Preparation of lead dodecyl sulfate nanorod materials mediated by mechanochemistry and green solvent-free catalytic synthesis of heterocyclic derivatives

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General Information

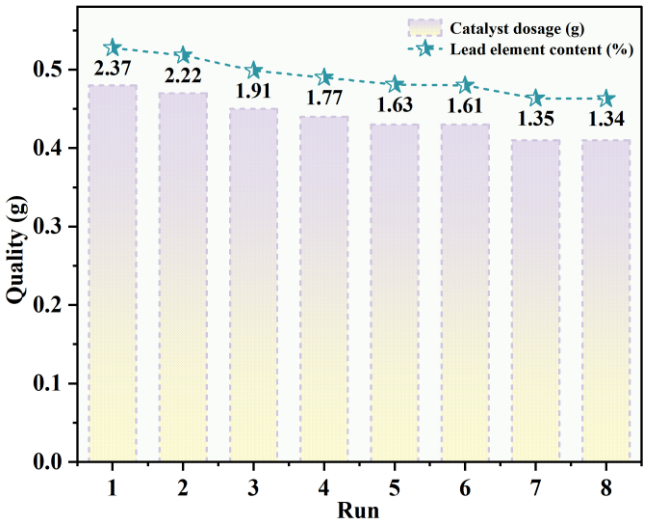
The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) instrument internally referenced to tetramethylsilane (TMS) or $CDCl_3$ signals. The NMR data were collected at ambient temperature and Chemical shifts are reported in parts per million (ppm) relative to the NMR solvent peaks. Data for ^{1}H-NMR are reported as follows: chemical shift, multiplicity (br: broad, s: singlet, d: doublet, t: triplet, m: multiplet), coupling constants, and integration. The high-resolution mass-spectra (HRMS) were acquired on an Agilent1290 Infinity separations module coupled to a 6230 time of flight (TOF) mass detector operating in ESI^{+} or ESI^{-} mode. The TLC was performed by using commercially prepared 200-400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. Processing of the NMR data was done using the standard Mestrenova 9.0.1 software. Melting points were measured with a melting point instrument and were uncorrected.

The powder X-ray diffraction patterns were recorded by a Bruker D8 Advance X-ray diffractometer using Cu-Ka (XRD). The scanning electron microscope was tested using German ZEISS Sigma 300 (SEM). The fourier transform infrared spectra were recorded in the range of 400-4000 cm^{-1} using a Thermo Scientific Nicolet iS50 FT-IR spectrometer employing potassium bromide (film) pellets technique at room temperature (FT-IR). The morphology of the materials was obtained on FEI Talos F200X High Resolution Transmission Electron Microscope (HRTEM). The X-ray photoemission spectra were performed at room temperature using a Thermo Scientific K-Alpha hemispherical electron energy analyser, and the working voltage of 12KV (XPS). Thermal gravimetric analysis was conducted on a TGA instrument (Hitachi 7200, Japan) under a N_2 atmosphere at a heating rate of 10 °C/min from 25 to 400°C (TGA). An inductively coupled plasma emission spectrometer ICP (Model: Agilent5110) and an organic element analyzer EA (Model: Vario EL cube) were used for elemental analysis of Pb, S and other elements in the material. The catalyst preparation and reaction evaluation were conducted using a semi-circular arc planetary ball mill (model: PBM-M-0.4·A; rated speed: 1050 r/min; actual operating speed: 600 r/min; power: 0.25 kW; Shenzhen Jitong Technology Development Co., Ltd, China).

Performance evaluation of catalyst for repeated use

Firstly, place a mixture of benzoyl (15 mmol; 3.15 g) and o-phenylenediamine (15 mmol; 1.62 g) into a ball mill, and then add catalyst ($Pb(DS)_2$; 10 wt%; 0.477g) and dispersant agent sodium chloride. The obtained mixture is first preheated in an oven at 75℃ for 20 minutes before being transferred to a ball mill for continuous ball milling reaction at a rate of 600 r/min, and the reaction was thoroughly completed under thin layer chromatography (TLC) monitoring (petroleum ether: ethyl acetate in a ratio of 25:1). During the repeated use of the catalyst, due to the insolubility of the catalyst material in water and ethyl acetate, the grinding aid sodium chloride is soluble in water but insoluble in ethyl acetate. Based on this, we first filtered and washed the recycled catalyst (including the grinding aid sodium chloride) multiple times with ethyl acetate (20 mL of ethyl acetate was used for dissolution and filtration for the first time, and 8-10 mL of ethyl acetate was added multiple times for washing during the filtration process). The filtered solution was obtained by column chromatography to obtain the reaction yield. The filter residue is a solid material consisting of catalyst and sodium chloride. The filter residue is subjected to secondary filtration, and a certain amount of deionized water is added for filtration and washing to remove sodium chloride. The catalyst material is retained and dried in a 45 ℃ oven for 20-24 h. Afterwards, use the dried catalyst and apply it to a new synthesis reaction for 8 cycles of reaction, and record the product yield after each cycle of reaction.

Fig. S1 Catalyst dosage and lead content during recycling process



Model reaction for the synthesis of *bis*(indole)methane derivatives from indole and benzaldehyde (Reaction I)

Firstly, place a mixture of indole (2.0 mmol; 234.3 mg) and benzaldehyde (1.0 mmol; 151.1 mg) into a ball mill jar (diameter: 5mm (with 6 additions) and 8mm (with 3 additions), volume ratio 1:4), followed by the addition of catalyst ($Pb(DS)_2$; 0.05 g) and dispersant sodium chloride (500 mg). The obtained mixture (ball powder mass ratio of 10:1) is first preheated in an oven at 100℃ for 20 minutes before being transferred to a ball mill for continuous ball milling reaction at a rate of 600 r/min, and the reaction was thoroughly completed under thin layer chromatography (TLC) monitoring (petroleum ether: ethyl acetate in a ratio of 3:1). After the reaction is complete, transfer the mixture from the ball milling tank to a beaker, and add ethyl acetate to dissolve the product (3×3.5 mL), filter and collect the catalyst. The process and collect the organic phase using a rotary evaporator. The purify using column chromatography (petroleum ether: ethyl acetate in a ratio of 3:1), weigh the product, and calculate the yield. All compound structures were tested by ^{1}H NMR and ^{13}C NMR.

Model reaction for the synthesis of quinoxaline derivatives from benzoyl and *o*-phenylenediamine (Reaction II)

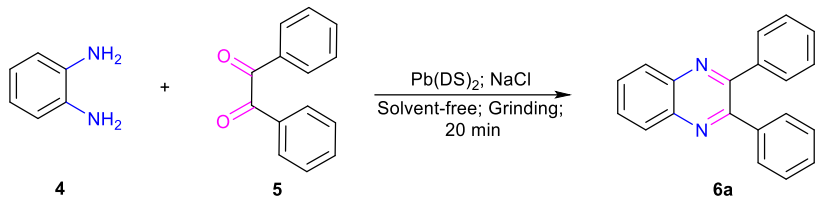
Firstly, place a mixture of benzoyl (0.5 mmol; 105.0 mg) and *o*-phenylenediamine (0.5 mmol; 54.0 mg) into a ball mill (diameter: 5mm (with 6 additions) and 8mm (with 3 additions), volume ratio 1:4), and then add catalyst ($Pb(DS)_2$; 10 wt%) and dispersant agent sodium chloride (500 mg). The obtained mixture (ball powder mass ratio of 14:1) is first preheated in an oven at 75℃ for 20 minutes before being transferred to a ball mill for continuous ball milling reaction at a rate of 600 r/min, and the reaction was thoroughly completed under thin layer chromatography (TLC) monitoring (petroleum ether: ethyl acetate in a ratio of 25:1). After the reaction is complete, transfer the mixture from the ball milling tank to a beaker, and add ethyl acetate to dissolve the product (3×3.5 mL), filter and collect the catalyst. The process and collect the organic phase using a rotary evaporator. The purify using column chromatography (petroleum ether: ethyl acetate in a ratio of 25:1), weigh the product, and calculate the yield. All compound structures were tested by ^{1}H NMR and ^{13}C NMR.

Model Reaction III Synthesis Method (Biginelli reaction)

Add benzaldehyde (0.5 mmol; 53.1 mg), urea (1.0 mmol; 60.1 mg), and ethyl acetoacetate (0.5 mmol; 65.1 mg) into a ball mill (diameter: 5mm (with 6 additions) and 8mm (with 3 additions), volume ratio 1:4), and then add catalyst ($Pb(DS)_2$; 10 wt%) and dispersant agent

sodium chloride (500 mg).The obtained mixture (ball powder mass ratio of 14:1) is first preheated in an oven at 100℃ for 20 minutes before being transferred to a ball mill for continuous ball milling reaction at a rate of 600 r/min, and the reaction was thoroughly completed under thin layer chromatography (TLC) monitoring (petroleum ether: ethyl acetate in a ratio of 1:2). After the reaction is complete, transfer the mixture from the ball milling tank to a beaker, and add ethyl acetate to dissolve the product (3×3.5 mL), filter and collect the catalyst. The process and collect the organic phase using a rotary evaporator. The purify using column chromatography (petroleum ether: ethyl acetate in a ratio of 1:2), weigh the product, and calculate the yield. All compound structures were tested by ^{1}H NMR and ^{13}C NMR.

Table. S1 The optimization of reaction conditions.



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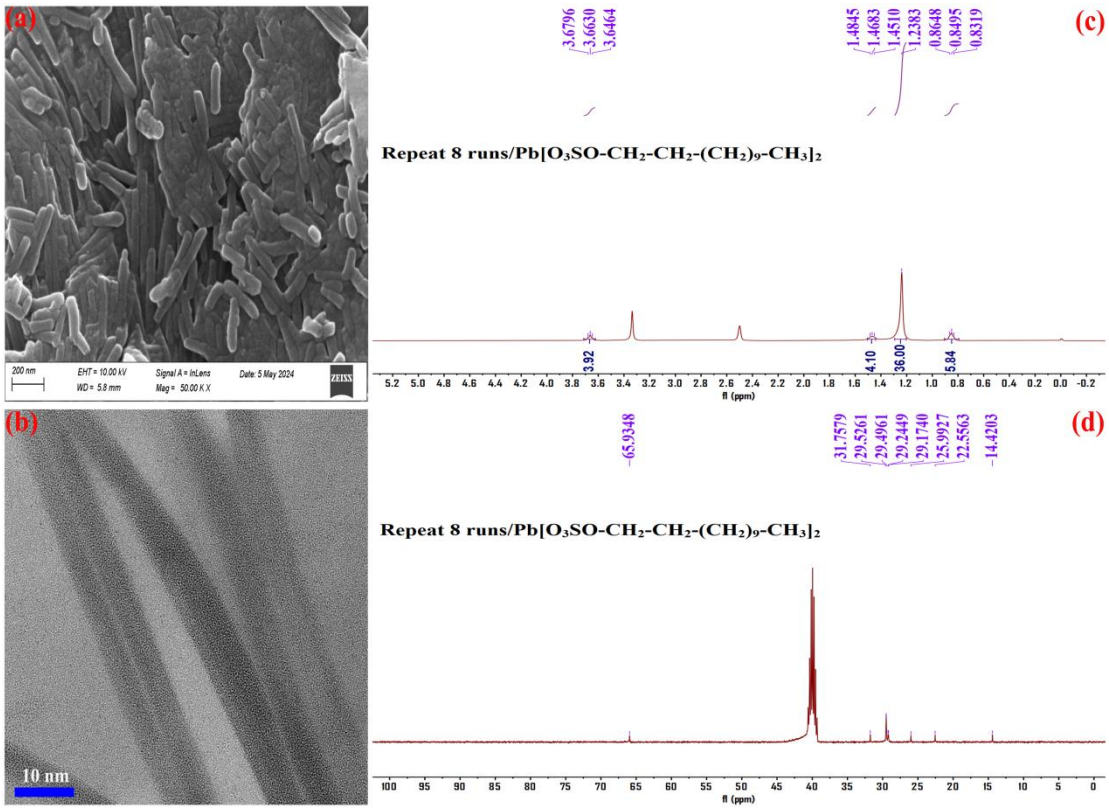
Entry[a]	Catalyst	Carrier[b] (g)	Time (min)	T (°C)	Yield[c] (%)
1			60	rt	Trace
2		NaCl	30	rt	<10
3	$Pb(DS)_2$	NaCl	30	rt	53
4	$Pb(DS)_2$	NaCl	30	50	67
5[e]	$Pb(DS)_2$	NaCl	30	75	98
6[e]	$Pb(DS)_2$	NaCl	30	75	97
7[e]	$Pb(DS)_2$	NaCl	30	75	74
8	$Pb(DS)_2$	NaCl	20	75	98
9	$La(DS)_3$	NaCl	10	75	72

[a] Reaction conditions: benzene-1,2-diamine **4** (0.5 mmol; 0.054 g); benzil **5** (0.5 mmol; 0.105 g); $Pb(DS)_2$: Lead dodecyl sulfate (10 wt%; 0.016 g); 75°C; Solvent-free; Solid phase grinding. [b] NaCl: sodium chloride (0.5 g). [c] Heating in an oven for 20 min prior to the ball milling reaction. [d] Isolated yields: All product yields were obtained by column chromatography. [e] The amount of $Pb(DS)_2$ was 10 wt% (0.016 g); 15 wt% (0.023 g); 5 wt% (0.008 g); respectively.

Fig. S2 SEM (a), TEM (b), and NMR spectra (^{1}H-NMR (c) and ^{13}C-NMR (d)) of the catalyst after 8 repeated uses.

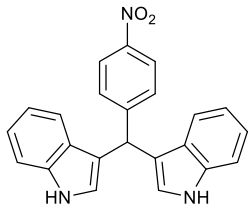


The Fig. S2 shows the SEM, HRTEM, and NMR images of $Pb(DS)_2$ catalyst synthesized by solid-phase grinding after eight cycles of use. From the SEM and HRTEM images, it can be seen that the morphology and structure of the catalytic material remain in the form of nano rod like structures after eight cycles of use, consistent with the fresh catalyst, proving that the material has good stability. During the cyclic use process, after multiple heating and mechanical ball milling, its morphological characteristics did not show significant changes, reflecting the good structural stability of $Pb(DS)_2$ catalyst material.

The ^{1}H NMR and ^{13}C NMR of $Pb(DS)_2$ material in DMSO after 8 cycles of use, The spectral data are as follows: ^{1}H NMR (400 MHz, DMSO) δ 3.66 (t, J=6.6 Hz, 4H), 1.51-1.44 (m, 4H), 1.24 (s, 36H), 0.86 (d, J=6.1 Hz, 6H). The chemical shift of methyl is 0.79-1.0, and the chemical shift of methylene is 0.98-1.54. Due to the induction effect of electron withdrawing groups caused by the connection of one end of the alkyl chain to the sulfate group, the chemical shift of the methylene group connected to the sulfate group is affected. Therefore, the chemical shift 3.66 corresponds to the methylene group directly connected to the sulfate group. However, although other methylene groups are also affected by the induction effect, they are directly connected to the sulfate group. The

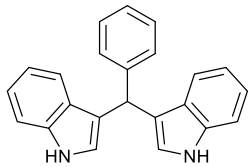
connected methylene groups have a weaker effect compared to others, and the peaks at chemical shifts 2.5 and 3.3 correspond to the peaks in DMSO and water, respectively. The ^{13}C NMR of $Pb(DS)_2$ (as shown in Figure. S2d) is at δ=65.93, 31.76, 29.53, 29.50, 29.24, 29.17, 25.99, 22.56,14.42. Figure. S2c-2d shows that in the fatty chain of lead dodecyl sulfate, the methylene group follows closely behind the lead sulfate, The peak of DMSO in the carbon spectrum appears at δ=40.0 ppm. This data result is consistent with the fresh $Pb(DS)_2$ material, and the catalyst material after repeated use maintains the intrinsic structure of the fresh catalyst.

Characterization data for all products
Reaction I



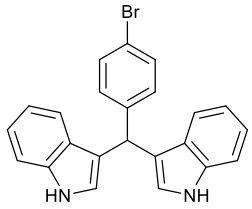
3,3'-((4-nitrophenyl)methylene)bis(1H-indole) (3a)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.93 (d, J = 2.6 Hz, 2H), 8.18-8.12 (m, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.06 (t, J = 7.6 Hz, 2H), 6.93-6.84 (m, 4H), 6.03 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 153.61, 146.21, 137.05, 129.92, 126.82, 124.33, 123.90, 121.57, 119.39, 118.89, 117.13, 112.06. **IR** (thin film) ν_{max} 3419.5; 2945.3; 2922.6; 1656.4; 1535.2; 1517.2; 1346.2; 1275.4; 1260.5; 764.0.



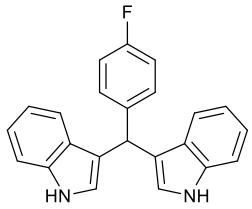
3,3'-(phenylmethylene)bis(1H-indole) (3b)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (d, J = 2.5 Hz, 2H), 7.38 (dd, J = 7.7, 4.5 Hz, 4H), 7.34-7.23 (m, 4H), 7.17 (t, J = 7.3 Hz, 1H), 7.05 (t, J = 7.3 Hz, 2H), 6.91-6.83 (m, 4H), 5.86 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 145.45, 137.07, 128.79, 128.51, 127.11, 126.26, 124.03, 121.36, 119.61, 118.66, 118.54, 111.93. **IR** (thin film) ν_{max} 3412.0; 3056.4; 2921.5; 2850.8; 1616.7; 1455.5; 1339.2; 1287.9; 1250.3; 744.8.



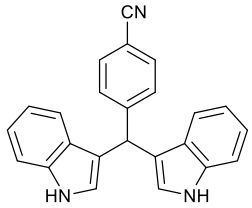
3,3'-((4-bromophenyl)methylene)bis(1H-indole) (3c)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.87 (d, J = 2.6 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.31 (dd, J = 8.2, 6.6 Hz, 4H), 7.06 (t, J = 7.5 Hz, 2H), 6.93 – 6.84 (m, 4H), 5.86 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 144.92, 137.10, 131.39, 131.03, 126.97, 124.13, 121.45, 119.52, 119.26, 118.76, 117.98, 112.00. **IR** (thin film) ν_{max} 3413.1; 3054.8; 2925.2; 2853.0; 1618.0; 1485.2; 1337.7; 1264.2; 1230.3; 785.0; 746.3; 703.1; 597.6.



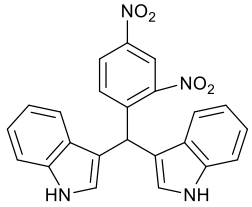
3,3'-((4-fluorophenyl)methylene)bis(1H-indole) (3d)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.87 (d, J = 2.6 Hz, 2H), 7.39 (dd, J = 8.4, 5.6 Hz, 4H), 7.30 (d, J = 8.0 Hz, 2H), 7.07 (dddd, J = 14.1, 8.2, 6.6, 1.6 Hz, 4H), 6.88 (t, J = 7.7 Hz, 2H), 6.85 (d, J = 2.4 Hz, 2H), 5.88 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 162.18, 159.78, 141.58, 141.55, 137.11, 130.48, 130.41, 127.02, 124.04, 121.41, 119.55, 118.71, 118.45, 115.25, 115.04, 111.96. **IR** (thin film) ν_{max} 3410.4;2922.6; 2854.1; 1647.5; 1456.5; 1341.8; 1278.9; 1263.4; 1221.8; 1158.8; 1095.8; 1024.5; 748.1.



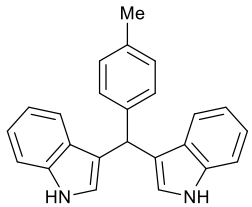
4-(di(1H-indol-3-yl)methyl)benzonitrile (3e)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (d, J = 2.6 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.12 – 7.03 (m, 2H), 6.95 – 6.87 (m, 4H), 6.00 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 151.38, 137.11, 132.59,129.81, 126.92, 124.32, 121.58, 119.58, 119.44, 118.91, 117.33, 112.08, 109.15. **IR** (thin film)ν_{max} 3411.7;3055.16;2226.39;1604.79;1456.19;1417.68;1337.45;1216.99;1094.39;1010.17;865.63;790.83;769.87;742.66;599.88;580.91;552.27;505.38;479.36;423.59.



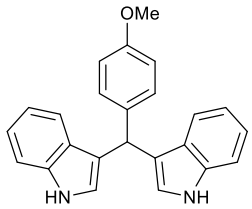
3,3'-((2,4-dinitrophenyl)methylene)bis(1H-indole) (3f)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.05 (d, J = 2.6 Hz, 2H), 8.76 (d, J = 2.4 Hz, 1H), 8.40(dd, J = 8.7, 2.5 Hz, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.14 – 7.06 (m, 2H), 6.97 – 6.88 (m, 4H), 6.53 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 149.58, 146.48, 145.11, 137.13, 132.55, 127.35, 126.62, 125.04, 121.87, 120.23, 119.29, 118.90, 115.28, 112.25, 35.15. **IR** (thin film) ν_{max} 1456.48;1418.3;1346.9;1123.51;1096.72;1062.45;1010.59;834.37;795.57;743.45;603.56;581.49;485.28;424.2.



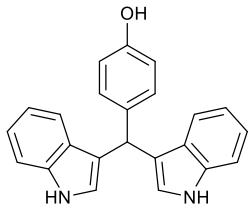
3,3'-(p-tolylmethylene)bis(1H-indole) (3g)

^{1}H NMR (400 MHz, DMSO-d6) δ 10.83 (s, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.27 (dd, J = 17.1, 7.8 Hz, 4H), 7.08 (s, 1H), 7.07-7.00 (m, 3H), 6.87 (t, J = 7.5 Hz, 2H), 6.83 (s, 2H), 5.80 (s, 1H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 142.43, 137.09, 135.04, 129.08, 128.67, 127.13, 123.97, 121.31, 119.63, 118.71, 118.60, 111.90, 21.10. **IR** (thin film) ν_{max} 3414.2; 3052.4; 2921.3; 2856.3; 1618.2; 1452.2; 1415.4; 1285.5; 1255.2; 742.8.



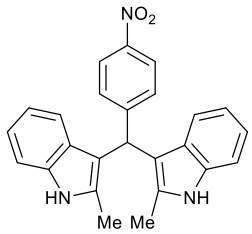
3,3'-((4-methoxyphenyl)methylene)bis(1H-indole) (3h)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 2.4 Hz, 2H), 5.85 (s, 1H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.92, 136.72, 136.26, 129.63, 127.09, 123.55, 121.91, 120.05, 120.00, 119.21, 113.60, 111.05, 55.24, 39.35. **IR** (thin film) ν_{max} 3412.7; 3054.7; 2927.8; 2835.7; 1609.7; 1456.1; 1338.0; 1252.7; 1226.7; 1174.7; 1092.3; 1028.3; 1009.9; 746.9.



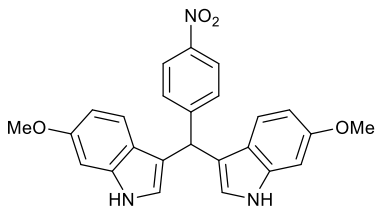
4-(di(1H-indol-3-yl)methyl)phenol (3i)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.78 (d, *J* = 2.4 Hz, 2H), 9.15 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.85(t, *J* = 7.5 Hz, 2H), 6.78 (d, *J* = 2.3 Hz, 2H), 6.65 (d, *J* = 8.3 Hz, 2H), 5.70 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 160.48, 141.82, 140.43, 134.34, 131.90, 128.59, 125.98, 124.39,123.90, 123.26, 119.97, 116.59. **IR** (thin film) ν_{max} 3413.55;3054.35;1613.35;1509.18;1455.82;1417.27;1337.45;1216.95; 1169.93; 1123.69; 1092.78;1009.87;786.1;743.31;702.02;598.35;583.04;533.71;458.58;423.94.



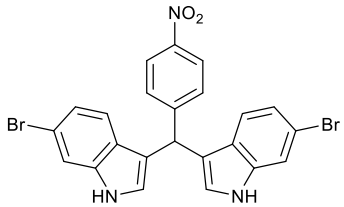
3,3'-((4-nitrophenyl)methylene)bis(2-methyl-1H-indole) (3j)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.91 (s, 2H), 8.21 – 8.13 (m, 2H), 7.48 – 7.42 (m, 2H), 7.30 – 7.25 (m, 2H), 6.93 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 2H), 6.84 (d, *J* = 7.7 Hz, 2H), 6.72 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 2H), 6.10 (s, 1H), 2.13 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 153.39, 146.17, 135.63, 133.08, 130.32, 128.39, 123.72, 120.26, 118.77, 118.70, 111.34, 111.02, 49.09, 12.42. **IR** (thin film) ν_{max} 3398.9; 2919.1; 1548.9; 1516.0; 1343.9; 1287.8; 1260.9; 747.9.



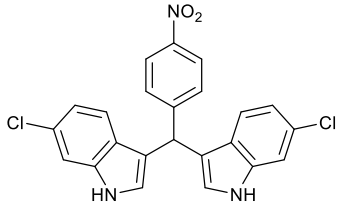
3,3'-((4-nitrophenyl)methylene)bis(6-methoxy-1H-indole)) (3k)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.74 (d, J = 2.4 Hz, 2H), 8.17 – 8.11 (m, 2H), 7.61 – 7.56 (m, 2H), 7.14 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 2.3 Hz, 2H), 6.76 (dd, J = 2.4, 0.9 Hz, 2H), 6.56 (dd, J = 8.7, 2.3 Hz, 2H), 5.92 (s, 1H), 3.74 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.02, 153.71, 146.18, 137.79, 129.87, 123.83, 122.94, 121.30, 120.00, 117.16, 109.11, 95.08, 55.59. **IR** (thin film) ν_{max} 3410.6; 2923.5; 2849.3; 1628.2; 1536.0; 1515.9; 1452.2; 1345.2; 1260.2; 1232.5; 1159.3; 1058.0; 1026.2.



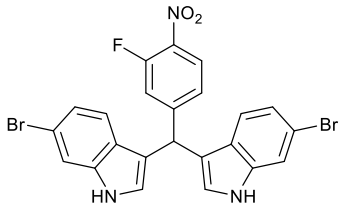
3,3'-((4-nitrophenyl)methylene)bis(6-bromo-1H-indole) (3l)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.12 (d, J = 2.5 Hz, 2H), 8.18 – 8.13 (m, 2H), 7.61 – 7.55 (m, 4H), 7.21 (d, J = 8.5 Hz, 2H), 7.02 (dd, J = 8.5, 1.8 Hz, 2H), 6.95 – 6.90 (m, 2H), 6.04 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 152.86, 146.36, 137.94, 129.89, 125.81, 125.45, 123.99, 121.86, 121.11, 117.26, 114.66, 114.49. **IR** (thin film) ν_{max} 3418.3; 2922.4; 2854.1; 1647.3; 1555.2; 1514.2; 1457.1; 1344.6; 1275.5; 1204.8; 783.8; 749.4; 708.6; 583.8



3,3'-((4-nitrophenyl)methylene)bis(6-chloro-1H-indole) (3m)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (d, J = 2.6 Hz, 2H), 8.15 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 2.0 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 6.97 – 6.88 (m, 4H), 6.04 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 152.89, 146.36, 137.45, 129.89, 126.45, 125.57, 125.52, 123.99, 120.70, 119.32, 117.25, 111.70. **IR** (thin film) ν_{max} 3430.3; 2997.5; 2924.9; 1594.4; 1454.6; 1345.5; 1242.8; 1225.6; 1098.0; 1061.8; 779.9; 747.9; 706.6.

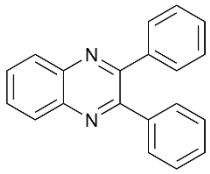


3,3'-((3-fluoro-4-nitrophenyl)methylene)bis(6-bromo-1H-indole) (3n)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.16 (d, J = 2.5 Hz, 2H), 8.09 (t, J = 8.2 Hz, 1H), 7.58 (d, J = 1.8 Hz, 2H), 7.48 (dd, J = 12.5, 1.8 Hz, 1H), 7.38 (dd, J = 8.6, 1.8 Hz, 1H), 7.24 (d, J = 8.5 Hz, 2H), 7.04 (dd, J = 8.5, 1.8 Hz, 2H), 6.98 (dd, J = 2.5, 0.9 Hz, 2H), 6.04 (s, 1H).**^{13}C NMR** (101 MHz, DMSO-d_6) δ 137.90, 126.82 (d, J = 2.2 Hz), 125.65 (d, J = 13.7 Hz), 125.34 (d, J = 3.2 Hz), 121.95, 121.05, 118.15 (d, J = 20.8 Hz), 116.72, 114.61 (d, J =

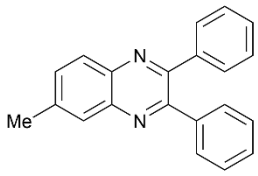
13.3 Hz), 40.49 (d, *J* = 21.0 Hz), 40.18, 39.97, 39.76, 39.55, 39.34.3429.89.**IR** (thin film)ν_{max}2 921.73;2850.75;1609.58;1520;1453.4;1396.75;1346.55;1243.34;1219.51;1094.65;1050.53;893.22;846. 46;802.17;748.44;736.71cm^{-1}.**ESI-MS**: $[M+H]^+$ calcd for $[C_{23}H_{14}Br_2FN_3O_2]^+$: 542.9416;found: 542.9412.

Reaction II



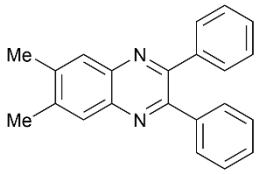
2,3-diphenylquinoxaline (3a)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (dt, *J* = 6.0, 2.6 Hz, 2H), 7.89 (dd, *J* = 6.6, 3.4 Hz, 2H), 7.52-7.43 (m, 4H), 7.42-7.32 (m, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 153.55, 140.94, 139.26, 130.88, 130.16, 129.26 (d, *J* = 5.1 Hz), 128.51. **IR** (thin film) ν_{max} 3415.6; 3058.2; 2921.3; 1618.3; 1477.4; 1440.8; 1344.3; 1219.1; 767.8; 697.4.



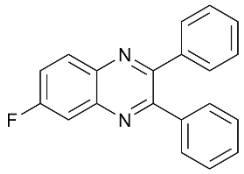
6-methyl-2,3-diphenylquinoxaline (3b)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.90 (s, 1H), 7.67 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.45 (t, *J* = 1.8 Hz, 2H), 7.43 (d, *J* = 2.0 Hz, 2H), 7.38 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.35 (dd, *J* = 4.2, 1.8 Hz, 3H), 7.31 (dd, *J* = 6.7, 1.8 Hz, 2H), 2.55 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 153.27, 152.53, 141.00, 139.41, 139.34, 132.99, 130.14, 130.12, 129.96, 129.14, 129.07, 128.80, 128.47, 127.95, 21.82. **IR** (thin film) ν_{max} 3415.6; 3058.0; 2921.7; 1620.9; 1485.2; 1444.9; 1401.3; 1345.6; 772.7; 697.5.



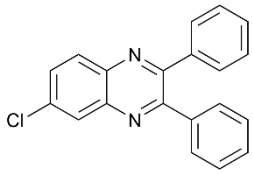
6,7-dimethyl-2,3-diphenylquinoxaline (3c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 2H), 7.55-7.47 (m, 4H), 7.34 (td, *J* = 3.9, 3.0, 1.8 Hz, 4H), 7.32-7.28 (m, 2H), 2.52 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.50, 140.53, 140.23, 139.40, 129.86, 128.54, 128.23, 128.20, 20.44. **IR** (thin film) ν_{max} 3415.6; 3058.0; 2922.1; 2852.1; 1635.5; 1615.7; 1481.5; 1344.5; 1207.5; 757.9; 697.0.



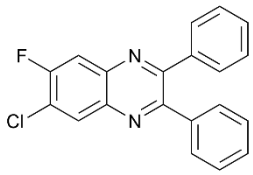
6-fluoro-2,3-diphenylquinoxaline (3d)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30-8.18 (m, 1H), 7.92 (dt, *J* = 9.7, 2.0 Hz, 1H), 7.80 (td, *J* = 8.8, 2.6 Hz, 1H), 7.46 (dq, *J* = 8.2, 1.8 Hz, 4H), 7.43-7.36 (m, 4H), 7.36-7.29 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.02, 161.54, 154.35, 153.09, 153.06, 141.72, 141.58, 139.01, 138.92, 138.31, 131.91, 131.80, 130.17, 130.13, 129.44, 129.28, 128.52, 121.15, 120.89, 112.82, 112.61. **IR** (thin film) ν_{max} 3415.6; 3057.2; 2925.3; 1636.5; 1479.9; 1435.6; 1343.0; 1204.5; 775.9; 695.2.



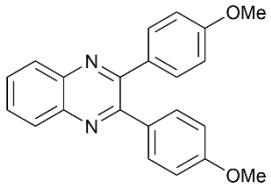
6-chloro-2,3-diphenylquinoxaline (3e)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18-8.04 (m, 2H), 7.82 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.44 (s, 2H), 7.42 (s, 2H), 7.37 (d, *J* = 6.9 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 4H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 154.40, 153.81, 141.19, 139.54, 138.84, 138.78, 135.05, 131.33, 131.06, 130.16, 130.13, 129.48, 129.40, 128.51, 127.91. **IR** (thin film) ν_{max} 3415.6; 3060.6; 2923.4; 2851.9; 1636.5; 1467.6; 1445.5; 1342.7; 767.6; 696.8.



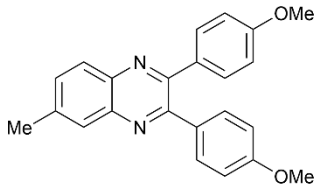
6-chloro-7-fluoro-2,3-diphenylquinoxaline (3f)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 9.8 Hz, 1H), 7.47 – 7.32 (m, 10H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 158.94, 156.44, 154.63, 154.01, 153.98, 140.49, 140.37, 138.64, 138.60, 138.30, 130.59, 130.16, 130.14, 129.62, 129.53, 128.56, 124.60, 124.39, 114.45, 114.24. **IR** (thin film) ν_{max} 3415.6; 3059.9; 2925.4; 1654.8; 1636.5; 1470.0; 1447.6; 1341.2; 1217.1; 757.4; 697.0.



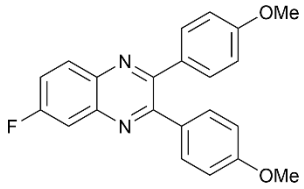
2,3-bis(4-methoxyphenyl)quinoxaline (3g)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12-8.04 (m, 2H), 7.81 (dt, *J* = 6.4, 3.4 Hz, 2H), 7.48-7.40 (m, 4H), 6.96-6.88 (m, 4H), 3.77 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 160.18, 153.01, 140.74, 131.66, 131.58, 130.39, 129.07, 115.29, 114.03, 55.64. **IR** (thin film) ν_{max} 3413.0; 3059.5; 2932.8; 2835.9; 1633.9; 1607.2; 1513.5; 1344.3; 1250.7; 1175.4; 1028.9; 832.8; 761.5.



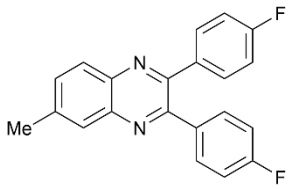
2,3-bis(4-methoxyphenyl)-6-methylquinoxaline (3h)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.85 (s, 1H), 7.63 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.41 (dt, *J* = 8.7, 2.2 Hz, 4H), 6.91 (d, *J* = 8.4 Hz, 4H), 3.87-3.68 (m, 6H), 2.55 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 160.12, 160.05, 152.81, 152.09, 140.81, 140.46, 139.21, 132.53, 131.78, 131.55, 131.51, 128.64, 127.81, 114.00, 55.62, 21.79. **IR** (thin film) v_{max} 3413.0; 2932.3; 2835.3; 1633.9; 1606.2; 1511.9; 1342.1; 1247.9; 1174.1; 1028.2; 834.6; 750.9.



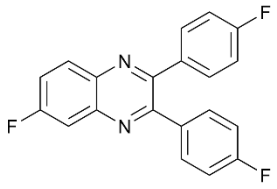
6-fluoro-2,3-bis(4-methoxyphenyl)quinoxaline (3i)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (dd, *J* = 9.2, 5.9 Hz, 1H), 7.84 (dd, *J* = 9.5, 2.8 Hz, 1H), 7.73 (td, *J* = 8.9, 2.9 Hz, 1H), 7.46-7.37 (m, 4H), 6.96-6.88 (m, 4H), 3.77 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 163.74, 161.26, 160.36, 160.21, 153.80, 152.57, 152.54, 141.47, 141.34, 138.07, 131.64, 131.62, 131.53, 131.43, 131.29, 120.57, 120.31, 114.05, 112.61, 112.40, 55.65, 55.64. **IR** (thin film) v_{max} 3415.6; 2933.0; 2836.1; 1636.5; 1606.4; 1511.9; 1340.9; 1250.8; 1174.7; 1027.7; 932.3; 758.2.



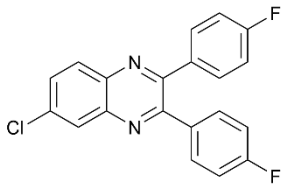
2,3-bis(4-fluorophenyl)-6-methylquinoxaline (3j)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 1.5 Hz, 1H), 7.72 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.50 (ddd, *J* = 9.0, 5.6, 1.8 Hz, 4H), 7.22 (ddt, *J* = 8.9, 6.6, 2.2 Hz, 4H), 2.58 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.04, 163.99, 161.59, 161.54, 152.35, 151.61, 141.20, 140.99, 139.40, 135.69, 135.66, 133.17, 132.50, 132.48, 132.42, 132.40, 128.81, 127.93, 115.72, 115.70, 115.50, 115.49, 21.83. **IR** (thin film) v_{max} 3415.6; 3058.8; 2924.6; 2852.2; 1636.5; 1600.0; 1509.2; 1347.6; 1220.4; 1163.7; 838.5; 799.3; 751.5.



6-fluoro-2,3-bis(4-fluorophenyl)quinoxaline (3k)

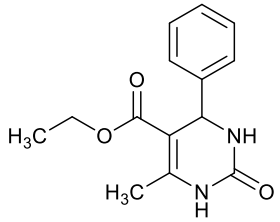
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (dd, *J* = 9.2, 5.9 Hz, 1H), 7.91 (dd, *J* = 9.5, 2.8 Hz, 1H), 7.81 (td, *J* = 8.9, 2.9 Hz, 1H), 7.50 (ddq, *J* = 8.5, 5.8, 3.0 Hz, 4H), 7.22 (ddt, *J* = 8.8, 6.6, 1.8 Hz, 4H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.19, 164.10, 164.04, 161.74, 161.65, 161.56, 153.35, 152.08, 152.05, 141.68, 141.55, 138.27, 135.34, 135.30, 135.24, 135.21, 132.58, 132.50, 132.42, 131.86, 131.76, 121.25, 120.99, 115.75, 115.54, 112.80, 112.59. **IR** (thin film) v_{max} 3415.6; 3071.9; 1621.2; 1602.9; 1510.4; 1481.3; 1344.2; 1231.2; 1204.7; 1156.8; 841.5; 760.0.



6-chloro-2,3-bis(4-fluorophenyl)quinoxaline (3l)

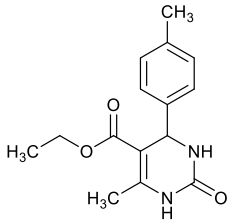
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, *J* = 2.4 Hz, 1H), 8.12 (d, *J* = 8.9 Hz, 1H), 7.85 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.54-7.45 (m, 4H), 7.21 (td, *J* = 8.8, 1.8 Hz, 4H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.24, 164.19, 161.78, 161.73, 153.43, 152.84, 141.17, 139.52, 135.19, 135.16, 135.13, 135.10, 132.56, 132.52, 132.47, 132.44, 131.46, 131.04, 127.88, 115.75, 115.54. **IR** (thin film) ν_{max} 3413.0; 3070.2; 2926.5; 1633.9; 1601.2; 1510.4; 1466.9; 1340.9; 1232.4; 1158.9; 1066.9; 838.6; 797.3; 729.3; 693.1; 660.4.

Reaction Ⅲ



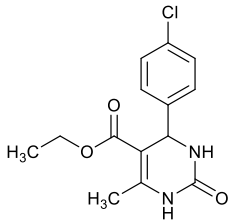
ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9a)

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 9.21 (s, 1H), 7.75 (t, J = 2.7 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 7.2 Hz, 3H), 5.15 (d, J = 3.3 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d$_6$) δ 165.77, 152.59, 148.83, 145.30, 128.85, 127.72, 126.69, 99.65, 59.65, 54.39, 18.24, 14.52. **IR** (thin film) ν_{max} 3241.7, 3113.2, 2980.8, 2930.2, 1726.8, 1703.4, 1648.9, 1468.8, 1286.7, 1220.5, 1092, 780.4 cm^{-1}.



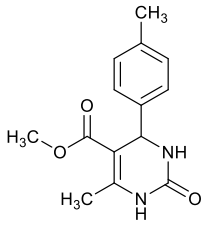
ethyl 6-methyl-2-oxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9b)

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 9.19 (d, J = 2.1 Hz, 1H), 7.72 (t, J = 2.6 Hz, 1H), 7.12 (s, 4H), 5.12 (d, J = 3.4 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.25 (d, J = 1.7 Hz, 6H), 1.10 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d$_6$) δ 165.81, 152.68, 148.64, 142.40, 136.85, 129.36, 126.62, 99.84, 59.65, 54.08, 21.11, 18.24, 14.56. **IR** (thin film) ν_{max} 3245.8, 3117, 2980.9, 2957.6, 2935, 1723.1, 1707.4, 1648.9, 1594.5, 1463, 1399.7, 1286.9, 1224.5, 1092, 784.4 cm^{-1}.



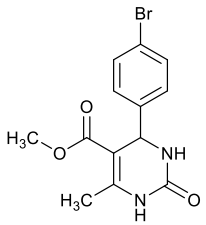
ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9c)

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 7.83 – 7.77 (m, 1H), 7.42 – 7.37 (m, 2H), 7.28 – 7.22 (m, 2H), 5.14 (d, *J* = 3.3 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.64, 152.39, 149.20, 144.22, 132.23, 128.85, 128.64, 99.23, 59.73, 53.85, 18.26, 14.52. **IR** (thin film) ν_{max} 3241.7, 3122, 2980.9, 2957.6, 2935, 1726.8, 1707.5, 1648.9, 1590.6, 1459, 1403.7, 1290.6, 1224.5, 1092, 784.4 cm^{-1}.



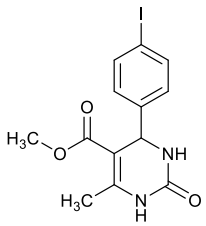
methyl 6-methyl-2-oxo-4-(*p*-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9d)

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (d, *J* = 2.0 Hz, 1H), 7.74 (t, *J* = 2.7 Hz, 1H), 7.12 (s, 4H), 5.13 (d, *J* = 3.4 Hz, 1H), 3.52 (s, 3H), 2.28 – 2.23 (m, 6H).**^{13}C NMR** (101 MHz, DMSO-d_6) δ 166.37,152.74, 149.01, 142.23, 136.97, 129.49, 126.60, 99.62, 53.98, 51.31, 21.15, 18.33.**IR** (thin film) ν_{max} 3244.8, 3117, 2981.8, 2957.5, 2935, 1721.9, 1707.7, 1648.9, 1594.4, 1462, 1340.6, 1286.9, 1224.4, 1092, 783.4 cm^{-1}.



methyl 4-(4-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9e)

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 3.5, 2.0 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.22 – 7.16 (m, 2H), 5.13 (d, *J* = 3.4 Hz, 1H), 3.52 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.72, 152.00, 149.06, 144.02, 131.41, 128.51, 120.40, 98.53, 53.36, 50.88, 17.90.**IR** (thin film) ν_{max} 3241.5, 3121, 2980.8, 2957.7, 2934, 1726.9, 1707.3, 1648.9, 1590.6, 1459, 1403.5, 1291.6, 1224.5, 1092, 783.8 cm^{-1}.

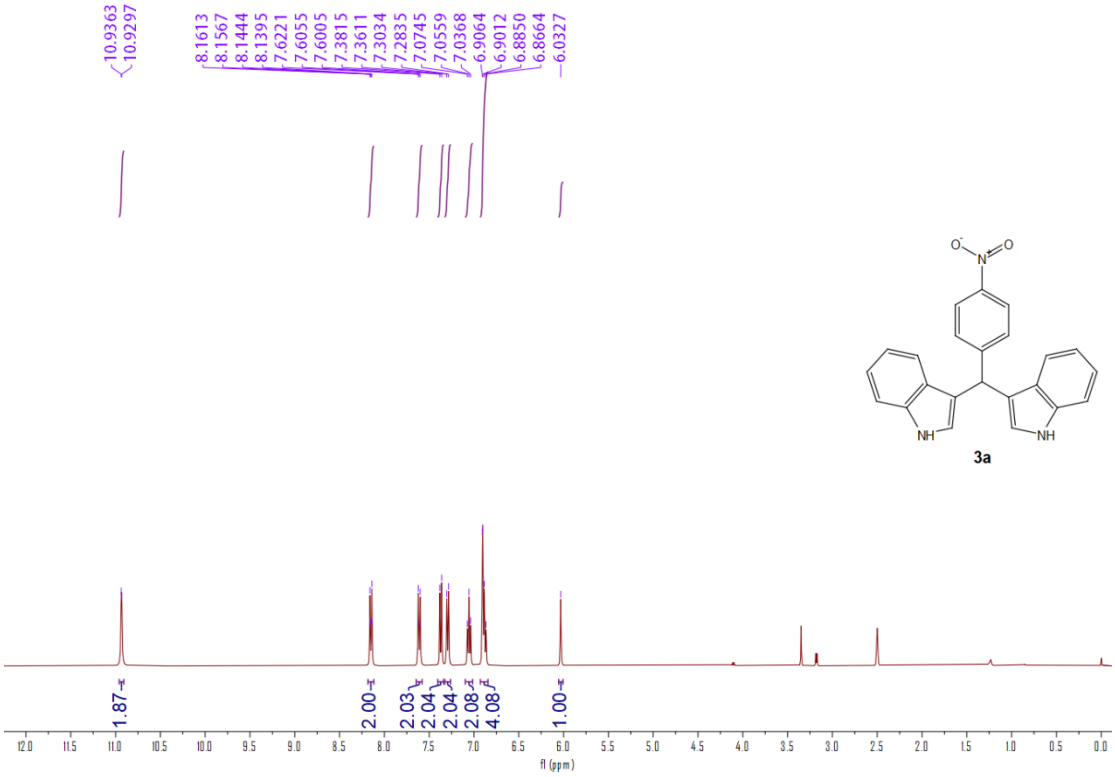


methyl 4-(4-iodophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9f)

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (s, 1H), 7.83 – 7.79 (m, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 5.11 (d, *J* = 3.4 Hz, 1H), 3.52 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.83, 152.14, 149.14, 144.53, 137.38, 128.77, 98.62, 93.48, 53.60, 51.02, 18.04. **IR** (thin film) ν_{max} 3242.7, 3122, 2980.8, 2958.4, 2934, 1726.9, 1707.3, 1646.9, 1590.6, 1459, 1401.5, 1290.8, 1223.4, 1092, 781.7 cm^{-1}.

NMR spectra for all compounds

Reaction I



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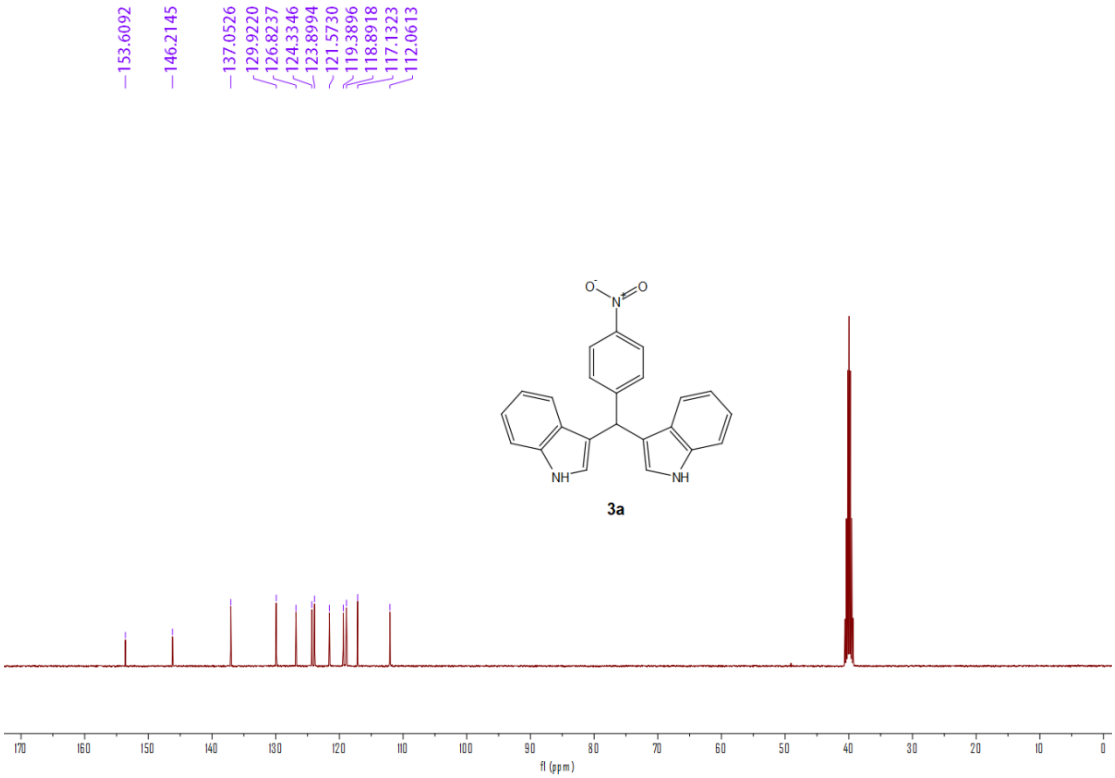

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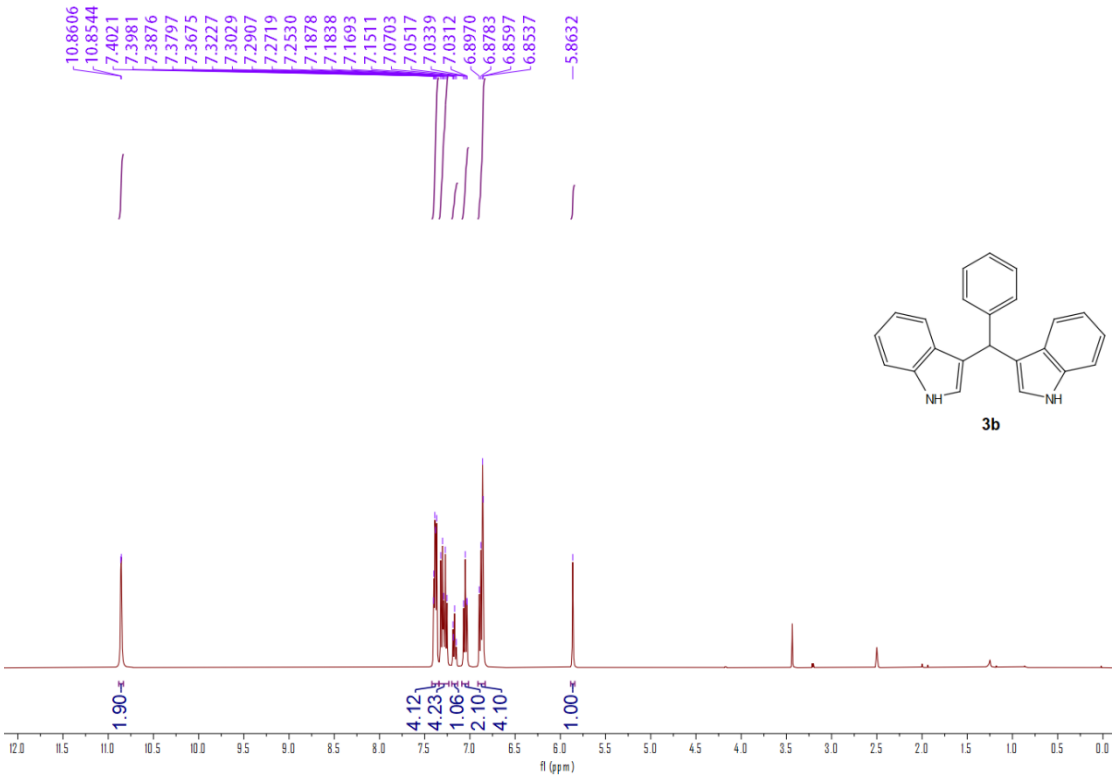
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7.0517
7.0339
7.0312
6.8970
6.8783
6.8597
6.8537
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NH
3b
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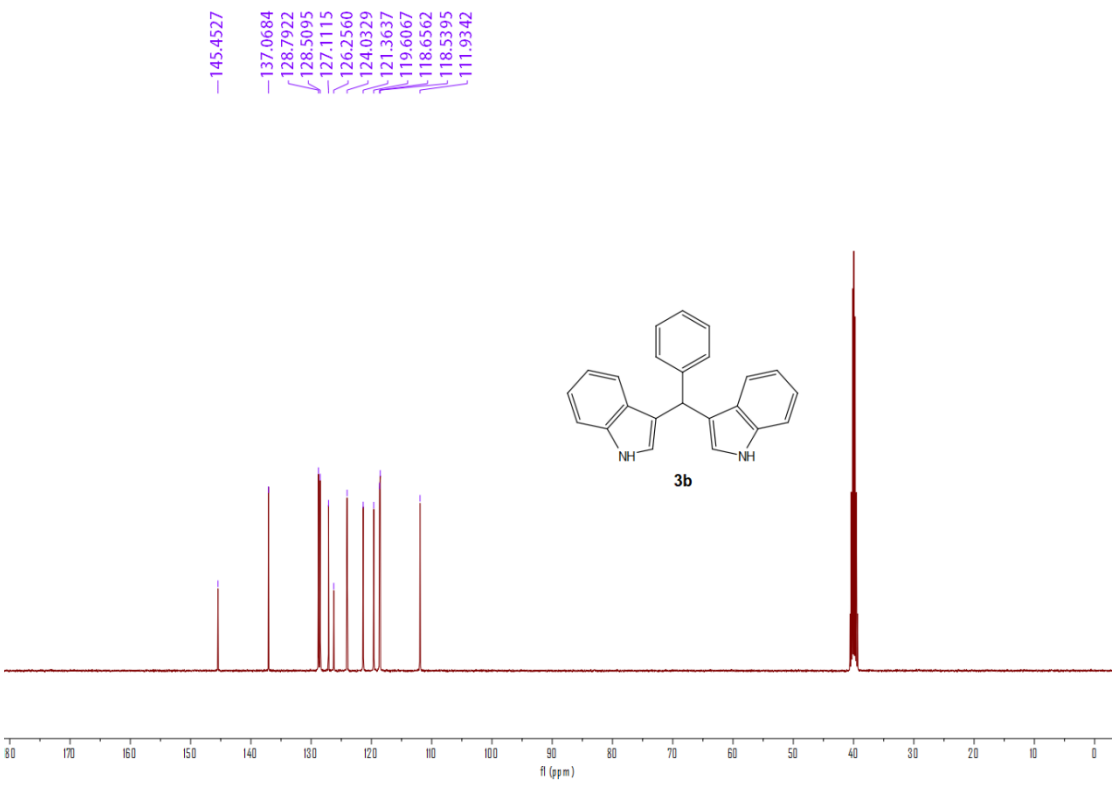
4.10
1.00
f1 (ppm)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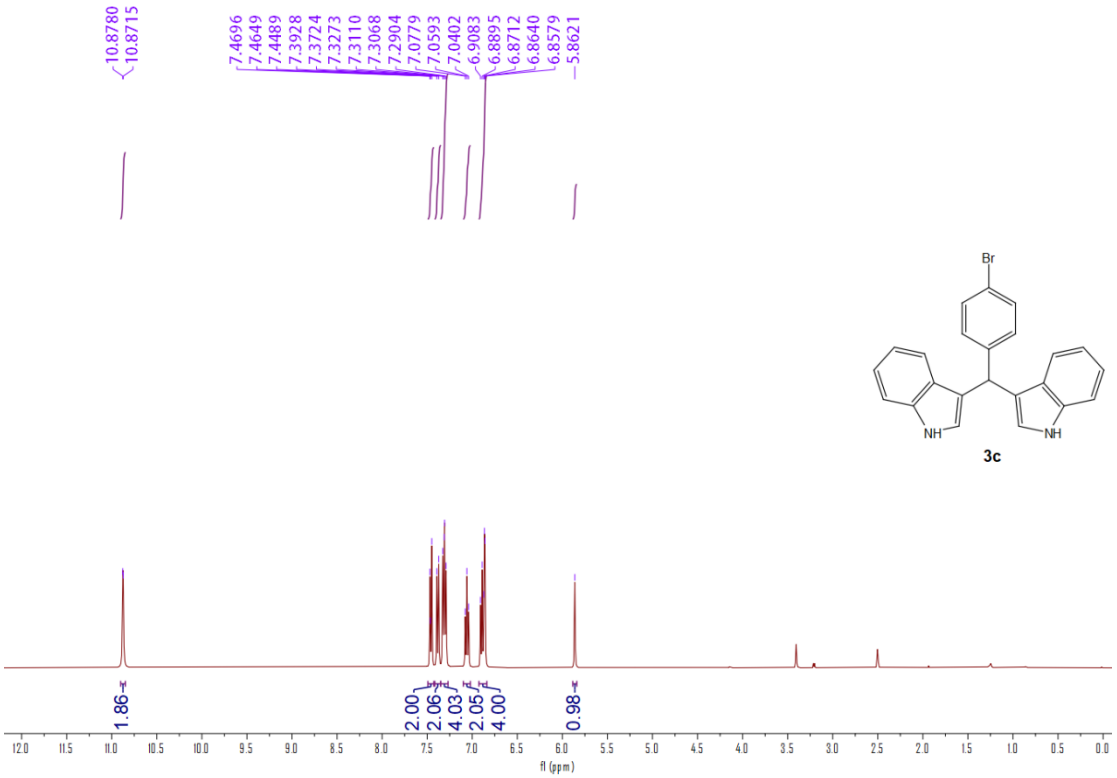
NH
3b
f1 (ppm)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7.2904
7.0779
7.0593
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NH
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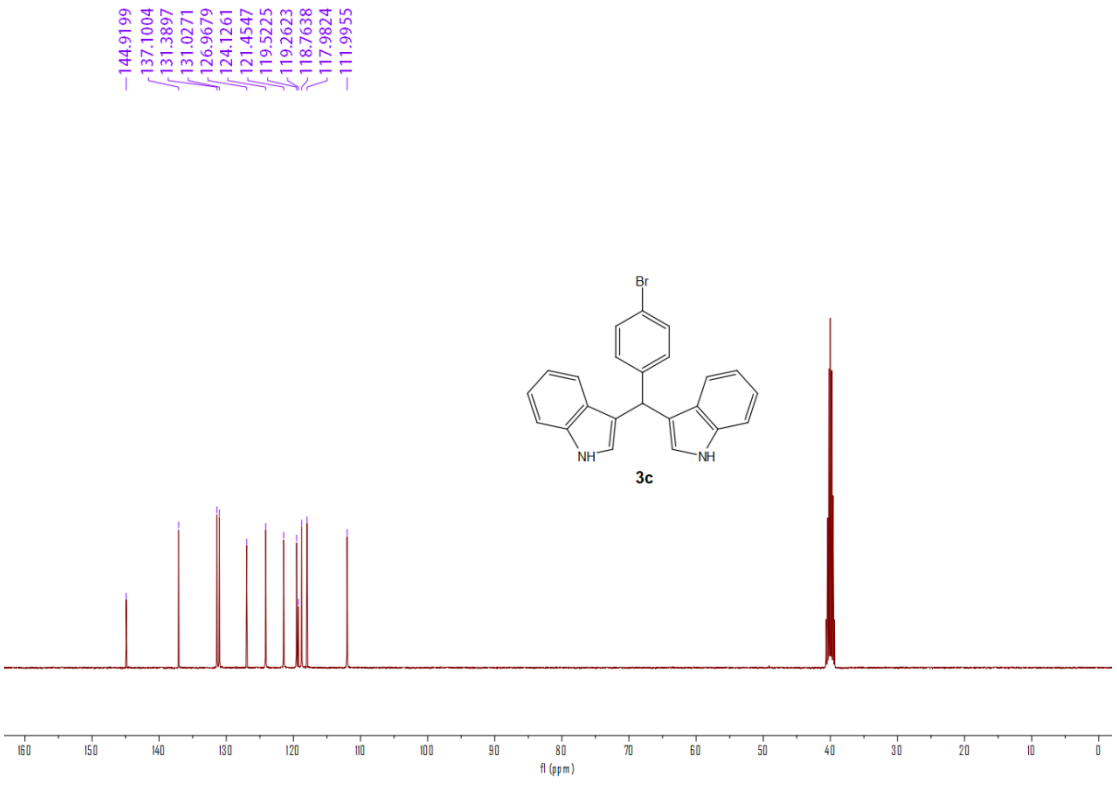
f1 (ppm)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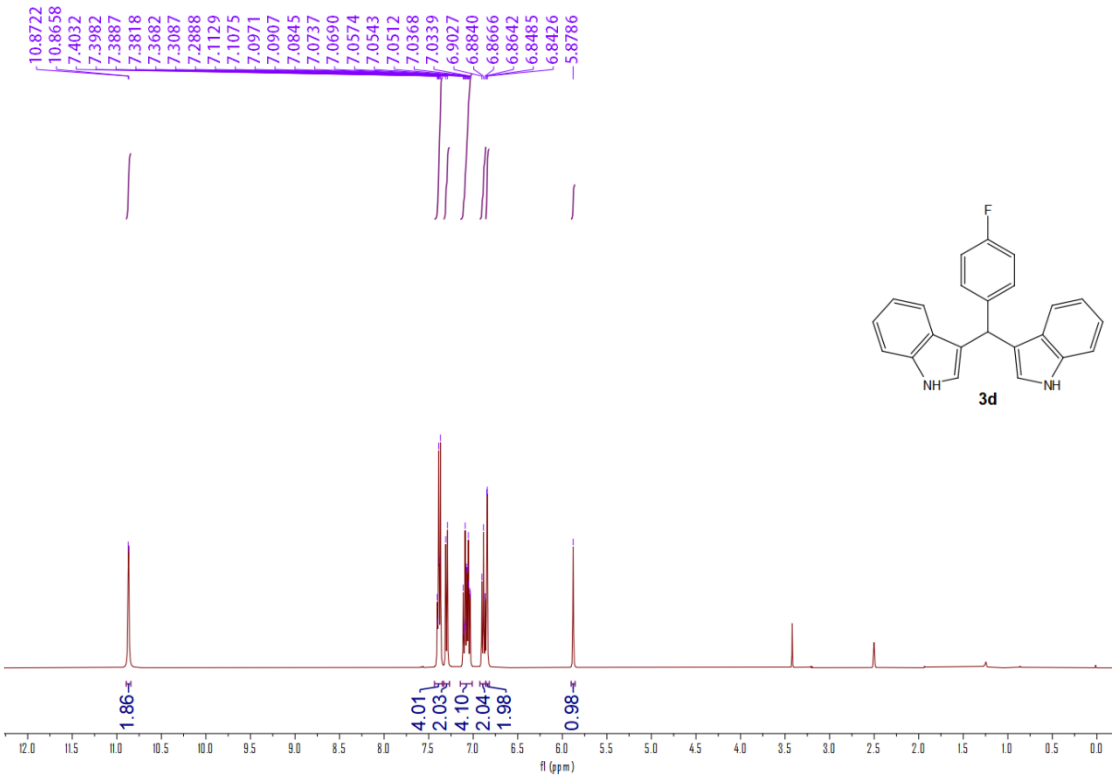
NH
3c
f1 (ppm)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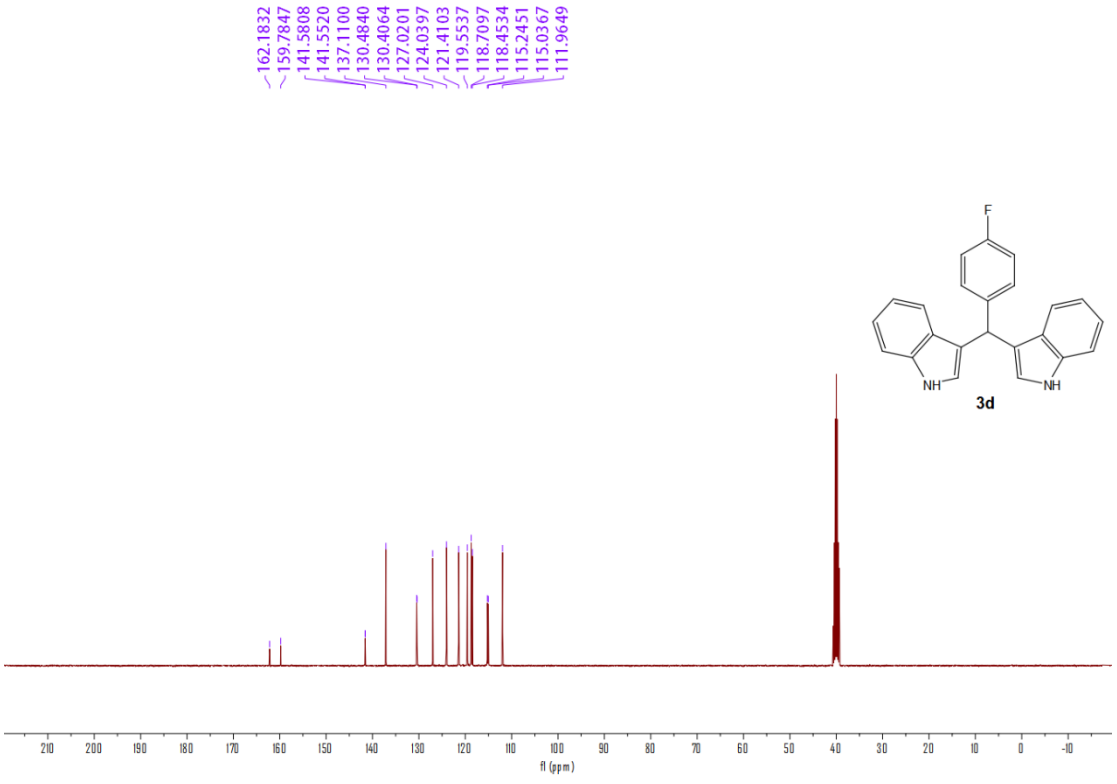
0.98
f1 (ppm)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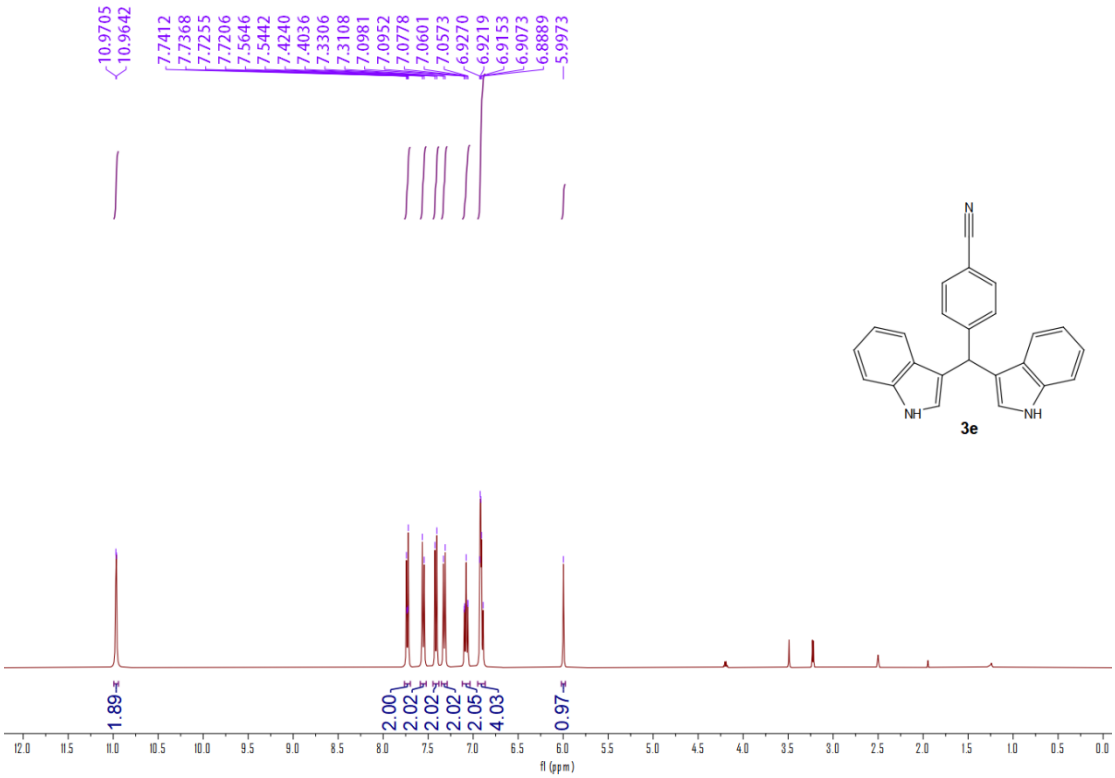
NH
3d
f1 (ppm)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7.3108
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7.0952
7.0778
7.0601
7.0573
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6.9153
6.9073
6.8889
5.9973
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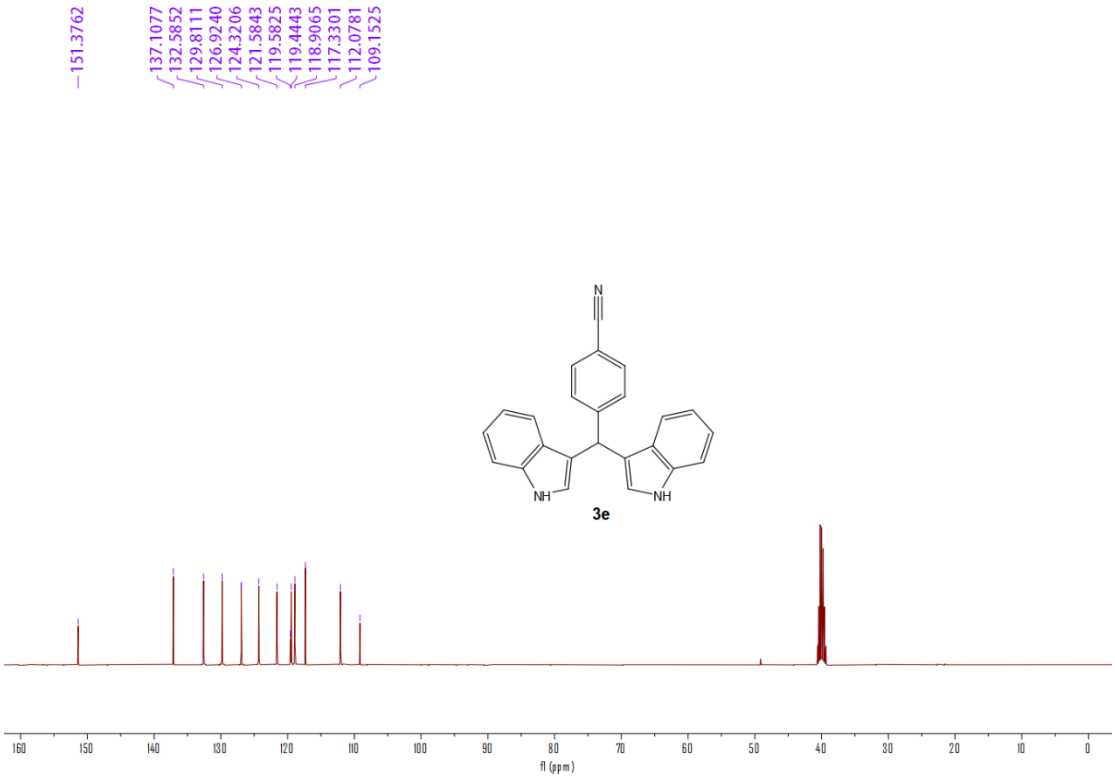
f1 (ppm)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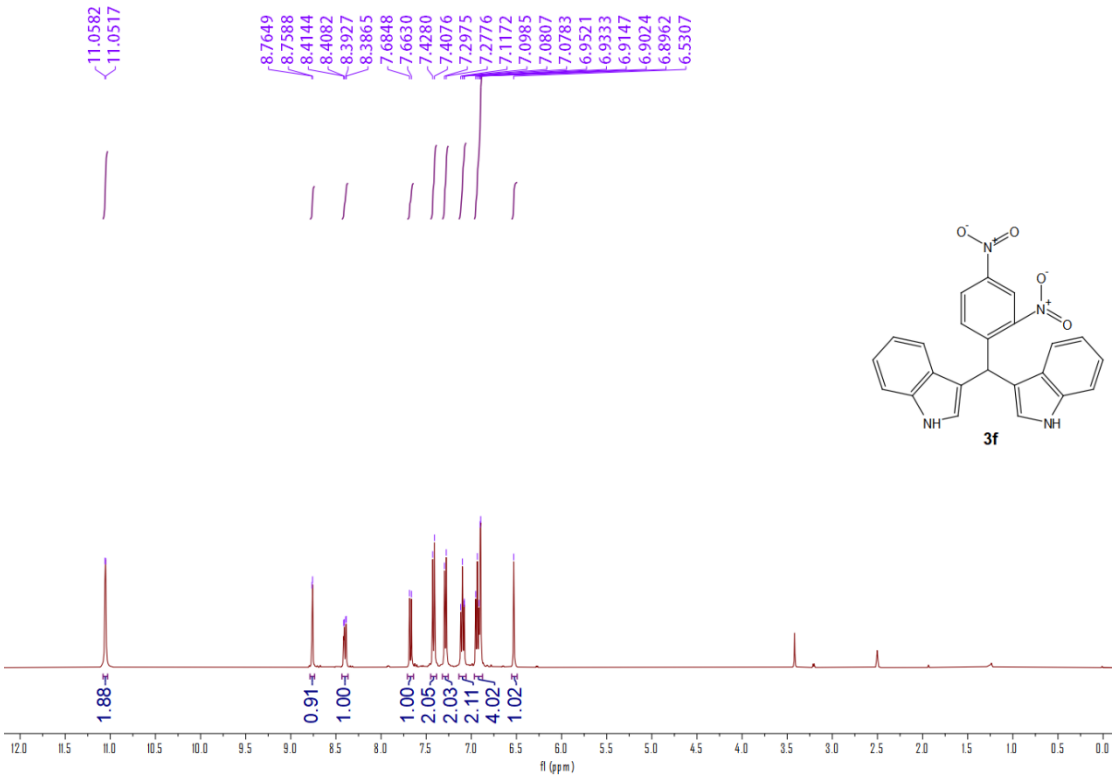
NH
NH
3e
f1 (ppm)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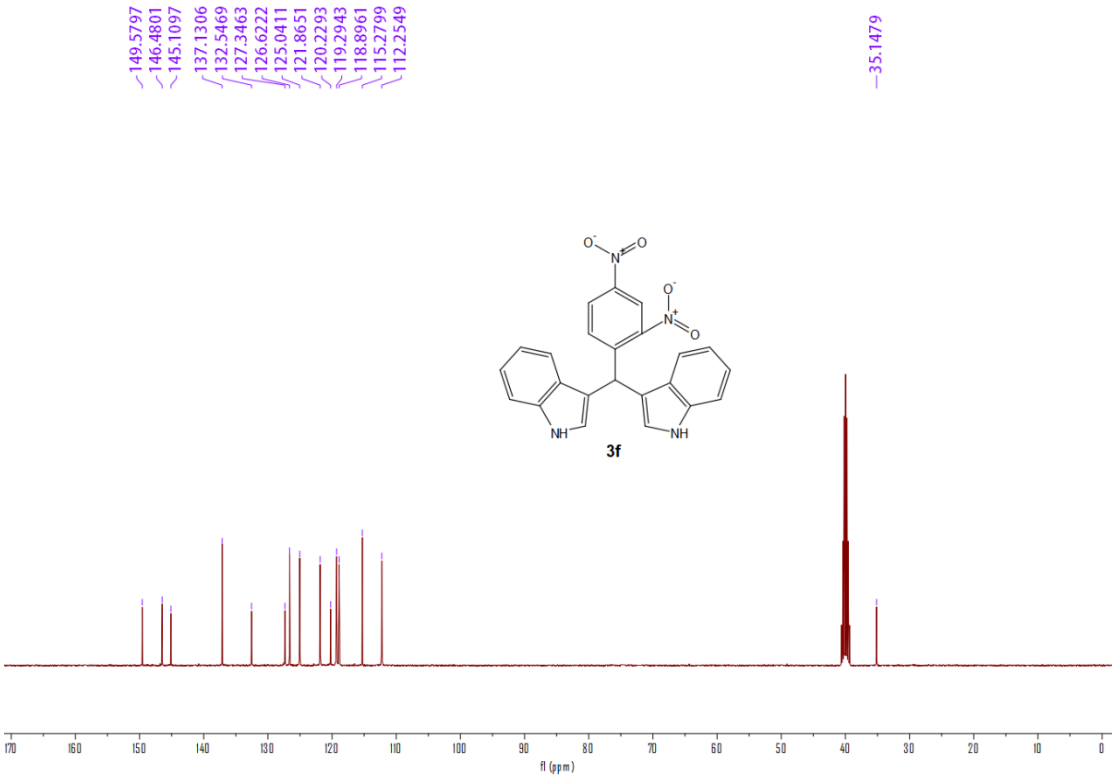
f1 (ppm)

3f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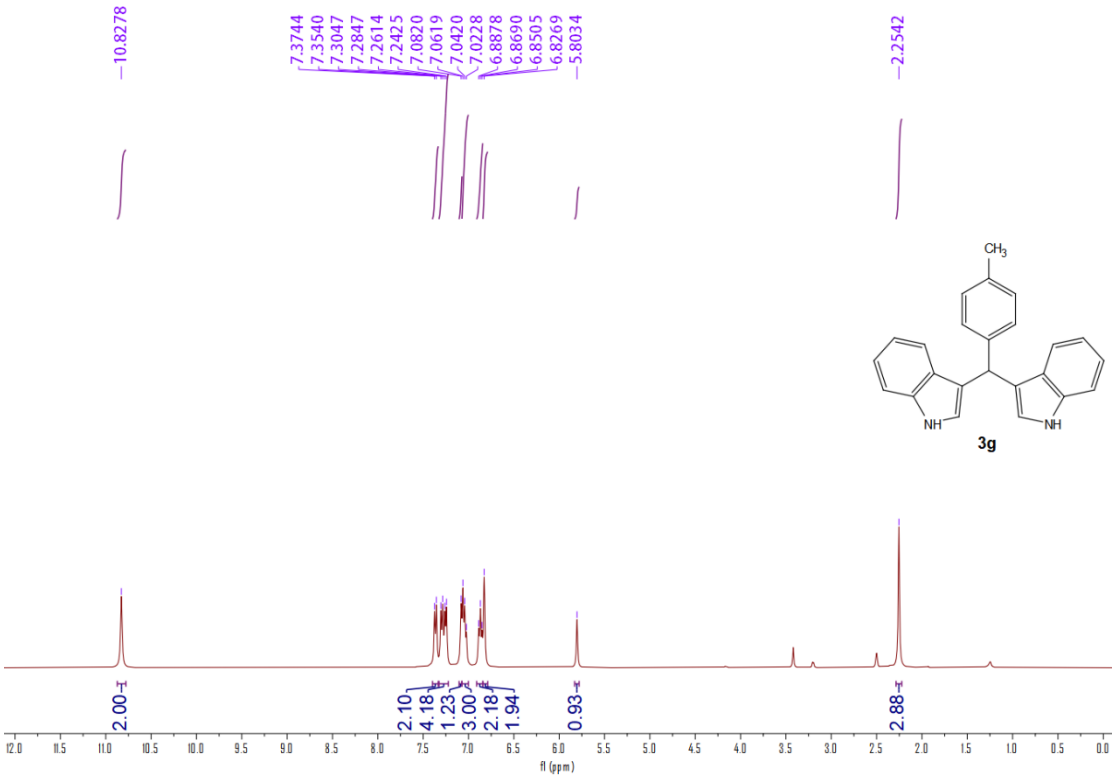
f1 (ppm)

3f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6.8269
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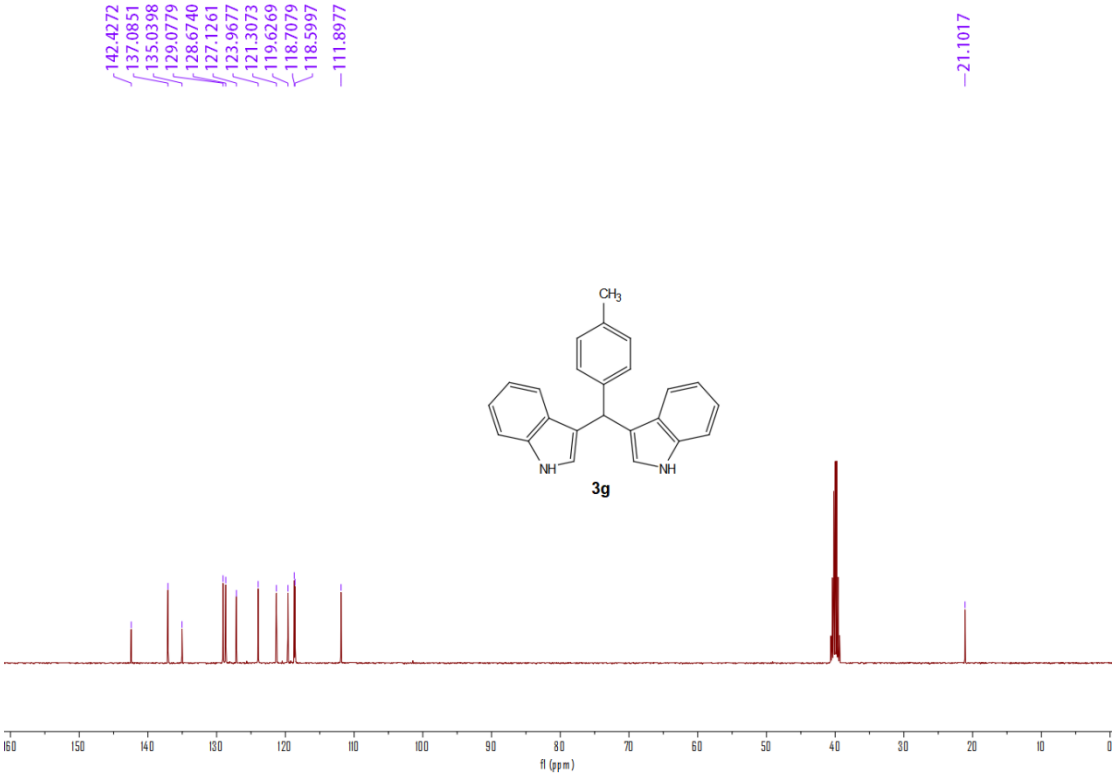
2.88
f1 (ppm)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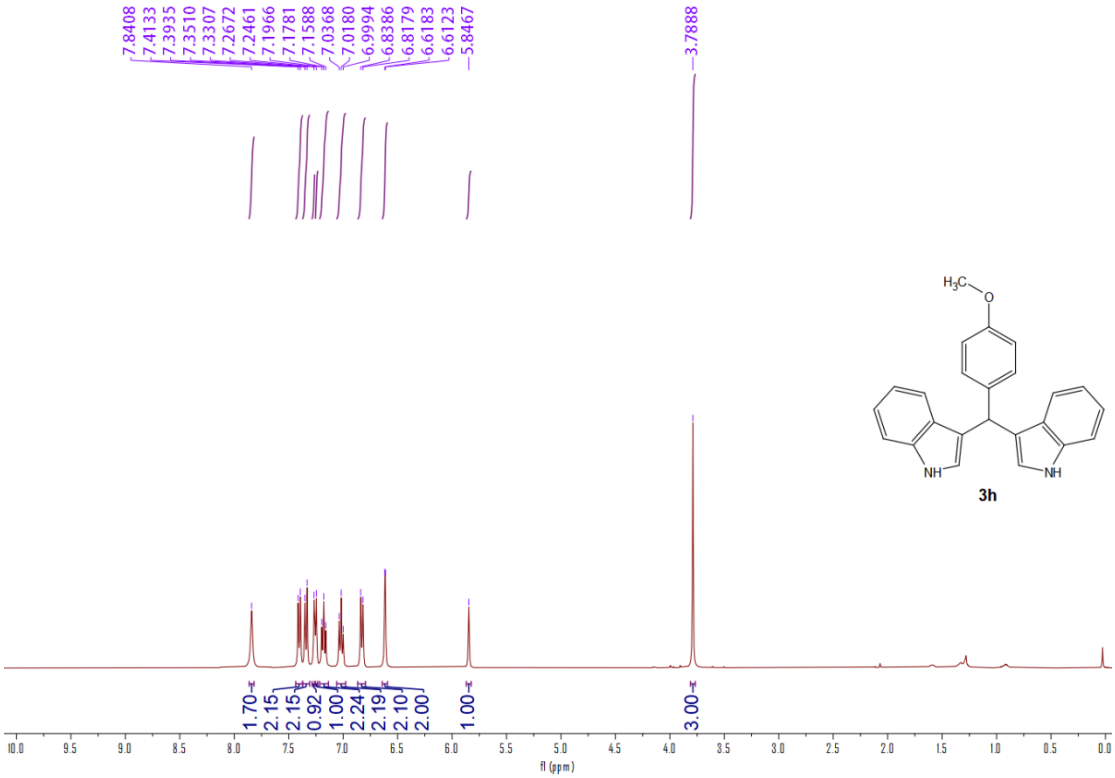
3g
f1 (ppm)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2.15
2.15
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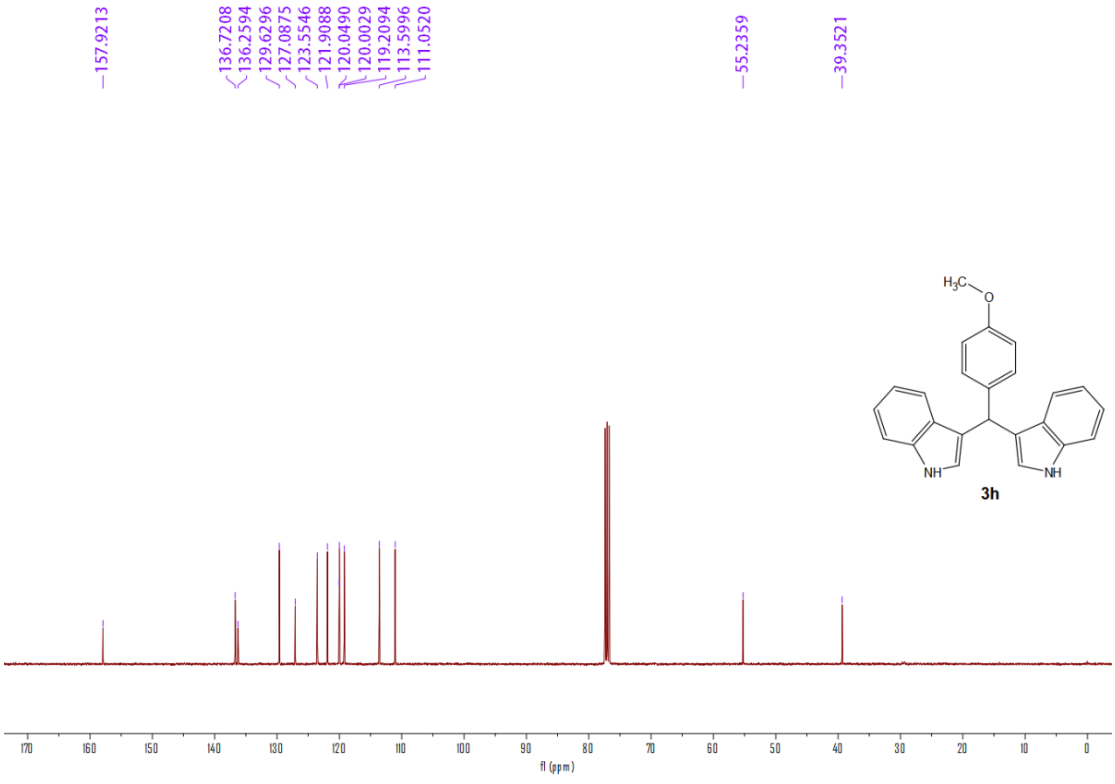
1.00
3.00
f1 (ppm)

H3C
O
NH
NH

3h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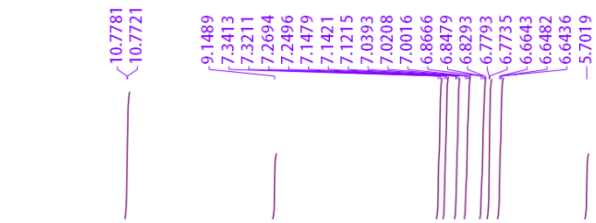
39.3521
f1 (ppm)

H3C
O
NH
NH

3h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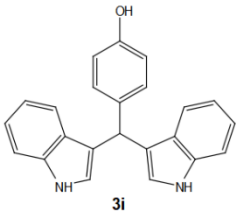
5.7019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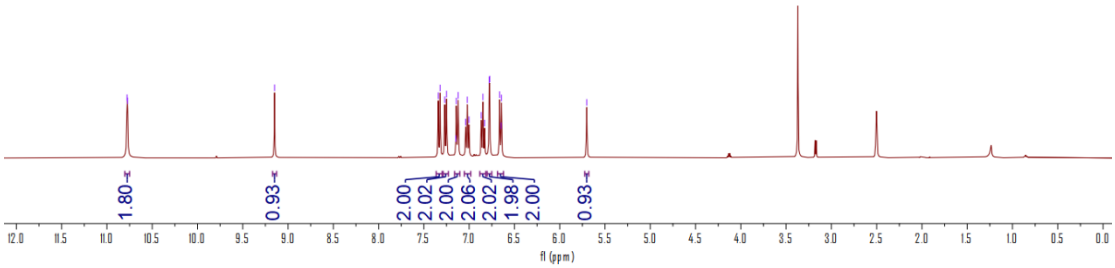
NH

3i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f1 (ppm)


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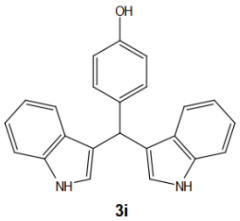
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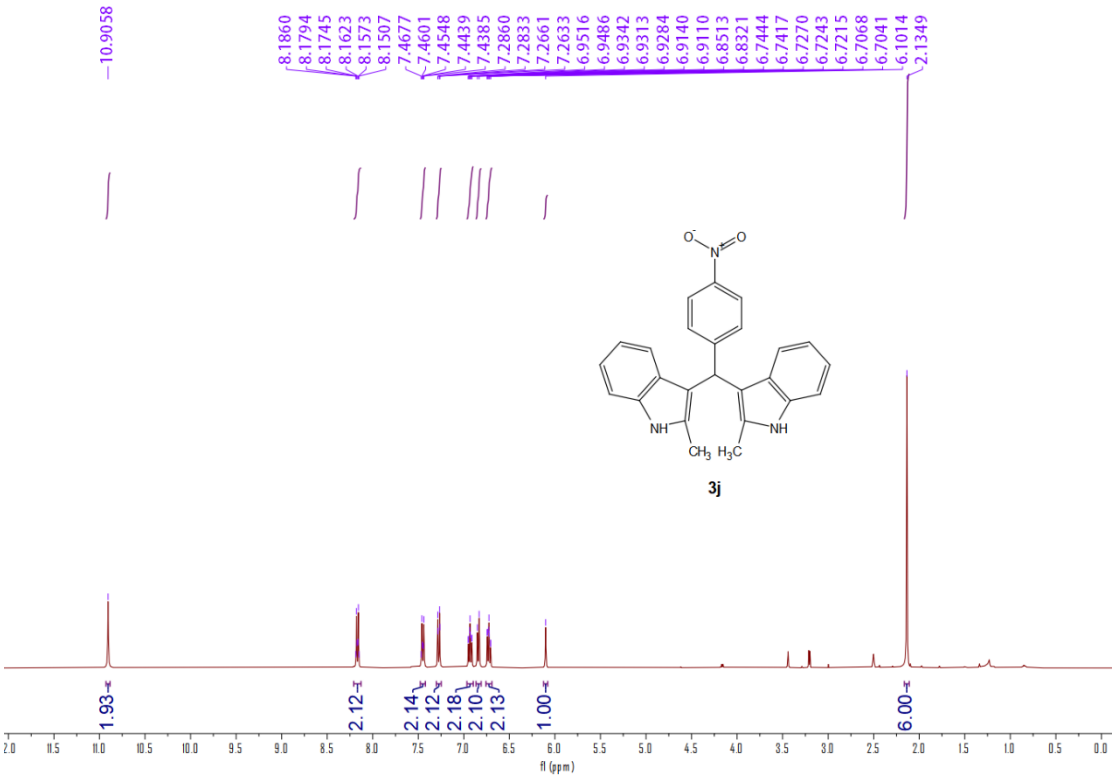
NH
NH

3i

f1 (ppm)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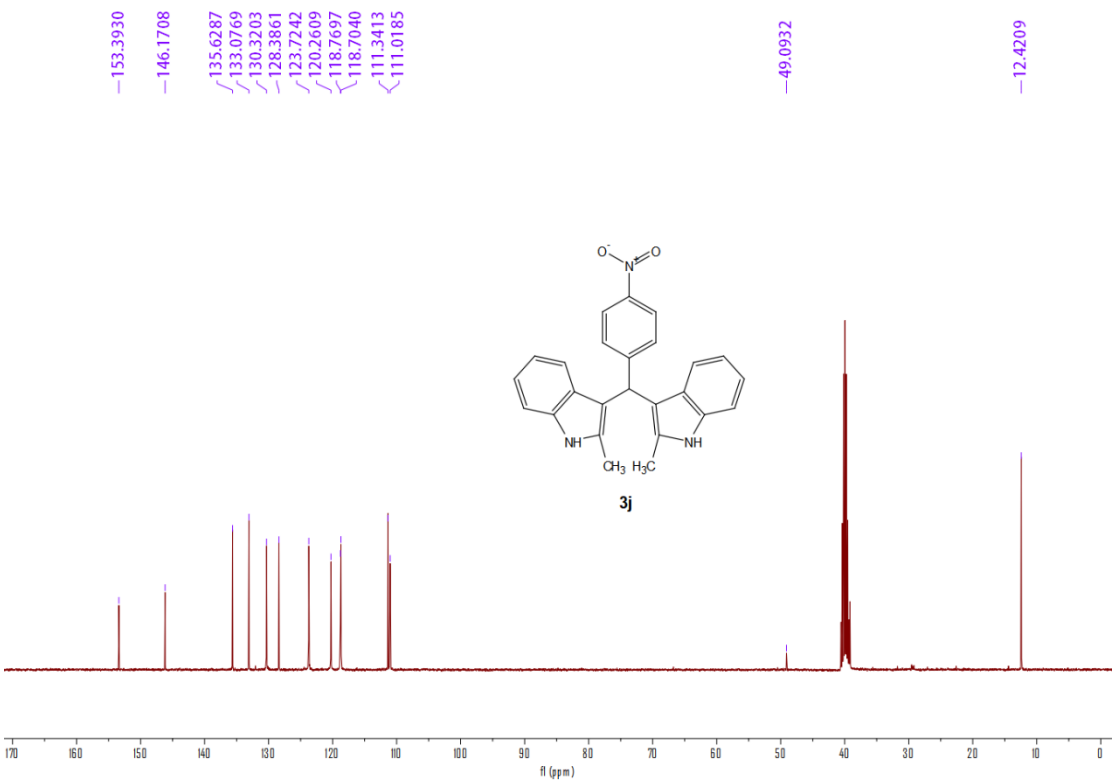
2.12
2.14
2.12
2.18
2.10
2.13
1.00
6.00
f1 (ppm)

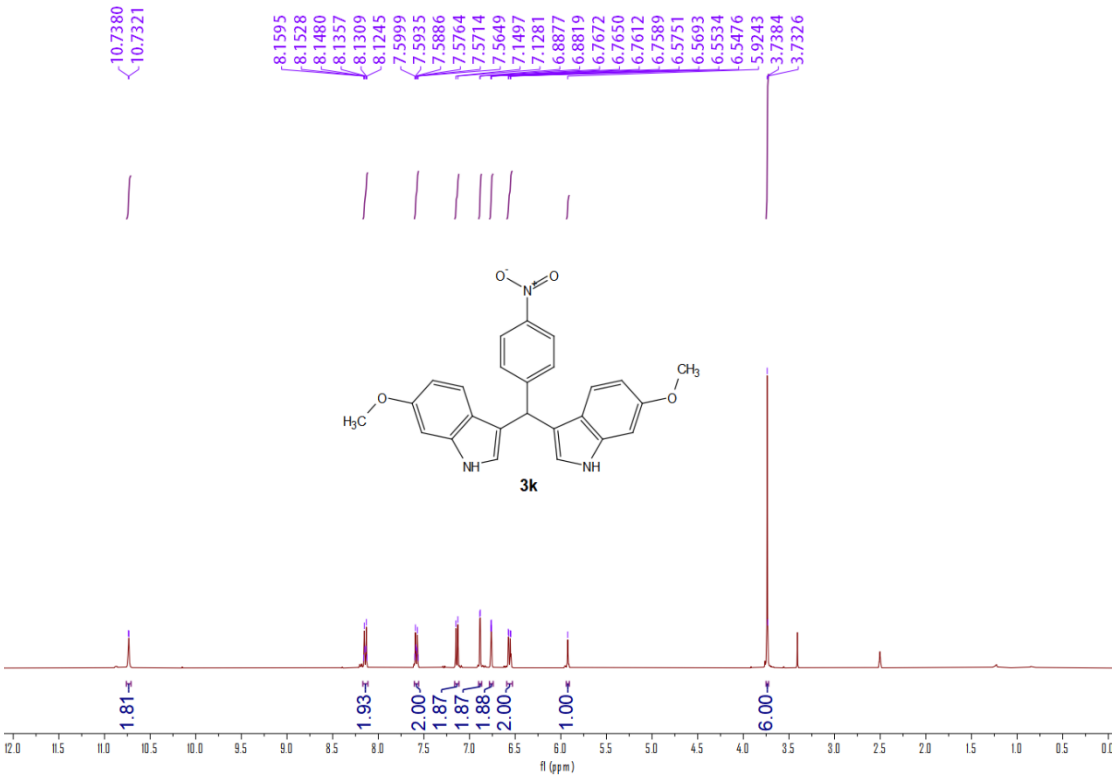
NH
NH
CH3 H3C

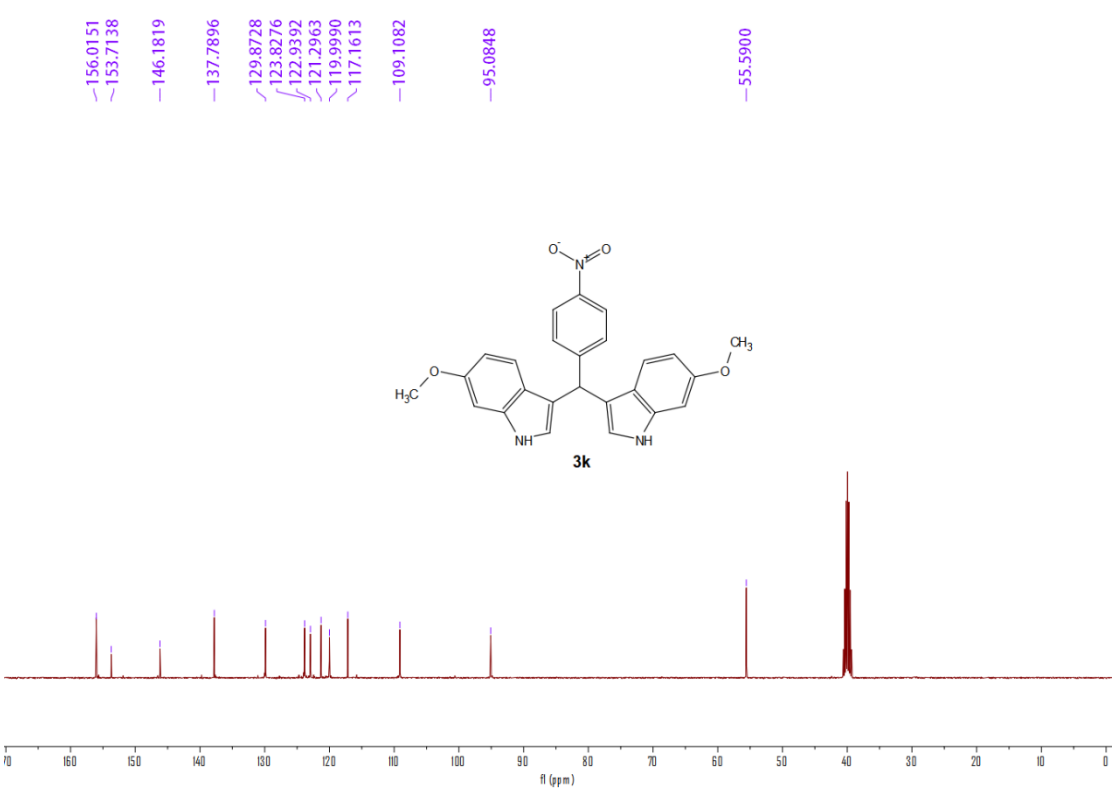
3j

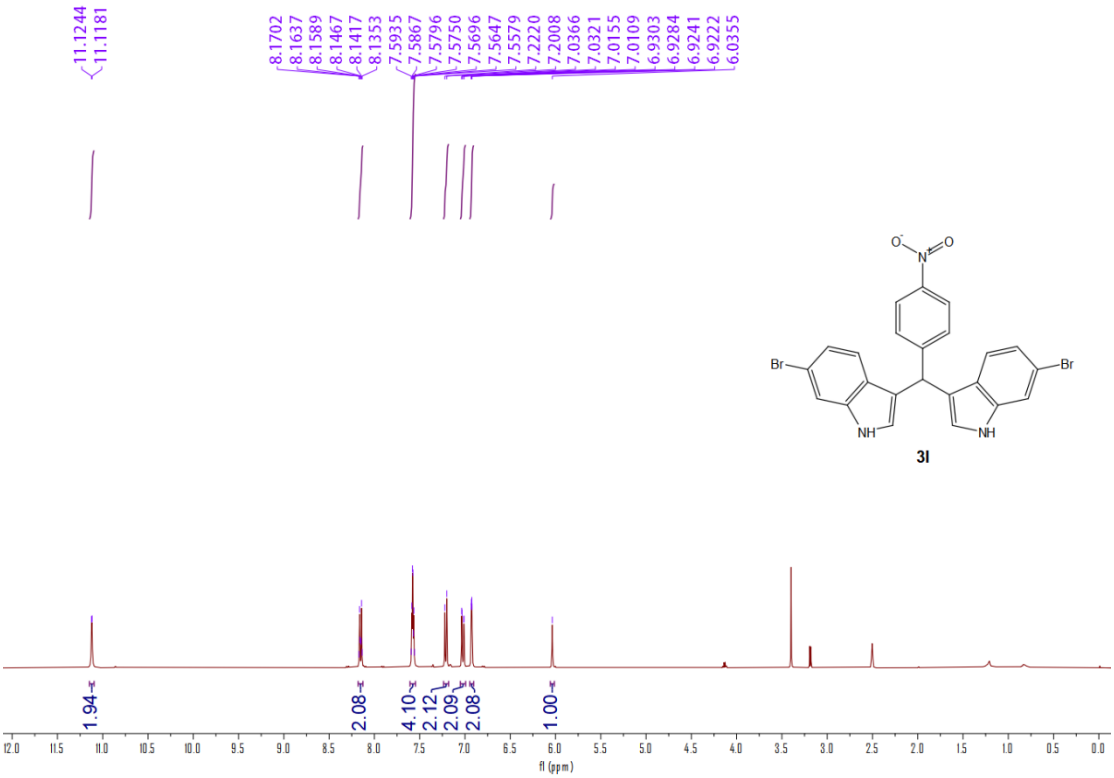

153.3930
146.1708
135.6287
133.0769
130.3203
128.3861
123.7242
120.2609
118.7697
118.7040
111.3413
111.0185
49.0932
12.4209
f1 (ppm)

NH
NH
CH3 H3C

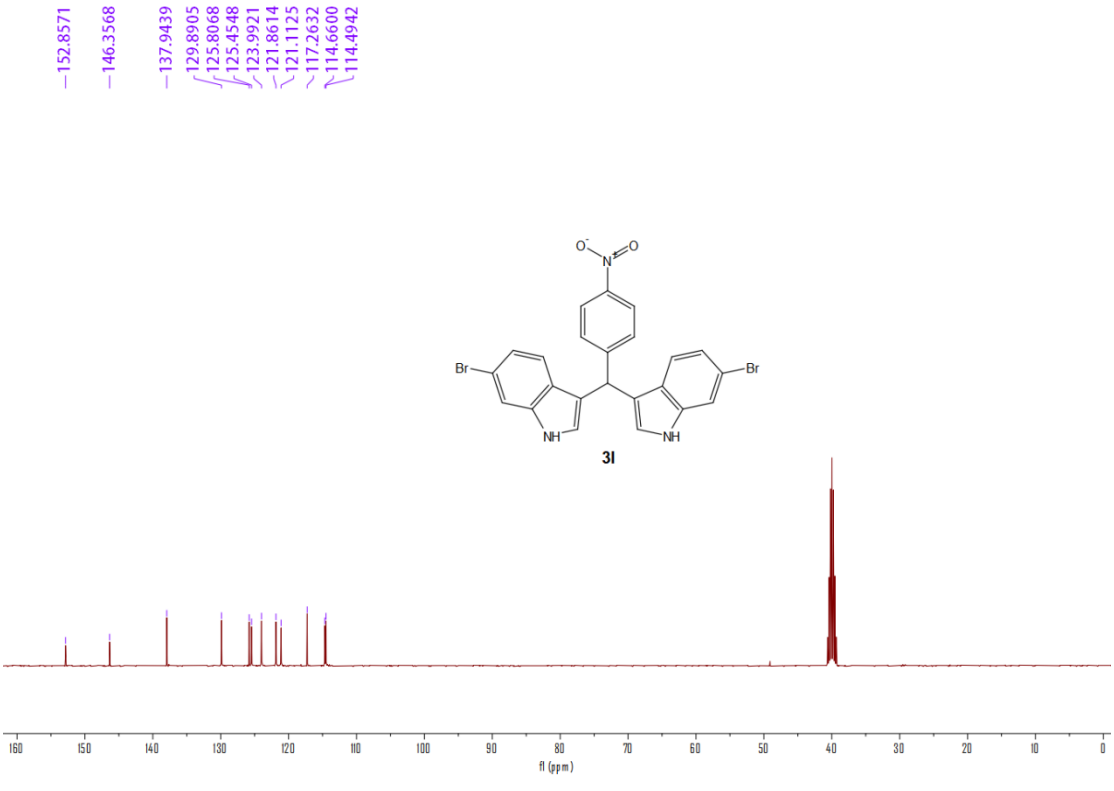
3j


10.7380
10.7321
8.1595
8.1528
8.1480
8.1357
8.1309
8.1245
7.5999
7.5935
7.5886
7.5764
7.5714
7.5649
7.1497
7.1281
6.8877
6.8819
6.7672
6.7650
6.7612
6.7589
6.5751
6.5693
6.5534
6.5476
5.9243
3.7384
3.7326
3k
1.81
1.93
2.00
1.87
1.87
1.88
2.00
1.00
6.00
f1 (ppm)

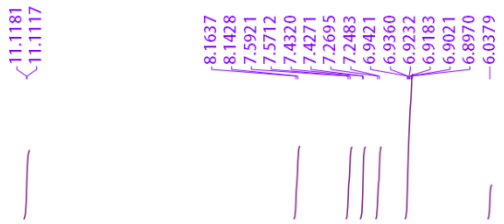

156.0151
153.7138
146.1819
137.7896
129.8728
123.8276
122.9392
121.2963
119.9990
117.1613
109.1082
95.0848
55.5900
3k
f1 (ppm)

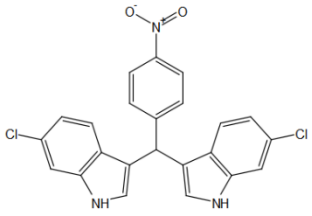

11.1244
11.1181
8.1702
8.1637
8.1589
8.1467
8.1417
8.1353
7.5935
7.5867
7.5796
7.5750
7.5696
7.5647
7.5579
7.2220
7.2008
7.0366
7.0321
7.0155
7.0109
6.9303
6.9284
6.9241
6.9222
6.0355
Br
Br
NH
NH
1.94
2.08
4.10
2.12
2.09
2.08
1.00
f1 (ppm)

3l

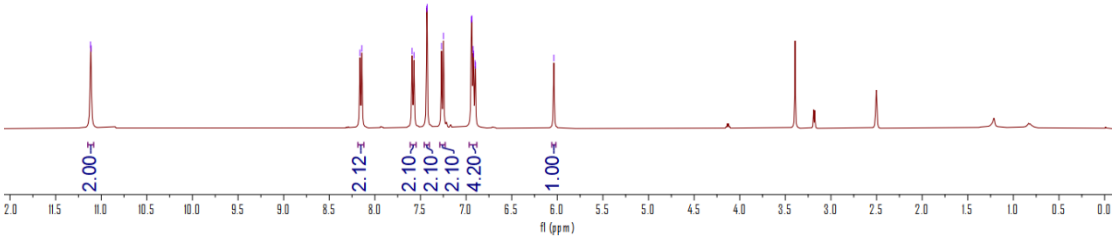

152.8571
146.3568
137.9439
129.8905
125.8068
125.4548
123.9921
121.8614
121.1125
117.2632
114.6600
114.4942
Br
Br
NH
NH
f1 (ppm)

3l

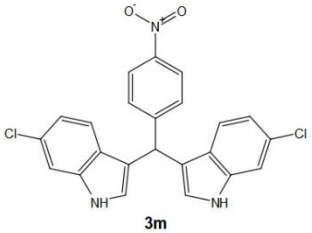

11.1181
11.1117
8.1637
8.1428
7.5921
7.5712
7.4320
7.4271
7.2695
7.2483
6.9421
6.9360
6.9232
6.9183
6.9021
6.8970
6.0379


O
N
O
Cl
Cl
NH
NH

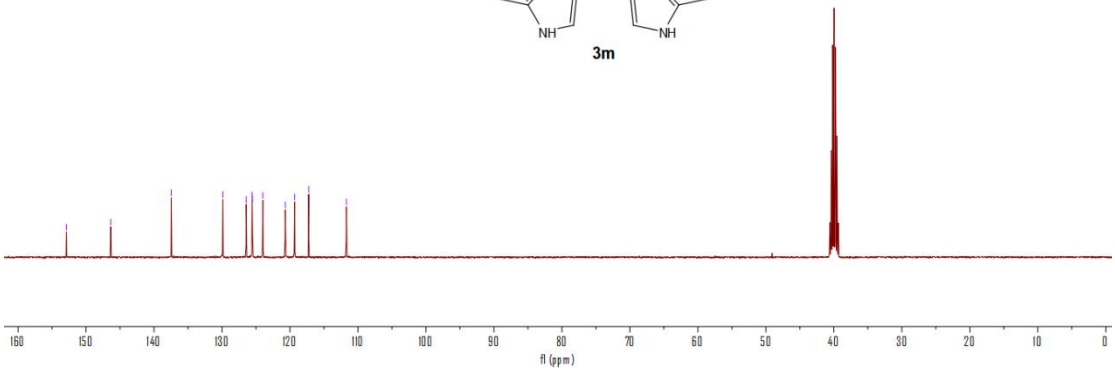
3m


2.00
2.12
2.10
2.10
2.10
4.20
1.00
f1 (ppm)

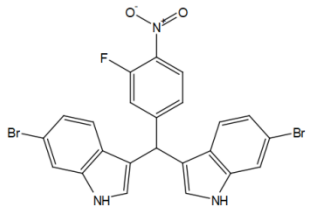

152.8930
146.3567
137.4468
129.8894
126.4497
125.5731
125.5217
123.9905
120.6972
119.3167
117.2460
111.7045


O
N
O
Cl
Cl
NH
NH

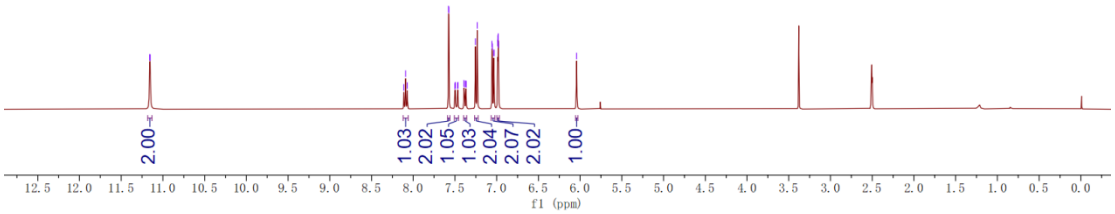
3m

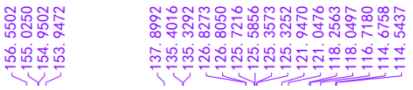

f1 (ppm)

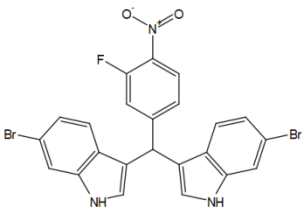

11.1588
11.1526
8.1126
8.0920
8.0715
7.5774
7.5730
7.5005
7.4961
7.4692
7.4647
7.3919
7.3874
7.3704
7.3660
7.2545
7.2333
7.0564
7.0519
7.0353
7.0307
6.9876
6.9855
6.9815
6.9792
6.9420


O
N
O
F
Br
Br
NH
NH

3n

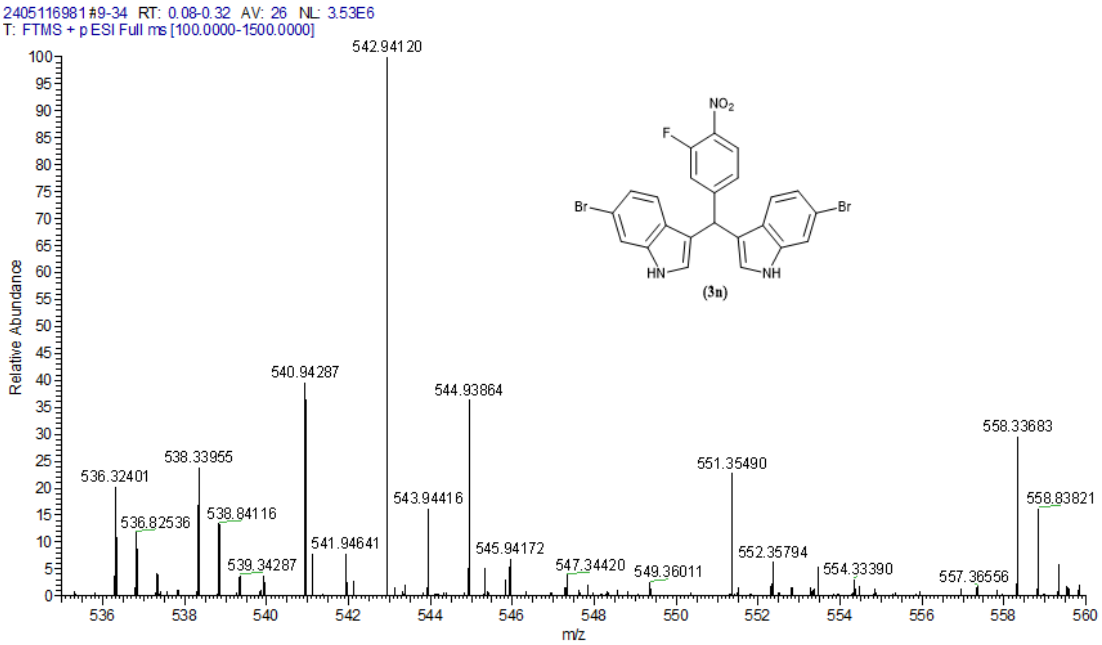

2.00
1.03
2.02
1.05
1.03
2.04
2.07
2.02
1.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.5502
155.0250
154.9502
153.9472
137.8992
135.4016
135.3292
126.8273
126.8050
125.7216
125.5856
125.3573
125.3252
121.9470
121.0476
118.2563
118.0497
116.7180
114.6758
114.5437

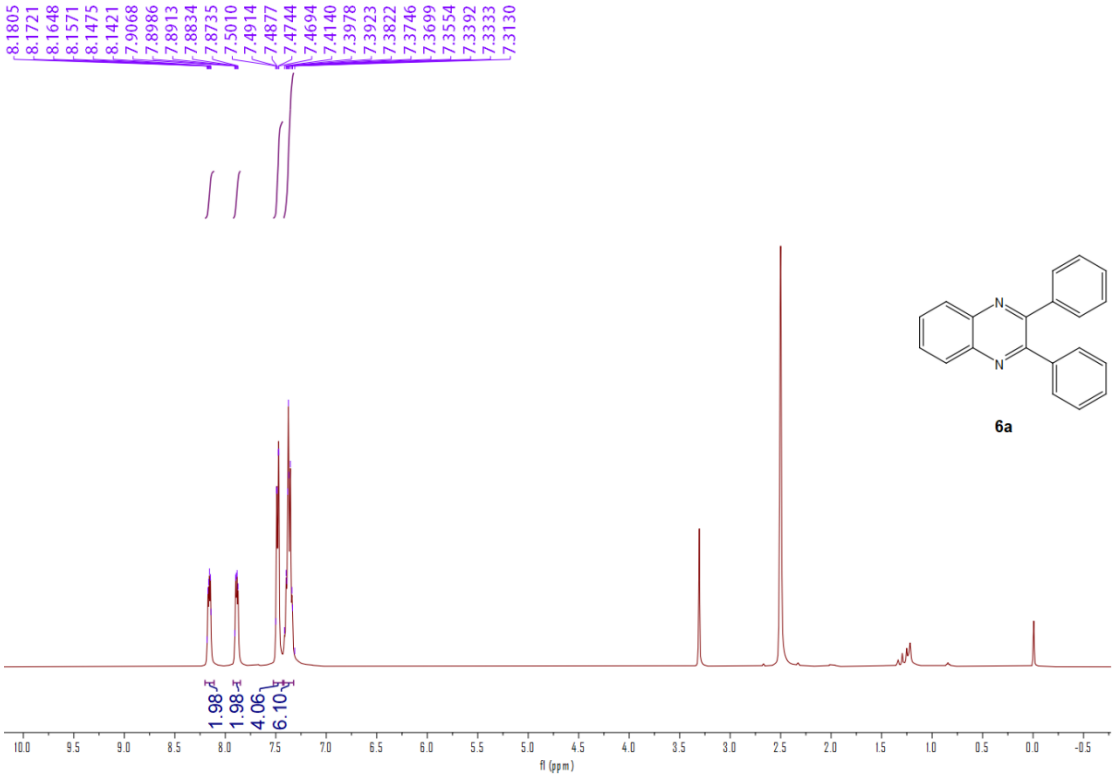

O
N
O
F
Br
Br
NH
NH

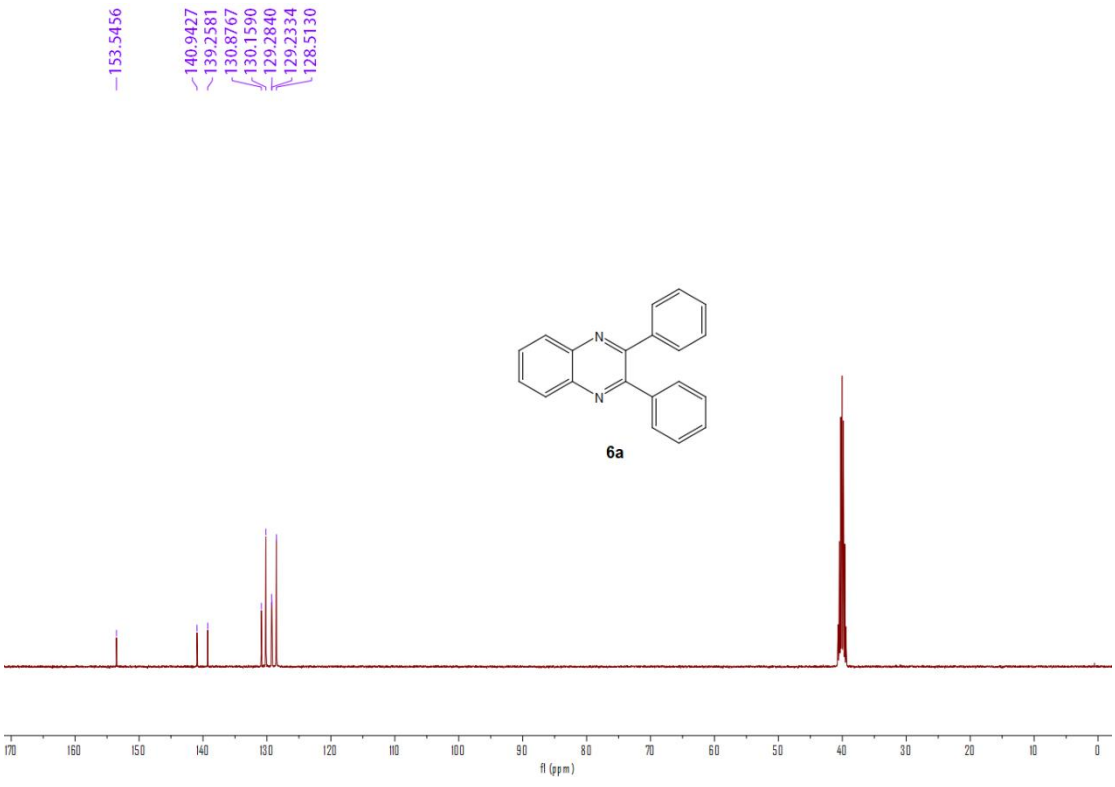
3n

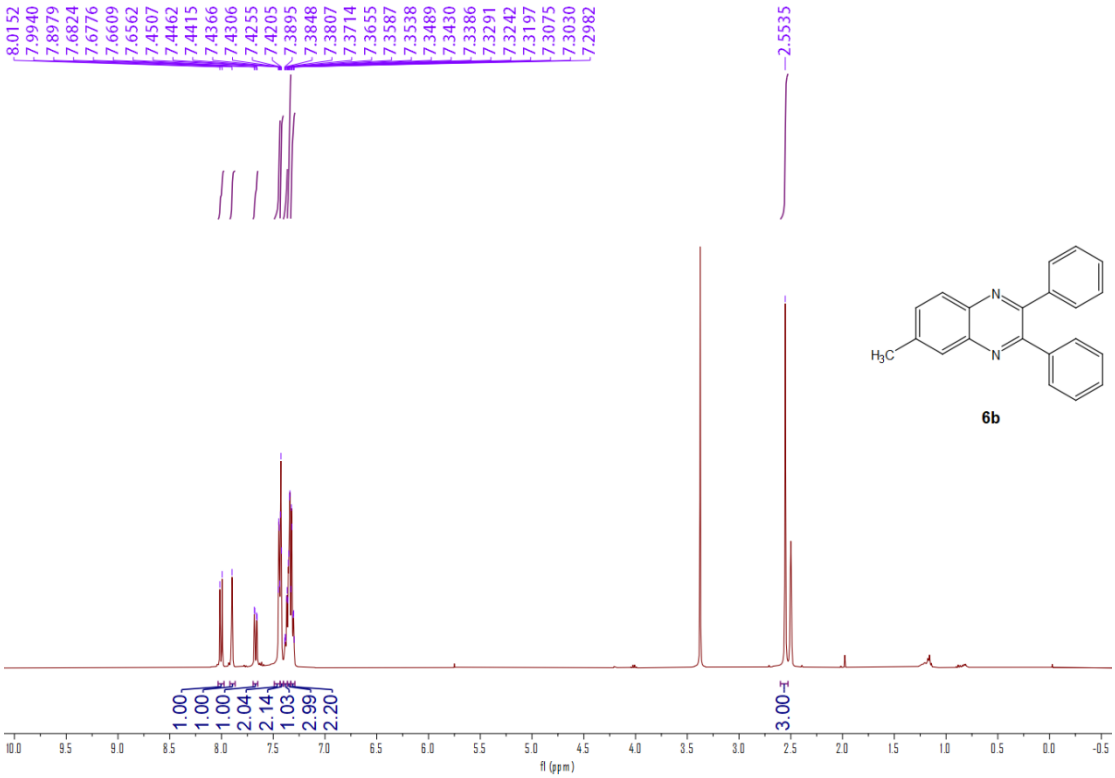
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30
f1 (ppm)


2405116981#9-34 RT: 0.08-0.32 AV: 26 NL: 3.53E6
T: FTMS + p ESI Full ms [100.0000-1500.0000]
542.94120
540.94287
544.93864
538.33955
536.32401
543.94416
538.84116
536.82536
541.94641
539.34287
545.94172
547.34420
549.36011
551.35490
552.35794
554.33390
557.36556
558.33683
558.83821
Relative Abundance
m/z
NO2
F
Br
Br
HN
NH
(3n)

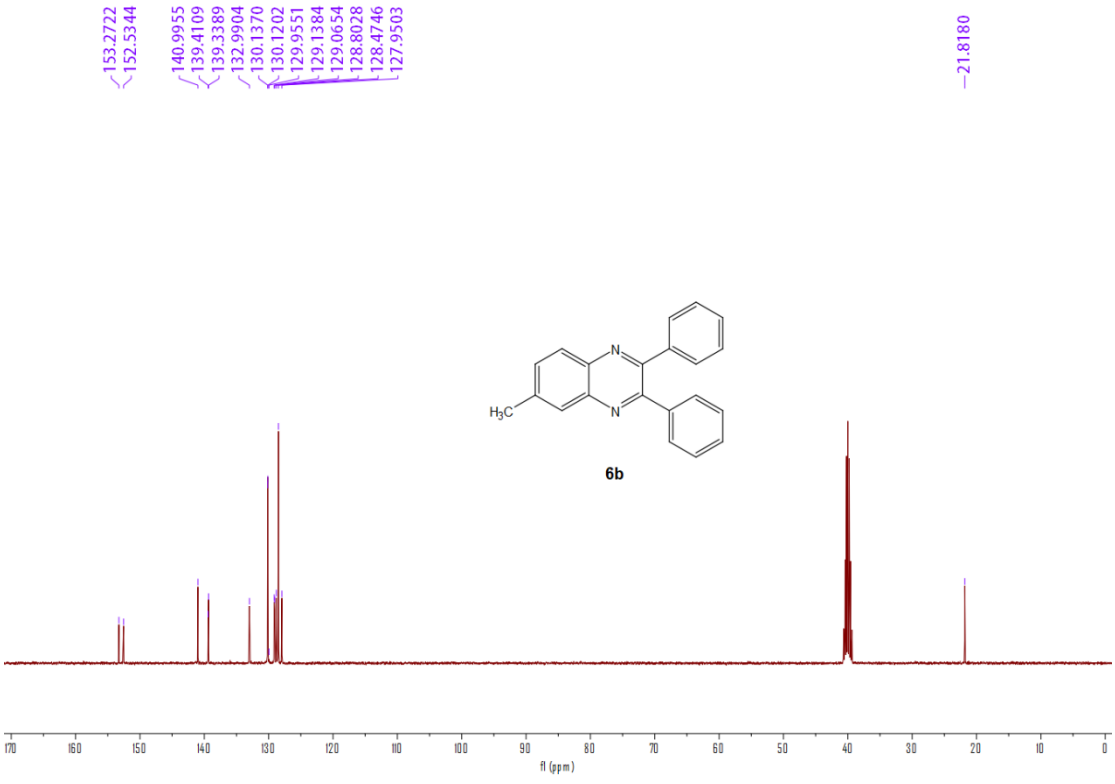
Reaction II


8.1805
8.1721
8.1648
8.1571
8.1475
8.1421
7.9068
7.8986
7.8913
7.8834
7.8735
7.5010
7.4914
7.4877
7.4744
7.4694
7.4140
7.3978
7.3923
7.3822
7.3746
7.3699
7.3554
7.3392
7.3333
7.3130
1.98
1.98
4.06
6.10
f1 (ppm)
6a

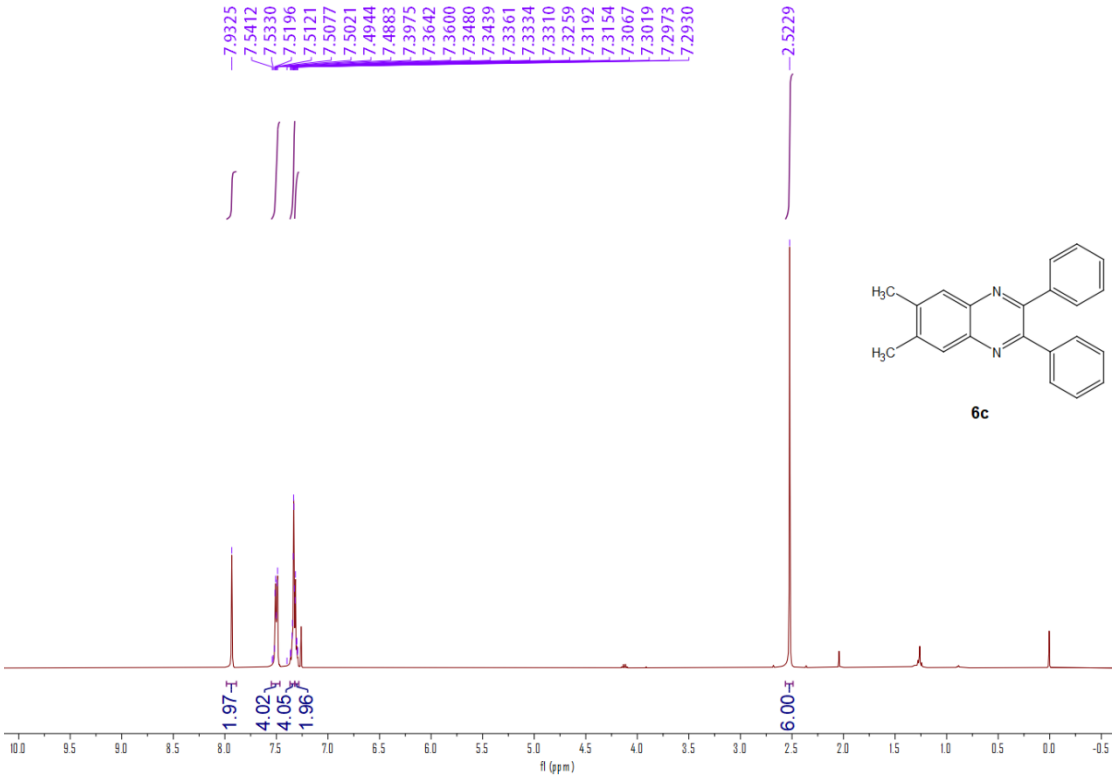

153.5456
140.9427
139.2581
130.8767
130.1590
129.2840
129.2334
128.5130
f1 (ppm)
6a


8.0152
7.9940
7.8979
7.6824
7.6776
7.6609
7.6562
7.4507
7.4462
7.4415
7.4366
7.4306
7.4255
7.4205
7.3895
7.3848
7.3807
7.3714
7.3655
7.3587
7.3538
7.3489
7.3430
7.3386
7.3291
7.3242
7.3197
7.3075
7.3030
7.2982
2.5535
1.00
1.00
1.00
2.04
2.14
1.03
2.99
2.20
3.00
f1 (ppm)

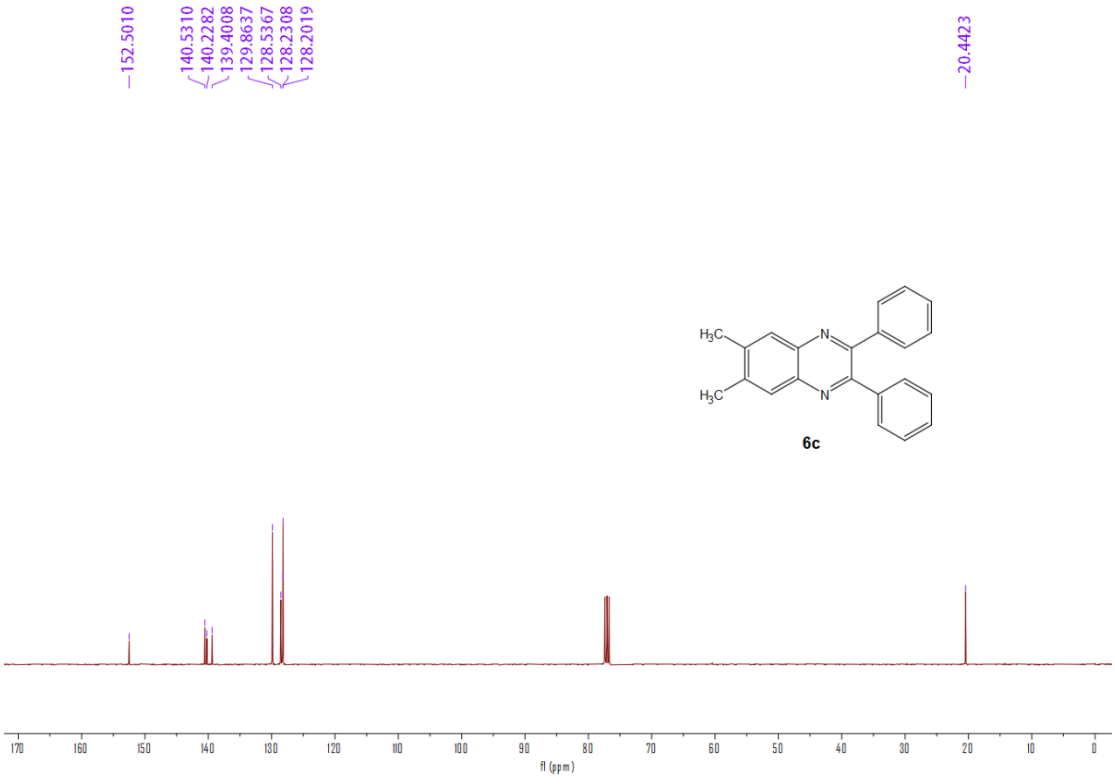
6b


153.2722
152.5344
140.9955
139.4109
139.3389
132.9904
130.1370
130.1202
129.9551
129.1384
129.0654
128.8028
128.4746
127.9503
21.8180
f1 (ppm)

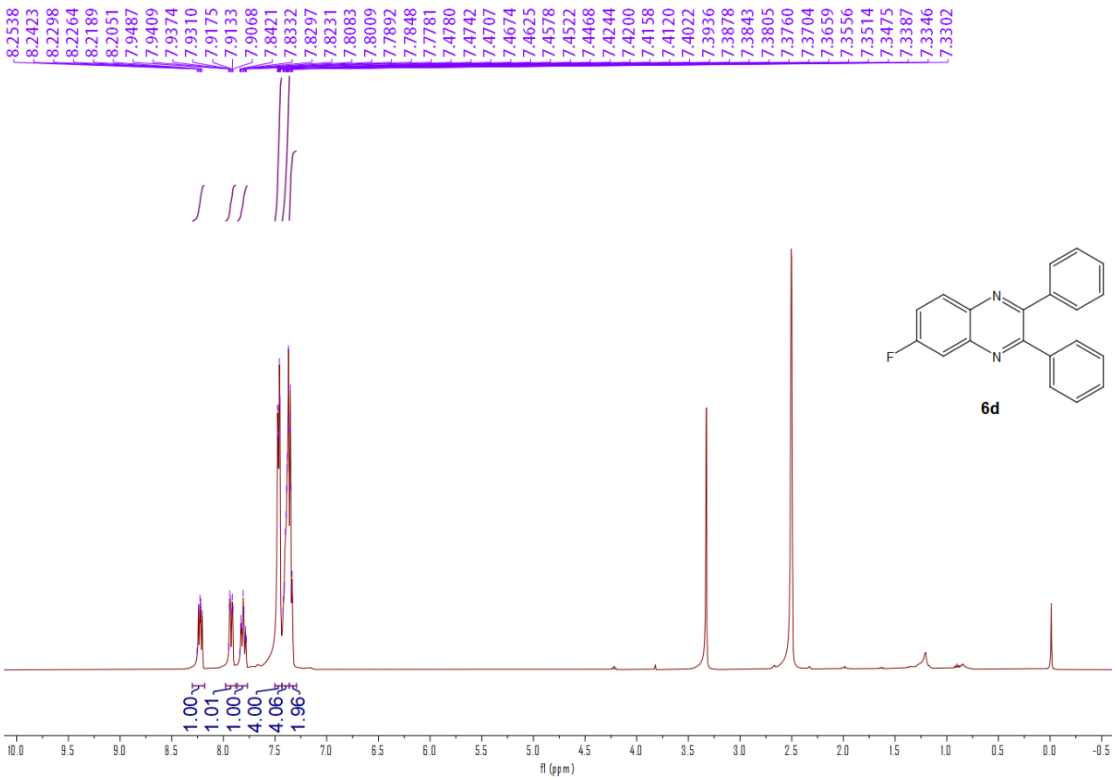
6b

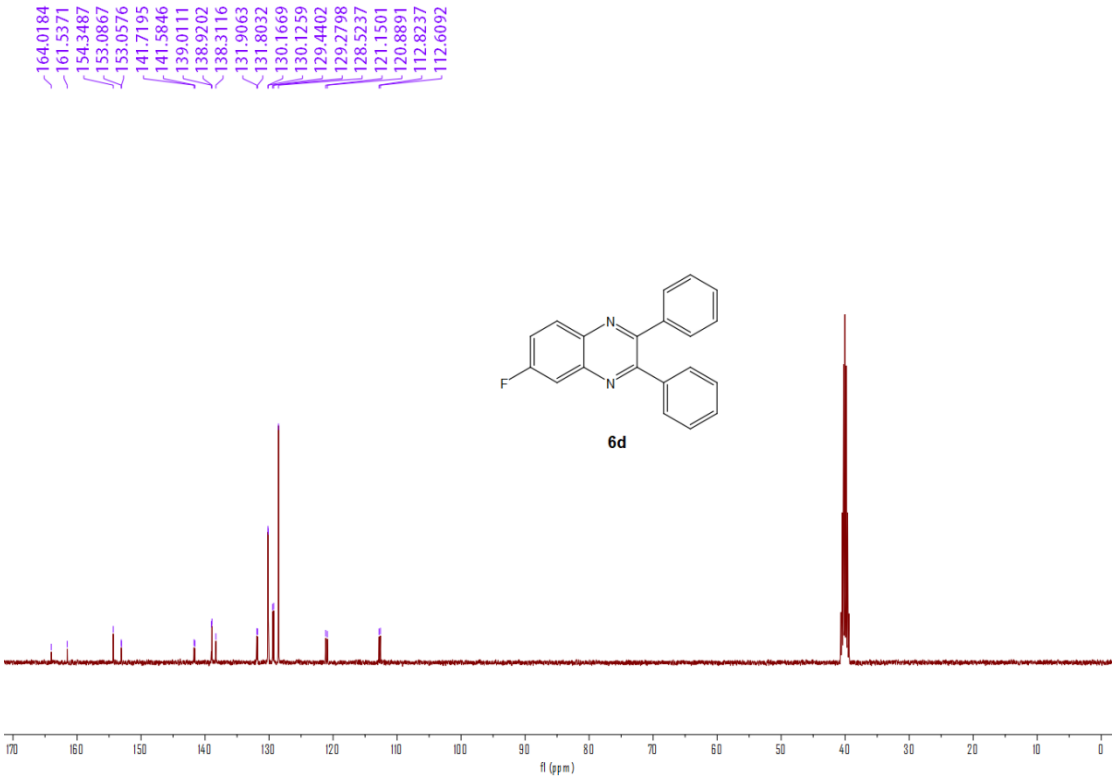

7.9325
7.5412
7.5330
7.5196
7.5121
7.5077
7.5021
7.4944
7.4883
7.3975
7.3642
7.3600
7.3480
7.3439
7.3361
7.3334
7.3310
7.3259
7.3192
7.3154
7.3067
7.3019
7.2973
7.2930
2.5229
1.97
4.02
4.05
1.96
6.00
f1 (ppm)

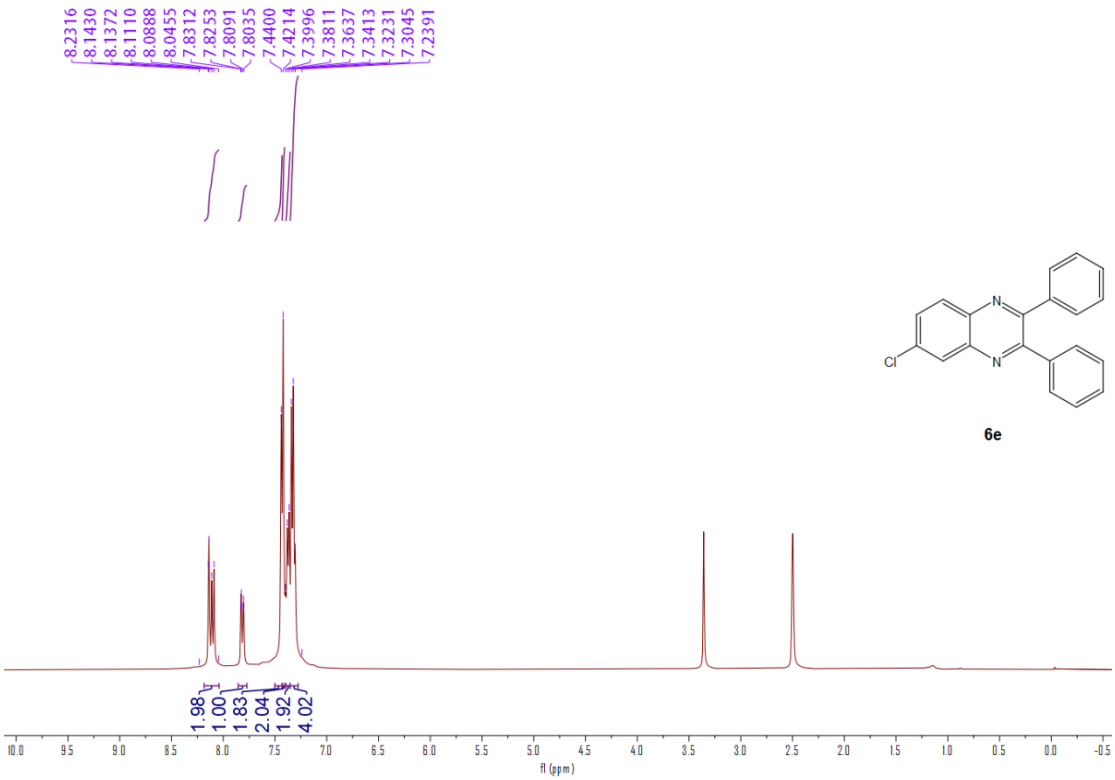
6c


152.5010
140.5310
140.2282
139.4008
129.8637
128.5367
128.2308
128.2019
20.4423
f1 (ppm)

6c

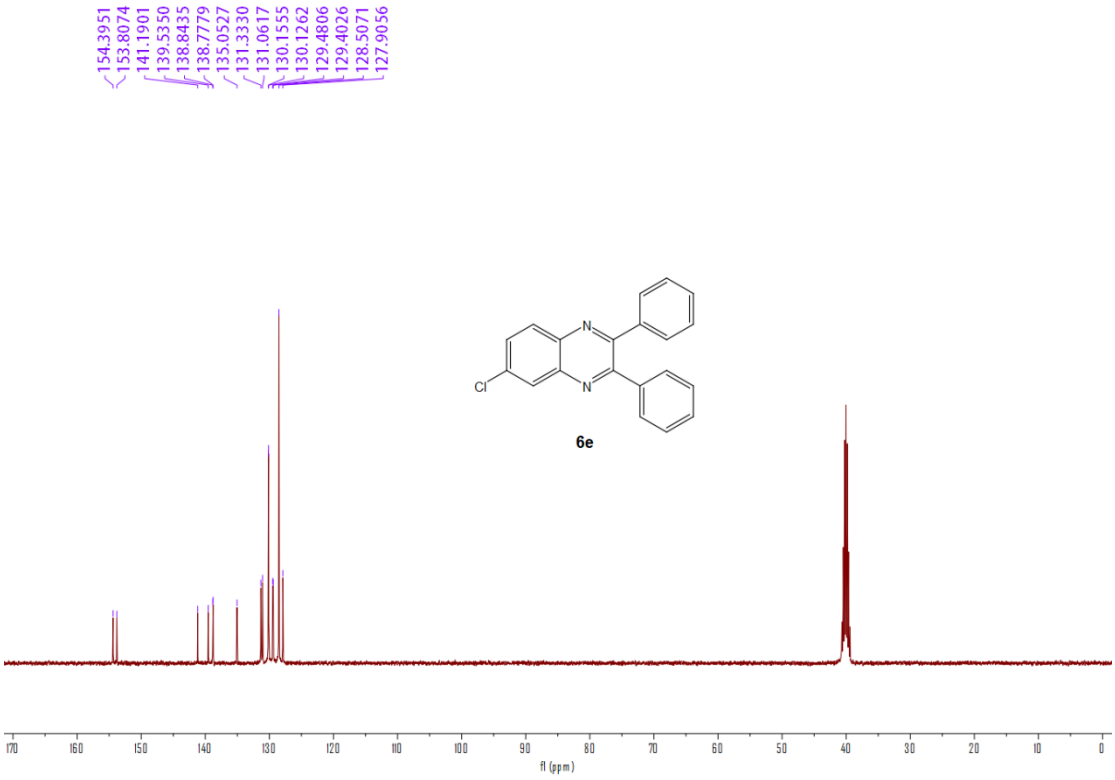

8.2538
8.2423
8.2298
8.2264
8.2189
8.2051
7.9487
7.9409
7.9374
7.9310
7.9175
7.9133
7.9068
7.8421
7.8332
7.8297
7.8231
7.8083
7.8009
7.7892
7.7848
7.7781
7.4780
7.4742
7.4707
7.4674
7.4625
7.4578
7.4522
7.4468
7.4244
7.4200
7.4158
7.4120
7.4022
7.3936
7.3878
7.3843
7.3805
7.3760
7.3704
7.3659
7.3556
7.3514
7.3475
7.3387
7.3346
7.3302
1.00
1.01
1.00
4.00
4.06
1.96
f1 (ppm)
6d


164.0184
161.5371
154.3487
153.0867
153.0576
141.7195
141.5846
139.0111
138.9202
138.3116
131.9063
131.8032
130.1669
130.1259
129.4402
129.2798
128.5237
121.1501
120.8891
112.8237
112.6092
f1 (ppm)
6d


8.2316
8.1430
8.1372
8.1110
8.0888
8.0455
7.8312
7.8253
7.8091
7.8035
7.4400
7.4214
7.3996
7.3811
7.3637
7.3413
7.3231
7.3045
7.2391
1.98
1.00
1.83
2.04
1.92
4.02
f1 (ppm)

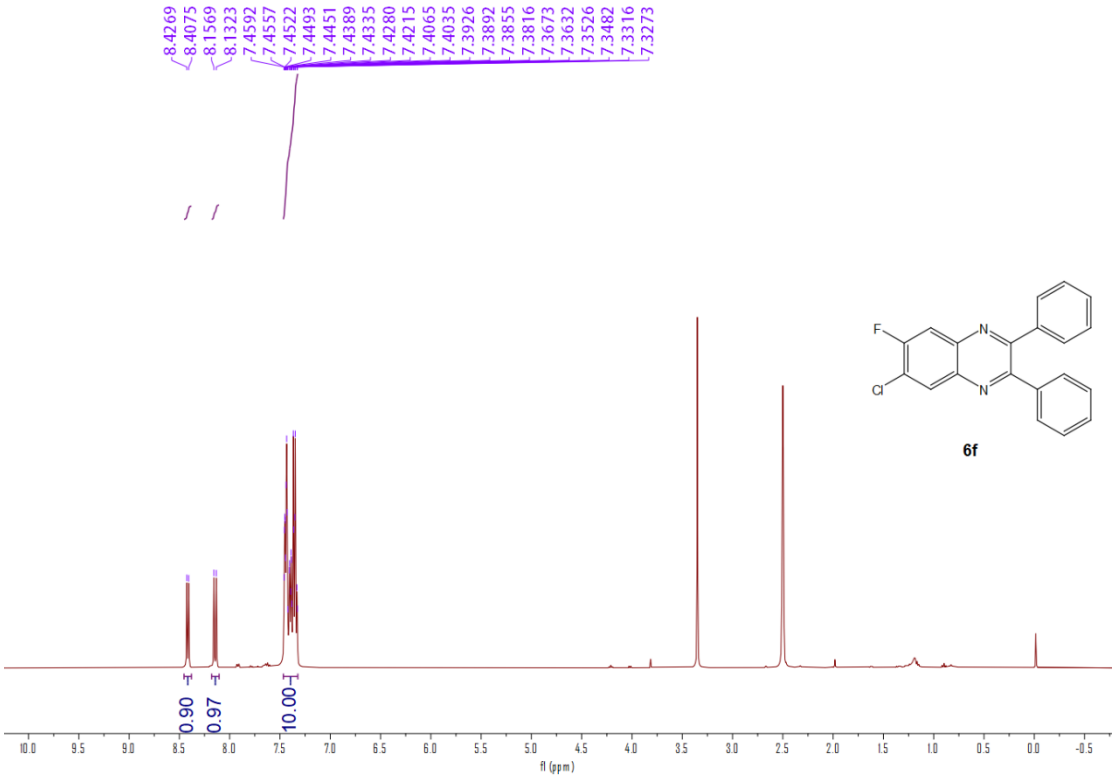
N
Cl
N

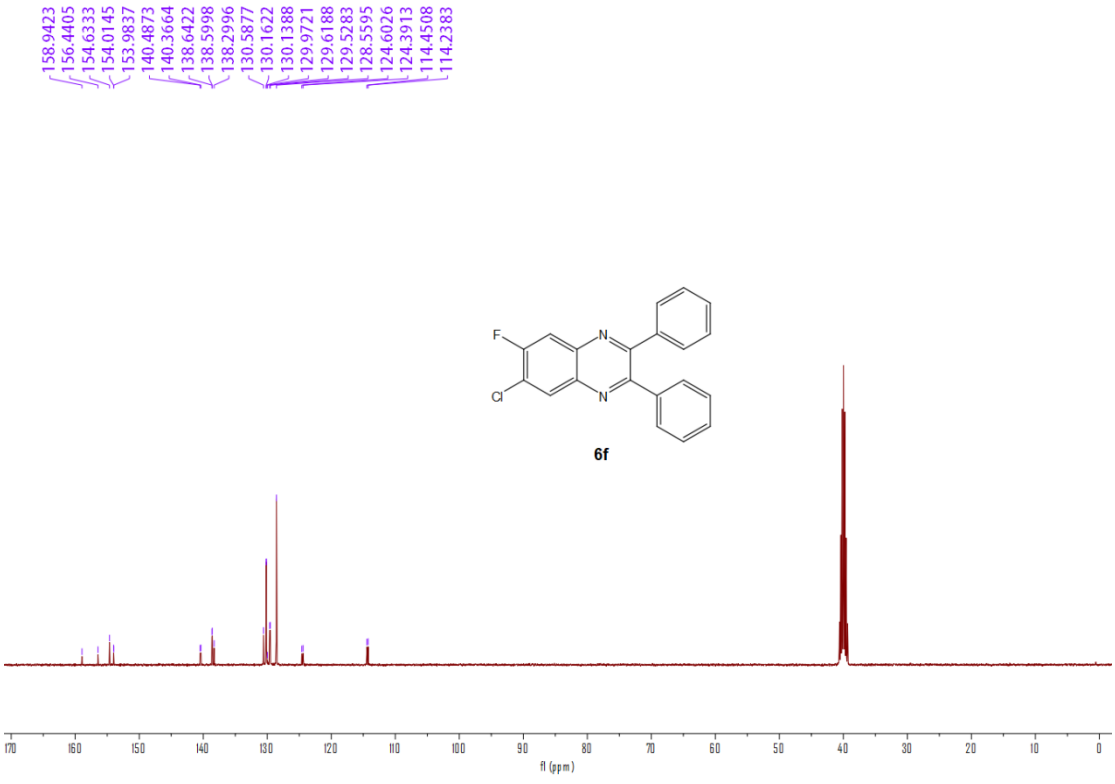
6e

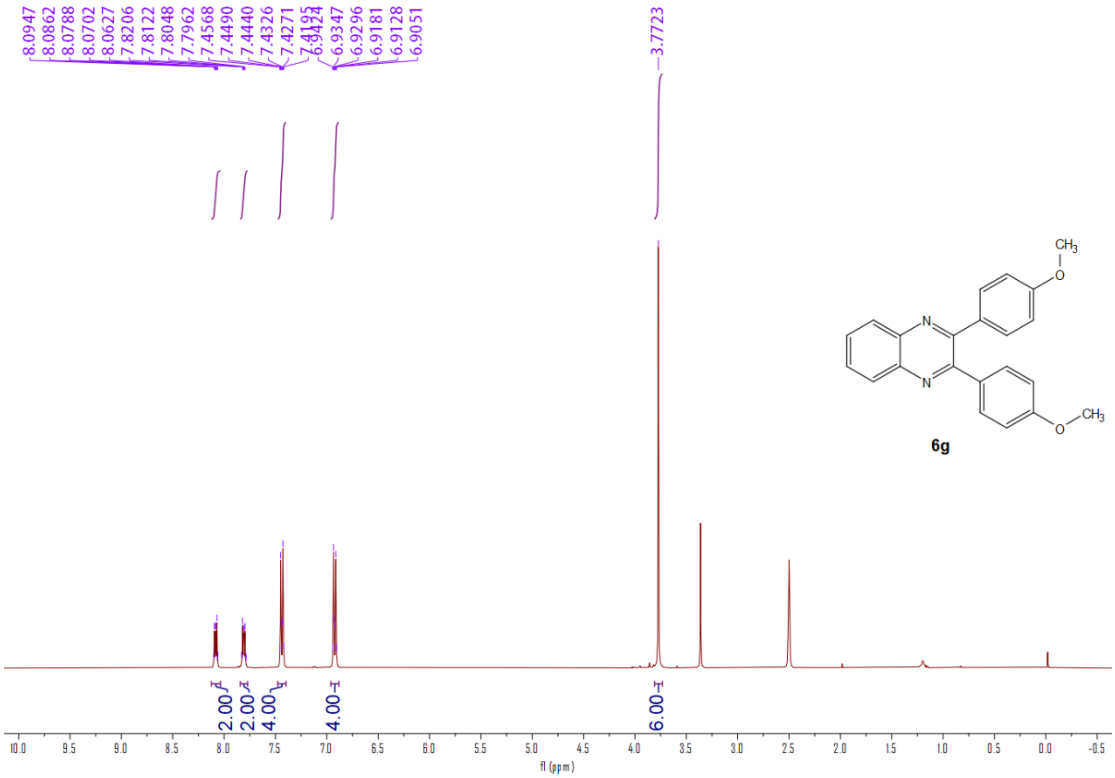

154.3951
153.8074
141.1901
139.5350
138.8435
138.7779
135.0527
131.3330
131.0617
130.1555
130.1262
129.4806
129.4026
128.5071
127.9056
f1 (ppm)

N
Cl
N

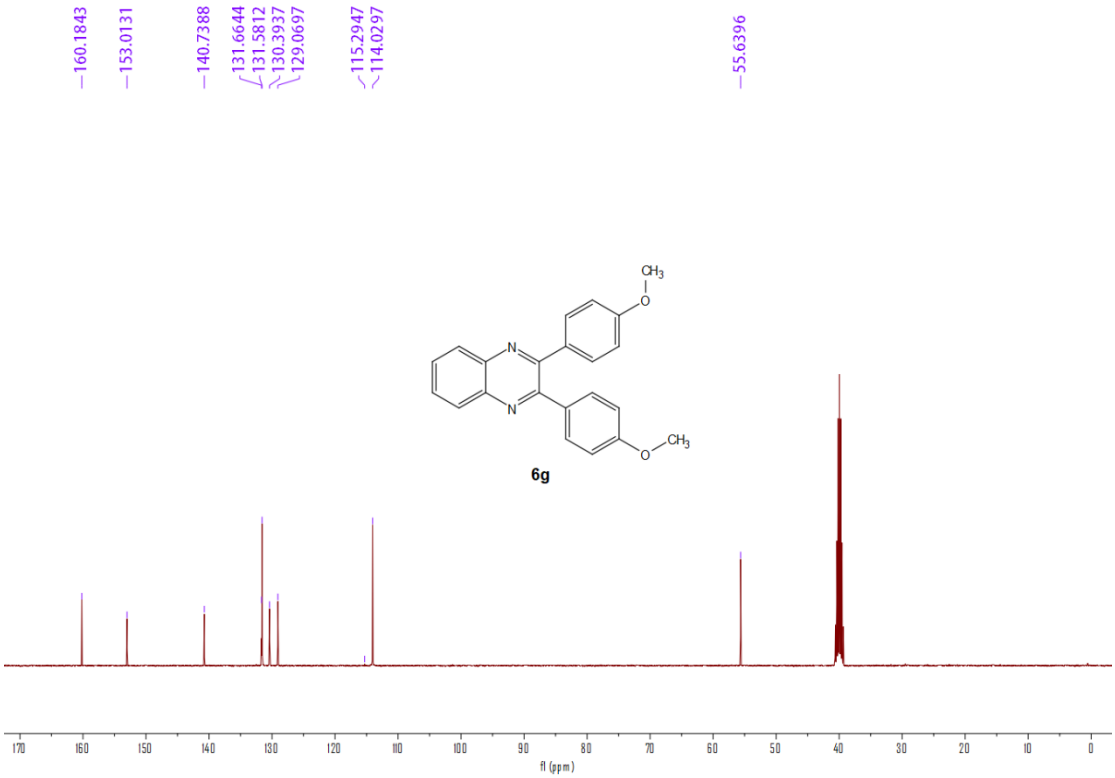
6e


8.4269
8.4075
8.1569
8.1323
7.4592
7.4557
7.4522
7.4493
7.4451
7.4389
7.4335
7.4280
7.4215
7.4065
7.4035
7.3926
7.3892
7.3855
7.3816
7.3673
7.3632
7.3526
7.3482
7.3316
7.3273
F
Cl
N
N
6f
0.90
0.97
10.00
f1 (ppm)

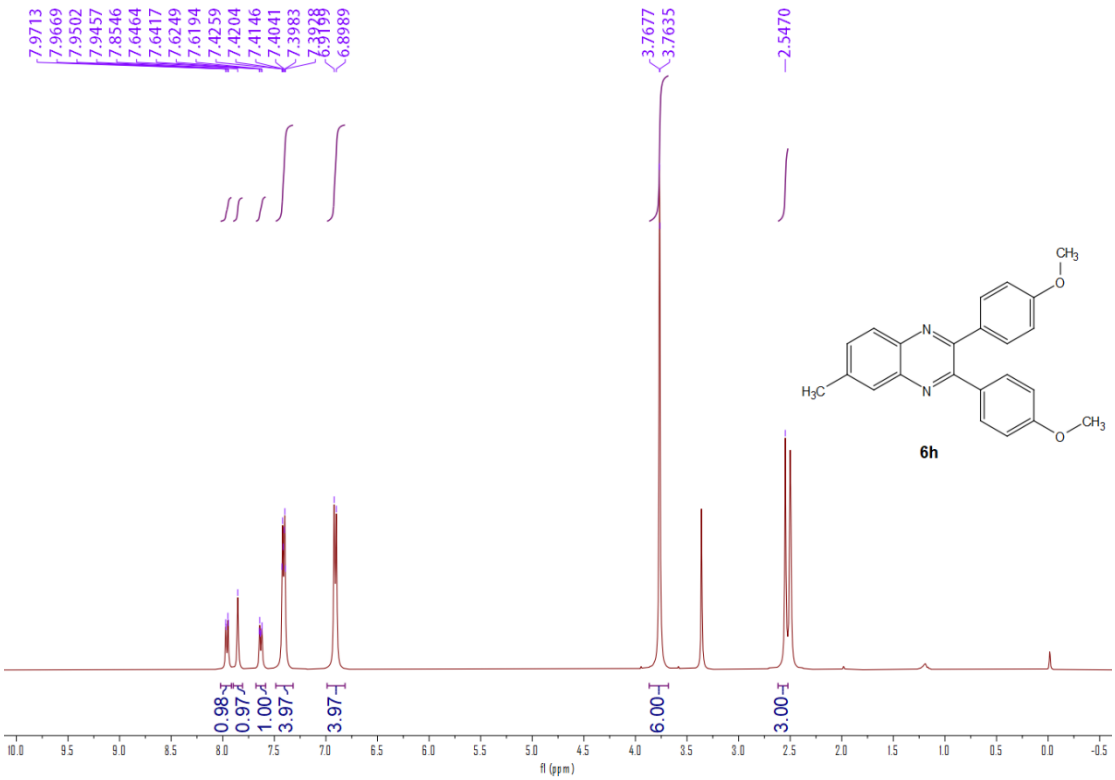

158.9423
156.4405
154.6333
154.0145
153.9837
140.4873
140.3664
138.6422
138.5998
138.2996
130.5877
130.1622
130.1388
129.9721
129.6188
129.5283
128.5595
124.6026
124.3913
114.4508
114.2383
F
Cl
N
N
6f
f1 (ppm)

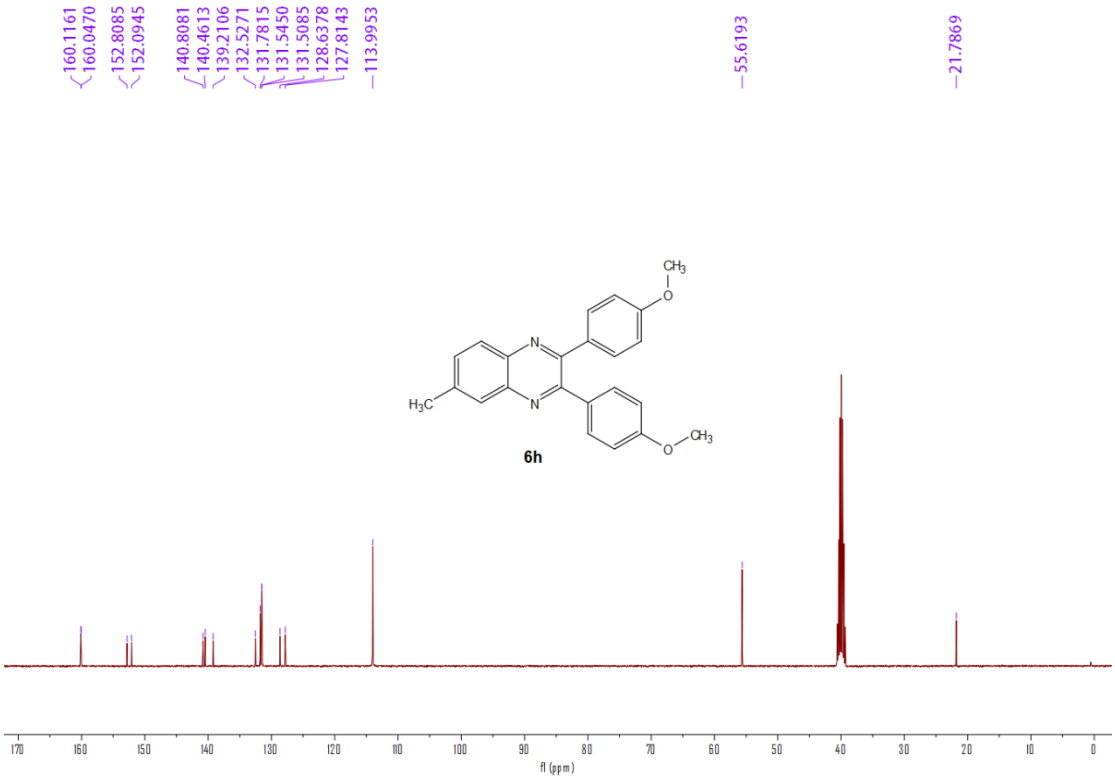

8.0947
8.0862
8.0788
8.0702
8.0627
7.8206
7.8122
7.8048
7.7962
7.4568
7.4490
7.4440
7.4326
7.4271
7.4195
6.9424
6.9347
6.9296
6.9181
6.9128
6.9051
3.7723
2.00
2.00
4.00
4.00
6.00
f1 (ppm)

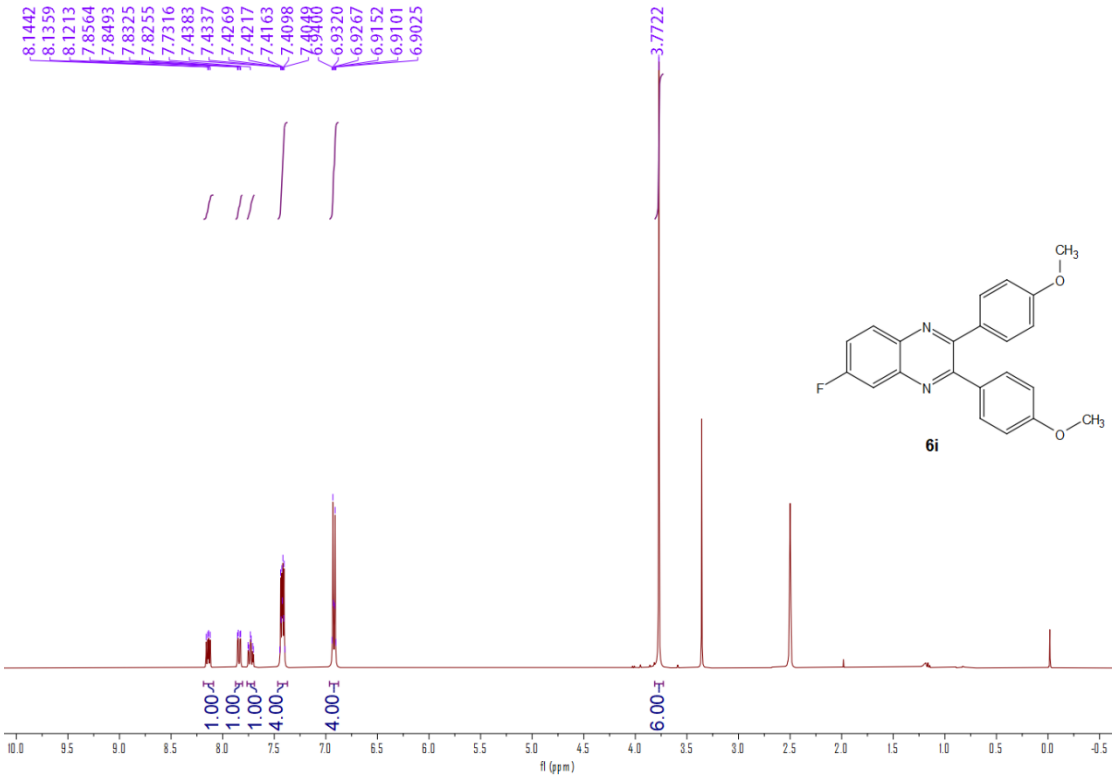
6g


160.1843
153.0131
140.7388
131.6644
131.5812
130.3937
129.0697
115.2947
114.0297
55.6396
f1 (ppm)

6g

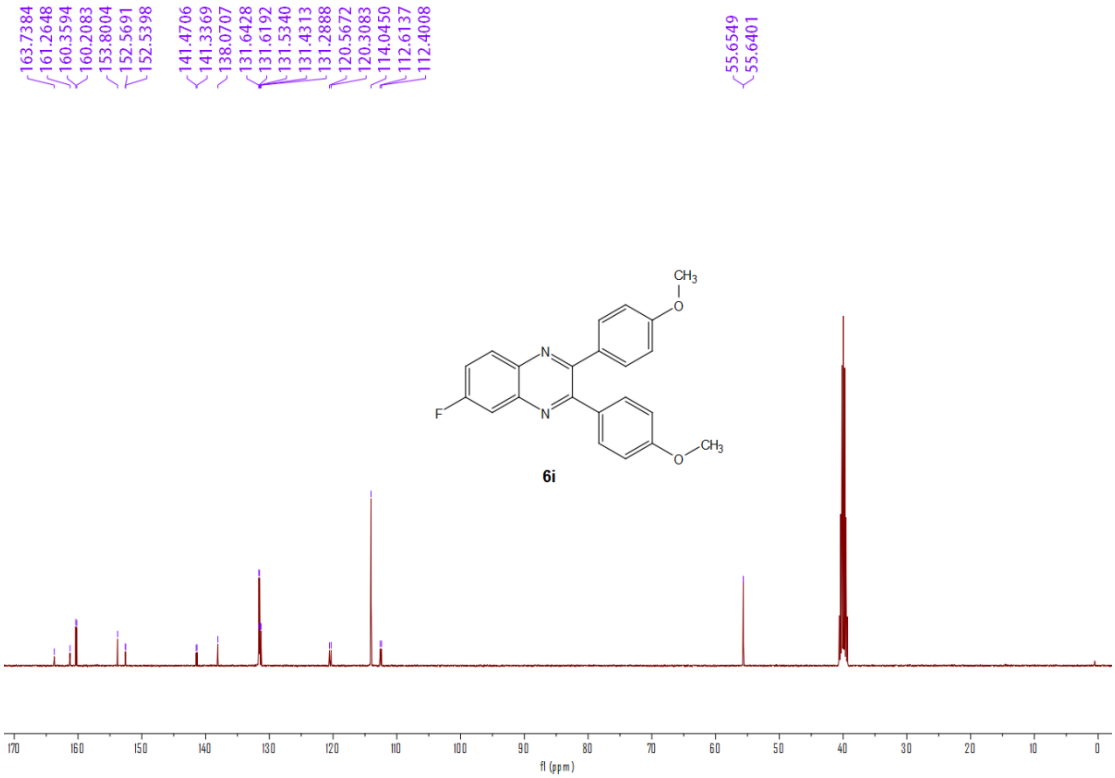

7.9713
7.9669
7.9502
7.9457
7.8546
7.6464
7.6417
7.6249
7.6194
7.4259
7.4204
7.4146
7.4041
7.3983
6.8989
3.7677
3.7635
2.5470
0.98
0.97
1.00
3.97
3.97
6.00
3.00
f1 (ppm)
6h


160.1161
160.0470
152.8085
152.0945
140.8081
140.4613
139.2106
132.5271
131.7815
131.5450
131.5085
128.6378
127.8143
113.9953
55.6193
21.7869
f1 (ppm)
6h


8.1442
8.1359
8.1213
7.8564
7.8493
7.8325
7.8255
7.7316
7.4383
7.4337
7.4269
7.4217
7.4163
7.4098
6.9320
6.9267
6.9152
6.9101
6.9025
3.7722
1.00
1.00
1.00
4.00
4.00
6.00
f1 (ppm)

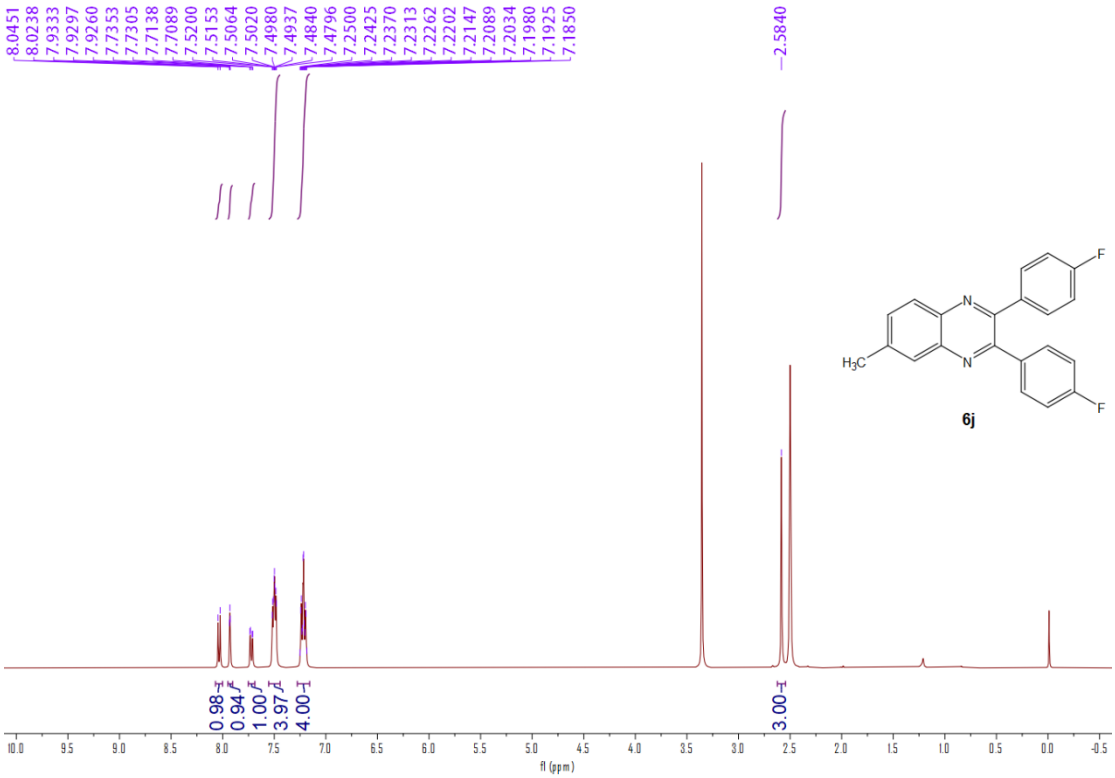
CH3
O
N
F
N
O
CH3

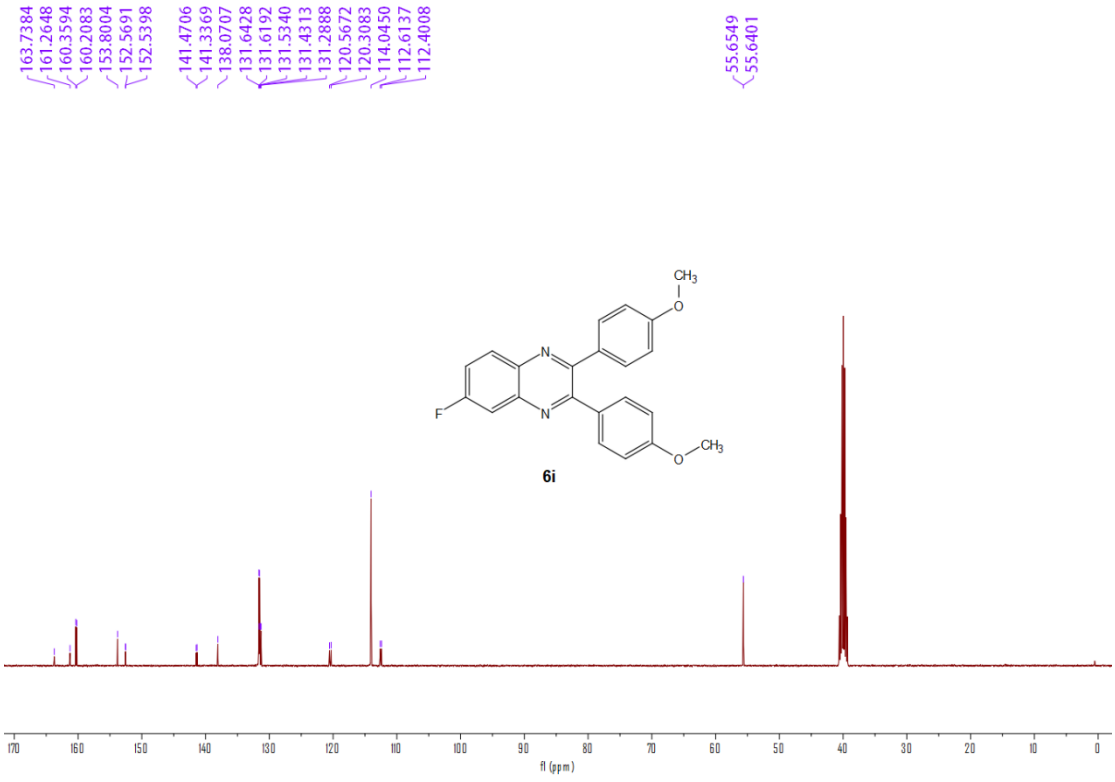
6i

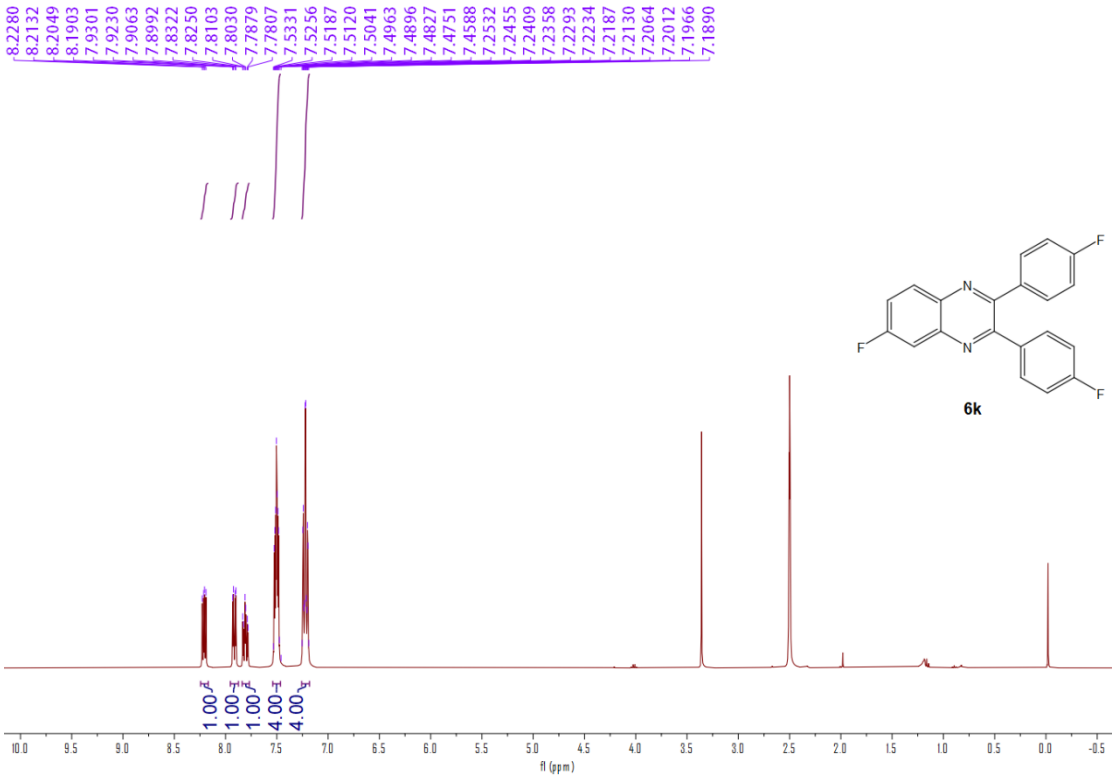

163.7384
161.2648
160.3594
160.2083
153.8004
152.5691
152.5398
141.4706
141.3369
138.0707
131.6428
131.6192
131.5340
131.4313
131.2888
120.5672
120.3083
114.0450
112.6137
112.4008
55.6549
55.6401
f1 (ppm)

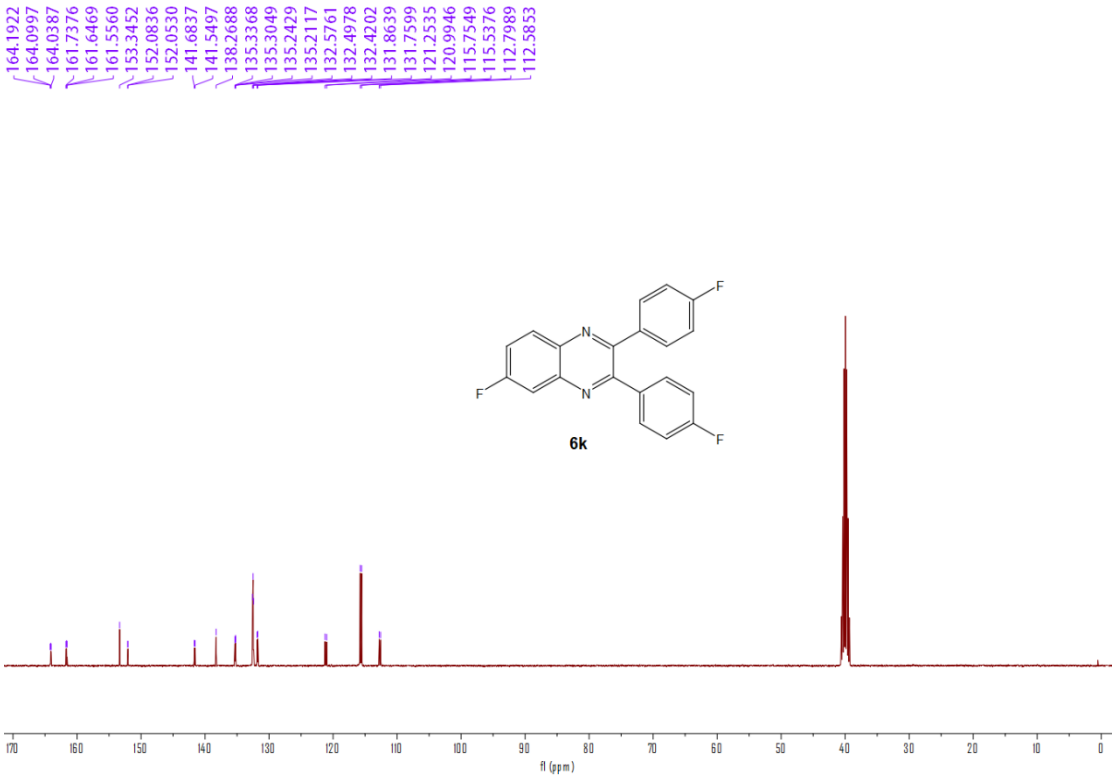
CH3
O
N
F
N
O
CH3

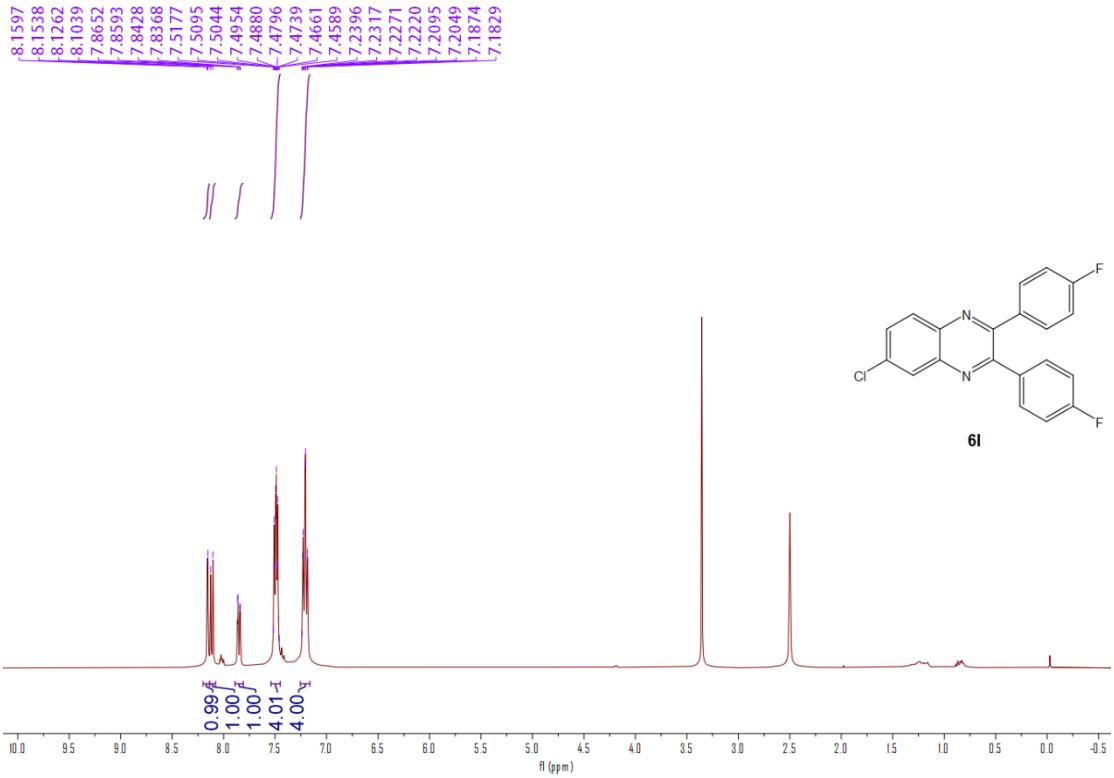
6i


8.0451
8.0238
7.9333
7.9297
7.9260
7.7353
7.7305
7.7138
7.7089
7.5200
7.5153
7.5064
7.5020
7.4980
7.4937
7.4840
7.4796
7.2500
7.2425
7.2370
7.2313
7.2262
7.2202
7.2147
7.2089
7.2034
7.1980
7.1925
7.1850
2.5840
0.98
0.94
1.00
3.97
4.00
3.00
F
N
N
H3C
F
6j
f1 (ppm)


163.7384
161.2648
160.3594
160.2083
153.8004
152.5691
152.5398
141.4706
141.3369
138.0707
131.6428
131.6192
131.5340
131.4313
131.2888
120.5672
120.3083
114.0450
112.6137
112.4008
55.6549
55.6401
CH3
O
N
N
F
O
CH3
6i
f1 (ppm)

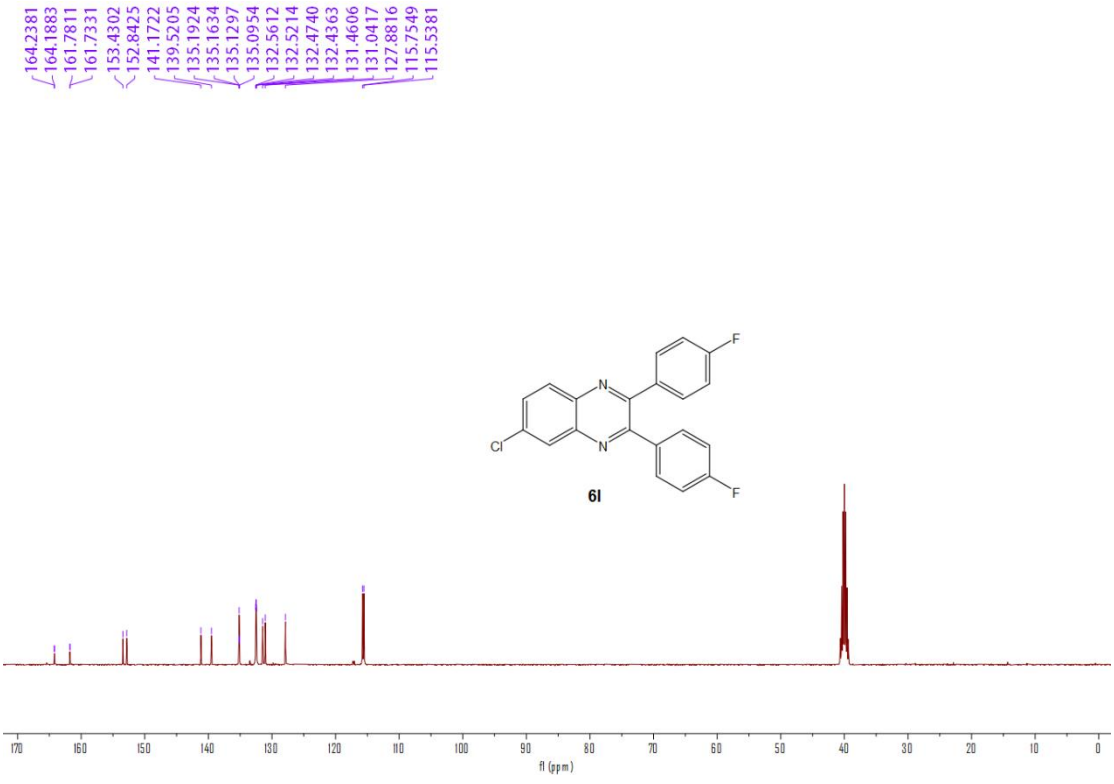

8.2280
8.2132
8.2049
8.1903
7.9301
7.9230
7.9063
7.8992
7.8322
7.8250
7.8103
7.8030
7.7879
7.7807
7.5331
7.5256
7.5187
7.5120
7.5041
7.4963
7.4896
7.4827
7.4751
7.4588
7.2532
7.2455
7.2409
7.2358
7.2293
7.2234
7.2187
7.2130
7.2064
7.2012
7.1966
7.1890
1.00
1.00
1.00
4.00
4.00
F
N
N
F
F
6k
f1 (ppm)


164.1922
164.0997
164.0387
161.7376
161.6469
161.5560
153.3452
152.0836
152.0530
141.6837
141.5497
138.2688
135.3368
135.3049
135.2429
135.2117
132.5761
132.4978
132.4202
131.8639
131.7599
121.2535
120.9946
115.7549
115.5376
112.7989
112.5853
F
N
N
F
F
6k
f1 (ppm)


8.1597
8.1538
8.1262
8.1039
7.8652
7.8593
7.8428
7.8368
7.5177
7.5095
7.5044
7.4954
7.4880
7.4796
7.4739
7.4661
7.4589
7.2396
7.2317
7.2271
7.2220
7.2095
7.2049
7.1874
7.1829
0.99
1.00
1.00
4.01
4.00
f1 (ppm)

F
N
Cl
N
F

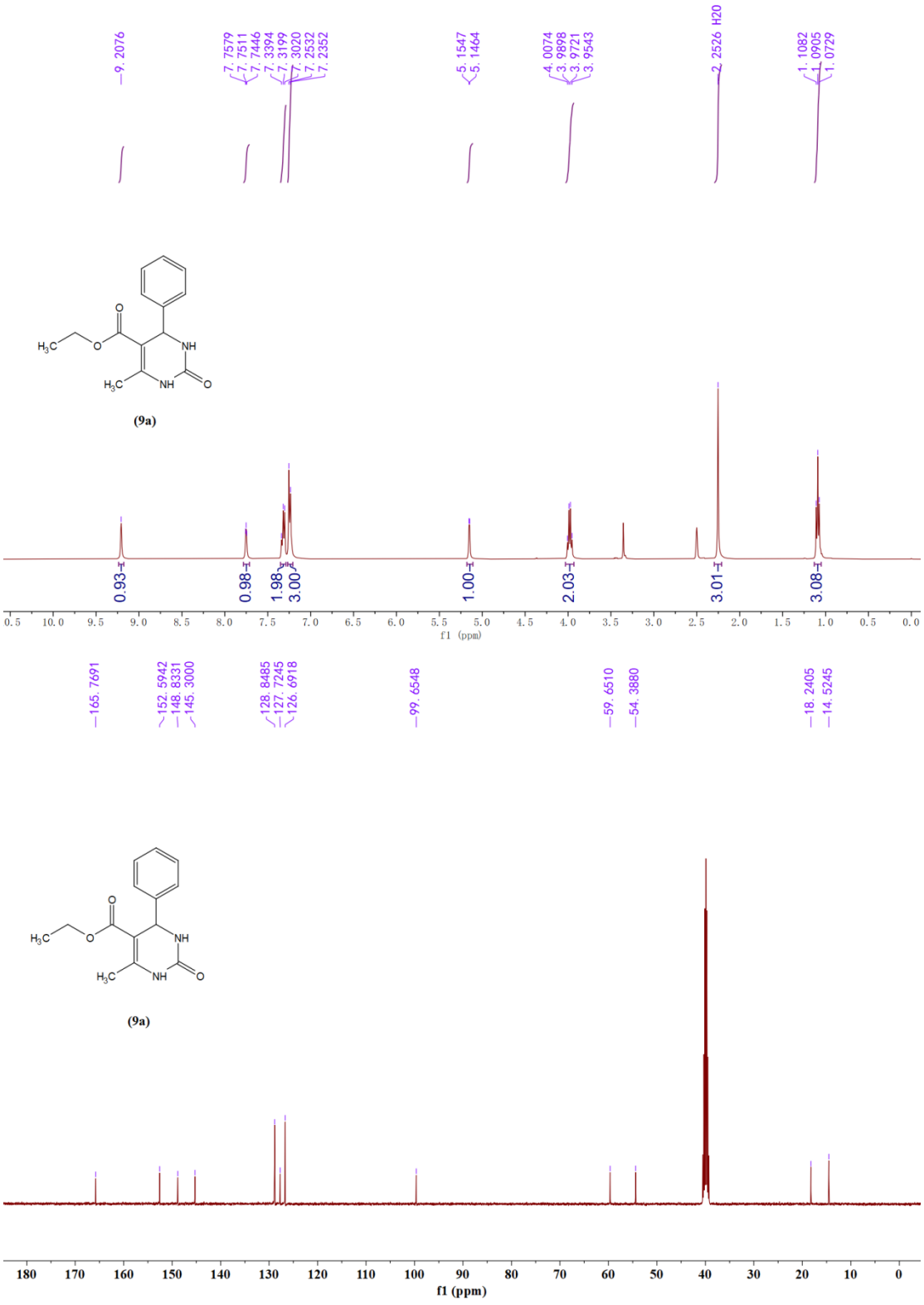
6l

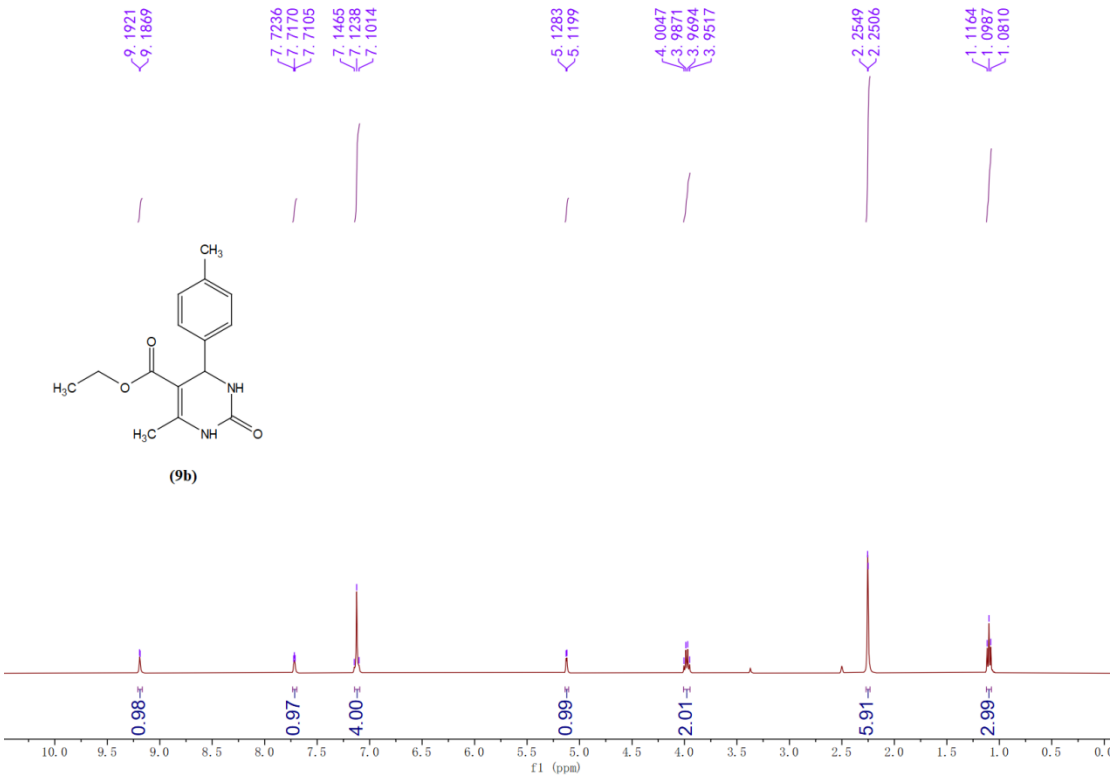

164.2381
164.1883
161.7811
161.7331
153.4302
152.8425
141.1722
139.5205
135.1924
135.1634
135.1297
135.0954
132.5612
132.5214
132.4740
132.4363
131.4606
131.0417
127.8816
115.7549
115.5381
f1 (ppm)

F
N
Cl
N
F

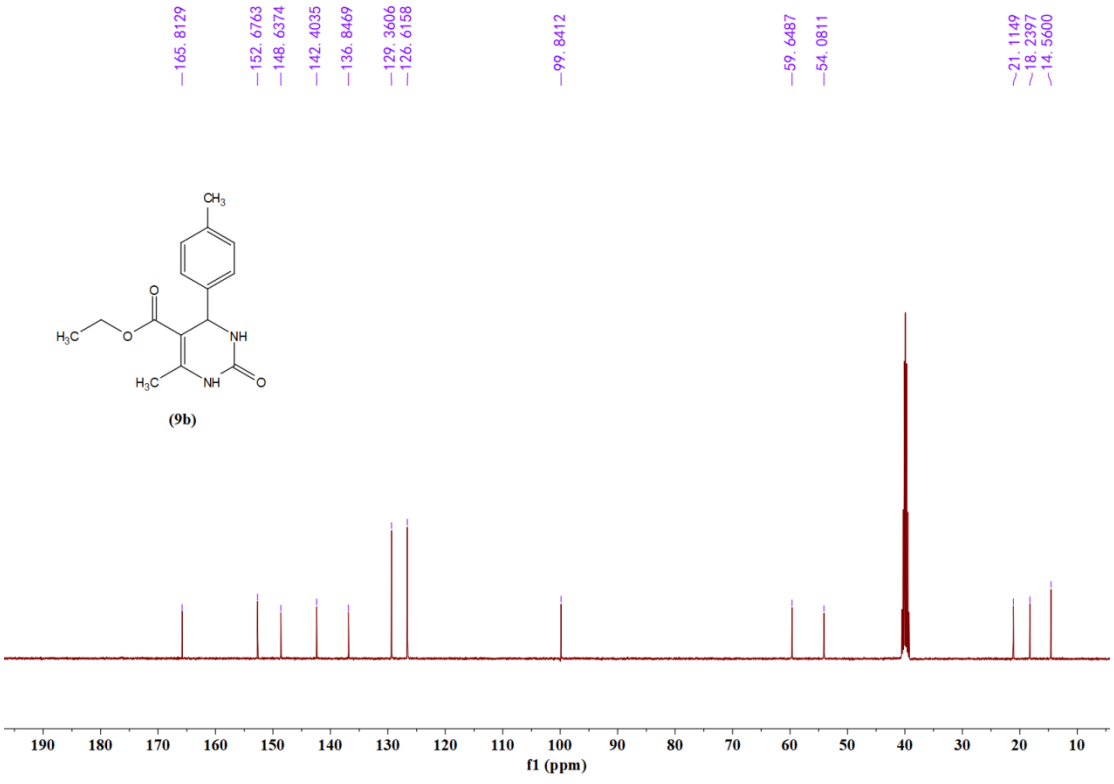
6l

Reaction III

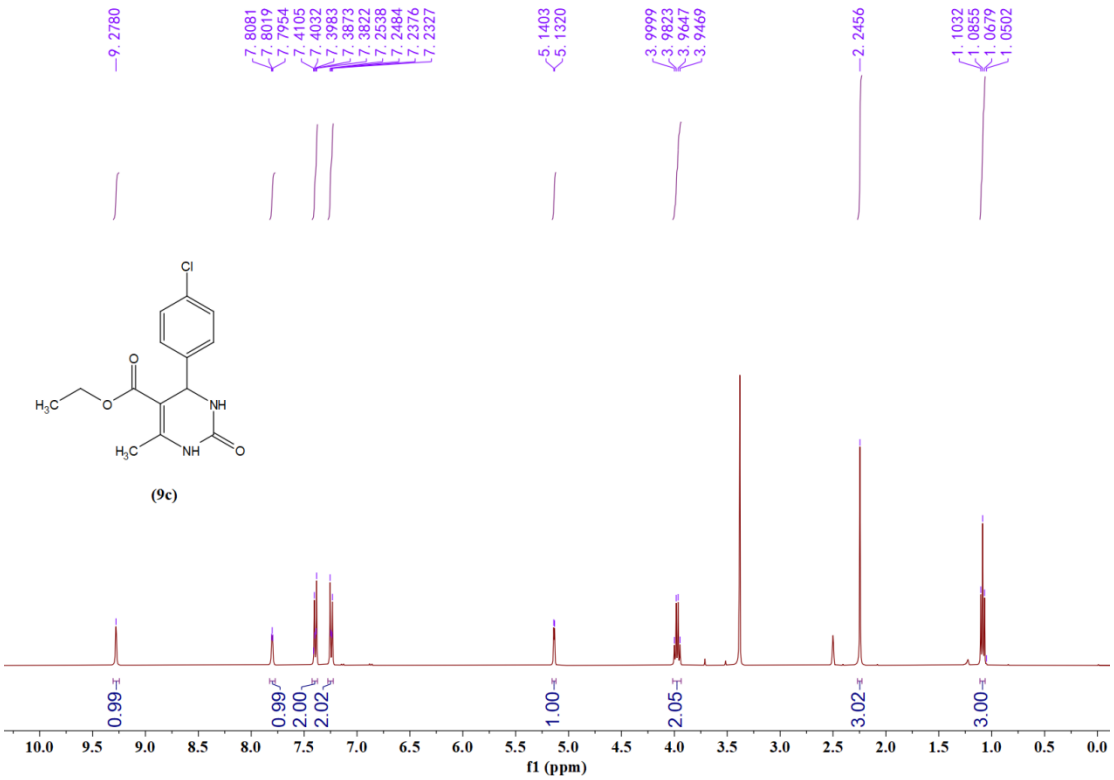



9.1921
9.1869
7.7236
7.7170
7.7105
7.1465
7.1238
7.1014
5.1283
5.1199
4.0047
3.9871
3.9694
3.9517
2.2549
2.2506
1.1164
1.0987
1.0810
CH3
O
O
H3C
NH
H3C
NH
O
0.98
0.97
4.00
0.99
2.01
5.91
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

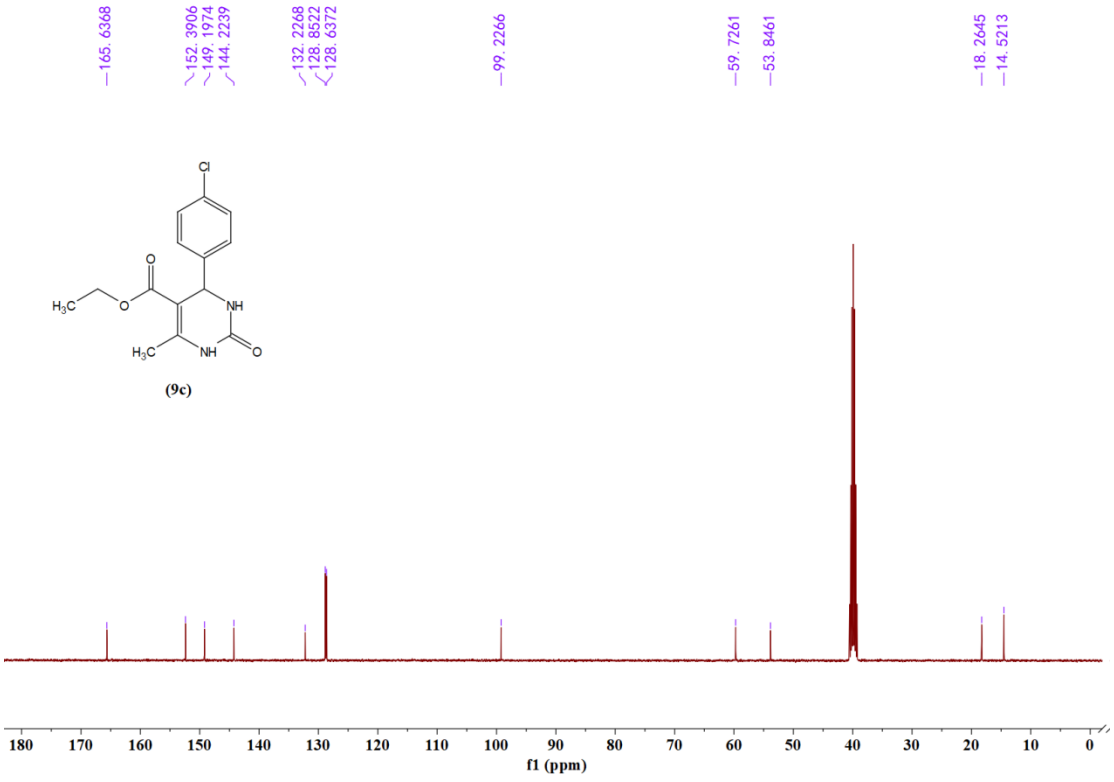
(9b)


165.8129
152.6763
148.6374
142.4035
136.8469
129.3606
126.6158
99.8412
59.6487
54.0811
21.1149
18.2397
14.5600
CH3
O
O
H3C
NH
H3C
NH
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

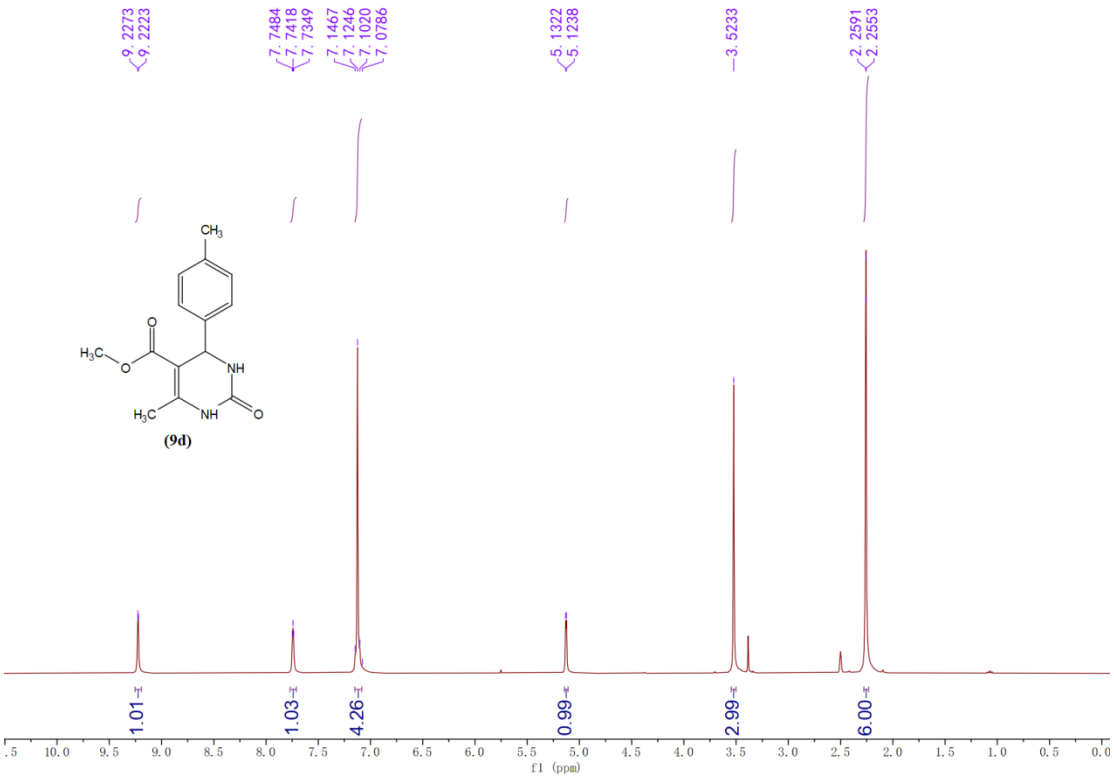
(9b)

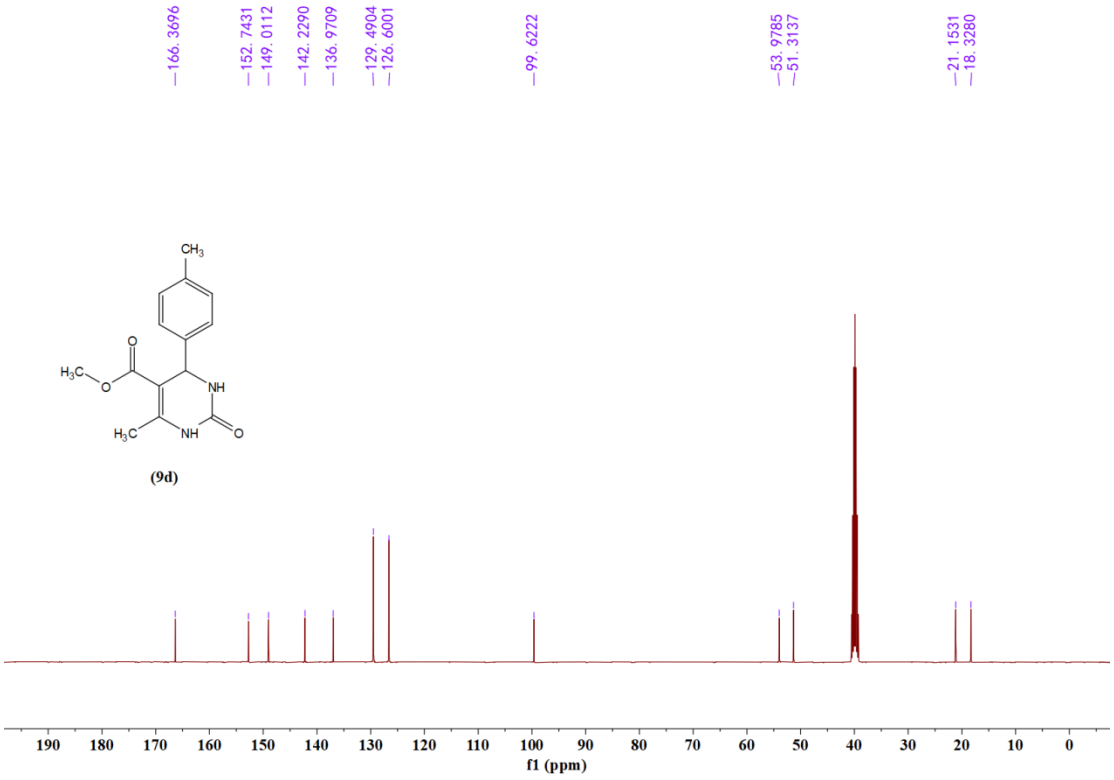

9.2780
7.8081
7.8019
7.7954
7.4105
7.4032
7.3983
7.3873
7.3822
7.2538
7.2484
7.2376
7.2327
5.1403
5.1320
3.9999
3.9823
3.9647
3.9469
2.2456
1.1032
1.0855
1.0679
1.0502
Cl
O
O
NH
H3C
NH
O
H3C
0.99
0.99
2.00
2.02
1.00
2.05
3.02
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

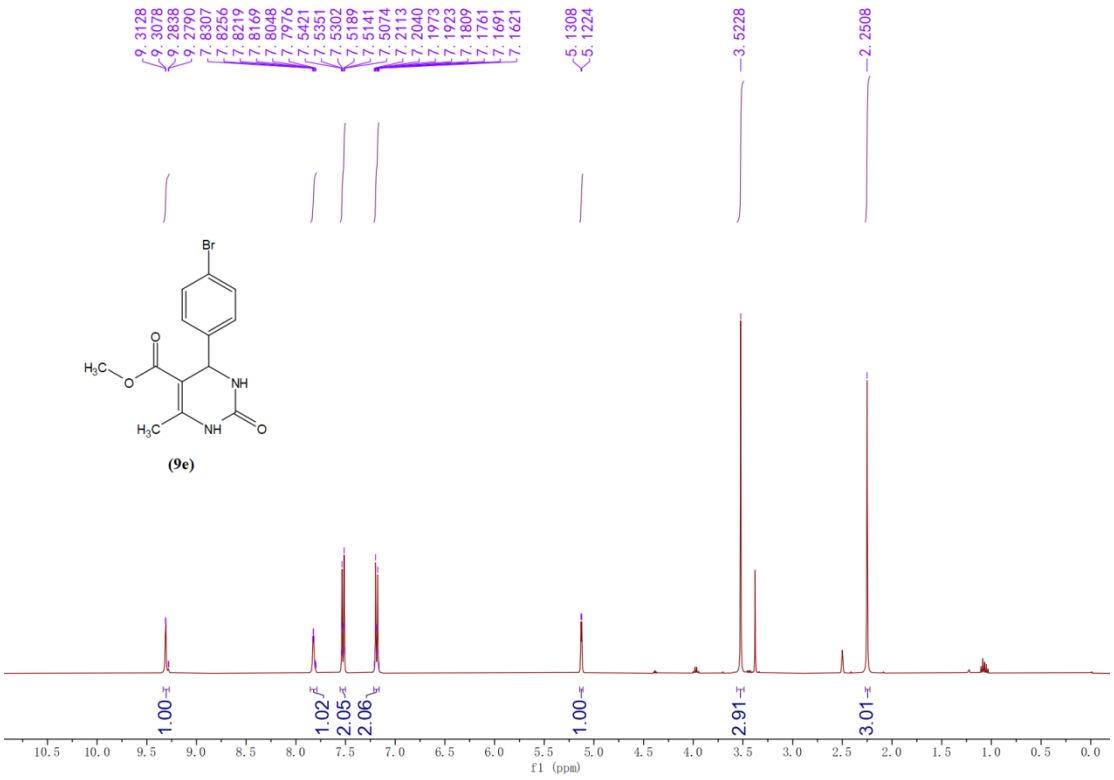
(9c)


165.6368
152.3906
149.1974
144.2239
132.2268
128.8522
128.6372
99.2266
59.7261
53.8461
18.2645
14.5213
Cl
O
O
NH
H3C
NH
O
H3C
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

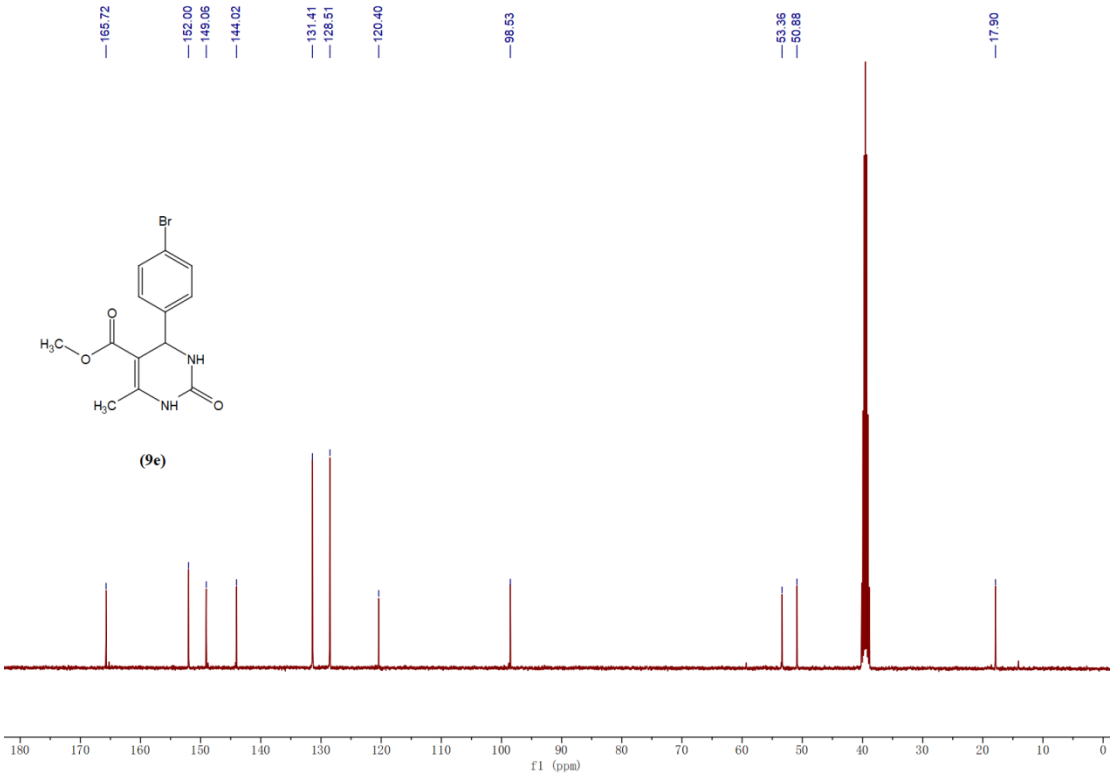
(9c)


9.2273
9.2223
7.7484
7.7418
7.7349
7.1467
7.1246
7.1020
7.0786
5.1322
5.1238
3.5233
2.2591
2.2553
CH3
O
H3C
O
NH
H3C
NH
O
(9d)
1.01
1.03
4.26
0.99
2.99
6.00
f1 (ppm)

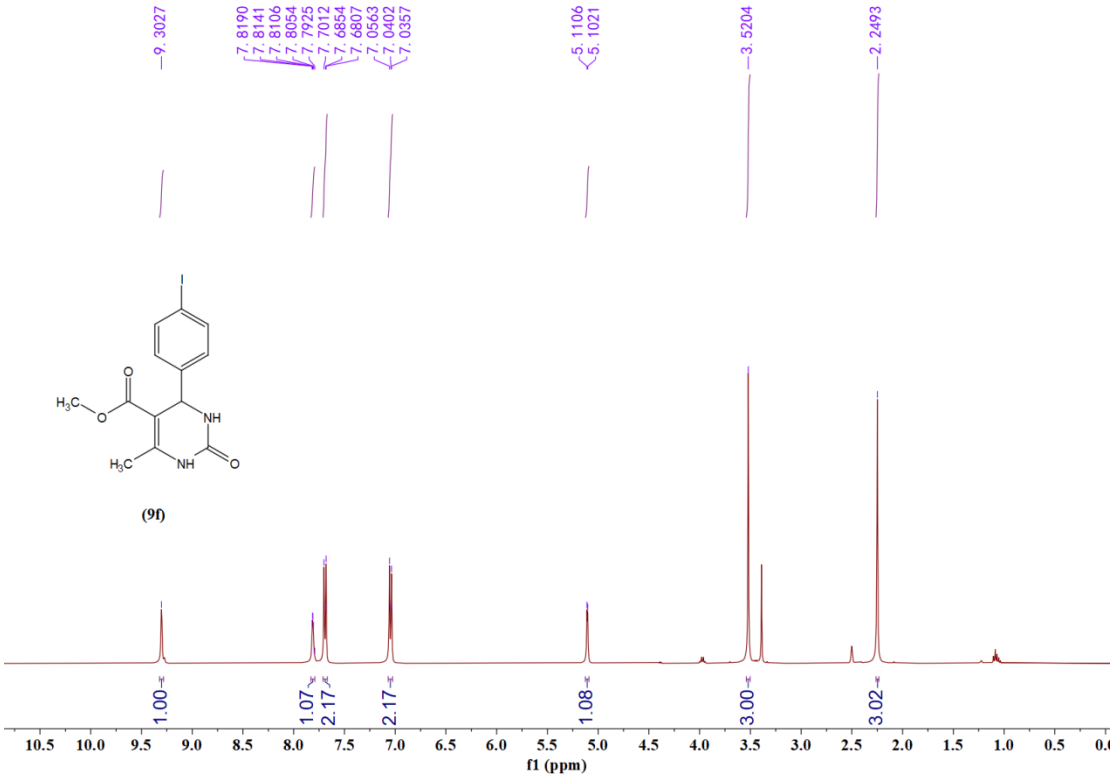

166.3696
152.7431
149.0112
142.2290
136.9709
129.4904
126.6001
99.6222
53.9785
51.3137
21.1531
18.3280
CH3
O
H3C
O
NH
H3C
NH
O
(9d)
f1 (ppm)


9.3128
9.3078
9.2838
9.2790
7.8307
7.8256
7.8219
7.8169
7.8048
7.7976
7.5421
7.5351
7.5302
7.5189
7.5141
7.5074
7.2113
7.2040
7.1973
7.1923
7.1809
7.1761
7.1691
7.1621
5.1308
5.1224
3.5228
2.2508
Br
O
H3C
O
NH
H3C
NH
O
1.00
1.02
2.05
2.06
1.00
2.91
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

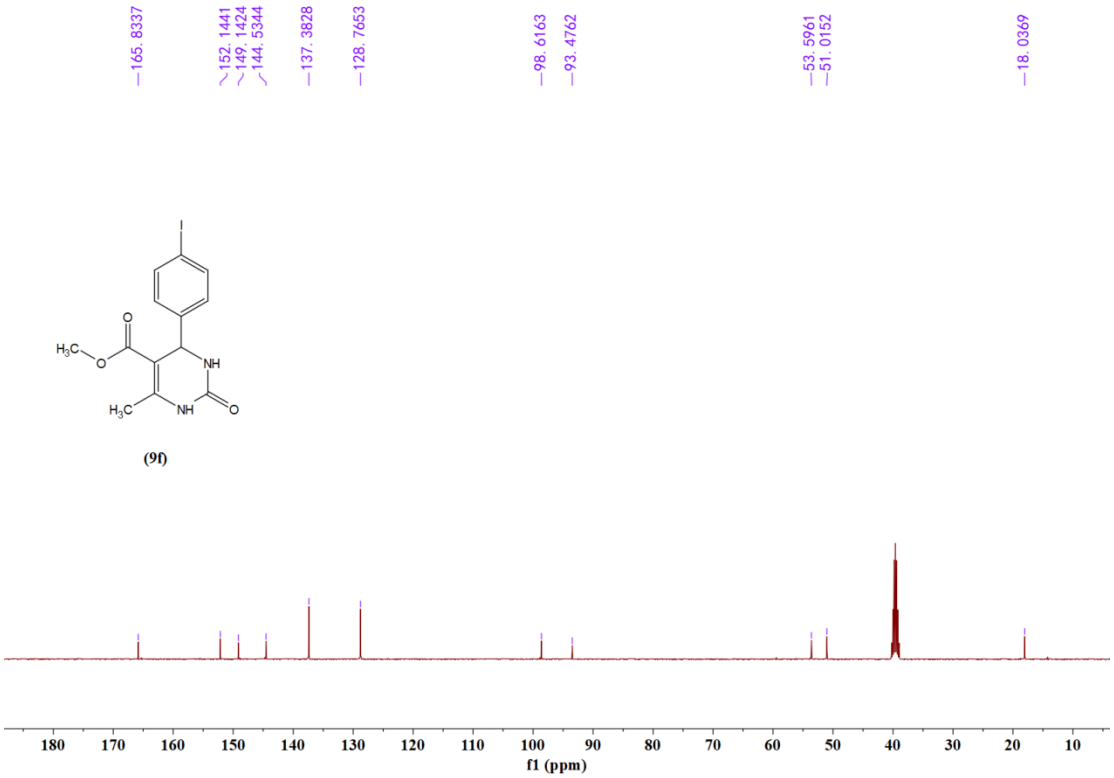
(9e)


165.72
152.00
149.06
144.02
131.41
128.51
120.40
98.53
53.36
50.88
17.90
Br
O
H3C
O
NH
H3C
NH
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

(9e)


9.3027
7.8190
7.8141
7.8106
7.8054
7.7925
7.7012
7.6854
7.6807
7.0563
7.0402
7.0357
5.1106
5.1021
3.5204
2.2493
I
O
H3C
O
NH
H3C
NH
O
1.00
1.07
2.17
2.17
1.08
3.00
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

(9f)


165.8337
152.1441
149.1424
144.5344
137.3828
128.7653
98.6163
93.4762
53.5961
51.0152
18.0369
I
O
H3C
O
NH
H3C
NH
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

(9f)