C.

The next step should be conducted behind a safety shield! A slightly modified literature procedure was used.^[11] 2-Iodo-1,3-bis((*E*)-2-nitrovinyl)benzene (**S7**, 1.66 g, 4.80 mmol, 1.0 equiv) was dissolved in DMF (50 mL) and NaN₃ (0.995 g, 14.4 mmol, 3.0 equiv) and *p*-TsOH•H₂O (0.914 g, 4.80 mmol, 1.0 equiv) were added. The mixture was stirred for 2 h at 60 °C, then diluted with H₂O (200 mL) and extracted with EtOAc (3 x 150 mL). The combined organic phases were washed with H₂O and brine (150 mL each), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified via a short silica column (cyclohexane/EtOAc 7:3) and (after removal of the solvent) the obtained product was further washed with hot cyclohexane/EtOAc (2:1) to give 4,4'-(2-iodo-1,3-phenylene)bis(1*H*-1,2,3-triazole) (**8**, 1.02 g, 3.02 mmol, 63%) as a beige solid.

¹H-NMR (*d*₆-DMSO, 601 MHz) δ (ppm) (15.26 (s_{br}, 2H, tautomeric NH),) 8.16 (s_{br}, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 2H). ¹³C-NMR (*d*₆-DMSO, 151 MHz) δ (ppm) 148.6 (br), 137.6 (br), 133.2 (br), 130.6, 128.2, 103.2. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3109, 2925, 1551, 1437, 1404, 1235, 1135, 1072, 1014, 800. HR-MS (ESI) Calculated for C₁₀H₈IN₆⁺ [M+H]⁺: *m/z* 338.98497, found 338.98463. Mp. 218–220 °C (decomp).

3,3'-(2-Iodo-1,3-phenylene)bis(1*H*-pyrazole) (**9**)



A slightly modified literature procedure was used.^[12] Tosylhydrazide (2.43 g, 13.0 mmol, 2.16 equiv) was dissolved in MeOH (30 mL) and 2-iodoisophthalaldehyde (**7**, 1.56 g, 6.00 mmol, 1.00 equiv) was added portionwise. After 5 min the reaction mixture completely solidifies and additional MeOH (15 mL) is added to enable stirring for further 25 min. Afterwards the solvent was removed under reduced pressure and the residue was suspended

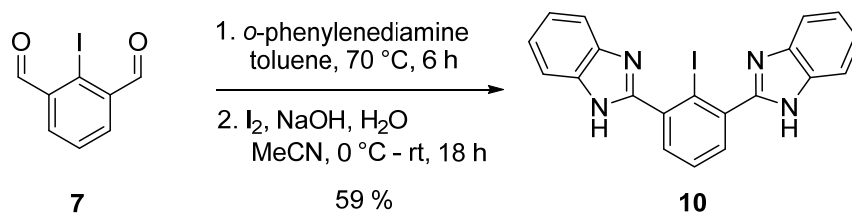
in MeOH (10 mL). After storing at 4 °C for 30 min, the precipitate is filtered off, washed with MeOH (5 mL) and dried *in vacuo* to give *N',N'''*-(2-iodo-1,3-phenylene)bis(methanylylidene))bis(4-methylbenzenesulfonohydrazide) (**S8**, 3.25 g, 5.45 mmol, 91%) as a colourless solid.

¹H-NMR (*d*₆-DMSO, 601 MHz) δ (ppm) 11.80 (s, 2H), 8.23 (s, 2H), 7.75 (d, *J* = 8.2 Hz, 4H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 4H), 7.37 (t, *J* = 7.8 Hz, 1H), 2.35 (s, 6H). ¹³C-NMR (*d*₆-DMSO, 151 MHz) δ (ppm) 150.0, 143.6, 136.5, 136.0, 129.8, 128.6, 128.1, 127.1, 104.3, 21.0. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3185, 1597, 1436, 1392, 1366, 1312, 1158, 1082, 890. HR-MS (ESI) Calculated for C₂₂H₂₂IN₄O₄S₂⁺ [M+H]⁺: *m/z* 597.01217, found 597.01141. Mp. 183–185 °C (decomp).

A slightly modified literature procedure was used.^[12] To a 150 mL pressure vial was added *N',N'''*-(2-iodo-1,3-phenylene)bis(methanylylidene))bis(4-methylbenzenesulfonohydrazide) (**S8**, 2.98 g, 5.00 mmol, 1.0 equiv) and dry toluene (65 mL) under an argon atmosphere. NaOEt (1.70 g, 25.0 mmol, 5.0 equiv) was added and the mixture was stirred for 15 min at room temperature. A solution of trimethylsilylacetylene (2.95 g, 30.0 mmol, 6.0 equiv) in dry toluene (15 mL) was added, the vial sealed, and the mixture was stirred at 90 °C for 16 h. The mixture was diluted with H₂O (70 mL), the pH adjusted to ~3 with aqueous 1 M HCl and extracted with EtOAc (3 x 100 mL). The combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was dissolved in dry THF (30 mL), TBAF (1 M in THF, 12.5 mL, 12.5 mmol, 2.5 equiv) was added and the mixture was stirred for 22 h at 50 °C. H₂O (50 mL) was added and the mixture extracted with DCM (3 x 50 mL). The combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (petrol ether/EtOAc 1:1→0:1) and the thus obtained product was further washed with hot EtOAc to give 3,3'-(2-iodo-1,3-phenylene)bis(1*H*-pyrazole) (**9**, 813 mg, 2.42 mmol, 48%) as a beige solid.

¹H-NMR (*d*₆-DMSO, 601 MHz) δ (ppm) 12.98 (s_{br}, 2H), 7.72 (s, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 6.49 (s, 2H). ¹³C-NMR (*d*₆-DMSO, 151 MHz) δ (ppm) 152.4 (br), 140.2 (br), 130.1, 129.5 (br), 127.7, 105.5, 103.1. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3142, 2831, 1732, 1458, 1396, 1298, 1241, 1099, 1046, 934. HR-MS (ESI) Calculated for C₁₂H₁₀IN₄⁺ [M+H]⁺: *m/z* 336.99447, found 336.99392. Mp. 202–204 °C (decomp).

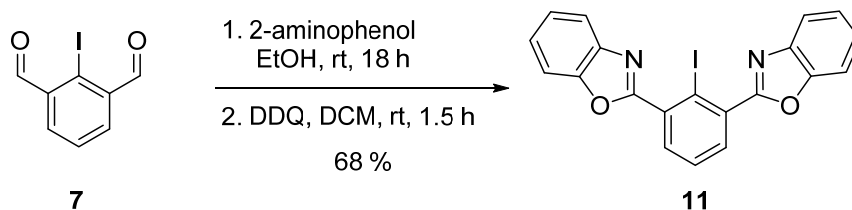
2,2'-(2-Iodo-1,3-phenylene)bis(1*H*-benzo[*d*]imidazole) (10)



A modified literature procedure was used.^[11] 2-Iodoisophthalaldehyde (**7**, 780 mg, 3.00 mmol, 1.0 equiv) and *o*-phenylenediamine (681 mg, 6.30 mmol, 2.1 equiv) were dissolved in toluene (30 mL) and the mixture was stirred for 6 h at 70 °C. Afterwards the solvent was removed under reduced pressure and the residue was suspended in MeCN (25 mL). Iodine (3.06 g, 12.0 mmol, 4.0 equiv) and aqueous 10% NaOH (11 mL, 30.0 mmol, 10 equiv) were added at 0 °C and the reaction mixture was slowly warmed up to room temperature and stirred for a total of 18 h. The solvent was removed under reduced pressure and the residue was suspended in DCM (20 mL) and quenched with sat. Na₂S₂O₃-solution (10 mL). The formed precipitate was filtered off, washed with H₂O (20 mL), and purified via column chromatography on silica gel (DCM/MeOH 20:1→10:1) to give 2,2'-(2-iodo-1,3-phenylene)bis(1*H*-benzo[*d*]imidazole) (**10**, 773 mg, 1.77 mmol, 59%) as a brownish solid.

¹H-NMR (*d*₆-DMSO, 601 MHz) δ (ppm) 12.79 (s, 2H), 7.72 – 7.70 (m, 2H), 7.69 – 7.67 (m, 3H), 7.59 – 7.51 (m, 2H), 7.27 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.23 (dd, *J* = 7.6, 1.3 Hz, 2H). ¹³C-NMR (*d*₆-DMSO, 151 MHz) δ (ppm) 153.2, 143.1, 138.7, 134.3, 131.9, 128.0, 122.6, 121.5, 119.2, 111.5, 101.4. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 2664, 1618, 1538, 1422, 1263, 1015, 739. HR-MS (ESI) Calculated for C₂₀H₁₄IN₄⁺ [M+H]⁺: *m/z* 437.02577, found 437.02543. Mp. 357–359 °C.

2,2'-(2-Iodo-1,3-phenylene)bis(benzo[*d*]oxazole) (11)

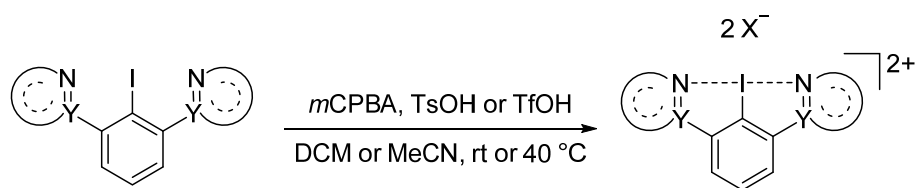


A slightly modified literature procedure was used.^[13] 2-Iodoisophthalaldehyde (**7**, 780 mg, 3.00 mmol, 1.0 equiv) and 2-aminophenol (655 mg, 6.00 mmol, 2.0 equiv) were dissolved in EtOH (30 mL) and the mixture was stirred for 18 h at room temperature. Afterwards the solvent was removed under reduced pressure and the residue was dissolved in DCM (60 mL). DDQ (1.50 g, 6.60 mmol, 2.2 equiv) was added portionwise and the mixture was stirred at room temperature for 1.5 h. The reaction was quenched with sat. NaHCO₃-solution (100 mL) and extracted with DCM (3 x 120 mL). The combined organic phases were washed with brine (120 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue

was purified via column chromatography on silica gel (cyclohexane/EtOAc 20:1) to give 2,2'-(2-iodo-1,3-phenylene)bis(benzo[d]oxazole) (**11**, 891 mg, 2.03 mmol, 68%) as an orange solid.

$^1\text{H-NMR}$ (CDCl_3 , 601 MHz) δ (ppm) 7.95 (d, $J = 7.7$ Hz, 2H), 7.92 – 7.85 (m, 2H), 7.69 – 7.61 (m, 3H), 7.47 – 7.39 (m, 4H). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz) δ (ppm) 162.9, 150.8, 141.4, 135.9, 133.6, 128.3, 125.8, 124.8, 120.7, 111.0, 96.7. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 1540, 1443, 1231, 1097, 857, 747. HR-MS (ESI) Calculated for $\text{C}_{20}\text{H}_{12}\text{IN}_2\text{O}_2^+ [\text{M}+\text{H}]^+$: m/z 438.99380, found 438.99351. Mp. 176–178 °C.

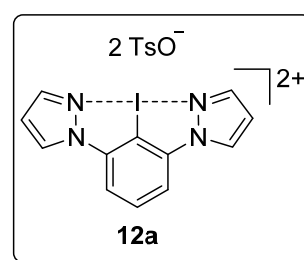
3. Preparation of λ^3 -Iodanes



General Procedure 1: The corresponding iodoarene (1.0 equiv) and *m*CPBA (85%, 1.2–1.5 equiv) were dissolved in the indicated solvent, TsOH or TfOH (2.2–2.4 equiv) was added, and the reaction mixture was stirred at room temperature or 40 °C for the indicated time. Afterwards the solvent was either removed under reduced pressure and the residue was suspended in Et_2O (and EtOAc for some) or Et_2O was directly added to the reaction mixture. After storing at 4 °C for 30 min the formed precipitate was filtered off and washed with additional Et_2O to give the desired λ^3 -iodanes.

(2,6-Bis(1*H*-pyrazol-1-yl)phenyl)- λ^3 -iodanediyl bistosylate (**12a**, Bis-Pyr-I-OTs)

Following GP1, 1,1'-(2-iodo-1,3-phenylene)bis(1*H*-pyrazole) (**4**, 672 mg, 2.00 mmol, 1.0 equiv) was stirred in DCM (20 mL) with *m*CPBA (607 mg, 3.00 mmol, 1.5 equiv) and *p*-TsOH· H_2O (837 mg, 4.40 mmol, 2.2 equiv) for 65 h at 40 °C. Afterwards Et_2O (60 mL) was directly added and after storing at 4 °C, the precipitate was filtered off and washed with Et_2O (2 x 10 mL) to give Bis-Pyr-I-OTs **12a** (1.27 g, 1.87 mmol, 94%) as a colourless solid.

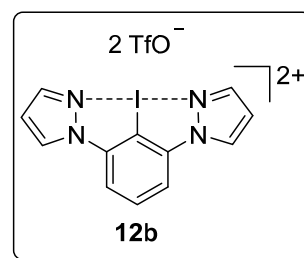


$^1\text{H-NMR}$ (d_6 -DMSO, 601 MHz) δ (ppm) 9.51 (d, $J = 2.9$ Hz, 2H), 8.71 (d, $J = 2.6$ Hz, 2H), 8.42 (d, $J = 8.1$ Hz, 2H), 8.15 (t, $J = 8.1$ Hz, 1H), 7.46 (d, $J = 7.9$ Hz, 4H), 7.13 (t, $J = 2.8$ Hz, 2H), 7.10 (d, $J = 7.8$ Hz, 4H), 2.28 (s, 6H). $^{13}\text{C-NMR}$ (d_6 -DMSO, 151 MHz) δ (ppm) 145.4, 142.3, 137.7, 134.8, 134.5, 132.1, 128.1, 125.4, 115.2, 112.2, 102.2, 20.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3098, 3035, 1511, 1217, 1145, 1076, 1003, 776. HR-MS (ESI) Calculated for $\text{C}_{12}\text{H}_{10}\text{IN}_4^+ [\text{M}-2\text{OTs}+\text{H}]^+$: m/z 336.99447, found 336.99422. Mp. 202–204 °C (decomp.).

(2,6-Bis(1*H*-pyrazol-1-yl)phenyl)-λ³-iodanediyl bistriflate (**12b**, Bis-Pyr-I-OTf)

In DCM:

Following GP1, 1,1'-(2-iodo-1,3-phenylene)bis(1*H*-pyrazole) (**4**, 2.69 g, 8.00 mmol, 1.0 equiv) was stirred in DCM (80 mL) with *m*CPBA (2.43 g, 12.0 mmol, 1.5 equiv) and TfOH (1.55 mL, 17.6 mmol, 2.2 equiv) for 65 h at 40 °C. Afterwards Et₂O (250 mL) was directly added and after storing at 4 °C, the precipitate was filtered off and washed with Et₂O (3 x 30 mL) to give Bis-Pyr-I-OTf **12b** (4.86 g, 7.66 mmol, 96%, estimated purity ~95% by ¹H-NMR) as a yellowish solid. Recrystallization from MeOH/Et₂O provides pure **12b** as a colourless solid (4.30 g, 6.78 mmol, 85%). (Note: At first this leads selectively to a mono-MeOH complex, see crystal structure. However, the additional MeOH can be removed by suspending in Et₂O, filtering and drying *in vacuo*)



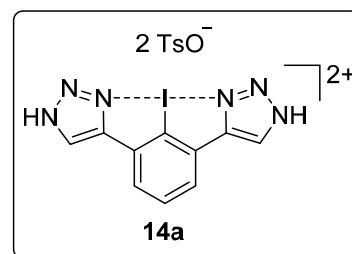
In MeCN:

Following GP1, 1,1'-(2-iodo-1,3-phenylene)bis(1*H*-pyrazole) (**4**, 1.34 g, 4.00 mmol, 1.0 equiv) was stirred in MeCN (40 mL) with *m*CPBA (1.21 g, 6.0 mmol, 1.5 equiv) and TfOH (777 μL, 8.80 mmol, 2.2 equiv) for 16 h at room temperature. Afterwards the solvent was removed under reduce pressure and the residue was suspended with Et₂O (100 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et₂O (3 x 20 mL) to give Bis-Pyr-I-OTf **12b** (2.52 g, 3.97 mmol, 99%, estimated purity ~98% by ¹H-NMR) as an off-white solid.

¹H-NMR (*d*₃-MeCN, 601 MHz) δ (ppm) 8.95 (dd, *J* = 3.0, 0.6 Hz, 2H), 8.53 (dd, *J* = 2.7, 0.6 Hz, 2H), 8.21 – 8.16 (m, 2H), 8.12 (dd, *J* = 9.1, 7.1 Hz, 1H), 7.02 (t, *J* = 2.8 Hz, 2H). ¹³C-NMR (*d*₃-MeCN, 151 MHz) δ (ppm) 142.4, 137.1, 135.2, 133.4, 121.8 (q, *J* = 320.1 Hz), 116.8, 113.9, 99.0. ¹⁹F-NMR (*d*₃-MeCN, 565 MHz) δ (ppm) –79.3. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3503, 3145, 1222, 1166, 1023, 793. HR-MS (ESI) Calculated for C₁₂H₉IN₄Na⁺ [M-2OTf+Na]⁺: *m/z* 358.97642, found 358.97615. Mp. 215–216 °C (decomp.).

(2,6-Bis(1*H*-1,2,3-triazol-4-yl)phenyl)-λ³-iodanediyl bistosylate (**14a**, Bis-NH-Tria-I-OTs)

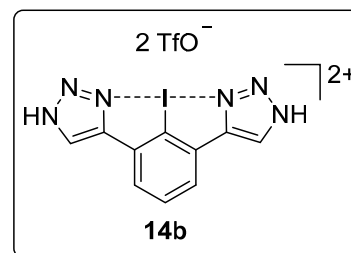
Following GP1, 4,4'-(2-iodo-1,3-phenylene)bis(1*H*-1,2,3-triazole) (**8**, 338 mg, 1.00 mmol, 1.0 equiv) was stirred in DCM (10 mL) with *m*CPBA (304 mg, 1.50 mmol, 1.5 equiv) and *p*-TsOH·H₂O (418 mg, 2.20 mmol, 2.2 equiv) for 14 h at room temperature. Afterwards the solvent was removed under reduced pressure and the residue was suspended in Et₂O/EtOAc (4:1, 20 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et₂O (2 x 5 mL) to give Bis-NH-Tria-I-OTs **14a** (627 mg, 0.921 mmol, 92%) as a beige solid.



$^1\text{H-NMR}$ (d_6 -DMSO, 601 MHz) δ (ppm) 8.64 (s, 2H), 8.20 (d, J = 7.6 Hz, 2H), 7.95 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 4H), 7.12 (d, J = 7.7 Hz, 4H), 2.29 (s, 6H). $^{13}\text{C-NMR}$ (d_6 -DMSO, 151 MHz) δ (ppm) 145.0, 140.9, 138.2, 132.8, 128.3, 127.2, 126.8, 126.2, 125.5, 122.4, 20.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3098, 2608, 1599, 1452, 1220, 1123, 1028, 1002, 820. HR-MS (ESI) Calculated for $\text{C}_{10}\text{H}_8\text{IN}_6^+ [\text{M-2OTs+H}]^+$: m/z 338.98497, found 338.98455. Mp. 112–114 °C (decomp.).

(2,6-Bis(1*H*-1,2,3-triazol-4-yl)phenyl)- λ^3 -iodanediyl bistriflate (14b, Bis-NH-Tria-I-OTf)

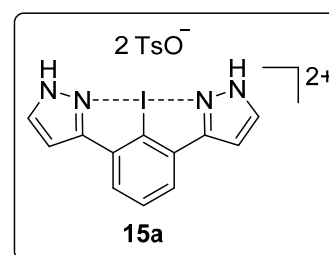
Following GP1, 4,4'-(2-iodo-1,3-phenylene)bis(1*H*-1,2,3-triazole) (**8**, 135 mg, 0.400 mmol, 1.0 equiv) was stirred in MeCN (4 mL) with *m*CPBA (121 mg, 0.600 mmol, 1.5 equiv) and TfOH (77.7 μL , 0.880 mmol, 2.2 equiv) for 14 h at room temperature. Afterwards the solvent was removed under reduce pressure and the residue was suspended in Et₂O/EtOAc (4:1, 5 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et₂O (2 x 5 mL) to give Bis-NH-Tria-I-OTf **14b** (223 mg, 0.365 mmol, 91%) as a beige solid.



$^1\text{H-NMR}$ (d_3 -MeCN, 601 MHz) δ (ppm) 8.97 (s, 2H), 8.47 (d, J = 7.7 Hz, 2H), 8.14 (t, J = 7.7 Hz, 1H). $^{13}\text{C-NMR}$ (d_3 -MeCN, 151 MHz) δ (ppm) 143.5, 135.2, 130.2, 127.0, 125.3, 121.8 (q, J = 319.8 Hz), 121.5. $^{19}\text{F-NMR}$ (d_3 -MeCN, 565 MHz) δ (ppm) –79.4. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3016, 2610, 1597, 1449, 1283, 1232, 1195, 1163, 1027, 806. HR-MS (ESI) Calculated for $\text{C}_{10}\text{H}_6\text{IN}_6^+ [\text{M-2OTf-H}]^+$: m/z 336.96932, found 336.96900. Mp. 187–188 °C (decomp.).

(2,6-Bis(1*H*-pyrazol-3-yl)phenyl)- λ^3 -iodanediyl bistosylate (15a, Bis-NH-Pyr-I-OTs)

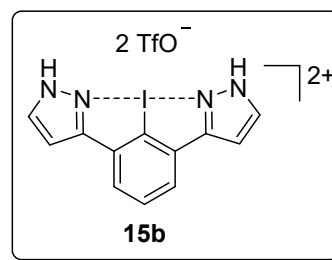
Following GP1, 3,3'-(2-iodo-1,3-phenylene)bis(1*H*-pyrazole) (**9**, 135 mg, 0.400 mmol, 1.0 equiv) was stirred in DCM (4 mL) with *m*CPBA (121 mg, 0.600 mmol, 1.5 equiv) and *p*-TsOH·H₂O (183 mg, 0.960 mmol, 2.4 equiv) for 42 h at room temperature. Afterwards Et₂O (6 mL) was directly added and after storing at 4 °C, the precipitate was filtered off and washed with Et₂O (2 x 5 mL) to give Bis-NH-Pyr-I-OTs **15a** (260 mg, 0.383 mmol, 96%) as a colourless solid.



$^1\text{H-NMR}$ (d_6 -DMSO, 601 MHz) δ (ppm) 8.26 (d, J = 7.6 Hz, 2H), 8.06 (s, 2H), 7.95 (t, J = 7.7 Hz, 1H), 7.48 (d, J = 7.7 Hz, 4H), 7.29 (s, 2H), 7.12 (d, J = 7.7 Hz, 4H), 2.29 (s, 6H). $^{13}\text{C-NMR}$ (d_6 -DMSO, 151 MHz) δ (ppm) 145.3, 145.1, 140.1, 137.9, 132.4, 129.5, 128.2, 125.8, 125.5, 119.5, 103.2, 20.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3090, 2634, 1440, 1244, 1223, 1155, 1119, 1031, 1009, 811. HR-MS (ESI) Calculated for $\text{C}_{12}\text{H}_8\text{IN}_4^+ [\text{M-2OTs-H}]^+$: m/z 334.97882, found 334.97830. Mp. 146–148 °C (decomp.).

(2,6-Bis(1*H*-pyrazol-3-yl)phenyl)-λ³-iodanediyl bistriflate (15b**, Bis-NH-Pyr-I-OTf)**

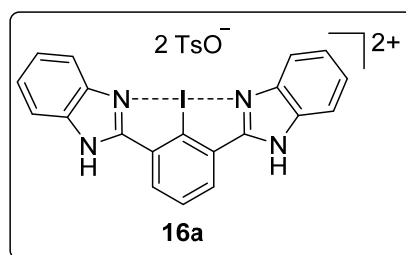
Following GP1, 3,3'-(2-iodo-1,3-phenylene)bis(1*H*-pyrazole) (**9**, 67.2 mg, 0.200 mmol, 1.0 equiv) was stirred in DCM (2 mL) with *m*CPBA (60.5 mg, 0.300 mmol, 1.5 equiv) and TfOH (42.4 μL, 0.480 mmol, 2.4 equiv) for 24 h at room temperature. Afterwards the solvent was removed under reduced pressure and the residue was suspended in Et₂O (2 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et₂O (3 x 1 mL) to give Bis-NH-Pyr-I-OTf **15b** (110 mg, 0.173 mmol, 87%) as a colourless solid.



¹H-NMR (*d*₆-DMSO, 601 MHz) δ (ppm) 8.26 (d, *J* = 7.6 Hz, 2H), 8.06 (s, 2H), 7.95 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 2.3 Hz, 2H). ¹³C-NMR (*d*₆-DMSO, 151 MHz) δ (ppm) 145.0, 140.2, 132.4, 129.6, 125.7, 120.7 (q, *J* = 322.3 Hz), 119.4, 103.1. ¹⁹F-NMR (*d*₆-DMSO, 565 MHz) δ (ppm) -77.7. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3218, 3152, 1628, 1528, 1461, 1277, 1245, 1220, 1148, 1028, 809. HR-MS (ESI) Calculated for C₁₂H₁₀IN₄⁺ [M-2OTf+H]⁺: *m/z* 336.99447, found 336.99423. Mp. 253–257 °C (decomp.).

(2,6-Bis(1*H*-benzo[*d*]imidazol-2-yl)phenyl)-λ³-iodanediyl bistosylate (16a**, Bis-Benzimi-I-OTs)**

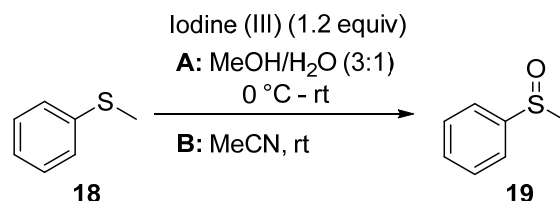
Following GP1, 2,2'-(2-iodo-1,3-phenylene)bis(1*H*-benzo[*d*]imidazole) (**10**, 87.3 mg, 0.200 mmol, 1.0 equiv) was stirred in DCM (2 mL) with *m*CPBA (49.2 mg, 0.240 mmol, 1.2 equiv) and *p*-TsOH·H₂O (83.6 mg, 0.440 mmol, 2.2 equiv) for 17 h at room temperature. Afterwards the solvent was removed under reduced pressure and the residue was suspended in Et₂O (4 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et₂O (2 x 2 mL) to give Bis-Benzimi-I-OTs **16a** (133 mg, 0.170 mmol, 85%) as a beige solid.



¹H-NMR (*d*₆-DMSO, 601 MHz) δ (ppm) 8.67 (d, *J* = 8.0, 2.4 Hz, 2H), 8.37 – 8.18 (m, 3H), 7.90 (dd, *J* = 7.0, 1.8 Hz, 2H), 7.61 – 7.44 (m, 8H), 7.13 (d, *J* = 7.8 Hz, 4H), 2.28 (s, 6H). ¹³C-NMR (*d*₆-DMSO, 151 MHz) δ (ppm) 151.2, 145.3, 137.9, 135.7, 133.6, 128.6, 128.2, 126.7, 125.5, 125.1, 124.8, 123.5, 116.4, 115.9, 20.8. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 2644, 1593, 1468, 1222, 1118, 1004, 808. HR-MS (ESI) Calculated for C₂₀H₁₄IN₄⁺ [M-2OTs+H]⁺: *m/z* 437.02577, found 437.02535. Mp. 260–262 °C (decomp.).

4. Applications

Oxidation of thioanisole (**18**)



Method A: A slightly modified literature procedure was used.^[11] The corresponding λ^3 -iodane (0.150 mmol, 1.2 equiv) was dissolved/suspended in MeOH/H₂O (2:1, 1.5 mL) and the mixture was cooled to 0 °C. A solution of thioanisole (**18**, 15.5 mg, 0.125 mmol, 1.0 equiv) in MeOH (0.5 mL) was added and the resulting mixture was stirred at room temperature for the indicated time. Afterwards sat. NaHCO₃-solution (4 mL) and sat. Na₂S₂O₃-solution (0.2 mL) were added, and the mixture was extracted with DCM (2 x 5 mL). The combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (EtOAc) to give (methylsulfinyl)benzene (**19**) as a colourless oil (For example: 17.1 mg, 0.122 mmol, 98% with Bis-Pyr-I-OTf **12b**).

Method B: A slightly modified literature procedure was used.^[14] The corresponding λ^3 -iodane (0.150 mmol, 1.2 equiv) was added to a solution of thioanisole (**18**, 15.5 mg, 0.125 mmol, 1.0 equiv) in MeCN (1 mL) and the resulting mixture was stirred at room temperature for the indicated time (Table 1). Afterwards sat. NaHCO₃-solution (4 mL) and sat. Na₂S₂O₃-solution (0.2 mL) were added, and the mixture was extracted with DCM (2 x 5 mL). The combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (EtOAc) to give (methylsulfinyl)benzene (**19**) as a colourless oil (For example: 16.4 mg, 0.117 mmol, 94% with Bis-Pyr-I-OTf **12b**).

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 7.67 – 7.60 (m, 2H), 7.56 – 7.41 (m, 3H), 2.72 (s, 3H). ¹³C-NMR (CDCl₃, 151 MHz): δ (ppm) 145.6, 131.0, 129.3, 123.5, 43.9. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3445, 3055, 2997, 1652, 1477, 1443, 1414, 1296, 1088, 1033. MS (APCI) m/z = 141.0 [M+H]⁺. Analytical data is in accordance with literature data.^[11]

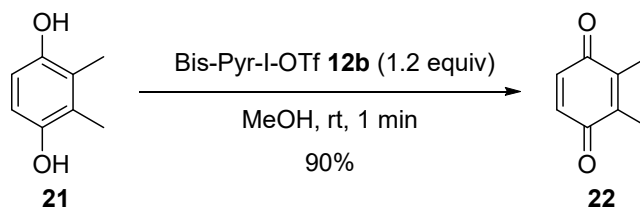
Table 1. Reaction times and yields for the oxidation of thioanisole **18**.

λ^3 -Iodane	Time A	Yield of 19 A ^a	Time B	Yield of 19 B ^a
Bis-Pyr-I-OTs 12a	<30 sec	95%	24 h	traces
Bis-Pyr-I-OTf 12b	<30 sec	98%	<30 sec	94%
Bis-NH-Tria-I-OTs 14a	4 h	89%	6 h	94%
Bis-NH-Tria-I-OTf 14b	3 h	92%	5 min	90%
Bis-NH-Pyr-I-OTs 15a	5 h	88%	24 h	traces

Bis-NH-Pyr-I-OTf 15b	4 h	90%	7 h	94%
Bis-Benzimi-I-OTs 16a	24 h	traces	24 h	0%
OH-Pyr-I-OTs 20	1 h	91%	3 h	88%

^aIsolated yield of (methylsulfinyl)benzene **19** after column chromatography.

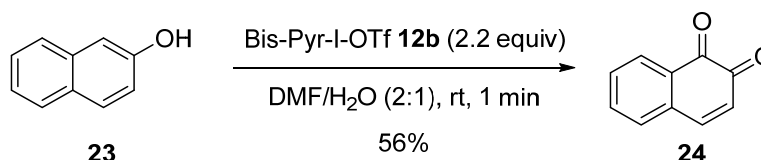
Oxidation of 2,3-dimethylhydroquinone (**21**)



A slightly modified literature procedure was used.^[15] Bis-Pyr-I-OTf **12b** (152 mg, 0.240 mmol, 1.2 equiv) was added to a solution of 2,3-dimethylhydroquinone (**21**, 27.6 mg, 0.200 mmol, 1.0 equiv) in MeOH (1 mL) and the resulting mixture was stirred at room temperature for 1 min. The mixture was directly loaded on silica gel and purified via column chromatography on silica gel (cyclohexane/EtOAc 5:1) to give 2,3-dimethyl-*p*-benzoquinone (**22**, 24.4 mg, 0.179 mmol, 90%) as a yellow solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 6.72 (s, 2H), 2.03 (s, 6H). ¹³C-NMR (CDCl₃, 151 MHz): δ (ppm) 187.4, 141.0, 136.2, 12.2. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3056, 2925, 2853, 1652, 1600, 1441, 1380, 1307, 1136, 1063. MS (EI) m/z = 136.07 [M]⁺. Mp. 54–55 °C. Analytical data is in accordance with literature data.^[16]

Oxidation of 2-naphthol (**23**) to naphthalene-1,2-dione (**24**)

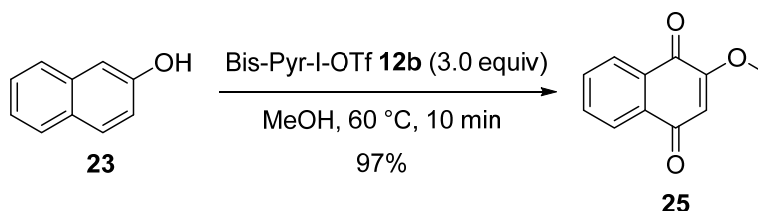


A slightly modified literature procedure was used.^[16] Bis-Pyr-I-OTf **12b** (279 mg, 0.440 mmol, 1.2 equiv) was added to a solution of 2-naphthol (**23**, 28.8 mg, 0.200 mmol, 1.0 equiv) in DMF/H₂O (2:1, 1 mL) and the resulting mixture was stirred at room temperature for 1 min. The reaction mixture was diluted with H₂O (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with brine (10 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (cyclohexane/EtOAc 5:1) to give naphthalene-1,2-dione (**24**, 17.6 mg, 0.111 mmol, 56%) as an orange solid, which turned dark brown over the course of a few hours and prolonged drying, already showing traces of decomposition after about an hour.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 8.17 – 8.09 (m, 1H), 7.66 (td, J = 7.5, 1.3 Hz, 1H), 7.52 (td, J = 7.6, 1.2 Hz, 1H), 7.45 (d, J = 10.1 Hz, 1H), 7.41 – 7.33 (m, 1H), 6.45 (d, J = 10.1 Hz, 1H).

^{13}C -NMR (CDCl_3 , 151 MHz): δ (ppm) 180.9, 178.9, 145.4, 135.8, 134.8, 131.6, 130.9, 130.2, 129.8, 127.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3052, 2921, 1695, 1651, 1585, 1565, 1399, 1285, 1196, 957. MS (APCI) m/z = 159.0 $[\text{M}+\text{H}]^+$. Mp. 116–117 °C. Analytical data is in accordance with literature data.^[16]

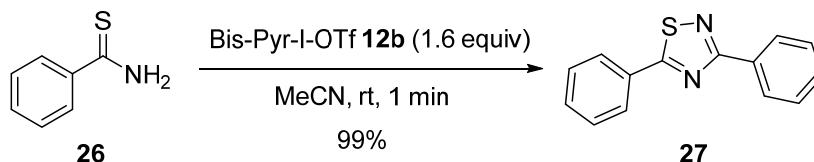
Oxidation of 2-naphthol (**23**) to 2-methoxynaphthalene-1,4-dione (**25**)



Bis-Pyr-I-OTf **12b** (381 mg, 0.600 mmol, 3.0 equiv) was added to a solution of 2-naphthol (**23**, 28.8 mg, 0.200 mmol, 1.0 equiv) in MeOH (1 mL) and the resulting mixture was stirred at 60 °C for 10 min. The reaction mixture was diluted with EtOAc (20 mL) and washed with sat. NaHCO_3 -solution (10 mL). The aqueous phase was extracted with EtOAc (10 mL) and the combined organic phases were washed with brine (10 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (cyclohexane/EtOAc 5:1) to give 2-methoxynaphthalene-1,4-dione (**25**, 36.6 mg, 0.194 mmol, 97%) as a yellow solid.

^1H -NMR (CDCl_3 , 601 MHz) δ (ppm) 8.14 (dd, J = 7.5, 1.5 Hz, 1H), 8.09 (dd, J = 7.7, 1.3 Hz, 1H), 7.76 (td, J = 7.5, 1.5 Hz, 1H), 7.72 (td, J = 7.5, 1.5 Hz, 1H), 6.18 (s, 1H), 3.91 (s, 3H). ^{13}C -NMR (CDCl_3 , 151 MHz): δ (ppm) 184.8, 180.1, 160.4, 134.3, 133.3, 132.0, 131.0, 126.7, 126.2, 109.9, 56.4. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3067, 2940, 1846, 1682, 1651, 1605, 1578, 1440, 1335, 1240, 1214, 1042. MS (APCI) m/z = 189.1 $[\text{M}+\text{H}]^+$. Mp. 177–180 °C. Analytical data is in accordance with literature data.^[17]

Oxidative cyclization of thiobenzamide (**26**) to 3,5-diphenyl-1,2,4-thiadiazole (**27**)

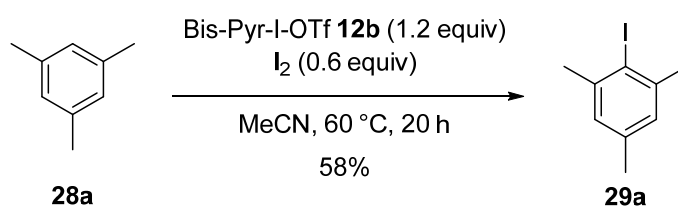


A reported literature procedure was used.^[14] To a solution of Bis-Pyr-I-OTf **12b** (244 mg, 0.384 mmol, 1.6 equiv) in MeCN (1.5 mL) was added thiobenzamide (**26**, 32.9 mg, 0.240 mmol, 1.0 equiv) and the reaction mixture was stirred at room temperature for 1 min. Sat. NaHCO_3 -solution (6 mL) and sat. $\text{Na}_2\text{S}_2\text{O}_3$ -solution (1 mL) were added, and the mixture was extracted with DCM (3 x 6 mL). The combined organic phases were dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by column

chromatography on silica gel (cyclohexane/EtOAc 20:1) to give 3,5-diphenyl-1,2,4-thiadiazole (**27**, 28.5 mg, 0.119 mmol, 99%) as a colourless solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 8.50 – 8.25 (m, 2H), 8.20 – 7.99 (m, 2H), 7.75 – 7.43 (m, 6H). ¹³C-NMR (CDCl₃, 151 MHz): δ (ppm) 188.1, 173.8, 132.9, 131.9, 130.7, 130.4, 129.3, 128.7, 128.3, 127.5. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3046, 2923, 1511, 1475, 1439, 1329, 1275, 1118, 1069, 988. MS (APCI) m/z = 239.1 [M+H]⁺. Mp. 86–87 °C. Analytical data is in accordance with literature data.^[14]

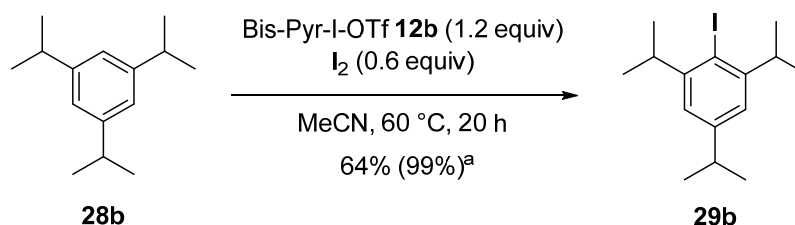
Iodination of mesitylene (**28a**)



A modified literature procedure was used.^[18] To a solution of mesitylene (**28a**, 24.0 mg, 0.200 mmol, 1.0 equiv) were added Bis-Pyr-I-OTf **12b** (152 mg, 0.240 mmol, 1.2 equiv) and iodine (30.5 mg, 0.120 mmol, 0.6 equiv) and the mixture was stirred at 60 °C for 20 h. The reaction was quenched with sat. Na₂S₂O₃-solution (5 mL) and extracted with DCM (2 x 10 mL). The combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (*n*-pentane) to give iodomesitylene (**29a**, 28.4 mg, 0.115 mmol, 58%) as a colourless solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 6.89 (s, 2H), 2.43 (s, 6H), 2.24 (s, 3H). ¹³C-NMR (CDCl₃, 151 MHz): δ (ppm) 141.7, 137.3, 127.9, 104.2, 29.5, 20.6. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 2964, 2916, 2850, 1572, 1462, 1434, 1376, 1301, 1021. MS (EI) m/z = 245.99 [M]⁺. Mp. 29–30 °C. Analytical data is in accordance with literature data.^[18]

Iodination of 1,3,5-triisopropylbenzene (**29b**)



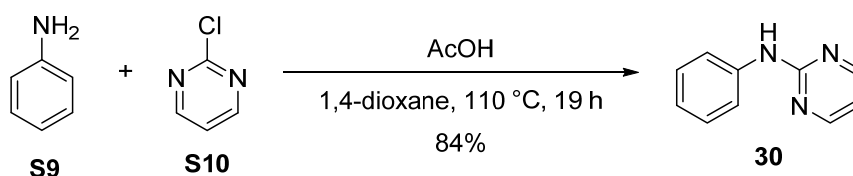
A modified literature procedure was used.^[18] To a solution of 1,3,5-triisopropylbenzene (**28b**, 40.9 mg, 0.200 mmol, 1.0 equiv) were added Bis-Pyr-I-OTf **12b** (152 mg, 0.240 mmol, 1.2 equiv) and iodine (30.5 mg, 0.120 mmol, 0.6 equiv) and the mixture was stirred at 60 °C for 20 h. The reaction was quenched with sat. Na₂S₂O₃-solution (5 mL) and extracted with DCM (2 x 10 mL). The combined organic phases were dried over Na₂SO₄, filtered and

concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (*n*-pentane) to give 1-iodo-2,4,6-triisopropylbenzene (**29b**, 42.4 mg, 0.128 mmol, 64%) as a colourless oil.

^a 1-Iodo-2,4,6-triisopropylbenzene (**29b**) was obtained in 99% yield (65.6 mg, 0.199 mmol) after 16 h when 1.5 equiv of Bis-Pyr-I-OTf **12b** (190 mg, 0.300 mmol) and iodine (76.1 mg, 0.300 mmol) were used.^[19]

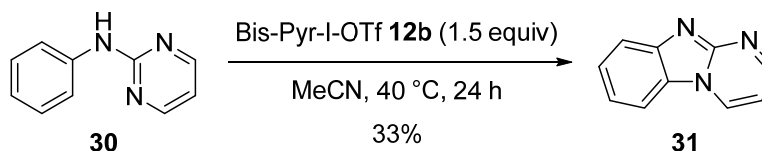
¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 6.95 (s, 2H), 3.39 (sept, *J* = 6.8 Hz, 2H), 2.87 (sept, *J* = 6.9 Hz, 1H), 1.24 (t, *J* = 6.7 Hz, 18H). ¹³C-NMR (CDCl₃, 151 MHz): δ (ppm) 150.7, 148.8, 122.0, 105.7, 39.2, 33.9, 24.0, 23.4. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 2958, 2925, 2868, 1566, 1460, 1420, 1361, 1101, 999. MS (EI) *m/z* = 330.10 [M]⁺. Analytical data is in accordance with literature data.^[18]

Oxidative cyclization of *N*-phenylpyrimidin-2-amine (**30**)



A slightly modified literature procedure was used.^[20] To a pressure vial were added 2-chloropyrimidine (**S10**, 286 mg, 2.50 mmol, 1.0 equiv), aniline (**S9**, 349 mg, 3.75 mmol, 1.5 equiv), AcOH (0.5 mL) and 1,4-dioxane (7.5 mL). The vial was sealed and stirred at 110 °C for 19 h. The mixture was diluted with H₂O (10 mL) and sat. NaHCO₃-solution (10 mL) and extracted with DCM (3 x 20 mL). The combined organic phases were washed with brine (20 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (cyclohexane/EtOAc 7:1→4:1) to give *N*-phenylpyrimidine-2-amine (**30**, 360 mg, 2.10 mmol, 84%) as a beige solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 8.42 (d, *J* = 4.8 Hz, 2H), 7.84 (s, 1H), 7.75 – 7.51 (m, 2H), 7.40 – 7.30 (m, 2H), 7.06 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.71 (t, *J* = 4.8 Hz, 1H). ¹³C-NMR (CDCl₃, 151 MHz): δ (ppm) 160.3, 158.0, 139.4, 129.0, 122.8, 119.7, 112.5. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3251, 3009, 1605, 1574, 1529, 1494, 1438, 1405, 1250, 994. MS (APCI) *m/z* = 172.0 [M+H]⁺. Mp. 114–115 °C. Analytical data is in accordance with literature data.^[20]

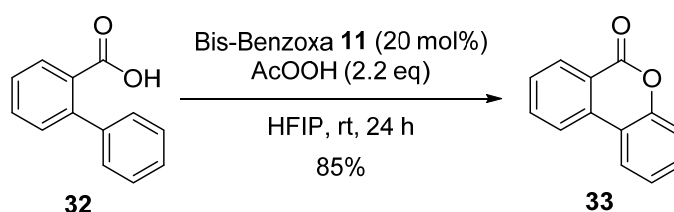


A modified literature procedure was used.^[20] To a solution of *N*-phenylpyrimidin-2-amine (**30**, 51.4 mg, 0.300 mmol, 1.0 equiv) was added Bis-Pyr-I-OTf **12b** (285 mg, 0.450 mmol, 1.5 equiv) and the solution was stirred at 40 °C for 24 h. The reaction was quenched with sat.

Na₂S₂O₃-solution (1 mL) and the phases were separated. The aqueous phase was extracted with EtOAc (3 x 2 mL) and the combined organic phases were dried over Na₂SO₄ and filtered. The filtrate was filtered through a short silica gel column with EtOAc as the eluent. The solvent was removed under reduced pressure and the residue was purified via column chromatography on silica gel (DCM/MeOH 10:1) to give benzo[4,5]imidazo[1,2-*a*]pyrimidine (**31**, 16.6 mg, 98.1 μmol, 33%) as a yellow solid.

¹H-NMR (CDCl₃, 601 MHz) δ (ppm) 8.97 – 8.68 (m, 2H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 6.99 (dd, *J* = 6.7, 4.1 Hz, 1H). ¹³C-NMR (CDCl₃, 151 MHz): δ (ppm) 155.8, 150.2, 143.4, 133.5, 126.9, 126.6, 122.4, 120.4, 110.8, 107.0. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3049, 1624, 1602, 1498, 1457, 1424, 1323, 1193, 1027. MS (APCI) *m/z* = 170.0 [M+H]⁺. Mp. 189–191 °C. Analytical data is in accordance with literature data.^[20]

Oxidative Cyclization of [1,1'-biphenyl]-2-carboxylic acid (**32**)



A reported literature procedure was used.^[21] [1,1'-Biphenyl]-2-carboxylic acid (**32**, 49.6 mg, 0.250 mmol, 1.0 equiv) and 2,2'-(2-iodo-1,3-phenylene)bis(benzo[*d*]oxazole) **11** (21.9 mg, 0.050 mmol, 20 mol%) were dissolved in HFIP (2.5 mL) and AcOOH (35%, 97.5 μL, 0.550 mmol, 2.2 equiv) was added. After stirring for 24 h at room temperature, the solvent was removed under reduced pressure and the residue was purified via column chromatography on silica gel (toluene/cyclohexane/EtOAc 20:20:1) to give 6*H*-benzo[*c*]chromen-6-one (**33**, 41.5 mg, 0.212 mmol, 85%) as a colourless solid.

¹H-NMR (CDCl₃, 601 MHz): δ (ppm) 8.42 (ddd, *J* = 7.9, 1.5, 0.6 Hz, 1H), 8.14 (dt, *J* = 8.1, 0.6 Hz, 1H), 8.08 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.84 (ddd, *J* = 8.1, 7.3, 1.4 Hz, 1H), 7.60 (ddd, *J* = 7.8, 7.3, 1.1 Hz, 1H), 7.49 (ddd, *J* = 8.3, 7.2, 1.5 Hz, 1H), 7.39 (ddd, *J* = 8.3, 1.3, 0.5 Hz, 1H), 7.35 (ddd, *J* = 8.0, 7.2, 1.3 Hz, 1H). ¹³C-NMR (CDCl₃, 151 MHz): δ (ppm) 161.2, 151.3, 134.8, 134.8, 130.6, 130.5, 128.9, 124.6, 122.8, 121.7, 121.3, 118.1, 117.8. IR (ATR): $\tilde{\nu}$ (cm⁻¹) 3033, 2923, 1726, 1606, 1483, 1432, 1303, 1237, 1077, 1032. MS (APCI) *m/z* = 196.9 [M+H]⁺. mp 89–91 °C. Analytical data is in accordance with literature data.^[21]

5. Crystallographic data

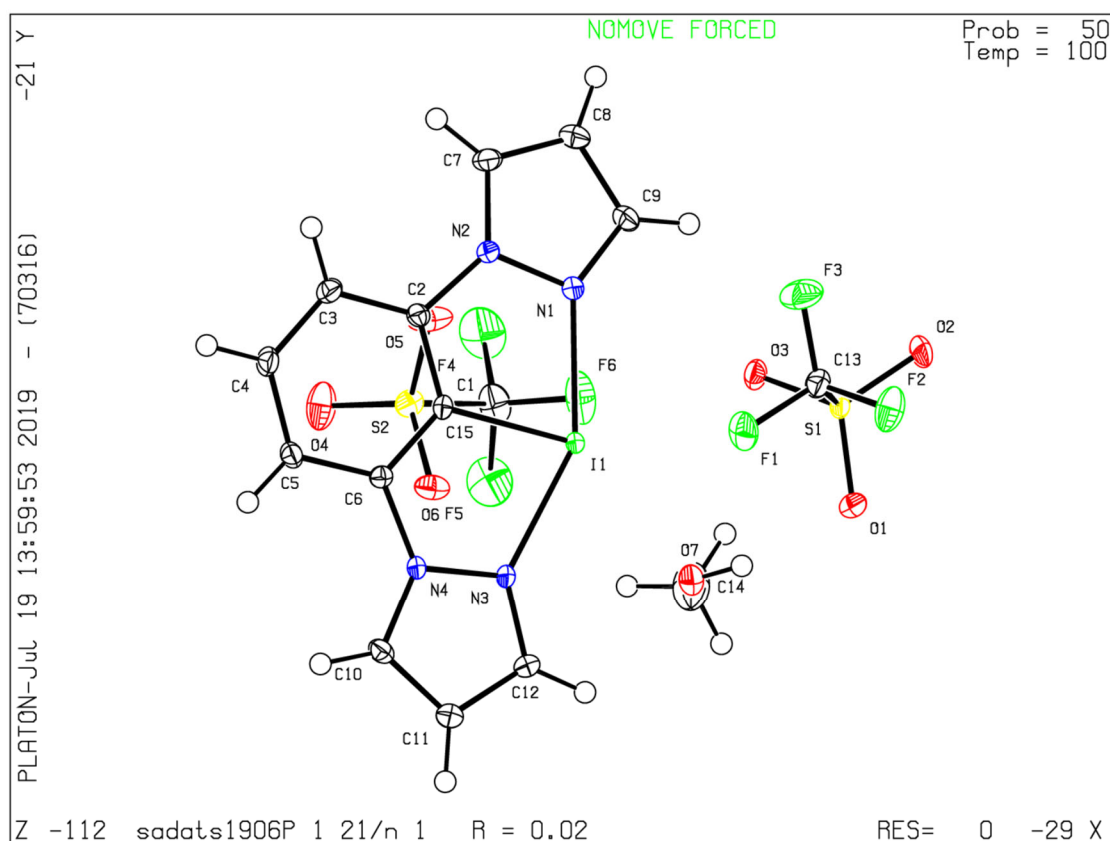
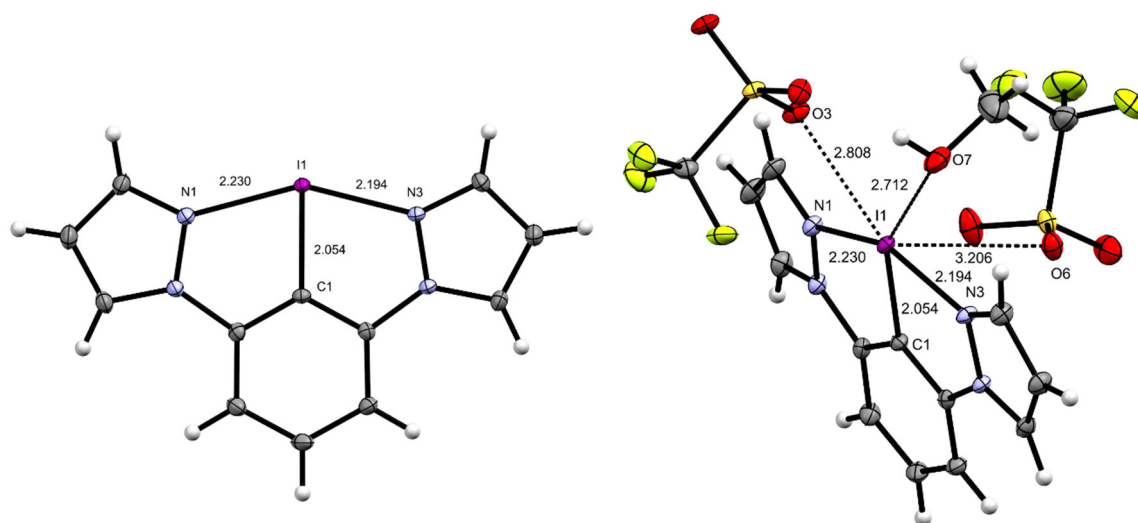


Table 2: Crystal data and structure refinement for Bis-Pyr-I-OTf **12b** (CCDC 2086526).

Empirical formula	$C_{15}H_{13}F_6IN_4O_7S_2$
Formula weight	666.31
Temperature/K	100.0

Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	8.7421(2)
b/Å	22.1857(6)
c/Å	11.8409(3)
α/°	90
β/°	93.6750(10)
γ/°	90
Volume/Å ³	2291.82(10)
Z	4
ρ _{calc} /cm ³	1.931
μ/mm ⁻¹	1.674
F(000)	1304.0
Crystal size/mm ³	0.3 × 0.25 × 0.2
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.018 to 59.998
Index ranges	-12 ≤ h ≤ 12, -31 ≤ k ≤ 31, -16 ≤ l ≤ 16
Reflections collected	124501
Independent reflections	6689 [R _{int} = 0.0377, R _{sigma} = 0.0136]
Data/restraints/parameters	6689/0/321
Goodness-of-fit on F ²	1.054
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0185, wR ₂ = 0.0422
Final R indexes [all data]	R ₁ = 0.0233, wR ₂ = 0.0439
Largest diff. peak/hole / e Å ⁻³	0.56/-0.44

Table 3: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Bis-Pyr-I-OTf **12b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
I1	3543.1(2)	6625.3(2)	7151.7(2)	9.77(3)
N1	5849.6(14)	6454.3(5)	8007.0(11)	12.5(2)
N2	6754.0(14)	6954.4(5)	8078.2(10)	12.0(2)
N3	1845.0(14)	7236.3(5)	6323.9(10)	11.5(2)
N4	2319.5(13)	7821.2(5)	6312.1(10)	10.3(2)
C1	4601.0(16)	7452.1(6)	7221.0(12)	10.3(2)
C2	6074.9(16)	7499.7(6)	7692.1(12)	11.6(3)
C3	6791.7(17)	8057.6(7)	7750.0(13)	15.5(3)
C4	5980.4(18)	8553.3(7)	7309.6(13)	16.2(3)
C5	4495.6(17)	8508.0(6)	6812.0(13)	13.7(3)
C6	3811.4(16)	7944.0(6)	6778.3(12)	10.4(2)
C7	8199.5(17)	6804.0(7)	8438.0(13)	16.7(3)
C8	8217.1(18)	6188.5(7)	8607.6(14)	19.9(3)
C9	6734.5(17)	5985.3(7)	8324.7(13)	16.6(3)
C10	1170.9(17)	8177.5(7)	5883.7(13)	13.9(3)

C11	-69.0(17)	7808.9(7)	5610.8(13)	16.4(3)
C12	390.0(16)	7224.3(7)	5904.0(13)	14.8(3)
S1	2531.1(4)	5132.8(2)	8605.8(3)	12.34(7)
F1	1926.9(12)	6157.6(4)	9591.5(9)	24.0(2)
F2	1329.8(13)	5365.4(5)	10520.6(9)	27.5(2)
F3	3693.5(13)	5632.3(5)	10475.3(10)	31.2(2)
O1	1011.5(13)	5159.5(5)	8044.8(10)	17.8(2)
O2	2972.5(14)	4556.1(5)	9065.0(10)	19.6(2)
O3	3686.5(12)	5443.5(5)	7999.7(10)	17.1(2)
C13	2366.3(18)	5594.4(7)	9868.2(14)	16.7(3)
S2	6122.1(4)	6890.4(2)	4581.8(3)	15.40(7)
F4	7514.6(16)	5949.9(6)	3777.0(12)	45.4(3)
F5	5243.1(17)	6100.8(6)	3022.5(10)	41.8(3)
F6	5559.9(16)	5734.9(5)	4704.5(11)	40.1(3)
O4	6807.6(17)	7256.9(6)	3746.1(11)	29.9(3)
O5	7002.3(14)	6824.7(7)	5643.8(10)	27.0(3)
O6	4508.3(13)	7004.6(5)	4683.3(9)	19.2(2)
C15	6113(2)	6129.6(8)	3990.0(16)	26.0(4)
O7	1159.1(14)	5956.8(5)	6269.8(11)	23.0(3)
C14	1558(3)	5674.2(10)	5249.2(18)	40.4(5)

Table 4: Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Bis-Pyr-I-OTf **12b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	9.31(4)	8.36(4)	11.63(4)	1.92(3)	0.46(3)	-0.54(3)
N1	11.6(5)	11.2(5)	14.5(6)	2.5(4)	-0.5(4)	-0.6(4)
N2	10.4(5)	12.5(5)	13.0(6)	1.9(4)	-0.7(4)	-0.9(4)
N3	10.6(5)	8.2(5)	15.5(6)	1.8(4)	0.0(4)	-1.4(4)
N4	10.8(5)	8.1(5)	12.1(5)	1.6(4)	0.6(4)	-0.6(4)
C1	11.1(6)	9.3(6)	10.6(6)	0.7(5)	1.5(5)	-1.3(5)
C2	11.9(6)	12.9(6)	9.9(6)	1.7(5)	0.4(5)	-0.2(5)
C3	14.5(7)	16.0(7)	15.5(7)	1.4(5)	-1.9(5)	-3.6(5)
C4	19.6(7)	12.2(6)	16.4(7)	0.9(5)	-1.6(6)	-4.9(5)
C5	15.7(7)	10.1(6)	15.0(7)	1.5(5)	-0.2(5)	-0.4(5)
C6	9.7(6)	11.8(6)	9.8(6)	0.3(5)	1.5(5)	0.0(5)
C7	11.3(6)	20.2(7)	18.1(7)	1.7(6)	-2.4(5)	0.2(5)
C8	13.9(7)	20.3(7)	25.0(8)	4.9(6)	-2.3(6)	4.2(6)
C9	14.7(7)	14.4(7)	20.5(8)	4.0(6)	0.0(6)	3.1(5)
C10	13.7(6)	12.9(6)	14.8(7)	2.6(5)	0.2(5)	3.1(5)
C11	12.6(6)	16.0(7)	20.3(7)	2.4(6)	-1.1(5)	1.3(5)
C12	10.4(6)	15.5(7)	18.5(7)	1.6(5)	-1.2(5)	-1.0(5)
S1	11.82(15)	8.40(14)	16.90(17)	1.58(12)	1.77(12)	-0.75(12)
F1	29.7(5)	12.0(4)	31.0(6)	-3.0(4)	7.1(4)	2.3(4)

F2	35.4(6)	25.6(5)	22.8(5)	-3.8(4)	13.7(4)	-10.8(4)
F3	24.7(5)	35.6(6)	31.5(6)	-8.4(5)	-11.0(4)	-2.4(5)
O1	13.7(5)	19.8(5)	19.5(5)	2.5(4)	-2.4(4)	-3.5(4)
O2	22.7(6)	9.1(5)	27.0(6)	4.0(4)	1.6(5)	1.3(4)
O3	14.3(5)	13.3(5)	24.5(6)	3.0(4)	6.6(4)	-0.9(4)
C13	16.2(7)	14.1(6)	19.8(7)	-0.4(6)	0.9(6)	-2.8(5)
S2	14.83(16)	20.59(18)	11.02(16)	-0.25(13)	2.70(12)	-1.56(13)
F4	43.9(7)	38.1(7)	57.0(9)	-1.5(6)	25.2(6)	16.5(6)
F5	62.2(9)	34.3(6)	28.0(6)	-14.1(5)	-3.5(6)	-3.2(6)
F6	53.8(8)	22.9(6)	45.6(7)	8.3(5)	18.5(6)	-1.9(5)
O4	41.6(8)	26.5(6)	23.3(6)	0.1(5)	16.0(6)	-9.8(6)
O5	13.9(5)	49.0(8)	17.5(6)	-2.5(5)	-2.4(4)	2.2(5)
O6	15.5(5)	26.8(6)	15.1(5)	0.1(4)	-1.4(4)	3.6(4)
C15	32.3(9)	21.1(8)	25.8(9)	1.5(7)	9.5(7)	3.4(7)
O7	23.4(6)	16.4(5)	28.4(7)	6.6(5)	-4.7(5)	-4.8(5)
C14	57.4(14)	33.9(11)	29.2(10)	-1.3(8)	-2.3(10)	-15.1(10)

Table 5: Bond Lengths for Bis-Pyr-I-OTf **12b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	N1	2.2301(12)	C8	C9	1.393(2)
I1	N3	2.1944(12)	C10	C11	1.379(2)
I1	C1	2.0533(13)	C11	C12	1.395(2)
N1	N2	1.3620(17)	S1	O1	1.4479(11)
N1	C9	1.3362(19)	S1	O2	1.4334(11)
N2	C2	1.4107(18)	S1	O3	1.4502(11)
N2	C7	1.3493(19)	S1	C13	1.8253(16)
N3	N4	1.3627(16)	F1	C13	1.3417(18)
N3	C12	1.3359(18)	F2	C13	1.3288(18)
N4	C6	1.4098(18)	F3	C13	1.3278(18)
N4	C10	1.3509(18)	S2	O4	1.4407(12)
C1	C2	1.375(2)	S2	O5	1.4389(13)
C1	C6	1.3769(19)	S2	O6	1.4459(12)
C2	C3	1.387(2)	S2	C15	1.8273(18)
C3	C4	1.392(2)	F4	C15	1.328(2)
C4	C5	1.394(2)	F5	C15	1.336(2)
C5	C6	1.3865(19)	F6	C15	1.330(2)
C7	C8	1.380(2)	O7	C14	1.425(3)

Table 6: Bond Angles for Bis-Pyr-I-OTf **12b**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N3	I1	N1	150.93(4)	N1	C9	C8	109.19(14)
C1	I1	N1	75.05(5)	N4	C10	C11	107.17(13)
C1	I1	N3	75.89(5)	C10	C11	C12	106.48(13)
N2	N1	I1	113.19(9)	N3	C12	C11	109.02(13)
C9	N1	I1	138.65(11)	O1	S1	O3	113.65(7)
C9	N1	N2	107.08(12)	O1	S1	C13	103.56(7)
N1	N2	C2	116.62(12)	O2	S1	O1	115.30(7)
C7	N2	N1	110.26(12)	O2	S1	O3	115.65(7)
C7	N2	C2	132.89(13)	O2	S1	C13	102.91(7)
N4	N3	I1	113.28(9)	O3	S1	C13	103.45(7)
C12	N3	I1	138.99(10)	F1	C13	S1	111.03(11)
C12	N3	N4	107.36(11)	F2	C13	S1	110.74(10)
N3	N4	C6	117.03(11)	F2	C13	F1	107.63(13)
C10	N4	N3	109.97(12)	F3	C13	S1	111.52(11)
C10	N4	C6	132.90(12)	F3	C13	F1	107.44(13)
C2	C1	I1	119.53(10)	F3	C13	F2	108.32(13)
C2	C1	C6	121.83(13)	O4	S2	O6	114.16(8)
C6	C1	I1	118.64(10)	O4	S2	C15	104.45(8)
C1	C2	N2	115.44(12)	O5	S2	O4	115.77(8)
C1	C2	C3	119.83(13)	O5	S2	O6	114.53(7)
C3	C2	N2	124.73(13)	O5	S2	C15	103.33(9)
C2	C3	C4	117.96(14)	O6	S2	C15	102.33(8)
C3	C4	C5	122.66(14)	F4	C15	S2	111.66(14)
C6	C5	C4	117.74(13)	F4	C15	F5	107.73(16)
C1	C6	N4	115.13(12)	F4	C15	F6	107.50(15)
C1	C6	C5	119.97(13)	F5	C15	S2	111.18(12)
C5	C6	N4	124.90(13)	F6	C15	S2	110.91(12)
N2	C7	C8	106.98(13)	F6	C15	F5	107.68(16)
C7	C8	C9	106.48(13)				

Table 7: Torsion Angles for Bis-Pyr-I-OTf **12b**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
I1	N1	N2	C2	4.70(15)	C6	C1	C2	N2	-178.07(13)
I1	N1	N2	C7	-170.41(10)	C6	C1	C2	C3	1.3(2)
I1	N1	C9	C8	166.91(12)	C7	N2	C2	C1	169.74(15)
I1	N3	N4	C6	2.39(15)	C7	N2	C2	C3	-9.6(3)
I1	N3	N4	C10	-174.53(9)	C7	C8	C9	N1	-0.52(19)
I1	N3	C12	C11	172.58(12)	C9	N1	N2	C2	175.10(13)
I1	C1	C2	N2	1.14(17)	C9	N1	N2	C7	-0.01(17)
I1	C1	C2	C3	-179.47(11)	C10	N4	C6	C1	174.40(15)
I1	C1	C6	N4	-0.03(17)	C10	N4	C6	C5	-5.7(2)

I1	C1	C6	C5	-179.96(11)	C10	C11	C12	N3	-0.62(18)
N1	N2	C2	C1	-3.99(18)	C12	N3	N4	C6	176.75(12)
N1	N2	C2	C3	176.65(14)	C12	N3	N4	C10	-0.16(16)
N1	N2	C7	C8	-0.31(17)	O1	S1	C13	F1	-58.49(12)
N2	N1	C9	C8	0.33(17)	O1	S1	C13	F2	61.02(12)
N2	C2	C3	C4	178.61(14)	O1	S1	C13	F3	-178.28(11)
N2	C7	C8	C9	0.50(18)	O2	S1	C13	F1	-178.91(10)
N3	N4	C6	C1	-1.64(18)	O2	S1	C13	F2	-59.40(12)
N3	N4	C6	C5	178.29(13)	O2	S1	C13	F3	61.30(12)
N3	N4	C10	C11	-0.23(17)	O3	S1	C13	F1	60.32(12)
N4	N3	C12	C11	0.48(17)	O3	S1	C13	F2	179.83(11)
N4	C10	C11	C12	0.51(17)	O3	S1	C13	F3	-59.46(12)
C1	C2	C3	C4	-0.7(2)	O4	S2	C15	F4	57.58(15)
C2	N2	C7	C8	-174.34(15)	O4	S2	C15	F5	-62.77(15)
C2	C1	C6	N4	179.18(13)	O4	S2	C15	F6	177.45(14)
C2	C1	C6	C5	-0.7(2)	O5	S2	C15	F4	-63.91(14)
C2	C3	C4	C5	-0.4(2)	O5	S2	C15	F5	175.74(13)
C3	C4	C5	C6	1.0(2)	O5	S2	C15	F6	55.96(15)
C4	C5	C6	N4	179.68(14)	O6	S2	C15	F4	176.85(13)
C4	C5	C6	C1	-0.4(2)	O6	S2	C15	F5	56.50(14)
C6	N4	C10	C11	-176.47(14)	O6	S2	C15	F6	-63.28(15)

Table 8: Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Bis-Pyr-I-OTf **12b**.

Atom	x	y	z	U(eq)
H3	7805.29	8100.01	8080.21	19
H4	6457.55	8938.07	7349.63	19
H5	3970.6	8851.95	6506.43	16
H7	9044.59	7071.08	8552.71	20
H8	9072.15	5950.33	8866.42	24
H9	6404.7	5577.85	8353.04	20
H10	1209.68	8602.22	5788.31	17
H11	-1043.48	7929.51	5286.99	20
H12	-231.8	6874.02	5818.67	18
H14A	2034.47	5970.81	4768.6	61
H14B	633.01	5511.94	4848.03	61
H14C	2282.29	5345.49	5428.85	61
H7A	1000(30)	5706(12)	6730(20)	46(8)

6. References

- [1] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, Elsevier, Amsterdam, **2009**.
- [2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, 42, 339.
- [3] G. M. Sheldrick, *Acta Cryst.* **2015**, A71, 3.
- [4] G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112.
- [5] F. Yang, L. Yan, K. Ma, L. Yang, J. Li, L. Chen, J. You, *Eur. J. Org. Chem.* **2006**, 1109.
- [6] Y.-S. Fan, Y.-J. Jiang, D. An, Di Sha, J. C. Antilla, S. Zhang, *Org. Lett.* **2014**, 16, 6112.
- [7] W. Feuerstein, C. Holzer, X. Gui, L. Neumeier, W. Kloppe, F. Breher, *Chem. Eur. J.* **2020**, 26, 17156.
- [8] R. Roth, G. Schmidt, A. Prud'homme, S. Abele, *Org. Process Res. Dev.* **2019**, 23, 234.
- [9] T. D. Krizan, J. C. Martin, *J. Org. Chem.* **1982**, 47, 2681.
- [10] D. Christopher Braddock, T. Cailleau, G. Cansell, S. A. Hermitage, R. H. Pouwer, J. M. Redmond, A. J.P. White, *Tetrahedron: Asymmetry* **2010**, 21, 2911.
- [11] A. Boelke, E. Lork, B. J. Nachtsheim, *Chem. Eur. J.* **2018**, 24, 18653.
- [12] A. Boelke, T. J. Kuczmera, L. D. Caspers, E. Lork, B. J. Nachtsheim, *Org. Lett.* **2020**, 22, 7261.
- [13] A. Boelke, B. J. Nachtsheim, *Adv. Synth. Catal.* **2020**, 362, 184.
- [14] J. Qurban, M. Elsherbini, H. Alharbi, T. Wirth, *Chem. Commun.* **2019**, 55, 7998.
- [15] S. Ficht, M. Mülbaier, A. Giannis, *Tetrahedron* **2001**, 57, 4863.
- [16] T. Dohi, T. Nakae, N. Takenaga, T. Uchiyama, K.-i. Fukushima, H. Fujioka, Y. Kita, *Synthesis* **2012**, 44, 1183.
- [17] R. Fiorot, R. Westphal, B. Lemos, R. Romagna, P. Gonçalves, M. Fernandes, C. Ferreira, A. Taranto, S. Greco, *J. Braz. Chem. Soc.* **2019**, 30, 1860.
- [18] T. Muraki, H. Togo, M. Yokoyama, *J. Org. Chem.* **1999**, 64, 2883.
- [19] Togo, Nabana, Yamaguchi, *J. Org. Chem.* **2000**, 65, 8391.
- [20] G. Qian, B. Liu, Q. Tan, S. Zhang, B. Xu, *Eur. J. Org. Chem.* **2014**, 4837.
- [21] X. Wang, J. Gallardo-Donaire, R. Martin, *Angew. Chem. Int. Ed.* **2014**, 53, 11084.

7. NMR spectra

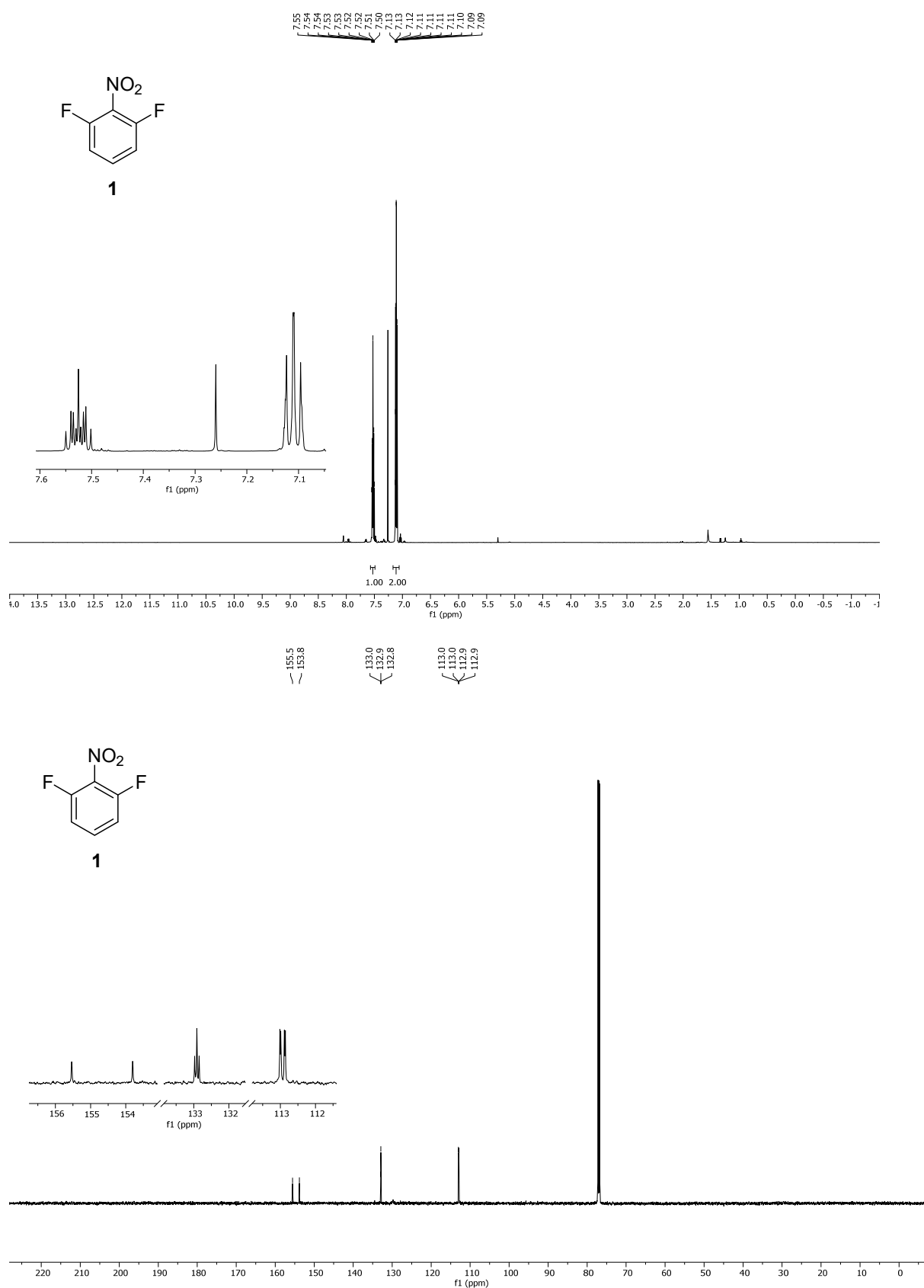


Figure S1: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **1** in CDCl₃.

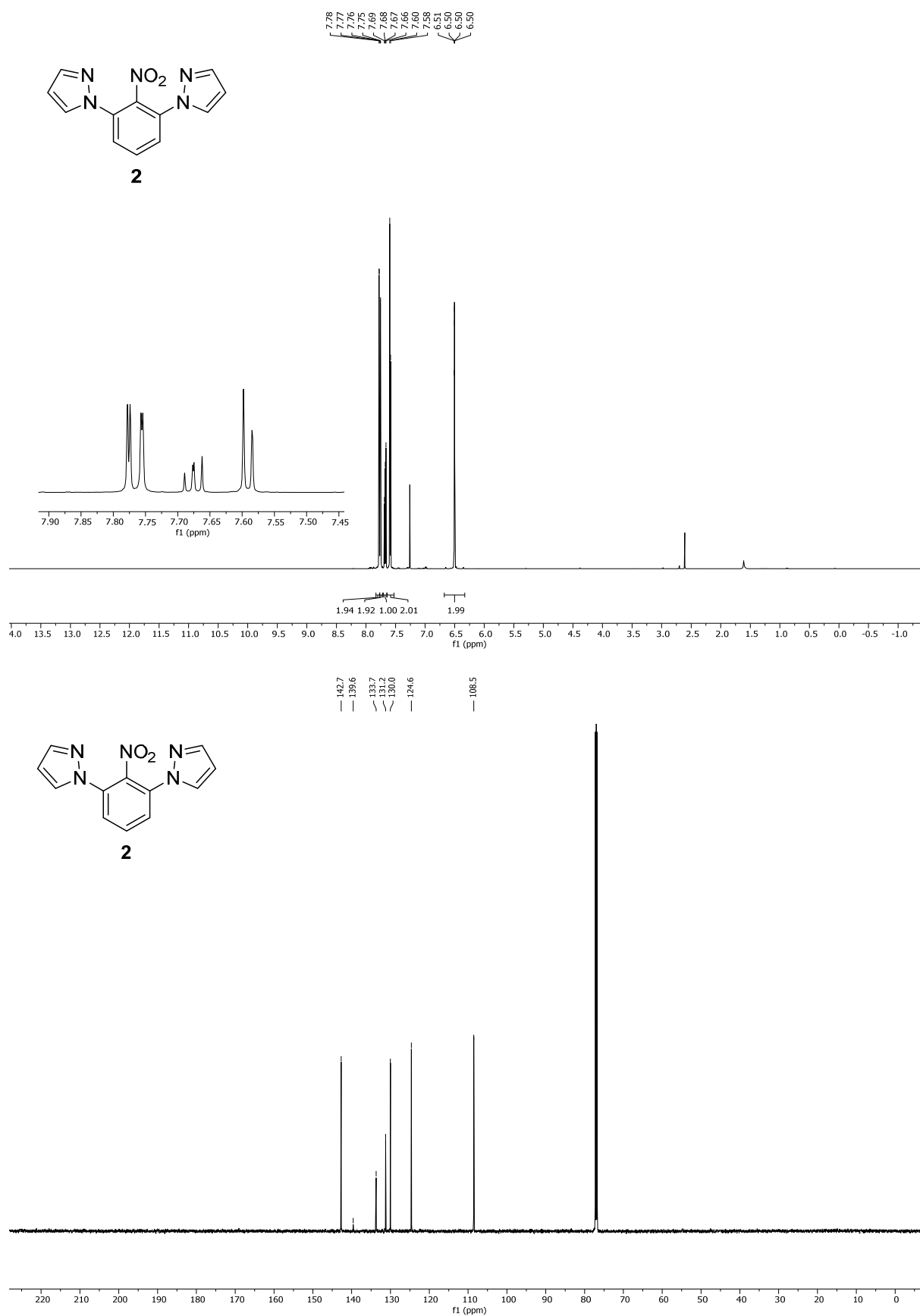


Figure S2: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **2** in CDCl₃.

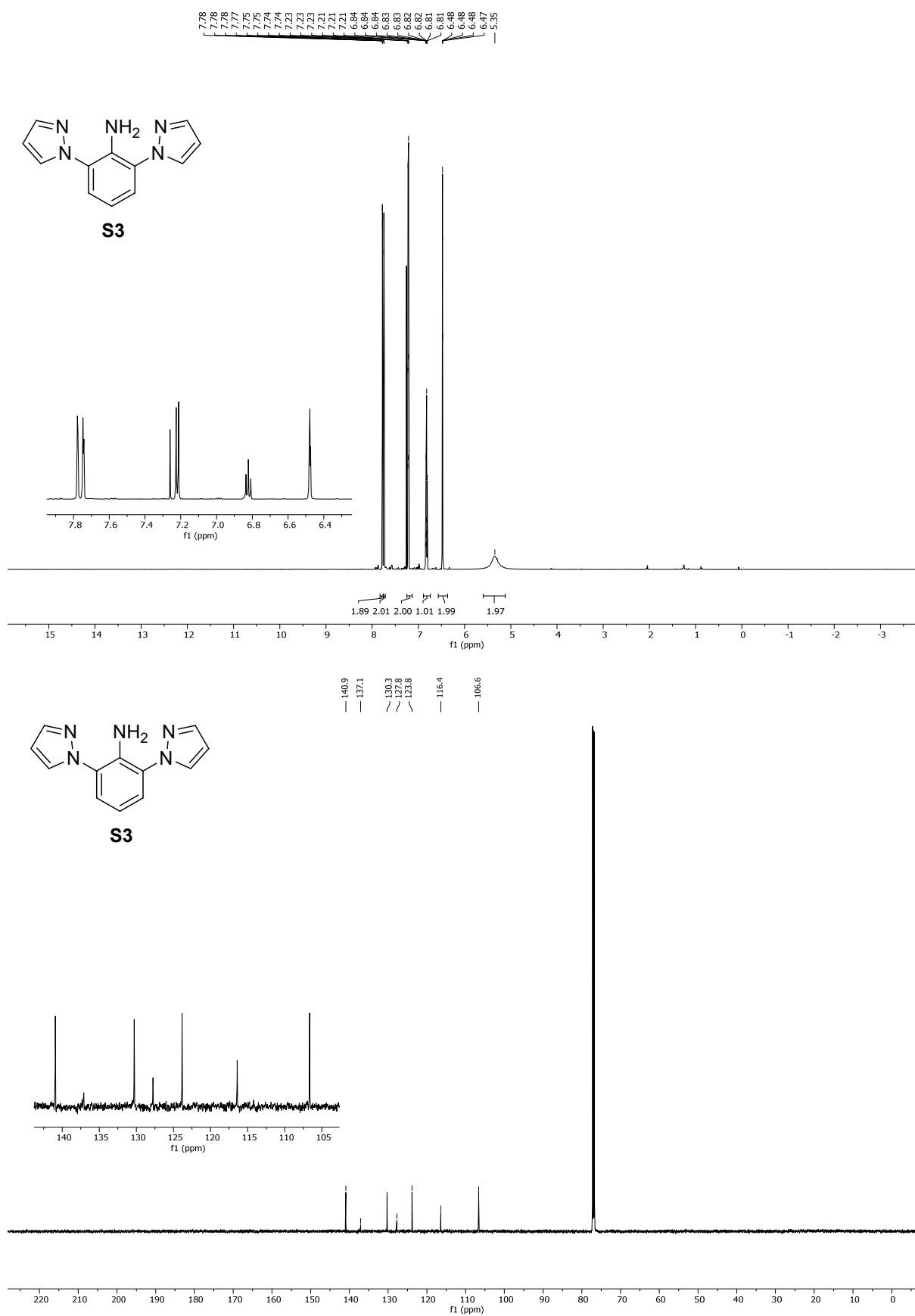


Figure S3: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **S3** in CDCl₃.

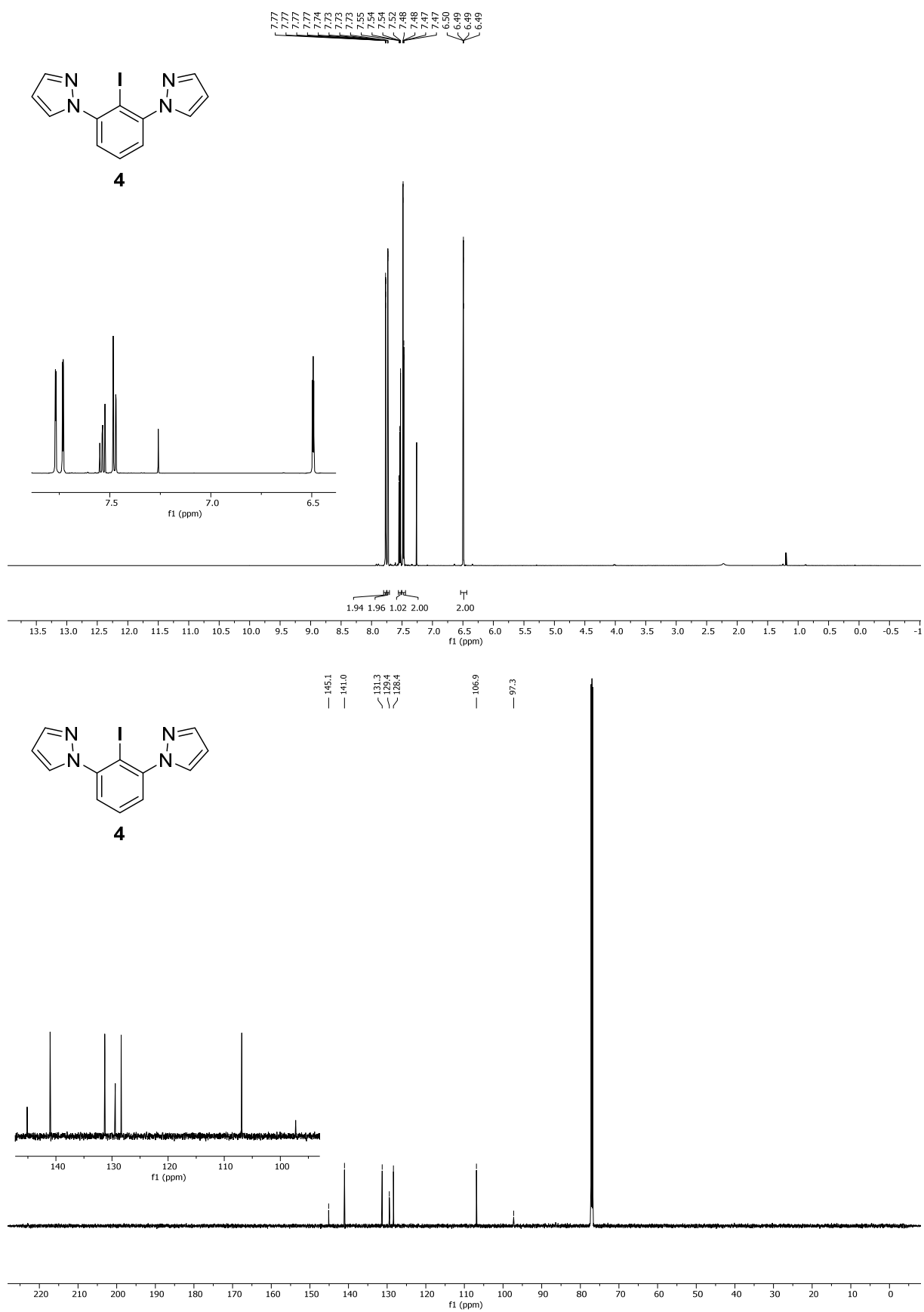


Figure S4: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **4** in CDCl_3 .

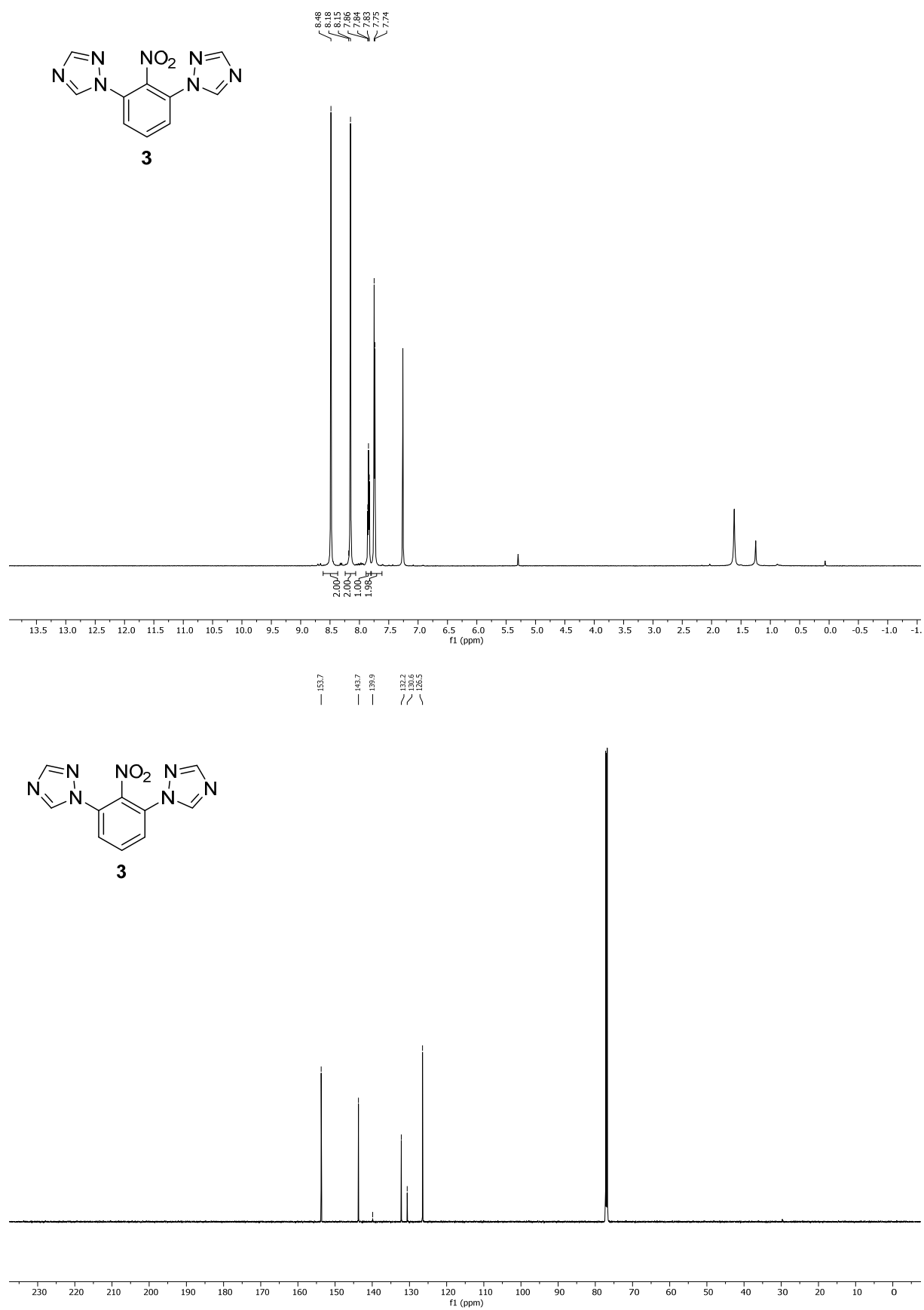


Figure S5: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **3** in CDCl₃.

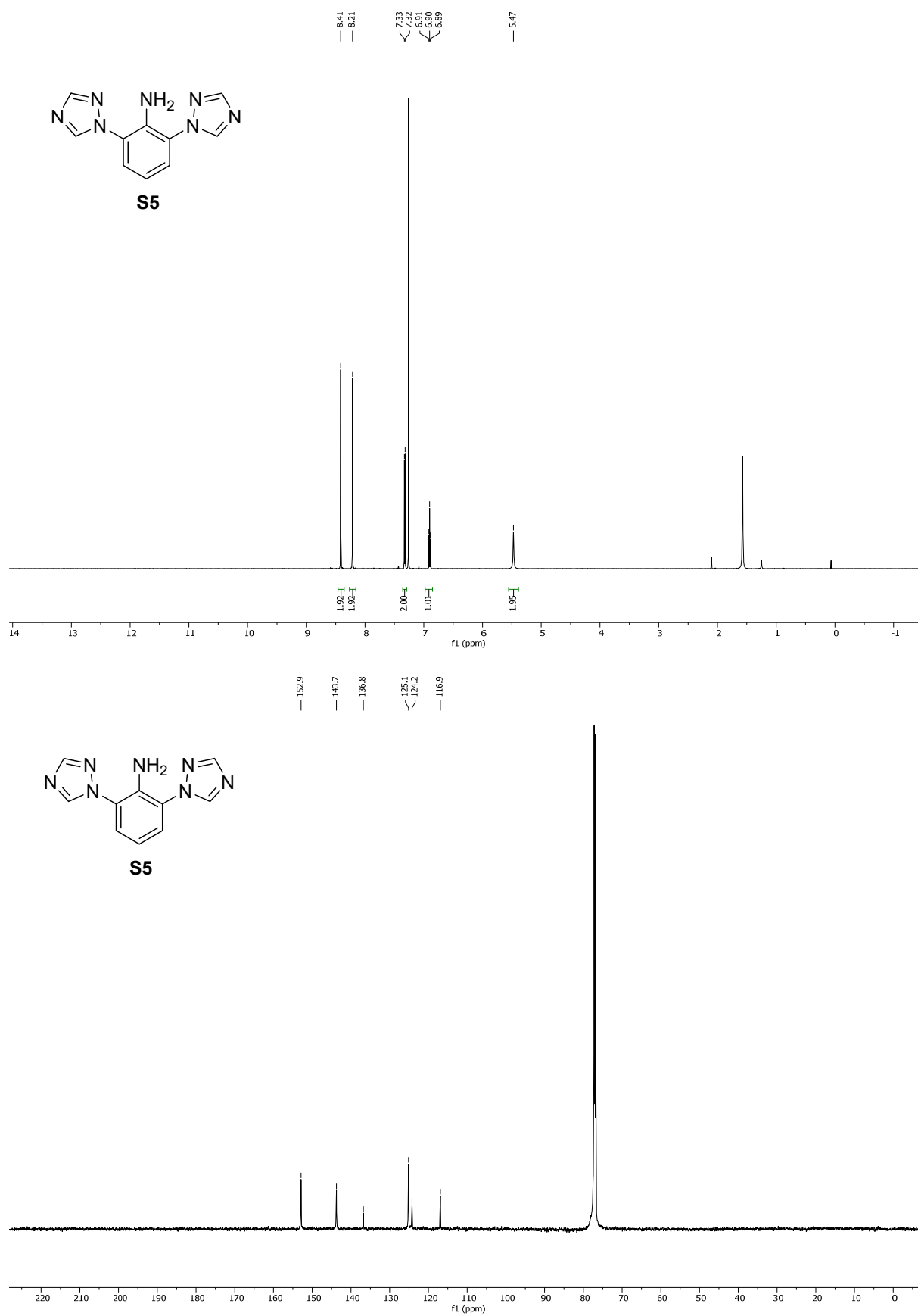


Figure S6: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **S5** in CDCl_3 .

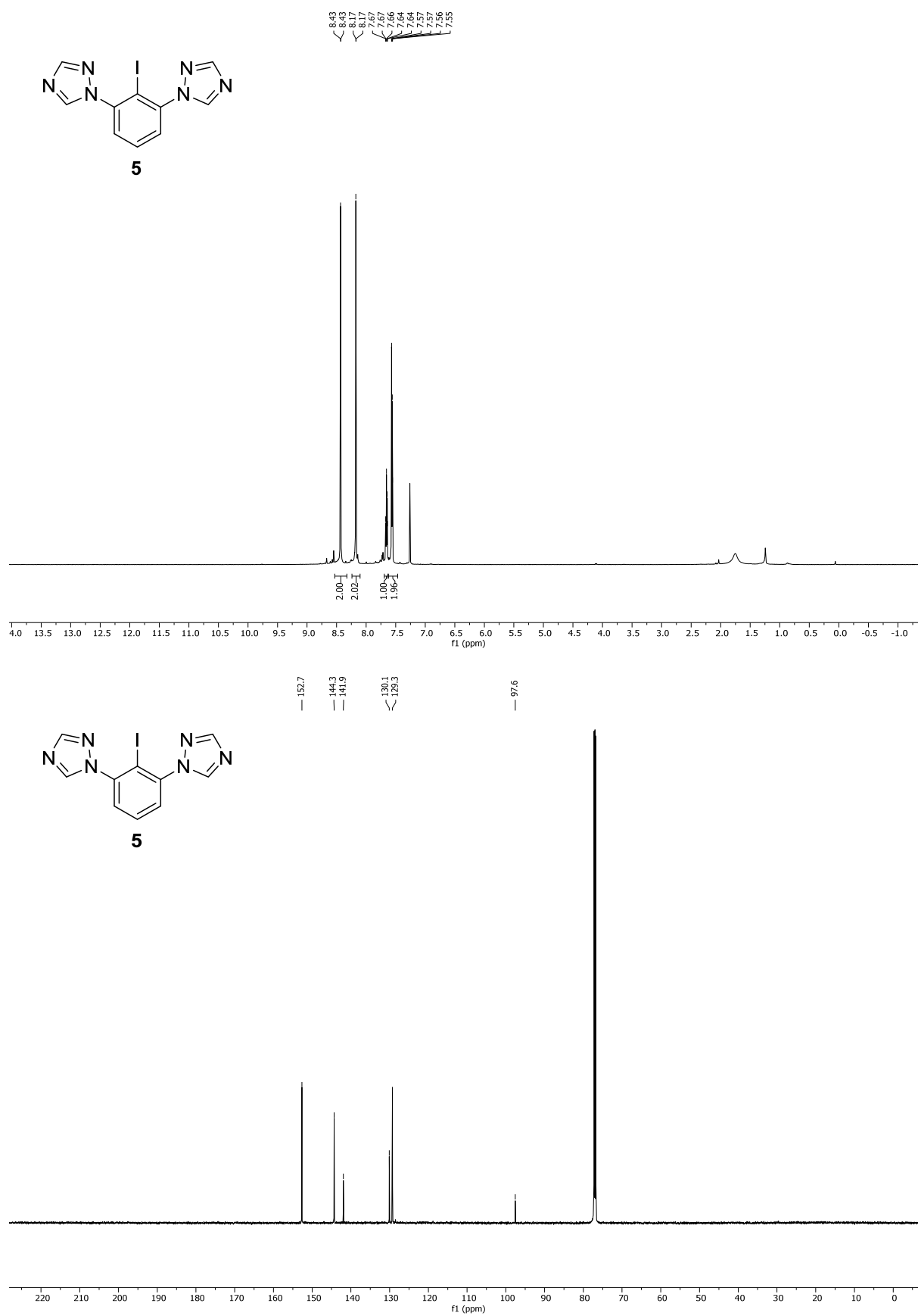


Figure S7: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **5** in CDCl_3 .

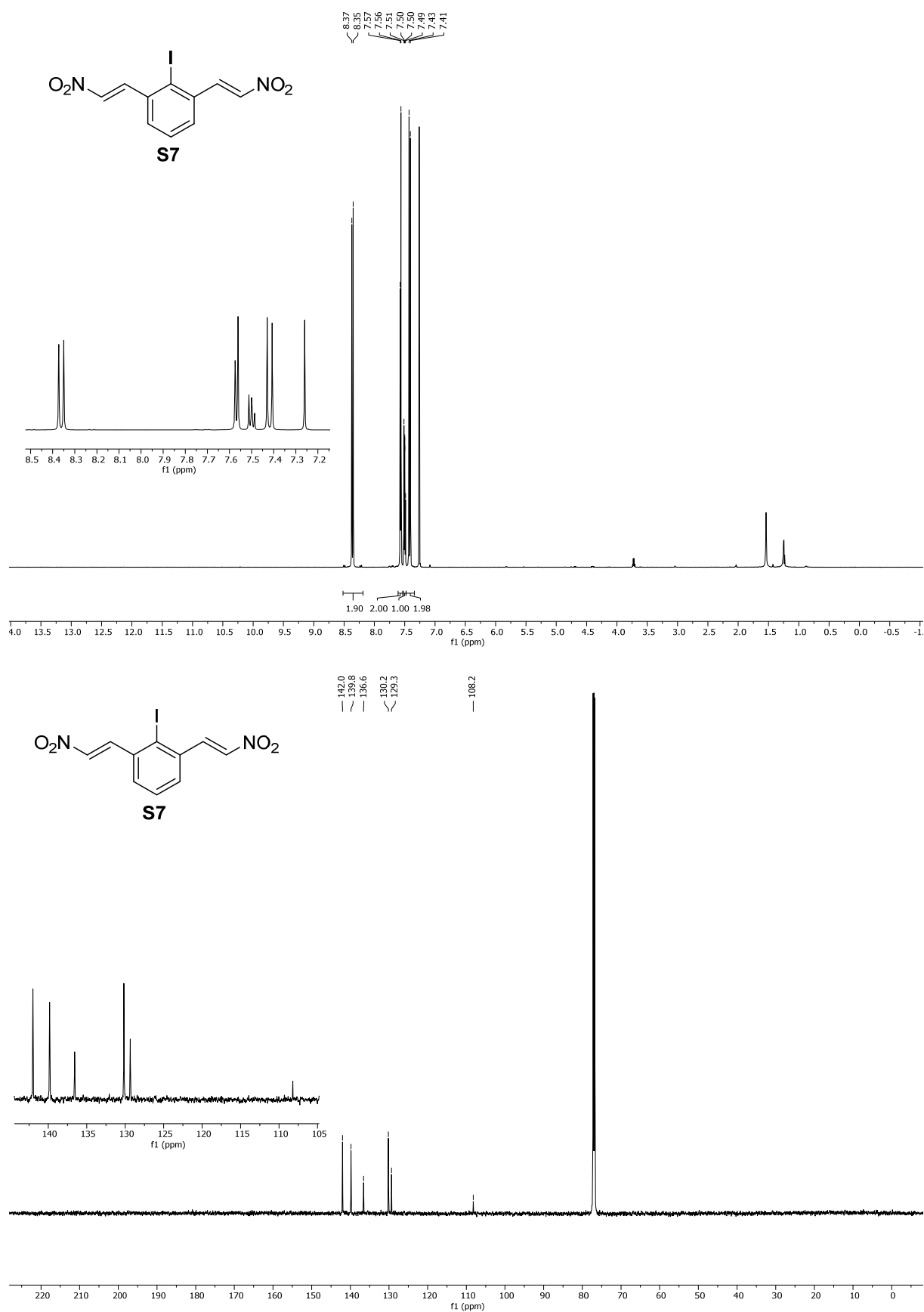
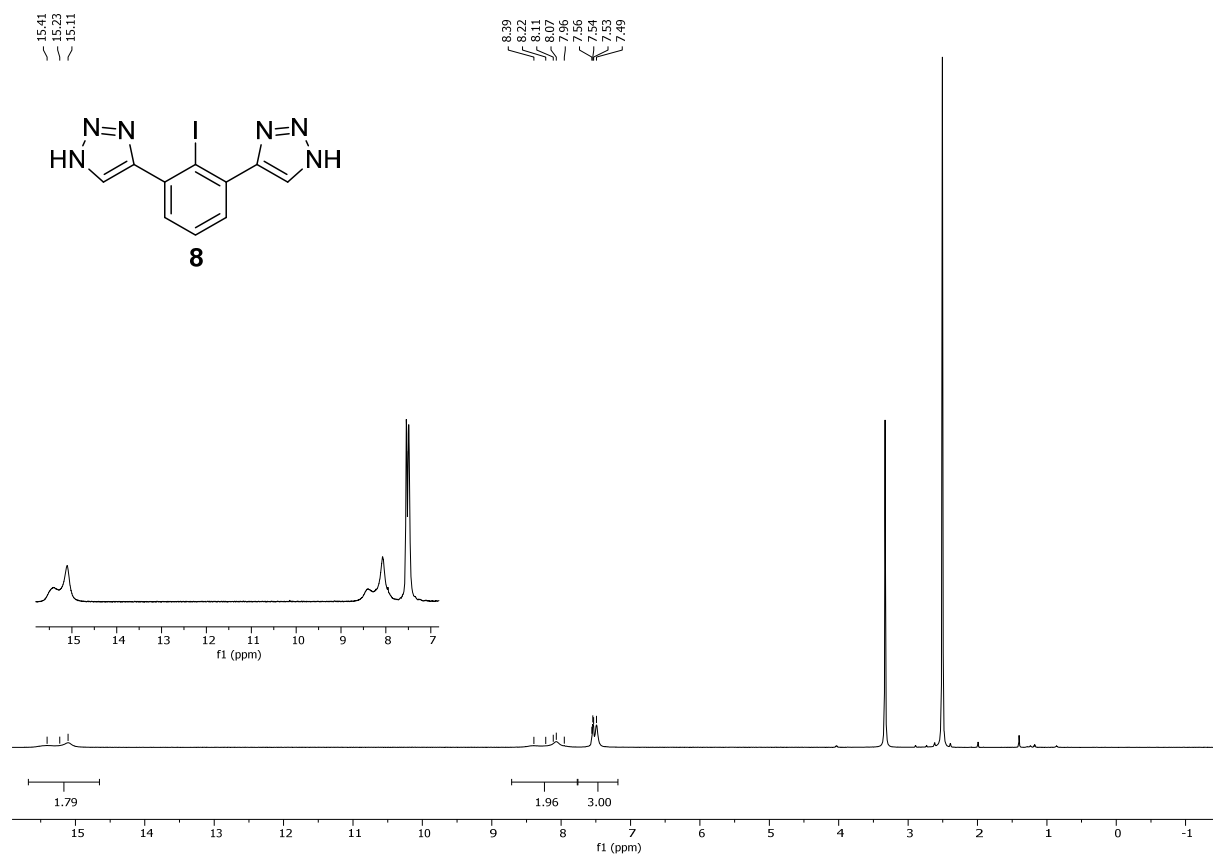
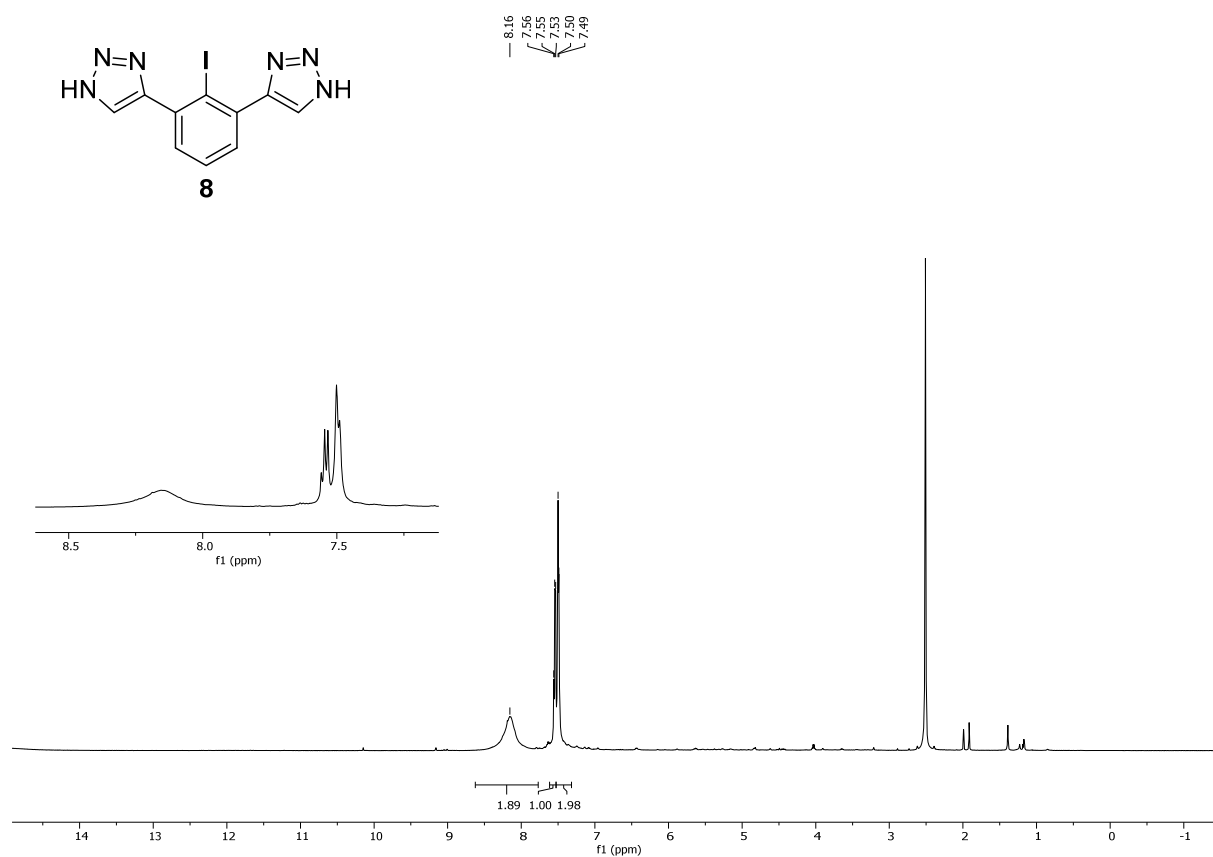


Figure S8: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **S7** in CDCl_3 .



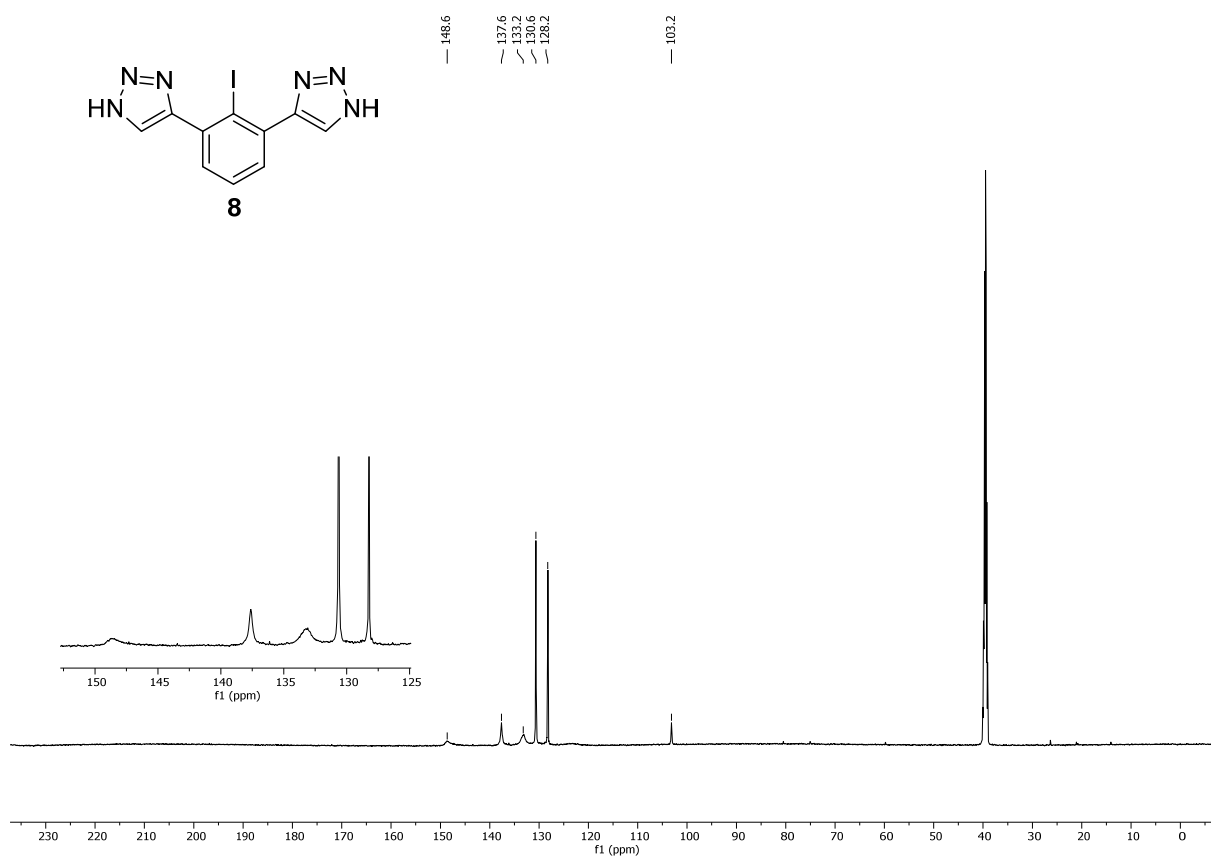
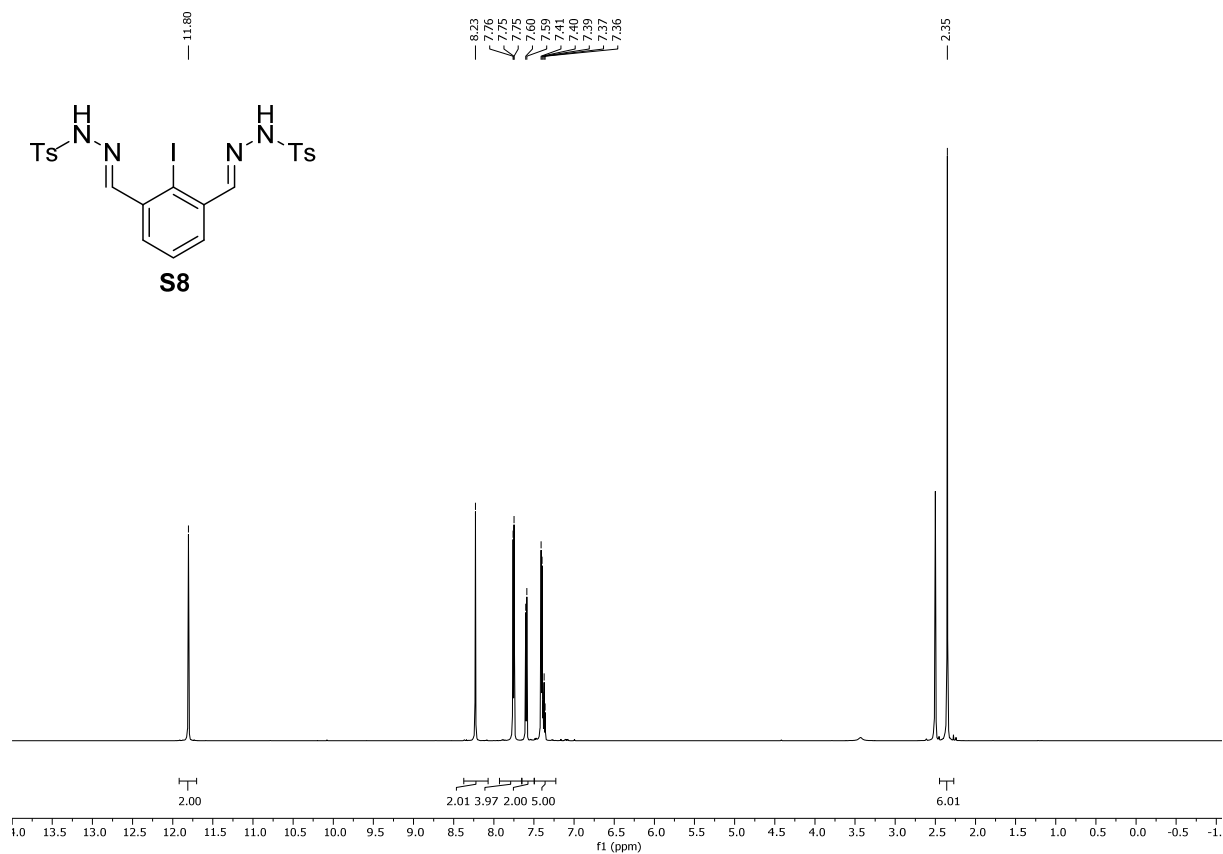


Figure S9: 600 MHz ¹H- (high and low concentration) and 151 MHz ¹³C-NMR spectra of **8** in *d*₆-DMSO.



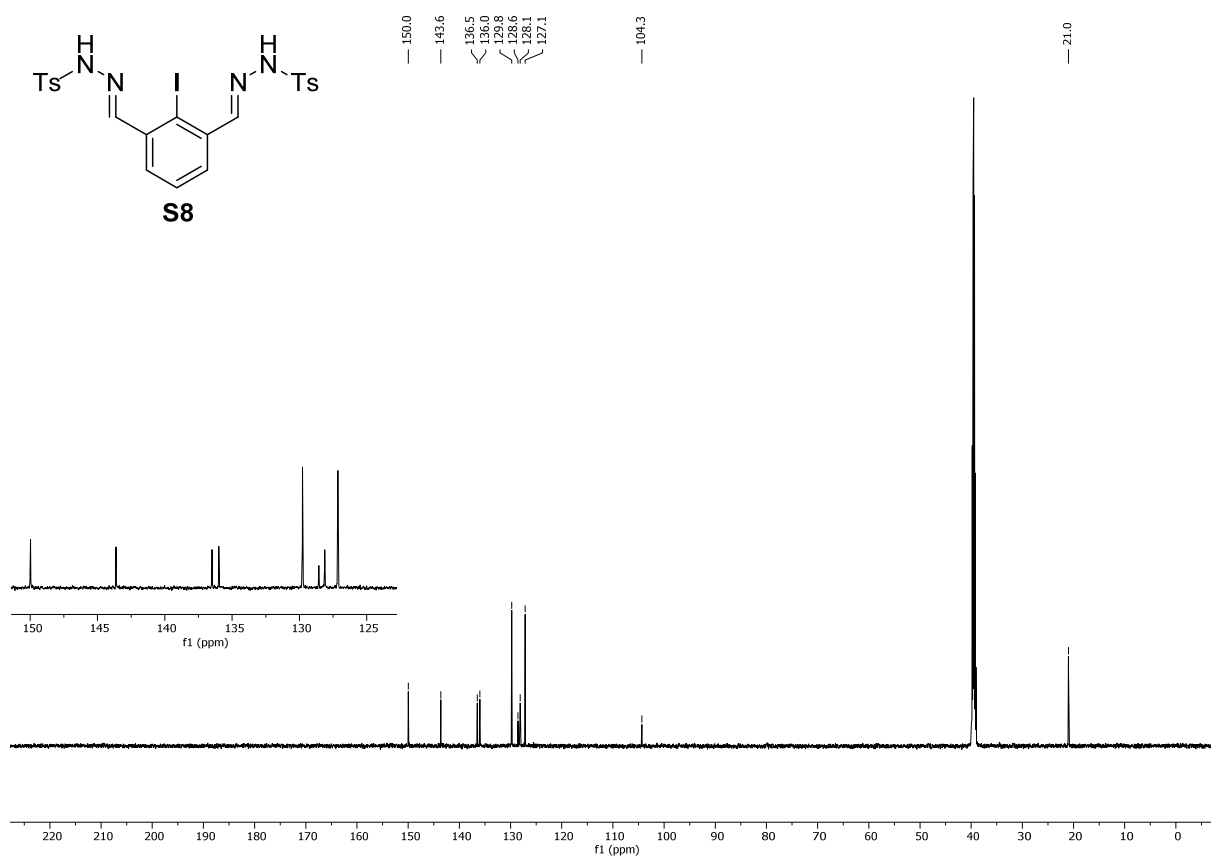
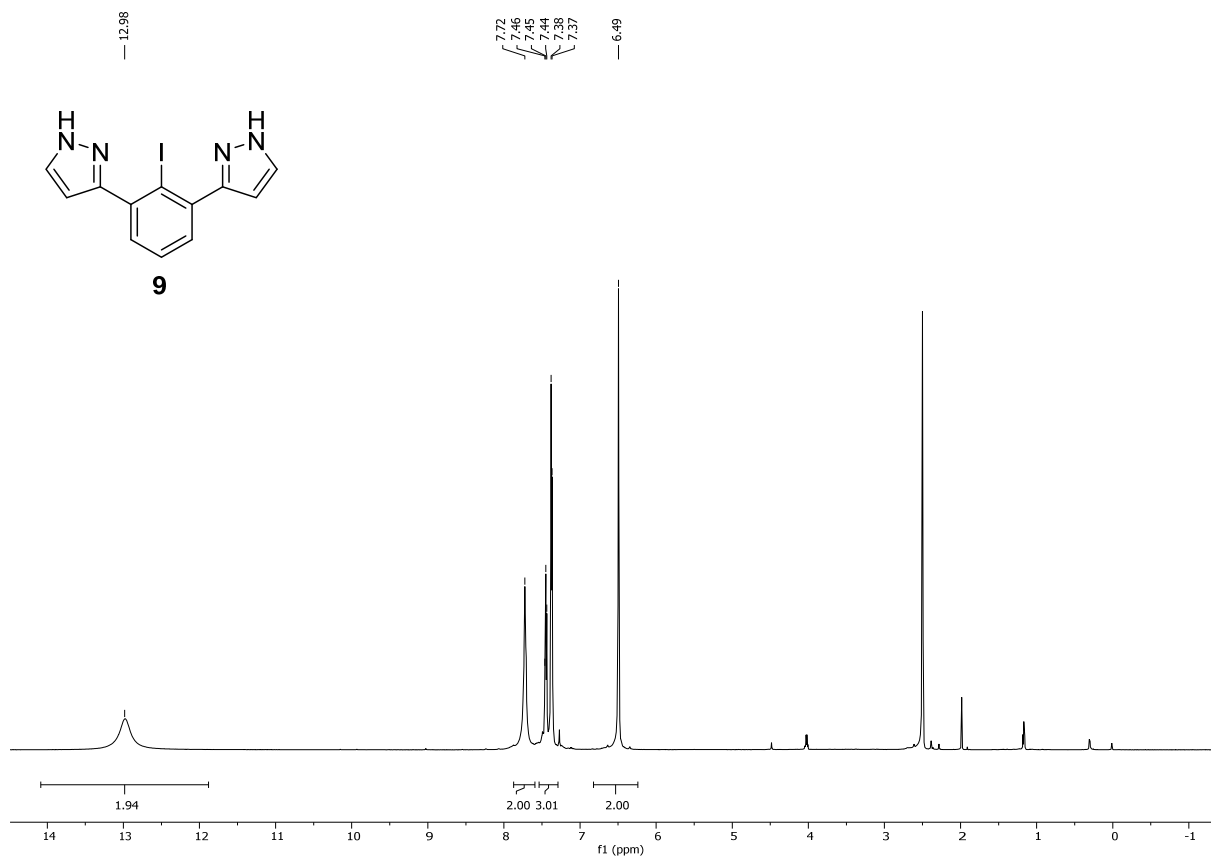


Figure S10: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **S8** in *d*₆-DMSO.



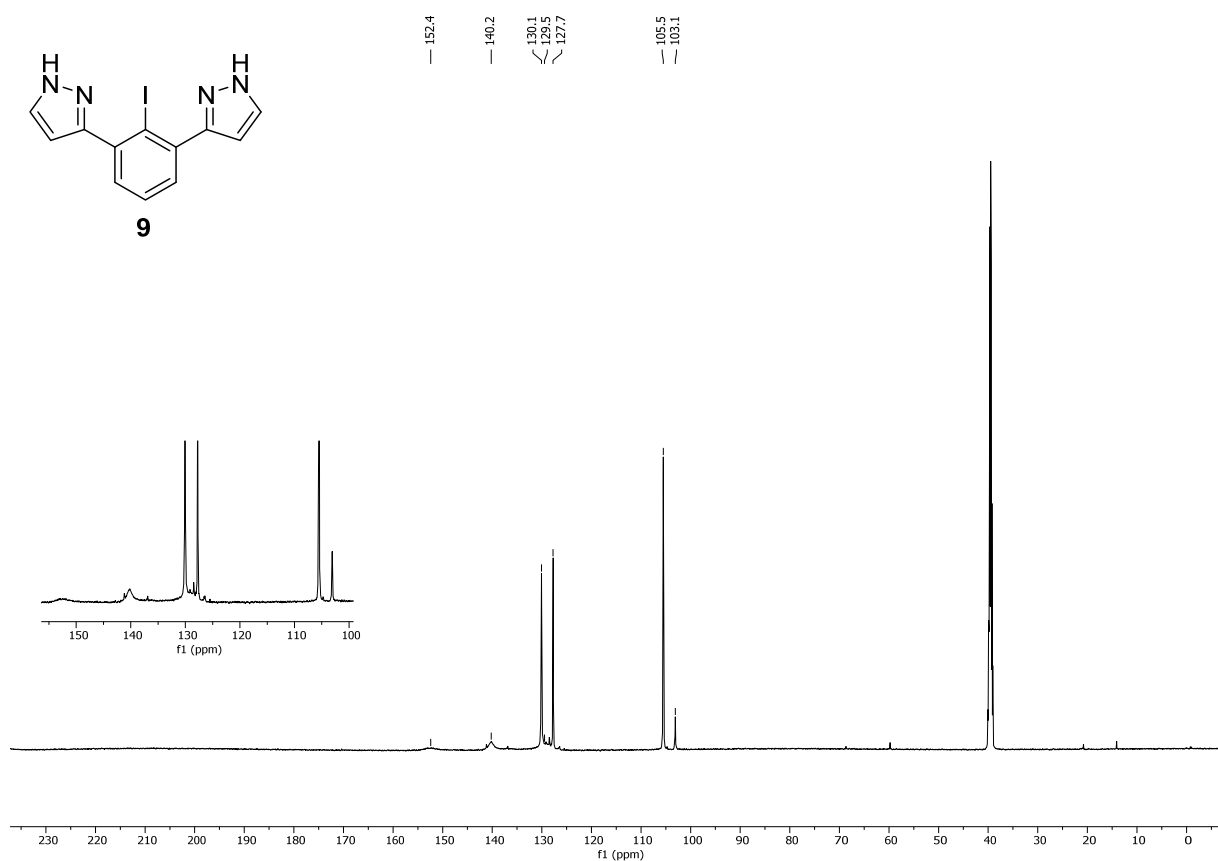
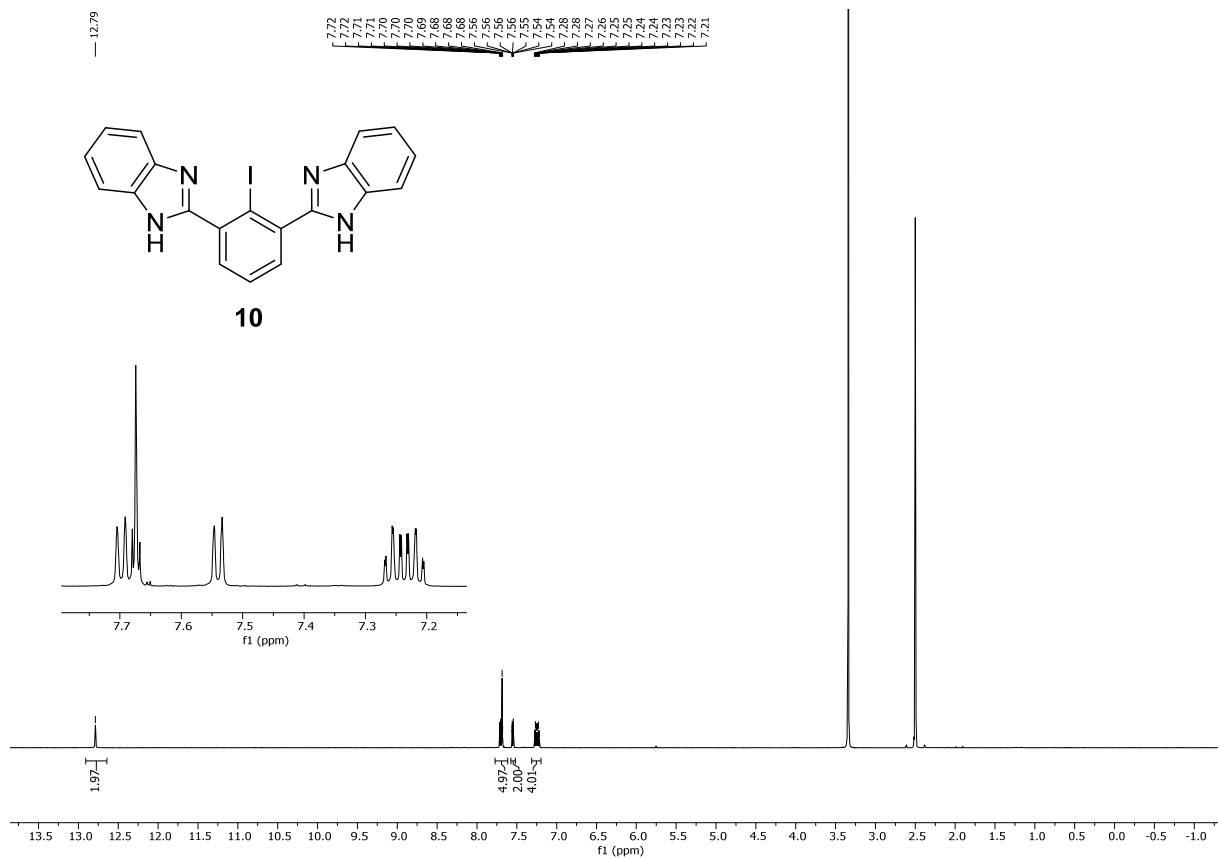


Figure S11: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **9** in *d*₆-DMSO.



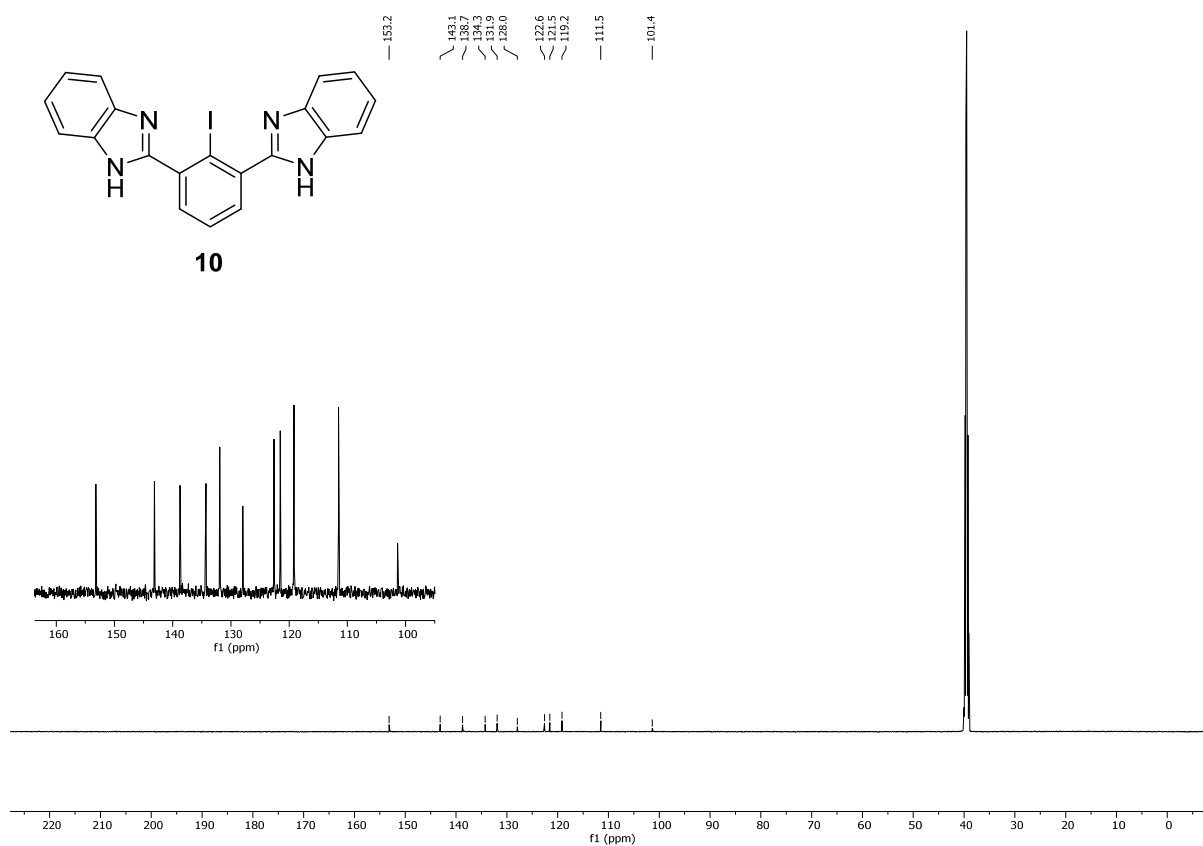
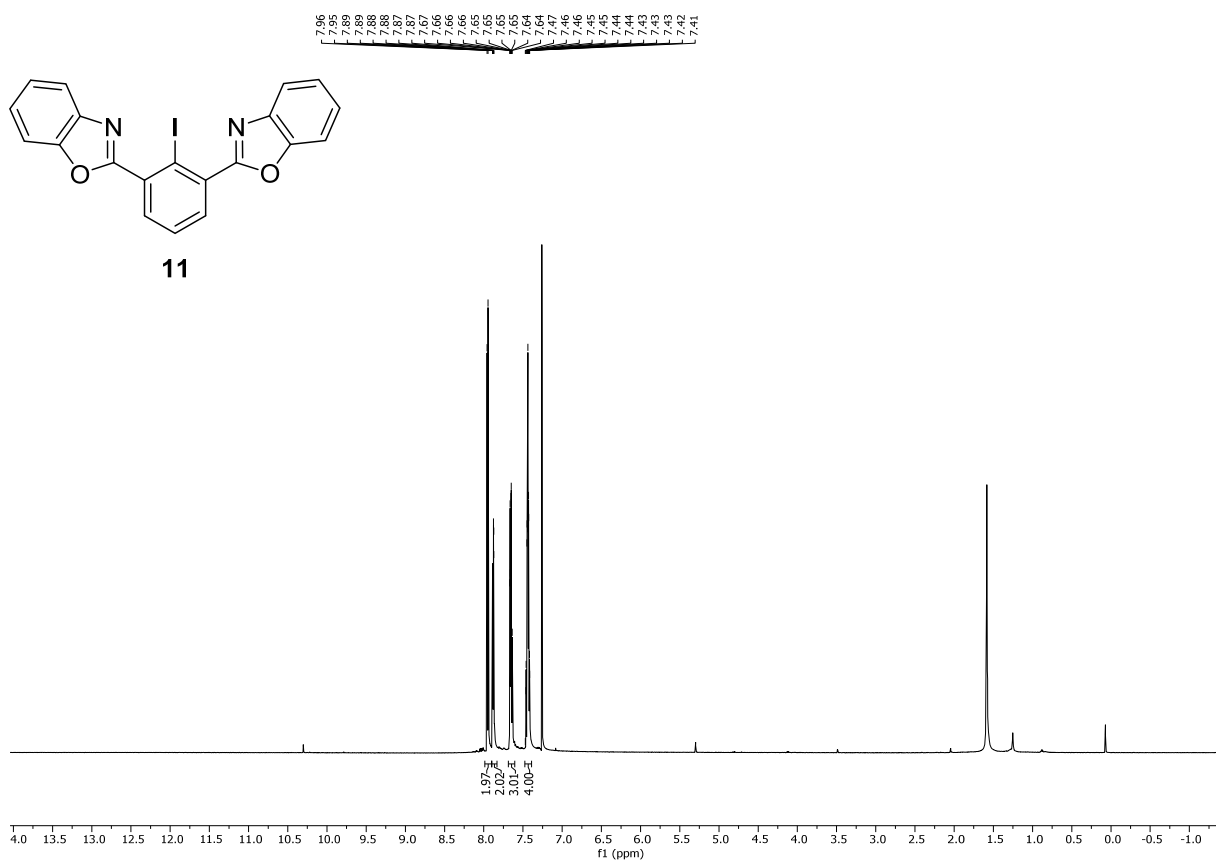


Figure S12: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **10** in d_6 -DMSO.



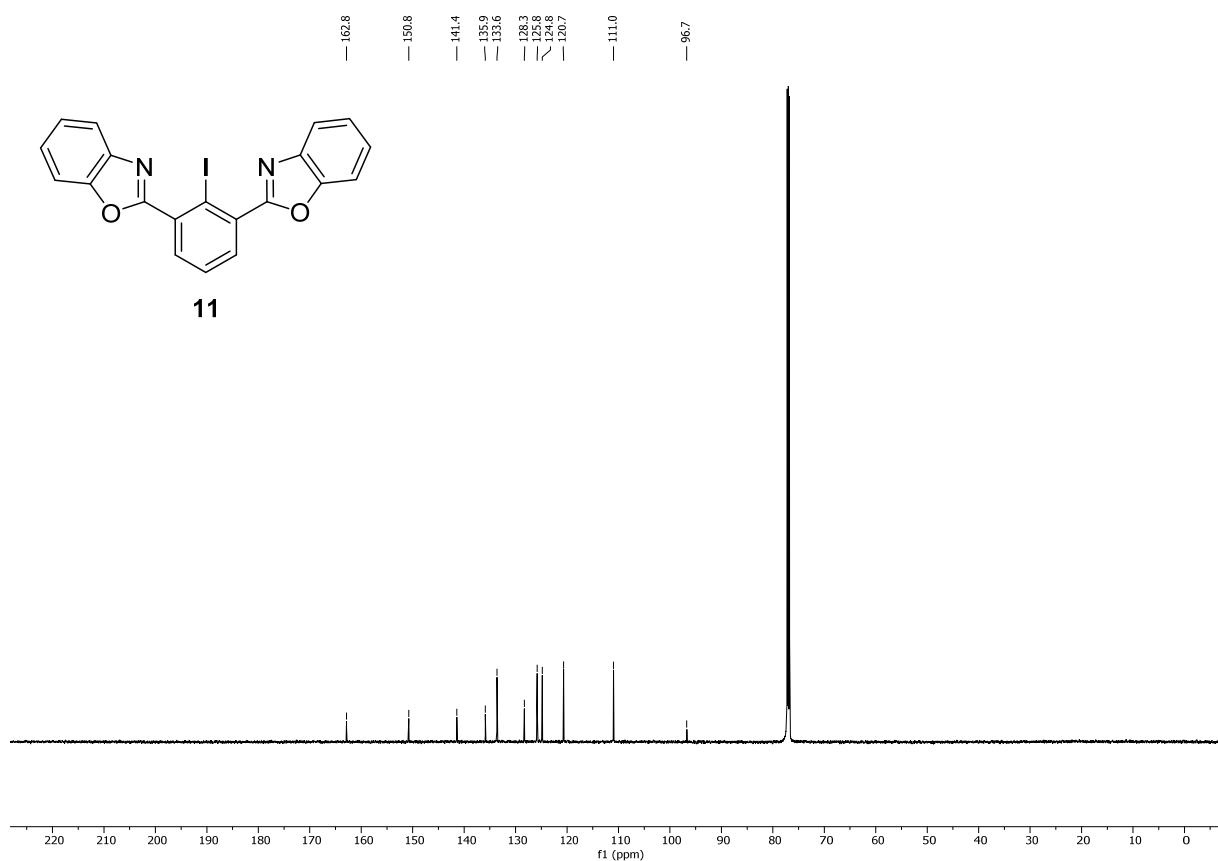
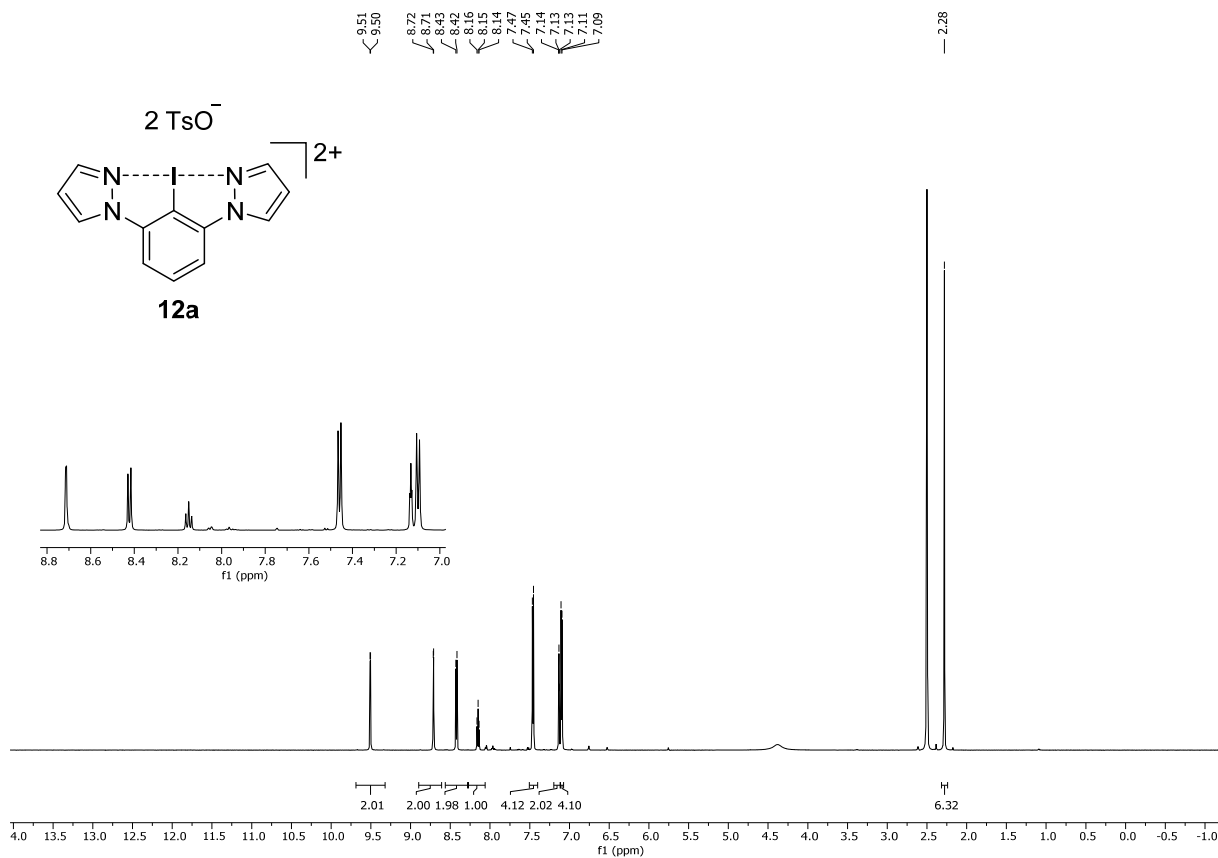


Figure S13: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **11** in CDCl_3 .



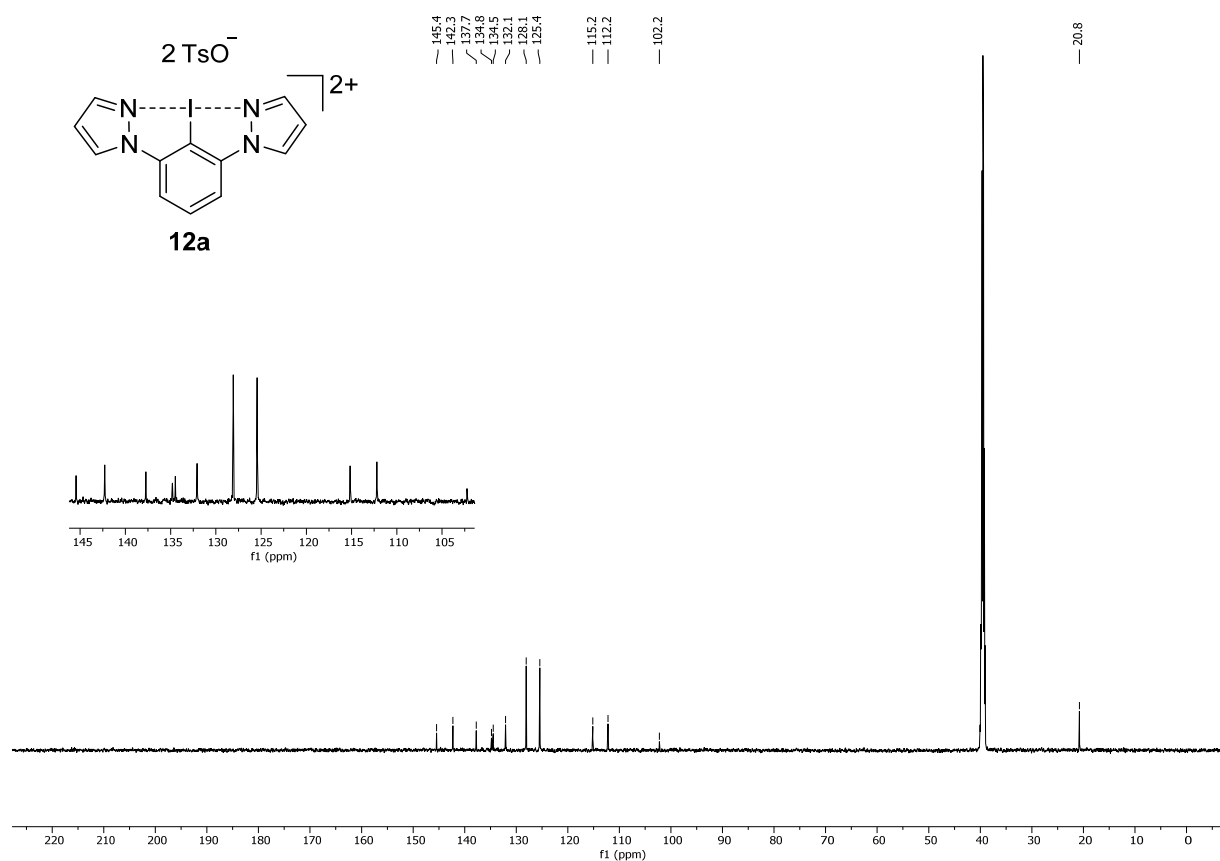
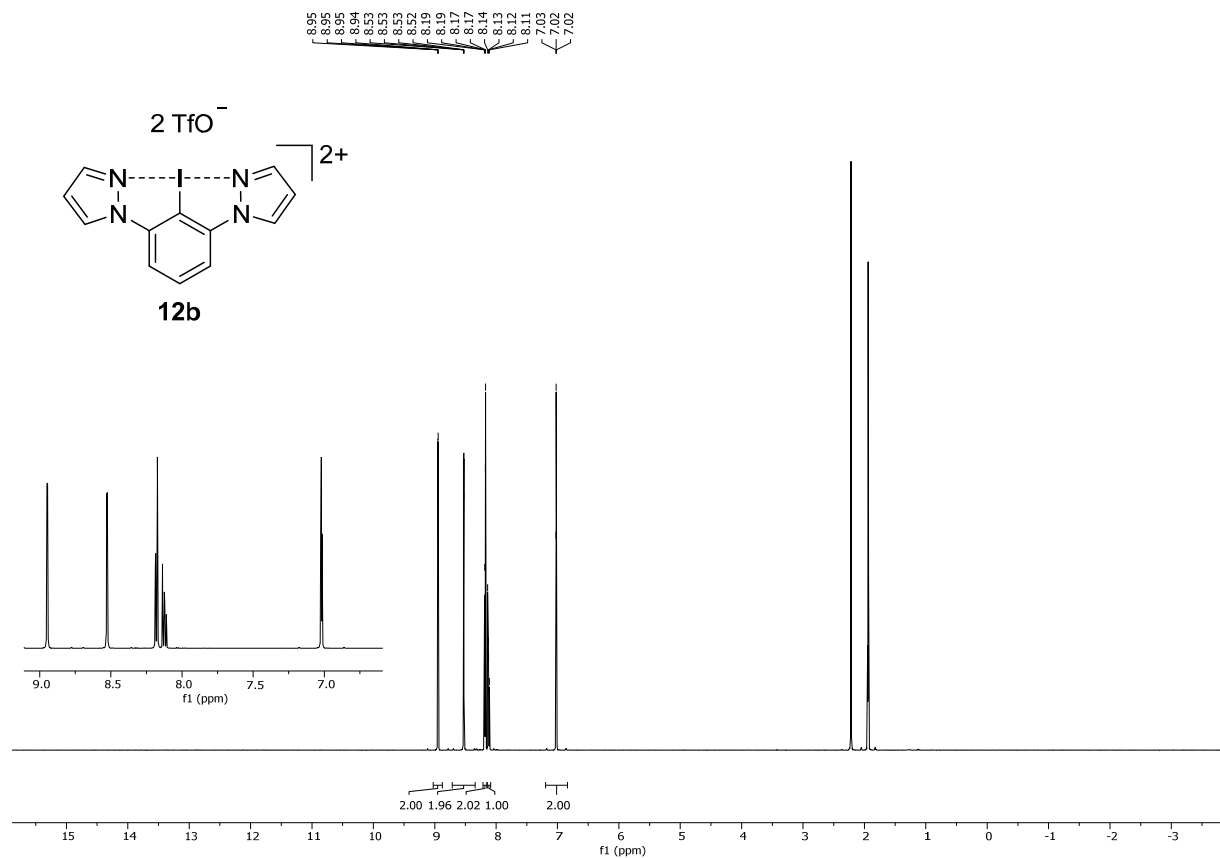


Figure S14: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **12a** in d_6 -DMSO.



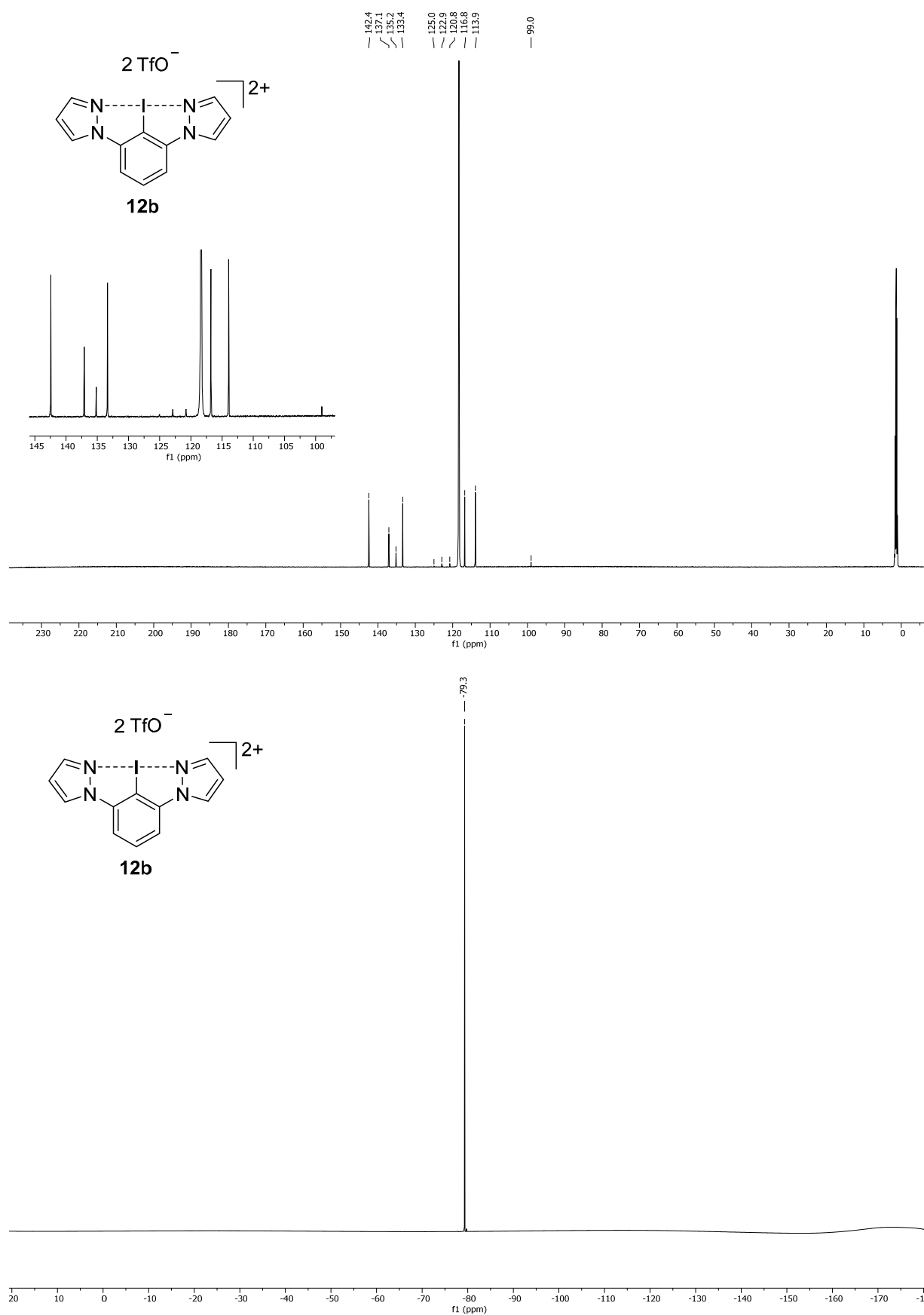


Figure S15: 600 MHz ¹H-, 151 MHz ¹³C and 565 MHz ¹⁹F-NMR spectra of **12b** in *d*₃-MeCN.

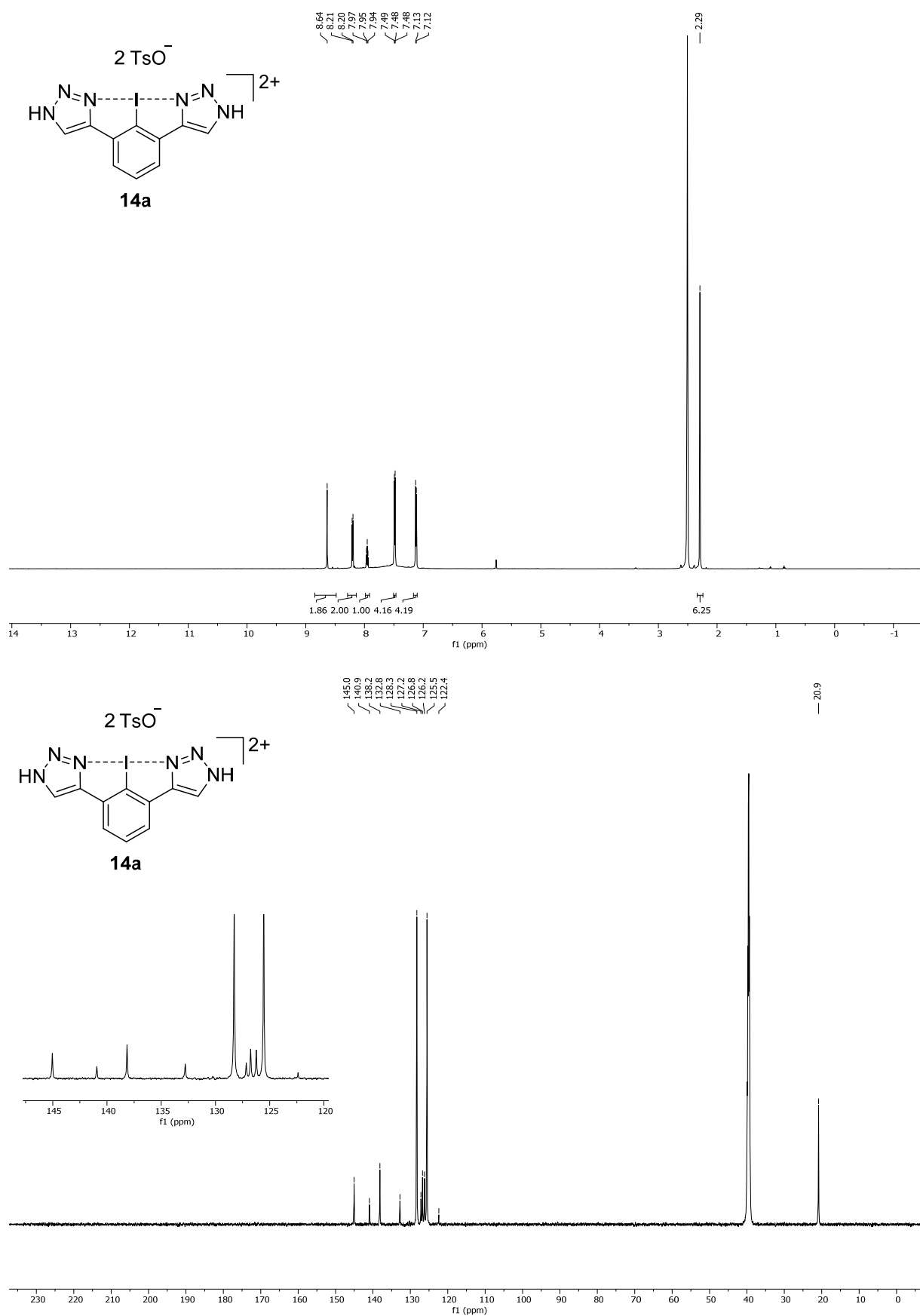
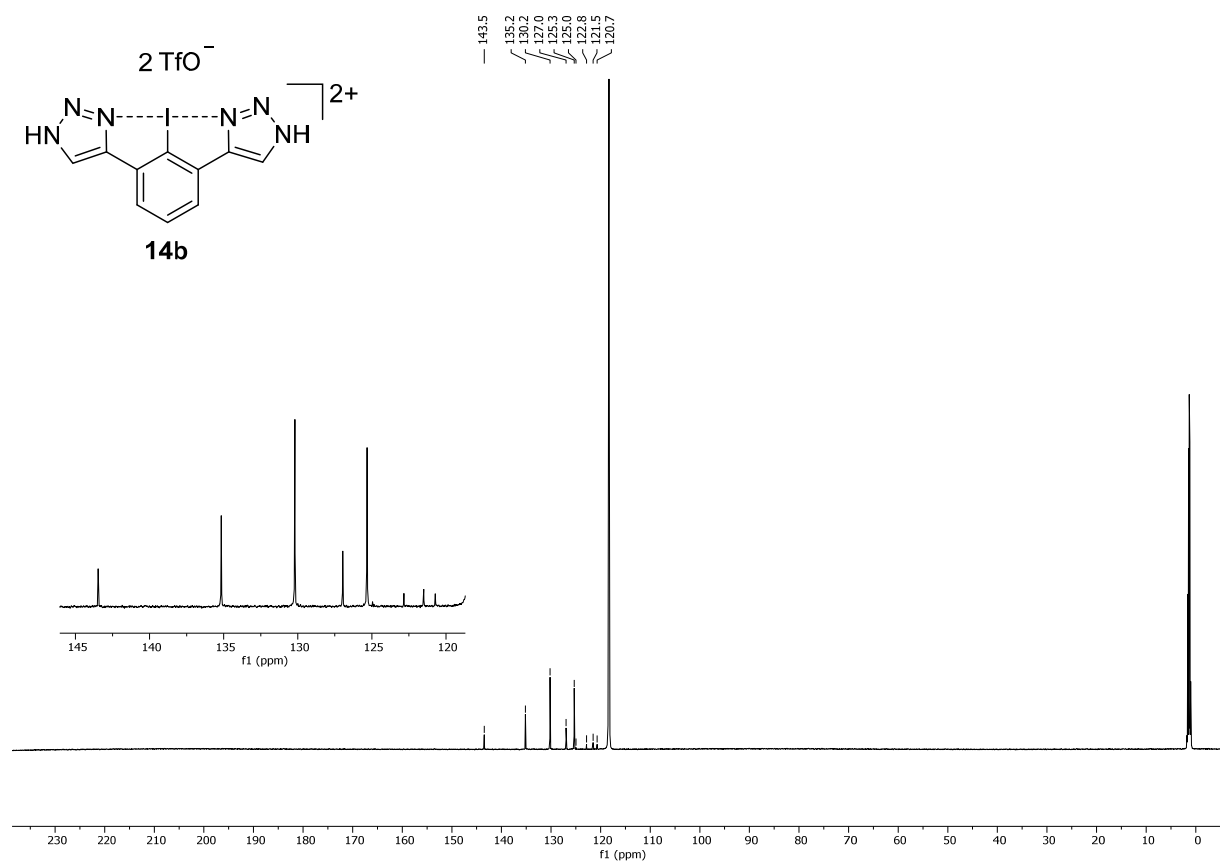
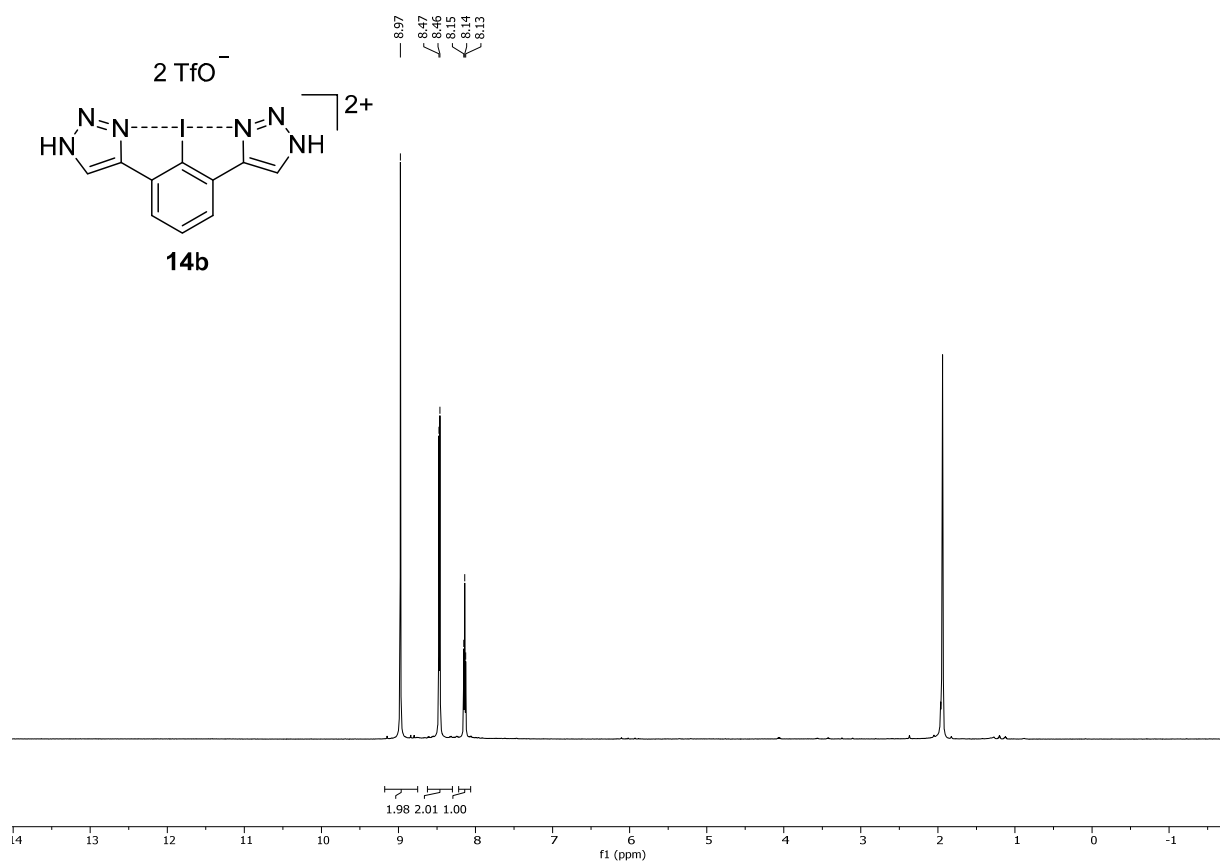


Figure S16: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **14a** in *d*₆-DMSO.



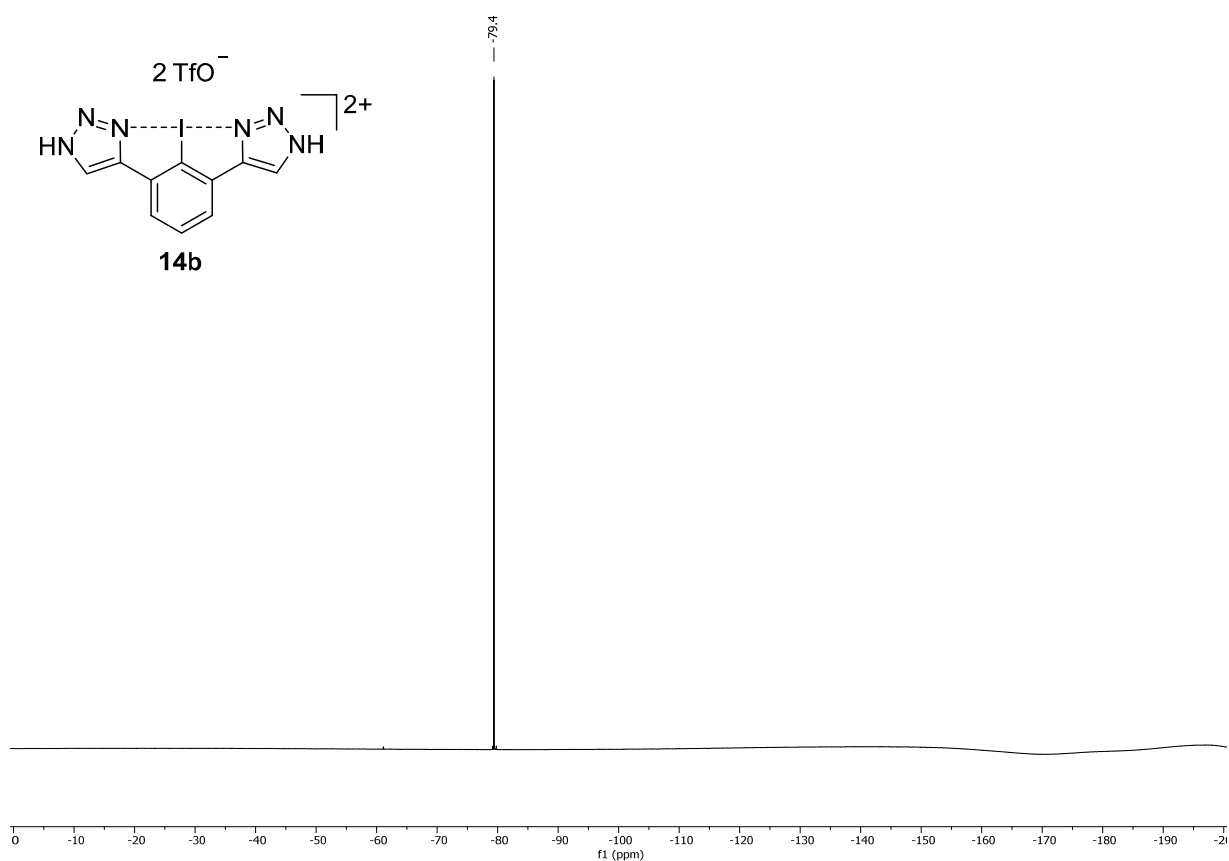
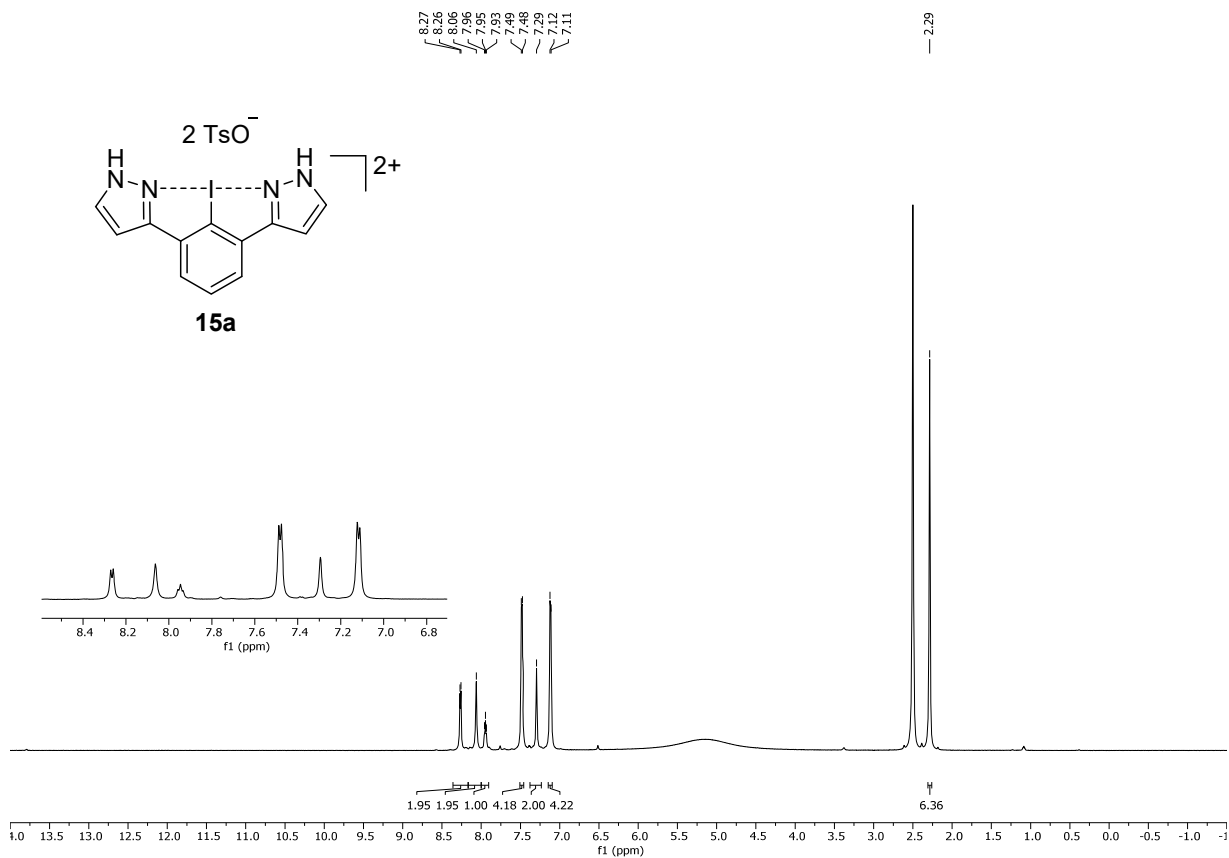


Figure S17: 600 MHz ^1H -, 151 MHz ^{13}C and 565 MHz ^{19}F -NMR spectra of **14b** in d_3 -MeCN.



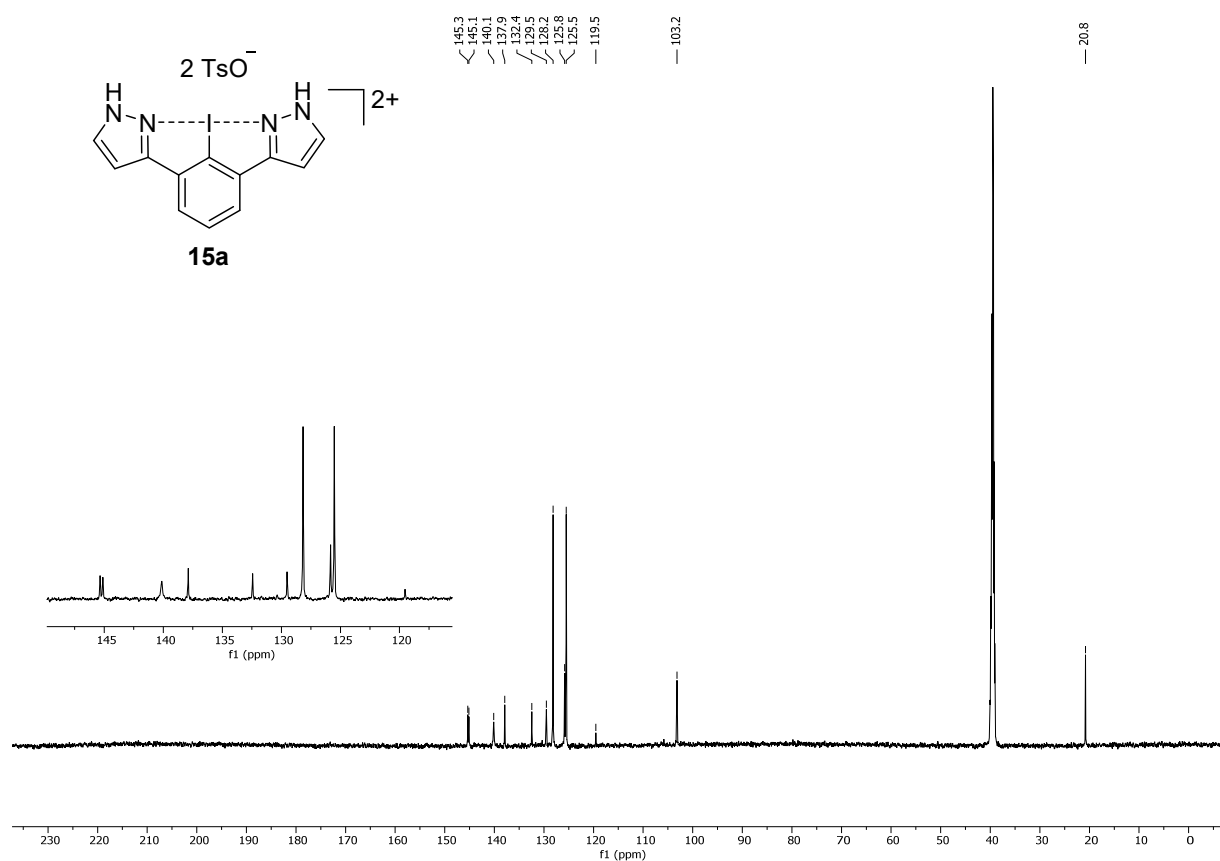
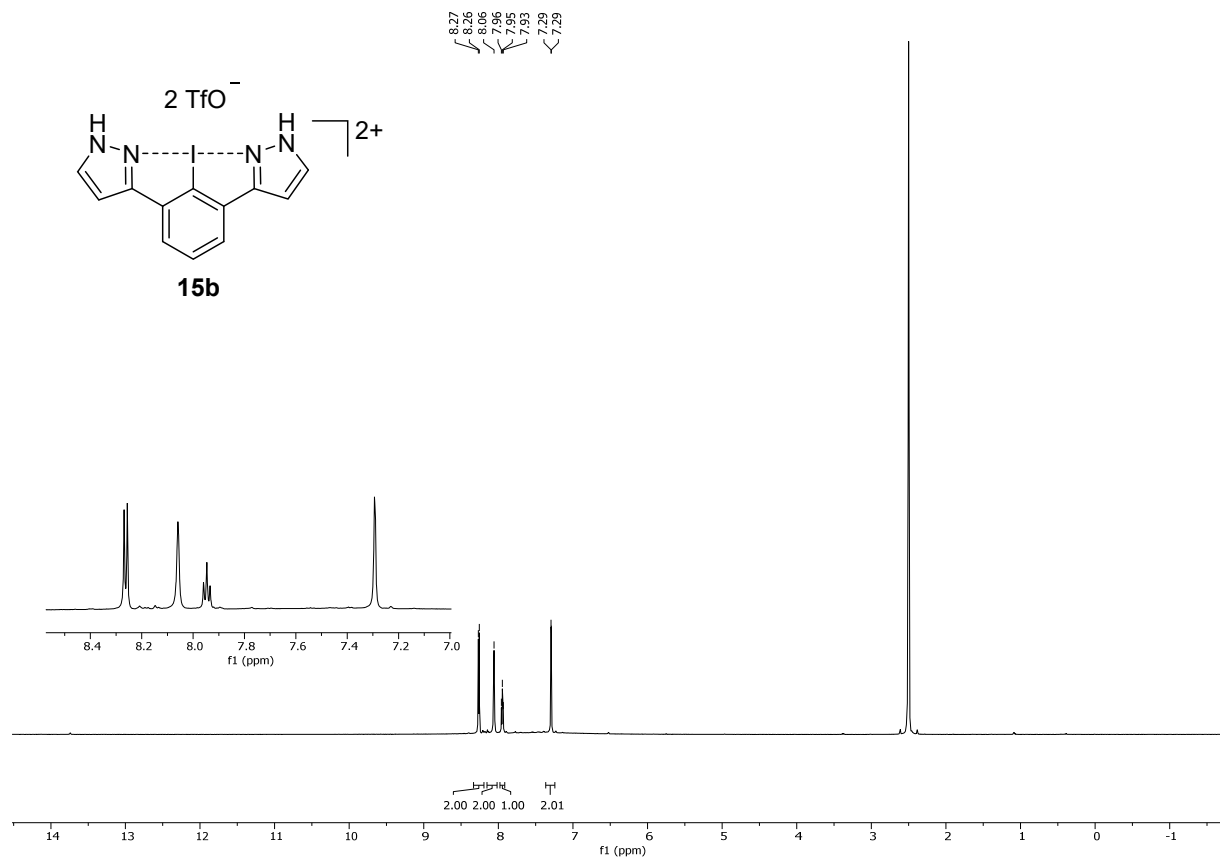


Figure S18: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **15a** in d_6 -DMSO.



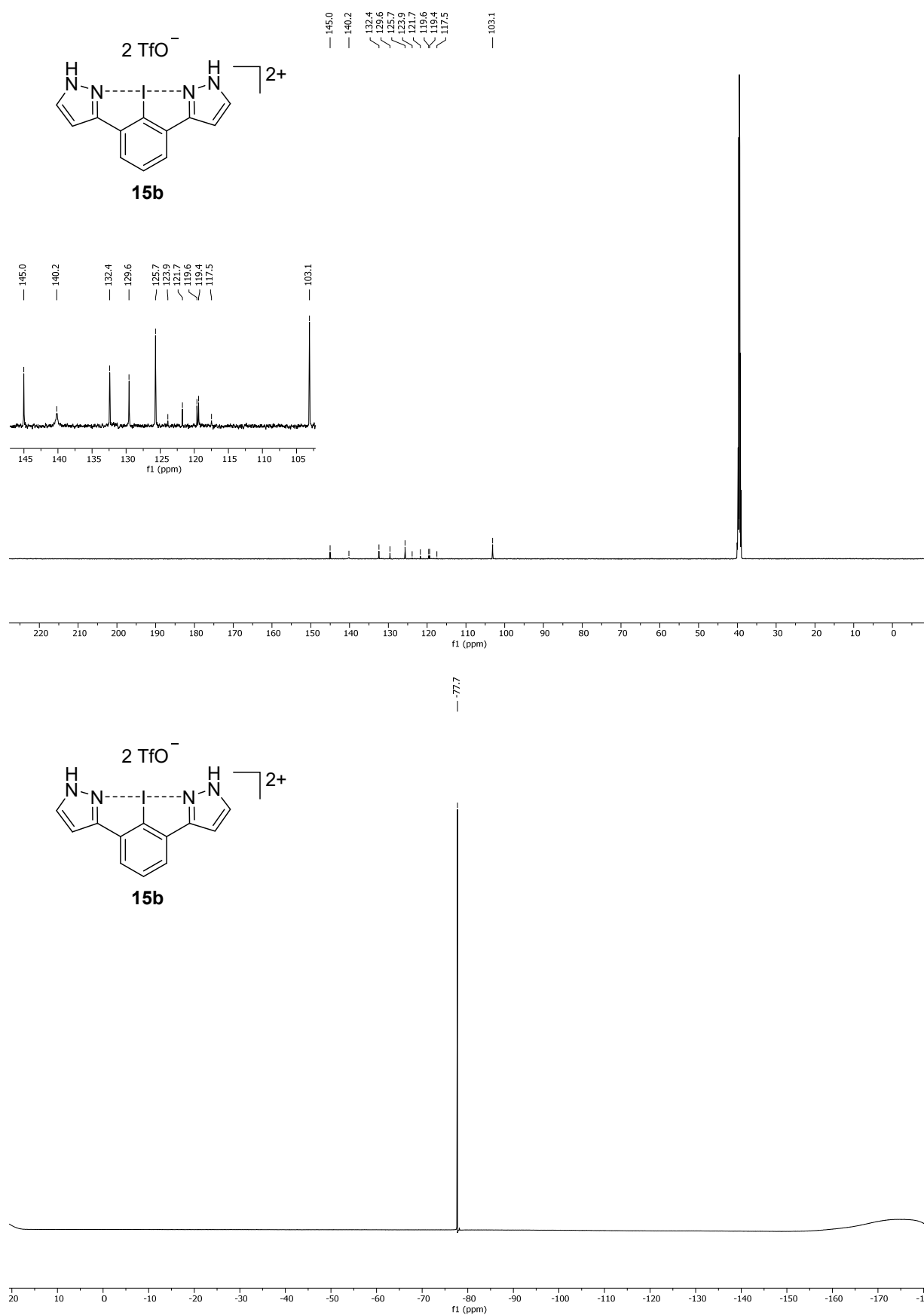


Figure S19: 600 MHz ¹H-, 151 MHz ¹³C- and 565 MHz ¹⁹F-NMR spectra of **15b** in *d*₆-DMSO.

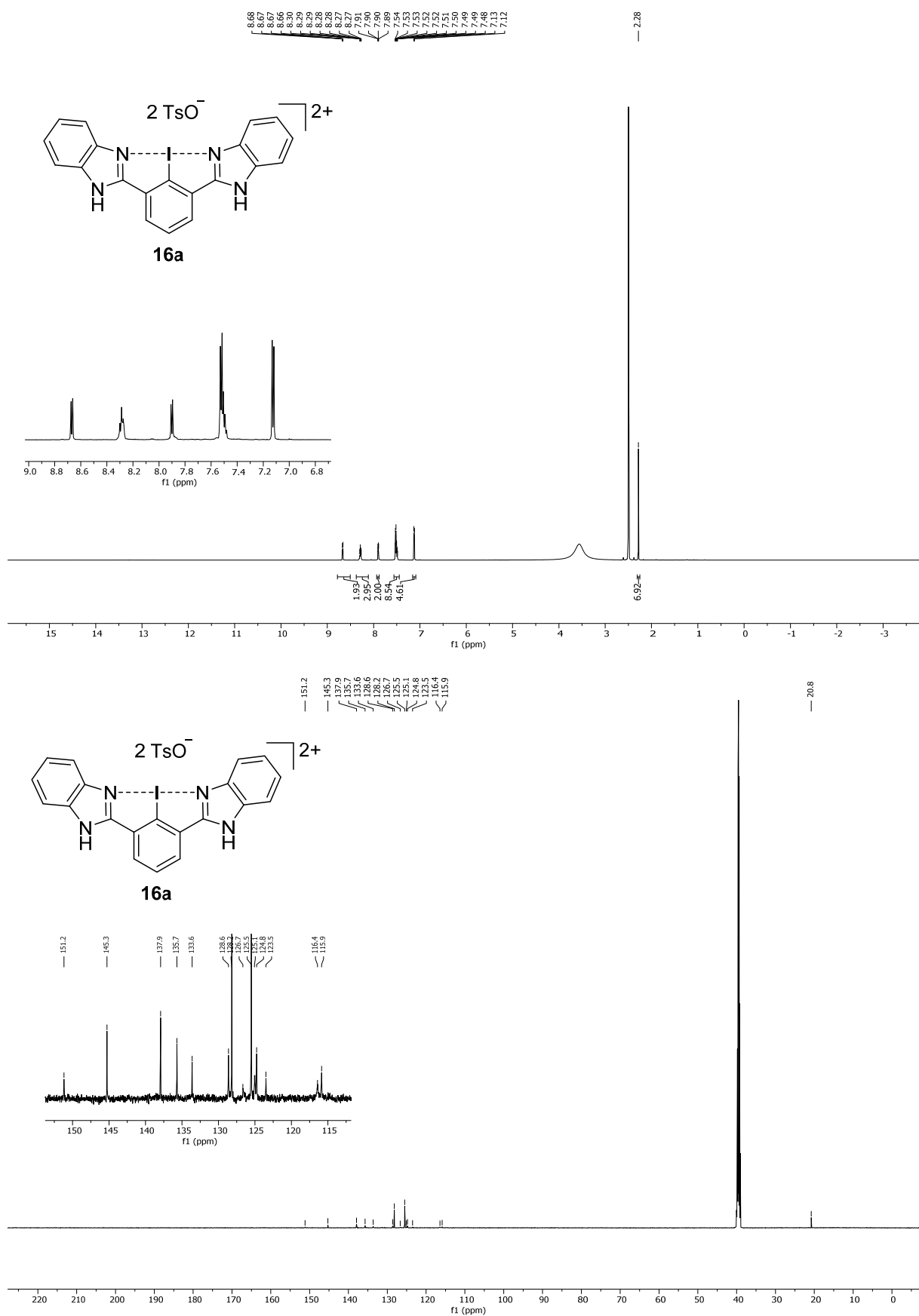


Figure S20: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **16a** in *d*₆-DMSO.

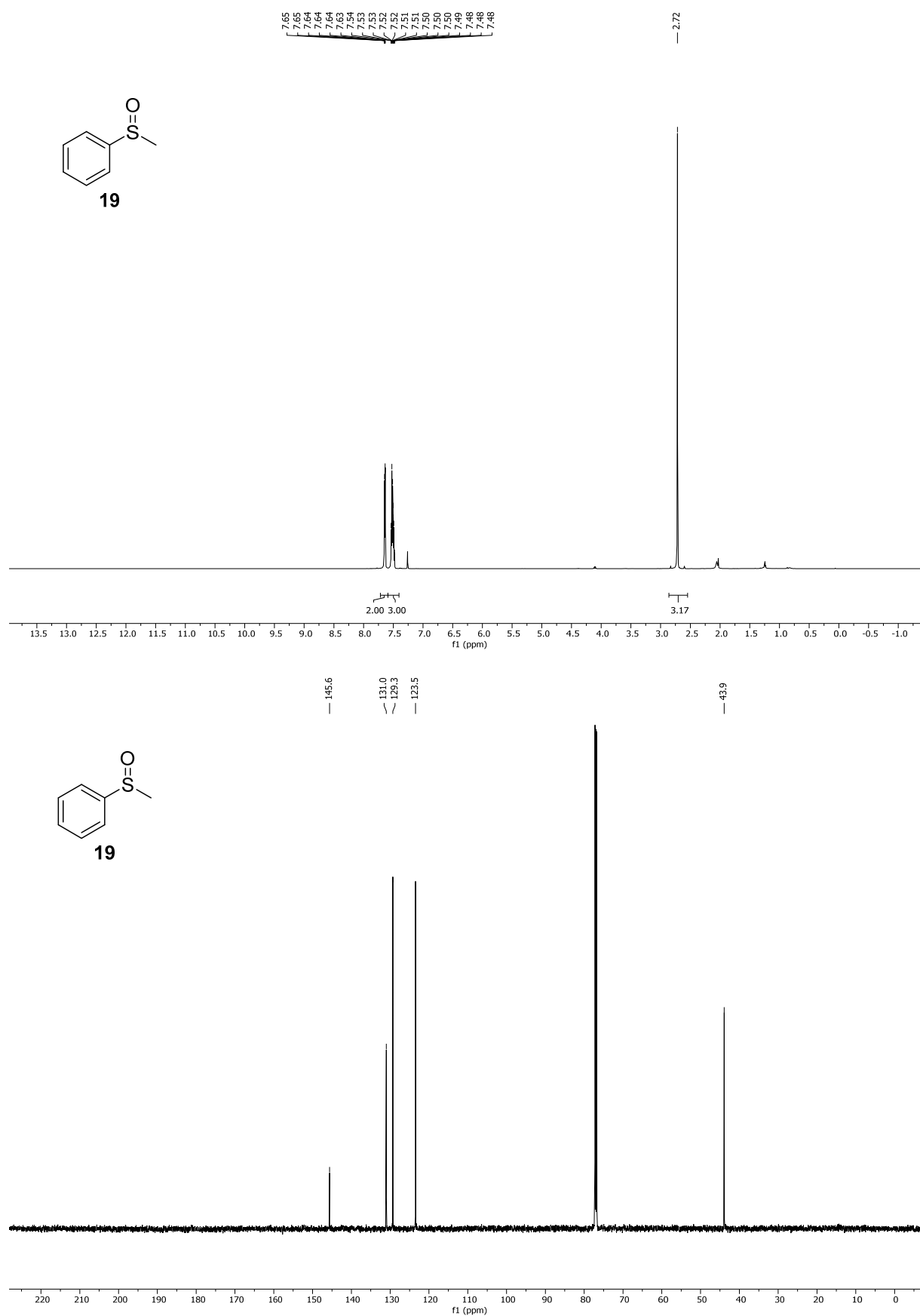


Figure S21: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **19** in CDCl₃.

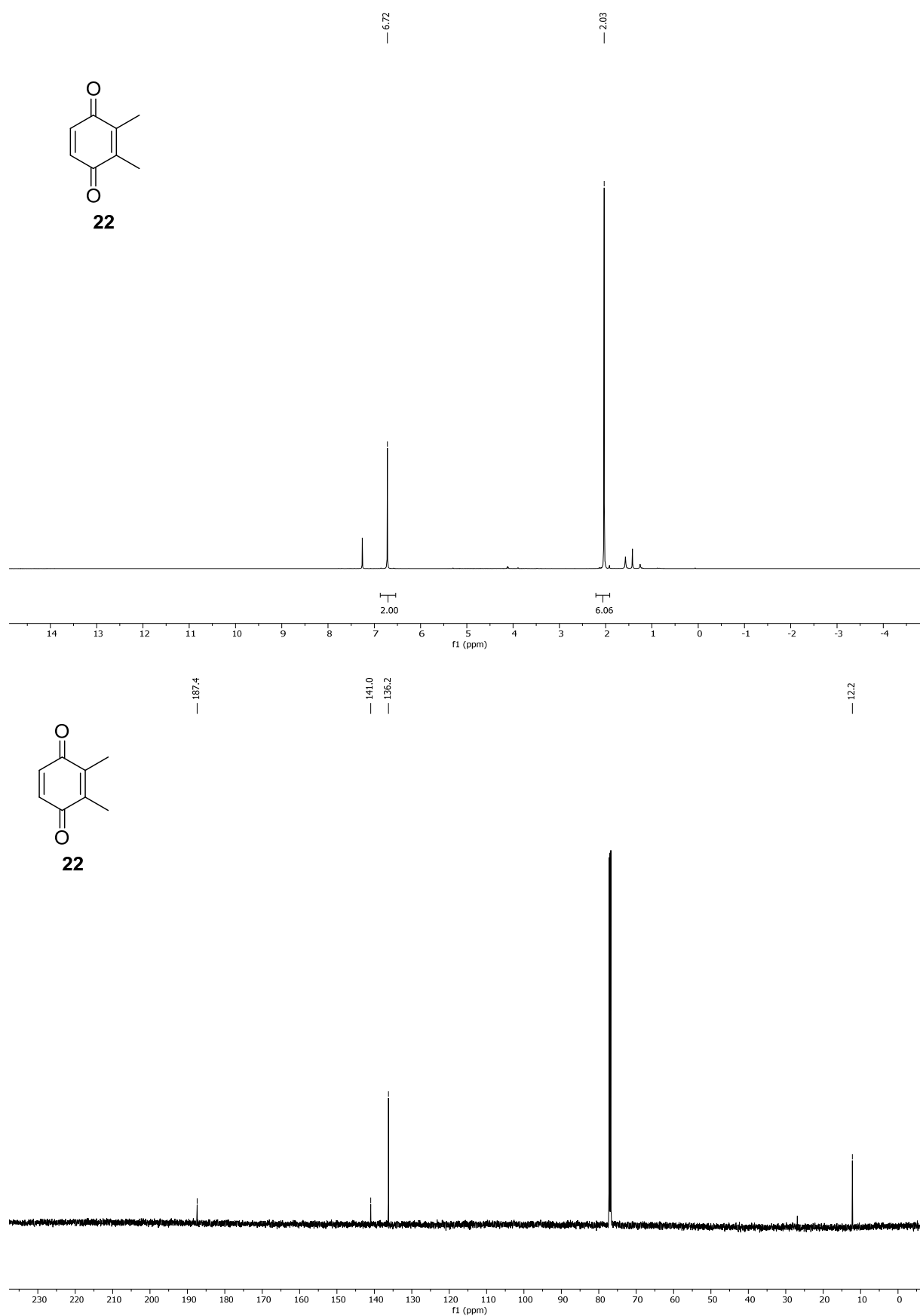


Figure S22: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **22** in CDCl_3 .

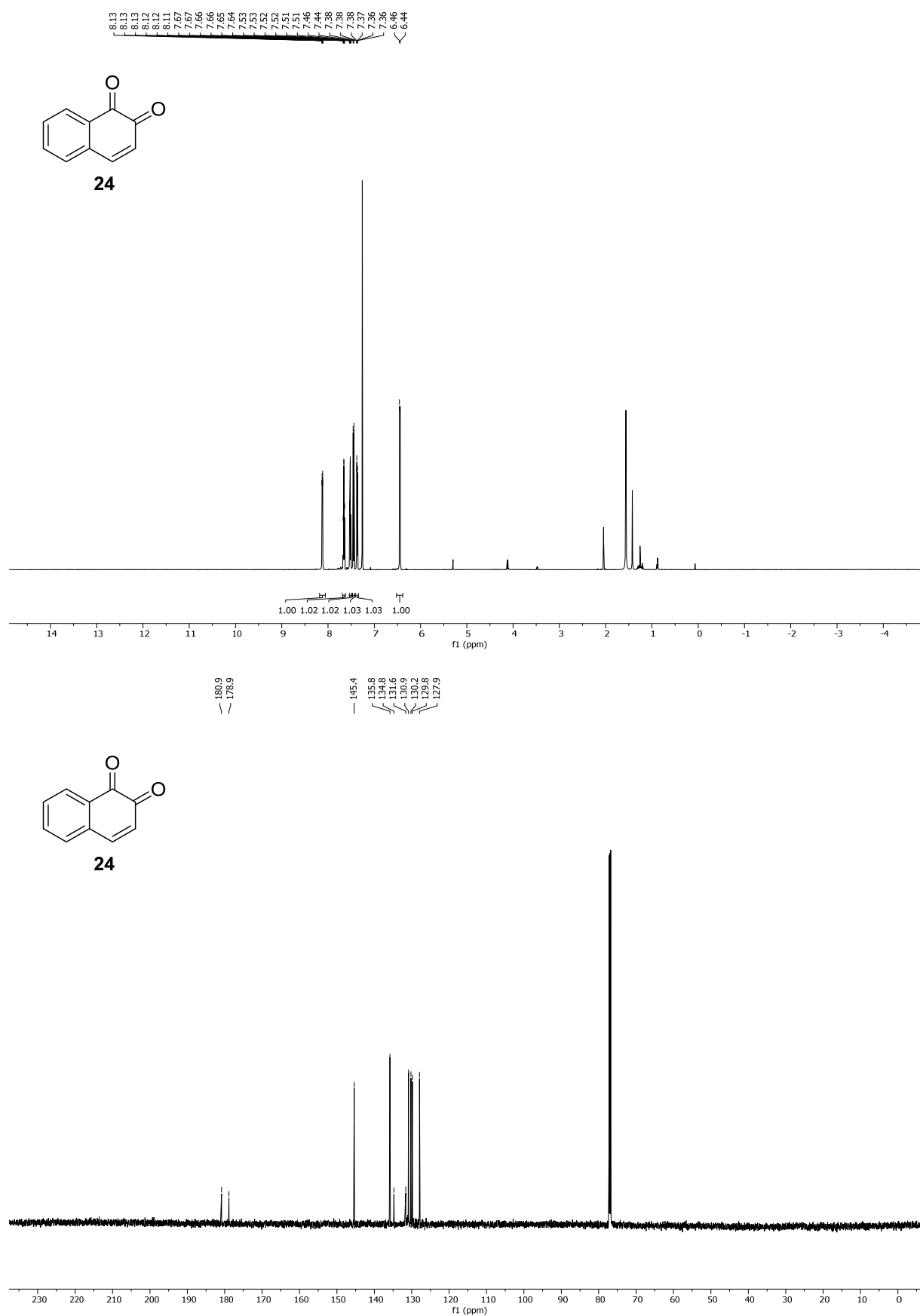


Figure S23: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **24** in CDCl₃.

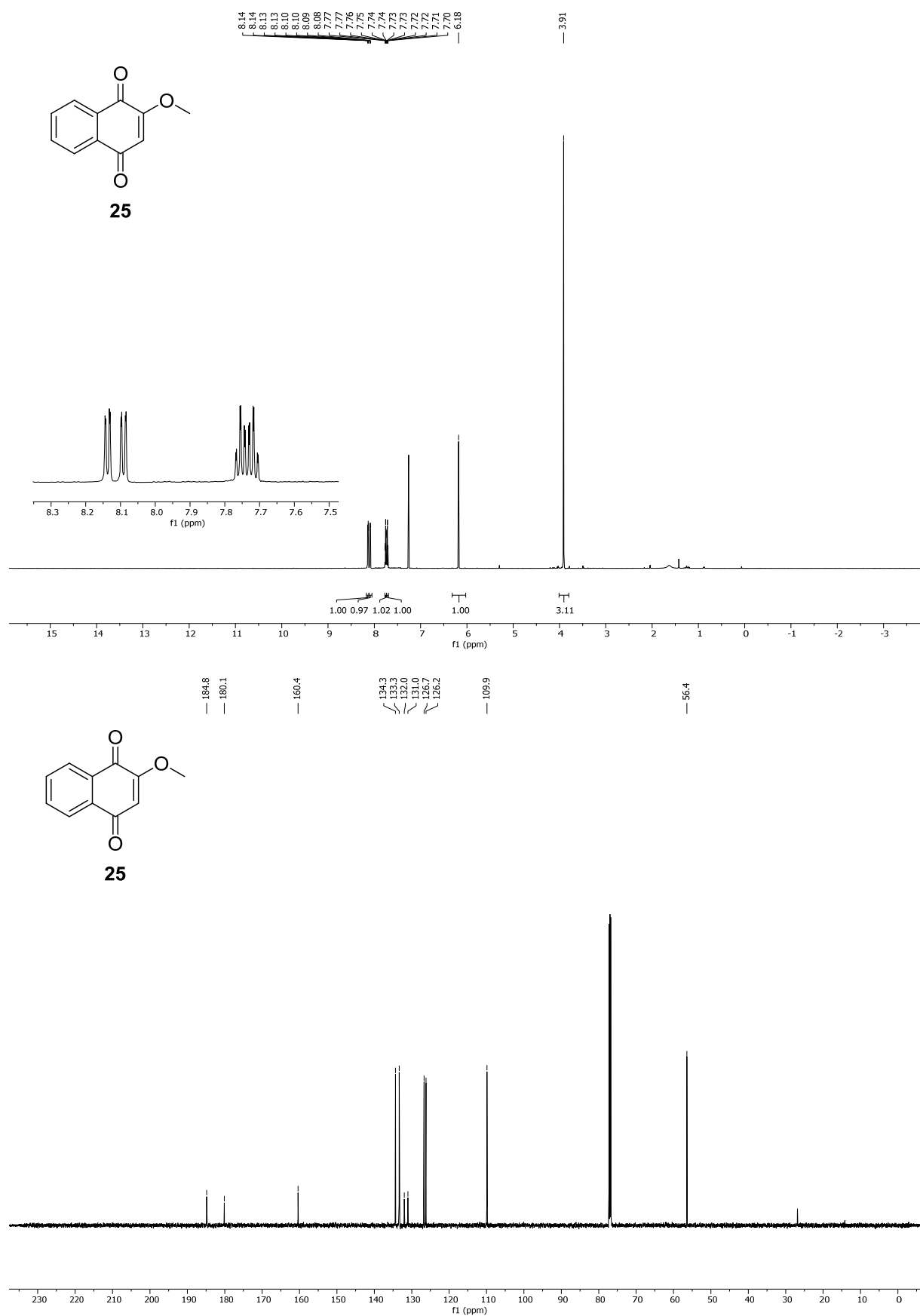


Figure S24: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **25** in CDCl₃.

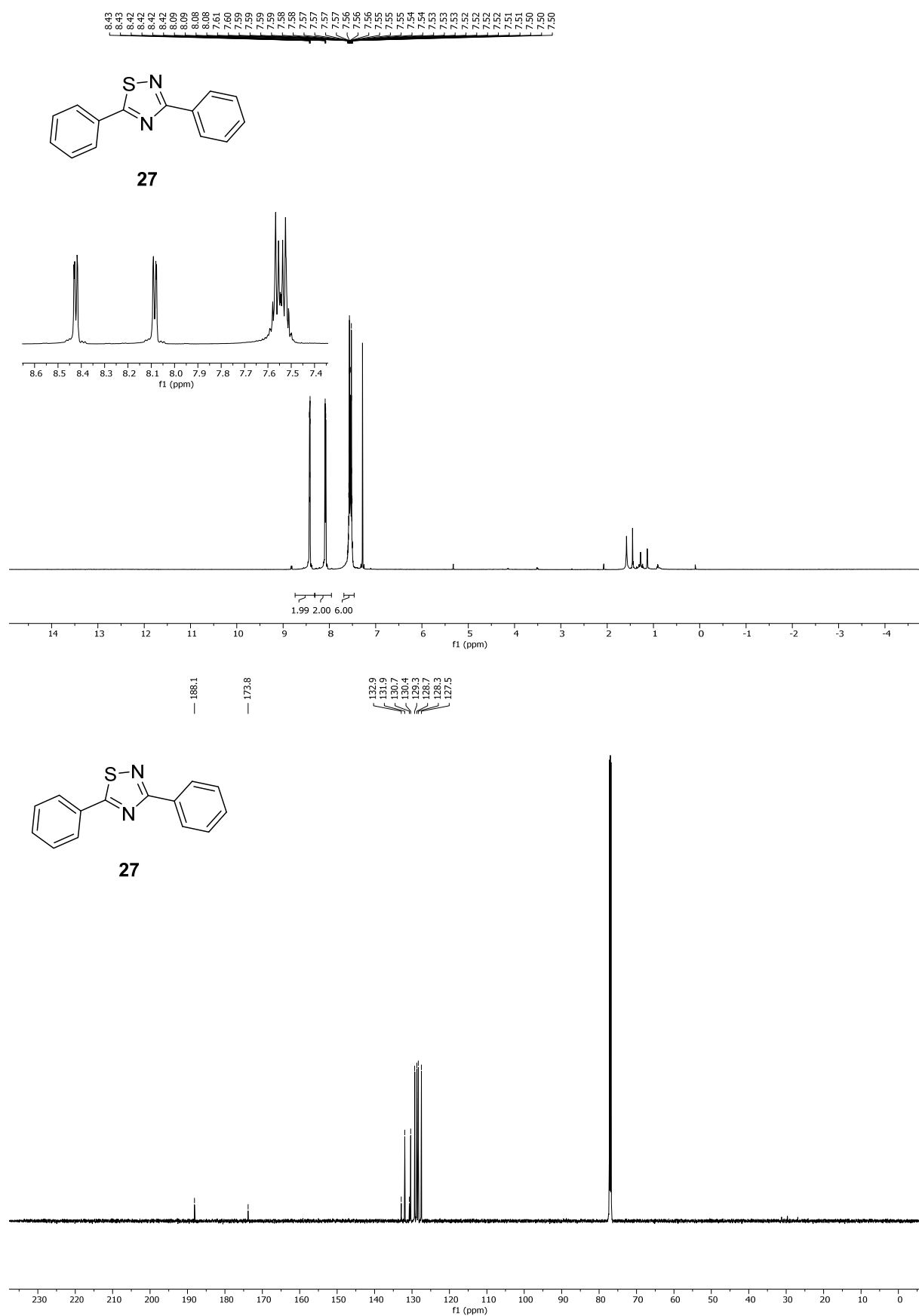


Figure S25: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **27** in CDCl₃.

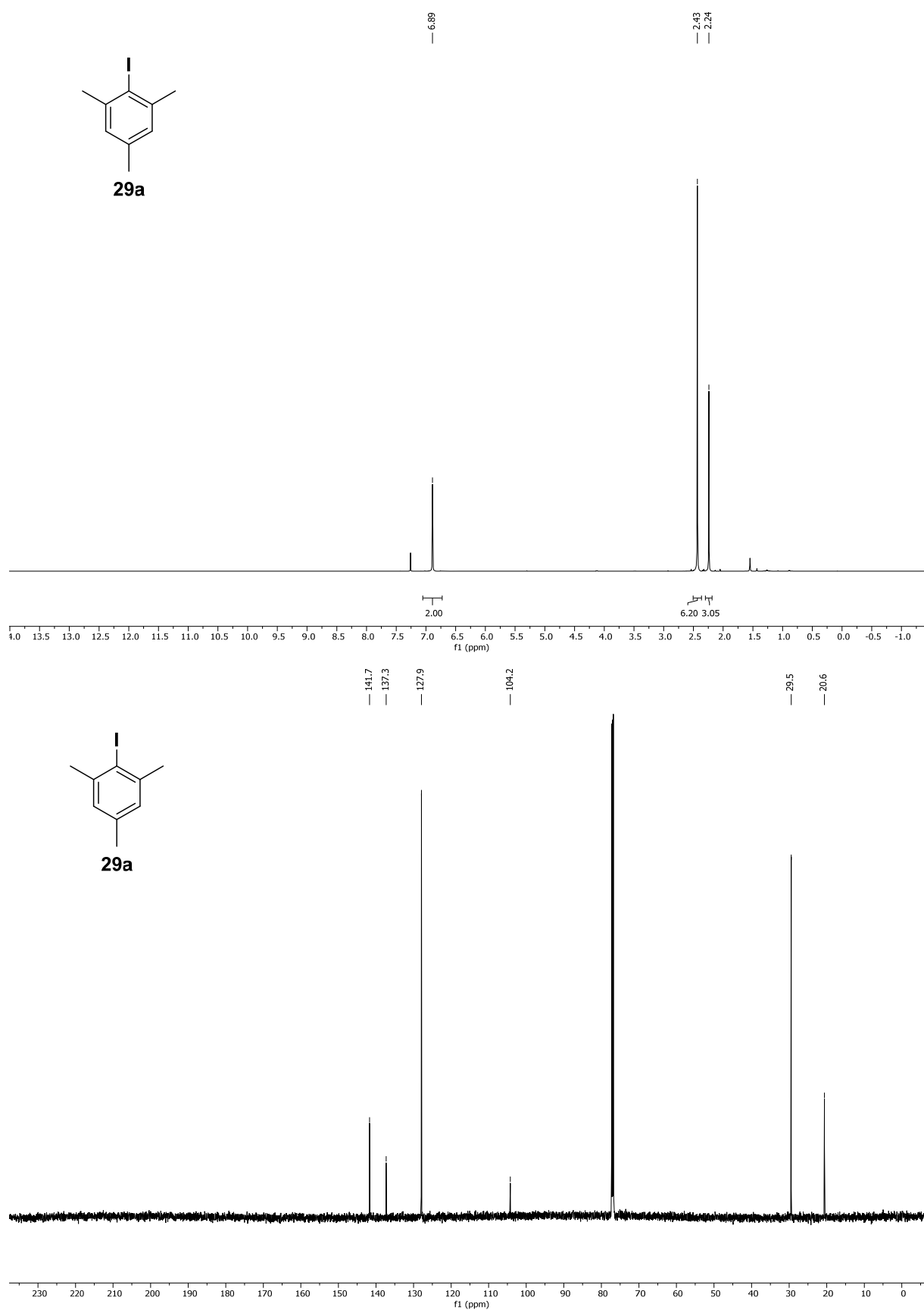


Figure S26: 600 MHz ^1H - and 151 MHz ^{13}C -NMR spectra of **29a** in CDCl_3 .

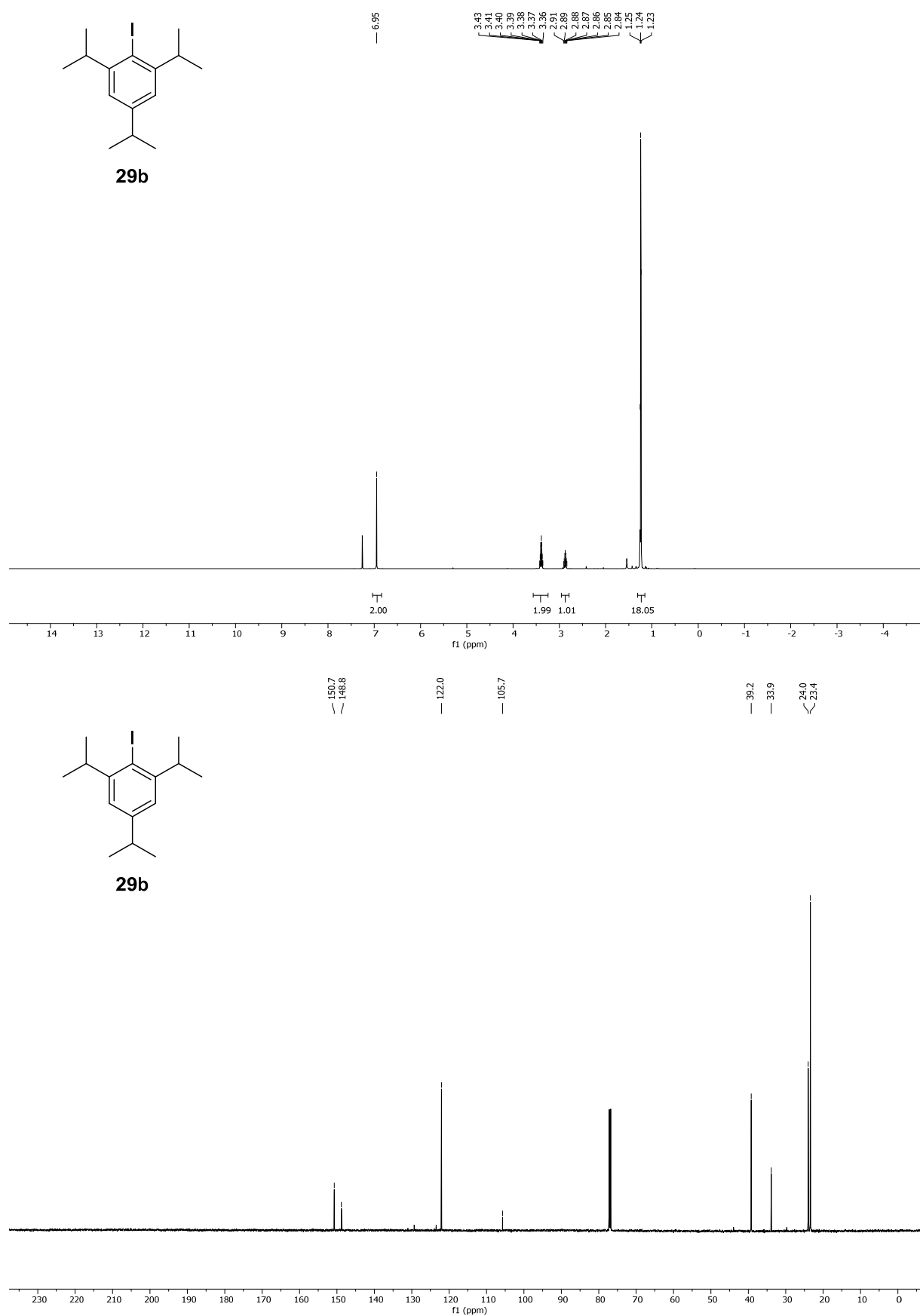


Figure S27: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **29b** in CDCl₃.

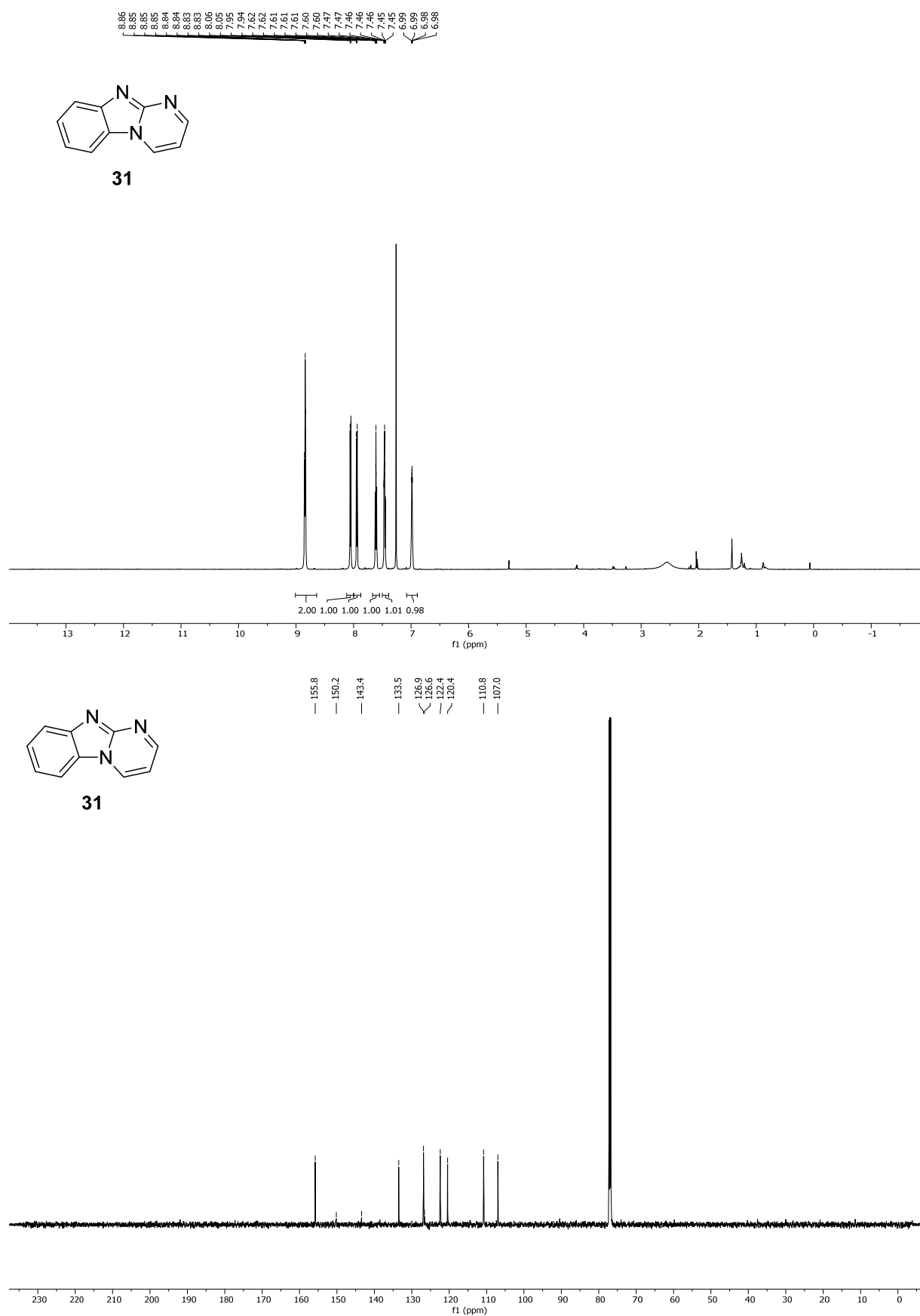


Figure S28: 600 MHz ¹H- and 151 MHz ¹³C-NMR spectra of **31** in CDCl₃.

Supporting Information-ChemRxiv.pdf (1.90 MiB)

[view on ChemRxiv](#) • [download file](#)
