Supporting Information

Synthesis of 1,3-dibromo-2-aryl-1*H*-indenes *via* NBS mediated unusual bromination of 2-alkynylbenzaldoximes

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1. General methods:

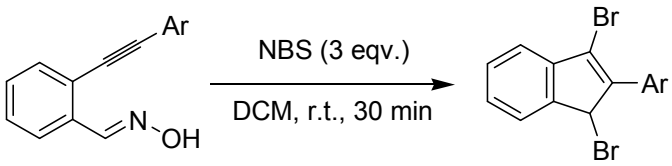
High quality reagents were purchased from Sigma Aldrich. Analytical grade commercial reagents and solvents were purified by standard procedures prior to use. Chromatographic purification was done with 60-120 mesh silica gel (Merck). For reaction monitoring, pre-coated silica gel 60 F254 sheets (Merck) were used. ^{1}H NMR (200 MHz) spectra were recorded on a BRUCKER-AC 200 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, bs = broad singlet), coupling constant (Hz). ^{13}C NMR (50 MHz) spectra were recorded on a BRUKER-AC 200 MHz. Spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 77.23 ppm). HRMS (ESI) spectra were taken using Waters Xevo G2 QTof mass spectrometer.

2. General procedures

2.1 *General procedure for the synthesis of 2-alkynylbenzaldoximes:* ***GP-1***

All the 2-alkynylbenzaldoximes were synthesized according to the Wu groups reported procedures.[1]

2.2 *General procedure for the synthesis of 1,3-dibromo-2-aryl-1H-indene:****GP-2***

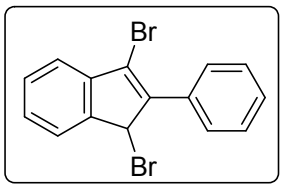


The 2-alkynylaldoxime (0.5 mmol) was taken in a round bottomed flask and 3 mL of dichloromethane (DCM) was added to it. Then 1.5 mmol of N-bromosuccinamide (NBS) was added in portion wise and the reaction mixture was stirred at room temperature for 30 min. After completion of the reaction, the reaction mixture was diluted with saturated aqueous solution of $Na_2S_2O_3$ and extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, evaporated under reduced pressure. Then

the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.

3. Spectroscopic data

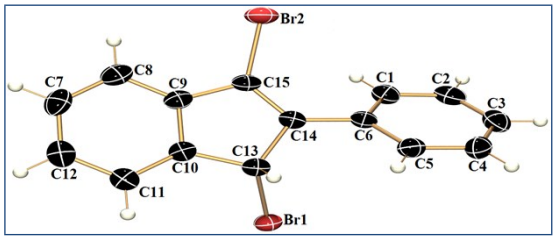
1,3-Dibromo-2-phenyl-1*H*-indene (2a):



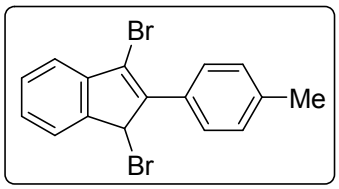
According to the *GP-2* the substrate 2-(2-phenylethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-phenyl-1*H*-indene (2a) as a yellow solid; Yield = 37 %; R_f = 0.50 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.74–7.68 (m, 2H), 7.61-7.35 (m, 7H), 5.92 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 143.29, 142.17, 141.72, 132.87, 129.49, 128.95 (2C), 128.80, 128.60 (2C), 128.01, 124.90, 121.54, 120.38, 48.25. ; **HRMS** (ESI) for $C_{15}H_{11}Br_2$: Calculated 348.9222 (M^++H); Found: 348.9225. The structure of the compound was also confirmed from its crystal structure which obtained by X-ray diffraction. Cell parameters: a = 16.202(2), b = 7.6187(11), c = 20.676(3), α = 90, β = 90, γ = 90; Space group: Pbca; CCDC No. 1407752.

ORTEP Structure of compound 2a.

(CCDC 1407752)

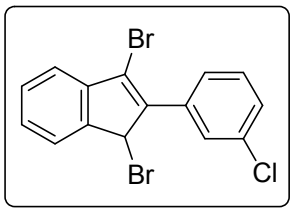


1,3-Dibromo-2-*p*-tolyl-1*H*-indene (2b):



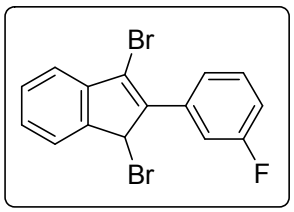
According to the *GP-2* the substrate 2-(2-*p*-tolylethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-*p*-tolyl-1*H*-indene (2b) as a yellow solid; Yield = 35 %; R_f = 0.5 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.64-7.56 (m, 2H), 7.45–7.28 (m, 6H), 5.90 (s, 1H), 2.42 (s, 3H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 143.29, 142.09, 141.85, 138.89, 129.96, 129.46, 129.38 (2c), 128.83 (2c), 127.84, 124.87, 121.40, 119.65, 48.34, 21.64. **HRMS** (ESI) for $C_{16}H_{13}Br_2$: Calculated 362.9379 (M^++H); Found: 362.9384.

1,3-Dibromo-2-(3-chlorophenyl)-1*H*-indene (2c):



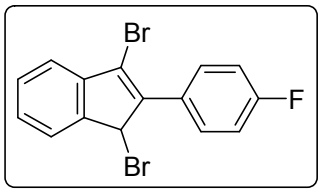
According to the *GP-2* the substrate 2-(2-(3-chlorophenyl)ethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-(3-chlorophenyl)-1*H*-indene (2c) as a yellow solid; Yield = 42 %; R_f = 0.41 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.71 (s, 1H), 7.61-7.55 (m, 2H), 7.48-7.35 (m, 5H), 5.87 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 142.10, 141.84, 141.38, 134.65, 134.58, 129.87, 129.60, 128.89, 128.81, 128.39, 127.12, 124.96, 121.79, 121.65, 47.91. **HRMS** (ESI) for $C_{15}H_{10}Br_2Cl$: Calculated 382.8832 (M^++H); Found: 382.8835.

1,3-Dibromo-2-(3-fluorophenyl)-1*H*-indene (2d):



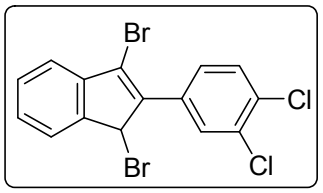
According to the *GP-2* the substrate 2-(2-(3-fluorophenyl)ethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-(3-fluorophenyl)-1*H*-indene (2d) as a yellow solid; Yield = 46 %; R_f = 0.40 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.62–7.34 (m, 7H), 7.17–7.07 (m, 1H), 5.87 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 162.81 (CF, d, *J* = 244.5 Hz), 142.11, 141.94 (d, *J* = 2.5 Hz), 141.44, 130.22, 130.06, 129.59, 128.37, 124.95, 124.71 (d, *J* = 3.0 Hz), 121.78, 121.53, 115.91 (d, *J* = 24 Hz), 115.71 (d, *J* = 22.0 Hz), 47.97. **HRMS** (ESI) for $C_{15}H_{10}Br_2F$: Calculated 366.9128 (M^++H); Found: 366.9130.

1,3-Dibromo-2-(4-fluorophenyl)-1*H*-indene (2e):



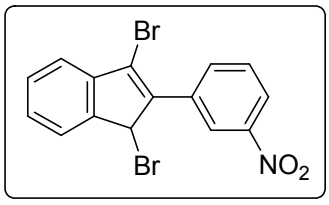
According to the *GP-2* the substrate 2-(2-(4-fluorophenyl)ethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-(4-fluorophenyl)-1*H*-indene (2e) as a yellow solid; Yield = 45 %; R_f = 0.40 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.74–7.67 (m, 2H), 7.59 (dd, *J* = 6.8, 1.4 Hz, 1H), 7.47–7.36 (m, 3H), 7.23–7.15 (m, 2H), 5.87 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 162.88 (CF, d, *J* = 248 Hz), 142.27, 142.03, 141.57, 130.82 (2C, d, *J* = 8.5 Hz), 129.56, 128.97 (d, *J* = 3.0 Hz), 128.10, 124.92, 121.56, 120.43, 115.74 (2C, d, *J* = 21.5 Hz), 48.27. **HRMS** (ESI) for $C_{15}H_{10}Br_2F$: Calculated 366.9128 (M^++H); Found: 366.9131.

1,3-Dibromo-2-(3,4-dichlorophenyl)-1*H*-indene (2f):



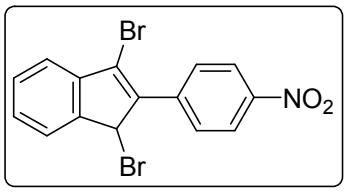
According to the *GP-2* the substrate 2-(2-(3,4-dichlorophenyl)ethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-(3,4-dichlorophenyl)-1*H*-indene (2f) as a yellow solid; Yield = 48 %; R_f = 0.33 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.83 (s, 1H), 7.61–7.36 (m, 6H), 5.83 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 142.05, 141.26, 140.84, 132.95, 132.88, 130.63 (3C), 129.68, 128.58, 128.17, 124.99, 122.11, 121.88, 47.70. **HRMS** (ESI) for $C_{15}H_9Br_2Cl_2$: Calculated 416.8443 (M^++H); Found: 416.8449.

1,3-Dibromo-2-(3-nitrophenyl)-1*H*-indene (2g):



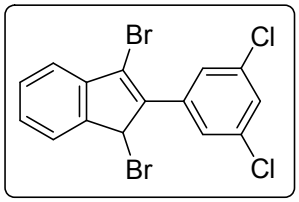
According to the *GP-2* the substrate 2-(2-(3-nitrophenyl)ethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-(3-nitrophenyl)-1*H*-indene (2g) as a yellow solid; Yield = 47 %; R_f = 0.20 (hexane/EtOAc 10:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 8.60 (s, 1H), 8.25 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.70–7.40 (m, 5H), 5.94 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 148.55, 142.09, 141.10, 140.78, 134.74, 134.62, 129.75, 129.61, 128.84, 125.07, 123.76, 123.31, 123.04, 122.06, 47.61. **HRMS** (ESI) for $C_{15}H_{10}Br_2NO_2$: Calculated 393.9073 (M^++H); Found: 393.9072.

1,3-Dibromo-2-(4-nitrophenyl)-1*H*-indene (2h):



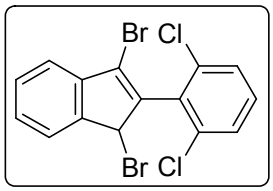
According to the *GP-2* the substrate 2-(2-(4-nitrophenyl)ethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-(4-nitrophenyl)-1*H*-indene (2h) as a yellow solid; Yield = 52 %; R_f = 0.20 (hexane/EtOAc 10:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 8.34 (d, *J* = 8.9 Hz, 2H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.64–7.42 (m, 4H), 5.93 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 147.52, 142.25, 141.15, 141.04, 139.36, 129.83, 129.73 (2C), 129.05, 125.10, 123.89 (3C), 122.23, 47.46. **HRMS** (ESI) for $C_{15}H_{10}Br_2NO_2$: Calculated 393.9073 (M^++H); Found: 393.9074.

1,3-Dibromo-2-(3,5-dichlorophenyl)-1*H*-indene (2i):



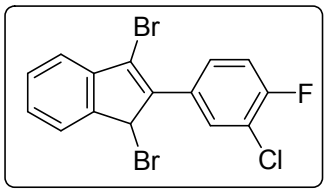
According to the *GP-2* the substrate 2-(2-(3,5-dichlorophenyl)ethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-(3,5-dichlorophenyl)-1*H*-indene (2j) as a yellow solid; Yield = 45 %; R_f = 0.32 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.68–7.35 (m, 7H), 5.82 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 142.07, 141.09, 140.58, 135.81, 135.27 (2C), 129.69, 128.75, 128.64, 127.25 (2C), 124.99, 122.85, 122.01, 47.58. **HRMS** (ESI) for $C_{15}H_9Br_2Cl_2$: Calculated 416.8443 (M^++H); Found: 416.8449.

1,3-Dibromo-2-(2,6-dichlorophenyl)-1*H*-indene (2j):



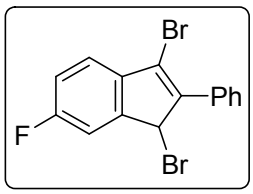
According to the *GP-2* the substrate 2-(2-(2,6-dichlorophenyl)ethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-(2,6-dichlorophenyl)-1*H*-indene (2k) as a yellow solid; Yield = 34 %; R_f = 0.30 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.62–7.27 (m, 7H), 6.09 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 143.18, 140.48, 140.38, 136.99, 135.10, 131.73, 130.63, 129.36, 128.77, 128.44, 128.11, 126.37, 125.08, 121.77, 48.28. **HRMS** (ESI) for $C_{15}H_9Br_2Cl_2$: Calculated 416.8443 (M^++H); Found: 416.8447.

1,3-Dibromo-2-(3-chloro-4-fluorophenyl)-1*H*-indene (2k):



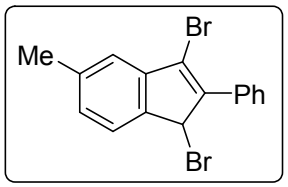
According to the *GP-2* the substrate 2-(2-(3-chloro-4-fluorophenyl)ethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-2-(3-chloro-4-fluorophenyl)-1*H*-indene (2l) as a yellow solid; Yield = 50 %; R_f = 0.30 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.82 (dd, *J* = 7.0, 2.3 Hz, 1H), 7.65–7.29 (m, 6H), 5.87 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 158.13 (CF, d, *J* = 249.5 Hz), 142.00 (d, *J* = 2.0 Hz), 141.27, 140.97, 131.15, 130.16 (d, *J* = 3.5 Hz), 129.64, 128.91 (d, *J* = 7.5 Hz), 128.44, 124.95, 121.77, 121.59, 121.28, 116.85 (d, *J* = 21.0 Hz), 47.94. **HRMS** (ESI) for $C_{15}H_9Br_2ClF$: Calculated 400.8738 (M^++H); Found: 400.8742.

1,3-Dibromo-6-fluoro-2-phenyl-1*H*-indene (2l):



According to the *GP-2* the substrate 5-fluoro-2-(2-phenylethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-6-fluoro-2-phenyl-1*H*-indene (2m) as a yellow solid; Yield = 42 %; R_f = 0.40 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.73 (d, *J* = 8.4 Hz, 2H), 7.57–7.30 (m, 5H), 7.18 (td, *J* = 8.8, 2.4 Hz, 1H), 5.90 (s, 1H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 163.15 (CF, d, *J* = 246 Hz), 144.18 (d, *J* = 9.0 Hz), 143.19 (d, *J* = 4.2 Hz), 137.69 (d, *J* = 2.6 Hz), 132.68 , 128.87, 128.83 (2C), 128.66 (2C), 122.63 (d, *J* = 8.7 Hz), 119.32 (d, *J* = 1.7 Hz), 116.34 (d, *J* = 23 Hz) , 112.92 (d, *J* =24.5 Hz), 47.35. **HRMS** (ESI) for $C_{15}H_{10}Br_2F$: Calculated 366.9128 (M^++H); Found: 366.9131.

1,3-Dibromo-5-methyl-2-phenyl-1*H*-indene (2m):

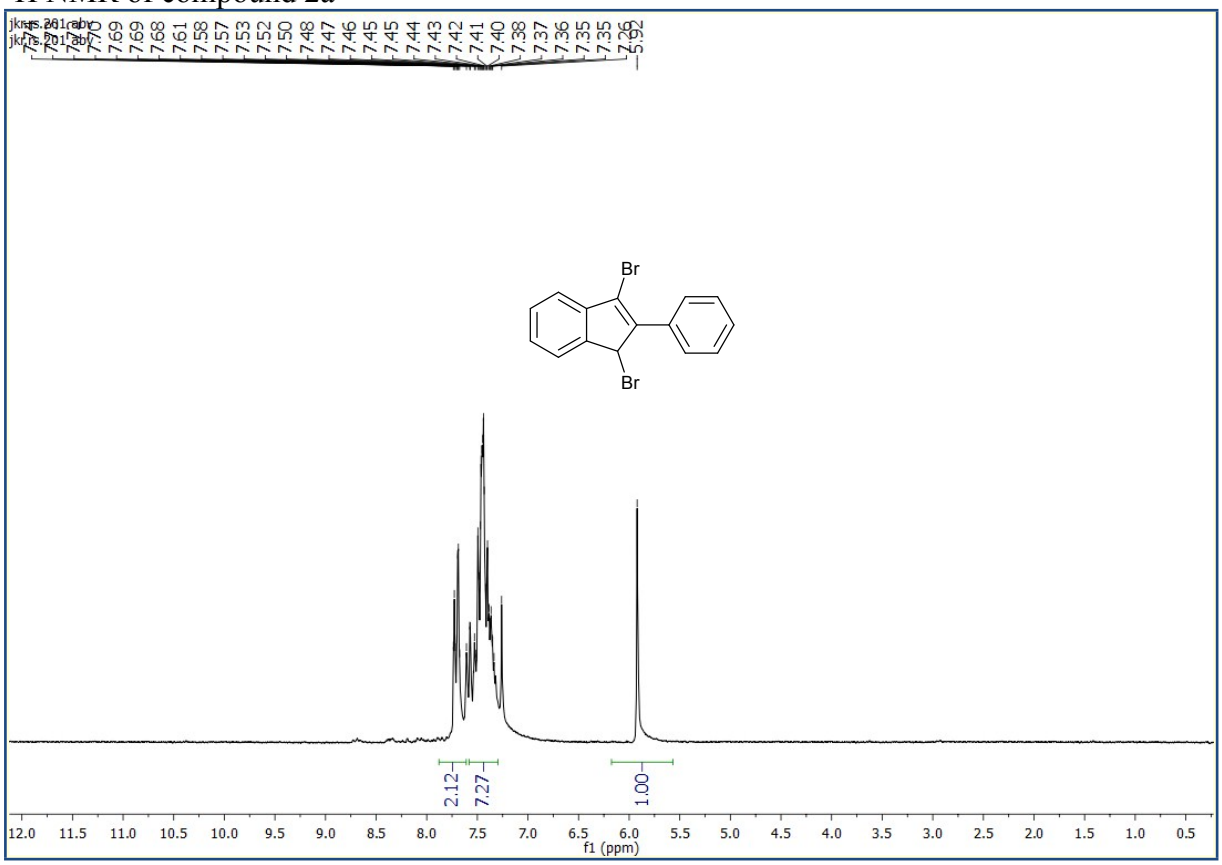


According to the *GP-2* the substrate 4-methyl-2-(2-phenylethynyl)benzaldehyde oxime afforded the product 1,3-dibromo-5-methyl-2-phenyl-1*H*-indene (2n) as a yellow solid; Yield = 35 %; R_f = 0.50 (hexane/EtOAc 50:1); **^{1}H NMR** (200 MHz, Chloroform-d) δ: 7.74–7.66 (m, 3H), 7.53–7.40 (m, 4H), 7.28 (d, *J* = 7.8 Hz, 1H), 5.85 (s, 1H), 2.50 (s, 3H); **^{13}C NMR** (50 MHz, Chloroform-d) δ: 143.75, 141.12, 139.38, 132.63, 128.97, 128.90 (3C), 128.83, 128.66 (2C), 124.33, 123.50, 119.44, 47.27, 23.55. **HRMS** (ESI) for $C_{16}H_{13}Br_2$: Calculated 362.9379 (M^++H); Found: 362.9383.

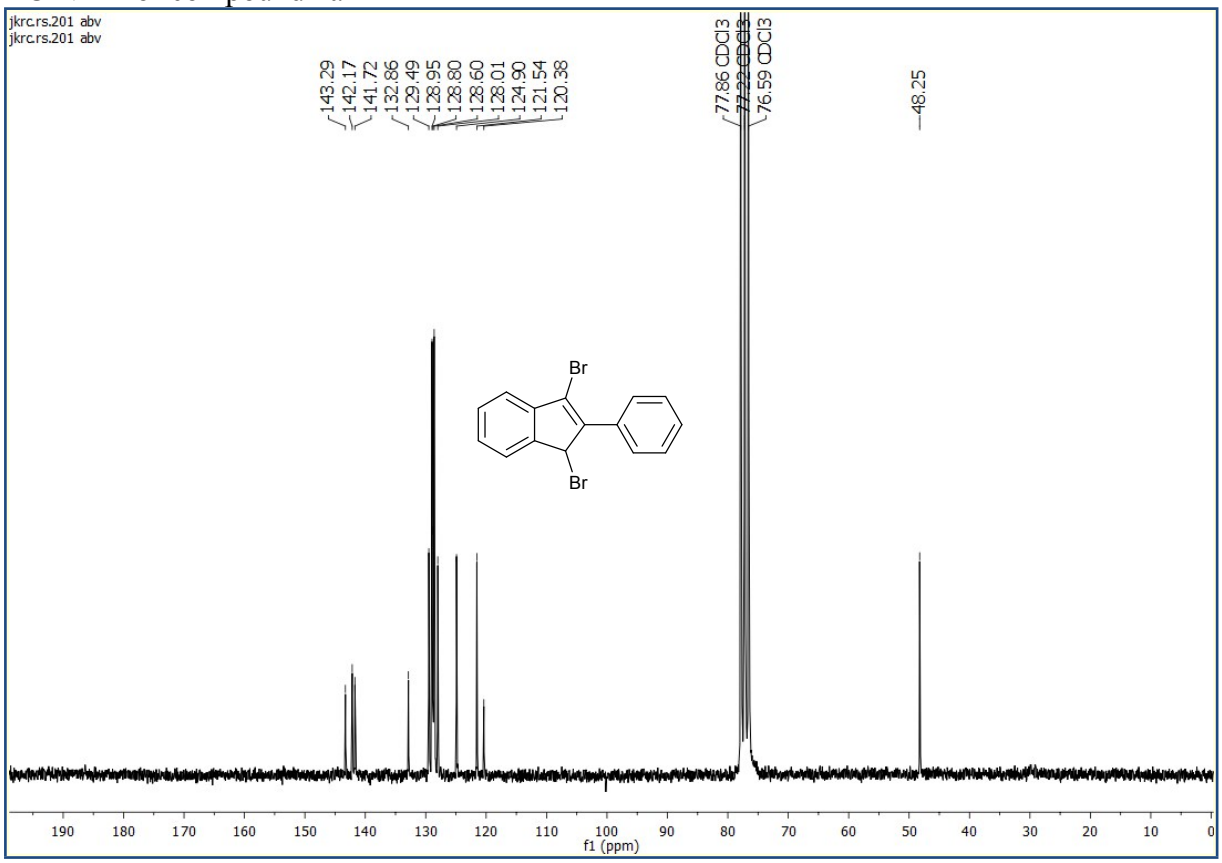
Reference

1. Q. Dinga and J. Wu, *Adv. Synth. Catal*., 2008, **350**, 1850.

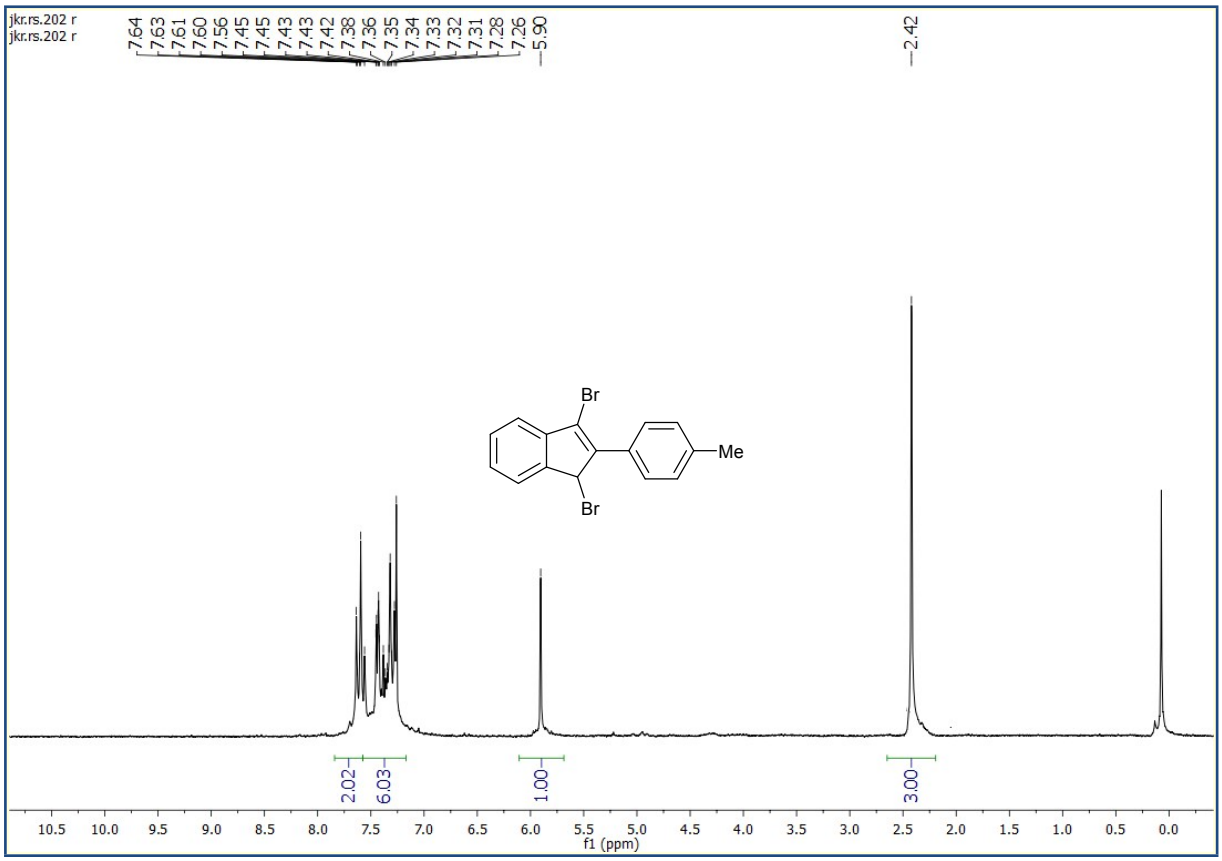
^{1}H NMR of compound 2a



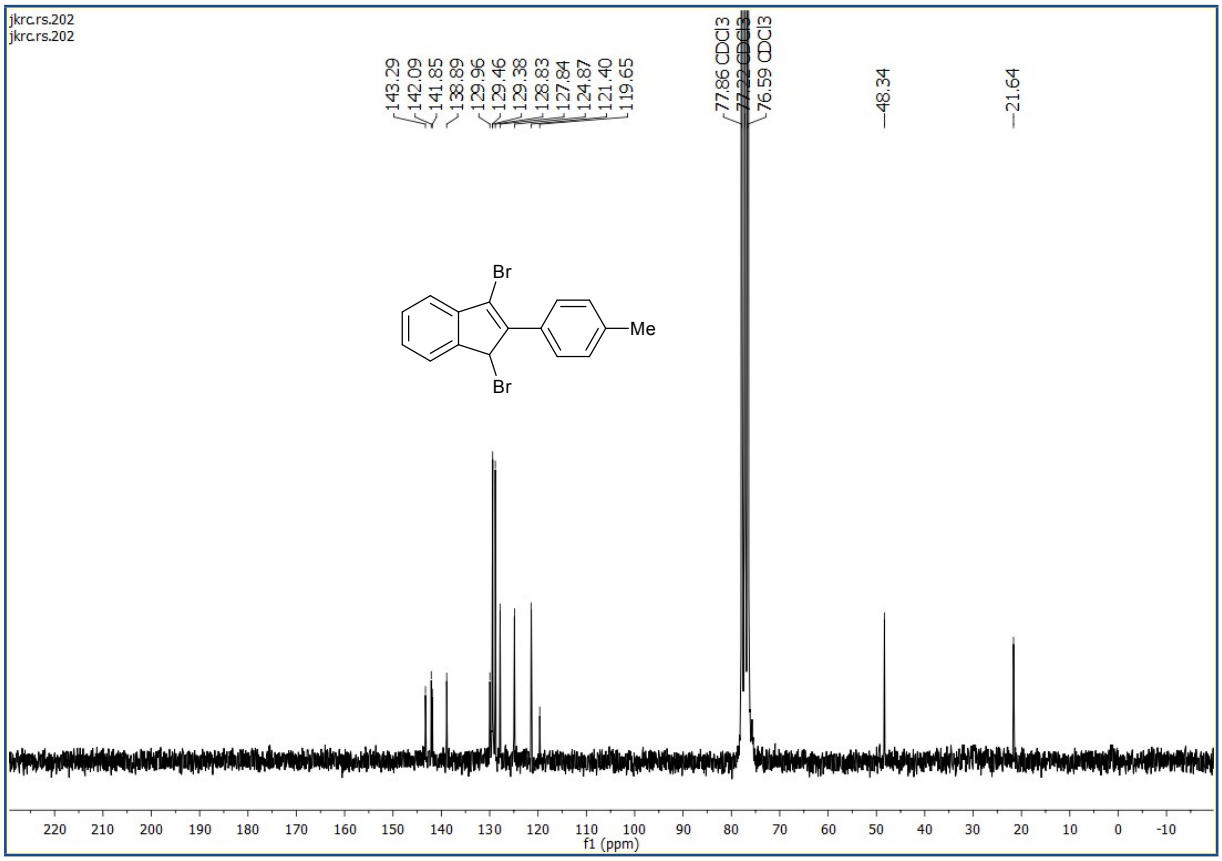
^{13}C NMR of compound 2a



^{1}H NMR of compound 2b



^{13}C NMR of compound 2b



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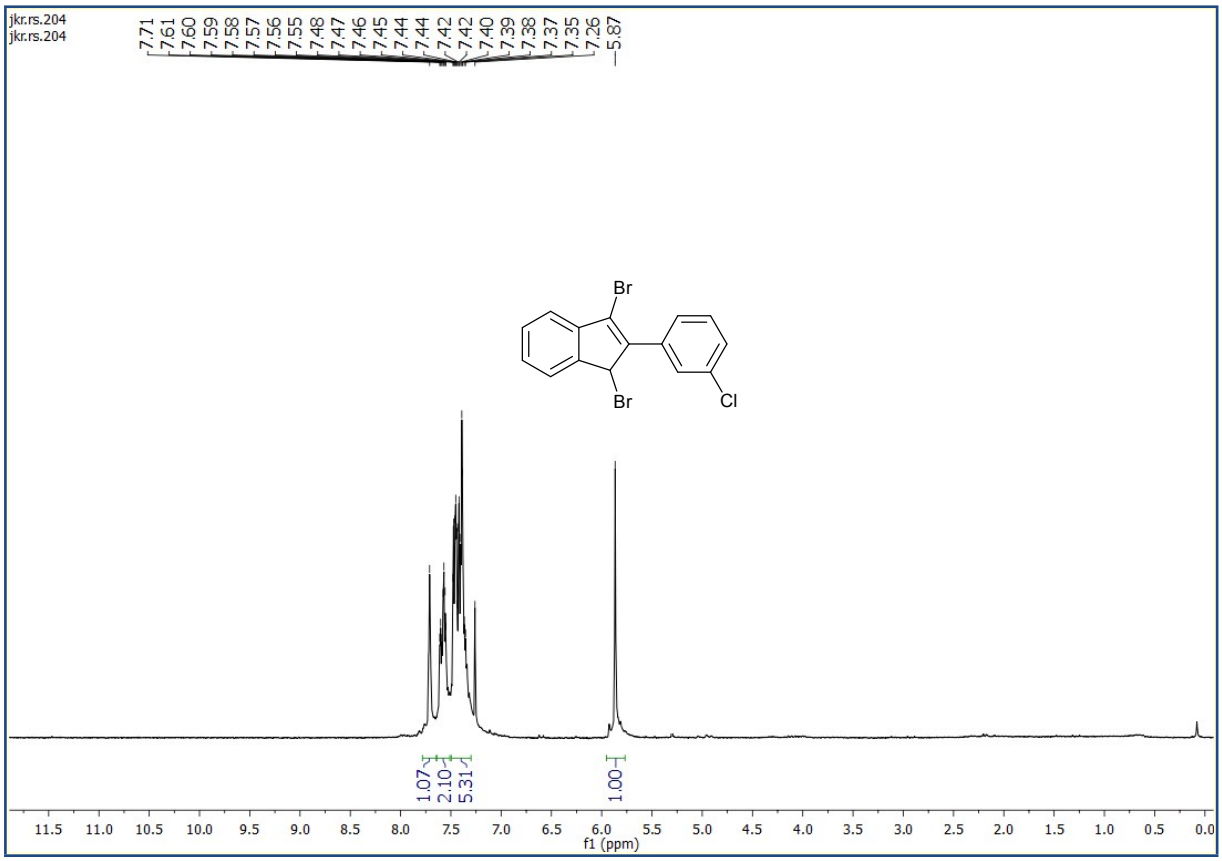

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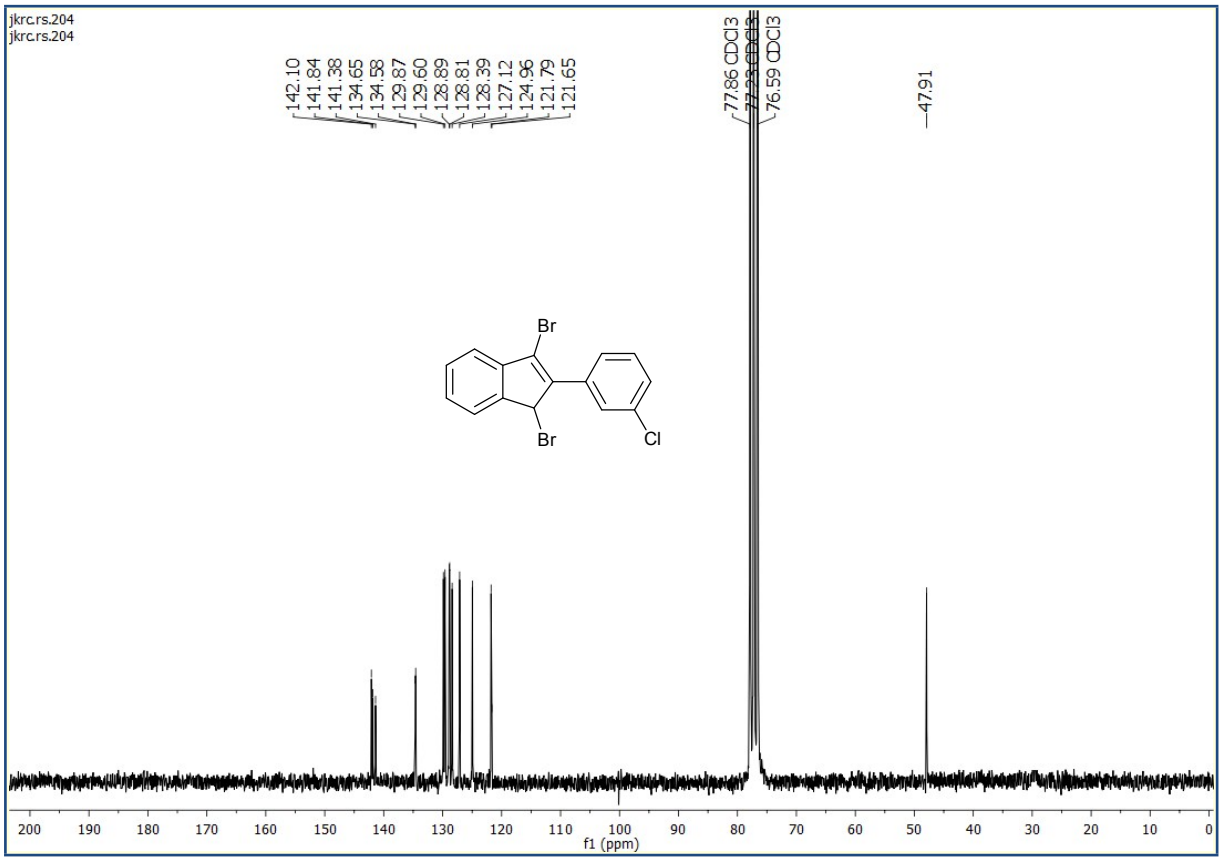
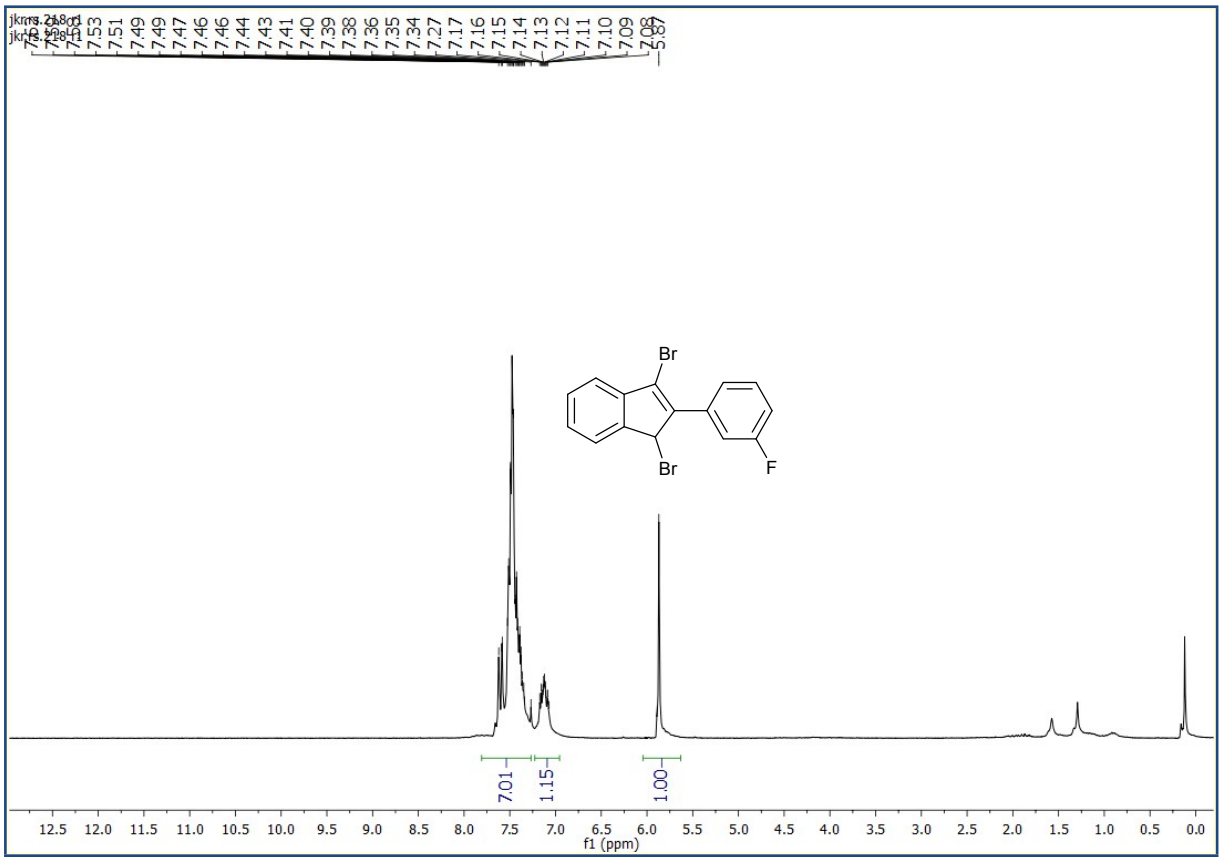
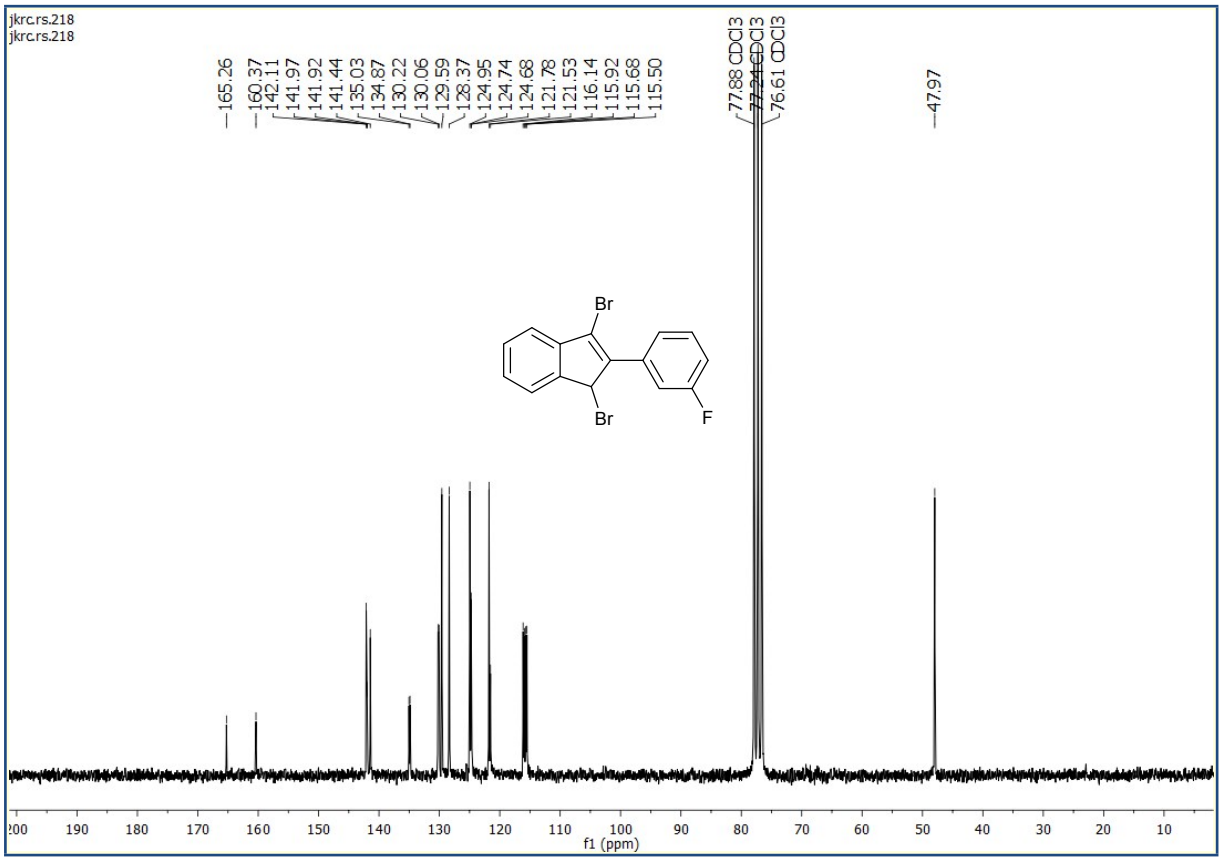


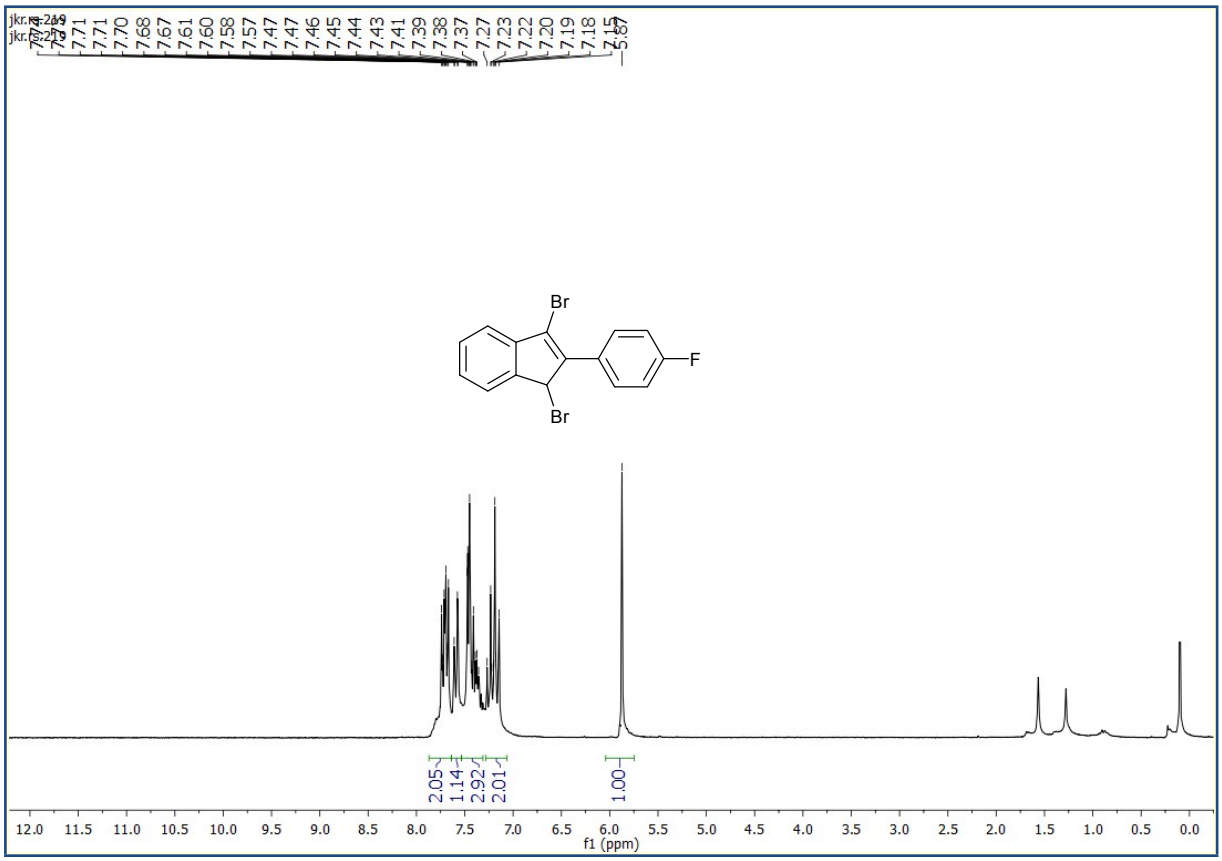
^{1}H NMR of compound 2d



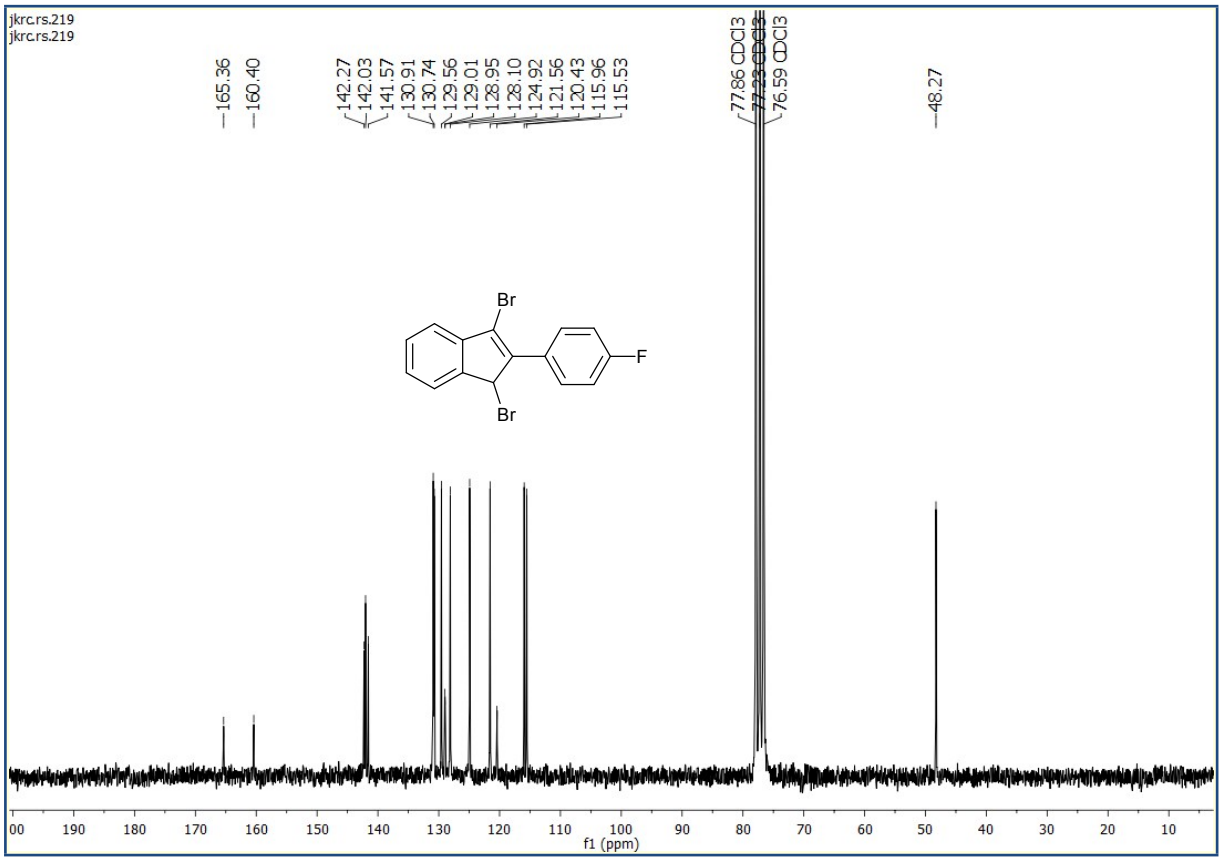
^{13}C NMR of compound 2d



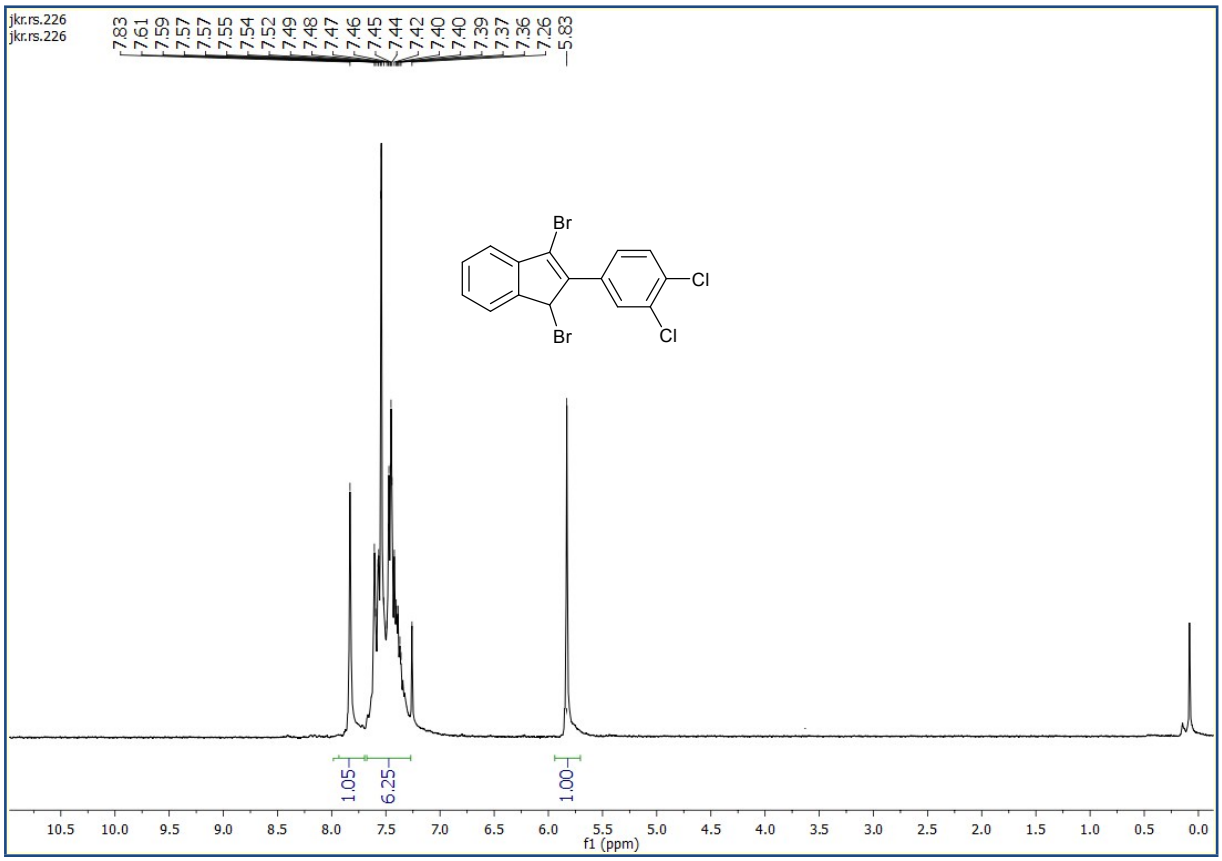
^{1}H NMR of compound 2e



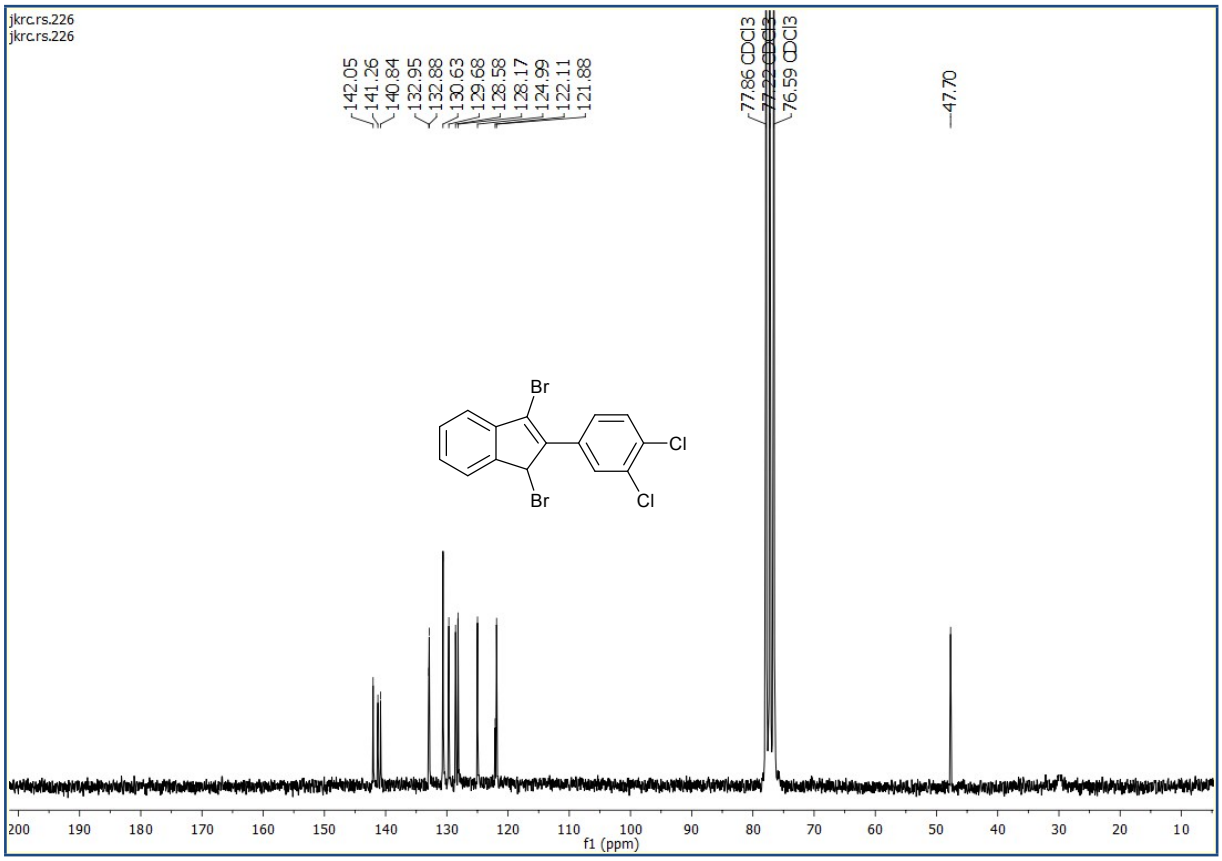
^{13}C NMR of compound 2e



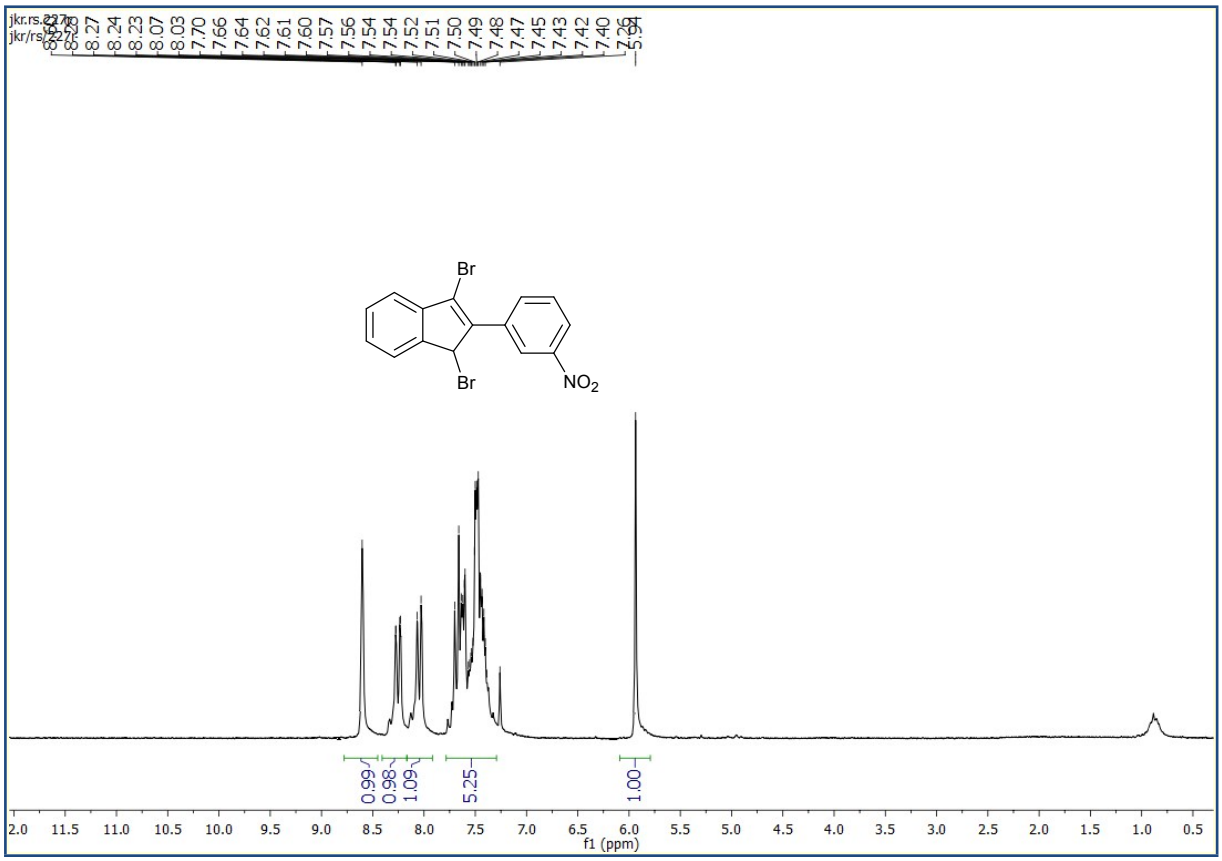
^{1}H NMR of compound 2f



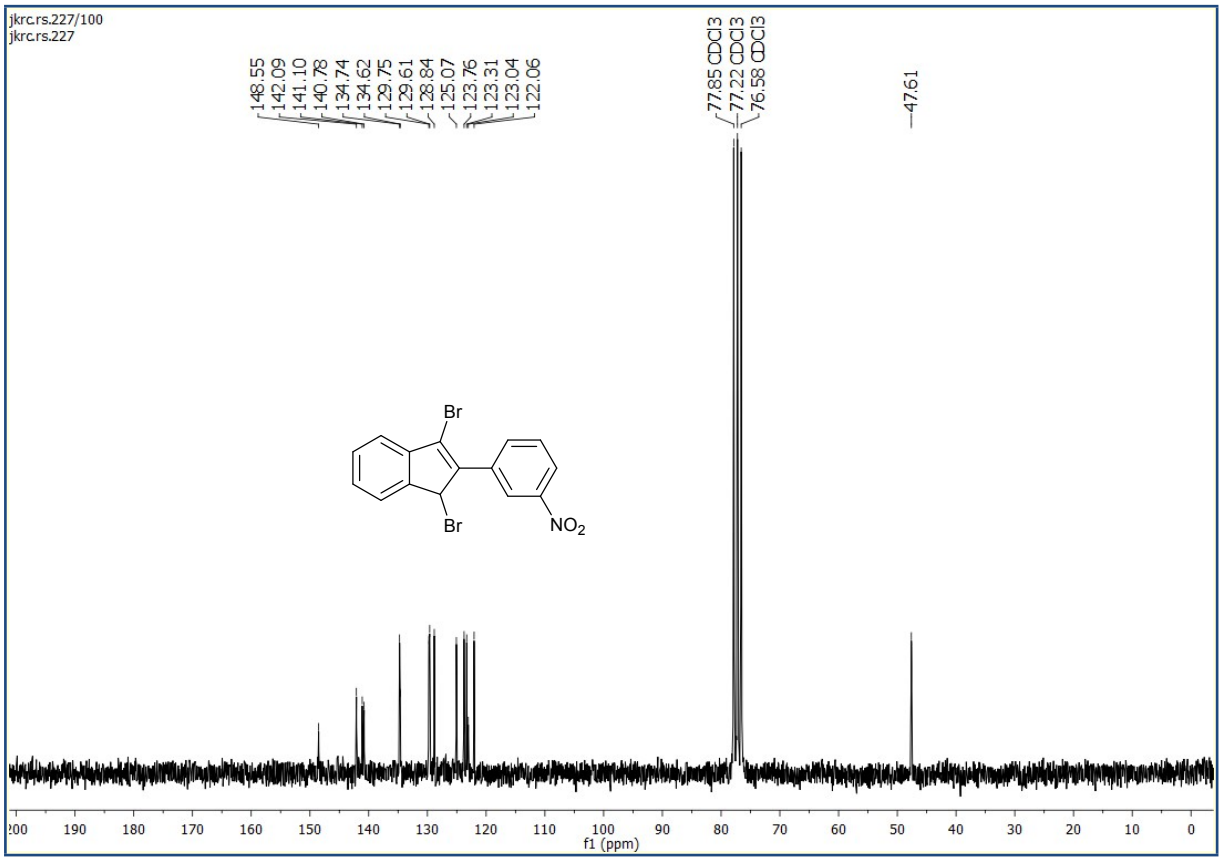
^{13}C NMR of compound 2f



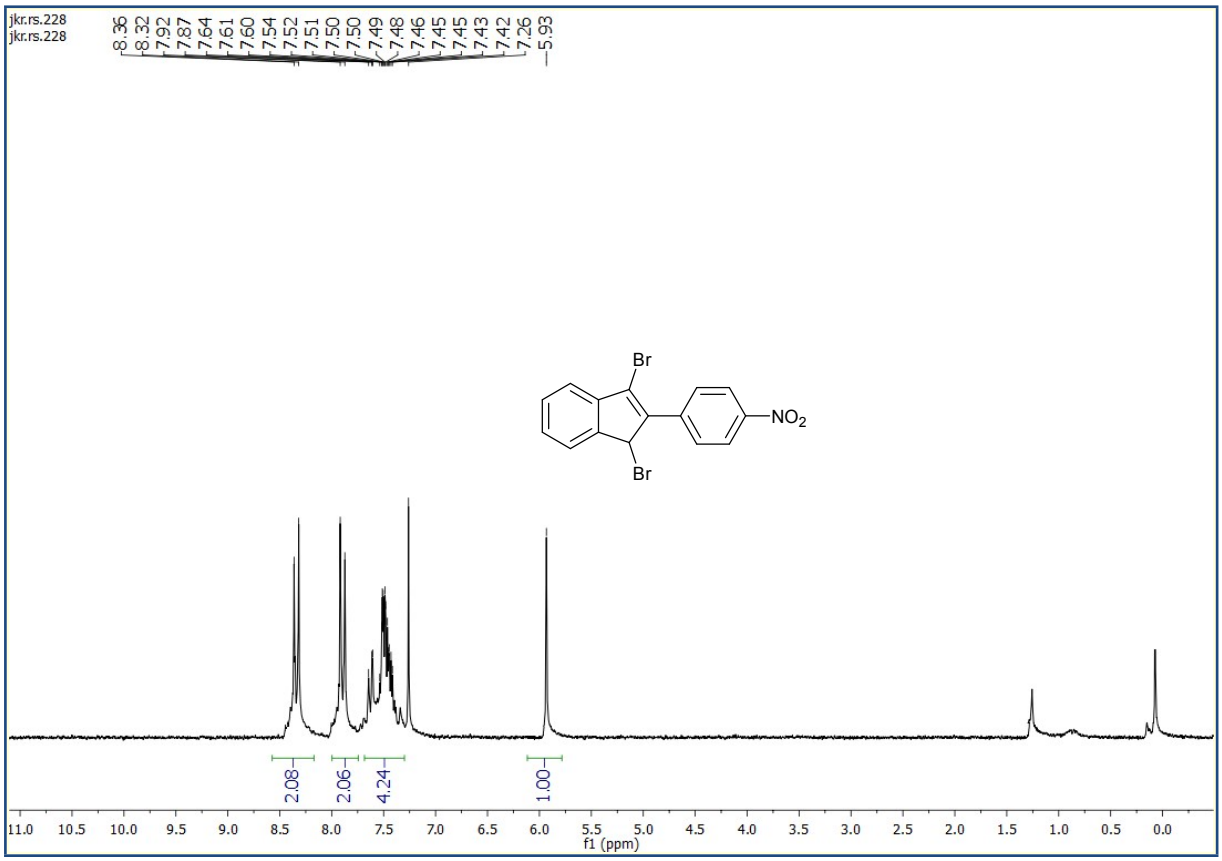
[1]H NMR of compound 2g



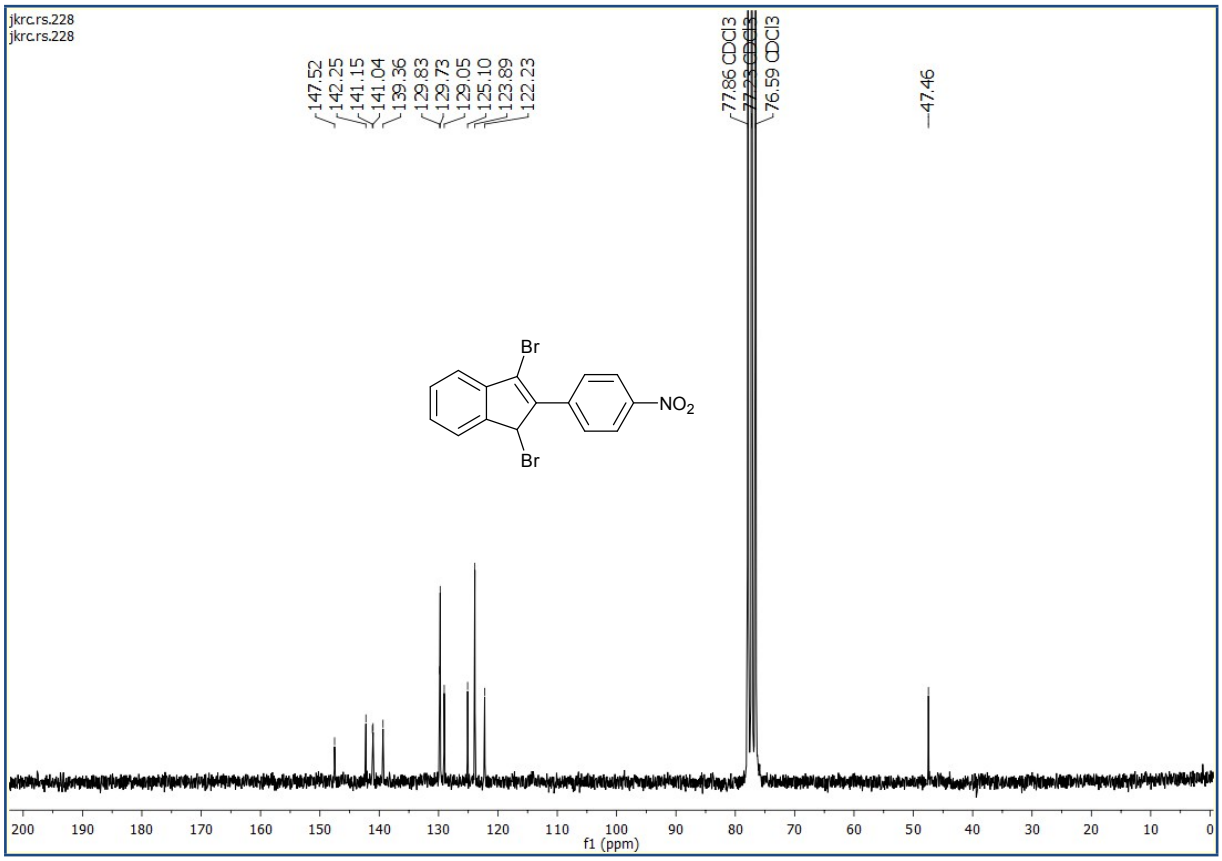
[13]C NMR of compound 2g



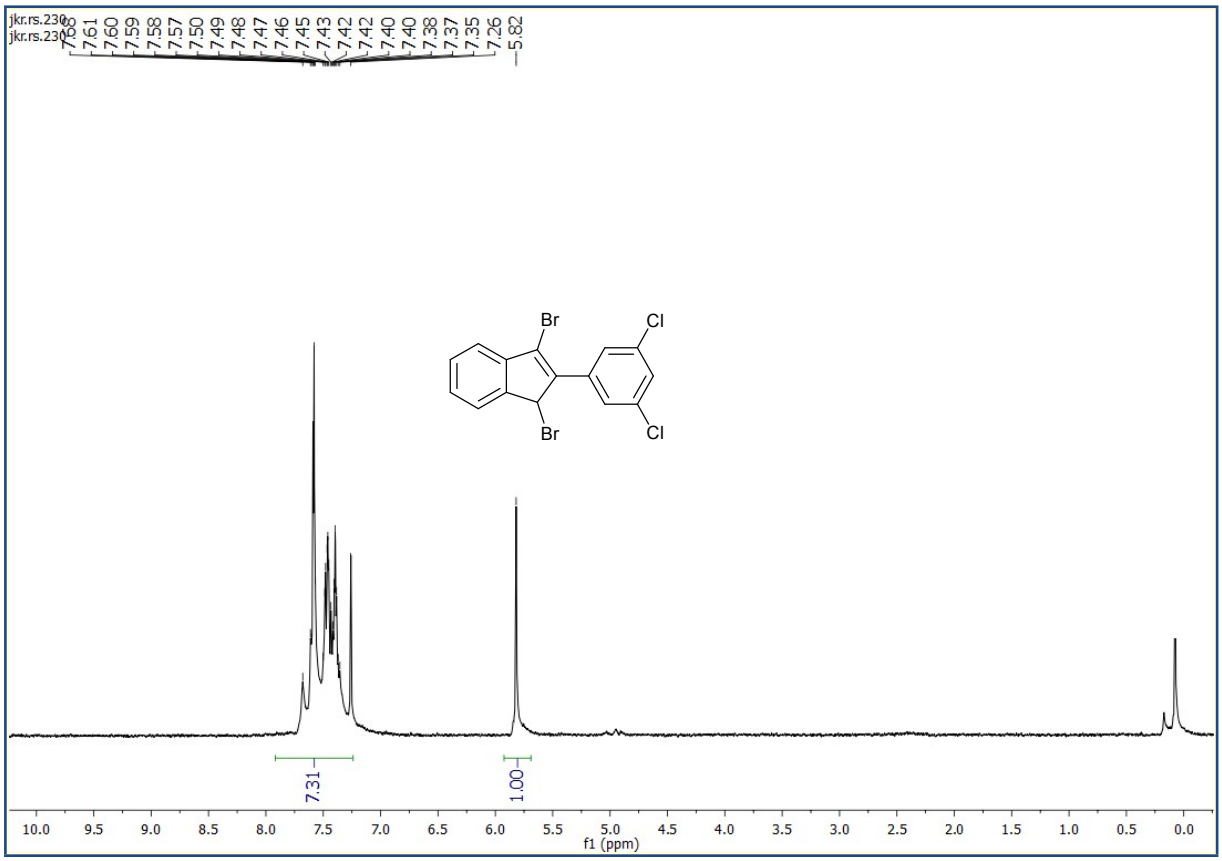
^{1}H NMR of compound 2h



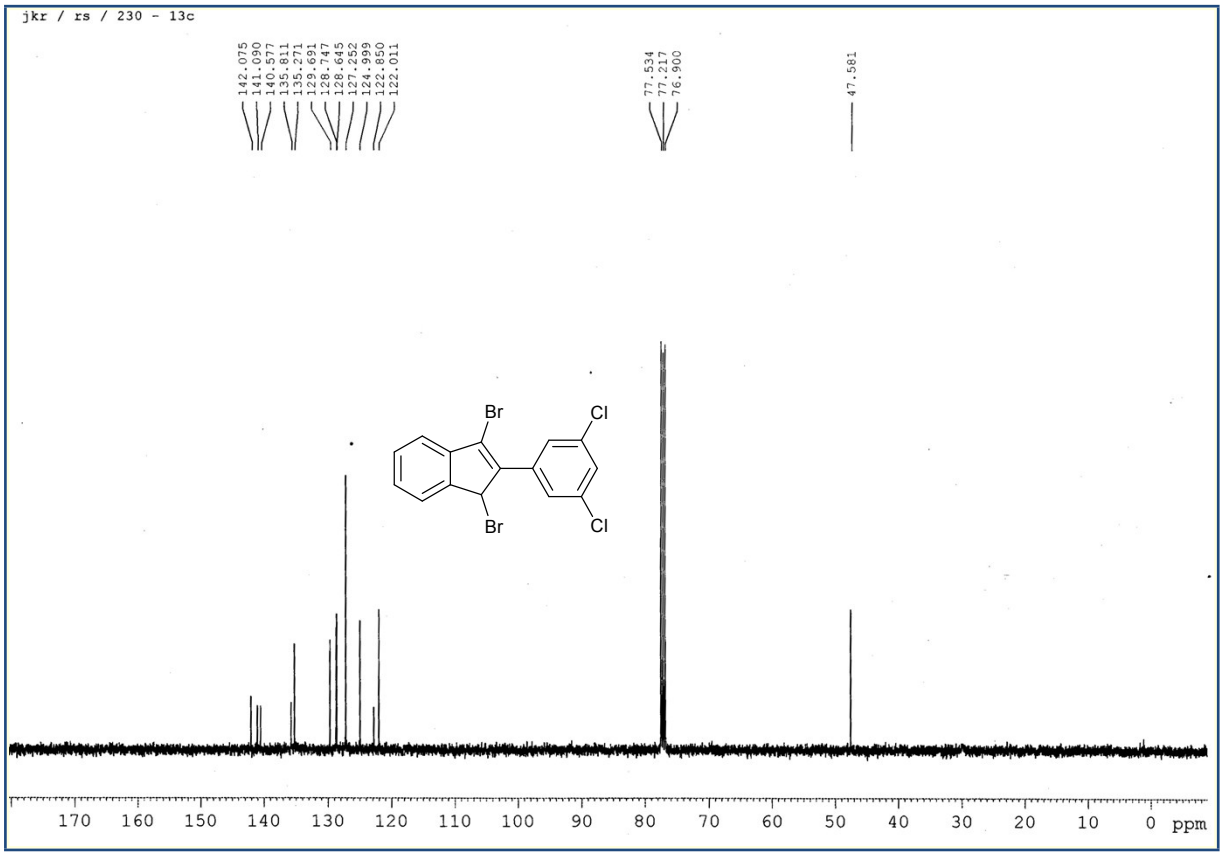
^{13}C NMR of compound 2h



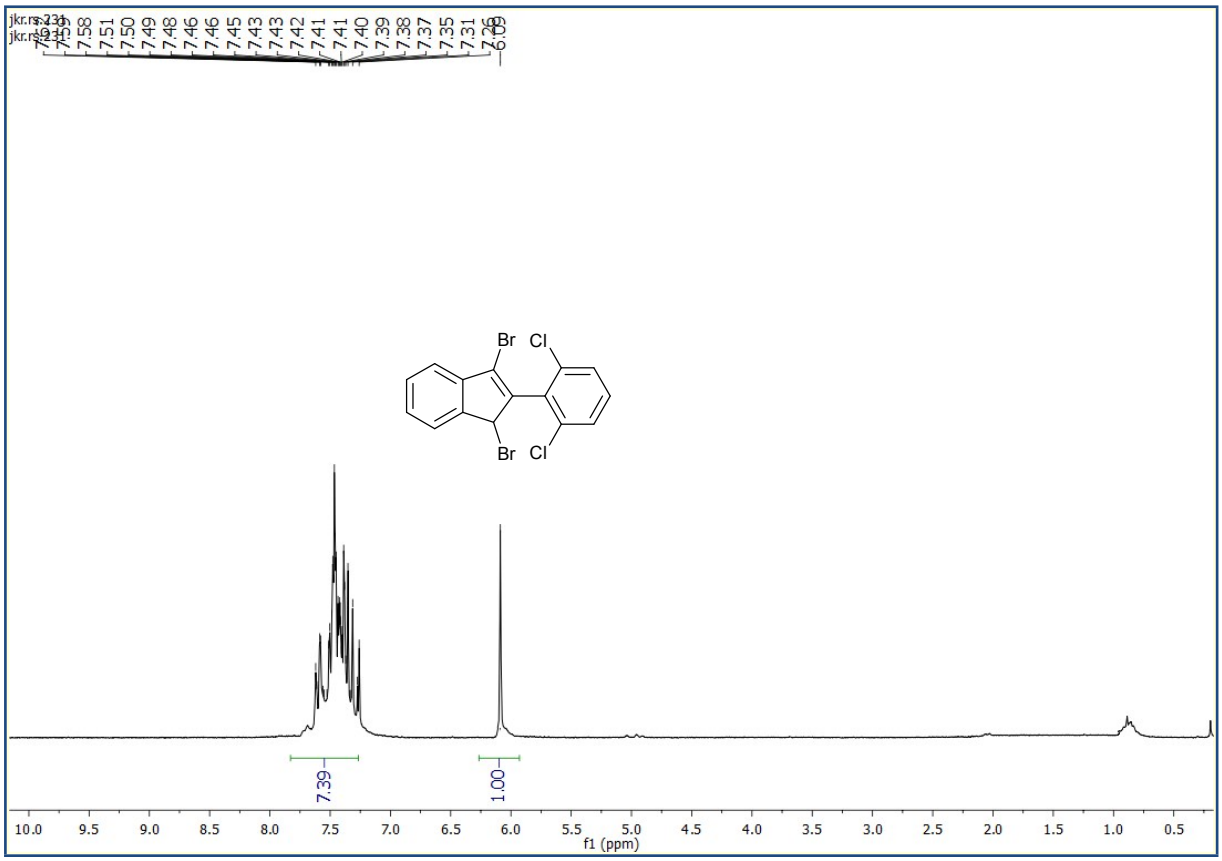
^{1}H NMR of compound 2i



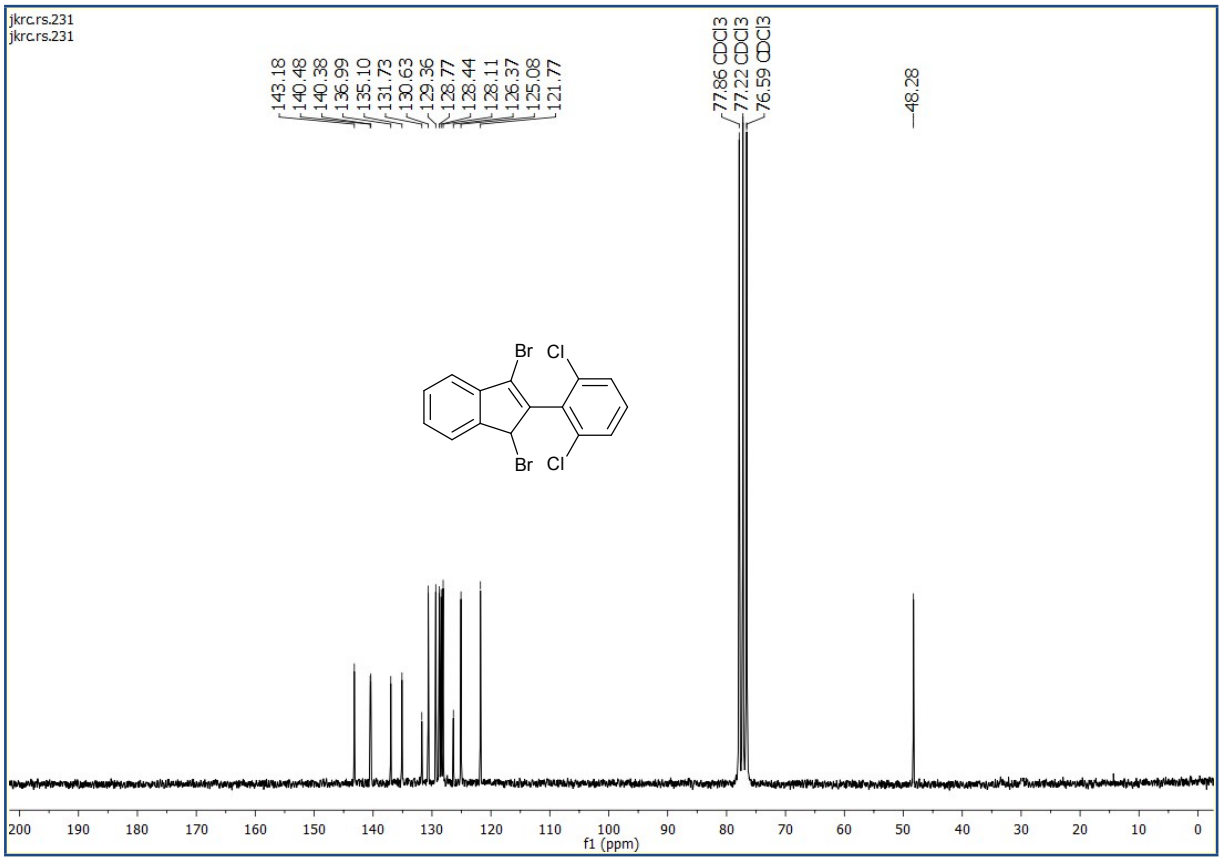
^{13}C NMR of compound 2i



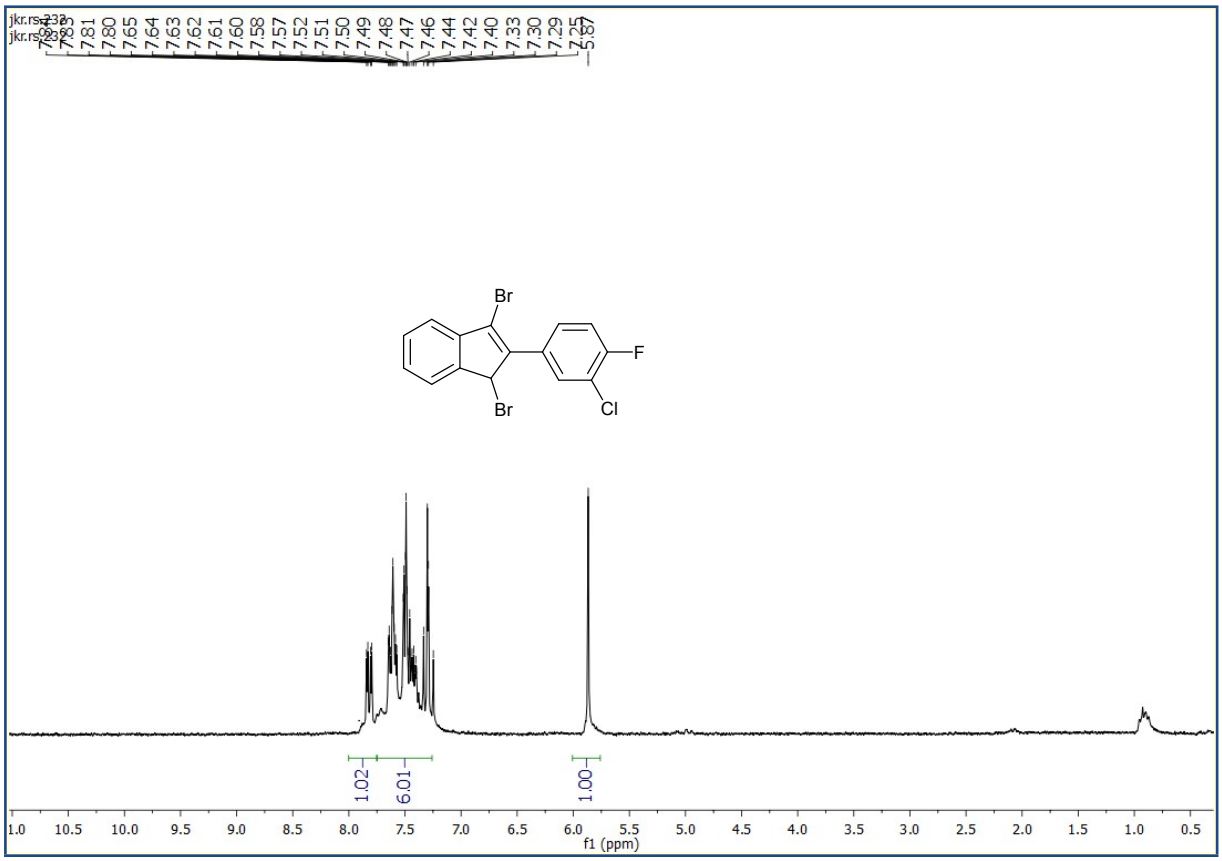
^{1}H NMR of compound 2j



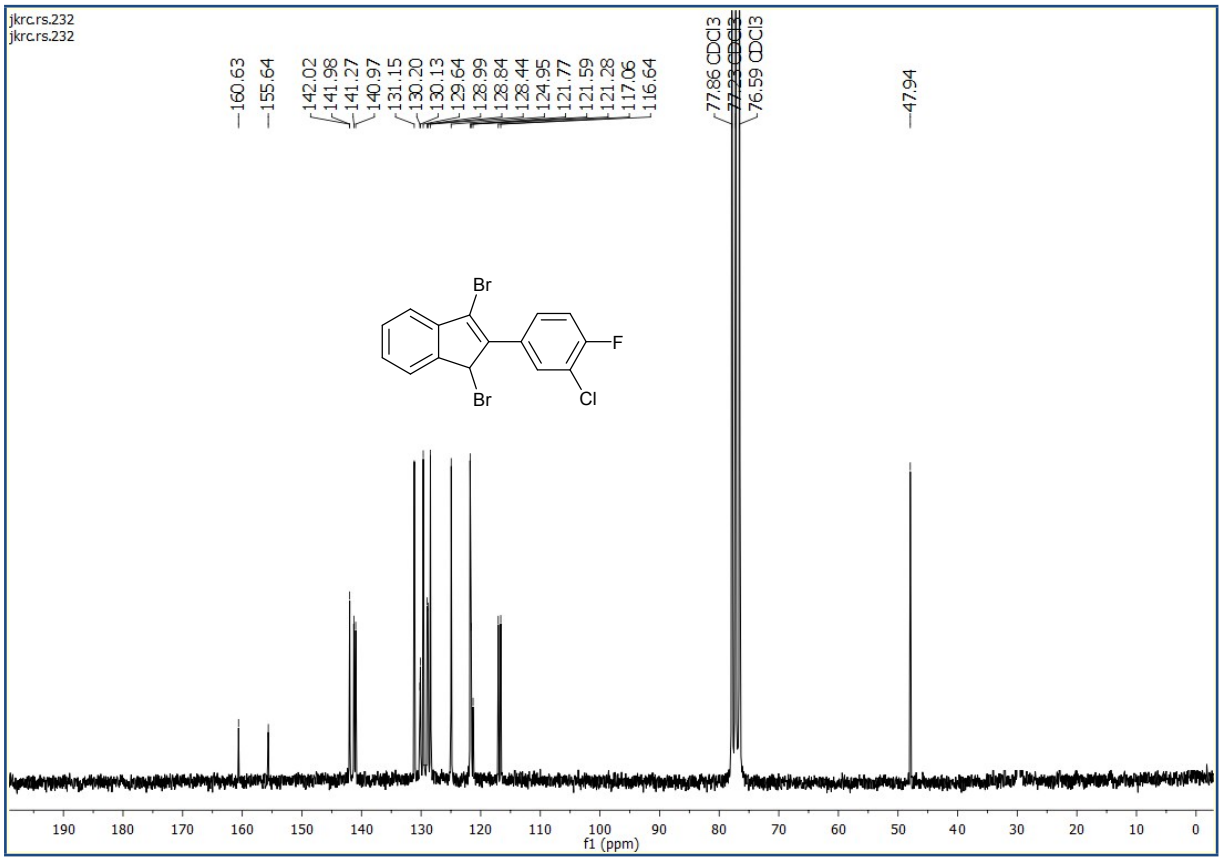
^{13}C NMR of compound 2j



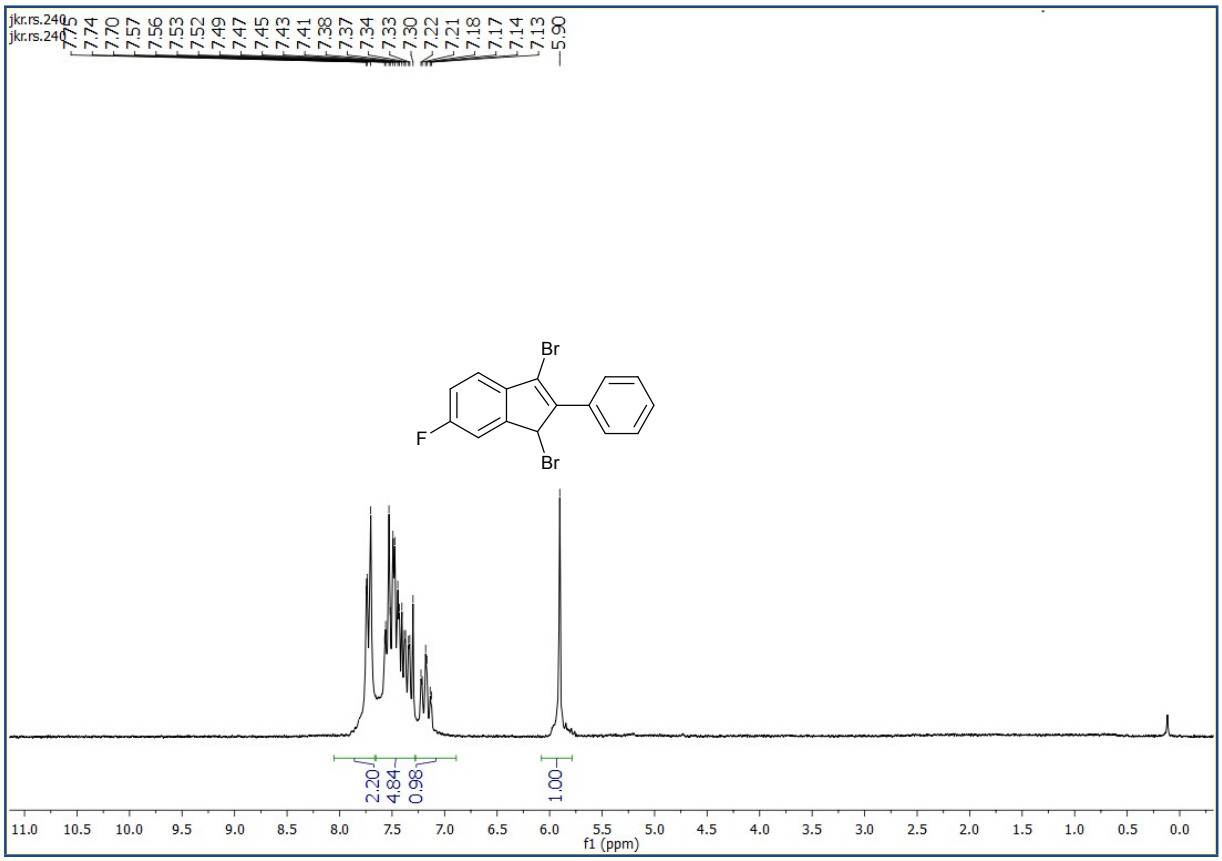
^{1}H NMR of compound 2k



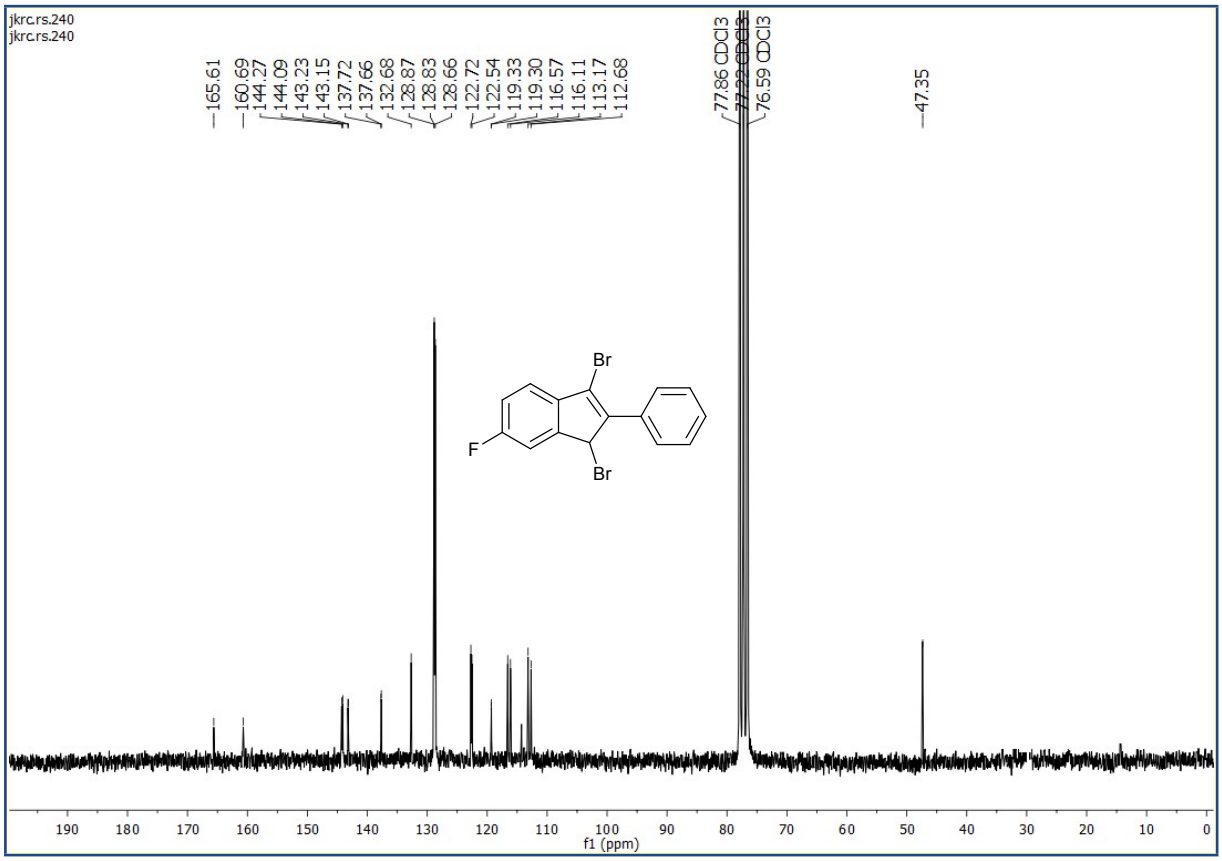
^{13}C NMR of compound 2k



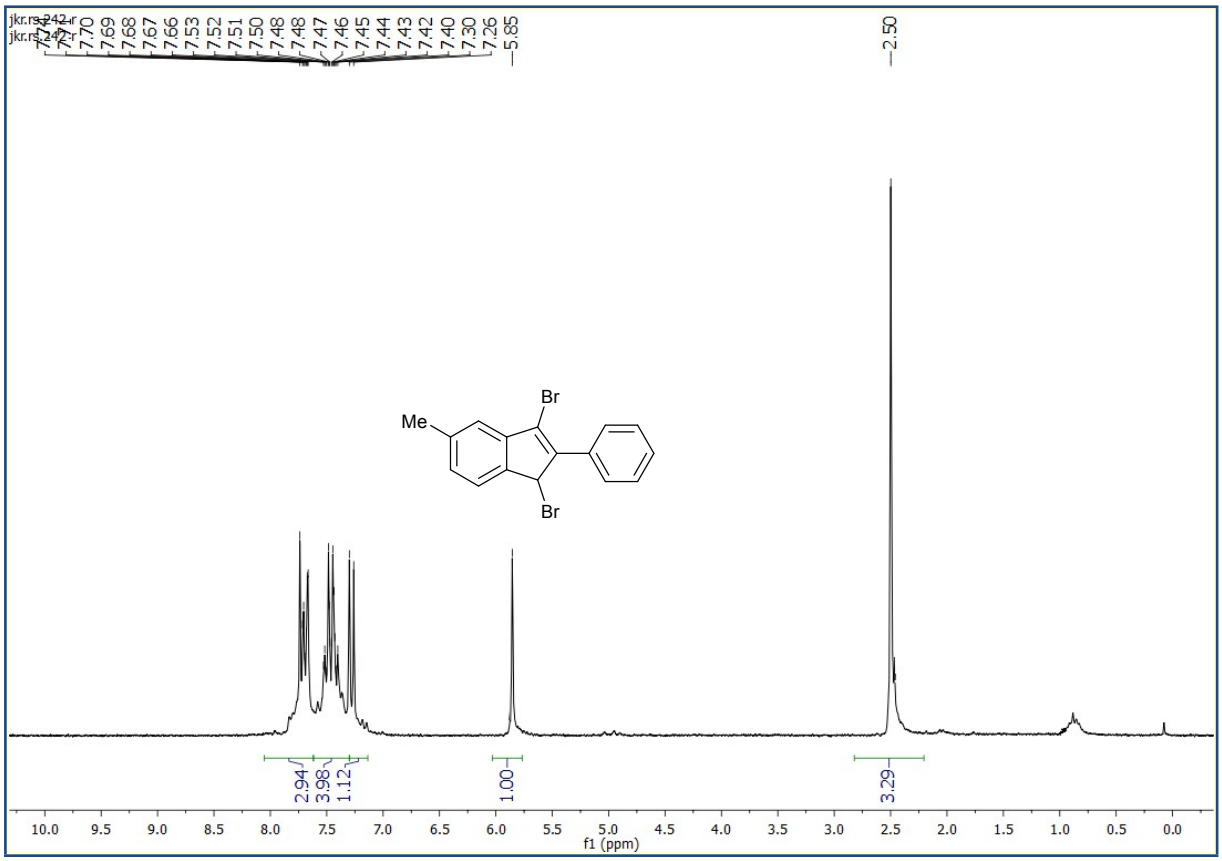
^{1}H NMR of compound 2l



^{13}C NMR of compound 2l



^{1}H NMR of compound 2m



^{13}C NMR of compound 2m