Supporting Information

for

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

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Table of Contents

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 ^{1}H-NMR spectroscopy.

Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (*Macherey-Nagel*, ALUGRAM Xtra SIL G/UV_{254}) 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.

^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded on *Bruker Avance Neo* 600-spectrometers. Chemical shifts for ^{1}H-NMR spectra were reported as δ (parts per million) relative to the residual signal of $CHCl_3$ 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 ^{13}C-NMR spectra were reported as δ (parts per million) relative to the signal of $CDCl_3$ 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.). ^{19}F-NMR spectra were reported as δ (parts per million) relative to $CFCl_3$ 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 ThemoQuest 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*.

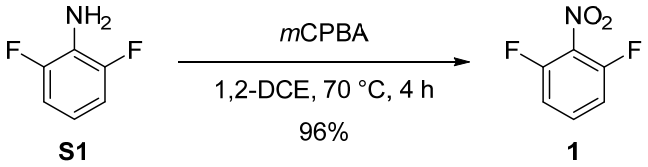
IR spectra were recorded on a *Nicolet* Thermo iS10 scientific spectrometer with a diamond ATR unit. The absorption bands were reported in cm^{-1}.

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 Et_2O 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

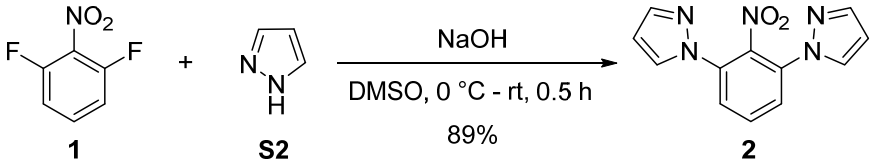
1,3-Difluoro-2-nitrobenzene (1)



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 Na_2SO_4, filtered, and concentrated under reduced pressure to give 1,3-difluoro-2-nitrobenzene (**1**, 30.5 g, 192 mmol, 96 %) as an orange liquid.

^{1}H-NMR ($CDCl_3$, 601 MHz): δ (ppm) 7.53 (tt, *J* = 8.6, 5.9 Hz, 1H), 7.14 – 7.09 (m, 2H). ^{13}C-NMR ($CDCl_3$, 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 $[M]^{+\bullet}$. Analytical data is in accordance with literature data.[5]

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

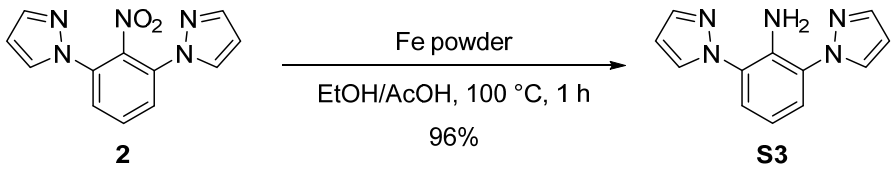


A modified literature procedure was used.[6] 1,3-Difluoro-2-nitrobenzene (**1**, 3.18 g, 20.0 mmol, 1.00 equiv) and 1*H*-pyrazole (**S2**, 3.06 g, 45.0 mmol, 2.25 equiv) were dissolved in DMSO (7.5 mL) and powdered NaOH (freshly ground pellets, 2.70 g, 67.5 mmol, 3.38 mmol) was slowly added while the 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 H_2O (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.

^{1}H-NMR ($CDCl_3$, 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).^{13}C-NMR ($CDCl_3$, 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)

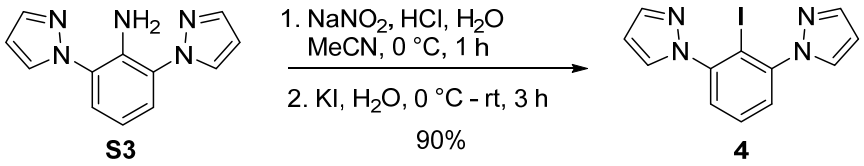


2 **S3**

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.

^{1}H-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)



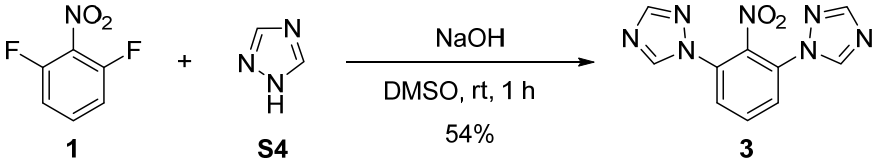
S3 **4**

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.

^{1}H-NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$,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 $C_{12}H_{10}IN_4^+$ [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)

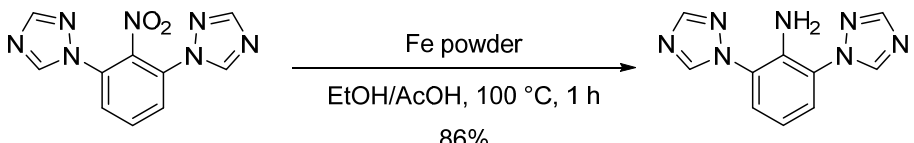


1 **S4** **3**

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 H_2O (100 mL) and extracted with EtOAc (3 x 150 mL). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, 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.

^{1}H-NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$, 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 $C_{10}H_8N_7O_2^+$ [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)



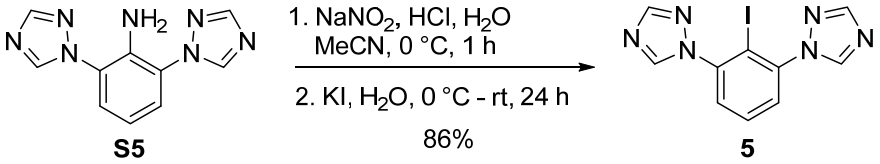
3 **S5**

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. $NaHCO_3$-solution and the formed precipitate was filtered off, washed with H_2O (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 Na_2SO_4, 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.

^{1}H-NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$, 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 $C_{10}H_9N_7Na^+$ [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)

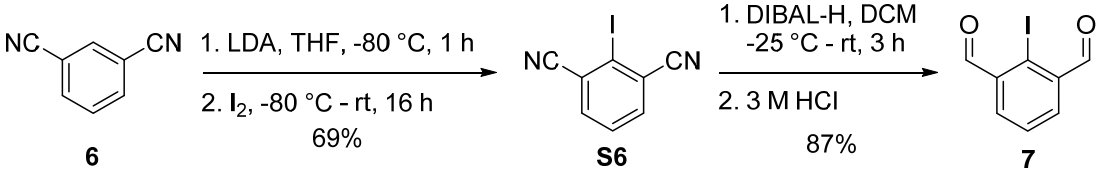


S5 **5**

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 $NaNO_2$ (0.730 g, 10.6 mmol, 1.15 equiv) in H_2O (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 H_2O (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 H_2O (200 mL) was added, and the mixture was extracted with EtOAc (4 x 300 mL). The combined organic phases were washed with sat. $Na_2S_2O_3$-solution (300 mL) and brine (300 mL), dried over Na_2SO_4, 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.

^{1}H-NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$, 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 $C_{10}H_8IN_6^+$ [M+H]$^+$: *m/z* 338.98497, found 338.98471. Mp. 170–172 °C.

2-Iodoisophthalaldehyde (7)



6 **S6** **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

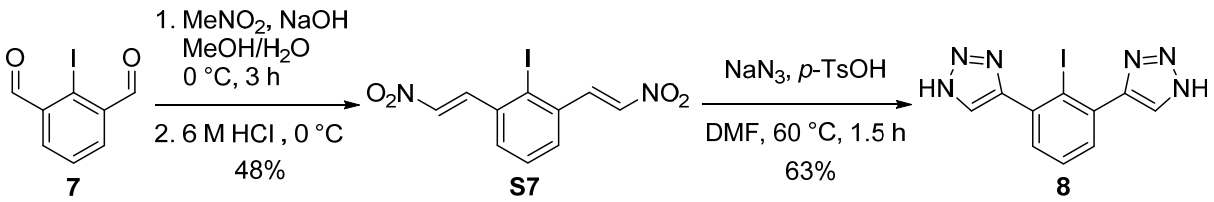
THF (200 mL, 60.0 mmol, 1.2 equiv) over the course of 0.5 h at –80 °C. After stirring at this temperature for 1 h, iodine (15.2 g, 60.0 mmol, 1.2 equiv) was added portionwise and stirring continued at –80 °C for 0.5 h before the mixture was slowly warmed up to room temperature (in total 16 h). The reaction was quenched with sat. $Na_2S_2O_3$-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 form cyclohexane/EtOAc to give 2-iodoisophthalonitrile (**S6**, 8.76 g, 34.5 mmol, 69%) as a colourless solid.

^{1}H-NMR ($CDCl_3$, 601 MHz) δ (ppm) 7.79 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H).^{13}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 $[M]^{+\bullet}$. Mp. 208–210 °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 °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}H-NMR ($CDCl_3$, 601 MHz) δ (ppm) 10.31 (s, 2H), 8.08 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.9, 6.9 Hz, 1H). ^{13}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 $[M]^{+\bullet}$. Mp. 132–134 °C. Analytical data is in accordance with literature data.[10]

4,4'-(2-Iodo-1,3-phenylene)bis(1*H*-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 °C. After stirring at 0 °C for 3 h, the reaction mixture was slowly

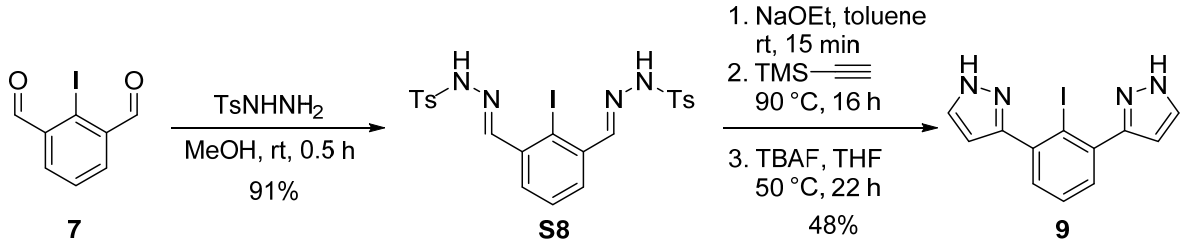
transferred to vigorously stirred aqueous 6 M HCl (75 mL) at 0 °C. The formed precipitate was filtered off and washed with H_2O. After drying *in vacuo*, the solid was recrystallized from EtOH to give 2-iodo-1,3-bis((*E*)-2-nitrovinyl)benzene (**S7**, 1.67 g, 4.83 mmol, 48%) as a yellowish solid.

^{1}H-NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$, 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 $C_{10}H_7IN_2O_4^+$ $[M]^{\bullet+}$: *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 NaN_3 (0.995 g, 14.4 mmol, 3.0 equiv) and *p*-TsOH•H_2O (0.914 g, 4.80 mmol, 1.0 equiv) were added. The mixture was stirred for 2 h at 60 °C, then diluted with H_2O (200 mL) and extracted with EtOAc (3 x 150 mL). The combined organic phases were washed with H_2O and brine (150 mL each), dried over Na_2SO_4, 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.

^{1}H-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). ^{13}C-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 $C_{10}H_8IN_6^+$ $[M+H]^+$: *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

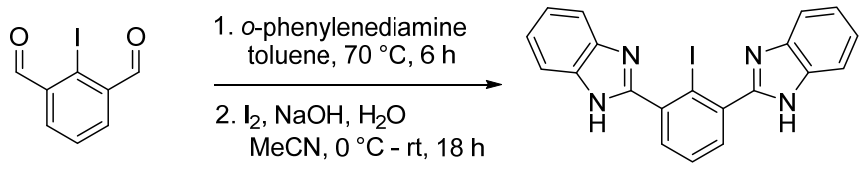
in MeOH (10 mL). After storing at 4 °C for 30 min, the precipitate is filtered off, washed with MeOH (5 mL) and dried *in vacuo* to give *N*',*N*'''-(2-iodo-1,3-phenylene)bis(methanylylidene))bis(4-methylbenzenesulfonohydrazide) (**S8**, 3.25 g, 5.45 mmol, 91%) as a colourless solid.

^{1}H-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). ^{13}C-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 $C_{22}H_{22}IN_4O_4S_2^+$ [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 H_2O (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 Na_2SO_4, 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. H_2O (50 mL) was added and the mixture extracted with DCM (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, 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.

^{1}H-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). ^{13}C-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 $C_{12}H_{10}IN_4^+$ [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)

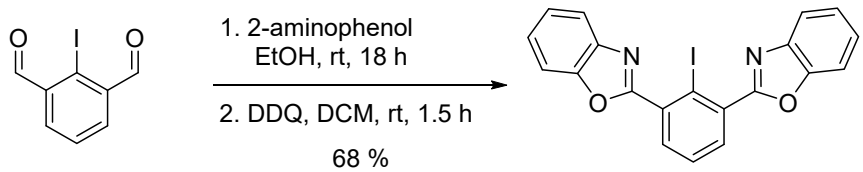


7 **10**

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. $Na_2S_2O_3$-solution (10 mL). The formed precipitate was filtered off, washed with H_2O (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.

^{1}H-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). ^{13}C-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 $C_{20}H_{14}IN_4^+$ [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)



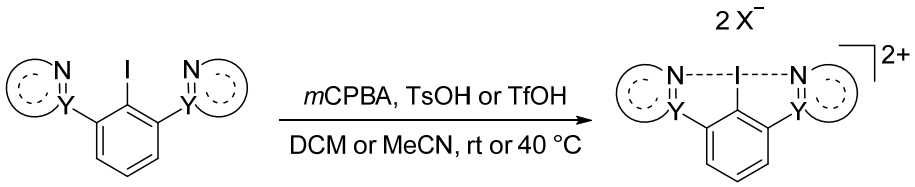
7 **11**

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. $NaHCO_3$-solution (100 mL) and extracted with DCM (3 x 120 mL). The combined organic phases were washed with brine (120 mL), dried over Na_2SO_4, 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.

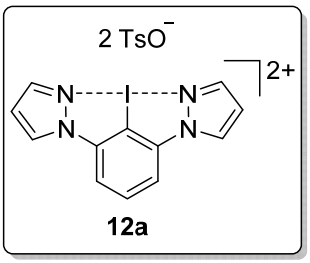
^{1}H-NMR ($CDCl_3$, 601 MHz) δ (ppm) 7.95 (d, *J* = 7.7 Hz, 2H), 7.92 – 7.85 (m, 2H), 7.69 – 7.61 (m, 3H), 7.47 – 7.39 (m, 4H). ^{13}C-NMR ($CDCl_3$, 151 MHz) δ (ppm) 162.9, 150.8, 141.4, 135.9, 133.6, 128.3, 125.8, 124.8, 120.7, 111.0, 96.7. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 1540, 1443, 1231, 1097, 857, 747. HR-MS (ESI) Calculated for $C_{20}H_{12}IN_2O_2^+$ [M+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.

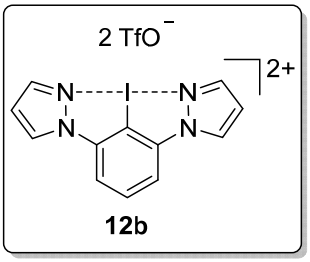
(2,6-Bis(1*H*-pyrazol-1-yl)phenyl)-λ^3-iodanediyl bistosylate (12a, Bis-Pyr-I-OTs)



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}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}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 $C_{12}H_{10}IN_4^+$ [M-2OTs+H]$^+$: *m/z* 336.99447, found 336.99422. Mp. 202–204 °C (decomp.).

(2,6-Bis(1*H*-pyrazol-1-yl)phenyl)-λ^3-iodanediyl bistriflate (12b, Bis-Pyr-I-OTf)



12b

In DCM:

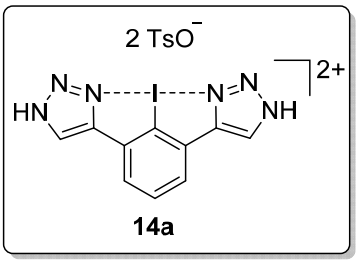
Following GP1, 1,1'-(2-iodo-1,3-phenylene)bis(1*H*-pyrazole) (**4**, 2.69 g, 8.00 mmol, 1.0 equiv) was stirred in DCM (80 mL) with *m*CPBA (2.43 g, 12.0 mmol, 1.5 equiv) and TfOH (1.55 mL, 17.6 mmol, 2.2 equiv) for 65 h at 40 °C. Afterwards Et_2O (250 mL) was directly added and after storing at 4 °C, the precipitate was filtered off and washed with Et_2O (3 x 30 mL) to give Bis-Pyr-I-OTf **12b** (4.86 g, 7.66 mmol, 96%, estimated purity ~95% by ^{1}H-NMR) as a yellowish solid. Recrystallization from MeOH/Et_2O 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 Et_2O, 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 Et_2O (100 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et_2O (3 x 20 mL) to give Bis-Pyr-I-OTf **12b** (2.52 g, 3.97 mmol, 99%, estimated purity ~98% by ^{1}H-NMR) as an off-white solid.

^{1}H-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). ^{13}C-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. ^{19}F-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 $C_{12}H_9IN_4Na^+$ [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)-λ^3-iodanediyl bistosylate (14a, Bis-NH-Tria-I-OTs)

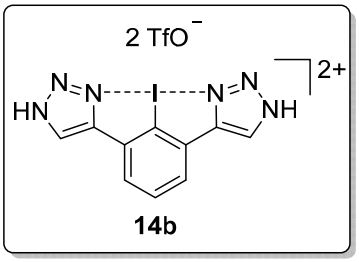


14a

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•H_2O (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 Et_2O/EtOAc (4:1, 20 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et_2O (2 x 5 mL) to give Bis-NH-Tria-I-OTs **14a** (627 mg, 0.921 mmol, 92%) as a beige solid.

^{1}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}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 $C_{10}H_8IN_6^+$ [M-2OTs+H]$^+$: *m/z* 338.98497, found 338.98455. Mp. 112–114 °C (decomp.).

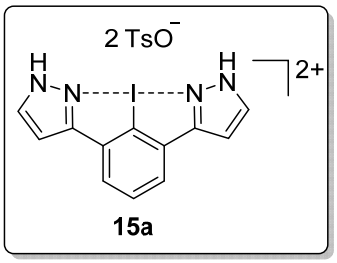
(2,6-Bis(1*H*-1,2,3-triazol-4-yl)phenyl)-λ^3-iodanediyl bistriflate (14b, Bis-NH-Tria-I-OTf)



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 Et_2O/EtOAc (4:1, 5 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et_2O (2 x 5 mL) to give Bis-NH-Tria-I-OTf **14b** (223 mg, 0.365 mmol, 91%) as a beige solid.

^{1}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}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}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 $C_{10}H_6IN_6^+$ [M-2OTf-H]$^+$: *m/z* 336.96932, found 336.96900. Mp. 187–188 °C (decomp.).

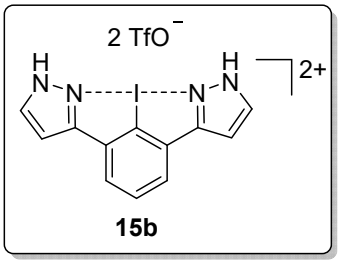
(2,6-Bis(1*H*-pyrazol-3-yl)phenyl)-λ^3-iodanediyl bistosylate (15a, Bis-NH-Pyr-I-OTs)



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•H_2O (183 mg, 0.960 mmol, 2.4 equiv) for 42 h at room temperature. Afterwards Et_2O (6 mL) was directly added and after storing at 4 °C, the precipitate was filtered off and washed with Et_2O (2 x 5 mL) to give Bis-NH-Pyr-I-OTs **15a** (260 mg, 0.383 mmol, 96%) as a colourless solid.

^{1}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}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 $C_{12}H_8IN_4^+$ [M-2OTs-H]$^+$: *m/z* 334.97882, found 334.97830. Mp. 146–148 °C (decomp.).

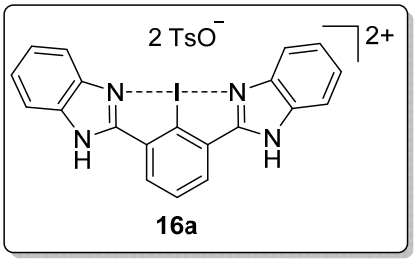
(2,6-Bis(1*H*-pyrazol-3-yl)phenyl)-λ^3-iodanediyl bistriflate (15b, Bis-NH-Pyr-I-OTf)



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 Et_2O (2 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et_2O (3 x 1 mL) to give Bis-NH-Pyr-I-OTf **15b** (110 mg, 0.173 mmol, 87%) as a colourless solid.

^{1}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* = 7.6 Hz, 1H), 7.29 (d, *J* = 2.3 Hz, 2H). ^{13}C-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. ^{19}F-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 $C_{12}H_{10}IN_4^+$ [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)-λ^3-iodanediyl bistosylate (16a, Bis-Benzimi-I-OTs)

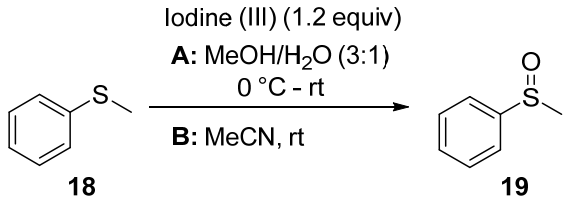


Following GP1, 2,2'-(2-iodo-1,3-phenylene)bis(1*H*-benzo[*d*]imidazole) (**10**, 87.3 mg, 0.200 mmol, 1.0 equiv) was stirred in DCM (2 mL) with *m*CPBA (49.2 mg, 0.240 mmol, 1.2 equiv) and *p*-TsOH•H_2O (83.6 mg, 0.440 mmol, 2.2 equiv) for 17 h at room temperature. Afterwards the solvent was removed under reduced pressure and the residue was suspended in Et_2O (4 mL). After storing at 4 °C, the precipitate was filtered off and washed with Et_2O (2 x 2 mL) to give Bis-Benzimi-I-OTs **16a** (133 mg, 0.170 mmol, 85%) as a beige solid.

^{1}H-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). ^{13}C-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 $C_{20}H_{14}IN_4^+$ [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/H_2O (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. $NaHCO_3$-solution (4 mL) and sat. $Na_2S_2O_3$-solution (0.2 mL) were added, and the mixture was extracted with DCM (2 x 5 mL). The combined organic phases were dried over Na_2SO_4, 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. $NaHCO_3$-solution (4 mL) and sat. $Na_2S_2O_3$-solution (0.2 mL) were added, and the mixture was extracted with DCM (2 x 5 mL). The combined organic phases were dried over Na_2SO_4, 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**).

^{1}H-NMR ($CDCl_3$, 601 MHz) δ (ppm) 7.67 – 7.60 (m, 2H), 7.56 – 7.41 (m, 3H), 2.72 (s, 3H). ^{13}C-NMR ($CDCl_3$, 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]

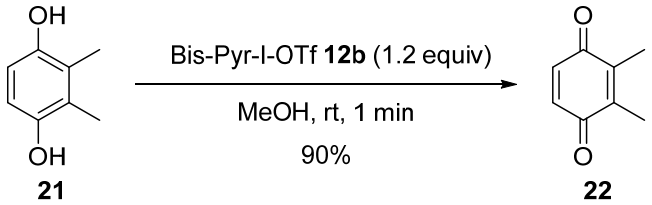
Table 1. Reaction times and yields for the oxidation of thioanisole **18**.

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%

[a]Isolated yield of (methylsulfinyl)benzene **19** after column chromatography.

Oxidation of 2,3-dimethylhydroquinone (21)

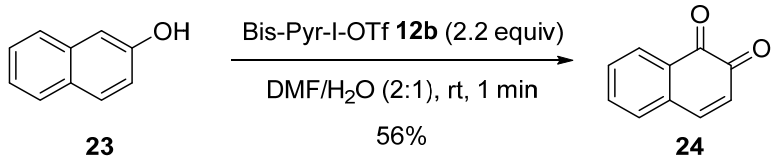


21 **22**

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.

^{1}H-NMR ($CDCl_3$, 601 MHz) δ (ppm) 6.72 (s, 2H), 2.03 (s, 6H). ^{13}C-NMR ($CDCl_3$, 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 $[M]^{\bullet+}$. Mp. 54–55 °C. Analytical data is in accordance with literature data.[16]

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



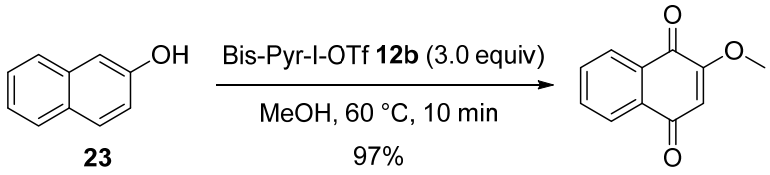
23 **24**

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/H_2O (2:1, 1 mL) and the resulting mixture was stirred at room temperature for 1 min. The reaction mixture was diluted with H_2O (10 mL) and extracted with EtOAc (3 x 10 mL). 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 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.

^{1}H-NMR ($CDCl_3$, 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 $[M+H]^+$. 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)

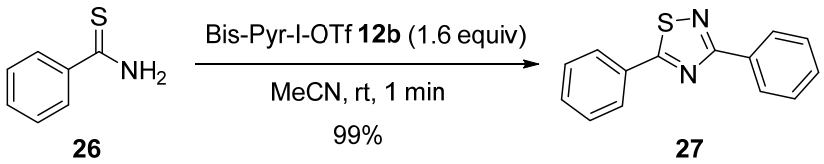


23 **25**

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.

^{1}H-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 $[M+H]^+$. 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)



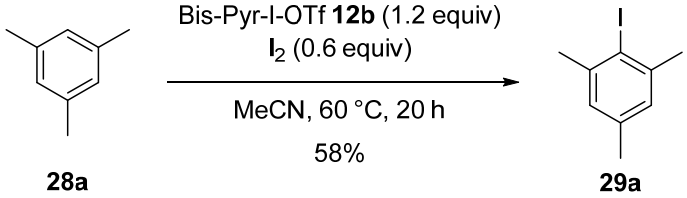
26 **27**

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. $Na_2S_2O_3$-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.

^{1}H-NMR ($CDCl_3$, 601 MHz) δ (ppm) 8.50 – 8.25 (m, 2H), 8.20 – 7.99 (m, 2H), 7.75 – 7.43 (m, 6H). ^{13}C-NMR ($CDCl_3$, 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]

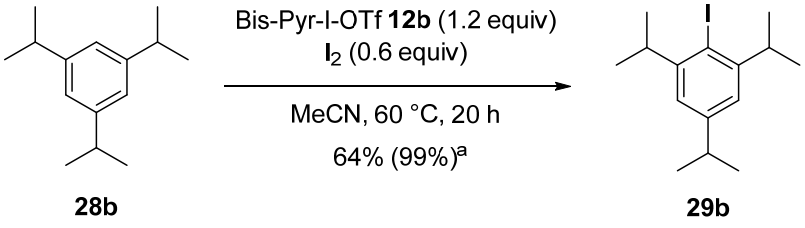
Iodination of mesitylene (28a)



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. $Na_2S_2O_3$-solution (5 mL) and extracted with DCM (2 x 10 mL). The combined organic phases were dried over Na_2SO_4, 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.

^{1}H-NMR ($CDCl_3$, 601 MHz) δ (ppm) 6.89 (s, 2H), 2.43 (s, 6H), 2.24 (s, 3H). ^{13}C-NMR ($CDCl_3$, 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 $[M]^{\bullet+}$. Mp. 29–30 °C. Analytical data is in accordance with literature data.[18]

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



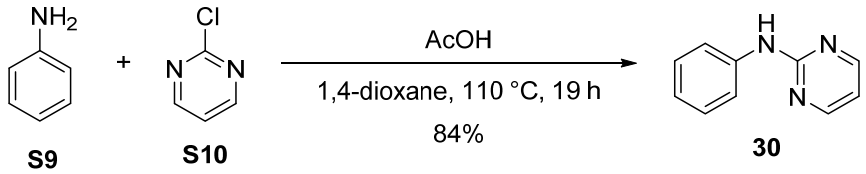
A modified literature procedure was used.[18] To a solution of 1,3,5-triisopropylbenzene (**28b**, 40.9 mg, 0.200 mmol, 1.0 equiv) were added Bis-Pyr-I-OTf **12b** (152 mg, 0.240 mmol, 1.2 equiv) and iodine (30.5 mg, 0.120 mmol, 0.6 equiv) and the mixture was stirred at 60 °C for 20 h. The reaction was quenched with sat. $Na_2S_2O_3$-solution (5 mL) and extracted with DCM (2 x 10 mL). The combined organic phases were dried over Na_2SO_4, 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]

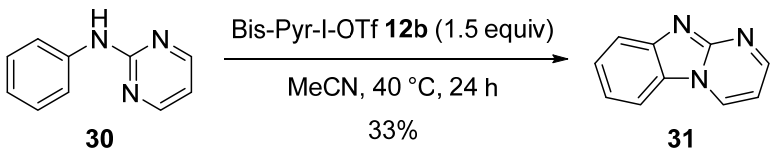
^{1}H-NMR ($CDCl_3$, 601 MHz) δ (ppm) 6.95 (s, 2H), 3.39 (sept, *J* = 6.8 Hz, 2H), 2.87 (sept, *J* = 6.9 Hz, 1H), 1.24 (t, *J* = 6.7 Hz, 18H). ^{13}C-NMR ($CDCl_3$, 151 MHz): δ (ppm) 150.7, 148.8, 122.0, 105.7, 39.2, 33.9, 24.0, 23.4. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 2958, 2925, 2868, 1566, 1460, 1420, 1361, 1101, 999. MS (EI) *m/z* = 330.10 $[M]^{\bullet+}$. 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 H_2O (10 mL) and sat. $NaHCO_3$-solution (10 mL) and extracted with DCM (3 x 20 mL). The combined organic phases were washed with brine (20 mL), dried over Na_2SO_4, 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.

^{1}H-NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$, 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]

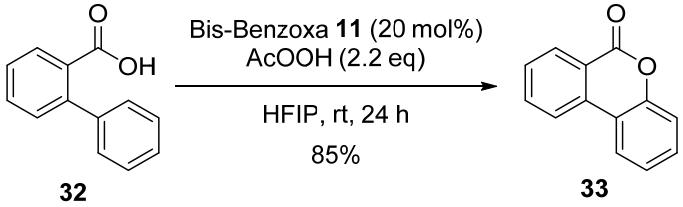


A modified literature procedure was used.[20] To a solution of *N*-phenylpyrimidin-2-amine (**30**, 51.4 mg, 0.300 mmol, 1.0 equiv) was added Bis-Pyr-I-OTf **12b** (285 mg, 0.450 mmol, 1.5 equiv) and the solution was stirred at 40 °C for 24 h. The reaction was quenched with sat.

$Na_2S_2O_3$-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 Na_2SO_4 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.

^{1}H-NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$, 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]

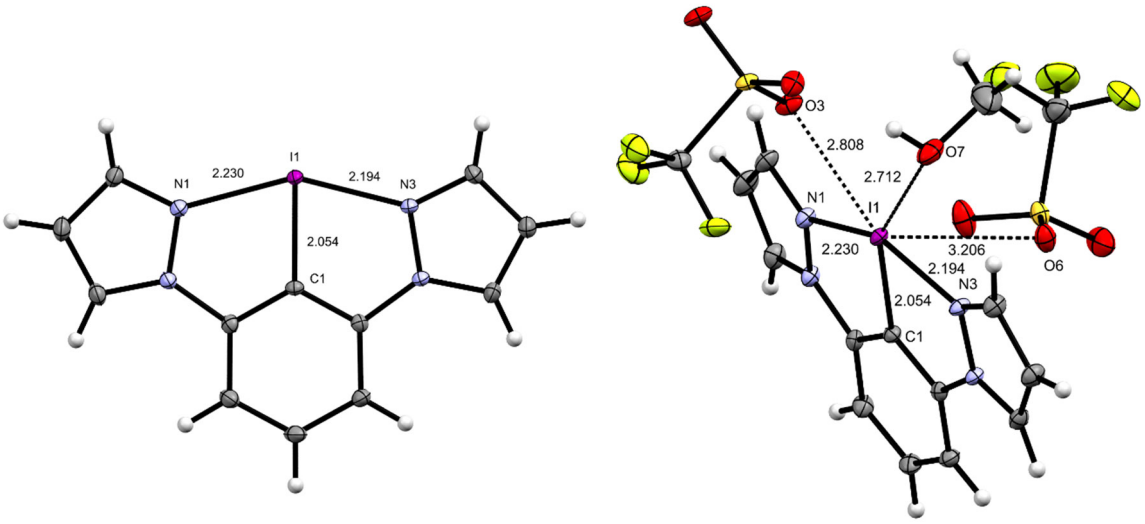
Oxidative Cyclization of [1,1'-biphenyl]-2-carboxylic acid (32)



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.

^{1}H-NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$, 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



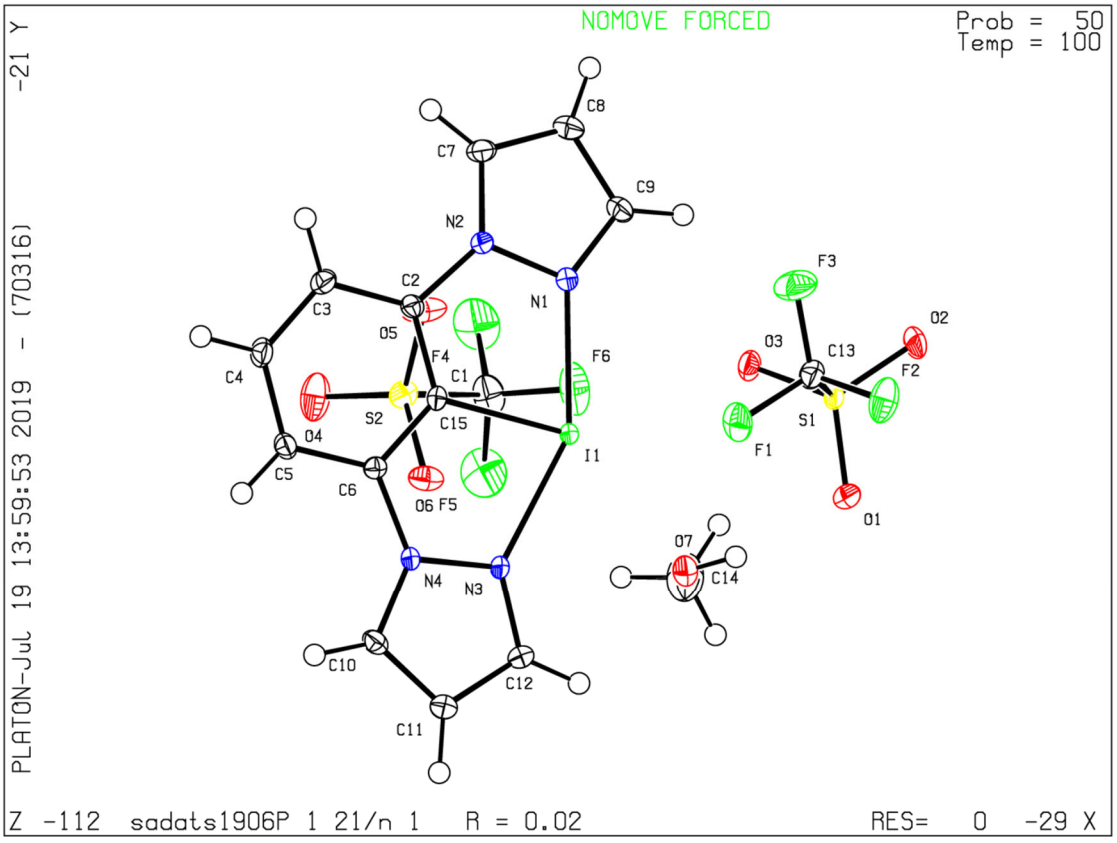


Table 2: Crystal data and structure refinement for Bis-Pyr-I-OTf **12b** (CCDC 2086526).

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}g/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 (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Bis-Pyr-I-OTf **12b**. U_{eq} is defined as 1/3 of 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 ($Å^2 \times 10^3$) for Bis-Pyr-I-OTf **12b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

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 (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) 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)

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7. NMR spectra

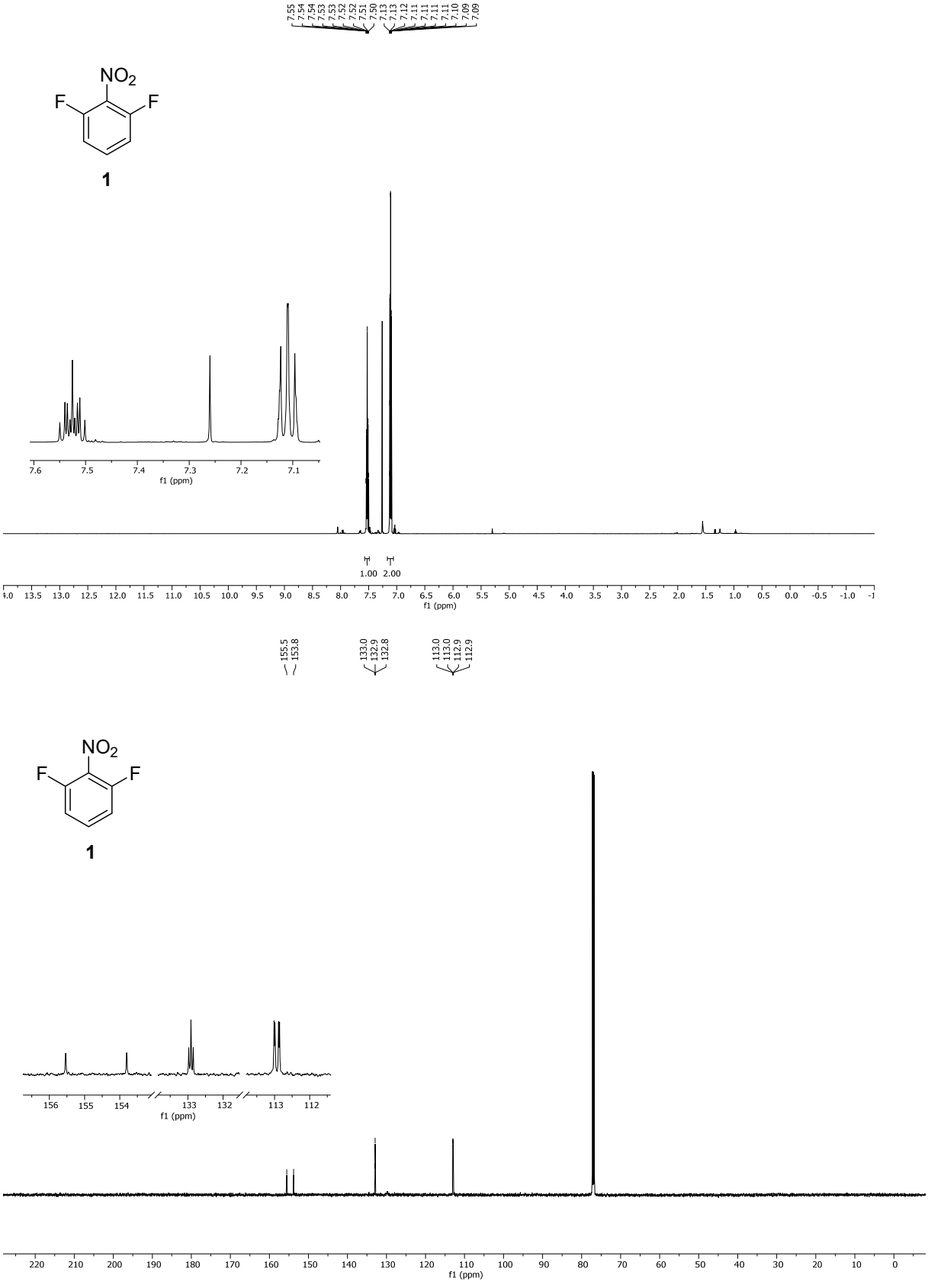


Figure S1: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **1** in $CDCl_3$.

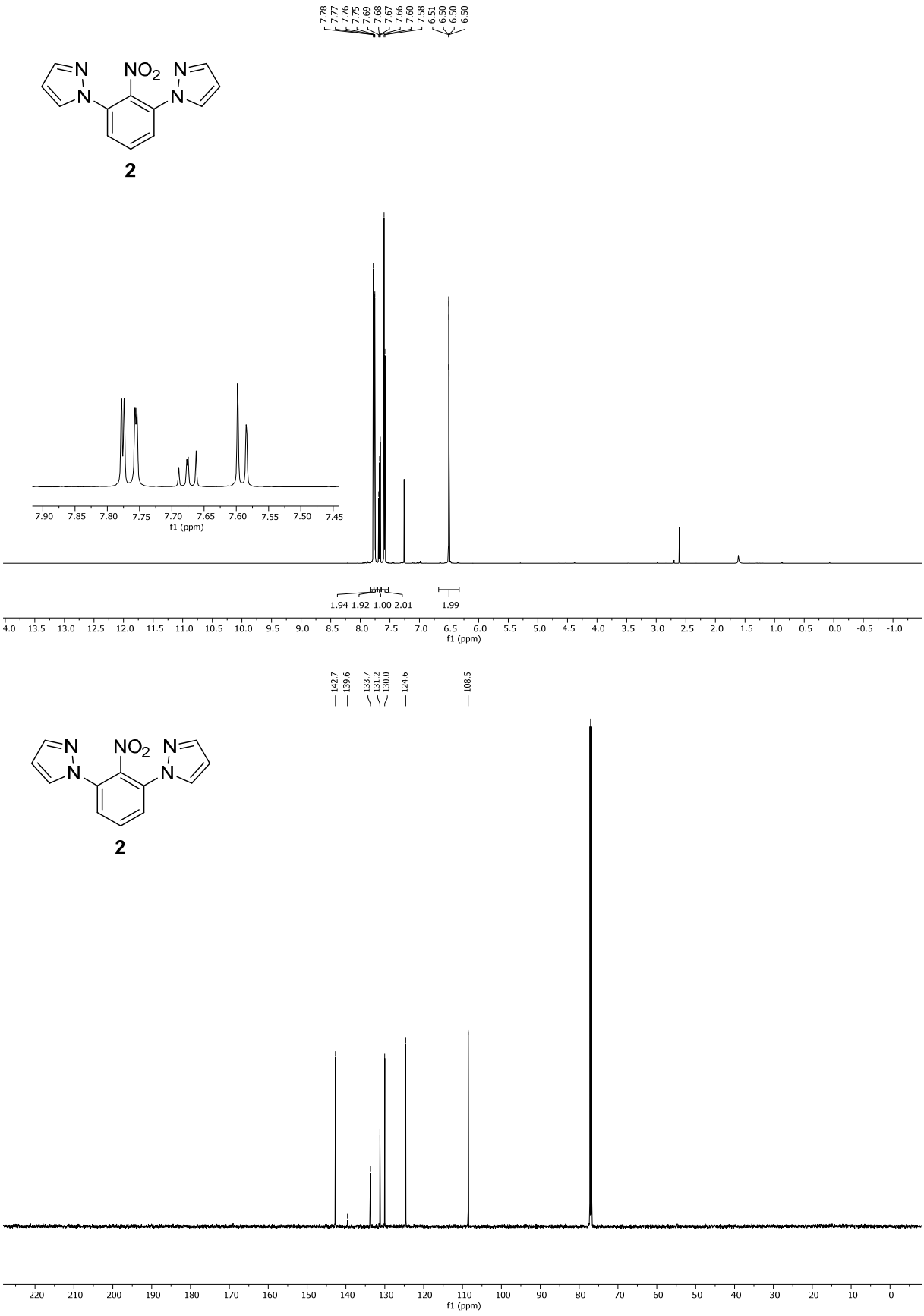


Figure S2: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **2** in $CDCl_3$.

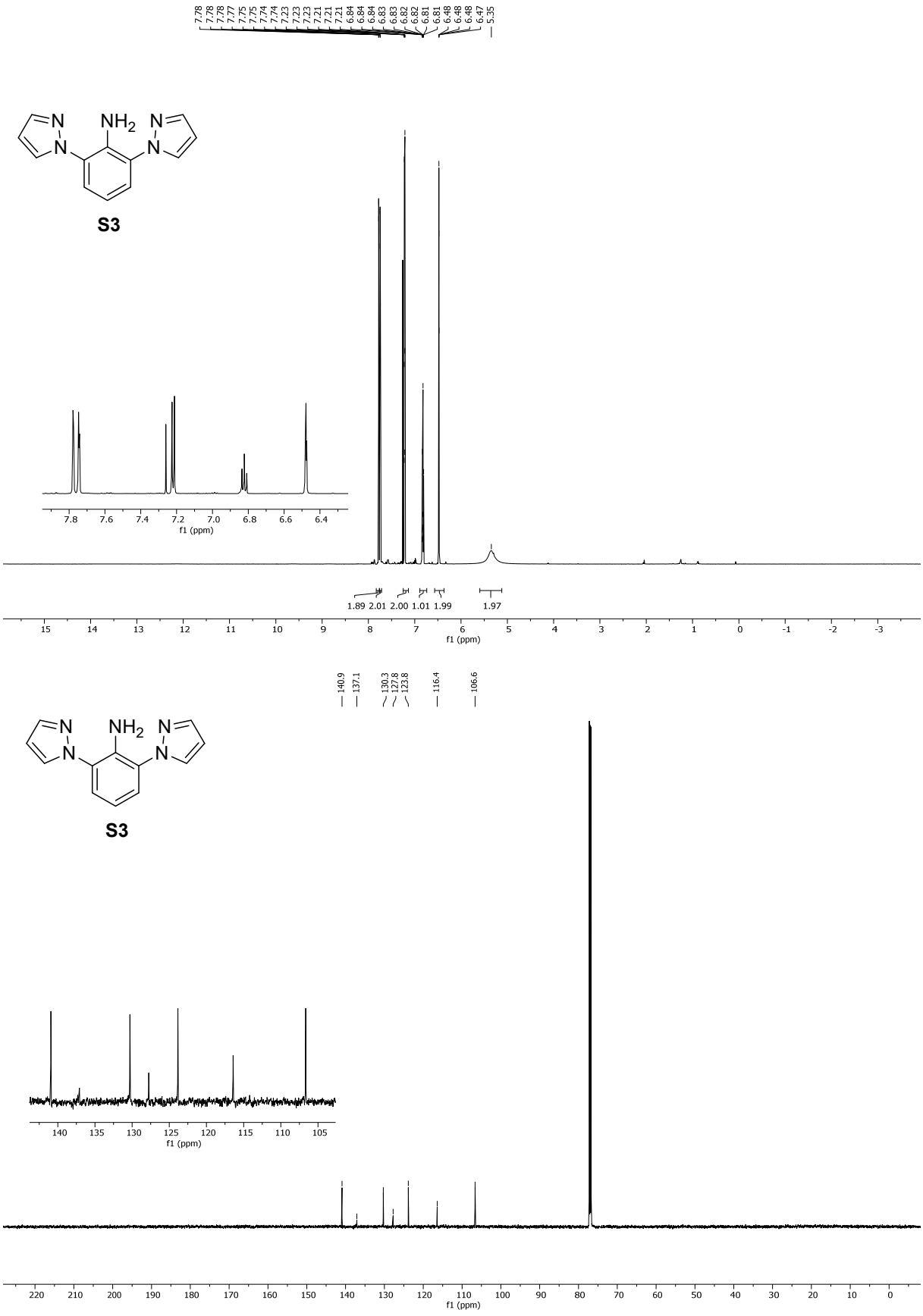


Figure S3: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **S3** in $CDCl_3$.

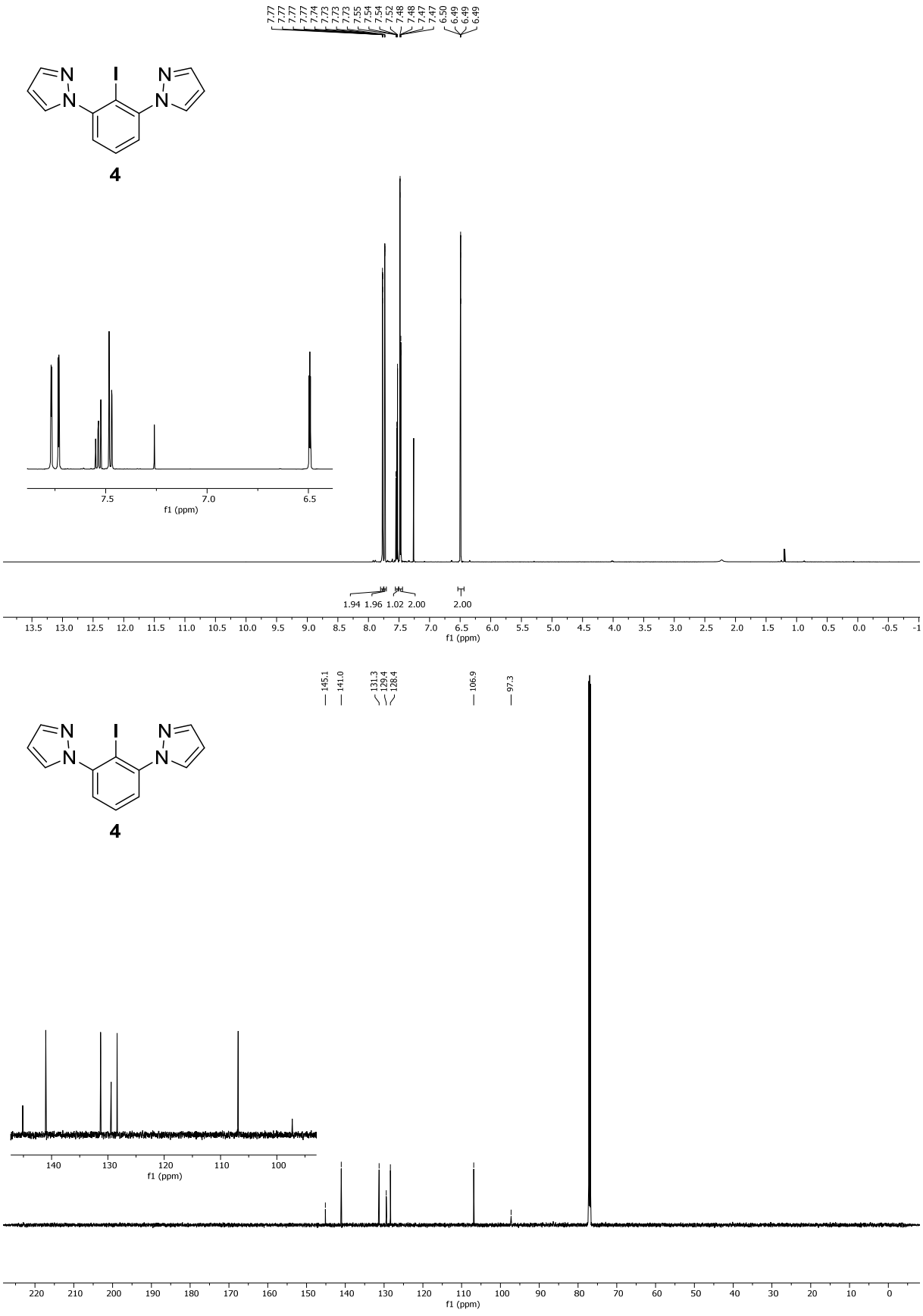


Figure S4: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **4** in $CDCl_3$.

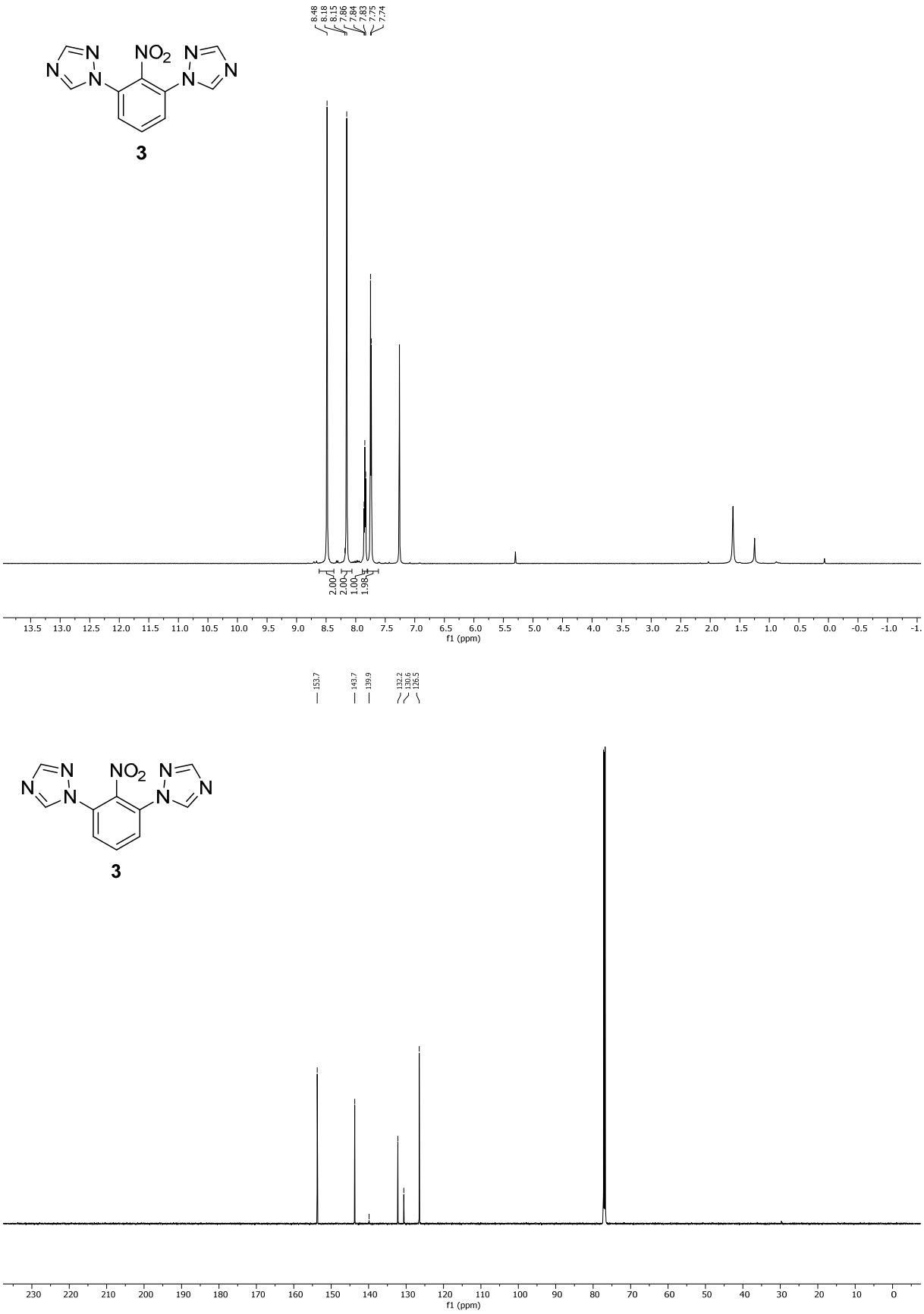


Figure S5: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **3** in $CDCl_3$.

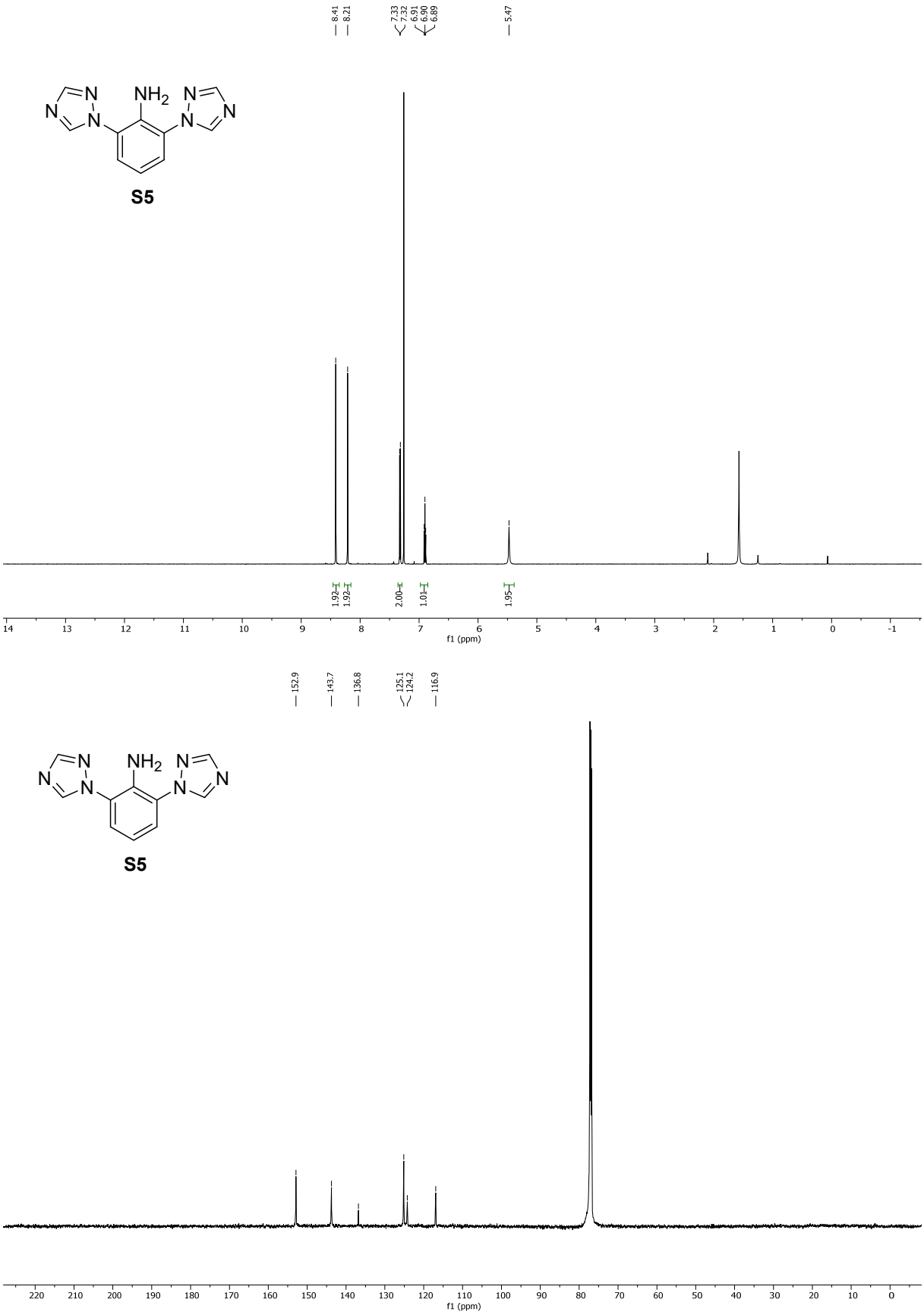


Figure S6: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **S5** in $CDCl_3$.

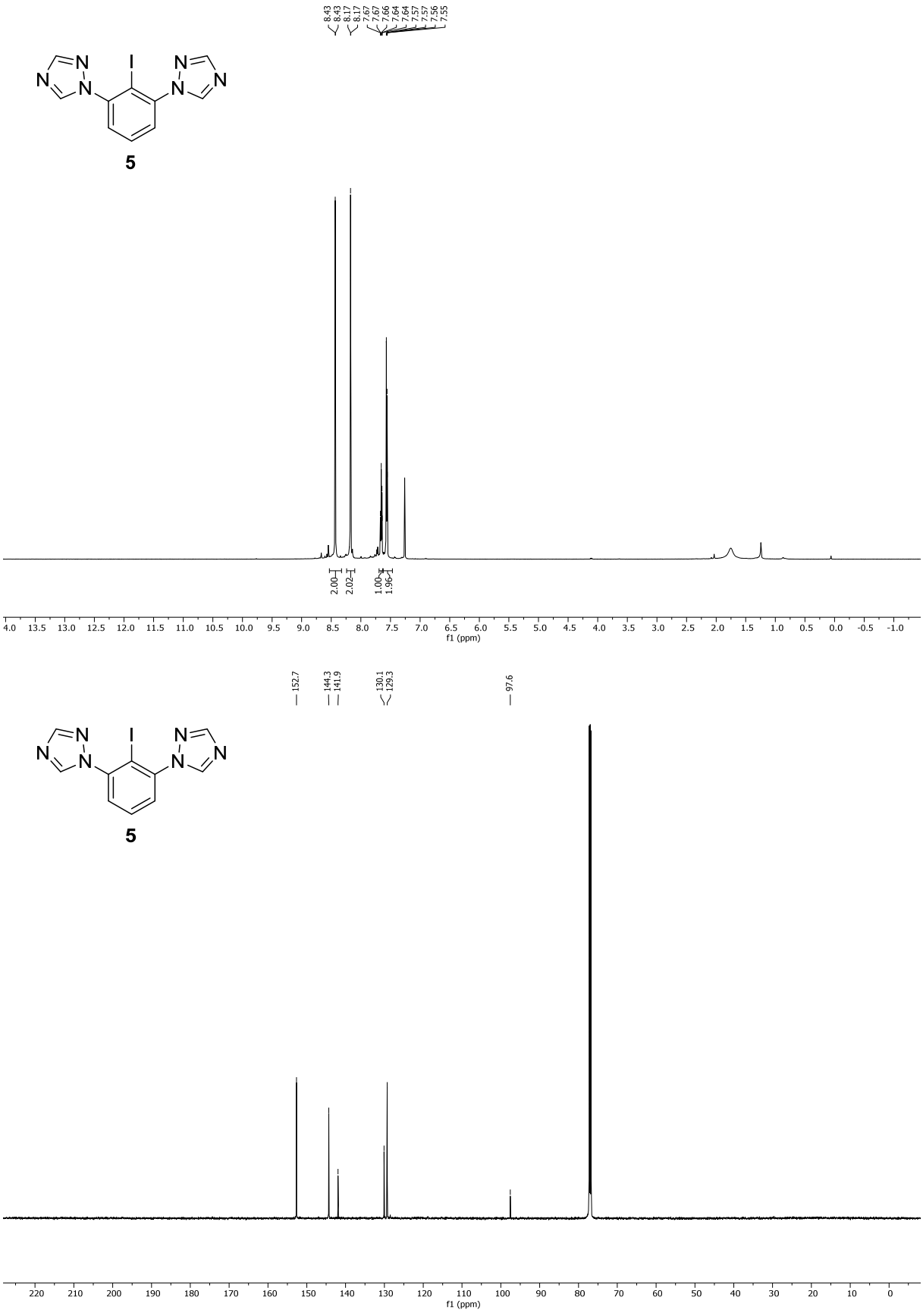


Figure S7: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **5** in $CDCl_3$.

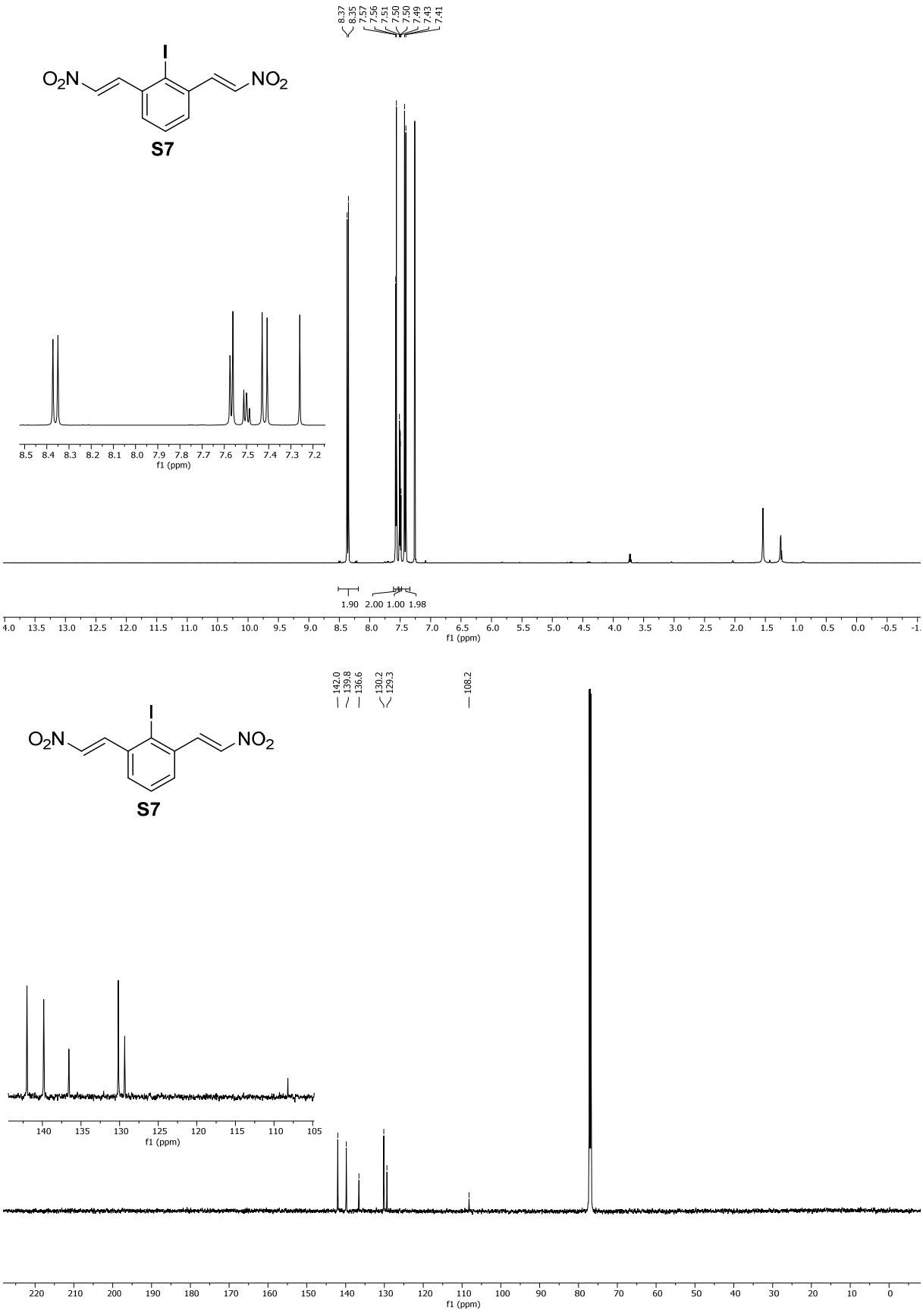
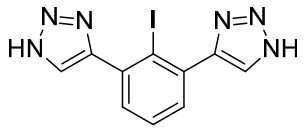


Figure S8: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **S7** in $CDCl_3$.



8

8.16
7.56
7.55
7.53
7.50
7.49
8.5
8.0
7.5
f1 (ppm)
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1.00
1.98
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

8

15.41
15.23
15.11
8.39
8.22
8.11
8.07
7.96
7.56
7.54
7.53
7.49
15
14
13
12
11
10
9
8
7
f1 (ppm)
1.79
1.96
3.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

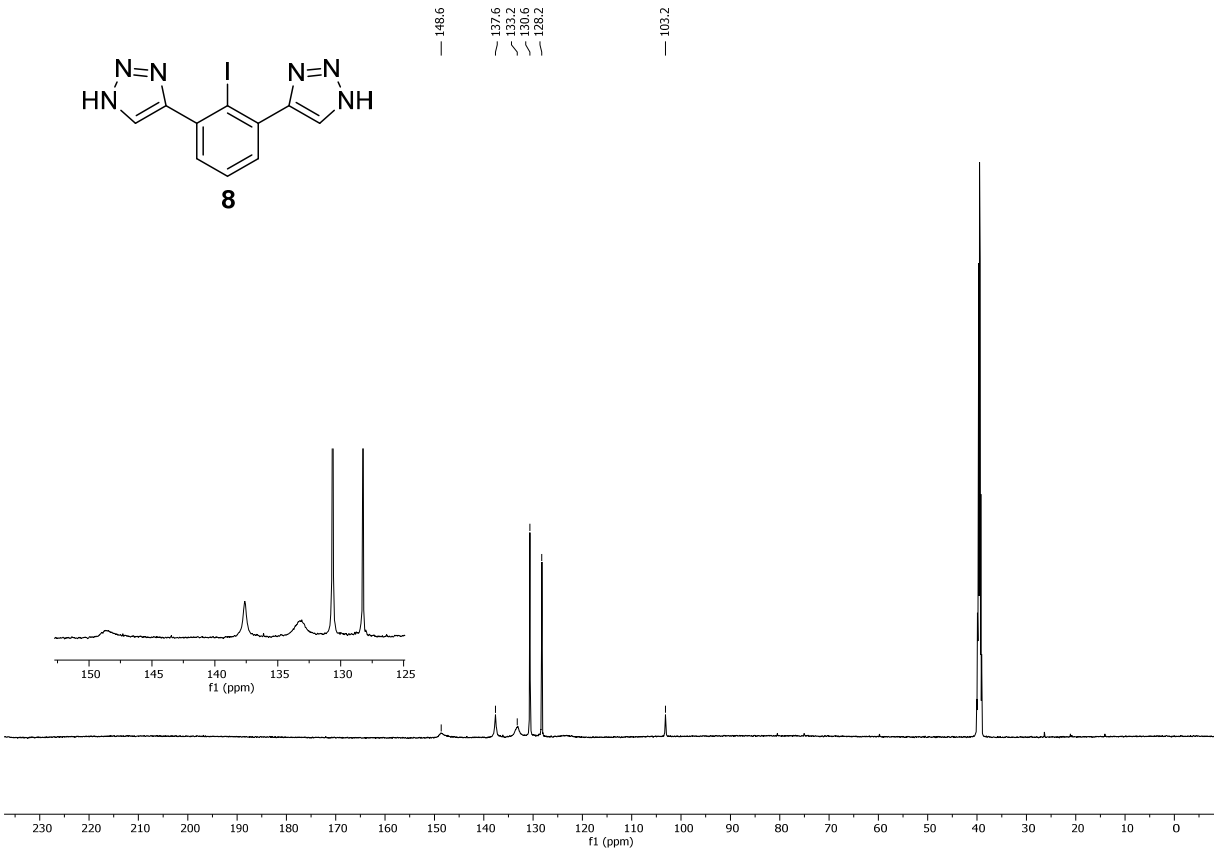
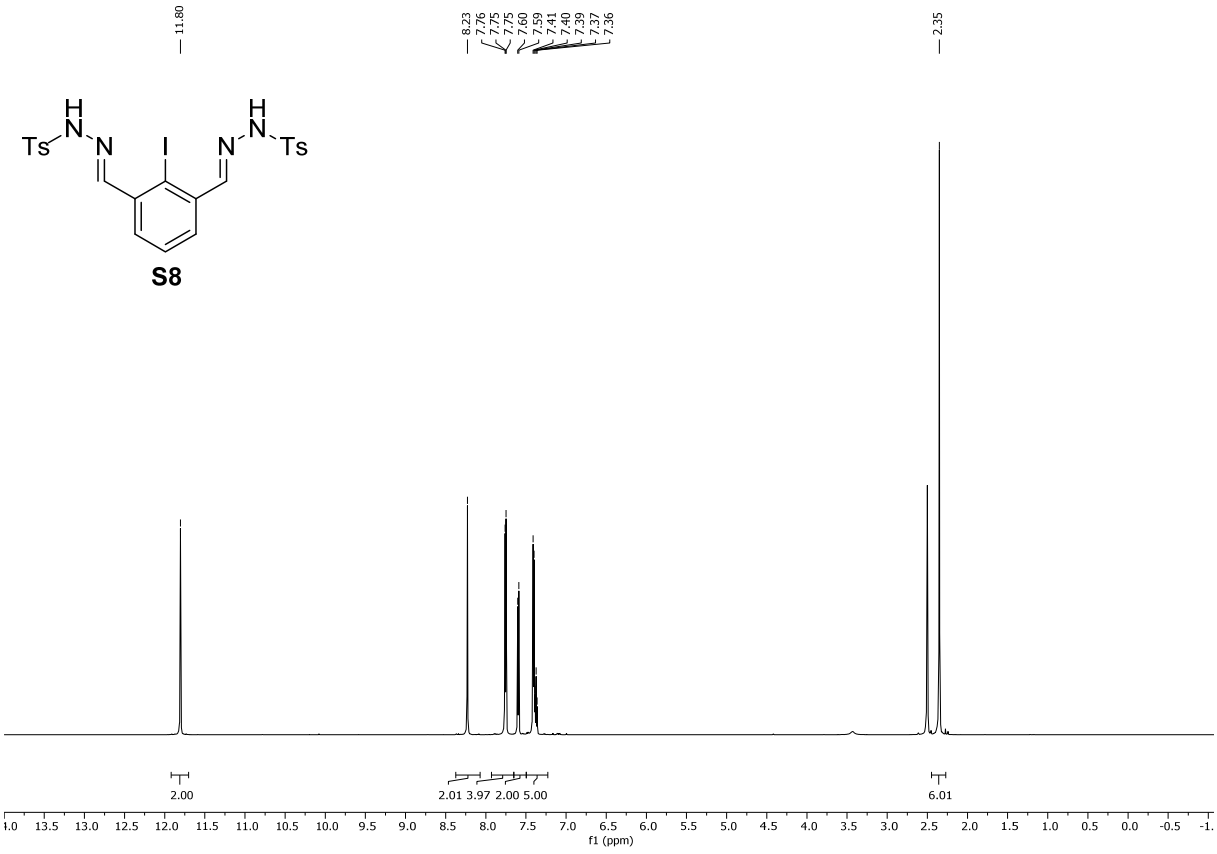


Figure S9: 600 MHz ^{1}H- (high and low concentration) and 151 MHz ^{13}C-NMR spectra of **8** in d_6-DMSO.



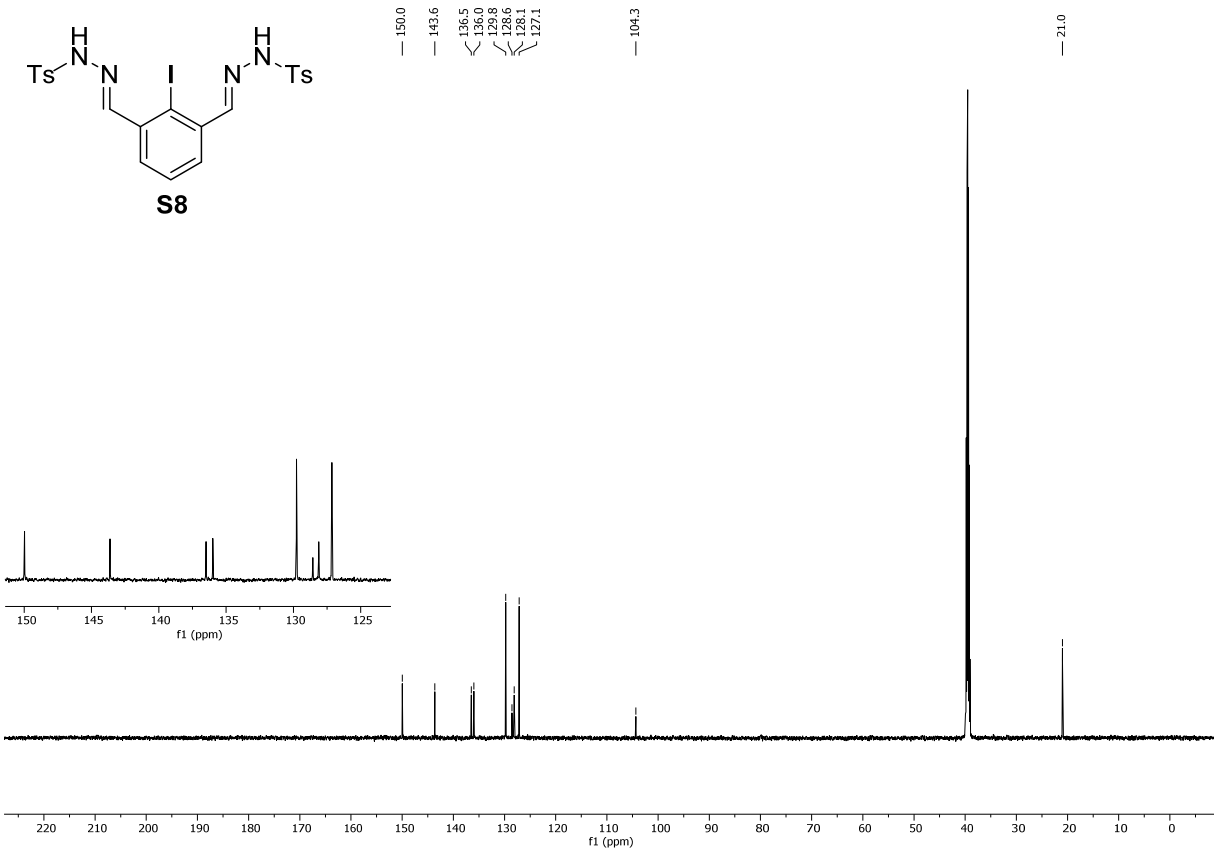
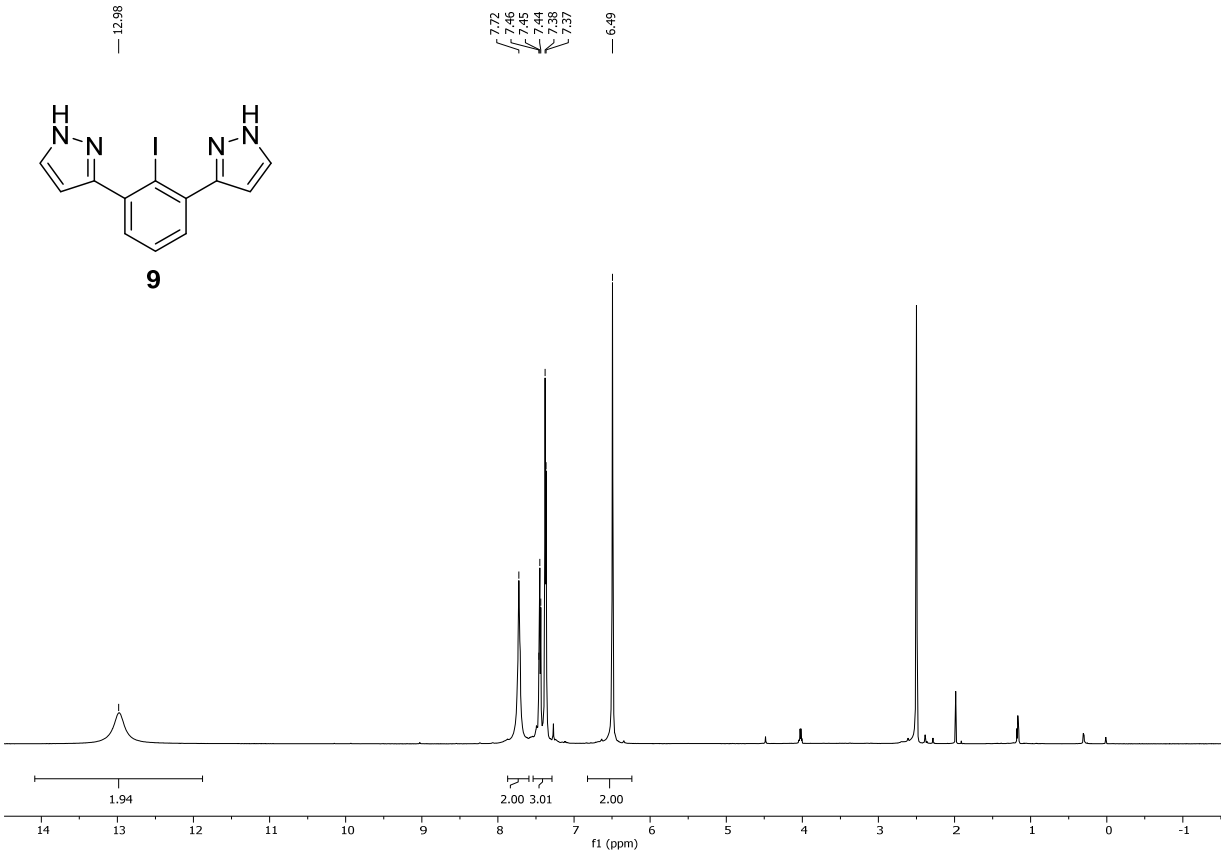


Figure S10: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **S8** in d_6-DMSO.



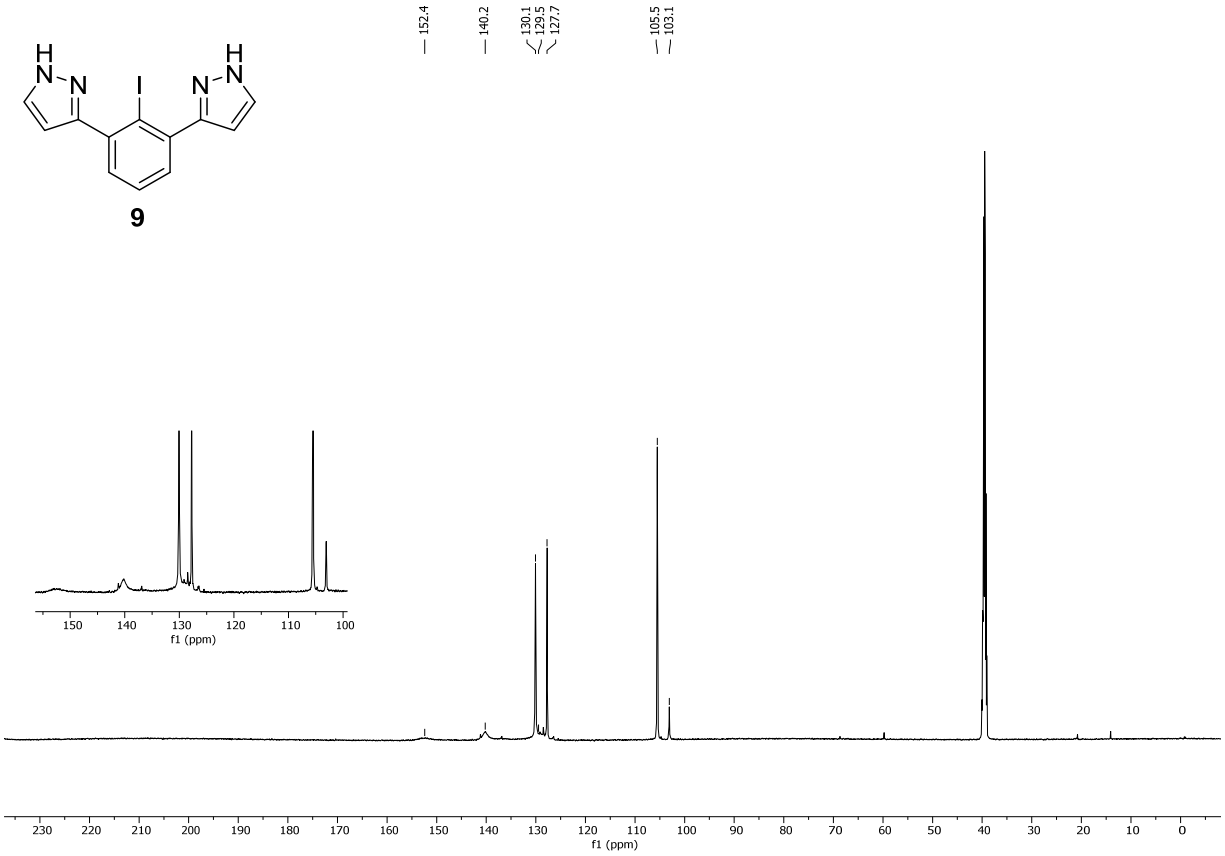
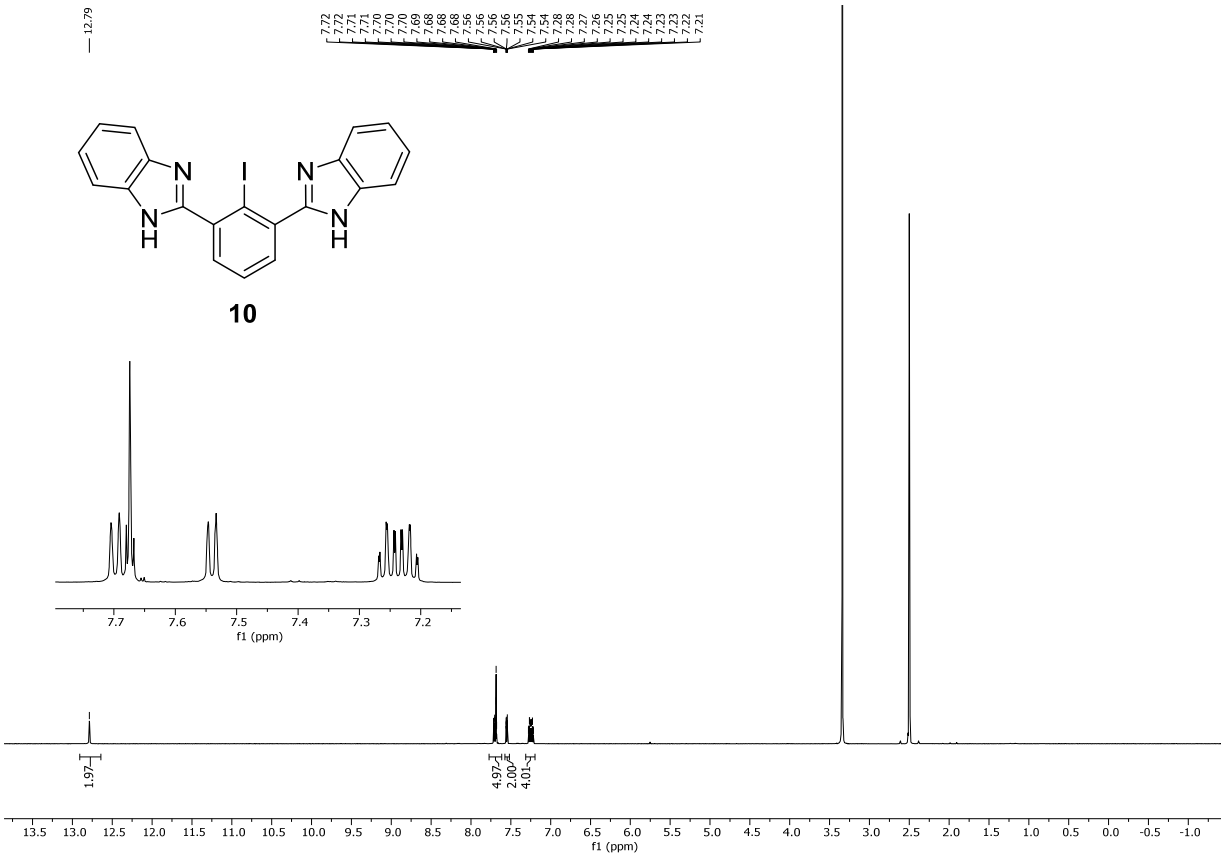


Figure S11: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **9** in d_6-DMSO.



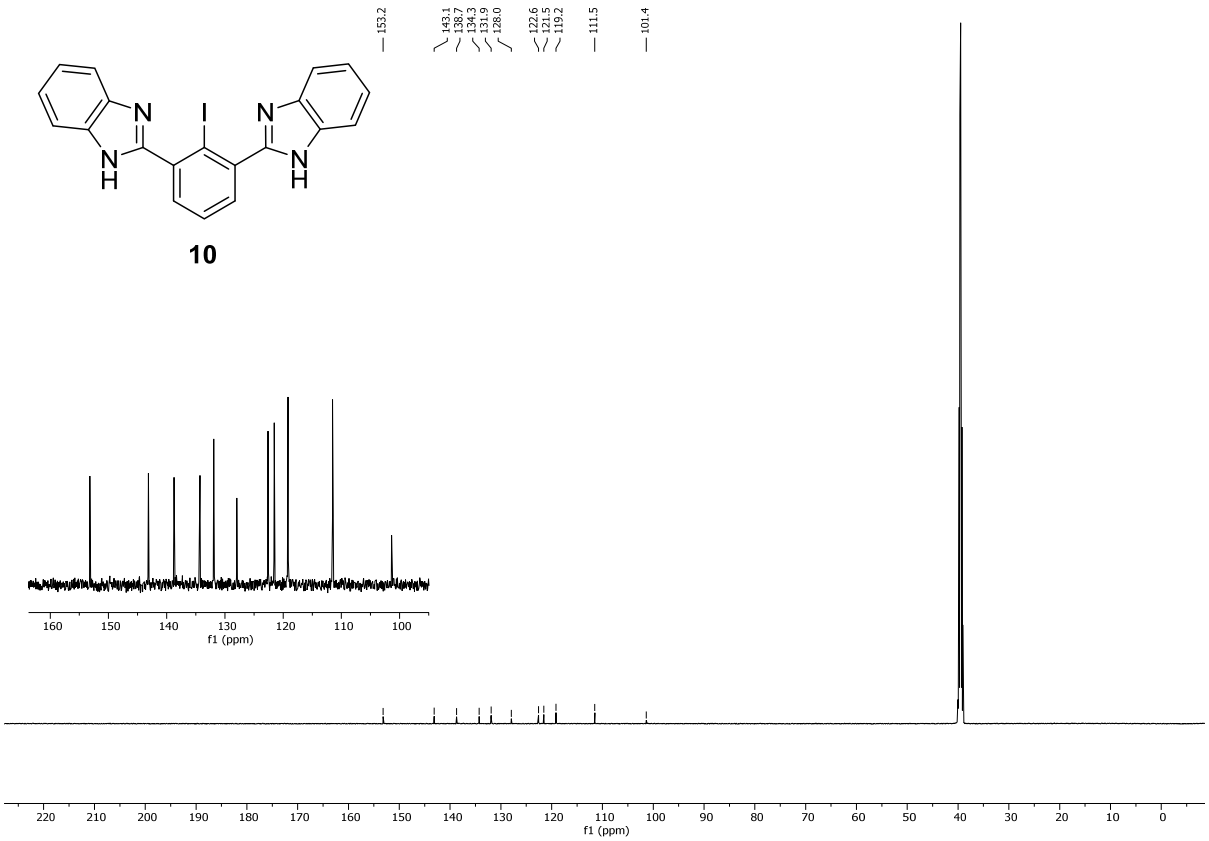
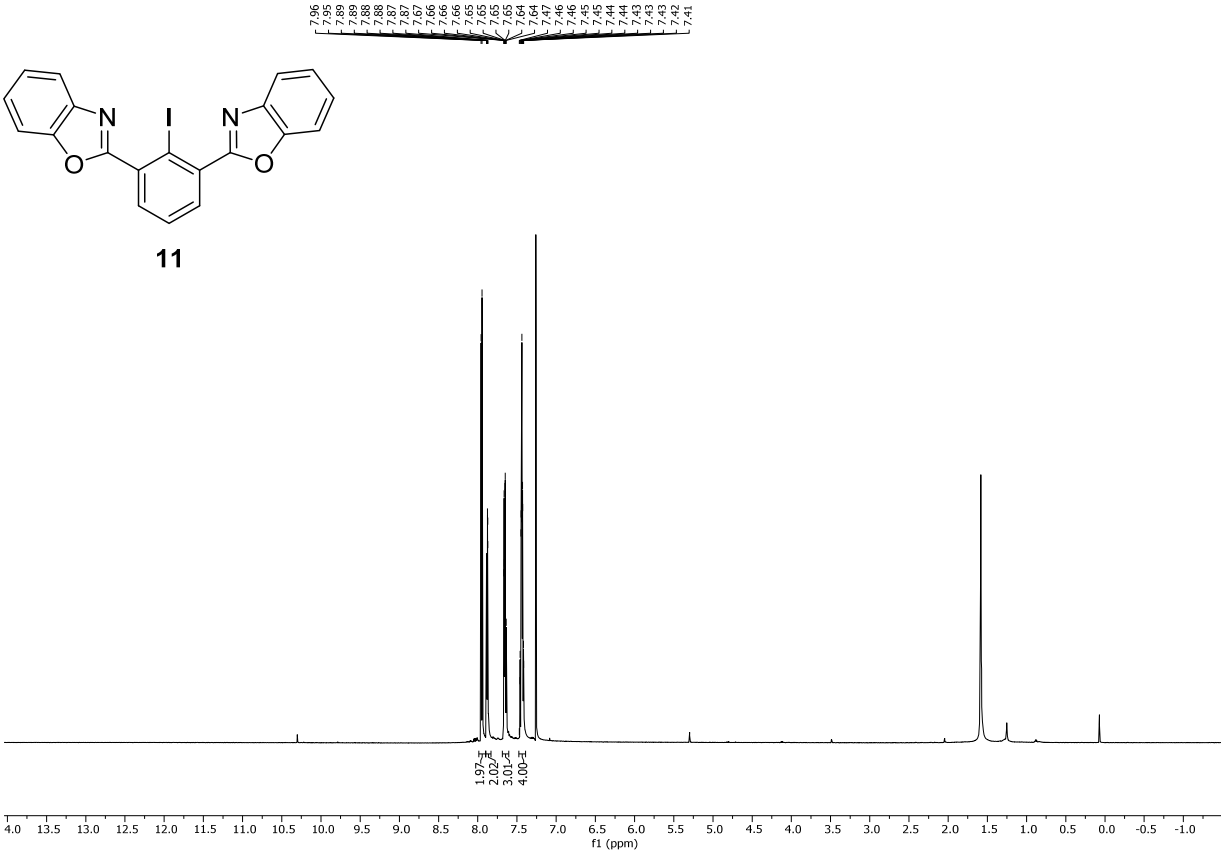


Figure S12: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **10** in d_6-DMSO.



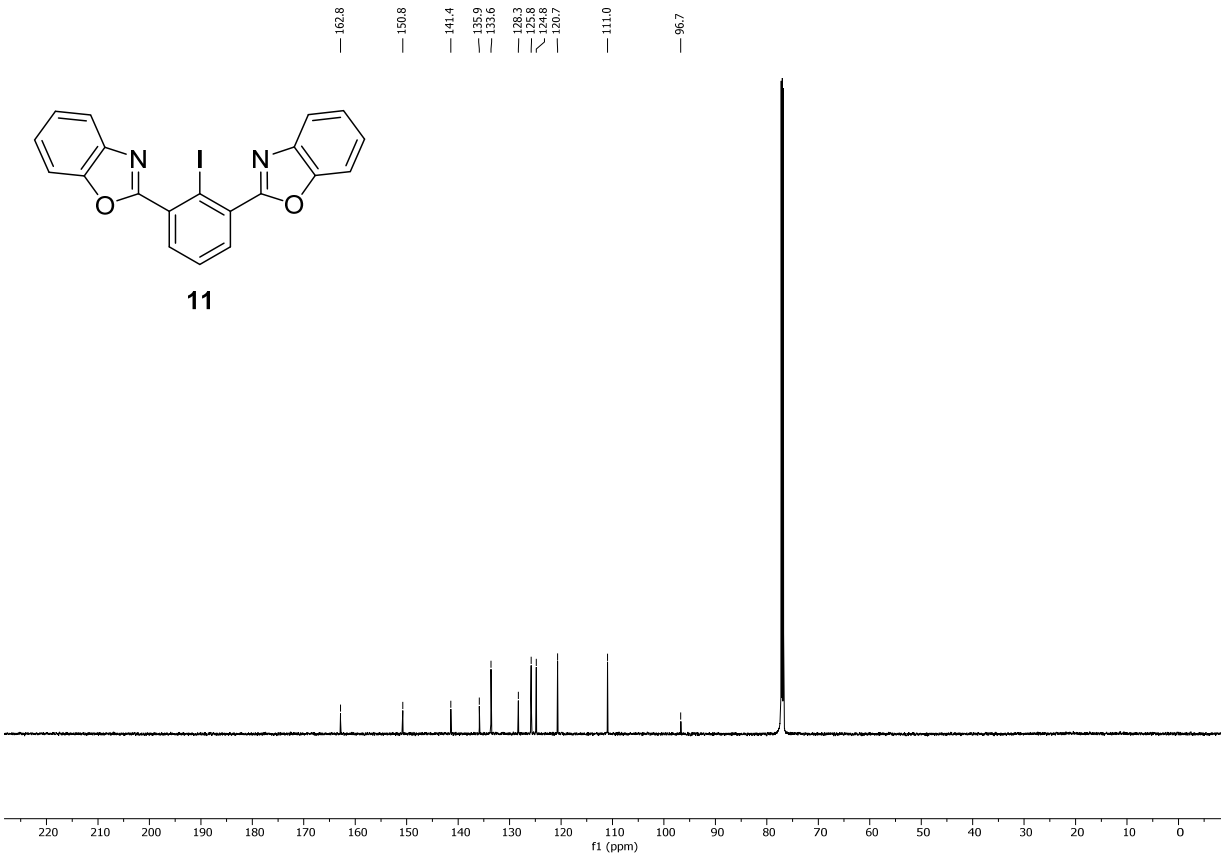
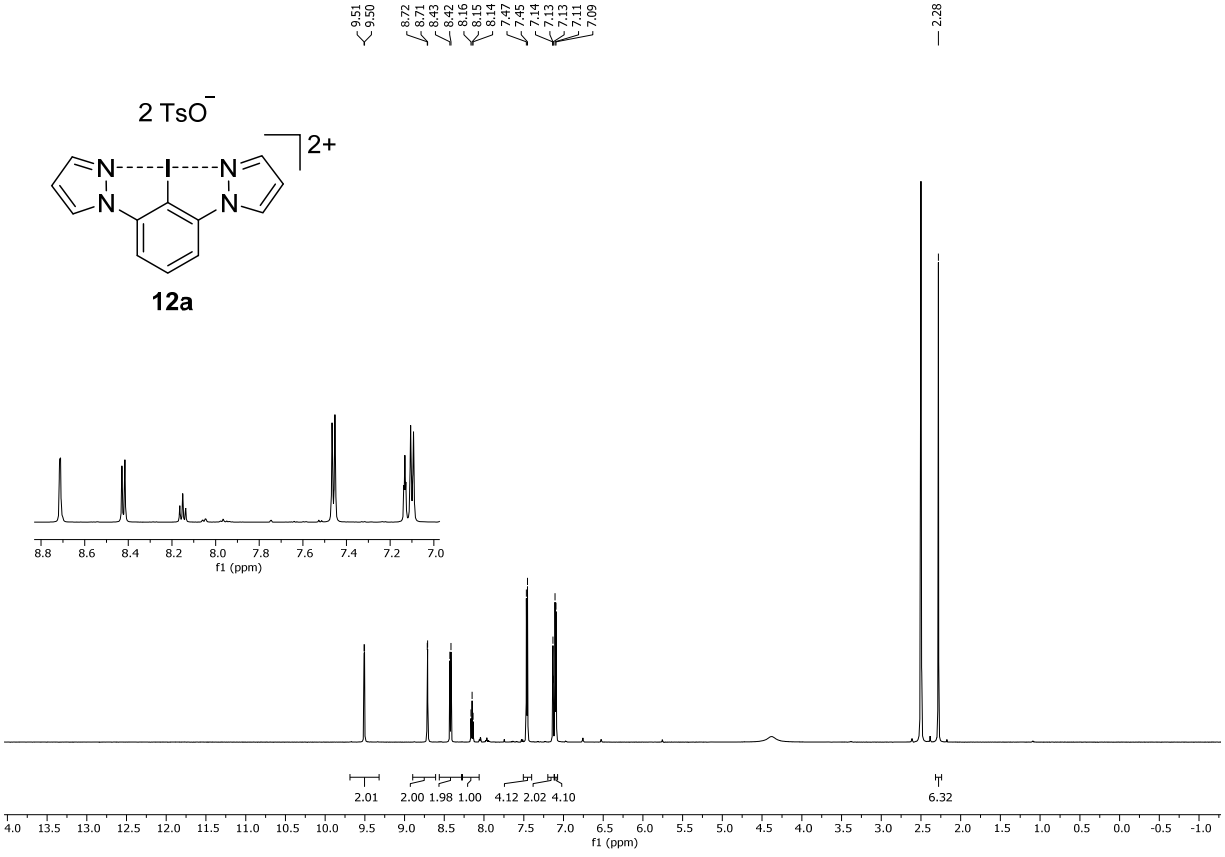


Figure S13: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **11** in $CDCl_3$.



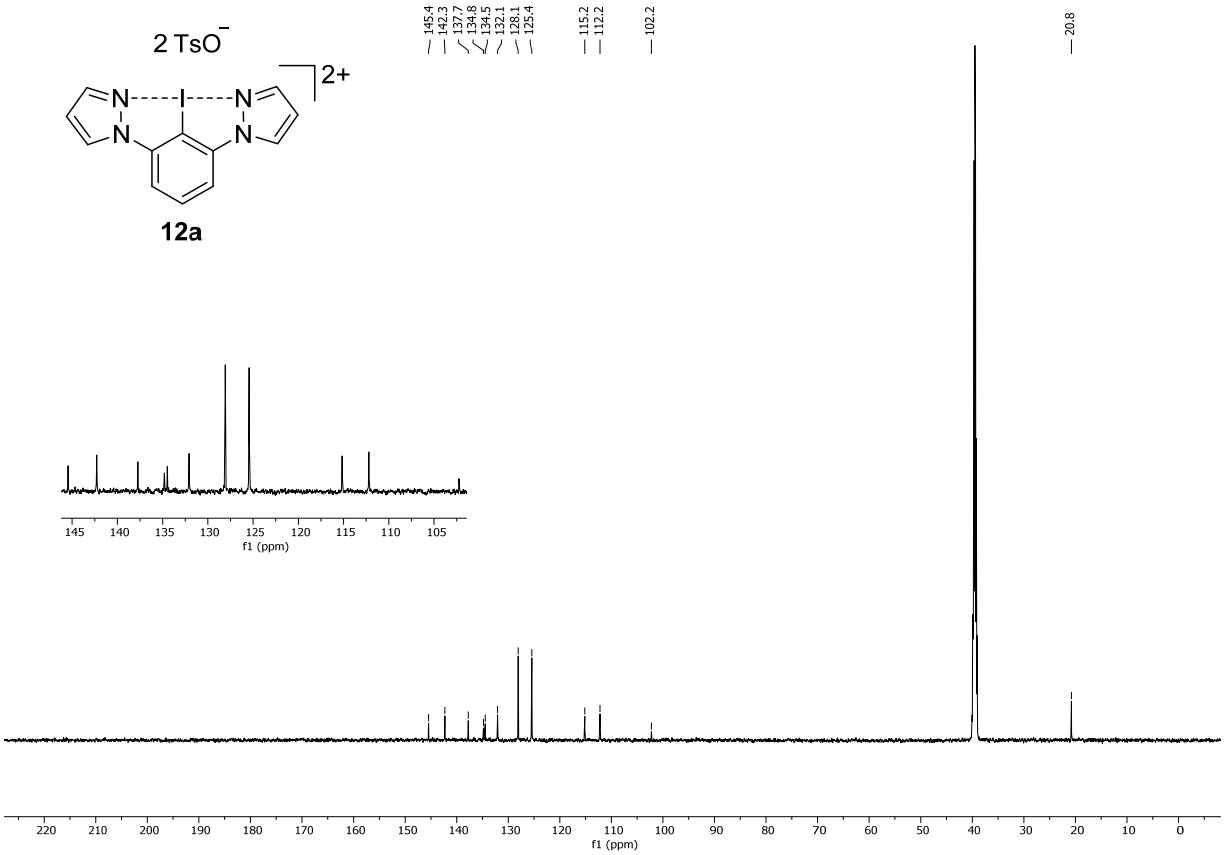
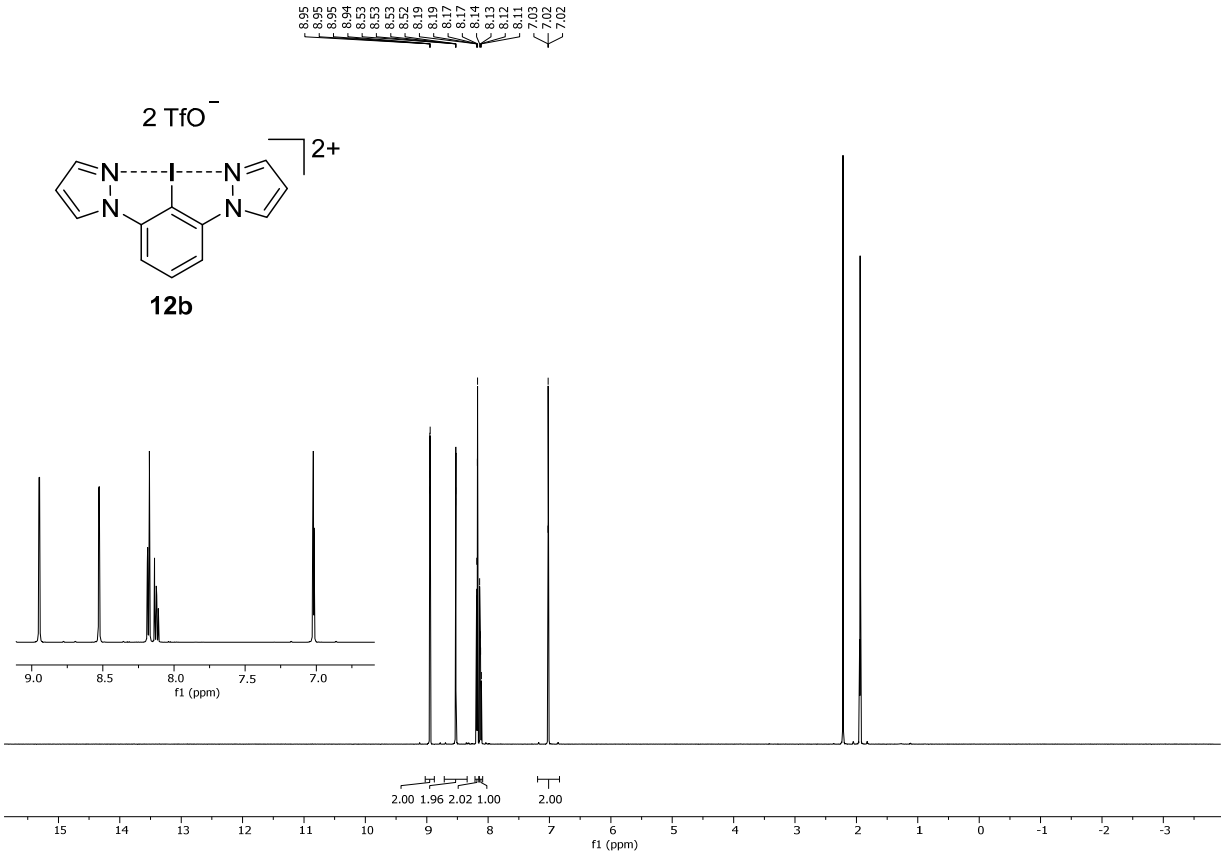


Figure S14: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **12a** in d_6-DMSO.



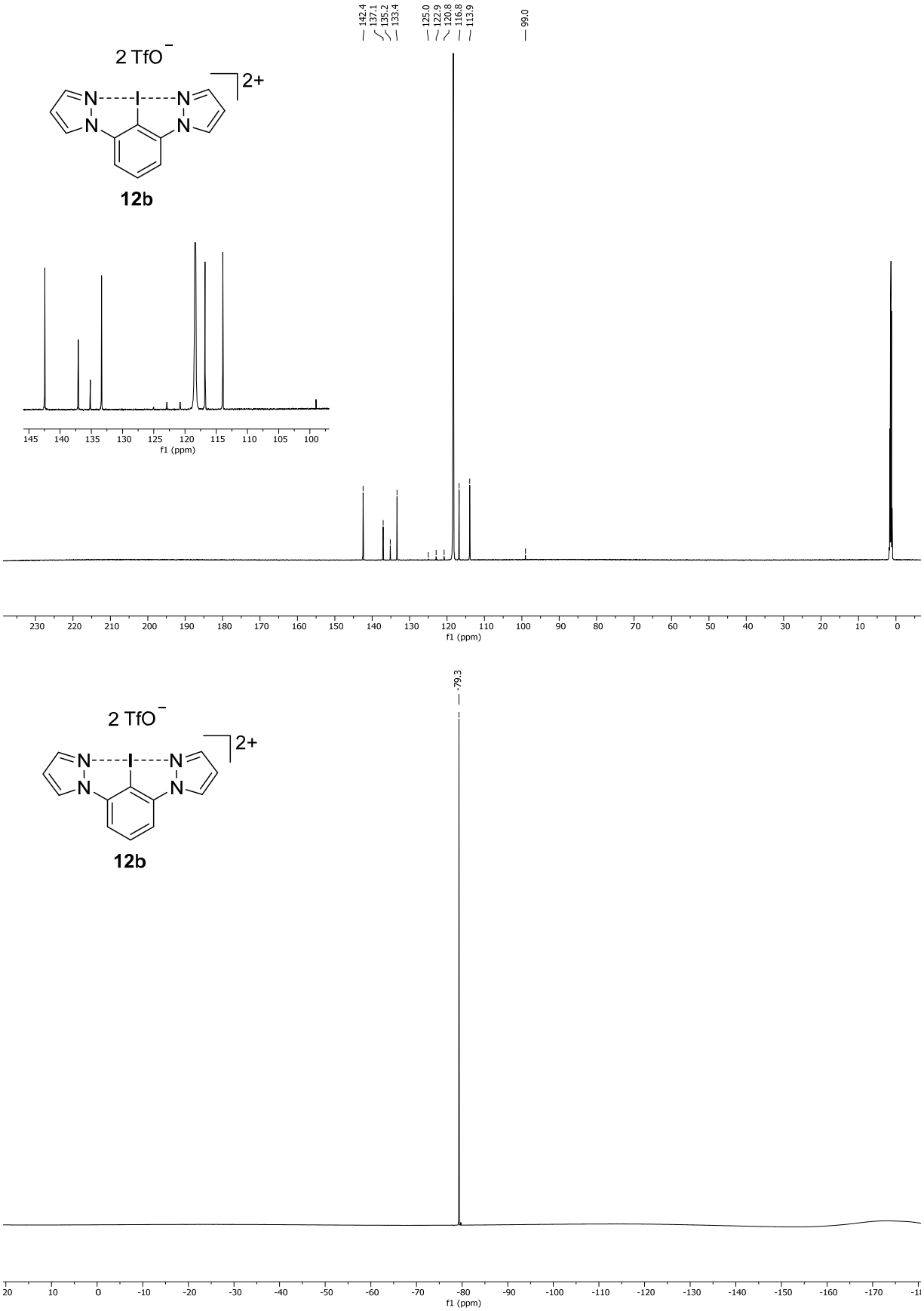


Figure S15: 600 MHz ^{1}H-, 151 MHz ^{13}C and 565 MHz ^{19}F-NMR spectra of **12b** in d_3-MeCN.

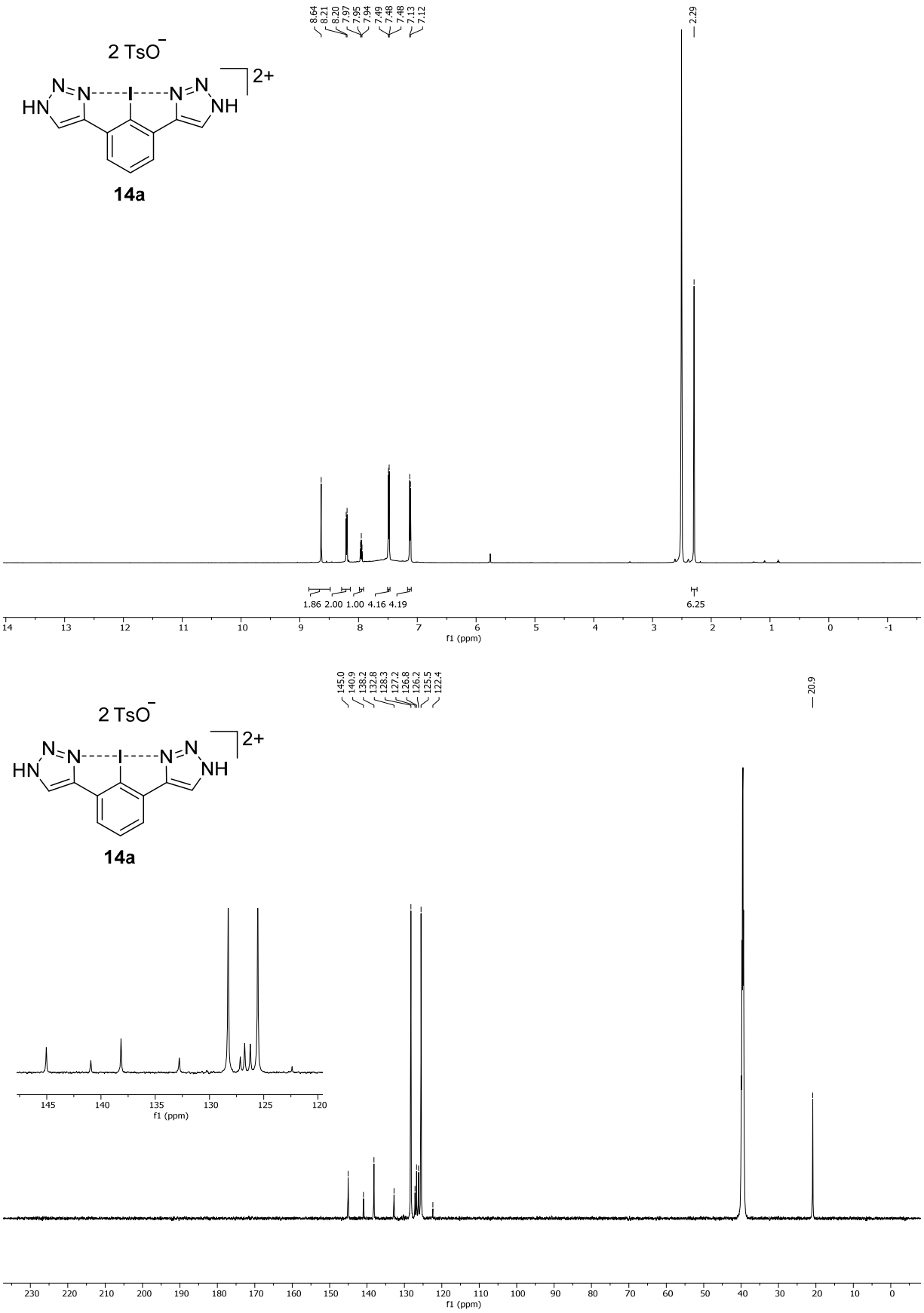
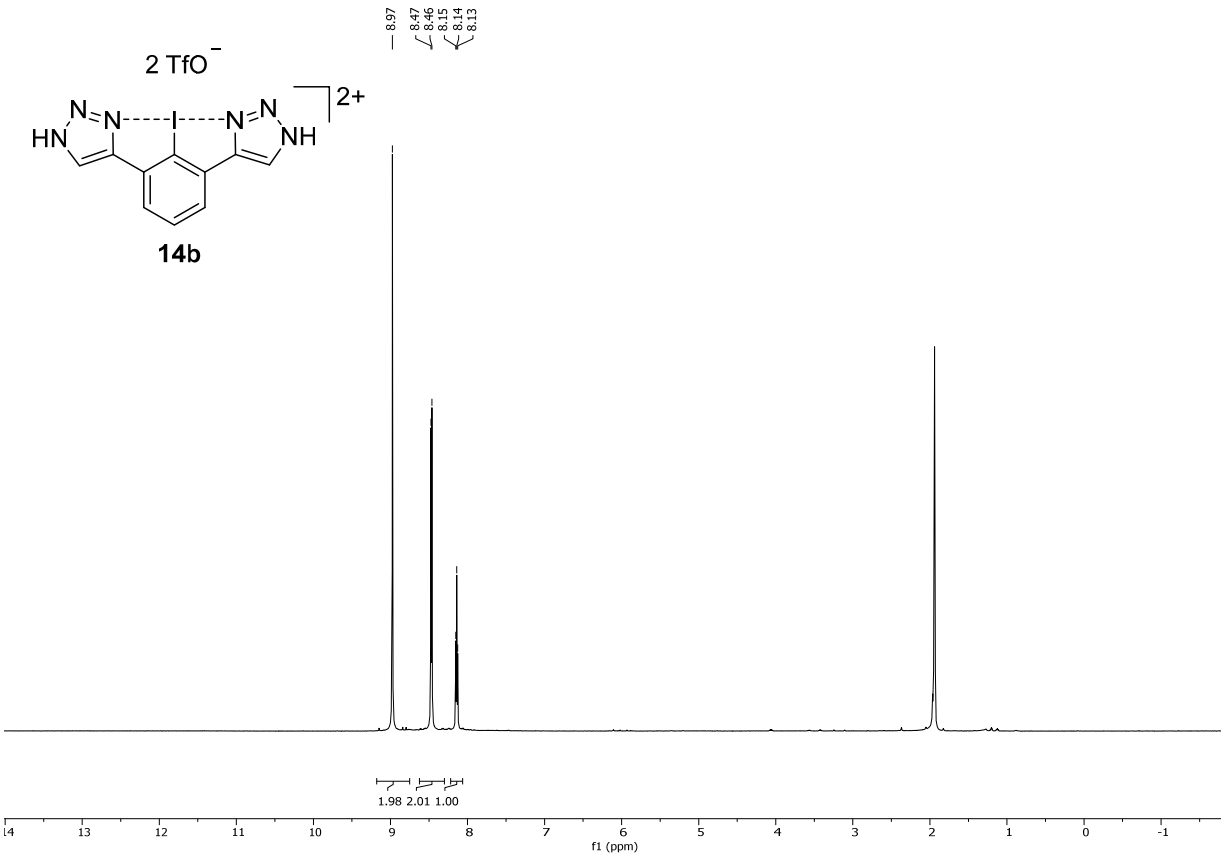
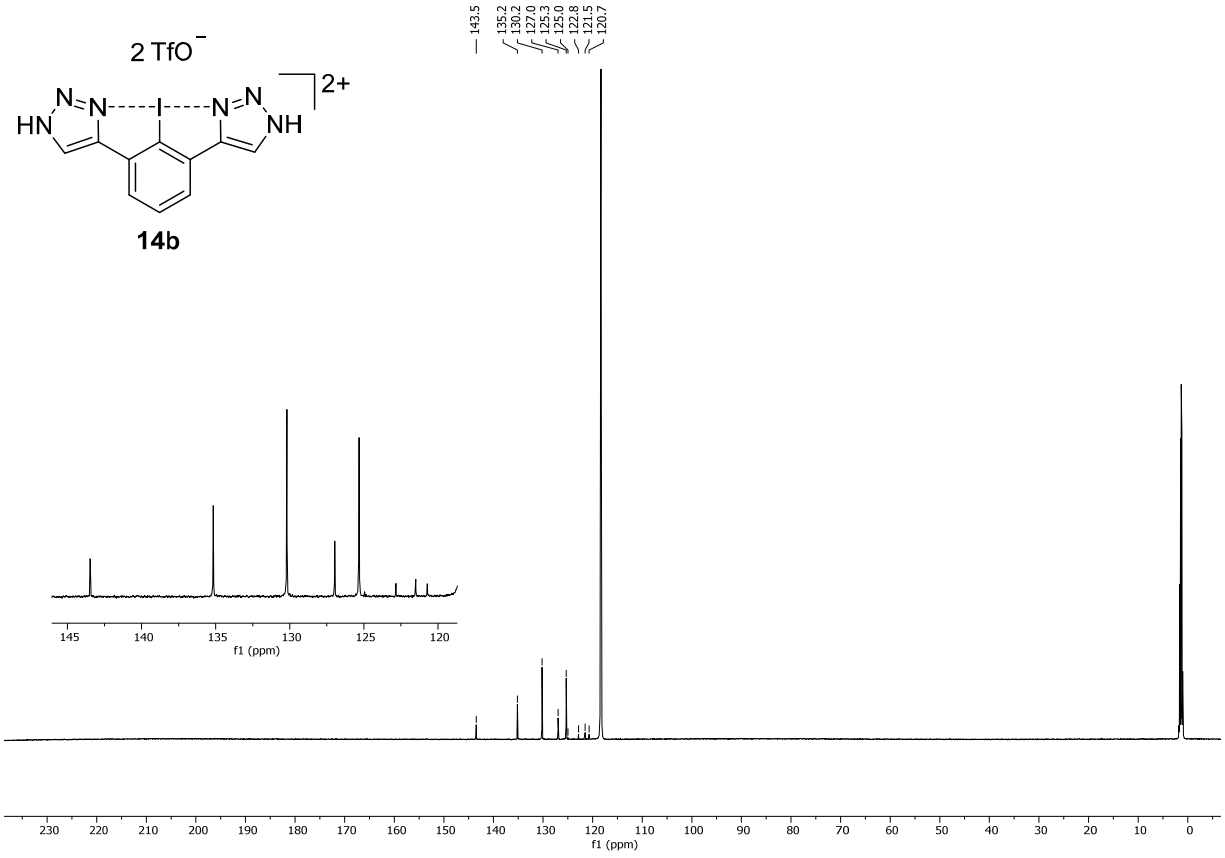


Figure S16: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **14a** in d_6-DMSO.


2 TfO⁻
2+
HN
NH
14b
8.97
8.47
8.46
8.15
8.14
8.13
1.98 2.01 1.00
f1 (ppm)


2 TfO⁻
2+
HN
NH
14b
143.5
135.2
130.2
127.0
125.3
125.0
122.8
121.5
120.7
f1 (ppm)

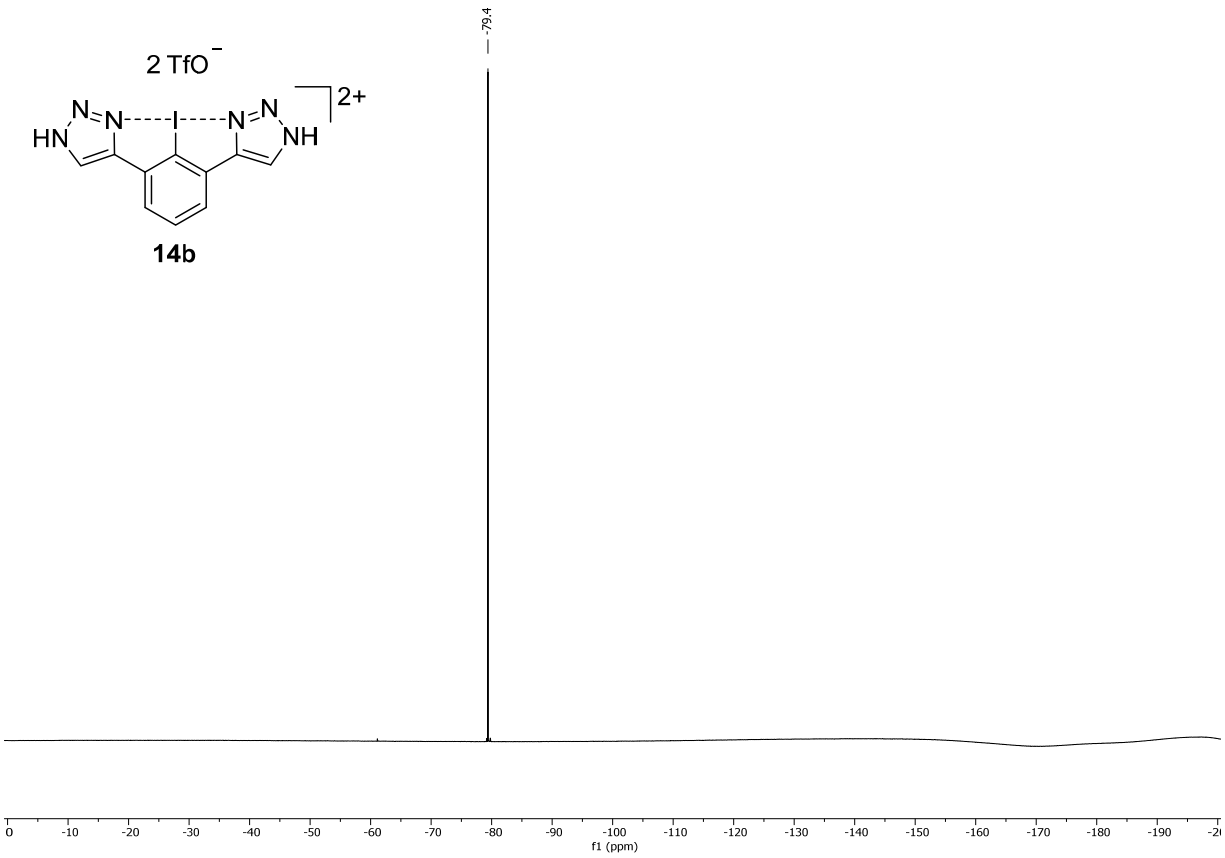
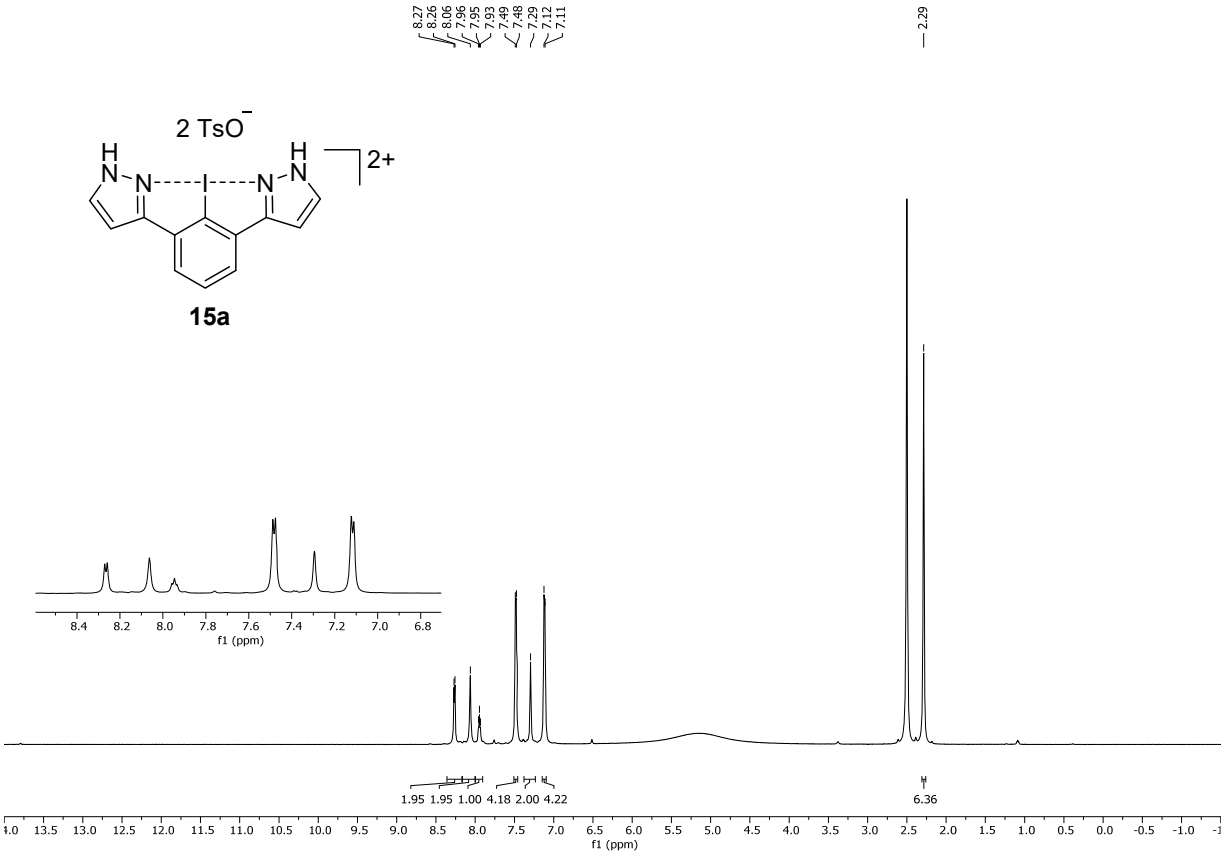


Figure S17: 600 MHz ^{1}H-, 151 MHz ^{13}C and 565 MHz ^{19}F-NMR spectra of **14b** in d_3-MeCN.



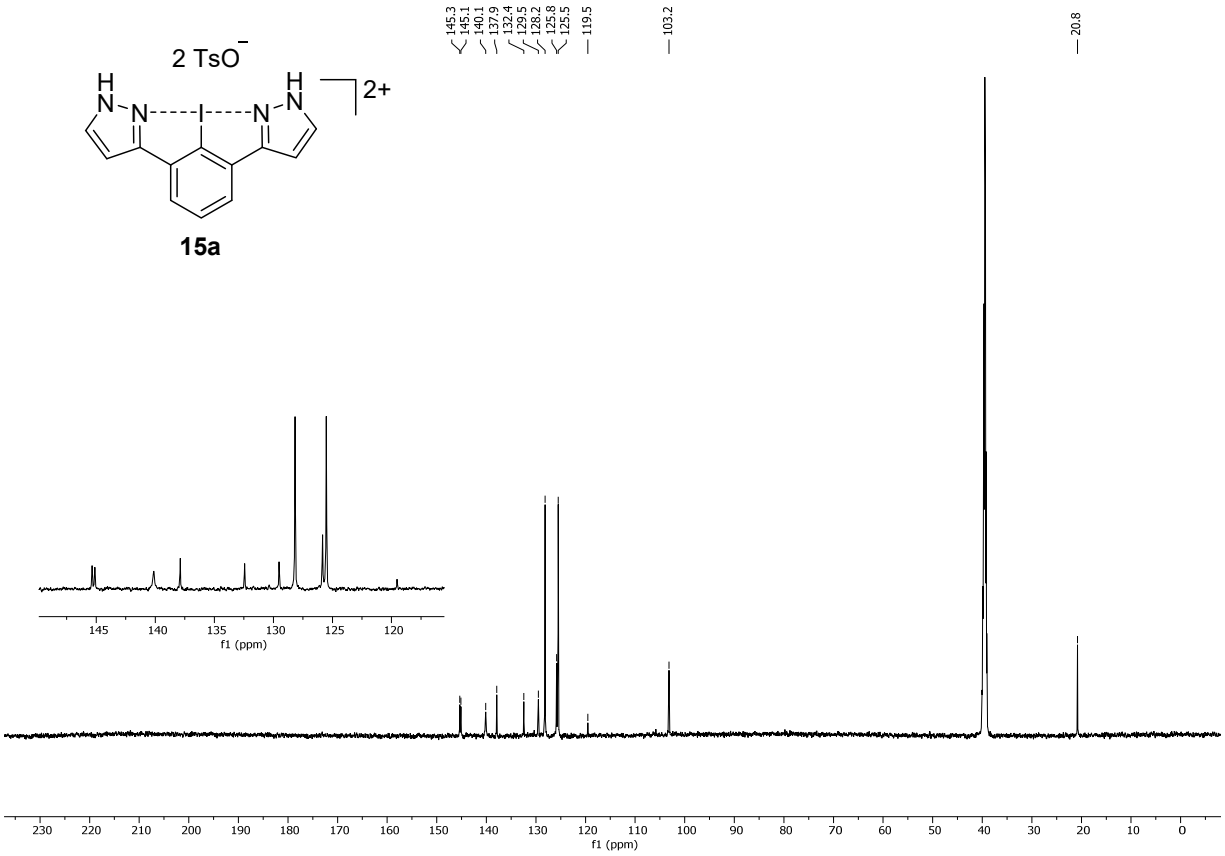
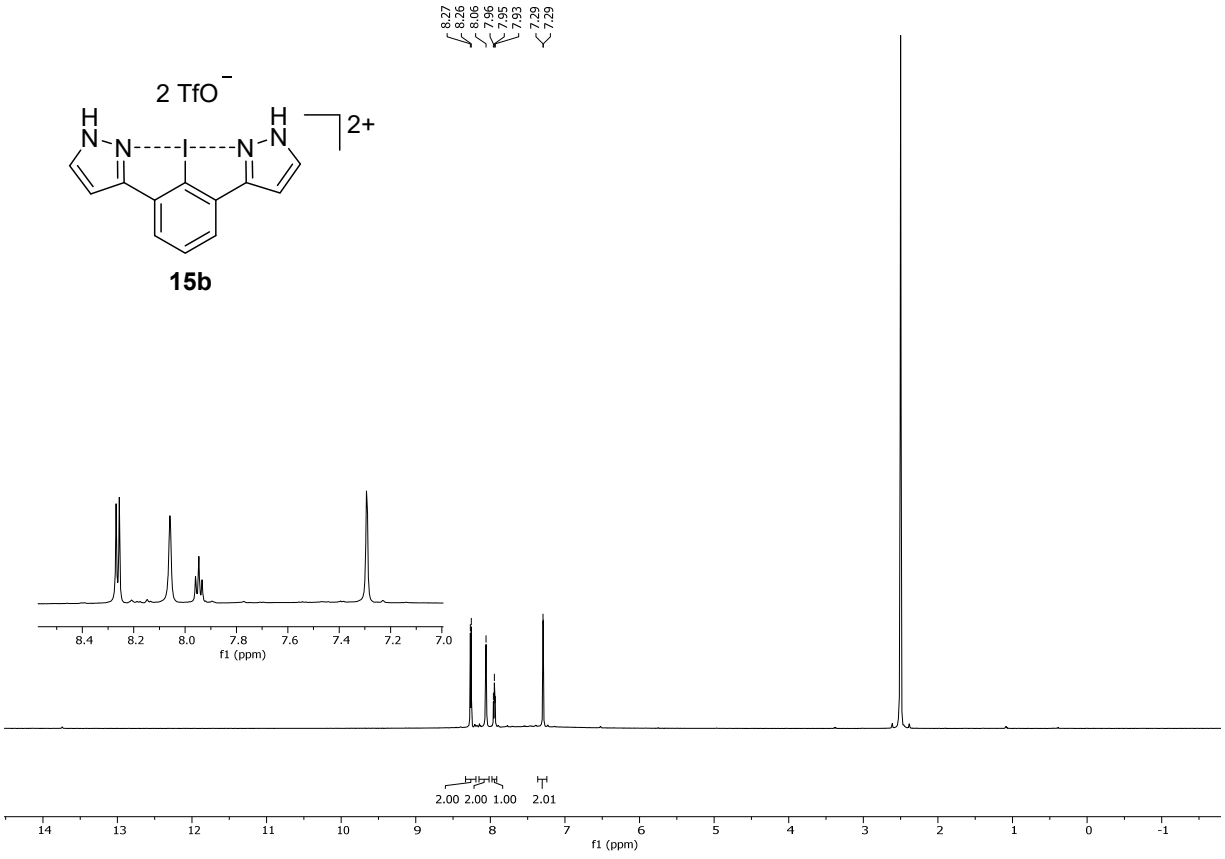


Figure S18: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **15a** in d_6-DMSO.



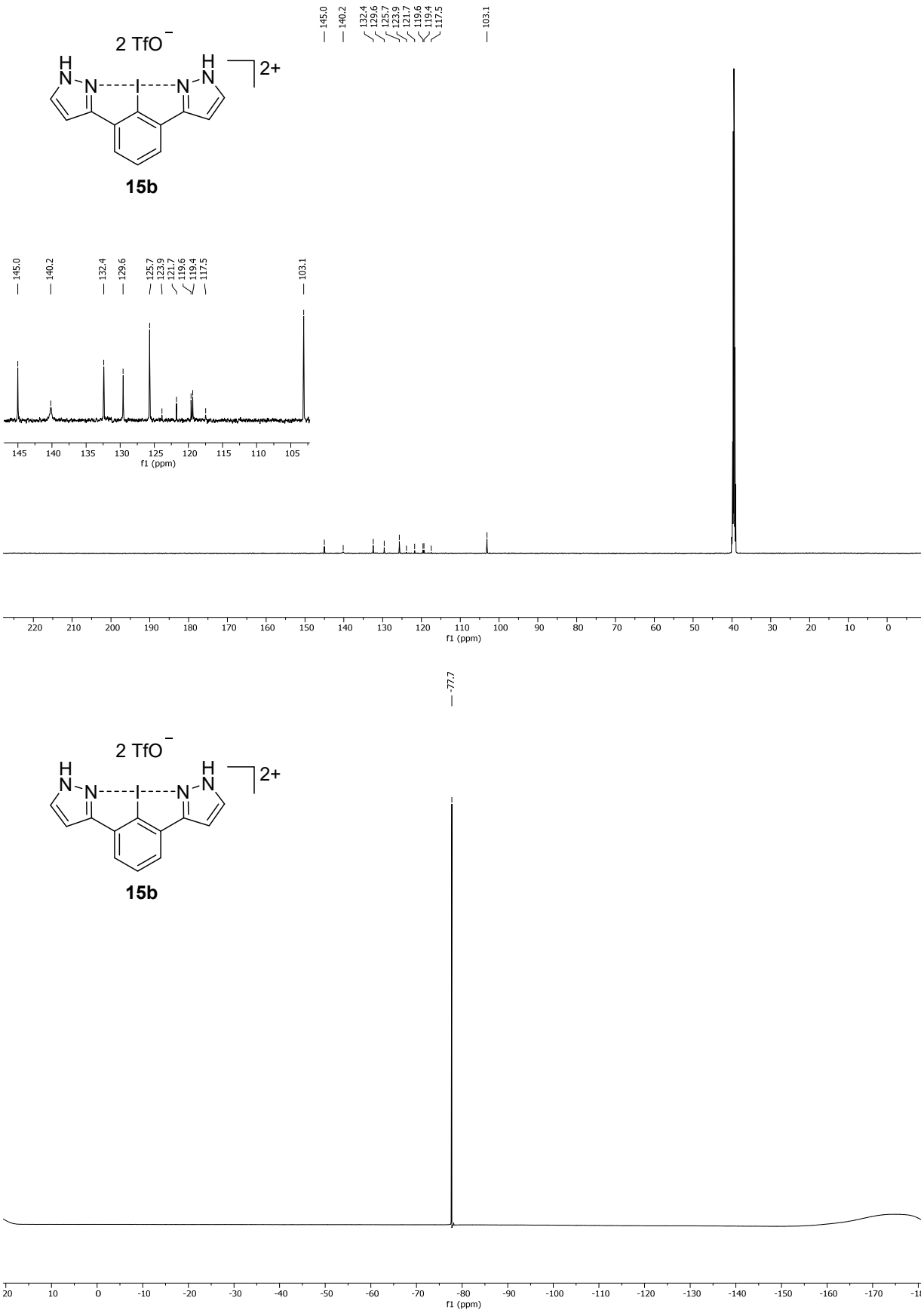


Figure S19: 600 MHz ^{1}H-, 151 MHz ^{13}C- and 565 MHz ^{19}F-NMR spectra of **15b** in d_6-DMSO.

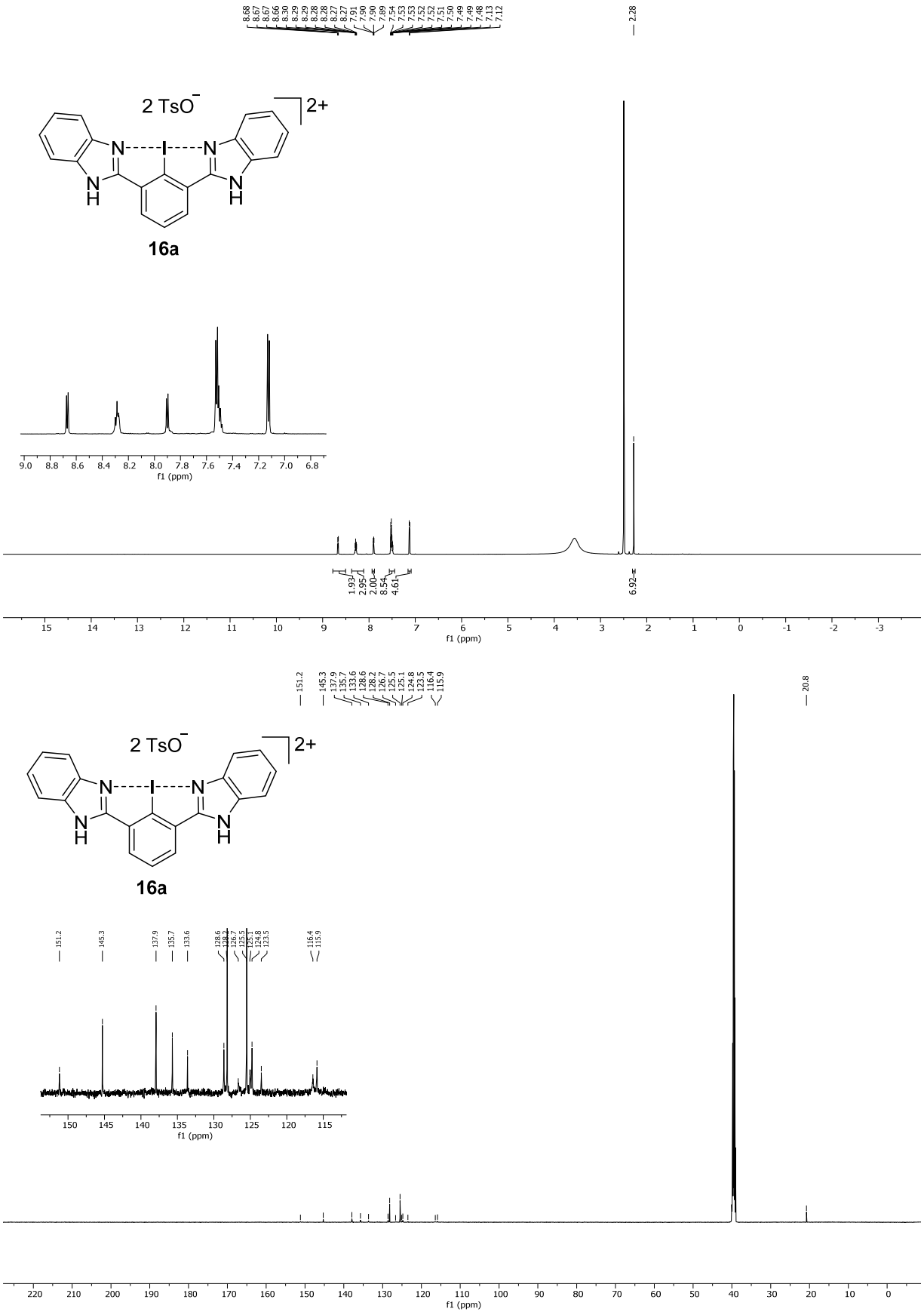


Figure S20: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **16a** in d_6-DMSO.

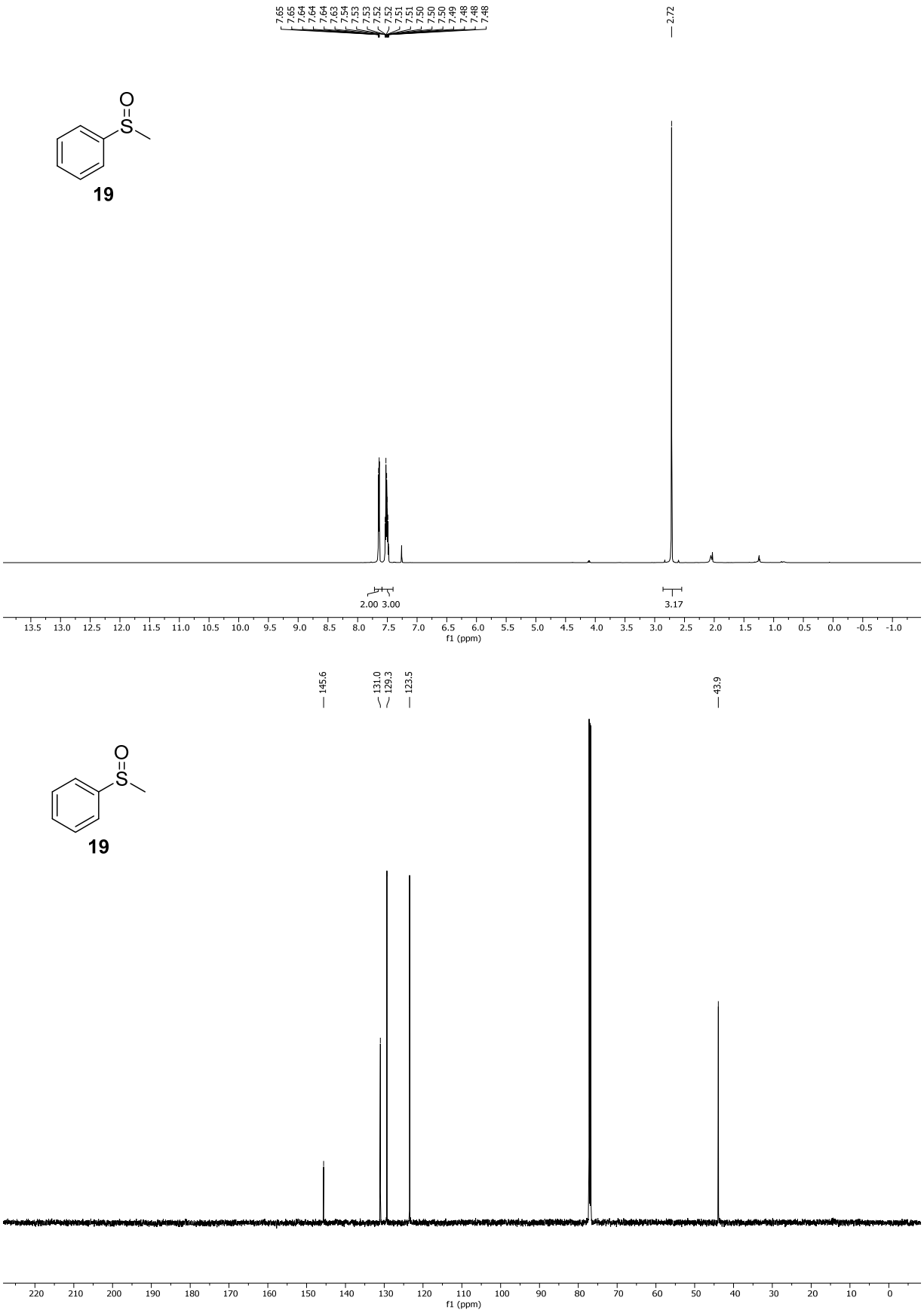


Figure S21: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **19** in $CDCl_3$.

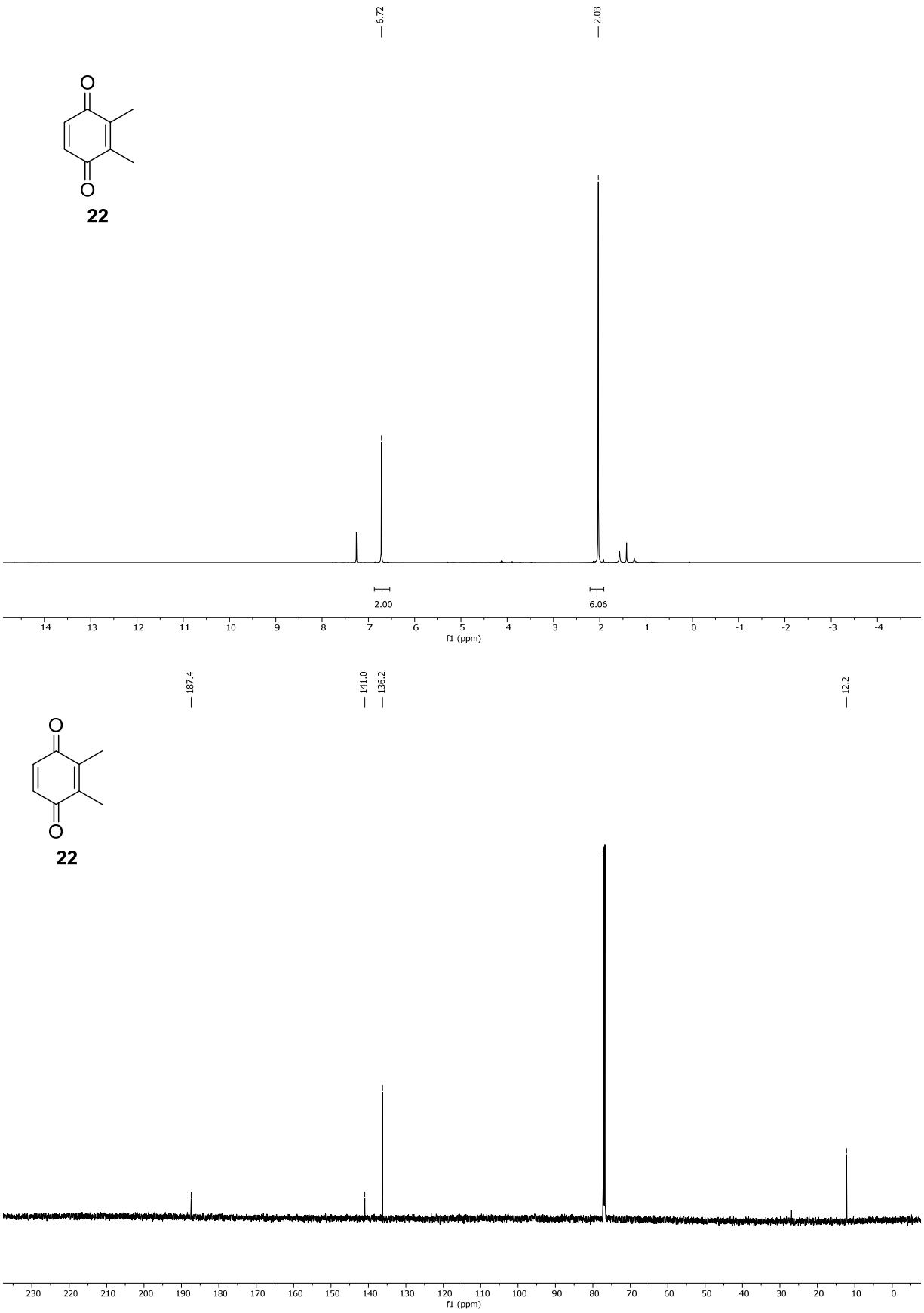


Figure S22: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **22** in $CDCl_3$.

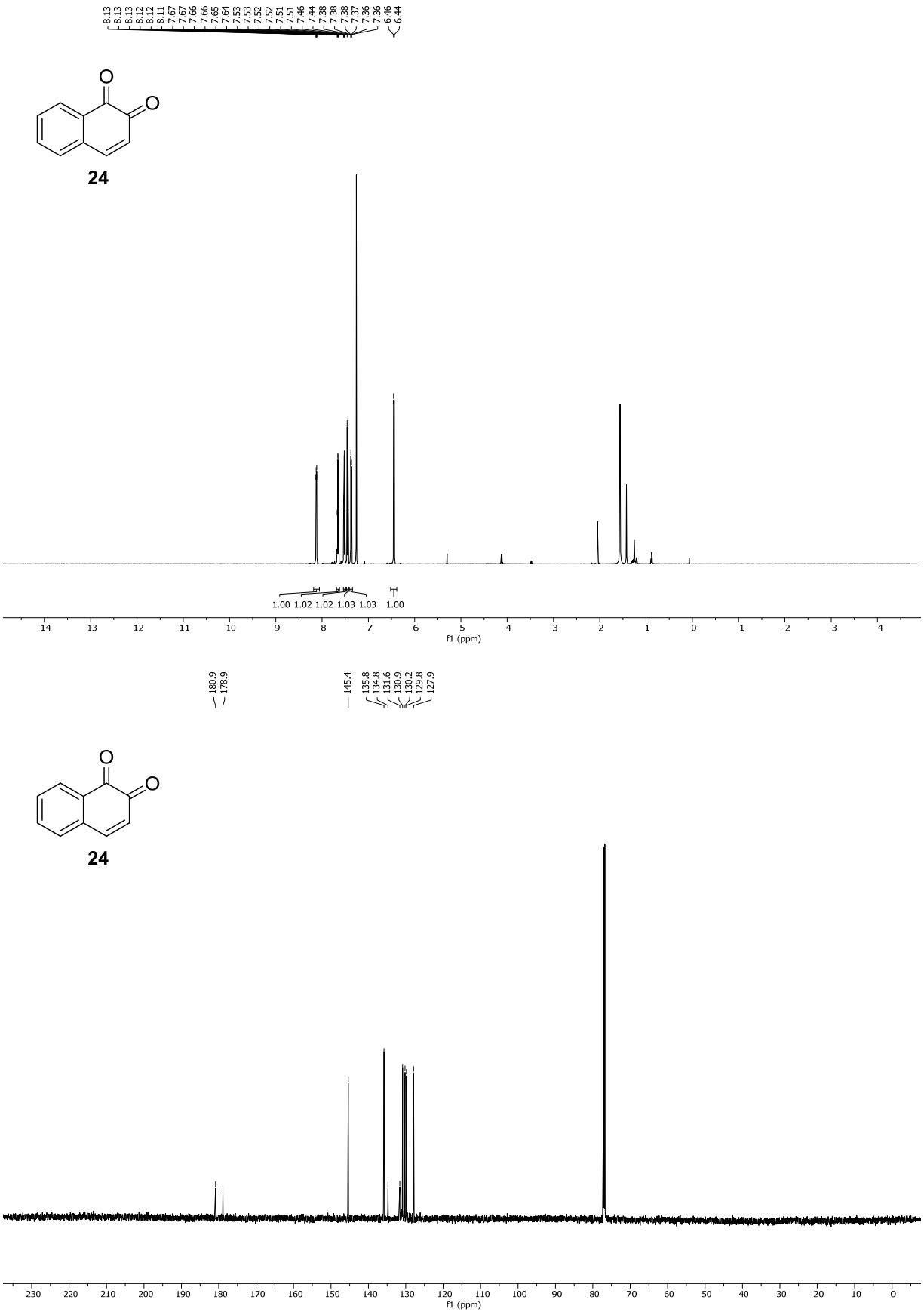


Figure S23: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **24** in $CDCl_3$.

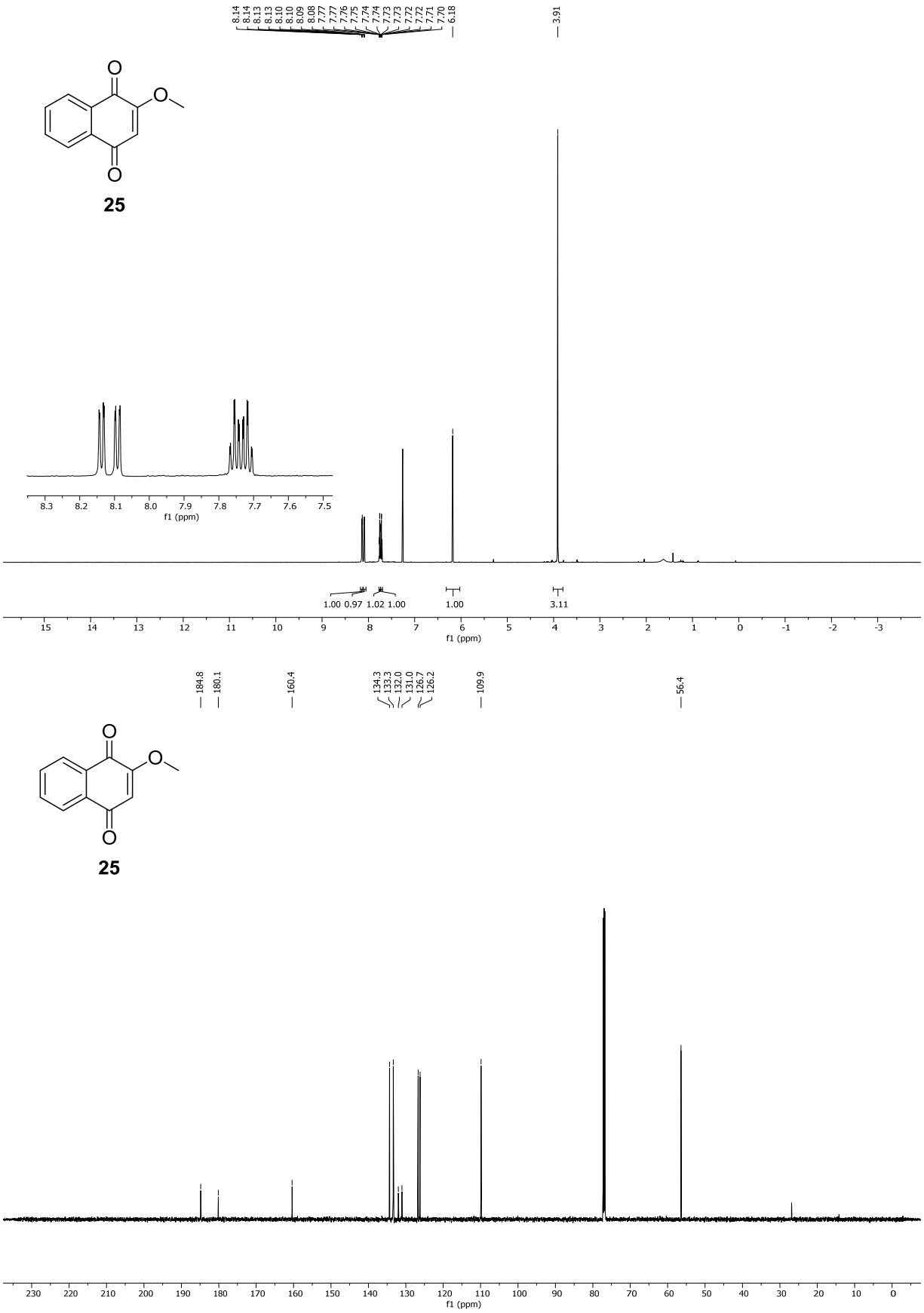


Figure S24: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **25** in $CDCl_3$.

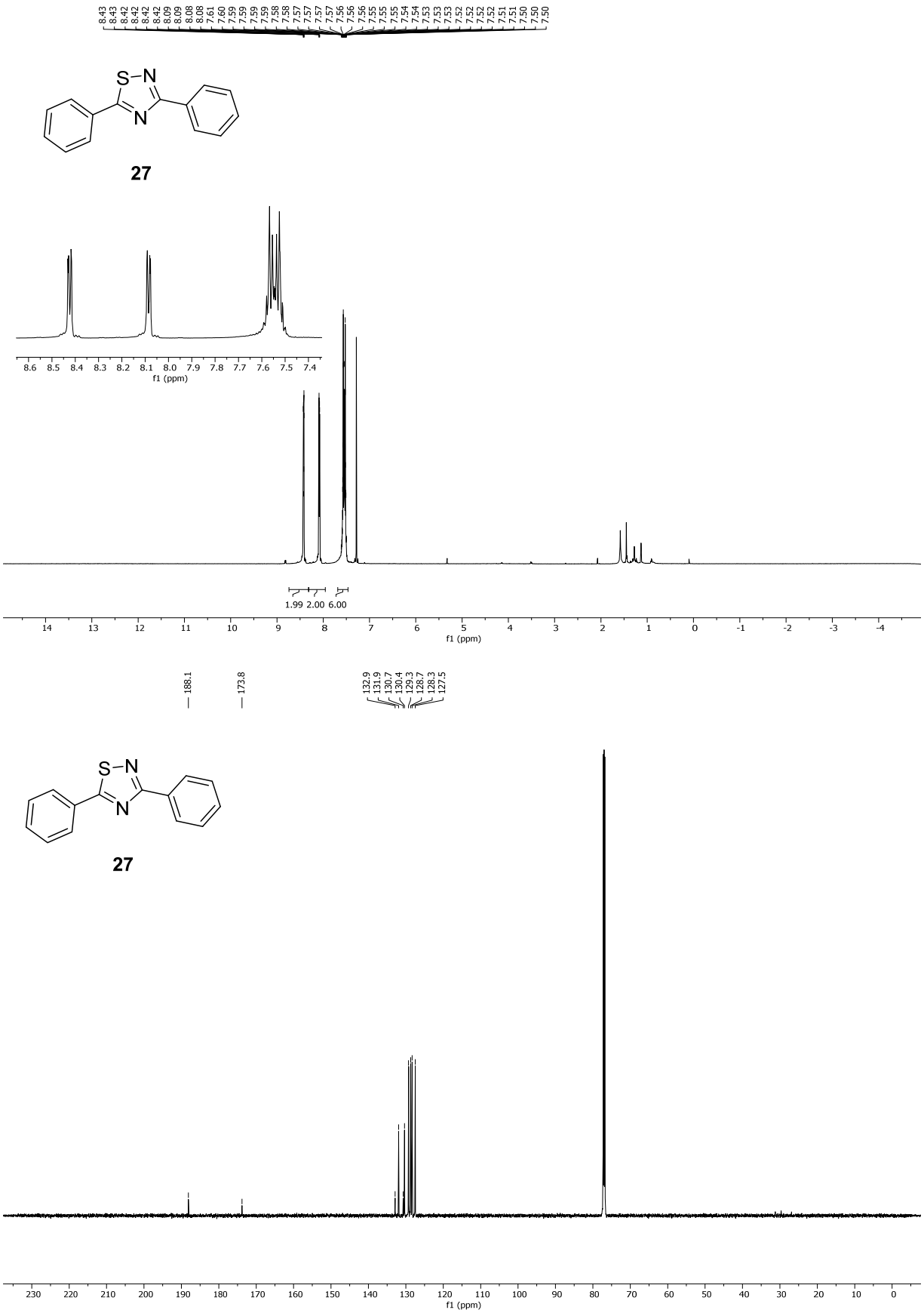


Figure S25: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **27** in $CDCl_3$.

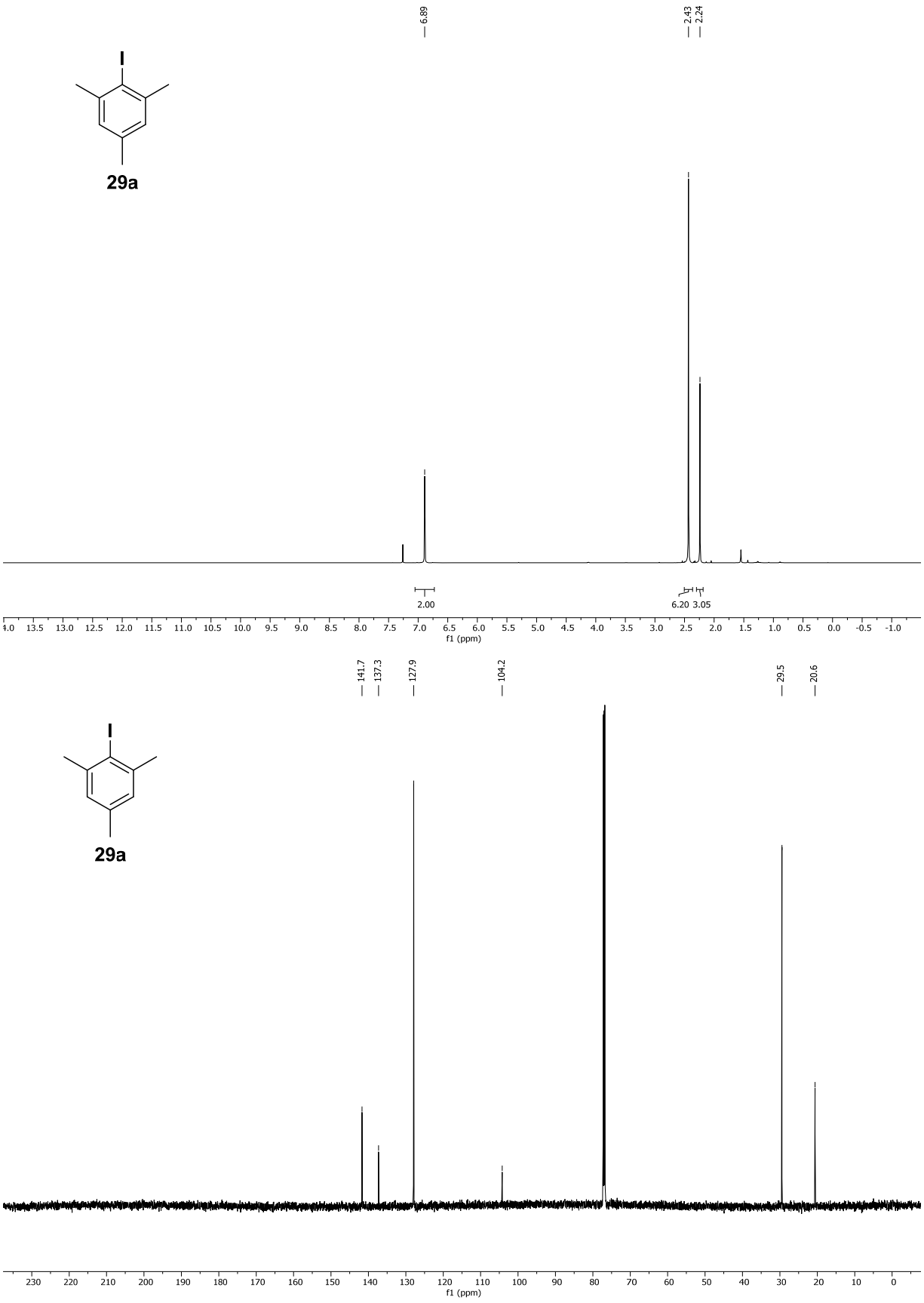
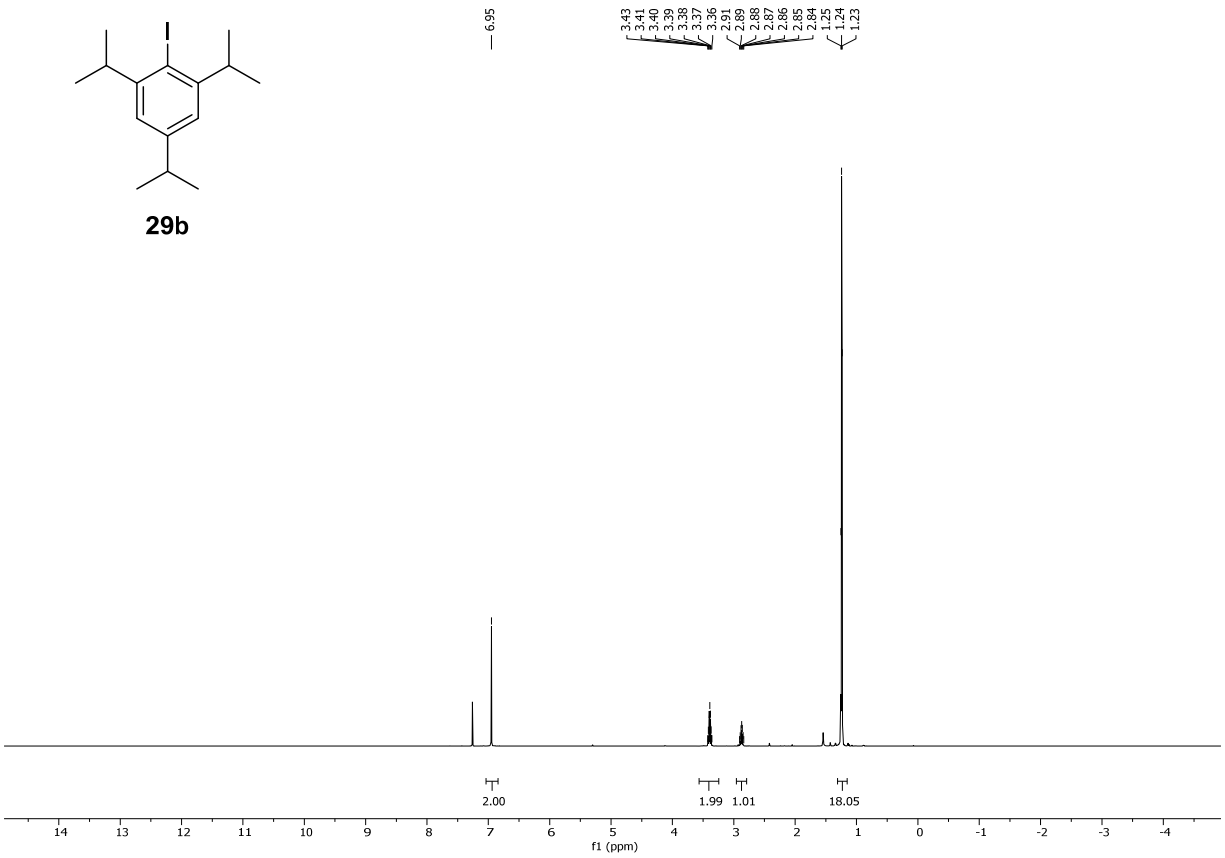
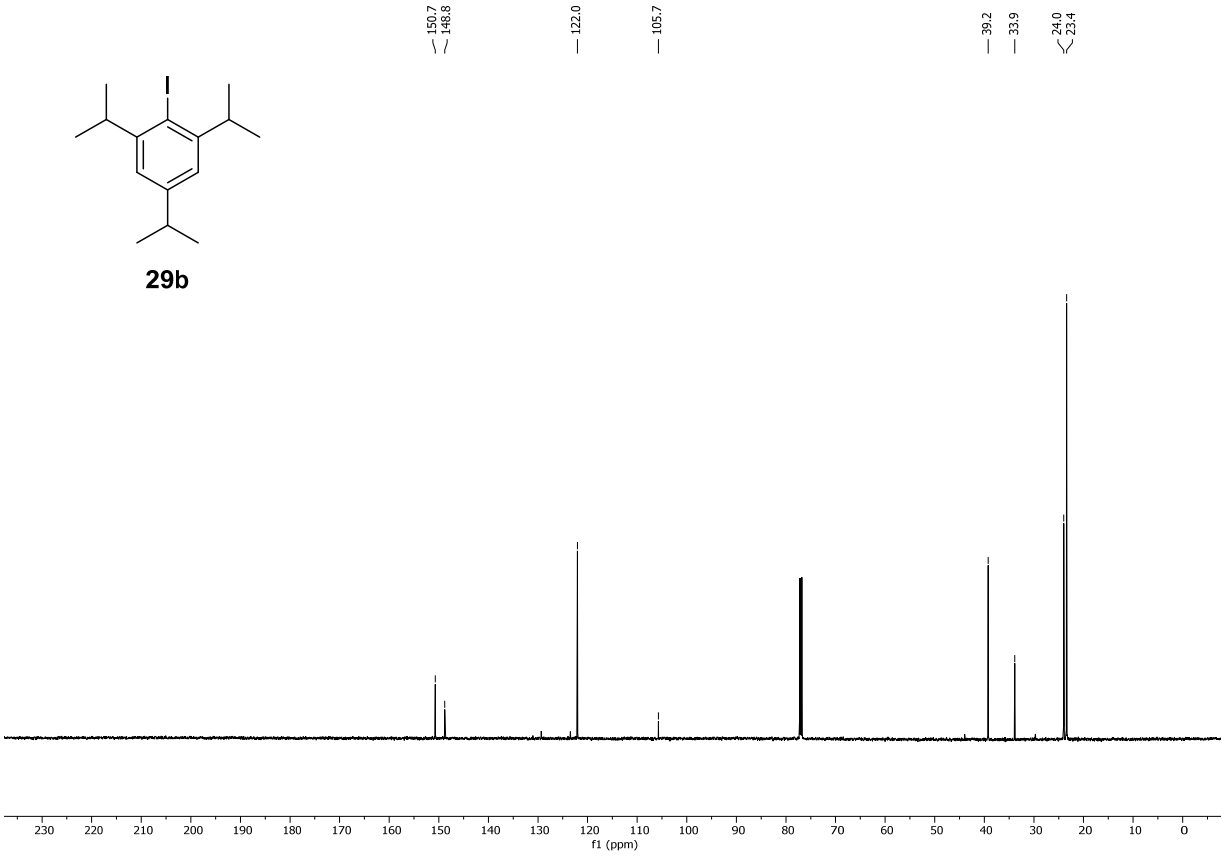


Figure S26: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **29a** in $CDCl_3$.

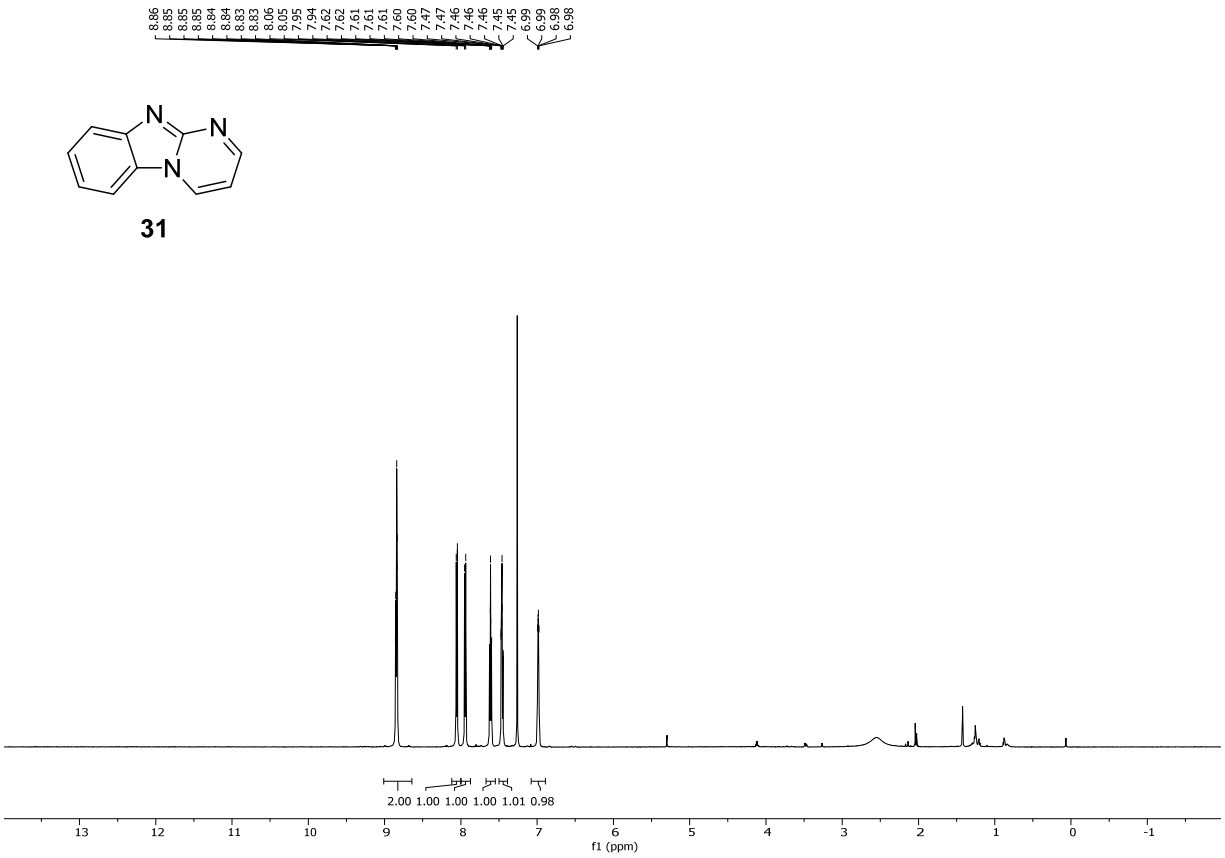


29b



29b

Figure S27: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **29b** in $CDCl_3$.



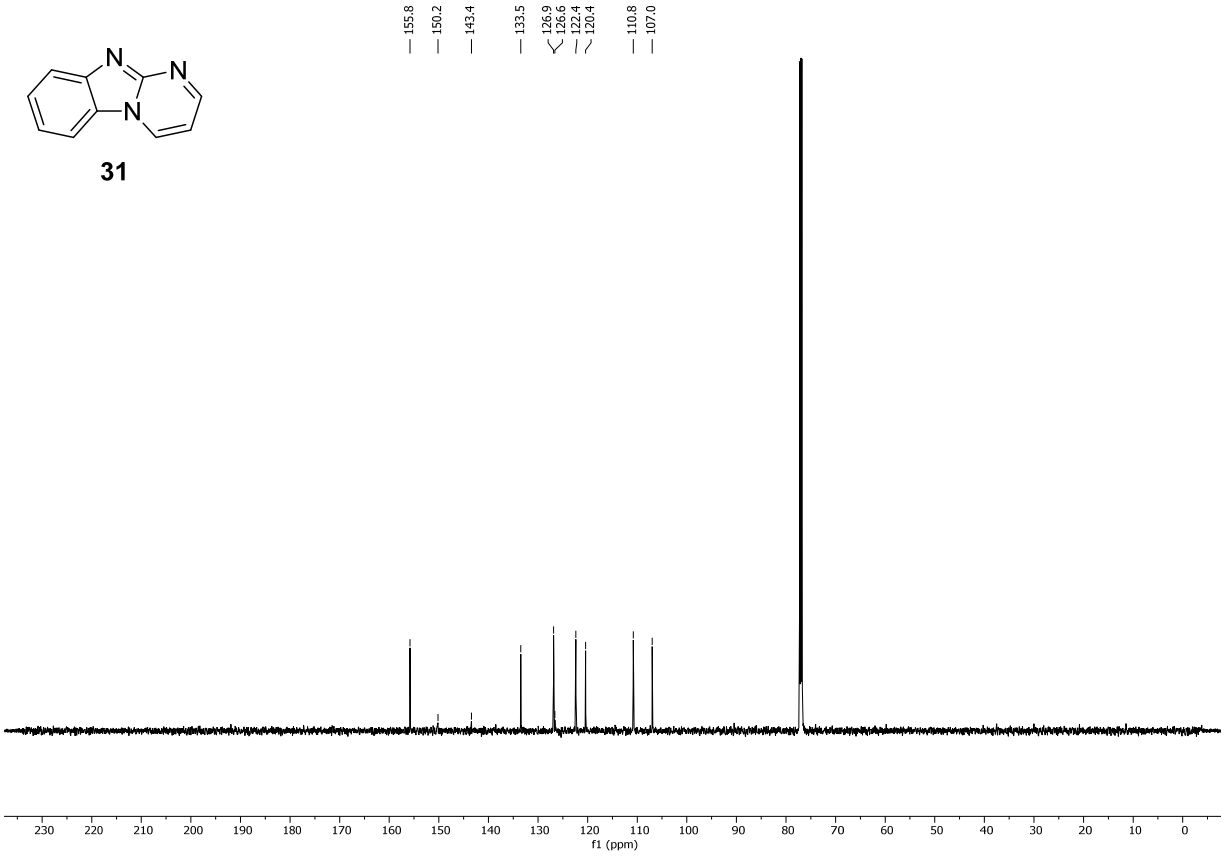


Figure S28: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **31** in $CDCl_3$.

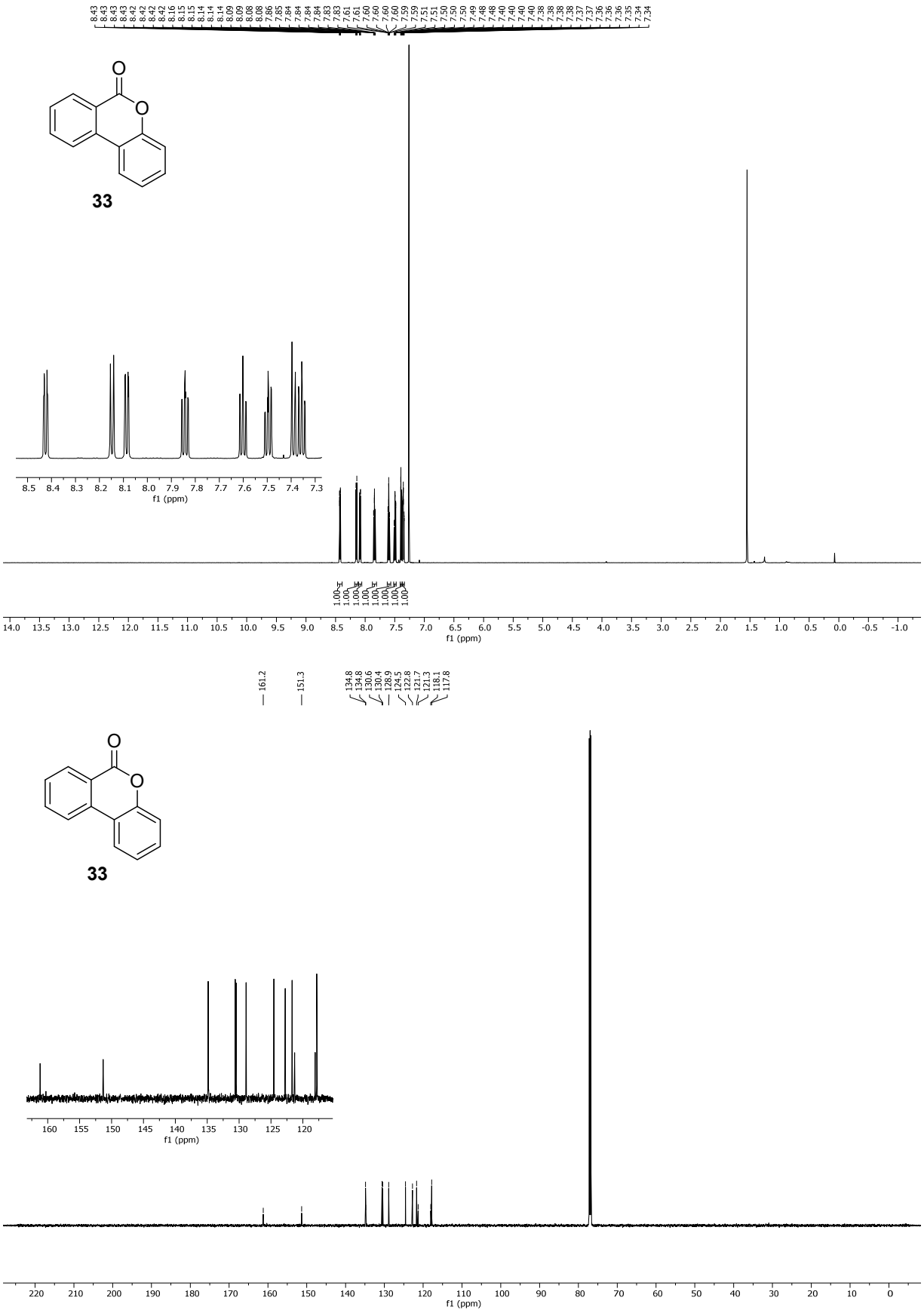


Figure S29: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR spectra of **33** in $CDCl_3$.