Electronic Supplementary Material (ESI) for Chemical Communications.

Ortho-Functionalization of Azobenzenes *via* Hypervalent Iodine Reagents

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1 General Experimental Procedures

Chemicals

*m*CPBA (<77 wt.%) was purchased from Sigma-Aldrich and dried under high vacuum at rt for 3 h, which was found important for the reproducibility of the reactions. The weight percent active oxidant was then determined by iodometric titration[1] and varied between 84-88% in different batches.
Unless otherwise stated, all other chemicals were purchased from commercial suppliers and used as received.

Solvents

CH_2Cl_2, TFE, Et_2O, EtOH, MeOH, cyclohexane and acetic acid were used as received. Toluene, THF, acetonitrile, and EtOAc were dried using a VAC-purification system and degassed for 30 minutes by bubbling argon through a long needle before all reactions. Anhydrous 1,4-dioxane was purchased from Acros Organics in an AcroSeal™ bottle with molecular sieves. For the reproducibility of the reactions, the purity of TFE was found crucial.

Purification and Analysis

TLC analysis was performed on pre-coated silica gel 60 F254 plates using UV light. The crude products were purified by flash column chromatography using 40-60 µm 60A silica gel as stationary phase or using automated flash system Teledyne ISCO CombiFlash Rf 200 with RediSep Rf columns.

Melting points were measured using either a STUART SMP3 and are reported uncorrected, or a Büchi Melting Point M-560 and are reported corrected. The melting point measurements refer to the solidified materials as the result of the given experimental procedures, no additional recrystallization was done.

NMR spectra were recorded on 400 MHz Bruker AVANCE II or 600 MHz Bruker Avance Neo 600 with a BBO probe at 298 K, using $CDCl_3$, DMSO-d_6, or MeOH-d_4 as solvents. Chemical shifts are given in ppm relative to the residual peak of $CDCl_3$ (^{1}H NMR δ 7.26, $^{13}C\{^1H\}$ NMR 77.16), DMSO-d_6 (^{1}H NMR δ 2.50, $^{13}C\{^1H\}$ NMR 39.52) or MeOH-d_4 (^{1}H NMR δ 3.31, $^{13}C\{^1H\}$ NMR 49.00) with multiplicity (s=singlet, ad= apparent doublet, d=doublet, dd=doublet of doublets, ddd= doublet of doublet of doublets, t=triplet, q=quartet, m=multiplet), integration and coupling constants (Hz). Complete analytical data is given for compounds that are novel or not fully characterized in the literature; ^{1}H NMR spectra and $^{13}C\{^1H\}$ NMR spectra are given for literature reported compounds.

High-resolution mass analyses were obtained using a Bruker microTOF ESI. High-resolution EI mass spectra were recorded on a Finnigan MAT 95XL double-focusing mass spectrometer at an ionization energy of 70 eV. Samples were measured by a direct inlet method with a source temperature of 200 C. High-resolution APCI mass spectra were measured by a direct inlet method on a Bruker Impact II mass spectrometer.

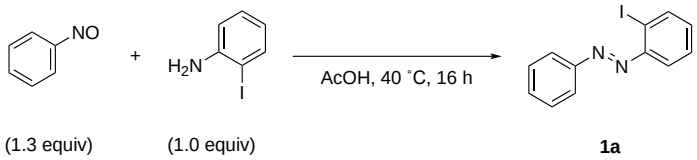
Single crystals were measured on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection. Using Olex2,[2] the structure was solved with the XT[3] structure solution program using Intrinsic Phasing and refined with the SHELXL[4] refinement package using Least Squares minimisation.

UV light illuminations were carried out using an array of three Seoul CUD4AF1B LEDs (340 nm with an optical performance of 55mW each), assembled by Sahlmann Photochemical Solutions. Illuminations with visible light were carried out using one Luxeon LXML-PX01 LED (450 nm with an optical performance of 900mW), assembled by Sahlmann Photochemical solutions. The distance between LED and sample was 1 cm.

UV spectra were recorded at 25 °C with a resolution of 0.5 nm using a UV-2700 spectrometer from Shimadzu with a double monochromator in $CHCl_3$ (spectroscopy grade). High precision quartz cuvettes with a light path length of 10 mm from Hellma Analytics were used. For analyzing the photostationary equilibrium *via* ^1H NMR spectroscopy, quartz NMR tubes from Deutero were used.

2 Synthesis of *ortho*-Iodoazobenzenes 1

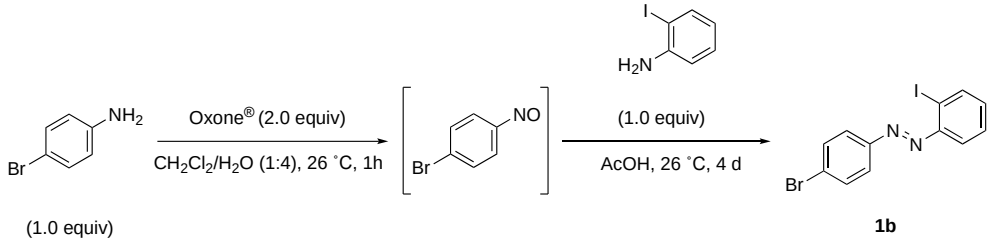
(*E*)-1-(2-Iodophenyl)-2-phenyldiazene (1a)



Following a reported procedure,[5] a solution of 2-iodoaniline (1.0 equiv, 65.0 mmol, 14.2 g) and nitrosobenzene (1.3 equiv, 84.5 mmol, 9.05 g) in acetic acid (400 mL) was stirred for 16 h at 40 °C. The solvent was evaporated, and the residue crystallized from MeOH at 65 °C to yield azobenzene **1a** as a red solid (8.32 g, 27.0 mmol, 42%).

Mp: 63 °C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.02 – 7.99 (m, 2H), 7.64 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.43 (ddd, *J* = 8.0, 7.2, 1.3 Hz, 1H), 7.17 (ddd, *J* = 7.9, 7.2, 1.6 Hz, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 152.5, 151.5, 140.0, 132.3, 131.7, 129.3, 129.1, 123.7, 117.5, 102.6. HRMS(ESI) m/z: calcd. for $C_{12}H_9IN_2^+$ $[M]^+$ 307.9805; found 307.9805 (71), 77.0 (100). Analytical data were in accordance with those previously reported.[5]

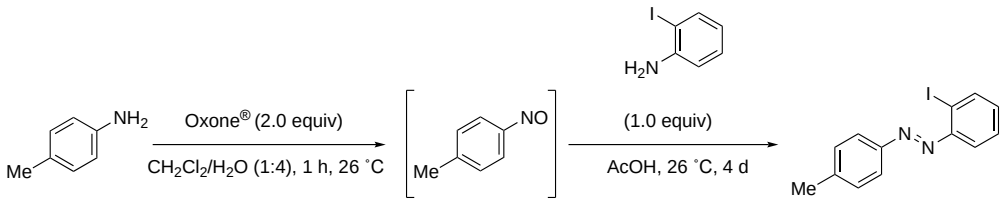
(*E*)-1-(4-Bromophenyl)-2-(2-iodophenyl)diazene (1b)



Following a reported procedure,[5] 4-bromoaniline (1.0 equiv, 12.0 g, 70.0 mmol) was dissolved in CH_2Cl_2 (150 mL). Oxone® (2.0 equiv, 86.1 g, 150 mmol) dissolved in water (600 mL) was added to this solution. The reaction mixture was stirred for 3 h at 26 °C under a nitrogen atmosphere, upon which the colour of the solution turned to green. After separation of the layers, the aqueous layer was extracted with DCM (3 × 200 mL). The combined organic layers were washed with 1 N HCl (300 mL), saturated $NaHCO_3$ solution (300 mL), water (300 mL), brine (300 mL) and dried over magnesium sulfate. The organic phase was filtered and concentrated under reduced pressure yielding the corresponding labile nitroso-arene, which was submitted to the next condensation step without further purification. The nitroso-arene (1.0 equiv, 11.9 g, 64.0 mmol) and 2-iodoaniline (1.0 equiv, 14.0 g, 64.0 mmol) were dissolved in acetic acid (200 mL) and stirred for 4 d at 26 °C. The formed precipitate was separated by filtration. The collected solid was washed with acetic acid (100 mL) and dried under reduced pressure to yield azobenzene **1b** as an orange solid (15.3 g, 39.4 mmol, 62%).

Mp: 116 °C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.64 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.43 (ddd, *J* = 8.0, 7.2, 1.3 Hz, 1H), 7.18 (ddd, *J* = 7.9, 7.2, 1.6 Hz, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 151.3, 151.2, 140.1, 132.7, 132.6, 129.1, 126.3, 125.1, 117.4, 103.0. HRMS(ESI) m/z: calcd. for $C_{12}H_8BrIN_2^+$ $[M]^+$ 385.8910; found 385.8914 (44), 76.0 (100). Analytical data were in accordance with those previously reported.[6]

(*E*)-1-(2-Iodophenyl)-2-(*p*-tolyl)diazene (1c)

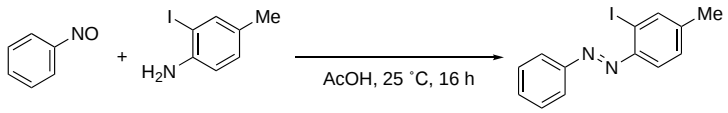


(1.0 equiv) **1c**

Following a reported procedure,[5] *p*-toluidine (1.0 equiv, 3.75 g, 35.0 mmol) was dissolved in CH_2Cl_2 (75 mL). Oxone® (2.0 equiv, 43.1 g, 70.0 mmol) dissolved in water (300 mL) was added to this solution. The reaction mixture was stirred for 1 h at 26 °C under a nitrogen atmosphere, upon which the colour of the solution turned to green. The layers were separated, and the organic phase was concentrated under reduced pressure yielding the corresponding labile nitroso-arene, which was submitted to the next condensation step without further purification. The nitroso-arene (1.0 equiv, 1.14 g, 9.41 mmol) and 2-iodoaniline (1.0 equiv, 2.06 g, 9.41 mmol) were dissolved in acetic acid (200 mL) and stirred for 15 h at 85 °C. After cooling down, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica (eluent: cyclohexane) to yield azobenzene **1c** as a red solid (906 mg, 2.81 mmol, 30%).

Mp: 80 °C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.42 (ddd, *J* = 8.0, 7.2, 1.3 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.15 (ddd, *J* = 7.9, 7.2, 1.6 Hz, 1H), 2.45 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 151.5, 150.7, 142.4, 139.9, 132.0, 130.0, 129.0, 123.7, 117.5, 102.4, 21.7. HRMS(ESI) m/z: calcd. for $C_{13}H_{11}IN_2^+$ $[M]^+$ 321.9961; found 321.9963 (33), 91.0 (100). Analytical data were in accordance with those previously reported.[5]

(*E*)-1-(2-Iodo-4-methylphenyl)-2-phenyldiazene (1d)

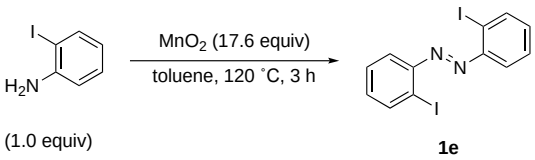


(1.3 equiv) (1.0 equiv) **1d**

Following a reported procedure,[5] A solution of 2-iodo-4-methylaniline (1.0 equiv, 25.0 mmol, 6.23 g) and nitrosobenzene (1.3 equiv, 32.5 mmol, 3.48 g) in acetic acid (400 mL) was stirred for 16 h at 25 °C. The solvent was evaporated, and the residue recrystallized from MeOH at 65 °C to yield azobenzene **1d** as a red solid (7.02 g, 20.8 mmol, 83%).

Mp: 56 °C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.87 (ad, *J* = 1.0 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.50 – 7.47 (m, 1H), 7.23 (dd, *J* = 8.2, 1.0 Hz, 1H), 2.39 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 152.5, 149.4, 143.3, 140.3, 131.4, 129.9, 129.3, 123.6, 117.0, 103.4, 21.0. HRMS(ESI) m/z: calcd. for $C_{13}H_{11}IN_2^+$ $[M]^+$ 307.9805; found 321.9963 (67), 77.0 (100). Analytical data were in accordance with those previously reported.[7]

(*E*)-1,2-Bis(2-iodophenyl)diazene (1e)

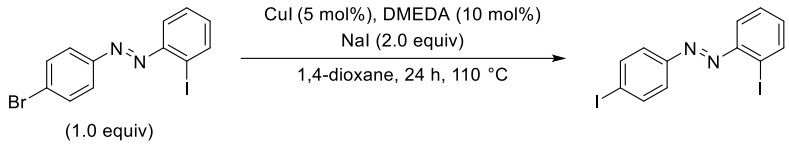


(1.0 equiv) **1e**

Following a reported procedure,[8] a solution of 2-iodoaniline (1.0 equiv, 45.7 mmol, 10.0 g) and activated manganese dioxide (17.6 equiv, 805 mmol, 70.0 g) in toluene (400 mL) was stirred for 3 h at 120 °C. The warm reaction mixture was filtered through silica and washed with toluene (400 mL). The solvent was evaporated yield azobenzene **1e** as a red solid (7.77 g, 17.9 mmol, 78%).

Mp: 141 °C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.77 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.46 (ddd, *J* = 8.0, 7.3, 1.3 Hz, 2H), 7.20 (ddd, *J* = 7.9, 7.3, 1.6 Hz, 2H). ^{13}C-NMR(151 MHz, $CDCl_3$) δ 151.0, 140.1, 132.9, 129.2, 118.4, 103.4 HRMS(APCI) m/z: calcd. for $[C_{12}H_8I_2N_2 + H]^+$ $[M + H]^+$ 434.8849; found 434.8845 (100). Analytical data were in accordance with those previously reported.[8]

(*E*)-1-(2-Iodophenyl)-2-(4-iodophenyl)diazene (1f)

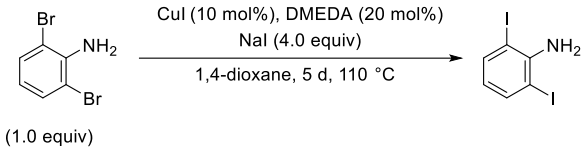


(1.0 equiv) **1b** **1f**

Under inert conditions, azobenzene **1b** (1.0 equiv, 38.8 mg, 100 µmol), copper iodide (5 mol%, 1.0 mg, 5.25 µmol), sodium iodide (2.0 equiv, 30.0 mg, 200 µmol) and *N,N'*-dimethylethylenediamine (10 mol%, 1.08 µL, 10.0 µmol) were dissolved in dry 1,4-dioxane (1 mL) in a high pressure tube. The reaction mixture was stirred for 24 h at 110 °C. The resulting suspension was allowed to reach 22 °C, diluted with $NaHCO_3$ solution (10 mL), poured into water (10 mL), and extracted with dichloromethane (3 × 15 mL). The combined organic phases were dried over magnesium sulfate, filtered and concentrated yielding azobenzene **1f** as an orange solid (38.3 mg, 88.2 µmol) in 88% yield.

Mp: 114 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.43 (ddd, *J* = 8.0, 7.2, 1.3 Hz, 1H), 7.18 (ddd, *J* = 7.9, 7.2, 1.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7, 151.2, 140.1, 138.6, 132.7, 129.1, 125.2, 117.4, 103.0, 98.7. HRMS(EI) m/z: calcd. for $C_{12}H_8I_2N_2^+$ $[M]^+$ 433.8771; found 433.8776. Analytical data were in accordance with those previously reported.[9]

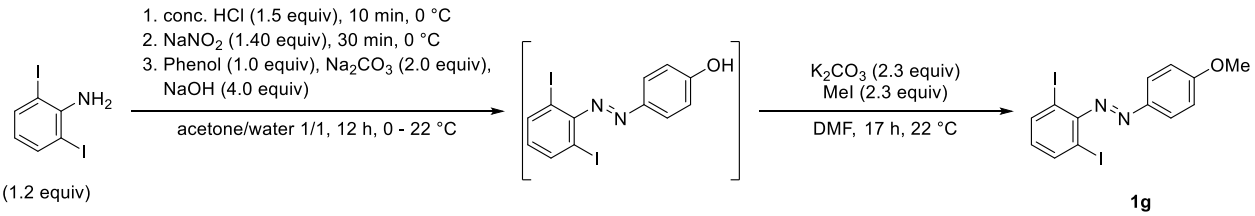
(*E*)-1-(2,6-Diiodophenyl)-2-(4-methoxyphenyl)diazene (1g)



(1.0 equiv)

Under inert conditions, 2,6-dibromoaniline (1.0 equiv, 3.76 g, 15.0 mmol), copper iodide (10 mol%, 286 mg, 1.50 mmol), sodium iodide (4.0 equiv, 8.99 g, 60.0 mmol) and *N,N'*-dimethyl-ethylenediamine (20 mol%, 323 µL, 3.00 mmol) were dissolved in dry 1,4-dioxane (75 mL) in a high pressure tube. The reaction mixture was stirred for 5 d at 110 °C. The resulting suspension was allowed to reach 22 °C, diluted with $NaHCO_3$ solution (50 mL), poured into water (50 mL), and extracted with dichloromethane (3 × 100 mL). The combined organic phases were dried over magnesium sulfate, filtered and concentrated yielding the product as a beige solid (5.04 g, 14.6 mol) in 98% yield.

Mp: 121 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2H), 6.16 (t, *J* = 7.8 Hz, 1H), 4.61 (s, br, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.2, 139.5, 121.4, 81.7. HRMS(EI) m/z: calcd. for $C_6H_5I_2N^+$ $[M]^+$ 344.8506; found 344.8503.



(1.2 equiv)

1g

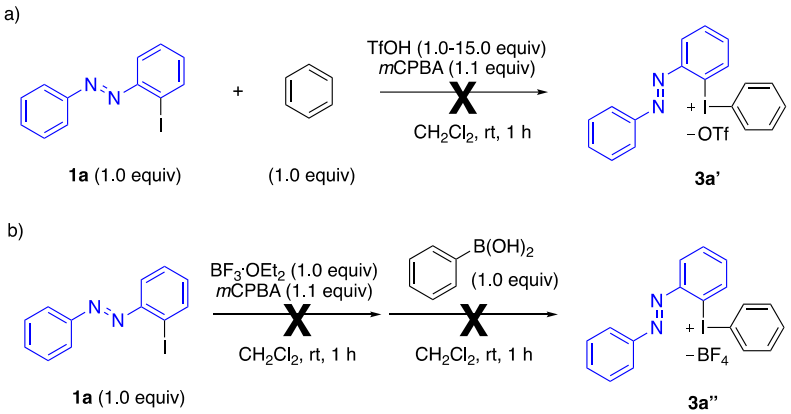
2,6-Diiodoaniline (1.2 equiv, 1.62 g, 4.70 mmol) was dissolved in a mixture of acetone/water (1:1, 20 mL) and cooled to 0 °C. Subsequently, conc. HCl (1.5 equiv, 5.88 mmol, 488 µL) was added dropwise to the solution and left to stir for another 10 min. Sodium nitrite (1.4 equiv, 37.8 mg, 5.48 mmol) dissolved in water (4 mL) was added dropwise and the reaction mixture was stirred for 30 min. Meanwhile, phenol (1.0 equiv, 369 mg, 3.91 mmol), Na_2CO_3 (2.0 equiv, 830 mg, 7.82 mmol) and NaOH (4.0 equiv, 626 mg, 15.7 mmol) were dissolved in acetone/water (1:1, 20 mL) and the obtained solution was cooled to 0 °C. The first prepared solution was slowly added to the solution containing the phenol over the course of 5 min. The resulting mixture was stirred for 12 h while slowly warmed to 21 °C. Subsequently, the mixture was diluted with an aqueous HCl solution (1 N, 30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic phases were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The obtained crude azobenzene (1.0 equiv, 1.76 g, 3.91 mmol), potassium carbonate (2.3 equiv, 1.24 g, 8.99 mmol) and iodomethane (2.3 equiv, 1.28 g, 560 µL, 8.99 mmol) were dissolved in DMF (10 mL) and stirred at 25 °C for 21 h. Water (100 mL) was added and the mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic phases were washed with an aqueous HCl solution (1 N, 100 mL), an aqueous $NaHCO_3$ solution (1 N, 100 mL), brine (100 mL), dried over magnesium sulfate and filtered. The solvent was removed under reduced pressure and the residue was purified by recrystallization from MeOH at 78 °C yielding azobenzene **1g** as a red solid (1.79 g, 3.80 mmol) in 97% yield.

Mp: 98 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.71 (t, *J* = 7.9 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4, 153.7, 145.7, 140.2, 130.2, 125.6, 114.6, 88.0, 55.9. HRMS(EI) m/z: calcd. for $C_{13}H_{10}I_2N_2O^+$ $[M]^+$ 463.8877; found 463.8875.

3 Synthesis of *ortho*-Azobenzene-Derived Diaryliodonium Salts 3

3.1 Optimization Studies

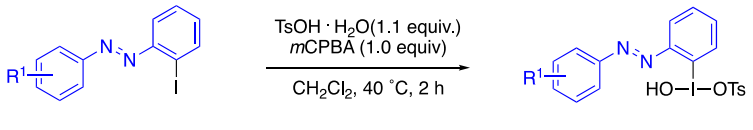
Initial screening of suitable conditions for the synthesis of diaryliodonium salts **3** from *ortho*-iodoazobenzene **1a** was performed. Our standard one-pot method[10] with *m*CPBA and triflic acid failed in delivering the diaryliodonium triflate **3a'**, as shown in **Scheme S1a**. Increasing the equivalents of TfOH (to 15 equiv) did not provide the desired product. In addition, our one-pot procedure[11] with arylboronic acid using $BF_3{\cdot}OEt_2$ failed, and product **3a''** could not be obtained (**Scheme S1b**). In both one-pot procedures, the unreacted *ortho*-iodoazobenzene **1a** and its decomposition to the unsubstituted azobenzene was detected by ^{1}H NMR spectroscopy of the crude mixture. Increasing the amount of triflic acid from 1.0 equiv to 15.0 equiv led to further decomposition: A black mixture was obtained and many side products were observed by ^{1}H NMR spectroscopy.



Scheme S1. One-pot synthesis from *ortho*-iodoazobenzene **1a** with a) benzene, TfOH and *m*CPBA; b) $BF_3{\cdot}OEt_2$, *m*CPBA, and arylboronic acid.

Further investigations focused on stepwise synthesis of reagents **3** through isolation of the corresponding Koser's reagents **21**.[12] Under literature conditions,[12-13] compound **21a** could be obtained in 68% yield (**Table S1**, entry 1). When TFE was used as the co-solvent, the product could not be detected (entry 2). Repeating the reaction at 0.5 mmol scale, product **21a** was isolated in 64% yield (entry 3), and further increased scale resulted in excellent yields of **21a** (entries 4, 5). Moreover, the reaction was performed with *p*-bromo-substituted azobenzene **1b** and product **21b** could be obtained in good yield of 88% (entry 6).

Table S1. Reaction conditions used for the synthesis of Koser's reagent **21**. [a] Isolated yield.

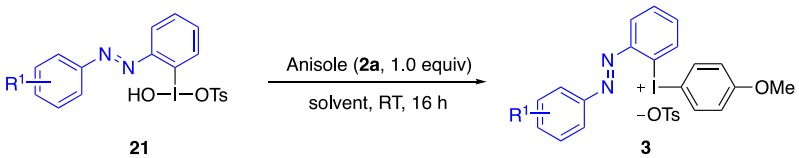


1 — 21 Koser's reagent

Entry	*n* (mmol)	R^1	Solvent	*T* (°C)	*t* (h)	Yield (%)[a]
1	0.30	H	CH_2Cl_2 (0.2 M)	40	2	**21a** 68
2	0.20	H	CH_2Cl_2/TFE (1:1)	40	2	-
3	0.50	H	CH_2Cl_2 (0.2 M)	40	2	**21a** 64
4	1.00	H	CH_2Cl_2 (0.2 M)	40	2	**21a** 92
5	2.00	H	CH_2Cl_2 (0.2 M)	40	2	**21a** 98
6	1.00	*p*-Br	CH_2Cl_2 (0.2 M)	40	2	**21b** 88

A small optimization was performed for the second step, where anisole (**2a**) was added to the Koser's reagent **21a**. With the idea of performing a sequential one-pot procedure, CH_2Cl_2 was used as the solvent of the reaction, which provided product **3a** in 67% yield (**Table S2**, entry 1). Next, TFE was added as the co-solvent in a ratio of 1:1 with CH_2Cl_2 and **3a** was obtained in good yield of 83% yield (entry 2). The diaryliodonium salt **3a** could also be obtained in 85% yield on a larger scale (entry 3). In entry 4, the product was isolated in lower yield (55%) compared to entry 3. We noticed a loss of product **3a** during the precipitation, and a detailed procedure for this step is described in **Section 3.2**. Finally, these conditions worked well in the case of *p*-bromo-substituted reagent **21b** delivering product **3b** in 90% yield (entry 5).

Table S2. Reaction conditions used for the synthesis of diaryliodonium salt **3**. [a] Isolated yield.

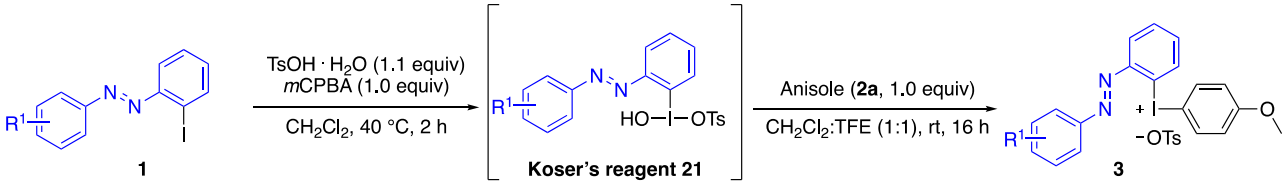


21 **3**

Entry	*n* (mmol)	R^1	Solvent	*T* (˚C)	*t* (h)	Yield (%)[a]
1	0.10	H	CH_2Cl_2	rt	16	**3a** 67
2	0.30	H	CH_2Cl_2/TFE (1:1)	rt	16	**3a** 83
3	1.80	H	CH_2Cl_2/TFE (1:1)	rt	16	**3a** 85
4	1.80	H	CH_2Cl_2/TFE (1:1)	rt	16	**3a** 55
5	0.60	*p*-Br	CH_2Cl_2/TFE (1:1)	rt	16	**3b** 90

Finally, a sequential one-pot procedure was developed,[12-14] with in situ formation of Koser's reagent **21** followed by addition of the arene **2a**. Surprisingly, salt **3a** could be isolated in 84% yield (**Table S3**, entry 1) as described in **Section 3.2**. To prove the strength of the sequential one-pot procedure, reactions were also performed on a large scale (2.0 and 3.2 mmol scale, entry 2 and 3), and the product **3a** could be successfully isolated in good yields of 89% and 77% respectively. The sequential one-pot procedure was also successful in case of EWG and EDG substituents. Indeed, on a larger scale, salt **3b** having *para*-bromine substituent was obtained in 71% yield and 84% yield (entry 4 and 5). Even salt **3d** could be isolated in good yield of 76% (entry 6), and 88% yield was obtained when the reaction scale was increased to 1.0 mmol scale (entry 7).

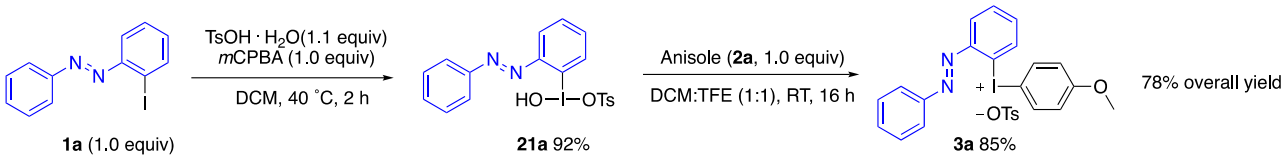
Table S3. A sequential one-pot procedure for the synthesis of diaryliodonium salt **3**. [a] Isolated yield.



1 **Koser's reagent 21** **3**

Entry	*n* (mmol)	R^1	Yield (%)[a]
1	1.00	H	**3a** 84
2	2.00	H	**3a** 89
3	3.20	H	**3a** 77
4	0.20	*p*-Br	**3b** 71
5	1.00	*p*-Br	**3b** 84
6	0.30	*p*-Me	**3c** 76
7	1.00	*p*-Me	**3c** 88

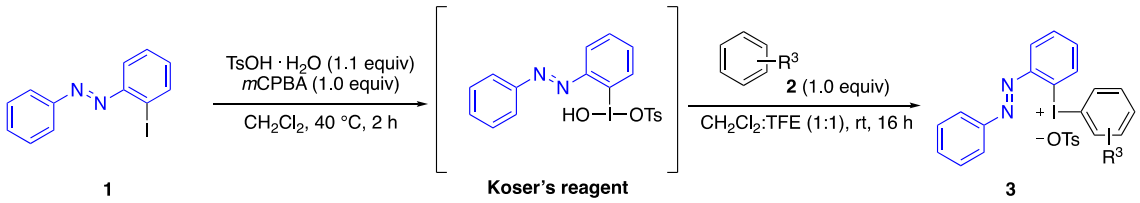
The efficiency of the sequential one-pot transformation was compared with the stepwise synthesis as depicted in **Scheme S2**. The stepwise synthesis *via* isolation of the Koser's reagent **21a** before adding the anisole **2a** yielded the diaryliodonium salt **3a** in a 78% overall yield. Therefore, the sequential one-pot procedure was used instead.



Scheme S2. Comparison of the sequential one-pot procedure with the stepwise synthesis.

Different dummy arenes, such as 1,3,5-trimethylbenzene (mesitylene, **2b**), 1,3,5-trimethoxybenzene (**2c**) and benzene (**2d**), were employed under the optimized condition in the sequential one-pot procedure (**Table S4**). When mesitylene was used, the diaryliodonium salt **3e** could only be obtained in 33% yield (entry 2). All attempts were in vain to get product **3e** in better yield even when solvents, temperature, and reaction time were changed. To the contrary, the reaction with **2c** delivered the product in good yield (entry 3). Finally, when benzene was used in the reaction, product **2d** could not be obtained but the corresponding Koser's reagent was isolated (entry 4). Different conditions were tried, e. g. mixture of solvents, prolongated reaction time and elevated temperature. However, in all cases, the Koser's reagent was obtained as the only product.

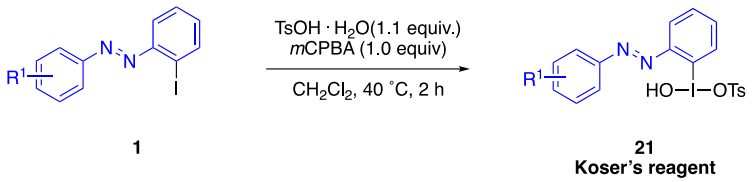
Table S4. A sequential one-pot procedure for synthesizing diaryliodonium salt **3** with different dummies. [a] Isolated yield.



Entry	Scale (mmol)	arene 2	Yield (%)[a]
1	1.0	anisole (**2a**)	**3a** 84
2	1.0	mesitylene (**2b**)	**3e** 33
3	0.2	1,3,5-trimethoxybenzene (**2c**)	**3f** 76
4	0.2	benzene (**2d**)	-

3.2 General Procedures

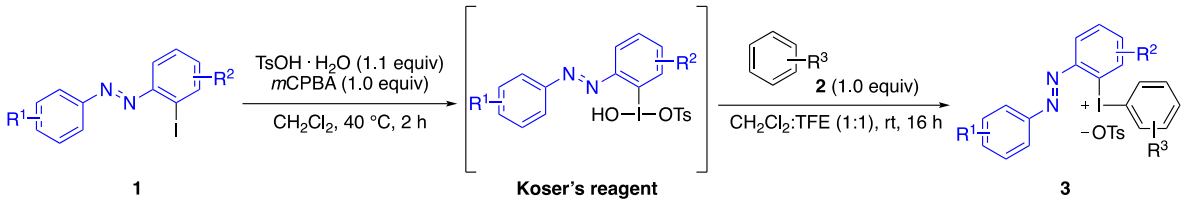
General Procedure for the Synthesis of Koser's Reagents 21



1 **21**
Koser's reagent

Following a reported procedure,[12] iodoazobenzene **1** (1.0 equiv, 1.0 mmol) was dissolved in CH_2Cl_2 0.2 M (5 mL) following by the addition of *m*CPBA (88%, 1.0 equiv, 1.0 mmol) and TsOH·H_2O (1.1 equiv, 1.1 mmol). The reaction mixture was stirred at 40 °C for 2 h. The solvent was removed under reduced pressure, and diethyl ether (5 mL) was added to the residue and stirred for 30 minutes. The solid was filtrated and washed with diethyl ether (5 mL) to obtain the pure compound **21**.

General One-Pot Procedure for the Synthesis of Diaryliodonium Salts 3



1 **Koser's reagent** **3**

*m*CPBA (1.0 equiv, 1.0 mmol) was added to the iodoazobenzene **1a** (1.0 equiv, 1.0 mmol) in CH_2Cl_2 (0.2 M, 5 mL), followed by the addition of TsOH·H_2O (1.1 equiv, 1.1 mmol) and the temperature was raised to 40 °C for 2 h. After cooling to rt, the solvent was evaporated *in vacuo*. The resulting mixture was then dissolved in a mixture of CH_2Cl_2/TFE (1:1, 0.2M) followed by the addition of the arene (1.0 mmol). The reaction was stirred for 16 h at rt, and the solvent was removed after this time. Et_2O (10 mL) was added, and the mixture was left in the -18 °C 16 h prior to filtration. *NB: It is essential to leave the mixture in the freezer due to its initial solid-oil form* (see **Figures S1-S2**). The precipitate was filtered and washed with Et_2O (3 x 20 mL). After drying the solid under vacuum, product **3** was obtained in analytically pure form and retained the *E*-configuration, which was fully characterized by NMR analysis (**Section 3.3**) and the configuration was confirmed by X-ray diffraction (**Section 4**). Some impurities were found to be challenging to remove through the procedure above, especially in product **3g** (see **Section 3.3**). Recrystallization from ethanol was then found to give the pure product.

In all cases, it is essential to leave the mixture in the freezer 16 h prior to filtration due to the initial solid-oil formation of the precipitate, which might affect the successful precipitation of the salt. Therefore, detailed pictures of the procedure of the synthesis of salt **3a** (2.00 mmol scale) are reported in **Figure S1**. After 16 h, the mixture should result as in **Figure S1-A** where precipitation is observed. After the solvents are removed *in vacuo*, the mixture results in a solid-oil form, as depicted in **Figure S1-B**. Next, 10 mL of diethyl ether was added, as shown in **Figure S1-C,** and it was stored in the freezer with a glass stopper for 16 h.

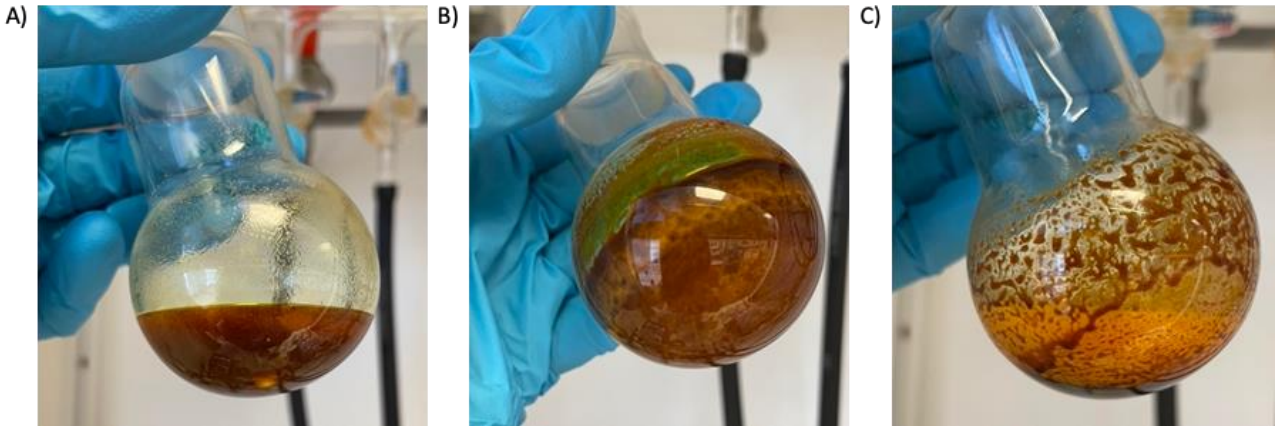


Figure S1. A) Reaction mixture stopped after 16 h; B) Solid-oil form obtained after removing the solvents; C) Addition of diethyl ether to the flask.

After this time, the flask is removed from the freezer, and the mixture is now a brown-yellow solid, as shown in **Figure S2-D**. Using a spatula, the solid is scratched and precipitates as in **Figure S2-E**. Finally, the solid is filtered, washed with diethyl ether (20 mL), and collected in a 20 mL vial with a cap (**Figure S2-F**). The salt must be stored in the dark and in the freezer to avoid decomposition of the salt due to exposure to light.

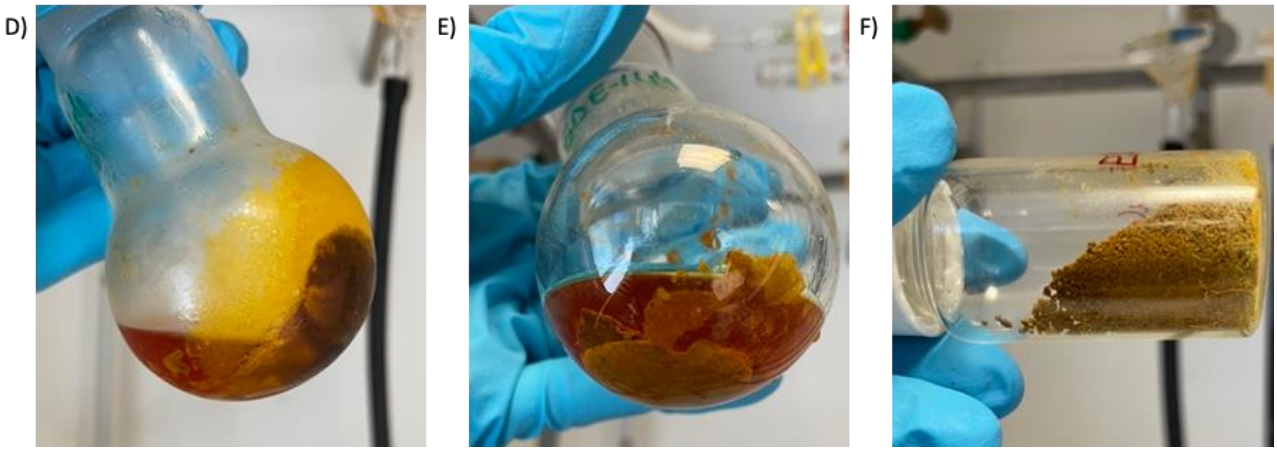
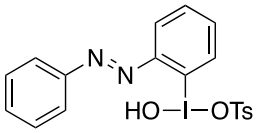


Figure S2. D) Solid formed after storing in the freezer for 16 h; E) The salt precipitation after scratching; F) Salt collected into a 20 mL vial.

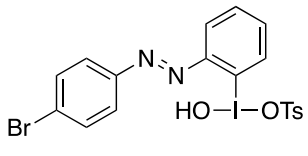
3.3 Analytical Data

(*E*)-Hydroxy(2-(phenyldiazenyl)phenyl)-λ³-iodaneyl 4-methylbenzenesulfonate (21a)



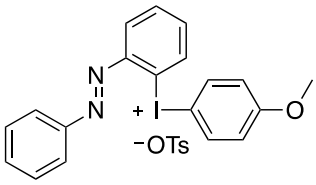
Prepared according to the general procedure, product **21a** was obtained as a yellow solid (994 mg, 2.00 mmol, 98%). Mp: 151 °C. ^{1}H-NMR (400 MHz, MeOD-*d*$_4$): δ 8.83 (dd, *J* = 7.6, 1.5 Hz, 1H), 8.23 – 8.02 (m, 5H), 7.86 – 7.78 (m, 1H), 7.77 – 7.66 (m, 4H), 7.26 – 7.17 (m, 2H), 2.36 (s, 3H). ^{13}C-NMR (101 MHz, MeOD-*d*$_4$) δ 151.2, 148.2, 143.6, 141.6, 138.6, 136.8, 136.4, 134.0, 131.9, 129.8, 129.1, 127.0, 124.9, 111.4, 21.3. HRMS(ESI) m/z: calcd. for $C_{12}H_{10}IN_2O$ [M-TsO$^-$]$^+$ 324.9838; found 324.9840.

(*E*)-(2-((4-Bromophenyl)diazenyl)phenyl)(hydroxy)-λ³-iodaneyl 4-methylbenzenesulfonate (21b)



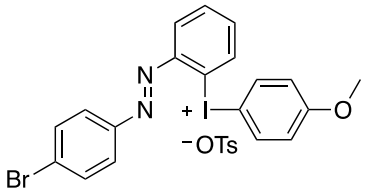
Prepared according to the reported procedure, product **21b** was obtained as a yellow solid (508 mg, 1.00 mmol, 88%). Mp: 161 °C. ^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ 10.03 (s, 1H), 8.80 (d, *J* = 7.7 Hz, 1H), 8.18 – 7.93 (m, 7H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 2.28 (s, 3H). ^{13}C-NMR (101 MHz, DMSO-*d*$_6$) δ 149.1, 145.9, 145.7, 137.6, 137.0, 135.1, 133.6, 132.5, 128.7, 128.1, 127.6, 125.5, 125.3, 112.0, 20.8. HRMS(ESI) m/z: calcd. for $C_{12}H_9BrIN_2O$ [M-TsO$^-$]$^+$ 402.8943; found 402.8949.

(*E*)-(4-Methoxyphenyl)(2-(phenyldiazenyl)phenyl)iodonium tosylate (3a)



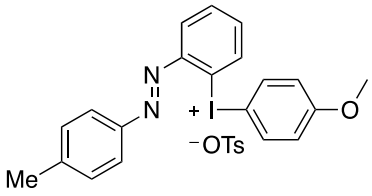
Prepared according to the general one-pot procedure, product **3a** was obtained as a yellow solid (495 mg, 0.84 mmol, 84%). Mp: 151 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.28 – 8.22 (m, 2H), 7.97 – 7.90 (m, 2H), 7.73 (td, *J* = 7.5, 1.1 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.60 – 7.48 (m, 3H), 7.41 (td, *J* = 8.9, 1.6 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.01 – 6.94 (m, 3H), 3.87 (s, 3H), 2.31 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 163.2, 149.1, 147.9, 143.1, 139.3, 139.2, 134.3, 134.0, 134.0, 131.7, 130.8, 130.2, 128.6, 126.2, 124.2, 118.0, 103.6, 102.7, 55.8, 21.4. HRMS(ESI) m/z: calcd. for $C_{19}H_{16}IN_2O$ [M-TsO$^-$]$^+$ 415.0302; found 415.0309.

(*E*)-(4-Methoxyphenyl)(2-(4-bromophenyldiazenyl)phenyl)iodonium tosylate (3b)



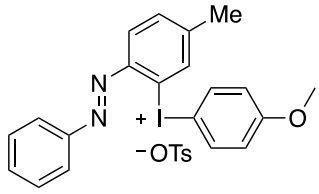
Prepared according to the general one-pot procedure obtained as a yellow solid (562 mg, 0.84 mmol, 84%). Mp: 167 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.33 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.18 – 8.11 (m, 2H), 7.98 – 7.91 (m, 2H), 7.74 (td, *J* = 7.6, 1.2 Hz, 1H), 7.69 – 7.59 (m, 4H), 7.43 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.11 – 7.04 (m, 2H), 7.04 – 6.97 (m, 3H), 3.89 (s, 3H), 2.34 (s, 3H).^{13}C-NMR (101 MHz,): δ 163.3, 148.0, 148.1, 139.6, 139.3, 134.5, 133.9, 133.5, 131.8, 130.8, 129.2, 128.7, 126.2, 125.6, 118.1, 104.1, 102.4, 55.8, 21.5. HRMS(ESI) m/z: calcd. for $C_{19}H_{15}BrIN_2O$ [M-TsO$^-$]$^+$ 492.9407; found 492.9400.

(*E*)-(4-Methoxyphenyl)(2-(*p*-tolyldiazenyl)phenyl)iodonium tosylate (3c)



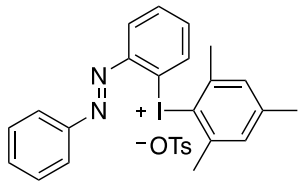
Prepared according to the general one-pot procedure obtained as a yellow solid (529 mg, 0.88 mmol, 88%). Mp: 163 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.31 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.20 – 8.12 (m, 2H), 7.98 – 7.90 (m, 2H), 7.72 (d, *J* = 1.2 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.35 (m, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.02 – 6.94 (m, 3H), 3.89 (s, 3H), 2.44 (s, 3H), 2.32 (s, 3H).^{13}C-NMR (101 MHz,): δ 163.2, 148.0, 147.2, 145.5, 143.2, 139.3, 139.2, 133.9, 133.7, 131.6, 130.9, 130.6, 128.6, 126.3, 124.3, 117.9, 103.4, 102.9, 55.8, 22.0, 21.4. HRMS(ESI) m/z: calcd. for $C_{20}H_{18}IN_2O$ $[M\text{-}TsO^-]^+$ 429.0458; found 429.0448.

(*E*)-(4-Methoxyphenyl)(5-methyl-2-(phenyldiazenyl)phenyl)iodonium tosylate (3d)



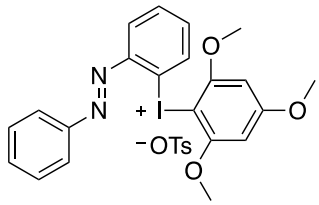
Prepared according to the general one-pot procedure obtained as slightly brown solid (93.6 mg, 0.16 mmol, 49%). Mp: 170 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.7 Hz, 3H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 3H), 7.54 (dd, *J* = 11.8, 7.2 Hz, 4H), 7.02 (dd, *J* = 23.8, 8.2 Hz, 5H), 6.75 (s, 1H), 3.88 (s, 3H), 2.31 (d, *J* = 3.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 149.1, 146.1, 146.1, 142.6, 139.6, 139.3, 133.7, 133.7, 132.4, 131.1, 130.1, 128.6, 126.3, 124.0, 117.9, 103.3, 102.6, 55.8, 22.0, 21.4. HRMS(ESI) m/z: calcd. for $C_{20}H_{18}IN_2O$ $[M\text{-}TsO^-]^+$ 429.0458; found 429.0448.

(*E*)-Mesityl(2-(phenyldiazenyl)phenyl)iodonium tosylate (3e)



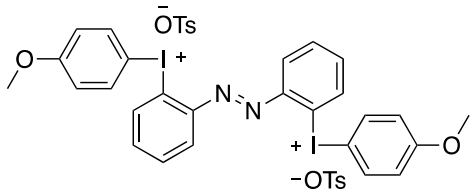
Prepared according to the general one-pot procedure obtained as a brown solid (200 mg, 0.33 mmol, 33%). Mp: 159 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.29 (m, 3H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.62 – 7.52 (m, 5H), 7.37 (td, *J* = 7.8, 1.6 Hz, 1H), 7.08 (s, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 2.55 (s, 6H), 2.40 (s, 3H), 2.31 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 149.5, 148.4, 144.2, 143.4, 143.3, 139.0, 134.4, 134.0, 133.6, 131.7, 130.2, 130.0, 129.4, 128.4, 126.1, 124.3, 120.2, 102.3, 26.8, 21.4. HRMS(ESI) m/z: calcd. for $C_{21}H_{20}I_2N_2$ $[M\text{-}TsO^-]^+$ 427.0660; found 427.0650.

(*E*)-(2,4,6-Trimethoxyphenyl)(2-(phenyldiazenyl)phenyl)iodonium tosylate (3f)



Prepared according to general one-pot procedure obtained as a green solid (108 mg, 0.17 mmol, 76%). Mp: 184 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.29 (m, 3H), 7.72 (td, *J* = 7.5, 1.2 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.59 – 7.50 (m, 3H), 7.39 (td, *J* = 7.7, 1.6 Hz, 1H), 7.07 – 7.00 (m, 3H), 6.21 (s, 2H) 3.91 (s, 3H), 3.79 (s, 6H), 2.31 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.5, 161.6, 149.1, 148.4, 143.4, 139.1, 134.7, 134.1, 133.8, 131.3, 130.1, 129.9, 128.5, 126.3, 124.3, 101.5, 91.8, 85.0, 57.1, 56.1, 21.4. HRMS(ESI) m/z: calcd. for $C_{21}H_{20}I_2N_2O_3$ $[M\text{-}TsO^-]^+$ 475.0513; found 475.0508.

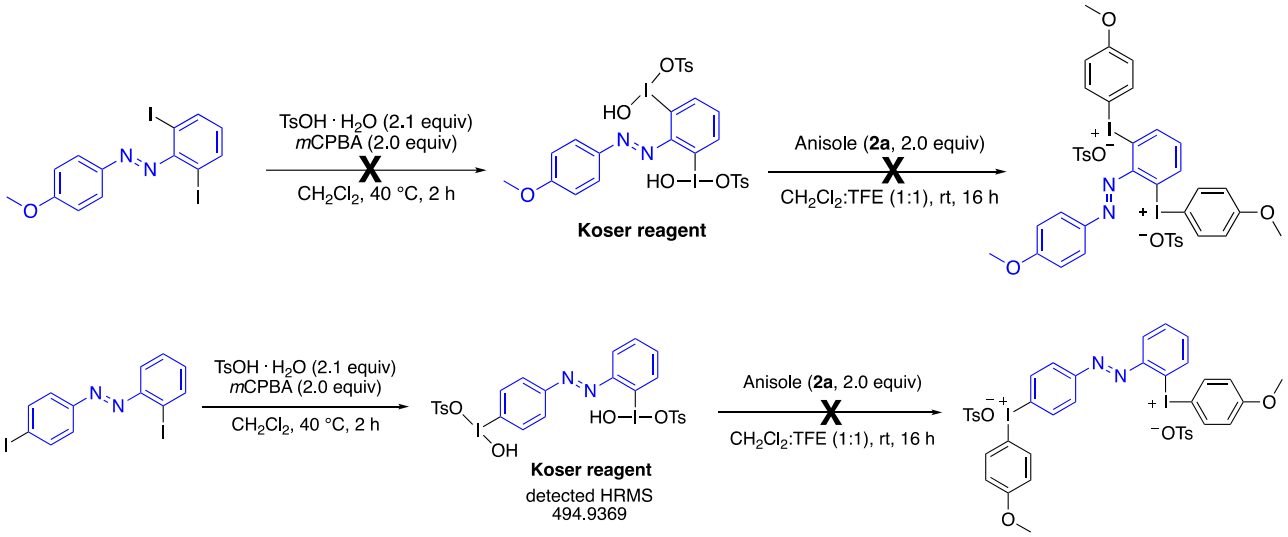
(*E*)-bis(4-Methoxyphenyl)(diazene-1,2-diylbis(2,1-phenylene))iodonium tosylate (3g)



Prepared according to the general one-pot procedure. In this case, increased equivalents of *m*CPBA (2.0 equiv), tosic acid (2.2 equiv), and anisole (2.0 equiv) were necessary to obtain salt **3g** as an orange solid (168 mg, 0.17 mmol, 56 %). ^{1}H-NMR (400 MHz, MeOD-d_4) δ 8.31 (dd, *J* = 7.9, 1.5 Hz, 2H), 8.08 – 8.00 (m, 4H), 7.99 – 7.91 (m, 4H), 7.77 (td, *J* = 8.4, 1.5 Hz, 2H), 7.68 – 7.61 (m, 4H), 7.22 – 7.15 (m, 4H), 7.09 – 7.01 (m, 4H), 3.86 (s, 6H), 2.35 (s, 6H). ^{13}C-NMR (101 MHz, MeOD-d_4) δ 165.0, 148.2, 143.6, 141.6, 139.7, 137.5, 135.7, 134.7, 129.8, 126.9, 125.5, 119.2, 116.9, 102.9, 56.5, 21.3. HRMS(ESI) m/z: calcd. for $C_{26}H_{22}I_2N_2O_2Na^+$ [M-TsO$^-$]$^+$ 693.9561; found 693.9626.

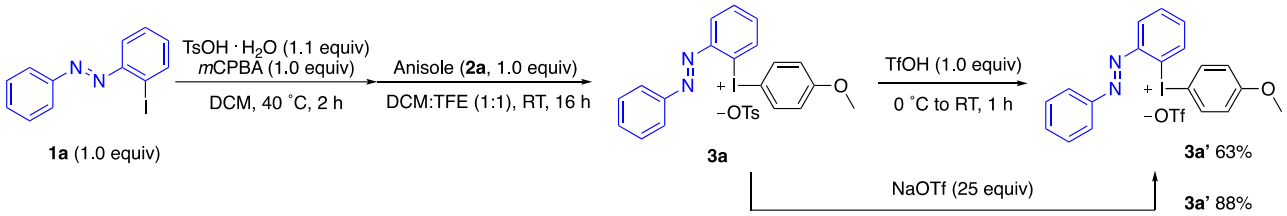
3.4 Scope Limitations

Other diiodinated azobenzenes were also evaluated in the diaryliodonium salt synthesis. Limitations were observed for the diiodinated substrates shown below. With the first substrate, we could not observe formation of any iodine(III) compound. The *ortho*- and *para*-diiodinated azobenzene was successfully oxidized to the corresponding Koser's reagent, which could be detected in HRMS and precipitated together with another product, where only one anisyl group had been incorporated. However, it was not possible to fully convert the mixture of these products into the targeted diaryliodonium salt despite evaluation of various reaction conditions.



3.5 Anion Exchange with the Diaryliodonium Salt 3a

The nature of the counterion has been shown to play an essential role in many reactions employing diaryliodonium salts.[15] We therefore investigated the possibility of an anion exchange from tosylate to triflate (**Scheme S3**). To our delight, adding 1.0 equiv of TfOH allowed the facile isolation of **3a'** in 63% yield (**Method 1**). Furthermore, salt **3a'** was obtained in 88% yield upon performing a work-up with 25 equiv of NaOTf after isolation of **3a** (**Method 2**).



Scheme S3. Anion exchange using *in situ* exchange and work-up methods.

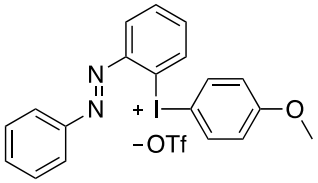
Method 1 – *in situ* with TfOH

After following the general procedure for the synthesis of salt **3a**, an *in situ* anion exchange was performed after full conversion to **3a**. The solvent was removed, and salt **3a** (97 mg, 0.32 mmol) was dissolved in CH_2Cl_2 (1 mL) and cooled to 0 °C. Triflic acid (28 µL, 1.0 equiv) was added, and the mixture was allowed to warm to rt and stirred for 1 h. The solvent was then removed, and Et_2O (5 mL) was added, and the mixture was kept in the freezer overnight prior filtration. After filtration and drying under vacuum, product **3a'** was obtained as a green solid (112 mg, 63% yield). The anion exchange was confirmed by NMR analysis.

Method 2 – work-up with NaOTf

Diaryliodonium salt **3a** (100 mg, 0.32 mmol) was dissolved in CH_2Cl_2 (15 mL) and extracted with NaOTf (1.4 g, 25 equiv) dissolved in H_2O (15 mL). The organic layer was concentrated without drying. Et_2O (10 mL) was added, and the mixture was stirred at rt for 30 min to precipitate a solid. The solid was filtrated and washed with Et_2O and dried *in vacuo* to give triflate salt **3a'** as an orange solid (162 mg, 88% yield). The anion exchange was confirmed by NMR analysis.

Analytical data for diaryliodonium salt 3a'



Mp: 156 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) 8.38 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.21 (dd, *J* = 7.5, 2.3 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.67 – 7.55 (m, 4H), 7.52 – 7.44 (m, 1H), 7.10 – 7.02 (m, 2H), 6.99 (d, *J* = 8.1 Hz, 1H), 3.88 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.7, 148.9, 147.1, 139.4, 134.9, 134.7, 134.4, 132.2, 130.3, 130.2, 124.1, 120.7 (q, *J* = 353.1 Hz, $CF_3SO_3^-$), 118.4, 100.9, 100.8, 55.9. ^{19}F-NMR (377 MHz, $CDCl_3$) δ −78.2. HRMS(ESI) m/z: calcd. for $C_{19}H_{16}IN_2O$ $[M\text{-}TfO^-]^+$ 415.0302; found 415.0309.

4 X-ray Diffraction Crystal Structure of Diaryliodonium Salt 3a

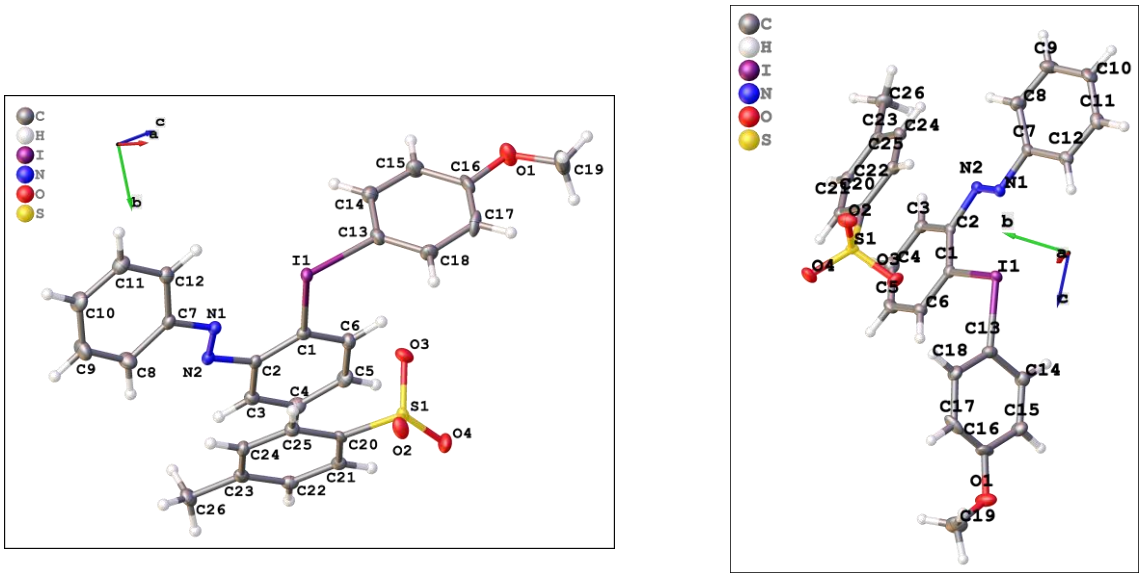


Figure S3. Crystal structure of diaryliodonium salt **3a**.

Single crystals of **3a** were grown by dissolving a small amount (ca. 5 mg) of the compound in CH_2Cl_2 (ca. 200 µL) in a snap cap sample vial. The solution was cautiously overlaid with *n*-hexane (ca. 1 mL) to prevent mixing of the solvents. Subsequently, the solvents were allowed to evaporate slowly at 25 °C by leaving the vial open for 7 d. CCDC Deposition Number: 2215795.

Table S5. Crystal data and structure refinement for **3a.**

Empirical formula	$C_{26}H_{23}IN_2O_4S$
Formula weight	586.42
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.8892(4)
b/Å	16.7789(11)
c/Å	14.1591(7)
α/°	90
β/°	98.131(2)
γ/°	90
Volume/Å^3	2325.8(2)
Z	4
ρ_{calc}g/cm^3	1.675
µ/mm^{-1}	1.504
F(000)	1176.0
Crystal size/mm^3	0.4 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.726 to 56.642
Index ranges	-13 ≤ h ≤ 12, -22 ≤ k ≤ 22, -18 ≤ l ≤ 18
Reflections collected	73815
Independent reflections	5789 [R_{int} = 0.0475, R_{sigma} = 0.0207]
Data/restraints/parameters	5789/0/308
Goodness-of-fit on F^2	1.108

Final R indexes [I>=2σ (I)]	R_1 = 0.0319, wR_2 = 0.0647
Final R indexes [all data]	R_1 = 0.0407, wR_2 = 0.0676
Largest diff. peak/hole / e Å^{-3}	2.02/-0.78

Table S6. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	2922.3(2)	5007.2(2)	5337.2(2)	12.72(5)
S1	5820.8(7)	7120.4(4)	5041.7(5)	13.45(13)
N2	255(2)	5972.5(13)	4197.8(16)	14.0(4)
O3	5797(2)	6300.6(12)	5415.3(15)	20.4(4)
N1	1091(2)	5485.4(13)	3936.3(16)	13.8(4)
O2	6686(2)	7190.7(14)	4293.7(14)	22.4(4)
O1	5471(2)	4067.5(15)	9460.6(16)	28.9(5)
O4	6089(2)	7709.0(13)	5794.7(15)	23.8(5)
C3	-219(3)	6823.3(16)	5459.6(19)	15.0(5)
C1	1736(3)	5952.5(15)	5785.5(19)	12.5(5)
C7	785(3)	5196.1(16)	2985.5(19)	15.2(5)
C2	622(3)	6234.1(15)	5155.2(18)	12.4(5)
C12	1332(3)	4461.2(17)	2797(2)	16.7(5)
C14	3205(3)	4176.7(18)	7230(2)	19.7(6)
C5	1206(3)	6866.2(17)	6987(2)	18.4(6)
C13	3874(3)	4727.6(18)	6728(2)	18.1(6)
C25	3696(3)	6998.0(16)	3567.1(19)	14.5(5)
C16	5026(3)	4319.9(18)	8548(2)	21.6(6)
C22	1945(3)	7947.6(16)	4453.6(19)	15.7(5)
C11	995(3)	4120.2(18)	1899(2)	19.9(6)
C6	2036(3)	6264.3(17)	6698.1(19)	16.5(5)
C23	1506(3)	7651.9(16)	3541.3(19)	15.0(5)
C21	3248(3)	7777.3(16)	4922.1(18)	14.1(5)
C15	3765(3)	3979.9(18)	8152(2)	21.6(6)
C10	154(3)	4516.6(19)	1196(2)	23.6(6)
C18	5103(3)	5070.7(18)	7115(2)	20.1(6)
C20	4129(3)	7306.3(15)	4476.6(18)	11.8(5)
C24	2392(3)	7171.6(16)	3106.1(19)	15.3(5)
C17	5686(3)	4836(2)	8062(2)	24.8(7)
C4	82(3)	7135.6(17)	6372(2)	19.0(6)
C19	6813(3)	4303(2)	9870(3)	35.0(8)
C9	-315(3)	5271(2)	1370(2)	25.8(7)
C8	-1(3)	5618.4(19)	2261(2)	22.3(6)
C26	93(3)	7845.4(19)	3040(2)	20.9(6)

Table S7. Anisotropic Displacement Parameters (Å^2×10^3) for **3a**. 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	10.52(8)	14.40(8)	12.72(8)	-1.01(7)	-0.16(5)	0.26(7)
S1	12.6(3)	15.4(3)	11.5(3)	1.7(2)	-1.1(2)	0.4(2)
N2	14.4(11)	13.5(11)	13.5(11)	-0.2(8)	-0.2(9)	-2.8(9)
O3	19.8(10)	17.7(10)	23.1(10)	6.6(8)	1.1(8)	3.7(8)
N1	14.9(11)	12.2(10)	13.6(10)	-0.9(8)	-0.4(8)	-0.7(9)
O2	13.2(9)	35.3(12)	18.7(10)	4.6(9)	2.5(8)	-0.8(9)
O1	24.4(12)	40.9(14)	20.2(11)	10.9(10)	-1.4(9)	-5.0(10)

Table S7. Anisotropic Displacement Parameters ($Å^2×10^3$) for **3a**. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O4	25.2(11)	23.4(11)	19.9(10)	-6.0(9)	-7.2(8)	-0.4(9)
C3	14.5(13)	14.8(12)	15.9(13)	1.7(10)	3.2(10)	-0.2(10)
C1	11.4(12)	12.4(12)	14.3(12)	0.2(10)	3.5(10)	-0.8(9)
C7	16.8(13)	15.2(13)	13.1(12)	-1.4(9)	0.7(10)	-3.7(10)
C2	12.5(12)	12.8(12)	11.8(11)	0.5(9)	1.8(9)	-3.2(10)
C12	13.4(13)	19.6(13)	17.1(13)	-0.4(11)	2.4(10)	-1.2(11)
C14	16.1(13)	20.3(14)	22.2(14)	1.0(11)	1.3(11)	-1.1(11)
C5	22.3(14)	20.5(14)	13.0(12)	-4.4(10)	4.4(11)	-2.3(11)
C13	18.2(14)	20.1(13)	15.0(13)	2.1(10)	-0.6(11)	2.4(11)
C25	13.6(12)	14.4(12)	15.8(12)	-0.7(10)	2.8(10)	0.7(10)
C16	23.3(15)	24.7(15)	14.5(13)	1.8(11)	-5.4(11)	8.3(12)
C22	17.3(13)	13.5(12)	17.2(13)	2.3(10)	6.1(10)	1.3(10)
C11	19.5(14)	20.8(14)	20.5(14)	-5.4(11)	7.3(11)	-2.8(11)
C6	16.4(13)	18.8(13)	13.7(12)	0.3(10)	-0.1(10)	-0.8(11)
C23	13.2(13)	14.7(12)	17.3(13)	4.5(10)	2.5(10)	-0.9(10)
C21	18.4(13)	13.0(12)	11.3(12)	1.7(10)	3.5(10)	-0.8(10)
C15	19.3(14)	23.7(15)	22.2(14)	6.5(12)	3.9(11)	-3.4(12)
C10	30.8(17)	26.0(16)	13.8(13)	-5.3(12)	2.2(12)	-2.3(13)
C18	20.1(13)	19.0(14)	21.4(13)	4.6(12)	3.8(11)	-4.5(12)
C20	13.0(12)	11.5(12)	10.5(11)	5.1(9)	0.5(9)	-0.2(9)
C24	15.6(13)	15.9(13)	13.7(12)	-0.5(10)	-0.3(10)	-1.8(10)
C17	9.9(12)	40.2(19)	23.5(14)	-15.2(13)	-0.2(11)	-3.7(12)
C4	19.9(14)	18.4(13)	20.1(14)	-3.3(11)	7.9(11)	1.6(11)
C19	20.9(16)	47(2)	33.2(18)	10.6(16)	-10.2(14)	-4.9(15)
C9	30.2(17)	30.5(16)	15.2(13)	0.4(12)	-2.1(12)	7.1(13)
C8	26.0(16)	20.0(14)	20.6(14)	-0.7(11)	2.1(12)	6.4(12)
C26	14.9(13)	24.0(15)	22.9(14)	3.4(12)	-0.5(11)	4.4(11)

Table S8. Bond Lengths for **3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C1	2.122(3)	C14	C13	1.389(4)
I1	C13	2.111(3)	C14	C15	1.385(4)
S1	O3	1.475(2)	C5	C6	1.399(4)
S1	O2	1.457(2)	C5	C4	1.388(4)
S1	O4	1.450(2)	C13	C18	1.386(4)
S1	C20	1.777(3)	C25	C20	1.398(4)
N2	N1	1.255(3)	C25	C24	1.392(4)
N2	C2	1.422(3)	C16	C15	1.413(4)
N1	C7	1.423(3)	C16	C17	1.333(5)
O1	C16	1.372(3)	C22	C23	1.395(4)
O1	C19	1.427(4)	C22	C21	1.392(4)
C3	C2	1.399(4)	C11	C10	1.374(4)
C3	C4	1.387(4)	C23	C24	1.396(4)
C1	C2	1.398(4)	C23	C26	1.510(4)
C1	C6	1.387(4)	C21	C20	1.392(4)
C7	C12	1.387(4)	C10	C9	1.383(4)
C7	C8	1.390(4)	C18	C17	1.438(4)
C12	C11	1.392(4)	C9	C8	1.384(4)

Table S9. Bond Angles for **3a**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C13	I1	C1	94.56(11)	C18	C13	I1	121.8(2)
O3	S1	C20	105.27(12)	C18	C13	C14	121.9(3)
O2	S1	O3	112.14(13)	C24	C25	C20	119.8(2)
O2	S1	C20	105.70(12)	O1	C16	C15	113.3(3)
O4	S1	O3	112.45(13)	C17	C16	O1	124.9(3)
O4	S1	O2	114.48(14)	C17	C16	C15	121.8(3)
O4	S1	C20	105.90(13)	C21	C22	C23	121.0(3)
N1	N2	C2	113.1(2)	C10	C11	C12	120.3(3)
N2	N1	C7	116.1(2)	C1	C6	C5	119.2(3)
C16	O1	C19	116.9(3)	C22	C23	C24	118.8(2)
C4	C3	C2	119.7(3)	C22	C23	C26	120.4(3)
C2	C1	I1	118.72(19)	C24	C23	C26	120.9(3)
C6	C1	I1	120.4(2)	C20	C21	C22	119.8(2)
C6	C1	C2	120.8(2)	C14	C15	C16	119.4(3)
C12	C7	N1	116.6(2)	C11	C10	C9	119.9(3)
C12	C7	C8	120.3(3)	C13	C18	C17	117.9(3)
C8	C7	N1	123.1(3)	C25	C20	S1	119.7(2)
C3	C2	N2	115.4(2)	C21	C20	S1	120.4(2)
C1	C2	N2	125.2(2)	C21	C20	C25	119.9(2)
C1	C2	C3	119.4(2)	C25	C24	C23	120.8(2)
C7	C12	C11	119.4(3)	C16	C17	C18	119.9(3)
C15	C14	C13	119.1(3)	C3	C4	C5	120.6(3)
C4	C5	C6	120.2(3)	C10	C9	C8	120.7(3)
C14	C13	I1	116.3(2)	C9	C8	C7	119.2(3)

Table S10. Torsion Angles for **3a**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
I1	C1	C2	N2	-4.3(3)	C13	C18	C17	C16	-1.8(5)
I1	C1	C2	C3	176.13(19)	C22	C23	C24	C25	-0.8(4)
I1	C1	C6	C5	-177.6(2)	C22	C21	C20	S1	177.1(2)
I1	C13	C18	C17	-179.1(2)	C22	C21	C20	C25	-0.9(4)
N2	N1	C7	C12	-155.3(2)	C11	C10	C9	C8	-3.1(5)
N2	N1	C7	C8	25.7(4)	C6	C1	C2	N2	177.9(2)
O3	S1	C20	C25	-78.7(2)	C6	C1	C2	C3	-1.7(4)
O3	S1	C20	C21	103.3(2)	C6	C5	C4	C3	-1.2(4)
N1	N2	C2	C3	175.4(2)	C23	C22	C21	C20	0.1(4)
N1	N2	C2	C1	-4.2(4)	C21	C22	C23	C24	0.7(4)
N1	C7	C12	C11	175.6(2)	C21	C22	C23	C26	-179.7(3)
N1	C7	C8	C9	-176.2(3)	C15	C14	C13	I1	-178.8(2)
O2	S1	C20	C25	40.1(2)	C15	C14	C13	C18	1.7(5)
O2	S1	C20	C21	-137.9(2)	C15	C16	C17	C18	1.1(5)
O1	C16	C15	C14	-179.3(3)	C10	C9	C8	C7	-0.6(5)
O1	C16	C17	C18	-178.6(3)	C20	C25	C24	C23	0.0(4)
O4	S1	C20	C25	162.0(2)	C24	C25	C20	S1	-177.2(2)
O4	S1	C20	C21	-16.0(2)	C24	C25	C20	C21	0.8(4)
C7	C12	C11	C10	1.6(4)	C17	C16	C15	C14	1.0(5)
C2	N2	N1	C7	179.8(2)	C4	C3	C2	N2	-177.9(2)

Table S10. Torsion Angles for **3a**.

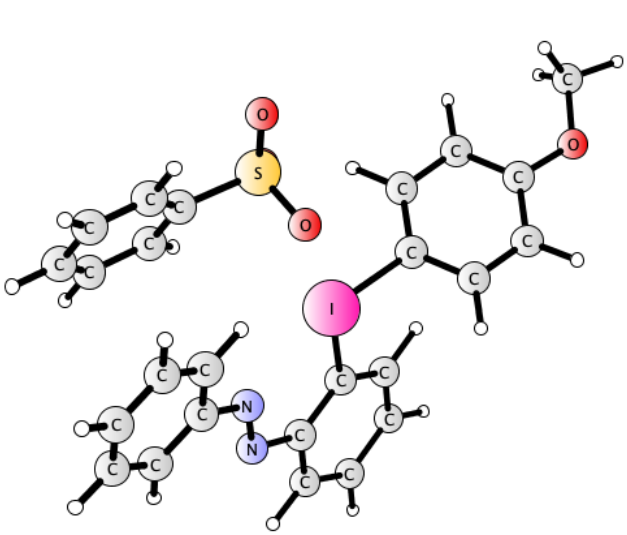
A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C2	C3	C4	C5	-0.3(4)	C4	C3	C2	C1	1.7(4)
C2	C1	C6	C5	0.2(4)	C4	C5	C6	C1	1.2(4)
C12	C7	C8	C9	4.8(5)	C19	O1	C16	C15	172.4(3)
C12	C11	C10	C9	2.6(5)	C19	O1	C16	C17	-7.9(5)
C14	C13	C18	C17	0.4(5)	C8	C7	C12	C11	-5.3(4)
C13	C14	C15	C16	-2.3(5)	C26	C23	C24	C25	179.6(3)

Table S11. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3a**.

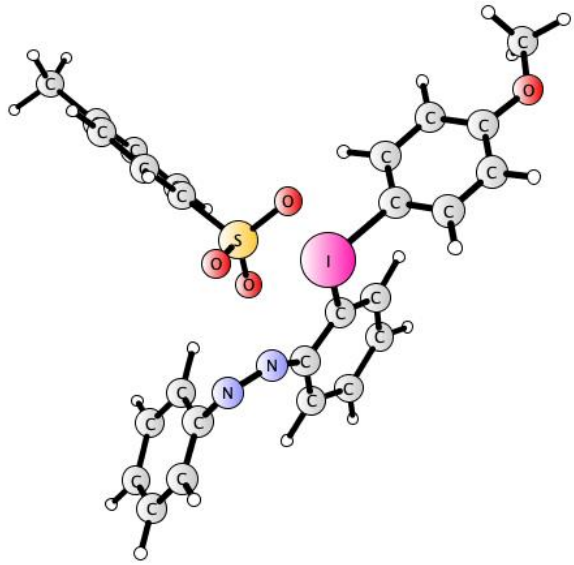
Atom	*x*	*y*	*z*	U(eq)
H3	-993.39	7008.61	5043.19	18
H12	1931.78	4193.06	3277.71	20
H14	2375.56	3938.48	6944.56	24
H5	1412.82	7091.07	7606.79	22
H25	4290.94	6670.74	3264.32	17
H22	1347.46	8269.87	4759.93	19
H11	1347.14	3610.91	1770.29	24
H6	2796.73	6071.43	7121.8	20
H21	3533.78	7981.9	5543.84	17
H15	3306.28	3619.58	8515.97	26
H10	-103.97	4272.57	592.04	28
H18	5546.88	5449.25	6765.01	24
H24	2101.02	6960.95	2488.01	18
H17	6540.42	5048.38	8341.51	30
H4	-487.23	7537.53	6578.09	23
H19A	7056.32	4036.98	10486.56	52
H19B	6837.82	4881.71	9962.4	52
H19C	7465.34	4151.4	9441.09	52
H9	-858.21	5554.47	873.33	31
H8	-318.45	6138.96	2376.05	27
H26A	-164.03	8383.24	3217.58	31
H26B	-562.78	7459.25	3228.44	31
H26C	88.49	7819.25	2347.94	31

5 Computational details

The Gaussian16 package[16] was employed and the functional Minnesota M06-2X[17] was used for all calculations presented in this work. Geometry optimizations were performed with def2-SVP basis set for all atoms. Energy corrections were applied to the optimized structures performing a single-point calculation using M06-2X with a larger basis set consisting of def2-TZVP for all atoms.



(*E*)-Salt **3a**



(*Z*)-Salt **3a**

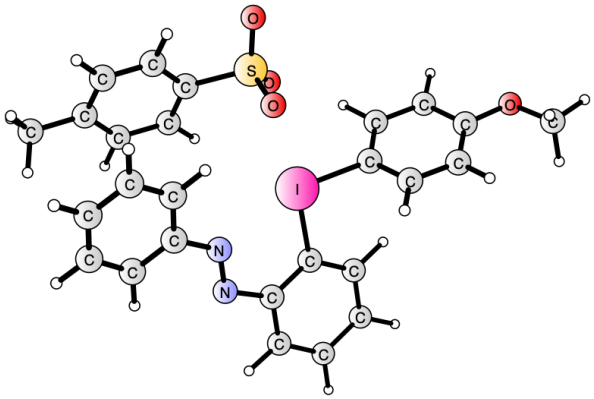
Table S12. Calculated absolute energies and energy corrections.

	M06-2X (def2-SVP) Electronic Energy (hartree)	M06-2X (def2-SVP) Free Energy correction	M06-2X (def2-TZVP) Electronic Energy (hartree)
(*E*)-Salt (3a)	-2108.8629649	0.373716	-2110.6567429
(Z)-Salt (3a)	-2108.8393281	0.374018	-2110.6336596

5.1 Cartesian Coordinates and Energies

Energies are given in Hartree
Sum of electronic and zero-point energies = $\varepsilon_0 + \varepsilon_{ZPE}$
Sum of electronic and thermal energies = $\varepsilon_0 + E_{tot}$
Sum of electronic and thermal enthalpies = $\varepsilon_0 + H_{corr}$
Sum of electronic and thermal free energies = $\varepsilon_0 + G_{corr}$

(*E*)-Salt **3a**



$\varepsilon_0 + \varepsilon_{ZPE}$ = -2108.422055
$\varepsilon_0 + E_{tot}$ = -2108.390465
$\varepsilon_0 + H_{corr}$ = -2108.389521
$\varepsilon_0 + G_{corr}$ = -2108.489249

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C	-2.58028293	0.78983660	-0.31104242
C	-3.50057747	0.32815965	-1.24647897
C	-4.82102702	0.77359738	-1.19427599
C	-5.19908555	1.69853873	-0.21070440
H	-4.56696905	2.90758426	1.44563883
H	-2.17859127	2.12912384	1.34167657
H	-3.20603682	-0.38491354	-2.01910312
H	-5.53498028	0.40605980	-1.92929296
I	-0.58756148	0.11189777	-0.43406386
O	-6.44316694	2.18946483	-0.08234416
C	-1.03087922	-1.88443991	0.21179025
C	-2.29820306	-2.23691779	0.66402031
C	0.00446986	-2.84321202	0.23038106
C	-2.54880446	-3.53543306	1.11535652
H	-3.10220593	-1.49954580	0.67454524
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N	1.34129794	-2.61104307	-0.17426870
O	0.04763200	1.92341100	-0.90436700
S	0.45023600	2.76041400	0.29164000
O	-0.28666500	2.31080900	1.48931700
O	0.45873900	4.18434400	-0.00124400
C	2.15427900	2.28751700	0.59808300
C	3.17915000	2.96453400	-0.05628800
C	2.43956000	1.22774300	1.45806200
C	4.49849100	2.55736100	0.13722300
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C	3.76102600	0.82619200	1.63602600
H	1.62009000	0.74407100	1.99355800
C	4.80859200	1.47948300	0.97474400
H	5.30663600	3.08691400	-0.37346800
H	3.98760500	-0.00893200	2.30382100
C	6.23214900	1.03098300	1.17589900
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H	6.90869500	1.51672300	0.46006800
H	6.58292400	1.27508000	2.19027800
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H	-8.34924506	2.30863327	-0.71798681
H	-7.15613815	2.05800068	-2.02925566
H	-7.60349051	0.69697330	-0.94586937
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C	3.97044854	-1.95211130	-0.79917630
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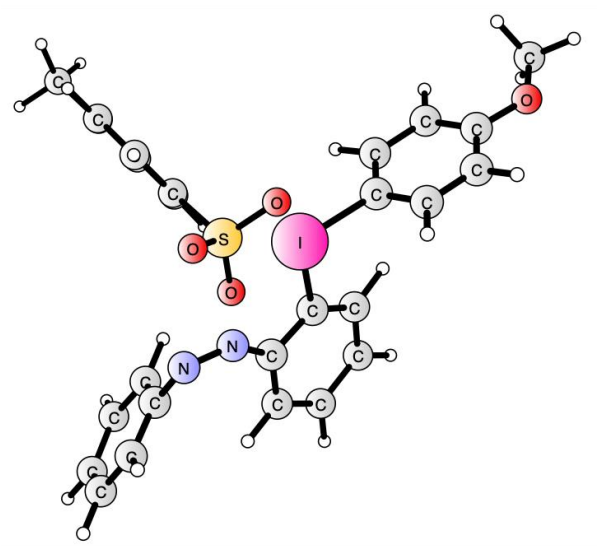
H	6.08789864	-2.17320455	-1.10585059
H	6.33855518	0.02894608	-2.23082319

(*Z*)-Salt **3a**



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C	0.84408500	-2.25506900	0.42084800
C	-0.30822000	-1.67500000	2.90438500
H	-1.94932200	-0.79108900	1.78303800
C	1.50120700	-2.63249500	1.59951600
C	0.91555600	-2.34061600	2.82665700
H	-0.73121600	-1.41868400	3.87593600
H	2.46633700	-3.13366600	1.55752300
H	1.43749700	-2.61874600	3.74255800
N	1.20324700	-2.48935000	-0.94127600
N	2.33452600	-2.63873200	-1.39910400
C	3.52079400	-2.45808300	-0.62952400
C	4.48475600	-3.46652800	-0.70391200
C	3.76190300	-1.27440200	0.07691900
C	5.67662700	-3.32518800	0.00333300
H	4.28058200	-4.35293900	-1.30589200
C	4.97018700	-1.13711900	0.75337300
H	3.00566000	-0.48864700	0.09880400
C	5.92041900	-2.16066600	0.73245500
H	6.42372500	-4.11946300	-0.02946300
H	5.16013600	-0.21813600	1.30941500
H	6.86002900	-2.04465600	1.27465200
C	-3.19060200	-0.69573300	-0.61064700
C	-3.38335300	0.61907600	-0.19607100
C	-4.22491000	-1.63809100	-0.58188700
C	-4.64513100	1.00221400	0.26044100
H	-2.54201100	1.31802300	-0.18572400
C	-5.47493400	-1.24848500	-0.13138400
H	-4.05713500	-2.66602500	-0.90592400
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H	-4.79014300	2.02867700	0.59288100
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H	-8.27742600	1.67013000	1.44371300
H	-6.60305800	1.93707600	2.02119700
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S	0.87226500	1.21988600	0.28635200
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O	-0.59900800	1.37390300	0.41244400
C	1.51014400	2.87393400	0.04994100
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C	1.63141100	3.39303600	-1.23493800
C	2.28129700	4.95120400	0.98138400
H	1.75580200	3.19988600	2.15630000
C	2.07688200	4.70296600	-1.40321000
H	1.38994900	2.75640200	-2.08738900
C	2.40610100	5.50047400	-0.30168100
H	2.54053000	5.55991300	1.85118700
H	2.17599700	5.11456600	-2.41040900
C	2.91633300	6.90620000	-0.48556700
H	4.01240100	6.94041700	-0.38614000
H	2.65957600	7.29715000	-1.47898100
H	2.49693900	7.58360100	0.27135000

6 Investigation of the Switching Behaviour of 1a and 3a

The influence of the hypervalent iodine moiety on the photo-switching behavior of the azobenzene was examined by ^{1}H NMR and UV/vis spectroscopy in $CDCl_3$ and $CHCl_3$, respectively. The diaryliodonium salt **3a** and the corresponding azobenzene **1a** were compared. Under ambient conditions, both molecules existed exclusively in the *E*-isomer. However, both molecules could be converted upon irradiation with UV light of 340 nm to the corresponding Z-isomer, which could be switched back to the *E*-isomer upon irradiation with visible light of 450 nm. The exact *E*/*Z*-ratio was determined by ^{1}H NMR spectroscopy. After 10 min of irradiation with 340 nm, the hypervalent azobenzene **3a** was switched by 71%, whereas the *Z*-isomer of the normal azobenzene **1a** was only obtained in 31% suggesting a faster *E*/*Z*-isomerization of the hypervalent azobenzene **3a**. Longer irradiation led to a higher *E*/*Z*-conversion (*E*/*Z*-ratio 32/68 for **1a** and 17/83 for **3a**). However, the hypervalent azobenzene **3a** started to decompose under such a long irradiation time, which is probably due to the high energy of the UV lamp and the sensitivity of iodine towards it. Free tosic acid became visible in the ^{1}H NMR spectrum (see **Figure S6**).

Upon irradiation with 450 nm, **1a** and **3a** re-isomerized to the corresponding *E*-isomer. For both molecules, the back-switching occurred faster than the *E*-*Z*-isomerization but a full conversion to the *E*-isomer could not be obtained. Again, **3a** switched faster than **1a**. The PSS450 of **3a** was obtained after irradiation with 450 nm for 1 min (*E*/*Z*-ratio: 72/28) and for **1a** after 2 min (*E*/*Z*-ratio: 90/10). However, this was in contrast to the UV/vis measurements. Here, the PSS340 and PSS450 of **1a** could be reached faster (PSS340: irradiation for 10 min; PSS450: irradiation for 1 min) and complete re-isomerization was possible. This is attributed to the concentration differences of NMR and absorption spectroscopy. The resistance against photo-bleaching was tested by reversible irradiation of **1a** and **3a** with UV and visible light. Both molecules showed no significant decomposition in the absorption spectra over five switching cycles. The incorporation of the hypervalent moiety had almost no influence on the absorption maxima of the azobenzene switch: **1a** showed the $\pi\pi^*$ transition at 325 nm and the weaker $n\pi^*$ transition at 434 nm; the hypervalent azobenzene **3a** at 338 nm ($\pi\pi^*$) and 436 nm ($n\pi^*$). However, the half-life time was significantly decreased by the incorporation of the hypervalent iodine bond: Whereas for **1a** a half-life time of 124.6 h was determined, for **3a** it was only 5.83 h, which we attributed to the strong electron acceptor character of the iodine(III) moiety. The thermal re-isomerization of azobenzene is a first order reaction. In the end, an equilibrium is reached where the equilibrium constant can be determined by the Van't Hoff equation. For the isomers of azobenzene the energy difference is ~ 40 kJ/mol leading to a rate constant of k = 0.984. In the case of our hypervalent azobenzene derivative, the energy difference between (*Z*)- and (*E*)-isomer is ~ 62.9 kJ/mol leading to a rate constant of k = 0.975. Hence, the concentration of the (*Z*)-isomer is negligible and the thermal re-isomerization should proceed completely.

6.1 ^{1}H NMR Analysis

To determine the ratio between *E* and *Z* isomer, ^{1}H NMR spectra of **1a** and **3a** in $CDCl_3$ were recorded without irradiation (ambient conditions) and after irradiation of the sample with 340 nm (PSS340) and 450 nm (PSS450), respectively. The sample concentration was approx. 3 mg/mL. For the analysis of the composition, the integral of two aromatic doublets were determined and set to one.

1-(2-Iodophenyl)-2-phenyldiazene (1a)

For the analysis of the composition, the doublets at 8.00 ppm (*E* isomer) and at 7.87 ppm (*Z* isomer) were chosen (**Table S13**).

Table S13. *E*/*Z* Ratio of **1a**.

Conditions	*E* isomer [%]	*Z* isomer [%]
No irradiation	100	0
340 nm 1 min	92	8
340 nm 2 min	90	10
340 nm 5 min	81	19
340 nm 10 min	69	31
340 nm 30 min	32	68
450 nm 1 min	90	10
450 nm 2 min	90	10
450 nm 5 min	90	10

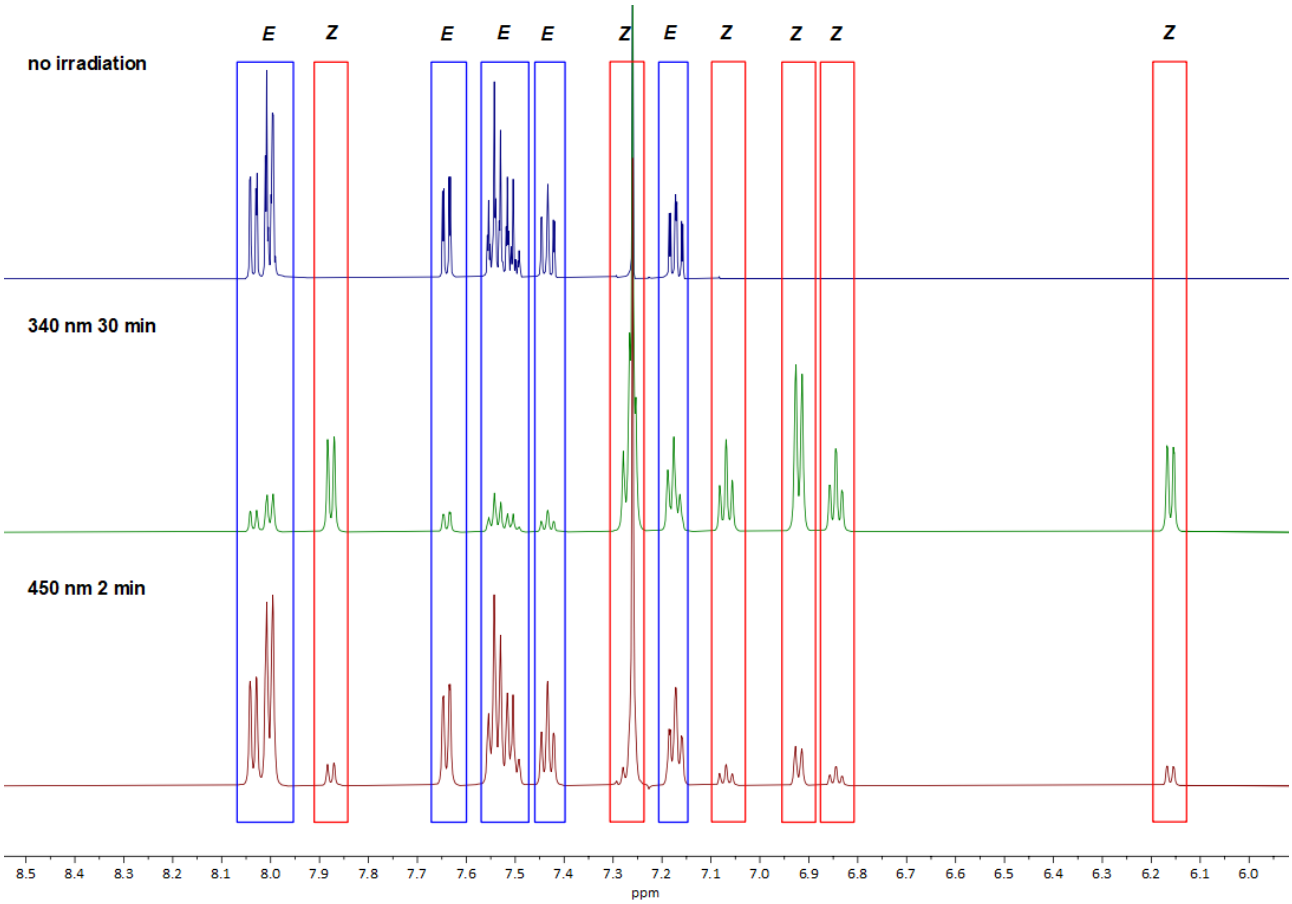


Figure S4. ^{1}H NMR spectra of **1a** in $CDCl_3$ under ambient conditions (top), PSS340 (middle) and PSS450 (bottom).

(4-Methoxyphenyl)(2-(phenyldiazenyl)phenyl)iodonium tosylate (3a)

For the analysis of the composition, the doublets at 8.27 ppm (*E* isomer) and at 8.05 ppm (*Z* isomer) were chosen (**Table S14**).

Table S14. *E*/*Z* Ratio of **3a**.

Conditions	*E* isomer [%]	*Z* isomer [%]
No irradiation	100	0
340 nm 1 min	78	22
340 nm 2 min	66	34
340 nm 5 min	53	47
340 nm 10 min	29	71
340 nm 30 min	17	83
450 nm 1 min	72	28
450 nm 2 min	72	28
450 nm 5 min	72	28

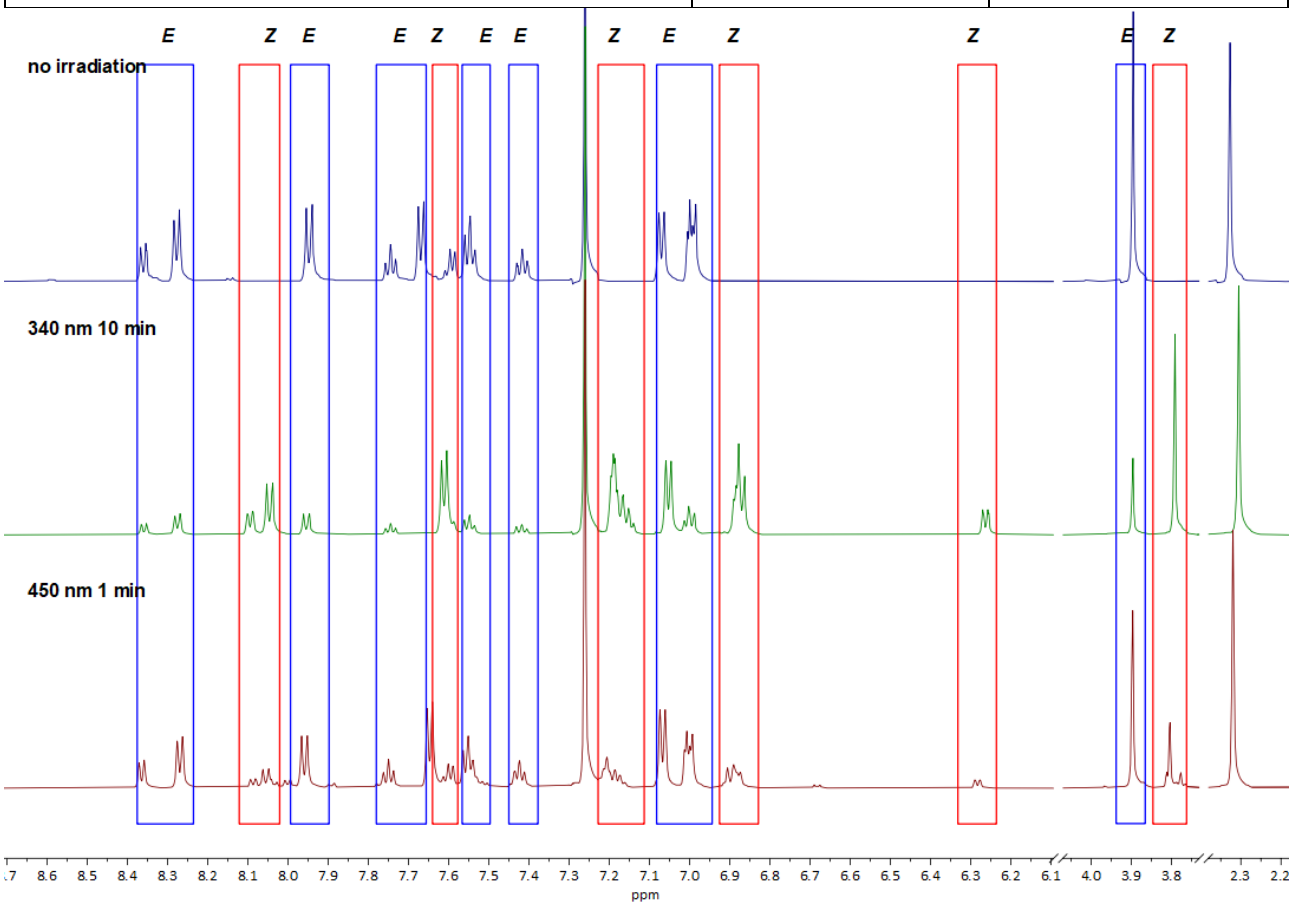


Figure S5. ^{1}H NMR spectra of **3a** in $CDCl_3$ under ambient conditions (top), PSS340 (middle) and PSS450 (bottom).

Upon irradiation with 340 nm for 30 min, the *Z* isomer was further enriched. However, decomposition of **3a** started to occur and free tosic acid became visible in the ^{1}H NMR spectrum, e.g. the broad singlet at 2.71 ppm (**Figure S6**).

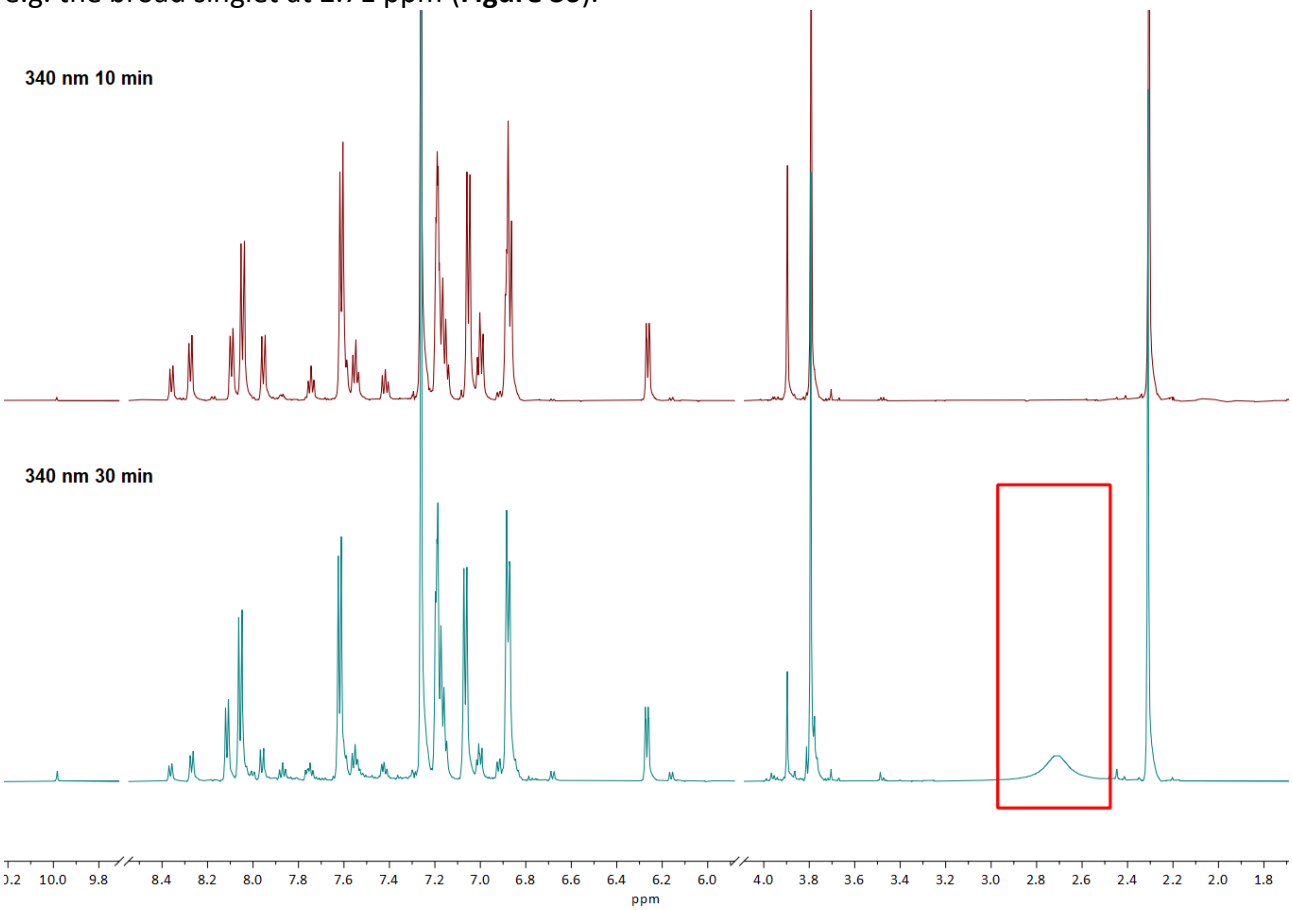


Figure S6. Comparison of ^{1}H NMR spectra of **3a** in $CDCl_3$ after irradiation with 340 nm for 10 min (top) and 30 min (bottom).

6.2 UV/vis Measurements

The sample concentration for the UV/vis measurements was approx. 0.1 µmol/mL. The samples were measured in $CHCl_3$.

1-(2-Iodophenyl)-2-phenyldiazene (1a)

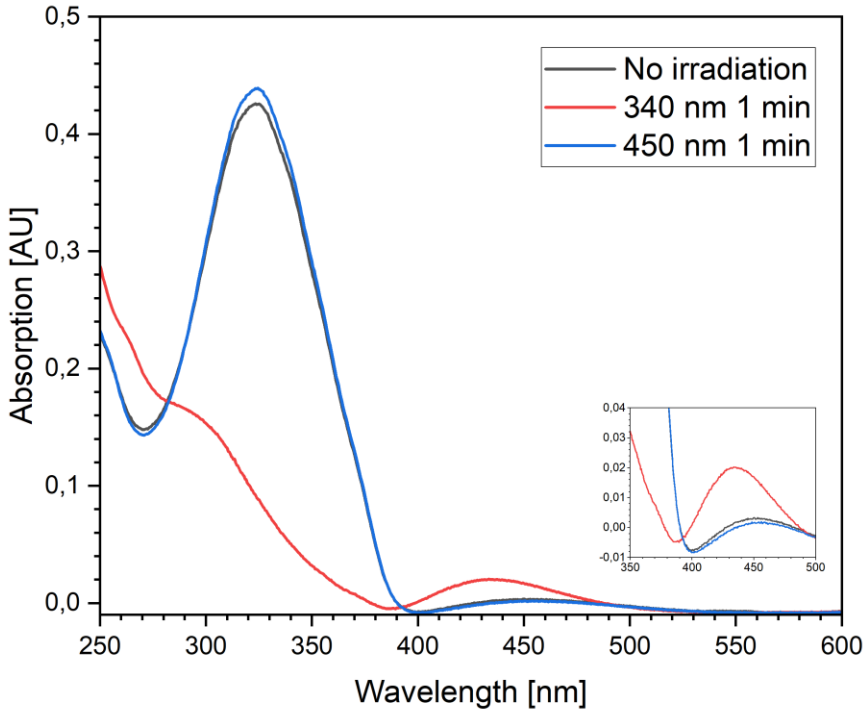


Figure S7. Absorption spectra of the **1a** without irradiation (black), of the PSS340 after irradiation for 1 min (red), and of the PSS450 after irradiation for 1 min (blue).

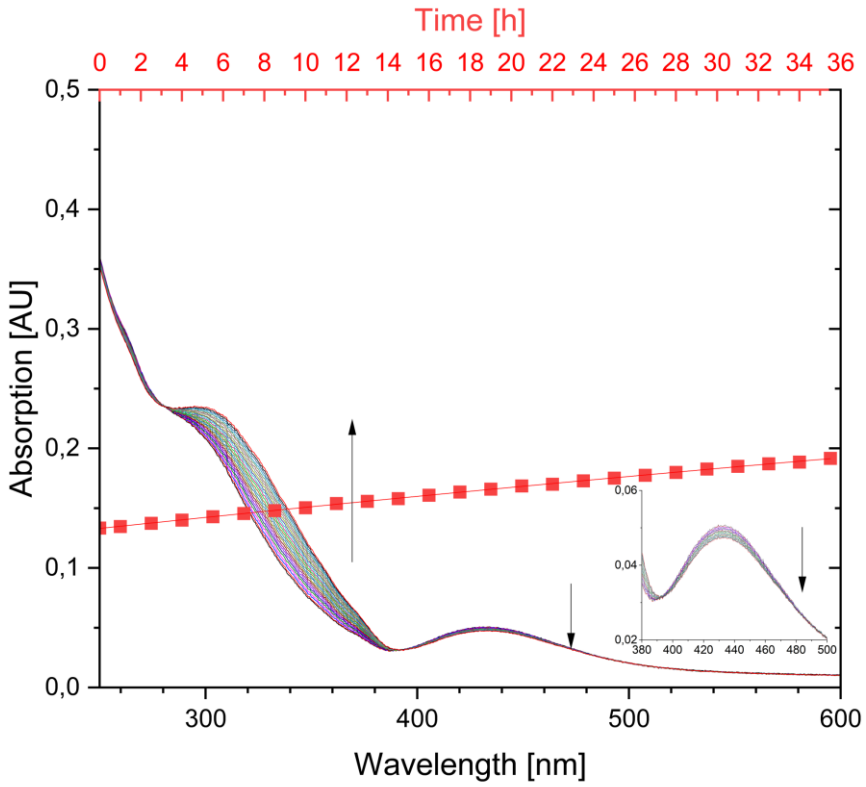


Figure S8. Thermal relaxation of **1a** after irradiation with 340 nm for 1min. The spectra were recorded with a delay of 30 min over the course of 36 h. Arrows indicate the change of absorption over time. The time profile of the thermal relaxation of the ππ* band (325 nm) is shown as red rectangles. This was used to determine the half-life time *via* an exponential fit to be 124.6 h.

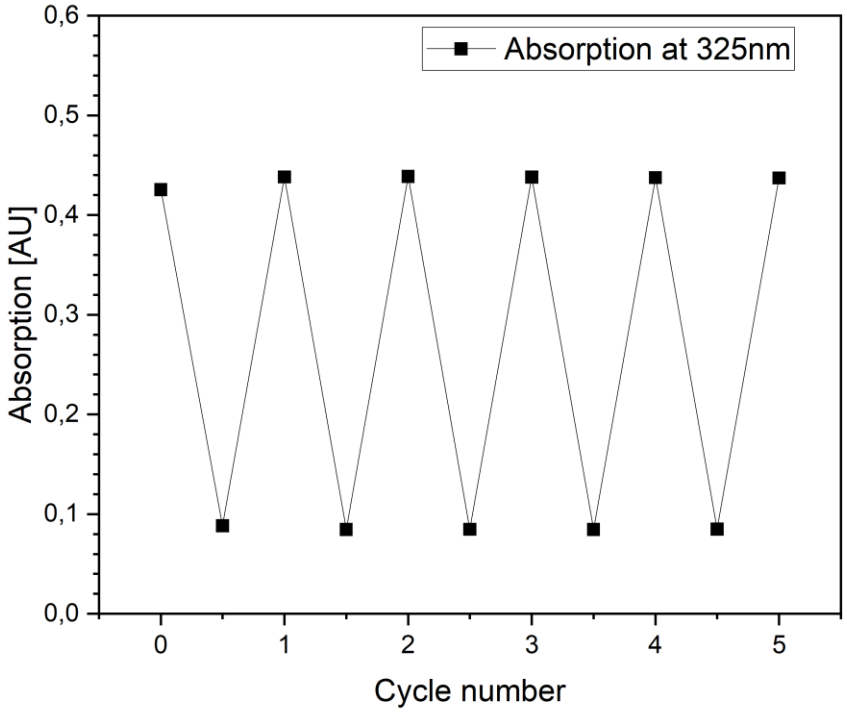


Figure S9. The stability of **1a** against photo-bleaching was tested by alternating switching between PSS340 and PSS450 in five cycles.

(4-Methoxyphenyl)(2-(phenyldiazenyl)phenyl)iodonium tosylate (3a)

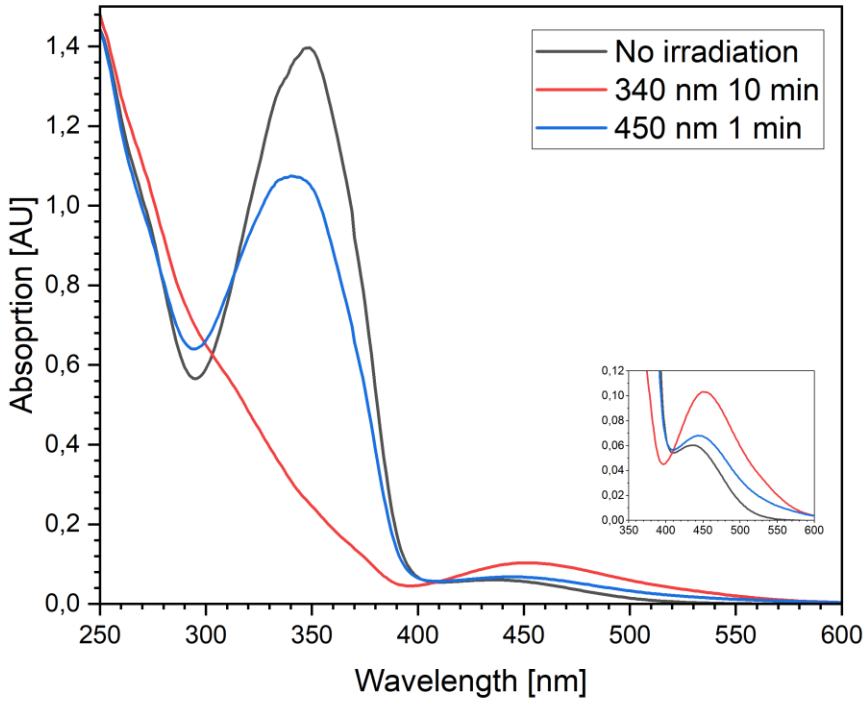


Figure S10. Absorption spectra of the **3a** without irradiation (black), of the PSS340 after irradiation for 10 min (red), and of the PSS450 after irradiation for 1 min (blue).

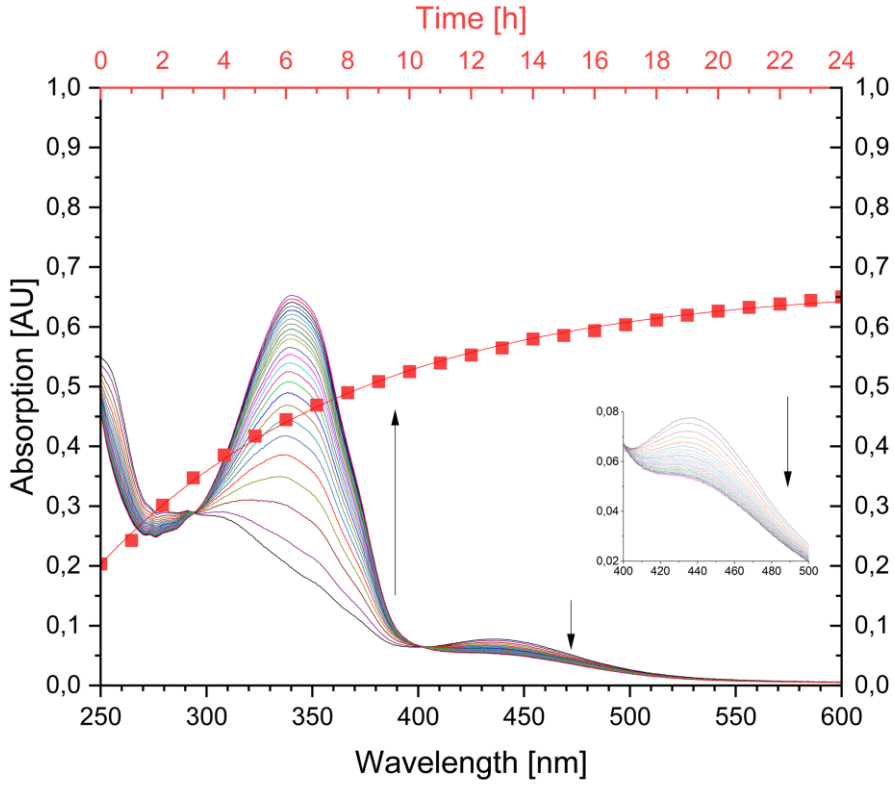


Figure S11. Thermal relaxation of **3a** after irradiation with 340 nm for 10min. The spectra were recorded with a delay of 60 min over the course of 24 h. Arrows indicate the change of absorption over time. The time profile of the thermal relaxation of the ππ* band (338 nm) is shown as red rectangles. This was used to determine the half-life time *via* an exponential fit to be 5.83 h.

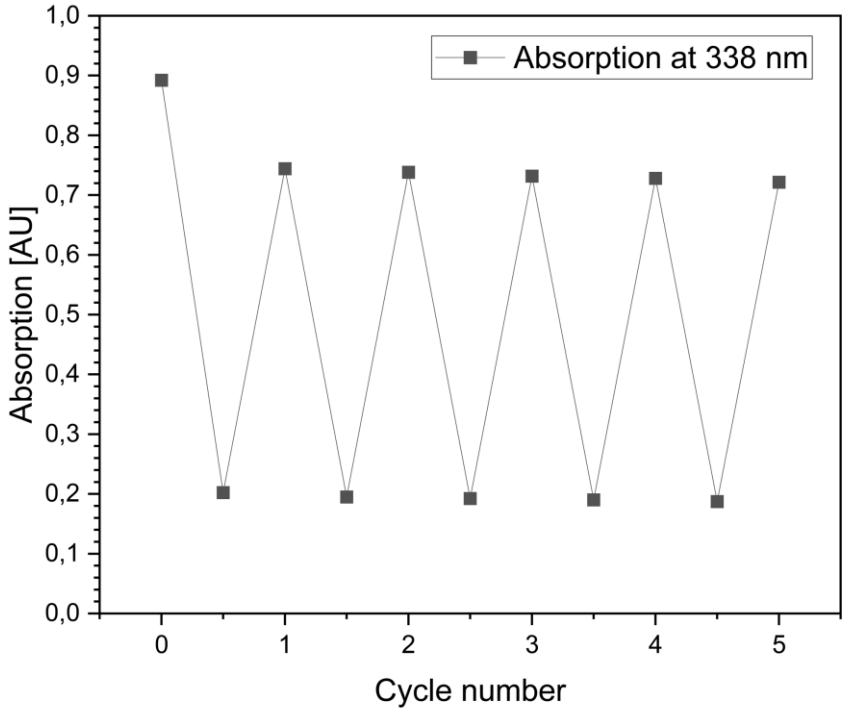
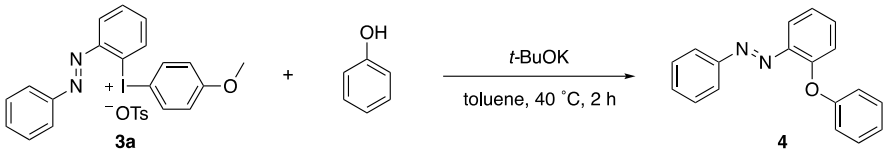


Figure S12. The stability of 3**a** against photo-bleaching was tested by alternating switching between PSS340 and PSS450 in five cycles.

7 Transition Metal-Free Arylations

7.1 Arylation with Oxygen Nucleophiles

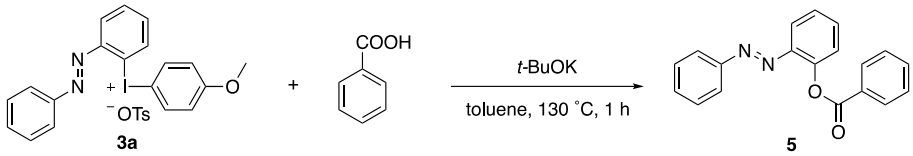
(*E*)-1-(2-Phenoxyphenyl)-2-phenyldiazene (4)



Following a reported procedure,[18] to a suspension of *t*-BuOK (1.2 equiv, 0.24 mmol, 27 mg) in anhydrous toluene (2.0 mL) was added phenol (1.2 equiv, 0.24 mmol, 22 mg) at 0 °C and the reaction was left to stir at this temperature for 15 min. Diaryliodonium salt **3a** (1.0 equiv, 0.20 mmol, 117 mg) was added in one portion, and the reaction was stirred at 40 °C for 2 h. The reaction was then quenched with H_2O at 0 °C, the organic phase was separated and the water phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried with Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica, 1% of Et_2O in *n*-pentane) to give diaryl ether **4** as a red oil (0.15 mmol, 41 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.48 – 7.39 (m, 4H), 7.36 – 7.28 (m, 2H), 7.23 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.17 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.10 – 7.02 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.9, 154.6, 153.1, 144.3, 132.5, 131.2, 129.8, 129.1, 124.4, 123.2, 123.0, 121.5, 118.3, 117.5. HRMS(ESI) *m/z*: calcd. for $C_{18}H_{14}N_2ONa^+$ $[M+Na]^+$ 297.0998; found 297.0980. Analytical data were in accordance with those previously reported.[19]

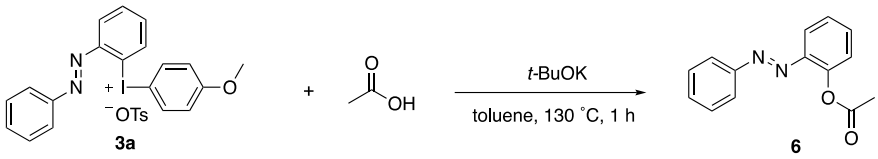
(*E*)-2-(Phenyldiazenyl)phenyl benzoate (5)



Following a reported procedure,[18] *t*-BuOK (1.2 equiv, 0.24 mmol, 27 mg) was dissolved in anhydrous toluene (2 mL). Benzoic acid (1.2 equiv, 0.24 mmol, 29 mg) and salt **3a** (1.0 equiv, 0.20 mmol, 117 mg) were added sequentially as solids. The flask was then heated to reflux in an oil bath for 1 h. The reaction mixture was diluted with CH_2Cl_2 (3 × 5 mL), washed with water (4 mL) and brine (4 mL), dried over magnesium sulfate and concentrated *in vacuo*. The crude material was purified by column chromatography (silica, 1% Et_2O in *n*-pentane) to yield aryl ester **5** as a red solid (0.16 mmol, 48 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.24 (m, 2H), 7.89 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.75 – 7.63 (m, 3H), 7.59 – 7.50 (m, 3H), 7.44 – 7.32 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 152.8, 149.4, 144.1, 133.7, 132.2, 131.4, 130.5, 129.6, 129.1, 128.8, 126.7, 123.7, 123.2, 118.0. HRMS(ESI) *m/z*: calcd. for $C_{19}H_{14}N_2O_2Na^+$ $[M+Na]^+$ 325.0947; found 325.0941. Analytical data were in accordance with those previously reported.[20]

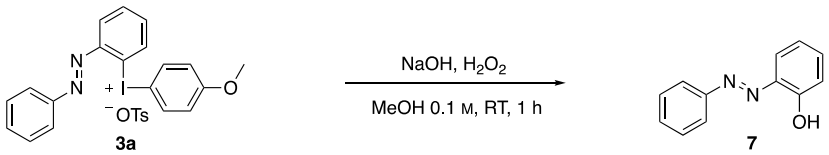
(*E*)-2-(Phenyldiazenyl)phenyl acetate (6)



Following a reported procedure,[18] *t*-BuOK (1.2 equiv, 0.24 mmol, 27 mg) was dissolved in anhydrous toluene (2 mL). Acetic acid (1.2 equiv, 0.24 mmol, 14 μL) and salt **3a** (1.0 equiv, 0.20 mmol, 117 mg) were added sequentially as solids. The reaction was then refluxed in an oil bath for 1 h. The mixture was allowed to cool down to rt and diluted with CH_2Cl_2 (3 × 5 mL), washed with water (4 mL) and brine (4 mL), dried over magnesium sulfate and concentrated *in vacuo*. The crude material was purified by column chromatography (silica, 1% Et_2O in *n*-pentane) to yield aryl ester **6** as a red solid (0.14 mmol, 33 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55 – 7.47 (m, 4H), 7.35 (ddd, *J* = 8.1, 7.3, 1.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.7, 152.9, 149.1, 144.1, 132.2, 131.5, 129.2, 126.7, 123.5, 123.1, 117.8, 20.9. Analytical data were in accordance with those previously reported.[21]

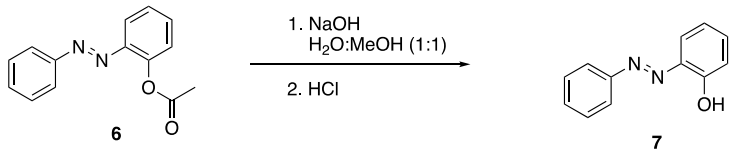
(*E*)-2-(Phenyldiazenyl)phenol (7)



Following a reported procedure,[22] sodium hydroxide (2.0 equiv, 0.40 mmol, 16 mg) was added to a microwave vial, followed by the addition of methanol (1.0 mL). Hydrogen peroxide (2.1 equiv, 0.42 mmol, 20 μL) was added followed by diaryliodonium salt **3a** (1.0 equiv, 0.2 mmol, 117 mg). Additional methanol (1.0 mL) was added, and the reaction was stirred at rt for 1 h. The reaction was quenched with the addition of sat. $NH_4Cl_{(aq)}$ and extracted with EtOAc (3 × 10 mL). The organic phases were washed with brine, dried over magnesium sulfate and concentrated *in vacuo*. The crude was purified using flash chromatography (silica, silica, 1% Et_2O in *n*-pentane) to provide 2-hydroxyazobenzene **7** as a red solid (0.08 mmol, 15 mg, 38% yield) .

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.92 (s, 1H), 7.96 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.58 – 7.46 (m, 3H), 7.36 (ddd, *J* = 8.5, 7.2, 1.7 Hz, 1H), 7.12 – 7.01 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.9, 150.7, 137.5, 133.4, 133.4, 131.3, 129.5, 122.4, 120.1, 118.4. Analytical data were in accordance with those previously reported.[21]

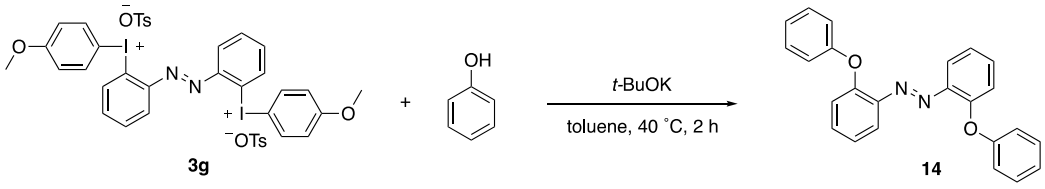
Synthesis of 2-Hydroxyazobenzene (7) by Hydrolysis



Following a reported procedure,[21] compound **6** (1.0 equiv, 0.14 mmol, 34 mg) and NaOH (10 equiv, 1.40 mmol, 56 mg) were added in a 5 mL vial followed by addition of 2 mL H_2O/MeOH (1:1). The reaction mixture was stirred vigorously at rt for 2 h. After this time, $HCl_{(aq)}$ (15 equiv, 2.10 mmol, 0.18 mL) was added to the mixture, and the reaction was stirred for additional 30 min. The orange product formed was filtered to obtain **7** (0.11 mmol, 23 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.92 (s, 1H), 7.96 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.58 – 7.46 (m, 3H), 7.36 (ddd, *J* = 8.5, 7.2, 1.7 Hz, 1H), 7.12 – 7.01 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.9, 150.7, 137.5, 133.4, 133.4, 131.3, 129.5, 122.4, 120.1, 118.4. Analytical data were in accordance with those previously reported.[21]

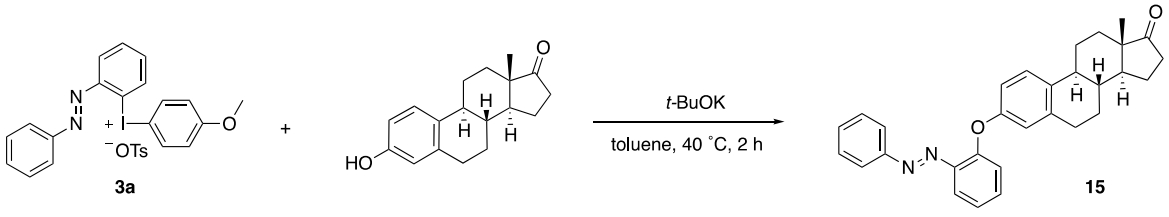
(*E*)-1,2-bis(2-Phenoxyphenyl)diazene (14)



Following a reported procedure,[18] to a suspension of *t*-BuOK (2.1 equiv, 0.21 mmol, 24 mg) in anhydrous toluene (1.0 mL) was added phenol (2.1 equiv, 0.21 mmol, 20 mg) at 0 °C and the reaction was left to stir at this temperature for 15 min. Diaryliodonium salt **3g** (1.0 equiv, 0.10 mmol, 98 mg) was added in one portion and the reaction was stirred at 40 °C. After quenching with H_2O at 0 °C, the organic phase was separated, and the water phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica, 1% of Et_2O in *n*-pentane) to give diaryl ether **14** as a red oil (0.06 mmol, 21 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 8H), 7.14 – 6.99 (m, 10H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.9, 154.6, 144.6, 132.5, 129.8, 124.3, 122.9, 121.3, 118.3, 117.8. HRMS(ESI) *m/z*: calcd. for $C_{24}H_{18}N_2O_2Na^+$ $[M+Na]^+$ 389.1260; found 389.1260. Analytical data were in accordance with those previously reported.[23]

Arylation of Estrone to give (8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(2-((*E*)-phenyldiazenyl)phenoxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (15)

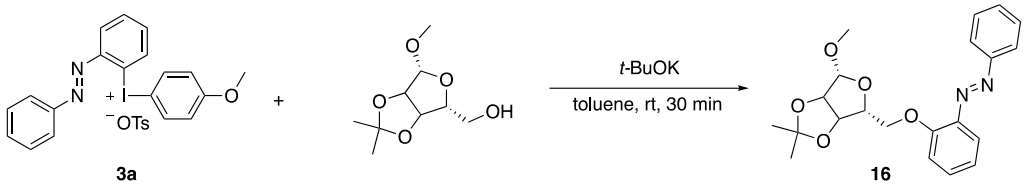


Following a reported procedure,[18] to a suspension of *t*-BuOK (1.2 equiv, 0.24 mmol, 27 mg) in anhydrous toluene (2.0 mL) was added estrone (1.2 equiv, 0.24 mmol, 65 mg) at 0 °C and the reaction was left to stir at this temperature for 15 min. Diaryliodonium salt **3a** (1.0 equiv, 0.20 mmol, 117 mg) was added in one portion, and the reaction was stirred at 40 °C. The reaction was then quenched with H_2O at 0 °C, the organic phase was separated, and the water phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried over sodium sulfate, filtered, and

concentrated *in vacuo*. The crude material was purified by flash chromatography (silica, 1% of Et_2O in *n*-pentane) to give diaryl ether **15** as a red sticky oil (0.12 mmol, 54 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.47 – 7.39 (m, 3H), 7.25 – 7.17 (m, 2H), 7.14 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.81 (d, *J* = 2.7 Hz, 1H), 2.92 – 2.79 (m, 2H), 2.55 – 2.45 (m, 1H), 2.44 – 2.34 (m, 1H), 2.32 – 2.22 (m, 1H), 2.20 – 1.89 (m, 4H), 1.69 – 1.35 (m, 6H), 0.92 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 220.9, 156.5, 154.9, 153.1, 144.2, 138.3, 134.6, 132.4, 131.1, 129.0, 126.7, 123.9, 123.2, 121.1, 118.6, 117.4, 116.0, 50.6, 48.1, 44.2, 38.4, 36.0, 31.7, 29.6, 26.6, 26.0, 21.7, 14.0. HRMS(ESI) *m/z*: calcd. for $C_{30}H_{30}N_2O_2Na^+$ $[M+Na]^+$ 473.2199; found 473.2183.

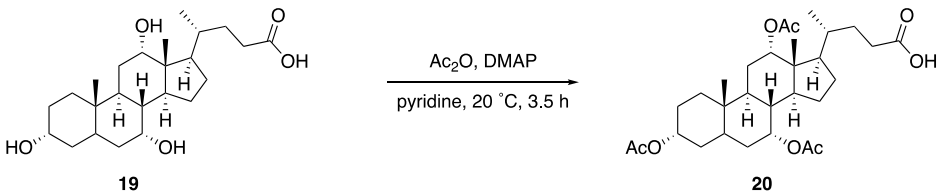
Arylation of a Protected Ribose to give (*E*)-1-(2-(((4*R*,6*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methoxy)phenyl)-2-phenyldiazene (16)



Following a reported procedure,[24] the protected ribose (1.0 equiv, 0.2 mmol, 41 mg) was stirred in a 5 mL screw-cap vial in toluene (2 mL) for 3 min. After this time, the mixture of salt **3a** (1.5 equiv, 0.30 mmol, 176 mg) and *t*-BuOK (1.5 equiv, 0.30 mmol, 34 mg) were added portion-wise under air. The reaction mixture was stirred for 30 min. The mixture was transferred to a round-bottom flask with EtOAc (3 x 5 mL), and celite was added. Then, the solvents were removed under reduced pressure and the residue was purified by column chromatography (silica, petroleum ether/EtOAc 4/1) to afford product **16** as a red oil (0.09 mmol, 34 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.68 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.55 – 7.38 (m, 4H), 7.13 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.07 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 5.02 (s, 1H), 4.94 (dd, J = 5.9, 1.0 Hz, 1H), 4.69 – 4.62 (m, 2H), 4.30 (dd, *J* = 9.8, 5.8 Hz, 1H), 4.20 (dd, *J* = 9.8, 8.7 Hz, 1H), 3.32 (s, 3H), 1.52 (s, 3H), 1.33 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.3, 153.2, 143.2, 132.4, 131.0, 129.2, 123.2, 122.1, 117.3, 116.6, 112.6, 109.7, 85.3, 84.6, 82.3, 71.3, 55.0, 26.6, 25.1. HRMS(ESI) *m/z*: calcd. for $C_{12}H_{24}N_2O_5Na^+$ $[M+Na]^+$ 407.1577; found 407.1576.

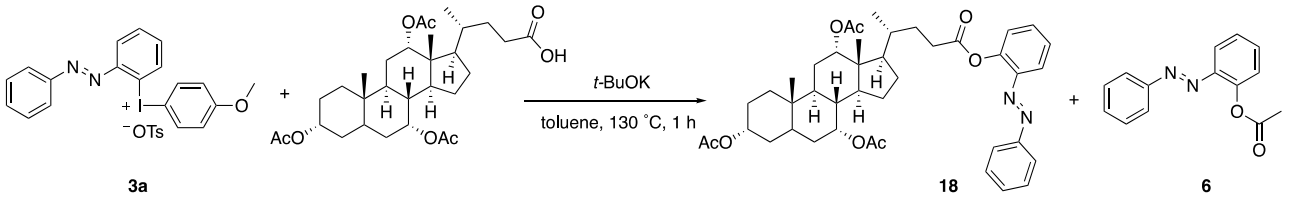
Protection of Cholic Acid (20)



Following a reported procedure,[25] to a suspension of cholic acid **19** (1.0 equiv, 4.90 mmol, 2.0 g) in acetic anhydride (4 mL), pyridine (6 mL) and 4-methylaminopyridine (DMAP) (0.6 equiv, 2.94 mmol, 359 mg) were added. The reaction mixture was stirred at 20 ˚C for 3.5 h and after this time, the solvent was removed under reduced pressure. The mixture was diluted with diethyl ether (40 mL) and washed with a solution of HCl 1 M (3 x 30 mL), sat. $NaHCO_3$(aq) (2 x 30 mL) and brine (30 mL). The organic phase was dried over sodium sulfate, filtrated and concentrated under reduced pressure to obtain the protected cholic acid **20** as a colourless solid (4.64 mmol, 2.5 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (m, 1H), 4.91 (m, 1H), 4.57 (m, 1H), 2.14 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 0.91 (s, 3H), 0.85 (s, 3H), 0.73 (s, 3H). Analytical data were in accordance with those previously reported.[25]

Arylation of the Protected Cholic Acid to give (3*R*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-5-oxo-5-(2-((*E*)-phenyldiazenyl)phenoxy)pentan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triyl triacetate (17)

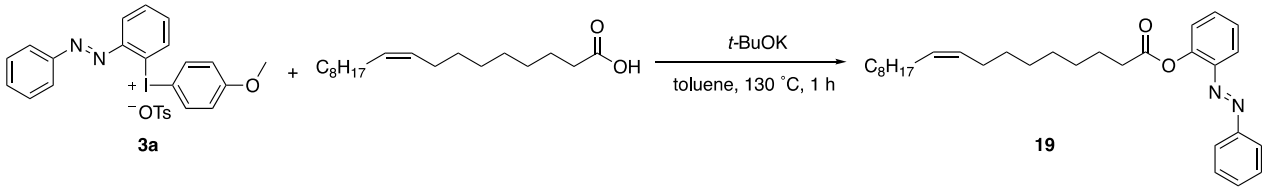


Following a reported procedure,[18] *t*-BuOK (1.2 equiv, 0.24 mmol, 27 mg) was dissolved in anhydrous toluene (2 mL). Protected cholic acid (1.2 equiv, 0.24 mmol, 128 mg) and salt **3a** (1.0 equiv, 0.20 mmol, 117 mg) were added sequentially. The mixture was refluxed in an oil bath for 1 h. and after cooling down diluted with CH_2Cl_2 (3 × 5 mL), washed with water (4 mL) and brine (4 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by column chromatography (silica, 1% Et_2O in *n*-pentane) to yield aryl ester **17** (0.09 mmol, 66 mg, 46%) as a red solid. In addition, the side-product **6** (0.04 mmol, 9 mg, 20%) was isolated as a red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.80 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.53 – 7.45 (m, 4H), 7.34 (td, *J* = 7.4, 1.4 Hz, 1H), 7.22 (dd, *J* = 8.1, 1.4 Hz, 1H), 5.10 (t, *J* = 3.0 Hz, 1H), 4.94 – 4.87 (m, 1H), 4.63 – 4.52 (m, 1H), 2.77 – 2.66 (m, 1H), 2.63 – 2.51 (m, 1H), 2.14 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 – 1.19 (m, 22H), 1.17 – 1.00 (m, 3H), 0.92 (s, 3H), 0.70 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.7, 170.7,170.6, 170.5, 152.9, 149.2, 144.1, 132.2, 131.5, 129.2, 126.6, 123.4, 123.1, 117.6, 75.5, 74.2, 70.8, 47.6, 45.2, 43.6, 41.1, 37.9, 34.8, 34.8, 34.7, 34.5, 31.4, 31.0, 30.9, 29.0, 27.4, 27.0, 25.7, 23.0, 22.7, 21.7, 21.6, 21.6, 17.7, 12.3. HRMS(ESI) *m/z*: calcd. for $C_{42}H_{54}N_2O_8Na^+$ $[M+Na]^+$ 737.3772; found 737.3771.

Analytical data for product **6**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55 – 7.47 (m, 4H), 7.35 (ddd, *J* = 8.1, 7.3, 1.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.7, 152.9, 149.1, 144.1, 132.2, 131.5, 129.2, 126.7, 123.5, 123.1, 117.8, 20.9. Analytical data were in accordance with those previously reported.[21]

Arylation of Oleic Acid to give 2-((*E*)-Phenyldiazenyl)phenyl (*E*)-octadec-9-enoate (18)



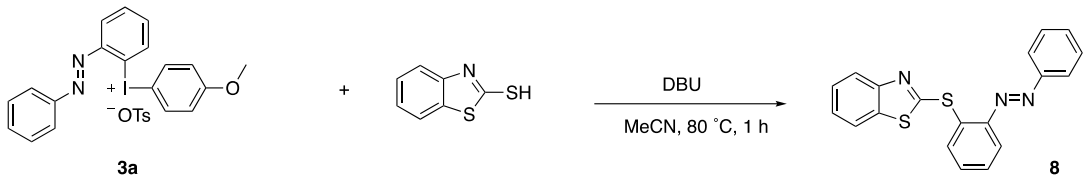
Following a reported procedure,[18] *t*-BuOK (1.2 equiv, 0.24 mmol, 27 mg) was dissolved in anhydrous toluene (2 mL). Oleic acid (1.2 equiv, 0.24 mmol, 76 μL) and salt **3a** (1.0 equiv, 0.20 mmol, 117 mg) were added sequentially. The reaction mixture was refluxed in an oil bath for 1 h and after

cooling down to rt diluted with CH_2Cl_2 (3 × 5 mL), washed with water (4 mL) and brine (4 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by column chromatography (silica, 1% Et_2O in *n*-pentane) to yield aryl ester **18** as a red oil (0.07 mmol, 34 mg, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.80 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.34 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.24 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.43 – 5.29 (m, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.02 (m, 4H), 1.81 (p, *J* = 7.5 Hz, 2H), 1.48 – 1.20 (m, 22H), 0.94 – 0.83 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 153.0, 149.2, 144.3, 132.1, 131.4, 130.2, 129.9, 129.2, 128.6, 126.6, 123.6, 123.2, 117.6, 34.3, 32.0, 29.9, 29.9, 29.7, 29.5, 29.4, 29.2, 27.3, 25.2, 22.8, 14.3. HRMS(ESI) *m/z*: calcd. for $C_{30}H_{42}N_2O_2Na^+$ $[M+Na]^+$ 485.3138; found 485.3134.

7.2 Arylation of Sulfur Nucleophiles

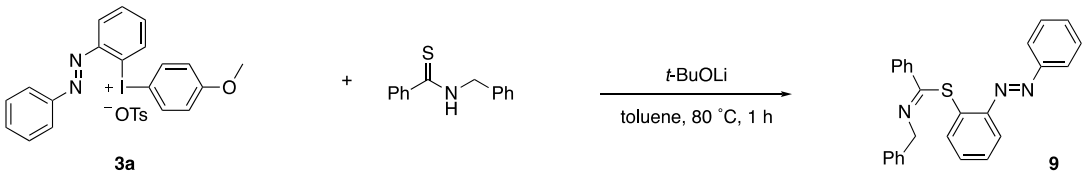
(*E*)-2-((2-(Phenyldiazenyl)phenyl)thio)benzo[*d*]thiazole (8)



Following a reported procedure,[26] a microwave vial was charged with mercaptothiazole (1.0 equiv, 0.20 mmol, 33 mg) and diaryliodonium salt **3a** (1.1 equiv, 0.22 mmol, 129 mg) caped and evacuated/backfilled with argon three times. Anhydrous acetonitrile (2.0 mL) was added followed by 1,8-diazabicyclo 5.4.0 undec-7-ene (DBU, 1.1 equiv, 0.22 mmol, 33 µL). The reaction was stirred for 1 h at 80 °C. After the reaction was cooled down to rt, a small amount of silica was added. Volatiles were removed *in vacuo* and the on silica absorbed crude loaded onto a silica column., The product was purified by column chromatography (silica, 1% Et_2O in *n*-pentane) to obtain the product **8** as a red oil (0.19 mmol, 65 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.79 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.68 (dt, *J* = 7.5, 0.8 Hz, 1H), 7.57 – 7.39 (m, 6H), 7.30 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2, 153.8, 152.7, 151.8, 136.4, 134.4, 132.4, 131.8, 131.8, 130.3, 129.3, 126.3, 124.9, 123.5, 122.5, 121.1, 118.2. HRMS(ESI) *m/z*: calcd. for $C_{19}H_{13}N_3S_2Na^+$ $[M+Na]^+$ 370.0443; found 370.0433.

2-((*E*)-Phenyldiazenyl)phenyl (*Z*)-*N*-benzylbenzimidothioate (9)



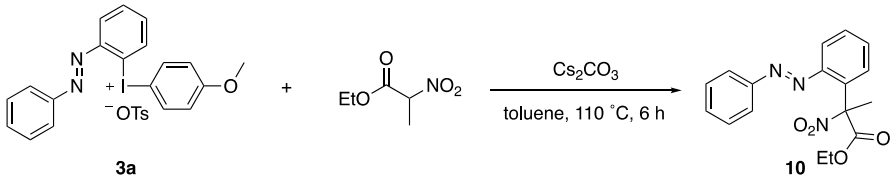
Following a reported procedure,[27] thioamide (1.0 equiv, 0.20 mmol, 45 mg), the diaryliodonium salt **3a** (1.1 equiv, 0.22 mmol, 129 mg) and *t*-BuOLi (1.1 equiv, 0.22 mmol, 18 mg) were weighed into an oven dried 4 mL microwave vial. The reaction was sealed with a metal cap, evacuated, and backfilled with argon three times. The solids were dissolved in degassed anhydrous toluene (1 mL) under argon and the mixture was stirred at 80 °C for 1 h. The reaction mixture was purified by

column chromatography (silica, 10% Et_2O in *n*-pentane) to obtain product **9** as a red oil (0.04 mmol, 17 mg, 21% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.65 – 7.58 (m, 2H), 7.58 – 7.37 (m, 9H), 7.35 – 7.31 (m, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 7.17 – 7.10 (m, 2H), 5.15 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.1, 152.7, 150.8, 139.9, 138.5, 134.7, 133.6, 131.6, 131.1, 129.8, 129.2, 129.2, 128.6, 128.5, 128.1, 127.9, 126.9, 123.5, 117.1, 59.0. HRMS(ESI) *m/z*: calcd. for $C_{26}H_{21}N_3SNa^+$ $[M+Na]^+$ 408.1529; 408.1524.

7.3 Arylation of Carbon Nucleophiles

Ethyl-(*E*)-2-nitro-2-(2-(phenyldiazenyl)phenyl)propanoate (10)

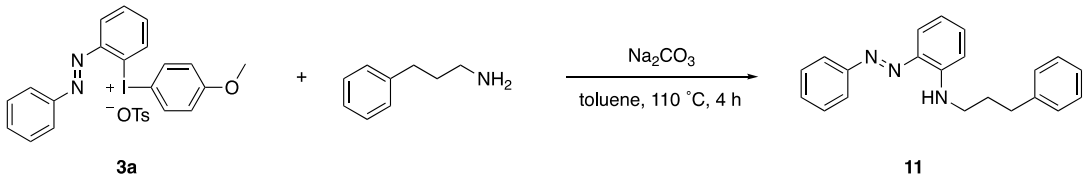


Following a reported procedure,[28] ethyl-2-nitropropanoate (1.0 equiv, 0.20 mmol, 29 mg), and Cs_2CO_3 (1.2 equiv, 0.24 mmol, 78 mg) were added to an oven-dry microwave vial. Anhydrous toluene (1.5 mL) was added to the vial at 0 °C and the solution was stirred at rt for 10 min. Diaryliodonium salt **3a** (1.0 equiv, 0.20 mmol, 117 mg) was then added to the reaction mixture at rt open to air. The reaction mixture was stirred at rt for 1 h followed by 6 h at 110 °C. After cooling to rt, the reaction mixture was quenched with brine (4 mL) and extracted CH_2Cl_2 (3 × 5 mL), washed with water (4 mL) and brine (4 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude was purified by flash column chromatography (silica, 1% Et_2O in pentane) to afford the propanoate **10** as a red oil (0.09 mmol, 29 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 1H), 7.84 – 7.78 (m, 2H), 7.57 – 7.47 (m, 5H), 7.40 – 7.36 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.5, 152.6, 148.9, 135.5, 131.9, 131.4, 130.4, 129.4, 126.8, 123.9, 116.2, 95.4, 63.2, 25.8, 13.9. HRMS(ESI) *m/z*: calcd. for $C_{17}H_{17}N_3O_4Na^+$ $[M+Na]^+$ 350.1111; found 350.1109.

7.4 Arylation of Nitrogen Nucleophiles

(*E*)-2-(Phenyldiazenyl)-*N*-(3-phenylpropyl)aniline (11)

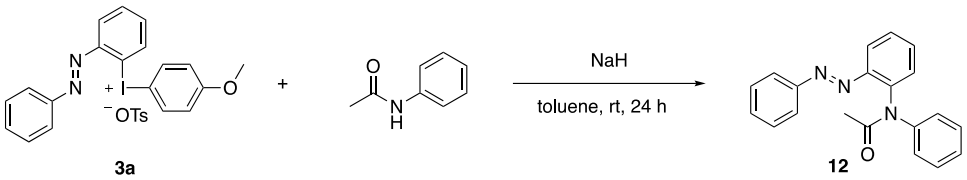


Following a reported procedure,[29] diaryliodonium salt **3a** (1.00 equiv, 200 μmol, 113 mg) and Na_2CO_3 (1.1 equiv, 0.22 mmol, 23 mg) were added to an oven-dried microwave vial and sealed with a cap. The vial was evacuated and backfilled with argon three times. Freshly distilled 3-phenylpropan-1-amine (1.1 equiv, 0.22 mmol, 31 μL) was added, followed by the addition of anhydrous and degassed toluene (1 mL). The mixture was stirred at 110 °C for 4 h and after

completion of the reaction, the mixture was diluted with CH_2Cl_2 (3 × 5 mL), washed with water (4 mL) and brine (4 mL), dried over magnesium sulfate and concentrated *in vacuo*. The crude material was purified by column chromatography (silica, 1% Et_2O in pentane) to yield the aniline product **11** as a red oil (0.04 mmol, 14 mg, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.87 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.53 – 7.46 (m, 2H), 7.43 – 7.36 (m, 1H), 7.34 – 7.27 (m, 3H), 7.25 – 7.18 (m, 3H), 6.82 – 6.71 (m, 2H), 3.36 – 3.28 (m, 2H), 2.85 – 2.77 (m, 2H), 2.13 – 2.02 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.0, 143.4, 141.5, 136.2, 132.8, 132.0, 129.7, 129.2, 128.6, 128.6, 126.2, 122.0, 115.7, 111.9, 42.0, 33.5, 30.8. HRMS(ESI) *m/z*: calcd. for $C_{21}H_{21}N_3Na^+$ $[M+Na]^+$ 338.1628; found 338.1624.

(*E*)-*N*-Phenyl-*N*-(2-(phenyldiazenyl)phenyl)acetamide (12)



Following a reported procedure,[30] acetanilide (1.0 equiv, 0.20 mmol, 27 mg), diaryliodonium salt **3a** (1.5 equiv, 0.30 mmol, 176 mg) and NaH (60%, 1.5 equiv, 0.30 mmol, 12 mg) were added to a dry 5 mL microwave vial, which was capped. The vial was evacuated and backfilled with nitrogen three times. Stirring was started and anhydrous toluene (4 mL) added. *NB: Gas evolved.* The solution was stirred at ambient temperature for 24 h. *NB: It is important that the stirring is vigorous*. The reaction mixture was diluted with CH_2Cl_2 (3 × 5 mL), washed with water (4 mL) and brine (4 mL), dried over magnesium sulfate and concentrated *in vacuo*. The crude was purified by column chromatography (silica, 1% Et_2O in pentane) to yield product **12** as a red oil (0.16 mmol, 50 mg, 79% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.94 – 7.88 (m, 2H, rotamer A), 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H, rotamer B), 7.54 – 7.47 (m, 4H), 7.46 – 7.39 (m, 2H), 7.38 – 7.28 (m, 5H), 7.19 (t, *J* = 7.2 Hz, 1H), 2.12 (s, 3H, rotamer B), 2.05 (s, 3H, rotamer A). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.0, 153.1, 142.4, 132.2, 131.8, 130.0, 129.4, 129.2, 128.9, 128.6, 128.3, 127.3, 126.6, 123.4, 117.4, 30.6, 23.6. HRMS(ESI) *m/z*: calcd. for $C_{20}H_{17}N_3ONa^+$ $[M+Na]^+$ 338.1264; found 338.1262. The product is previously reported,[31] but comparison of the NMR data is complicated by the the restricted rotation around the C-N bond causing tertiary amides to exist as rotamers. For this compound, the presence of rotamers caused the peaks broadening at ambient temperature. Therefore, the ^{1}H- and ^{13}C-NMR were recorded at 263 K, 298 K and 323 K in both $CDCl_3$ and DMSO-d_6. In the spectra, peaks of the methyl group are consistent with varying degrees of restricted rotation of the amide group. When the ^{1}H-NMR spectra were recorded in $CDCl_3$, the two rotamers were established to be in a 1:7 ratio (**Figure S3**). Instead, it was established that these peaks coalesce when recording the ^{1}H (**Figure S3**, above) and ^{13}C NMR spectra (**Figure S3**, below), going from 263 K to 323 K in DMSO-d_6.

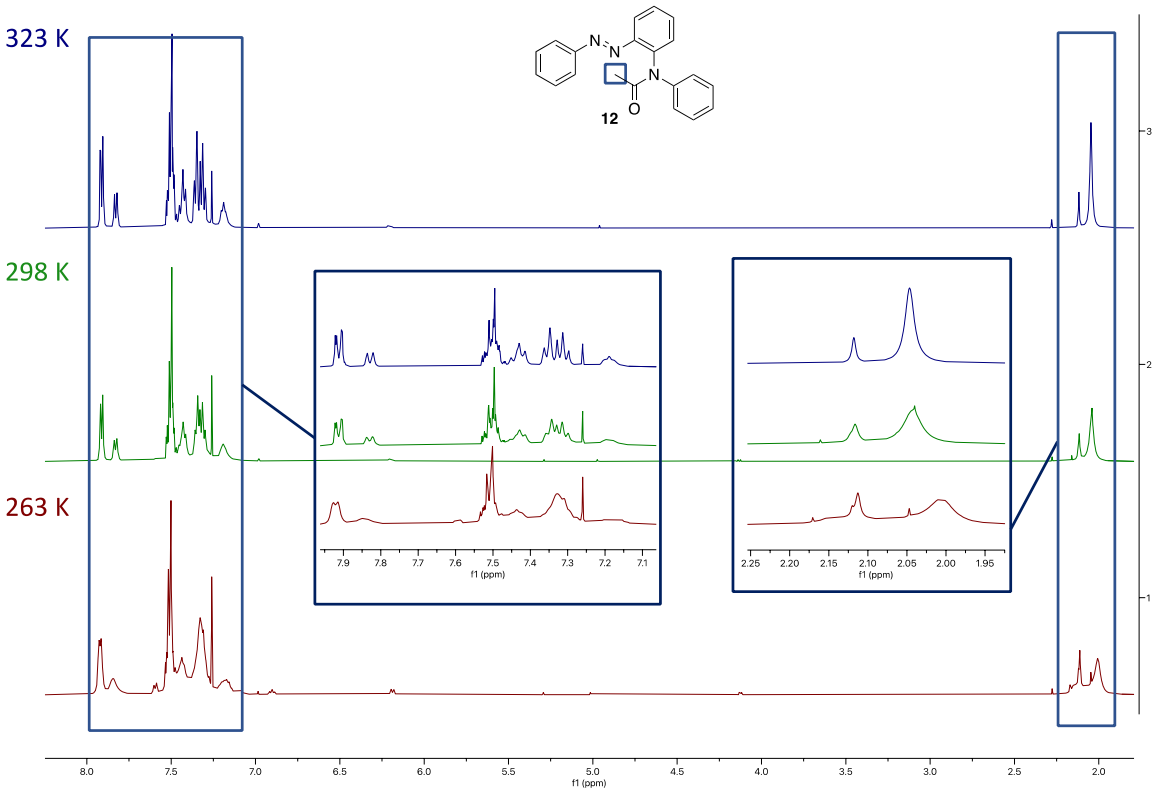


Figure S13. ^{1}H NMR spectra of amide **11** from 263 K to 323 K in $CDCl_3$.

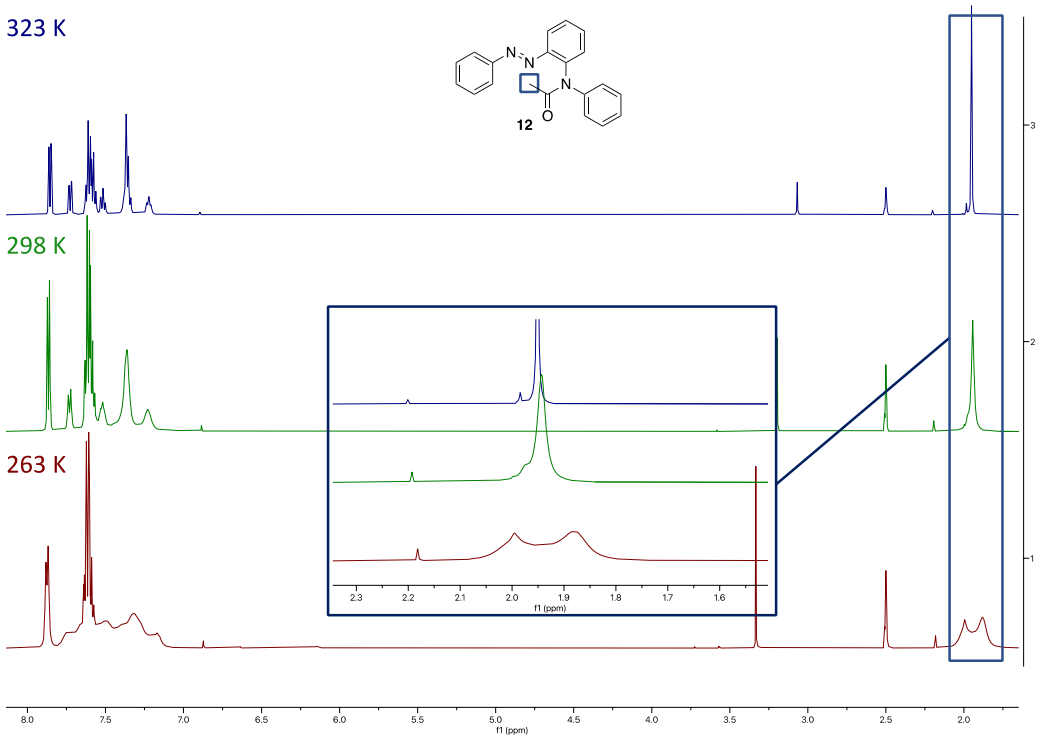


Figure S14. ^{1}H NMR spectra of amide **11** from 263 K to 323 K in DMSO-d_6.

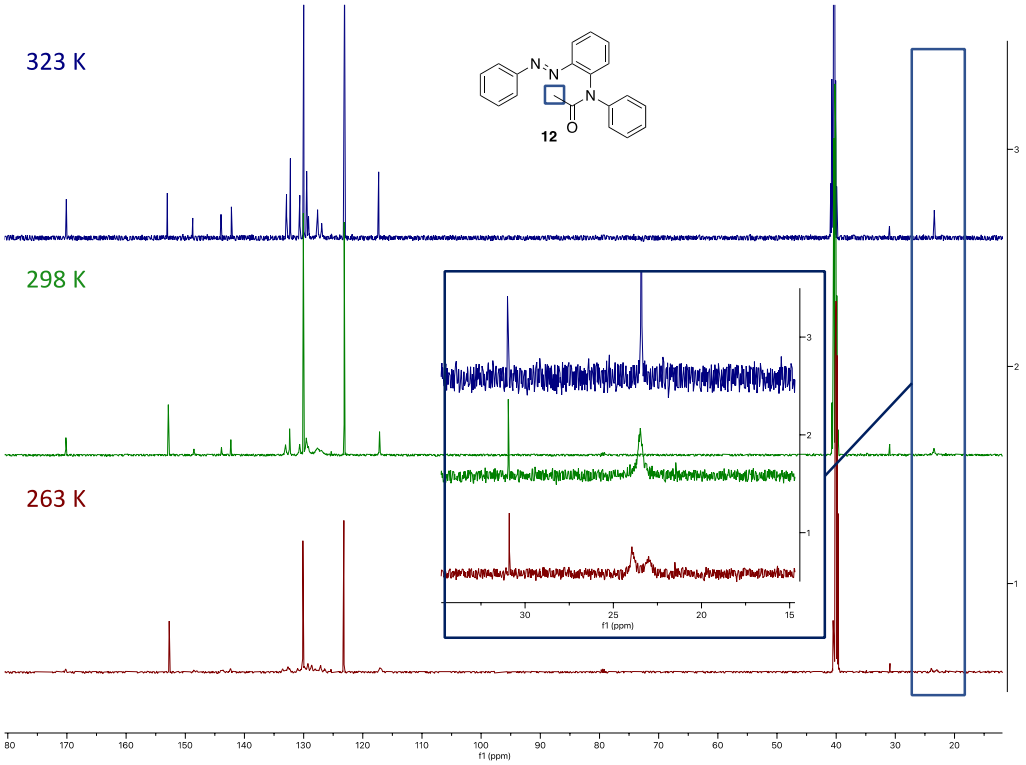
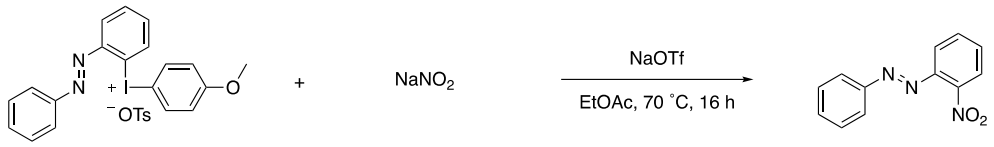


Figure S15. ^{13}C NMR spectra of amide **11** from 263 K to 323 K in DMSO-d_6.

(*E*)-1-(2-Nitrophenyl)-2-phenyldiazene (13)



3a **13**

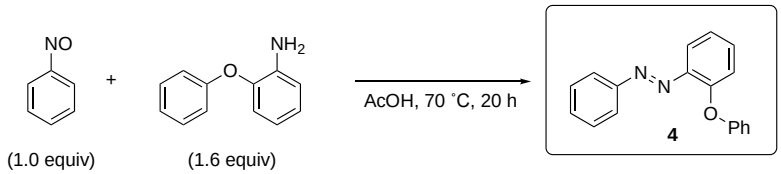
Following a reported procedure,[32] diaryliodonium salt **3a** (1.0 equiv, 0.20 mmol, 117 mg), sodium nitrite (1.1 equiv, 0.22 mmol, 15 mg) and sodium triflate (1.0 equiv, 0.20 mmol, 34 mg) were added to a microwave vial followed by EtOAc (1 mL). The vial was capped, and the solution was stirred at 70 °C for 16 h. The solvent was evaporated, and the crude was loaded onto silica and purified by flash chromatography (silica, 1% of Et_2O in *n*-pentane) to yield product **13** as a red oil (0.13 mmol, 29 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 3H), 7.74 – 7.67 (m, 2H), 7.63 – 7.53 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.6, 147.6, 145.6, 133.2, 132.5, 130.6, 129.4, 124.2, 123.8, 118.6. HRMS(ESI) *m/z*: calcd for $C_{12}H_9N_3O_2Na^+$ $[M+Na]^+$ 250.0587; found 250.0590. Analytical data were in accordance with those previously reported.[33]

7.5 Comparison with Literature Methods for Synthesis of Products 4-7 and 12-14

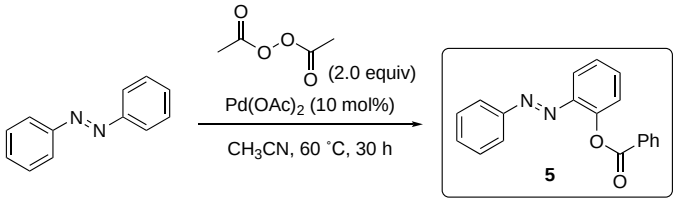
To evaluate the efficiency of the presented methodology, a comparison with reported routs to the know products **4-7** and **12-14** are given below.

Product 4: Previously obtained through an oxidative coupling from the corresponding aniline (a Mills reaction), no yield was reported (**Scheme S4**).[19] In a similar manner, the product was later obtained in 48% yield.[23] Yield with our method: 75% from **3a**.



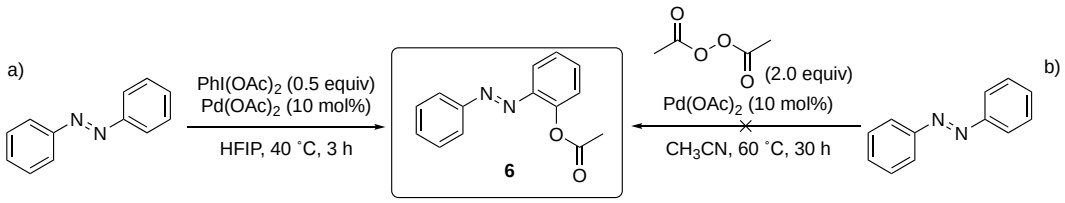
Scheme S4. Synthesis of product **4**.

Product 5: Previously obtained in 82% yield through a Pd-catalyzed *ortho*-functionalization of azoarenes (**Scheme S5**).[20] Yield with our method: 79% from **3a**.



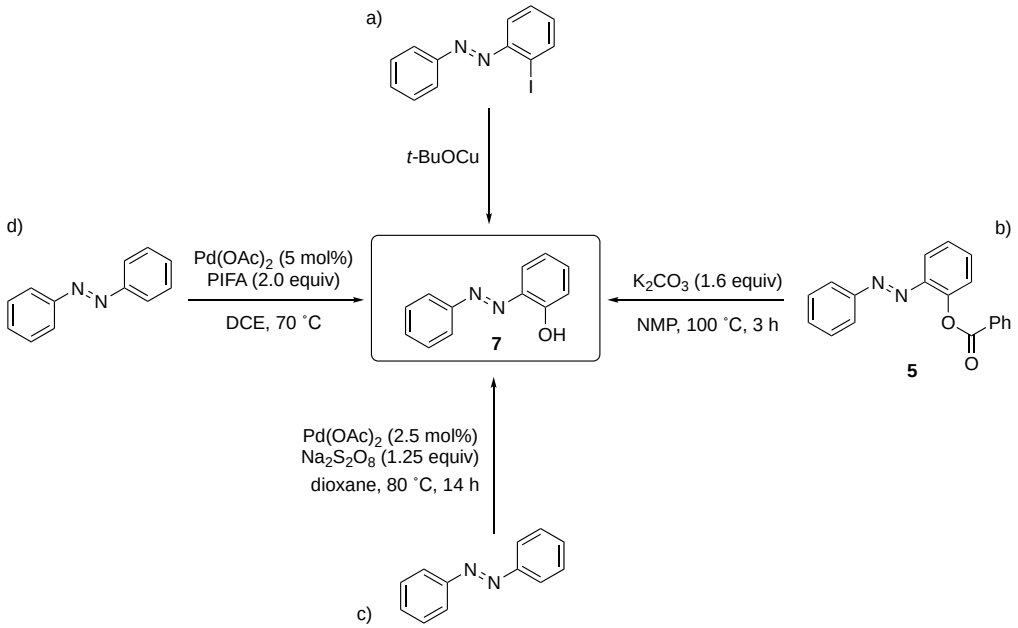
Scheme S5. Synthesis of product **5**.

Product 6: Previously synthesized *via* a Pd-catalyzed C-H acetoxylation of azobenzene with (diacetoxyiodo)benzene to give **6** in excellent yield using expensive hexafluoroisopropanol (HFIP) as solvent (**Scheme S6a**).[21] The synthesis of product **6** was also attempted *via* Pd-catalyzed *ortho*-functionalization of azoarenes with acylperoxides used in the synthesis of **5** (above) but the product could not be detected (**Scheme S6b**).[20] Yield with our method: 70% from **3a**.



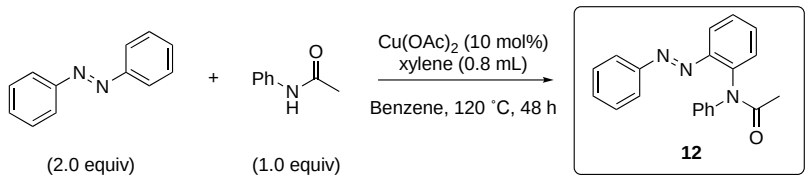
Scheme S6. Methodologies for the synthesis of product **6**.

Product 7: Several methods are reported for the synthesis of product **7**. Despite the traditional approach of a Mills reaction,[34] it was obtained in 42% yield as side product in a reaction with iodoazobenzene and stoichiometric amount of copper salt (**Scheme S7a**).[35] Alternatively, it could be obtained by hydrolysis of product **5**, formed through Pd-catalyzed detailed above (75% from azobenzene over two steps) (**Scheme S7b**).[20] Moreover, a Pd-catalyzed hydroxylation of azoarenes delivered **7** in 61% yield upon heating to 80 °C for prolonged time (**Scheme S7c**).[36] Finally, a Pd-catalyzed oxidation using excess PIFA in the toxic solvent DCE gave **7** in 81% (**Scheme S7d**).[37] Yield with our method: 81% from **6** (57% over two steps from **3a**); 38% directly from **3a**.



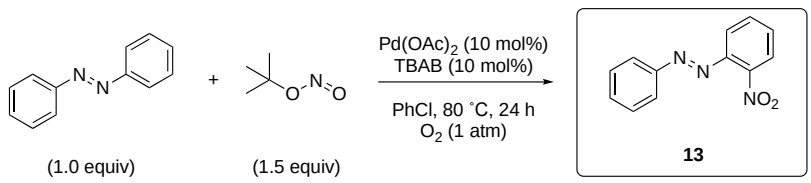
Scheme S7. Methodologies for the synthesis of product **7**.

Product 12: A copper(II)-catalyzed dehydrogenation amidation of azoarenes was used to synthetize the azobenzene amide **12** in 56% yield.[31] The protocol required extended heating to 120 °C in toxic benzene, in a pressurized reaction vessel (bp of benzene = 80 °C) (**Scheme S8**). Yield with our method: 79% from **3a**.



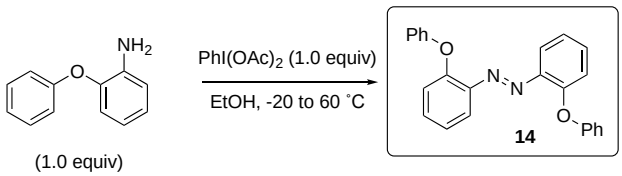
Scheme S8. Cu(II)-catalyzed amidation to obtain product **12**.

Product 13: Previously obtained in 72% yield *via* a Pd-catalyzed C-H functionalization of azobenzene in presence of tetrabutyl ammonium bromide (TBAB) upon heating to 80 °C in chlorobenzene for 24 h (**Scheme S9**)[33] or by traditional Mills reaction in 77-81% yield.[38] Yield with our method: 63% from **3a**.



Scheme S9. Pd-catalyzed nitration to obtain product **13**.

Product 14: Previously obtained in only 8% yield through an oxidative coupling from the corresponding aniline (**Scheme S10**).[23] Yield with our method: 57% from **3h**.



Scheme S10. Pd-catalyzed nitration to obtain product **14**.

In summary, a range of Pd-catalyzed methods have previously been reported to reach target products **5**-**7** and **13**, whereas Cu-catalysis was employed to reach product **12**. Finally, metal-free oxidative couplings from pre-functionalized anilines have been employed to obtain products **4**, **7**, **13** and **14** in differing yields.
The majority of the methods require a transition metal catalyst, prolonged heating and/or a toxic solvent. Furthermore, nitroso compounds are not always stable. While our methodology cannot always compete in terms of yield, it is a mild and transition metal-free method to reach the target products, as well as several novel structures with a variety of O, S, and N-functional groups.

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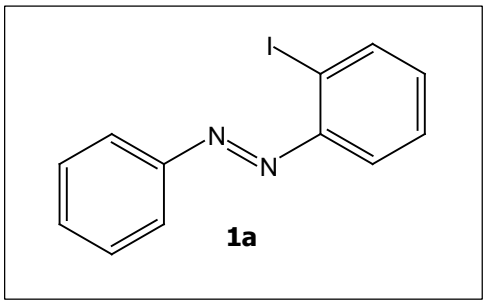
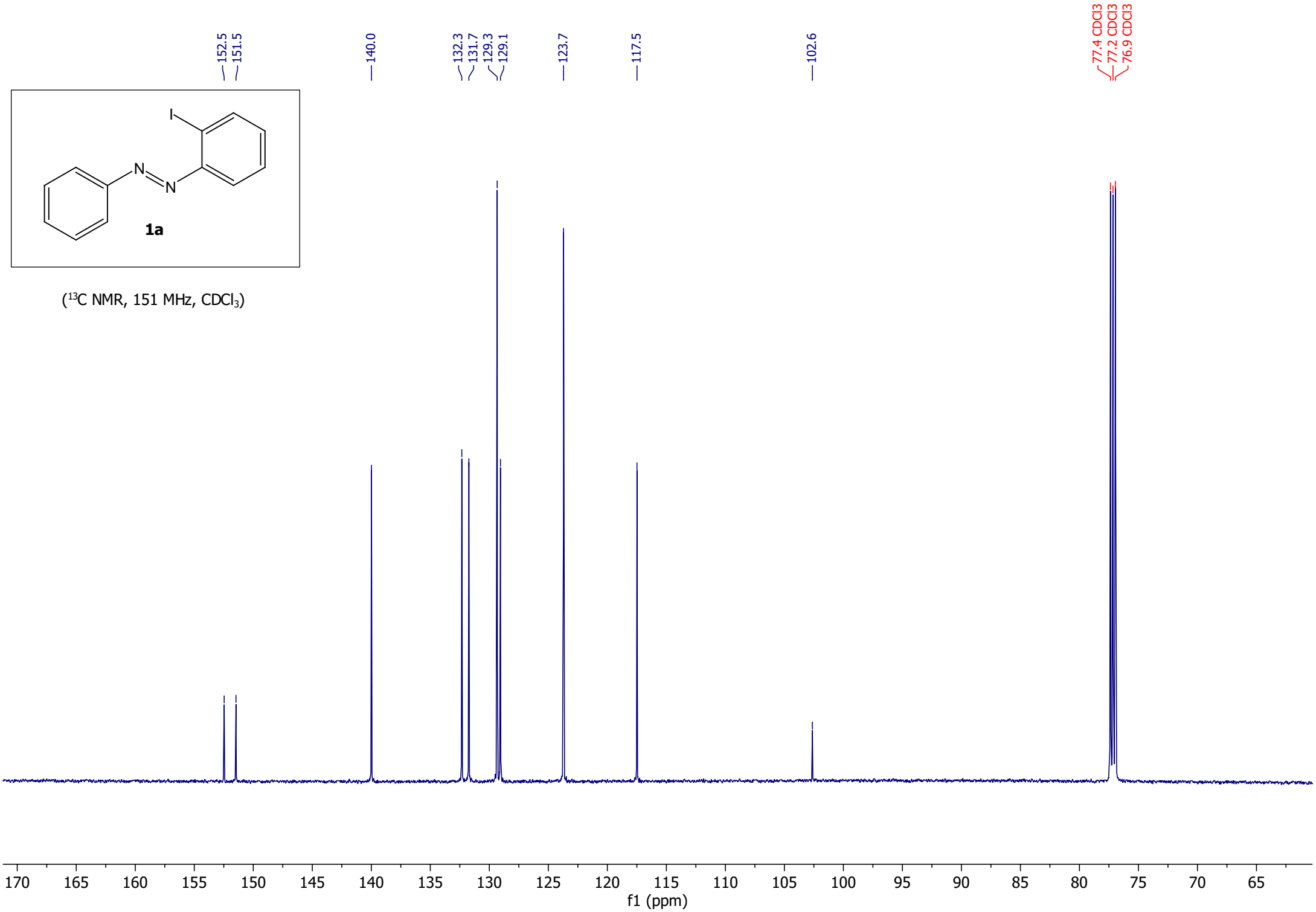
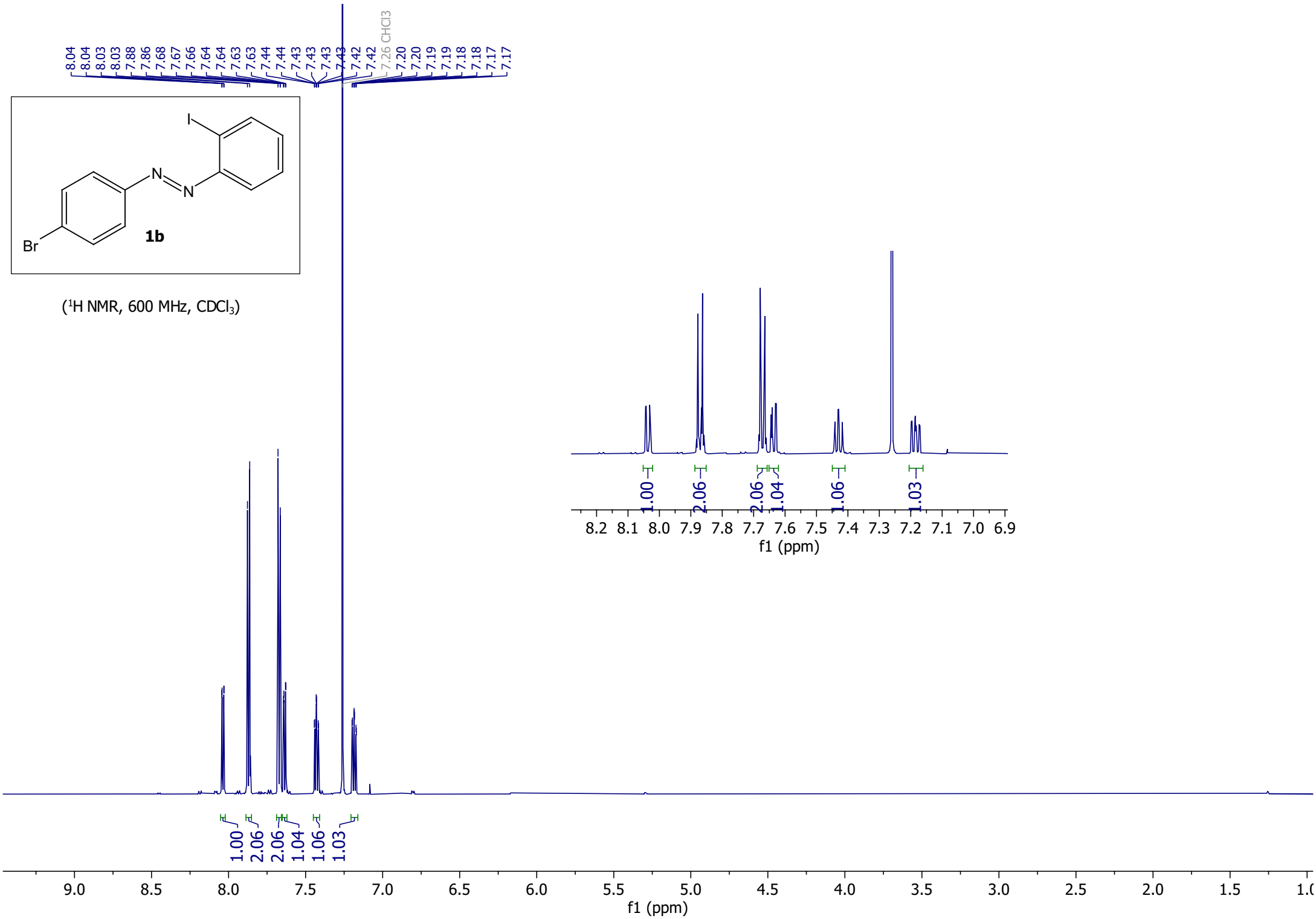
9 ^{1}H- and ^{13}C-NMR Spectra

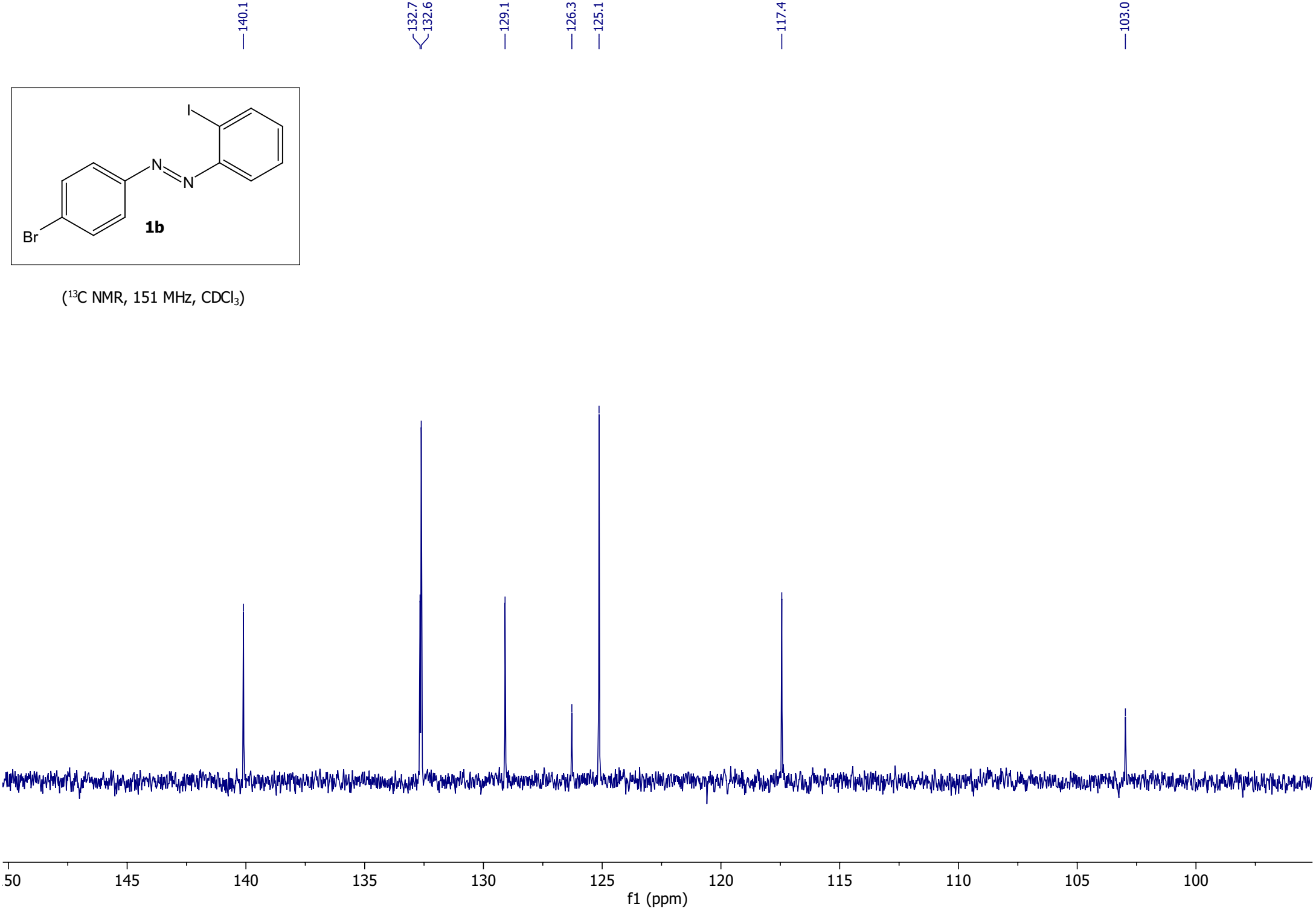


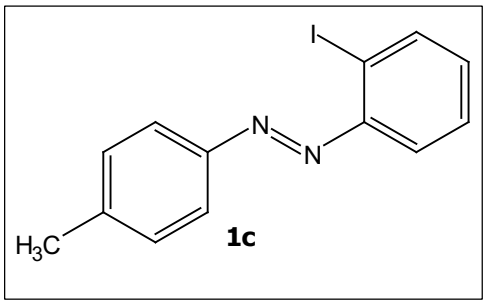
1a

(^{1}H NMR, 600 MHz, $CDCl_3$)

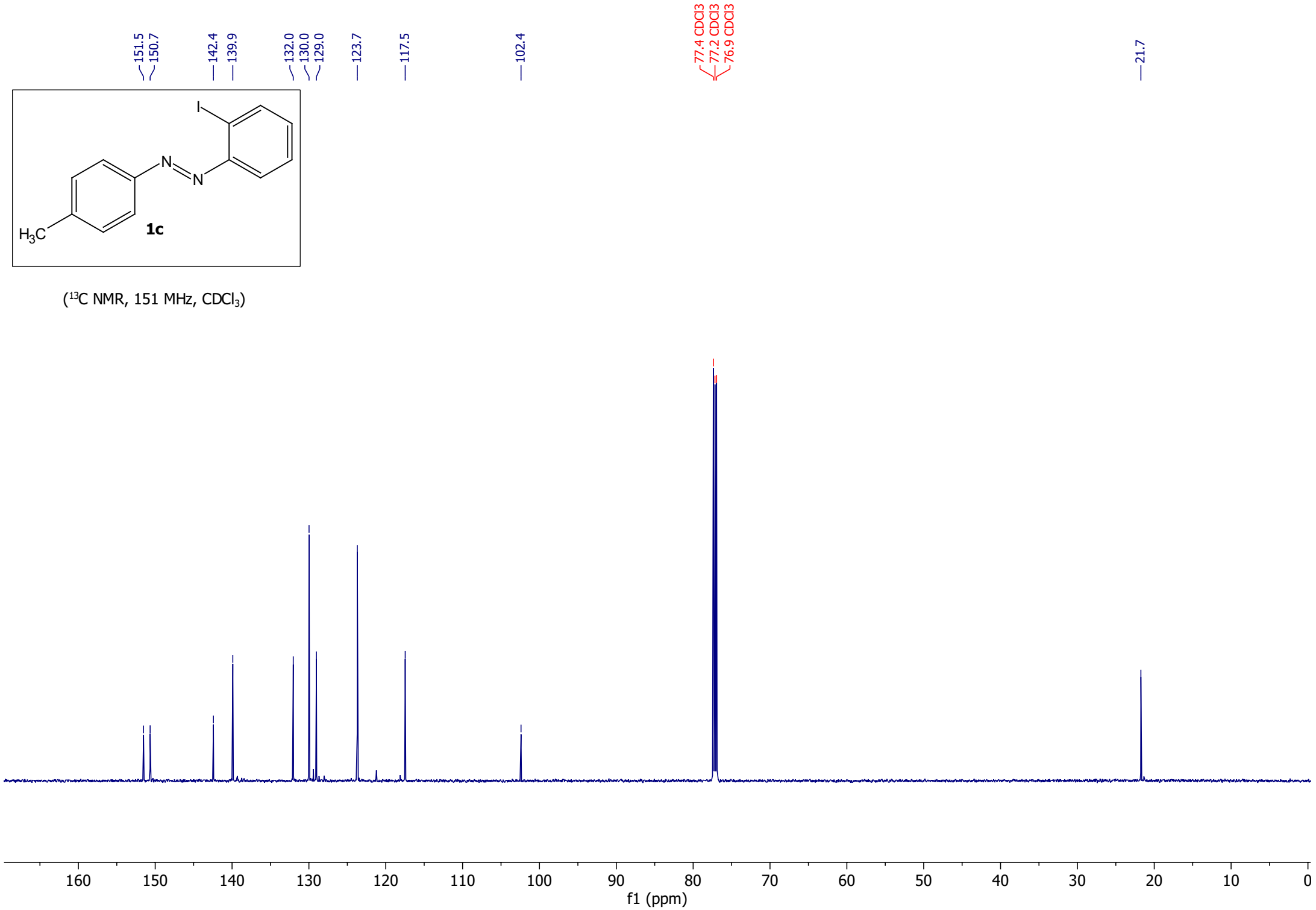

152.5
151.5
140.0
132.3
131.7
129.3
129.1
123.7
117.5
102.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
I
N
N
1a
(13C NMR, 151 MHz, CDCl3)
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
f1 (ppm)


8.04
8.04
8.03
8.03
7.88
7.86
7.68
7.67
7.66
7.64
7.64
7.63
7.63
7.44
7.44
7.43
7.43
7.43
7.43
7.42
7.42
7.26 CHCl3
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.17
I
N
N
Br
1b
(1H NMR, 600 MHz, CDCl3)
1.00
2.06
2.06
1.04
1.06
1.03
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

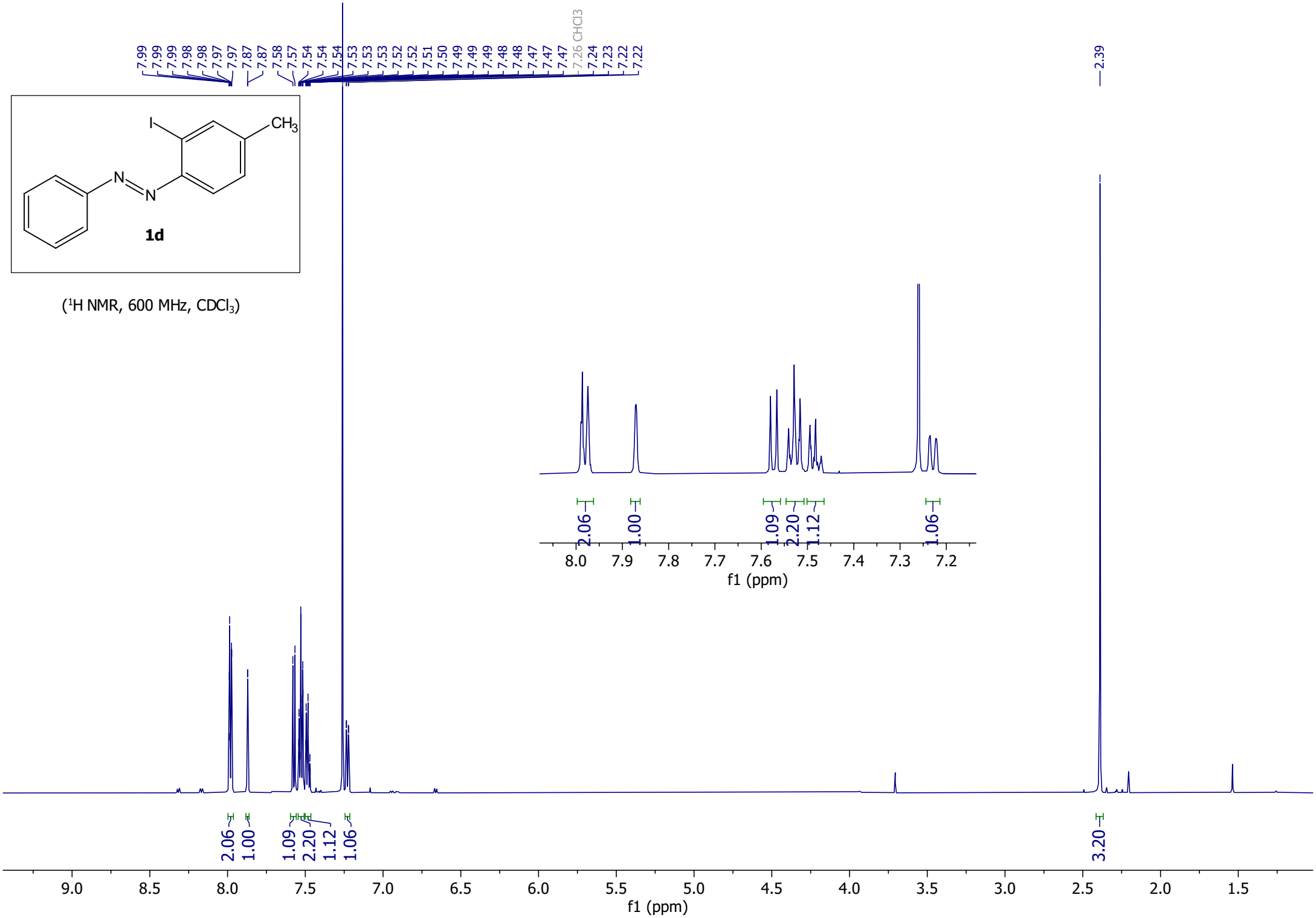

140.1
132.7
132.6
129.1
126.3
125.1
117.4
103.0
I
N
N
Br
1b
(13C NMR, 151 MHz, CDCl3)
50
145
140
135
130
125
120
115
110
105
100
f1 (ppm)

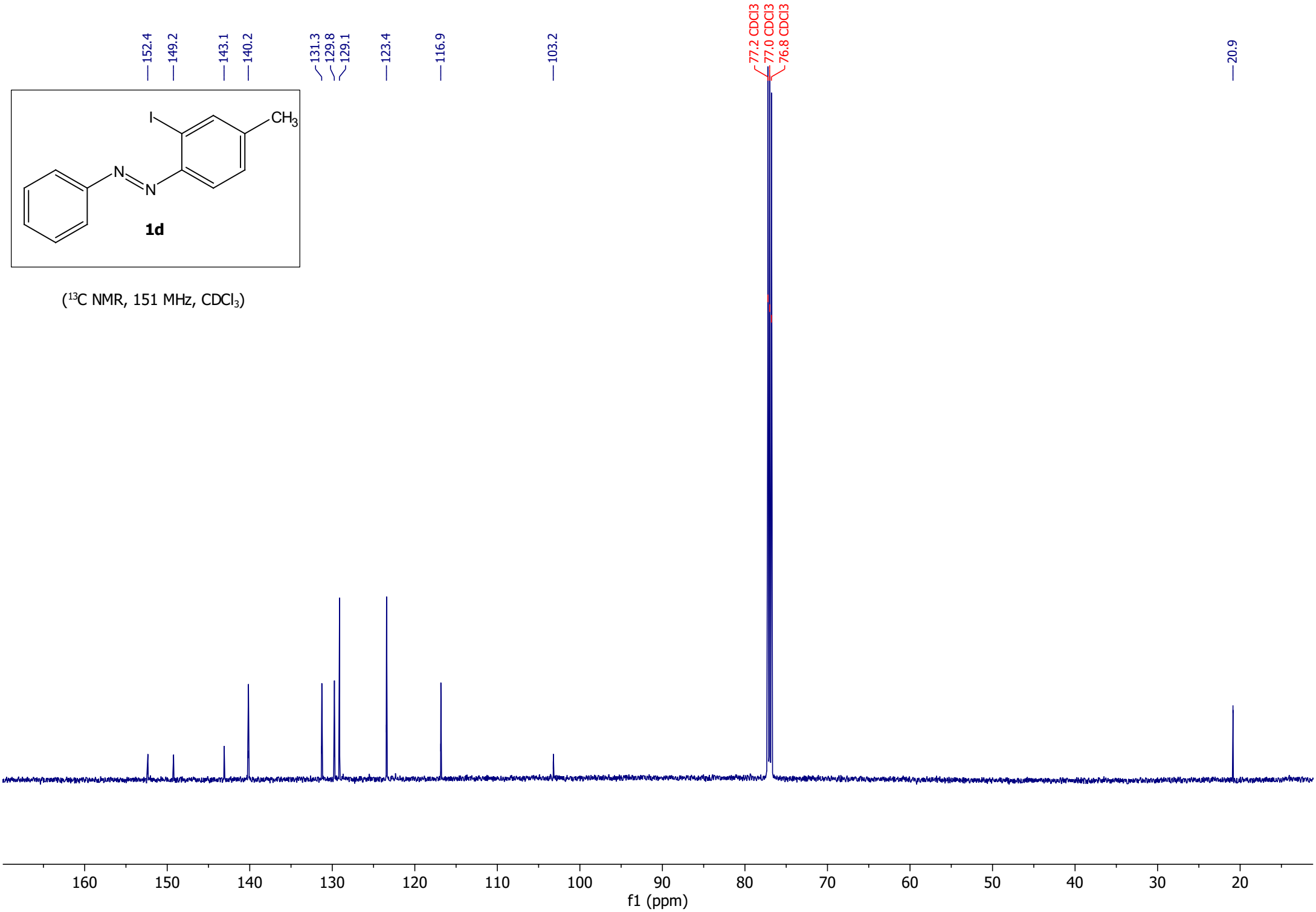


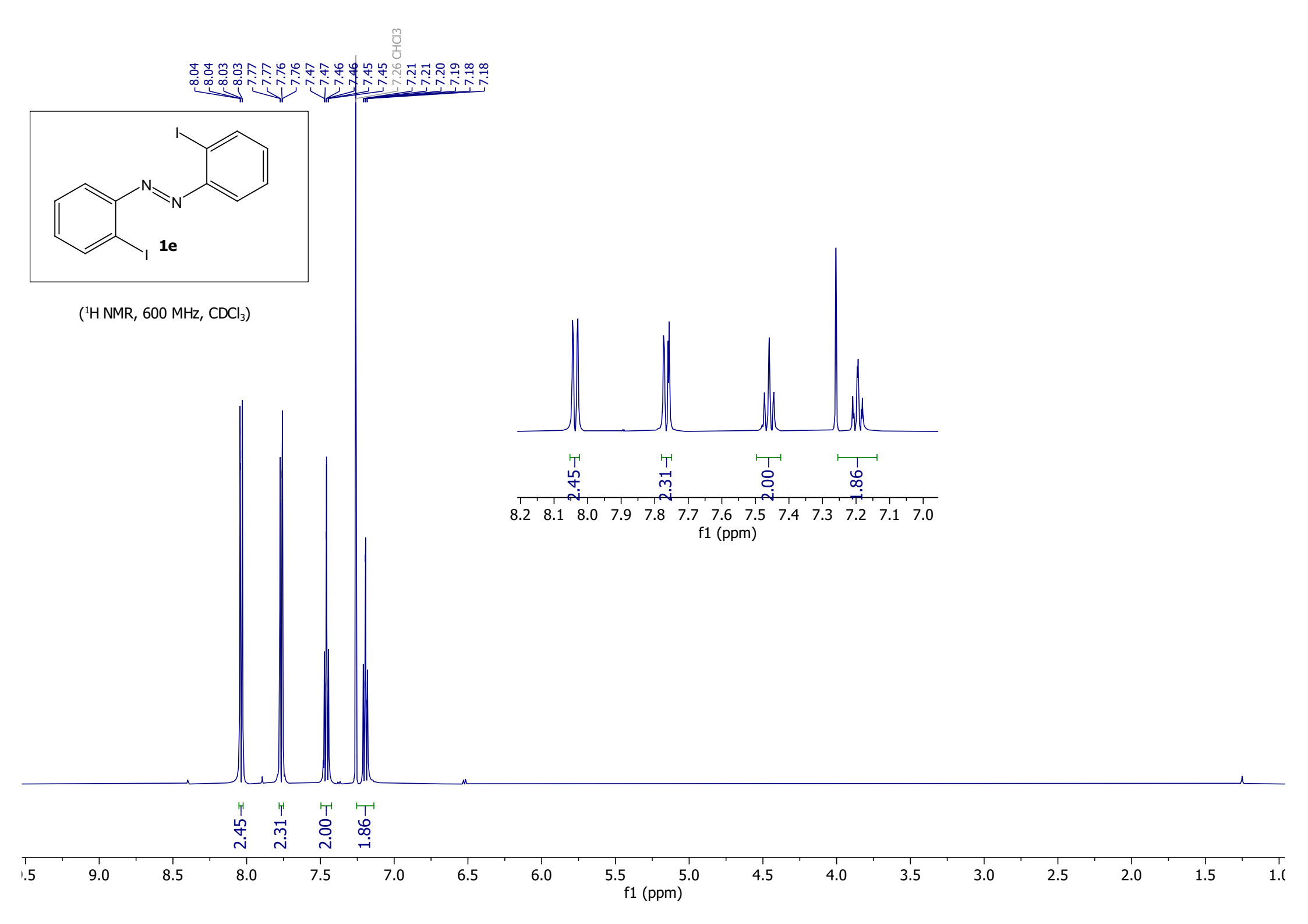
(^{1}H NMR, 600 MHz, $CDCl_3$)

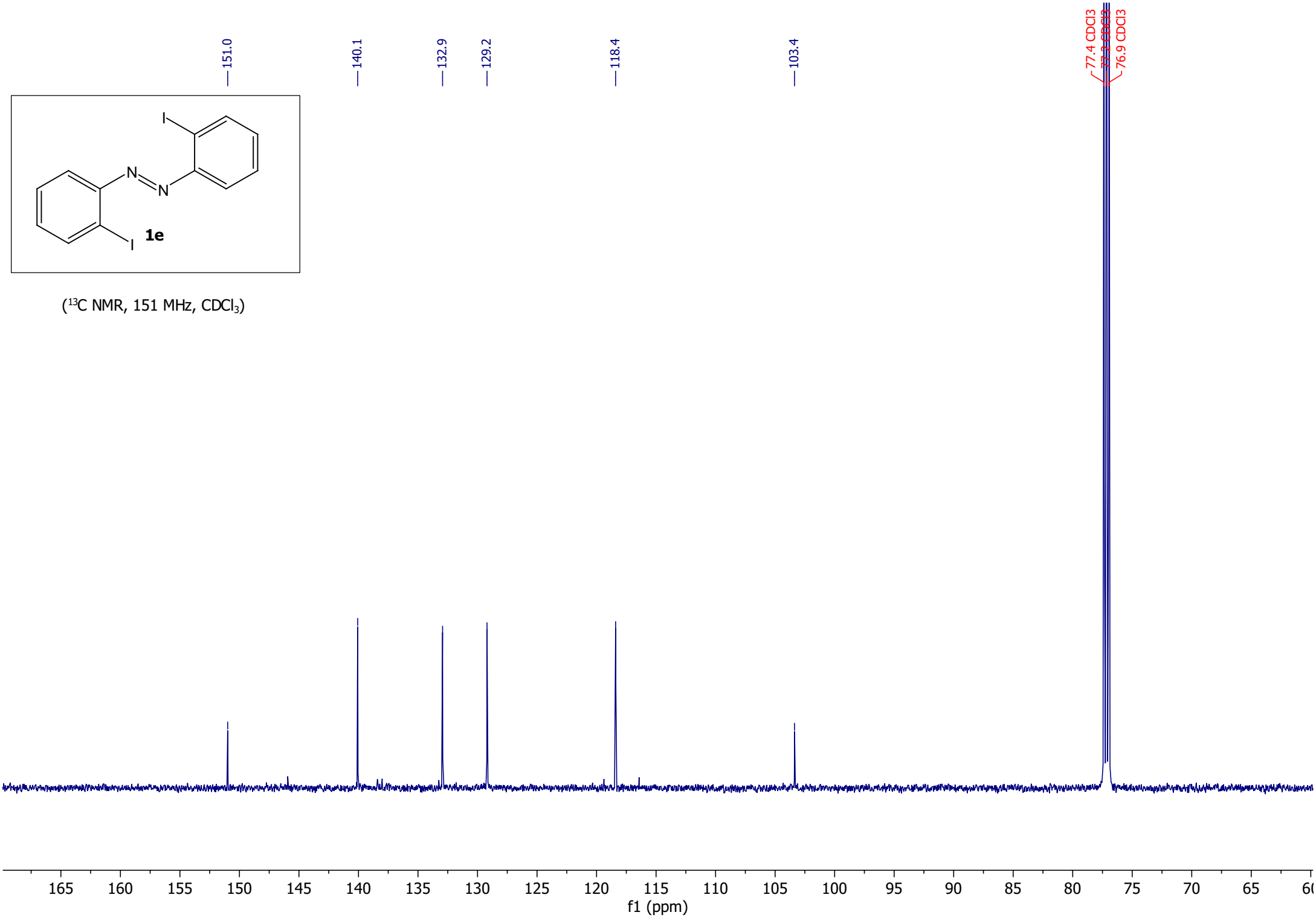


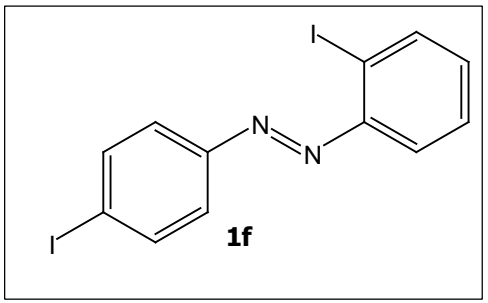
(^{13}C NMR, 151 MHz, $CDCl_3$)


7.99
7.99
7.99
7.98
7.98
7.97
7.97
7.87
7.87
7.58
7.57
7.54
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.50
7.49
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.26 CHCl3
7.24
7.23
7.22
7.22
2.39
I
CH3
N
N
1d
(1H NMR, 600 MHz, CDCl3)
2.06
1.00
1.09
2.20
1.12
1.06
3.20
f1 (ppm)

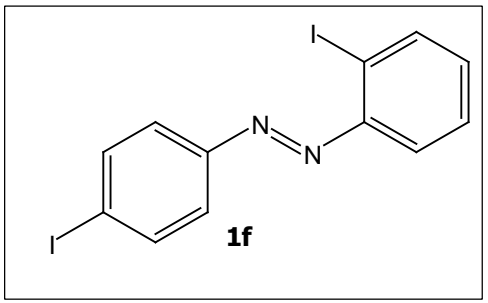

152.4
149.2
143.1
140.2
131.3
129.8
129.1
123.4
116.9
103.2
77.2 CDCl3
77.0 CDCl3
76.8 CDCl3
20.9
I
CH3
N
N
1d
(13C NMR, 151 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


8.04
8.04
8.03
8.03
7.77
7.77
7.76
7.76
7.47
7.47
7.46
7.46
7.45
7.45
7.26 CHCl3
7.21
7.21
7.20
7.19
7.18
7.18
I
N
N
I
1e
(1H NMR, 600 MHz, CDCl3)
2.45
2.31
2.00
1.86
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
2.45
2.31
2.00
1.86
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

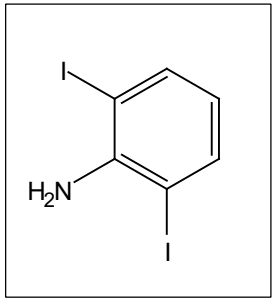

151.0
140.1
132.9
129.2
118.4
103.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
I
N
N
I
1e
(13C NMR, 151 MHz, CDCl3)
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)



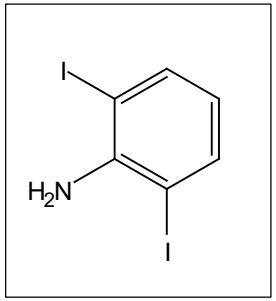
(^{1}H NMR, 600 MHz, $CDCl_3$)



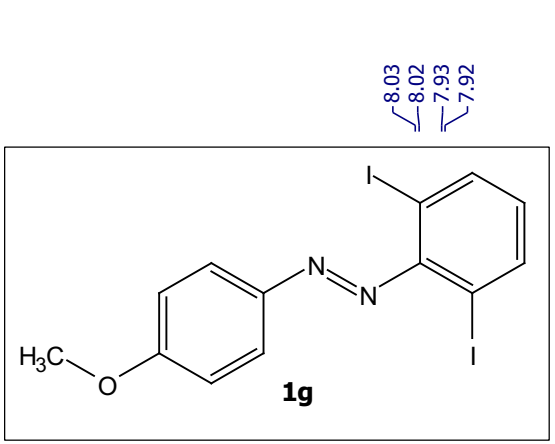
(^{13}C NMR, 151 MHz, $CDCl_3$)



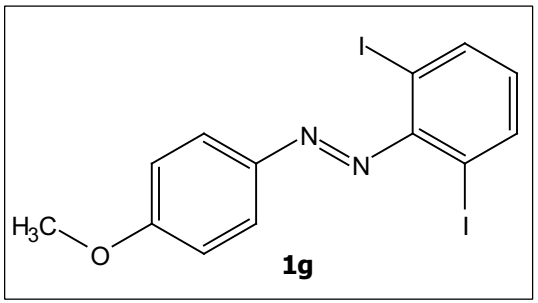
(^{1}H NMR, 600 MHz, $CDCl_3$)



(^{13}C NMR, 151 MHz, $CDCl_3$)

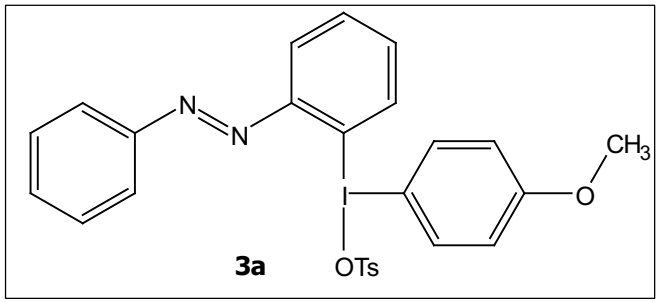


(^{1}H NMR, 600 MHz, $CDCl_3$)



1g

(^{13}C NMR, 151 MHz, $CDCl_3$)



3a

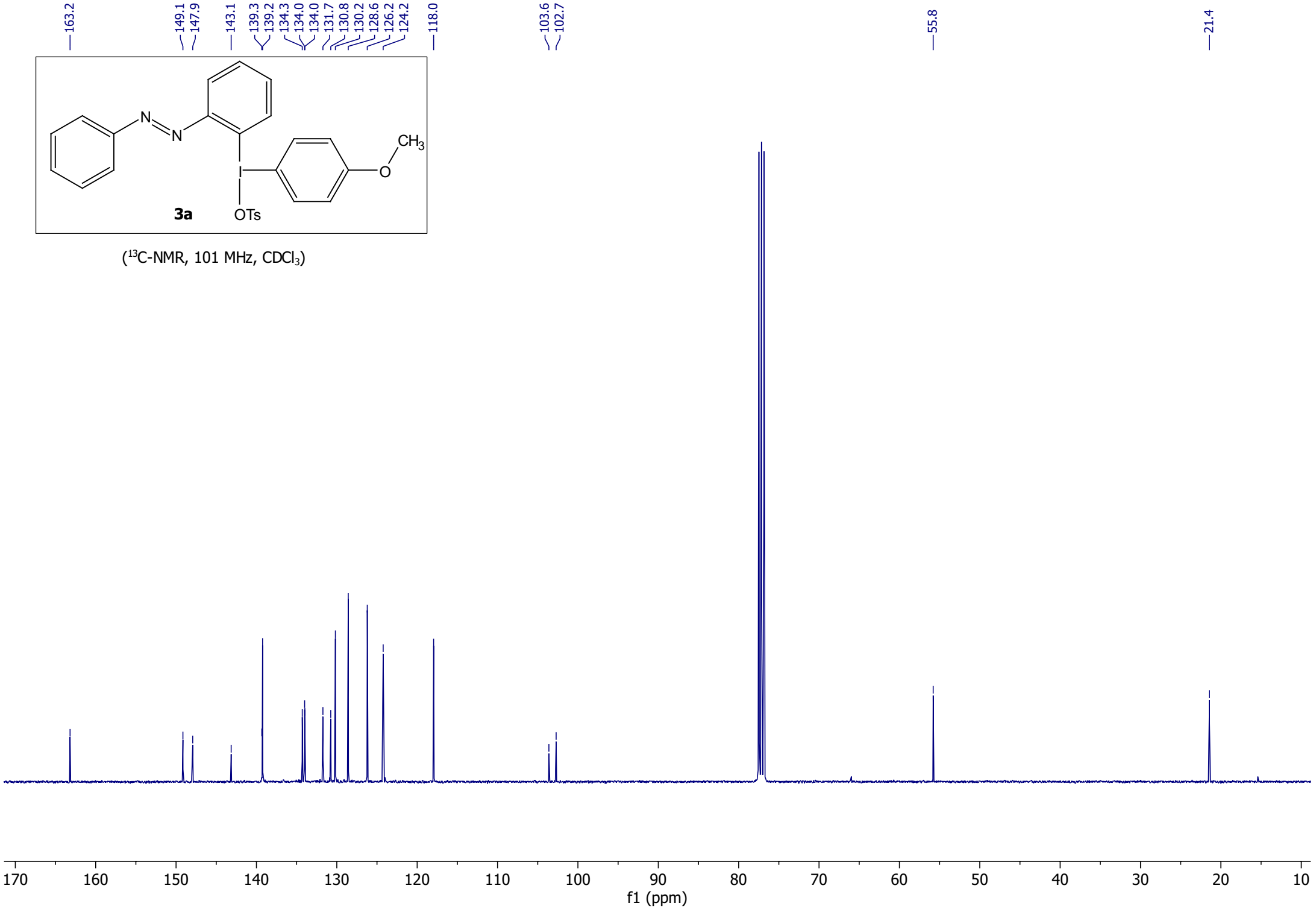
(^{1}H-NMR, 400 MHz, $CDCl_3$)

8.35 8.35 8.33 8.33 8.26 8.26 8.26 8.24 8.24 7.96 7.95 7.94 7.93 7.92 7.92 7.75 7.75 7.73 7.73 7.71 7.71 7.66 7.65 7.64 7.64 7.60 7.58 7.57 7.56 7.56 7.56 7.54 7.54 7.54 7.53 7.52 7.51 7.51 7.50 7.43 7.42 7.41 7.41 7.40 7.39 7.39 7.06 7.04 6.99 6.99 6.98 6.97 6.97 6.97 3.87 2.31

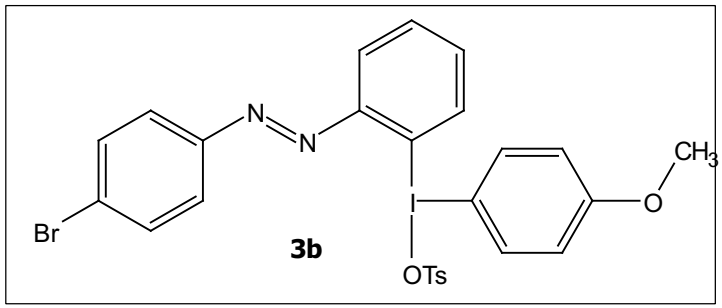
1.00 1.93 1.93 1.03 2.08 3.06 0.99 2.08 2.87 2.88 3.09

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0

f1 (ppm)

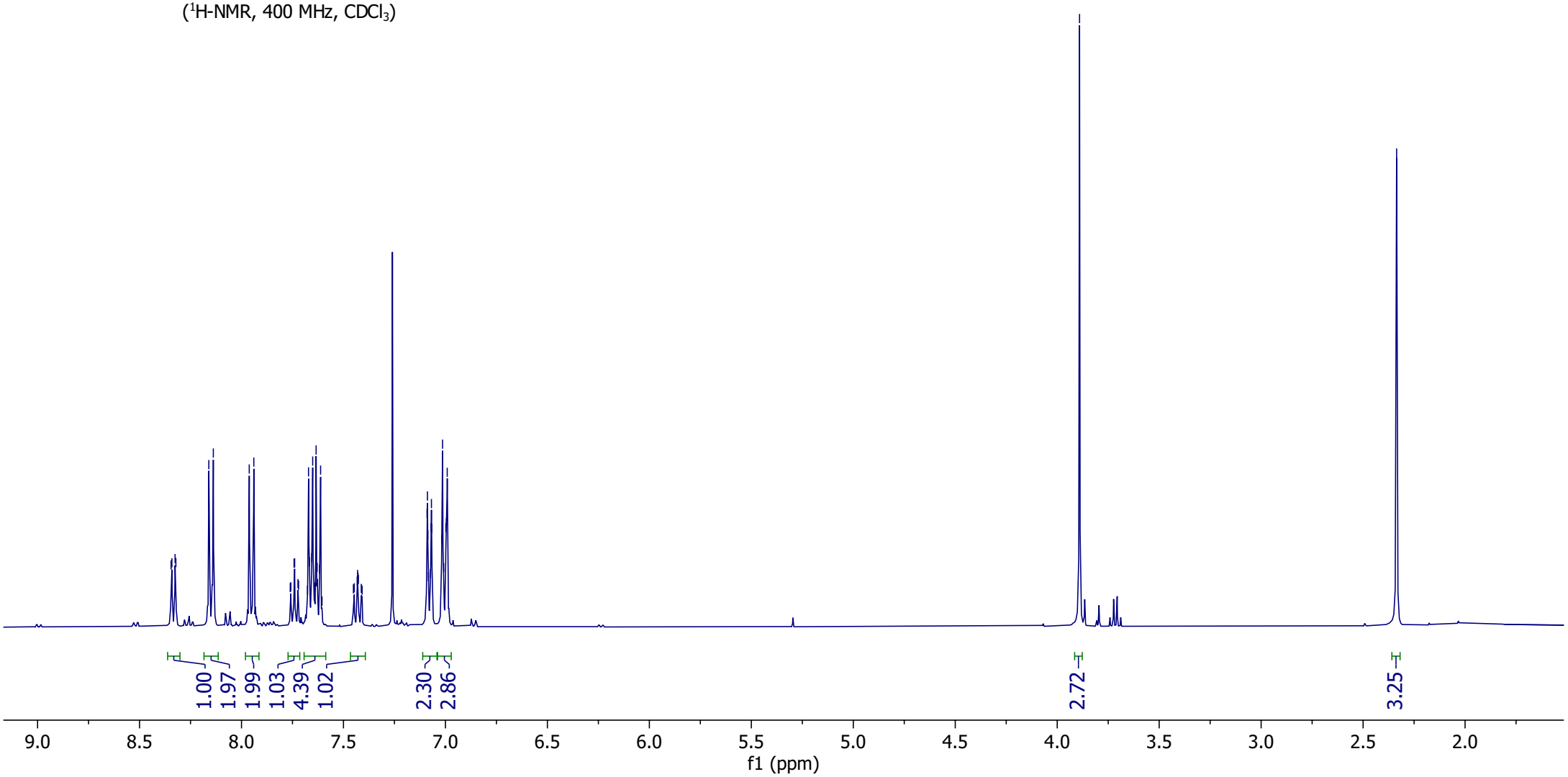


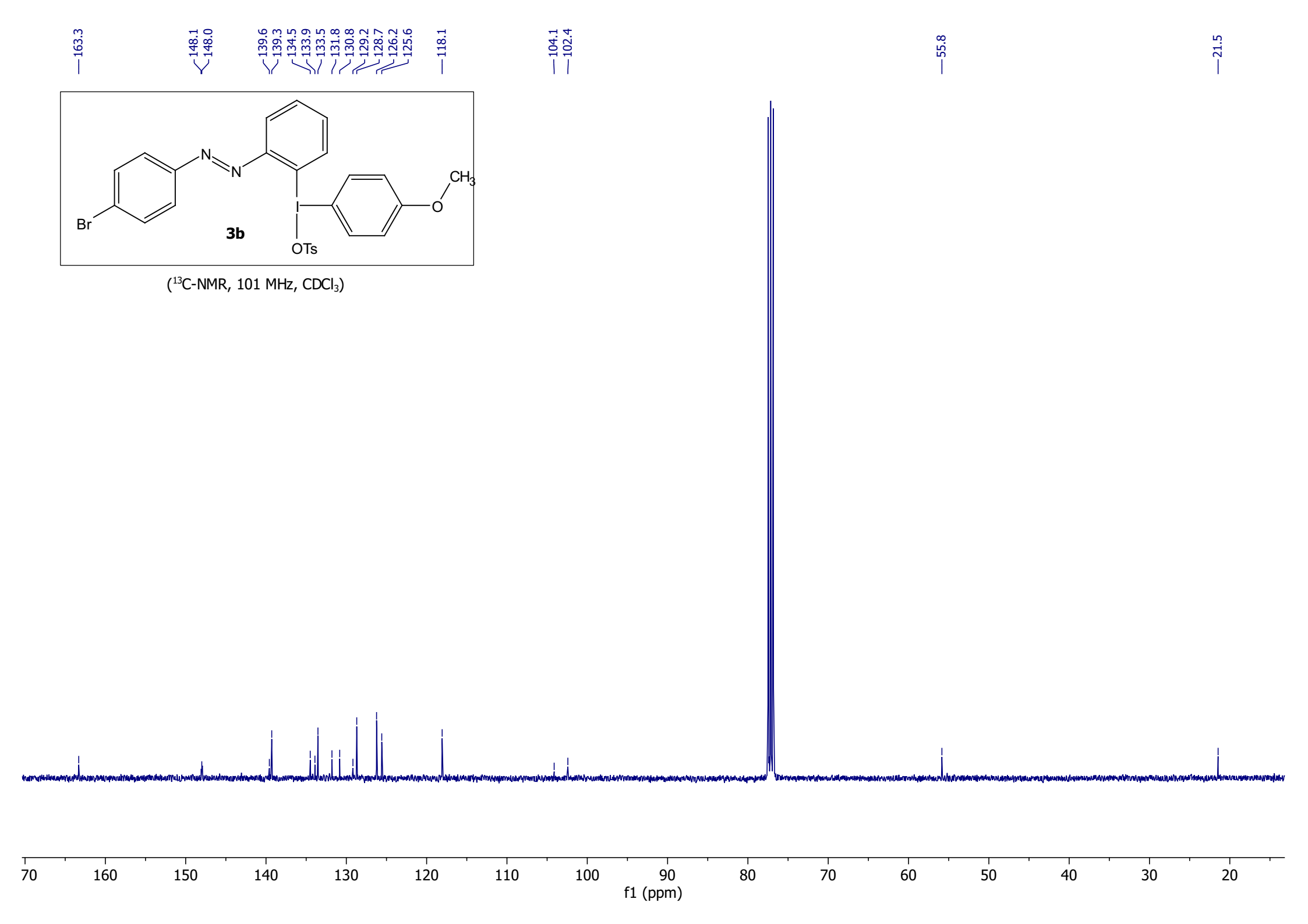
(^{13}C-NMR, 101 MHz, $CDCl_3$)



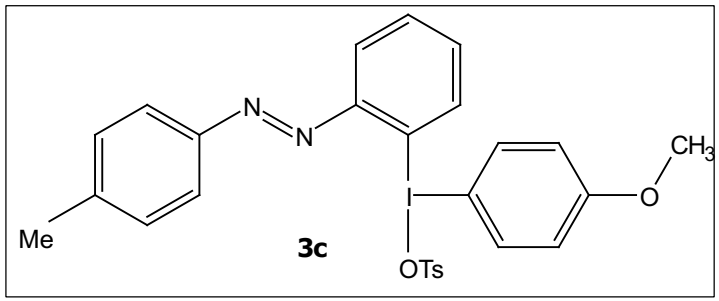
3b

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



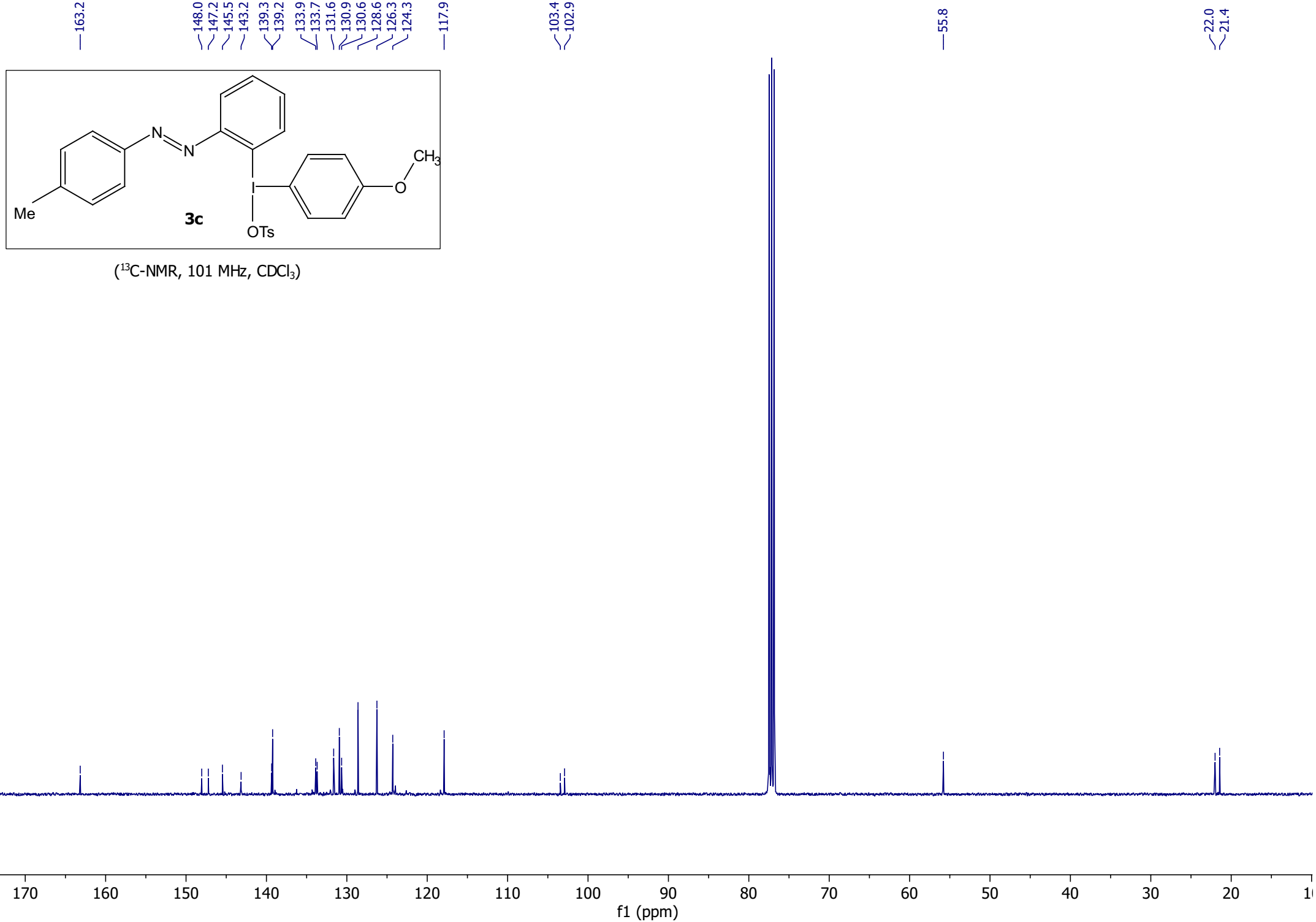


(^{13}C-NMR, 101 MHz, $CDCl_3$)

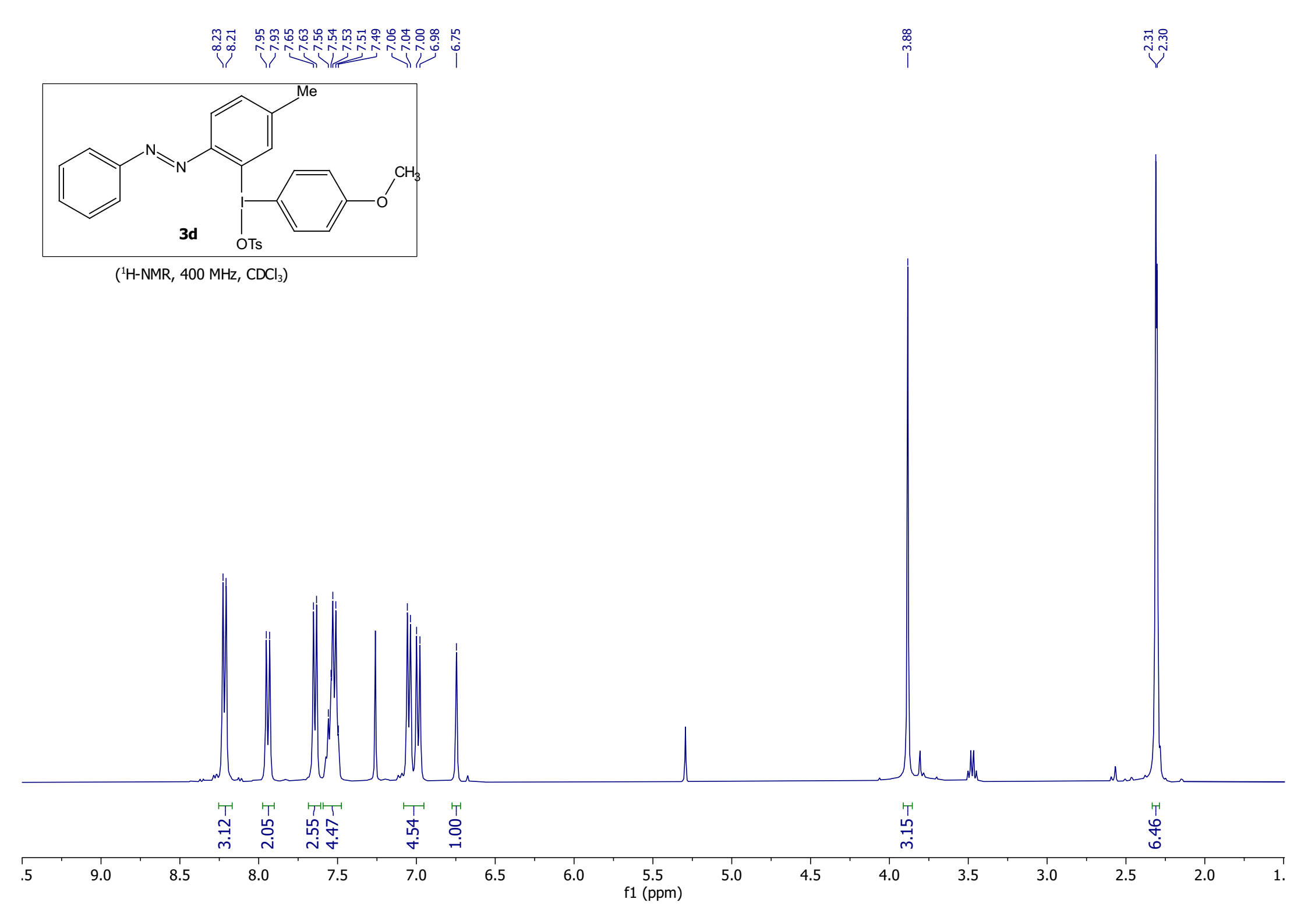


3c

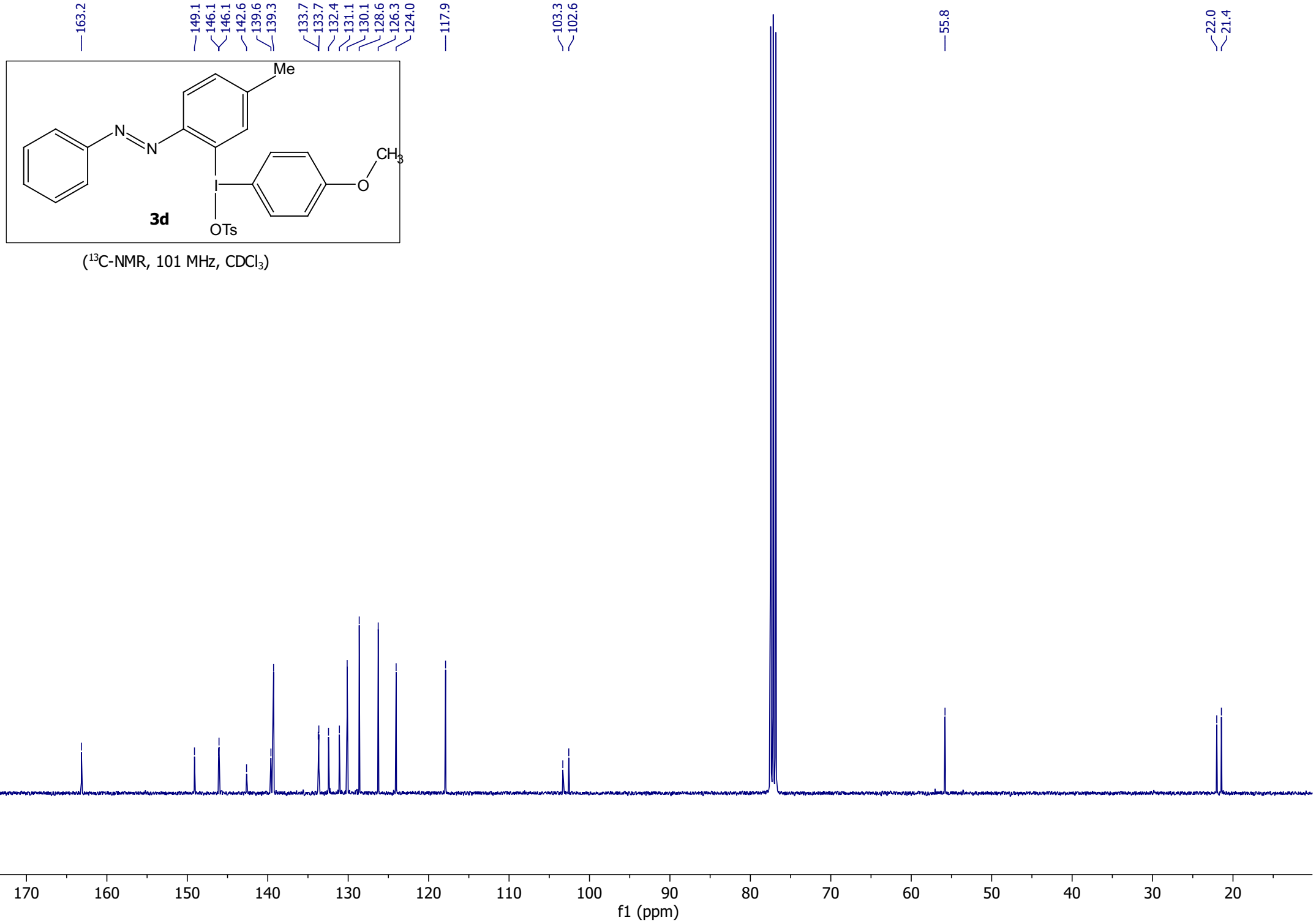
(^{1}H-NMR, 400 MHz, $CDCl_3$)



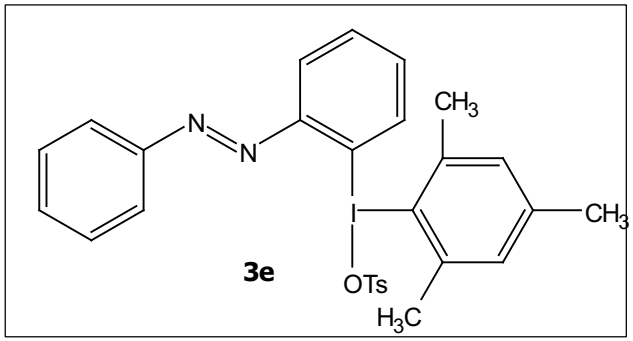
(^{13}C-NMR, 101 MHz, $CDCl_3$)



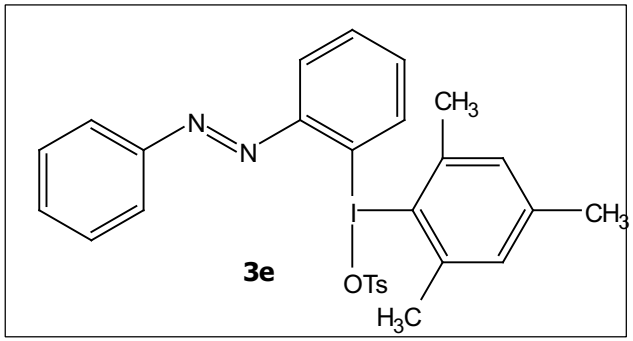
(^{1}H-NMR, 400 MHz, $CDCl_3$)



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



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

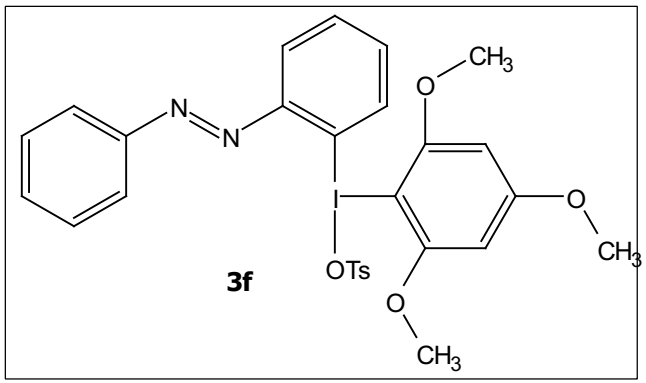


(^{13}C-NMR, 101 MHz, $CDCl_3$)

149.5
148.4
144.2
143.4
143.3
139.0
134.4
134.0
133.6
131.7
130.2
130.0
129.4
128.4
126.1
124.3
120.2
102.3
26.8
21.4

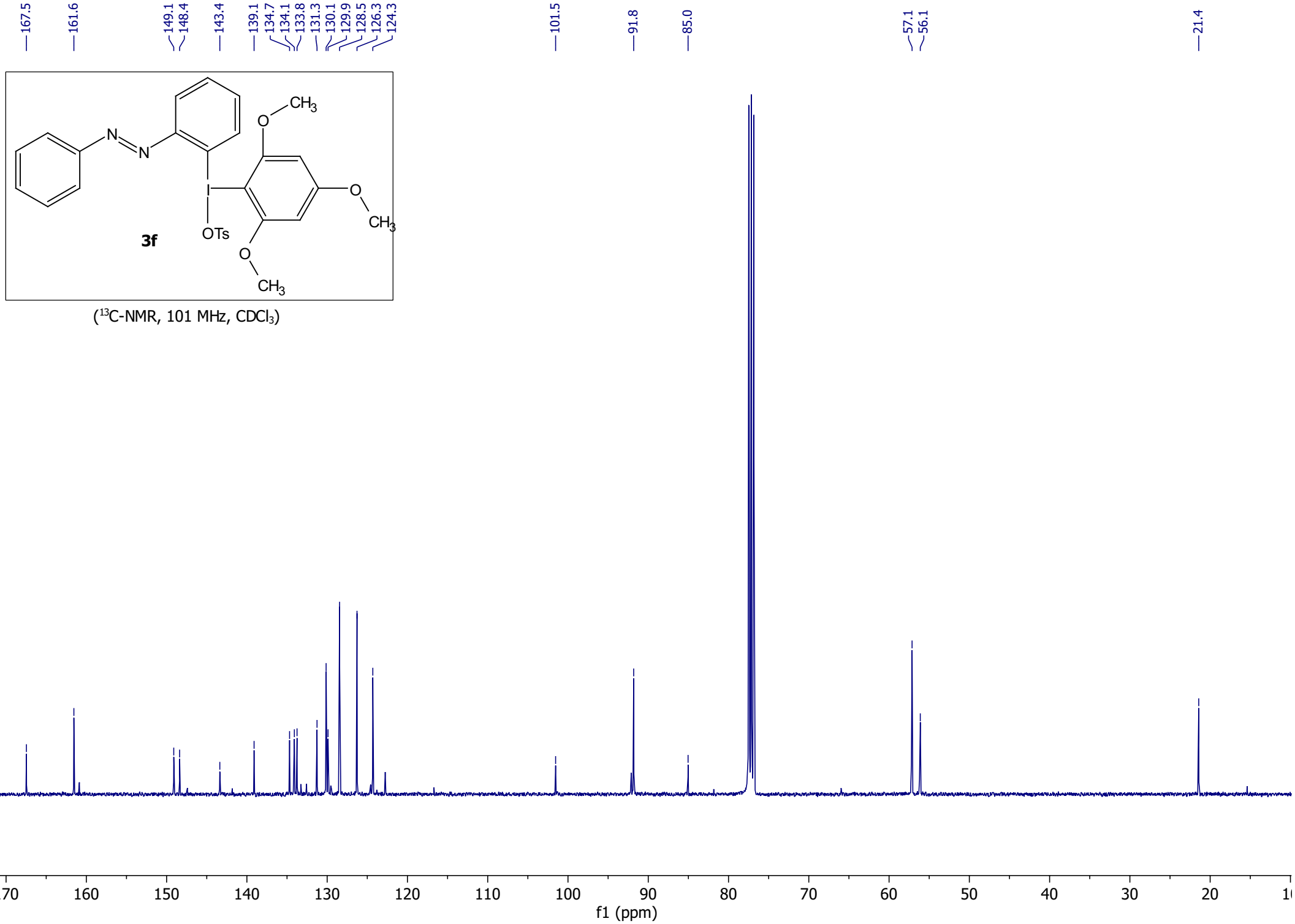
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

f1 (ppm)

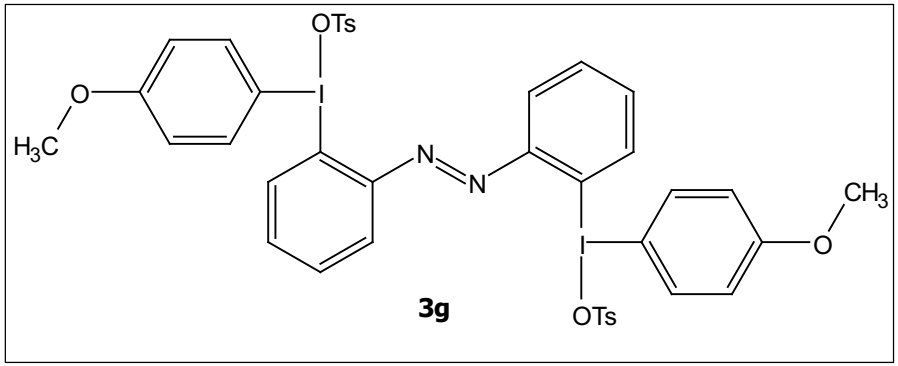


3f

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

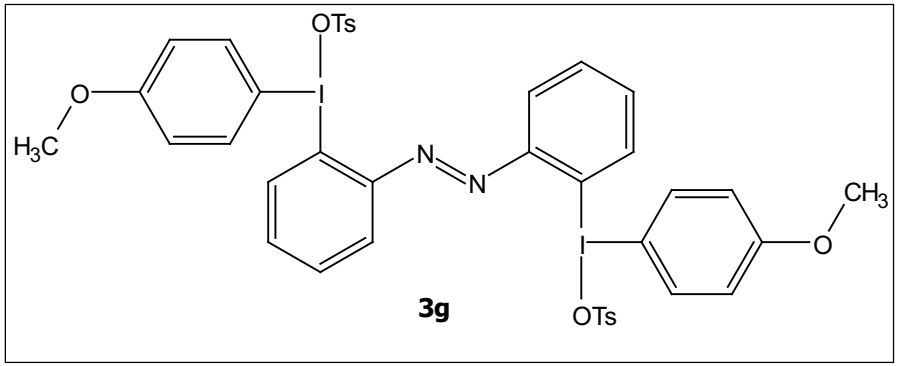


(^{13}C-NMR, 101 MHz, $CDCl_3$)



3g

(^{1}H-NMR, 400 MHz, MeOD-d_4)



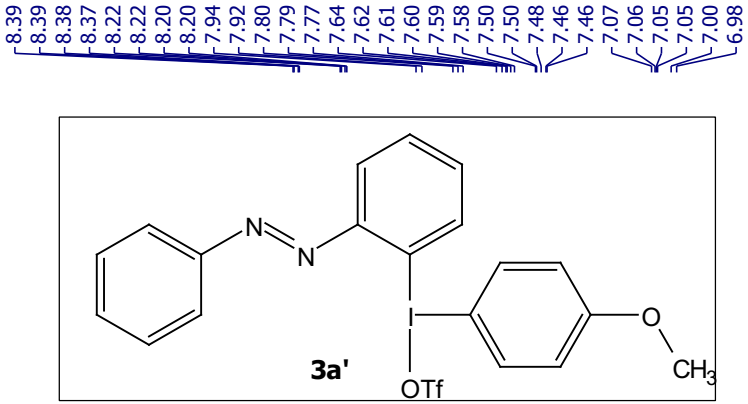
3g

(^{13}C-NMR, 101 MHz, MeOD-d_4)

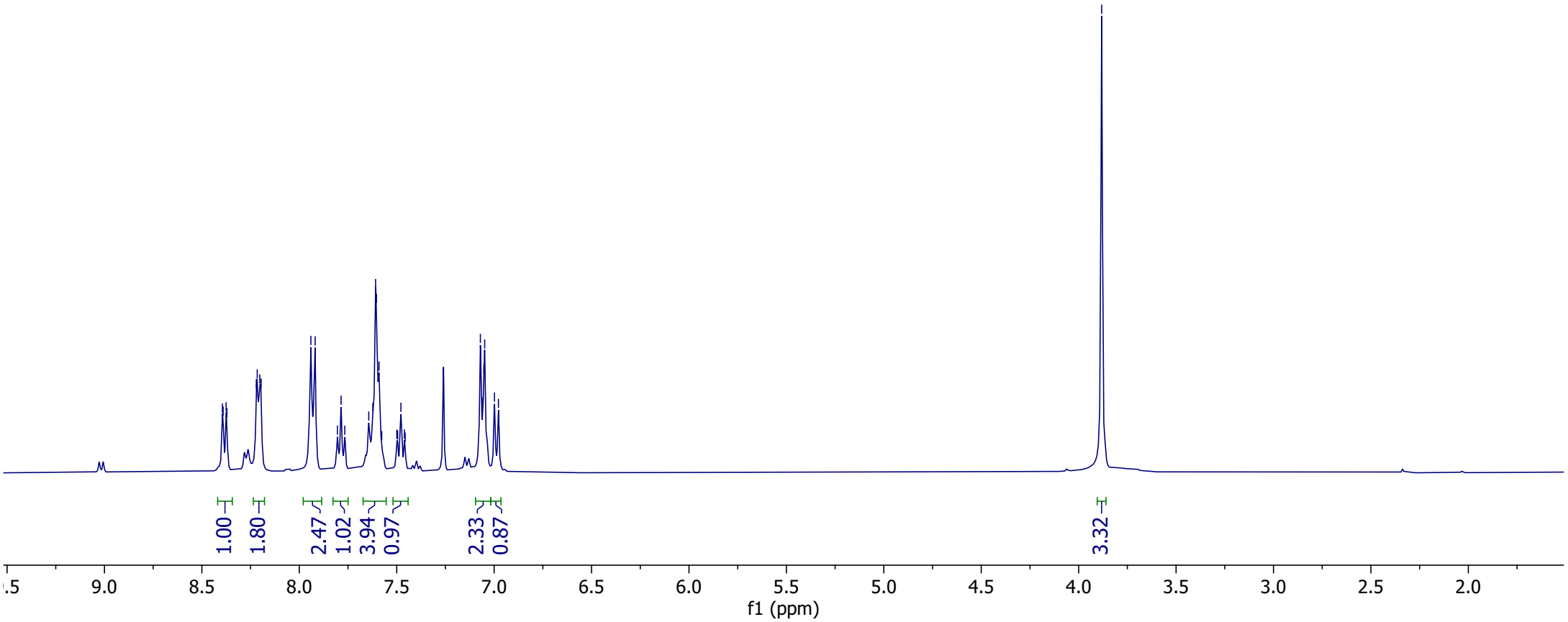
165.0
148.2
143.6
141.6
139.7
137.5
135.7
134.7
129.8
126.9
125.5
119.2
116.9
102.9
56.5
21.3

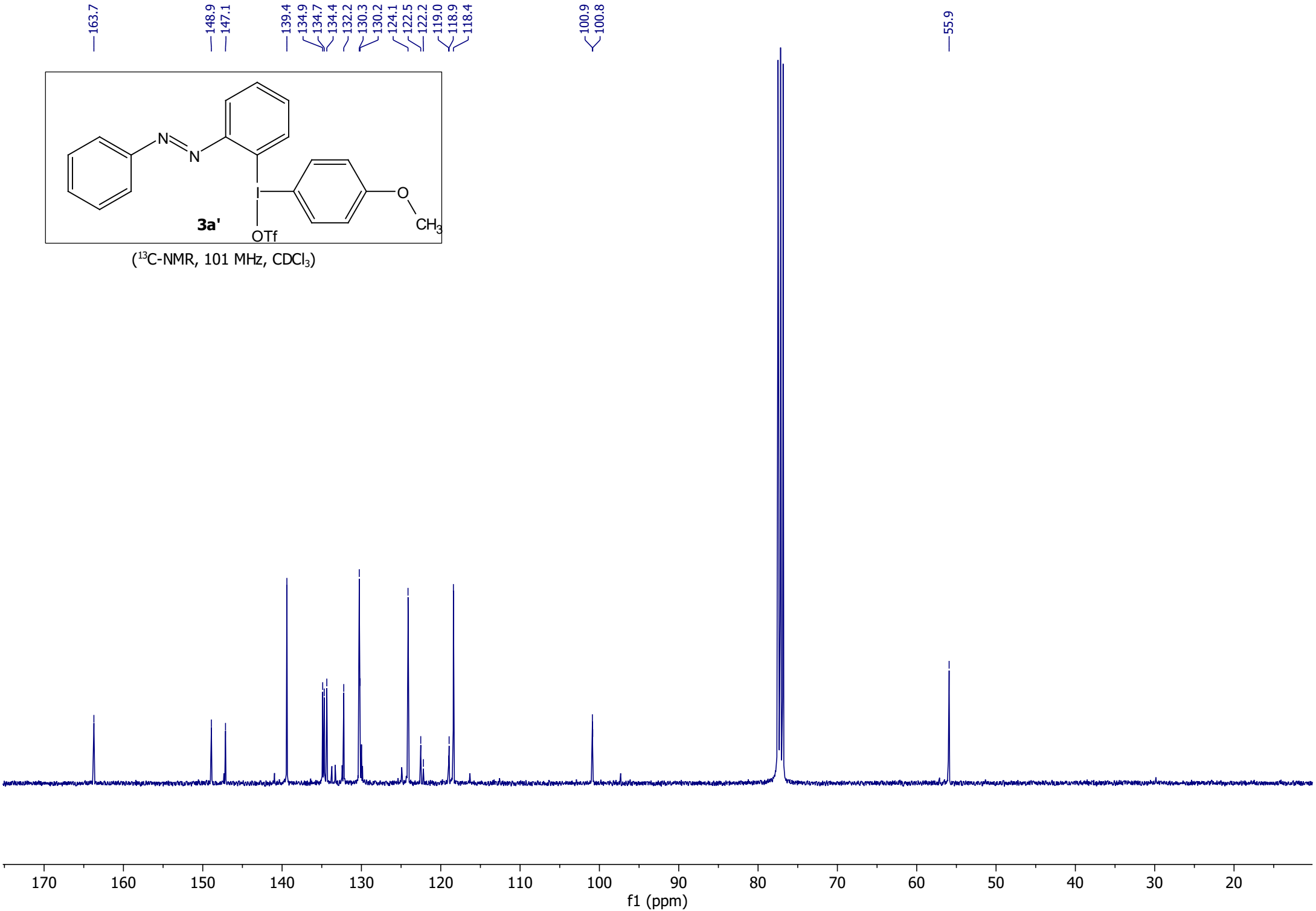
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

f1 (ppm)

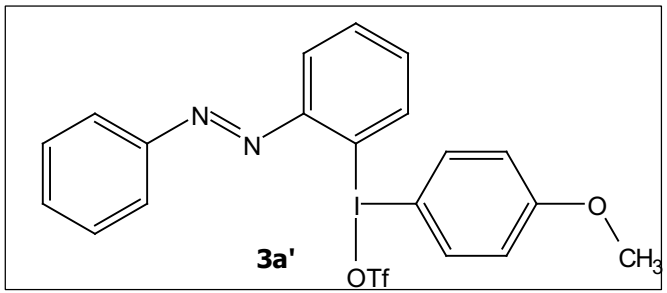


(^{1}H-NMR, 400 MHz, $CDCl_3$)



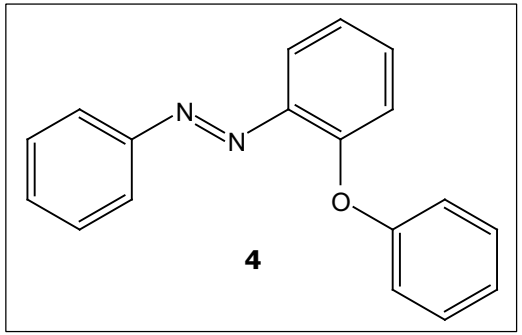


(^{13}C-NMR, 101 MHz, $CDCl_3$)



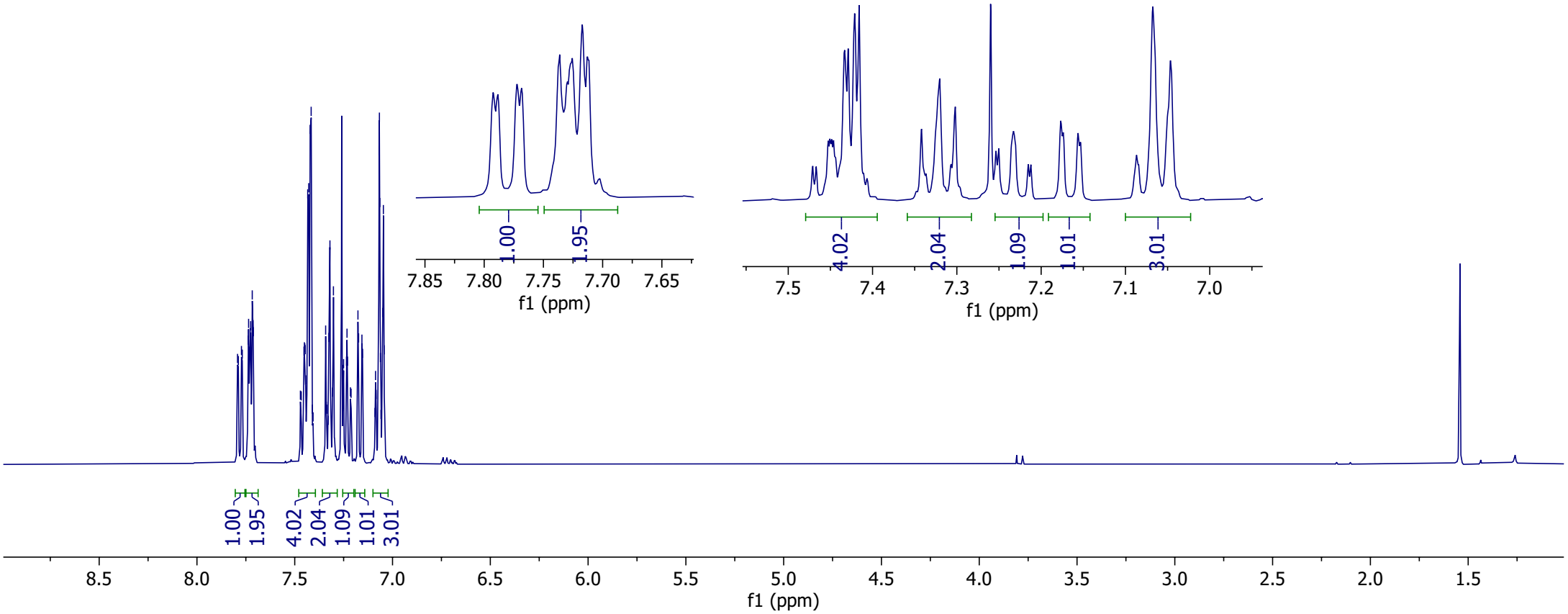
3a'

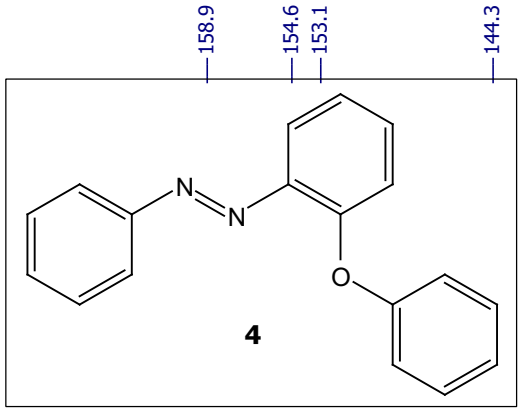
(^{19}F-NMR, 377 MHz, $CDCl_3$)



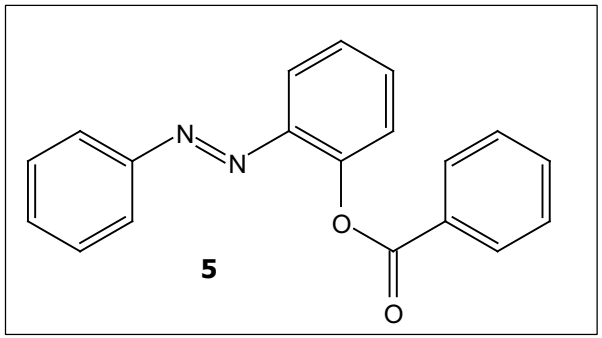
4

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

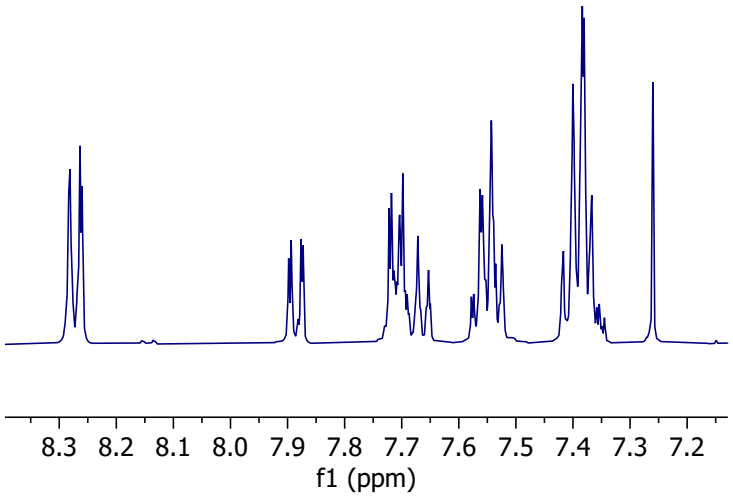


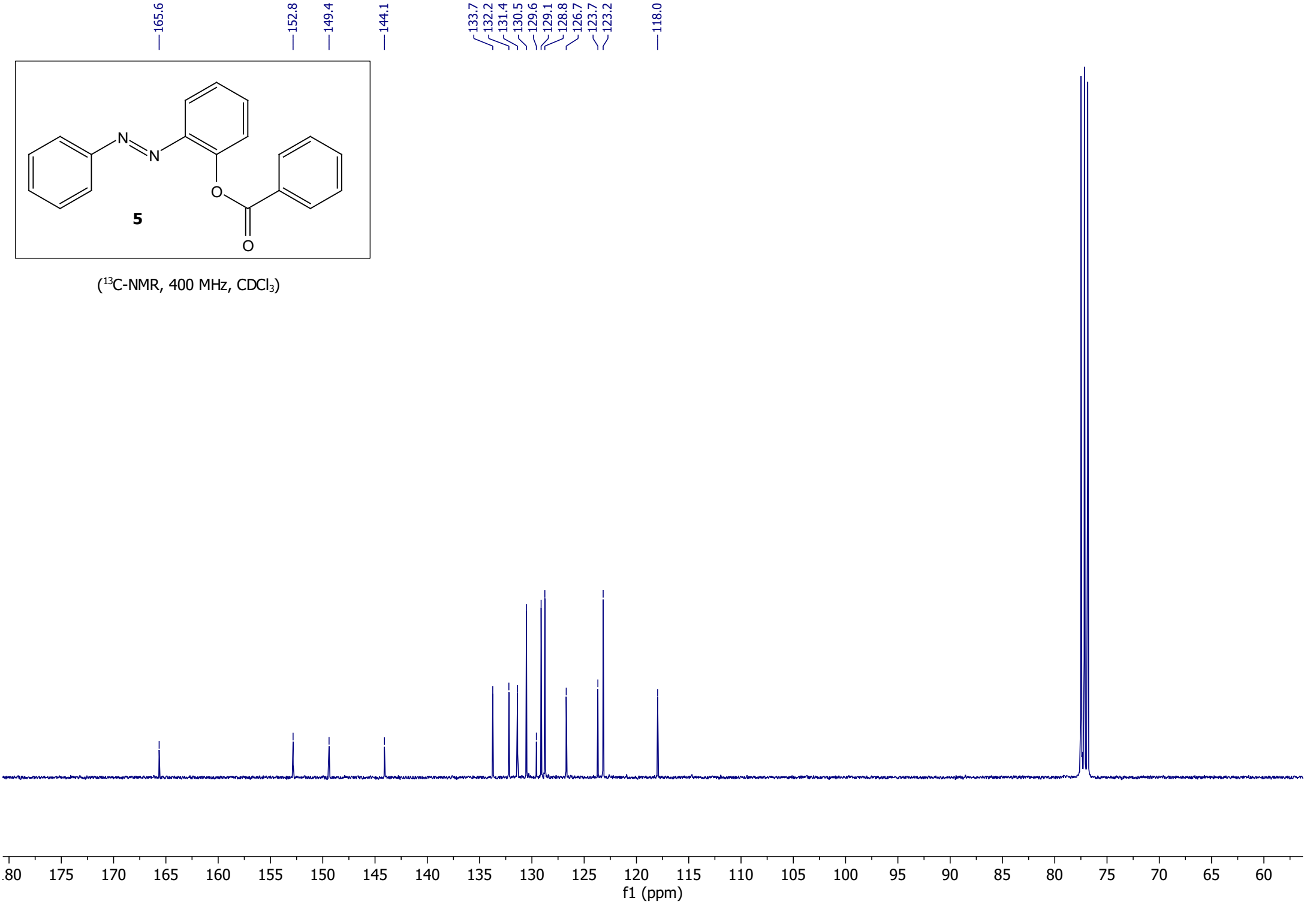


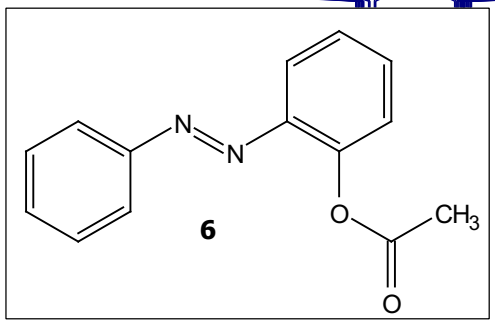
(^{13}C-NMR, 101 MHz, $CDCl_3$)



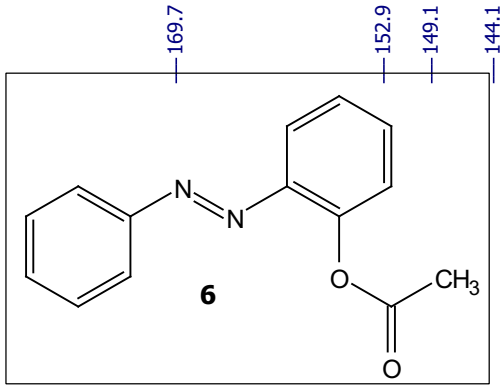
(^{1}H-NMR, 400 MHz, $CDCl_3$)



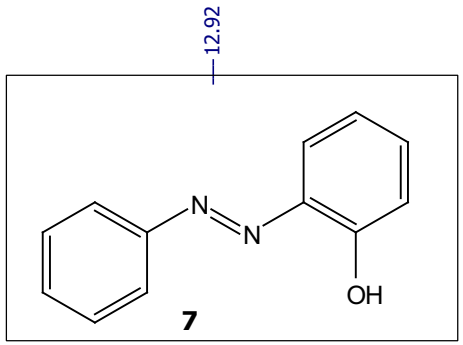

165.6
152.8
149.4
144.1
133.7
132.2
131.4
130.5
129.6
129.1
128.8
126.7
123.7
123.2
118.0
N
N
O
O
5
(13C-NMR, 400 MHz, CDCl3)
f1 (ppm)



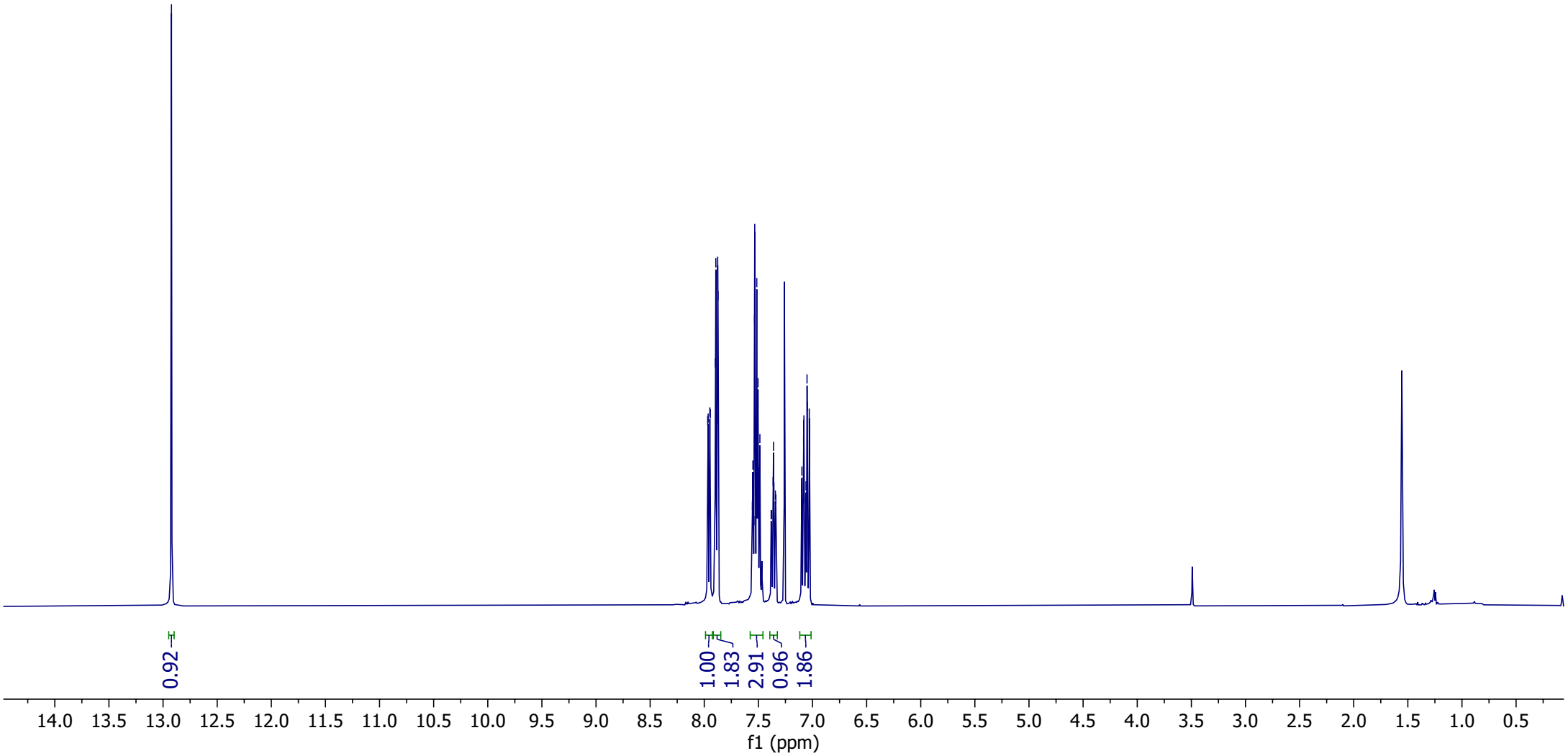
(^{1}H-NMR, 400 MHz, $CDCl_3$)

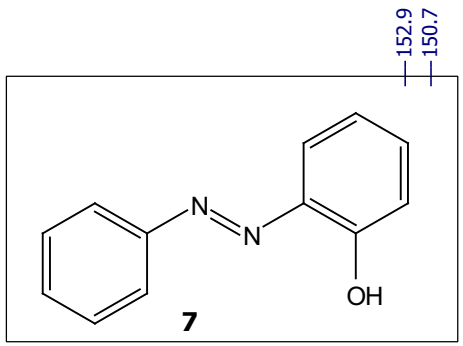


(^{13}C-NMR, 101 MHz, $CDCl_3$)



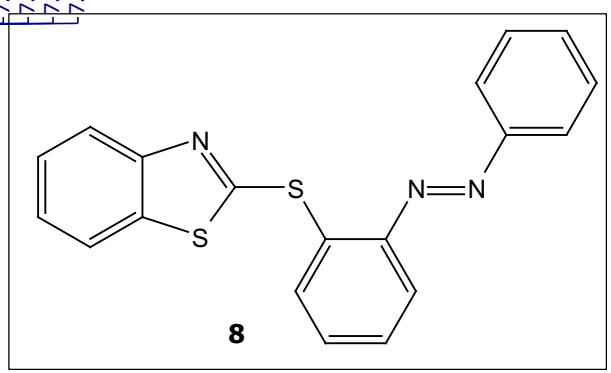
(^{1}H-NMR, 400 MHz, $CDCl_3$)





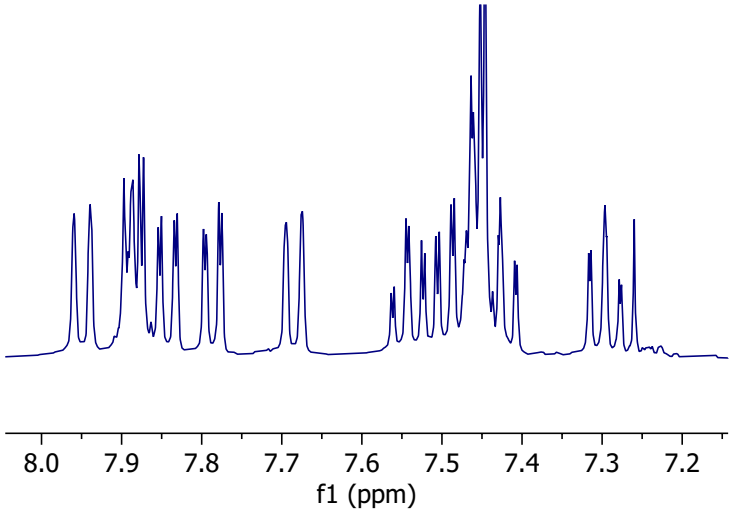
7

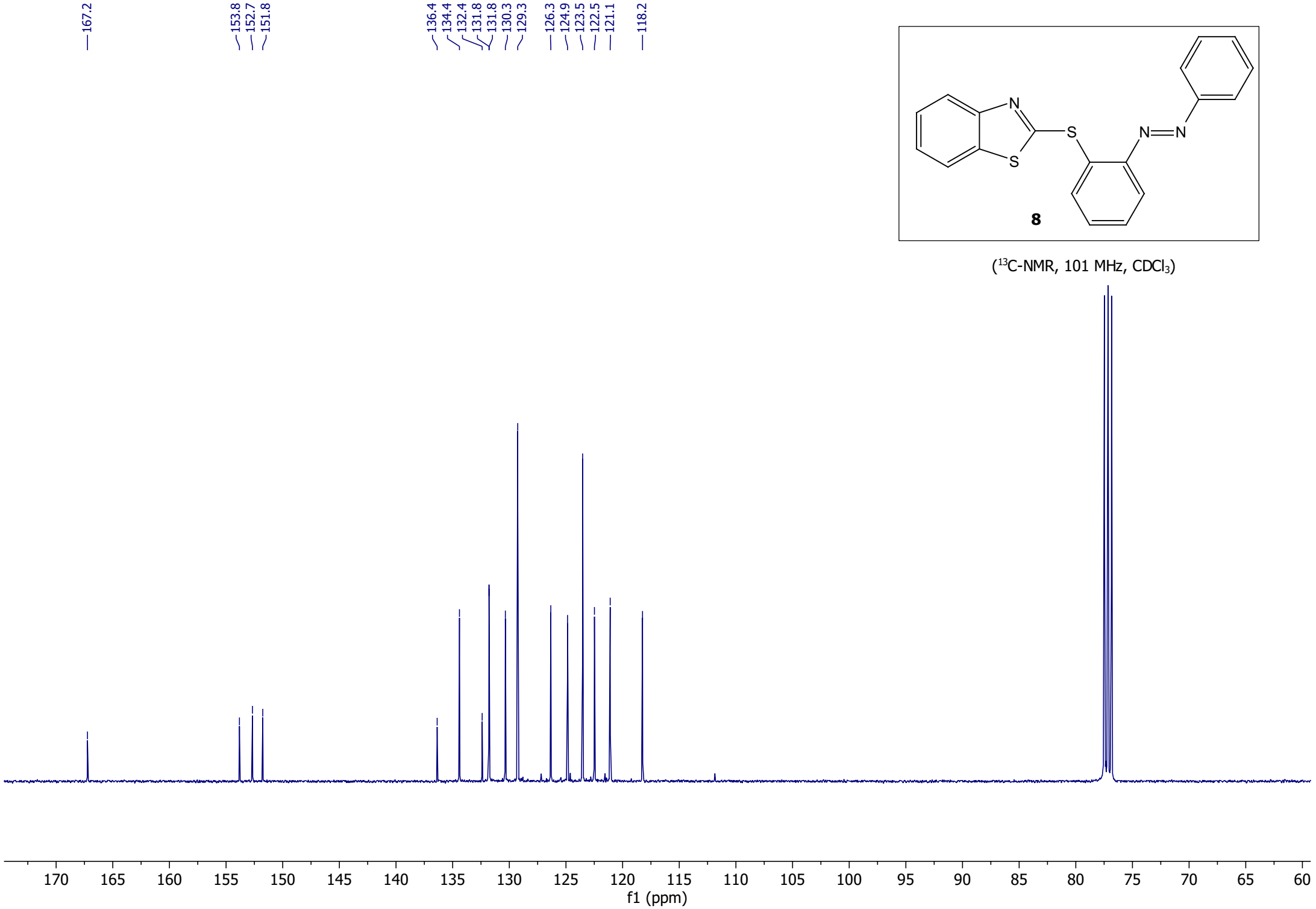
(^{13}C-NMR, 101 MHz, $CDCl_3$)



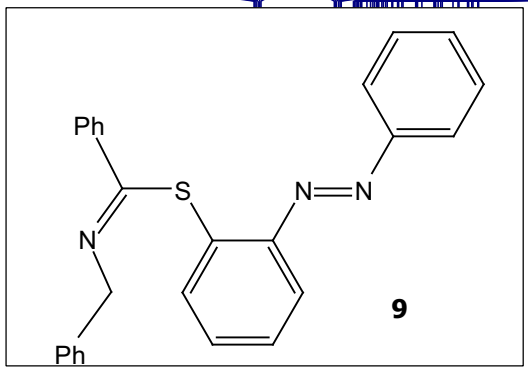
8

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




167.2
153.8
152.7
151.8
136.4
134.4
132.4
131.8
131.8
130.3
129.3
126.3
124.9
123.5
122.5
121.1
118.2
N
S
S
N=N
8
(13C-NMR, 101 MHz, CDCl3)
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)

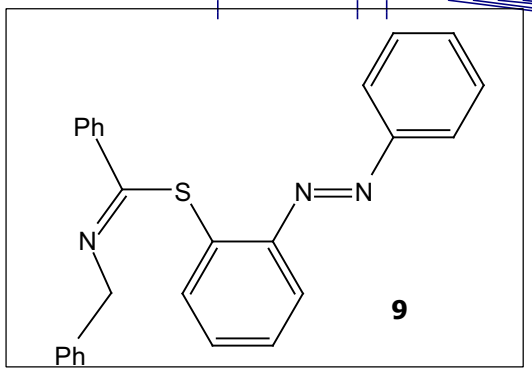
ED-E-150-2.1.fid



9

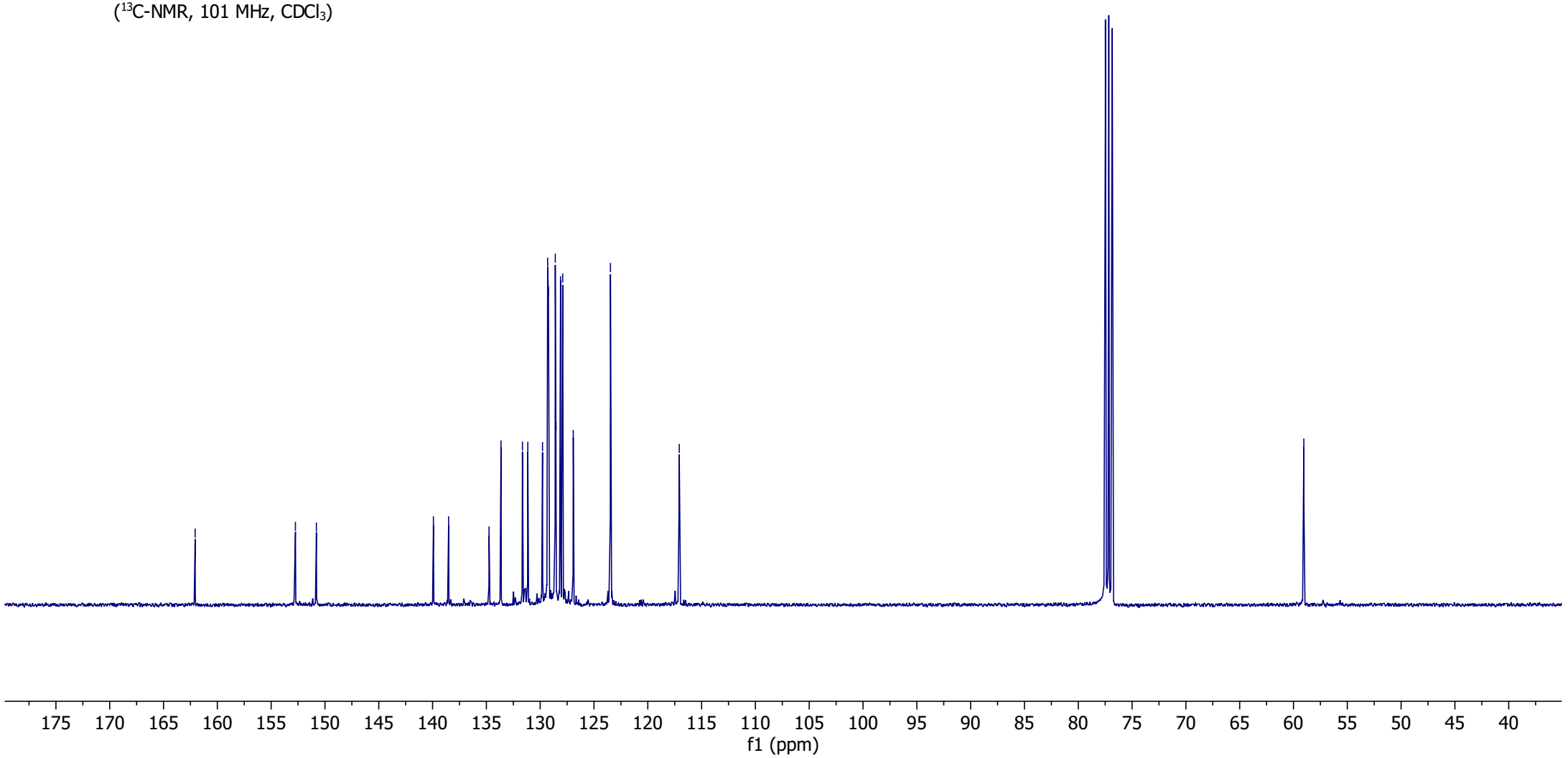
(^{1}H-NMR, 400 MHz, $CDCl_3$)

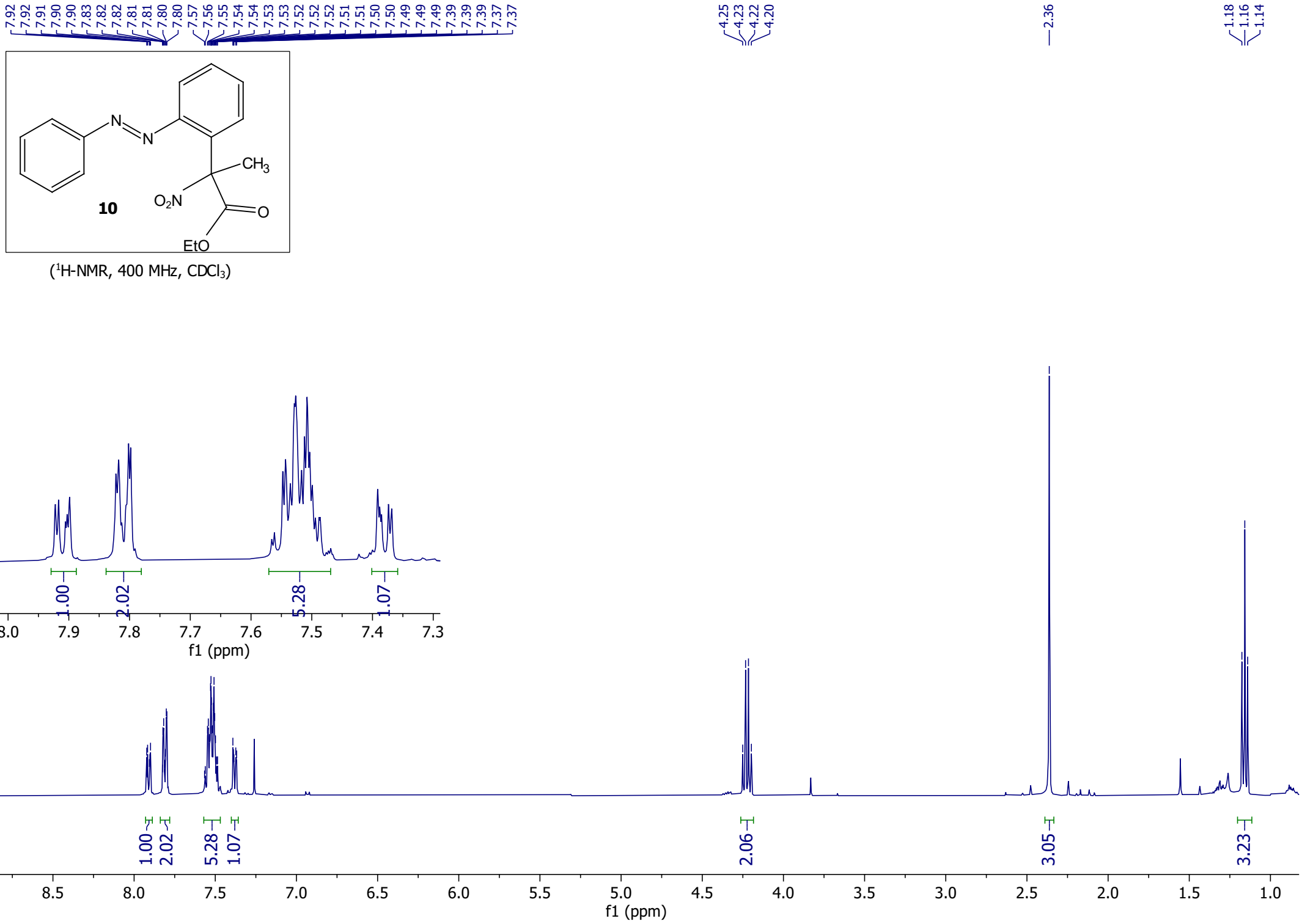
ED-E-150-2.4.fid

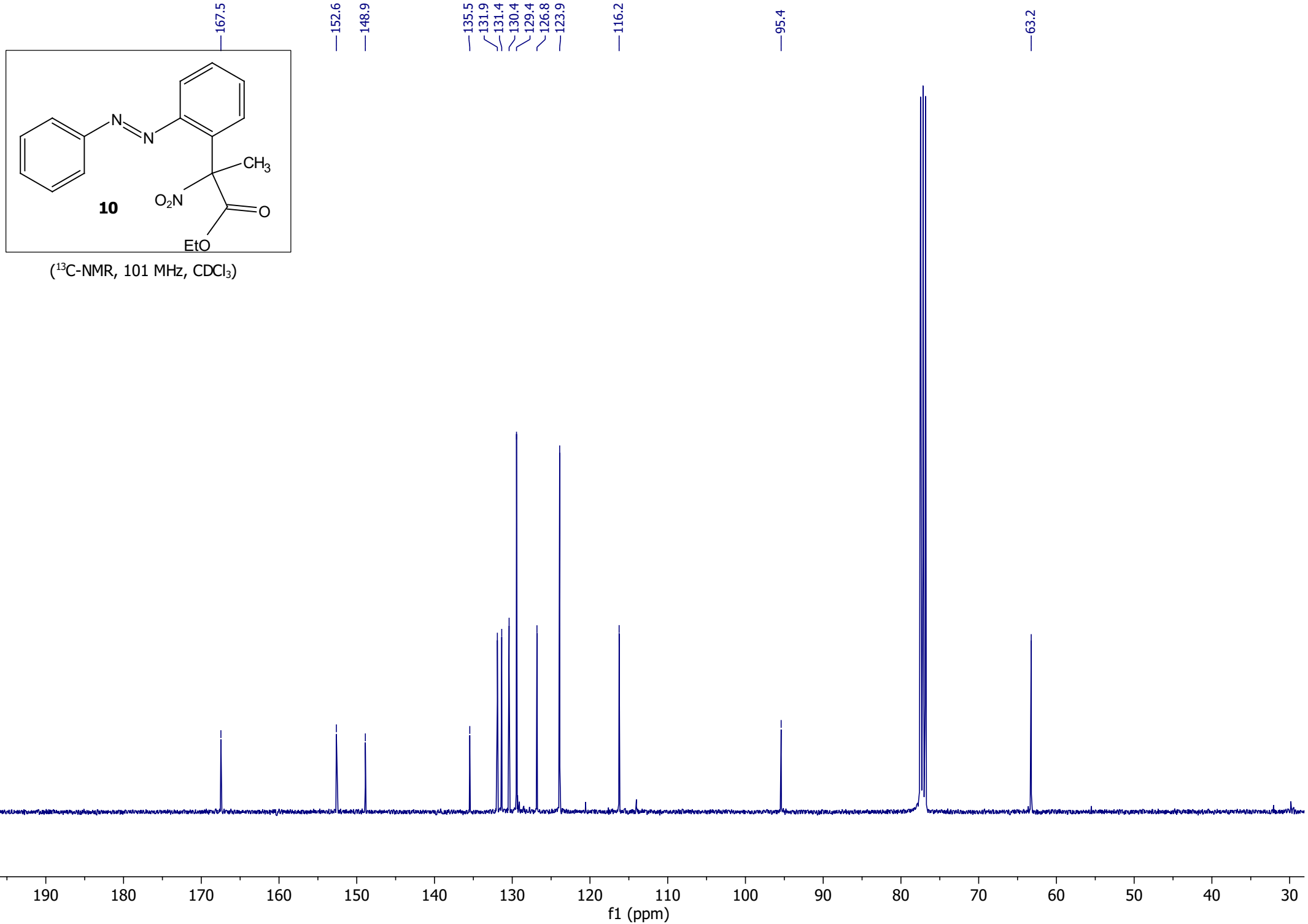


9

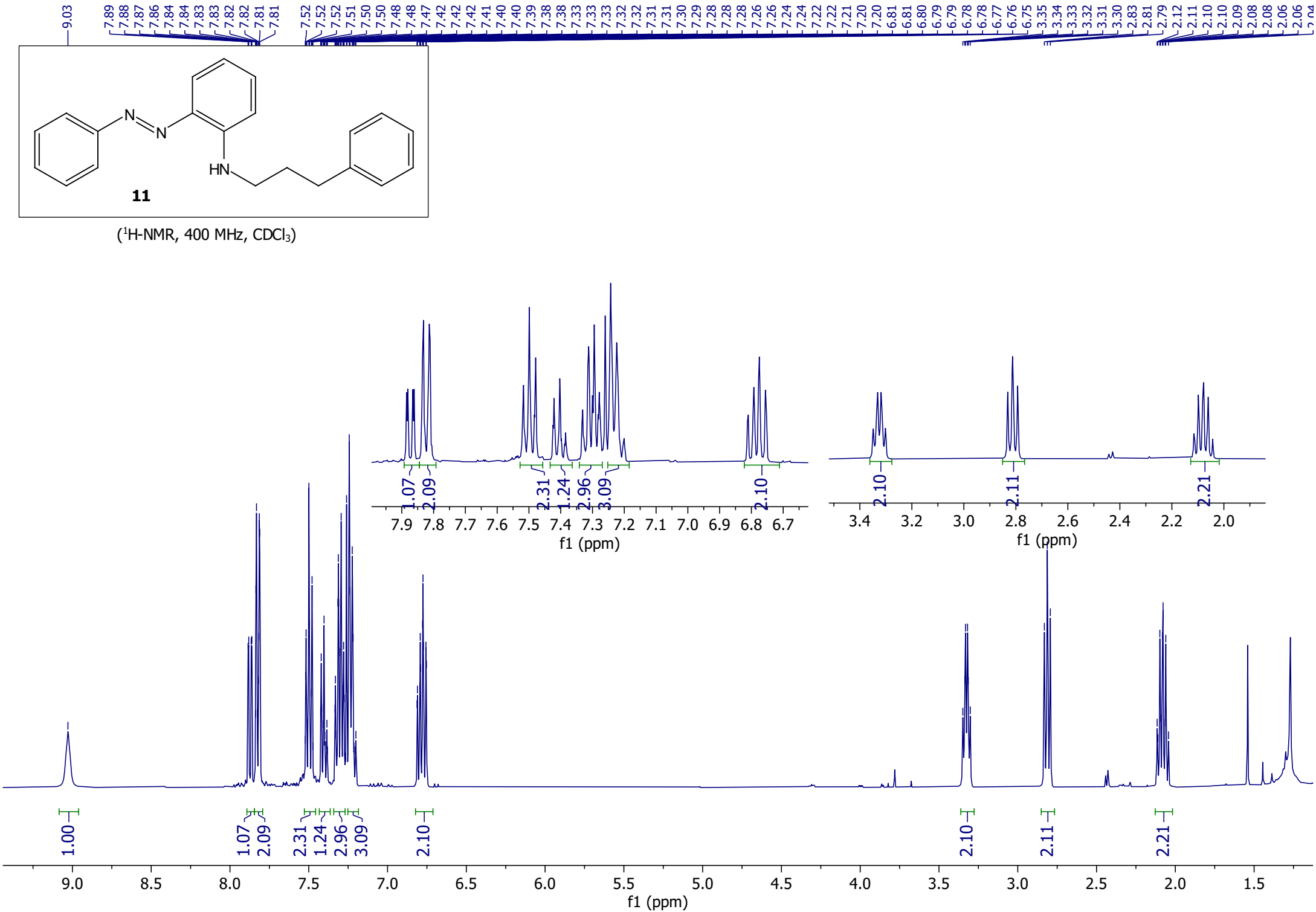
(^{13}C-NMR, 101 MHz, $CDCl_3$)

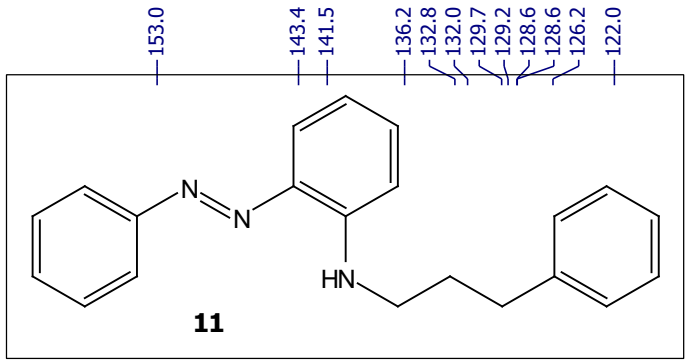



7.92 7.92 7.91 7.90 7.90 7.83 7.82 7.82 7.81 7.81 7.80 7.80 7.57 7.56 7.55 7.54 7.54 7.53 7.53 7.52 7.52 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.49 7.39 7.39 7.37 7.37
4.25 4.23 4.22 4.20
2.36
1.18 1.16 1.14
N
N
CH3
O2N
O
EtO
10
(1H-NMR, 400 MHz, CDCl3)
1.00 2.02 5.28 1.07
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
1.00 2.02 5.28 1.07 2.06 3.05 3.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

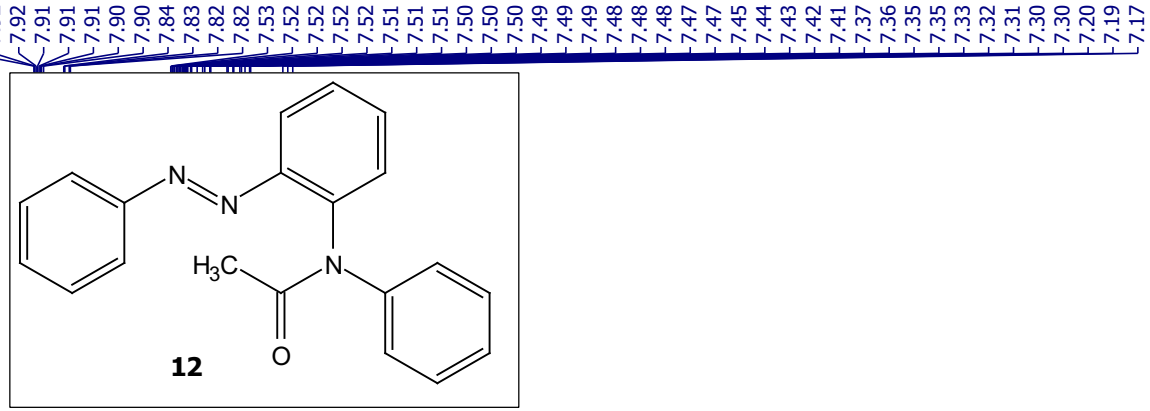


(^{13}C-NMR, 101 MHz, $CDCl_3$)

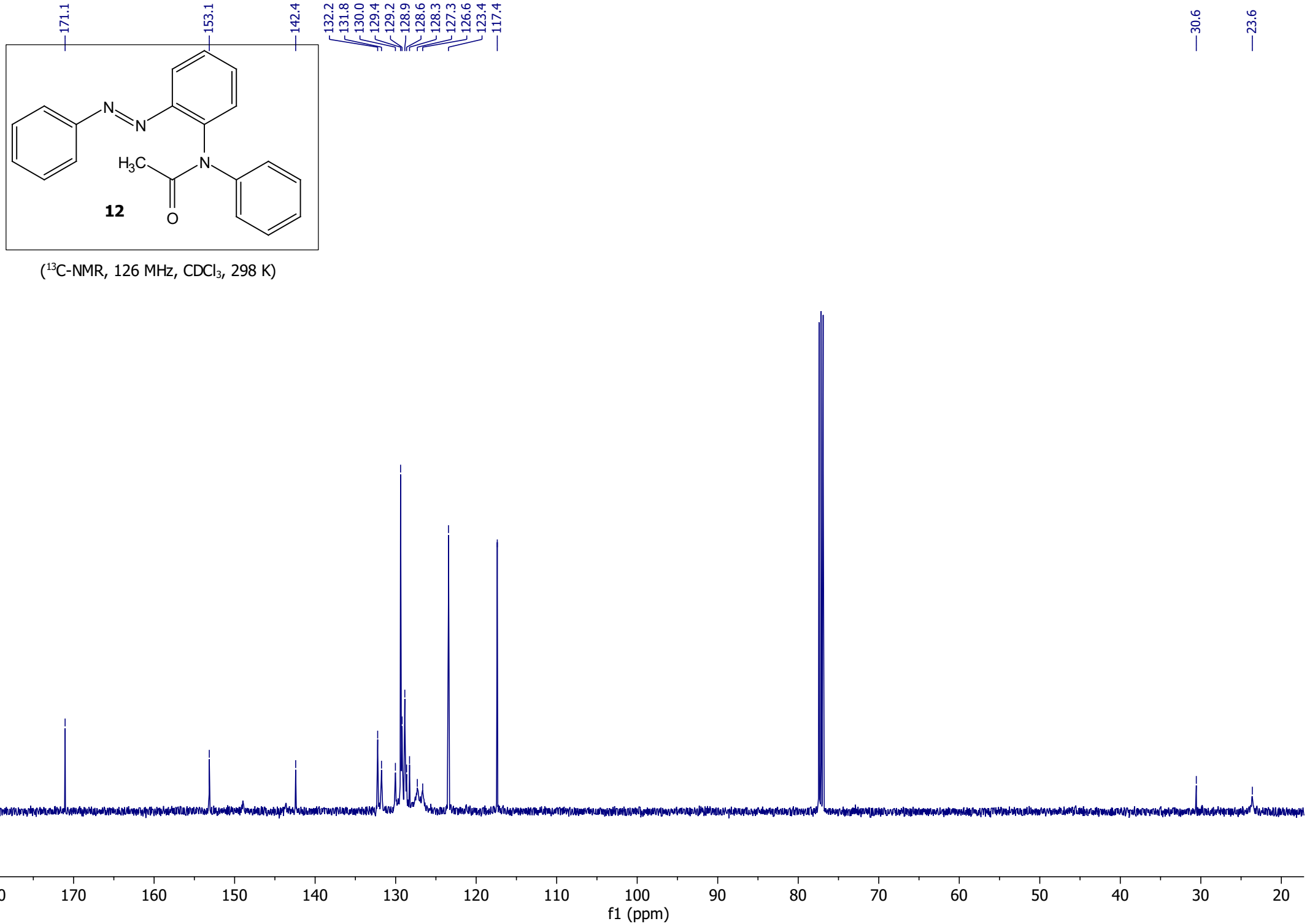

11
(1H-NMR, 400 MHz, CDCl3)
f1 (ppm)



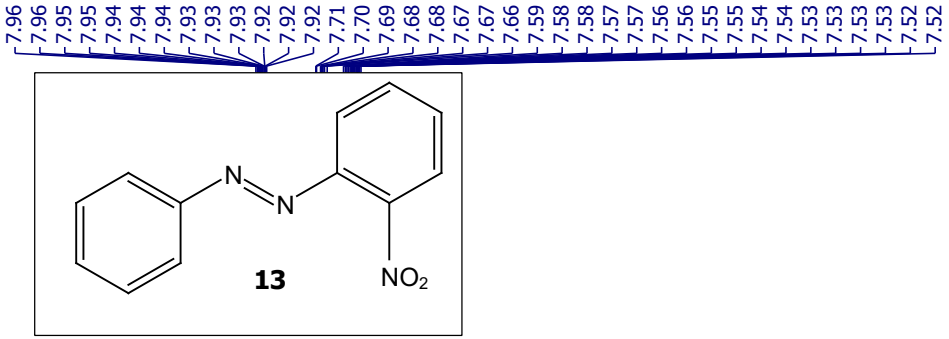
(^{13}C-NMR, 101 MHz, $CDCl_3$)



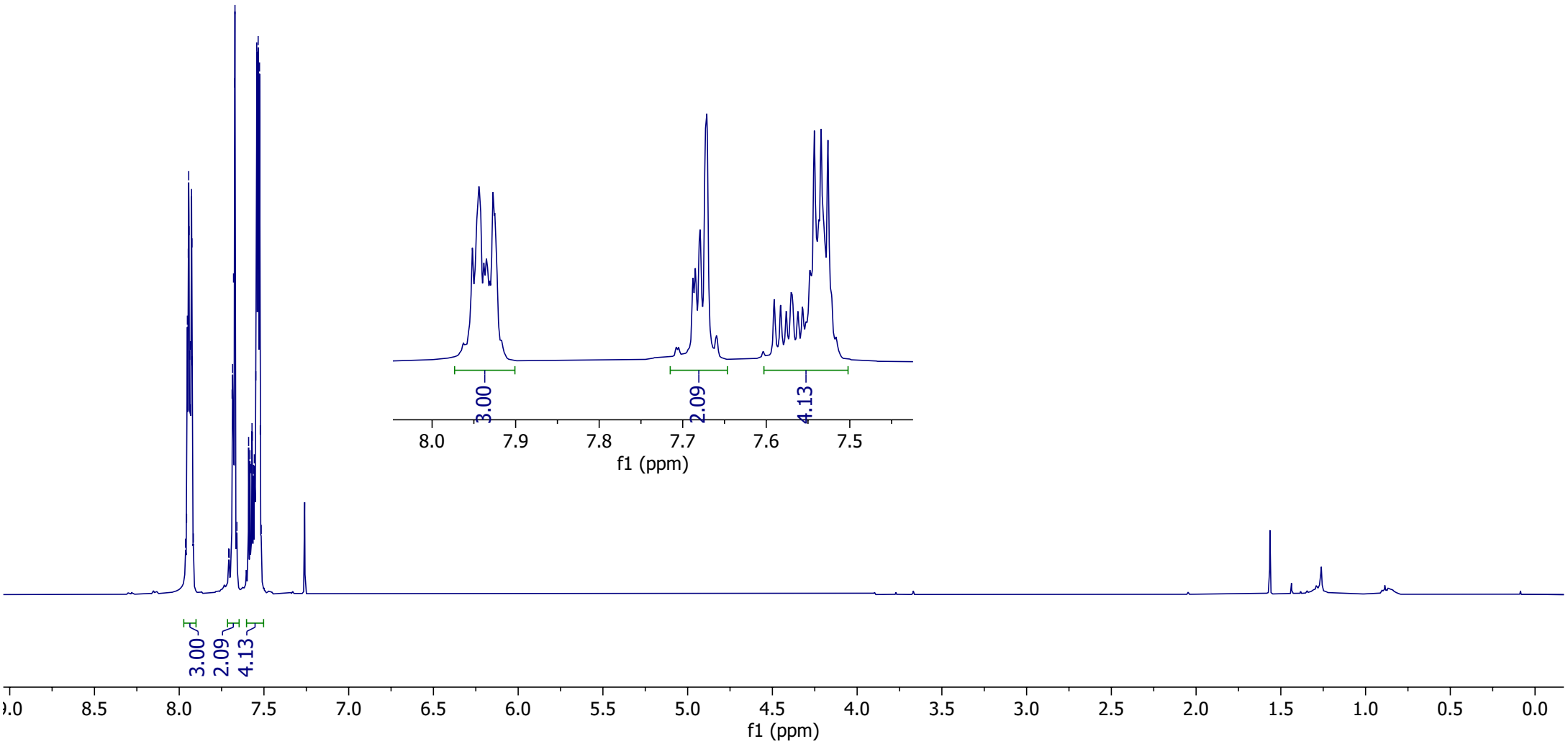
(¹H-NMR, 500 MHz, $CDCl_3$, 298 K)

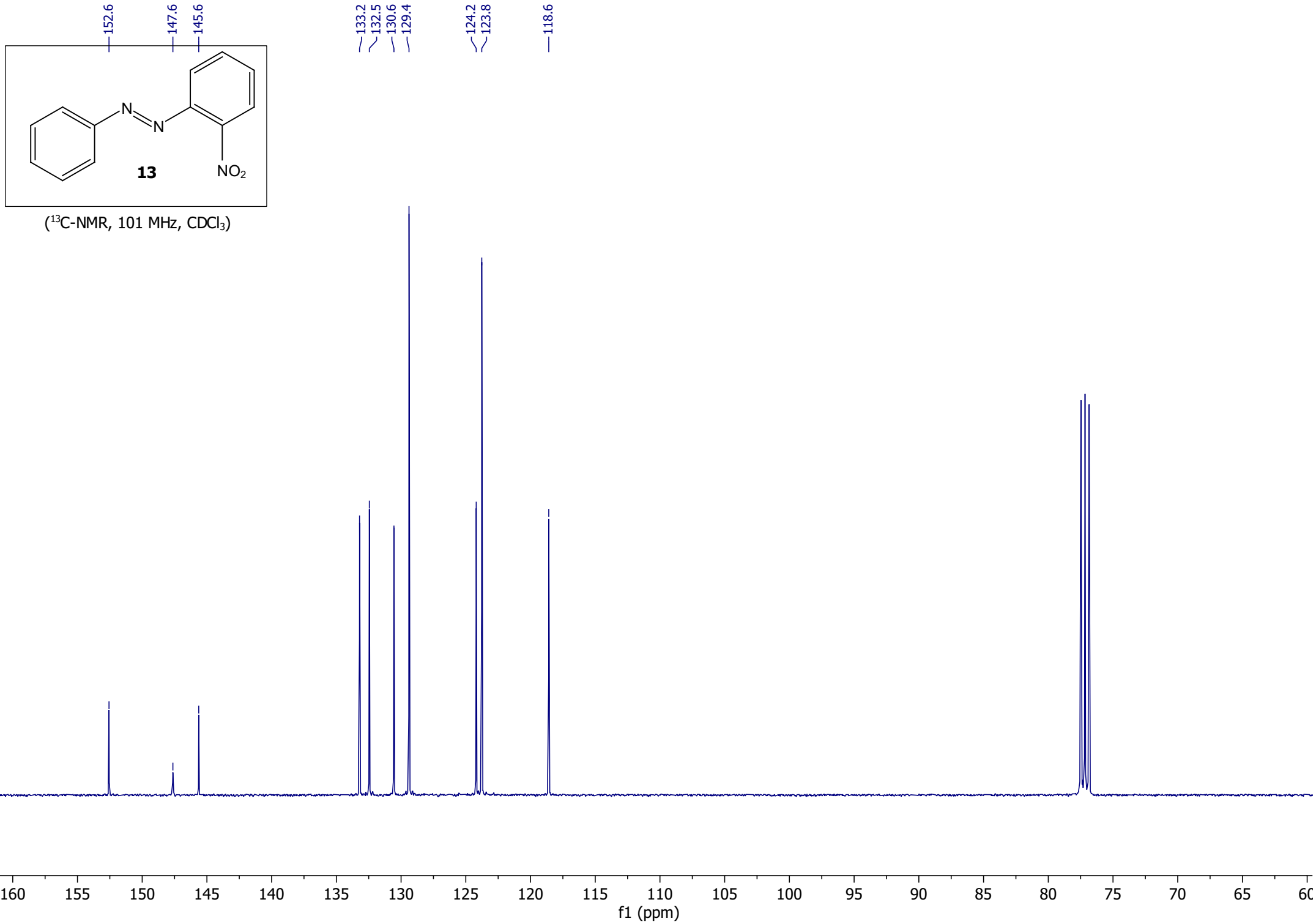


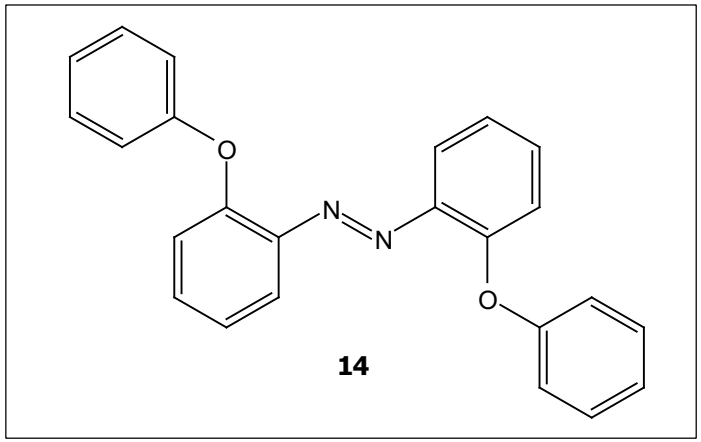
(^{13}C-NMR, 126 MHz, $CDCl_3$, 298 K)



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

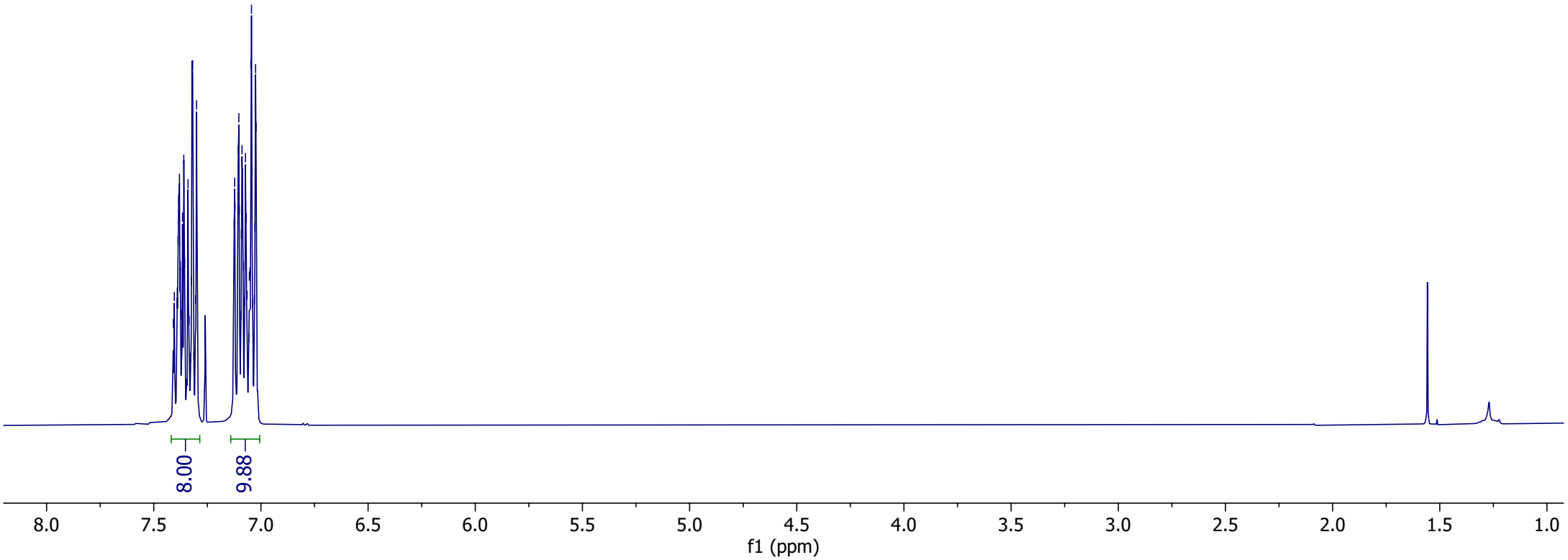


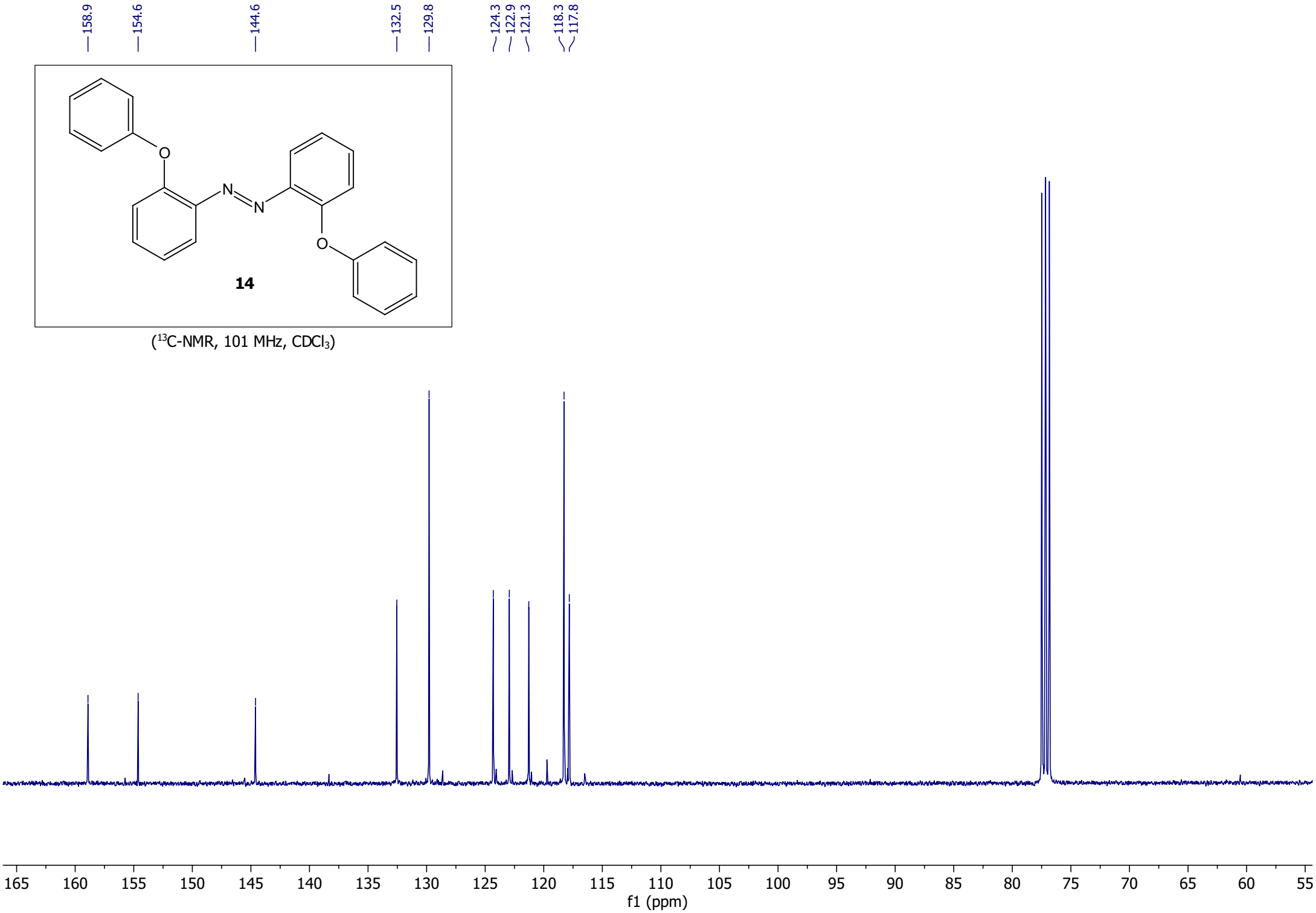

152.6
147.6
145.6
133.2
132.5
130.6
129.4
124.2
123.8
118.6
N
N
NO2
13
(13C-NMR, 101 MHz, CDCl3)
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)

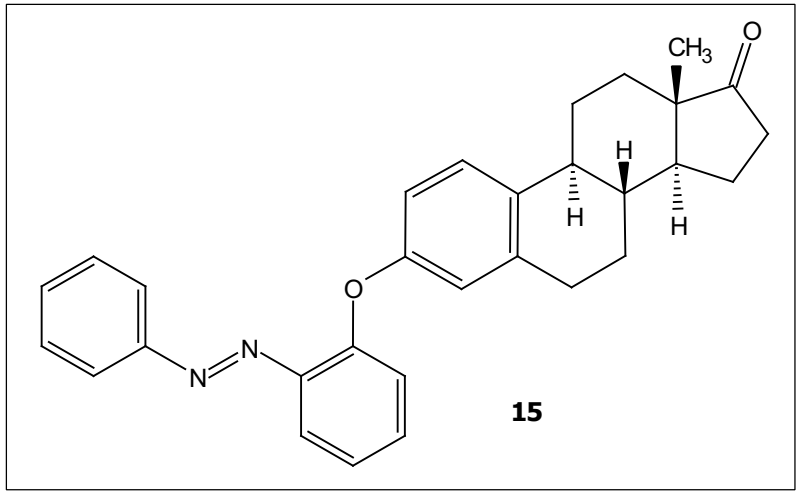


14

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

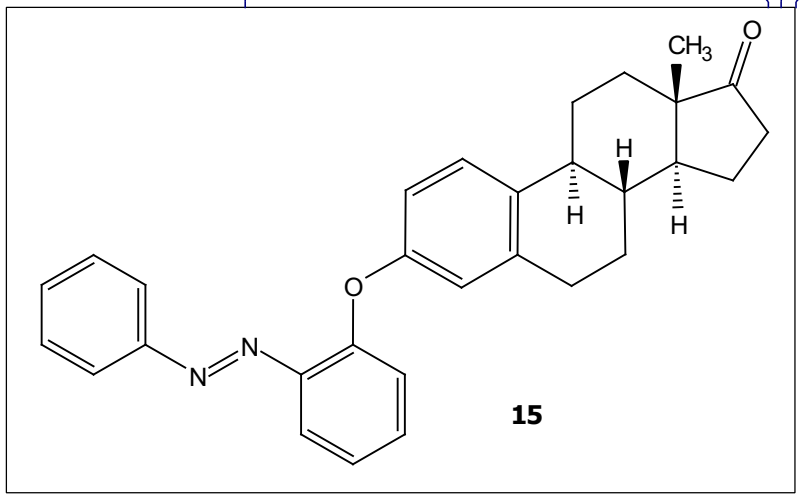



158.9
154.6
144.6
132.5
129.8
124.3
122.9
121.3
118.3
117.8
O
N
N
O
14
(13C-NMR, 101 MHz, CDCl3)
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)



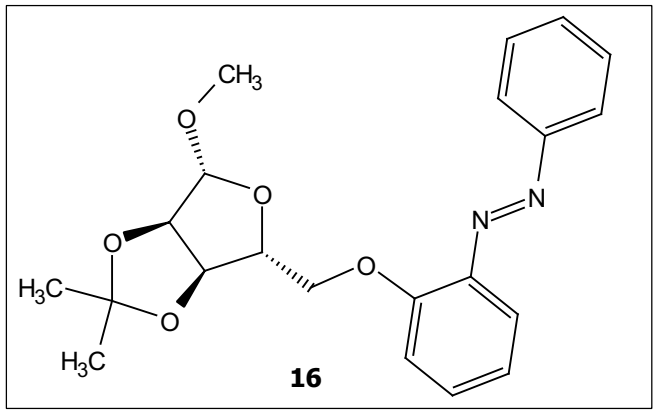
15

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



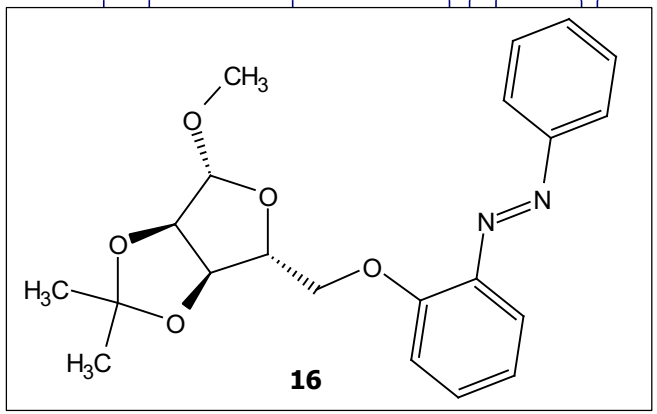
15

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



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

f1 (ppm)



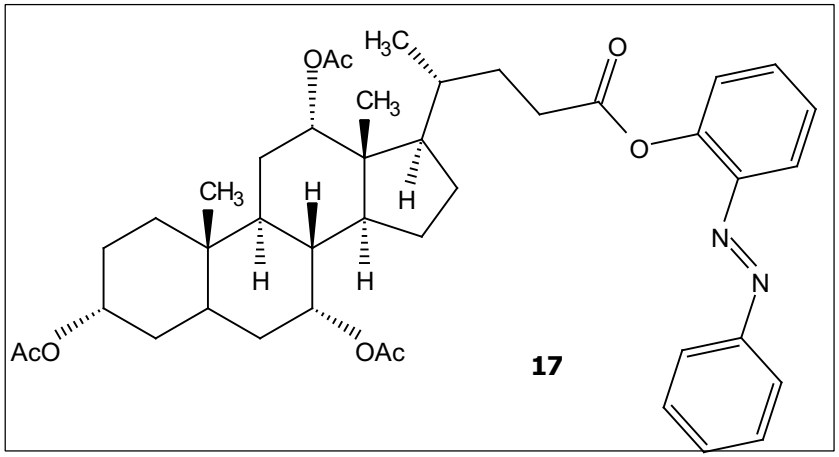
16

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

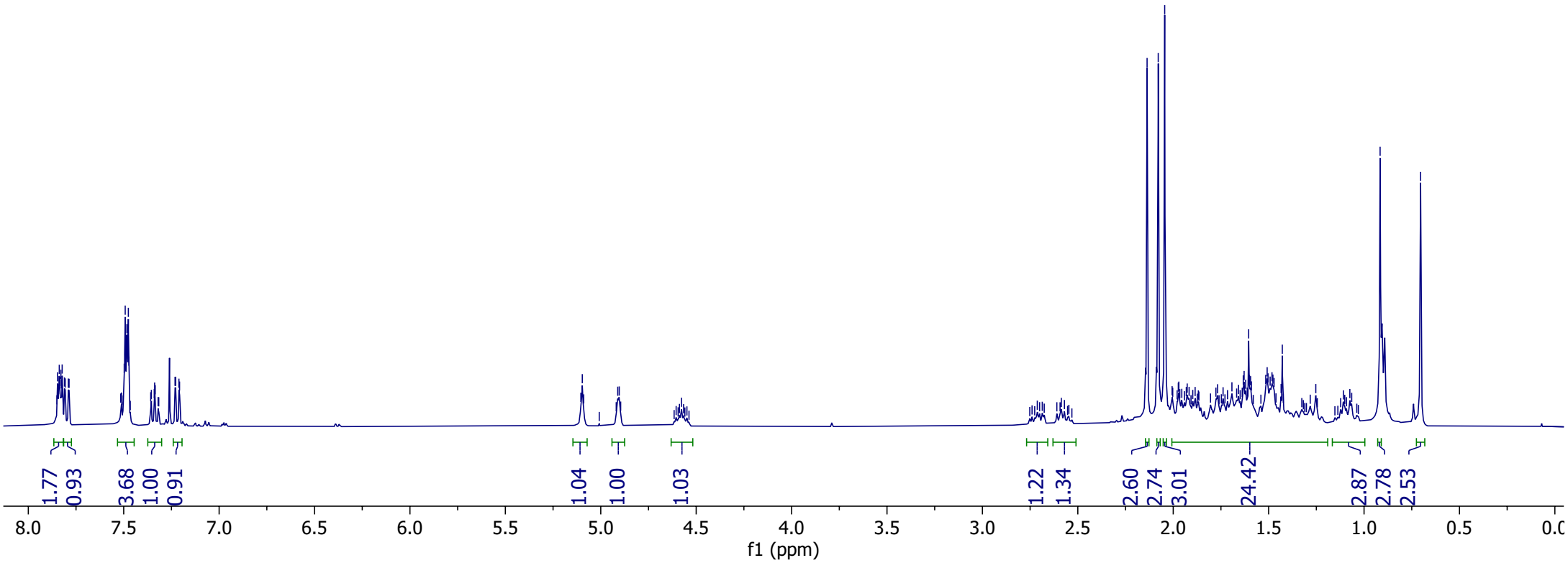
156.3
153.2
143.2
132.4
131.0
129.2
123.2
122.1
117.3
116.6
112.6
109.7
85.3
84.6
82.3
71.3
55.0
26.6
25.1

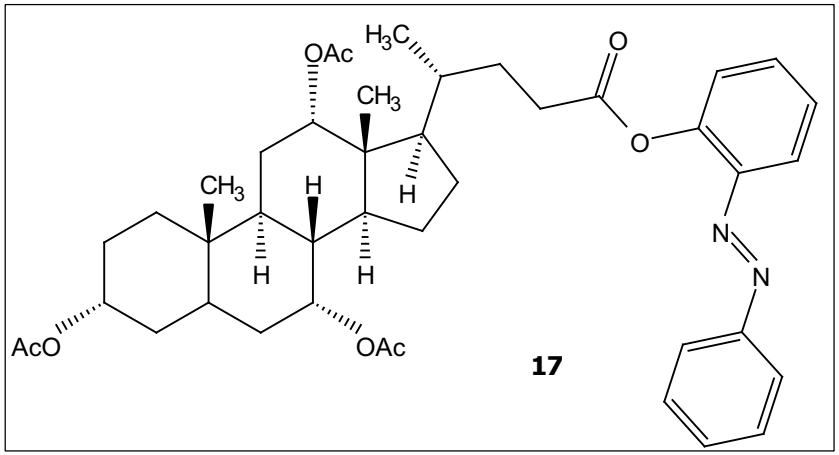
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15

f1 (ppm)



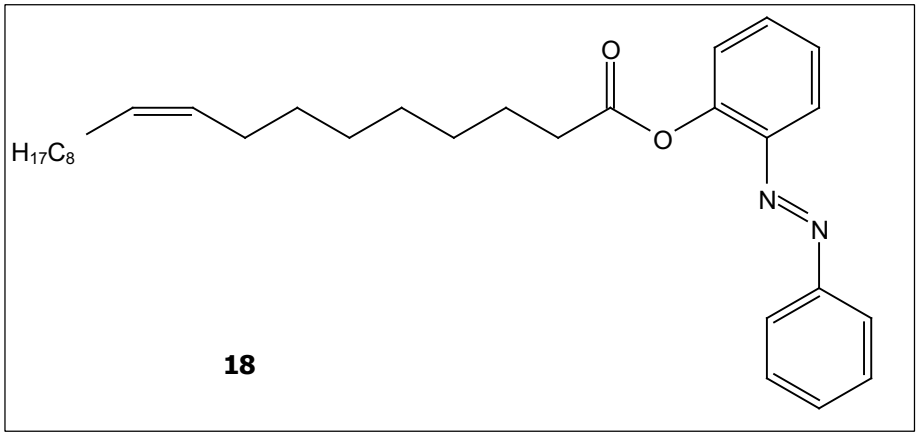
(^{1}H-NMR, 400 MHz, $CDCl_3$)





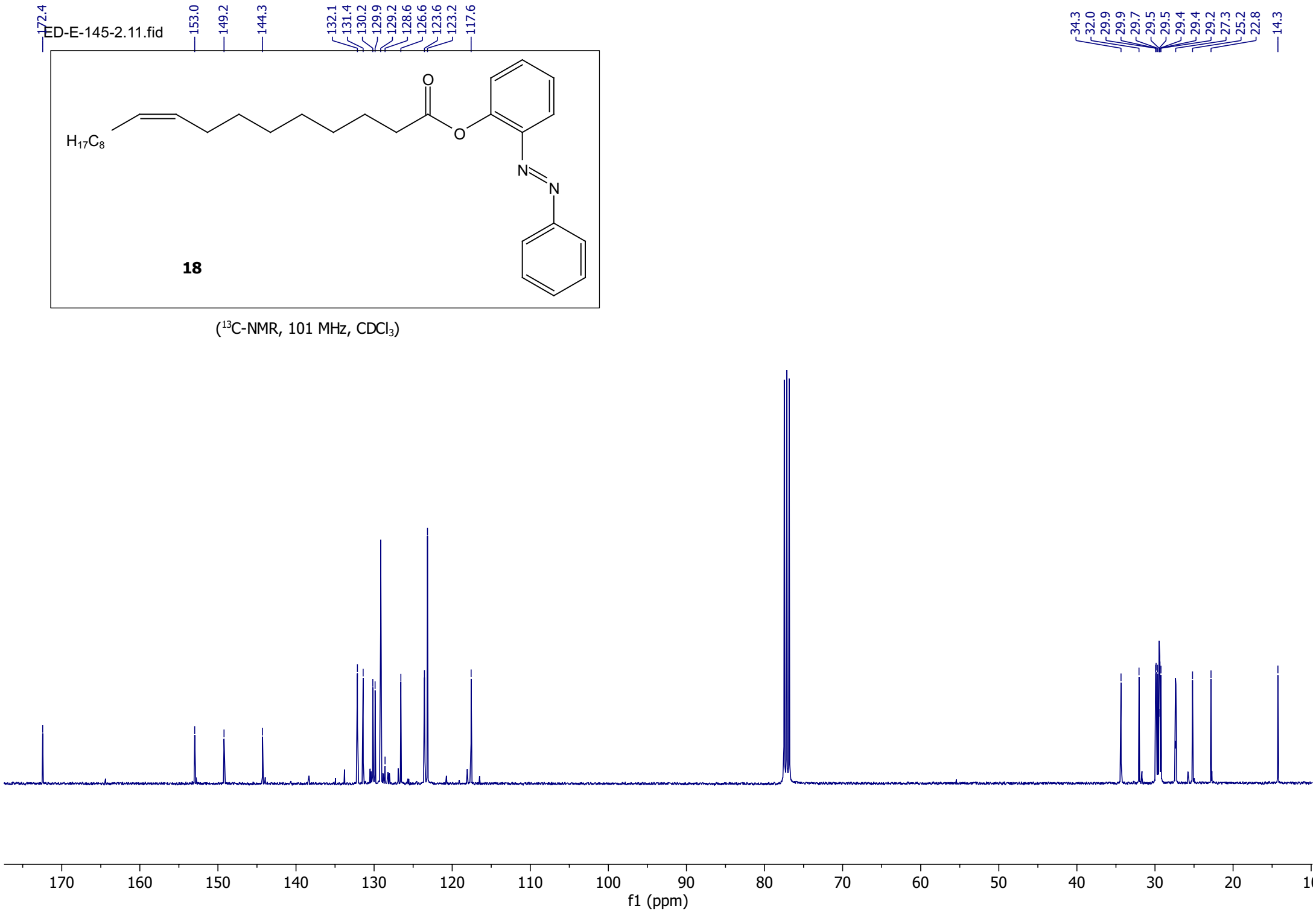
(^{13}C-NMR, 101 MHz, $CDCl_3$)

ED-E-145-2 10.fid

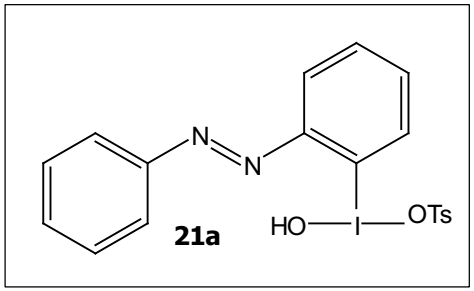


18

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

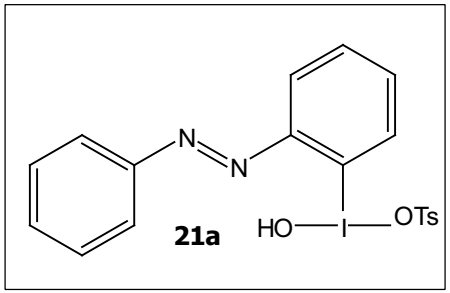


(^{13}C-NMR, 101 MHz, $CDCl_3$)



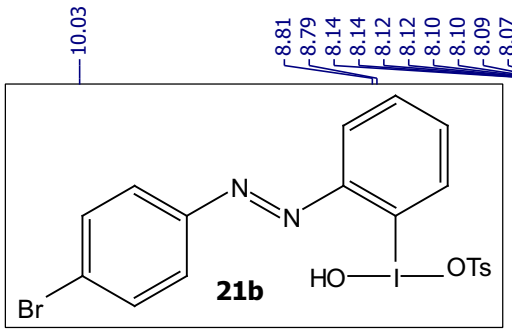
21a

(^{1}H-NMR, 400 MHz, MeOD-d_4)

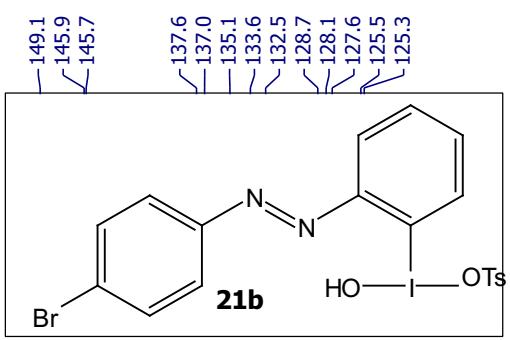


21a

(^{13}C-NMR, 101 MHz, MeOD-d_4)



(^{1}H-NMR, 400 MHz, DMSO-d_6)



(^{13}C-NMR, 101 MHz, DMSO-d_6)