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Photo-induced metal-free dehydrogenative N–N homo-coupling

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1. General Information

All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under nitrogen atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh). Analytical thin layer chromatography (TLC) were performed using aluminum-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a BrukerAvance 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz) spectrometer at 298 K. Coupling constants (*J*) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Mass spectrometry was performed on either a Waters AQUITY UPLC system equipped with PDA and SQD2 electrospray (ESI) MS detector or by GC-MS/FID analysis on an Agilant 7890A GC equipped with an HP-5 column and a 5975C VLMSD with triple-axis detector (EI). High-resolution mass spectrometry was performed on an Agilent 1290 UHPLC system (column: Agilent phenyl hexyl) coupled to an Agilent 6545 QTOF mass spectrometer (ESI). Photochemical reactions were performed in a HepatoChem photoreactor. Light sources used were EvoluChem cold white, 365 nm or 425 nm LEDs of comparable light intensities (425 nm, 33 mW/cm^{2}; 365 nm, 25 mW/cm^{2}; white, 29 mW/cm^{2}) although the wattage is different (425 nm, 18 W; 365 nm, 30 W; white, 18 W).

2. Synthesis of Benzophenone Imine Derivatives

Note: Some of the imines prepared below are sensitive to hydrolysis. To prevent hydrolysis, these compounds were stored in a argon-filled glovebox. Benzophenone imine is commercially available from Sigma Aldrich and used as received.

2.1. General Procedure A

To a stirring solution of ketone (10 mmol) in Et_2O (10 mL) was added a $KN(SiMe_3)_2$ (13 mmol, 0.5 M solution in toluene, 1.3 equiv). After addition of $KN(SiMe_3)_2$, the solution began to warm and slowly turned deep yellow orange in color. After 2 h, the volatiles were removed in vacuo and the resulting oily-solid was extracted into hexanes (25 mL) to give a cloudy solution. The solution was filtered through a Celite plug supported on a medium porosity glass frit, leaving behind a large plug of tan solid on the Celite pad, which was discarded. The volatiles were removed from the filtrate in vacuo and the resulting oil was extracted into hexanes (10 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). To the filtrate was added methanol (2 mL) and a 10:1 pentane/Et_2O solution, which resulted in a color change to bright yellow and subsequent precipitation of a yellow solid. The solid was collected on a medium porosity glass frit and rinsed with additional hexanes (5 mL) affording the title compounds.

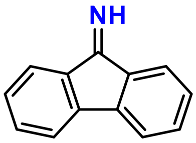
2.2 General Procedure B

Methoxyphenyl magnesium bromide (26 mL, 1.0 M, 26 mmol, 1.3 equiv) in THF was transferred to a 100 mL nitrogen-filled flask fitted with a reflux condenser, and the solution was cooled to 0 ºC. A solution of 4-methoxybenzonitrile (20.0 mmol) in dry THF (15 mL) was added to the flask, and the syringe rinsed with THF (3 mL). The reaction mixture was heated at reflux for 15 h, then cooled to 0 ºC, and then quenched with dry methanol (5 mL). The reaction mixture was diluted with hexanes (20 mL), filtered through a pad of Celite, and concentrated under reduced pressure. The resulting crude mixture was purified by column chromatography (on prebasified silica) to give the title compounds.

2.3 General Procedure C

Dry magnesium turnings (365 mg, 15.0 mmol, 1.50 equiv), dry THF (20 mL), and a magnetic stir bar were placed in a nitrogen-filled flask, and the flask was connected to a reflux condenser. Aryl bromide (15.0 mmol, 1.50 equiv) was dissolved in THF (3 mL), and a small amount of this solution was transferred to the reaction flask. The reaction was initiated with a single iodine crystal. The remaining aryl bromide solution was slowly transferred to the reaction flask. The syringe was rinsed with THF (3 mL), and the mixture was stirred at ambient temperature for 2.5 h at which time the majority of the magnesium was visibly consumed. The reaction mixture was then cooled to 0 ºC. A solution of a benzonitrile derivative (10 mmol, 1.0 equiv) in THF (10 mL) was added to the flask, and the syringe rinsed with THF (3 mL). The reaction mixture was heated to reflux for 15 h, cooled to 0 ºC, and then quenched with dry methanol (3 mL). The reaction mixture was diluted with hexanes (30 mL), filtered through a pad of Celite, and concentrated under reduced pressure. The resulting crude mixture was purified by column chromatography to give the title compounds.

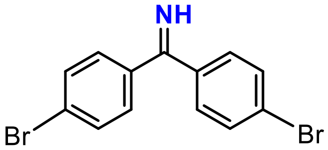
9*H*-Fluoren-9-imine (1b)



Synthesized via General Procedure A. Purified via silica gel chromatography (5% trimethylamine, 10% EtOAc, 85% hexane). Isolated as a yellow solid (465 mg, 47% yield). The spectral data are consistent with the data reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (bs, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.61 (dd, *J* = 20.1, 7.5 Hz, 3H), 7.49 (td, *J* = 7.5, 1.2 Hz, 2H), 7.36 (d, *J* = 6.9 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 142.8, 142.0, 137.3, 133.2, 132.4 (2C), 128.6, 128.1, 123.3, 121.5, 120.4, 120.1.
MS (EI) *m/z* ($M^{\cdot +}$) calcd for $C_{13}H_9N$: 179, found 179.

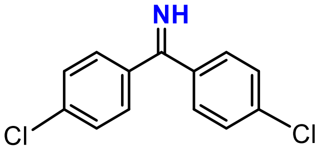
4,4′-Dibromobenzophenone imine (1c)



Synthesized via General Procedure A. Purified via silica gel chromatography (5% triethylamine in hexane). Isolated as a yellow solid (0.677 g, 68% yield). The spectral data are consistent with the data reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (bs, 1H), 7.59 (d, *J* = 8.5 Hz, 4H), 7.45 (d, *J* = 8.5 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 137.6 (2C), 131.9 (4C), 130.1 (4C), 125.4 (2C).
MS (EI) *m/z* ($M^{\cdot +}$) calcd for $C_{13}H_9Br_2NO$: 339, found 339.

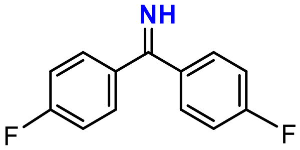
4,4′-Dichlorobenzophenone imine (1d)



Synthesized via General Procedure B. Purified via silica gel chromatography (5% triethylamine in hexane). Isolated as a pale-yellow solid (3.73 g, 74% yield). The spectral data are consistent with the data reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (bs, 1H), 7.57 – 7.47 (m, 4H), 7.46 – 7.37 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 137.4 (2C), 136.9 (2C), 129.8 (4C), 128.9 (4C).
MS (EI) *m/z* ($M^{\cdot +}$) calcd for $C_{13}H_9Cl_2N$: 249, found 249.

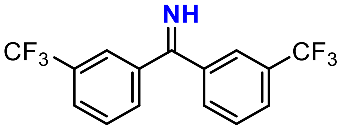
4,4′-Difluorobenzophenone imine (1e)



Synthesized via General Procedure B. Purified via silica gel chromatography (5% triethylamine in hexane). Isolated as a yellow oil (2.96 g, 68% yield). The spectral data are consistent with the data reported in the literature.[2]

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.45 (bs, 1H), 7.56 – 7.39 (m, 4H), 7.10 – 6.94 (m, 3H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 176.1, 164.1 (d, $^{1}J_{\text{C-F}}$ = 251.5 Hz, 2C), 135.4 (d, $^{4}J_{\text{C-F}}$ = 3.0 Hz, 2C), 130.5 (d, $^{3}J_{\text{C-F}}$ = 8.1 Hz, 4C), 115.5 (d, $^{2}J_{\text{C-F}}$ = 21.8 Hz, 4C).
^{19}F NMR (377 MHz, CDCl$_3$) δ -109.81.
MS (EI) *m/z* (M$^{\bullet+}$) calcd for $C_{13}H_9NF_2$: 217, found 217.

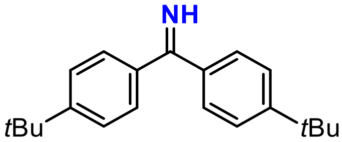
Bis(3-(trifluoromethyl)phenyl)methanimine (1f)



Synthesized via General Procedure C. Purified via silica gel chromatography (5% triethylamine in hexane). Isolated as a pale-red oil (4.48 g, 69% yield). The spectral data are consistent with the data reported in the literature.[2]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (bs, 2H), 7.83 – 7.77 (m, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 2H).
^{19}F NMR (377 MHz, CDCl$_3$) δ -62.80.
^{13}C NMR (101 MHz, CDCl$_3$) δ 175.7, 139.5 (2C), 131.7 (2C), 131.3 (q, $^{2}J_{\text{C-F}}$ = 31.8 Hz, 2C), 129.4 (2C), 127.5 (q, $^{3}J_{\text{C-F}}$ = 3.9 Hz, 2C), 125.2 (2C), 123.9 (q, $^{1}J_{\text{C-F}}$ = 267.7 Hz, 2C).
MS (EI) *m/z* (M$^{\bullet+}$) calcd for $C_{15}H_9F_6N$: 317, found 317.

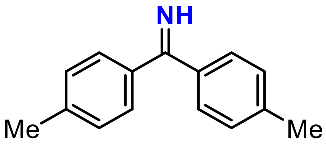
Bis(4-(*tert*-butyl)phenyl)methanimine (1g)



Synthesized via General Procedure C. Purified via silica gel chromatography (5% triethylamine in hexane). Isolated as a yellow oil (1.29 g, 44% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.58 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 4H), 7.36 (d, *J* = 8.4 Hz, 4H), 1.28 (s, 18H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 178.1, 153.7 (2C), 136.3 (2C), 128.4 (4C), 125.2 (4C), 34.9 (2C), 31.3 (6C).
HRMS (ESI/QTOF) m/z: [M+H]$^+$ Calcd for $C_{21}H_{28}N^+$; 294.2216, Found 294.2232.

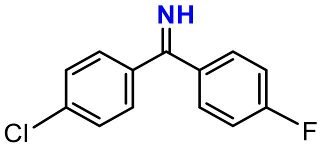
4,4’-Dimethylbenzophenone imine (1h)



Synthesized via General Procedure C. Purified via silica gel chromatography (5% triethylamine in hexane). Isolated as a pale-yellow solid (3.17 g, 76% yield). The spectral data are consistent with the data reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (bs, 1H), 7.49 (d, *J* = 7.7 Hz, 4H), 7.24 (d, *J* = 7.9 Hz, 4H), 2.43 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 140.5 (2C), 136.9 (2C), 129.1 (4C), 128.6 (4C), 21.5 (2C).
MS (EI) *m/z* ($M^{\bullet+}$) calcd for $C_{15}H_{15}N$: 209, found 209.

(4-Chlorophenyl)(4′-fluorophenyl)methanimine (1i)



Synthesized via General Procedure B. Purified via silica gel chromatography (5% triethylamine, 5% EtOAc, 90% hexane). Isolated as a colorless liquid (1.84 g, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.67 – 7.46 (m, 4H), 7.46 – 7.38 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H).
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -109.68.
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 164.1 (d, $^1J_{C\text{-}F}$ = 251.5 Hz), 137.6, 135.1, 131.3, 130.5 (2C), 129.7 (2C), 128.7 (2C), 115.5 ($^2J_{C\text{-}F}$ = 21.2 Hz, 2C).
HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{10}ClFN^+$; 234.0486, Found 234.0504.

3. General Procedure D: Photo-Induced N–N Homo-Coupling of Benzophenone Imines

A 4 mL vial was charged with the diarylimine **1a-i** (0.6 mmol; 1.0 equiv) and di-*tert*-butyl peroxide (20 equiv). The vial was loaded with a stirring bar and capped with a PTFE-lined septum cap. The vial was placed in a HepatoChem photoreactor equipped with either a 365 nm or a 425 nm LED lamp. The reaction was stirred for 40 h (365 nm) or 72 h (425 nm). The measured reaction temperature was 35 °C (no fan used). Then, the reaction mixture was concentrated under reduced pressure, and the resulting solids washed with hexane (2x3 mL). The title compounds were collected as the solids.

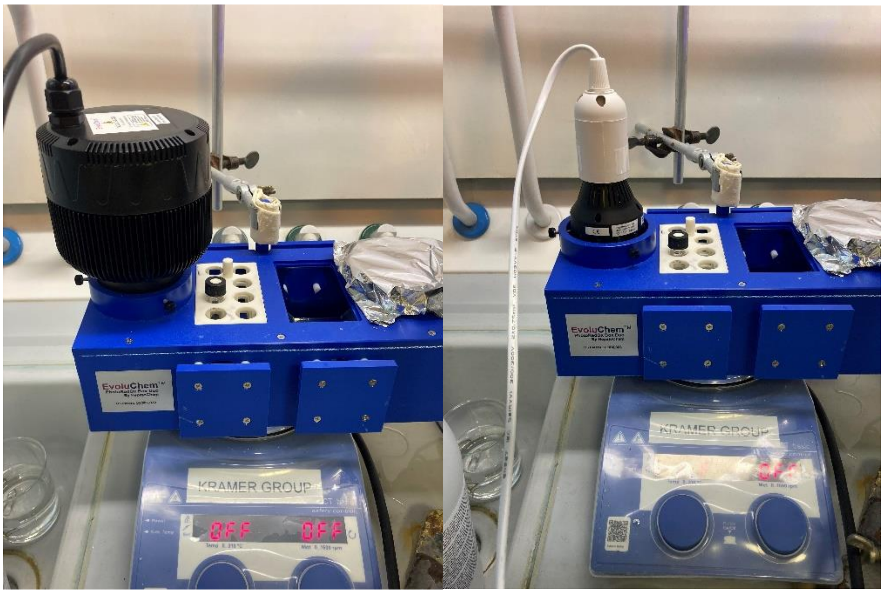
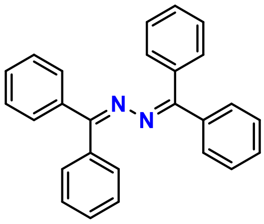


Figure S1. Hepatochem photoreactor. Left: 365 nm setup. Right: 425 nm setup.

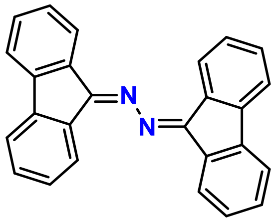
1,2-Bis(diphenylmethylene)hydrazine (2a)



Synthesized via General Procedure D. Purified by washing procedure using n-pentane (2x3 mL). Isolated as a pale-yellow solid (99.4 mg, 92% yield under 365 nm and 95.6 mg, 89% yield under 425 nm). The spectral data are consistent with the reported data in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 4H), 7.47 – 7.27 (m, 16H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (2C), 138.2 (2C), 135.5 (2C), 129.6 (2C), 129.3 (4C), 128.7 (4C), 128.7 (2C), 128.0 (4C), 127.9 (4C).
GCMS (EI): m/z Calcd for $C_{26}H_{20}N_2^+$; 360.2 Found 360.2.

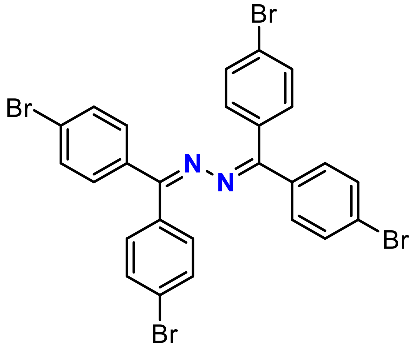
1,2-Di(9*H*-fluoren-9-ylidene)hydrazine (2b)



Synthesized via General Procedure D. Purified by washing procedure using n-pentane (2x3 mL). Isolated as a pale-red solid (87.3 mg, 81% yield under 365 nm and 61.2 mg, 75% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dt, *J* = 7.6, 0.9 Hz, 1H), 8.09 (dt, *J* = 7.3, 1.0 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.43 (tt, *J* = 7.5, 1.3 Hz, 2H), 7.31 – 7.23 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (2C), 142.3 (2C), 141.3 (2C), 136.5 (2C), 131.40 (2C), 131.38 (2C), 131.0 (2C), 129.8 (2C), 128.3 (2C), 128.2 (2C), 122.9 (2C), 120.1 (2C), 120.0 (2C).
LCMS m/z: $[M]^+$ Calcd for $C_{26}H_{16}N_2^+$ 356.1; Found 356.1.

1,2-Bis(bis(4-bromophenyl)methylene)hydrazine (2c)

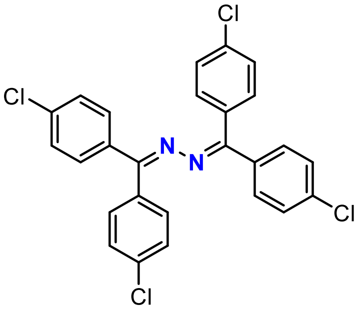


Synthesized via General Procedure D. Purified by washing procedure using n-pentane (2x3 mL). Isolated as a yellow solid (152.6 mg, 75% yield under 365 nm and 138 mg, 68% yield under 425 nm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 4H), 7.47 (d, *J* = 8.6 Hz, 4H), 7.40 – 7.31 (m, 4H), 7.24 – 7.12 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (2C), 136.4 (2C), 133.7 (2C), 131.7 (4C), 131.5 (4C), 131.1 (4C), 130.3 (4C), 125.0 (2C), 123.6 (2C).
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{17}Br_4N_2^+$ 672.8125; Found 672.8106.

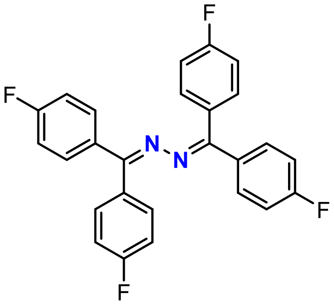
1,2-Bis(bis(4-chlorophenyl)methylene)hydrazine (2d)



Synthesized via General Procedure D. Purified by washing procedure using 5% EtOAc in hexane (2x3 mL). Isolated as a pale-yellow solid (98.3 mg, 66% yield under 365 nm and 103 mg, 69% yield under 425 nm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 4H), 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (2C), 136.5 (2C), 136.0 (2C), 135.3 (2C), 133.3 (2C), 130.9 (4C), 130.0 (4C), 128.7 (4C), 128.5 (4C).
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{17}Cl_4N_2^+$ 497.0146; Found 497.0143.

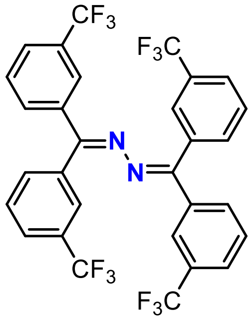
1,2-Bis(bis(4-fluorophenyl)methylene)hydrazine (2e)



Synthesized via General Procedure D. Purified by washing procedure with n-pentane (2x3 mL). Isolated as a yellow solid (108 mg, 83% yield under 365 nm and 86 mg, 66% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 8.7, 5.6 Hz, 1H), 7.33 (dd, J = 8.5, 5.6 Hz, 1H), 7.14 (t, J = 8.7 Hz, 1H), 7.02 (t, J = 8.7 Hz, 1H).
^{19}F NMR (377 MHz, $CDCl_3$) δ -110.48, -111.26.
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (d, $^{1}J_{C\text{-}F}$ = 252.5 Hz, 2C), 162.8 (d, $^{1}J_{C\text{-}F}$ = 250.5 Hz, 2C), 159.0 (2C), 134.0 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz, 2C), 131.4 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz, 4C), 131.2 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz, 2C), 130.6 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz, 4C), 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, 4C), 115.1 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, 4C).
MS (EI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{16}F_4N_2^+$ 432.1; Found 432.1.

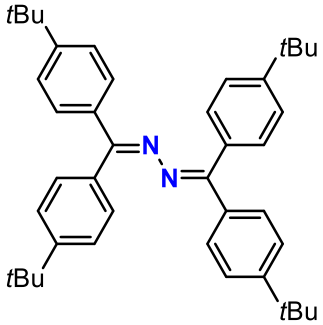
1,2-Bis(bis(3-(trifluoromethyl)phenyl)methylene)hydrazine (2f)



Synthesized via General Procedure D. Purified via prebasified silica gel chromatography (5% triethylamine, 5% EtOAc, 90% hexane). Isolated as a yellow solid (93 mg, 49% yield under 365 nm and 79.2 mg, 42% yield under 425 nm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 4H), 7.71 – 7.59 (m, 8H), 7.54 – 7.44 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (2C), 137.6 (2C), 134.9 (2C), 132.3 (2C), 131.1 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz, 2C), 130.9 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz, 2C), 128.9 (4C), 127.1 (q, $^{3}J_{C\text{-}F}$ = 4.2 Hz, 2C), 126.3-126.1 (m, 4C),125.2-125.0 (4C), 123.5 (q, $^{1}J_{C\text{-}F}$ = 267.7 Hz, 4C).
^{19}F NMR (377 MHz, $CDCl_3$) δ -62.84, -62.98.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{17}F_{12}N_2^+$ 633.1200; Found 633.1176.

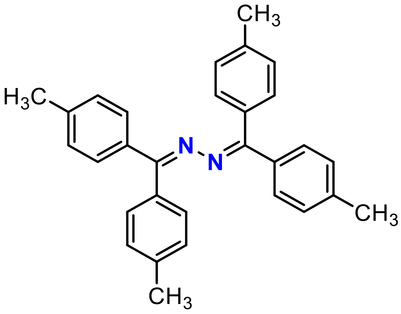
1,2-Bis(bis(4-(*tert*-butyl)phenyl)methylene)hydrazine (2g)



Synthesized via General Procedure D. Purified by washing procedure using 5% EtOAc in hexane (2x3 mL). Isolated as a yellow solid (136.4 mg, 78% yield under 365 nm and 116 mg, 66% yield under 425 nm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 8H), 7.28 – 7.20 (m, 8H), 1.28 (s, 18H), 1.23 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1 (2C), 152.5 (2C), 151.5 (2C), 136.0 (2C), 132.7 (2C), 129.4 (4C), 128.6 (4C), 124.8 (4C), 124.6 (4C), 34.8 (2C), 34.7 (2C), 31.3 (6C), 31.2 (6C).
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{52}N_2^+$ 585.4130; Found 585.4126.

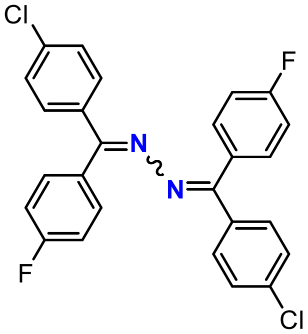
1,2-Bis(di-*p*-tolylmethylene)hydrazine (2h)



Synthesized via General Procedure D. Purified via prebasified silica gel chromatography (5% triethylamine, 5% EtOAc, 90% hexane). Isolated as a yellow solid (49.2 mg, 39% yield under 365 nm and 54 mg, 43% yield under 425 nm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.38 (d, *J* = 13.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (2C), 139.6 (2C), 138.5 (2C), 136.1 (2C), 132.9 (2C), 129.7 (4C), 128.9 (4C), 128.8 (4C), 128.5 (4C), 21.6 (2C), 21.5 (2C).
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{29}N_2^+$ 417.2331; Found 417.2326.

1,2-((4-Chlorophenyl)(4-fluorophenyl)methylene)hydrazine (2i)



Synthesized via General Procedure D. Purified by washing procedure using 5% EtOAc in hexane (2x3 mL). Isolated as a yellow solid (103 mg, 74% yield under 365 nm and 72 mg, 52% yield under 425 nm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.40 (m, 6H), 7.37 – 7.24 (m, 6H), 7.14 (td, *J* = 8.7, 2.7 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 (d, $^1J_{C\text{-}F}$ = 251.5 Hz), 162.86 (d, $^1J_{C\text{-}F}$ = 250.5 Hz), 159.1, 158.9, 158.8, 158.6, 136.2, 135.0 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 133.7 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 133.5 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 131.5 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 131.41 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 130.8 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 130.66, 130.57, 129.9, 128.5, 128.3, 115.3 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 15.2 (d, $^2J_{C\text{-}F}$ = 21.3 Hz).
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -110.20, -110,21, -110.96, -111.04.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{17}Cl_2F_2N_2^+$ 465.0737; Found 465.0763.

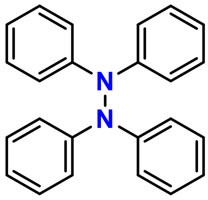
4. Gram-Scale Procedure for Photo-Induced N–N Homo-Coupling of Benzophenone Imine

A 20 mL vial was charged with benzophenone imine **1a** (1.45 g, 8.0 mmol) and di-*tert*-butyl peroxide (80.0 mmol, 14.6 mL, 10 equiv). The vial was loaded with a stirring bar and capped with a PTFE-lined septum cap. The vial was placed in a HepatoChem photoreactor equipped with a 365 nm LED lamp, and the reaction stirred for 72 h under irradiation. The measured reaction temperature was 37 °C. Then, the reaction mixture was concentrated under reduced pressure, and the resulting solids washed with hexane (2x30 mL). The title compound was collected as pale-yellow solid (1.21 g, 84%).

5. General Procedure E: Photo-Induced N–N Homo-Coupling of Diaryl Amines and Carbazoles

A 4 mL vial was charged with diarylamine (**3a-d**) or carbazole (**3e-h**) derivative (0.6 mmol; 1.0 equiv) and di-*tert*-butyl peroxide (10 equiv). The vial was loaded with a stirring bar and capped with a PTFE-lined septum cap. The vial was placed in a HepatoChem photoreactor equipped with either a 365 nm or a 425 nm LED lamp. The reaction was stirred for 40 h (365 nm) or 72 h (425 nm). The measured reaction temperature was 35 °C. Then, the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel.

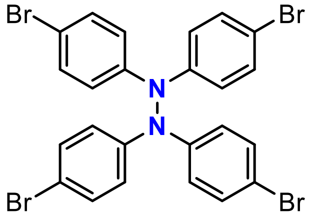
1,1,2,2-Tetraphenylhydrazine (4a)



Synthesized via General Procedure E. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a pale-brown solid (68 m, 67% yield under 365 nm and 56 mg, 55% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.3 Hz, 8H), 7.22 (d, 7.2 Hz, 8H), 6.92 (t, *J* = 7.3 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5 (4C), 129.1 (8C), 122.1 (4C), 118.1 (8C).
MS (ESI) Calculated for $C_{24}H_{20}N_2$ $[M]^+$: 336.2, Found: 336.2.

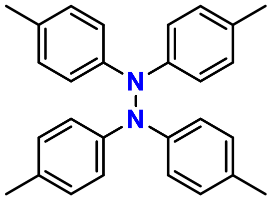
1,1,2,2-Tetrakis(4-bromophenyl)hydrazine (4b)



Synthesized via General Procedure E. Purified via pre-basified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a colorless solid (113 mg, 58% yield under 365 nm and 98 mg, 50% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (d, *J* = 9.1 Hz, 8H), 7.10 (d, *J* = 9.1 Hz, 8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8 (4C), 132.6 (8C), 119.8 (4C), 115.3 (8C).
MS (ESI) Calculated for $C_{24}H_{16}Br_4N_2$ $[M]^+$: 649.8, Found: 649.8.

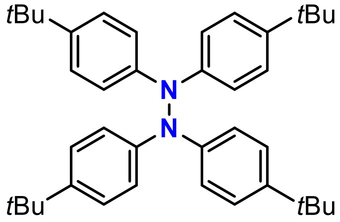
1,1,2,2-Tetra-*p*-tolylhydrazine (4c)



Synthesized via General Procedure E. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a yellow solid (77 mg, 65% yield under 365 nm and 49 mg, 42% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[6]

^{1}H NMR (400 MHz, C_6D_6) δ 6.95 (d, *J* = 8.2 Hz, 8H), 6.84 (d, *J* = 8.4 Hz, 7H), 2.15 (s, 12H).
^{13}C NMR (101 MHz, C_6D_6) δ 141.4 (4C), 129.7 (4C), 129.6 (8C), 118.0 (8C), 20.3 (4C).
MS (ESI) Calculated for $C_{28}H_{28}N_2$ $[M]^+$: 392.2, Found: 392.2.

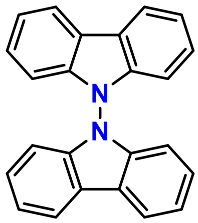
1,1,2,2-Tetrakis(4-(*tert*-butyl)phenyl)hydrazine (4d)



Synthesized via General Procedure E. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a pale-brown solid (124 mg, 74% yield under 365 nm and 78 mg, 46% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[6]

^{1}H NMR (400 MHz, C_6D_6) δ 7.48 (d, *J* = 8.8 Hz, 8H), 7.15 (d, J = 8.9 Hz, 8H), 1.13 (s, 36H).
^{13}C NMR (101 MHz, C_6D_6) δ 144.2 (4C), 141.9 (4C), 126.1 (4C), 117.8 (4C), 33.8 (4C), 31.1 (4C).
MS (ESI) Calculated for $C_{40}H_{52}N_2$ $[M]^+$: 560.4, Found: 560.4.

9,9'-Bicarbazole (4e)

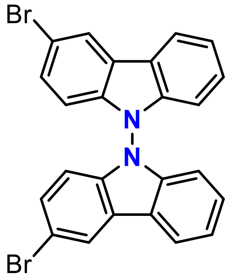


Synthesized via General Procedure E. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a colorless solid (54 mg, 54% yield under 365 nm and 36.8 mg, 37% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.16 (m, 4H), 7.35 (dd, *J* = 6.4, 2.8 Hz, 8H), 7.00 – 6.85 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0 (4C), 126.7 (4C), 122.1 (4C), 121.4 (4C), 120.8 (4C), 109.2 (4C).
MS (ESI) Calculated for $C_{24}H_{20}N_2$ $[M]^+$: 332.1, Found: 332.1.

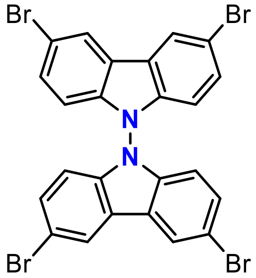
3,3'-dibromo-9,9'-bicarbazole (4f)



Synthesized via General Procedure E. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a colorless solid (107 mg, 73% yield under 365 nm and 98.3 mg, 67% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 1.8 Hz, 2H), 8.22 – 8.12 (m, 2H), 7.45 (dd, J = 8.6, 1.8 Hz, 2H), 7.39 (dd, J = 6.0, 3.1 Hz, 4H), 6.90 (dd, J = 6.2, 3.0 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0 (2C), 138.4 (2C), 129.4 (2C), 127.5 (2C), 123.8 (2C), 123.6 (2C), 121.9 (2C), 121.0 (2C), 121.0 (2C), 114.4 (2C), 110.4 (2C), 109.2 (2C).
LCMS-ESI: Calculated for $C_{24}H_{14}Br_2N_2$ $[M]^+$: 489.9, Found: 489.9.

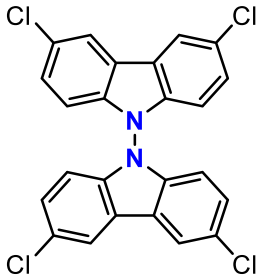
3,3',6,6'-Tetrabromo-9,9'-bicarbazole (4g)



Synthesized via General Procedure E. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a colorless solid (159 mg, 82% yield under 365 nm and 119 mg, 61% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 1.8 Hz, 4H), 7.49 (dd, J = 8.6, 1.9 Hz, 4H), 6.77 (d, J = 8.6 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 (4C), 130.4 (4C), 123.9 (4C), 122.7 (4C), 115.0 (4C), 110.5 (4C).
LCMS-ESI: Calculated for $C_{24}H_{12}Br_4N_2$ $[M]^+$: 645.8, Found: 645.8.

3,3',6,6'-Tetrachloro-9,9'-bicarbazole (4h)



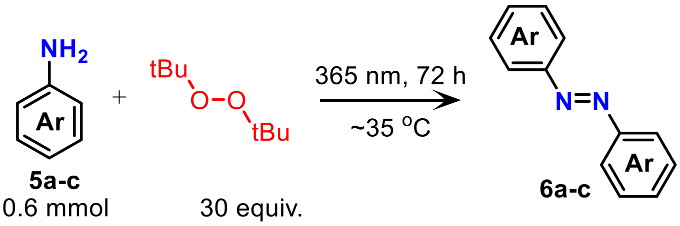
Synthesized via General Procedure E. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a colorless solid (89 mg, 63% yield under 365 nm and 74 mg, 52% yield under 425 nm). The spectral data are consistent with the data reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.0 Hz, 4H), 7.34 (dd, *J* = 8.6, 1.4 Hz, 4H), 6.80 (d, *J* = 8.6 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 (4C), 127.9 (4C), 127.8 (4C), 122.4 (4C), 121.1 (4C), 110.3 (4C).
LCMS-ESI: Calculated for $C_{24}H_{12}Cl_4N_2$ $[M]^+$: 470.0, Found: 470.0.

6. Gram-Scale Procedure: Photo-Induced N–N Homo-Coupling 3,6-Dibromo-Carbazole

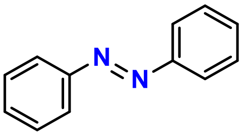
A 20 mL vial was charged with 3,6-dibromo-carbazole **4g** (1.95 g, 6.0 mmol) and di-*tert*-butyl peroxide (60.0 mmol, 10.9 mL, 10 equiv). The vial was loaded with a stirring bar and capped with a PTFE-lined septum cap. The vial was placed in a HepatoChem photoreactor equipped with a 365 nm LED lamp, and the reaction stirred for 40 h under irradiation. The measured reaction temperature was 37 °C. Then, the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel using 0-5% EtOAc in hexane to afford the title compound as a colorless solid (1.49 g, 77%).

7. General Procedure F: Photo-Induced Double Dehydrogenative N–N Homo-Coupling of Anilines



A 4 mL vial was charged with aniline derivative **5a-c** (0.6 mmol; 1 equiv) and di-*tert*-butyl peroxide (30 equiv). The vial was loaded with a stirring bar and capped with a PTFE-lined septum cap. The vial was placed in a HepatoChem photoreactor equipped with a 365 nm LED lamp and stirred under irradiation for 72 h. The measured reaction temperature was typically 35 °C. Then, the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel.

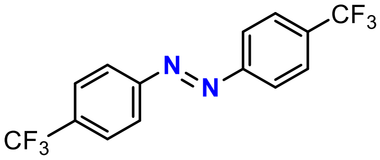
1,2-Diphenyldiazene (6a)



Synthesized via General Procedure F. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a pale-red solid in 57% yield (31.2 mg). The spectral data are consistent with the data reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 8.0, 1.7 Hz, 4H), 7.65 – 7.41 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7 (2C), 131.0 (4C), 129.1 (2C), 122.8 (4C).
MS (EI) *m/z* ($M^{•+}$) calcd for $C_{12}H_{10}N_2$: 182, found 182.

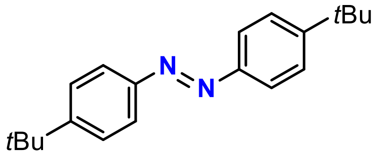
1,2-Bis(4-(trifluoromethyl)phenyl)diazene (6b)



Synthesized via General Procedure F. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a pale-red solid in 53% yield (50.7 mg). The spectral data are consistent with the data reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 4H), 7.83 (d, *J* = 8.3 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1 (2C), 133.0 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz, 2C), 126.4 (q, $^{3}J_{C\text{-}F}$ = 32.3 Hz, 4C),123.8 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz, 4C) 123.3 (2C).
^{19}F NMR (377 MHz, $CDCl_3$) δ -62.73.
MS (EI) *m/z* ($M^{•+}$) calcd for $C_{14}H_8F_6N_2$: 318, found 318.

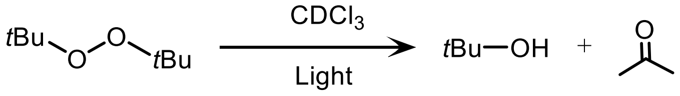
1,2-Bis(4-(*tert*-butyl)phenyl)diazene (6c)



Synthesized via General Procedure F. Purified via prebasified silica gel chromatography (3% triethylamine in hexane). The title compound was obtained as a pale-red solid in 63% yield (55.8 mg). The spectral data are consistent with the data reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 4H), 7.53 (d, *J* = 8.6 Hz, 4H), 1.37 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4 (2C), 150.9 (2C), 126.1 (4C), 122.6 (4C), 35.1 (2C), 31.4 (6C).
MS (EI) *m/z* ($M^{\bullet +}$) calcd for $C_{20}H_{26}N_2$: 294, found 294.

8. Photolysis of DTBP



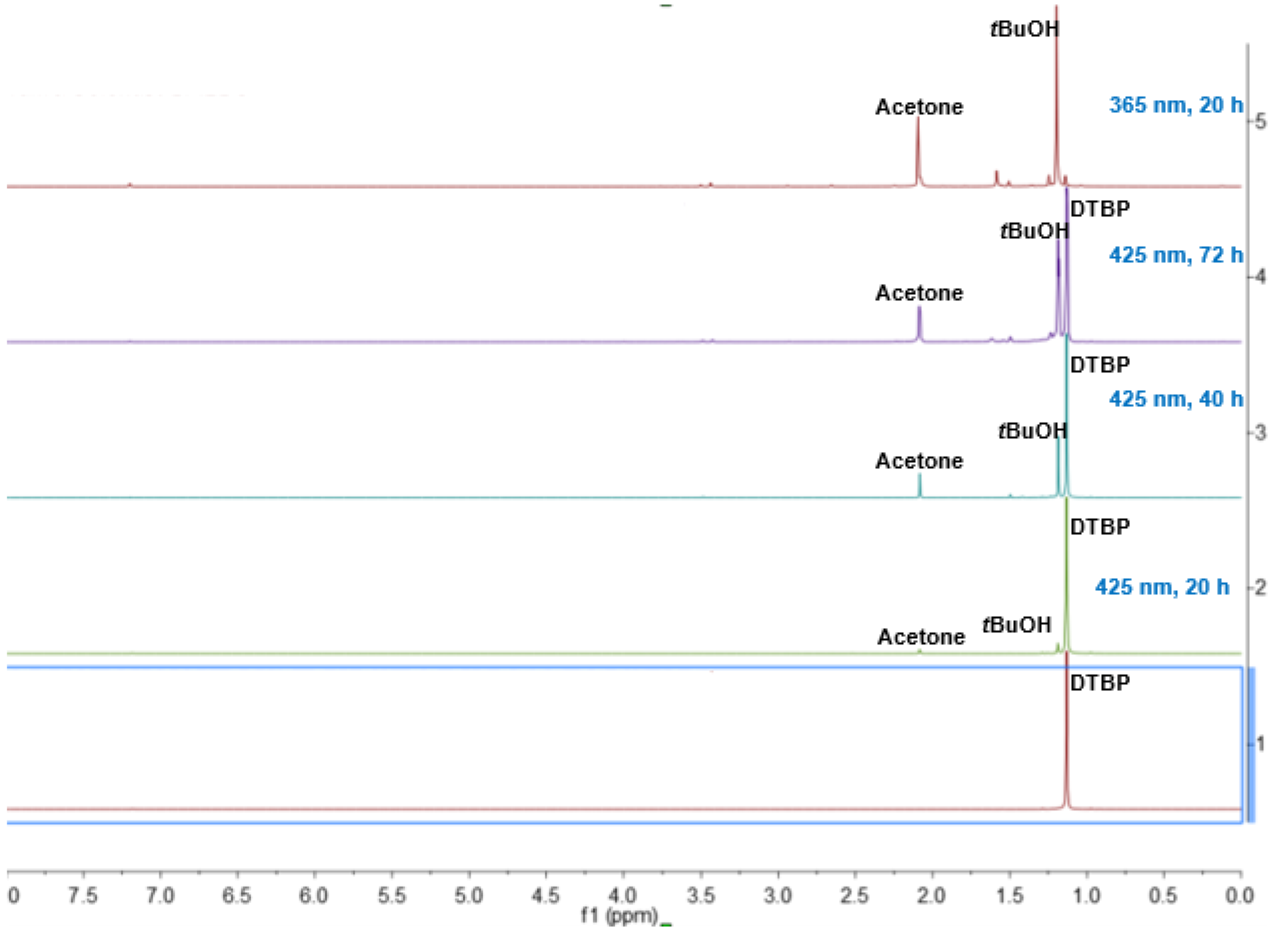
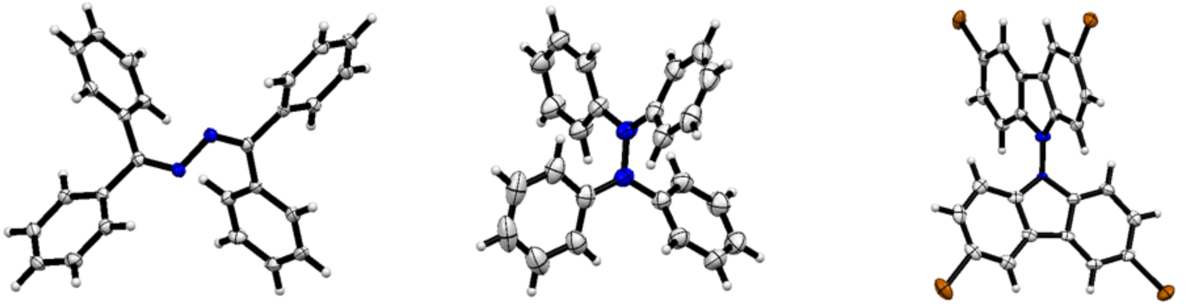


Figure S2. Complete conversion of DTBP to *t*-BuOH and acetone under 365 nm LED irradiation in 20 h in $CDCl_3$.

9. X-Ray Crystallography Data



X-ray structure of **2a** X-ray structure of **4a** X-ray structure of **4g**

Figure S3: X-ray structures of N-N homo coupled products (ORTEP drawings showing thermal ellipsoids at 50% probability).

Table S1 Crystal data and structure refinement for 2a.

Identification code	BB-296
Empirical formula	$C_{26}H_{20}N_2$
Formula weight	360.44
Temperature/K	119.97(11)
Crystal system	monoclinic
Space group	C2/c
a/Å	21.8743(10)
b/Å	5.4117(2)
c/Å	16.0179(7)
α/°	90
β/°	94.488(4)
γ/°	90
Volume/$Å^3$	1890.34(14)
Z	4
ρ_{calc}g/cm^3	1.266
μ/mm^{-1}	0.074
F(000)	760.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.556 to 51.358
Index ranges	$-26 \leq h \leq 26, -6 \leq k \leq 6, -19 \leq l \leq 19$
Reflections collected	13668
Independent reflections	1807 [R_{int} = 0.1034, R_{sigma} = 0.0456]
Data/restraints/parameters	1807/0/127
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.1152
Final R indexes [all data]	R_1 = 0.0493, wR_2 = 0.1192
Largest diff. peak/hole / e Å^{-3}	0.17/-0.25

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2a. U$_{eq}$ is defined as 1/3 of of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	*x*	*y*	*z*	U(eq)
N$^{(001)}$	5278.0(5)	1873(2)	7744.1(7)	19.4(3)
C$^{(002)}$	5742.1(6)	2784(2)	7403.4(9)	18.5(3)
C$^{(003)}$	5716.7(6)	4116(3)	6585.0(9)	19.3(3)
C$^{(004)}$	6348.5(6)	2574(3)	7888.4(9)	19.3(3)
C$^{(005)}$	6791.1(7)	4388(3)	7813.0(9)	23.0(3)
C$^{(006)}$	5364.7(7)	6242(3)	6453.4(9)	24.2(4)
C$^{(007)}$	6477.8(7)	617(3)	8443.5(9)	23.5(3)
C$^{(008)}$	6069.0(7)	3301(3)	5949.6(9)	24.6(4)
C$^{(009)}$	7349.4(7)	4283(3)	8290.8(10)	26.8(4)
C$^{(00A)}$	5701.8(7)	6679(3)	5074.1(9)	28.1(4)
C$^{(00B)}$	7469.7(7)	2354(3)	8845.3(10)	28.7(4)
C$^{(00C)}$	5362.7(7)	7528(3)	5705.9(10)	28.3(4)
C$^{(00D)}$	6053.8(7)	4572(3)	5195.0(9)	29.1(4)
C$^{(00E)}$	7034.6(7)	522(3)	8915.3(10)	28.3(4)

Table S3 Anisotropic Displacement Parameters (Å^2×10^3) for 2a. 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$_{12}$
N$^{(001)}$	17.3(6)	20.1(6)	20.8(6)	-1.3(5)	0.7(5)	1.3(5)
C$^{(002)}$	18.0(7)	17.1(7)	20.6(7)	-3.0(5)	2.5(6)	2.2(5)
C$^{(003)}$	15.4(7)	22.8(7)	19.3(7)	-1.7(6)	-0.8(5)	-4.1(5)
C$^{(004)}$	17.3(7)	22.9(7)	17.9(7)	-2.4(6)	3.3(6)	3.0(6)
C$^{(005)}$	21.6(7)	25.3(8)	22.0(7)	1.3(6)	1.7(6)	0.6(6)
C$^{(006)}$	26.1(8)	25.8(8)	20.9(7)	-0.4(6)	2.8(6)	1.6(6)
C$^{(007)}$	21.9(7)	24.6(8)	24.4(8)	1.6(6)	3.5(6)	2.9(6)
C$^{(008)}$	18.8(7)	30.9(8)	23.9(8)	-2.8(6)	0.3(6)	1.1(6)
C$^{(009)}$	19.4(8)	33.1(9)	28.0(8)	-3.9(7)	1.9(6)	-2.4(6)
C$^{(00A)}$	28.3(8)	37.6(9)	18.3(7)	5.1(6)	0.1(6)	-8.1(7)
C$^{(00B)}$	20.0(8)	41.3(9)	24.0(8)	-4.6(7)	-3.6(6)	6.4(7)
C$^{(00C)}$	32.1(9)	26.6(8)	25.9(8)	5.0(6)	0.8(7)	0.3(7)
C$^{(00D)}$	23.6(8)	45.4(10)	18.6(8)	-5.3(7)	4.2(6)	-3.7(7)
C$^{(00E)}$	28.2(8)	31.4(9)	24.9(8)	3.1(6)	0.6(6)	9.6(7)

Table S4 Bond Lengths for 2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N$^{(001)}$	N$^{(001)1}$	1.393(2)	C$^{(005)}$	C$^{(009)}$	1.391(2)
N$^{(001)}$	C$^{(002)}$	1.2877(18)	C$^{(006)}$	C$^{(00C)}$	1.385(2)
C$^{(002)}$	C$^{(003)}$	1.4932(19)	C$^{(007)}$	C$^{(00E)}$	1.383(2)
C$^{(002)}$	C$^{(004)}$	1.488(2)	C$^{(008)}$	C$^{(00D)}$	1.389(2)

$C^{(003)}$	$C^{(006)}$	1.391(2)	$C^{(009)}$	$C^{(00B)}$	1.383(2)
$C^{(003)}$	$C^{(008)}$	1.395(2)	$C^{(00A)}$	$C^{(00C)}$	1.380(2)
$C^{(004)}$	$C^{(005)}$	1.391(2)	$C^{(00A)}$	$C^{(00D)}$	1.381(2)
$C^{(004)}$	$C^{(007)}$	1.397(2)	$C^{(00B)}$	$C^{(00E)}$	1.385(2)

[1] 1-X,+Y,3/2-Z

Table S5 Bond Angles for 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$C^{(002)}$	$N^{(001)}$	$N^{(001)1}$	116.40(13)	$C^{(004)}$	$C^{(005)}$	$C^{(009)}$	120.73(14)
$N^{(001)}$	$C^{(002)}$	$C^{(003)}$	125.48(13)	$C^{(00C)}$	$C^{(006)}$	$C^{(003)}$	120.73(14)
$N^{(001)}$	$C^{(002)}$	$C^{(004)}$	116.72(13)	$C^{(00E)}$	$C^{(007)}$	$C^{(004)}$	120.10(14)
$C^{(004)}$	$C^{(002)}$	$C^{(003)}$	117.75(12)	$C^{(00D)}$	$C^{(008)}$	$C^{(003)}$	120.09(14)
$C^{(006)}$	$C^{(003)}$	$C^{(002)}$	120.96(12)	$C^{(00B)}$	$C^{(009)}$	$C^{(005)}$	119.94(14)
$C^{(006)}$	$C^{(003)}$	$C^{(008)}$	118.79(13)	$C^{(00C)}$	$C^{(00A)}$	$C^{(00D)}$	119.87(14)
$C^{(008)}$	$C^{(003)}$	$C^{(002)}$	120.20(13)	$C^{(009)}$	$C^{(00B)}$	$C^{(00E)}$	119.68(14)
$C^{(005)}$	$C^{(004)}$	$C^{(002)}$	119.94(13)	$C^{(00A)}$	$C^{(00C)}$	$C^{(006)}$	120.09(15)
$C^{(005)}$	$C^{(004)}$	$C^{(007)}$	118.85(14)	$C^{(00A)}$	$C^{(00D)}$	$C^{(008)}$	120.40(14)
$C^{(007)}$	$C^{(004)}$	$C^{(002)}$	121.18(13)	$C^{(007)}$	$C^{(00E)}$	$C^{(00B)}$	120.69(15)

[1] 1-X,+Y,3/2-Z

Table S6 Torsion Angles for 2a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
$N^{(001)1}$	$N^{(001)}$	$C^{(002)}$	$C^{(003)}$	8.39(18)	$C^{(003)}$	$C^{(008)}$	$C^{(00D)}$	$C^{(00A)}$	1.5(2)
$N^{(001)1}$	$N^{(001)}$	$C^{(002)}$	$C^{(004)}$	-174.35(9)	$C^{(004)}$	$C^{(002)}$	$C^{(003)}$	$C^{(006)}$	-118.56(15)
$N^{(001)}$	$C^{(002)}$	$C^{(003)}$	$C^{(006)}$	58.7(2)	$C^{(004)}$	$C^{(002)}$	$C^{(003)}$	$C^{(008)}$	58.65(18)
$N^{(001)}$	$C^{(002)}$	$C^{(003)}$	$C^{(008)}$	-124.12(16)	$C^{(004)}$	$C^{(005)}$	$C^{(009)}$	$C^{(00B)}$	0.3(2)
$N^{(001)}$	$C^{(002)}$	$C^{(004)}$	$C^{(005)}$	-148.51(13)	$C^{(004)}$	$C^{(007)}$	$C^{(00E)}$	$C^{(00B)}$	0.0(2)
$N^{(001)}$	$C^{(002)}$	$C^{(004)}$	$C^{(007)}$	29.45(19)	$C^{(005)}$	$C^{(004)}$	$C^{(007)}$	$C^{(00E)}$	0.9(2)
$C^{(002)}$	$C^{(003)}$	$C^{(006)}$	$C^{(00C)}$	177.29(13)	$C^{(005)}$	$C^{(009)}$	$C^{(00B)}$	$C^{(00E)}$	0.6(2)
$C^{(002)}$	$C^{(003)}$	$C^{(008)}$	$C^{(00D)}$	-178.72(13)	$C^{(006)}$	$C^{(003)}$	$C^{(008)}$	$C^{(00D)}$	-1.5(2)
$C^{(002)}$	$C^{(004)}$	$C^{(005)}$	$C^{(009)}$	176.95(13)	$C^{(007)}$	$C^{(004)}$	$C^{(005)}$	$C^{(009)}$	-1.1(2)
$C^{(002)}$	$C^{(004)}$	$C^{(007)}$	$C^{(00E)}$	-177.09(13)	$C^{(008)}$	$C^{(003)}$	$C^{(006)}$	$C^{(00C)}$	0.0(2)
$C^{(003)}$	$C^{(002)}$	$C^{(004)}$	$C^{(005)}$	28.96(19)	$C^{(009)}$	$C^{(00B)}$	$C^{(00E)}$	$C^{(007)}$	-0.8(2)
$C^{(003)}$	$C^{(002)}$	$C^{(004)}$	$C^{(007)}$	-153.08(13)	$C^{(00C)}$	$C^{(00A)}$	$C^{(00D)}$	$C^{(008)}$	0.0(2)
$C^{(003)}$	$C^{(006)}$	$C^{(00C)}$	$C^{(00A)}$	1.4(2)	$C^{(00D)}$	$C^{(00A)}$	$C^{(00C)}$	$C^{(006)}$	-1.4(2)

[1] 1-X,+Y,3/2-Z

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a.

Atom	*x*	*y*	*z*	U(eq)
H$^{(005)}$	6711.31	5712.44	7430.87	28
H$^{(006)}$	5123.01	6817.37	6881.12	29
H$^{(007)}$	6182.75	-650.12	8496.83	28
H$^{(008)}$	6319.47	1874.35	6033.31	30
H$^{(009)}$	7647.82	5536.09	8236.23	32
H$^{(00A)}$	5693.28	7542.13	4556.85	34
H$^{(00B)}$	7848.98	2285.21	9176.62	34
H$^{(00C)}$	5127.39	8997.32	5628.06	34
H$^{(00D)}$	6287.03	3988.09	4759.37	35
H$^{(00E)}$	7119.5	-814.48	9291.24	34

Table S8 Crystal data and structure refinement for 4a.

Identification code	exp_1985_BB_598_autored
Empirical formula	$C_{24}H_{20}N_2$
Formula weight	336.42
Temperature/K	229.99(10)
Crystal system	orthorhombic
Space group	C222$_1$
a/Å	12.66060(10)
b/Å	35.4705(2)
c/Å	12.01470(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5395.54(7)
Z	12
ρ_{calc}g/cm^3	1.242
μ/mm^{-1}	0.560
F(000)	2136.0
Crystal size/mm^3	0.4 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.414 to 153.28
Index ranges	$-15 \le h \le 15$, $-44 \le k \le 41$, $-15 \le l \le 15$
Reflections collected	56056
Independent reflections	5670 [R_{int} = 0.0389, R_{sigma} = 0.0154]
Data/restraints/parameters	5670/0/352
Goodness-of-fit on F^2	1.045

Final R indexes [I>=2σ (I)]	$R_1 = 0.0289$, $wR_2 = 0.0763$
Final R indexes [all data]	$R_1 = 0.0299$, $wR_2 = 0.0776$
Largest diff. peak/hole / e Å^{-3}	0.10/-0.13
Flack parameter	0.02(11)

Table S9 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N001	6130.2(10)	6519.6(3)	5599.8(11)	41.9(3)
N002	6029.7(10)	6825.6(3)	4876.8(11)	40.0(3)
N003	9554.5(12)	5434.7(4)	7840.5(11)	47.6(3)
C004	4564.2(14)	7076.4(4)	5945.0(14)	46.1(3)
C005	5457.5(11)	7140.0(4)	5304.3(12)	36.4(3)
C006	5552.6(12)	6190.3(4)	5335.5(13)	39.7(3)
C007	6888.2(12)	6559.0(4)	6453.6(13)	40.1(3)
C008	6504.2(12)	6798.7(4)	3825.9(13)	41.2(3)
C009	9637.9(13)	5639.4(4)	8843.7(12)	40.9(3)
C00A	8690.2(14)	5211.6(4)	7502.8(13)	44.9(3)
C00B	5799.6(13)	7507.3(4)	5135.5(14)	43.8(3)
C00C	6299.4(15)	7060.2(5)	2987.2(14)	49.8(4)
C00D	5863.9(14)	5834.6(4)	5712.9(14)	46.1(3)
C00E	10335.4(13)	5943.4(4)	8916.0(14)	45.6(3)
C00F	10417.5(14)	6146.2(5)	9892.5(15)	50.6(4)
C00G	7725.3(13)	6813.0(5)	6312.4(15)	47.8(4)
C00H	8845.2(16)	4913.7(5)	6759.1(15)	52.2(4)
C00I	3995.3(15)	7373.9(5)	6380.6(15)	53.1(4)
C00J	7172.1(13)	6495.1(5)	3592.0(17)	51.5(4)
C00K	9053.2(14)	5541.0(4)	9787.3(13)	46.4(4)
C00L	5265.0(16)	5520.7(4)	5447.6(16)	53.6(4)
C00M	9143.5(16)	5749.2(5)	10756.8(14)	52.0(4)
C00N	4311.7(15)	7739.3(5)	6185.4(16)	54.5(4)
C00O	4677.4(13)	6215.5(4)	4642.1(15)	49.3(4)
C00P	8468.5(15)	6859.6(5)	7142.6(18)	58.6(5)
C00Q	6803.3(14)	6365.1(4)	7458.1(14)	47.9(4)
C00R	5213.9(15)	7804.0(4)	5570.1(16)	53.2(4)
C00S	9818.9(16)	6054.7(5)	10813.9(14)	53.8(4)
C00T	8404.7(17)	6657.2(6)	8118.6(18)	63.4(5)
C00U	4099.8(16)	5896.3(5)	4375.0(18)	56.4(4)
C00V	8009.3(19)	4690.9(6)	6435.8(17)	62.4(5)
C00W	7664.1(15)	5288.0(5)	7862.0(15)	51.6(4)
C00X	7567.9(18)	6412.5(5)	8275.8(15)	58.8(5)
C00Y	4378.1(16)	5548.6(5)	4793.1(17)	56.0(4)
C00Z	6769.8(18)	7021.6(6)	1949.7(16)	64.7(5)
C010	6841.6(16)	5057.4(6)	7544.5(18)	62.5(5)
C011	7621.9(15)	6459.9(6)	2552(2)	66.5(6)

C012	7007.9(18)	4753.6(6)	6841.7(19)	66.3(5)
C013	7429.8(18)	6720.3(7)	1728.1(18)	73.2(7)

Table S10 Anisotropic Displacement Parameters ($Å^2×10^3$) for 4a. 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}
N001	45.8(7)	31.0(5)	48.9(7)	1.7(5)	-7.8(6)	0.7(5)
N002	44.9(6)	32.1(5)	42.9(6)	1.0(5)	1.9(5)	4.2(5)
N003	56.3(8)	44.5(6)	41.9(6)	-2.8(5)	19.0(6)	-3.6(6)
C004	47.9(8)	41.0(7)	49.4(8)	3.4(6)	6.6(7)	-2.5(7)
C005	38.2(7)	34.6(6)	36.5(6)	0.2(5)	-1.9(6)	1.9(5)
C006	41.0(7)	32.5(6)	45.6(7)	-2.0(5)	-0.8(6)	2.2(5)
C007	40.7(7)	34.9(7)	44.8(7)	-9.2(6)	-2.8(6)	8.4(6)
C008	35.7(7)	42.9(7)	45.1(7)	-9.6(6)	-0.5(6)	-6.6(6)
C009	50.4(8)	35.3(7)	36.9(7)	4.6(5)	8.9(6)	7.8(6)
C00A	57.1(9)	38.5(7)	39.0(7)	6.9(6)	7.7(7)	3.0(6)
C00B	45.9(8)	36.4(7)	49.2(8)	1.0(6)	5.7(7)	-2.2(6)
C00C	52.0(9)	54.3(9)	43.2(8)	-4.8(7)	0.0(7)	-7.6(7)
C00D	52.5(9)	35.3(7)	50.4(8)	-1.4(6)	-7.0(7)	6.0(6)
C00E	50.4(8)	45.1(8)	41.2(7)	4.8(6)	8.3(7)	1.0(6)
C00F	53.1(9)	50.1(8)	48.5(8)	-0.4(7)	-1.1(7)	1.7(7)
C00G	43.9(8)	43.9(8)	55.7(9)	-10.0(7)	-2.2(7)	3.4(6)
C00H	63.1(10)	49.2(9)	44.4(8)	-1.8(7)	2.3(8)	7.1(8)
C00I	48.4(9)	60.1(10)	50.9(9)	0.7(8)	11.5(7)	6.2(7)
C00J	40.4(8)	49.7(9)	64.4(10)	-17.8(8)	1.9(7)	-3.0(7)
C00K	59.6(9)	36.9(7)	42.7(7)	6.7(6)	14.4(7)	5.5(6)
C00L	69.3(11)	31.6(7)	59.9(10)	0.4(7)	-6.9(9)	2.1(7)
C00M	64.6(10)	54.2(9)	37.1(7)	7.3(7)	12.8(7)	14.4(8)
C00N	59.7(10)	51.1(9)	52.7(9)	-4.5(7)	2.5(8)	19.1(8)
C00O	49.6(9)	36.5(7)	61.9(10)	2.2(7)	-11.7(8)	3.0(6)
C00P	47.1(9)	55.9(9)	72.9(12)	-21.0(9)	-10.9(8)	3.5(8)
C00Q	54.5(9)	42.9(7)	46.3(8)	-7.1(7)	-1.1(7)	10.0(7)
C00R	65.7(11)	34.6(7)	59.4(10)	1.0(7)	2.8(8)	5.0(7)
C00S	62.7(11)	59.3(10)	39.4(8)	-6.3(7)	-0.3(7)	10.4(8)
C00T	62.7(11)	63.7(11)	63.9(11)	-23.8(9)	-23.7(9)	17.9(9)
C00U	53.5(9)	46.3(8)	69.5(11)	-3.0(8)	-17.3(9)	-2.4(7)
C00V	78.5(13)	54.5(10)	54.2(10)	-7.0(8)	-13.0(10)	4.4(9)
C00W	58.0(10)	47.4(8)	49.5(9)	5.5(7)	7.7(8)	6.1(7)
C00X	77.5(12)	55.9(10)	43.1(8)	-11.0(7)	-10.0(9)	23.1(9)
C00Y	62.2(10)	38.1(8)	67.6(11)	-4.3(7)	-7.0(9)	-8.3(7)
C00Z	70.2(12)	80.1(13)	43.7(9)	-7.3(9)	3.6(8)	-23.9(11)
C010	54.2(10)	73.2(12)	60.0(10)	13.3(10)	-0.4(9)	4.4(9)
C011	49.1(9)	71.5(11)	78.9(13)	-38.1(11)	14.9(9)	-11.5(9)
C012	68.2(12)	66.2(11)	64.6(11)	6.9(10)	-15.6(10)	-7.7(10)

C013	63.6(12)	99.7(16)	56.4(11)	-37.2(12)	18.4(10)	-30.1(12)

Table S11 Bond Lengths for 4a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N001	N002	1.3960(17)	C00C	C00Z	1.388(3)
N001	C006	1.4143(18)	C00D	C00L	1.384(2)
N001	C007	1.412(2)	C00E	C00F	1.380(2)
N002	C005	1.4257(18)	C00F	C00S	1.380(3)
N002	C008	1.402(2)	C00G	C00P	1.381(3)
N003	N003[1]	1.394(3)	C00H	C00V	1.377(3)
N003	C009	1.411(2)	C00I	C00N	1.377(3)
N003	C00A	1.410(2)	C00J	C011	1.379(3)
C004	C005	1.387(2)	C00K	C00M	1.384(2)
C004	C00I	1.381(2)	C00L	C00Y	1.374(3)
C005	C00B	1.388(2)	C00M	C00S	1.382(3)
C006	C00D	1.397(2)	C00N	C00R	1.380(3)
C006	C00O	1.389(2)	C00O	C00U	1.386(2)
C007	C00G	1.401(2)	C00P	C00T	1.377(3)
C007	C00Q	1.393(2)	C00Q	C00X	1.389(3)
C008	C00C	1.394(2)	C00T	C00X	1.383(3)
C008	C00J	1.398(2)	C00U	C00Y	1.377(2)
C009	C00E	1.396(2)	C00V	C012	1.377(3)
C009	C00K	1.398(2)	C00W	C010	1.378(3)
C00A	C00H	1.398(2)	C00Z	C013	1.382(3)
C00A	C00W	1.396(3)	C010	C012	1.385(3)
C00B	C00R	1.389(2)	C011	C013	1.376(4)

[1] 2-X,+Y,3/2-Z

Table S12 Bond Angles for 4a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N002	N001	C006	117.09(12)	C00Z	C00C	C008	120.23(19)
N002	N001	C007	115.92(12)	C00L	C00D	C006	119.80(16)
C007	N001	C006	126.62(12)	C00F	C00E	C009	120.20(15)
N001	N002	C005	115.49(12)	C00E	C00F	C00S	121.19(17)
N001	N002	C008	117.94(12)	C00P	C00G	C007	120.31(18)
C008	N002	C005	126.56(12)	C00V	C00H	C00A	120.43(18)
N003[1]	N003	C009	116.16(16)	C00N	C00I	C004	120.21(16)
N003[1]	N003	C00A	117.34(14)	C011	C00J	C008	120.1(2)
C00A	N003	C009	126.35(13)	C00M	C00K	C009	120.37(16)
C00I	C004	C005	120.77(15)	C00Y	C00L	C00D	121.43(15)
C004	C005	N002	119.15(13)	C00S	C00M	C00K	120.75(16)
C004	C005	C00B	119.24(14)	C00I	C00N	C00R	119.26(16)

C00B	C005	N002	121.54(13)	C00U	C00O	C006	120.48(15)
C00D	C006	N001	121.80(14)	C00T	C00P	C00G	120.83(19)
C00O	C006	N001	119.60(13)	C00X	C00Q	C007	119.94(17)
C00O	C006	C00D	118.54(14)	C00N	C00R	C00B	121.15(16)
C00G	C007	N001	119.33(15)	C00F	C00S	C00M	118.96(16)
C00Q	C007	N001	121.87(14)	C00P	C00T	C00X	119.24(17)
C00Q	C007	C00G	118.73(15)	C00Y	C00U	C00O	120.81(17)
C00C	C008	N002	121.74(14)	C012	C00V	C00H	121.01(19)
C00C	C008	C00J	118.68(16)	C010	C00W	C00A	120.18(17)
C00J	C008	N002	119.54(15)	C00T	C00X	C00Q	120.87(19)
C00E	C009	N003	119.85(13)	C00L	C00Y	C00U	118.82(16)
C00E	C009	C00K	118.49(15)	C013	C00Z	C00C	120.6(2)
C00K	C009	N003	121.64(14)	C00W	C010	C012	121.0(2)
C00H	C00A	N003	119.96(16)	C013	C011	C00J	121.23(19)
C00W	C00A	N003	121.64(15)	C00V	C012	C010	118.8(2)
C00W	C00A	C00H	118.36(17)	C011	C013	C00Z	119.16(18)
C005	C00B	C00R	119.31(15)				

[1] 2-X,+Y,3/2-Z

Table S13 Torsion Angles for 4a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N001	N002	C005	C004	-39.60(19)	C007	N001	C006	C00O	165.96(16)
N001	N002	C005	C00B	137.50(15)	C007	C00G	C00P	C00T	0.3(3)
N001	N002	C008	C00C	169.07(14)	C007	C00Q	C00X	C00T	1.5(2)
N001	N002	C008	C00J	-8.6(2)	C008	N002	C005	C004	141.44(15)
N001	C006	C00D	C00L	179.02(16)	C008	N002	C005	C00B	-41.5(2)
N001	C006	C00O	C00U	-179.87(17)	C008	C00C	C00Z	C013	1.2(3)
N001	C007	C00G	C00P	179.19(15)	C008	C00J	C011	C013	0.2(3)
N001	C007	C00Q	C00X	-179.99(14)	C009	N003	C00A	C00H	-154.26(15)
N002	N001	C006	C00D	155.70(15)	C009	N003	C00A	C00W	28.0(2)
N002	N001	C006	C00O	-21.4(2)	C009	C00E	C00F	C00S	0.0(3)
N002	N001	C007	C00G	-23.26(19)	C009	C00K	C00M	C00S	-0.7(3)
N002	N001	C007	C00Q	153.75(13)	C00A	N003	C009	C00E	-157.84(15)
N002	C005	C00B	C00R	-179.95(15)	C00A	N003	C009	C00K	23.6(2)
N002	C008	C00C	C00Z	-178.94(16)	C00A	C00H	C00V	C012	-0.6(3)
N002	C008	C00J	C011	178.30(15)	C00A	C00W	C010	C012	-1.9(3)
N003[1]	N003	C009	C00E	26.8(2)	C00C	C008	C00J	C011	0.6(2)
N003[1]	N003	C009	C00K	-151.78(14)	C00C	C00Z	C013	C011	-0.5(3)
N003[1]	N003	C00A	C00H	21.1(2)	C00D	C006	C00O	C00U	2.9(3)

N003[1]	N003	C00A	C00W	-156.64(15)	C00D	C00L	C00Y	C00U	1.5(3)
N003	C009	C00E	C00F	179.66(15)	C00E	C009	C00K	C00M	2.0(2)
N003	C009	C00K	C00M	-179.37(15)	C00E	C00F	C00S	C00M	1.3(3)
N003	C00A	C00H	C00V	179.10(16)	C00G	C007	C00Q	C00X	-3.0(2)
N003	C00A	C00W	C010	-177.96(16)	C00G	C00P	C00T	C00X	-1.8(3)
C004	C005	C00B	C00R	-2.8(2)	C00H	C00A	C00W	C010	4.3(3)
C004	C00I	C00N	C00R	-1.3(3)	C00H	C00V	C012	C010	3.0(3)
C005	N002	C008	C00C	-12.0(2)	C00I	C004	C005	N002	179.46(16)
C005	N002	C008	C00J	170.34(14)	C00I	C004	C005	C00B	2.3(2)
C005	C004	C00I	C00N	-0.2(3)	C00I	C00N	C00R	C00B	0.7(3)
C005	C00B	C00R	C00N	1.4(3)	C00J	C008	C00C	C00Z	-1.3(2)
C006	N001	N002	C005	109.50(15)	C00J	C011	C013	C00Z	-0.2(3)
C006	N001	N002	C008	-71.45(17)	C00K	C009	C00E	C00F	-1.7(2)
C006	N001	C007	C00G	149.47(15)	C00K	C00M	C00S	C00F	-1.0(3)
C006	N001	C007	C00Q	-33.5(2)	C00O	C006	C00D	C00L	-3.9(3)
C006	C00D	C00L	C00Y	1.7(3)	C00O	C00U	C00Y	C00L	-2.5(3)
C006	C00O	C00U	C00Y	0.2(3)	C00P	C00T	C00X	C00Q	0.9(3)
C007	N001	N002	C005	-77.05(16)	C00Q	C007	C00G	C00P	2.1(2)
C007	N001	N002	C008	102.00(15)	C00W	C00A	C00H	C00V	-3.1(3)
C007	N001	C006	C00D	-17.0(2)	C00W	C010	C012	C00V	-1.8(3)

[1] 2-X,+Y,3/2-Z

Table S14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4a.

Atom	*x*	*y*	*z*	U(eq)
H004	4343.49	6827.85	6084.5	55
H00B	6421.15	7554.84	4731.2	53
H00C	5841.2	7263.49	3124.71	60
H00D	6478.13	5808.57	6145.67	55
H00E	10750.23	6010.06	8297.72	55
H00F	10889.56	6350.32	9930.81	61
H00G	7781.34	6952.32	5649.52	57
H00H	9524.52	4865.1	6477.87	63
H00I	3390.01	7326.77	6811.81	64
H00J	7314.88	6314.53	4144.58	62
H00K	8596.2	5332.32	9763.05	56
H00L	5469.36	5283.39	5721.02	64
H00M	8740.9	5682.1	11383.61	62
H00N	3917.58	7942.45	6468.14	65
H00O	4475.56	6450.82	4351.93	59
H00P	9024.81	7031.63	7040.27	70

H00Q	6229.34	6202.37	7582.39	57
H00R	5436.13	8053.17	5442.77	64
H00S	9869.9	6197.93	11470	65
H00T	8924.15	6685.1	8671.52	76
H00U	3510.77	5917.22	3902.75	68
H00V	8124.12	4492.84	5930.15	75
H00W	7533.58	5497.28	8321.75	62
H00X	7515.54	6276.3	8944.74	71
H00Y	3968.73	5334.2	4633.65	67
H00Z	6638.36	7201.81	1393.1	78
H010	6156.88	5107.07	7809.08	75
H011	8068.06	6254.21	2403.2	80
H012	6446.98	4593.21	6645.49	80
H013	7743.38	6693.78	1023.31	88

Table S15 Crystal data and structure refinement for 4g.

Identification code	BB_657
Empirical formula	$C_{24}H_{12}Br_4N_2$
Formula weight	646.00
Temperature/K	120.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.5392(7)
b/Å	14.9833(9)
c/Å	27.7960(16)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4389.3(5)
Z	8
ρ_{calc}g/cm^3	1.955
μ/mm^{-1}	7.348
F(000)	2472.0
Crystal size/mm^3	0.4 × 0.1 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.832 to 59.466
Index ranges	$-9 \leq h \leq 14$, $-20 \leq k \leq 15$, $-34 \leq l \leq 38$
Reflections collected	22392
Independent reflections	5515 [R_{int} = 0.0547, R_{sigma} = 0.0573]
Data/restraints/parameters	5515/0/271
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0516, wR_2 = 0.1052
Final R indexes [all data]	R_1 = 0.0882, wR_2 = 0.1216
Largest diff. peak/hole / e Å^{-3}	1.80/-1.42

Table S16 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for 4g. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
$\mathrm{Br}^{(01)}$	3697.0(6)	3755.0(4)	1270.0(2)	29.96(15)
$\mathrm{Br}^{(02)}$	-1690.8(5)	7111.4(4)	2786.9(2)	33.02(16)
$\mathrm{Br}^{(03)}$	3870.2(6)	1242.2(4)	5002.3(2)	36.15(17)
$\mathrm{Br}^{(04)}$	7873.8(6)	6201.9(4)	4554.7(2)	43.51(18)
$\mathrm{N}^{(005)}$	2511(4)	4608(3)	3333.7(14)	25.3(10)
$\mathrm{C}^{(006)}$	3176(4)	4481(3)	3755.0(14)	12.2(9)
$\mathrm{C}^{(007)}$	3397(5)	4022(3)	1929.8(17)	20.1(10)
$\mathrm{C}^{(008)}$	350(5)	5904(3)	2631.4(18)	20.5(10)
$\mathrm{C}^{(009)}$	2426(5)	4602(3)	2044.1(16)	20.5(10)
$\mathrm{C}^{(00A)}$	4453(5)	2952(3)	4626.4(16)	23.9(11)
$\mathrm{C}^{(00B)}$	-330(5)	6353(3)	2977.3(19)	24.9(11)
$\mathrm{C}^{(00C)}$	4161(5)	3615(3)	2278.0(18)	23.7(11)
$\mathrm{C}^{(00D)}$	3934(5)	3772(3)	2762.8(18)	24.5(11)
$\mathrm{C}^{(00E)}$	1310(5)	5338(3)	2785.3(16)	19.6(10)
$\mathrm{C}^{(00F)}$	2202(5)	4776(3)	2531.6(17)	19.1(10)
$\mathrm{C}^{(00G)}$	5981(5)	4898(4)	4452.3(19)	27.4(12)
$\mathrm{C}^{(00H)}$	2962(5)	4347(3)	2880.0(16)	20.7(10)
$\mathrm{C}^{(00I)}$	3611(5)	2255(4)	4600.4(17)	26.2(12)
$\mathrm{C}^{(00J)}$	4232(5)	3686(4)	4320.7(16)	23.6(11)
$\mathrm{C}^{(00K)}$	1540(5)	5231(3)	3278.6(17)	22.4(11)
$\mathrm{C}^{(00L)}$	4242(5)	4985(4)	3882.3(17)	25.1(11)
$\mathrm{C}^{(00M)}$	-96(5)	6258(3)	3466(2)	28.4(12)
$\mathrm{C}^{(00N)}$	853(5)	5686(3)	3627.3(18)	26.0(12)
$\mathrm{C}^{(00O)}$	4900(5)	4516(4)	4246.7(17)	23.9(11)
$\mathrm{C}^{(00P)}$	6378(5)	5707(4)	4281.8(19)	31.0(13)
$\mathrm{C}^{(00Q)}$	2555(6)	2261(4)	4299.8(18)	29.5(12)
$\mathrm{C}^{(00R)}$	3188(5)	3679(3)	4012.4(17)	23.8(11)
$\mathrm{C}^{(00S)}$	5746(6)	6166(4)	3918(2)	34.0(13)
$\mathrm{C}^{(00T)}$	4641(6)	5809(4)	3715.1(18)	29.2(12)
$\mathrm{C}^{(00U)}$	2330(5)	2981(4)	3994.4(18)	28.9(12)

Table S17 Anisotropic Displacement Parameters ($Å^2\times10^3$) for 4g. 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}
$\mathrm{Br}^{(01)}$	38.5(3)	28.9(3)	22.5(3)	-5.1(2)	4.3(2)	2.6(2)
$\mathrm{Br}^{(02)}$	21.9(3)	23.2(3)	53.9(4)	2.0(2)	3.0(3)	4.0(2)
$\mathrm{Br}^{(03)}$	42.2(4)	38.4(3)	27.8(3)	11.8(2)	5.0(2)	0.7(3)
$\mathrm{Br}^{(04)}$	31.3(3)	53.6(4)	45.6(3)	-17.9(3)	11.1(3)	-17.1(3)
$\mathrm{N}^{(005)}$	29(2)	31(2)	15.6(19)	-2.0(18)	-2.0(18)	8.4(19)
$\mathrm{C}^{(006)}$	14(2)	15(2)	7.6(19)	2.5(16)	-3.1(17)	0.9(17)

C$^{(007)}$	21(3)	19(2)	20(2)	-2.8(19)	0(2)	-4(2)
C$^{(008)}$	17(3)	20(2)	25(3)	-0.3(19)	-2(2)	1(2)
C$^{(009)}$	25(3)	18(2)	19(2)	0.7(19)	-2(2)	-3(2)
C$^{(00A)}$	21(3)	35(3)	16(2)	-1(2)	-1(2)	7(2)
C$^{(00B)}$	19(3)	18(2)	38(3)	-1(2)	0(2)	-4(2)
C$^{(00C)}$	22(3)	19(3)	30(3)	-3(2)	2(2)	-1(2)
C$^{(00D)}$	24(3)	24(3)	26(3)	0(2)	-3(2)	3(2)
C$^{(00E)}$	18(3)	21(2)	20(2)	0.8(19)	-2.9(19)	-2.9(19)
C$^{(00F)}$	17(3)	18(2)	22(2)	-1.3(19)	-4(2)	0.4(19)
C$^{(00G)}$	22(3)	36(3)	25(3)	-5(2)	3(2)	0(2)
C$^{(00H)}$	24(3)	20(2)	19(2)	0.7(19)	0(2)	-1(2)
C$^{(00I)}$	36(3)	29(3)	14(2)	3(2)	4(2)	1(2)
C$^{(00J)}$	25(3)	34(3)	12(2)	-2(2)	1.6(19)	1(2)
C$^{(00K)}$	20(3)	22(3)	25(2)	-2(2)	-1(2)	0(2)
C$^{(00L)}$	24(3)	34(3)	17(2)	0(2)	4(2)	2(2)
C$^{(00M)}$	23(3)	26(3)	36(3)	-9(2)	11(2)	5(2)
C$^{(00N)}$	32(3)	27(3)	19(2)	-2(2)	-1(2)	-1(2)
C$^{(00O)}$	21(3)	32(3)	18(2)	-2(2)	5(2)	0(2)
C$^{(00P)}$	25(3)	41(3)	27(3)	-14(2)	8(2)	-5(2)
C$^{(00Q)}$	29(3)	32(3)	27(3)	-4(2)	4(2)	-6(2)
C$^{(00R)}$	27(3)	27(3)	18(2)	0(2)	-3(2)	5(2)
C$^{(00S)}$	42(4)	28(3)	32(3)	-8(2)	15(3)	-2(3)
C$^{(00T)}$	34(3)	30(3)	24(3)	-1(2)	7(2)	6(2)
C$^{(00U)}$	30(3)	35(3)	21(2)	-2(2)	-6(2)	-3(2)

Table S18 Bond Lengths for 4g.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br$^{(01)}$	C$^{(007)}$	1.903(5)	C$^{(00D)}$	C$^{(00H)}$	1.379(7)
Br$^{(02)}$	C$^{(00B)}$	1.905(5)	C$^{(00E)}$	C$^{(00F)}$	1.446(7)
Br$^{(03)}$	C$^{(00I)}$	1.905(5)	C$^{(00E)}$	C$^{(00K)}$	1.402(7)
Br$^{(04)}$	C$^{(00P)}$	1.900(6)	C$^{(00F)}$	C$^{(00H)}$	1.411(7)
N$^{(005)}$	C$^{(006)}$	1.378(6)	C$^{(00G)}$	C$^{(00O)}$	1.398(7)
N$^{(005)}$	C$^{(00H)}$	1.403(6)	C$^{(00G)}$	C$^{(00P)}$	1.367(8)
N$^{(005)}$	C$^{(00K)}$	1.393(6)	C$^{(00I)}$	C$^{(00Q)}$	1.392(8)
C$^{(006)}$	C$^{(00L)}$	1.399(7)	C$^{(00J)}$	C$^{(00O)}$	1.443(7)
C$^{(006)}$	C$^{(00R)}$	1.398(6)	C$^{(00J)}$	C$^{(00R)}$	1.395(7)
C$^{(007)}$	C$^{(009)}$	1.381(7)	C$^{(00K)}$	C$^{(00N)}$	1.389(7)
C$^{(007)}$	C$^{(00C)}$	1.398(7)	C$^{(00L)}$	C$^{(00O)}$	1.415(7)
C$^{(008)}$	C$^{(00B)}$	1.375(7)	C$^{(00L)}$	C$^{(00T)}$	1.384(7)
C$^{(008)}$	C$^{(00E)}$	1.388(7)	C$^{(00M)}$	C$^{(00N)}$	1.392(7)
C$^{(009)}$	C$^{(00F)}$	1.400(7)	C$^{(00P)}$	C$^{(00S)}$	1.392(8)
C$^{(00A)}$	C$^{(00I)}$	1.372(7)	C$^{(00Q)}$	C$^{(00U)}$	1.393(7)
C$^{(00A)}$	C$^{(00J)}$	1.409(7)	C$^{(00R)}$	C$^{(00U)}$	1.383(8)
C$^{(00B)}$	C$^{(00M)}$	1.387(8)	C$^{(00S)}$	C$^{(00T)}$	1.401(8)

C$^{(00C)}$	C$^{(00D)}$	1.388(7)

Table S19 Bond Angles for 4g.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C$^{(006)}$	N$^{(005)}$	C$^{(00H)}$	123.5(4)	C$^{(00A)}$	C$^{(00I)}$	Br$^{(03)}$	118.9(4)
C$^{(006)}$	N$^{(005)}$	C$^{(00K)}$	124.0(4)	C$^{(00A)}$	C$^{(00I)}$	C$^{(00Q)}$	123.0(5)
C$^{(00K)}$	N$^{(005)}$	C$^{(00H)}$	109.7(4)	C$^{(00Q)}$	C$^{(00I)}$	Br$^{(03)}$	118.1(4)
N$^{(005)}$	C$^{(006)}$	C$^{(00L)}$	123.3(4)	C$^{(00A)}$	C$^{(00J)}$	C$^{(00O)}$	132.7(5)
N$^{(005)}$	C$^{(006)}$	C$^{(00R)}$	123.9(4)	C$^{(00R)}$	C$^{(00J)}$	C$^{(00A)}$	119.6(5)
C$^{(00R)}$	C$^{(006)}$	C$^{(00L)}$	109.1(4)	C$^{(00R)}$	C$^{(00J)}$	C$^{(00O)}$	107.7(4)
C$^{(009)}$	C$^{(007)}$	Br$^{(01)}$	118.5(4)	N$^{(005)}$	C$^{(00K)}$	C$^{(00E)}$	108.2(4)
C$^{(009)}$	C$^{(007)}$	C$^{(00C)}$	122.8(4)	C$^{(00N)}$	C$^{(00K)}$	N$^{(005)}$	129.5(5)
C$^{(00C)}$	C$^{(007)}$	Br$^{(01)}$	118.7(4)	C$^{(00N)}$	C$^{(00K)}$	C$^{(00E)}$	122.4(5)
C$^{(00B)}$	C$^{(008)}$	C$^{(00E)}$	117.6(5)	C$^{(006)}$	C$^{(00L)}$	C$^{(00O)}$	107.8(4)
C$^{(007)}$	C$^{(009)}$	C$^{(00F)}$	117.7(4)	C$^{(00T)}$	C$^{(00L)}$	C$^{(006)}$	129.9(5)
C$^{(00I)}$	C$^{(00A)}$	C$^{(00J)}$	117.1(5)	C$^{(00T)}$	C$^{(00L)}$	C$^{(00O)}$	122.3(5)
C$^{(008)}$	C$^{(00B)}$	Br$^{(02)}$	119.3(4)	C$^{(00B)}$	C$^{(00M)}$	C$^{(00N)}$	120.4(5)
C$^{(008)}$	C$^{(00B)}$	C$^{(00M)}$	122.8(5)	C$^{(00K)}$	C$^{(00N)}$	C$^{(00M)}$	116.9(5)
C$^{(00M)}$	C$^{(00B)}$	Br$^{(02)}$	117.8(4)	C$^{(00G)}$	C$^{(00O)}$	C$^{(00J)}$	133.8(5)
C$^{(00D)}$	C$^{(00C)}$	C$^{(007)}$	120.0(5)	C$^{(00G)}$	C$^{(00O)}$	C$^{(00L)}$	119.3(5)
C$^{(00H)}$	C$^{(00D)}$	C$^{(00C)}$	117.6(5)	C$^{(00L)}$	C$^{(00O)}$	C$^{(00J)}$	106.9(5)
C$^{(008)}$	C$^{(00E)}$	C$^{(00F)}$	132.8(4)	C$^{(00G)}$	C$^{(00P)}$	Br$^{(04)}$	117.5(4)
C$^{(008)}$	C$^{(00E)}$	C$^{(00K)}$	119.9(5)	C$^{(00G)}$	C$^{(00P)}$	C$^{(00S)}$	122.9(5)
C$^{(00K)}$	C$^{(00E)}$	C$^{(00F)}$	107.3(4)	C$^{(00S)}$	C$^{(00P)}$	Br$^{(04)}$	119.6(4)
C$^{(009)}$	C$^{(00F)}$	C$^{(00E)}$	133.6(4)	C$^{(00I)}$	C$^{(00Q)}$	C$^{(00U)}$	120.4(5)
C$^{(009)}$	C$^{(00F)}$	C$^{(00H)}$	119.0(4)	C$^{(00J)}$	C$^{(00R)}$	C$^{(006)}$	108.3(5)
C$^{(00H)}$	C$^{(00F)}$	C$^{(00E)}$	107.4(4)	C$^{(00U)}$	C$^{(00R)}$	C$^{(006)}$	128.7(5)
C$^{(00P)}$	C$^{(00G)}$	C$^{(00O)}$	118.1(5)	C$^{(00U)}$	C$^{(00R)}$	C$^{(00J)}$	122.9(5)
N$^{(005)}$	C$^{(00H)}$	C$^{(00F)}$	107.3(4)	C$^{(00P)}$	C$^{(00S)}$	C$^{(00T)}$	120.1(5)
C$^{(00D)}$	C$^{(00H)}$	N$^{(005)}$	129.7(4)	C$^{(00L)}$	C$^{(00T)}$	C$^{(00S)}$	117.3(5)
C$^{(00D)}$	C$^{(00H)}$	C$^{(00F)}$	123.0(4)	C$^{(00R)}$	C$^{(00U)}$	C$^{(00Q)}$	116.9(5)

Table S20 Torsion Angles for 4g.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br$^{(01)}$	C$^{(007)}$	C$^{(009)}$	C$^{(00F)}$	178.7(4)	C$^{(00E)}$	C$^{(008)}$	C$^{(00B)}$	Br$^{(02)}$	-178.1(4)
Br$^{(01)}$	C$^{(007)}$	C$^{(00C)}$	C$^{(00D)}$	-177.7(4)	C$^{(00E)}$	C$^{(008)}$	C$^{(00B)}$	C$^{(00M)}$	-0.2(8)
Br$^{(02)}$	C$^{(00B)}$	C$^{(00M)}$	C$^{(00N)}$	177.4(4)	C$^{(00E)}$	C$^{(00F)}$	C$^{(00H)}$	N$^{(005)}$	2.6(5)
Br$^{(03)}$	C$^{(00I)}$	C$^{(00Q)}$	C$^{(00U)}$	-179.2(4)	C$^{(00E)}$	C$^{(00F)}$	C$^{(00H)}$	C$^{(00D)}$	-178.7(5)
Br$^{(04)}$	C$^{(00P)}$	C$^{(00S)}$	C$^{(00T)}$	-179.8(4)	C$^{(00E)}$	C$^{(00K)}$	C$^{(00N)}$	C$^{(00M)}$	0.4(8)
N$^{(005)}$	C$^{(006)}$	C$^{(00L)}$	C$^{(00O)}$	-162.4(4)	C$^{(00F)}$	C$^{(00E)}$	C$^{(00K)}$	N$^{(005)}$	-1.6(6)
N$^{(005)}$	C$^{(006)}$	C$^{(00L)}$	C$^{(00T)}$	19.4(8)	C$^{(00F)}$	C$^{(00E)}$	C$^{(00K)}$	C$^{(00N)}$	179.4(5)
N$^{(005)}$	C$^{(006)}$	C$^{(00R)}$	C$^{(00J)}$	161.5(4)	C$^{(00G)}$	C$^{(00P)}$	C$^{(00S)}$	C$^{(00T)}$	1.0(8)

N$^{(005)}$	C$^{(006)}$	C$^{(00R)}$	C$^{(00U)}$	-20.2(8)	C$^{(00H)}$	N$^{(005)}$	C$^{(006)}$	C$^{(00L)}$	73.6(7)
N$^{(005)}$	C$^{(00K)}$	C$^{(00N)}$	C$^{(00M)}$	-178.3(5)	C$^{(00H)}$	N$^{(005)}$	C$^{(006)}$	C$^{(00R)}$	-82.5(7)
C$^{(006)}$	N$^{(005)}$	C$^{(00H)}$	C$^{(00D)}$	15.9(9)	C$^{(00H)}$	N$^{(005)}$	C$^{(00K)}$	C$^{(00E)}$	3.3(6)
C$^{(006)}$	N$^{(005)}$	C$^{(00H)}$	C$^{(00F)}$	-165.5(4)	C$^{(00H)}$	N$^{(005)}$	C$^{(00K)}$	C$^{(00N)}$	-177.8(5)
C$^{(006)}$	N$^{(005)}$	C$^{(00K)}$	C$^{(00E)}$	165.0(5)	C$^{(00I)}$	C$^{(00A)}$	C$^{(00J)}$	C$^{(00O)}$	-179.5(5)
C$^{(006)}$	N$^{(005)}$	C$^{(00K)}$	C$^{(00N)}$	-16.1(9)	C$^{(00I)}$	C$^{(00A)}$	C$^{(00J)}$	C$^{(00R)}$	0.3(7)
C$^{(006)}$	C$^{(00L)}$	C$^{(00O)}$	C$^{(00G)}$	-177.4(4)	C$^{(00I)}$	C$^{(00Q)}$	C$^{(00U)}$	C$^{(00R)}$	-0.9(8)
C$^{(006)}$	C$^{(00L)}$	C$^{(00O)}$	C$^{(00J)}$	2.7(6)	C$^{(00J)}$	C$^{(00A)}$	C$^{(00I)}$	Br$^{(03)}$	179.6(4)
C$^{(006)}$	C$^{(00L)}$	C$^{(00T)}$	C$^{(00S)}$	178.7(5)	C$^{(00J)}$	C$^{(00A)}$	C$^{(00I)}$	C$^{(00Q)}$	-1.8(8)
C$^{(006)}$	C$^{(00R)}$	C$^{(00U)}$	C$^{(00Q)}$	-178.7(5)	C$^{(00J)}$	C$^{(00R)}$	C$^{(00U)}$	C$^{(00Q)}$	-0.6(8)
C$^{(007)}$	C$^{(009)}$	C$^{(00F)}$	C$^{(00E)}$	179.0(5)	C$^{(00K)}$	N$^{(005)}$	C$^{(006)}$	C$^{(00L)}$	-85.7(7)
C$^{(007)}$	C$^{(009)}$	C$^{(00F)}$	C$^{(00H)}$	-0.7(7)	C$^{(00K)}$	N$^{(005)}$	C$^{(006)}$	C$^{(00R)}$	118.3(6)
C$^{(007)}$	C$^{(00C)}$	C$^{(00D)}$	C$^{(00H)}$	-1.2(7)	C$^{(00K)}$	N$^{(005)}$	C$^{(00H)}$	C$^{(00D)}$	177.7(5)
C$^{(008)}$	C$^{(00B)}$	C$^{(00M)}$	C$^{(00N)}$	-0.5(8)	C$^{(00K)}$	N$^{(005)}$	C$^{(00H)}$	C$^{(00F)}$	-3.6(6)
C$^{(008)}$	C$^{(00E)}$	C$^{(00F)}$	C$^{(009)}$	0.4(10)	C$^{(00K)}$	C$^{(00E)}$	C$^{(00F)}$	C$^{(009)}$	179.8(5)
C$^{(008)}$	C$^{(00E)}$	C$^{(00F)}$	C$^{(00H)}$	-180.0(5)	C$^{(00K)}$	C$^{(00E)}$	C$^{(00F)}$	C$^{(00H)}$	-0.6(6)
C$^{(008)}$	C$^{(00E)}$	C$^{(00K)}$	N$^{(005)}$	177.8(5)	C$^{(00L)}$	C$^{(006)}$	C$^{(00R)}$	C$^{(00J)}$	2.6(6)
C$^{(008)}$	C$^{(00E)}$	C$^{(00K)}$	C$^{(00N)}$	-1.2(8)	C$^{(00L)}$	C$^{(006)}$	C$^{(00R)}$	C$^{(00U)}$	-179.2(5)
C$^{(009)}$	C$^{(007)}$	C$^{(00C)}$	C$^{(00D)}$	1.6(8)	C$^{(00O)}$	C$^{(00G)}$	C$^{(00P)}$	Br$^{(04)}$	-178.5(4)
C$^{(009)}$	C$^{(00F)}$	C$^{(00H)}$	N$^{(005)}$	-177.7(4)	C$^{(00O)}$	C$^{(00G)}$	C$^{(00P)}$	C$^{(00S)}$	0.7(8)
C$^{(009)}$	C$^{(00F)}$	C$^{(00H)}$	C$^{(00D)}$	1.0(8)	C$^{(00O)}$	C$^{(00J)}$	C$^{(00R)}$	C$^{(006)}$	-0.8(6)
C$^{(00A)}$	C$^{(00I)}$	C$^{(00Q)}$	C$^{(00U)}$	2.2(8)	C$^{(00O)}$	C$^{(00J)}$	C$^{(00R)}$	C$^{(00U)}$	-179.2(5)
C$^{(00A)}$	C$^{(00J)}$	C$^{(00O)}$	C$^{(00G)}$	-1.2(10)	C$^{(00O)}$	C$^{(00L)}$	C$^{(00T)}$	C$^{(00S)}$	0.7(8)
C$^{(00A)}$	C$^{(00J)}$	C$^{(00O)}$	C$^{(00L)}$	178.7(5)	C$^{(00P)}$	C$^{(00G)}$	C$^{(00O)}$	C$^{(00J)}$	178.2(5)
C$^{(00A)}$	C$^{(00J)}$	C$^{(00R)}$	C$^{(006)}$	179.3(4)	C$^{(00P)}$	C$^{(00G)}$	C$^{(00O)}$	C$^{(00L)}$	-1.7(7)
C$^{(00A)}$	C$^{(00J)}$	C$^{(00R)}$	C$^{(00U)}$	0.9(8)	C$^{(00P)}$	C$^{(00S)}$	C$^{(00T)}$	C$^{(00L)}$	-1.7(8)
C$^{(00B)}$	C$^{(008)}$	C$^{(00E)}$	C$^{(00F)}$	-179.7(5)	C$^{(00R)}$	C$^{(006)}$	C$^{(00L)}$	C$^{(00O)}$	-3.3(6)
C$^{(00B)}$	C$^{(008)}$	C$^{(00E)}$	C$^{(00K)}$	1.0(7)	C$^{(00R)}$	C$^{(006)}$	C$^{(00L)}$	C$^{(00T)}$	178.5(5)
C$^{(00B)}$	C$^{(00M)}$	C$^{(00N)}$	C$^{(00K)}$	0.4(8)	C$^{(00R)}$	C$^{(00J)}$	C$^{(00O)}$	C$^{(00G)}$	178.9(5)
C$^{(00C)}$	C$^{(007)}$	C$^{(009)}$	C$^{(00F)}$	-0.6(7)	C$^{(00R)}$	C$^{(00J)}$	C$^{(00O)}$	C$^{(00L)}$	-1.2(6)
C$^{(00C)}$	C$^{(00D)}$	C$^{(00H)}$	N$^{(005)}$	178.4(5)	C$^{(00T)}$	C$^{(00L)}$	C$^{(00O)}$	C$^{(00G)}$	1.0(8)
C$^{(00C)}$	C$^{(00D)}$	C$^{(00H)}$	C$^{(00F)}$	-0.1(8)	C$^{(00T)}$	C$^{(00L)}$	C$^{(00O)}$	C$^{(00J)}$	-178.9(5)

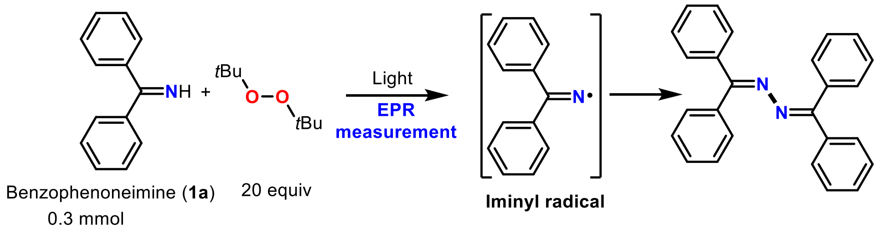
Table S21 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4g.

Atom	***x***	***y***	***z***	**U(eq)**
H$^{(008)}$	169.45	5979.54	2298.96	25
H$^{(009)}$	1926.49	4874.54	1800.28	25
H$^{(00A)}$	5153.81	2940.58	4841.25	29
H$^{(00C)}$	4833.5	3231.68	2182.95	28
H$^{(00D)}$	4431.78	3492.29	3004.91	29
H$^{(00G)}$	6427.9	4603.76	4703.4	33
H$^{(00M)}$	-586.72	6586.32	3691.39	34
H$^{(00N)}$	1021.83	5609.8	3960.44	31

$H^{(00Q)}$	1984.23	1769.93	4302.8	35
$H^{(00S)}$	6065.62	6722.58	3807.49	41
$H^{(00T)}$	4183.45	6119.43	3472.66	35
$H^{(00U)}$	1620.77	2992.15	3783.68	35

10. EPR Experiments

EPR studies on the *in-situ* generated iminyl radical (from 1a)



In an argon-filled glovebox, a 4 mL vial was charged with benzophenone imine **1a** (54 mg, 0.3 mmol) and di-*tert*-butylperoxide, (DTBP, 1.1 mL, 6 mmol, 20 equiv). From this stock solution, 100 μL was transferred to a 4mm Ø EPR tube inside the glovebox and the tube sealed with a cap and parafilm.

The EPR tube was placed in a ST4102 cavity with a grating to allow irradiation. The cavity was part of a Bruker EMX EPR instrument. EPR spectra were obtained continuously for approx.10.5 minutes with a spectral resolution of 1 spectrum per 23 second while irradiating with a DYMAX Blue Wave 75 UV lamp fitted with an optical fiber ending just in front of the grating. The *in-situ* experiment revealed a clear signal, which is indicative of the nitrogen centered radical (Figure S4 left; main text Figure 3). The signal is *only* observed during irradiation and disappears instantly when the light is turned off.

Control experiments of either a) benzophenone imine (**1a**) in benzene or b) neat DTBP under exactly the same conditions as the *in-situ* protocol, the same instrument settings, and the same experimental parameters did not show any signal (Figure S4 middle and right).

The spectral data was collected at 295 K with the following spectrometer settings:

Microwave power = 20.95 mW; frequency 9.75 GHz, center field = 348 mT, sweep width = 20 mT, sweep time = 20 s, modulation frequency = 100 KHz, modulation amplitude = 0.05 mT, time constant = 10 ms, conversion time = 10 ms. The g-values were corrected versus 2,2-diphenyl-1-picrylhydrazyl (dpph) and all spectra were baseline corrected by subtracting the average of 5 spectra obtained on a reference solution using the same experimental parameters.

The experiment was replicated twice on independently prepared 1:20 benzophenone imine:DTBP solutions and repeated using different ratios between substrate and oxidant (1:5, 1:10 1:30, and 1:40). The results were all similar, including the signal decay profile. The solution in the EPR tube was not stirred during the experiment and the tube was only irradiated on one side. The experiment was also repeated using a visible light source (Thor labs White light). The EPR signal was much weaker compared to UV light, but still clearly detectable and the same g-value and ^{14}N coupling constant were observed.

The simulated spectrum shown in red in Figure S4, left was obtained using Easyspin[10] with the garlic routine (isotropic, fast motion) with the following spin Hamiltonian parameters: g_{iso} = 2.0032, ^{14}N (triplet, I = 1) coupling constant A = 1.001 mT line width = 0.014 mT, line shape gaussian.

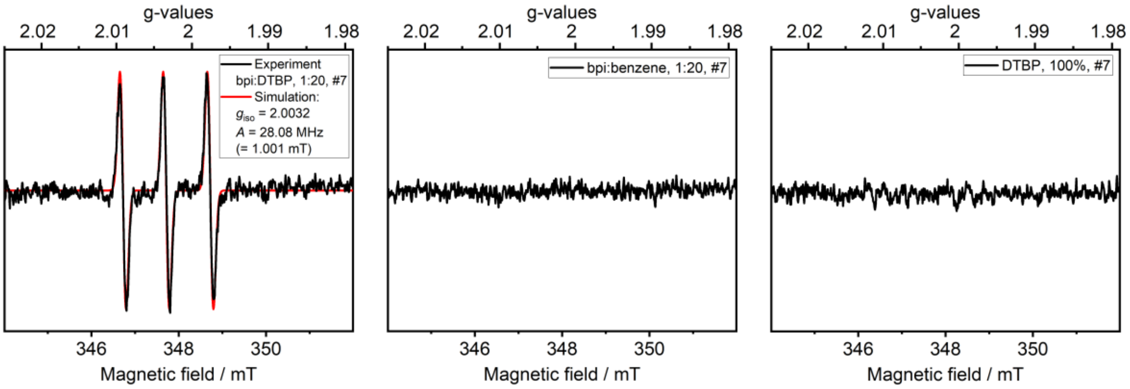


Figure S4: *In-situ* EPR experiments to detect formation of aminyl radical during UV irradiation. Left: benzophenone imine:DTBP = 1:20. Middle: benzophenone imine in benzene, no DTBP. Right: Neat DTBP, no benzophenone imine. In all three cases EPR spectrum number 7 are shown corresponding to light irradiation for approximately 30 seconds.

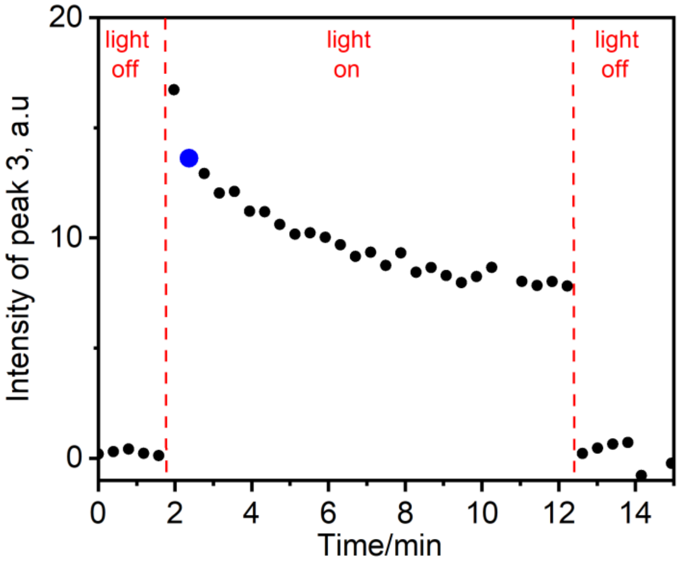
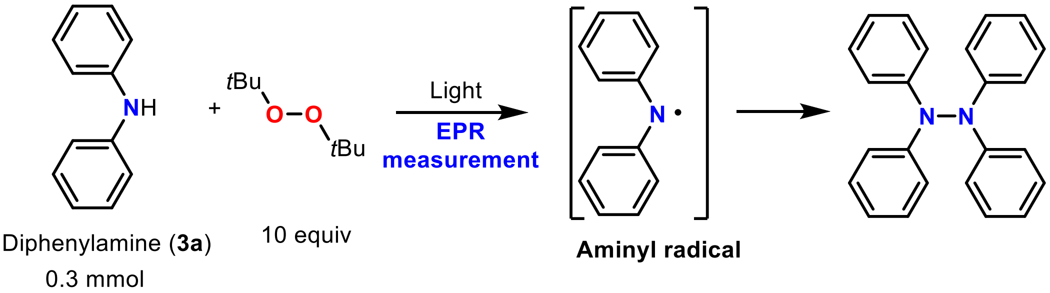


Figure S5: Integrated signal intensity of the third peak in the EPR spectrum of the N-centered radical in a solution with benzophenone imine:DTBP as a function of time. Light on and light off of the DYMAX Blue wave 75 are indicated with red dashed lines. The individual spectrum shown in Figure 3 of the main text and in Figure S4 left is indicated with a blue dot. A single point (#28) has been removed since the corresponding spectrum had a bad baseline.

EPR studies on the *in-situ* generated aminyl radical (from 3a)



In an argon-filled glovebox, a 4 mL vial was charged with diphenylamine **3a** (DPA, 50.5 mg, 0.3 mmol) and di-*tert*-butylperoxide, (DTBP, 0.55 mL, 3.0 mmol, 10 equiv). From this stock solution, 100 μL was transferred to a 4mm Ø LPV (low pressure vacuum) EPR tube inside the glovebox and the tube sealed with a cap and parafilm.

The EPR experiments were performed in the same way as above using the same experimental protocol and using the same UV light source. The parameters were the same except that the frequency was 9.744 GHz, the microwave power was 20.98 mW, the sweep width was 10 mT and the modulation amplitude 0.05 mT.

Upon switching on the light, a complicated multi-line EPR spectrum appears instantly (Figure S6, left). The simulated spectrum shown in red in Figure S6, left was obtained using Easyspin[10] with the garlic routine (isotropic, fast motion) with the following spin Hamiltonian parameters: g_{iso} = 2.0033, ^{14}N (triplet, I = 1) coupling constant A(N, 1 nucleus) = 0.888 mT, ^{1}H (I = 1/2) coupling constants A(ortho H, 4 nuclei) = 0.367 mT, A(meta H, 4 nuclei) = 0.150 mT and A(para H, 2 nuclei) = 0.428 mT, line width 0.004 mT, line shape lorentzian. The simulated spectrum was not independently fitted to the experimental spectrum, but was reproduced using values given in the literature[11] with adjustment of g-value (of 0.0001 which is within experimental uncertainty) and fitted line width. The acceptable fit of all line positions show that the diphenylaminyl radical is positively identified. The multiline signal from the diphenylaminyl radical disappears again when the light is off.

The experiment is not as clean as for **1a** since the signal from a second radical appears within a few minutes. The signal of the second radical is shown in Figure S6, middle. The shown spectrum is obtained while the light source has been on for 10 minutes but the light is off during the recording of the spectrum. The radical giving the second signal is persistent and has a long lifetime of many minutes in the reactant mixture. It is still possible to identify the diphenylaminyl radical EPR signal when light is turned on a second time and subtraction of the spectrum with and without light indicates that the diphenylaminyl radical signal is still switching on and off with the light and is not influenced by the presence of the persistent radical.

The persistent radical has not been positively identified at the present stage, but it can be satisfyingly reproduced using a simple model with 2 ^{14}N, see Figure S6, middle. It is thought to be either a byproduct in the reaction or a radical related to the dimeric product.

A control experiment was performed on diphenylamine in benzene which showed no signal, see Figure S6, right. For the control experiment with neat DTPB, see Figure S4, right.

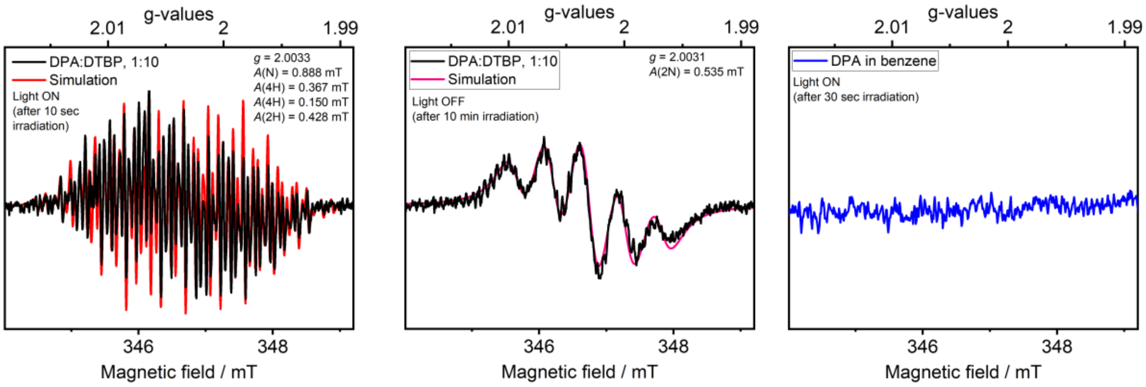


Figure S6: *In-situ* EPR experiments to detect radicals formed by reaction with diphenylamine (DPA) and DTBP. Left: DPA:DTBP = 1:10 during light ON after 20 sec irradiation. Middle: same experiment after the light has been turned OFF after 10 min irradiation. Right: DPA in benzene during light ON.

11. References

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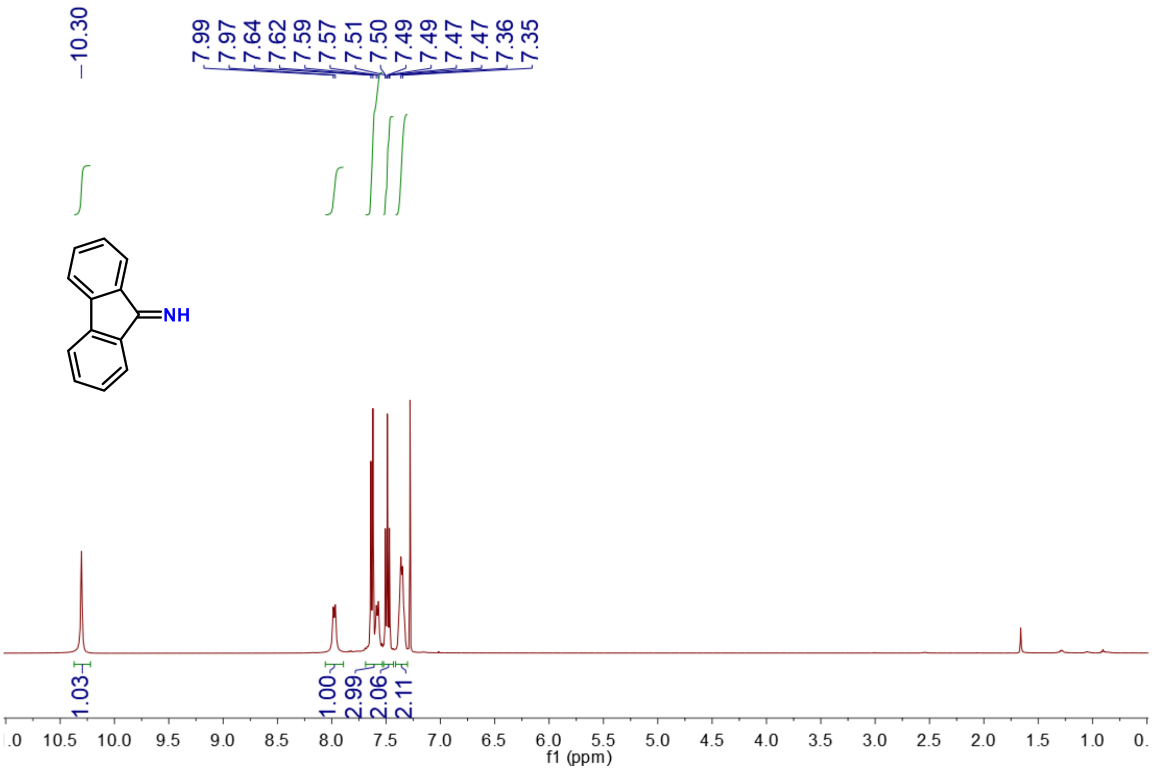
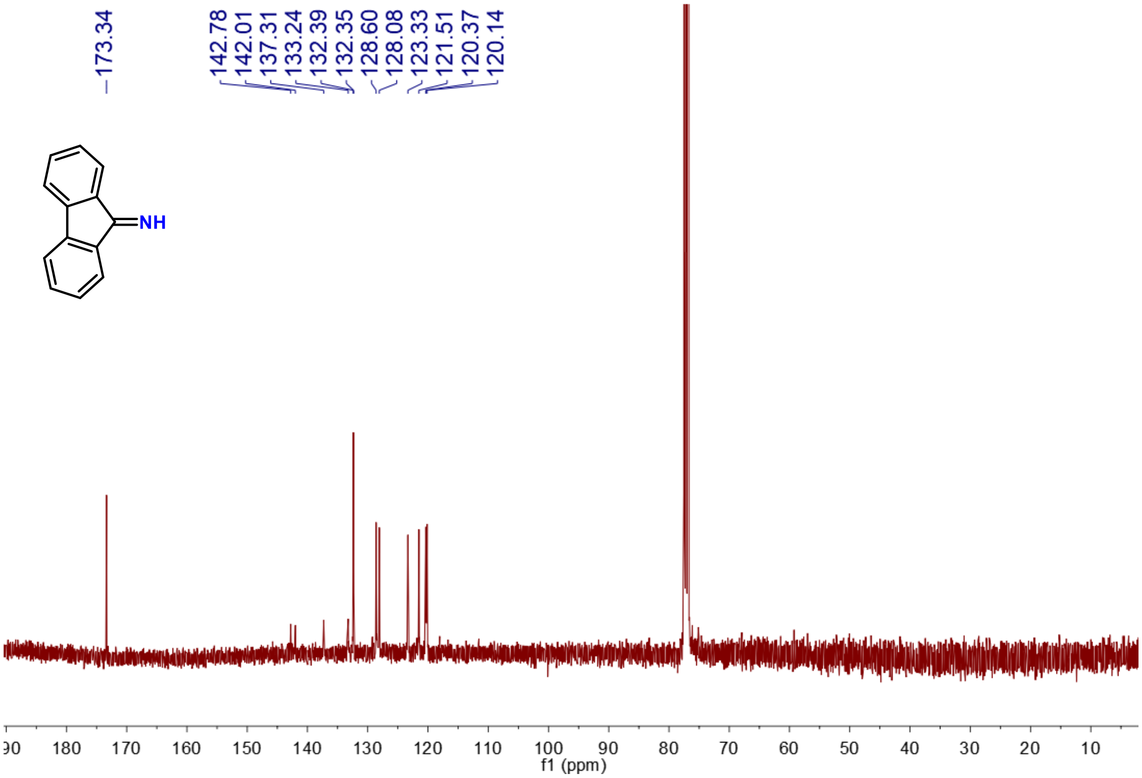
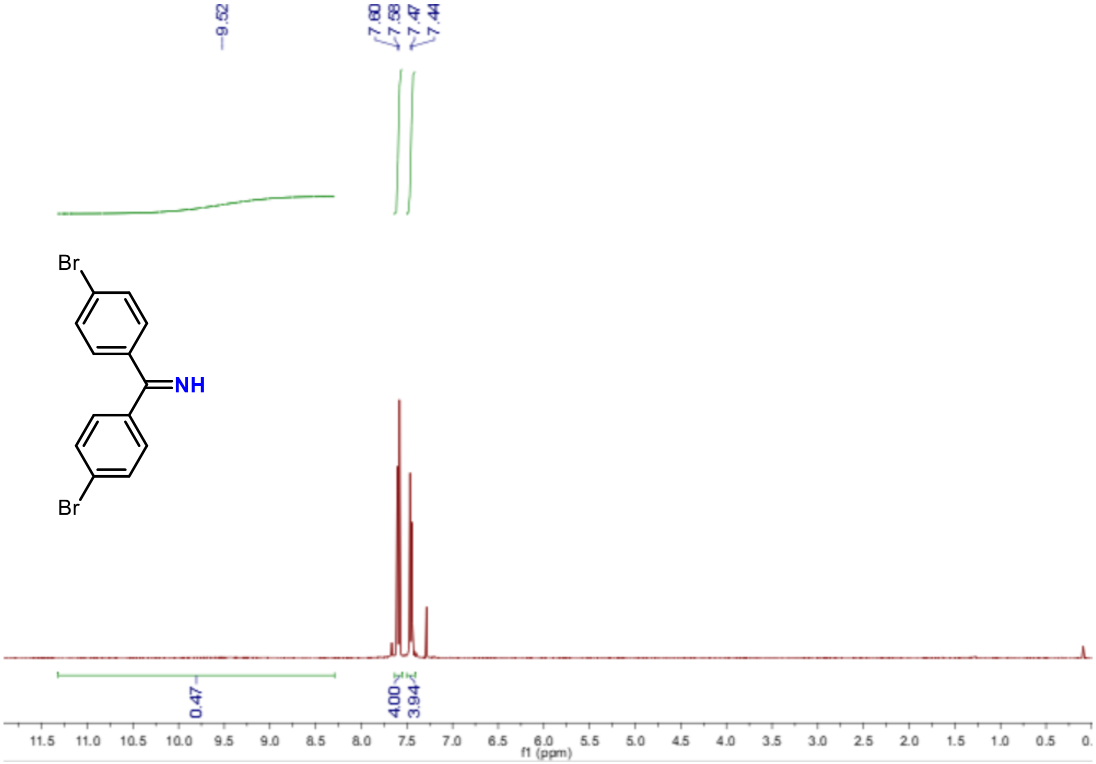
12. NMR Spectra



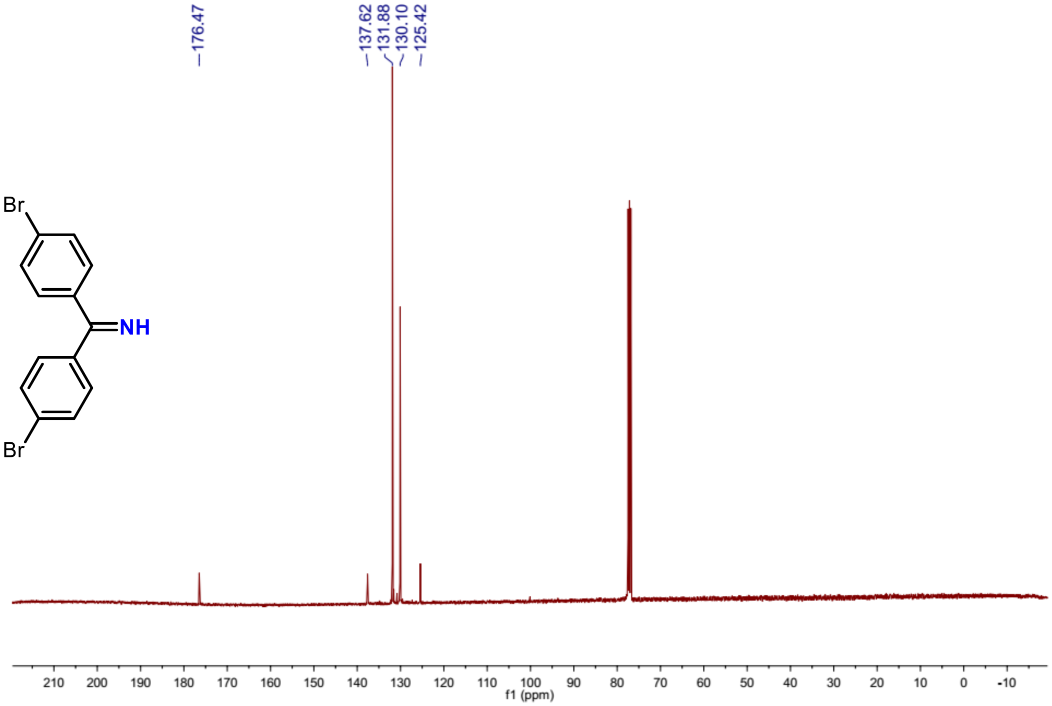
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **1b**.



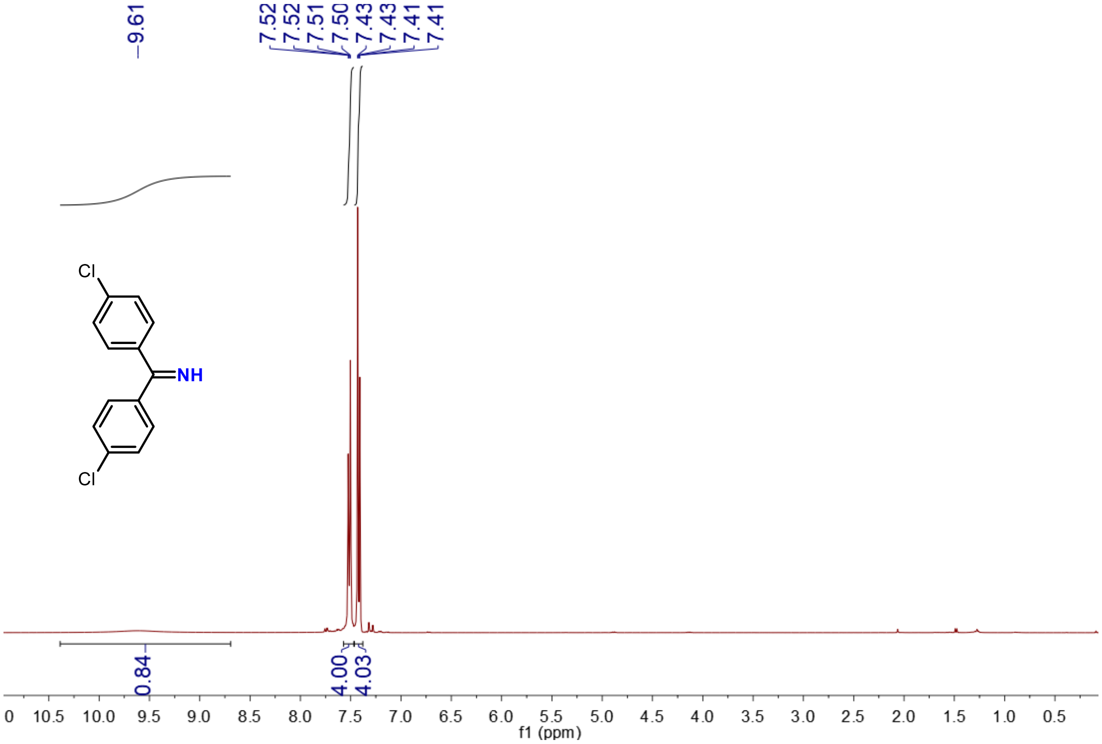
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **1b**.



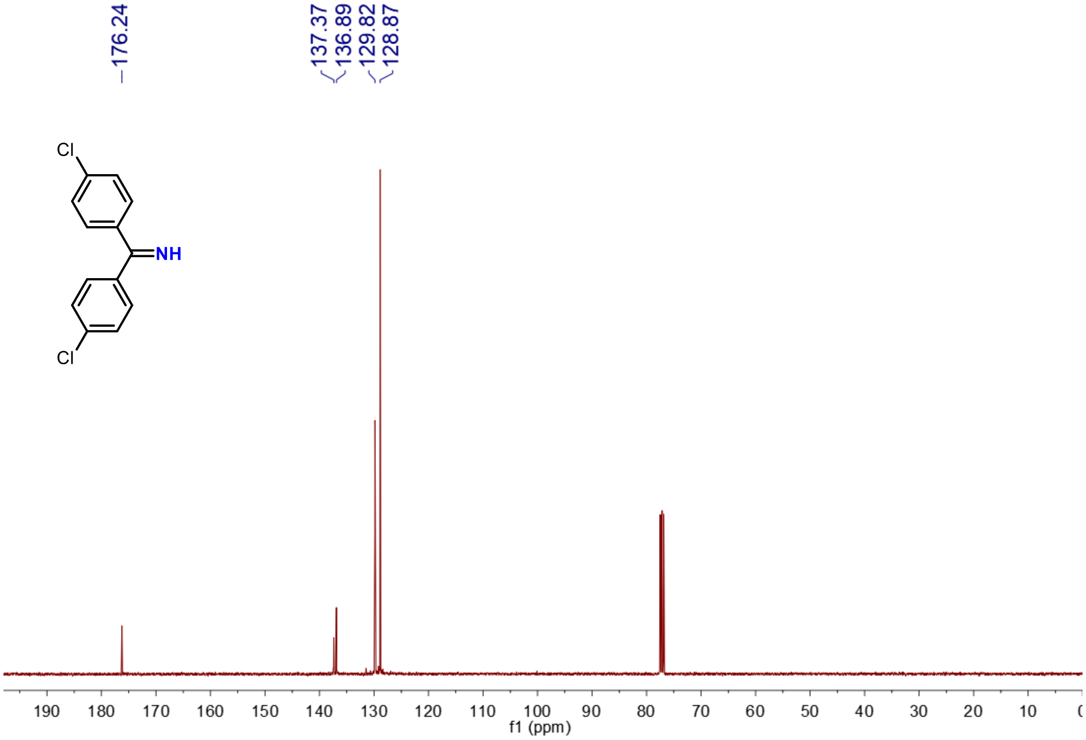
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **1c**.



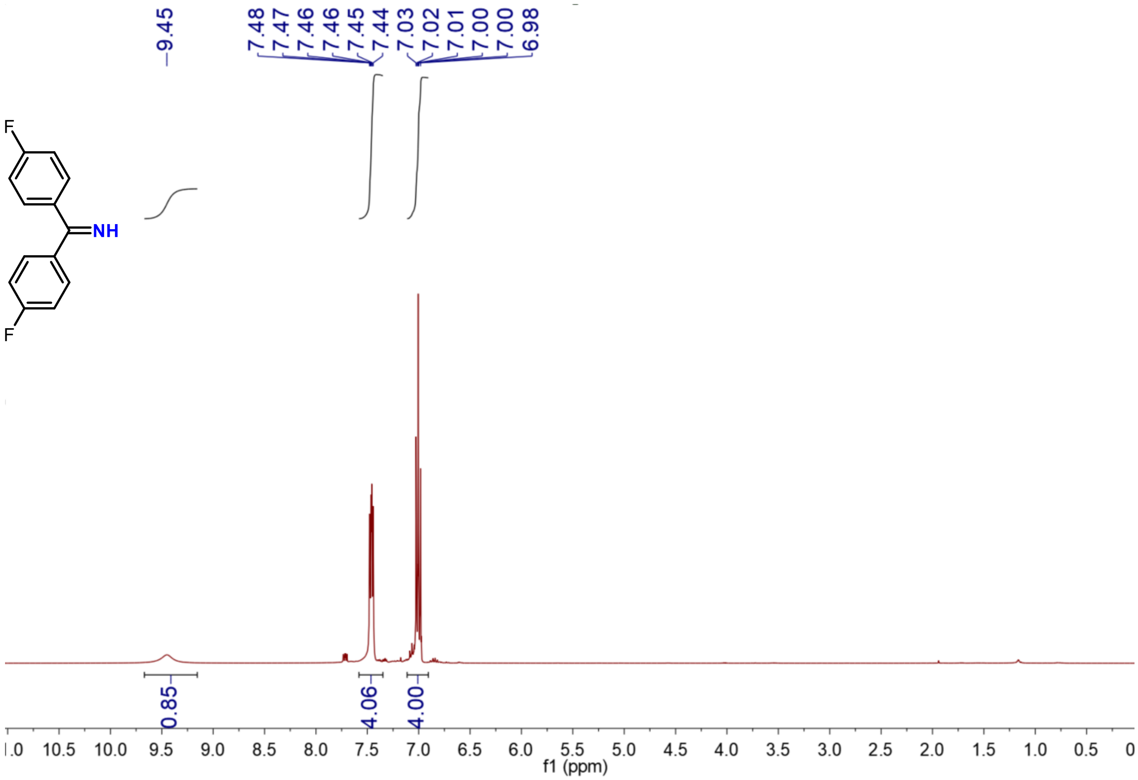
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **1c.**



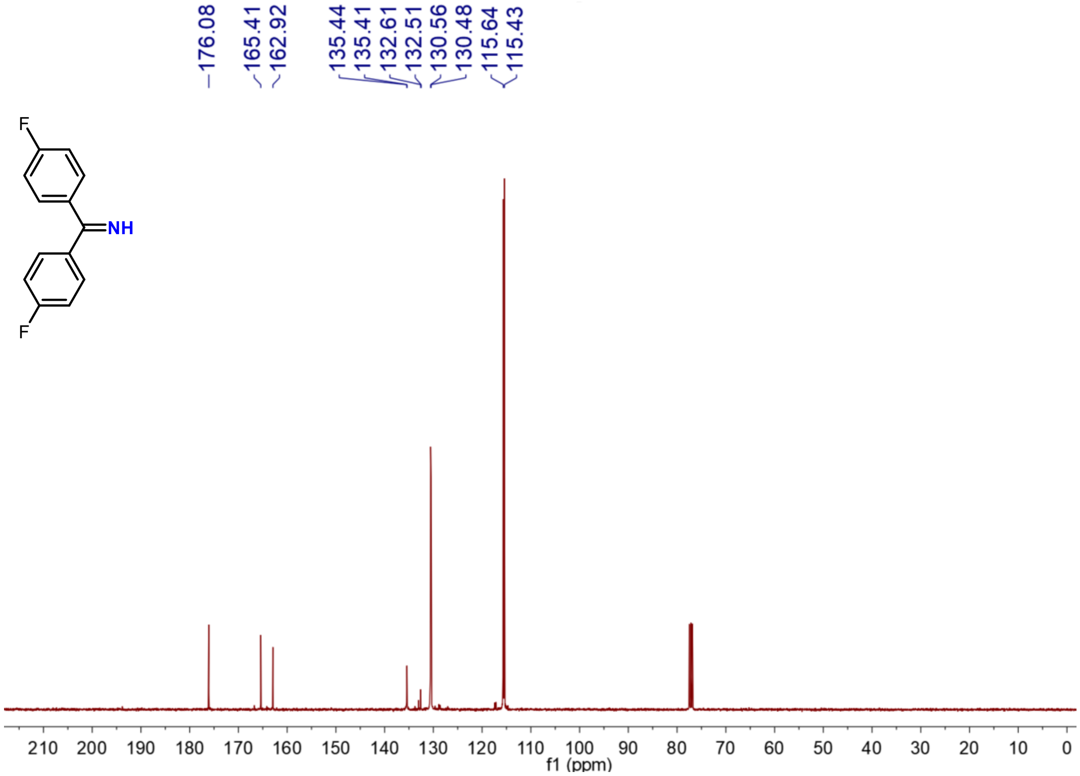
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **1d**.



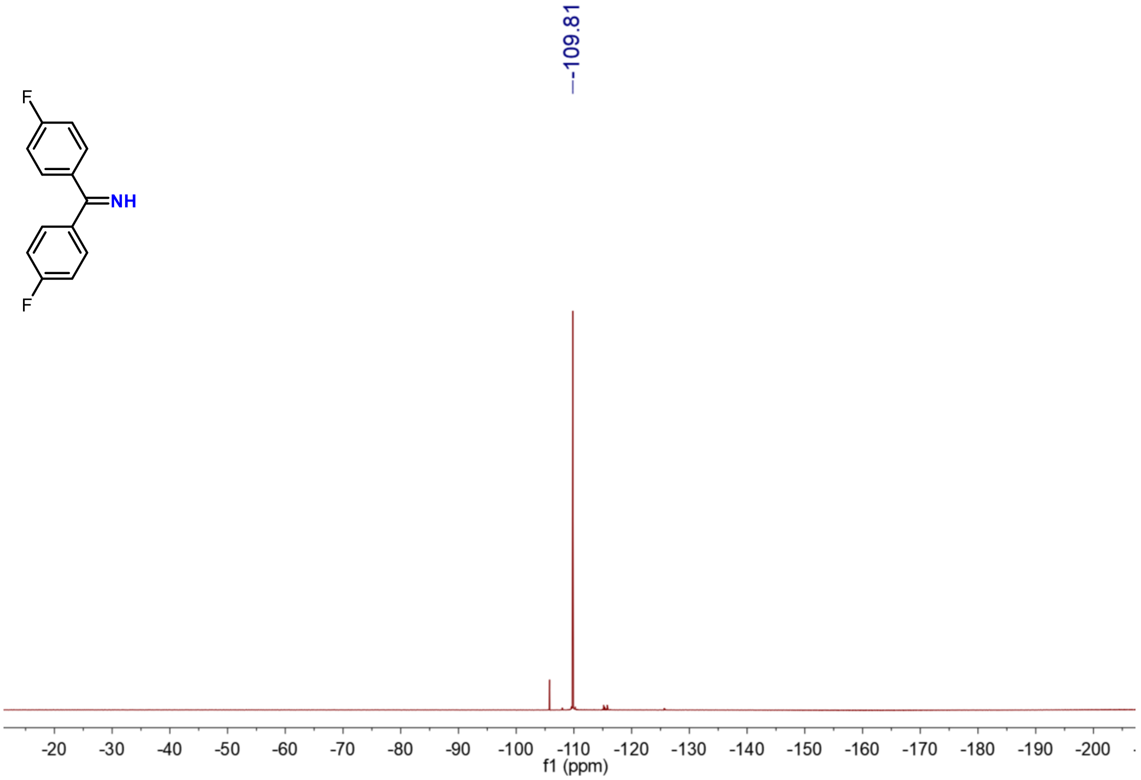
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **1d**.



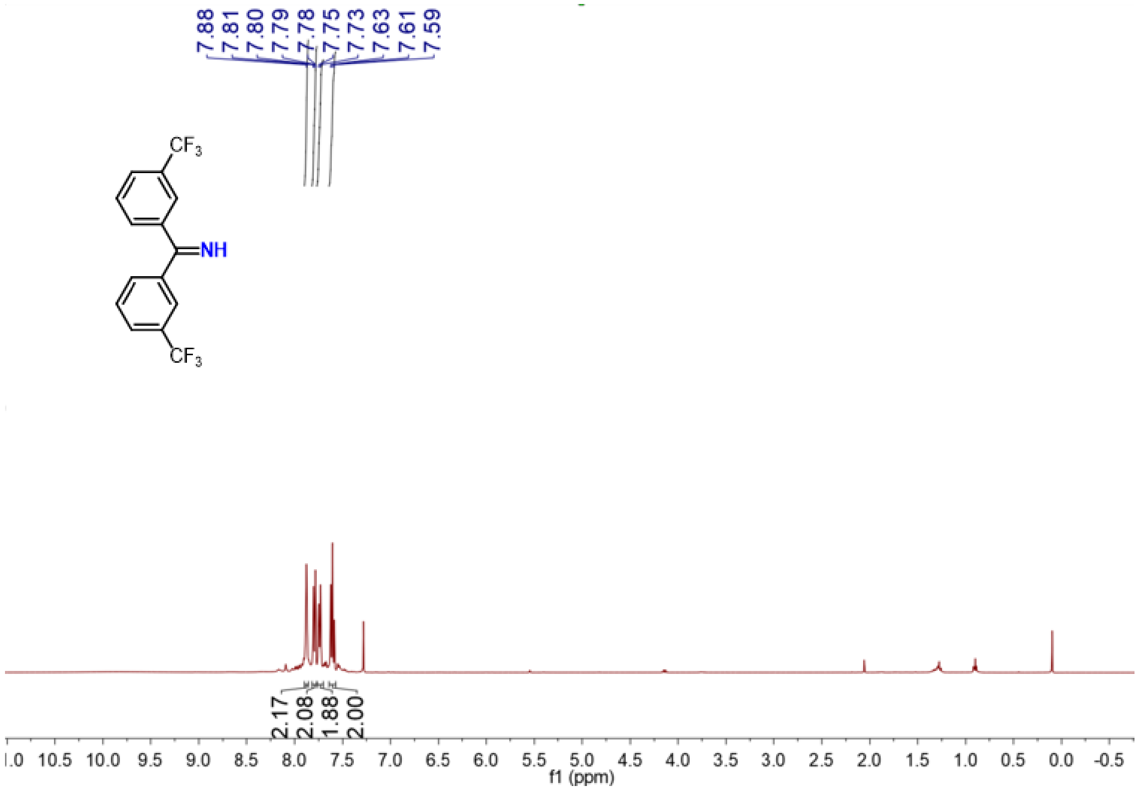
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **1e**.



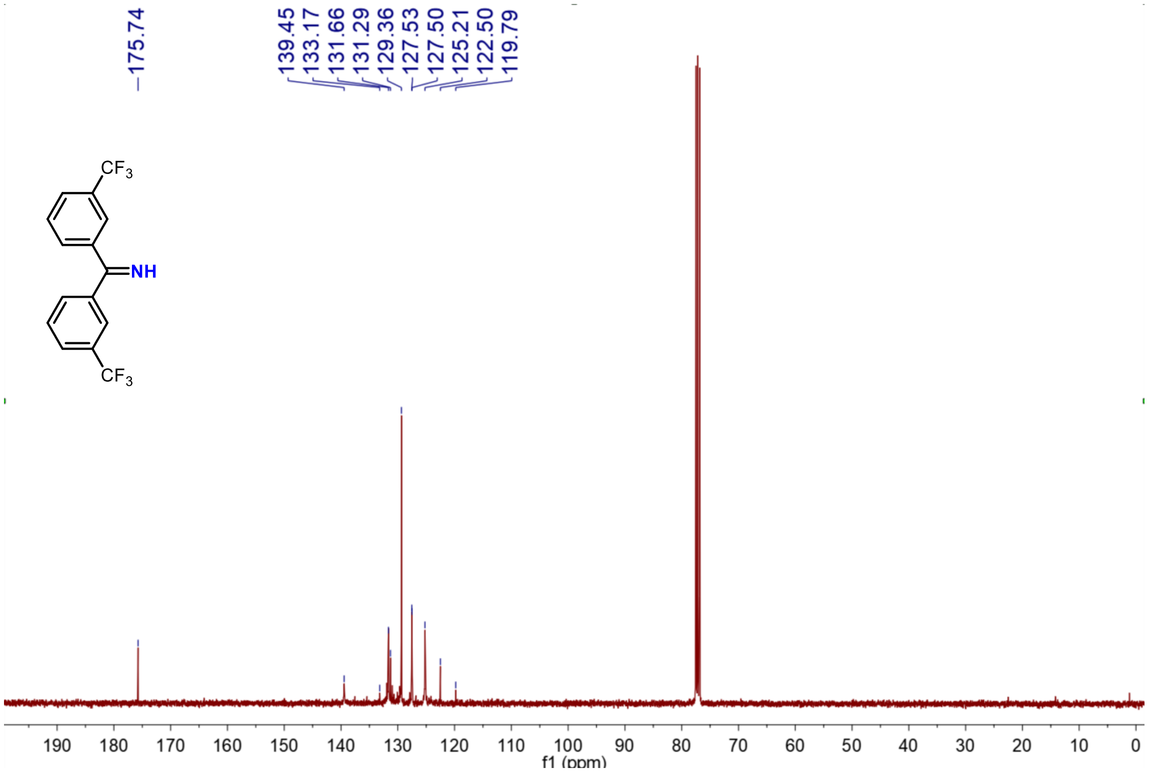
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **1e**.



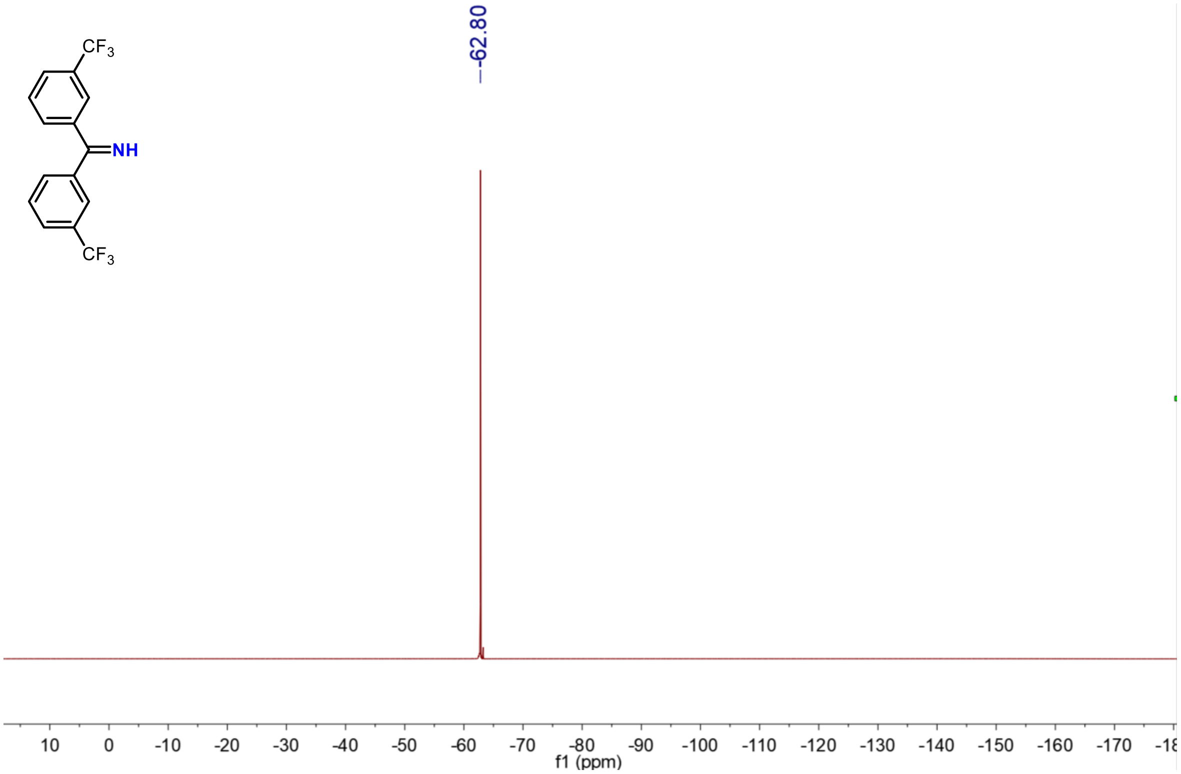
$^{19}F\{^1H\}$-NMR spectrum (377 MHz, $CDCl_3$, 298 K) of compound **1e**.



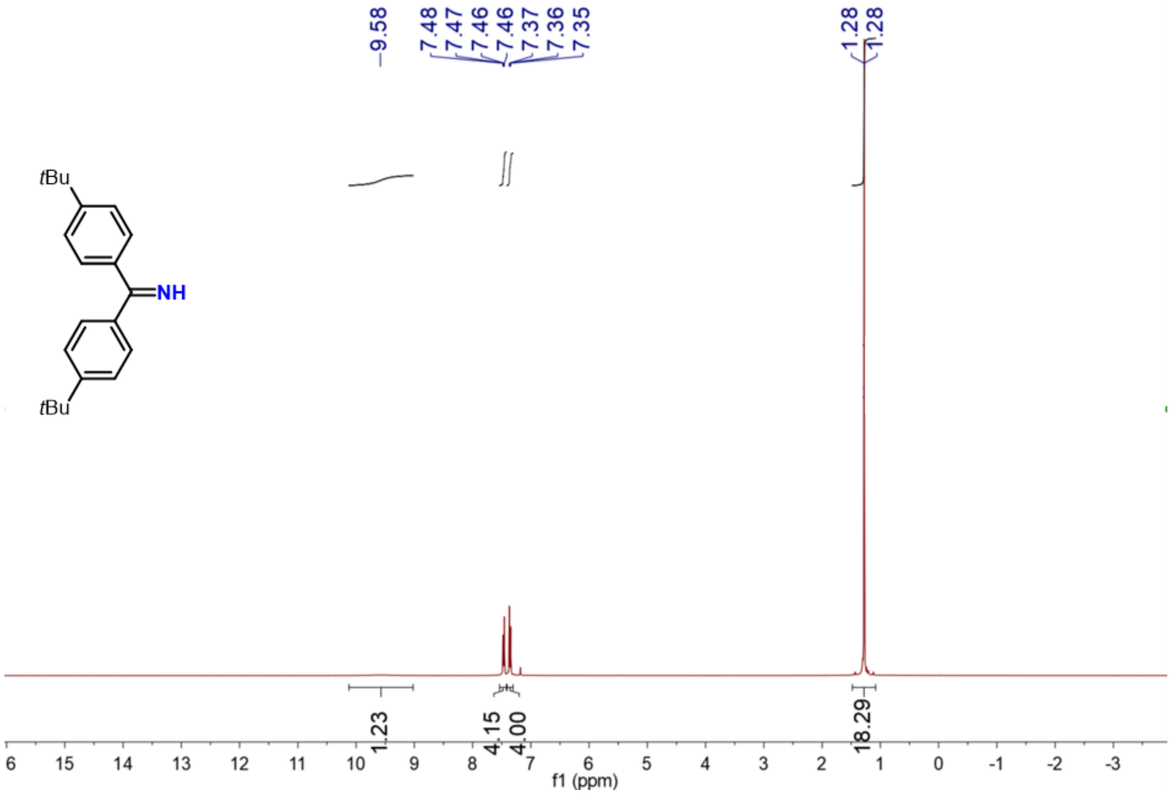
^1H-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **1f**.



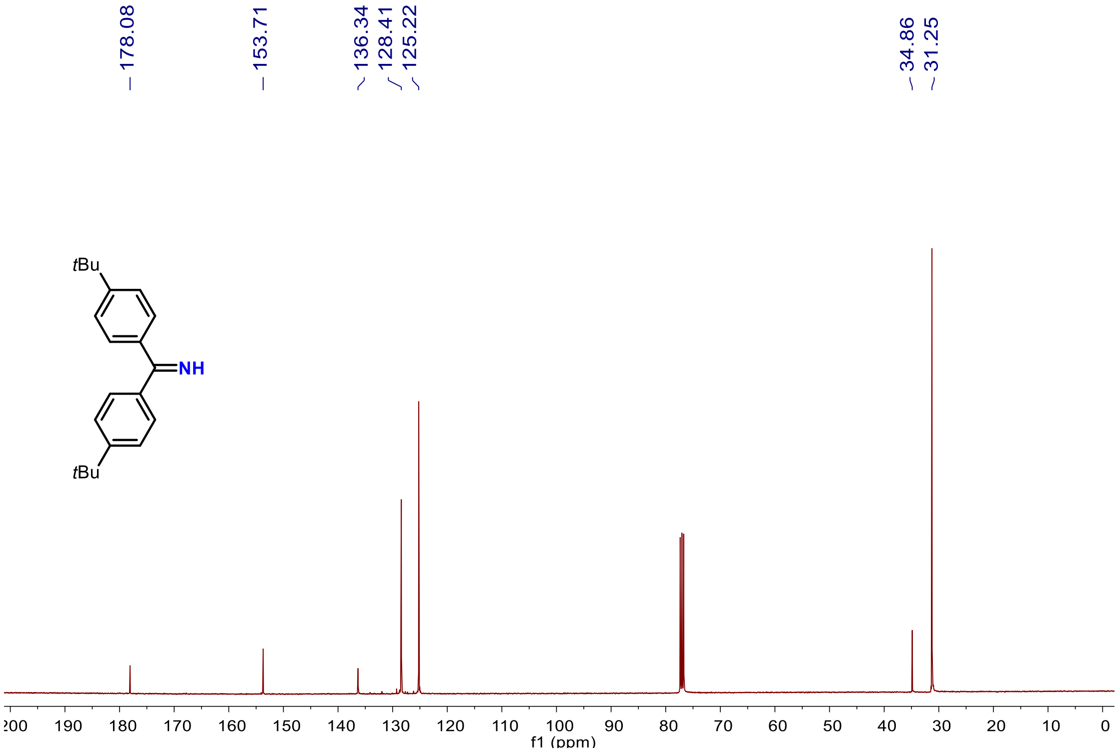
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **1f.**



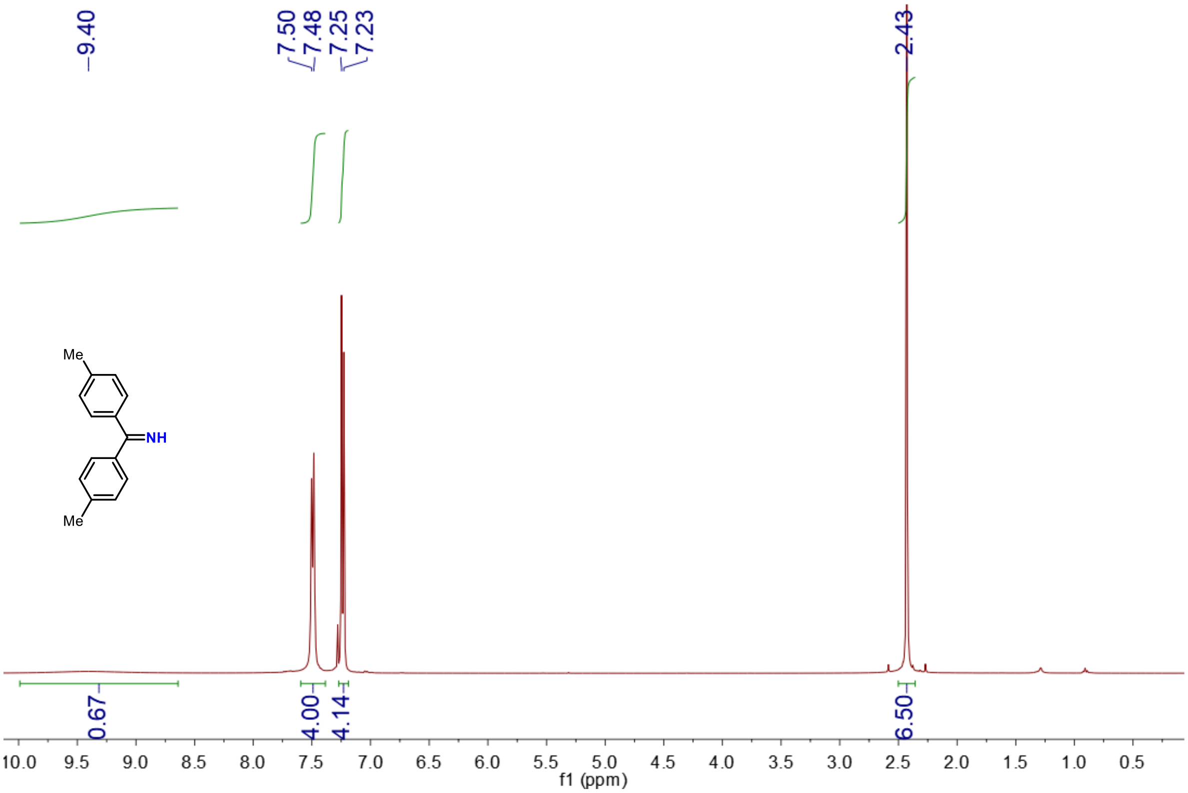
^{19}F{^{1}H}-NMR spectrum (377 MHz, CDCl$_3$, 298 K) of compound **1f**.



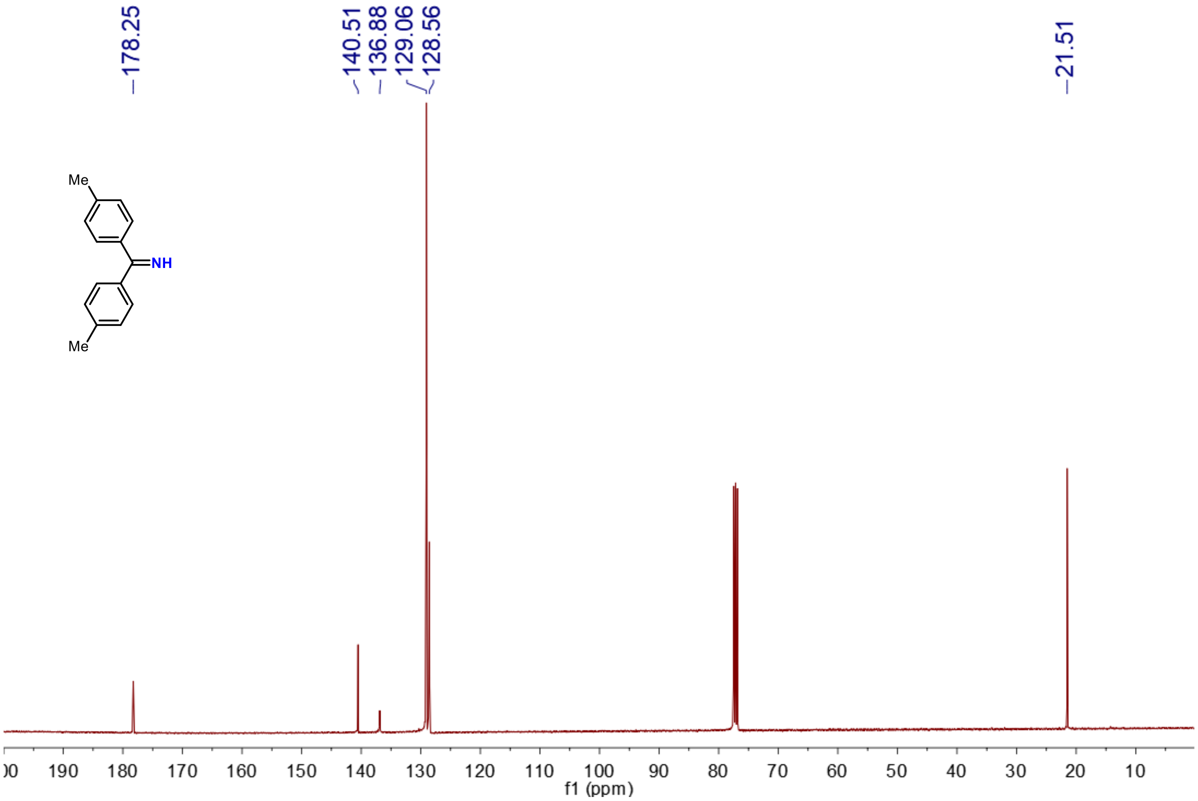
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **1g**.



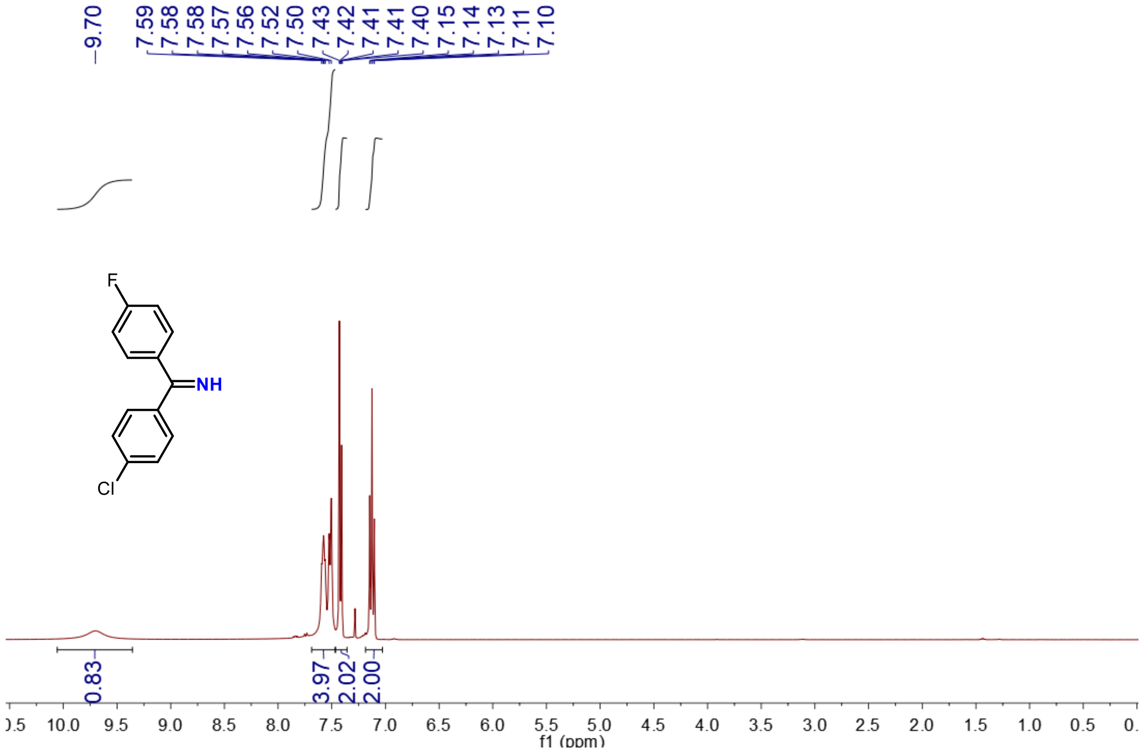
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **1g**.



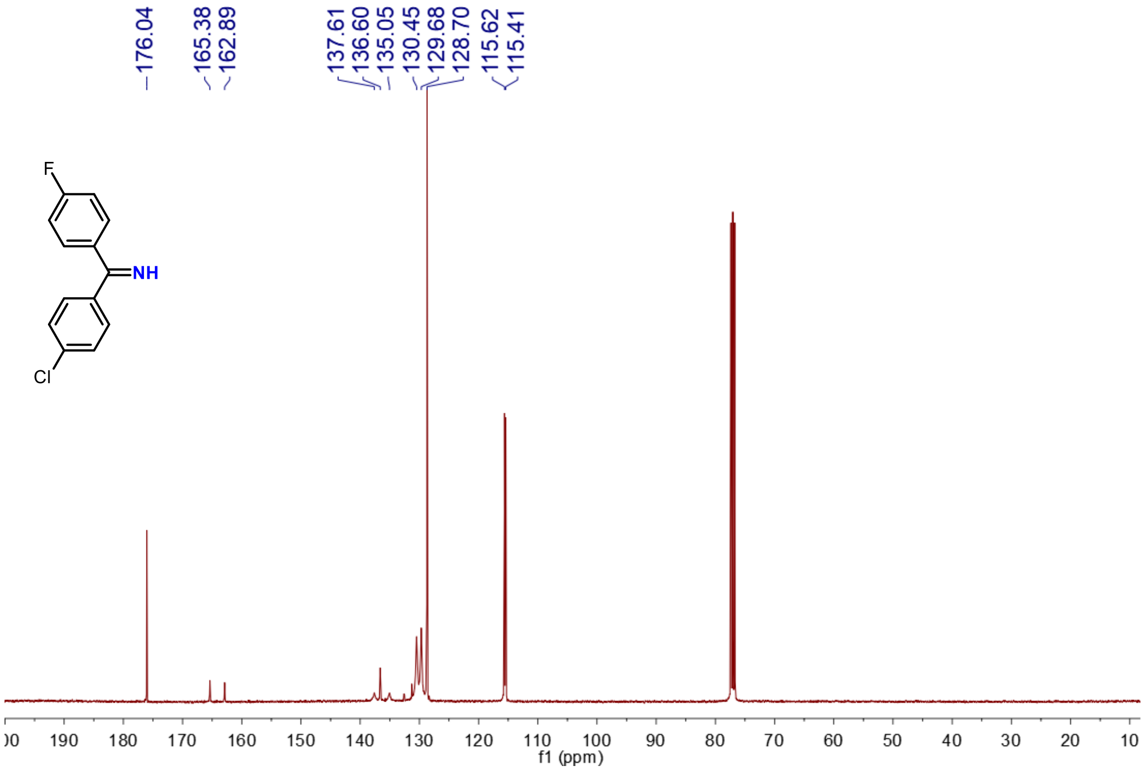
^{1}H-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **1h**.



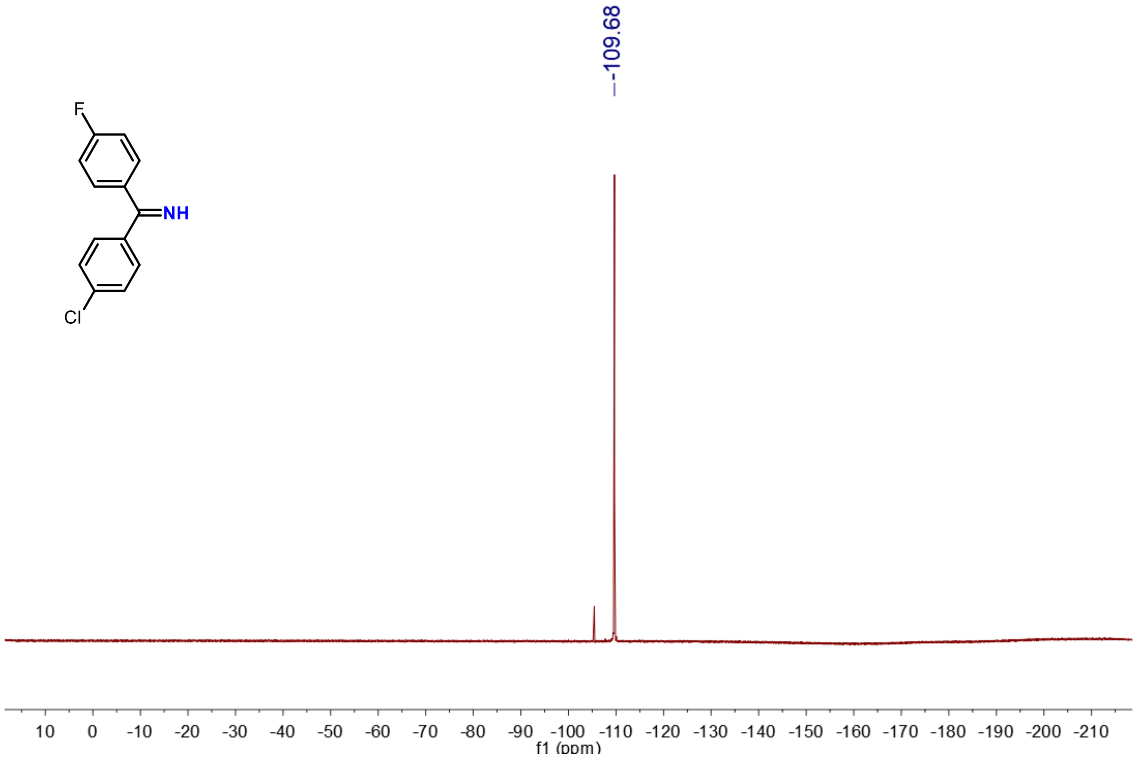
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **1h**.



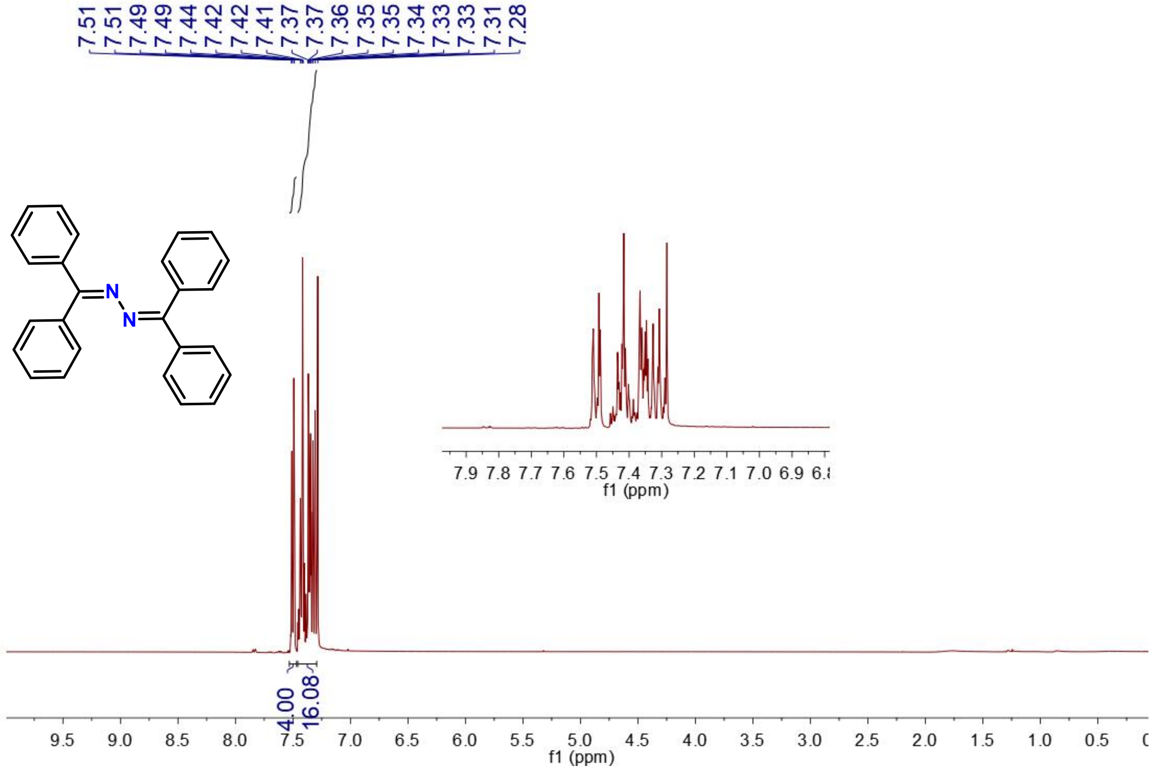
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **1i**.



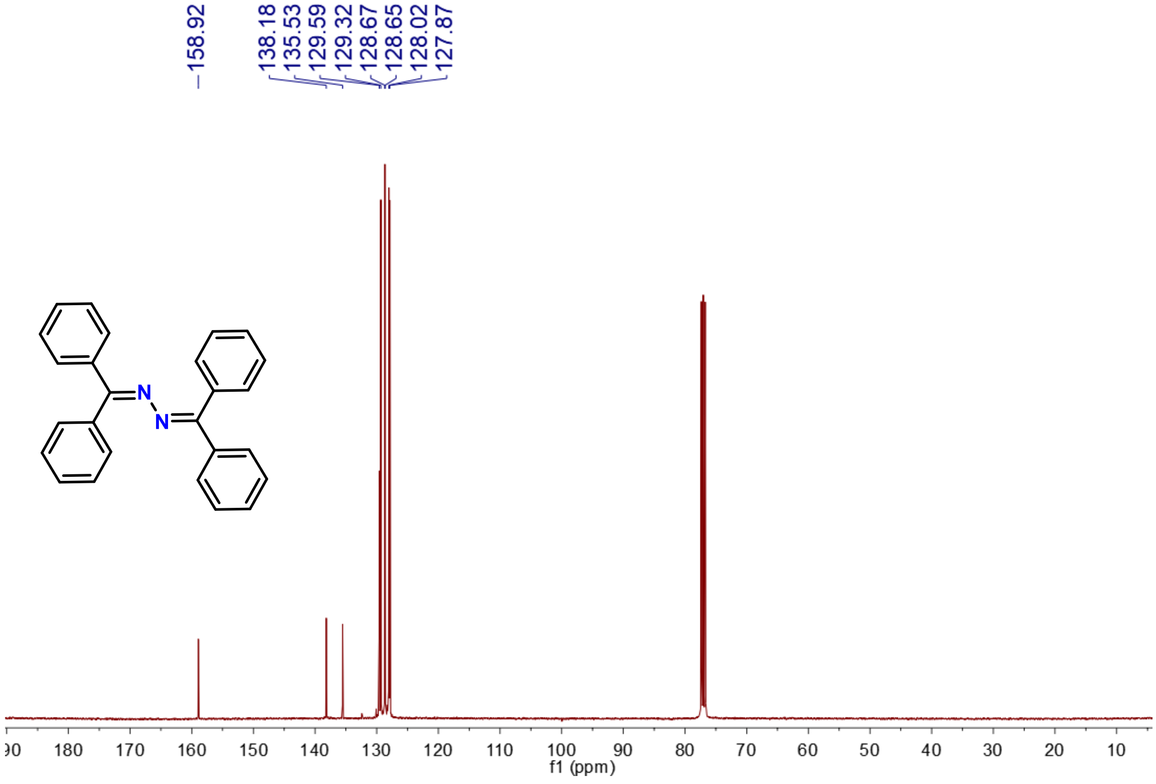
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **1i**.



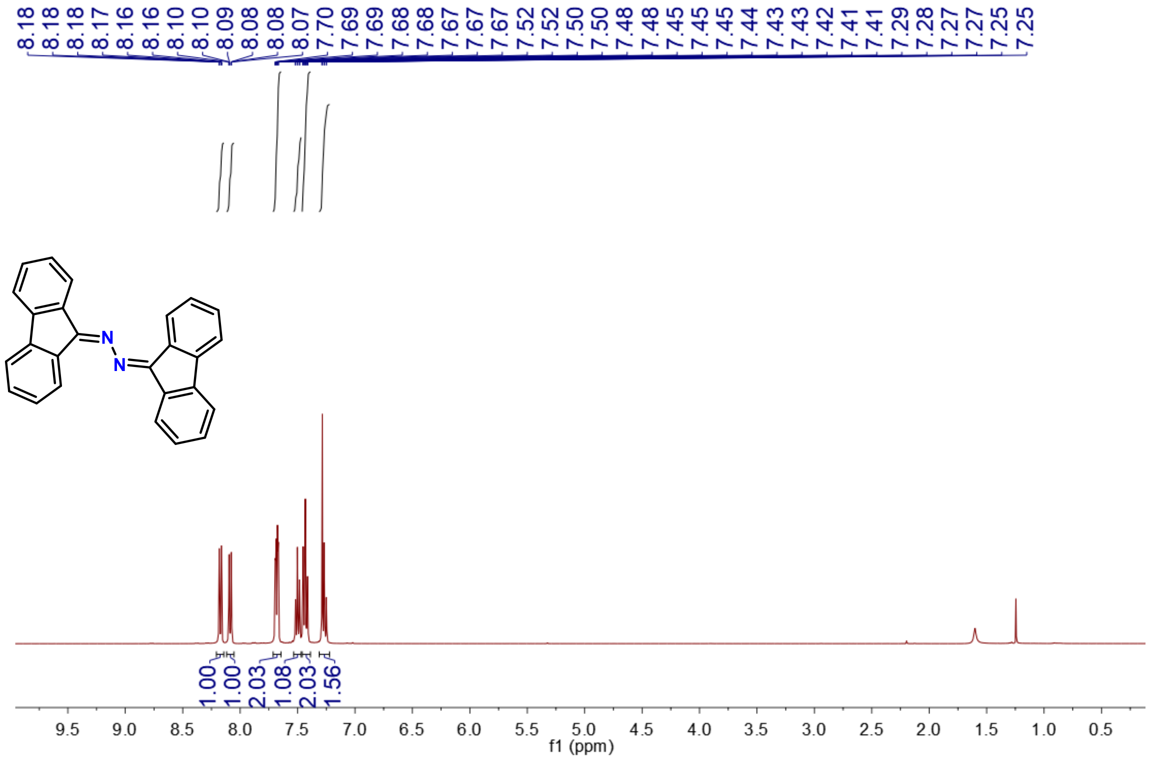
^{19}F{1H}-NMR spectrum (377 MHz, $CDCl_3$, 298 K) of compound **1i**.



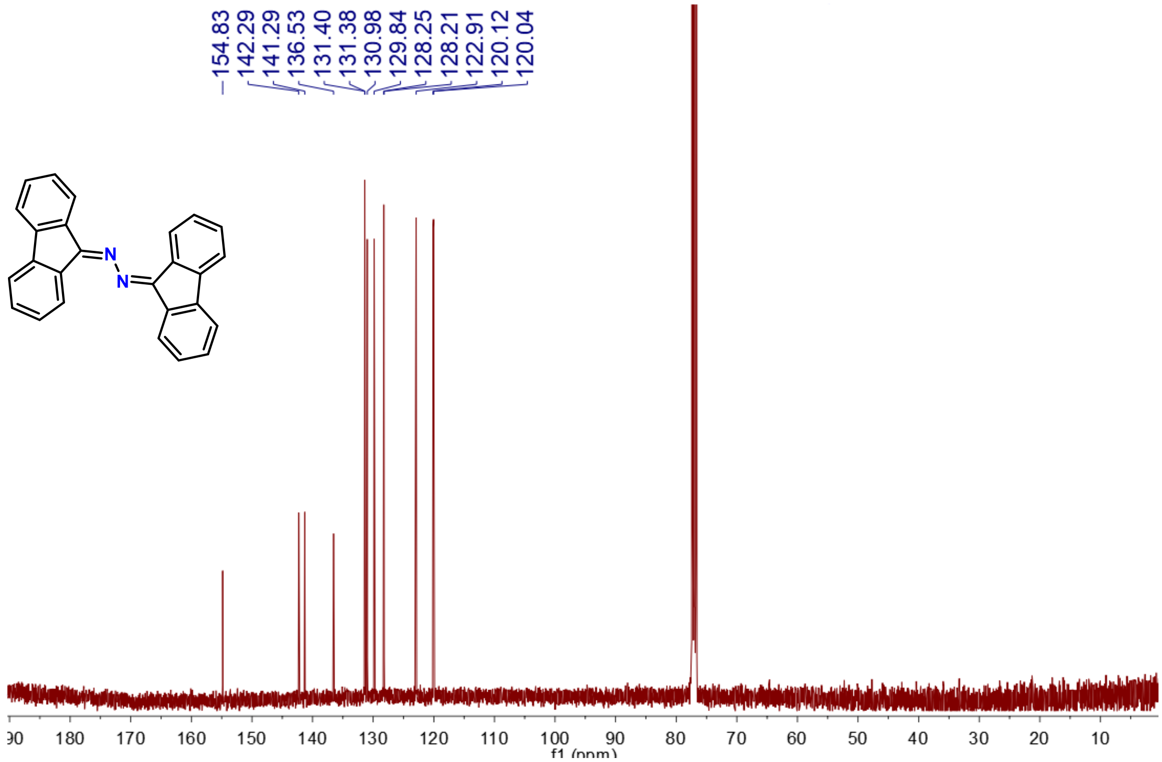
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **2a**.



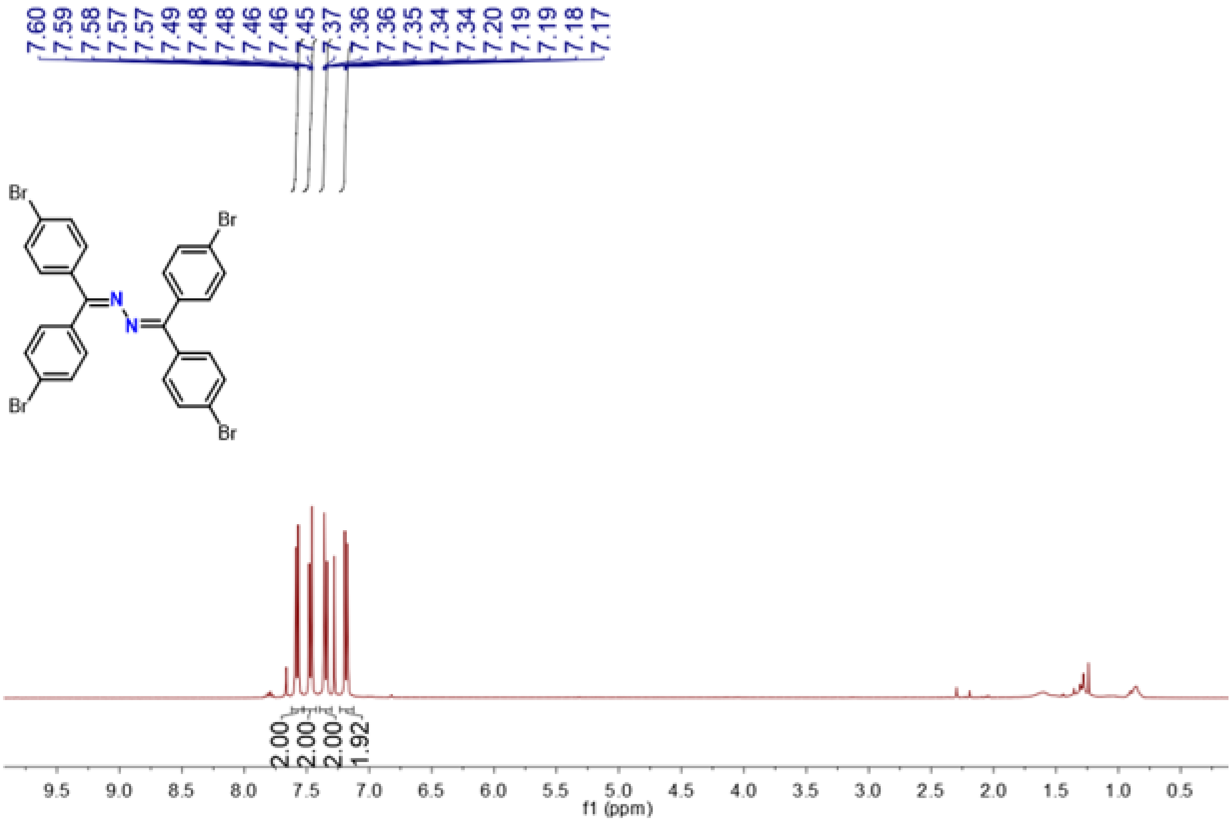
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **2a**.



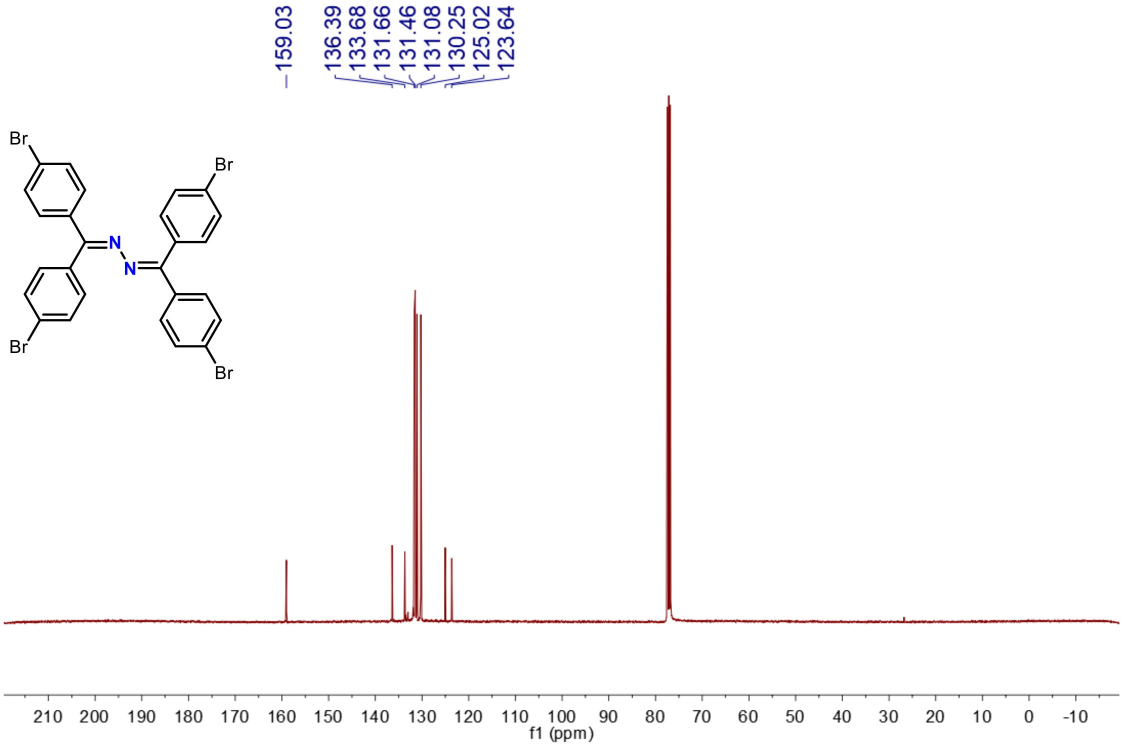
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **2b**.



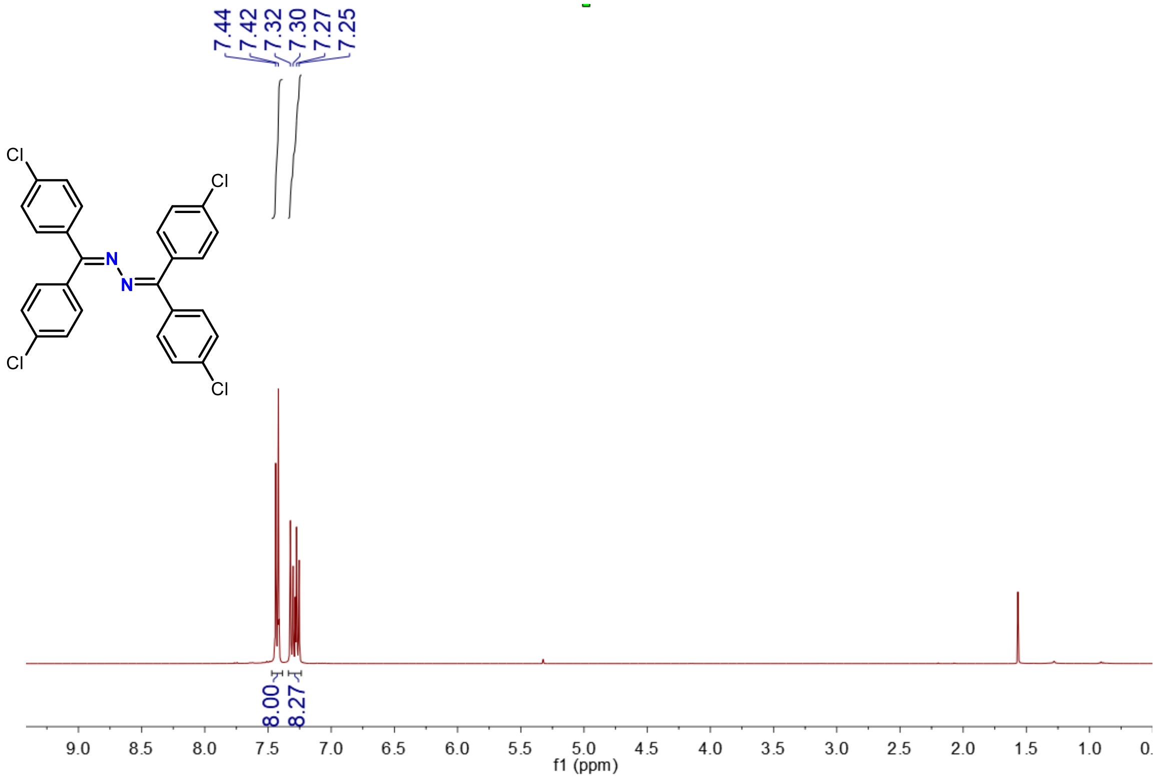
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **2b**.



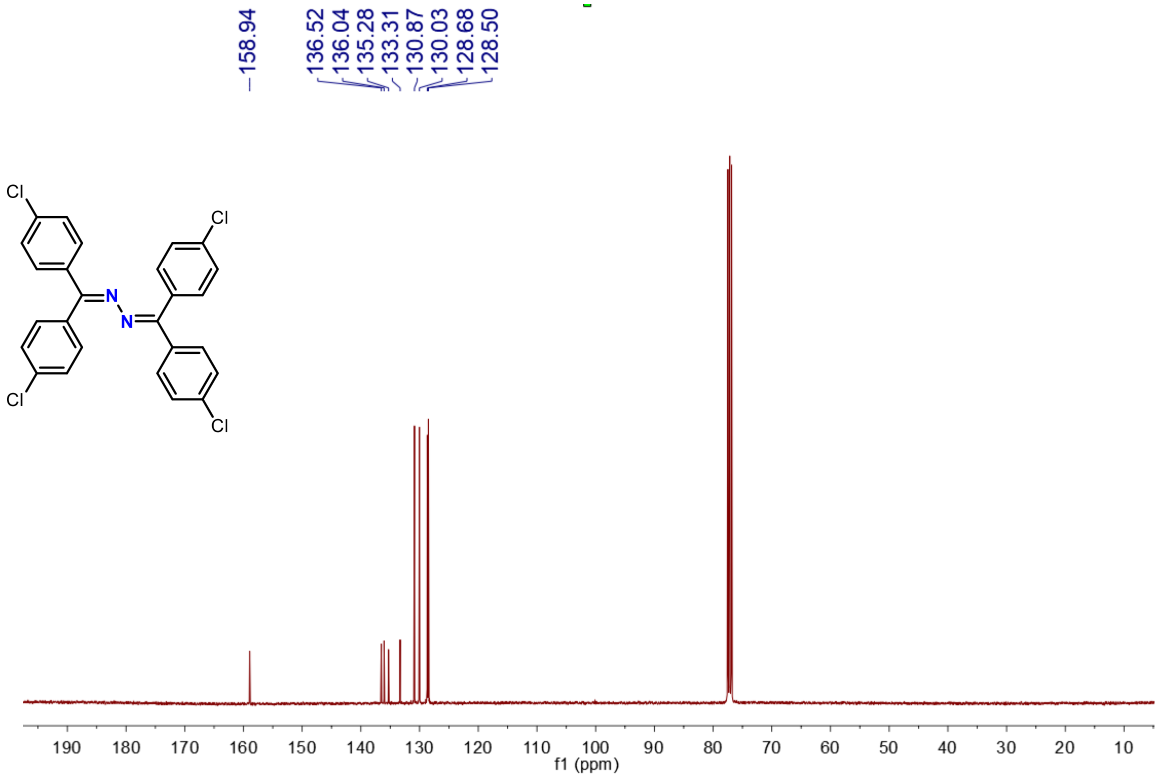
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **2c.**



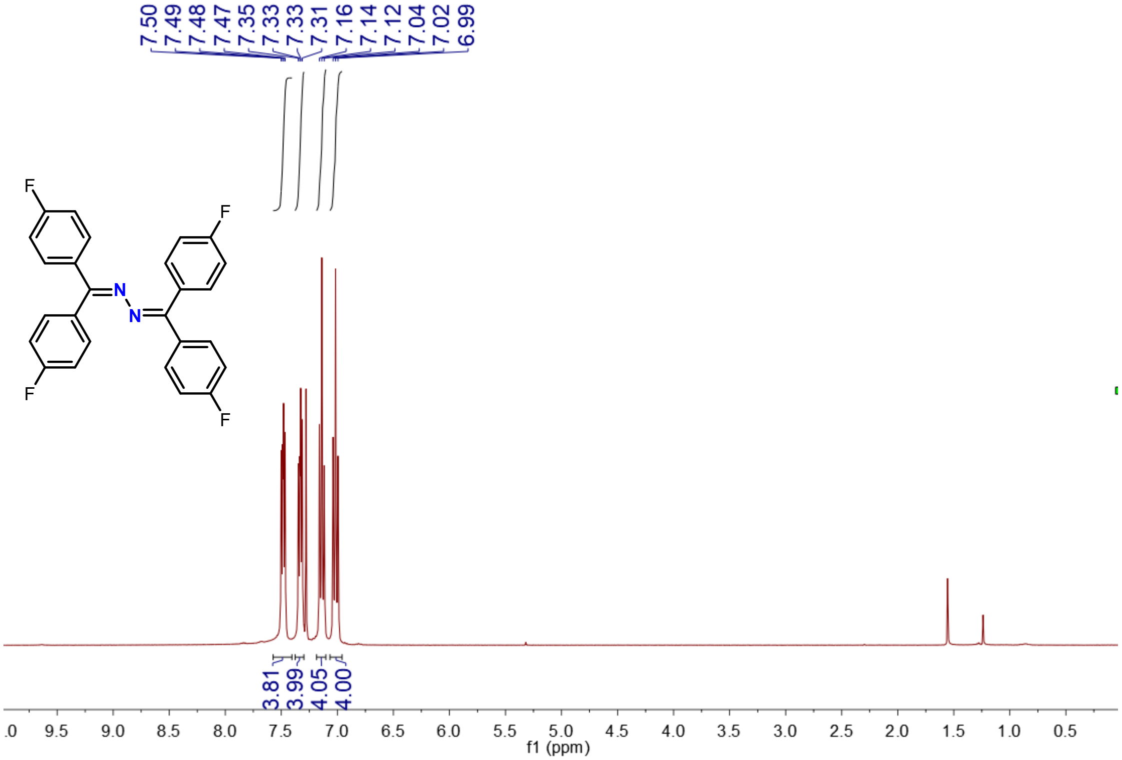
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **2c.**



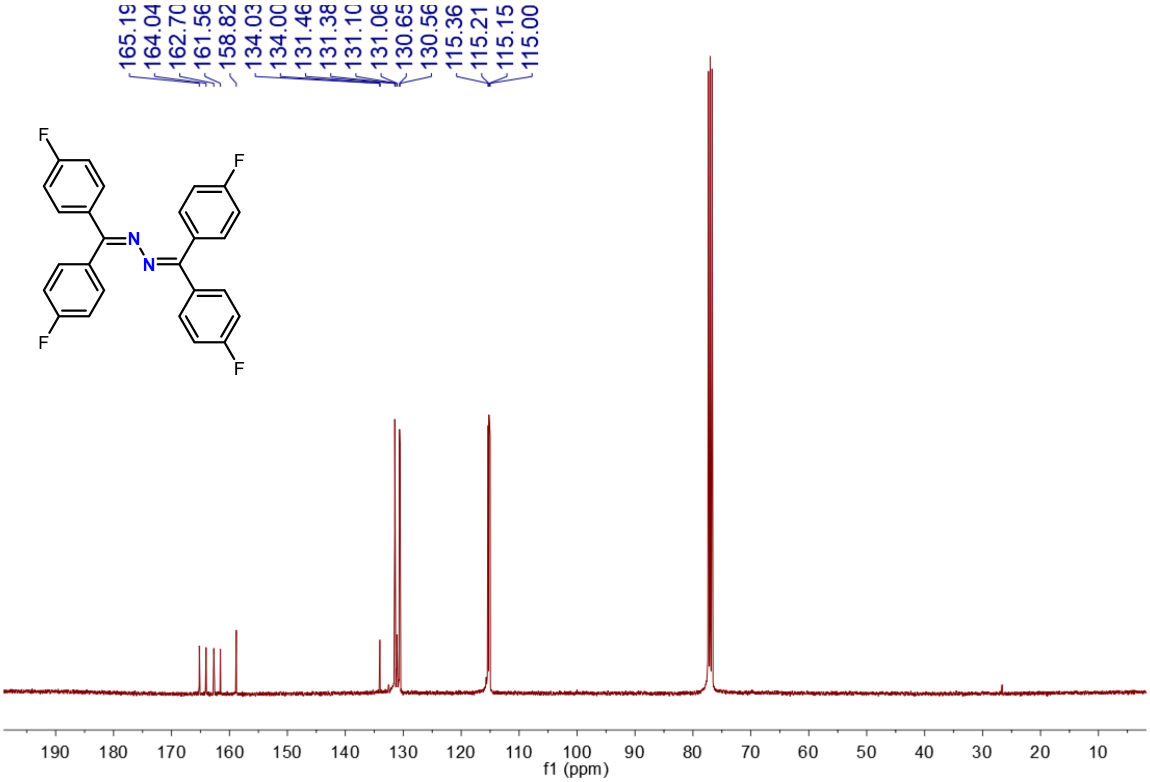
^{1}H-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **2d**.



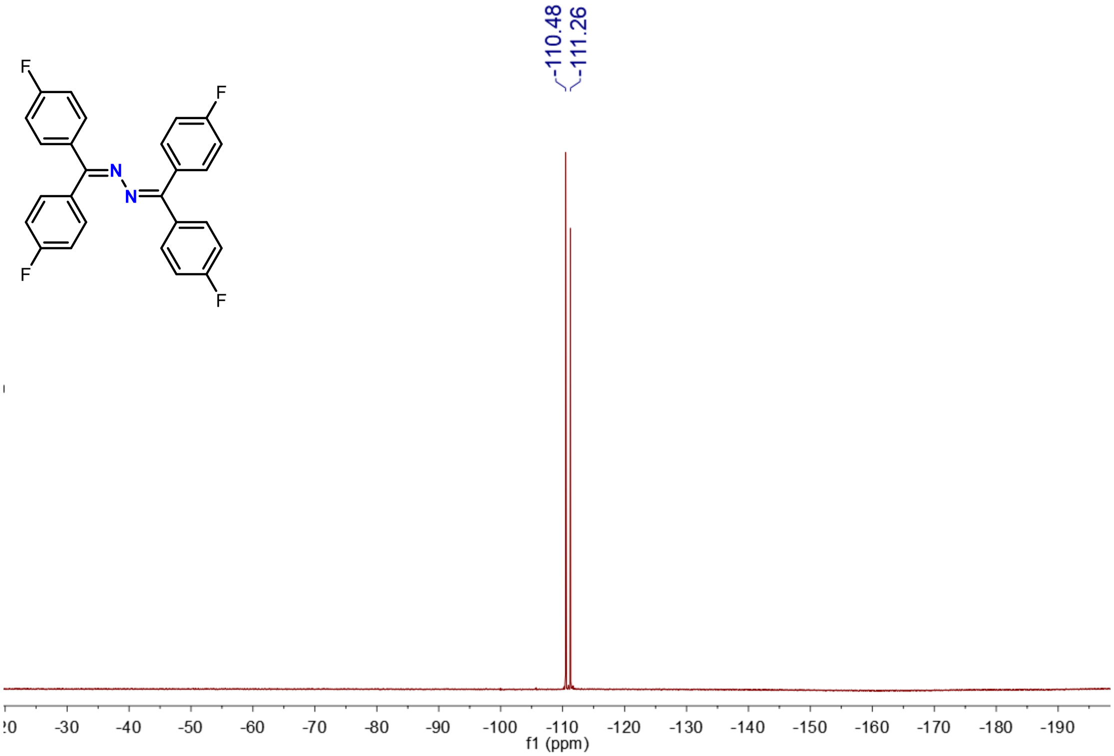
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **2d**.



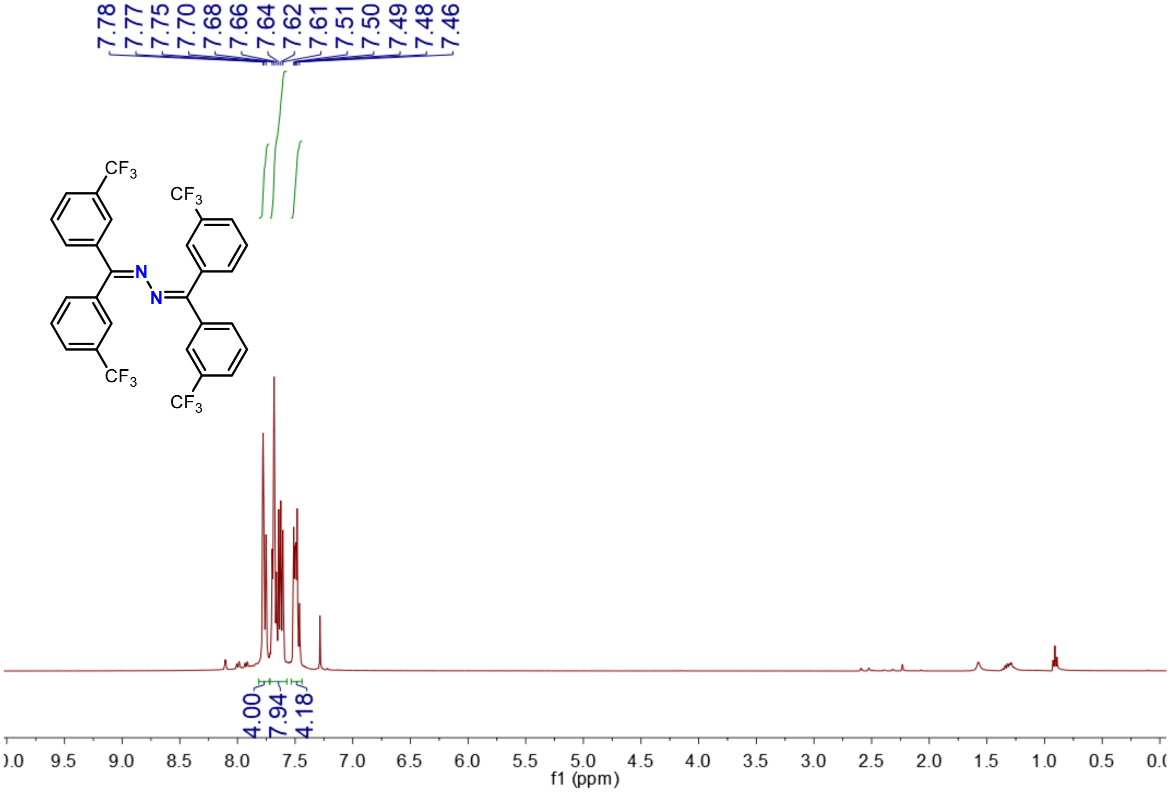
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **2e**.



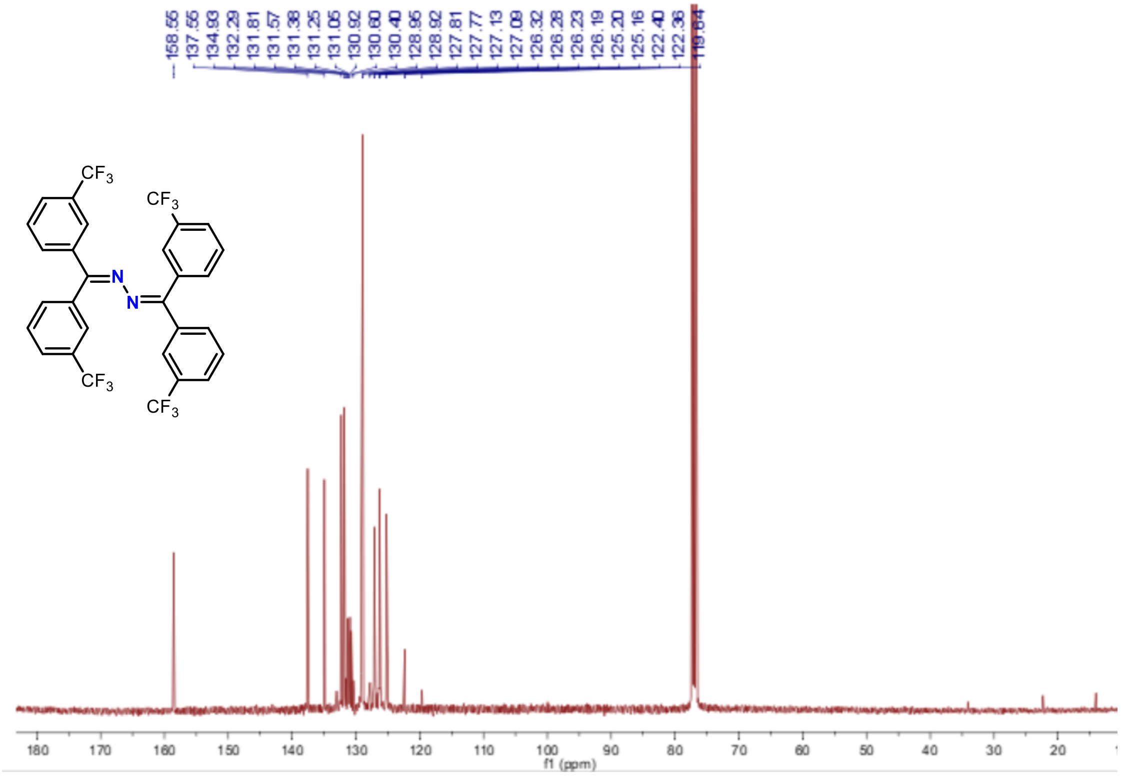
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **2e**.



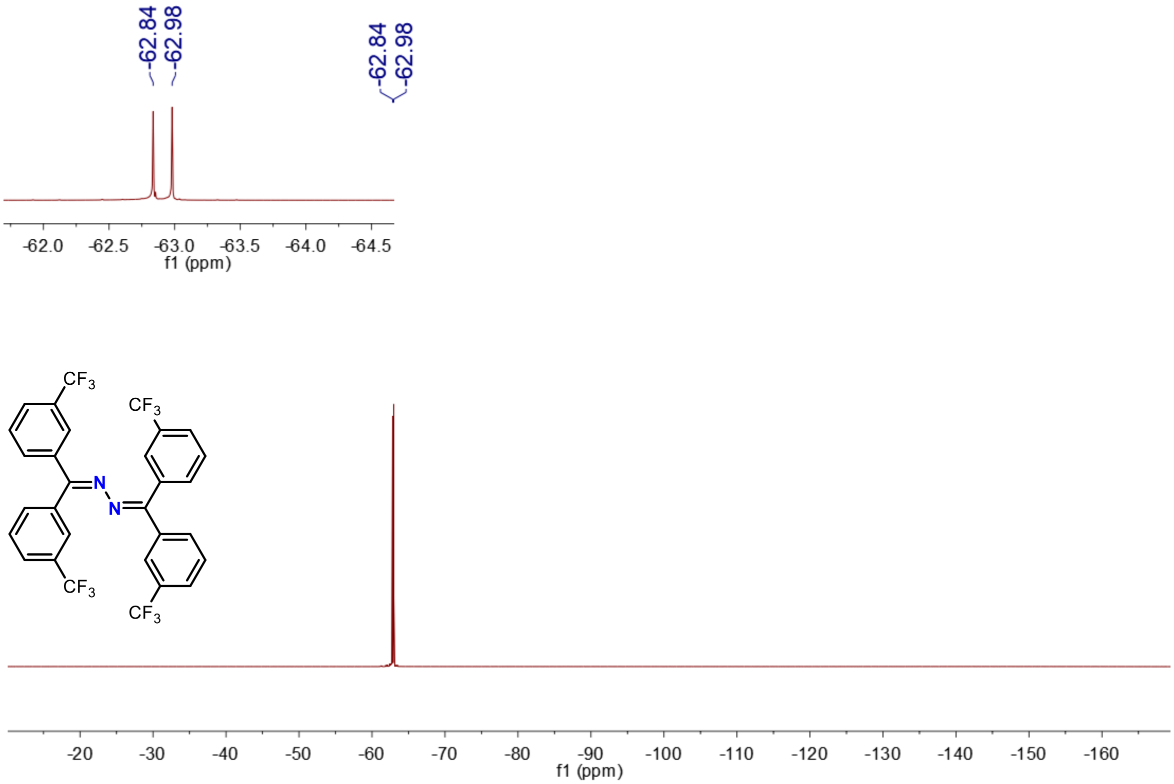
^{19}F-NMR spectrum (377 MHz, $CDCl_3$, 298 K) of compound **2e**.



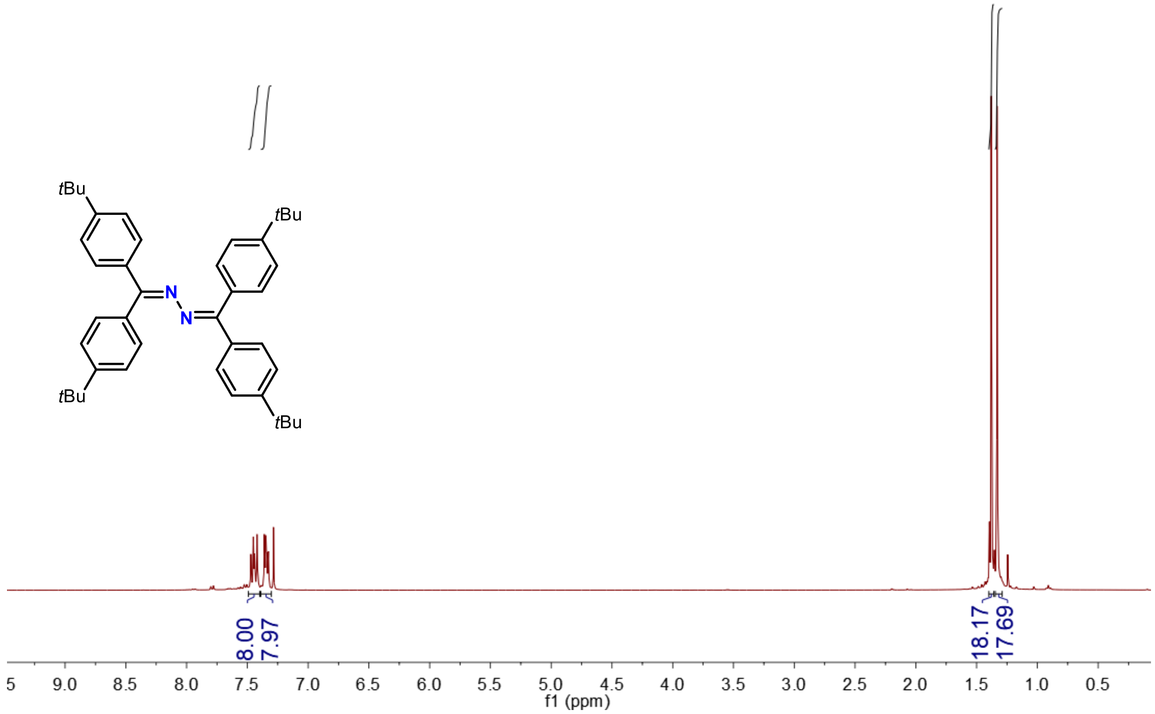
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **2f**.



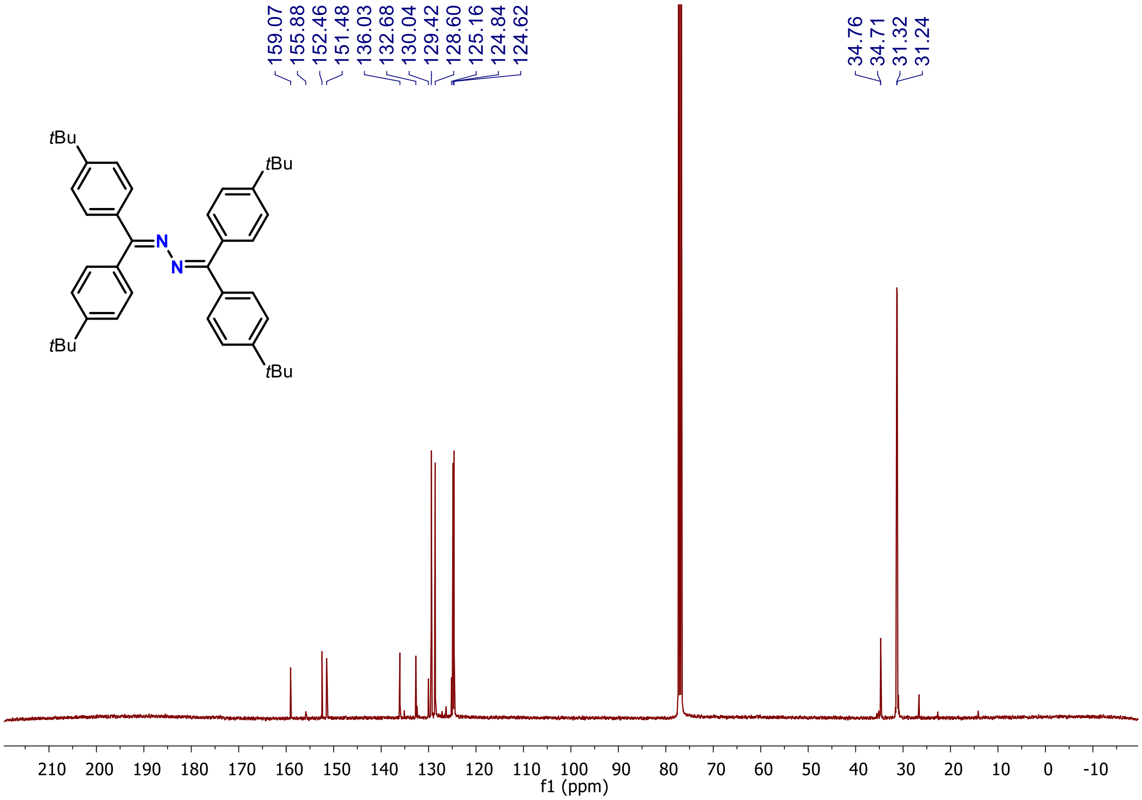
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **2f**.



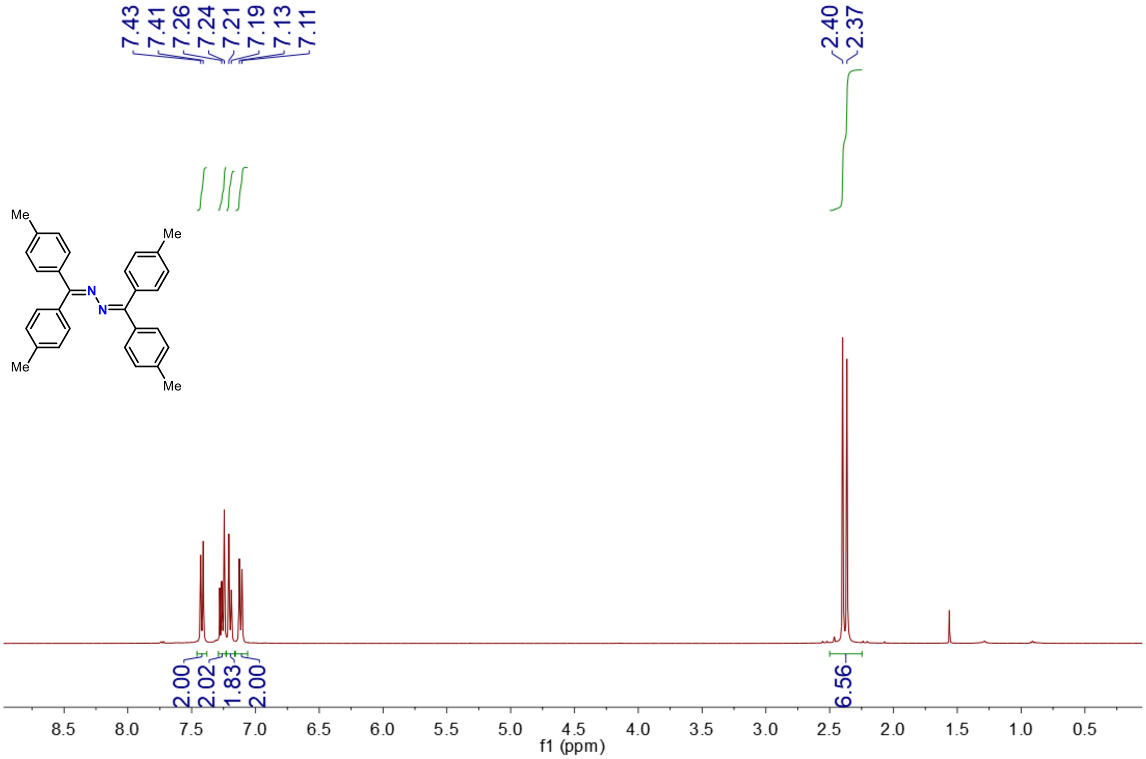
^{19}F{^{1}H}-NMR spectrum (377 MHz, CDCl$_3$, 298 K) of compound **2f**.



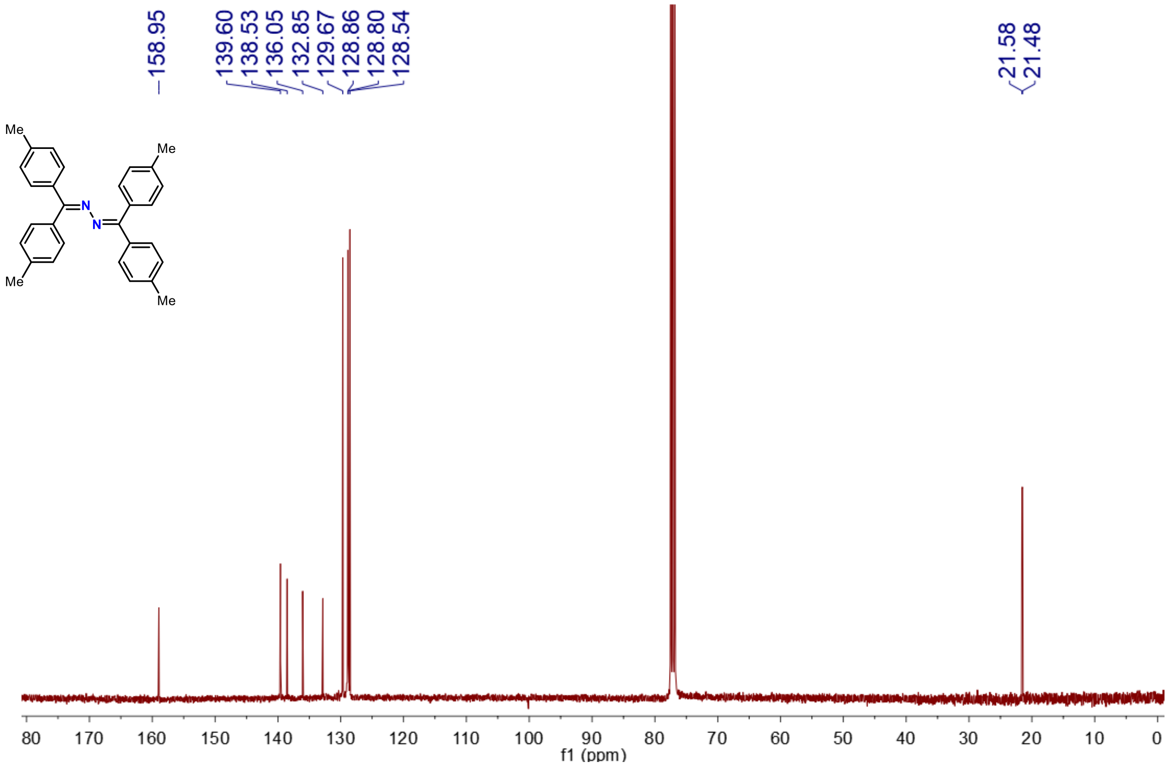
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **2g**



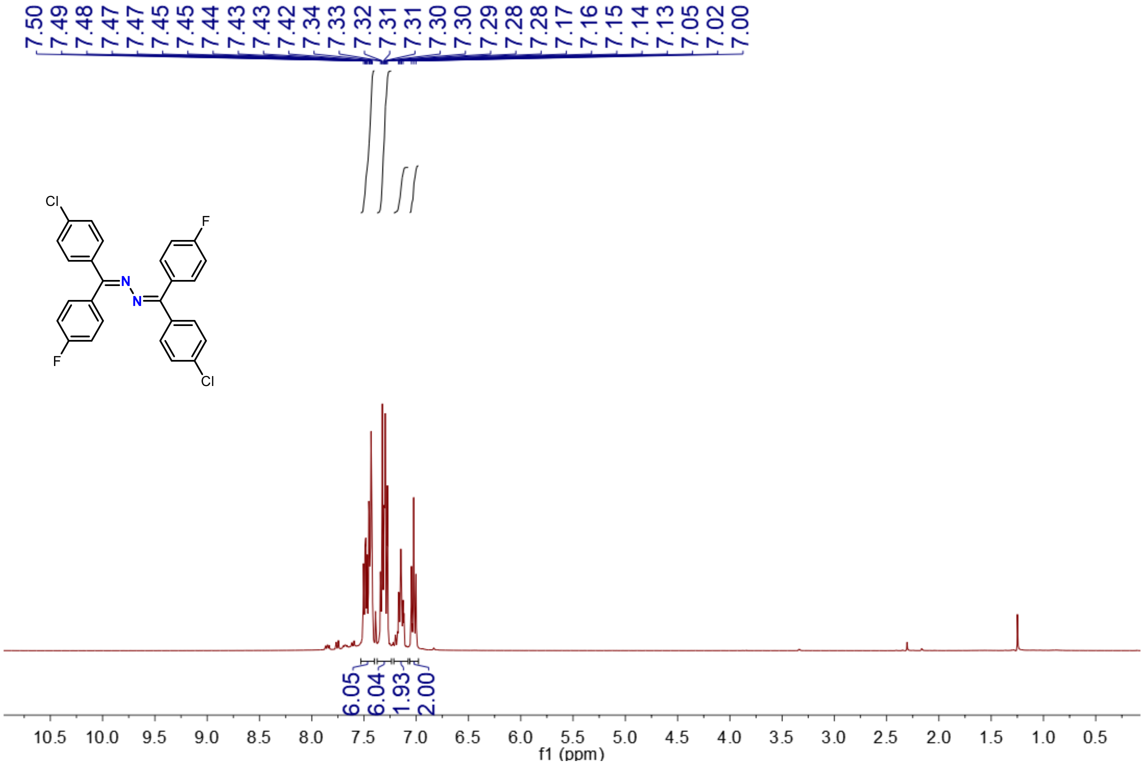
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **2g**.



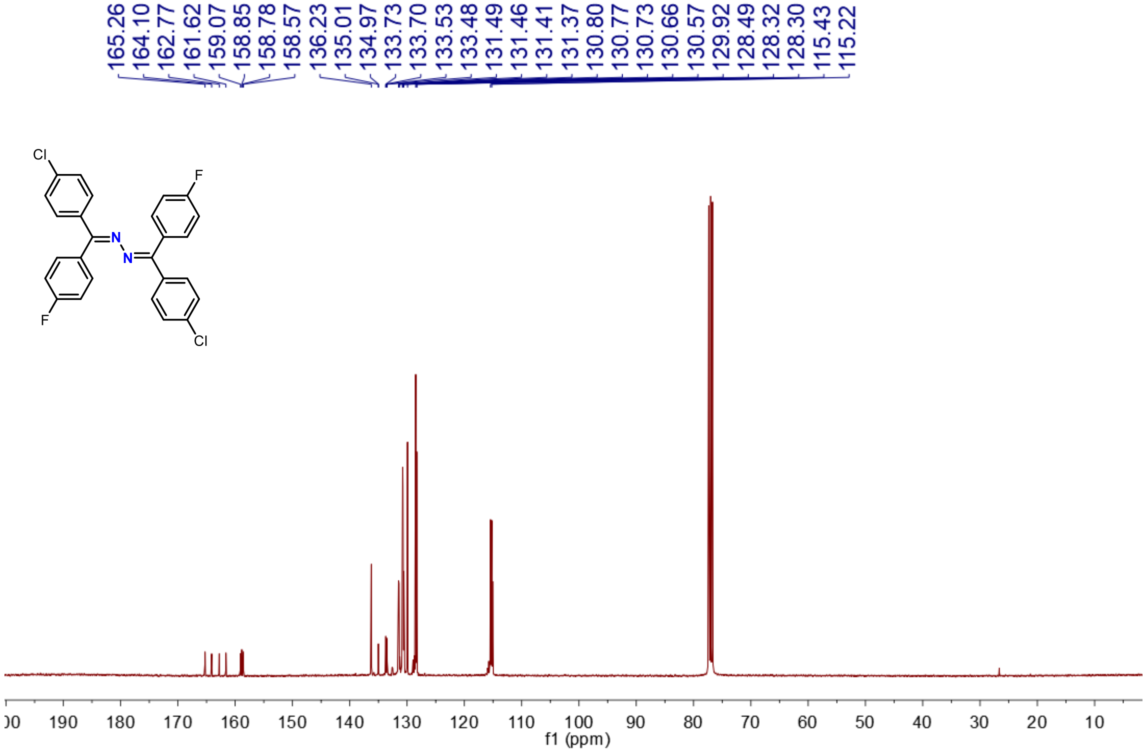
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **2h**.



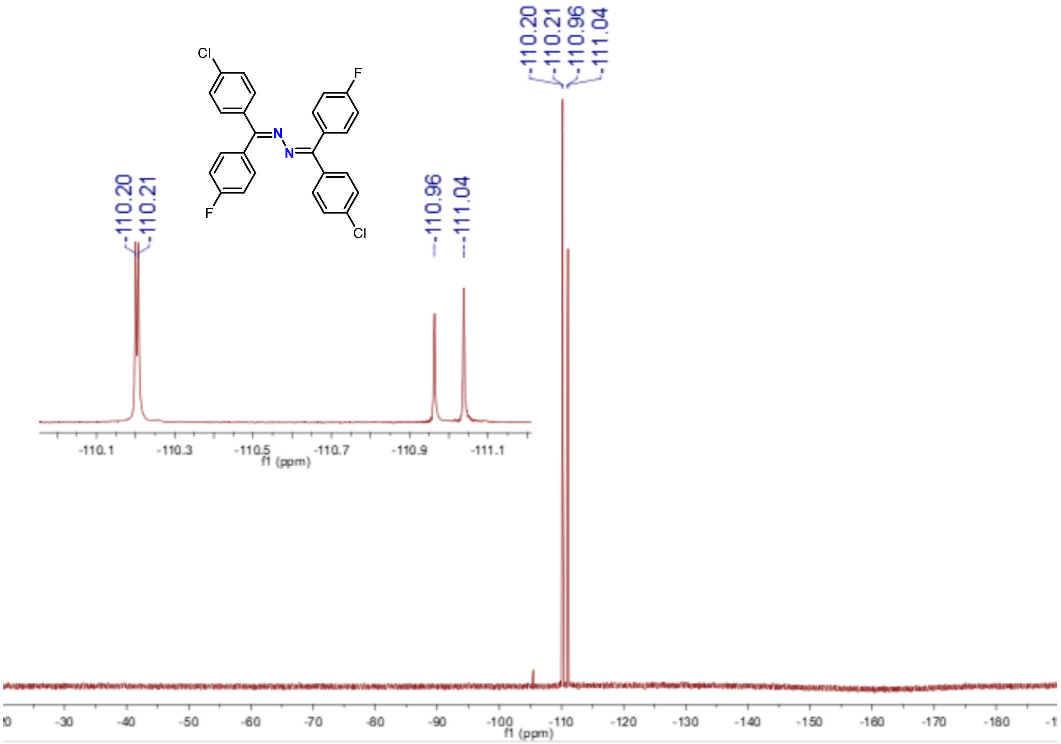
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **2h**.



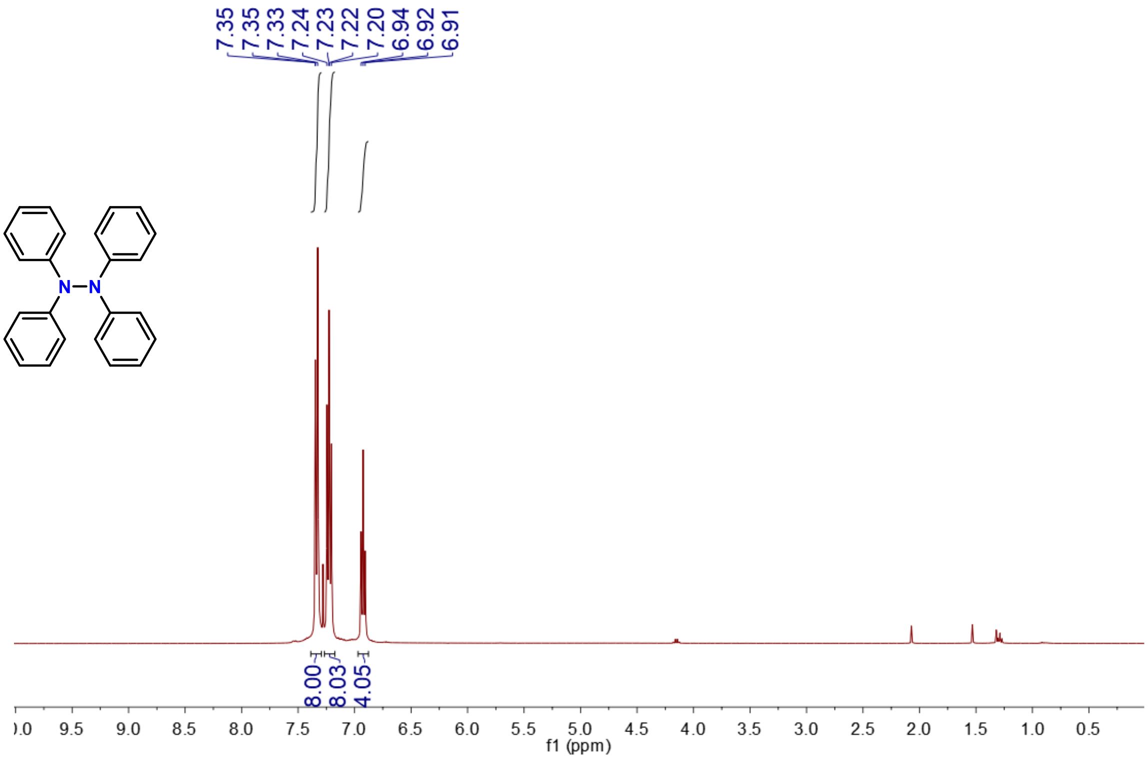
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **2i**.



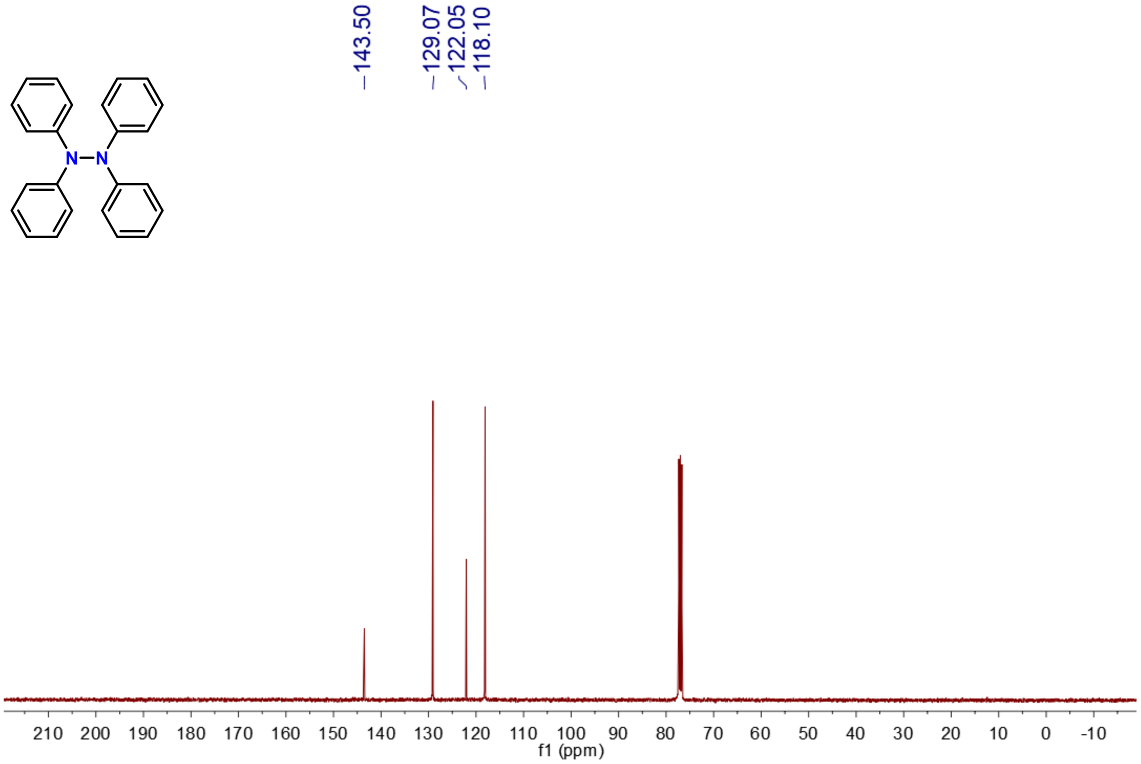
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **2i**.



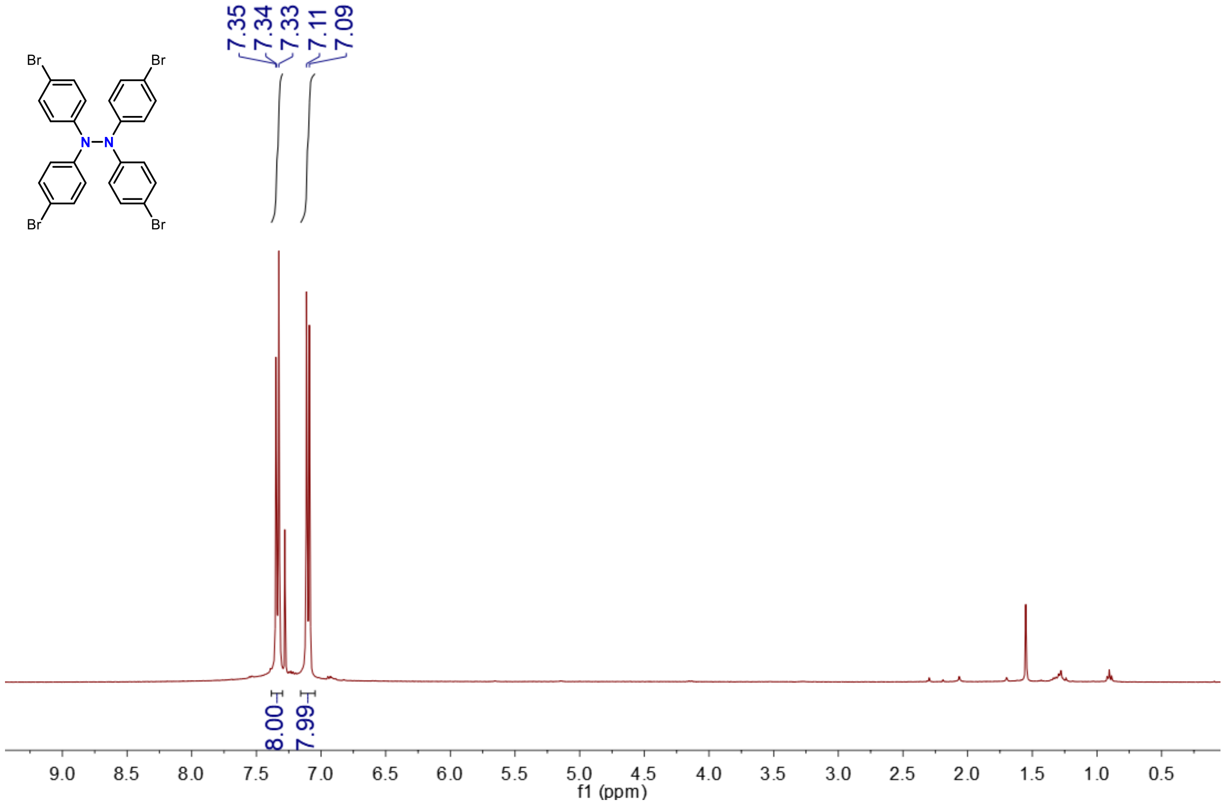
$^{19}F\{^{1}H\}$-NMR spectrum (377 MHz, $CDCl_3$, 298 K) of compound **2i**.



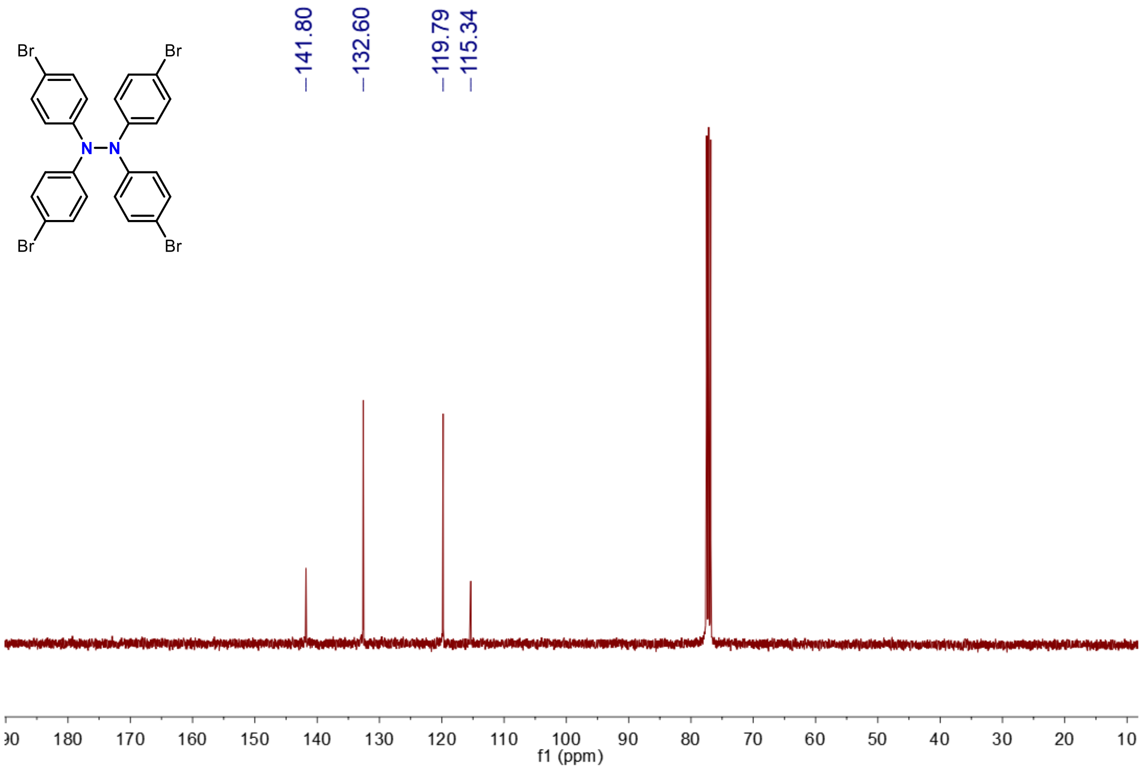
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **4a**.



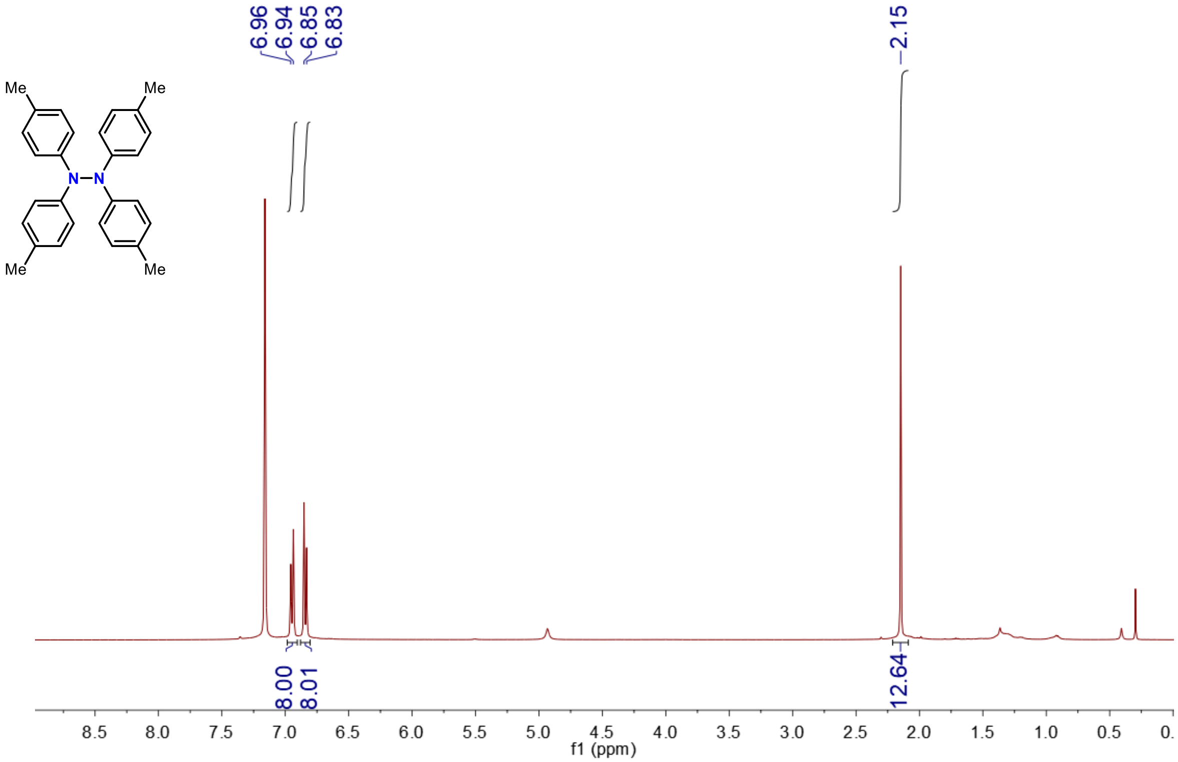
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **4a**.



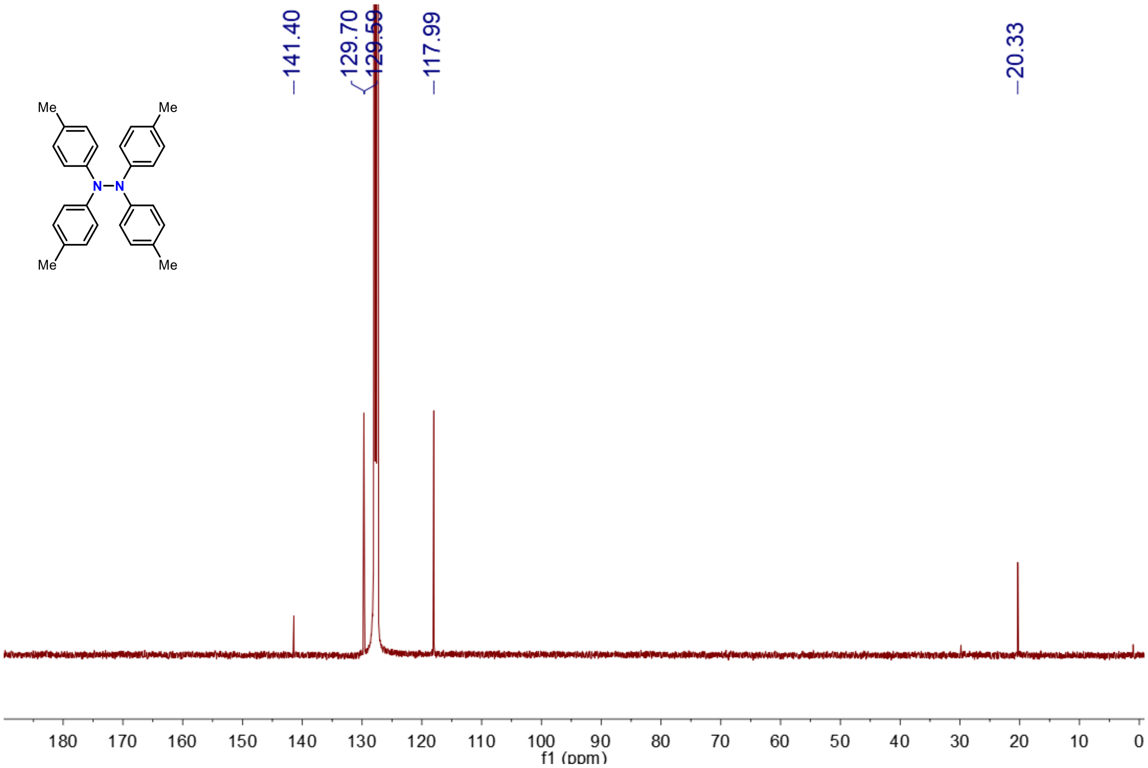
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **4b**.



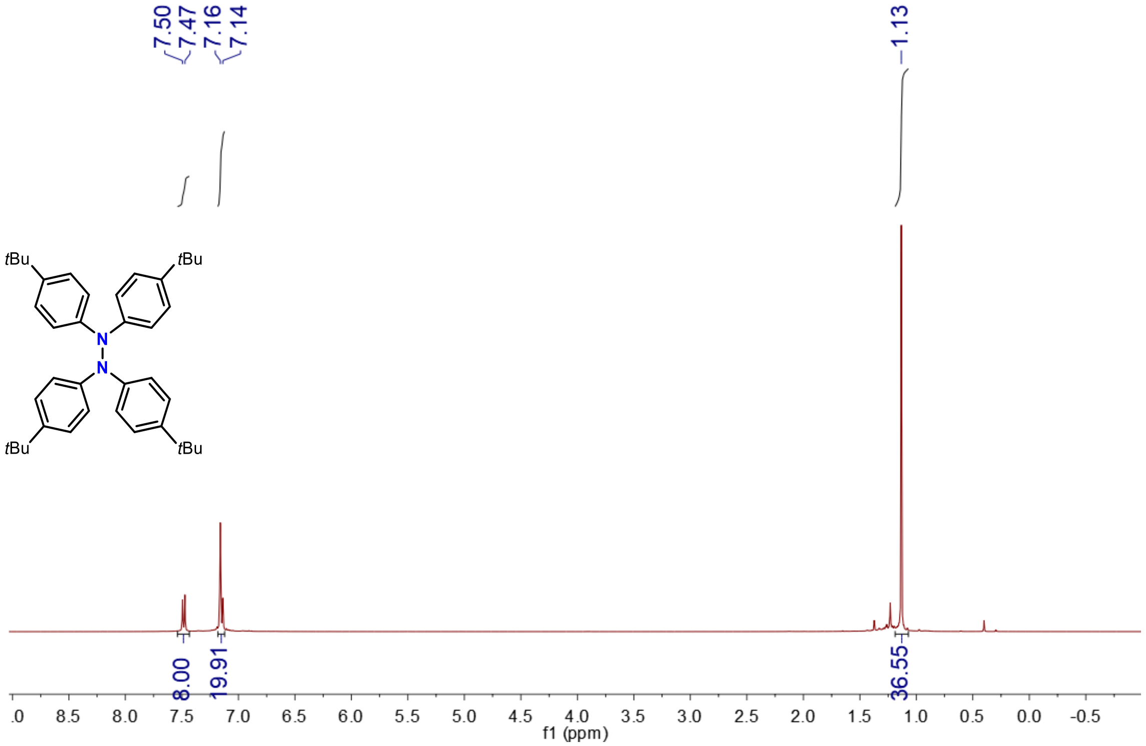
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **4b**.



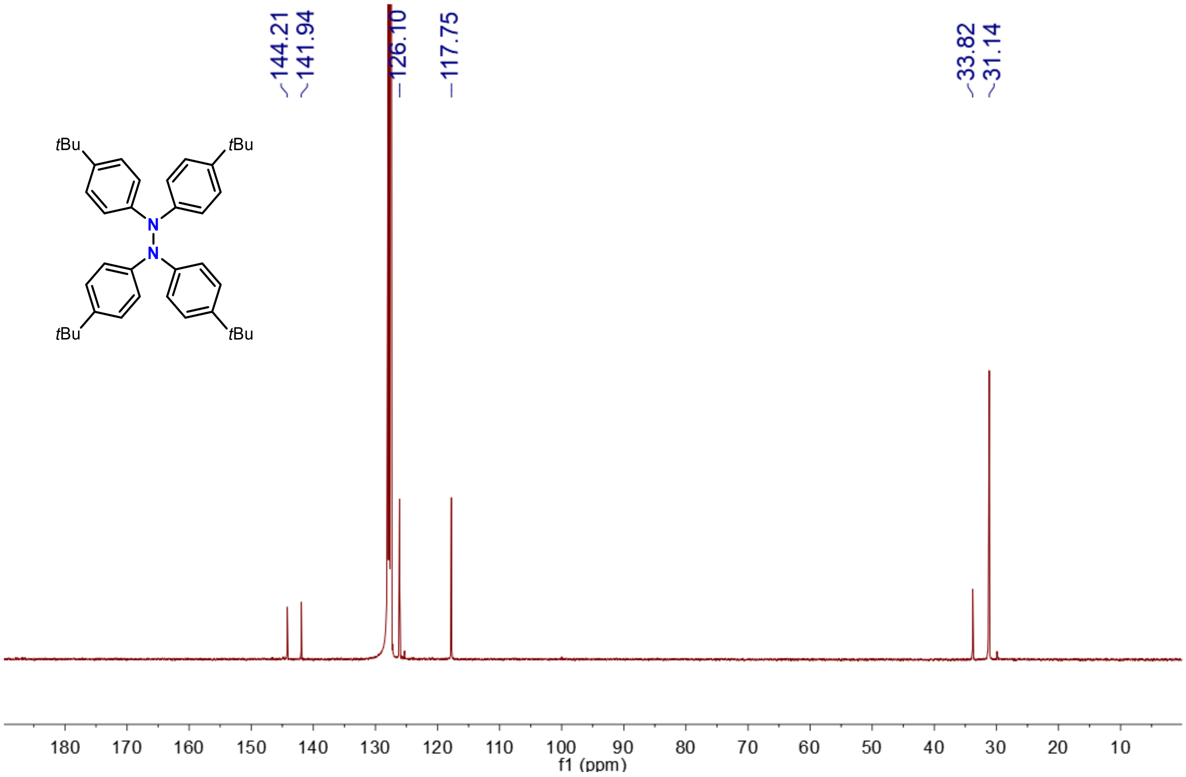
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **4c**.



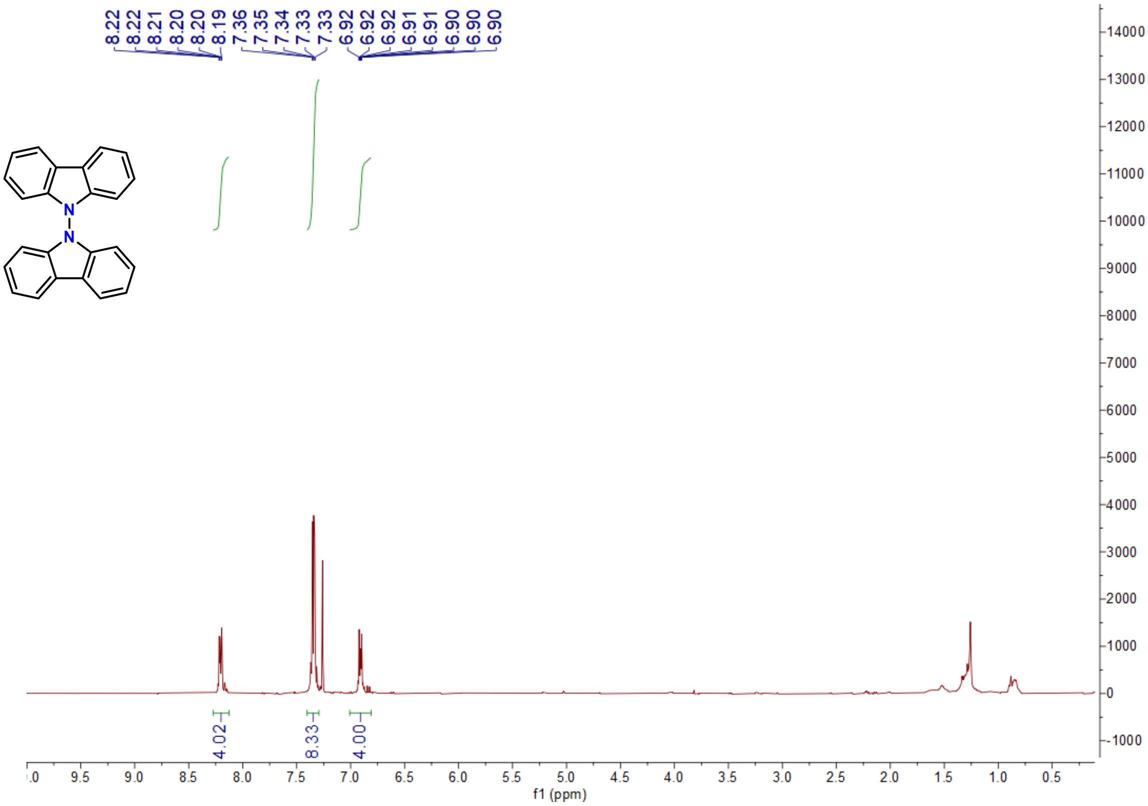
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **4c**.



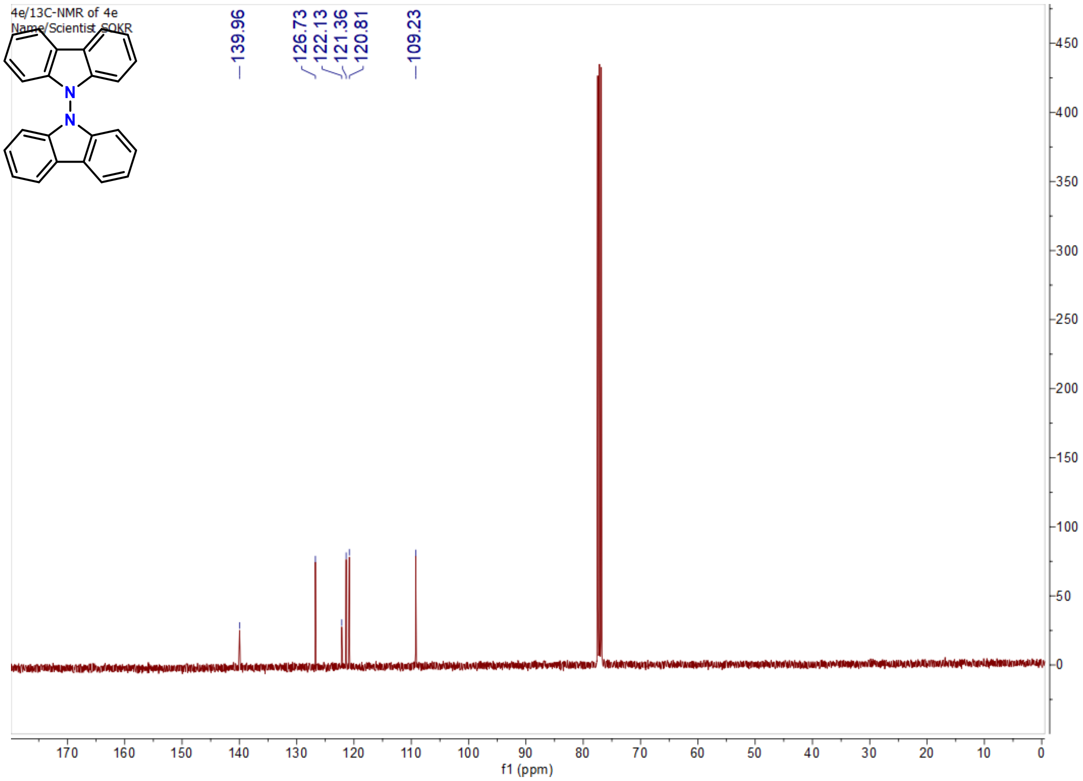
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **4d**



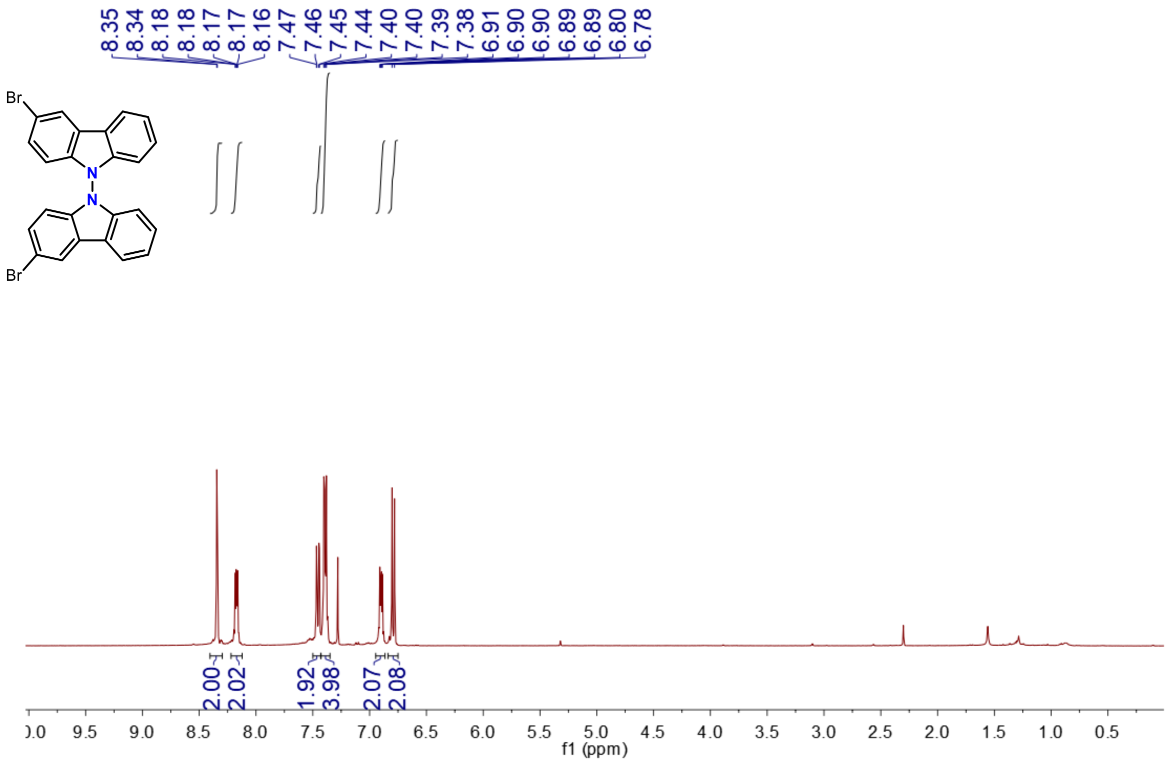
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **4d**.



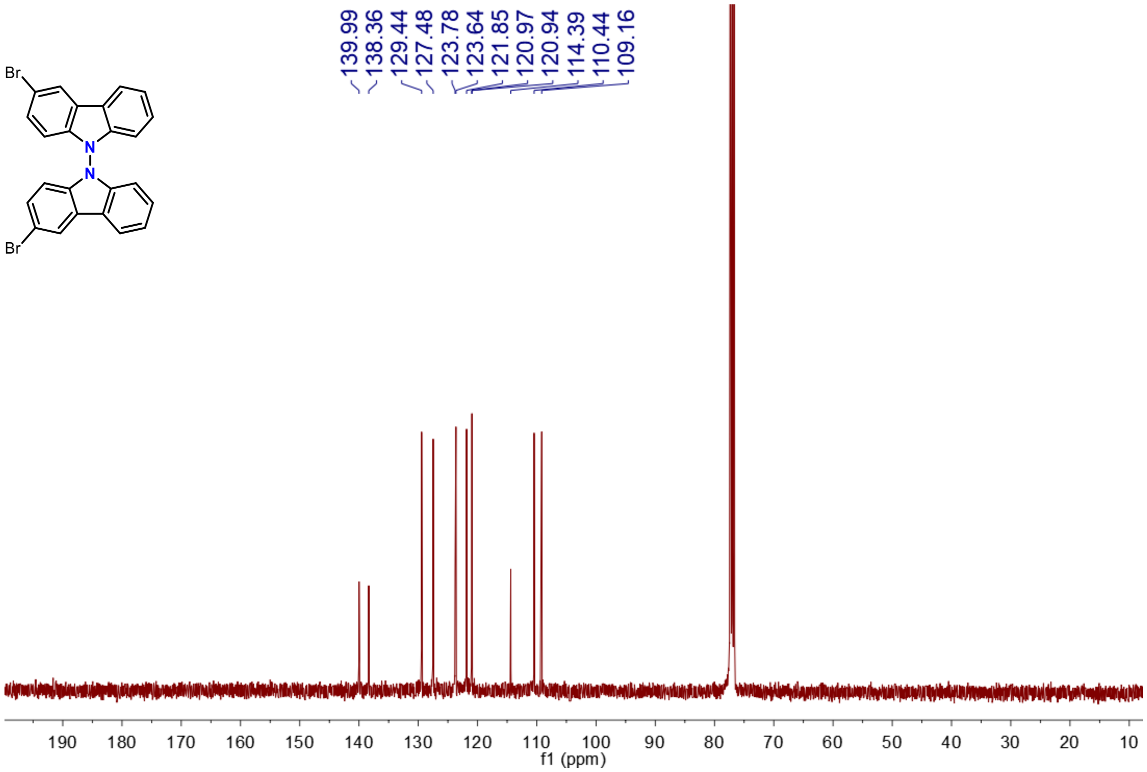
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **4e**.



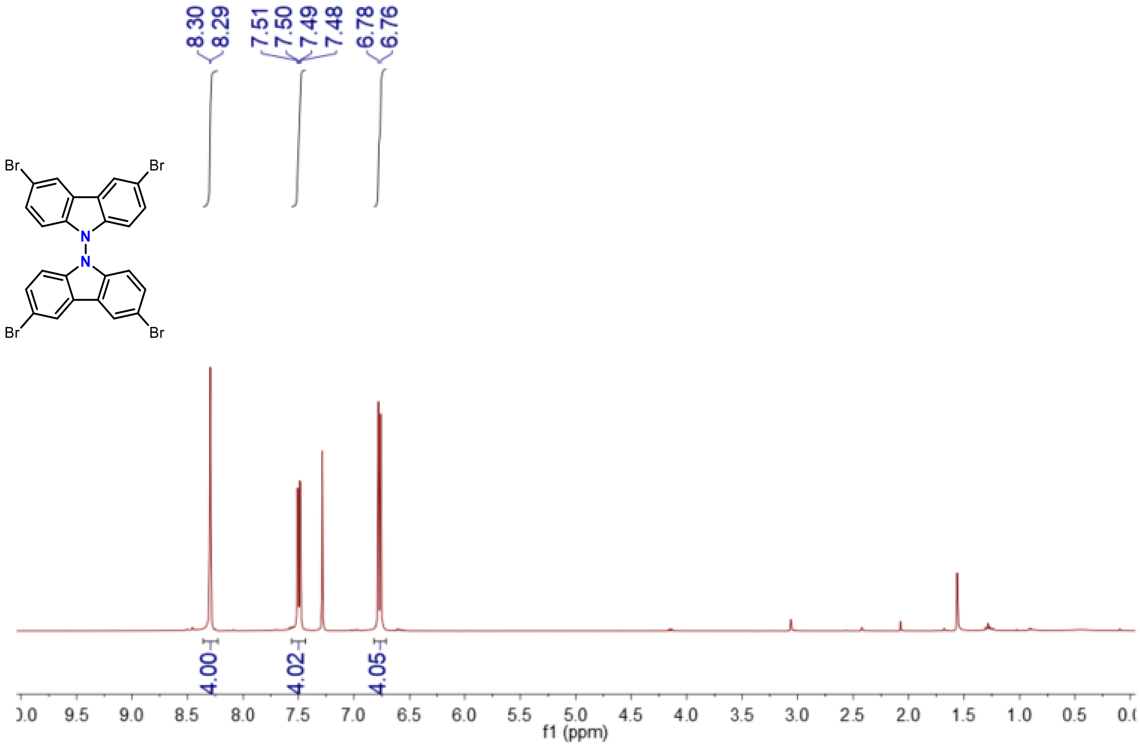
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **4e**.



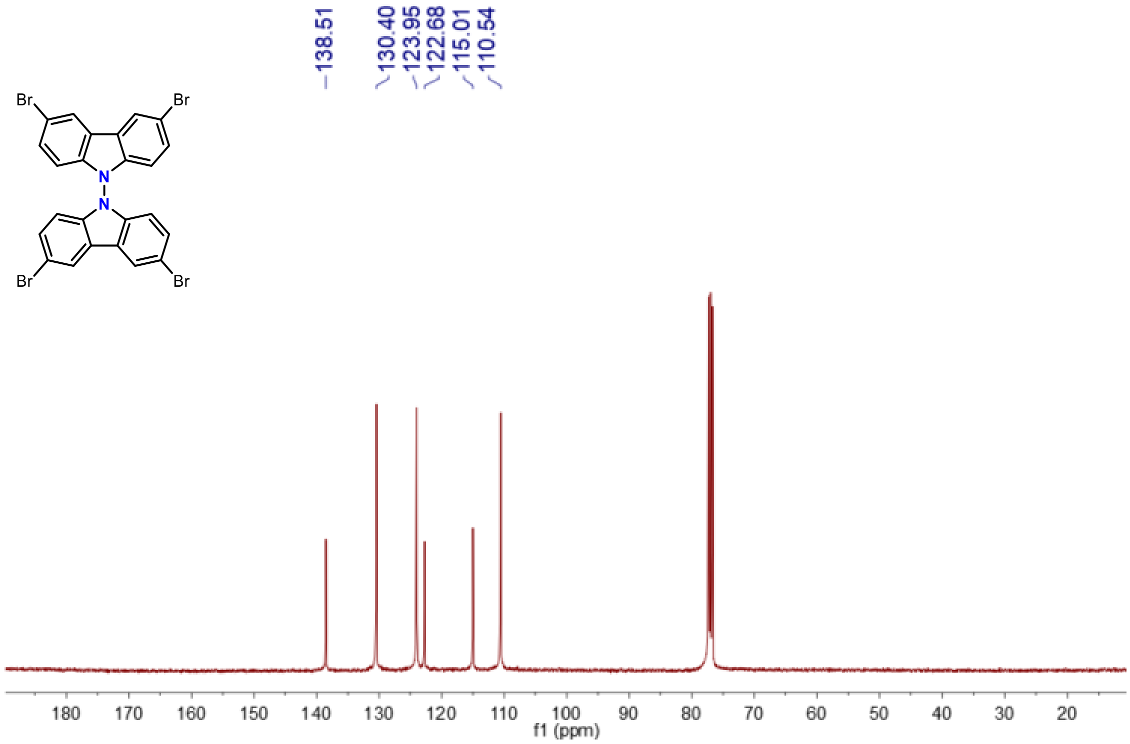
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **4f**.



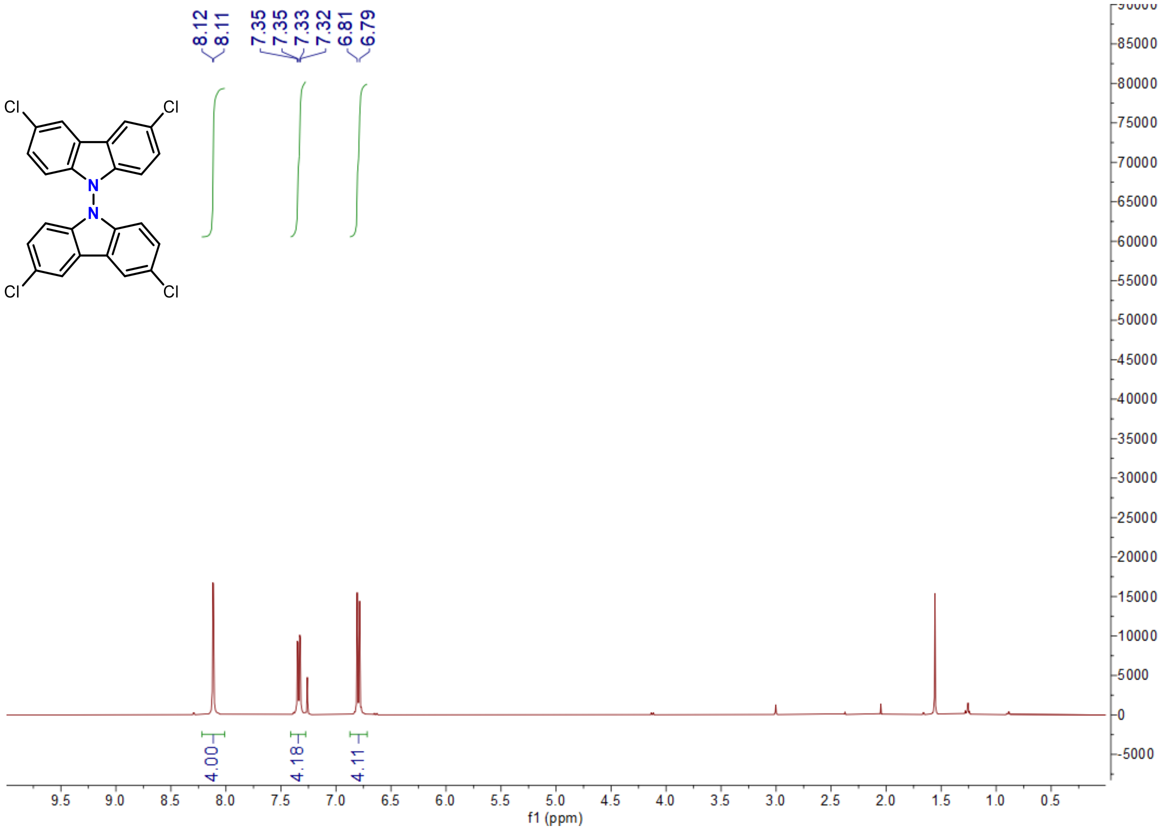
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **4f**.



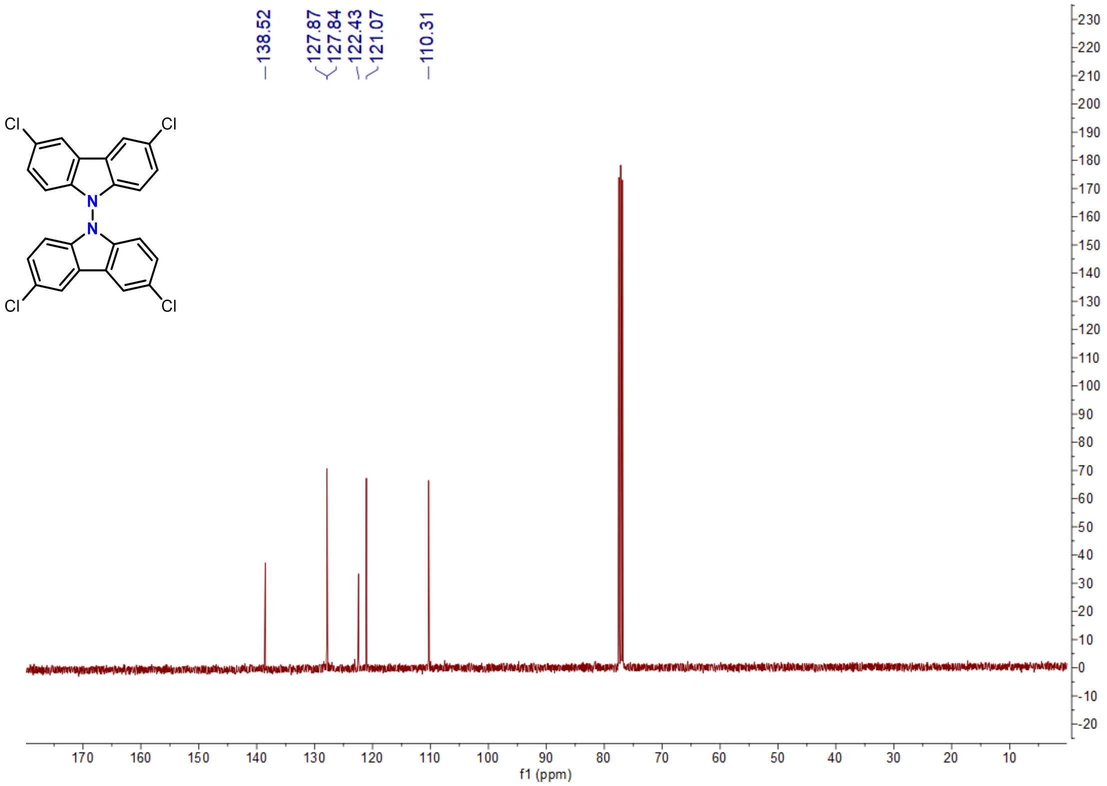
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **4g**.



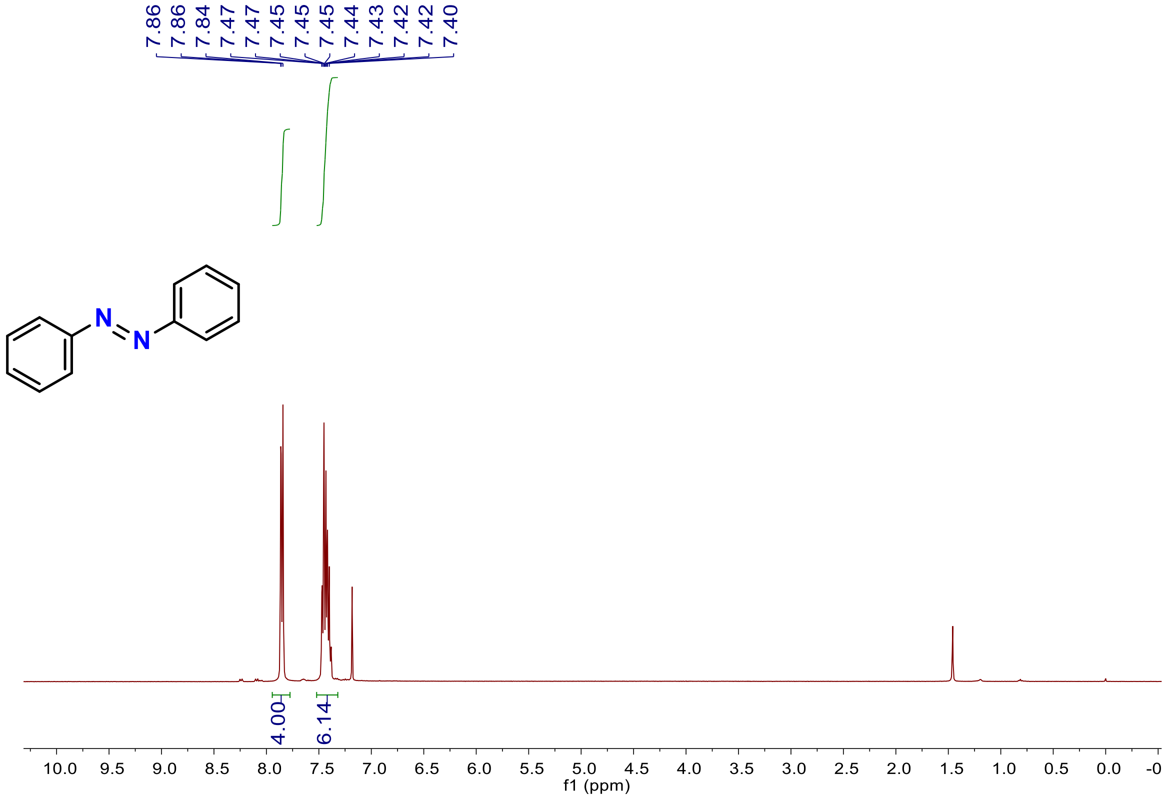
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **4g**.



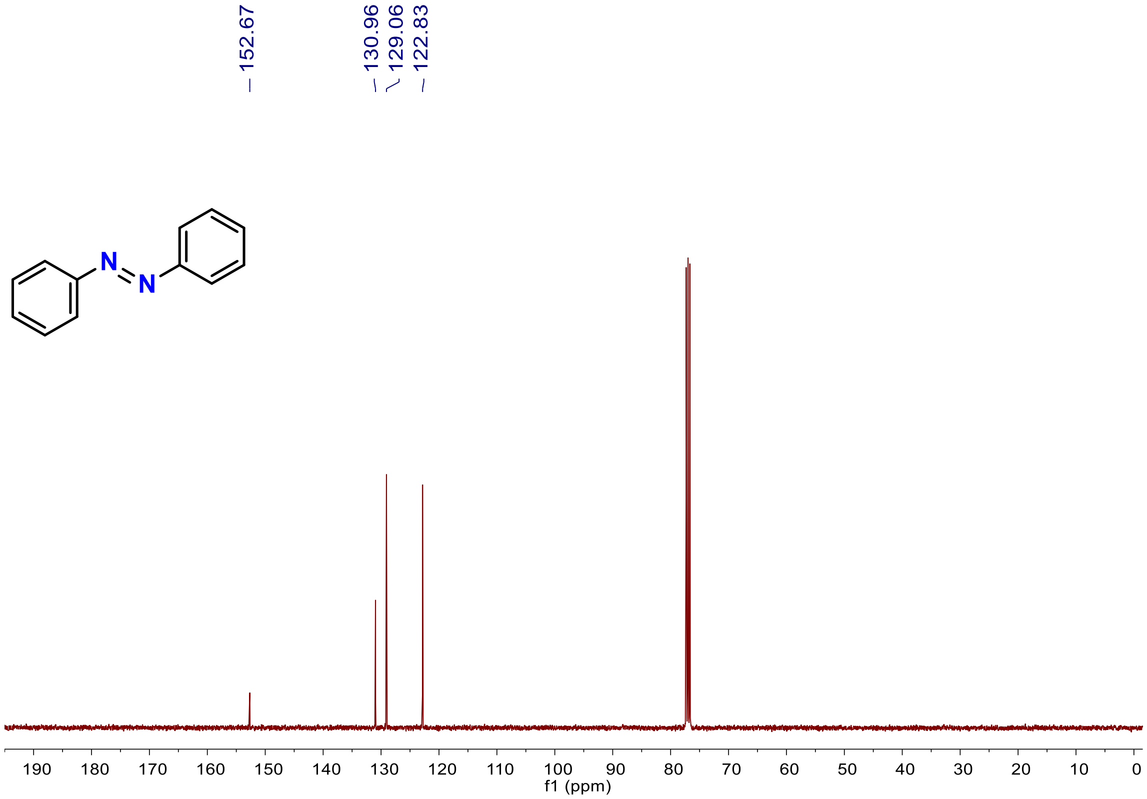
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **4h**.



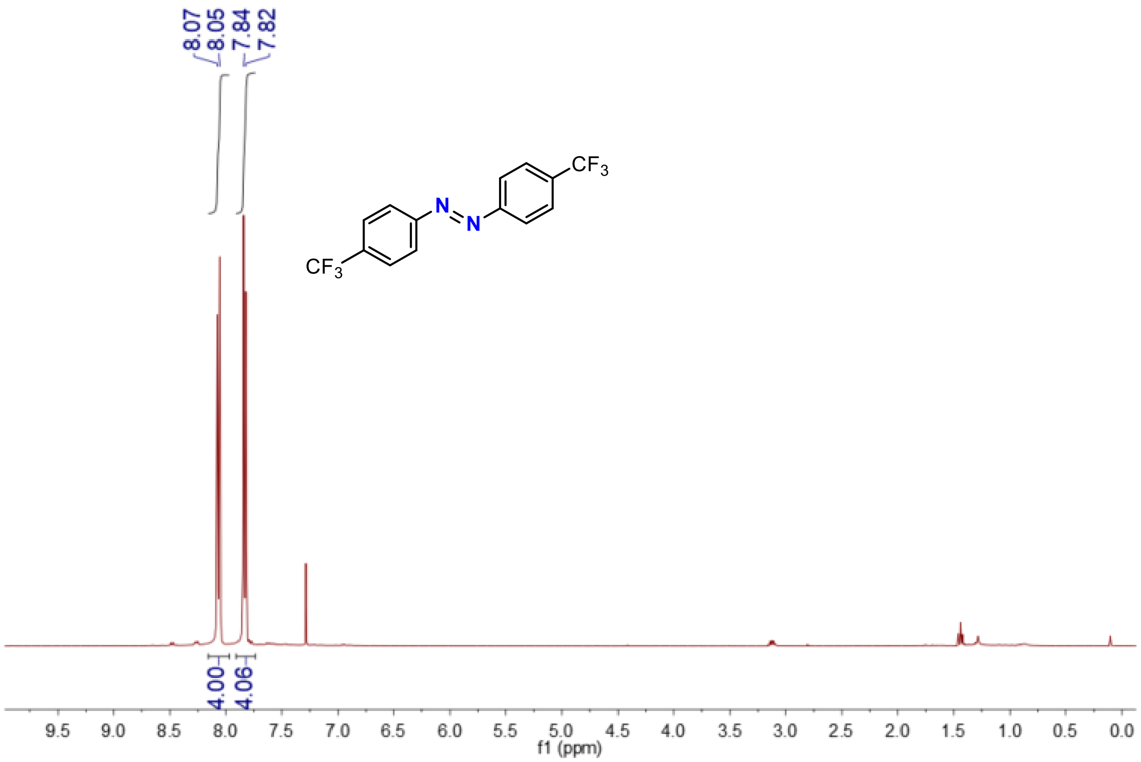
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **4h**.



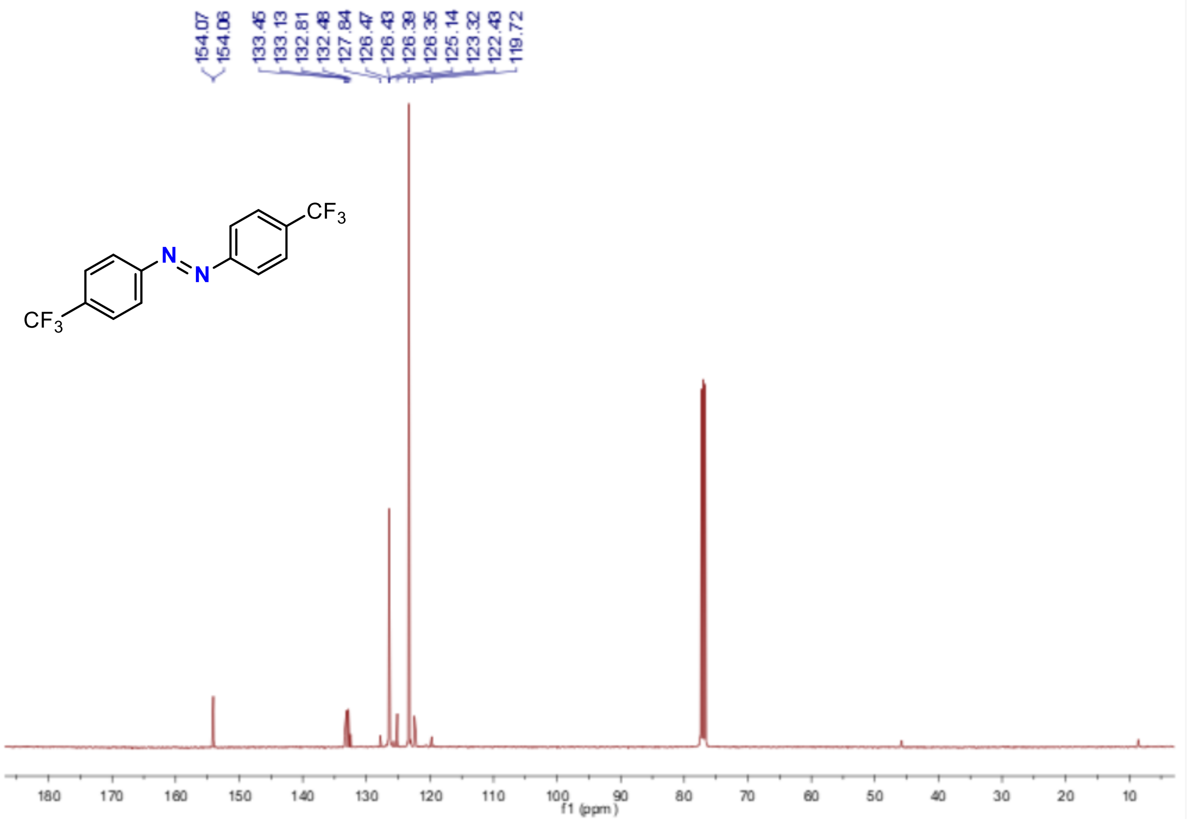
^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **6a**.



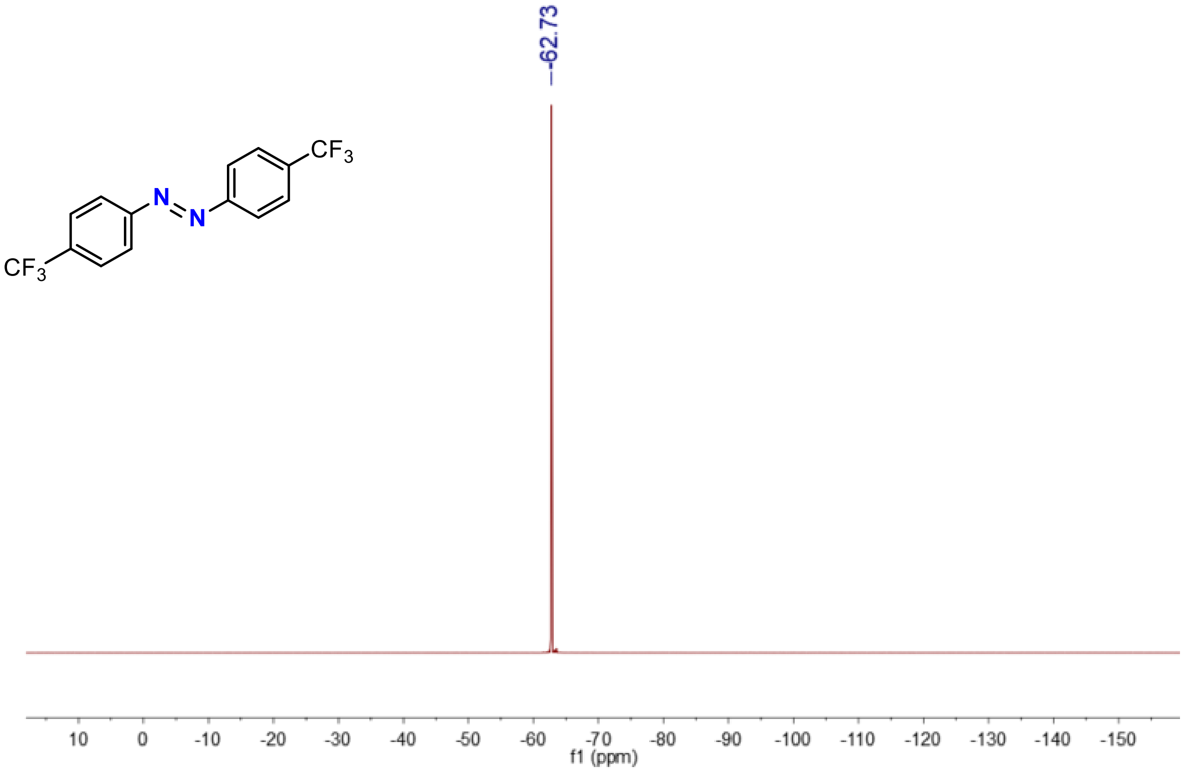
^{13}C-NMR spectrum (101 MHz, CDCl$_3$, 298 K) of compound **6a**.



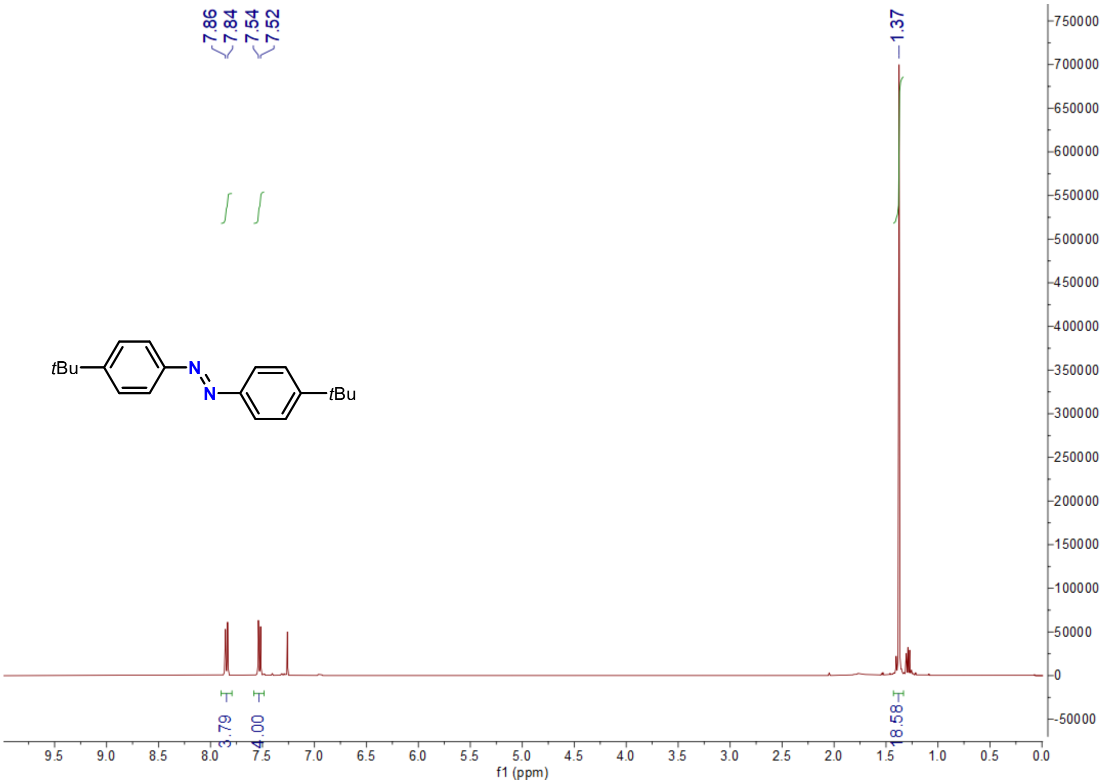
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **6b**.



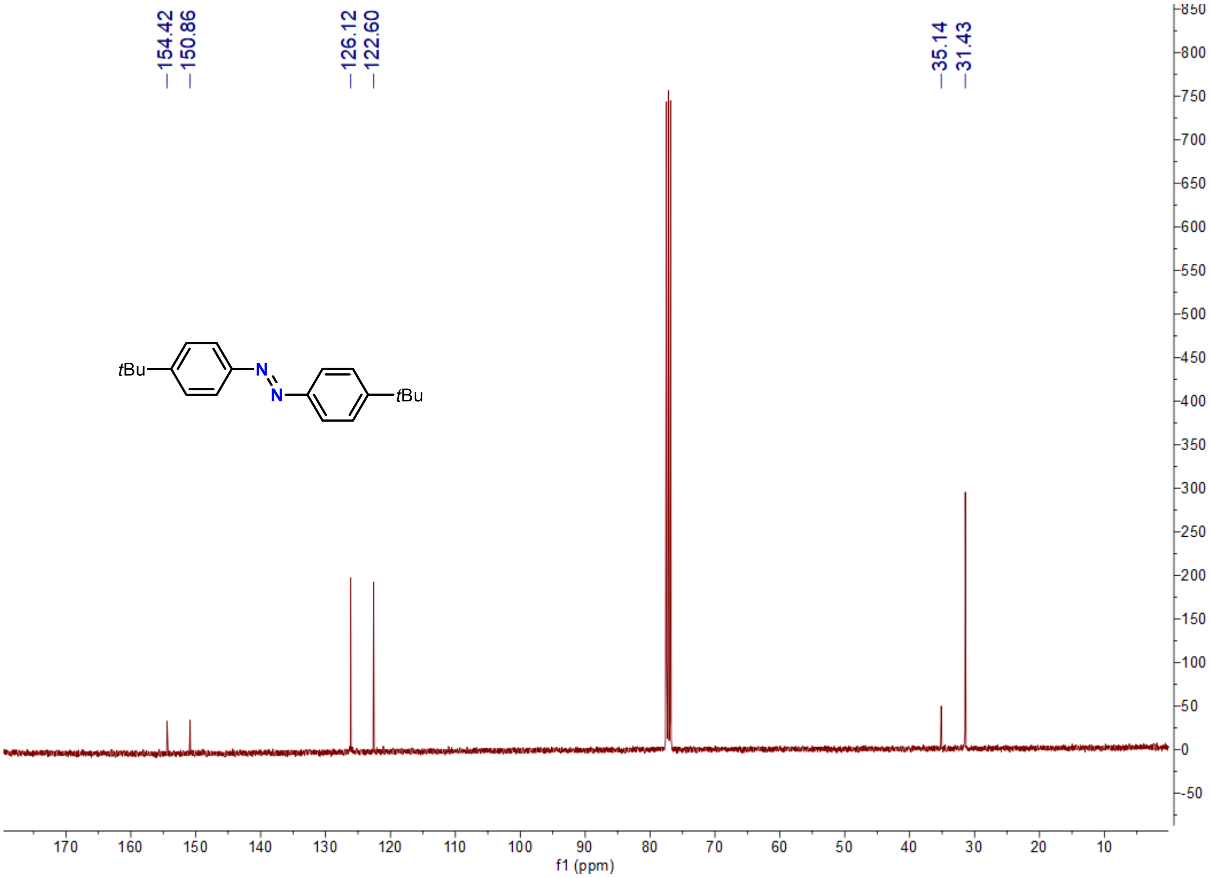
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **6b**.



$^{19}F\{^1H\}$-NMR spectrum (377 MHz, $CDCl_3$, 298 K) of compound **6b**.



^1H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **6c**.



^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **6c**.