

Supporting Information

for

Synthesis, structural, and photophysical properties of pyrazolyl bis(pentafluorophenyl) boron complexes

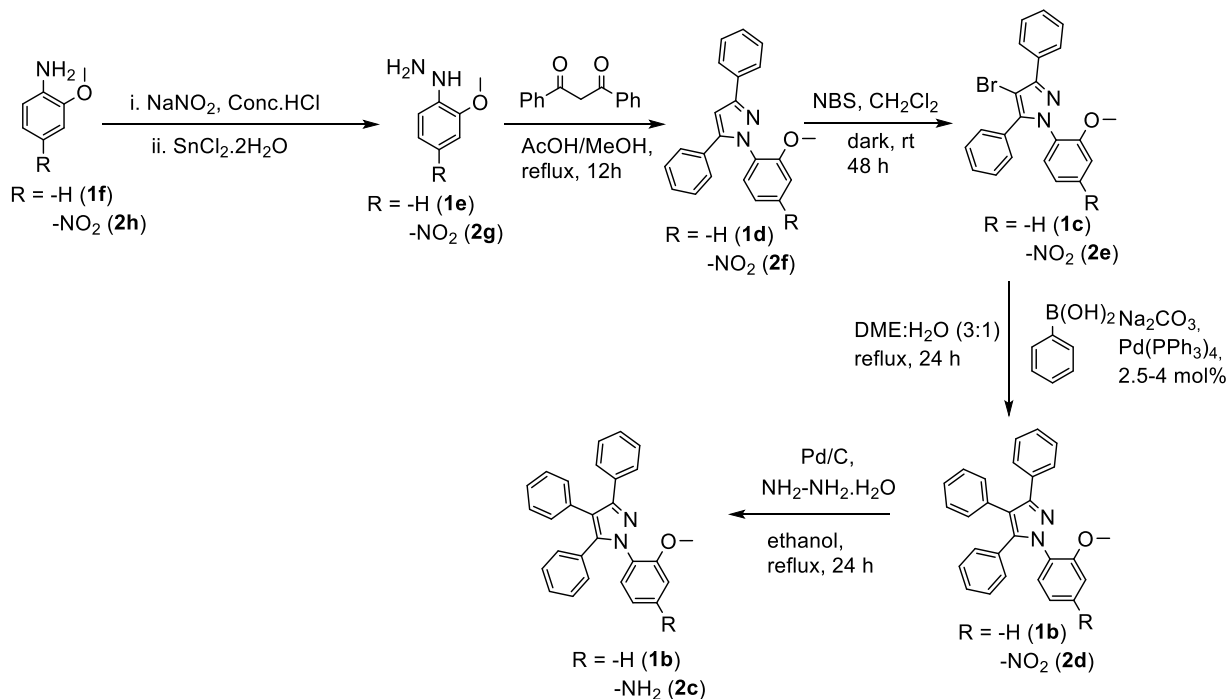
Anna Chandrasekar Murali,^[a] Preeta Pratakshya,^[a] Pratiksha Patel,^[a] Prakash Nayak,^[a] Saravanan Peruncheralathan,^[a] Krishnan Venkatasubbaiah*^[a]

^aSchool of Chemical Sciences, National Institute of Science Education and Research (NISER), an OCC of Homi Bhabha National Institute, Bhubaneswar-752050, Odisha (India). *E-mail: krishnv@niser.ac.in

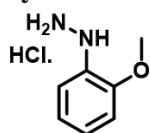
Experimental section:

General information: All the reactions were carried out under N₂ atmosphere using standard glove box, Schlenk line and vacuum line techniques. Solvents and other general reagents were purified according to standard procedures. All the reactions were monitored by thin layer chromatography. Nuclear magnetic resonance spectra were recorded on a 400 MHz or 700MHz Fourier transform NMR spectrometer (JEOL or Bruker) with CDCl₃ as a solvent. ¹¹B and ¹⁹F NMR spectra were externally referenced to BF₃.Et₂O in CDCl₃ (δ=0 ppm) and α,α,α-trifluoro toluene in CDCl₃ (δ=-63.73 ppm), respectively. Chemical shifts are reported in δ ppm (parts per million) using residual solvent protons as the internal standard (δ 7.26 for CDCl₃ in ¹H NMR, δ 77.16 for CDCl₃ in ¹³C NMR). Coupling constants are reported as J values in hertz (Hz). Splitting patterns are designated as s(singlet), d(doublet), t(triplet), q(quartet), dd(doublet of doublet), dt(doublet of triplet), m(multiplet) and br(broad). HRMS were recorded using Waters XEVO G2-XS QTOF mass spectrometer. Elemental analyses were performed in a Euro Vector EA 3000 CHNS analyzer. UV – Visible spectra were recorded on Agilent Technologies Cary 60 UV/Visible spectrometer. Fluorescence spectra and quantum yield were measured using Edinburgh spectrofluorimeter instrument FS5. For the measurement of absolute quantum yield, the concentration of the boron compounds was such as to give an absorbance of around 0.1 at excitation wavelength. Absolute total quantum yields were measured using an integrating sphere (Edinburgh instrument FS5) mounted in SC-30 compartment of the spectrofluorimeter, The time-resolved fluorescence studies, a time-correlated single-photon counting (TCSPC) spectrometer (Edinburgh, OB920) has been used with a laser of 330 nm as a source of excitation and an MCP photomultiplier (Hamamatsu R3809U-50) is used as a detector. In order to check the laser profile, a water:ludox (4:1) solution has been used. Using water:ludox (4:1) solution, the instrument response function (IRF) has been obtained. Single crystal X-ray diffraction data were collected on Rigaku Super Nova fine-focused dual diffractometer, with Cu Kα radiation (λ = 1.54178 Å) and Mo-Kα radiation (0.71073 Å) equipped with a PILATUS200K. The structures were solved by direct methods using SHELXT program and refined with least squares minimization with SHELXL using Olex2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. The SQUEEZE procedure of Olex2 was applied for removing one of the disorder chloroform solvent in compound 4 and 5. Boron compounds **1-6** are not stable in the acidic medium. Hence, we avoided column chromatography for purification. Photo stability of compound **1** and **4** are investigated with continuous illumination of 365 nm UV light for 30 min. The ¹H-NMR result that both the boron compounds are stable under UV light conditions. The films were prepared by mixing of polymethylmethacrylate (PMMA) (95 mg) and compound **2** (5 mg) in distilled THF, stirred (1h) and coated in a glass plate, then dried at open air for 24 h.

Starting materials: Commercially available 1,3-diphenylpropanedione, acetophenone, *o*-anisidine, 4-nitro-2-methoxyaniline, phenylboronic acid, stannous chloride, sodium nitrite, hydrazine monohydrate, Pd/C, 4-nitrophenylhydrazine, N-bromosuccinimide, copper(I) iodide, 1,10-phenanthroline, sodium carbonate, phenylboronic acid, iodobenzene, sodium cyanoborohydride, boron tribromide, potassium *tert*-butoxide, formaldehyde (37%) solution, magnesium flakes, carbon disulphide, methyl iodide, Palladium tetrakis(triphenylphosphine), sodium hydride, tris(pentafluorophenyl)borane were purchased from Alfa aesar and Sigma Aldrich. Glacial acetic acid, HCl, H₂SO₄ was obtained from Spectrochem.

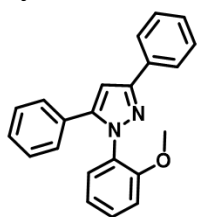


Synthesis of (2-methoxyphenyl)hydrazine hydrochloride (1e)



o-Anisidine (3.9 mL, 34.35 mmol, 1.0 eq) was added slowly to conc. HCl (50 mL) at 0 °C to form a suspension. A solution of sodium nitrite (2.40 g, 34.69 mmol, 1.1 eq) in distilled water was added dropwise to the suspension at -30 °C. The temperature was slowly allowed to reach 0 °C over a period of 2h. The reaction mixture was then added slowly to a suspension of stannous chloride (13.20 g, 69.39 mmol, 2.0 eq) in conc. HCl (25 mL) at -30 °C. The temperature was slowly allowed to reach room temperature while continuing stirring over a period of 3-4h. The reaction mixture was filtered and the precipitate was washed with cold conc. HCl and then vacuum dried. Without further purification the compound was used for the next reaction.

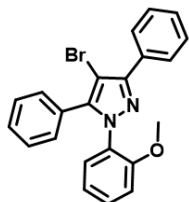
Synthesis of 1-(2-methoxyphenyl)-3,5-diphenyl-1H-pyrazole (1d)



A mixture of 1,3-diphenylpropanedione (4.70 g, 20.90 mmol, 1.0 eq), (2-methoxyphenyl)hydrazine hydrochloride (1e) (4.80 g, 27.24 mmol, 1.3 eq), glacial acetic acid (45 mL) and methanol (45 mL) was refluxed for 12h. To the reaction mixture water was added (100 mL), the reaction mixture was extracted using dichloromethane (3 x 150 mL). The extracted organic phase was washed with brine and dried over anhydrous sodium sulphate. The solvent was concentrated and the product (1d) was purified using silica gel column chromatography (*n*-hexane/EtOAc (98:2)). Yield: 4.33 g (63.0%). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.48

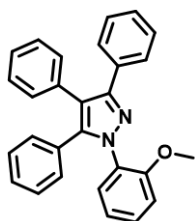
– 7.29 (m, 4H), 7.26 (s, 5H), 7.11 – 7.02 (m, 1H), 6.90 – 6.82 (m, 2H), 3.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 154.2, 152.0, 146.3, 133.3, 131.2, 130.1, 129.5, 129.0, 128.6, 128.3, 128.0, 127.9, 127.6, 126.0, 121.1, 112.4, 103.4, 55.5. HR-MS (ESI): calculated for C₂₂H₁₉N₂O ([M + H]⁺): 327.1492, observed : 327.1441.

Synthesis of 4-bromo-1-(2-methoxyphenyl)-3,5-diphenyl-1H-pyrazole (1c)



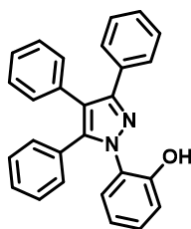
A mixture of 1-(2-methoxyphenyl)-3,5-diphenyl-1H-pyrazole (**1d**) (3.30 g, 10.20 mmol, 1.0 eq) and N-bromosuccinimide (2.20 g, 12.20 mmol, 1.2 eq) was taken in dichloromethane (60 mL). The reaction mixture was stirred at room temperature for 24h. After completion of the reaction, the product was extracted using water and dichloromethane (3 x 60 mL). The organic phase was collected and dried over anhydrous sodium sulphate. The solvent was concentrated and the product (**1c**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (98:2)). Yield: 4.00 g (96.0%). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.45 (m, 3H), 7.43 – 7.38 (m, 1H), 7.35–7.30 (m, 6H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.8, 149.7, 143.8, 132.2, 130.3, 129.4, 129.3, 129.0, 128.8, 128.6, 128.3, 128.2, 128.0, 120.9, 112.1, 96.2, 93.1, 55.3. HR-MS (ESI): calculated for C₂₂H₁₈BrN₂O ([M+H]⁺): 405.0597, 407.0578 observed : 405.0619, 407.0601.

Synthesis of 1-(2-methoxyphenyl)-3,4,5-triphenyl-1H-pyrazole (1b):



A mixture of dimethoxyethane (DME) (70 mL) and water (23 mL) was degassed for 30 minutes and added to a mixture of 4-bromo-1-(2-methoxyphenyl)-3,5-diphenyl-1H-pyrazole (**1c**) (3.50 g, 8.61 mmol, 1.0 eq), tetrakis(triphenylphosphine)palladium (0.40 g, 0.35 mmol, 0.04 eq), phenylboronic acid (1.40 g, 11.4 mmol, 1.2 eq) and sodium carbonate (2.70 g, 27.55 mmol, 3.0 eq) under nitrogen atmosphere. The reaction mixture was refluxed for 24h. After completion of the reaction (monitored via TLC), the reaction mixture was passed through a column of celite. The resultant mixture was extracted using water (100 mL) and dichloromethane (3 x 150 mL). The extracted organic phase was washed with brine and dried over anhydrous sodium sulphate. The solvent was concentrated and the product (**1b**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (98:2)). Yield: 1.65 g (48 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.55 – 7.49 (m, 3H), 7.34 – 7.28 (m, 1H), 7.27 – 7.23 (m, 3H), 7.22 – 7.18 (m, 3H), 7.16 – 7.07 (m, 5H), 7.04 – 6.98 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 154.1, 150.2, 143.2, 133.5, 133.5, 130.9, 130.6, 130.0, 129.6, 129.3, 129.2, 128.6, 128.2, 128.2, 127.8, 127.8, 127.5, 126.6, 120.9, 119.1, 112.1, 55.3. HR-MS (ESI): calculated for C₂₈H₂₃N₂O ([M+H]⁺): 403.1805, observed : 403.1823.

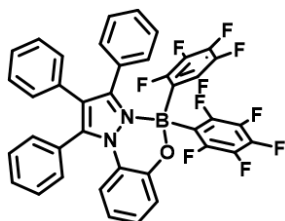
Synthesis of 2-(3,4,5-triphenyl-1H-pyrazol-1-yl)phenol (1a):



1-(2-Methoxyphenyl)-3,4,5-triphenyl-1H-pyrazole (**1b**) (2.00 g, 4.95 mmol, 1.0 eq) was taken in dry CH₂Cl₂ (25 mL). BBr₃ (2.36 mL, 24.85mmol, 5.0 eq) in dry CH₂Cl₂ (30 mL) was added dropwise to the reaction mixture under nitrogen atmosphere at -78 °C. The temperature was slowly allowed to reach to room temperature while stirring for 12h. The reaction mixture was then added to ice-cold water and filtered. The filtrate was collected and extracted using water and dichloromethane (3 x 100 mL). The extracted organic phase was washed with brine and dried over anhydrous sodium sulphate. The solvent was concentrated and the product (**1a**) was purified using silica gel column chromatography (*n*-hexane/EtOAc/ CH₂Cl₂

(80:10:10)). Crystallisation was done using CH₂Cl₂/EtOH. Yield: 1.5 g (78 %). ¹H NMR (400 MHz, CDCl₃) δ = 9.83 (s, 1H), 7.54 – 7.48 (m, 2H), 7.34 – 7.22 (m, 9H), 7.18 – 7.13 (m, 2H), 7.13 – 7.07 (m, 4H) 6.63 – 6.56 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ = 150.8, 149.9, 142.2, 133.6, 132.4, 132.2, 130.8, 130.4, 129.6, 128.8, 128.6, 128.4, 128.4, 128.4, 128.3, 128.3, 127.1, 125.4, 120.8, 119.1, 118.6. HR-MS (ESI): calculated for C₂₇H₂₁N₂O ([M+H]⁺): 389.1648, observed : 389.1676.

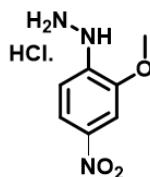
Synthesis of complex 1: 2-(3,4,5-Triphenyl-1H-pyrazol-1-yl)phenol (**1a**) (0.30 g, 0.77 mmol,



1.0 eq) was taken in a sealed tube and tris(pentafluorophenyl)borane (0.43 g, 0.85 mmol, 1.1 eq) was added to it under nitrogen atmosphere followed by dry toluene (10 mL) and refluxed for 24h. The reaction mixture was cooled transferred to a round bottom flask and the solvent was evaporated by vacuum distillation leaving behind a glassy residue. Dry hexane (25 mL) was added to the round bottom flask and sonicated for 5 min. The white precipitate formed was collected by

filtration and dried under vacuum. Crystallisation was done using CH₂Cl₂/*n*-hexane. Yield: 0.30 g (54 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.51 (t, *J*=8.0, 1H), 7.43 (t, *J*=8.0, 2H), 7.35 – 7.28 (m, 2H), 7.22 – 7.12 (m, 2H), 7.11 – 6.98 (m, 8H), 6.81 (d, *J*=8.0, 2H), 6.55 (d, *J*=4.0, 2H). ¹³C NMR (101 MHz, CDCl₃) δ = 150.4, 148.1 (d, *J* = 243.41 Hz), 147.9, 140.3 (d, *J* = 260.58 Hz) 136.9 (d, *J* = 248.92 Hz) 130.6, 130.5, 130.3, 129.8, 129.6, 129.5, 128.7, 128.4, 128.2, 127.9, 127.5, 124.7, 123.8, 120.9, 120.8, 120.0. ¹⁹F NMR (376 MHz, CDCl₃) δ = -132.98 (bs, 4F, Pf), -156.33 (t, 2F, Pf), -164.12 (bs, 4F, Pf). ¹¹B NMR (128 MHz, CDCl₃) δ -0.72. HR-MS (ESI): calculated for C₃₉H₂₀BF₁₀N₂O ([M+H]⁺): 733.1545, observed : 733.1591. Anal. Calcd for C₃₉H₁₉BF₁₀N₂O: C, 63.96; H, 2.62, N, 3.83. Found: C, 64.35; H, 1.99, N, 4.19.

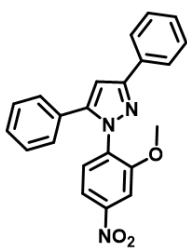
Synthesis of (2-methoxy-4-nitrophenyl)hydrazine hydrochloride (2g)



2-Methoxy-4-nitroaniline (15.10 g, 90.00 mmol, 1.0 eq) was added slowly to conc. HCl (100 mL) at 0 °C to form a suspension. A solution of sodium nitrite (9.3 g, 135.00 mmol, 1.5 eq) in distilled water was added dropwise to the suspension at -30 °C. The temperature was then slowly allowed to reach 0 °C over a period of 2h. The reaction mixture was then added slowly to a suspension of stannous chloride (40.6 g, 180.00

mmol, 2.0 eq) in conc. HCl (50 mL) at -30 °C. The temperature was slowly allowed to reach room temperature while continuing stirring over a period of 3-4h. The reaction mixture was filtered and the precipitate was washed with cold conc. HCl and then vacuum dried. Without further purification the compound was used for the next reaction.

Synthesis of 1-(2-methoxy-4-nitrophenyl)-3,5-diphenyl-1H-pyrazole (2f)

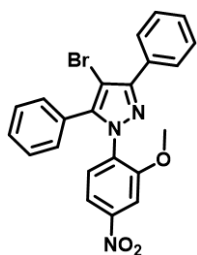


Compound **2f** was prepared following a procedure similar to that used for **1d**. The quantities involved are as follows: 1,3-Diphenylpropanedione (10.10 g, 45.09 mmol, 1.0 eq), (2-methoxy-4-nitrophenyl) hydrazine hydrochloride (**2g**) (19.00 g, 90.18 mmol, 2.0 eq), glacial acetic acid (90 mL) and methanol (90 mL). The product (**2f**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (98:2)). Crystallisation was done using CH₂Cl₂/*n*-hexane. Yield: 10.2 g (60.0%). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.80 (d, *J* = 8.0

Hz, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.32 – 7.28 (m, 3H) 7.28 – 7.18 (m, 2H), 6.87 (s, 1H), 3.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.9, 153.3, 148.3,

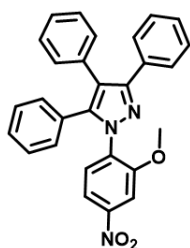
146.7, 135.1, 132.8, 130.9, 129.2, 128.8, 128.6 (2C), 128.4, 127.3, 126.0, 116.5, 107.6, 104.5, 55.9. HR-MS (ESI): calculated for $C_{22}H_{17}N_3O_3Na$ ($[M+Na]^+$): 394.1162, observed : 394.1185.

Synthesis of 4-bromo-1-(2-methoxy-4-nitrophenyl)-3,5-diphenyl-1H-pyrazole (2e)



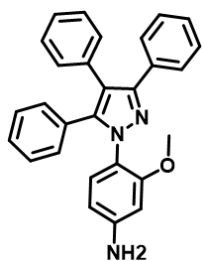
Compound **2e** was prepared following a procedure similar to that used for **1c**. The quantities involved are as follows: 1-(2-Methoxy-4-nitrophenyl)-3,5-diphenyl-1H-pyrazole (**2f**) (8.10 g, 21.81 mmol, 1.0 eq) and N-bromosuccinimide (4.60 g, 26.17 mmol, 1.2 eq). Yield: 9.56 g (97.0%). 1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $J = 8.0$ Hz, 2H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.66 (s, 1H), 7.53 – 7.39 (m, 4H), 7.39 – 7.31 (m, 2H), 7.31 (d, $J = 5.6$ Hz, 2H), 3.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 150.9, 148.4, 144.0, 134.3, 131.6, 129.1, 129.0, 129.0, 128.7, 128.4, 128.4, 128.3, 128.1, 116.2, 107.4, 94.3, 55.8. HR-MS (ESI): calculated for $C_{22}H_{16}BrN_3O_3Na$ ($[M+Na]^+$): 472.0267, 474.0248 observed : 472.0281, 474.0263.

Synthesis of 1-(2-methoxy-4-nitrophenyl)-3,4,5-triphenyl-1H-pyrazole (2d)



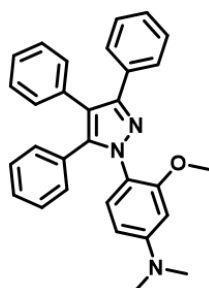
Compound **2d** was prepared following a procedure similar to that used for **1b**. The quantities involved are as follows: 4-Bromo-1-(2-methoxy-4-nitrophenyl)-3,5-diphenyl-1H-pyrazole (**2e**) (9.30 g, 20.52 mmol, 1.0 eq), palladium tetrakis(triphenylphosphine) (0.60 g, 0.51 mmol, 0.025 eq), phenylboronic acid (3.30 g, 26.67 mmol) and sodium carbonate (6.50 g, 61.54 mmol, 3.0 eq). The product (**2d**) was purified using silica gel column chromatography (*n*-hexane/EtOAc/ CH_2Cl_2 (80:10:10)). Yield: 7.00 g (76.0%). 1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 1H), 7.68 (s, 1H), 7.55 – 7.46 (m, 2H), 7.33 – 7.27 (m, 3H), 7.27 – 7.08 (m, 8H), 7.04 – 6.96 (m, 2H), 3.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 151.0, 148.4, 143.5, 136.3, 134.4, 132.6, 132.5, 130.8, 130.0, 129.6, 129.2, 128.6, 128.4, 128.4, 128.2, 127.0, 120.1, 119.0, 116.3, 107.4, 55.9. HR-MS (ESI): calculated for $C_{28}H_{22}N_3O_3$ ($[M+H]^+$): 448.1661, observed : 448.1631.

Synthesis of 4-(3,4,5-triphenyl-1H-pyrazol-1-yl)-3-methoxyaniline (2c)



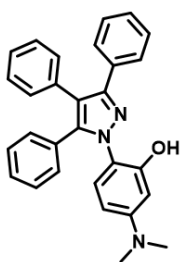
A mixture of 1-(2-methoxy-4-nitrophenyl)-3,4,5-triphenyl-1H-pyrazole (**2d**) (5.60 g, 12.6 mmol, 1.0 eq), hydrazine hydrate (6.2 mL, 126.00 mmol, 10.0 eq), Pd/C (0.13 g, 1.26 mmol, 0.1 eq) and ethanol (120 mL) was refluxed for 12h. After completion of the reaction, the reaction mixture was passed through a column of celite and was extracted using water and ethyl acetate (3 x 150 mL). The extracted organic phase was washed with brine and then dried over anhydrous sodium sulphate. The solvent was concentrated and the product (**2c**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (70:30)). Crystallisation was done using CH_2Cl_2/n -hexane. Yield: 5.30 g (98.0%). 1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.30 – 7.17 (m, 7H), 7.16 – 7.07 (m, 5H), 7.07 – 6.99 (m, 2H), 6.46 (d, $J = 8.0$ Hz, 1H), 6.32 (s, 1H), 4.37 (s, 2H), 3.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 149.6, 148.1, 143.3, 133.7, 133.6, 130.8, 130.7, 130.0, 129.7, 128.6, 128.2, 128.1, 127.8, 127.6, 127.4, 126.4, 120.5, 118.8, 107.1, 99.0, 55.2. HR-MS (ESI): calculated for $C_{28}H_{24}N_3O$ ($[M+H]^+$): 418.1914, observed : 418.1931.

Synthesis of 3-methoxy-*N,N*-dimethyl-4-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)aniline (**2b**):



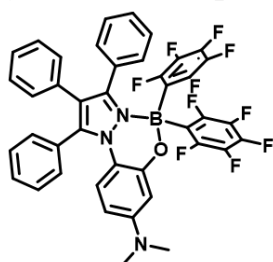
A mixture of 3-methoxy-4-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)aniline (**2c**) (1.90 g, 4.56 mmol, 1.0 eq), sodium cyanoborohydride (1.40 g, 21.96 mmol, 5.0 eq), 37% formaldehyde solution (5.6 mL, 68.43 mmol, 15.0 eq) and acetic acid (0.52 mL, 9.12 mmol, 2.0 eq) was taken in acetonitrile (60 mL). The reaction mixture was stirred at room temperature for 6h. The reaction mixture was extracted using water and dichloromethane (3 x 100 mL). The extracted organic phase was washed with brine and then dried over anhydrous sodium sulphate. The solvent was concentrated and the product (**2b**) was purified using silica gel column chromatography (*n*-hexane/EtOAc/CH₂Cl₂ (80:10:10)). Crystallisation was done using CH₂Cl₂/Ethanol. Yield: 1.96 g (97 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.56 – 7.49 (m, 2H), 7.31 (d, *J* = 8.7 Hz, 1H), 7.28 – 7.18 (m, 6H), 7.17 – 7.10 (m, 5H), 7.08 – 7.02 (m, 2H), 6.31 (d, *J* = 8.0 Hz, 1H), 6.07 (d, *J* = 2.6 Hz, 1H), 3.43 (s, 3H), 2.96 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ = 154.9, 152.0, 149.5, 143.2, 133.8, 133.7, 130.9, 129.7, 129.5, 128.6, 128.2, 128.1, 127.7, 127.5, 127.3, 126.4, 118.7, 118.7, 104.5, 96.1, 55.2, 40.7. HR-MS (ESI): calculated for C₃₀H₂₈N₃O ([M+H]⁺): 446.2227, observed : 446.2252.

Synthesis of 5-(dimethylamino)-2-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)phenol (**2a**):



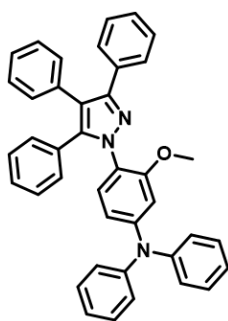
Compound **2a** was prepared following a procedure similar to that used for **1a**. The quantities involved are as follows: 3-Methoxy-*N,N*-dimethyl-4-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)aniline (**2b**) (1.60 g, 3.59 mmol, 1.0 eq) and BBr₃ (1.7 mL, 17.91 mmol, 5.0 eq) The product (**2a**) was purified using silica gel column chromatography (*n*-hexane/EtOAc/CH₂Cl₂ (80:10:10)). Crystallisation was done using CH₂Cl₂/EtOH. Yield: 0.80 g (52 %), ¹H NMR (400 MHz, CDCl₃) δ = 9.56 (s, 1H), 7.53 – 7.47 (m, 2H), 7.34 – 7.18 (m, 9H), 7.16 – 7.04 (m, 4H), 6.50 – 6.39 (m, 2H), 5.97 – 5.91 (m, 1H), 2.92 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ = 151.6, 150.6, 149.2, 141.5, 132.8, 132.6, 130.8, 130.5, 129.9, 128.5(2C), 128.4, 128.3 (2C), 128.0, 126.9, 125.0, 120.1, 115.7, 103.5, 101.2, 40.4. HR-MS (ESI): calculated for C₂₉H₂₆N₃O ([M+H]⁺): 432.2070, observed : 432.2076.

Synthesis of complex **2**: Compound **2** was prepared following a procedure similar to that used for **1**.



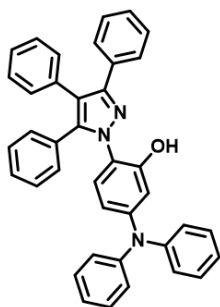
The quantities involved are as follows: 5-(Dimethylamino)-2-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)phenol (**2a**) (0.25 g, 0.58 mmol, 1.0 eq) and tris(pentafluorophenyl)borane (0.32 g, 0.62 mmol, 1.2 eq). Crystallisation was done using CH₂Cl₂/*n*-hexane. Yield: 0.29 g (64 %). ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.39 (m, 3H), 7.31 (d, *J* = 6.9 Hz, 2H), 7.22 – 6.98 (m, 8H), 6.83 – 6.75 (m, 2H), 6.38 – 6.32 (m, 1H), 6.29 (d, *J* = 4.0 Hz, 1H), 5.85 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.87 (s, 6H). ¹³C NMR (176 MHz, CDCl₃) δ 151.1, 148.1 (d, *J* = 241.12 Hz) 146.4, 140.1 (d, *J* = 251.68 Hz), 139.8, 138.0, 136.8 (d, *J* = 248.16 Hz), 130.5, 130.4, 130.2, 129.6, 129.4, 129.1, 128.6, 128.3, 128.2, 128.0, 127.9, 127.6, 125.4, 122.9, 121.3, 114.6, 103.8, 102.4, 96.2, 40.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -132.82 (bs, 4F, Pf), -156.74 (t, 2F, Pf), -164.30 (s, 4F, Pf). ¹¹B NMR (128 MHz, CDCl₃) δ -0.85. HR-MS (ESI): calculated for C₄₁H₂₅BF₁₀N₃O ([M+H]⁺): 776.1967, observed : 776.2048. Anal. Calcd for C₄₁H₂₄BF₁₀N₃O.0.2(C₆H₁₄): C, 63.94; H, 3.41, N, 5.30. Found: C, 64.50; H, 3.15, N, 5.76.

Synthesis of 3-methoxy-*N,N*-diphenyl-4-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)aniline (**3b**):



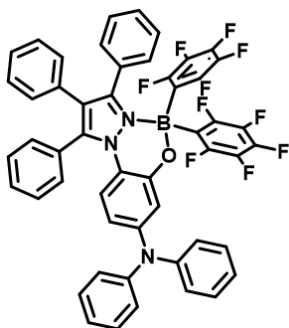
A mixture of 4-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)-3-methoxyaniline (**2c**) (5.20 g, 12.47 mmol, 1.0 eq), iodobenzene (4.2 mL, 37.27 mmol, 3.0 eq), copper iodide (0.14 g, 0.74 mmol, 0.06 eq), 1,10-phenanthroline (0.15 g, 0.84 mmol, 0.07 eq), potassium *tert*-butoxide (4.20 g, 37.27 mmol, 3.0 eq) was taken in a round bottom flask with degassed dry toluene (100 mL). The reaction mixture was refluxed for 36 h. After completion of the reaction, the reaction mixture was passed through a column of celite, the resultant solution was extracted using water and dichloromethane (3 x 100 mL). The extracted organic phase was washed with brine and dried over anhydrous sodium sulphate. The solvent was concentrated and the product (**3b**) was purified using silica gel column chromatography (*n*-hexane/EtOAc/CH₂Cl₂ (80:10:10)). Crystallisation was done using CH₂Cl₂/Ethanol. Yield: 5.60 g, (79 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.58 – 7.50 (m, 2H), 7.37 – 7.32 (m, 1H), 7.30 – 7.11 (m, 15H), 7.12 – 6.99 (m, 8H), 6.69 – 6.62 (m, 1H), 6.54 – 6.50 (m, 1H), 3.24 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 154.8, 149.9, 149.5, 147.4, 143.2, 133.5, 133.5, 130.8, 130.7, 129.7, 129.7, 129.4, 128.6, 128.2, 128.1, 127.8, 127.7, 127.4, 126.5, 124.8, 123.5, 123.4, 118.9, 115.5, 107.0, 55.3. HR-MS (ESI): calculated for C₄₀H₃₂N₃O ([M+H]⁺): 570.2540, observed : 570.2564.

Synthesis of 5-(diphenylamino)-2-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)phenol (**3a**):



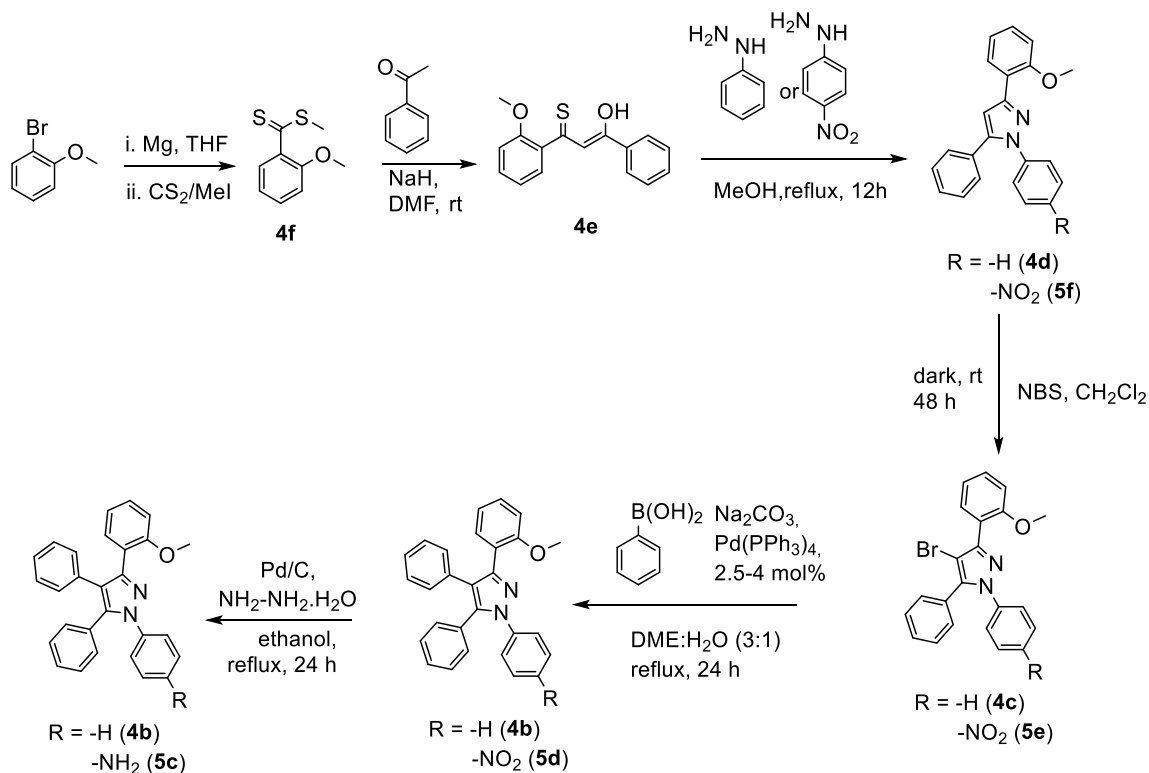
Compound **3a** was prepared following a procedure similar to that used for **1a**. The quantities involved are as follows: 3-Methoxy-*N,N*-diphenyl-4-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)aniline (**3b**) (3.50 g, 6.13 mmol, 1.0 eq) and BBr₃ (2.9 mL, 30.67 mmol, 5.0 eq) The product (**3a**) was purified using silica gel column chromatography (*n*-hexane/EtOAc/CH₂Cl₂ (80:10:10)). Crystallisation was done using CH₂Cl₂/EtOH. Yield: 2.60 g, (76.5 %). ¹H NMR (400 MHz, CDCl₃): δ = 9.72 (s, 1H), 7.57 – 7.46 (m, 2H), 7.35 – 7.25 (m, 13H), 7.21 – 7.02 (m, 10H), 6.83 (d, *J* = 4.0 Hz, 1H), 6.46 – 6.40 (m, 1H), 6.29 (dd, *J* = 8.0, 4.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 151.4, 149.5, 147.8, 147.3, 141.8, 132.5, 132.3, 130.8, 130.4, 129.7, 129.4, 128.7, 128.6, 128.44 (2C), 128.41, 128.2, 127.0, 125.1, 124.7, 123.5, 120.5, 119.8, 113.4, 111.8. HR-MS (ESI): calculated for C₃₉H₃₀N₃O ([M+H]⁺): 556.2389, observed : 556.2344.

Synthesis of complex **3**: Compound **3** was prepared following a procedure similar to that used

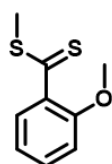


for **1**. The quantities involved are as follows: 5-(Diphenylamino)-2-(3,4,5-triphenyl-1*H*-pyrazol-1-yl)phenol (**3a**) (0.25 g, 0.45 mmol, 1.0eq) and tri(pentafluorophenyl)borane (0.23 g, 0.54 mmol, 1.2 eq). Crystallisation was done using CH₂Cl₂/*n*-hexane. Yield: 0.32 g (80 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.49 – 7.39 (m, 3H), 7.38 – 7.32 (m, 2H), 7.28 – 7.21 (m, 5H), 7.08 - 7.03 (m, 9H), 6.98 (d, *J* = 8.0 Hz, 4H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 4.0 Hz, 1H), 6.34 – 6.29 (m, 1H), 6.17 (dd, *J* = 8.0, 4.0 Hz, 1H). ¹³C NMR (176 MHz, CDCl₃) δ = 151.0, 148.8, 148.2 (d, *J* = 281.6 Hz) 147.0, 146.6, 140.6, 140.1 (d, *J* = 248.16 Hz) 136.8 (d, *J* = 248.16 Hz) 130.5, 130.5, 130.3, 129.5, 129.5, 129.5, 128.8, 128.3, 128.1, 127.7, 127.6, 125.5, 124.1, 123.3, 121.0, 118.6, 112.8, 112.4. ¹⁹F NMR (376 MHz, CDCl₃) δ = -132.94 (bs, 4F, Pf), -156.55 (t, 2F, Pf), -164.14 (bs, 4F, Pf). ¹¹B NMR (128 MHz, CDCl₃) δ = -1.02. HR-MS (ESI): calculated for C₅₁H₂₉BF₁₀N₃O ([M+H]⁺): 900.2280, observed

: 900.2245. Anal. Calcd for $C_{51}H_{28}BF_{10}N_3O$: C, 68.09; H, 3.14, N, 4.67. Found: C, 67.89; H, 3.74, N, 4.62.

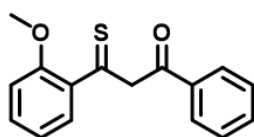


Synthesis of methyl 2-methoxybenzodithiolate (**4f**)



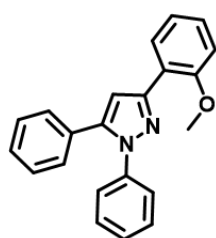
Activated magnesium turnings (0.84 g, 34.70 mmol, 1.3 eq) were added to 60 mL of dry THF under N_2 atmosphere to a two neck RB and the solution was warmed till brisk effervescence was observed. After activation of Mg, the solution was immersed in an ice-cooled water bath and 2-bromoanisole (5.00 g, 3.33 mL, 26.69 mmol, 1.0 eq) was added dropwise. The solution was stirred for about 2h at room temperature; CS_2 (2.23 g, 1.77mL, 29.36 mmol, 1.1 eq) was added dropwise to the reaction mixture at 0 °C. Then the reaction mixture was stirred at room temperature for another 2h after which methyl iodide (4.16 g, 1.83 mL, 29.36 mmol, 1.1 eq) was added dropwise to it at 0 °C. The reaction mixture was allowed to stir at rt, overnight. After completion of the reaction, it was quenched with ice-cold water. The reaction mixture was extracted using water and ethyl acetate (3 x 100 mL). The extracted organic phase was washed with brine and dried over anhydrous sodium sulphate. The solvent was concentrated under reduced pressure and the product was purified using silica gel column chromatography (*n*-hexane/EtOAc (99.5:0.5)). Yield: 4.79 g (90.0%). 1H NMR (400 MHz,) δ 7.40 (dd, $J = 8.0$ Hz, 2.0 Hz 1H), 7.36 (dd, $J = 8.0$ Hz, 2.0 Hz, 1H), 7.00 – 6.92 (m, 2H), 3.85 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 229.7, 154.8, 136.6, 131.3, 129.0, 120.5, 111.9, 56.1, 21.1. HR-MS (ESI): calculated for $C_9H_{10}OS_2K$ ($[M + K]^+$): 236.9810, observed : 237.0095.

Synthesis of 3-(2-methoxyphenyl)-1-phenyl-3-thioxopropan-1-one (4e)



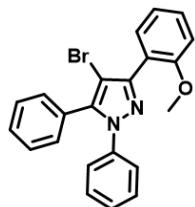
The compound **(4e)** has been synthesized following a procedure reported in literature.¹ To a stirred suspension of NaH (1.28 g, 26.8 mmol, 1.2 eq) in DMF (50 mL) under N₂ atmosphere was added a solution of acetophenone (2.68 g, 2.61 mL, 22.33 mmol, 1.0 eq) and methyl 2-methoxybenzodithioate (**4f**) (5.00 g, 26.8 mmol, 1.2 eq) in DMF (30 mL) at 0 °C, dropwise. The reaction mixture was further stirred at room temperature for about 5 h (monitored by TLC) and was poured into ice-cold water (100 mL) and acidified with acetic acid. The product **(4e)** was extracted using water and EtOAc (3 x 150 mL). The extracted organic phase was washed with brine and dried over anhydrous sodium sulphate. The solvent was concentrated under reduced pressure to give crude product 3-(2-methoxyphenyl)-1-phenyl-3-thioxopropan-1-one, (**4e**) which was used for the next reaction without purification.

Synthesis of 3-(2-methoxyphenyl)-1,5-diphenyl-1H-pyrazole (4d)



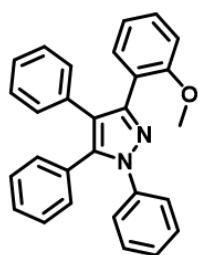
A mixture of 3-(2-methoxyphenyl)-1-phenyl-3-thioxopropan-1-one, (**4e**) (5.00 g 18.45 mmol, 1.0 eq), phenylhydrazine (2.20 g, 20.34 mmol, 1.1 eq) in ethanol (45 mL) was refluxed for 12h. The reaction mixture was extracted using water and dichloromethane (3 x 150 mL). The extracted organic phase was washed with brine and dried over anhydrous sodium sulphate. The solvent was concentrated under reduced pressure and the product **(4d)** was purified using silica gel column chromatography (*n*-hexane/EtOAc (96:4)). Yield: 3.32 g (40%). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.41 – 7.28 (m, 11H), 7.09 (s, 1H), 7.07 – 7.00 (m, 2H), 3.95 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.0, 149.0, 143.4, 140.4, 131.0, 129.2, 129.0, 128.9 (2C), 128.5, 128.1, 127.3, 125.4, 122.1, 121.0, 111.3, 109.4, 55.6. HR-MS (ESI): calculated for C₂₂H₁₉N₂O ([M + H]⁺): 327.1492, observed : 327.1494.

Synthesis of 4-Bromo-3-(2-methoxyphenyl)-1,5-diphenyl-1H-pyrazole (4c)



Compound **4c** was prepared following a procedure similar to that used for **1c**. The quantities involved are as follows: 3-(2-Methoxyphenyl)-1,5-diphenyl-1H-pyrazole (**4d**) (2.00 g, 6.12 mmol, 1.0 eq) and N-bromosuccinimide (1.31 g, 7.35 mmol, 1.2 eq). The product was purified using silica gel column chromatography (*n*-hexane/EtOAc (94:6)). Yield: 1.31 g (53.0%). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.23 (m, 11H), 7.12 – 7.00 (m, 2H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.7, 149.5, 141.0, 140.0, 131.9, 130.4, 130.3, 129.3, 128.9, 128.8, 128.5, 127.4, 124.9, 121.1, 120.6, 111.3, 97.8, 55.7. HR-MS (ESI): calculated for C₂₂H₁₈BrN₂O ([M+H]⁺): 405.0597, 407.0578 observed : 405.0574, 407.0558.

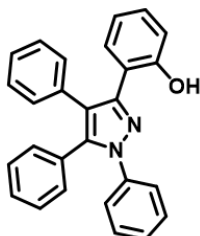
Synthesis of 3-(2-methoxyphenyl)-1,4,5-triphenyl-1H-pyrazole (4b):



Compound **4b** was prepared following a procedure similar to that used for **1b**. The quantities involved are as follows: 4-Bromo-3-(2-methoxyphenyl)-1,5-diphenyl-1H-pyrazole (**4c**) (1.67 g, 4.12 mmol, 1.0 eq), Pd(PPh₃)₄ (0.14 g, 0.12 mmol, 0.03 eq), phenylboronic acid (0.586 g, 4.81 mmol, 1.2 eq), and sodium carbonate (1.31 g, 12.40 mmol, 3.0 eq). The product (**4b**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (96:4)). Yield: 1.34 g (90 %). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.11 (m, 9H), 7.11 – 6.99 (m, 5H),

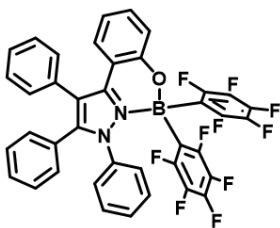
6.95 (t, $J = 8.0$ Hz, 1H), 6.89 – 6.84 (m, 2H), 6.72 (d, $J = 8.0$ Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.0, 148.9, 140.1, 134.3, 131.8, 130.7, 130.4, 129.7, 129.2, 129.1, 128.7, 128.4, 128.2, 127.8, 127.1, 125.9, 125.5, 122.8, 122.0, 120.8, 111.2, 54.8. HR-MS (ESI): calculated for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{ONa}$ ($[\text{M} + \text{Na}]^+$): 425.1630, observed : 425.1639.

Synthesis of 2-(1,4,5-triphenyl-1H-pyrazol-3-yl)phenol (**4a**):



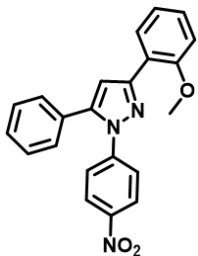
Compound **4a** was prepared following a procedure similar to that used for **1a**. The quantities involved are as follows: 3-(2-Methoxyphenyl)-1,4,5-triphenyl-1H-pyrazole (**4b**) (1.50 g, 3.73 mmol, 1.0 eq) and BBr_3 (1.41 mL, 14.92 mmol, 4.0 eq). The product (**4a**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (94:06)). Yield: 1.00 g (69 %). ^1H NMR (400 MHz, CDCl_3) δ = 10.87 (s, 1H), 7.30 – 7.20 (m, 8H), 7.10 – 7.06 (m, 6H), 7.00 – 6.93 (m, 4H), 6.53 (t, $J = 7.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ = 156.5, 148.3, 141.8, 139.3, 133.1, 131.1, 130.4, 129.3, 129.3, 129.0, 128.6, 128.6, 128.4, 128.3, 127.6, 127.4, 124.9, 121.1, 118.8, 117.2, 116.6. HR-MS (ESI): calculated for $\text{C}_{27}\text{H}_{21}\text{N}_2\text{O}$ ($[\text{M} + \text{H}]^+$): 389.1648, observed : 389.1641

Synthesis of complex **4**: Compound **4** was prepared following a procedure similar to that used



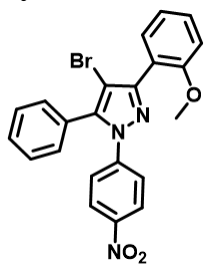
for **1**. The quantities involved are as follows: 2-(1,4,5-Triphenyl-1H-pyrazol-3-yl)phenol (**4a**) (0.25 g, 0.64 mmol, 1.0 eq) and tri(pentafluorophenyl)borane (0.40 g, 0.77 mmol, 1.2 eq). Crystallisation was done using CH_2Cl_2 /*n*-hexane. Yield: 0.25 g (54 %). ^1H NMR (400 MHz, CDCl_3) δ = 7.39 (m, 3H), 7.36 – 7.29 (m, 2H), 7.24 – 7.15 (m, 3H), 7.11 (m, 6H), 6.99 (m, 4H), 6.62 (t, $J = 8.3$, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ = 155.5, 148.1 (d, $J = 243.41$ Hz) 147.2, 142.8, 140.1 (d, $J = 252.5$ Hz) 136.9 (d, $J = 247.45$ Hz) 134.8, 132.5, 130.9, 130.7, 130.4, 130.2, 129.8, 129.2, 129.0, 128.7, 128.5, 126.7, 126.2, 119.0, 115.1. ^{19}F NMR (376 MHz, CDCl_3) δ = -134.34 (bs, 4F, Pf), -156.65 (t, 2F, Pf), -163.94 (bs, 4F, Pf). ^{11}B NMR (128 MHz, CDCl_3) δ = -0.60. HR-MS (ESI): calculated for $\text{C}_{39}\text{H}_{20}\text{BF}_{10}\text{N}_2\text{O}$ ($[\text{M} + \text{H}]^+$): 733.1545, observed : 733.1526. Anal. Calcd for $\text{C}_{39}\text{H}_{19}\text{BF}_{10}\text{N}_2\text{O} \cdot 0.2(\text{C}_6\text{H}_{14})$: C, 64.41; H, 2.93, N, 3.74. Found: C, 64.79; H, 2.51, N, 4.20.

Synthesis of 3-(2-methoxyphenyl)-1-(4-nitrophenyl)-5-phenyl-1H-pyrazole (**5f**)



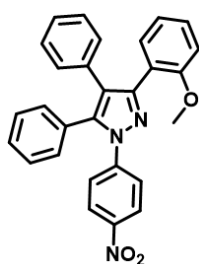
Compound **5f** was prepared following a procedure similar to that used for **4d**. The quantities involved are as follows: 3-(2-methoxyphenyl)-1-phenyl-3-thioxopropan-1-one, (**4e**) (5.00 g, 14.37 mmol, 1.0 eq), and 4-nitrophenylhydrazine (2.20 g, 18.51 mmol, 1.3 eq). The product (**5f**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (96:4)). Yield: 3.32 g (62%). ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.0$ Hz, 2H), 8.09 (d, $J = 8.0$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.43 – 7.36 (m, 4H), 7.34 – 7.30 (m, 2H), 7.12 – 7.00 (m, 3H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.2, 150.6, 145.8, 145.0, 144.0, 130.4, 129.9, 129.07 (2C), 129.01 (2C), 124.6, 124.5, 121.1, 121.1, 111.4, 111.4, 55.6. HR-MS (ESI): calculated for $\text{C}_{27}\text{H}_{17}\text{N}_3\text{O}_3\text{Na}$ ($[\text{M} + \text{Na}]^+$): 394.1168, observed : 394.1163.

Synthesis of 4-bromo-3-(2-methoxyphenyl)-1-(4-nitrophenyl)-5-phenyl-1H-pyrazole (**5e**)



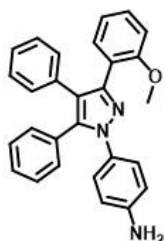
Compound **5e** was prepared following a procedure similar to that used for **1c**. The quantities involved are as follows: 3-(2-Methoxyphenyl)-1-(4-nitrophenyl)-5-phenyl-1H-pyrazole (**5f**) (2.30 g, 6.12 mmol, 1.0 eq) and N-bromosuccinimide (1.31 g, 7.35 mmol, 1.2 eq). The product (**5e**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (94:6)). Yield: 2.28 g (83%). ¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.11 (m, 2H), 7.51 (dd, 8.0 Hz, 2.0 Hz 1H), 7.49 – 7.44 (m, 6H), 7.41 – 7.37 (m, 2H), 7.12 – 7.01 (m, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.6, 151.2, 146.0, 144.6, 141.5, 131.7, 130.9, 130.2, 129.7, 129.1, 128.7, 124.5, 124.2, 120.7, 120.4, 111.4, 100.2, 55.7. HR-MS (ESI): calculated for C₂₂H₁₆BrN₃O₃Na ([M+Na]⁺): 472.0267, 474.0248 observed : 472.0281, 474.0263.

Synthesis of 3-(2-methoxyphenyl)-1-(4-nitrophenyl)-4,5-diphenyl-1H-pyrazole (**5d**)



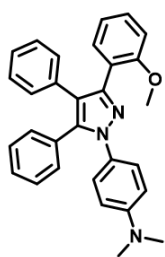
Compound **5d** was prepared following a procedure similar to that used for **1b**. The quantities involved are as follows: 4-bromo-3-(2-methoxyphenyl)-1-(4-nitrophenyl)-5-phenyl-1H-pyrazole (**5e**) (1.55 g, 3.70 mmol, 1.0 eq), Pd(PPh₃)₄ (0.13 g, 0.11 mmol, 0.035 eq), phenylboronic acid (0.58 g, 4.81 mmol, 1.3 eq), Sodium carbonate (1.17 g, 11.10 mmol, 3.0 eq). The product (**5d**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (96:4)). Yield: 1.52 g (92%). ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.26 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.08 (m, 3H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.97 – 6.89 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.25 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.0, 150.7, 145.7, 144.9, 140.4, 133.2, 131.5, 130.6, 130.2, 129.8, 129.1, 129.0, 129.0, 127.9, 126.4, 124.7, 124.4, 121.9, 120.9, 115.4, 111.3, 54.9. HR-MS (ESI): calculated for C₂₈H₂₂N₃O₃ ([M+H]⁺): 448.1661, observed : 448.1631.

Synthesis of 4-(3-(2-methoxyphenyl)-4,5-diphenyl-1H-pyrazol-1-yl)aniline (**5c**)



Compound **5c** was prepared following a procedure similar to that used for **2c**. The quantities involved are as follows: 3-(2-Methoxyphenyl)-1-(4-nitrophenyl)-4,5-diphenyl-1H-pyrazole (**5d**) (5.60 g, 12.6 mmol, 1.0 eq), hydrazine hydrate (6.2 mL, 126.00 mmol, 10.0 eq), and Pd/C (0.13 g, 1.26 mmol, 0.1 eq). The product (**5c**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (70:30)). Yield: 5.05 g (96%). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.31 (td, *J* = 7.9, 1.8 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.16 – 7.07 (m, 7H), 7.00 (td, *J* = 7.5, 1.1 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.78 (d, *J* = 7.3 Hz, 2H), 3.22 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.0, 148.1, 145.6, 139.9, 134.5, 131.8, 131.5, 130.7, 130.5, 129.5, 129.2, 128.2, 127.9, 127.7, 126.8, 125.8, 122.9, 121.2, 120.8, 114.9, 111.1, 54.8. HR-MS (ESI): calculated for C₂₈H₂₄N₃O ([M+H]⁺): 418.1914, observed : 418.1931.

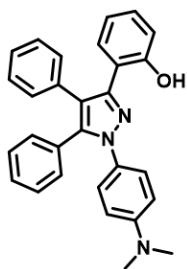
Synthesis of 4-(3-(2-methoxyphenyl)-4,5-diphenyl-1H-pyrazol-1-yl)-N,N-dimethylaniline (**5b**)



Compound **5b** was prepared following a procedure similar to that used for **2b**. The quantities involved are as follows: 4-(3-(2-Methoxyphenyl)-4,5-diphenyl-1H-pyrazol-1-yl)aniline (**5c**) (1.90 g, 4.56 mmol, 1.0 eq), sodium cyanoborohydride (1.4 g, 21.96 mmol, 4.8 eq), 37% formaldehyde solution (5.6 mL, 68.43 mmol, 15.0 eq) and acetic acid (0.52 mL, 9.12 mmol, 2.0 eq). The product was purified using silica gel column chromatography (*n*-hexane/EtOAc/CH₂Cl₂ (80:10:10)). Yield: 1.83 g (90 %). ¹H NMR (400 MHz,

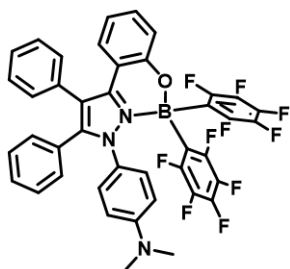
CDCl₃) δ 7.64 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.24 – 7.12 (m, 7H), 7.04 (t, J = 8.0 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.81 (d, J = 8.0 Hz, 1H), 6.64 – 6.66 (m, 2H), 3.24 (s, 3H), 2.96 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 157.0, 149.5, 148.0, 139.9, 134.7, 131.9, 130.8, 130.7, 129.8, 129.4, 129.2, 128.2, 127.8, 127.7, 126.4, 125.7, 123.1, 121.2, 120.8, 112.1, 111.2, 54.8, 40.6. HR-MS (ESI): calculated for C₃₀H₂₈N₃O ([M+H]⁺): 446.2227, observed : 446.2252.

Synthesis of 2-(1-(4-(dimethylamino)phenyl)-4,5-diphenyl-1H-pyrazol-3-yl)phenol (**5a**):



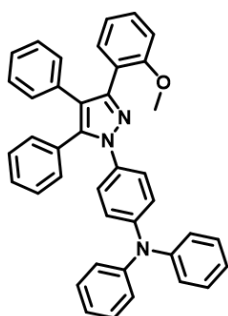
Compound **5a** was prepared following a procedure similar to that used for **1a**. The quantities involved are as follows: Compound **5b** (1.00 g, 2.24 mmol, 1.0 eq) and BBr₃ (1.06 mL, 11.2 mmol, 5.0 eq). The product (**5a**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (94:06)). Crystallisation was done using CH₂Cl₂/*n*-hexane. Yield: 0.88 g (92 %). ¹H NMR (400 MHz, CDCl₃) δ = 11.09 (s, 1H), 7.30 – 7.29 (m, 3H), 7.22 – 7.12 (m, 8H), 7.06 – 7.03 (m, 4H), 6.65 – 6.55 (m, 3H), 2.97 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ = 156.5, 149.7, 147.4, 141.5, 135.3, 133.5, 131.1, 130.5, 129.6, 129.0, 128.7, 128.6, 128.2, 127.2, 126.0, 120.2, 118.7, 117.4, 117.1, 116.9, 111.9, 40.5. HR-MS (ESI): calculated for C₂₉H₂₆N₃O ([M+H]⁺): 432.2070, observed: 432.2076.

Synthesis of complex **5**: Compound **5** was prepared following a procedure similar to that used for **1**.



Compound **5** was prepared following a procedure similar to that used for **1**. The quantities involved are as follows: Compound **5a** (0.30 g, 0.69 mmol, 1.0 eq) and tris(pentafluorophenyl)borane (0.39 g, 0.76 mmol, 1.2 eq). Crystallisation was done using CH₂Cl₂/*n*-hexane. Yield: 0.34 g (63 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.42 – 7.31 (m, 5H), 7.30 – 7.10 (m, 4H), 7.09 – 7.03 (m, 2H), 7.02 – 6.94 (m, 2H), 6.93 – 6.83 (m, 2H), 6.60 (t, J = 8.0 Hz, 1H), 6.24 (d, J = 8.0 Hz, 2H), 2.87 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ = 155.6, 150.9, 148.1 (d, J = 245.43 Hz), 147.3, 142.3, 142.2 (d, J = 233.31), 137.0 (d, J = 250.48), 132.2, 131.0, 130.7, 130.5, 129.5, 129.1, 128.5, 128.4, 126.7, 126.6, 123.1, 119.7, 118.7, 115.3, 111.4, 40.3. ¹⁹F NMR (376 MHz, CDCl₃) δ = -132.53 (bs, 4F, Pf), -157.63 (t, 2F, Pf), -164.42 (s, 4F, Pf). ¹¹B NMR (128 MHz, CDCl₃) δ = -0.77. HR-MS (ESI): calculated for C₄₁H₂₅BF₁₀N₃O ([M+H]⁺): 776.1967, observed : 776.2001. Anal. Calcd for C₄₁H₂₄BF₁₀N₃O: C, 63.50; H, 3.12, N, 5.42. Found: C, 64.02; H, 3.27, N, 5.82.

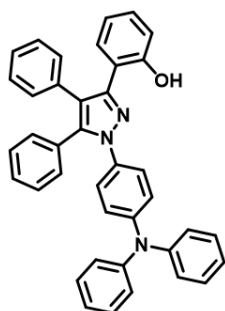
Synthesis of 4-(3-(2-methoxyphenyl)-4,5-diphenyl-1H-pyrazol-1-yl)-N,N-diphenylaniline (**6b**):



Compound **6b** was prepared following a procedure similar to that used for **3b**. 4-(3-(2-Methoxyphenyl)-4,5-diphenyl-1H-pyrazol-1-yl)aniline (**5c**) (5.20 g, 12.47 mmol, 1.0 eq), iodobenzene (4.20 mL, 37.27 mmol, 3.0 eq), copper iodide (0.14 g, 0.74 mmol, 0.02 eq), 1,10-phenanthroline monohydrate (0.15 g, 0.74 mmol, 0.02 eq), and potassium *tert*-butoxide (4.20 g, 37.27 mmol, 3.0 eq). The product (**6b**) was purified using silica gel column chromatography (*n*-hexane/EtOAc/CH₂Cl₂ (80:10:10)). Yield: 6.09 g (86 %). ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 6.2 Hz, 7H), 7.21 – 7.17 (m, 4H), 7.15 – 7.09 (m, 8H), 7.08 – 7.03 (m, 2H), 7.02 – 6.96 (m, 4H), 6.82 (d, J = 8.2 Hz, 1H), 3.25 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.0, 148.7, 147.6, 146.8, 139.5, 134.4, 134.4, 131.9, 130.7, 130.5, 129.6, 129.4, 129.2, 128.3, 128.2, 127.8, 126.4, 125.9, 124.6, 123.2,

122.8, 121.7, 120.8, 117.4, 111.2, 54.8. HR-MS (ESI): calculated for $C_{40}H_{32}N_3O$ ($[M+H]^+$): 570.2540, observed : 570.2564.

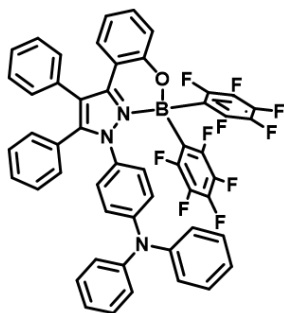
Synthesis of 2-(1-(4-(diphenylamino)phenyl)-4,5-diphenyl-1H-pyrazol-3-yl)phenol (6a):



Compound **6a** was prepared following a procedure similar to that used for **1a**. The quantities involved are as follows: Compound **6b** (1.50 g, 2.63 mmol, 1.0 eq), BBr_3 (1.25 mL, 13.18 mmol, 5.0 eq). The product (**6a**) was purified using silica gel column chromatography (*n*-hexane/EtOAc (94:06)). Crystallisation was done using CH_2Cl_2/n -hexane. Yield: 1.0 g (69 %). 1H NMR (400 MHz, $CDCl_3$) δ = 11.01 (s, 1H, -OH), 7.30 – 7.18 (m, 12H), 7.16 – 7.01 (m, 13H), 6.99 (d, J = 8.0 Hz, 2H), 6.60 (t, J = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.4, 147.8, 147.3, 147.3, 141.6, 133.2, 132.5, 131.0, 130.4, 129.5, 129.4, 129.2, 128.6, 128.5, 128.3, 128.3, 127.4, 125.7,

124.9, 123.6, 122.6, 120.7, 118.8, 117.1, 116.7. HR-MS (ESI): calculated for $C_{39}H_{30}N_3O$ ($[M+H]^+$): 556.2389, observed : 556.2392.

Synthesis of complex 6: Compound **6** was prepared following a procedure similar to that used for **1**. The quantities involved are as follows: Compound **6a** (0.30 g,



0.54 mmol, 1.0 eq) and tris(pentafluorophenyl)borane (0.33 g, 0.64 mmol, 1.2 eq) Crystallisation was done using $CHCl_3/n$ -hexane. Yield: 0.25 g (52 %), 1H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.35 (m, 3H), 7.36 – 7.28 (m, 7H), 7.22 – 7.16 (m, 3H), 7.15 – 7.09 (m, 2H), 7.05 – 6.95 (m, 8H), 6.81 (d, J = 8.0 Hz, 2H), 6.64 – 6.58 (m, 1H), 6.54 (d, J = 8.0, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.5, 149.4, 148.3 (d, J = 282.8 Hz) 147.3, 146.1, 142.3, 140.0 (d, J = 274.72 Hz), 139.8, 137.2 (d, J = 226.24 Hz) 133.0, 132.3, 130.9, 130.5, 129.9, 129.6,

129.1, 128.9, 128.6, 129.5, 128.4, 127.3, 126.7, 126.2, 125.2, 124.7, 119.7, 119.7, 118.9, 118.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -134.27 (bs, 4F, Pf), -156.85 (t, 2F, Pf), -163.79 (t, 4F, Pf). ^{11}B NMR (128 MHz, $CDCl_3$) δ = -0.85. HR-MS (ESI): calculated for $C_{51}H_{29}BF_{10}N_3O$ ($[M+H]^+$): 900.2358, observed : 900.2347. Anal. Calcd for $C_{51}H_{28}BF_{10}N_3O$: C, 68.09; H, 3.14, N, 4.67. Found: C, 67.89; H, 3.32, N, 4.27.

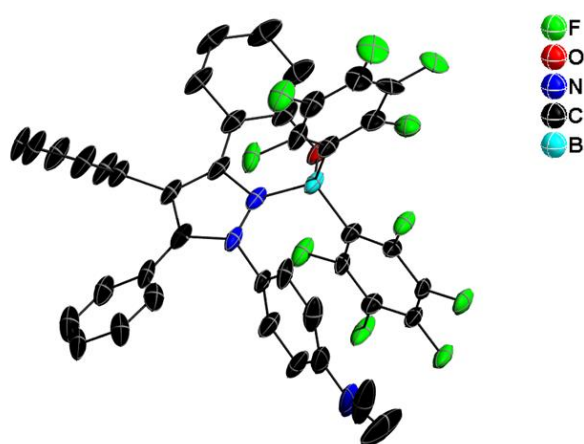
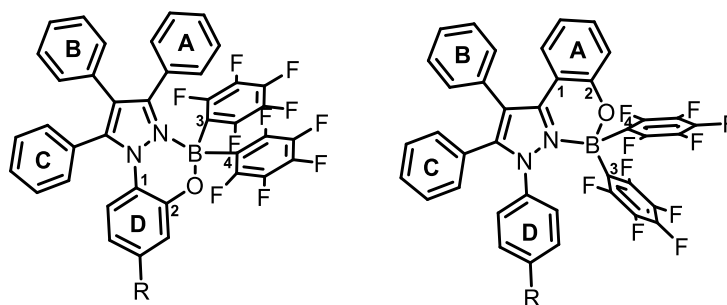


Figure S1. Molecular structures of compounds 5 with 30% probability level of thermal ellipsoids (hydrogen atoms are omitted for clarity).

Table S1. Bond length, bond angle and plane deviation measurement data for compounds **1**, **4**, and **5**.



Compound	1	4	5
B-N1 (Å)	1.596 (2)	1.603 (2)	1.577 (10)
B-O (Å)	1.474 (2)	1.462 (2)	1.468 (12)
B-C3 (Å)	1.644 (2)	1.626 (3)	1.646 (10)
B-C4 (Å)	1.627 (2)	1.650 (3)	1.659 (10)
N1-B-O (deg)	105.1 (1)	104.2 (1)	104.4 (6)
N1-B-C3 (deg)	109.7 (1)	111.8 (1)	110.7 (6)
O-B-C4 (deg)	107.1 (1)	108.8 (1)	105.1 (6)
C3-B-C4 (deg)	117.3 (1)	114.8 (1)	116.4 (5)
Deviation of B from N₂C₂OB plane (Å)	0.405 (1)	-	-
Deviation of B from NC₃OB plane (Å)	-	0.354 (1)	0.343 (1)
Angle between pyrazole ring and plane A (°)	62.7 (5)	11.1 (6)	14.2 (2)
Angle between pyrazole ring and plane B (°)	45.2 (5)	82.2 (7)	60.9 (3)
Angle between pyrazole ring and plane C (°)	58.6 (4)	54.7 (7)	41.5 (3)
Angle between pyrazole ring and plane D (°)	26.5 (5)	85.8 (8)	78.5 (3)

Table S2. Photophysical data of compound **1-6** in different solvents

Compound	Solvent	λ_{abs}^a /nm ($\epsilon \times 10^4/\text{M}^{-1}$ cm^{-1})	λ_{ems}^b (nm)	Stokes Shift (cm^{-1})	Φ_{F}^d (%)	τ_{av} (ns)
1	Toluene	312 (1.28)	506	12289	4.6,	
	THF	307 (1.18)	515	19417	1.4(5.6) ^f	1.3
	ACN	307 (1.17)	517	13231	0.5	
			380 ^c		3.7 ^e	
2	Toluene	356 (1.42)	500	8089	1.7,	
	THF	352 (1.85)	533	9648	0.5(41.6) ^f	2.8
	ACN	348 (1.71)	555	10717	0.7	
			485 ^c		30.8 ^e	
3	Toluene	367 (1.86)	477	6283	16.4,	
	THF	365 (1.56)	508	7712	14.0(32.1) ^f	1.6
	ACN	360 (1.73)	541	9293	12.0	
			(452, 549) ^c		11.8 ^e	
4	Toluene	323 (0.74)	434	7918	20.4,	
	THF	319 (1.00)	440	8620	18.9(19.6) ^f	3.8
	ACN	318 (1.04)	446	9025	14.5	
			380 ^c		5.4 ^e	
5	Toluene	318 (1.81)	438	8615	<0.1	
	THF	318 (1.27)	475	10394	<0.1(15.5) ^f	-
	ACN	316 (1.44)	500	11645	0.2	
			408 ^c		28.2 ^e	
6	Toluene	328 (1.99)	432	7339	4.0,	
	THF	324 (1.65)	446	8443	1.6(29.6) ^f	2.9
	ACN	320 (1.99)	468	9883	5.3	
			438 ^c		23.2 ^e	

^aAbsorption maximum (concentration = 5.0×10^{-5} M), ^bexcited at λ_{max} , ^csolid state emission maxima,

^dabsolute quantum yield using integrating sphere module, ^eSolid state quantum yield using integrating

sphere module, ^fabsolute quantum yield of AIE (99 : 1) (H₂O : THF) of using integrating sphere module.

Table S3. Fluorescence lifetime of compound **1-6** in THF with concentration of 5.0×10^{-5} M.

Compound	B ₁	τ_1 (ns)
1	1.00	1.3
2	1.00	0.2
3	1.00	1.6
4	1.00	3.9
5	1.00	2.2
6	1.00	0.9

B₁ represent the fractional amount of molecules in each environment.

Table S4. Fluorescence lifetime of compound **1-6** in water fraction ($f_w=99\%$) with concentration of 5.0×10^{-5} M.

Compounds	B ₁ /B ₂ /B ₃	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
1	0.78/0.22/0	0.6	3.1	-
2	0.26/0.74/0	3.8	7.9	-
2 (Thin film)	0.16/0.84	2.2	5.2	-
3	0.26/0.64/0.10	1.5	4.9	16.1
4	0.47/0.53/0	1.6	4.4	-
5	0.18/0.56/0.26	1.4	4.4	10.0
6	0.51/0.49/0	2.3	6.1	-

B₁B₂B₃ represent the fractional amount of molecules in each environment.

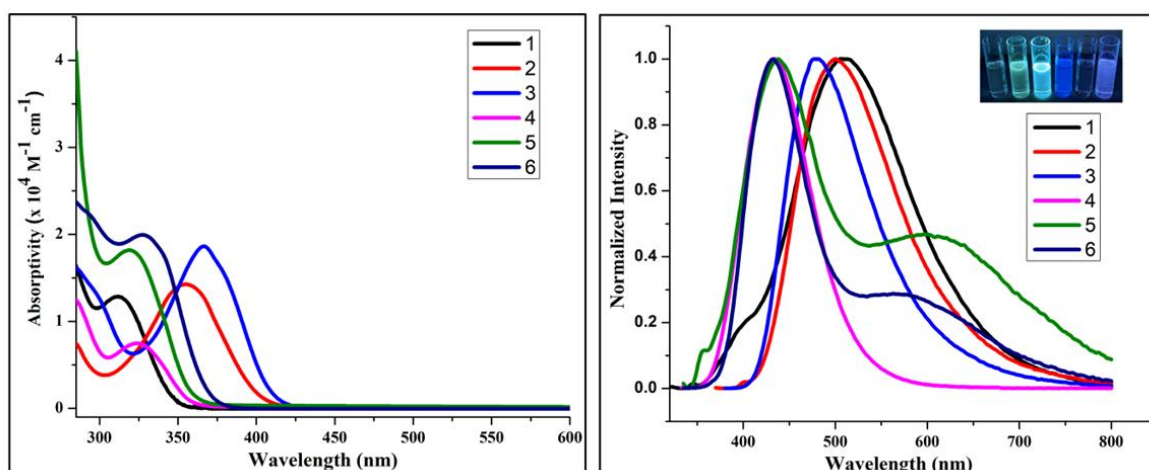


Figure S2: Absorption spectra of compounds **1-6** (Left) and normalized emission spectra of compounds **1-6** (Right) in toluene (5.0×10^{-5} M concentration) inset (Right): photograph of compounds **1-6** taken under hand-held UV lamp 365nm.

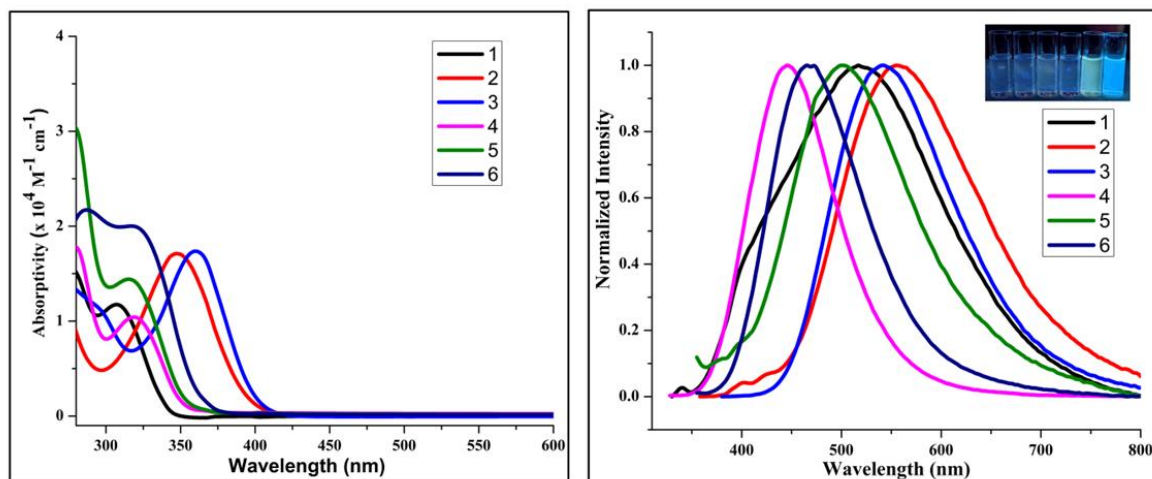


Figure S3: Absorption spectra of compounds **1-6** (Left) and normalized emission spectra of compounds **1-6** (Right) in acetonitrile (5.0×10^{-5} M concentration) inset (Right): photograph of compounds **1-6** taken under hand-held UV lamp 365nm.

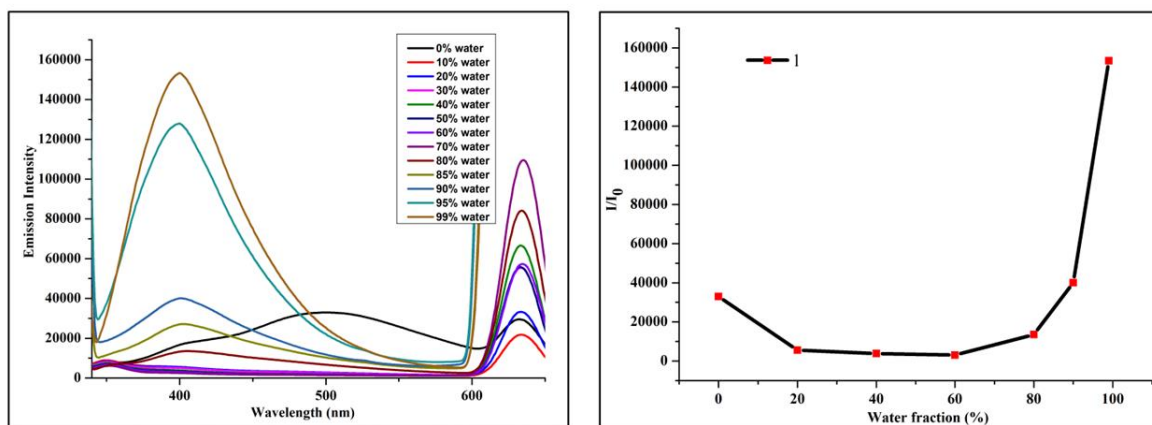


Figure S4: Fluorescence spectra of compound **1** (5.0×10^{-5} M) in a THF/ H_2O mixture with different water fraction (f_w) (left). I/I_0 vs water fraction plot for compound **1** (vol%) (right).

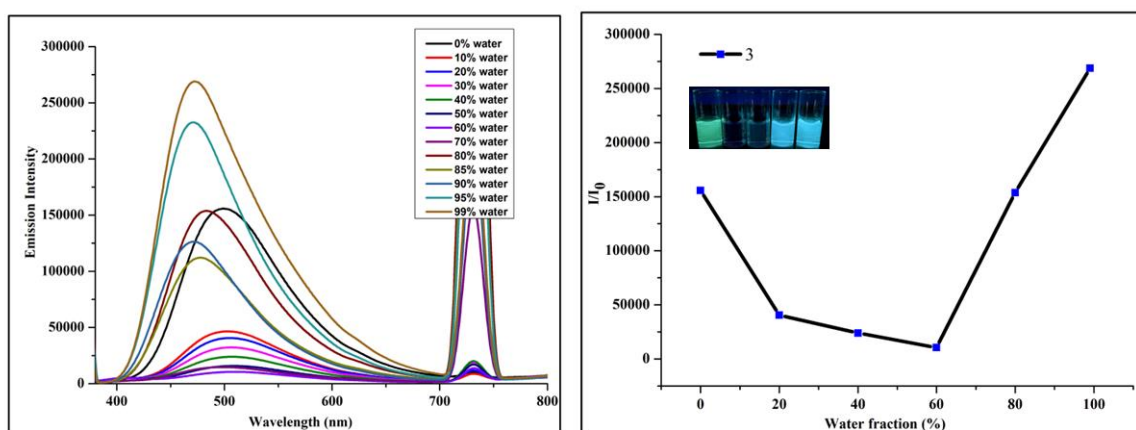


Figure S5: Fluorescence spectra of compound **3** (5.0×10^{-5} M) in a THF/ H_2O mixture with different water fraction (f_w) (left). I/I_0 vs water fraction plot for compound **3** (vol%) (right).

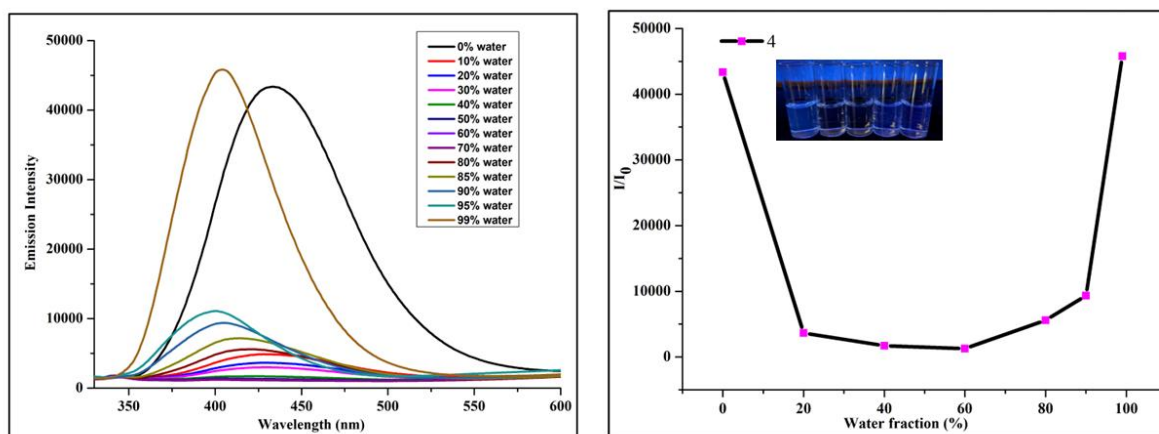


Figure S6: Fluorescence spectra of compound **4** (5.0×10^{-5} M) in a THF/H₂O mixture with different water fraction (f_w) (left). I/I_0 vs water fraction plot for compound **4** (vol%) (right).

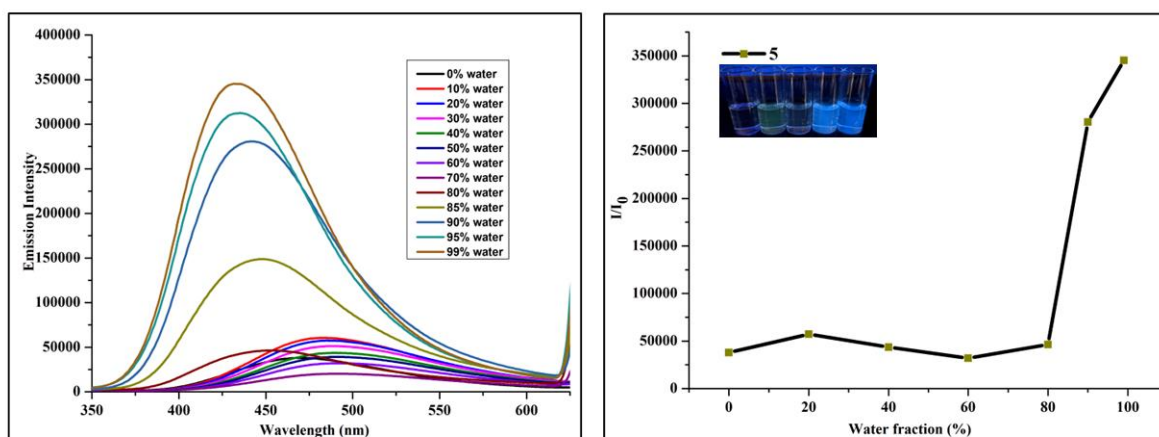


Figure S7: Fluorescence spectra of compound **5** (5.0×10^{-5} M) in a THF/H₂O mixture with different water fraction (f_w) (left). I/I_0 vs water fraction plot for compound **5** (vol%) (right).

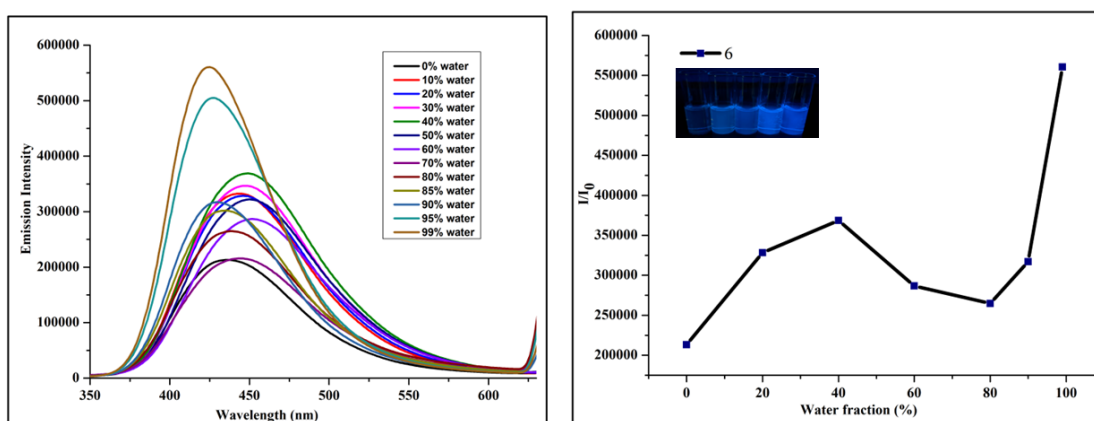


Figure S8: Fluorescence spectra of compound **6** (5.0×10^{-5} M) in a THF/H₂O mixture with different water fraction (f_w) (left). I/I_0 vs water fraction plot for compound **6** (vol%) (right).

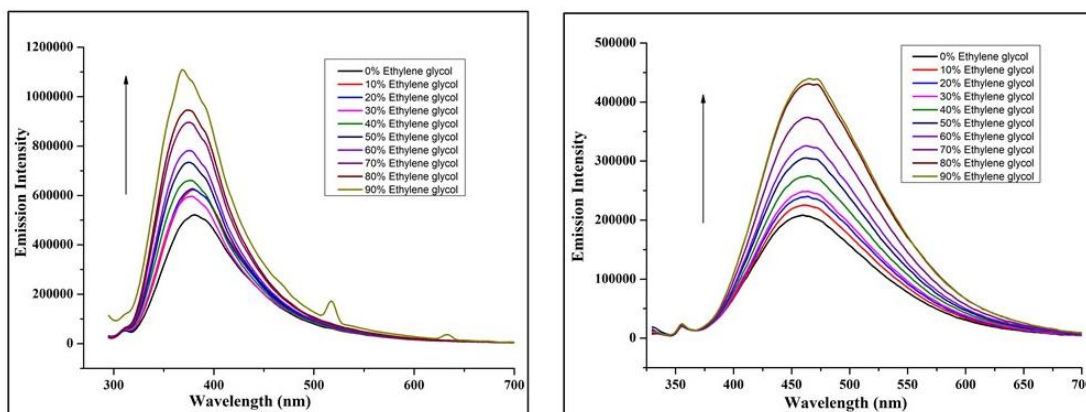


Figure S9: Emission spectra of compound **1** (Left) and compound **2** (Right) with the addition of different percentage of MeOH/Ethylene glycol mixture (10^{-5} M concentration).

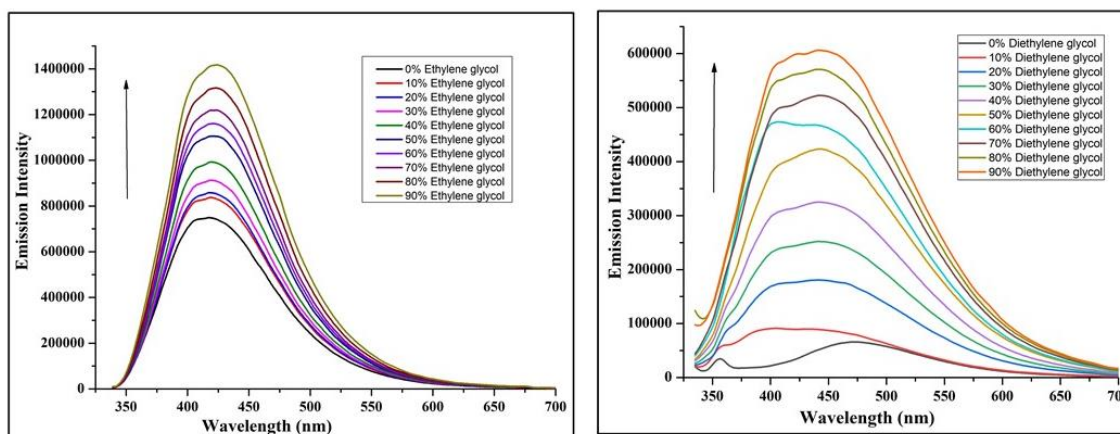


Figure S10: Emission spectra of compound **3** (Left) and Compound **4** (Right) with the addition of different percentage of MeOH/Ethylene glycol or Diethylene glycol mixture (10^{-5} M concentration).

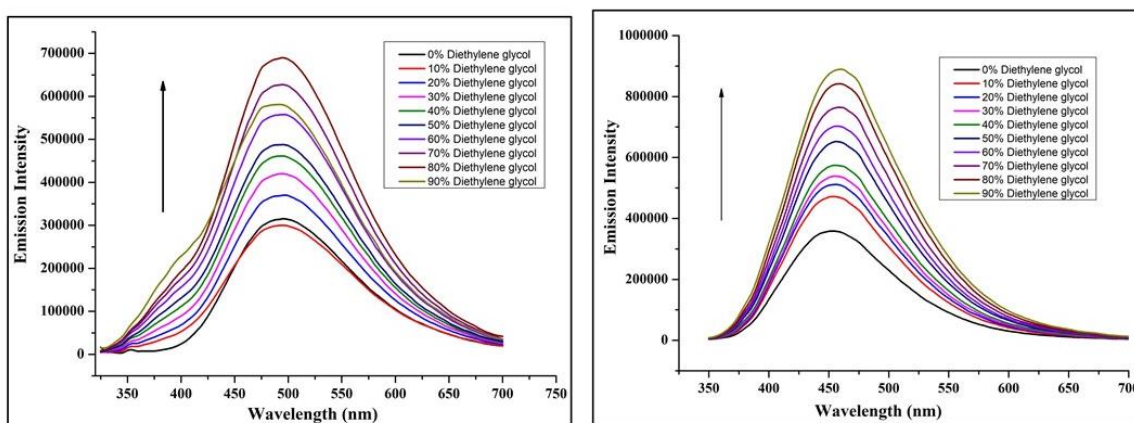


Figure S11: Emission spectra of compound **5** (Left) and Compound **6** (Right) with the addition of different percentage of MeOH/Diethylene glycol mixture (10^{-5} M concentration).

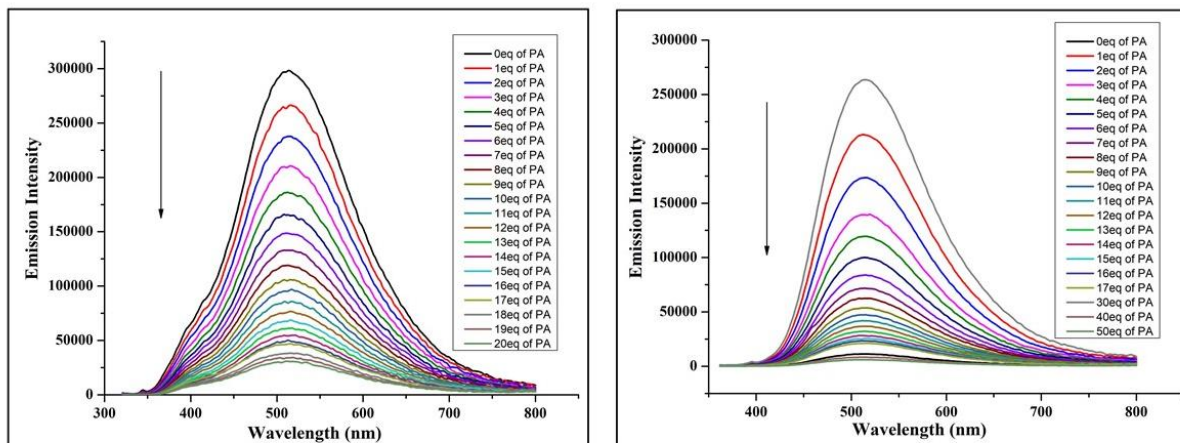


Figure S12: Emission spectra of compound 1 (Left) and Compound 2 (Right) with the addition of different equivalents of picric acid in dichloromethane (10^{-5} M concentration).

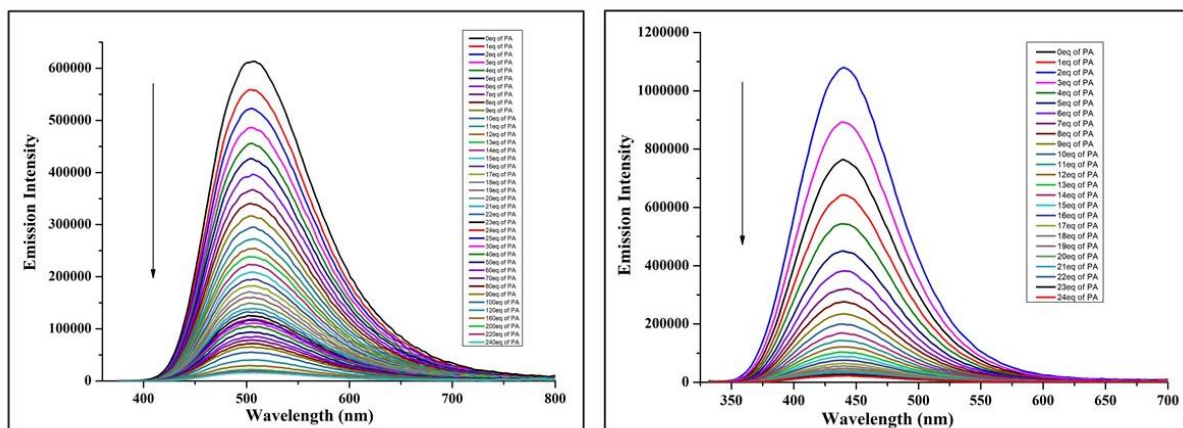


Figure S13: Emission spectra of compound 3 (Left) and Compound 4 (Right) with the addition of different equivalents of picric acid in dichloromethane (10^{-5} M concentration).

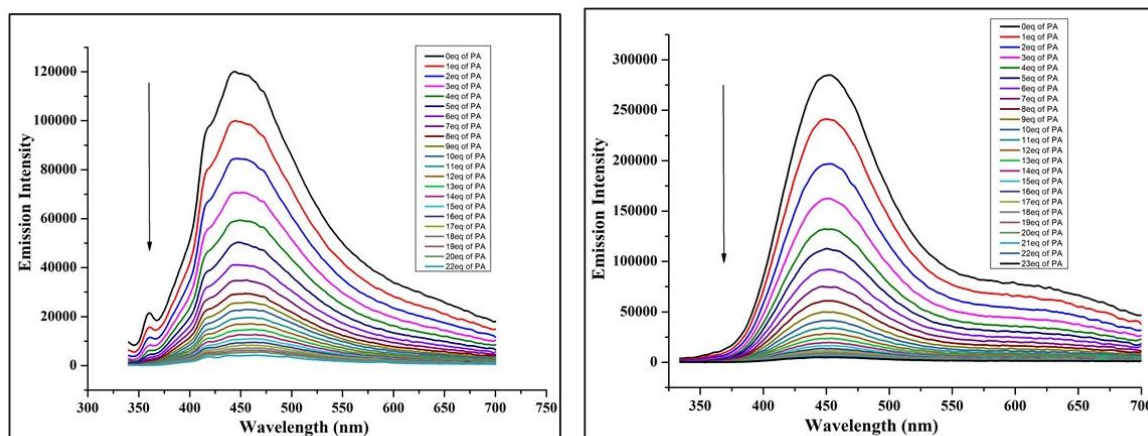


Figure S14: Emission spectra of compound 5 (Left) and Compound 6 (Right) with the addition of different equivalents of picric acid in dichloromethane (10^{-5} M concentration).

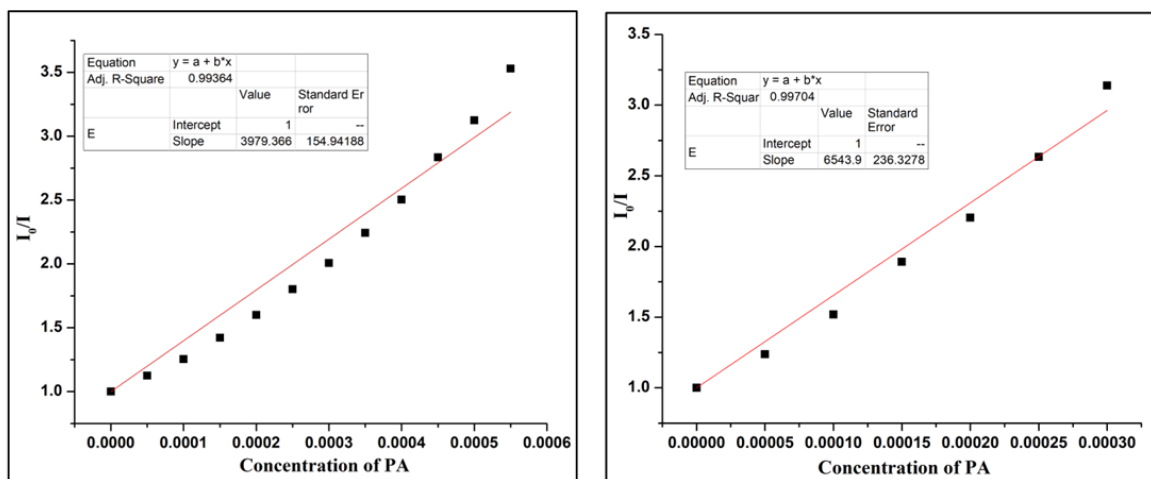


Figure S15: Stern-Volmer plot of compound 1 (Left) and 2 (Right).

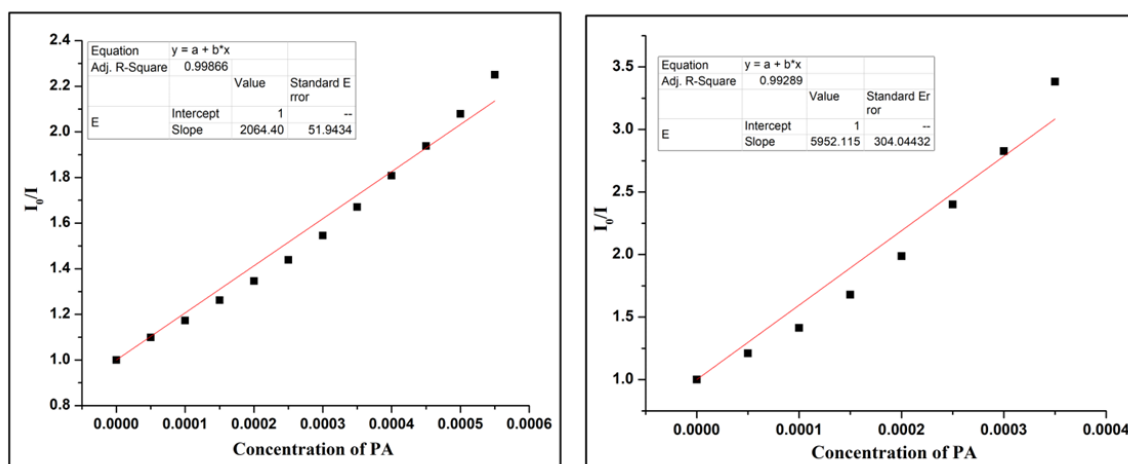


Figure S16: Stern-Volmer plot of compound 3 (Left) and 4 (Right).

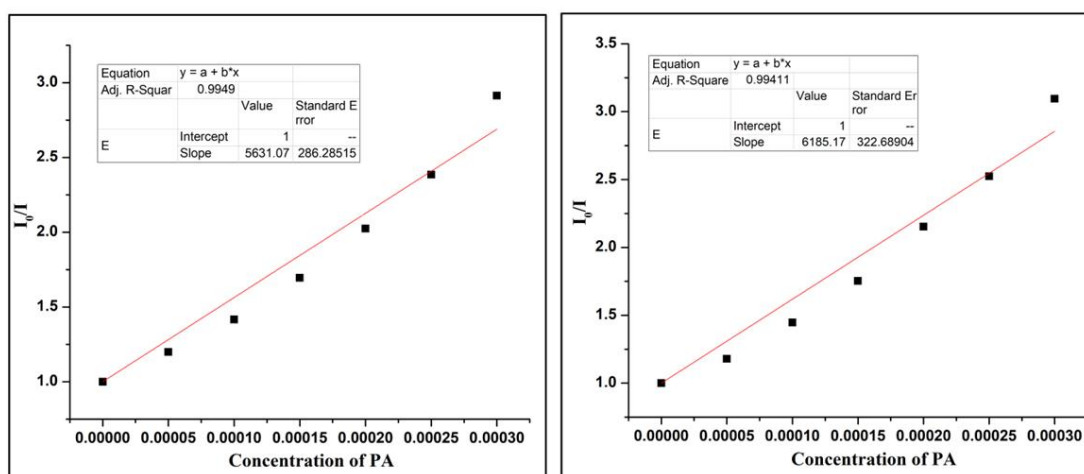


Figure S17: Stern-Volmer plot of compound 5 (Left) and 6 (Right).

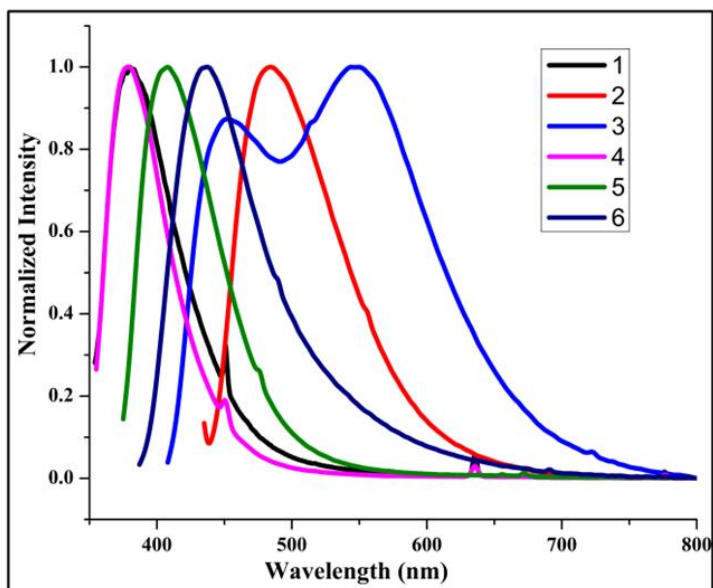


Figure S18: Solid-state emission spectra of pyrazole compound **1-6**.

Table S5. Crystal data and structure refinement for Compound 1, 4, 5.

	Compound 1	Compound 4	Compound 5
Empirical formula	C ₃₉ H ₁₉ BF ₁₀ N ₂ O	C ₄₀ H ₂₀ BCl ₃ F ₁₀ N ₂ O	C ₄₁ H ₂₄ BF ₁₀ N ₃ O
Formula weight	732.37	851.74	775.44
Temperature/K	100.00(10)	299.6(9)	113(18)
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P2 ₁
a/Å	7.88670(10)	8.8799(2)	12.4589(13)
b/Å	13.1605(3)	14.0601(3)	12.9868(9)
c/Å	17.5175(4)	16.9083(3)	12.6311(11)
α/°	109.877(2)	75.691(2)	90
β/°	90.082(2)	81.675(2)	107.763(10)
γ/°	107.239(2)	78.457(2)	90
Volume/Å ³	1622.45(6)	1994.05(8)	1946.3(3)
Z	2	2	2
ρ _{calc} /cm ³	1.499	1.419	1.323
μ/mm ⁻¹	0.130	2.808	0.113
F(000)	740.0	856.0	788.0
Crystal size/mm ³	0.15 × 0.12 × 0.11	0.14 × 0.13 × 0.11	0.14 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)	Cu Kα (λ = 1.54184)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.94 to 49.998	7.53 to 156.84	6.668 to 52.732
Index ranges	-9 ≤ h ≤ 9, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20	-11 ≤ h ≤ 11, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20	-15 ≤ h ≤ 14, -15 ≤ k ≤ 16, -15 ≤ l ≤ 15
Reflections collected	22626	37407	32402
Independent reflections	5704 [R _{int} = 0.0314, R _{sigma} = 0.0223]	8039 [R _{int} = 0.0632, R _{sigma} = 0.0320]	7671 [R _{int} = 0.1186, R _{sigma} = 0.0627]
Data/restraints/parameters	5704/0/478	8039/0/479	7671/1107/516
Goodness-of-fit on F ²	1.035	1.082	1.066
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0332, wR ₂ = 0.0871	R ₁ = 0.0583, wR ₂ = 0.1726	R ₁ = 0.0859, wR ₂ = 0.1948
Final R indexes [all data]	R ₁ = 0.0361, wR ₂ = 0.0892	R ₁ = 0.0673, wR ₂ = 0.1823	R ₁ = 0.0927, wR ₂ = 0.2002
Largest diff. peak/hole / e Å ⁻³	0.30/-0.23	0.21/-0.27	0.49/-0.38
Flack parameter	-	-	-1.3(5)

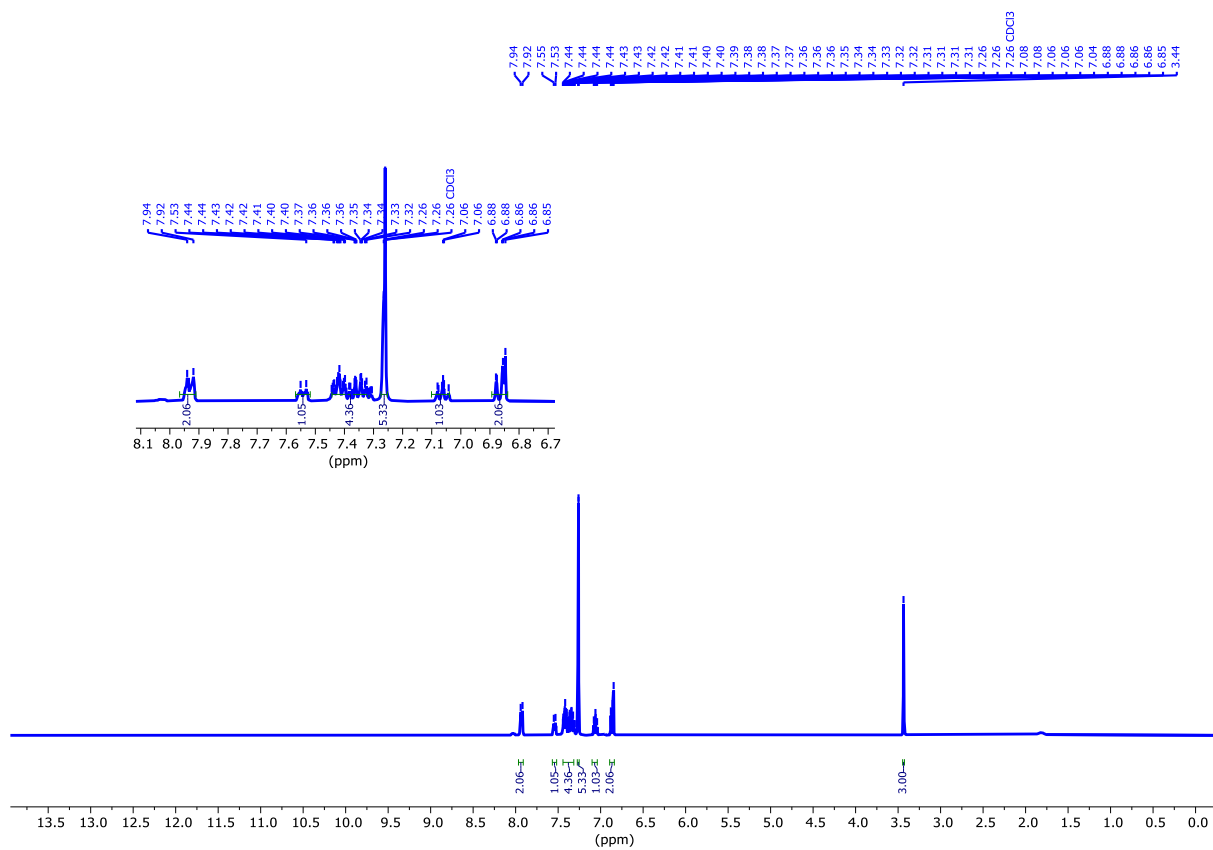


Figure S19: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 1d in CDCl_3

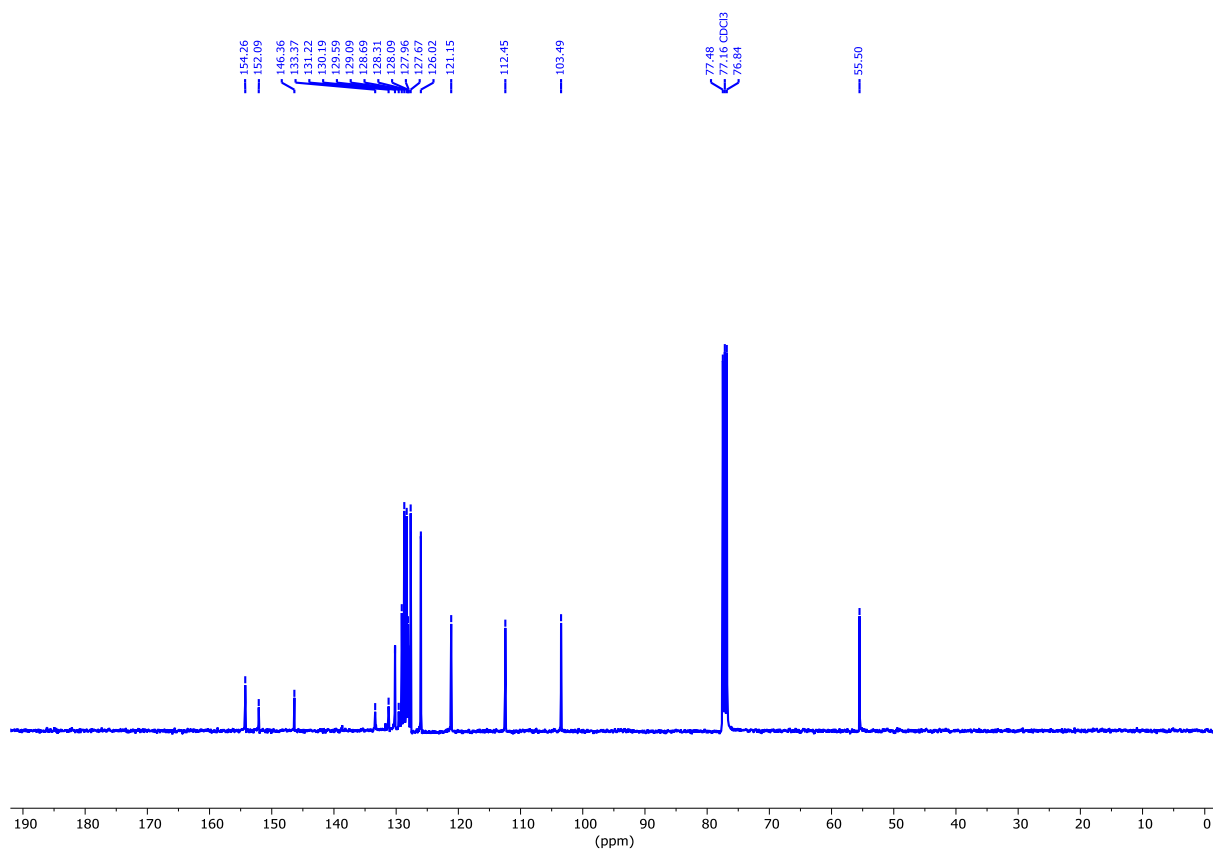


Figure S20: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 1d in CDCl_3

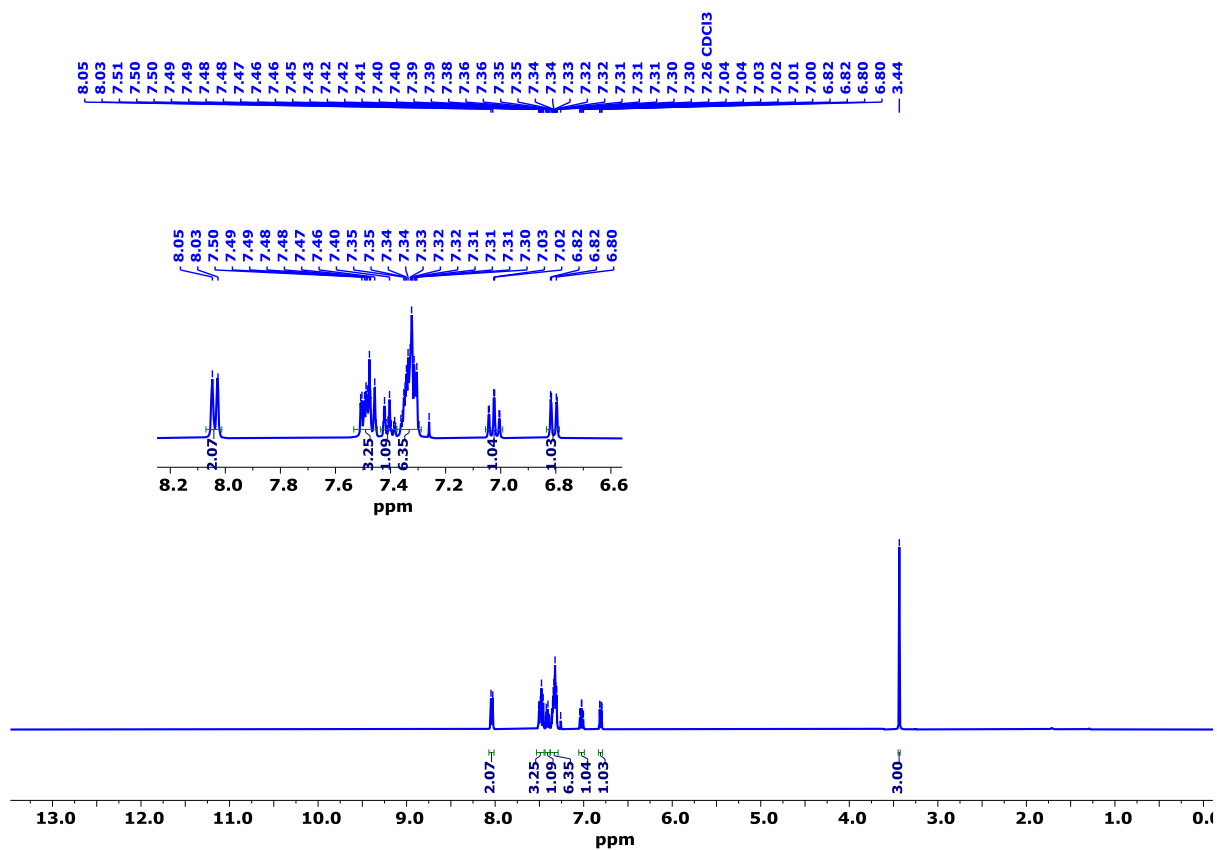


Figure S21: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 1c in CDCl_3

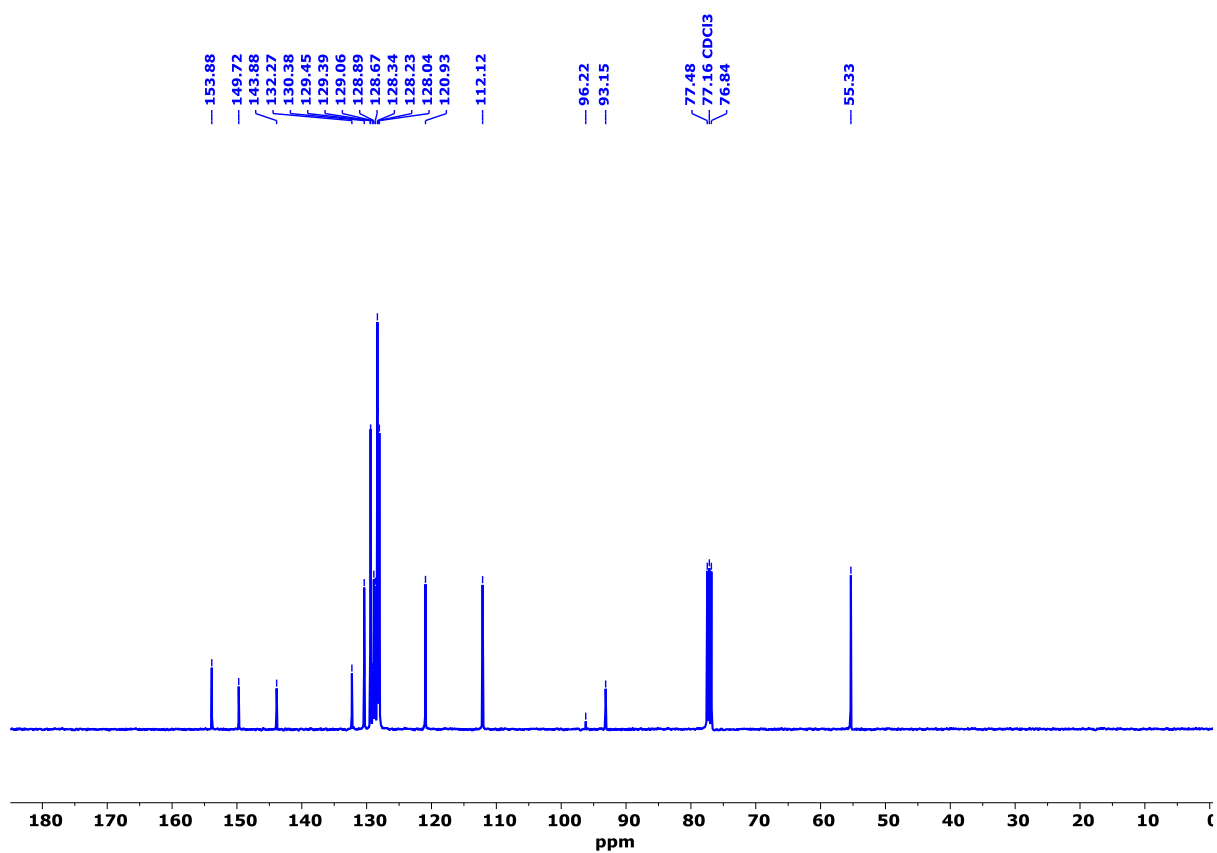


Figure S22: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 1c in CDCl_3

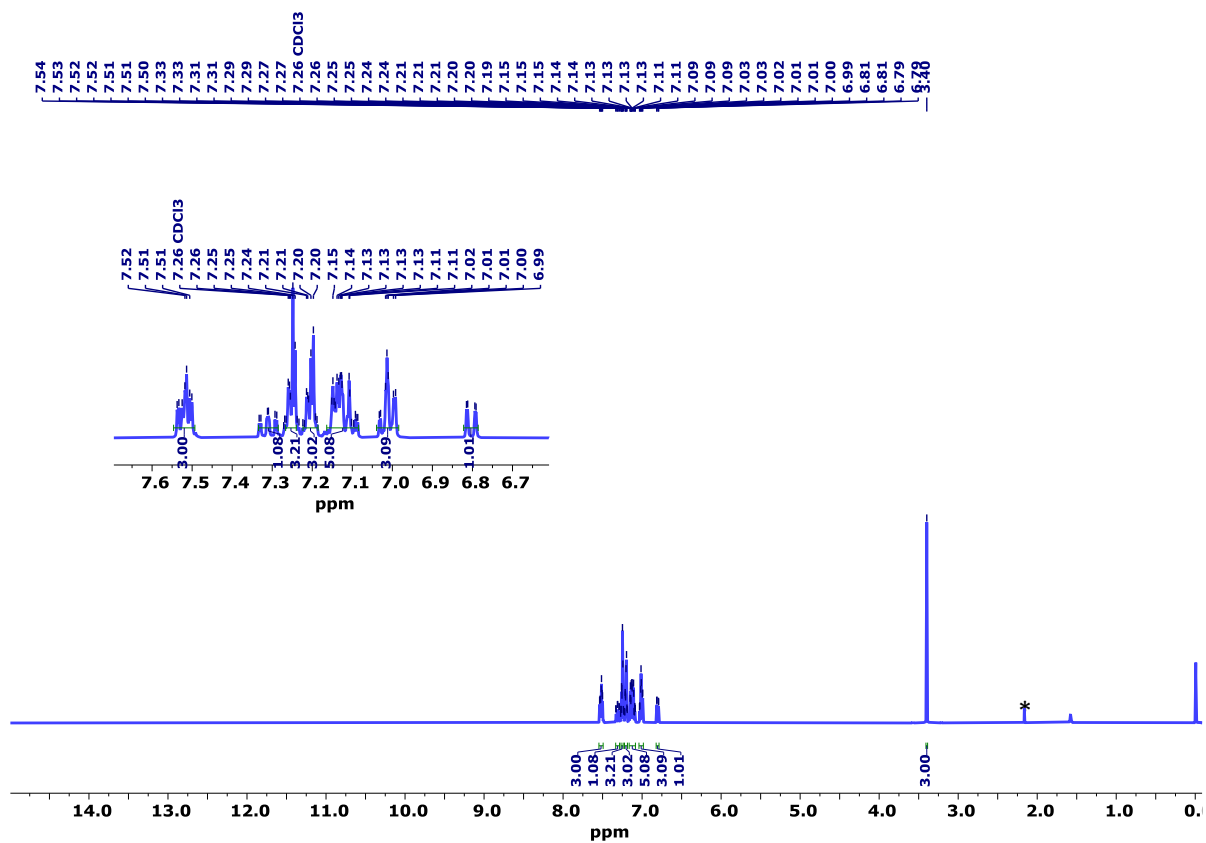


Figure S23: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 1b in CDCl_3 (*Toluene $-\text{CH}_3$ peak)

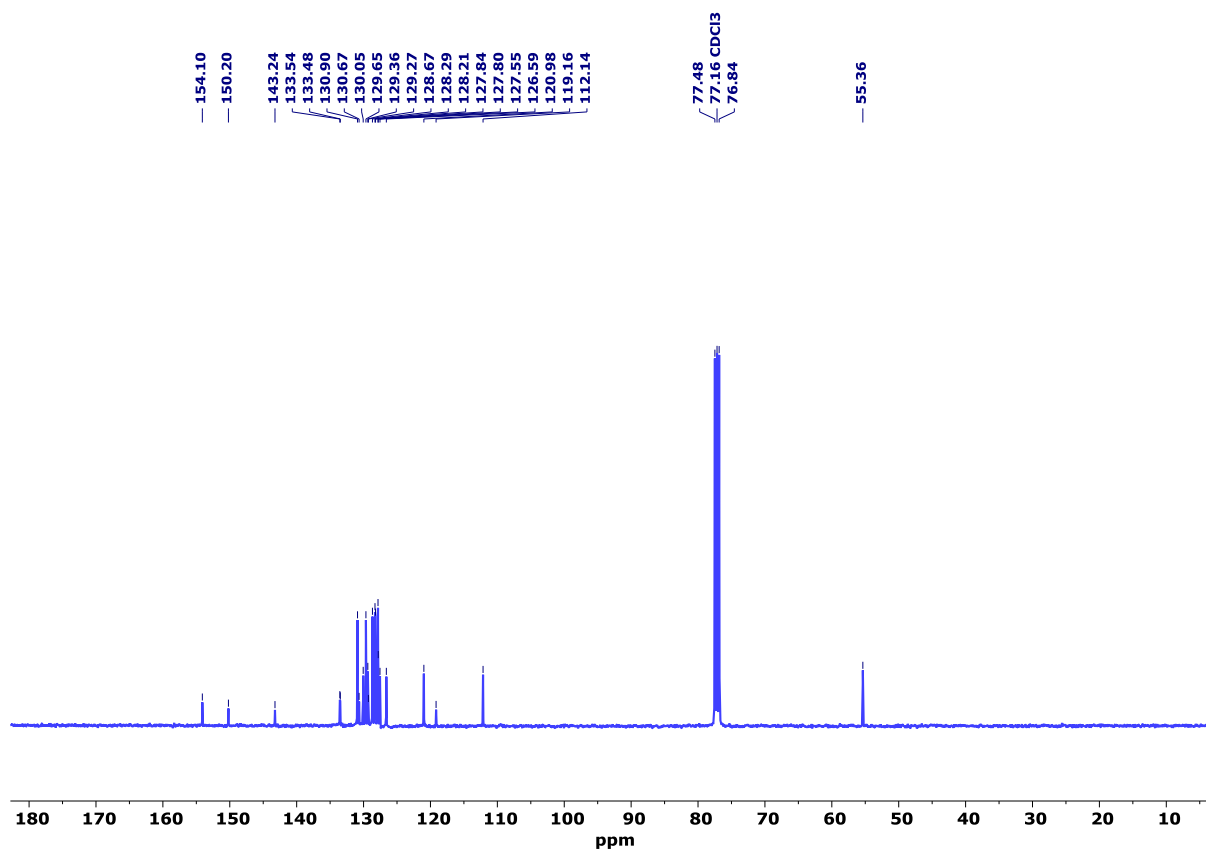


Figure S24: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 1b in CDCl_3

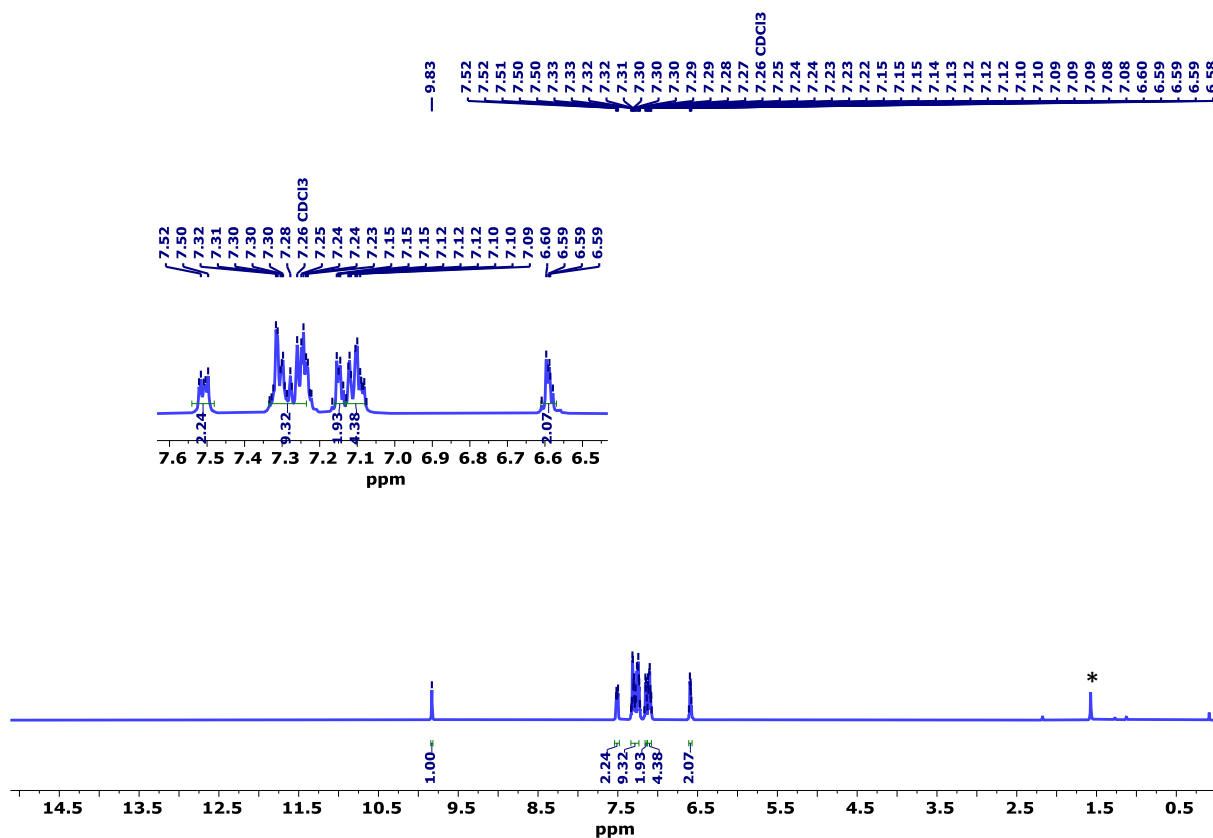


Figure S25: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 1a in CDCl_3 (* H_2O peak)

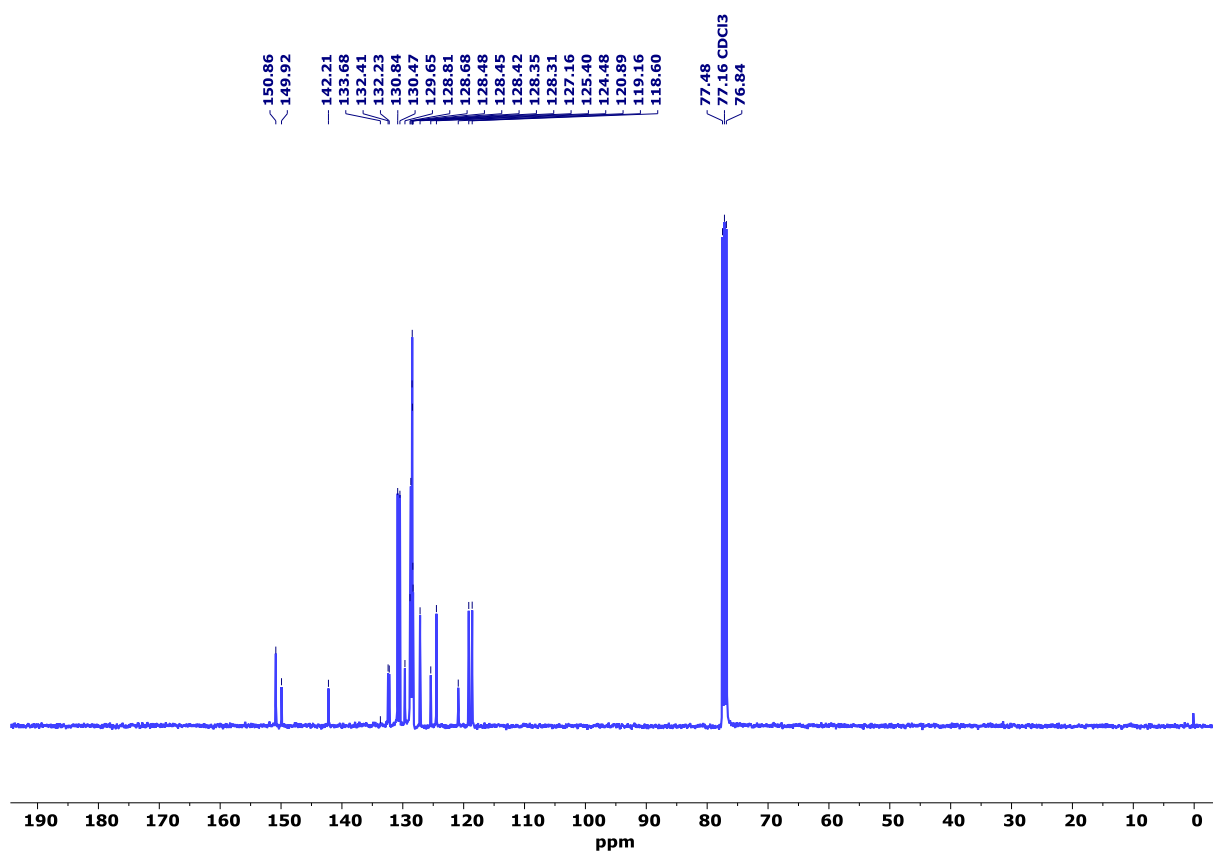


Figure S26: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 1a in CDCl_3

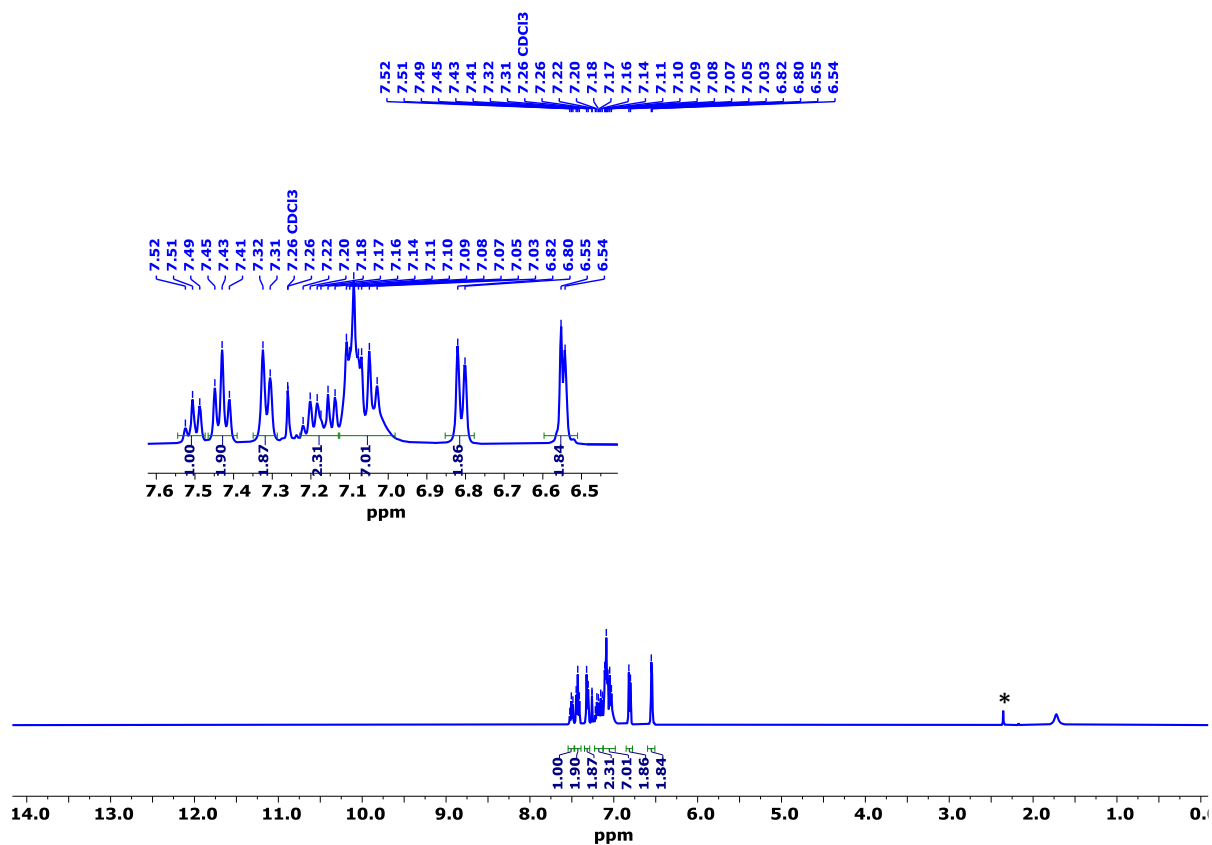


Figure S27: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 1 in CDCl_3 (* Toluene $-\text{CH}_3$)

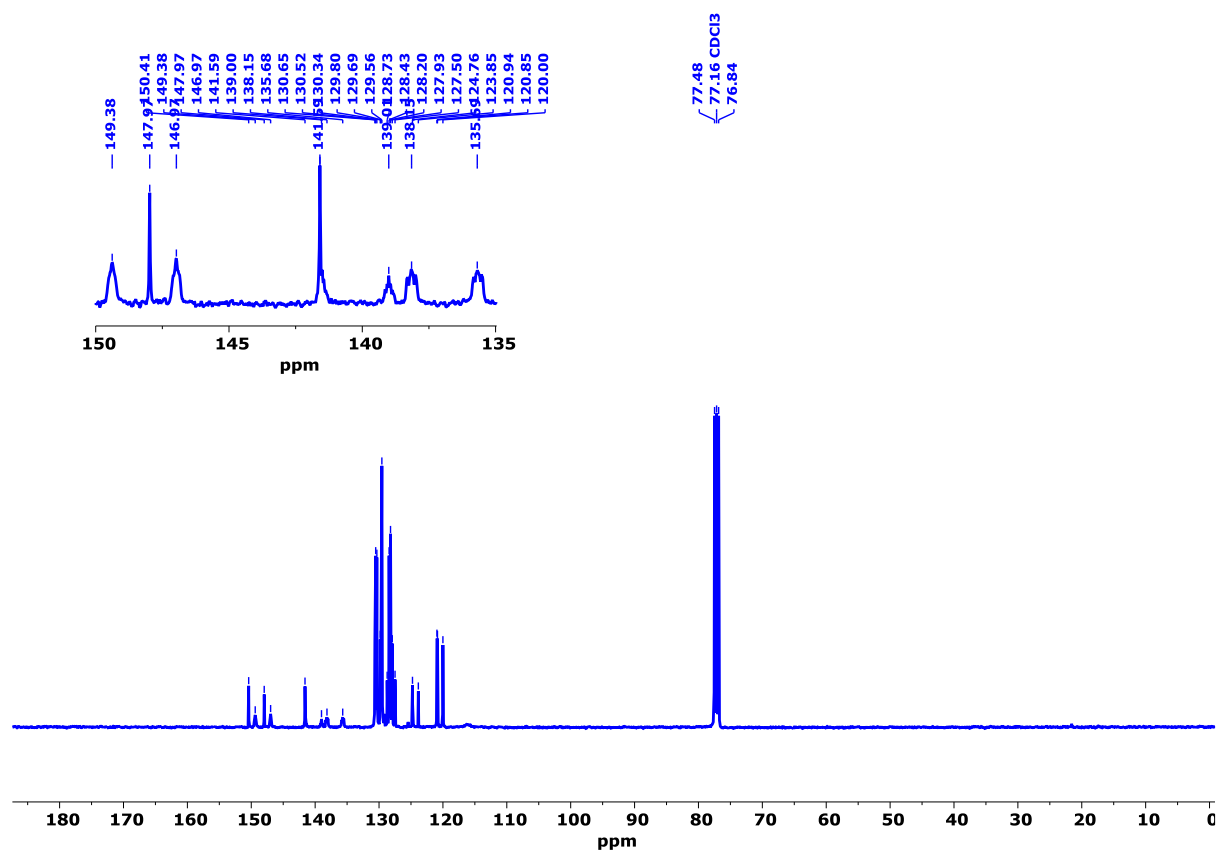


Figure S28: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 1 in CDCl_3

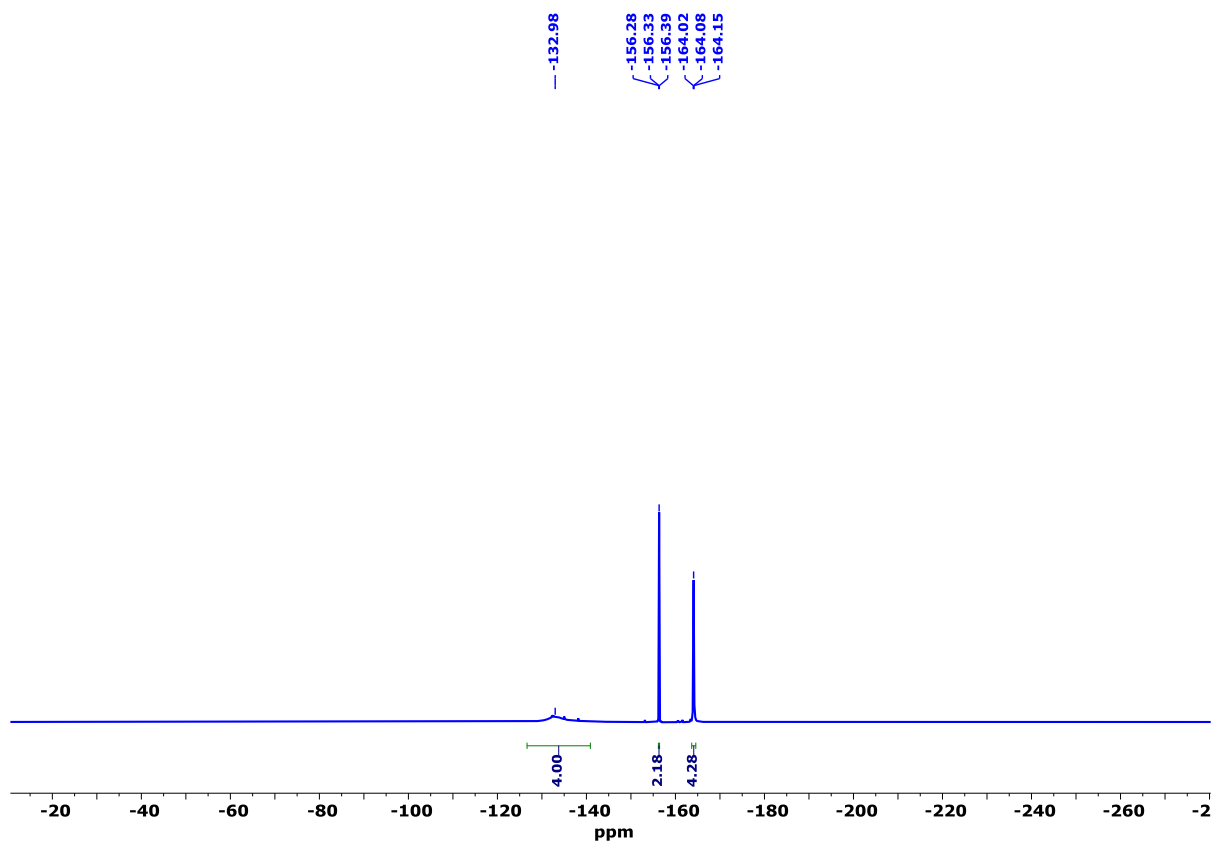


Figure S29: ^{19}F -NMR (376 MHz) spectrum of compound 1 in CDCl_3

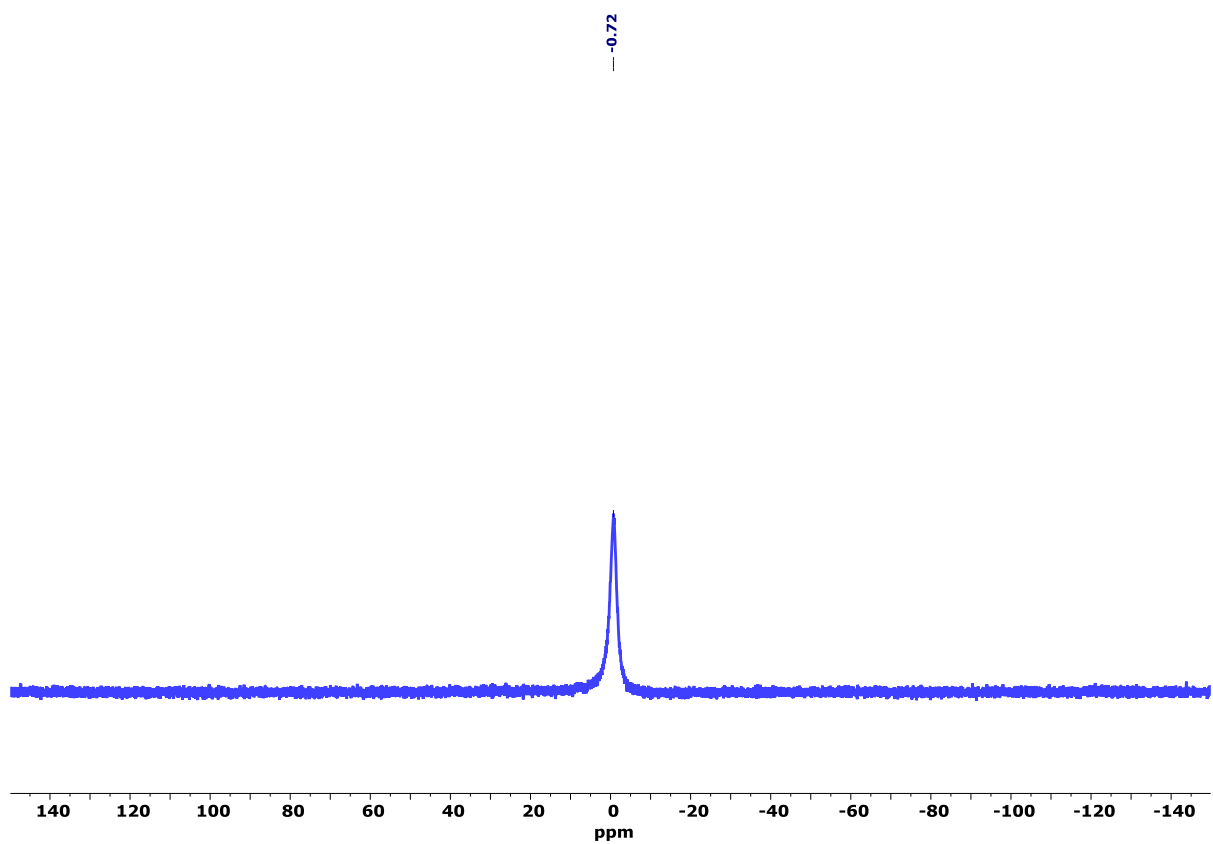


Figure S30: ^{11}B -NMR (128 MHz) spectrum of compound 1 in CDCl_3

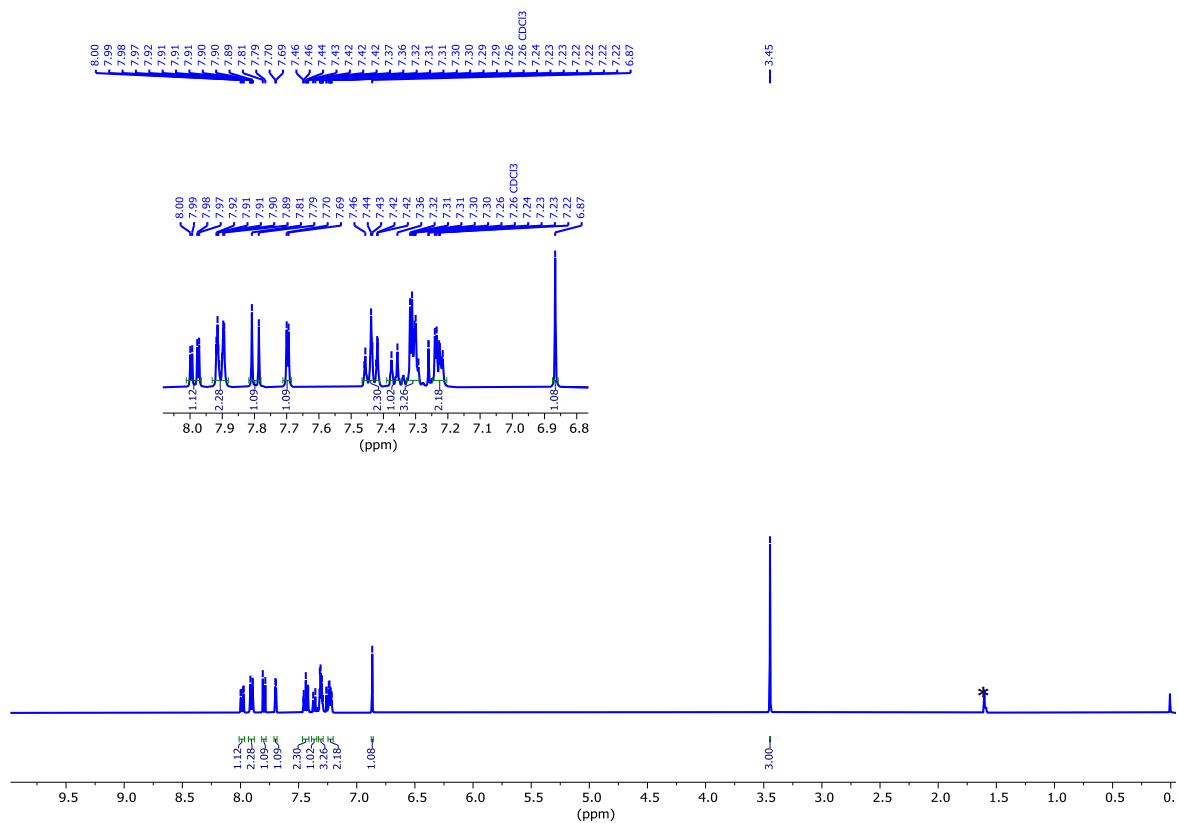


Figure S31: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 2f in CDCl_3 (* H_2O peak)

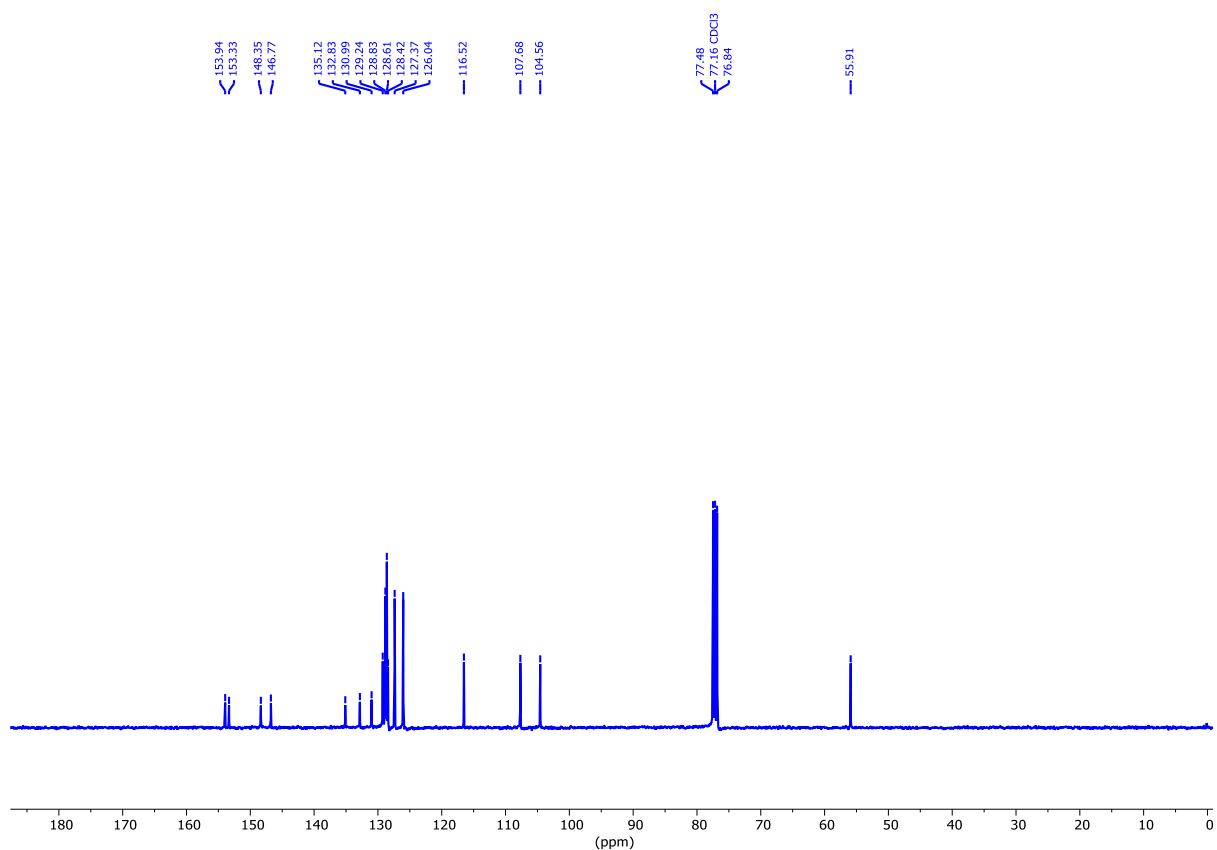


Figure S32: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 2f in CDCl_3

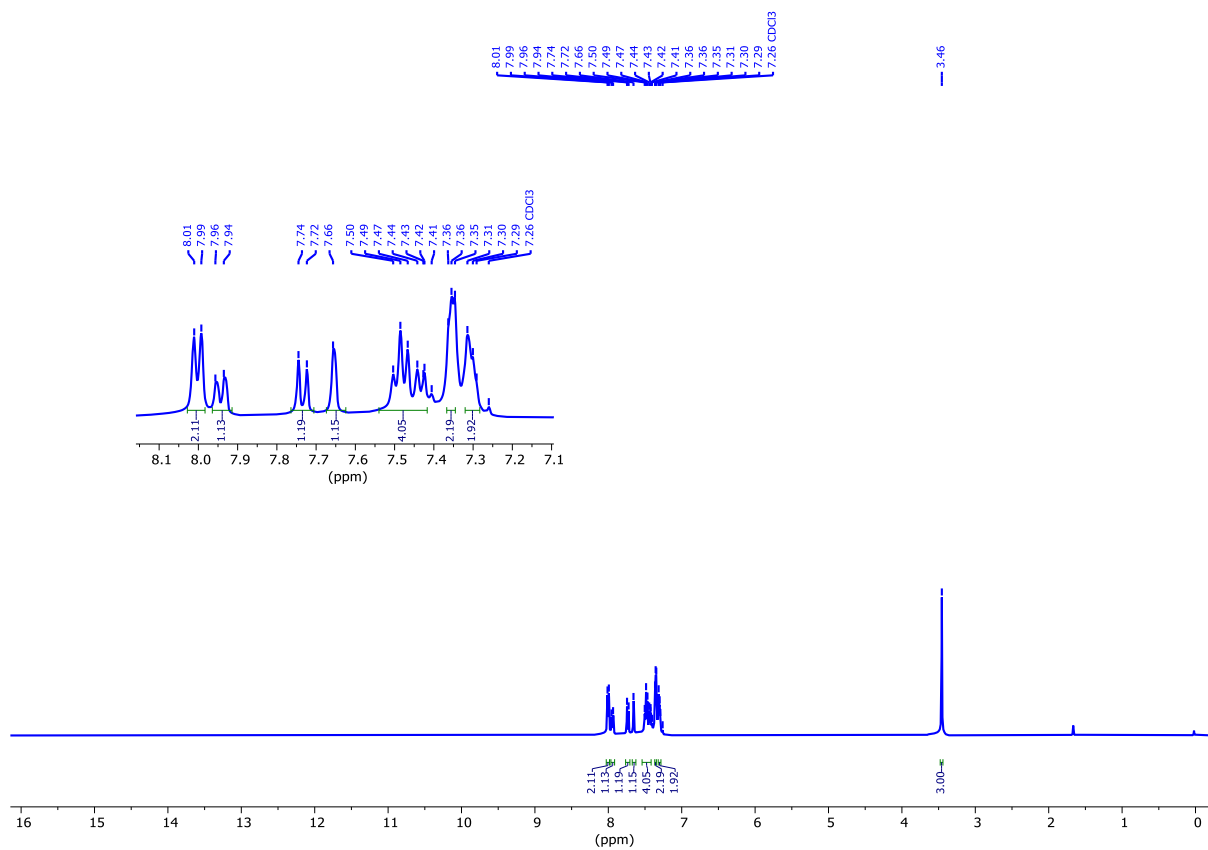


Figure S33: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 2e in CDCl_3

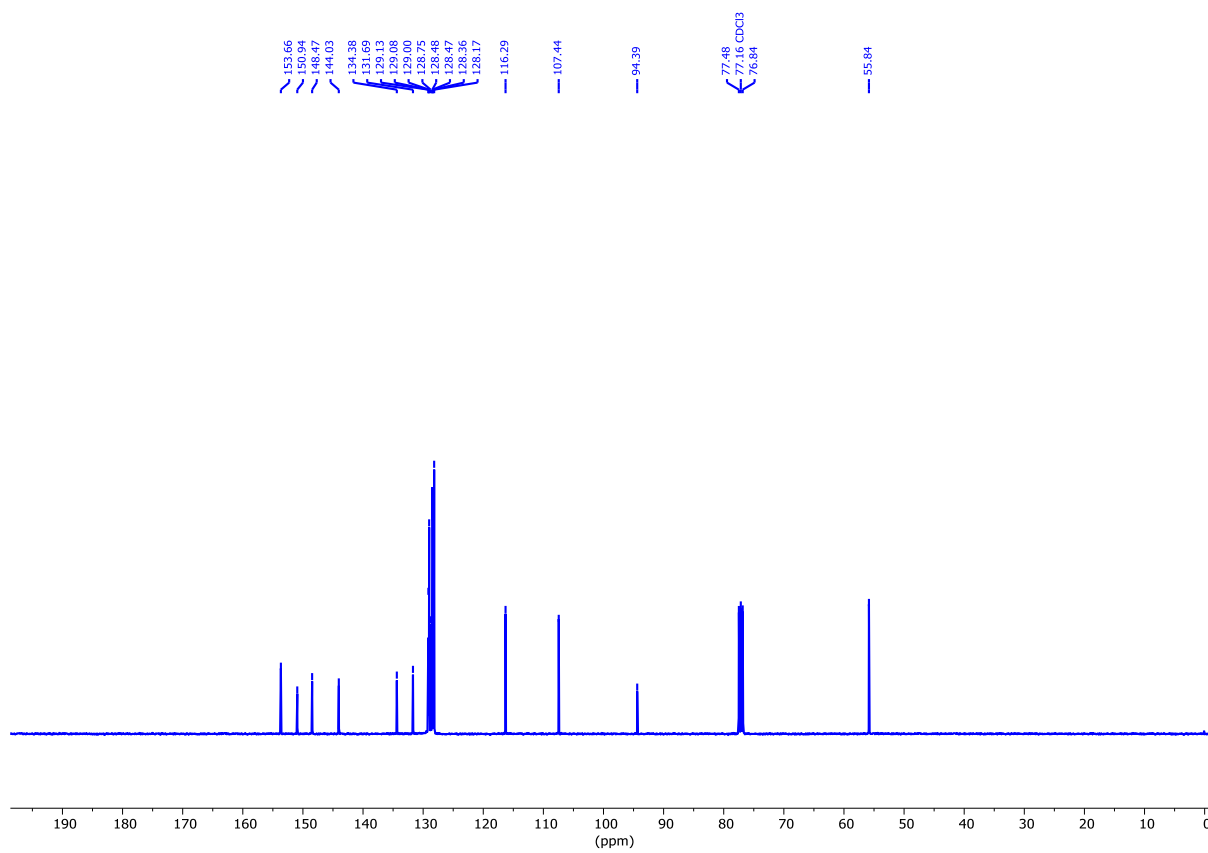


Figure S34: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 2e in CDCl_3

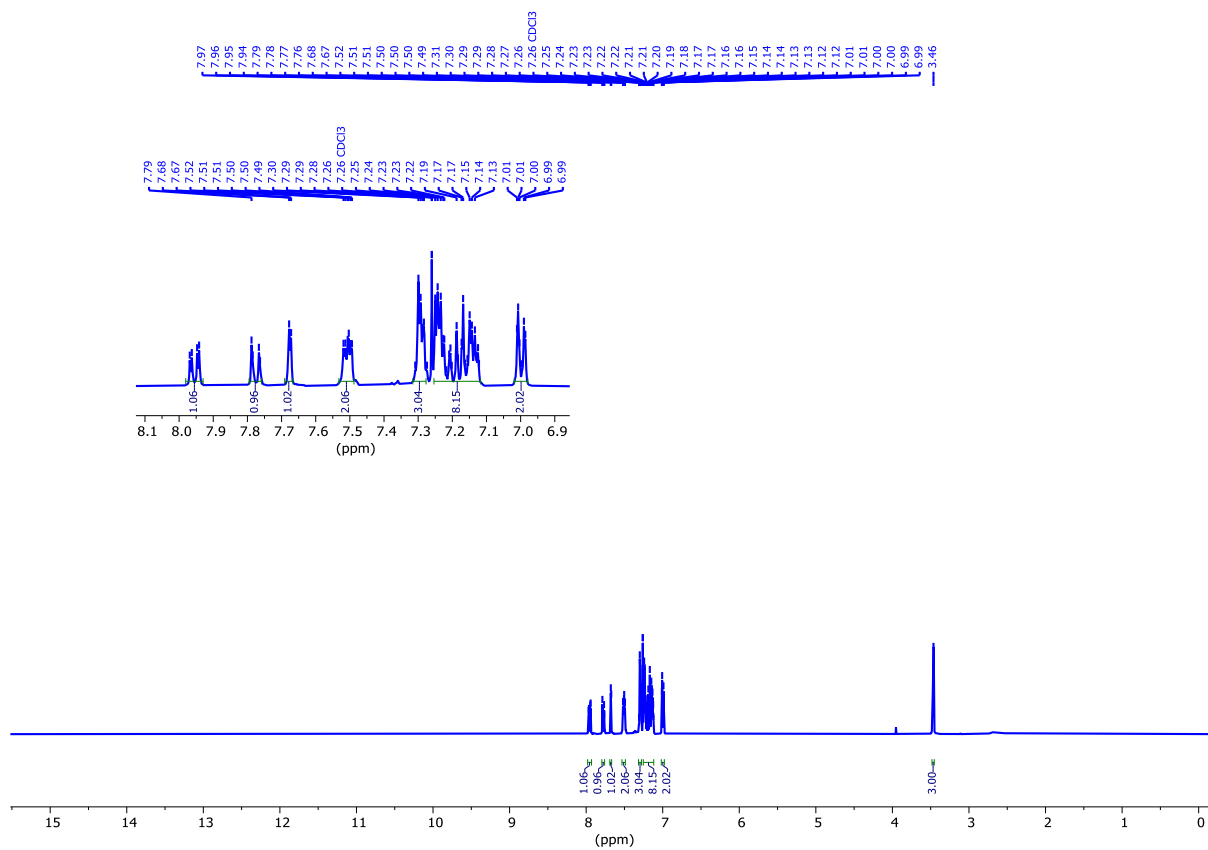


Figure S35: ¹H-NMR (400 MHz) spectrum of compound 2d in CDCl₃

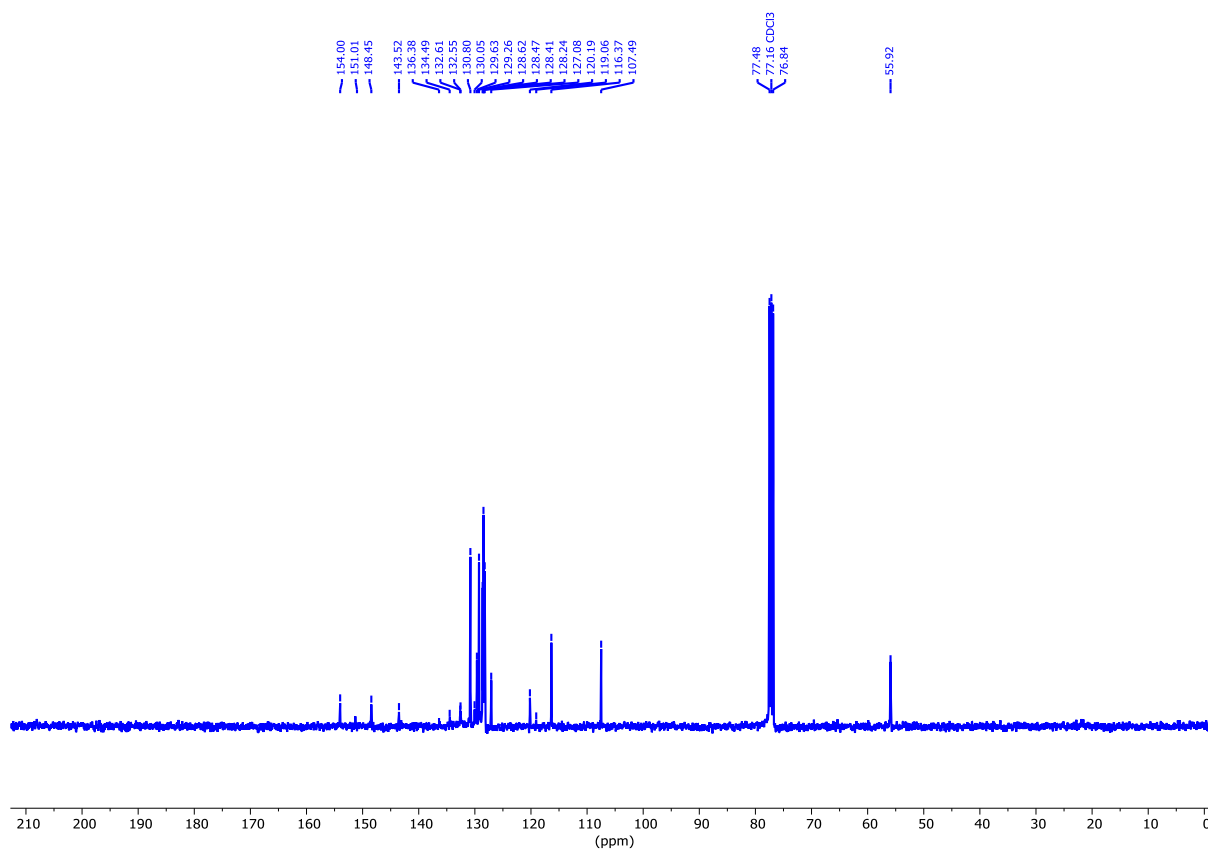


Figure S36: ¹³C-NMR (101 MHz) spectrum of compound 2d in CDCl₃

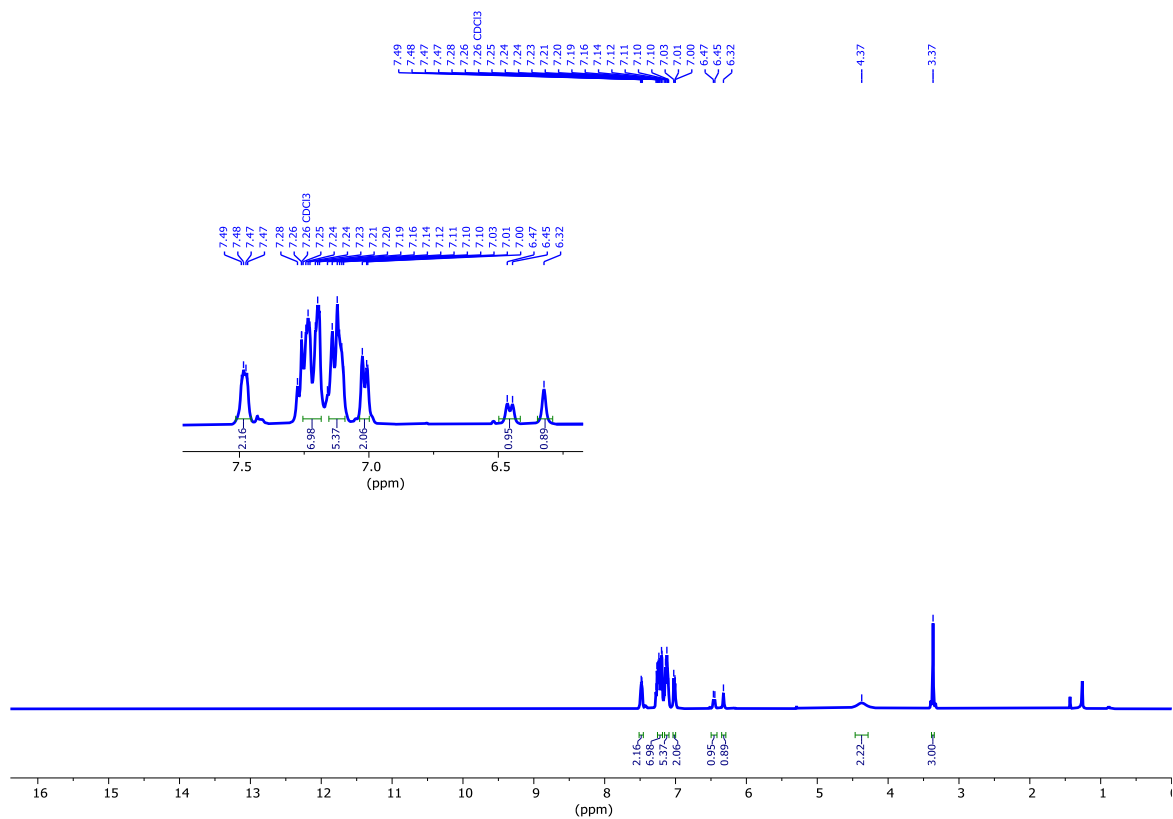


Figure S37: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 2c in CDCl_3

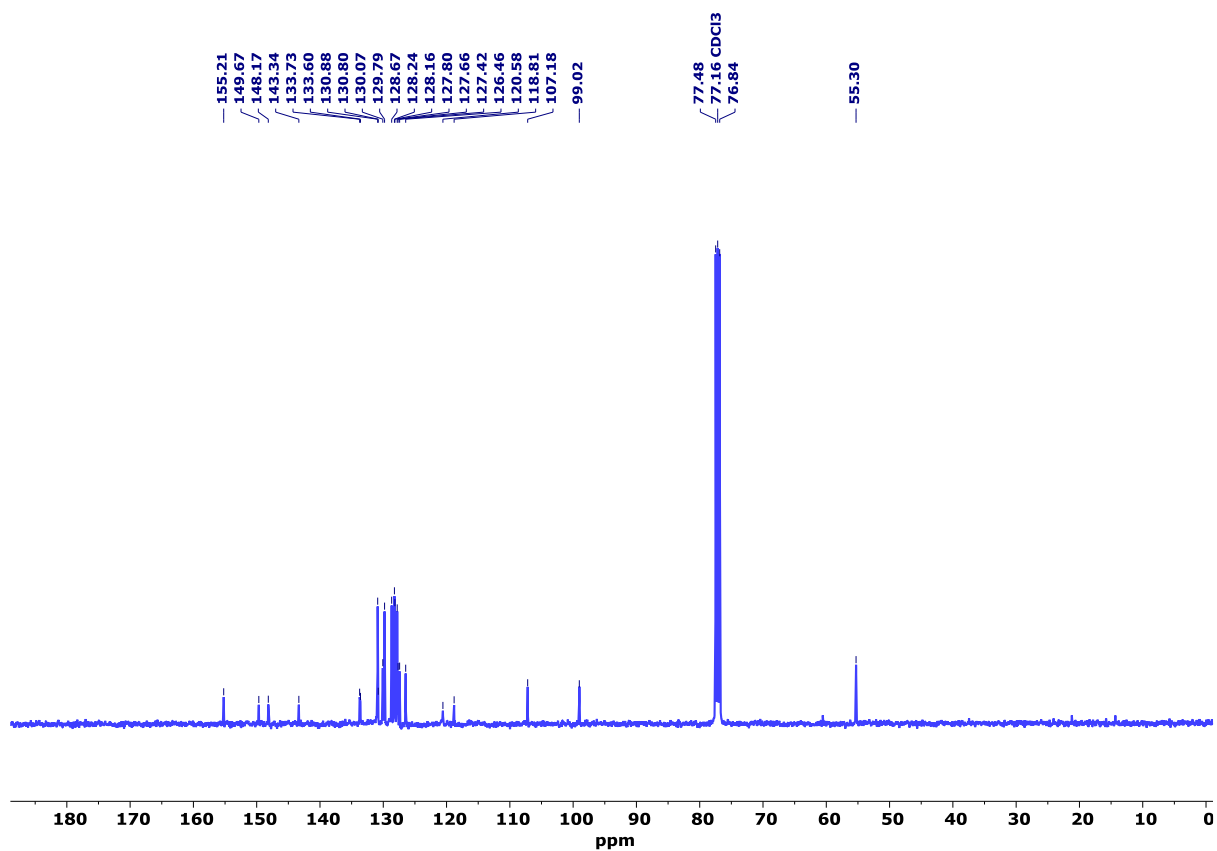


Figure S38: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 2c in CDCl_3

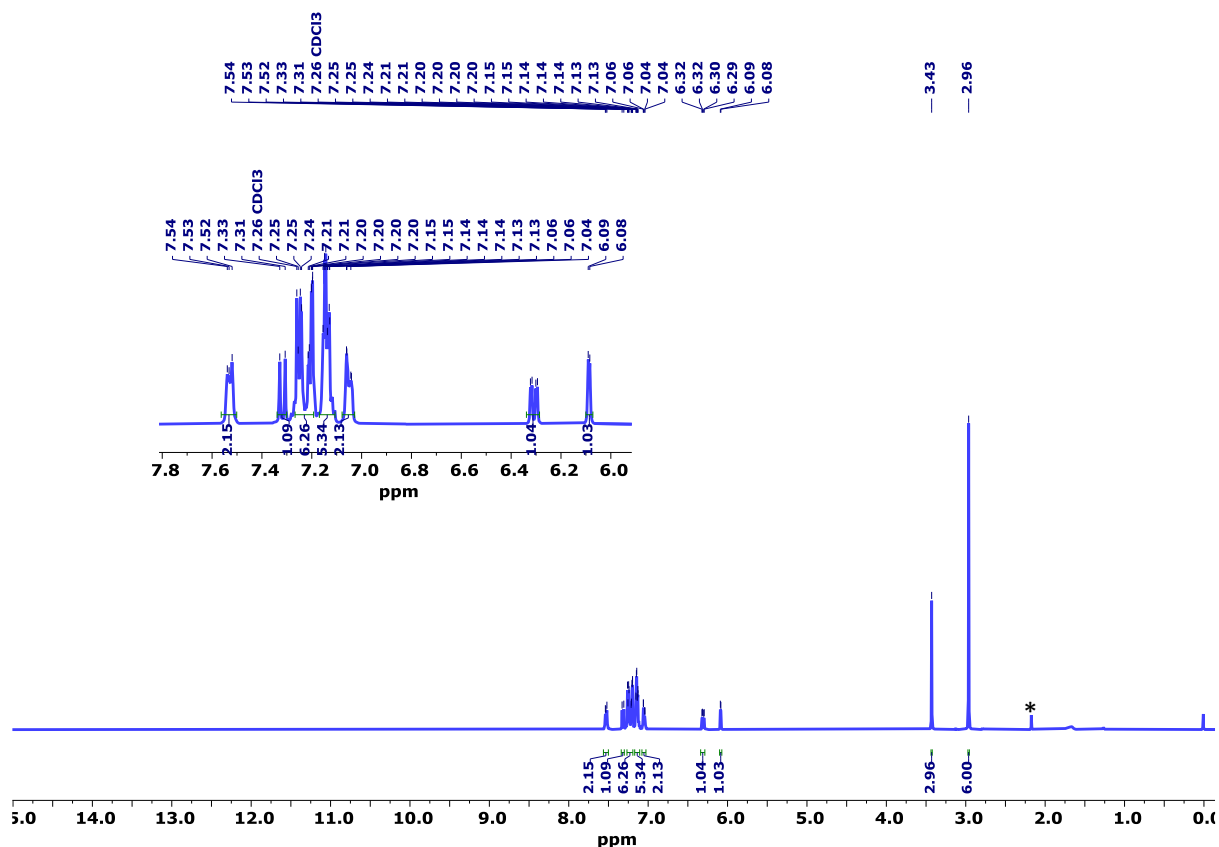


Figure S39: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 2b in CDCl_3 (*Toluene $-\text{CH}_3$ peak)

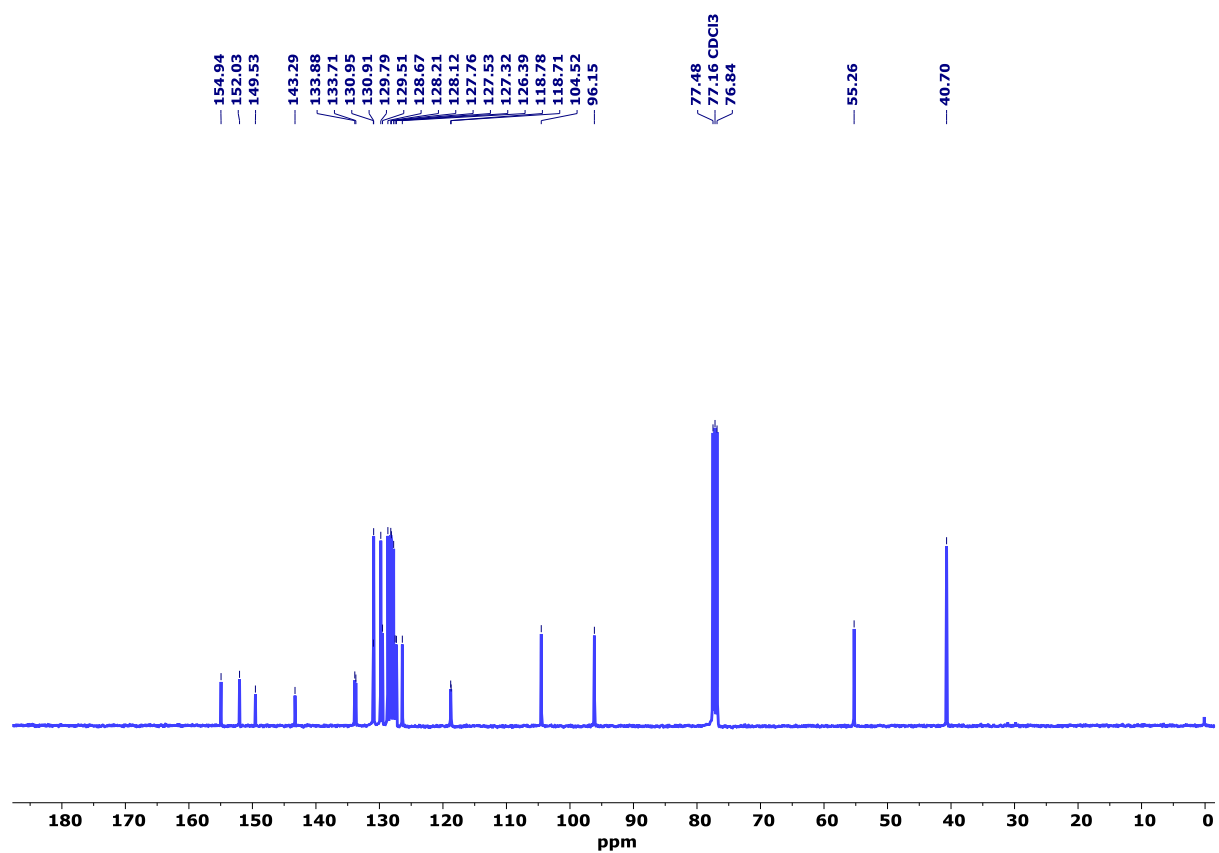


Figure S40: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 2b in CDCl_3

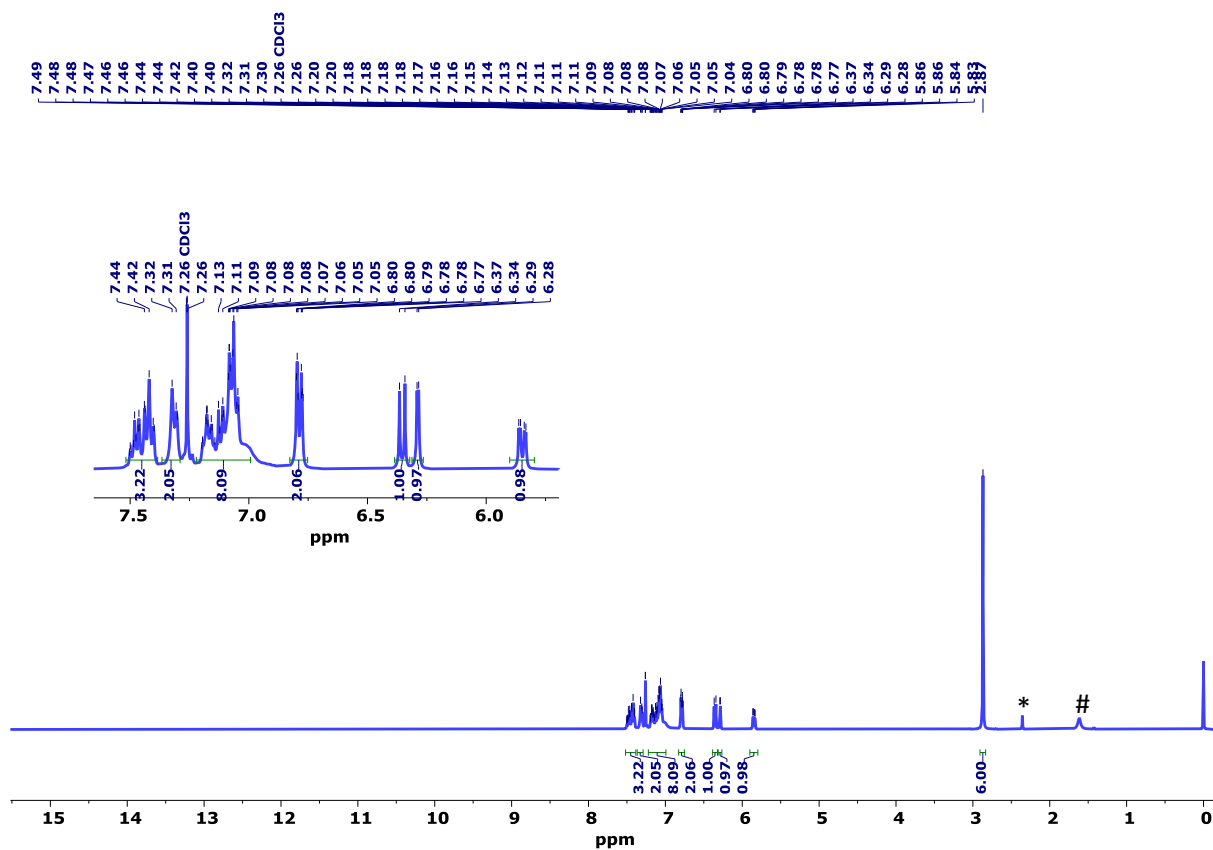


Figure S43: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 2 in CDCl_3 (* Toluene $-\text{CH}_3$) (# H_2O)

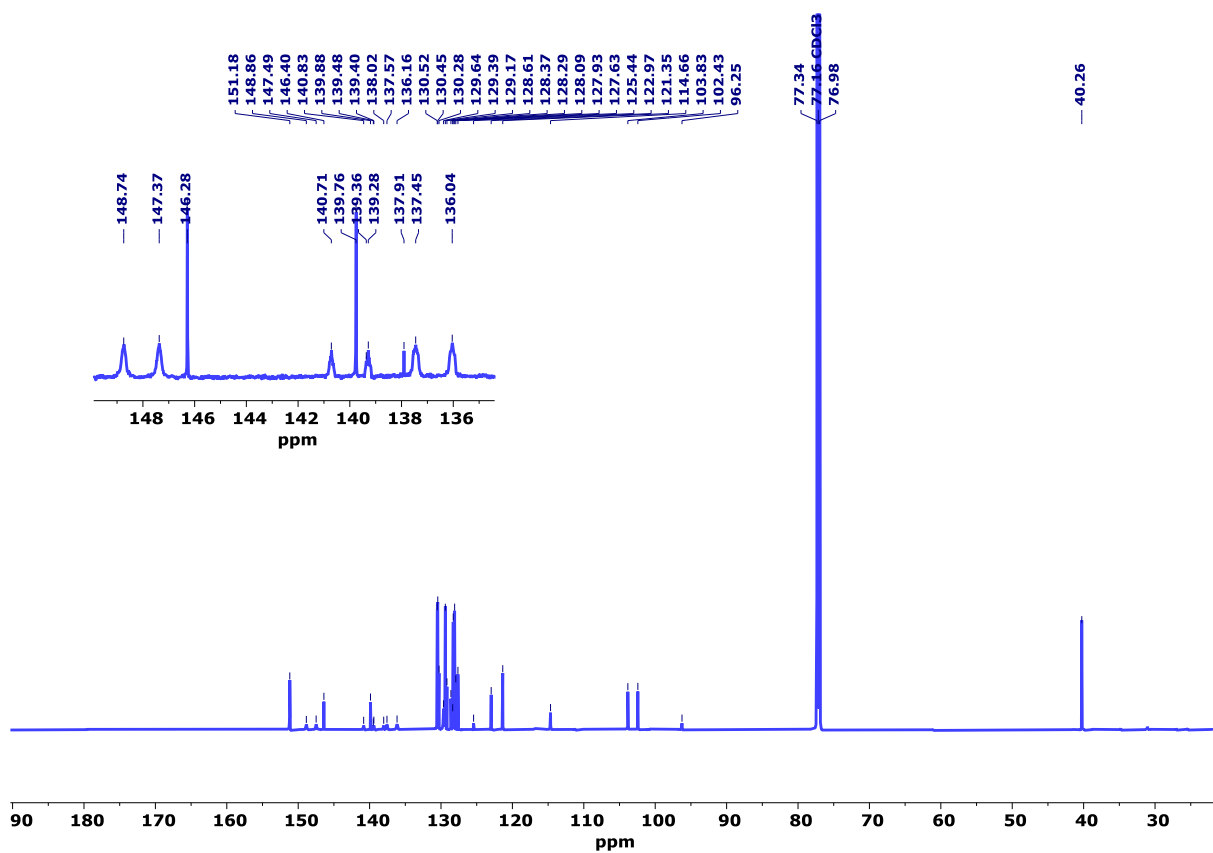


Figure S44: $^{13}\text{C-NMR}$ (176 MHz) spectrum of compound 2 in CDCl_3

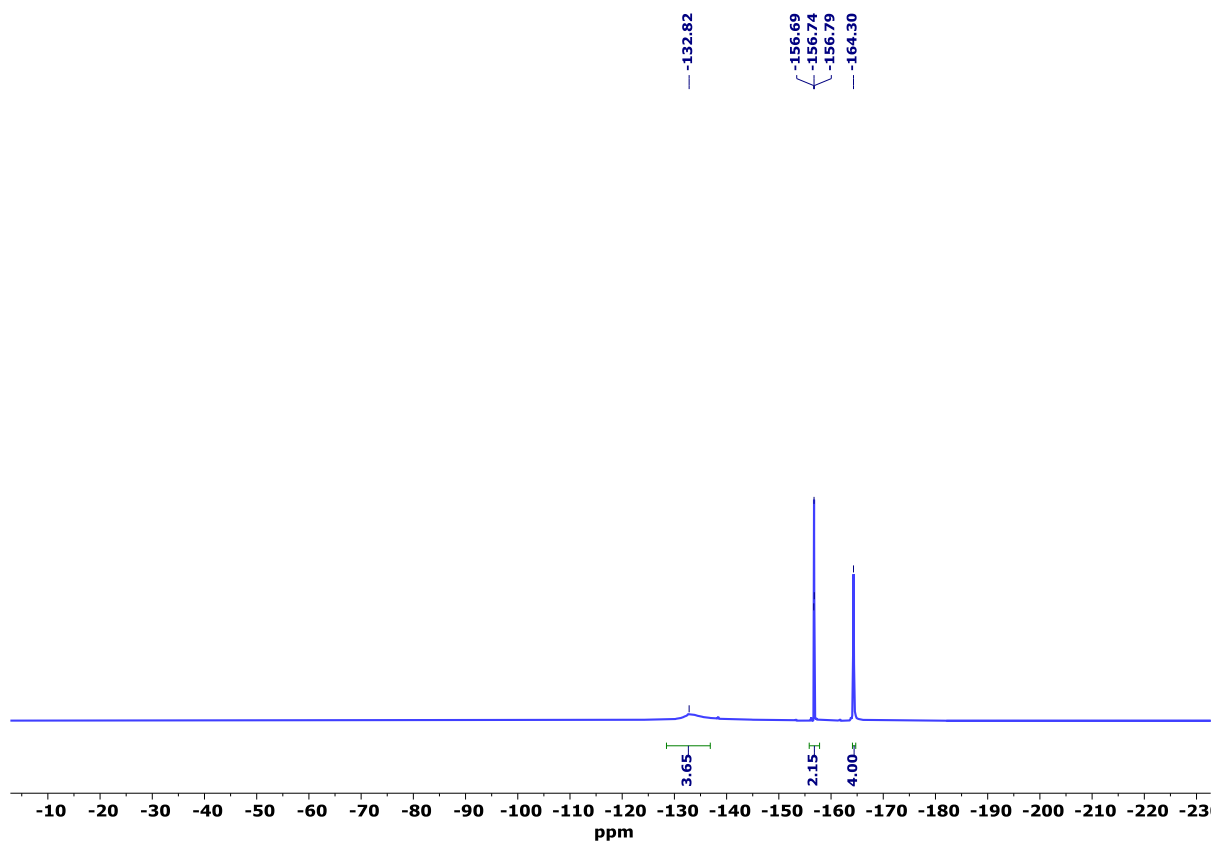


Figure S45: ^{19}F -NMR (376 MHz) spectrum of compound 2 in CDCl_3

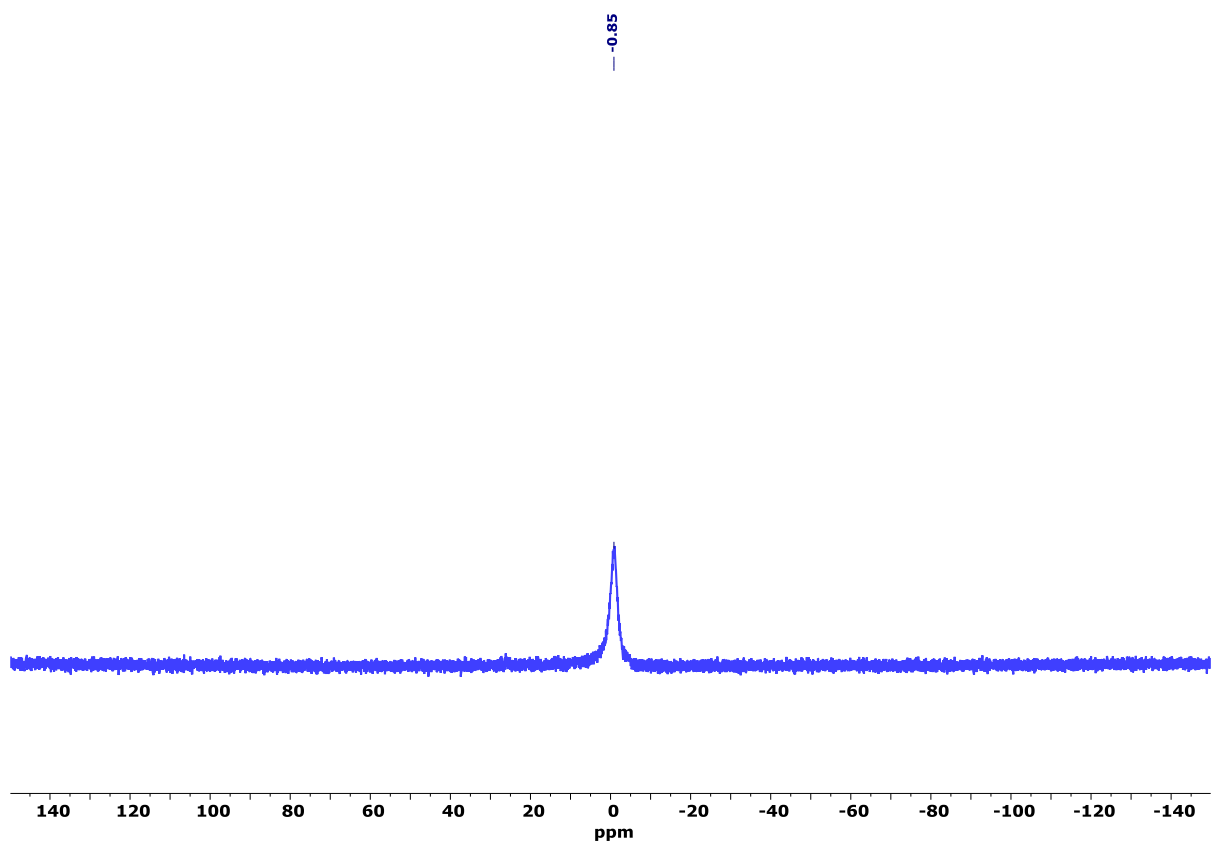


Figure S46: ^{11}B -NMR (128 MHz) spectrum of compound 2 in CDCl_3

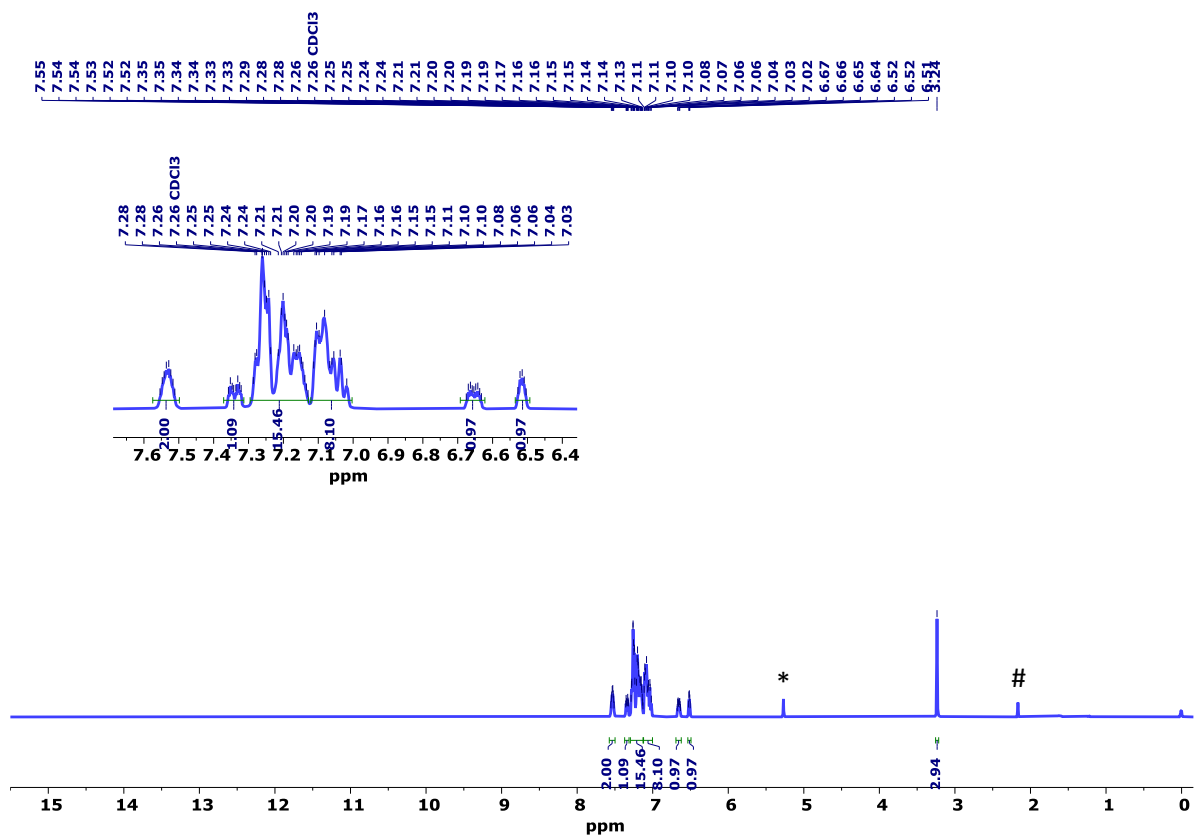


Figure S47: ¹H-NMR (400 MHz) spectrum of compound 3b in CDCl₃ (*CH₂Cl₂ peak & #H₂O peak)

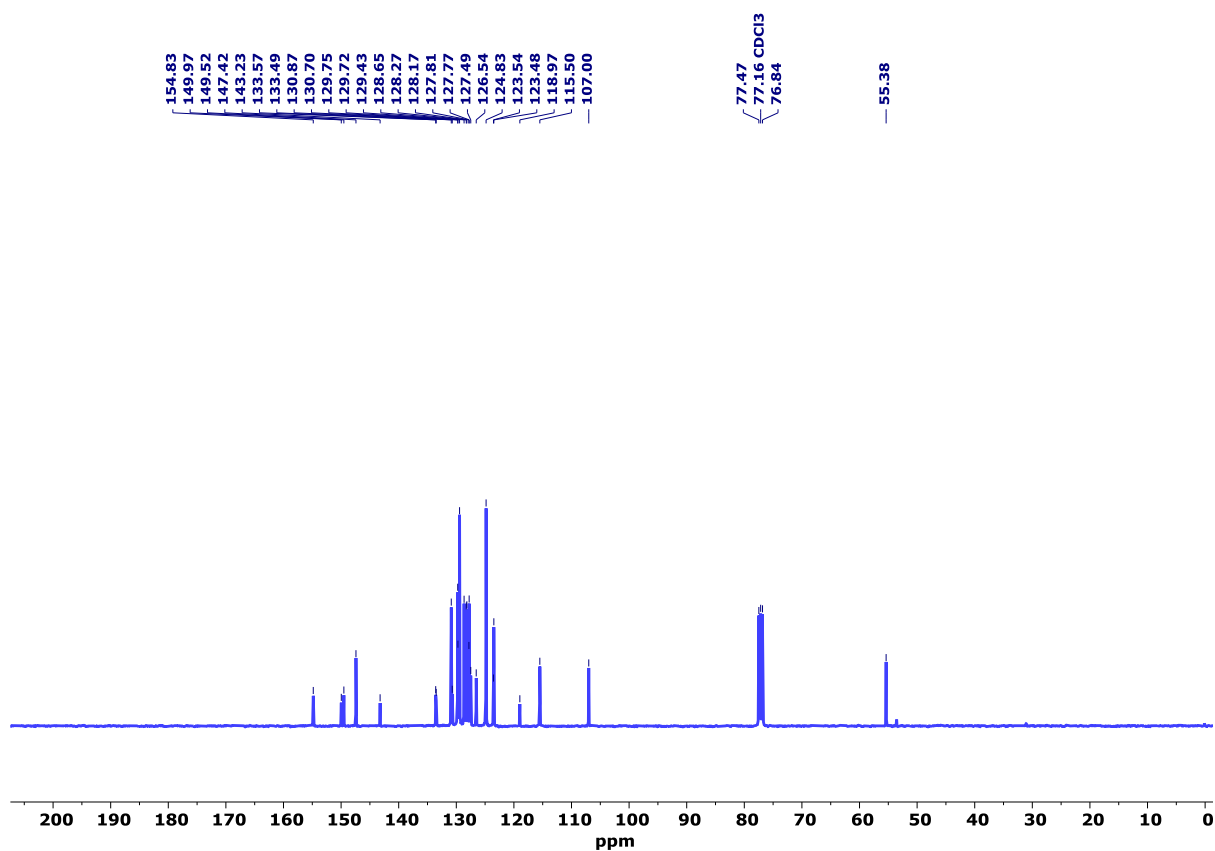


Figure S48: ¹³C-NMR (101 MHz) spectrum of compound 3b in CDCl₃

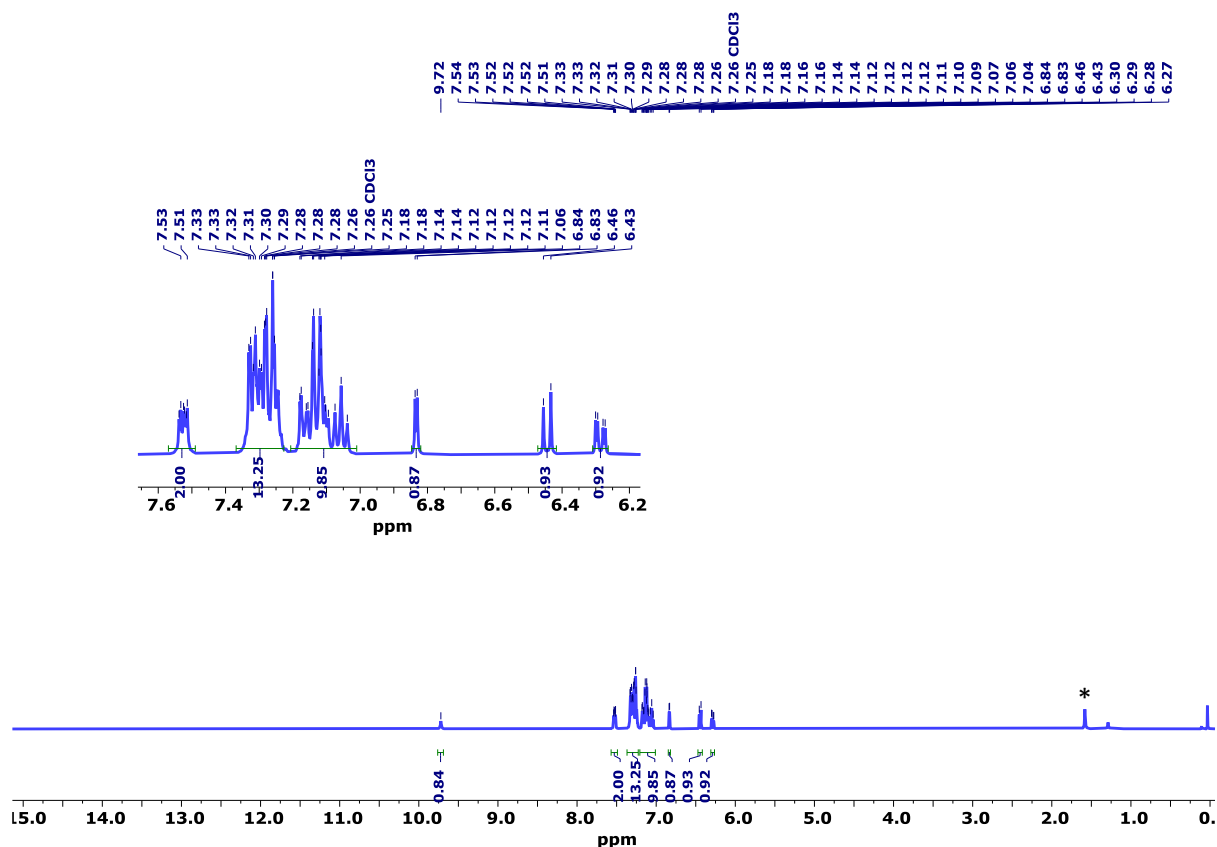


Figure S49: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 3a in CDCl_3 (* H_2O peak)

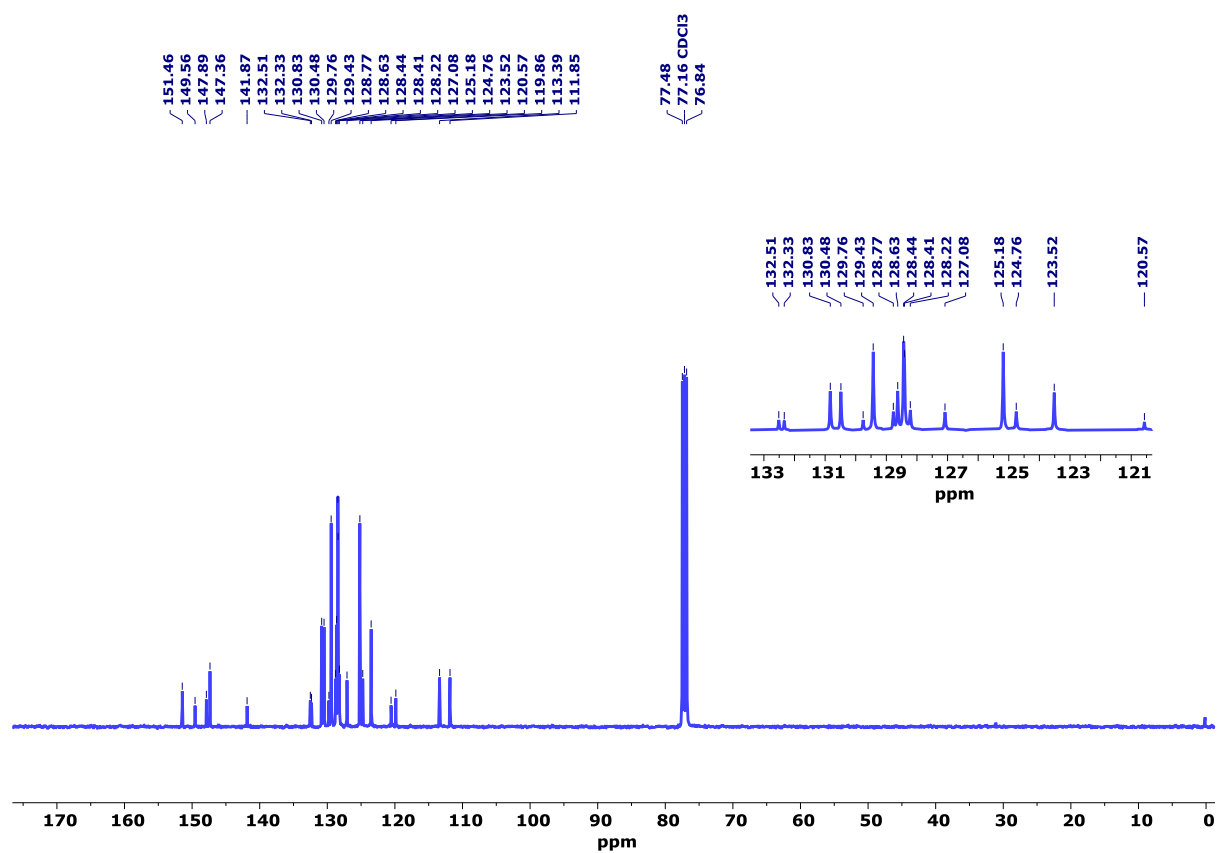


Figure S50: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 3a in CDCl_3

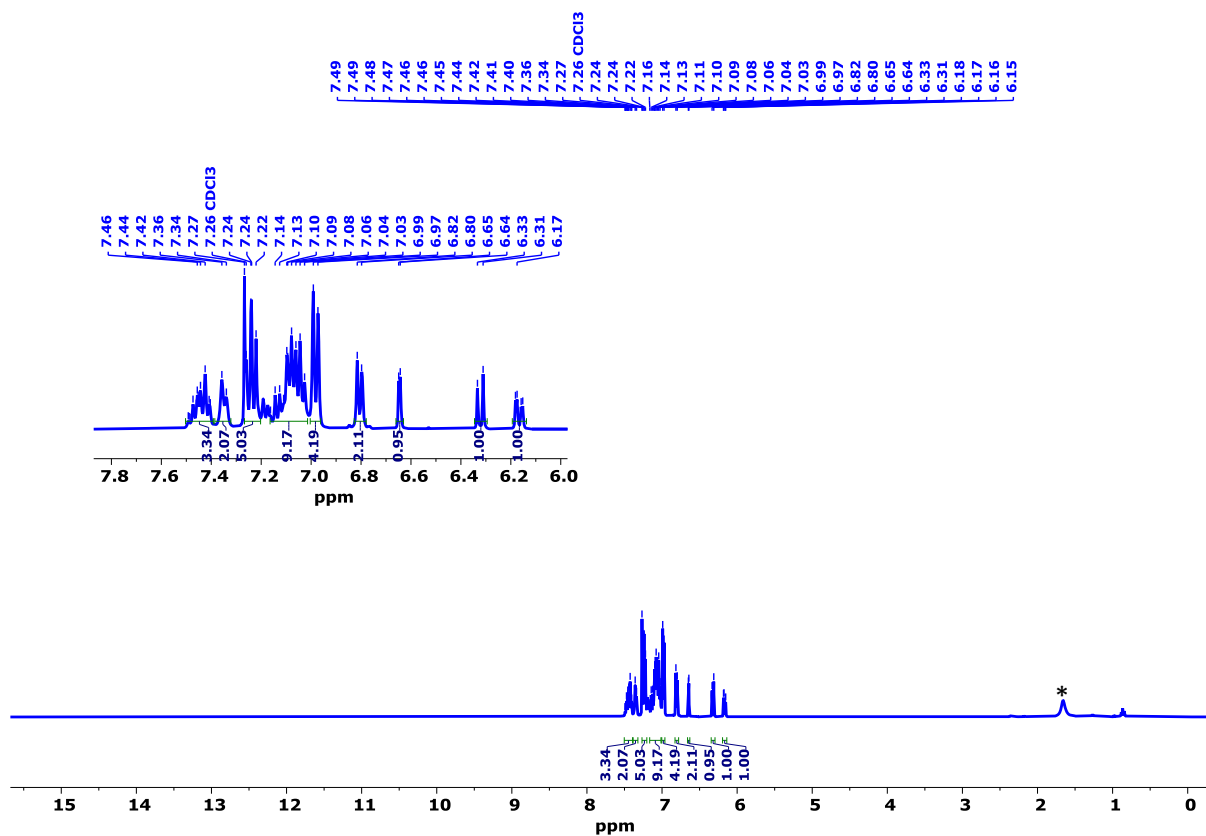


Figure S51: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 3 in CDCl_3 (* H_2O peak)

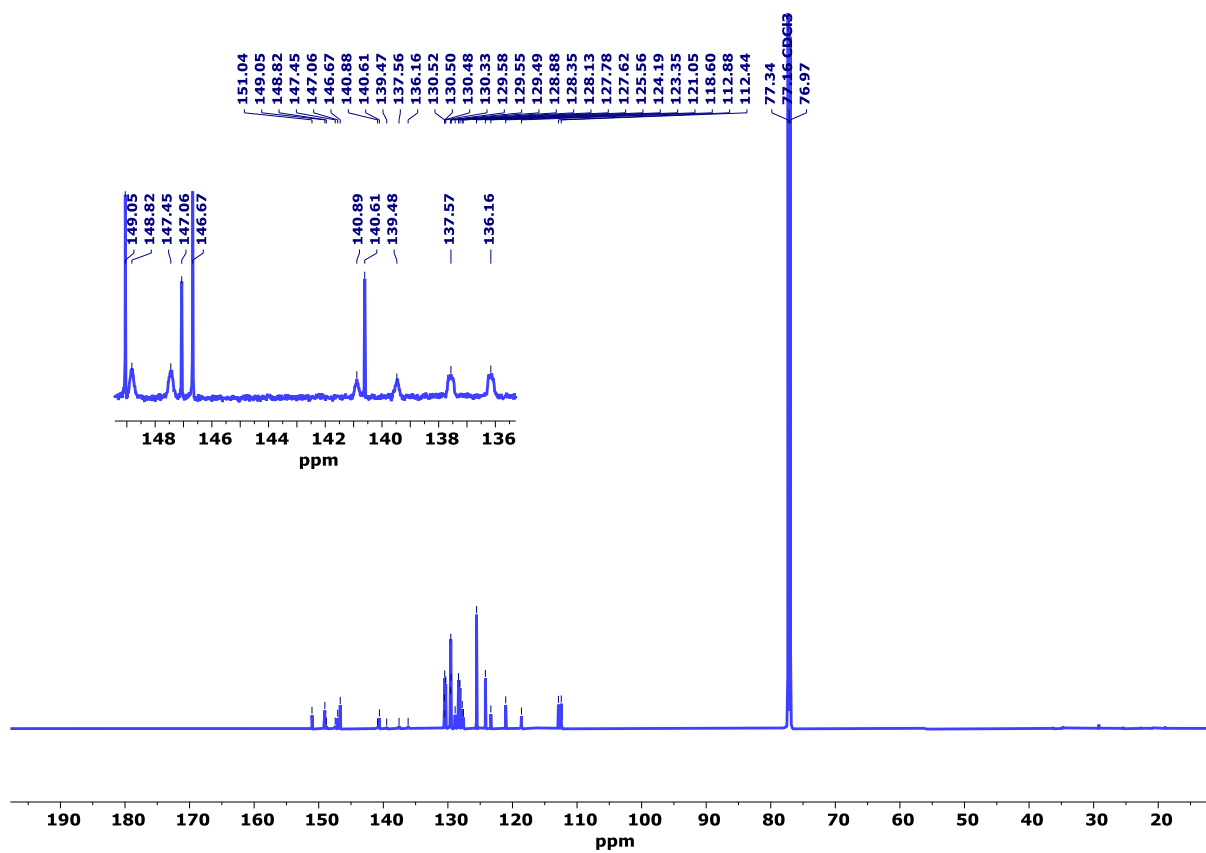


Figure S52: $^{13}\text{C-NMR}$ (176 MHz) spectrum of compound 3 in CDCl_3

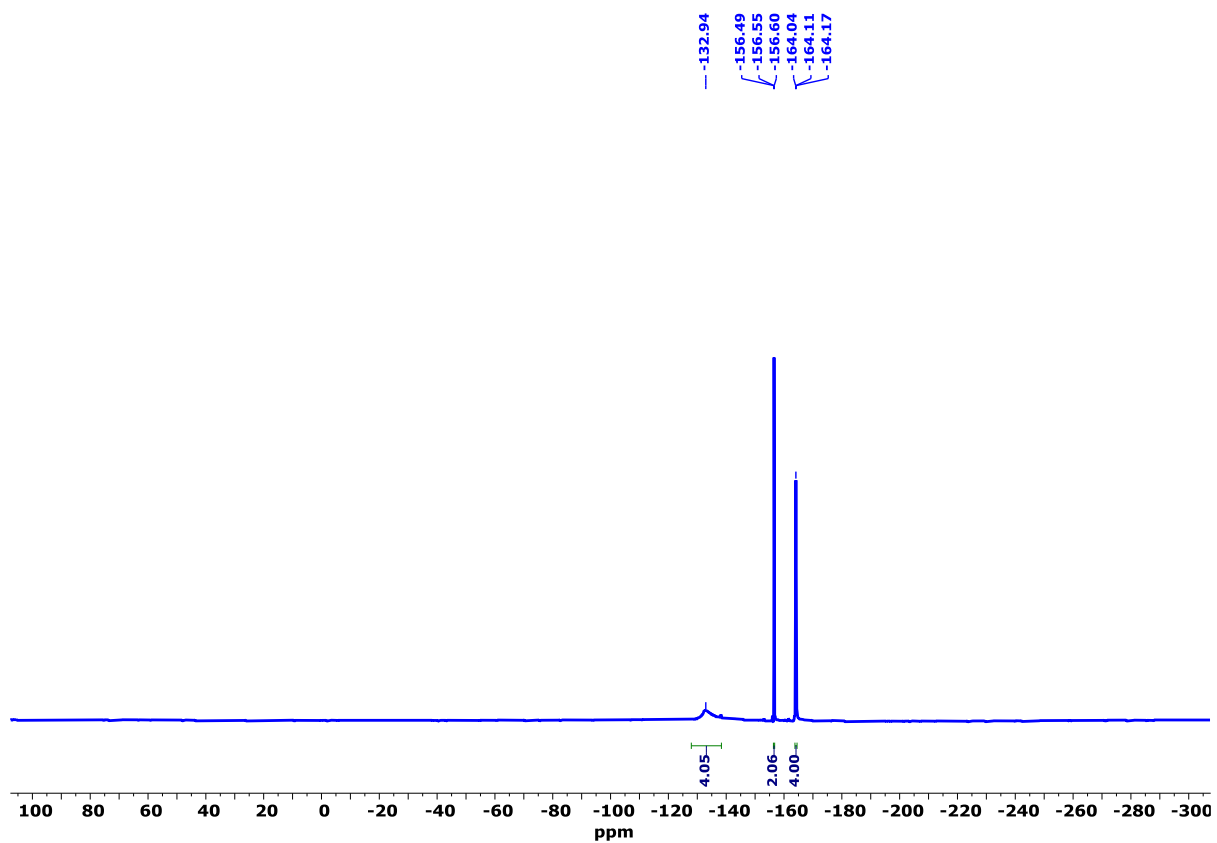


Figure S53: ^{19}F -NMR (376 MHz) spectrum of compound 3 in CDCl_3

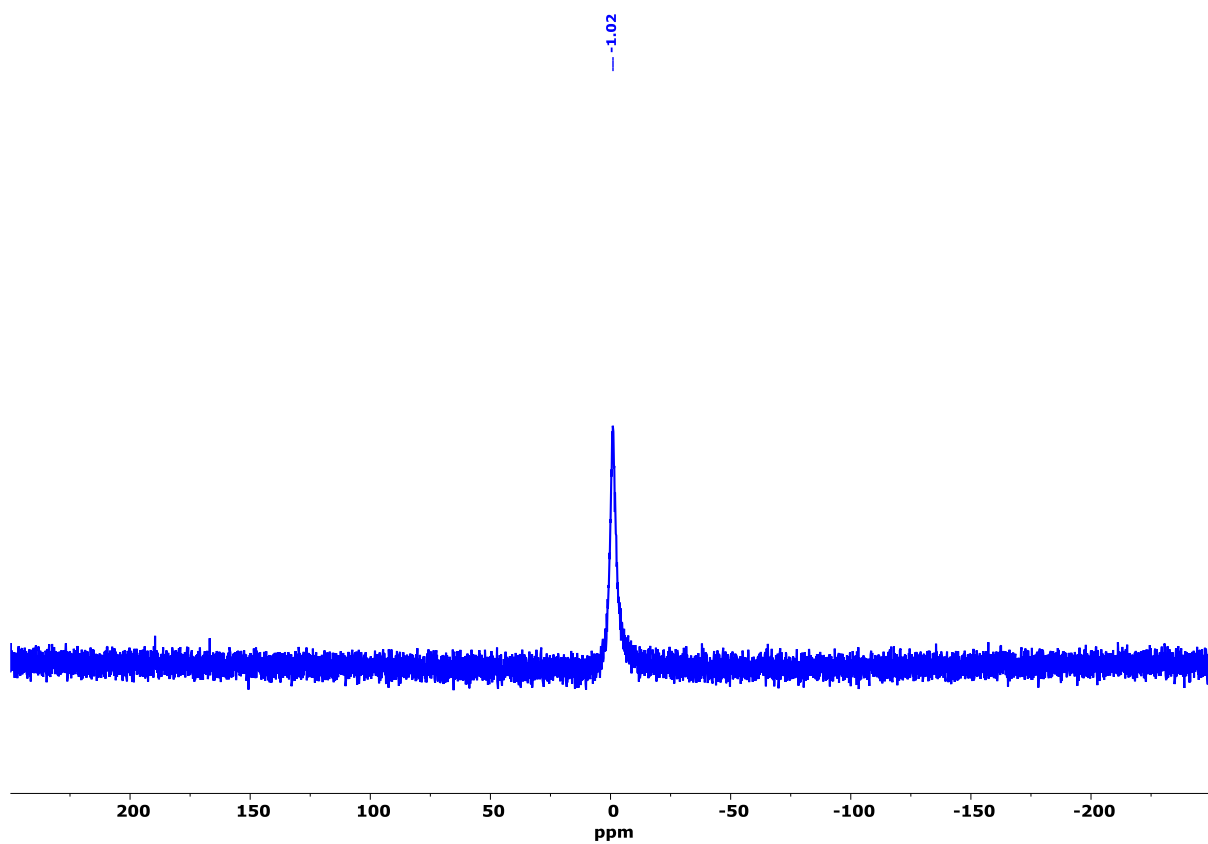


Figure S54: ^{11}B -NMR (128 MHz) spectrum of compound 3 in CDCl_3

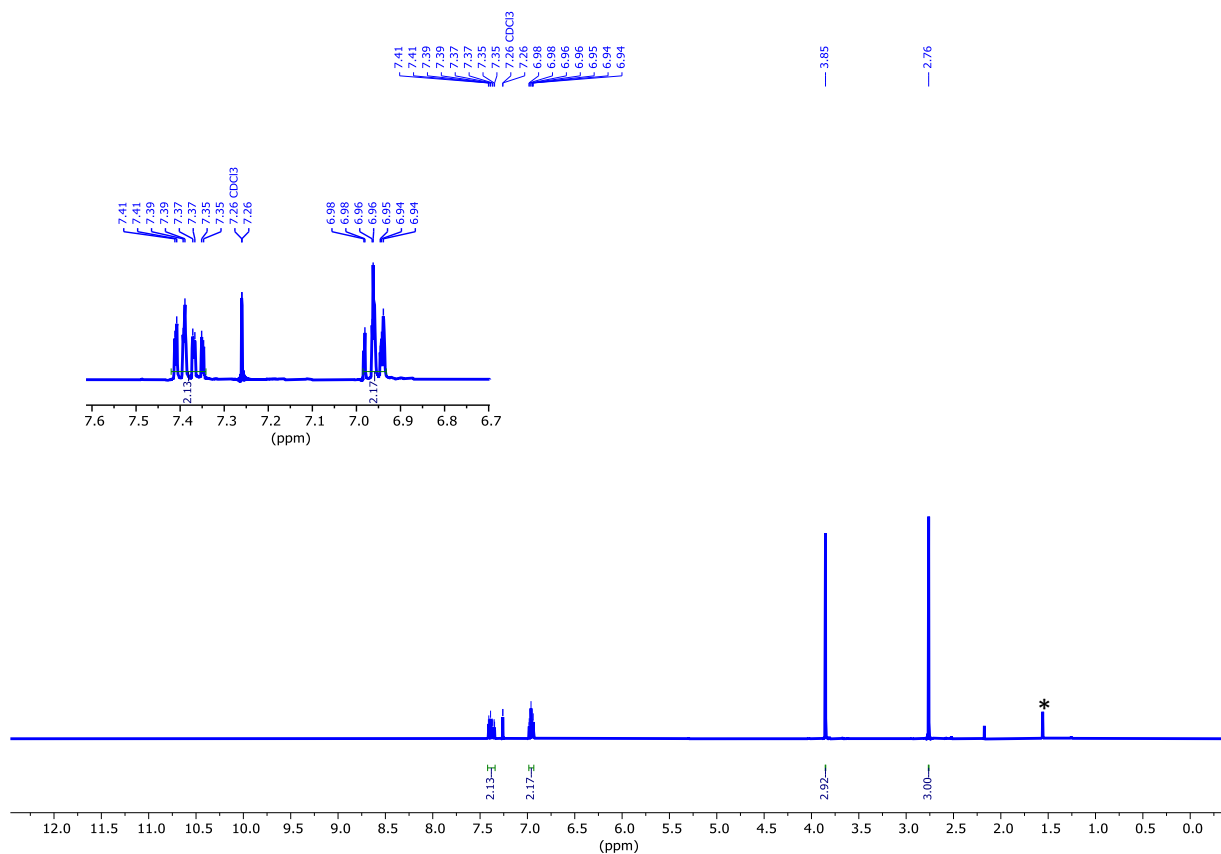


Figure S55: ¹H-NMR (400 MHz) spectrum of compound 4f in CDCl₃ (*H₂O peak)

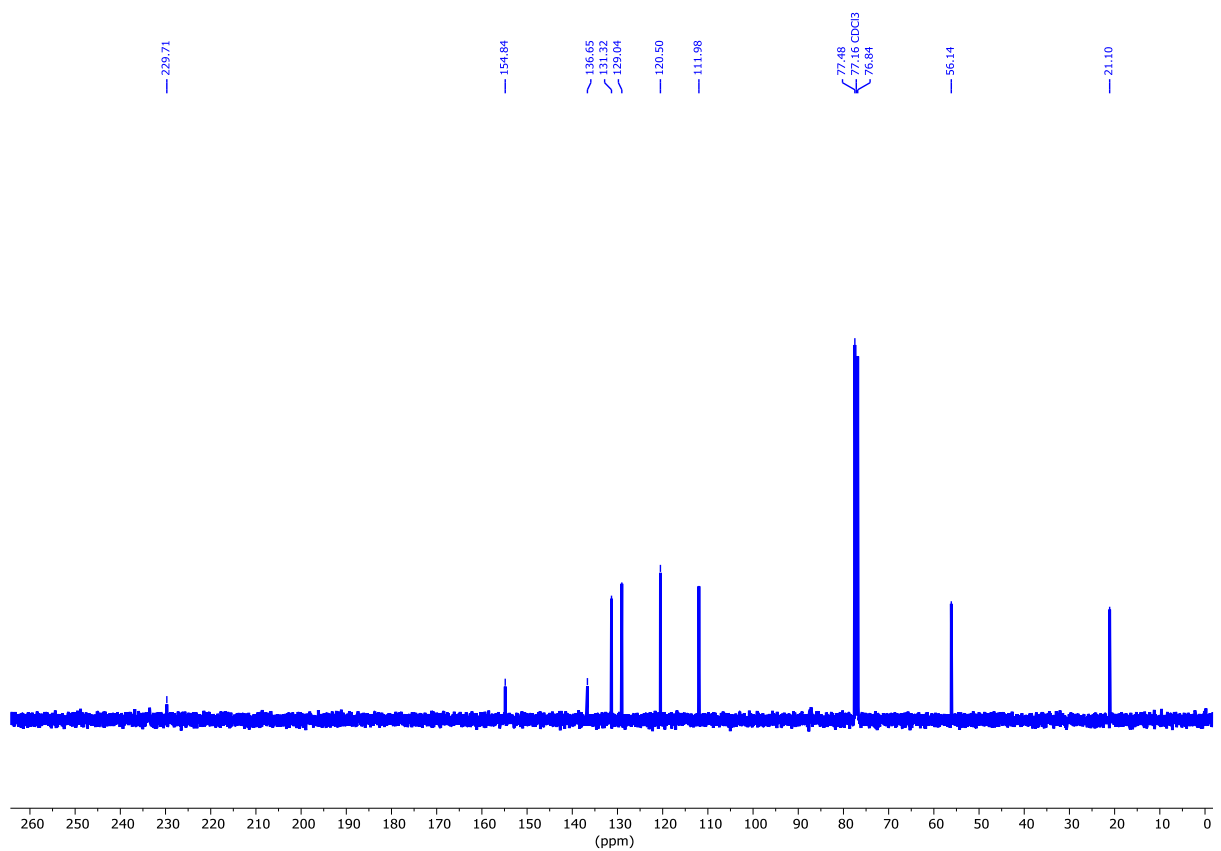


Figure S56: ¹³C-NMR (101 MHz) spectrum of compound 4f in CDCl₃

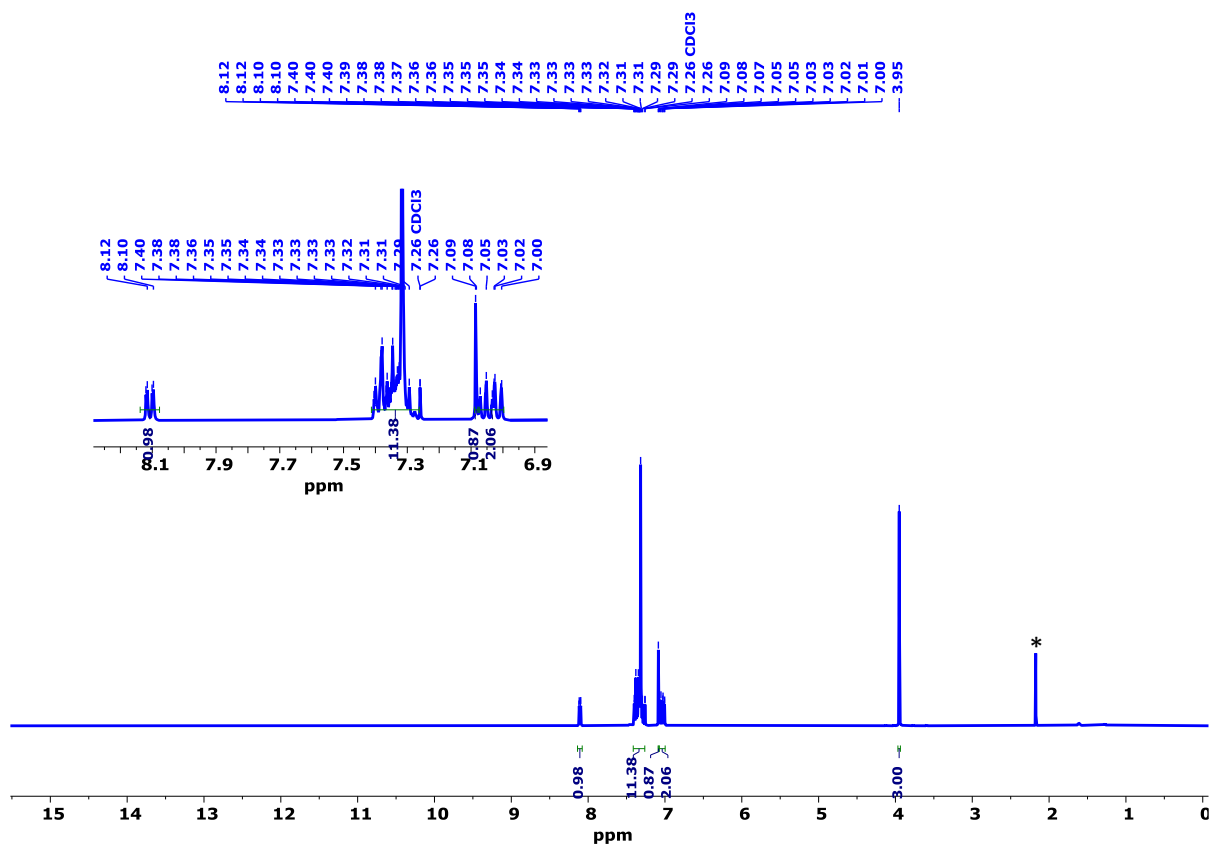


Figure S57: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 4d in CDCl_3 (*Acetone peak)

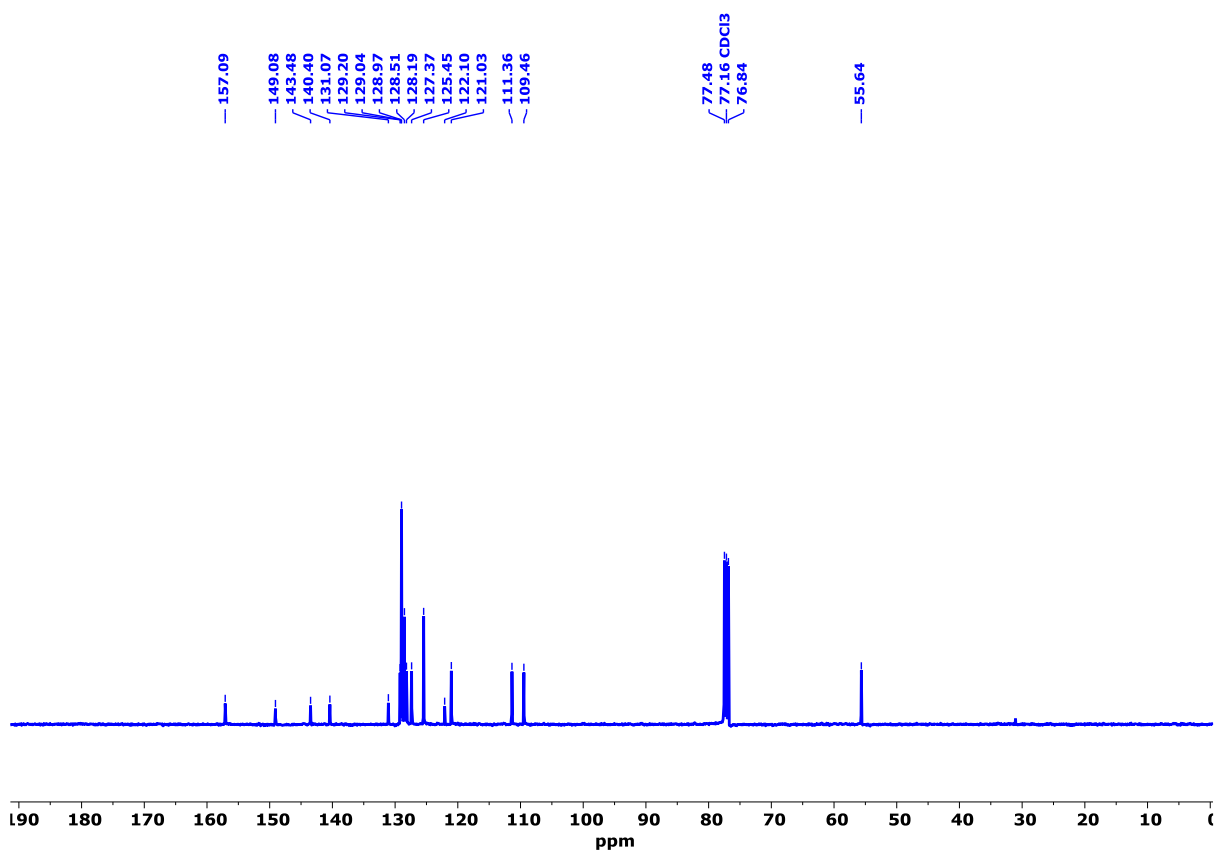


Figure S58: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 4d in CDCl_3

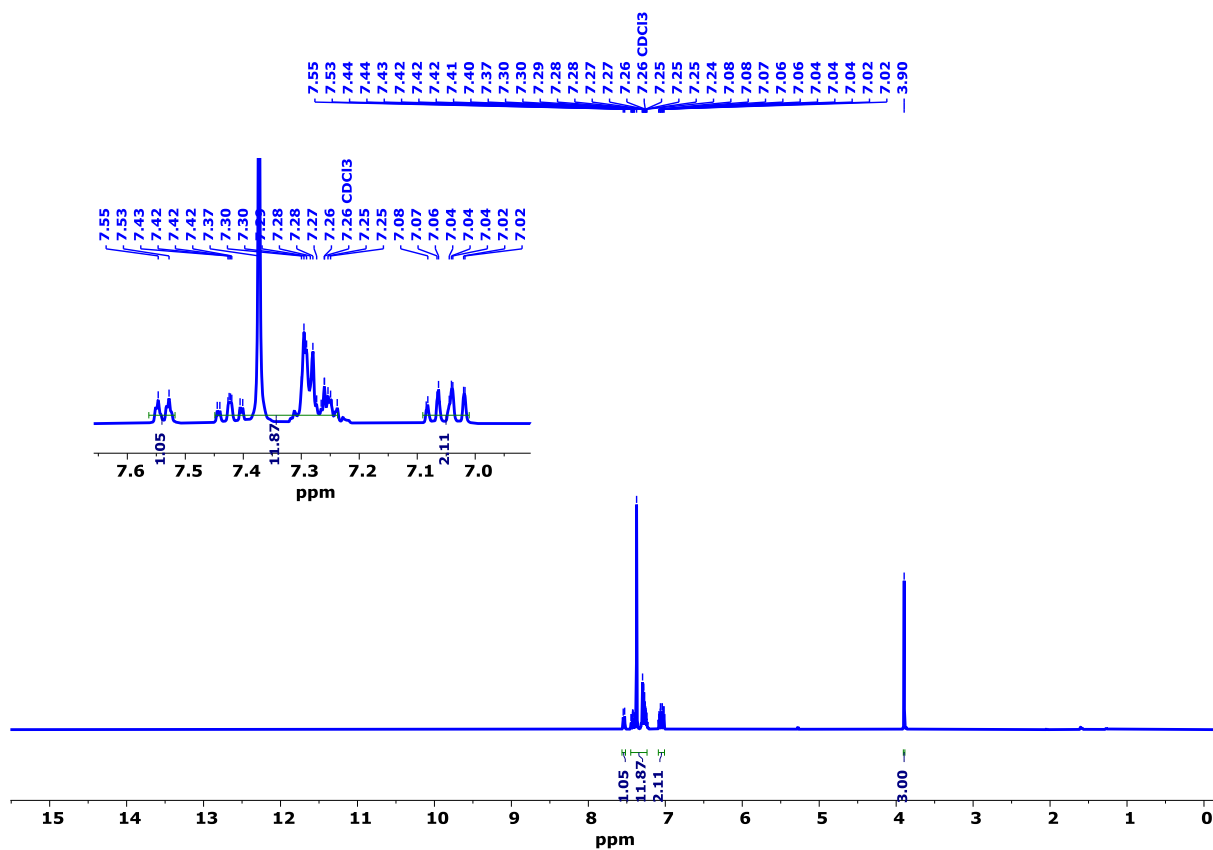


Figure S59: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 4c in CDCl_3

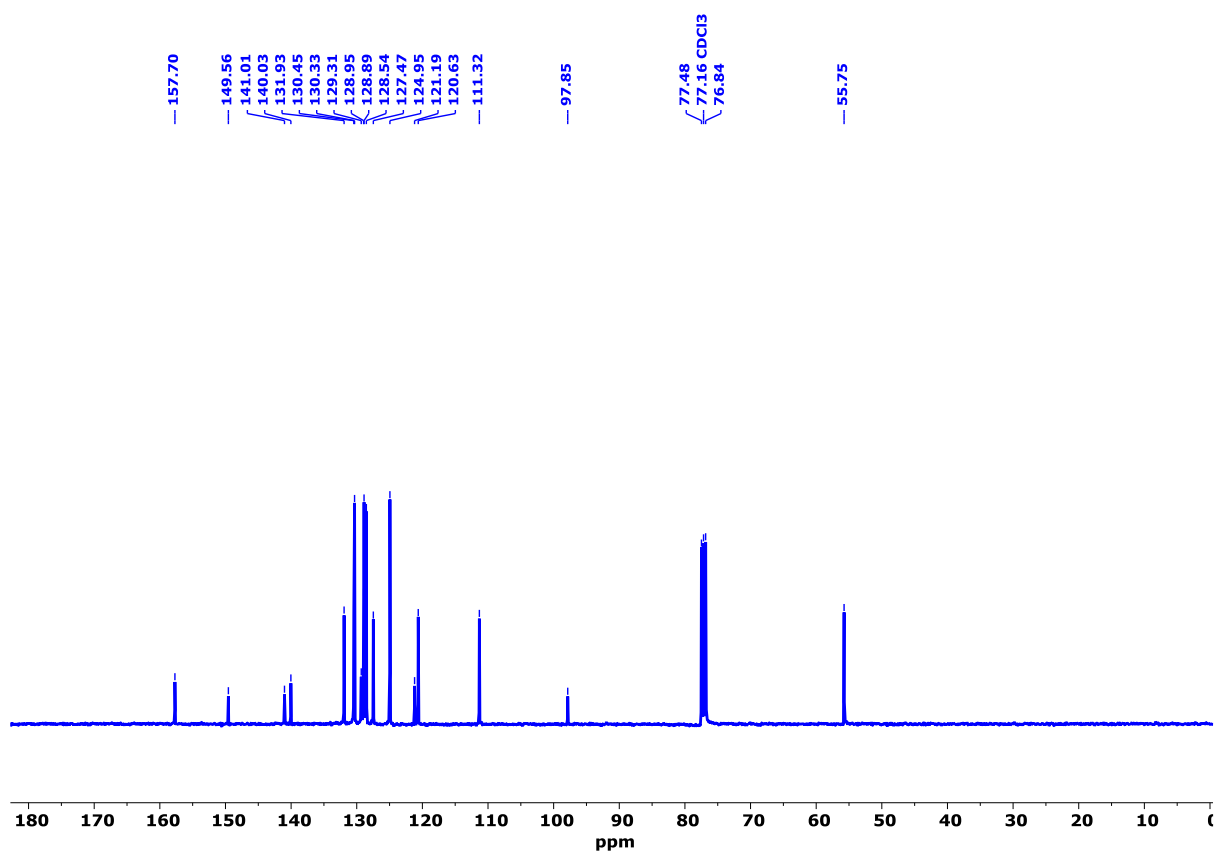


Figure S60: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 4c in CDCl_3

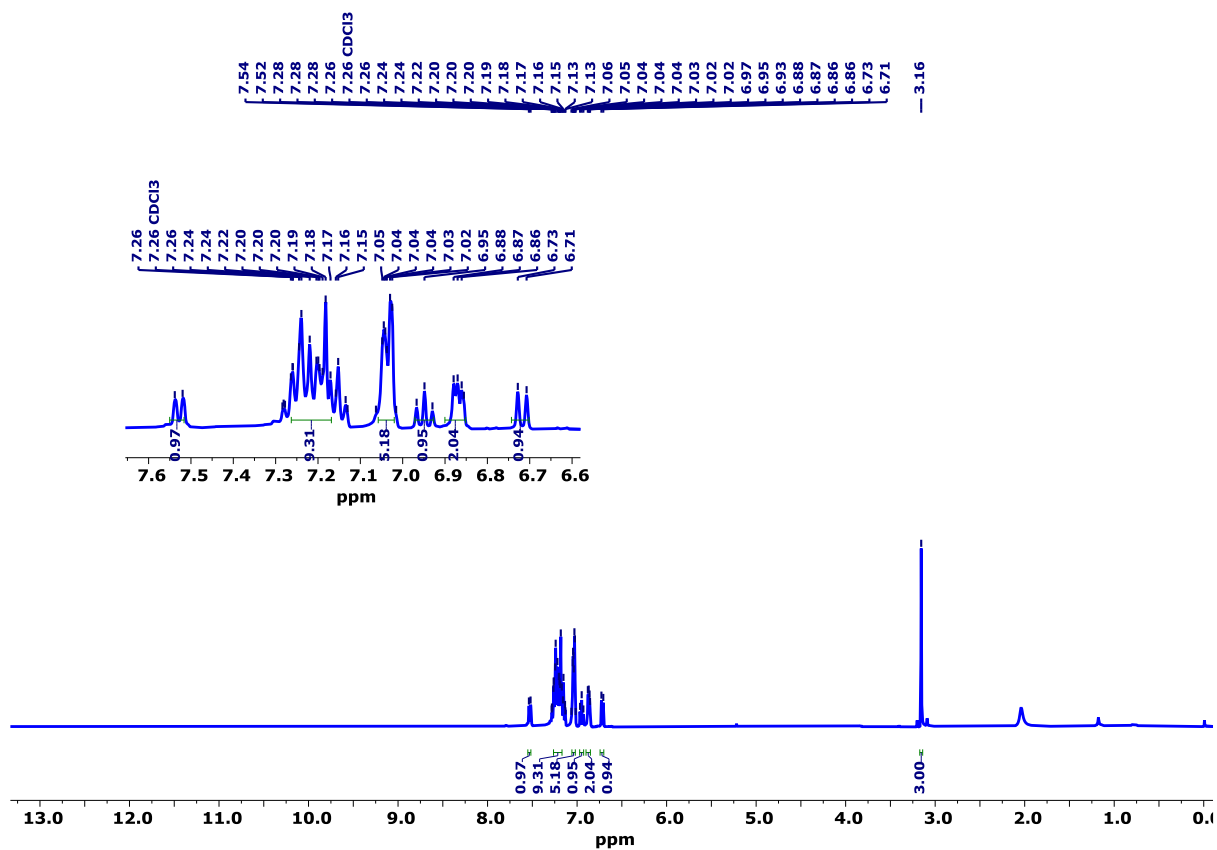


Figure S61: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 4b in CDCl_3

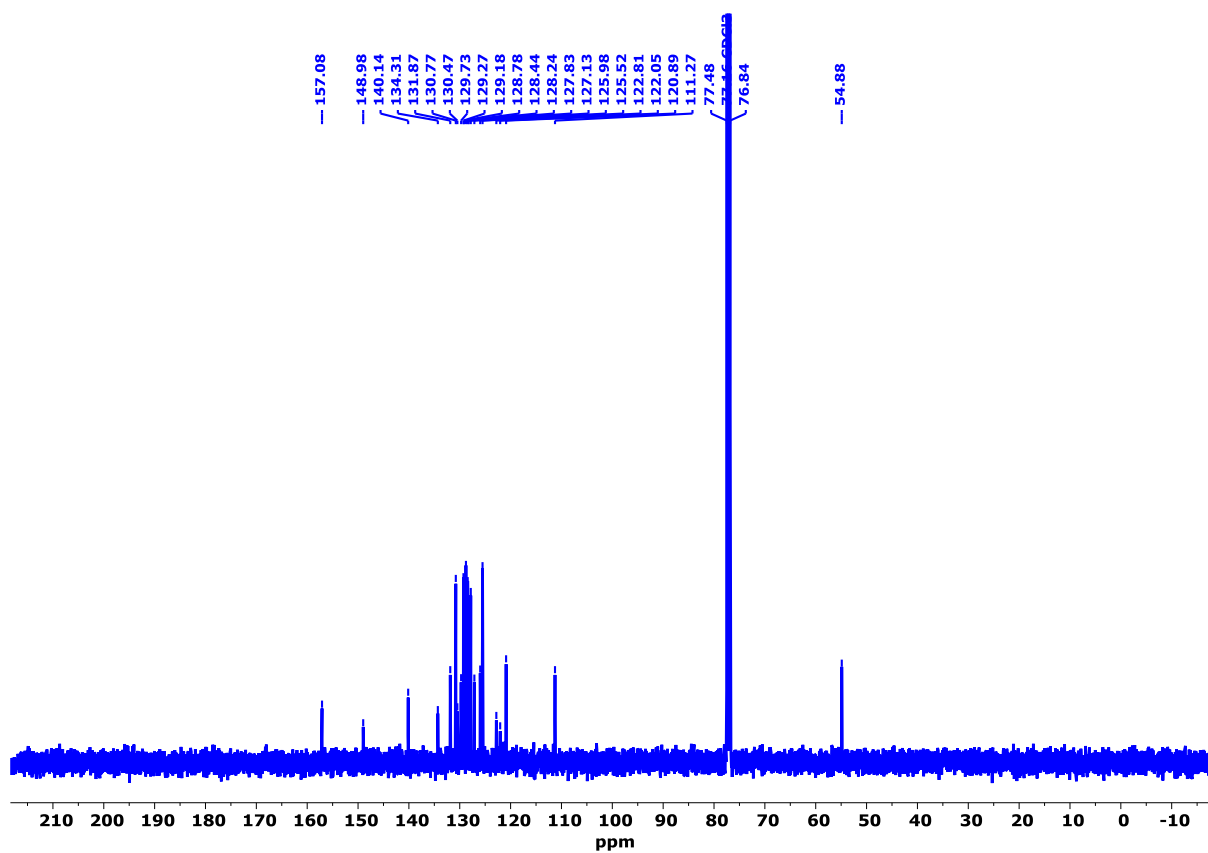


Figure S62: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 4b in CDCl_3

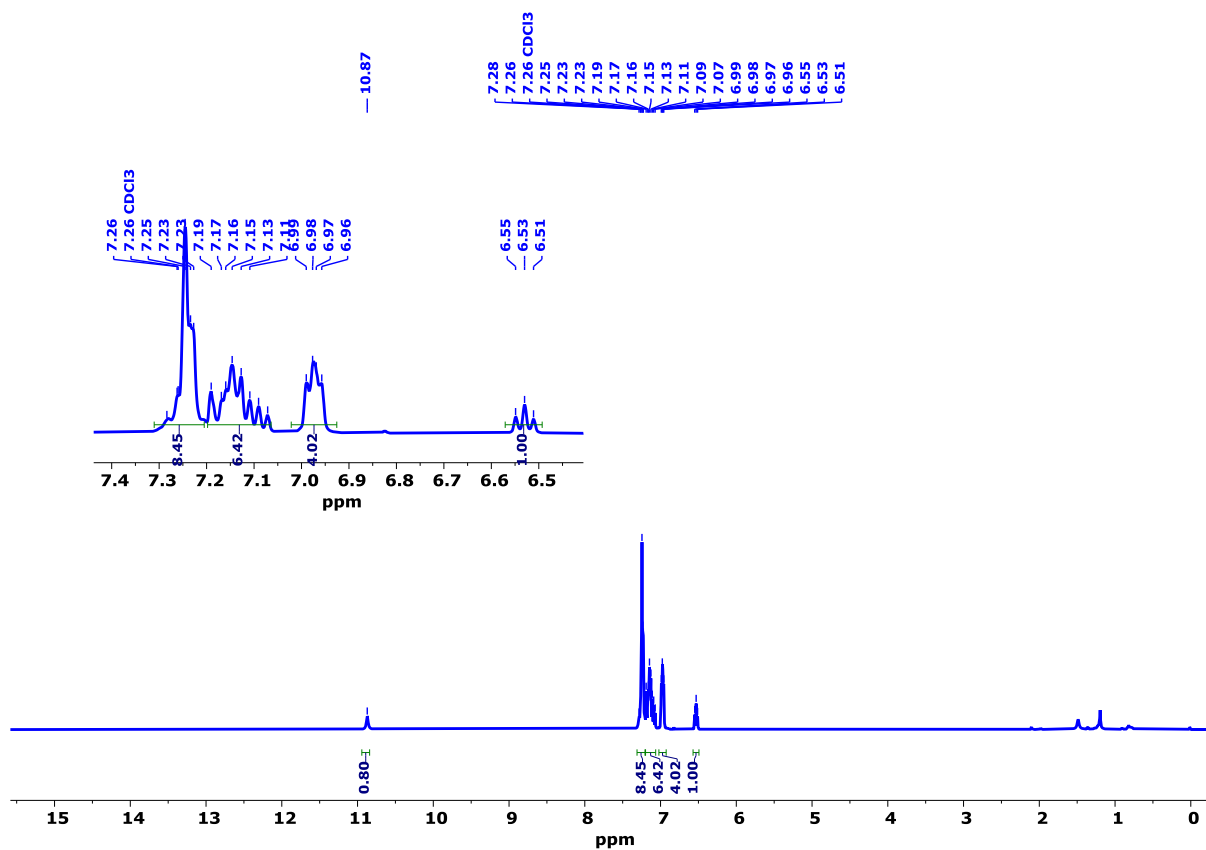


Figure S63: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 4a in CDCl_3

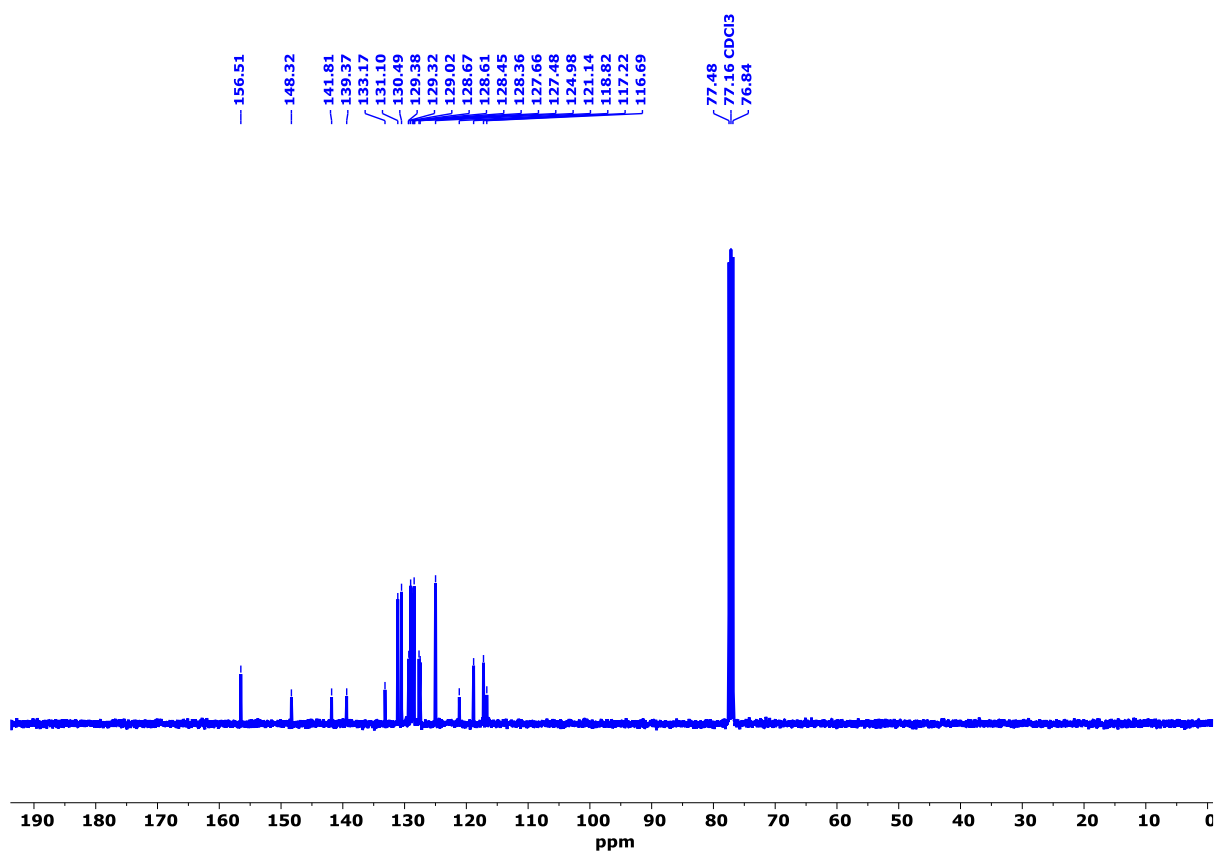


Figure S64: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 4a in CDCl_3

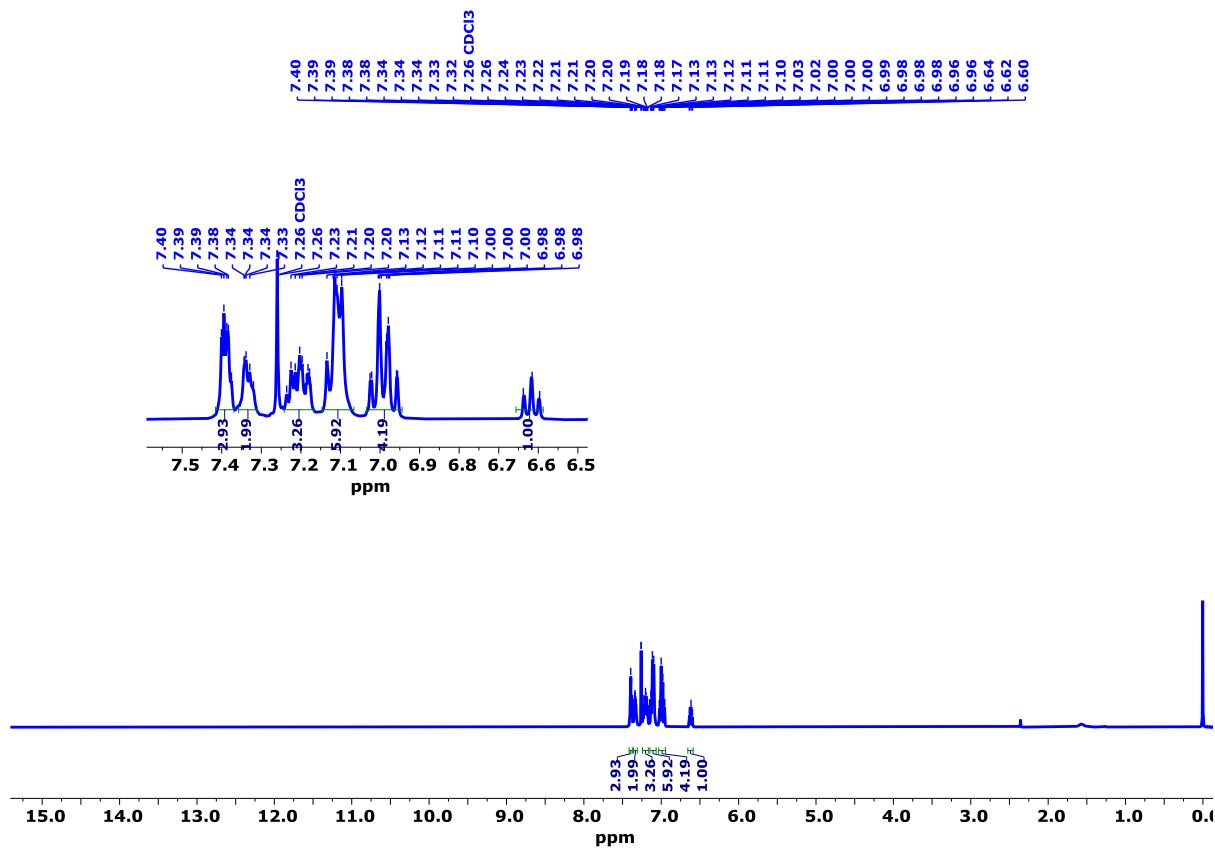


Figure S65: ¹H-NMR (400 MHz) spectrum of compound 4 in CDCl₃

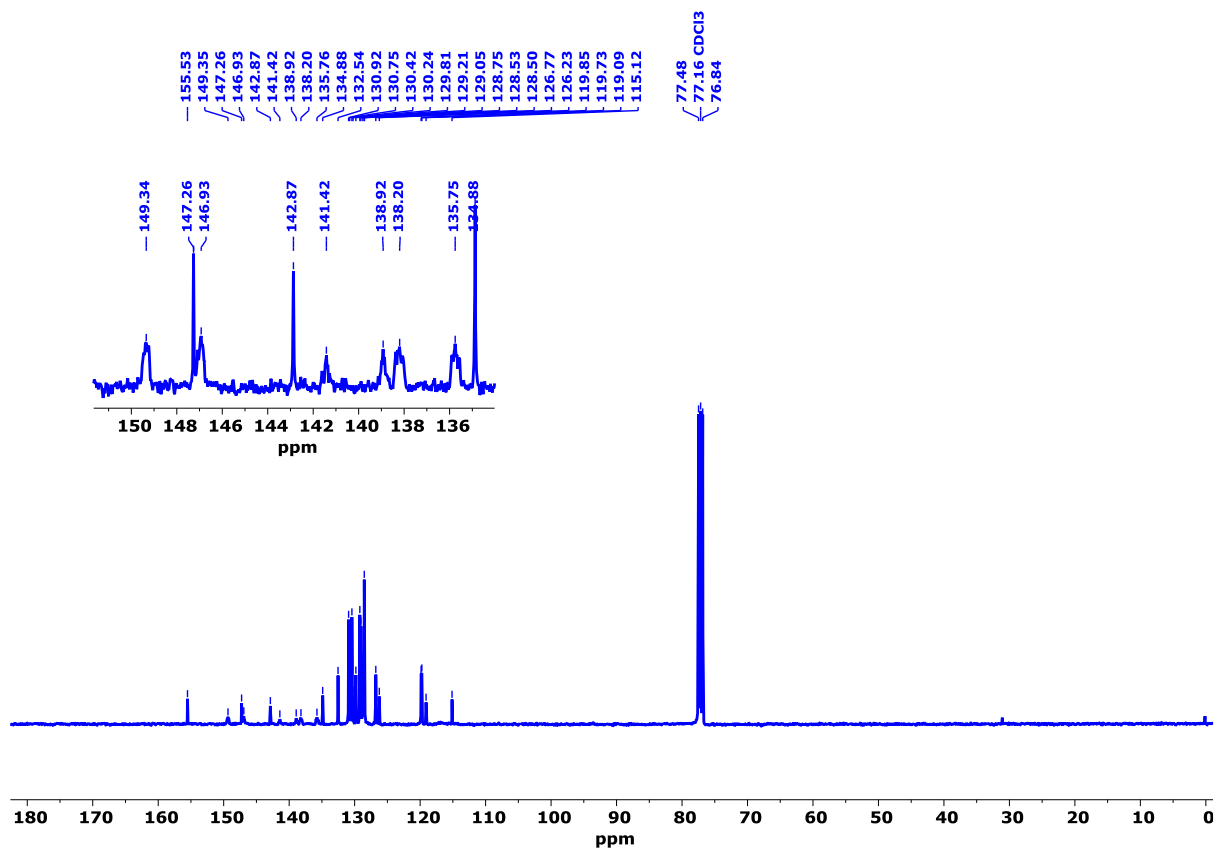


Figure S66: ¹³C-NMR (101 MHz) spectrum of compound 4 in CDCl₃

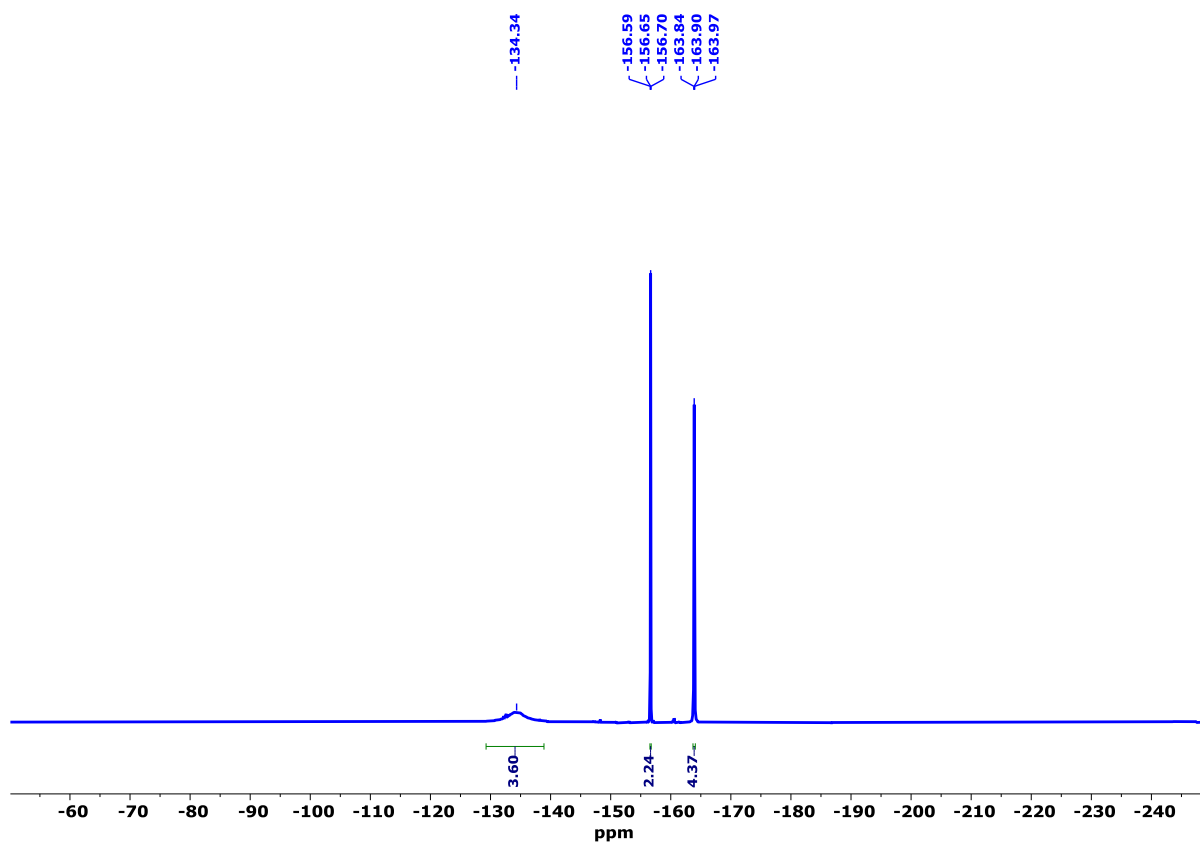


Figure S67: ^{19}F -NMR (376 MHz) spectrum of compound 4 in CDCl_3

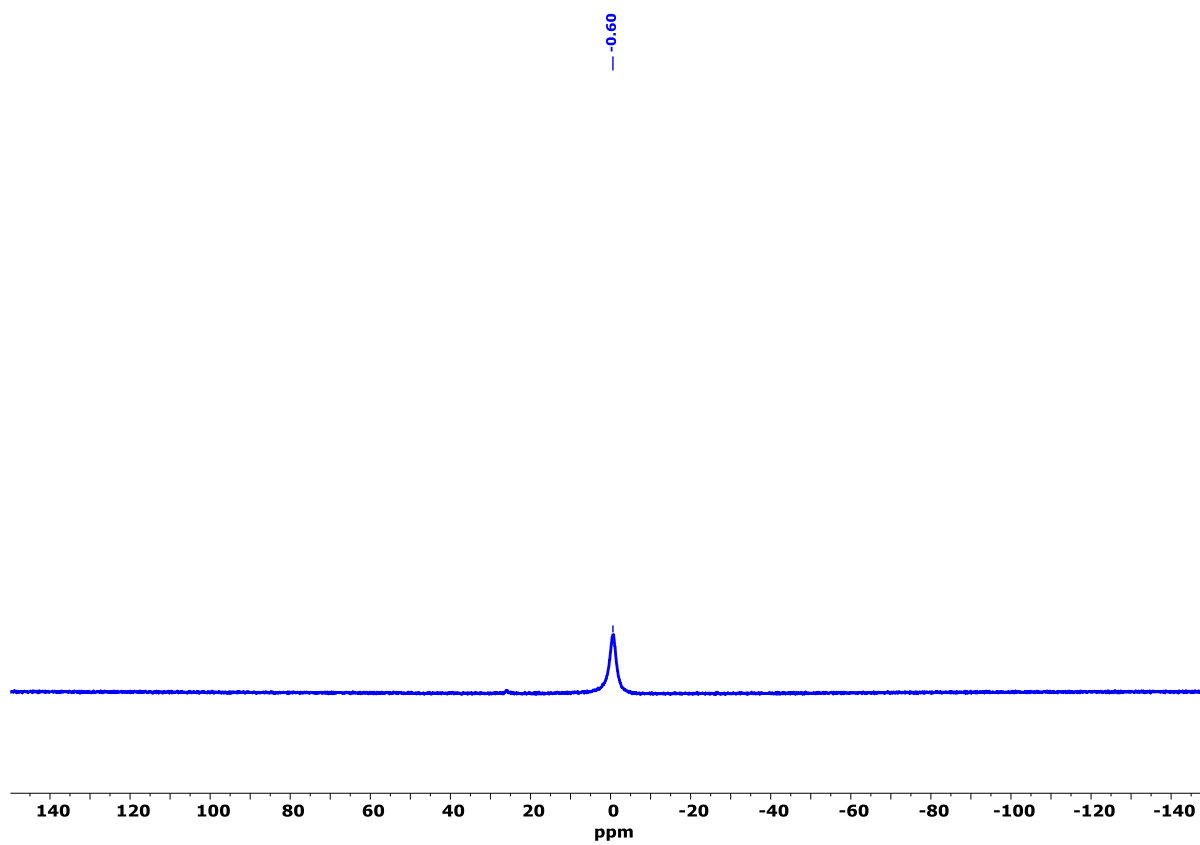


Figure S68: ^{11}B -NMR (128 MHz) spectrum of compound 4 in CDCl_3

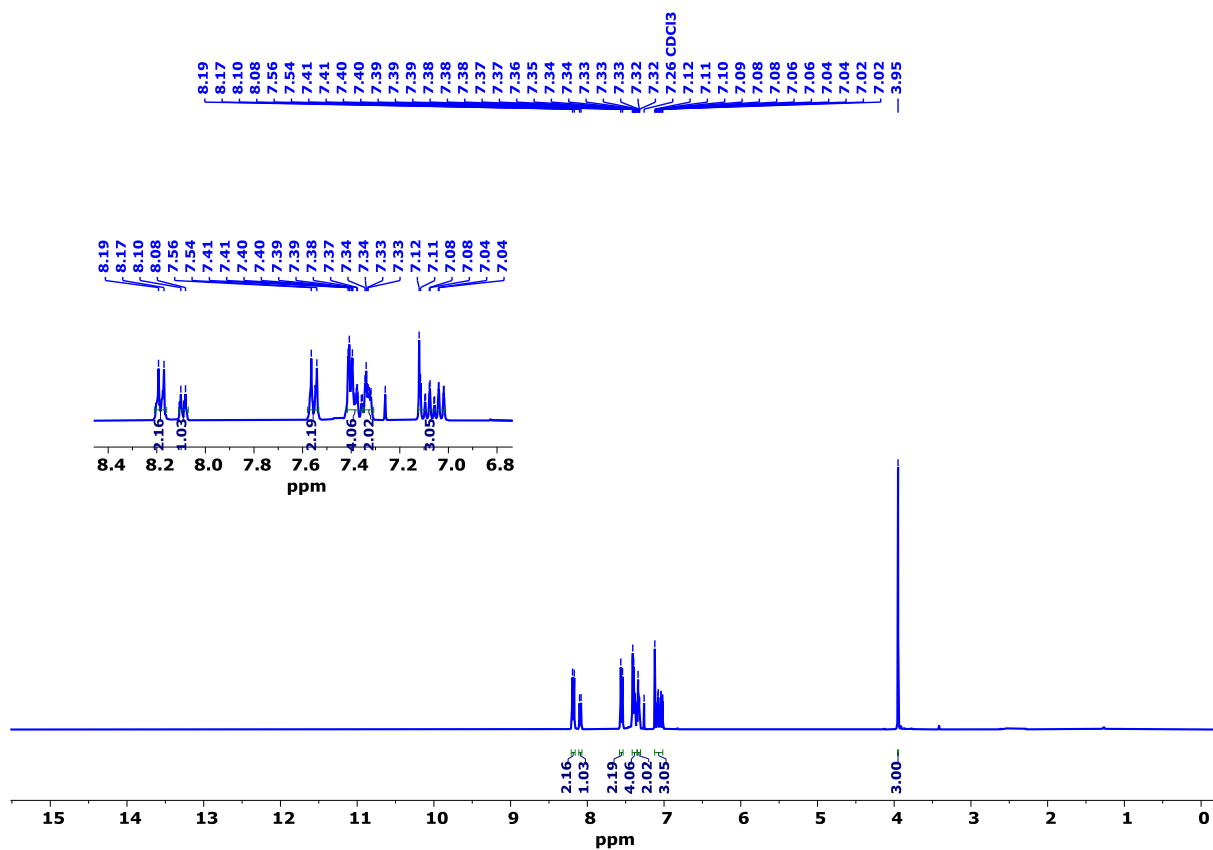


Figure S69: ¹H-NMR (400 MHz) spectrum of compound 5f in CDCl₃

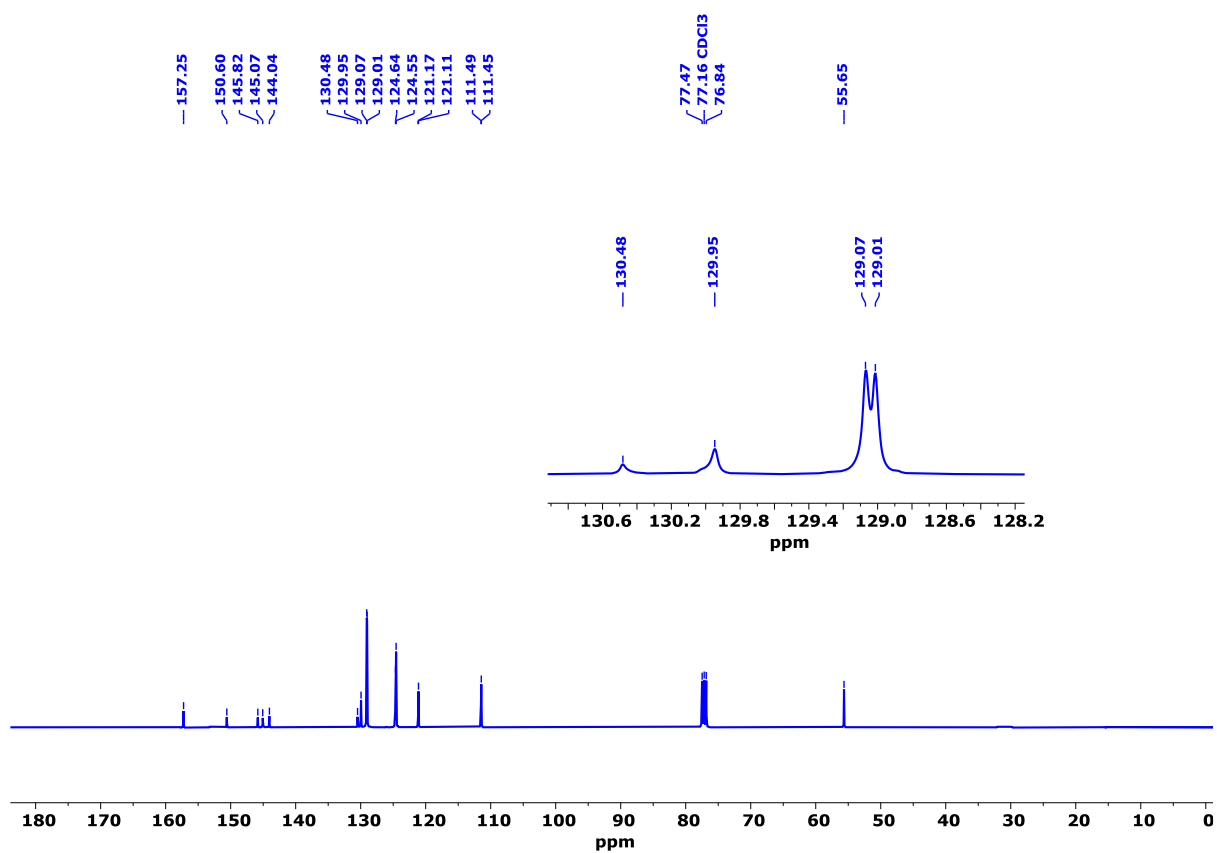


Figure S70: ¹³C-NMR (101 MHz) spectrum of compound 5f in CDCl₃

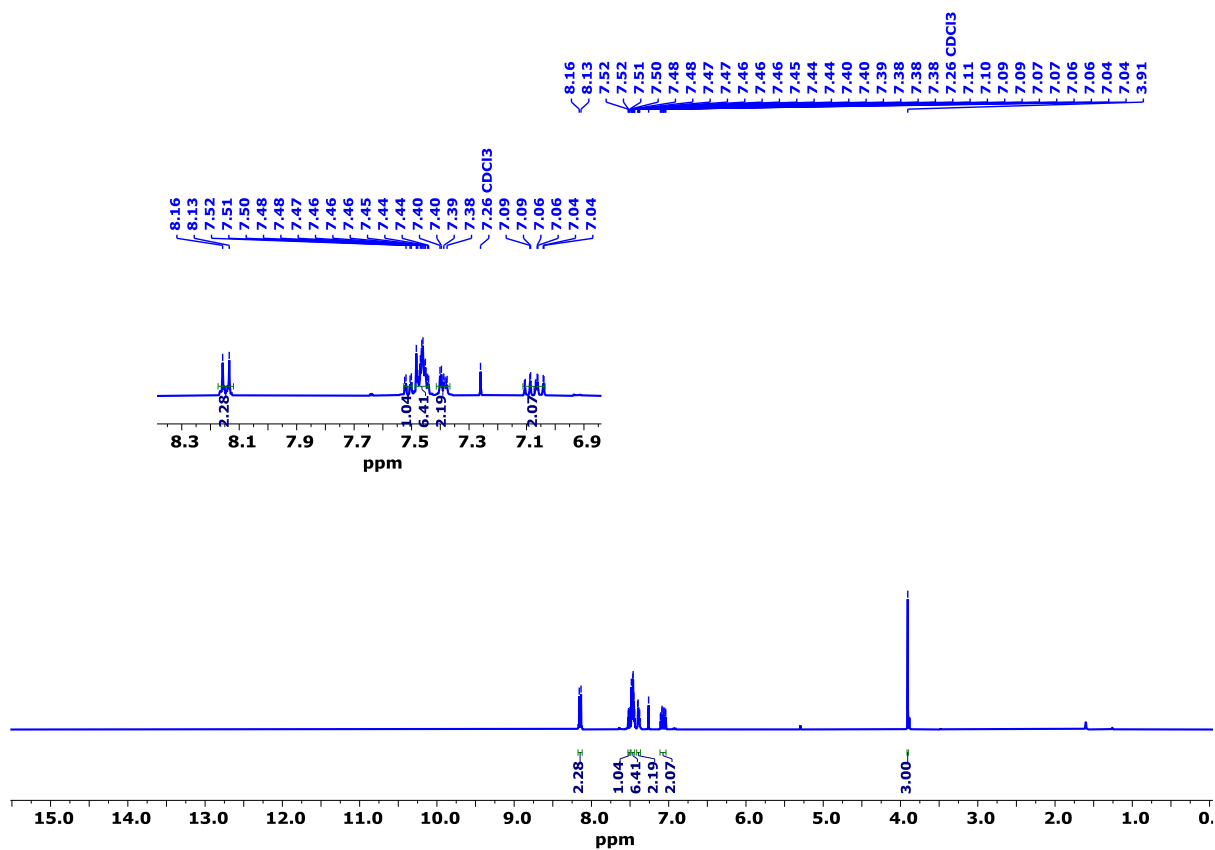


Figure S71: ¹H-NMR (400 MHz) spectrum of compound 5e in CDCl₃

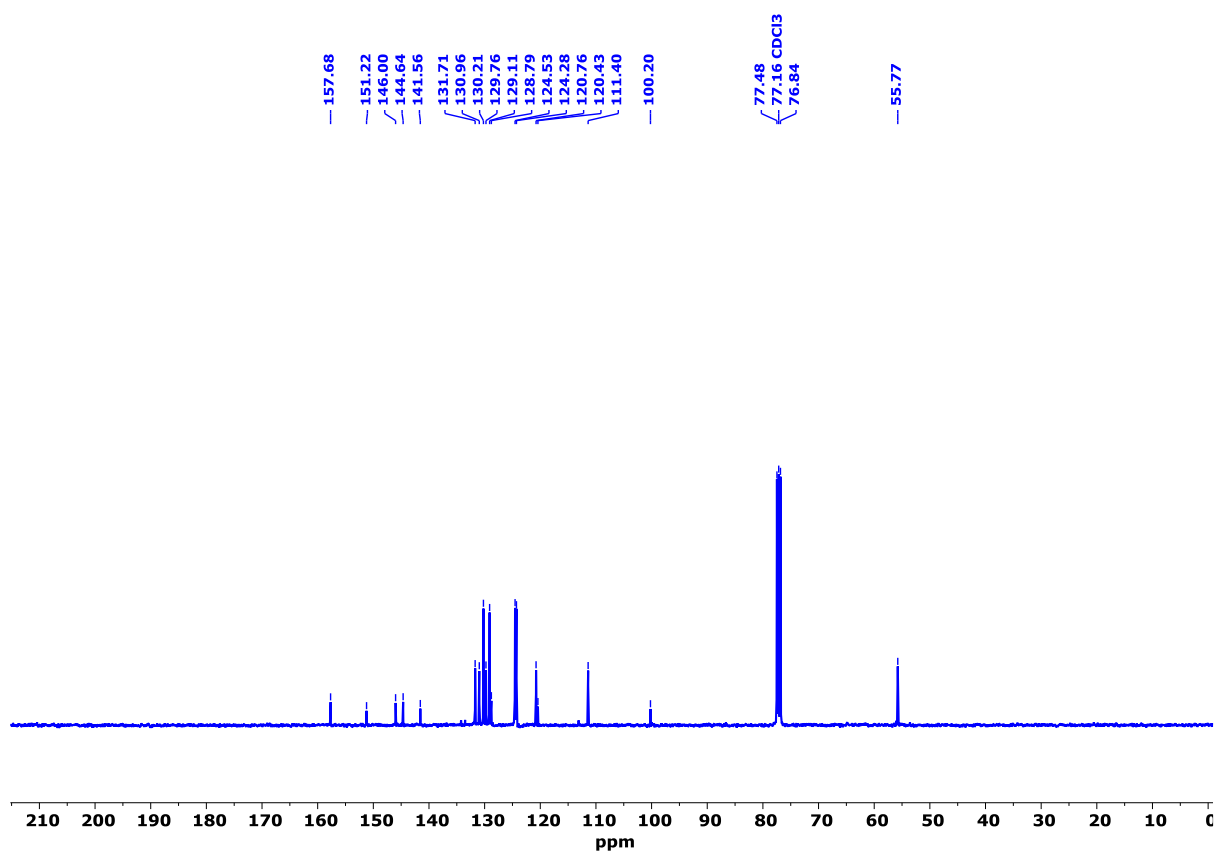


Figure S72: ¹³C-NMR (101 MHz) spectrum of compound 5e in CDCl₃

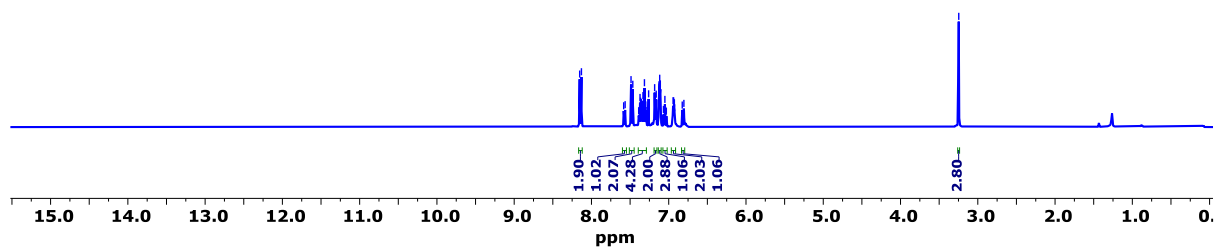
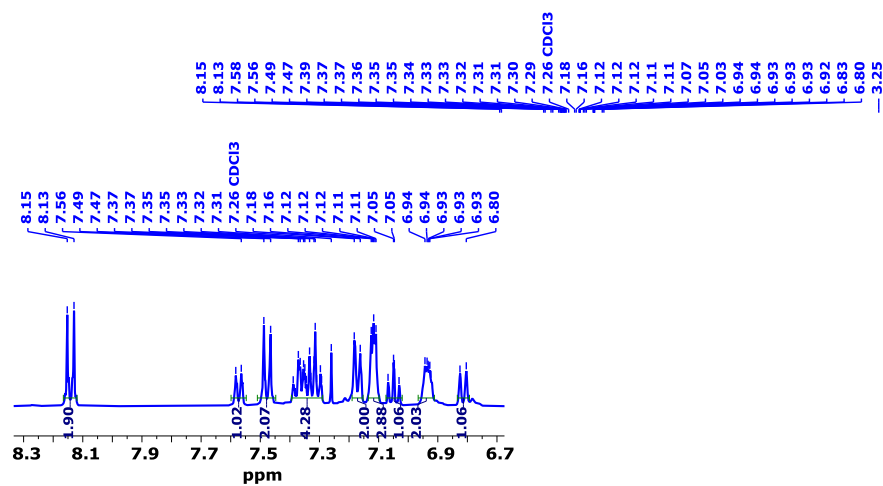


Figure S73: ¹H-NMR (400 MHz) spectrum of compound 5d in CDCl₃

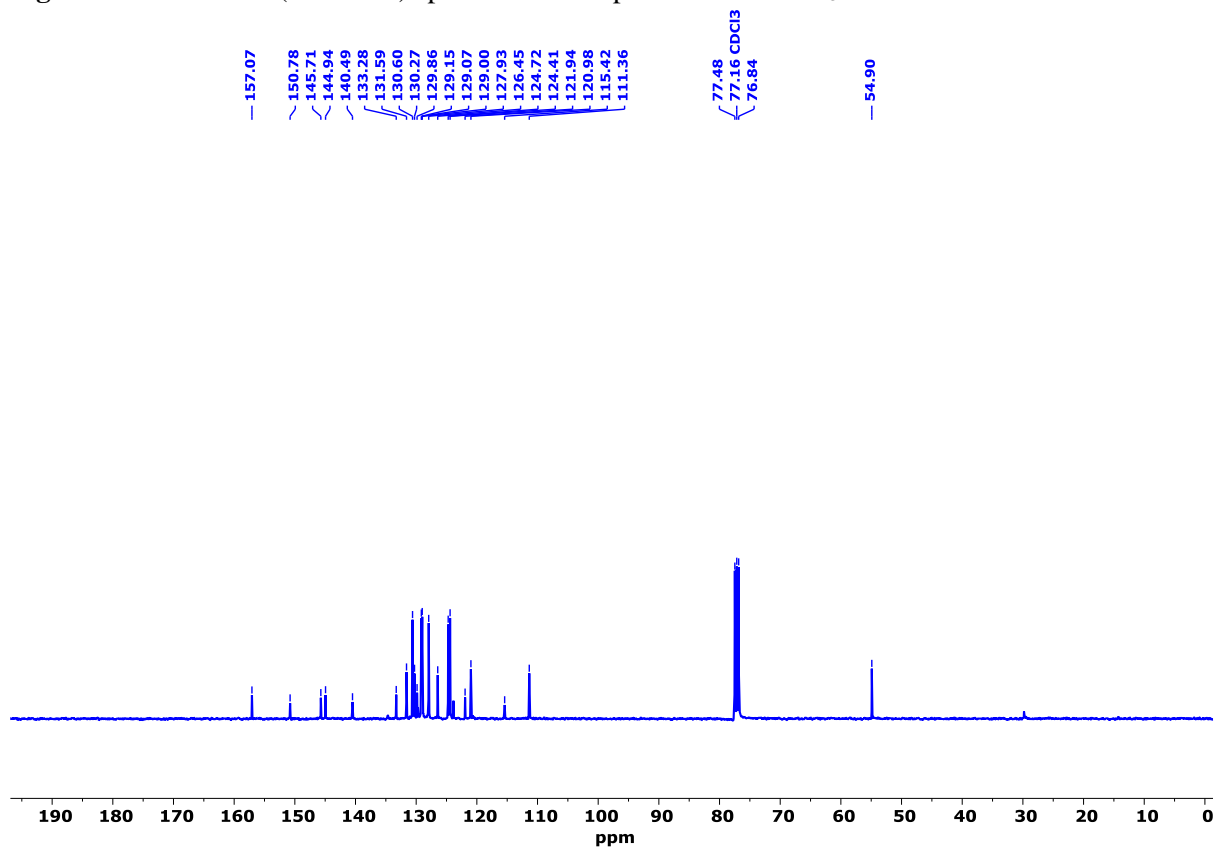


Figure S74: ¹³C-NMR (101 MHz) spectrum of compound 5d in CDCl₃

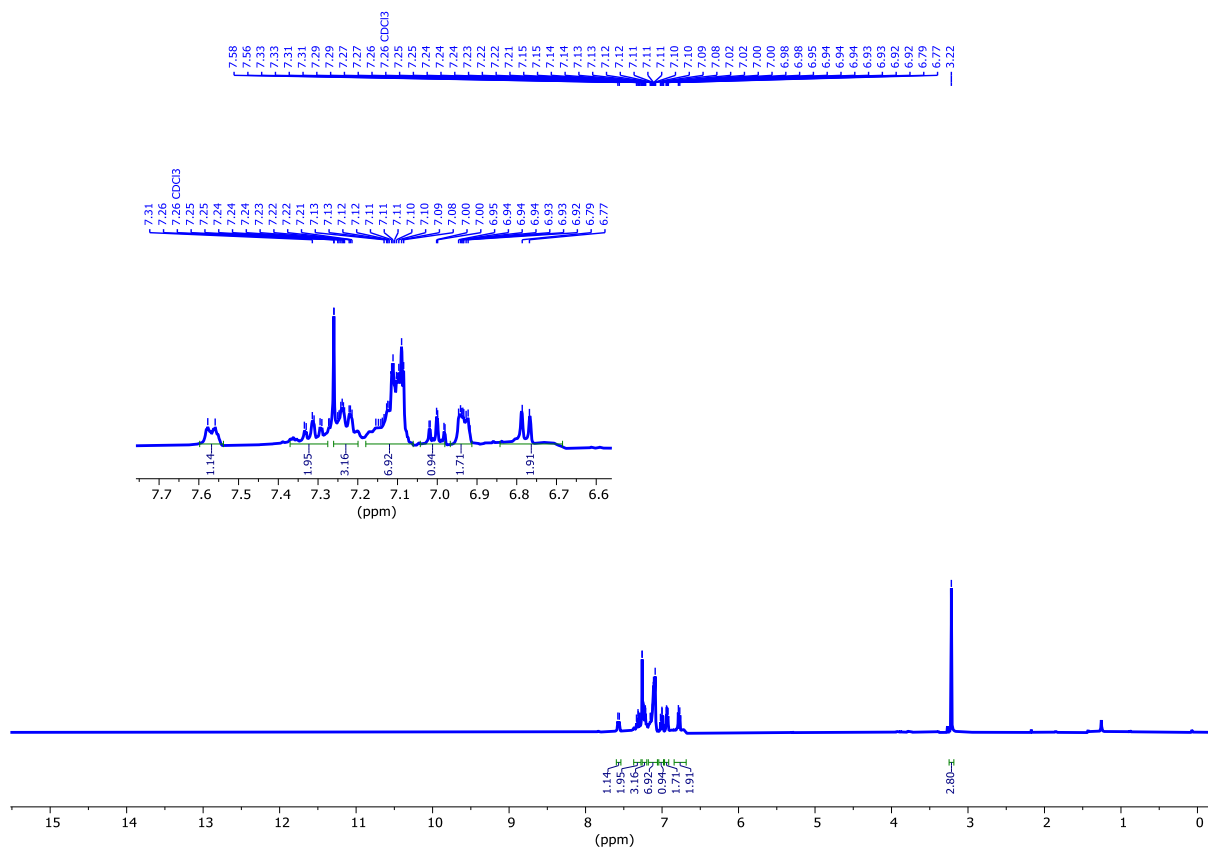


Figure S75: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 5c in CDCl_3

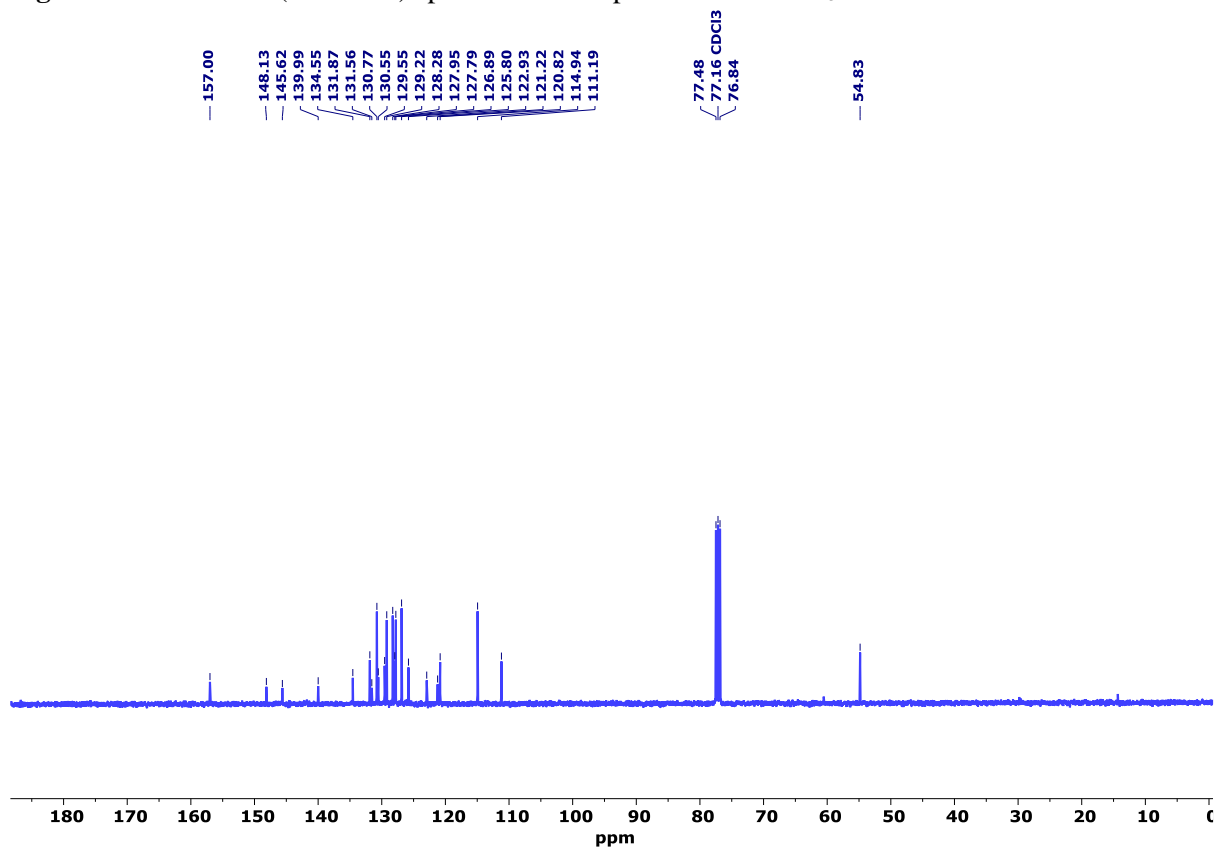


Figure S76: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 5c in CDCl_3

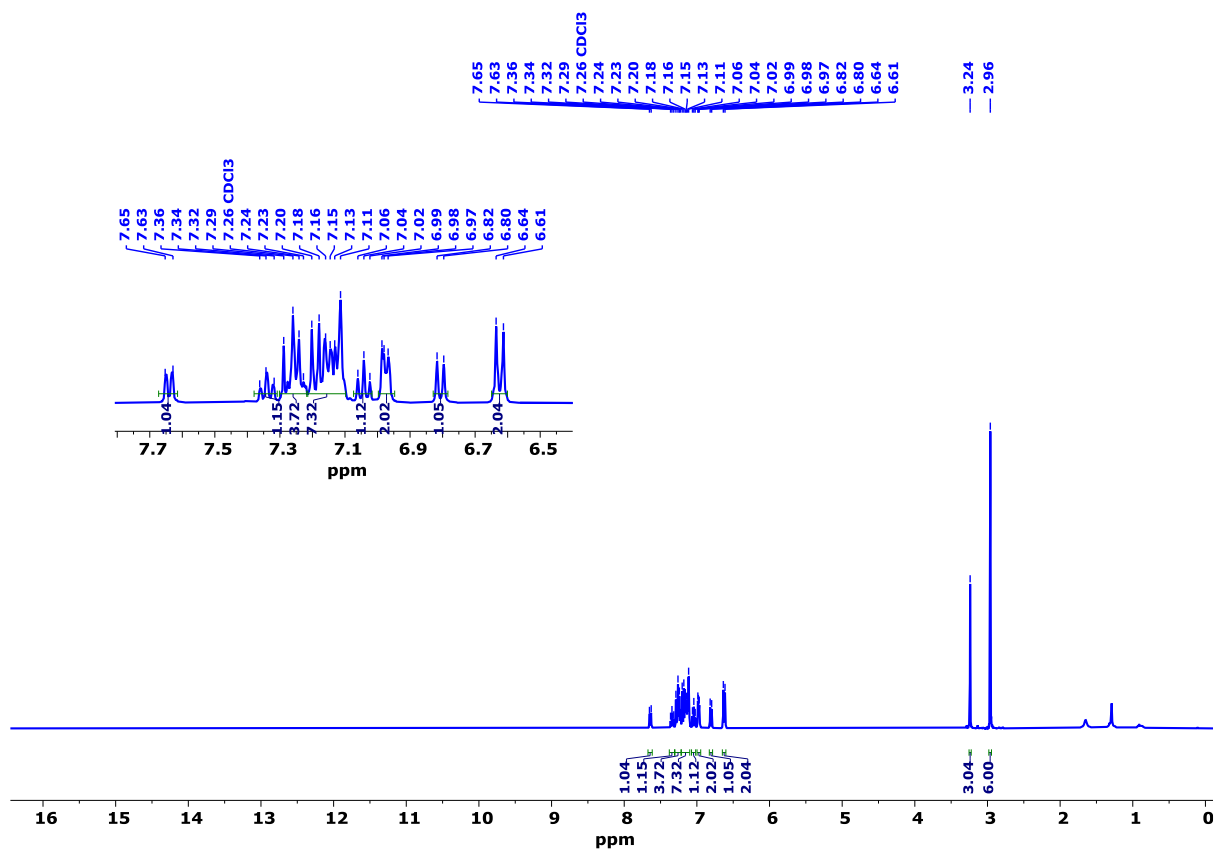


Figure S77: ¹H-NMR (400 MHz) spectrum of compound 5b in CDCl₃

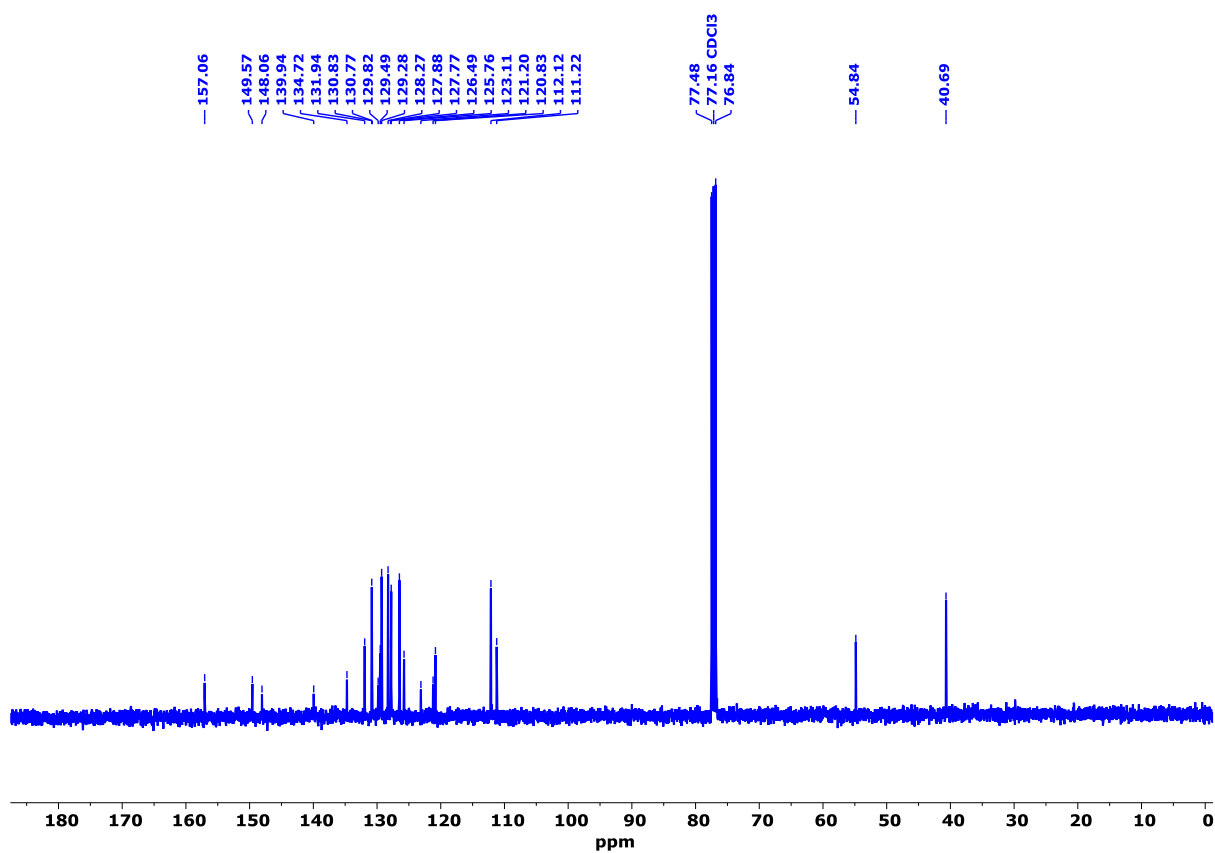


Figure S78: ¹³C-NMR (101 MHz) spectrum of compound 5b in CDCl₃

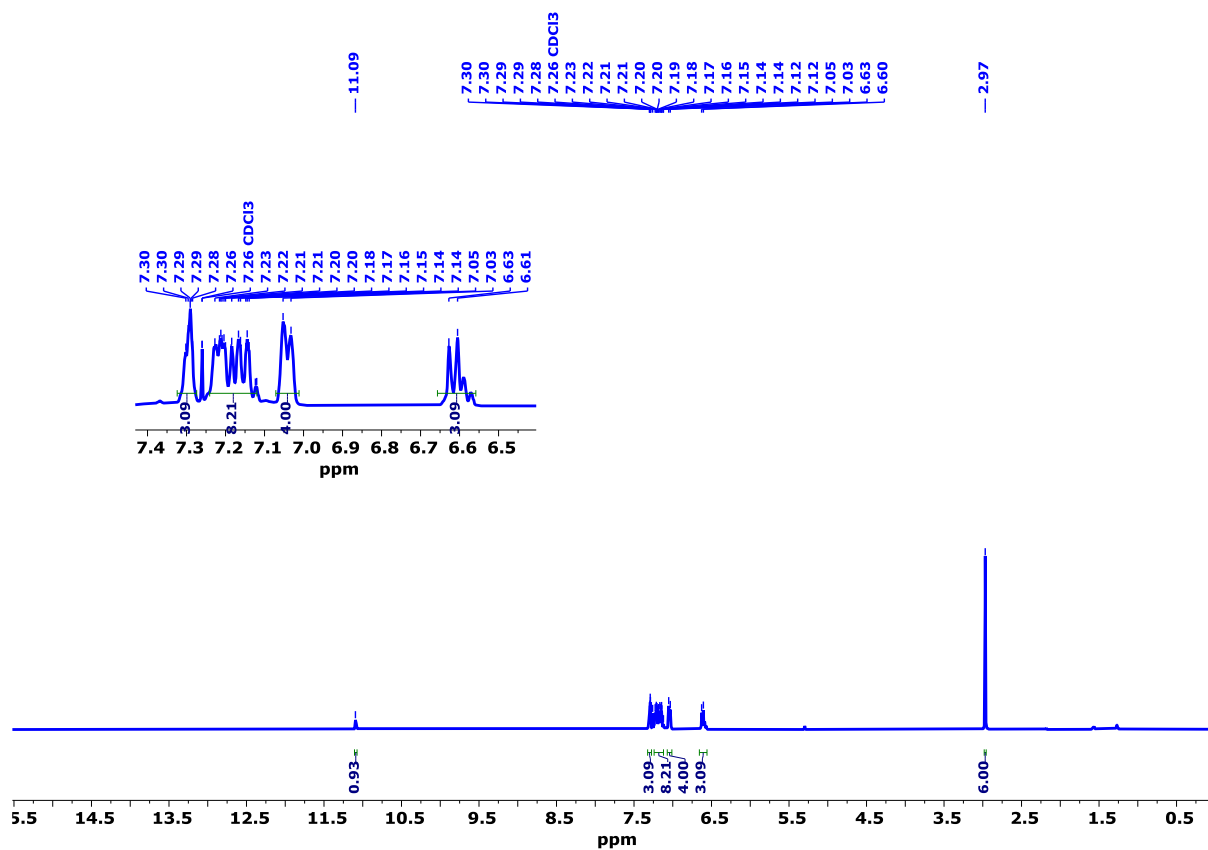


Figure S79: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 5a in CDCl_3

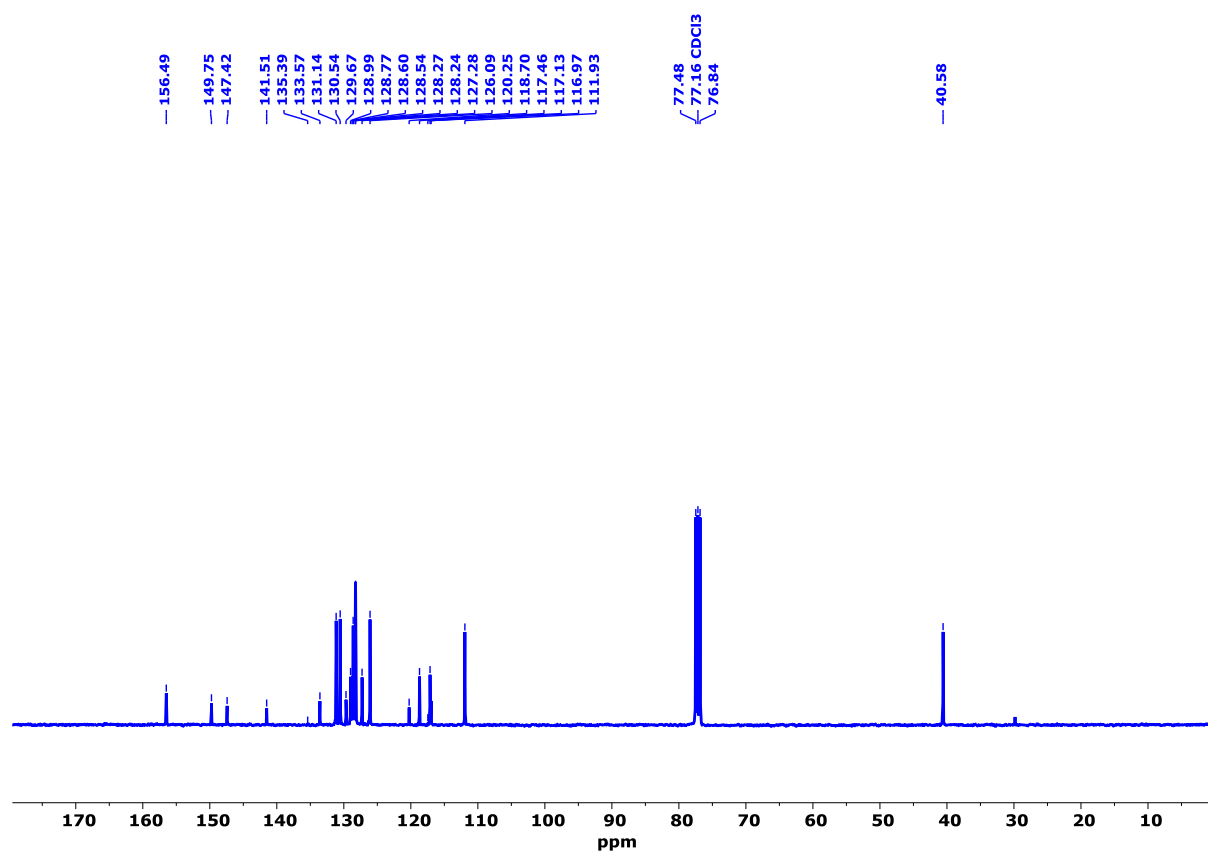


Figure S80: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 5a in CDCl_3

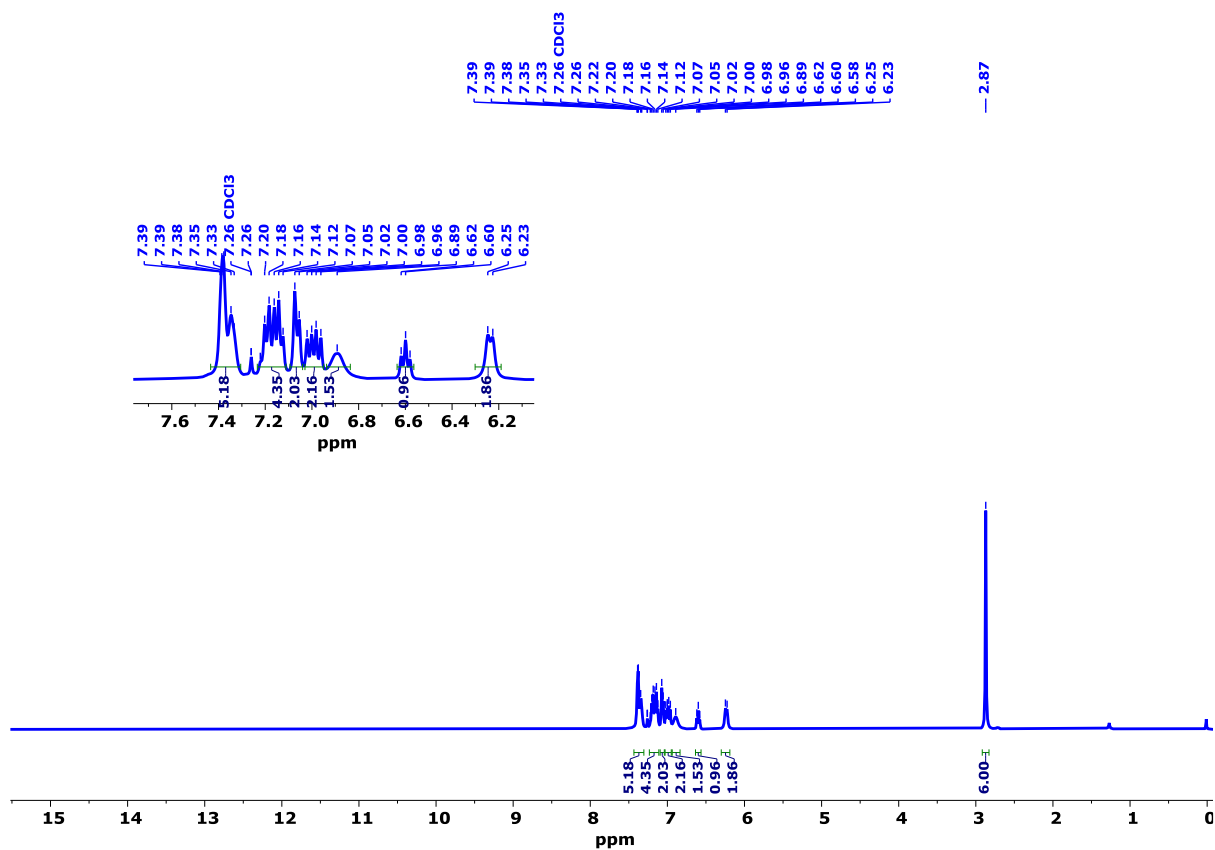


Figure S81: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 5 in CDCl_3

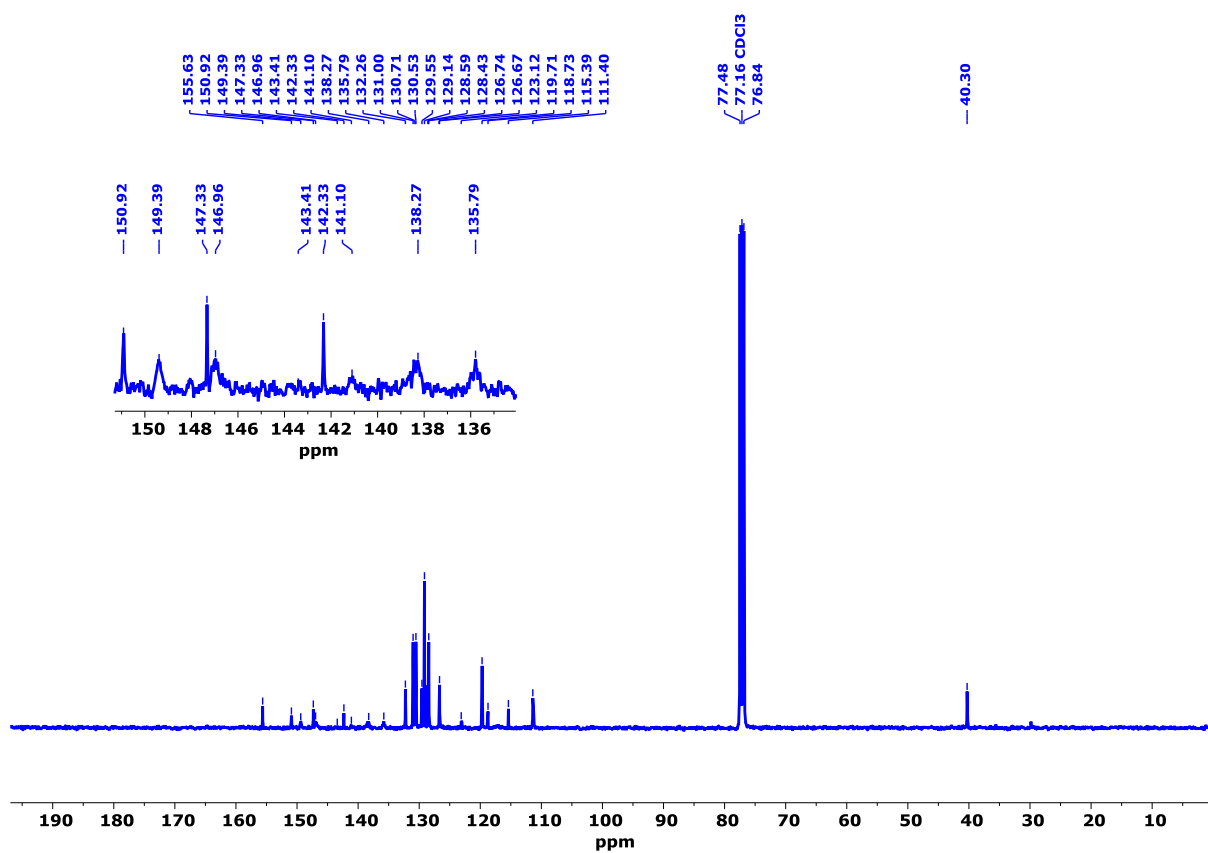


Figure S82: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 5 in CDCl_3

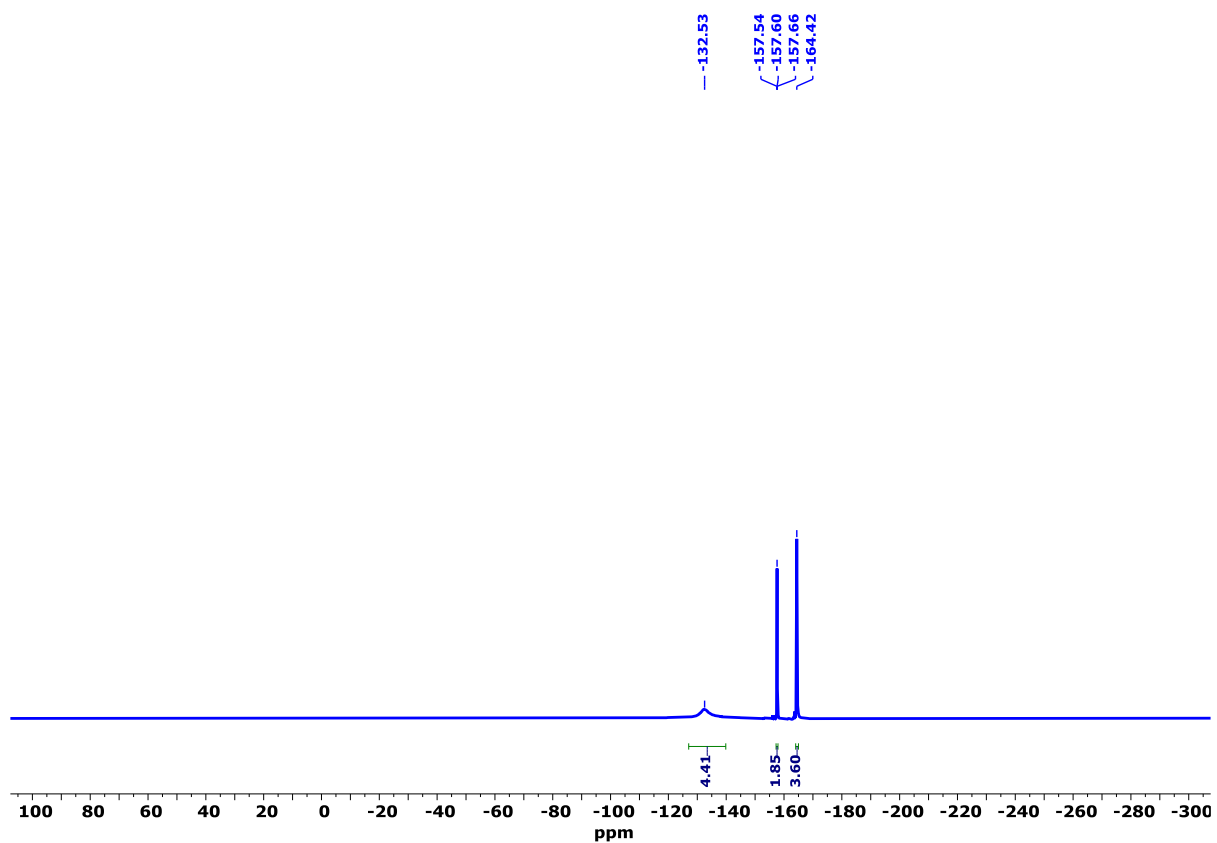


Figure S83: ^{19}F -NMR (376 MHz) spectrum of compound 5 in CDCl_3

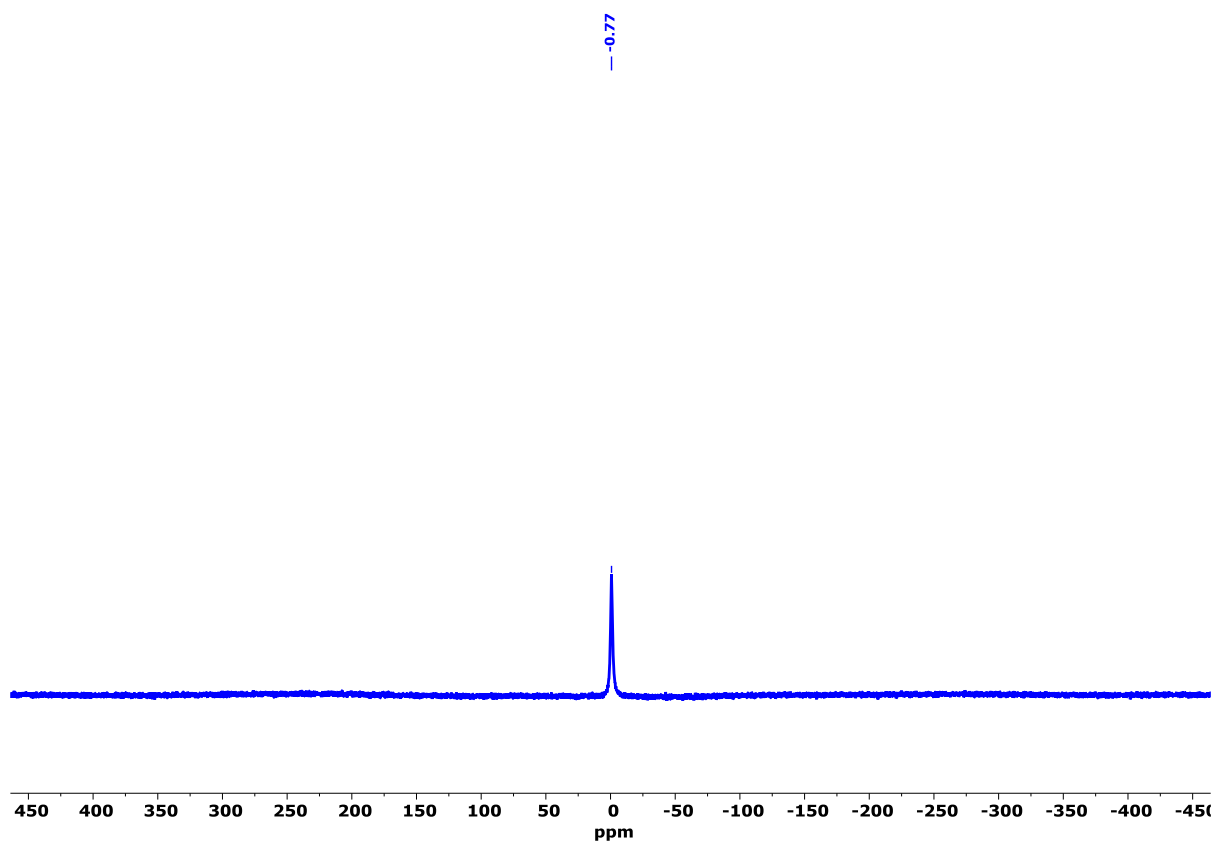
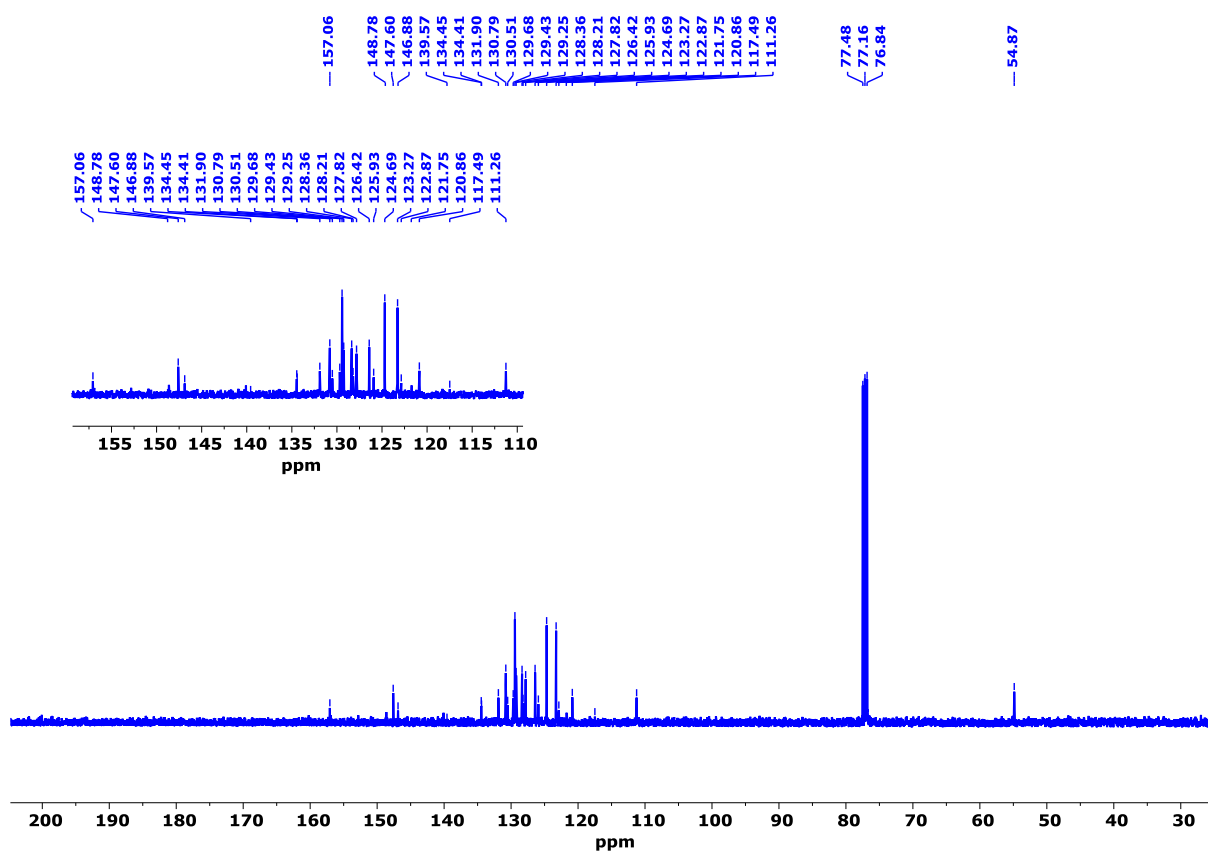
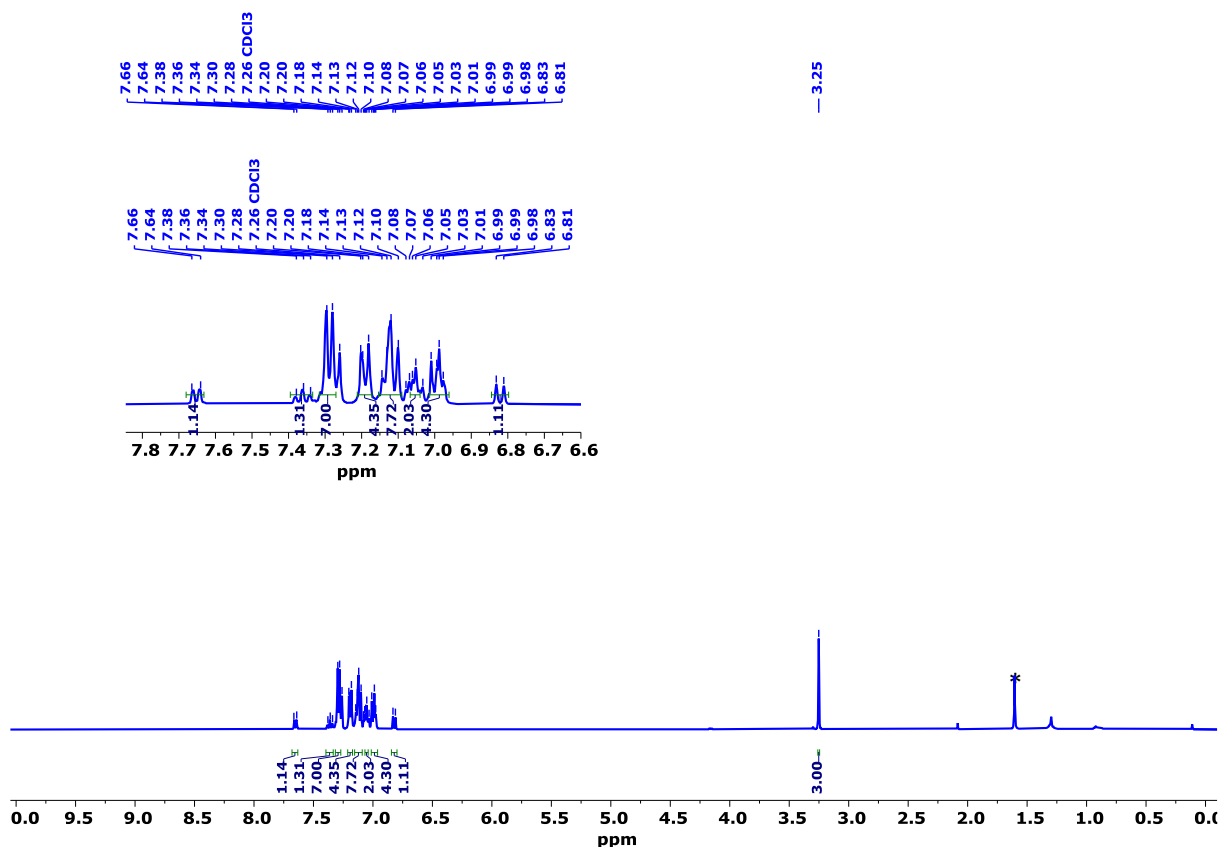


Figure S84: ^{11}B -NMR (128 MHz) spectrum of compound 5 in CDCl_3



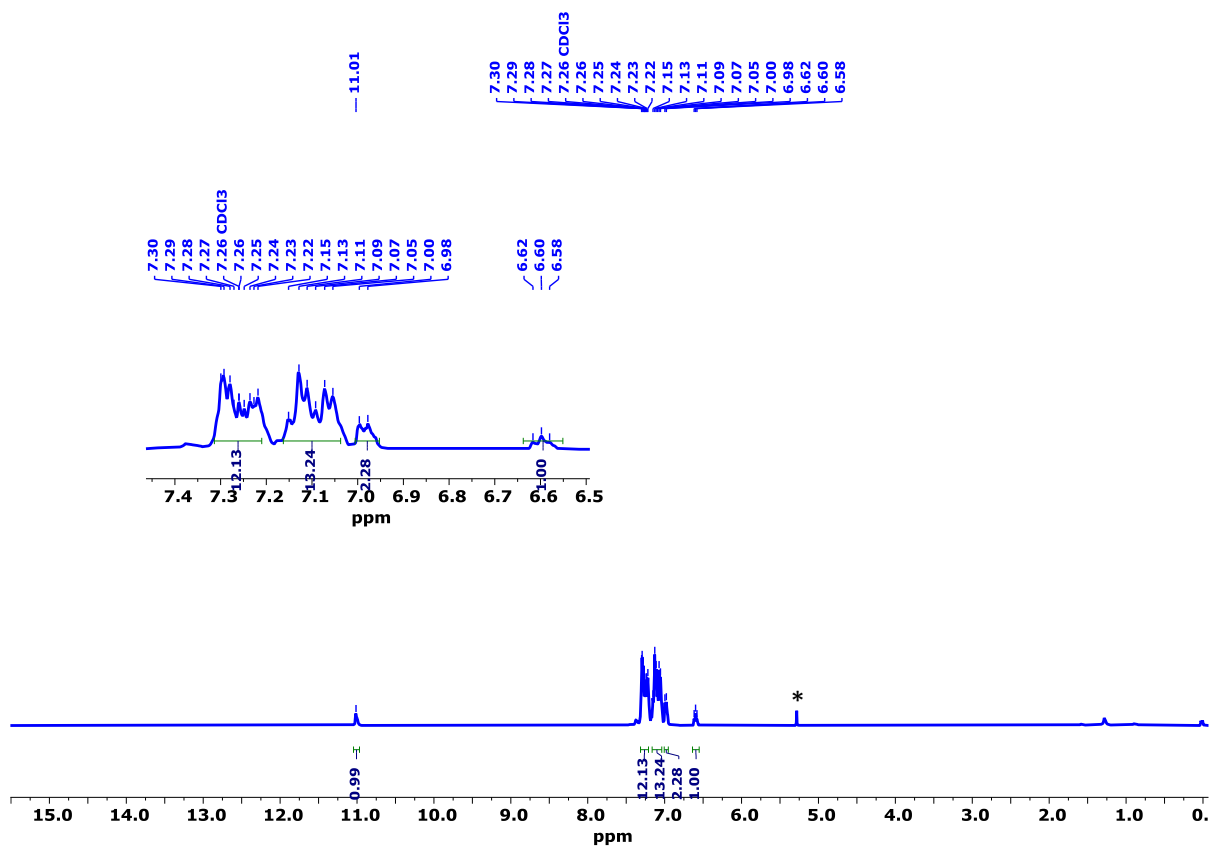


Figure S87: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 6a in CDCl_3 (* CH_2Cl_2 peak)

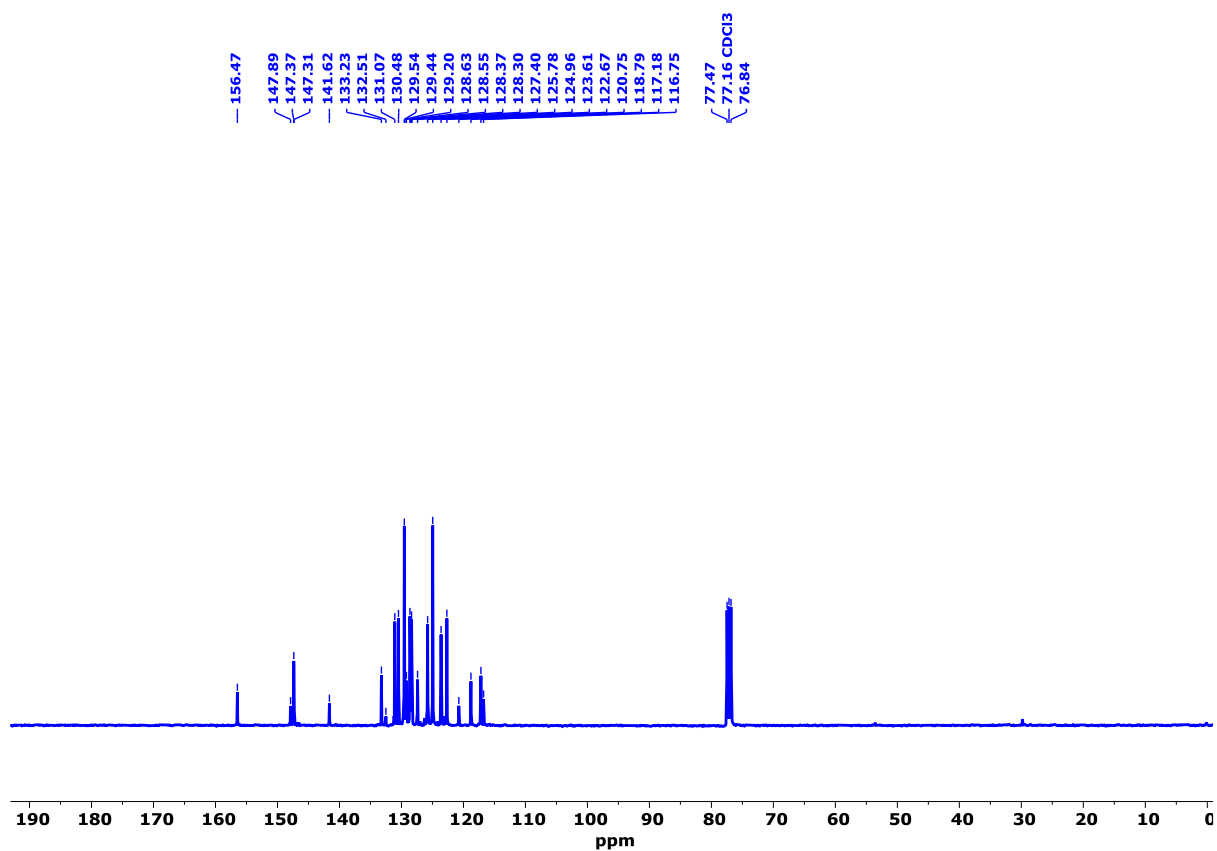


Figure S88: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 6a in CDCl_3

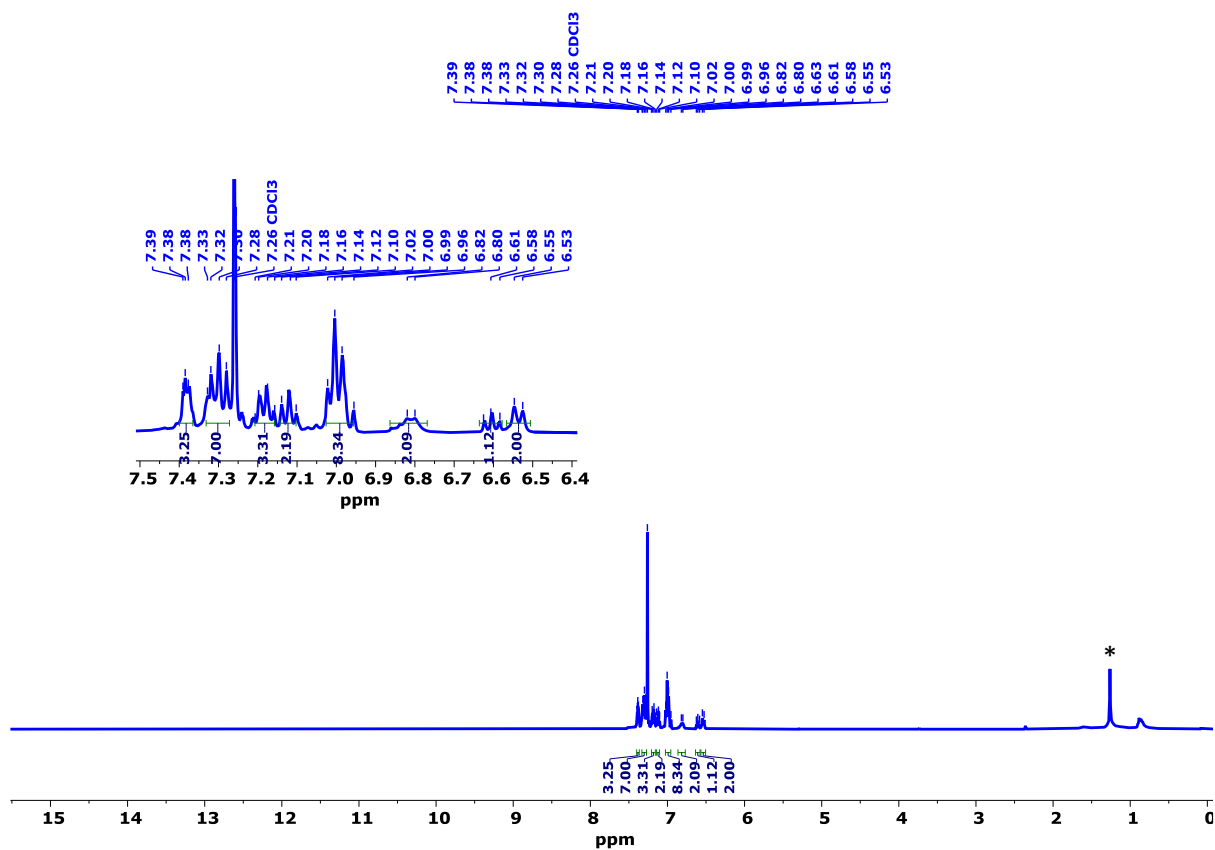


Figure S89: $^1\text{H-NMR}$ (400 MHz) spectrum of compound 6 in CDCl_3 (*grease peak)

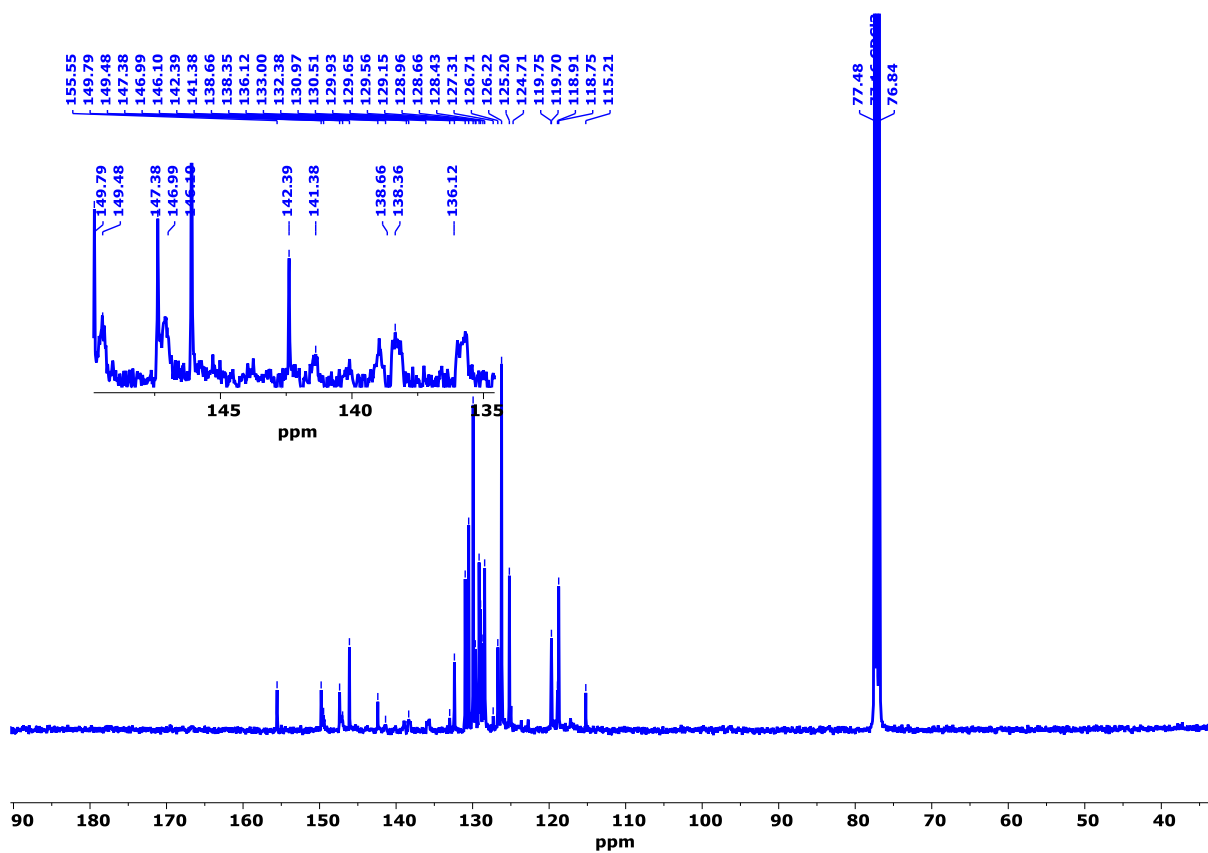


Figure S90: $^{13}\text{C-NMR}$ (101 MHz) spectrum of compound 6 in CDCl_3

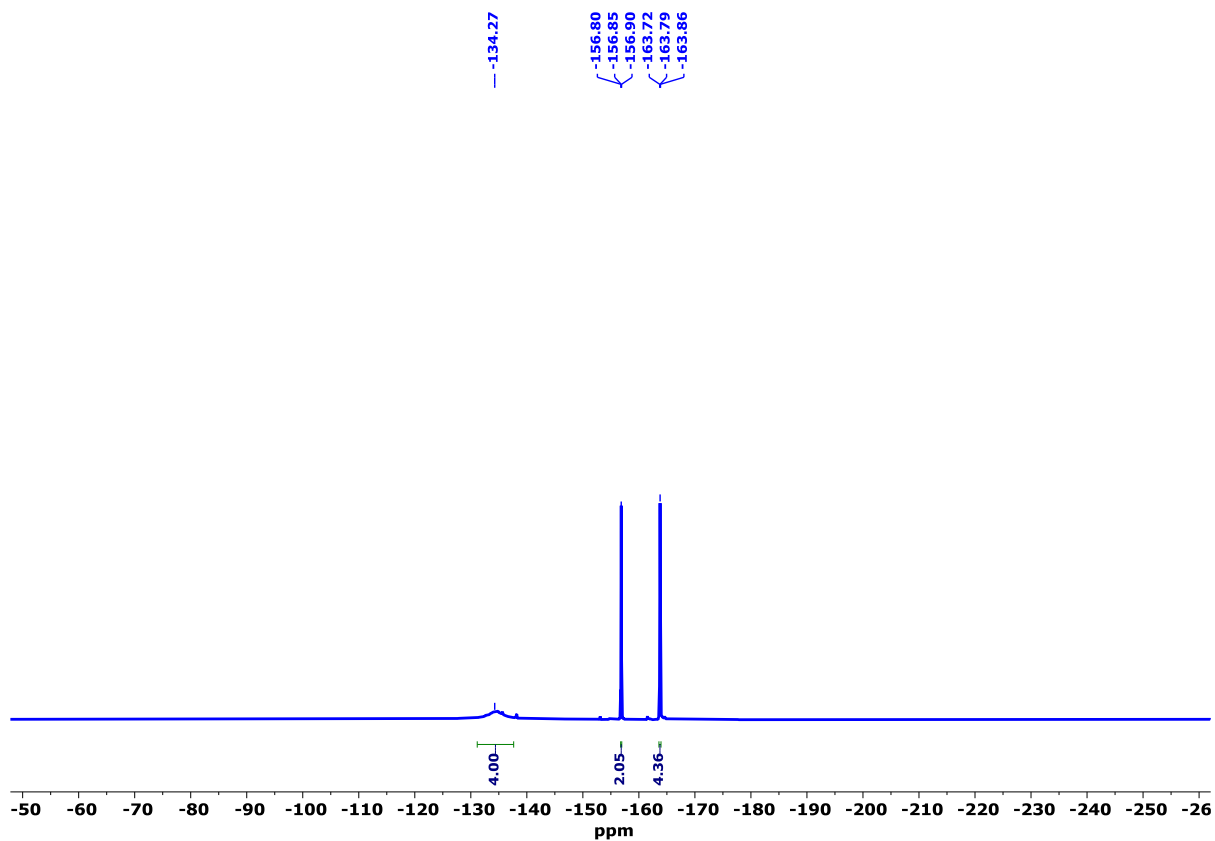


Figure S91: ^{19}F -NMR (376 MHz) spectrum of compound 6 in CDCl_3

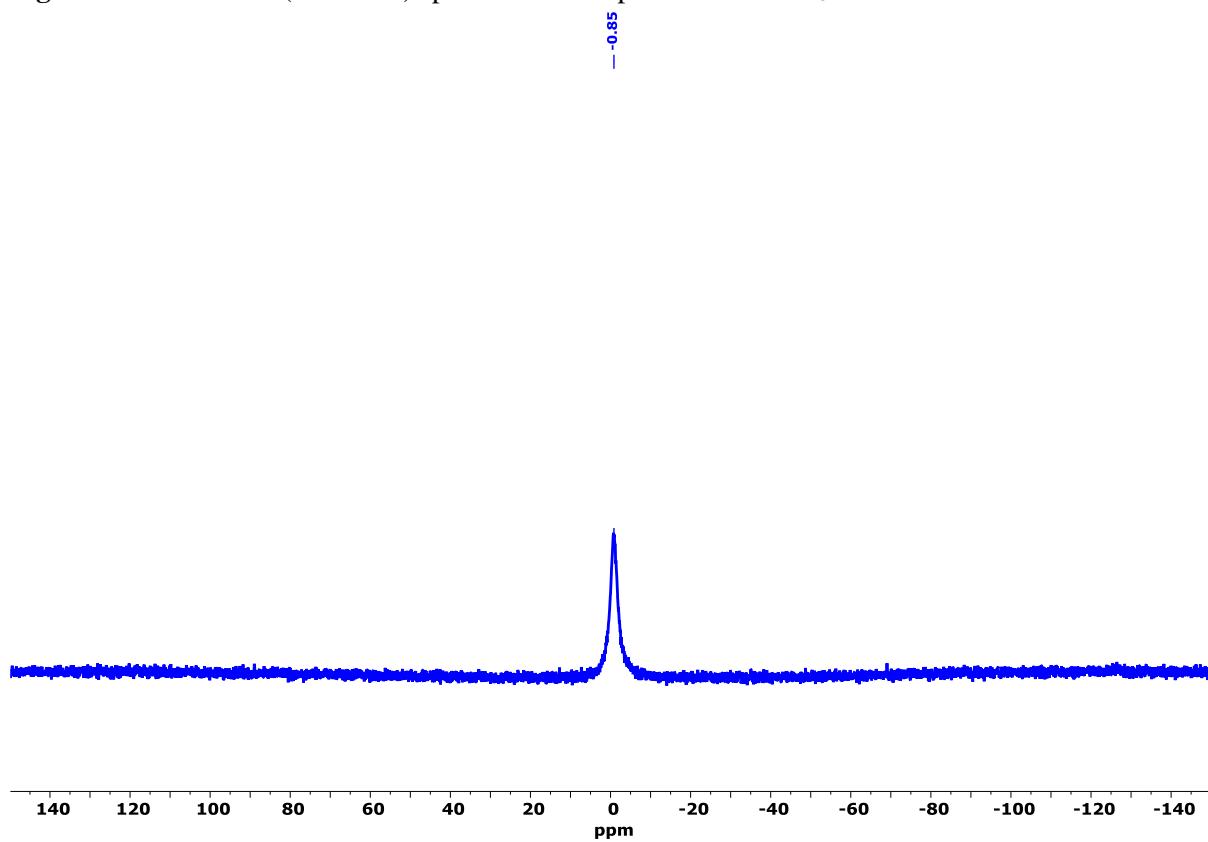


Figure S92: ^{11}B -NMR (128 MHz) spectrum of compound 6 in CDCl_3

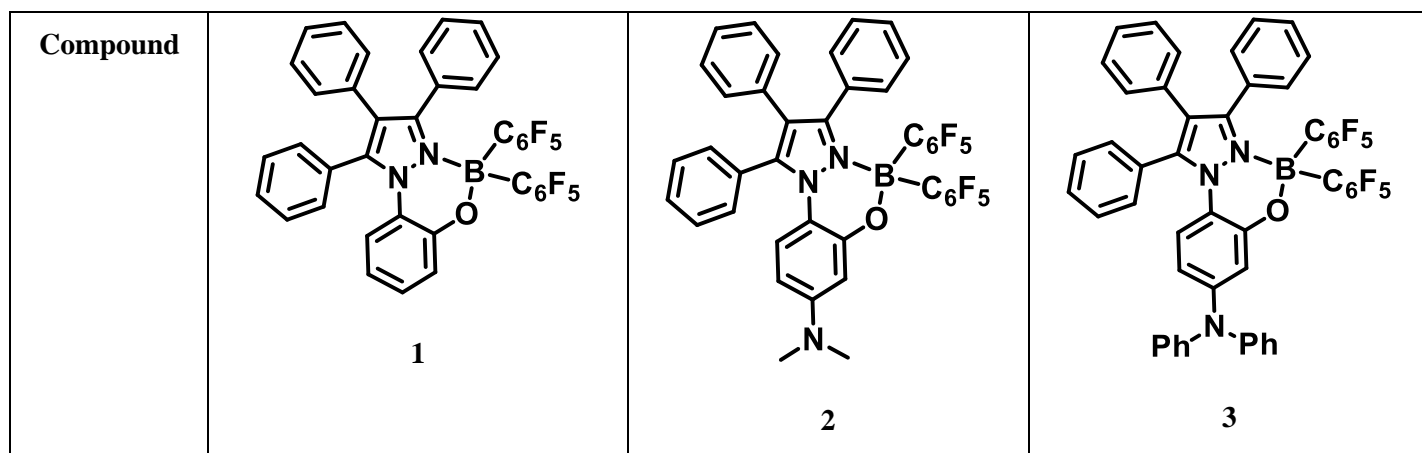
DFT calculations were performed with the Gaussian 16 program.² The structures were optimized using 6-31G(d,p) (B3LYP) as the basis set. Frequency calculations confirmed the optimized structures to be local minimum structures. Excitation data were determined using TD-DFT (B3LYP/631g(d,p)) calculations.

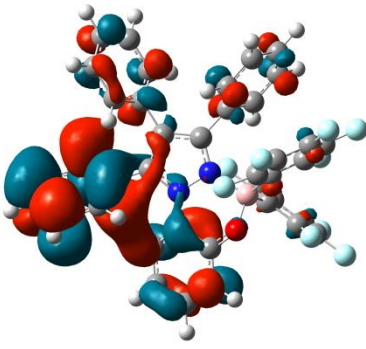
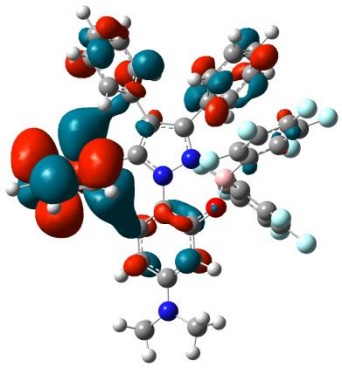
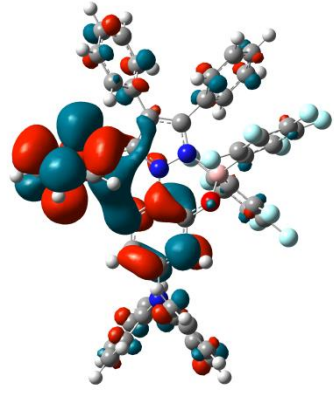
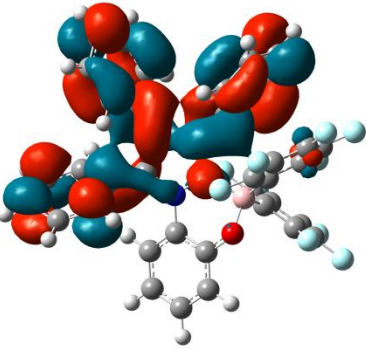
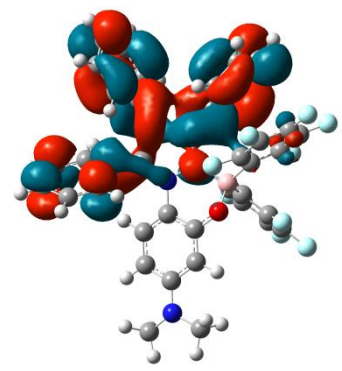
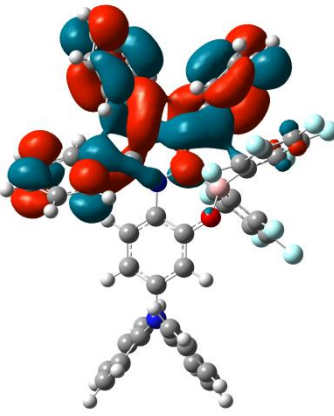
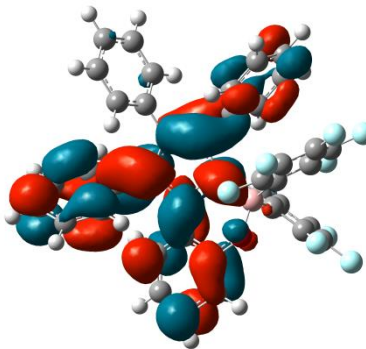
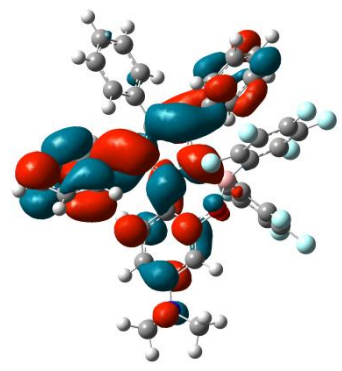
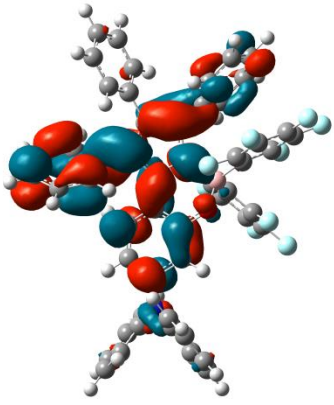
Table S6. Calculated electronic transitions for compound **1-6**

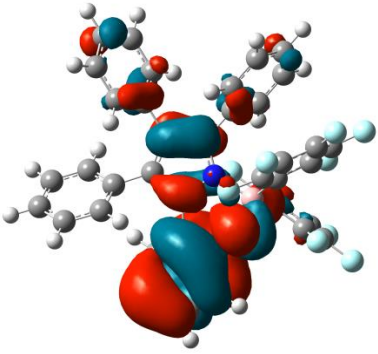
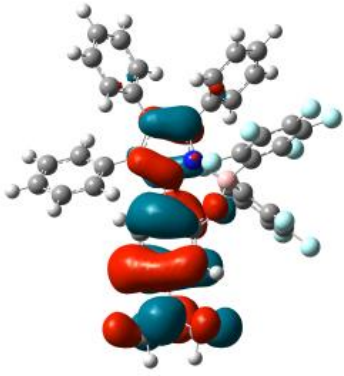
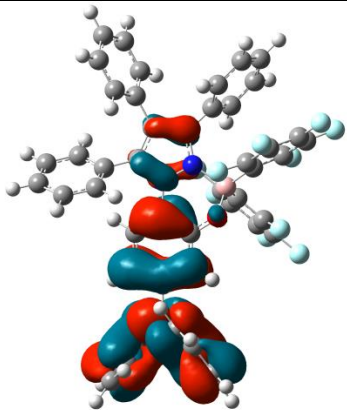
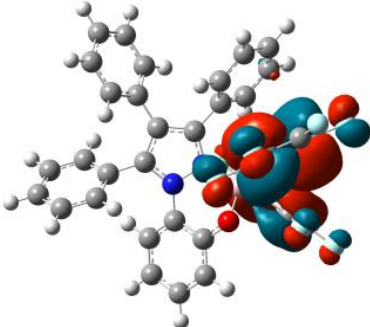
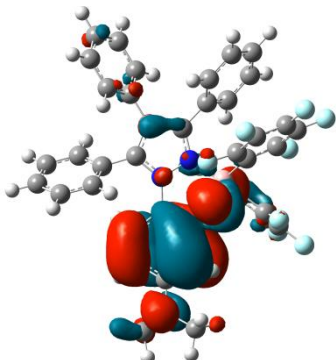
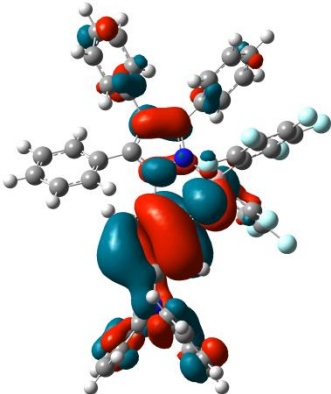
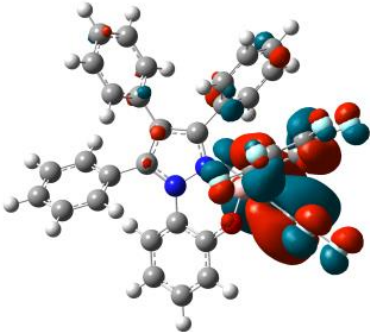
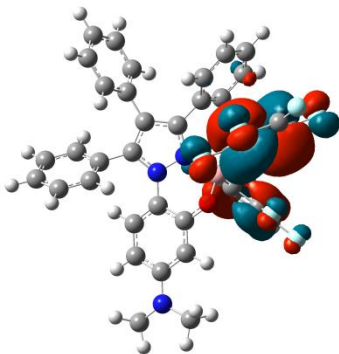
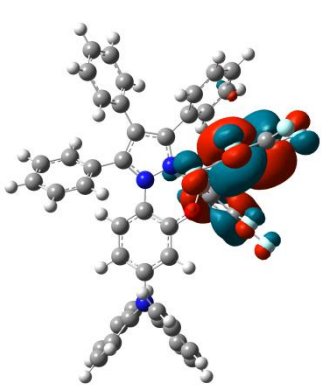
Compound	Transition	MO contributions	Energy gap eV (nm)	Oscillator strength/f
1	S ₀ →S ₁	HOMO→LUMO	3.74 (331)	0.1292
	S ₀ →S ₂	HOMO-1→LUMO	4.07 (304)	0.0019
	S ₀ →S ₃	HOMO-3→LUMO HOMO-2→LUMO	4.15 (298)	0.0280
2	S ₀ →S ₁	HOMO→LUMO	3.29 (375)	0.2707
	S ₀ →S ₂	HOMO-1→LUMO	3.98 (311)	0.0008
		HOMO→LUMO+1		
		HOMO→LUMO+2		
S ₀ →S ₃	HOMO-1→LUMO HOMO→LUMO+1	4.00 (309)	0.0153	
3	S ₀ →S ₁	HOMO→LUMO	3.05 (406)	0.3580
	S ₀ →S ₂	HOMO-1→LUMO	3.82 (324)	0.0221
		HOMO→LUMO+1		
		HOMO→LUMO+2		
		HOMO→LUMO+3		
		HOMO→LUMO+4		
	S ₀ →S ₃	HOMO-1→LUMO	3.86 (320)	0.0533
		HOMO→LUMO+1		
HOMO→LUMO+2				
HOMO→LUMO+3				

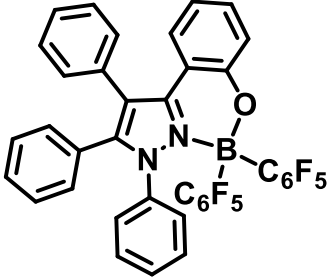
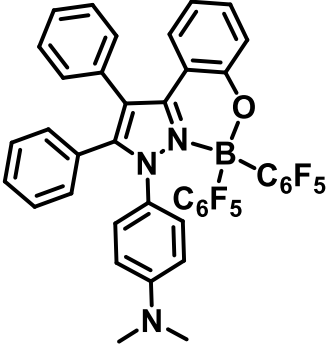
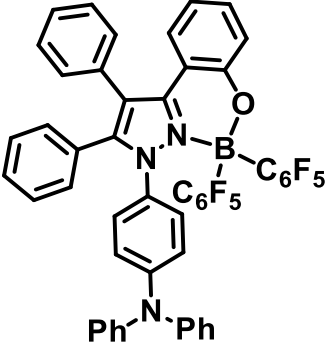
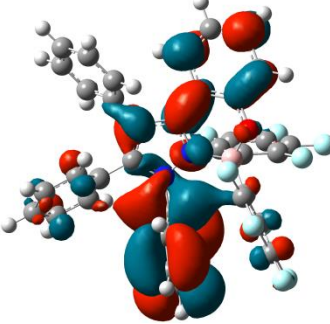
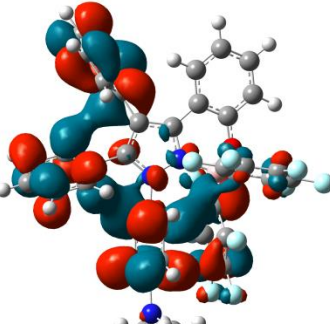
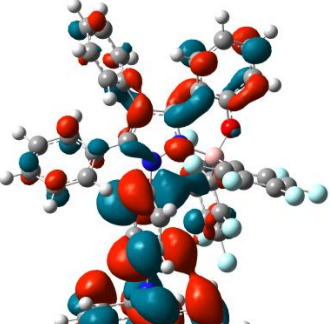
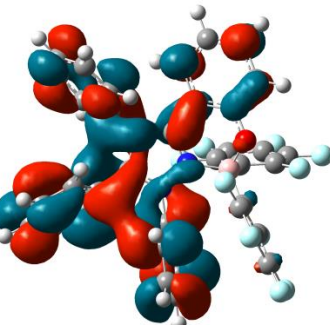
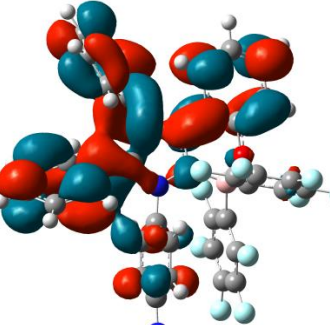
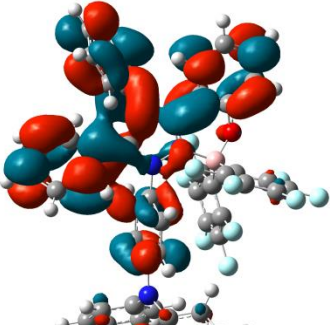
4	$S_0 \rightarrow S_1$	HOMO \rightarrow LUMO	3.63 (341)	0.0659
	$S_0 \rightarrow S_2$	HOMO-3 \rightarrow LUMO	4.16 (297)	0.0398
		HOMO \rightarrow LUMO+1		
		HOMO \rightarrow LUMO+2		
$S_0 \rightarrow S_3$	HOMO-1 \rightarrow LUMO	4.24 (292)	0.0021	
5	$S_0 \rightarrow S_1$	HOMO \rightarrow LUMO	3.65 (339)	0.0614
	$S_0 \rightarrow S_2$	HOMO-1 \rightarrow LUMO	3.72 (333)	0.0450
	$S_0 \rightarrow S_3$	HOMO-3 \rightarrow LUMO	4.17 (297)	0.0388
		HOMO-1 \rightarrow LUMO+1		
		HOMO \rightarrow LUMO+1		
6	$S_0 \rightarrow S_1$	HOMO \rightarrow LUMO	3.57 (347)	0.0761
	$S_0 \rightarrow S_2$	HOMO-1 \rightarrow LUMO	3.70 (334)	0.0657
	$S_0 \rightarrow S_3$	HOMO \rightarrow LUMO+1	4.00 (309)	0.0425
		HOMO \rightarrow LUMO+2		
		HOMO \rightarrow LUMO+3		

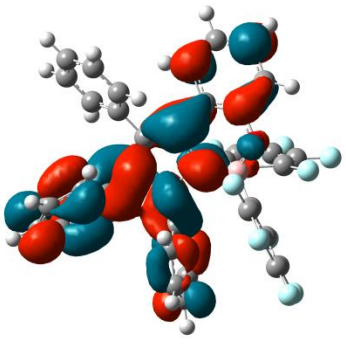
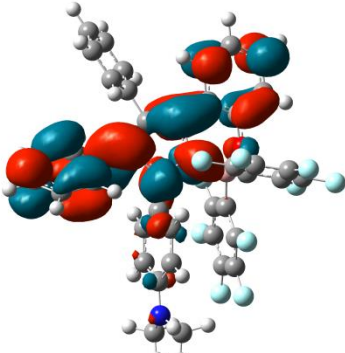
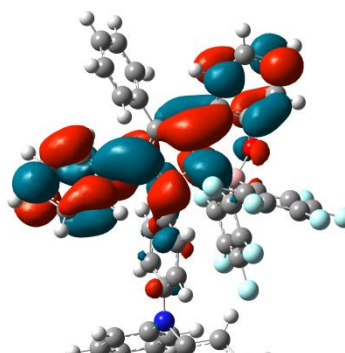
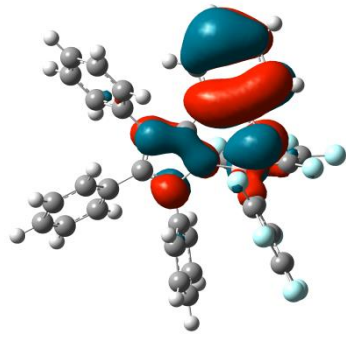
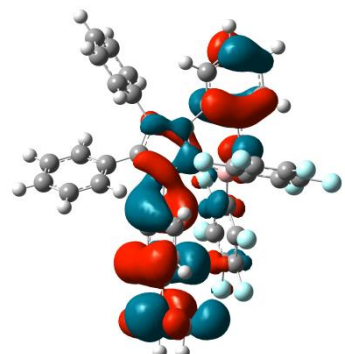
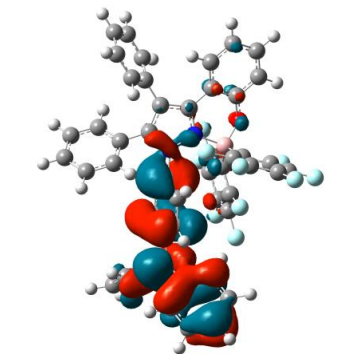
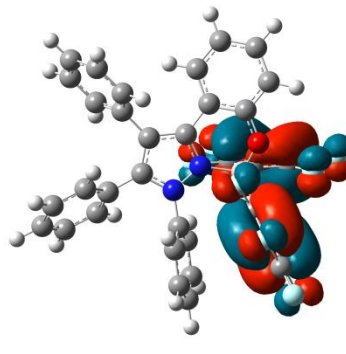
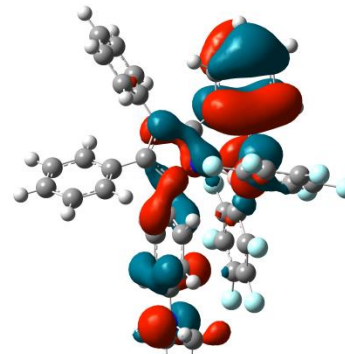
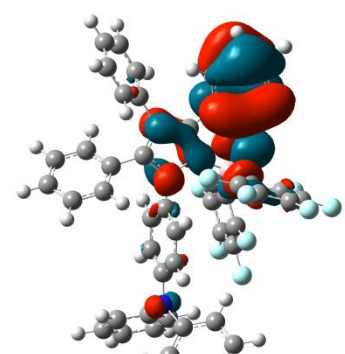
Table S7. Computed orbitals for compounds 1-6

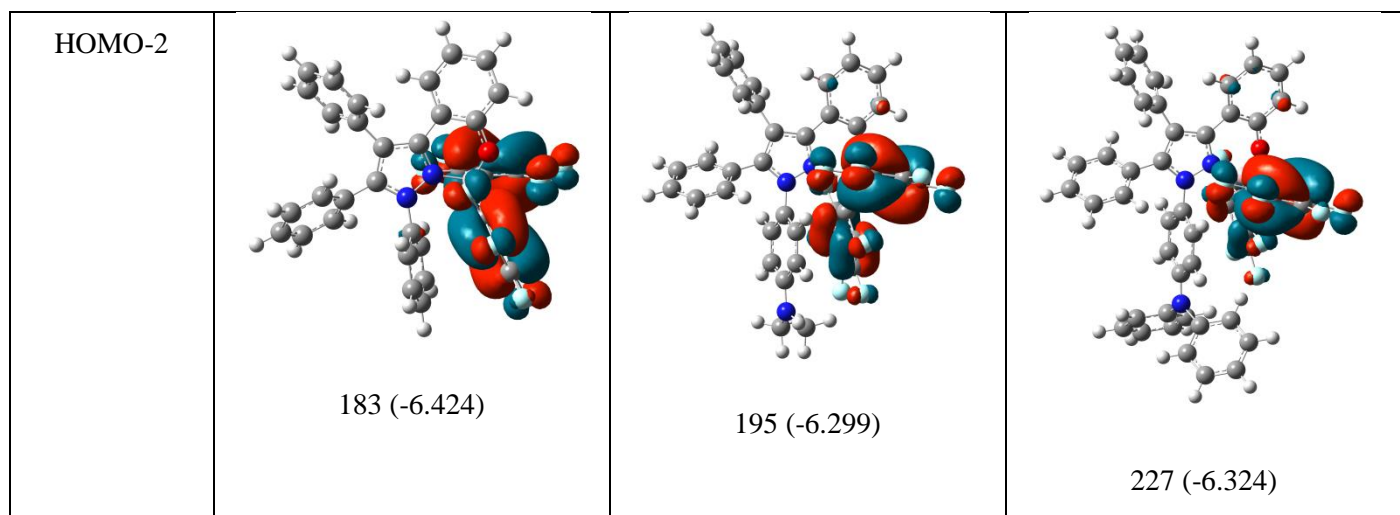


LUMO+2	 <p>188 (-0.768)</p>	 <p>200 (-0.622)</p>	 <p>232 (-0.720)</p>
LUMO+1	 <p>187 (-0.951)</p>	 <p>199 (-0.807)</p>	 <p>231 (-0.891)</p>
LUMO	 <p>186 (-1.725)</p>	 <p>198 (-1.483)</p>	 <p>230(-1.634)</p>

HOMO	 <p>185 (-6.092)</p>	 <p>197 (-5.276)</p>	 <p>229 (-5.143)</p>
HOMO-1	 <p>184 (-6.337)</p>	 <p>196 (-6.115)</p>	 <p>228 (-6.117)</p>
HOMO-2	 <p>183 (-6.419)</p>	 <p>195 (-6.235)</p>	 <p>227 (-6.288)</p>

Compound	 <p style="text-align: center;">4</p>	 <p style="text-align: center;">5</p>	 <p style="text-align: center;">6</p>
LUMO+2	 <p style="text-align: center;">188 (-0.994)</p>	 <p style="text-align: center;">200 (-0.603)</p>	 <p style="text-align: center;">232 (-0.750)</p>
LUMO+1	 <p style="text-align: center;">187 (-1.093)</p>	 <p style="text-align: center;">199 (-0.943)</p>	 <p style="text-align: center;">231 (-0.951)</p>

LUMO	 <p>186 (-1.574)</p>	 <p>198 (-1.409)</p>	 <p>230 (-1.403)</p>
HOMO	 <p>185 (-5.794)</p>	 <p>197 (-5.641)</p>	 <p>229 (-5.511)</p>
HOMO-1	 <p>184 (-6.357)</p>	 <p>196 (-5.723)</p>	 <p>228 (-5.698)</p>



Compound 1

Center Atomic Atomic Coordinates (Angstroms)

Number Number Type X Y Z

F	-0.368062	-1.492600	2.188560
F	-3.799018	-1.322804	-1.108764
F	-0.034264	1.190088	-2.737297
F	-3.462937	1.123353	0.563329
F	-1.901409	-3.066517	3.680968
F	-3.240138	4.613653	-2.559432
F	-4.428613	3.403533	-0.414946
O	-0.970645	-1.239323	-1.857323
N	1.351666	-1.105052	-0.450539
N	0.386146	-0.214161	-0.071892
C	-1.588738	-1.813945	1.684671
C	-3.288231	-1.737921	0.066289
C	-2.008068	-1.322195	0.450237
C	-2.368470	-2.635490	2.498952
C	2.392749	0.604815	0.524251
C	0.997436	0.818451	0.538910
C	0.270634	1.965826	1.126047
C	-1.733778	1.000742	-1.076397
C	0.549177	3.267969	0.683228
H	1.273706	3.421248	-0.109879
C	-0.220945	-2.348220	-1.788684
C	-1.151801	1.674587	-2.156169
C	0.966256	-2.350672	-1.033019
C	-2.758301	3.458210	-2.086183
C	-1.637502	2.874087	-2.668067
C	3.437656	1.500790	1.069188
C	3.857361	-1.279376	-0.484924
C	-0.656053	1.772540	2.160909
H	-0.843774	0.771078	2.527689
C	-2.842249	1.637685	-0.516757
C	-3.360581	2.839097	-0.997281
C	-1.311497	2.866080	2.725689

H	-2.031149	2.706470	3.522588
C	-0.111612	4.355877	1.248872
H	0.100949	5.358975	0.891951
C	-0.597566	-3.517976	-2.458886
H	-1.507890	-3.495289	-3.047931
C	3.364708	1.955168	2.395659
H	2.536274	1.641905	3.022719
C	-1.045353	4.157163	2.268727
H	-1.560738	5.006595	2.706738
C	0.173195	-4.669903	-2.338946
H	-0.131954	-5.574133	-2.856843
C	4.790268	-1.593127	0.514288
H	4.558131	-1.373890	1.551344
C	4.516599	1.914897	0.271917
H	4.581089	1.578425	-0.757832
C	4.166614	-1.553191	-1.826798
H	3.451709	-1.304313	-2.604649
C	6.306254	-2.460764	-1.158293
H	7.254766	-2.920299	-1.419342
C	5.497710	2.759096	0.789848
H	6.324187	3.072200	0.158767
C	4.345556	2.801574	2.910063
H	4.274263	3.143149	3.938413
C	5.385497	-2.140908	-2.158557
H	5.616615	-2.347391	-3.199041
C	6.006852	-2.185157	0.176755
H	6.720413	-2.429282	0.957703
C	5.415380	3.205443	2.109663
H	6.179102	3.864734	2.511328
B	-1.130569	-0.442713	-0.623774
C	-3.633212	-3.016780	2.070224
C	-4.100755	-2.558306	0.841019
F	-4.397069	-3.809123	2.831467
C	2.584549	-0.617575	-0.127870
F	-5.321437	-2.915423	0.417763
F	-1.031810	3.474906	-3.703964
C	1.712832	-3.521108	-0.870751
H	2.591903	-3.525057	-0.239598
C	1.316239	-4.679997	-1.532381
H	1.895688	-5.588993	-1.411461

Rotational constants (GHZ): 0.0671746 0.0526944 0.0414231

Compound 2

Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z

F 0.539481 0.321931 2.570374

F	3.784718	-1.081307	-0.619798
F	-0.516492	-0.900233	-2.800964
F	2.030097	-3.218684	0.485168
F	2.458104	0.563782	4.392453
F	0.417969	-5.472761	-3.297397
F	1.791510	-5.459041	-0.932478
O	1.447541	0.467072	-1.429317
N	-0.758405	1.373477	-0.119793
N	-0.462910	0.054045	0.077659
C	1.803585	0.025103	2.170303
C	3.413088	-0.665319	0.606572
C	2.064768	-0.396500	0.868278
C	2.782929	0.156610	3.155150
C	-2.656978	0.359490	0.453734
C	-1.599995	-0.572332	0.442974
C	-1.666308	-2.012185	0.779503
C	0.822728	-1.922857	-1.114804
C	-2.509604	-2.862227	0.047933
H	-3.082564	-2.462725	-0.782515
C	1.391185	1.777766	-1.141459
C	0.112289	-1.992314	-2.318499
C	0.293995	2.285838	-0.422452
C	0.547426	-4.337259	-2.600018
C	-0.031504	-3.159611	-3.062416
C	-4.076322	0.094455	0.779219
C	-2.765265	2.878743	-0.155453
C	-0.935254	-2.529547	1.859105
H	-0.310826	-1.867221	2.446219
C	1.367187	-3.133911	-0.685546
C	1.245812	-4.325770	-1.398521
C	-1.031422	-3.882010	2.185021
H	-0.458356	-4.274410	3.019416
C	-2.597890	-4.213397	0.375247
H	-3.243816	-4.866044	-0.204162
C	2.416818	2.630570	-1.541229
H	3.239657	2.180285	-2.079271
C	-4.424774	-0.545880	1.979331
H	-3.643755	-0.844318	2.671226
C	-1.857297	-4.726628	1.442562
H	-1.926303	-5.780444	1.695205
C	2.387861	4.004224	-1.220532
C	-3.532884	3.459279	0.864836
H	-3.602058	2.965658	1.828601
C	-5.099972	0.474082	-0.103685
H	-4.845613	0.961648	-1.039356
C	-2.688921	3.515102	-1.404858
H	-2.103022	3.066364	-2.200581
C	-4.115860	5.293965	-0.598998
H	-4.638051	6.230439	-0.770744
C	-6.435470	0.223381	0.208000
H	-7.214120	0.521855	-0.487779
C	-5.760714	-0.798570	2.287132
H	-6.011946	-1.294246	3.220185
C	-3.360766	4.716053	-1.622104

H	-3.296589	5.199260	-2.592282
C	-4.201096	4.663104	0.642900
H	-4.788984	5.106116	1.440980
C	-6.770527	-0.413713	1.403782
H	-7.811016	-0.610383	1.644732
B	1.004381	-0.477084	-0.384653
C	4.106105	-0.125642	2.842129
C	4.424473	-0.546450	1.553363
F	5.064093	-0.000978	3.769020
C	-2.091158	1.582932	0.070868
F	5.698505	-0.825174	1.239825
F	-0.729190	-3.162586	-4.209238
C	0.285955	3.627880	-0.036327
H	-0.520443	4.016265	0.572703
C	1.309465	4.477545	-0.428293
H	1.271546	5.509747	-0.107717
N	3.389131	4.856834	-1.645812
C	4.549127	4.317341	-2.336428
H	4.248674	3.765436	-3.233792
H	5.190971	5.140138	-2.653608
H	5.143836	3.640636	-1.704895
C	3.447201	6.216341	-1.135434
H	4.290396	6.733835	-1.594211
H	2.538587	6.774885	-1.389463
H	3.575610	6.254974	-0.043479

 Rotational constants (GHZ): 0.0527875 0.0506596 0.0361310

Compound 3

 Center Atomic Atomic Coordinates (Angstroms)
 Number Number Type X Y Z

F	-0.856723	0.008098	2.770954
F	0.530837	-3.640951	0.044678
F	-1.672022	-0.442041	-2.779665
F	-2.370457	-3.544887	0.762625
F	0.278943	-1.152050	4.874229
F	-4.558544	-4.098896	-3.347116
F	-4.042299	-4.916786	-0.789649
O	0.387578	-0.926082	-1.025318
N	-0.481726	1.449137	-0.023967
N	-1.339457	0.396763	0.137307
C	-0.237879	-1.182234	2.553311
C	0.451740	-2.987352	1.219452
C	-0.218157	-1.760075	1.285665
C	0.339429	-1.765165	3.681597
C	-2.527639	2.304056	0.188209
C	-2.581534	0.898147	0.286442
C	-3.774759	0.057378	0.529335

C	-1.882431	-1.952599	-0.947506
C	-4.858755	0.106987	-0.360209
H	-4.801786	0.740390	-1.239429
C	1.315395	-0.022903	-0.675628
C	-2.199391	-1.567815	-2.255106
C	0.919837	1.200834	-0.103009
C	-3.701784	-3.412930	-2.580852
C	-3.082569	-2.267812	-3.071743
C	-3.663662	3.248857	0.274277
C	-0.572852	3.944838	-0.273428
C	-3.856758	-0.751925	1.672016
H	-3.034321	-0.763356	2.376642
C	-2.543605	-3.096270	-0.496870
C	-3.435579	-3.826192	-1.280822
C	-4.998105	-1.518052	1.905973
H	-5.050280	-2.146168	2.789834
C	-5.994957	-0.663217	-0.122766
H	-6.824337	-0.628054	-0.822553
C	2.671850	-0.295060	-0.850368
H	2.947065	-1.248844	-1.283243
C	-4.554929	3.195619	1.358015
H	-4.404368	2.456182	2.137891
C	-6.065672	-1.479583	1.008565
H	-6.951236	-2.081151	1.190114
C	3.645198	0.629995	-0.444936
C	-0.739029	4.977992	0.660562
H	-1.290770	4.788162	1.575407
C	-3.873562	4.213203	-0.724426
H	-3.198712	4.259839	-1.573045
C	0.131207	4.197915	-1.461582
H	0.254890	3.404207	-2.191452
C	0.506855	6.483057	-0.764433
H	0.927019	7.466155	-0.954229
C	-4.943226	5.103053	-0.638255
H	-5.091910	5.840972	-1.421063
C	-5.625814	4.084263	1.439973
H	-6.304763	4.029639	2.285786
C	0.667290	5.461023	-1.702789
H	1.208920	5.647657	-2.625042
C	-0.197304	6.239413	0.415630
H	-0.327088	7.031113	1.147103
C	-5.822946	5.041576	0.443550
H	-6.657293	5.733607	0.508771
B	-0.764976	-1.105709	-0.118511
C	0.992308	-2.984887	3.559887
C	1.044473	-3.606351	2.314588
F	1.558877	-3.559980	4.627691
C	-1.180800	2.619993	-0.027491
F	1.667028	-4.786488	2.184866
F	-3.350106	-1.844098	-4.316833
C	1.885008	2.100697	0.357118
H	1.587540	3.022804	0.839176
C	3.233587	1.827958	0.176052
H	3.973678	2.541426	0.516365

N	5.016398	0.355341	-0.632541
C	5.979433	0.785470	0.326223
C	7.181767	1.371745	-0.097025
C	5.747029	0.616150	1.699771
C	8.132519	1.775217	0.838385
H	7.363852	1.504372	-1.158269
C	6.695744	1.039664	2.628524
H	4.824582	0.151643	2.031733
C	7.894337	1.617222	2.205075
H	9.059044	2.226576	0.495416
H	6.501835	0.901236	3.688218
H	8.634655	1.938176	2.931304
C	5.455289	-0.394086	-1.764024
C	4.978610	-0.089037	-3.047796
C	6.378977	-1.437616	-1.606145
C	5.410925	-0.825283	-4.148852
H	4.269021	0.721799	-3.174103
C	6.819699	-2.156606	-2.715674
H	6.745703	-1.679094	-0.614160
C	6.336272	-1.858978	-3.990996
H	5.031092	-0.579986	-5.136357
H	7.533912	-2.963212	-2.578218
H	6.675529	-2.426623	-4.851877

Compound 4

Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z

F	0.132721	1.316341	2.125919
O	-1.059398	1.403873	-1.831033
F	-3.681603	1.825748	-0.682227
F	-3.437800	-0.749366	0.867073
F	-0.600473	-1.071755	-2.942647
F	-4.737090	3.535071	1.091080
F	-0.939329	3.014749	3.862136
N	0.935406	-0.873258	0.368567
N	0.422390	0.189338	-0.322762
F	-4.210682	-4.021302	-2.401666
F	-4.865674	-2.803507	-0.041960
F	-3.383060	4.157620	3.384445
F	-2.060622	-3.124768	-3.835151
C	0.130548	-1.948883	0.885435
C	2.296271	-0.785710	0.393130
C	-0.119348	2.342538	-2.005763
C	-1.978418	-0.757341	-1.022577
C	1.452092	0.967702	-0.715647
C	2.666583	0.368382	-0.297907
C	1.171007	2.201618	-1.442722
C	3.154144	-1.794301	1.049870
C	4.058769	0.821970	-0.534265

C	-1.077207	1.847773	1.794905
C	-3.071147	-1.270419	-0.322025
C	-1.717032	1.493316	0.609588
C	-2.962492	2.103966	0.421927
C	2.973975	-2.133655	2.399861
H	2.186190	-1.658653	2.974387
C	-0.416958	3.463363	-2.793351
H	-1.408655	3.534398	-3.226720
C	-1.674807	-1.431953	-2.210776
C	-3.828749	-2.353882	-0.764617
C	2.115341	3.227068	-1.628654
H	3.092350	3.143860	-1.169425
C	4.191241	-2.400709	0.324461
H	4.341992	-2.135912	-0.716661
C	5.023108	-3.337074	0.935476
H	5.819074	-3.802759	0.362518
C	0.139229	-3.175899	0.218638
H	0.718659	-3.289311	-0.691084
C	-3.498500	-2.976320	-1.962490
C	0.538595	4.453982	-2.981718
H	0.294078	5.324912	-3.583140
C	4.576185	0.885415	-1.838320
H	3.939950	0.620808	-2.677541
C	-1.612214	2.726418	2.736819
C	1.803171	4.347354	-2.388036
H	2.538815	5.134076	-2.519225
C	-3.536469	2.988359	1.328756
C	4.833904	-3.674321	2.276559
H	5.483537	-4.403222	2.751698
C	-0.603437	-1.767091	2.057803
H	-0.573949	-0.810706	2.563295
C	-2.405794	-2.515240	-2.690336
C	3.809975	-3.068758	3.006864
H	3.663007	-3.320802	4.052637
C	5.891982	1.289746	-2.059115
H	6.277584	1.334992	-3.073329
B	-1.117008	0.570601	-0.618226
C	-2.850332	3.308284	2.497905
C	4.890554	1.167563	0.541077
H	4.498870	1.123477	1.552578
C	6.711604	1.631816	-0.981552
H	7.736556	1.946064	-1.154639
C	-0.613306	-4.231382	0.728772
H	-0.617058	-5.186694	0.213751
C	6.207842	1.568903	0.318250
H	6.838597	1.835146	1.161186
C	-1.365406	-4.057286	1.893418
H	-1.956202	-4.880039	2.283883
C	-1.358493	-2.829064	2.555503
H	-1.941298	-2.693163	3.460703

Compound 5

 Center Atomic Atomic Coordinates (Angstroms)
 Number Number Type X Y Z

F	-3.128594	0.998483	-0.581669
F	-5.182246	-0.318184	0.474069
F	-4.952922	-1.554625	2.893119
F	0.775022	1.132844	-2.192034
F	-0.479397	-0.166848	3.202876
F	0.392798	2.969246	-4.071569
F	-2.073374	3.581168	0.738106
F	-2.583767	-1.416892	4.267774
F	-2.439494	5.416366	-1.180418
O	0.158934	2.100738	1.796555
N	0.814208	0.234975	0.368020
N	0.752504	-0.999467	-0.223105
F	-1.212111	5.140191	-3.608721
C	2.112351	0.521478	0.601279
C	-0.486388	-1.660106	-0.521753
C	-3.920989	-0.851923	2.400442
C	-4.031965	-0.225392	1.166981
C	-0.615860	2.274506	-0.607705
C	-2.936307	0.451336	0.635727
C	2.461038	1.815062	1.182410
C	4.375503	-0.753885	0.295150
C	2.281492	-2.847687	-0.901640
C	2.010519	-1.510950	-0.333263
C	-1.636480	-0.119079	2.513599
C	2.906747	-0.577475	0.191113
C	-2.712411	-0.794229	3.085662
C	-0.022819	2.185816	-1.864759
C	-1.227588	-1.309991	-1.650024
H	-0.846425	-0.555296	-2.326909
C	-1.428446	3.400291	-0.430790
C	-2.463719	-1.897613	-1.883315
H	-3.028479	-1.573444	-2.746960
C	-1.695556	0.523770	1.271401
C	4.040162	3.551157	1.808109
H	5.049181	3.950041	1.793934
C	3.764212	2.343179	1.179854
H	4.557951	1.805062	0.677044
C	2.851050	-5.379608	-1.963907
H	3.070554	-6.360395	-2.375118
C	5.001126	-0.796680	1.551928
H	4.401800	-0.676794	2.449477
C	3.051313	-3.767648	-0.173080
H	3.427217	-3.493463	0.806808
C	-0.962436	-2.652644	0.337354
H	-0.380358	-2.935315	1.208436
C	-0.208763	3.123004	-2.881083
N	-4.261964	-3.396011	-1.182967
C	5.161525	-0.909867	-0.856354

H	4.687685	-0.876444	-1.832482
C	-2.193946	-3.245974	0.107597
H	-2.544565	-3.989842	0.810584
C	2.091472	-4.467006	-2.697936
H	1.721505	-4.732985	-3.683432
C	1.807297	-3.208065	-2.172615
H	1.224149	-2.499321	-2.750061
C	6.539424	-1.102182	-0.754215
H	7.134052	-1.219238	-1.655362
C	6.378649	-0.986048	1.651900
H	6.847702	-1.016024	2.630961
C	-1.020842	4.225507	-2.649995
C	-1.643093	4.362579	-1.411615
C	1.421509	2.550932	1.798085
C	3.330867	-5.026336	-0.701835
H	3.923524	-5.730896	-0.126319
C	7.151700	-1.140017	0.499183
H	8.224650	-1.287954	0.578019
C	-2.999910	-2.859887	-0.993340
C	3.012571	4.247161	2.457685
H	3.226387	5.187985	2.956907
B	-0.371536	1.287785	0.691186
C	1.713245	3.755127	2.453544
H	0.897732	4.287110	2.931399
C	-5.160092	-2.743260	-2.129667
H	-4.741276	-2.759298	-3.140302
H	-5.371332	-1.700990	-1.851037
H	-6.101547	-3.293156	-2.160049
C	-4.891013	-4.117943	-0.082075
H	-5.865018	-4.482146	-0.411138
H	-5.038436	-3.488807	0.808644
H	-4.297802	-4.991894	0.202943

Compound 6

Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z

F	-1.625331	2.290369	0.253543
F	-3.726947	1.795319	1.805713
F	-3.459448	0.344631	4.101228
F	1.905503	1.118971	-2.168942
F	1.126340	-0.188441	3.251717
F	1.913505	3.122295	-3.910530
F	0.428159	4.116282	1.226432
F	-0.995105	-0.628783	4.809013
F	0.445333	6.116162	-0.556248
O	2.237252	1.895820	1.837895
N	1.886432	0.022985	0.306835
N	1.251932	-1.041460	-0.276077
F	1.188335	5.650647	-3.147348

C	3.206512	-0.250492	0.353408
C	-0.171986	-1.098373	-0.453404
C	-2.385939	0.599835	3.342555
C	-2.511895	1.345865	2.178355
C	1.167842	2.515067	-0.364305
C	-1.393208	1.588565	1.384256
C	4.121849	0.756339	0.882622
C	4.696316	-2.303276	-0.278993
C	1.800367	-3.302308	-1.179323
C	2.167605	-2.006681	-0.570499
C	-0.041582	0.368221	2.872285
C	3.425103	-1.547116	-0.173436
C	-1.134170	0.107317	3.695955
C	1.540619	2.341202	-1.695414
C	-0.781932	-0.413912	-1.507006
H	-0.170976	0.133577	-2.213845
C	0.811645	3.827280	-0.032327
C	-2.162481	-0.431845	-1.643970
H	-2.619859	0.108797	-2.462696
C	-0.116300	1.117667	1.691980
C	6.335505	1.680330	1.264925
H	7.407517	1.644325	1.101008
C	5.513782	0.721112	0.686523
H	5.947102	-0.058711	0.072872
C	1.170223	-5.783386	-2.324628
H	0.925352	-6.743838	-2.768271
C	5.408342	-2.663909	0.876671
H	5.029508	-2.365563	1.849579
C	2.214322	-4.494858	-0.565706
H	2.783507	-4.451750	0.356682
C	-0.951055	-1.849186	0.428321
H	-0.475211	-2.398411	1.233922
C	1.549423	3.366287	-2.641643
N	-4.366153	-1.070891	-0.795965
C	5.197371	-2.692733	-1.530101
H	4.655891	-2.417116	-2.429731
C	-2.332785	-1.859310	0.304807
H	-2.923766	-2.421117	1.016468
C	0.761361	-4.601525	-2.944723
H	0.201096	-4.638629	-3.874030
C	1.073202	-3.367199	-2.378094
H	0.759274	-2.452591	-2.868499
C	6.381985	-3.423456	-1.623581
H	6.757728	-3.715516	-2.599750
C	6.593650	-3.391645	0.781164
H	7.133054	-3.661761	1.684217
C	1.184743	4.650084	-2.258096
C	0.806541	4.882415	-0.937991
C	3.560351	1.806945	1.645194
C	1.897566	-5.726814	-1.134828
H	2.219763	-6.642041	-0.647634
C	7.083475	-3.774173	-0.469329
H	8.006456	-4.341579	-0.543255
C	-2.974508	-1.114848	-0.711987

C	5.773427	2.689278	2.057563
H	6.413184	3.436653	2.518251
B	1.259613	1.405676	0.851280
C	4.398651	2.755969	2.246797
H	3.940176	3.539112	2.840888
C	-5.059999	-0.064740	-1.549067
C	-4.758729	1.296769	-1.401107
C	-6.090067	-0.454160	-2.414260
C	-5.472200	2.248049	-2.129500
H	-3.977104	1.608011	-0.718162
C	-6.809290	0.505290	-3.125423
H	-6.325421	-1.508135	-2.519741
C	-6.499529	1.859400	-2.991273
H	-5.231160	3.299984	-2.008381
H	-7.607480	0.191169	-3.791567
H	-7.056042	2.605738	-3.549882
C	-5.167356	-1.856933	0.106000
C	-5.422455	-3.203972	-0.170105
C	-5.690240	-1.267189	1.262737
C	-6.208699	-3.956211	0.703761
H	-5.001500	-3.650796	-1.065579
C	-6.479222	-2.022924	2.129675
H	-5.457569	-0.229604	1.481302
C	-6.741612	-3.366142	1.851311
H	-6.408040	-5.001086	0.485008
H	-6.881623	-1.563480	3.027413
H	-7.355730	-3.951928	2.528630

References

1. (a) Kumar, S. V.; Yadav, S. K.; Raghava, B.; Saraiah, B.; Ila, H.; Rangappa, K. S.; Hazra, A. Cyclocondensation of Arylhydrazines with 1,3-Bis(het)arylmonothio-1,3-diketones and 1,3-Bis(het)aryl-3-(methylthio)-2-propenones: Synthesis of 1-Aryl-3,5-bis(het)arylpyrazoles with Complementary Regioselectivity. *J. Org. Chem.* **2013**, *78*, 4960-4973; (b) Yugandar, S.; Konda, S.; Ila, H. Synthesis of Substituted Benzo[b]thiophenes via Sequential One-Pot, Copper-Catalyzed Intermolecular C-S Bond Formation and Palladium-Catalyzed Intramolecular Arene-Alkene Coupling of Bis(het)aryl/alkyl-1,3-monothiodiketones and o-Bromoiodoarenes. *Org. Lett.* **2017**, *19*, 1512-1515.
2. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.