Electronic Supplementary Information

AIEE Phenomenon: Tetraaryl vs Triaryl Pyrazoles

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EXPERIMENTAL SECTION

General Consideration

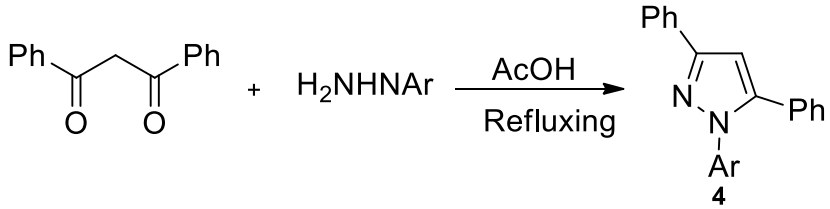
Reagents

All experiments were carried out in oven–dried glasswares under nitrogen atmosphere. 1,3-Diphenylpropan-1,3-dione, aryl and heteroaryl hydrazines were purchased from Aldrich and Acros and used as received. $Pd(PPh_3)_4$, aryl and heteroaryl boronic acids were purchased from Aldrich. N-Bromosuccinimide was purchase from Aldrich and recrystallized from water. Cs_2CO_3, KOH, K_2CO_3 and Et_3N were purchased from Aldrich, Acros, Merck or Alfa-Aesar and used as received. All other reagents were purchased from common suppliers and used without further purification. Flash chromatography was performed by using Merck Silica gel 60 (230–400 mesh). Reactions were monitored by thin–layer chromatography on pre-coated with silica gel 60 F254 plates (Merck & co.) and were visualized by UV. 1,3,4-triphenylpyrazole was synthesized by reported method.[1]

Analytical Methods

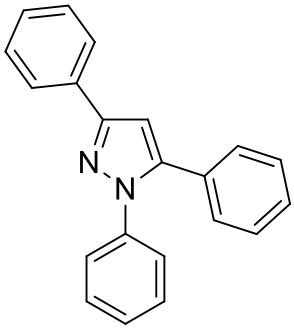
^1H and ^{13}C spectra were recorded in $CDCl_3$ solution using Brucker Avance DRX(400 MHz). The signals were referenced to residual chloroform (7.26 ppm, 77.16 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), dd (doublet of a doublet). Gas chromatography analysis was performed on ThermoFisher ITQ 900 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using helium as carrier gas. Gas chromatography-mass analysis was carried out on ThermoFisher ITQ 900 instrument (EI) and TG-SQC capillary column using helium carrier gas. ESI HR-MS measurements were performed on Bruker micrOTOF-Q-II mass-spectrometer. The fluorescence spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. The electronic absorption spectra were recorded with Shimadzu 3101PC UV-Vis-NIR Scanning spectrophotometer. DLS analyses were carried out with a Zetasizer Nano S from Malvern Instruments at 25°C. The X-ray quality crystals for the compounds were grown by slow diffusion of *n*-hexane over CH_2Cl_2 solution. Single-crystal X-ray diffraction data of **2a**, **2i** and **4a** were collected in a Bruker KAPPA APEX-II, four angle rotation system, Mo-Kα radiation (0.71073 Å).

Scheme 1: General Procedure for Synthesis of 1,3,5-Triaryl-1*H*-pyrazoles



To a solution of 1,3-diphenylpropan-1,3-dione (2.46 g, 11 mmol) in AcOH (20 mL) was added arylhydrazine (13 mmol) at room temperature. The reaction mixture was refluxed until 1,3-diketone was consumed. The reaction mixture was cooled and neutralized by saturated sodium carbonate solution. The aqueous phase was extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude product by flash chromatography afforded the corresponding pyrazole as a colourless solid.

1,3,5-Triphenyl-1*H*-pyrazole (4a)[2]



Yield: 2.61 g (80%) as a colourless solid.

Melting point: 130 – 132 °C

R_f: 0.31 in 5% ethyl acetate in hexane

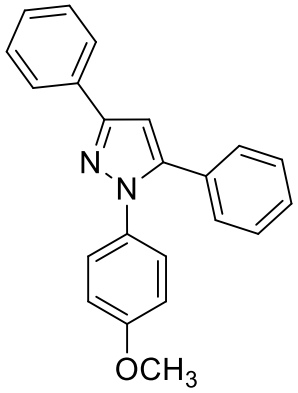
IR (ν cm^{-1}, in KBr): 3448, 3120, 3061, 1596, 1497, 1482, 1457, 1433, 1363, 1213, 1174, 1065, 1021, 972, 957, 921, 814, 765, 700, 693, 504.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.92 (m, 2H), 7.46 – 7.42 (m, 2H), 7.34 – 7.28 (m, 11H), 6.83 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.10, 144.53, 140.26, 133.17, 130.71, 129.05, 128.88, 128.78, 128.61, 128.43, 128.13, 127.57, 125.95, 125.45, 105.34.

HR–MS (ESI): Calcd. for $C_{21}H_{16}N_2$ (M+H):297.1386, found: 297.1354.

1-(4-Methoxyphenyl)-3,5-diphenyl-1*H*-pyrazole (4b)[3]



Yield: 2.69 g (75%) as a colourless solid.

Melting point: 101 – 104 °C

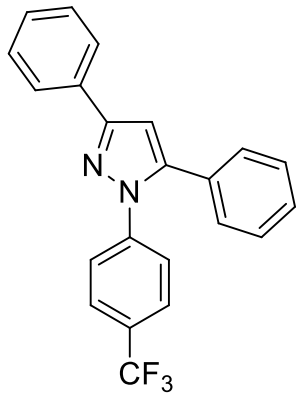
R_f: 0.68 in 10% ethyl acetate in hexane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.36 – 7.27 (m, 8H), 6.90 – 6.84 (m, 2H), 6.81 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.99, 151.77, 144.49, 133.59, 133.30, 130.75, 128.84, 128.77, 128.59, 128.32, 128.03, 126.89, 125.93, 114.25, 104.78, 55.64.

HR–MS (ESI): Calcd. for $C_{22}H_{18}N_2O$ (M+H): 327.1492, found: 327.1520.

1-(4-Trifluoromethylphenyl)-3,5-diphenyl-1*H*-pyrazole (4c)



Yield: 3.12 g (78%) as a colourless solid.

Melting point: 113 – 115 °C

R_f: 0.51 in 2% ethyl acetate in hexane

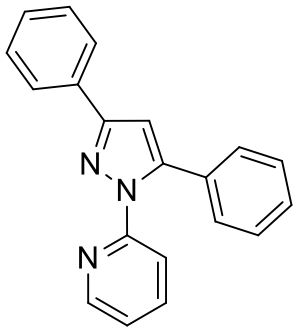
IR (ν cm^{-1}, in KBr): 3064, 2372, 1611, 1523, 1509, 1484, 1458, 1410, 1364, 1325, 1168, 1159, 1125, 1108, 1075, 1057, 1016, 969, 851, 766, 697, 613.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.86 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.31 (dt, *J* = 7.6, 3.9 Hz, 2H), 6.85 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.81, 144.74, 142.94, 132.76, 130.38, 129.05 (q, *J* = 33 Hz), 128.92, 128.87 (2C), 128.84, 128.44, 126.14 (q, *J* = 4 Hz), 125.97, 124.91, 124.00 (q, *J* = 271 Hz), 106.39.

HR–MS (ESI): Calcd. for $C_{22}H_{15}N_2F_3$ (M+H): 365.1260, found: 365.1245.

1-(2-Pyridyl)-3,5-diphenyl-1*H*-pyrazole (4d)[4]



Yield: 1.80 g (55%) as a colourless solid.

Melting point: 104 – 106 °C

R_f: 0.26 in 20 % ethyl acetate in hexane

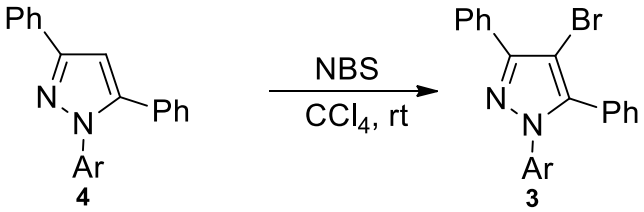
IR (ν cm^{-1}, in KBr): 2373, 2345, 1580, 1469, 1362, 1329, 1074, 791, 765, 742, 699, 670, 460.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.77 (ddd, *J* = 8.0, 7.4, 2.0 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.47 – 7.41 (m, 2H), 7.39 – 7.28 (m, 6H), 7.22 (ddd, *J* = 7.4, 4.9, 0.8 Hz, 1H), 6.84 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.79, 152.71, 148.61, 145.23, 138.34, 132.95, 131.20, 128.85, 128.77, 128.40, 128.37 (2C), 126.15, 122.55, 119.09, 106.57.

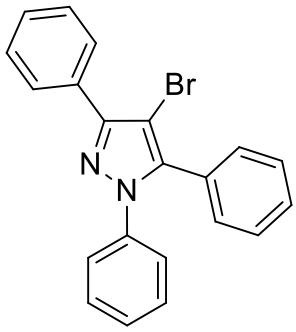
HR–MS (ESI): Calcd. for $C_{20}H_{15}N_3$ (M+H): 298.1339, found: 298.1372.

Scheme 2: General Procedure for Synthesis of 4–Bromo–1,3,5-triaryl-1*H*-pyrazoles



To a solution of 1,3,5-triarylpyrazole (8 mmol) in CCl_4 (50 mL) was added N-bromosuccinimide (1.71 g, 9.6 mmol) at room temperature. The reaction mixture was stirred at the same temperature until the pyrazole was consumed. The reaction mixture was poured into H_2O and was extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude product by flash chromatography afforded the corresponding pyrazole as a colourless solid.

4–Bromo–1,3,5–triphenyl-1*H*-pyrazole (3a)[2]



Yield: 2.43 g (81%) as a colourless solid.

Melting point: 224 – 226 °C

R_f: 0.35 in 5% ethyl acetate in hexane

IR (ν cm^{-1}, in KBr): 3047, 1482, 1492, 1453, 1358, 1157, 1091, 1072, 1029, 963, 769, 760, 693, 674.

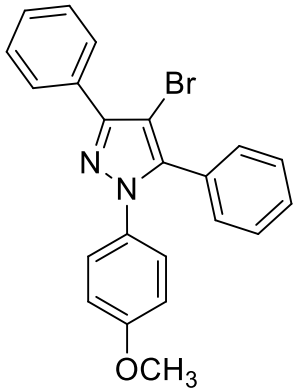
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 – 7.99 (m, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.38 (m, 4H), 7.36 – 7.27 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.87, 142.15, 139.91, 132.08, 130.34, 129.16, 129.12, 129.03, 128.65, 128.58, 128.50, 128.21, 127.73, 124.94, 95.04.

HR–MS (ESI): Calcd. for $C_{21}H_{15}N_2Br$ (M+H): 375.0491, found: 375.0497.

377.0471, found: 377.0479.

4-Bromo-1-(4-methoxyphenyl)-3,5-diphenyl-1*H*-pyrazole (3b)



Yield: 3.14 g (97%) as a colourless solid.

Melting point: 109 –110 °C

R_f: 0.36 in 20 % ethyl acetate in hexane

IR (ν cm^{-1}, in KBr): 2933, 2835, 2345, 1542, 1509, 1479, 1458, 1357, 1301, 1243, 1169, 1108, 1026, 968, 837, 806, 768, 730, 699, 615, 531.

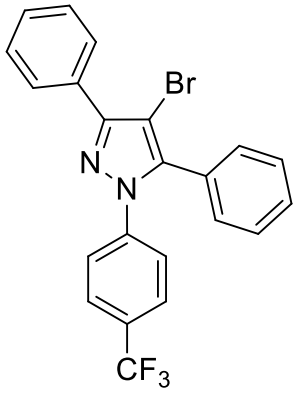
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 – 7.98 (m, 2H), 7.49 – 7.44 (m, 2H), 7.42 – 7.32 (m, 6H), 7.20 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.81 (dd, *J* = 6.8, 2.0 Hz, 2H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.02, 149.50, 142.15, 133.22, 132.21, 130.36, 129.19, 129.03, 128.59, 128.47 (2C), 128.19, 126.41, 114.16, 94.42, 55.60.

HR–MS (ESI): Calcd. for $C_{22}H_{17}N_2OBr$ (M+H): 405.0471, found: 405.0552.

407.0451, found: 407.0533.

4-Bromo-1-(4-trifluoromethylphenyl)-3,5-diphenyl-1*H*-pyrazole (3c)



Yield: 3.44 g (97%) as a colourless solid.

Melting point: 104 –106 °C

R_f: 0.51 in 20 % ethyl acetate in hexane

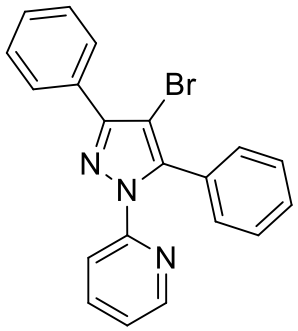
IR (ν cm^{-1}, in KBr): 3448, 2372, 2345, 1701, 1324, 1167, 1121, 1065, 842, 765, 695, 460.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 – 8.00 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.48 (m, 2H), 7.47 – 7.42 (m, 6H), 7.38 – 7.34 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.66, 142.57, 142.40, 131.74, 130.29, 129.61, 129.36 (q, *J* = 33 Hz), 128.99, 128.88, 128.86, 128.59, 128.21, 126.22 (q, *J* = 4 Hz), 123.88 (q, *J* = 270 Hz), 124.48, 96.29.

HR–MS (ESI): Calcd. for $C_{22}H_{14}N_2F_3Br$ (M+H): 443.0365, found: 443.0377.
445.0346, found: 445.0364.

4-Bromo-1-(2-pyridyl)-3,5-diphenyl-1*H*-pyrazole (3d)[4]



Yield: 2.86 g (95%) as a colourless solid.

Melting point: 121 °C

R_f: 0.28 in 20 % ethyl acetate in hexane

IR (ν cm^{-1}, in KBr): 3056, 1590, 1483, 1471, 1360, 1313, 1161, 1143, 1087, 1074, 1030, 995, 980, 967, 925, 771, 706, 697, 617, 512, 463.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 8.04 – 8.01 (m, 2H), 7.74 (ddd, *J* = 8.1, 7.4, 2.0 Hz, 1H), 7.53 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.44 – 7.34 (m, 6H), 7.20 (ddd, *J* = 7.4, 4.8, 0.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.27, 150.60, 148.57, 142.70, 138.37, 131.92, 130.17, 129.74, 128.94, 128.77, 128.47, 128.39 (2C), 122.76, 118.58, 96.45.

HR–MS (ESI): Calcd. for $C_{20}H_{14}N_3Br$ (M+H): 376.0443, found: 376.0100.
378.0424, found: 378.0079.

Scheme 3: Optimization of Cross-coupling of 4-Bromo-1,3,5-triphenyl-1*H*-pyrazole with Phenyl boronic Acid

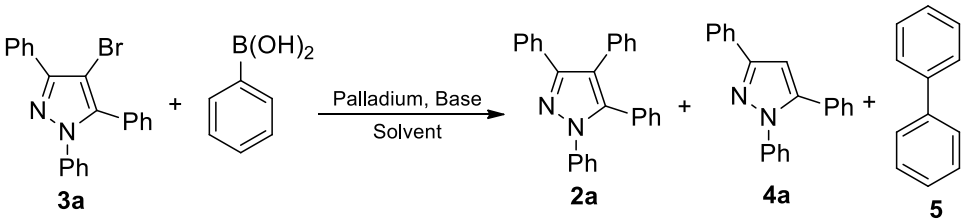
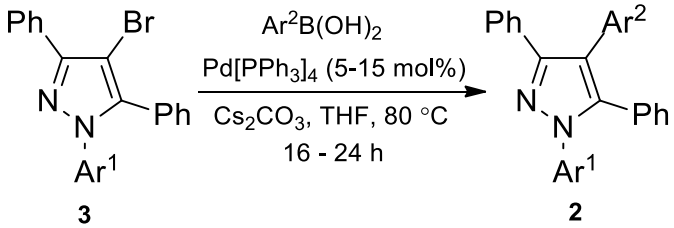


Table 1: Standardization of Cross-coupling Reaction[a]

S. No	Base	Solvent	Catalyst	Product 2a	4a	5
1	Na_2CO_3 (2M)	^{i}PrOH	$Pd(PPh_3)_4$	11%	36%	20%
2	Na_2CO_3 (2M)	^{i}PrOH	$Pd(dba)_2$	-	70%	15 %
3	$Ba(OH)_2$(2M)	Toluene	$Pd(PPh_3)_4$	38%	17%	5 %
4	Cs_2CO_3	Toluene	$Pd(PPh_3)_4$	38%	17	-
5	Cs_2CO_3	THF	$Pd(PPh_3)_4$	38%	17	-
6	Cs_2CO_3	Toluene	$Pd(PPh_3)_4$	16%	-	-
7[b]	Cs_2CO_3	THF	$Pd(PPh_3)_4$	64%	-	-
7[b,c]	Cs_2CO_3	THF	$Pd(PPh_3)_4$	75%	-	-

[a]Reaction Conditions: 4-Bromopyrazole (0.5 mmol), Phenyl Boronic Acid (0.6 mmol), Catalyst (5 mol-%), Base (1.5 mmol), Solvent (2 mL), 80 °C, 12 h; [b]Reaction was performed in Sealed tube; [c]Reaction time was 16 h.

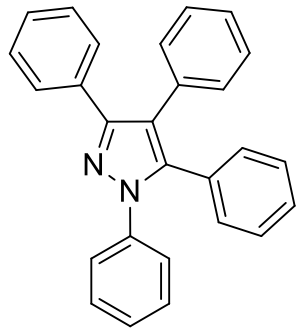
Scheme 4: General Procedure for Synthesis of 1,3,4,5-Tetraaryl-1*H*-pyrazoles by Suzuki Reaction



An oven-dried sealed tube was charged with $Pd(PPh_3)_4$ (5-15 mol%), 4-bromo-1,3,5-triarylpyrazole (0.45 mmol), arylboronic acid (0.54 mmol) and Cs_2CO_3 (0.67 mmol) in THF (5 mL) and was stirred at 80°C. The reaction was monitored by TLC or GC/MS analysis. After the

starting material was completely consumed, the reaction mixture was then cooled to room temperature and was purified by flash chromatography.

1,3,4,5-Tetraphenyl-1*H*-pyrazole (2a)[5]



Yield: 0.126 g (75%) as a colourless solid.

Melting point: 202 °C

R_f: 0.47 in 20 % ethyl acetate in hexane

UV (λ_{max}): 240 nm (15 µM solution in CH_3CN)

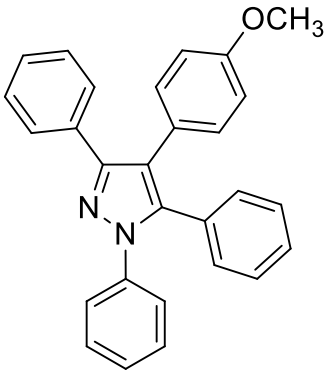
IR (ν cm^{-1}, in KBr): 2925, 2854, 2372, 2345, 1594, 1496, 1458, 1362, 1074, 964, 921, 793, 746, 768, 700, 650.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.52 (m, 2H), 7.36 – 7.28 (m, 8H), 7.24 – 7.18 (m, 6H), 7.13 – 7.10 (m, 2H), 7.08 – 7.05 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.30, 141.54, 140.0, 133.21, 133.19, 133.16, 130.84, 130.56, 130.17, 128.89, 128.54, 128.39, 128.32, 128.29, 127.78, 127.37, 126.80, 125.47, 120.85.

HR–MS (ESI): Calcd. for $C_{27}H_{20}N_2$(M+H): 373.1699, Found: 373.1728.

4-(4-Methoxyphenyl)-1,3,5-triphenyl-1*H*-pyrazole (2b)



Yield: 0.116 g (64%) as a colourless solid.

Melting point: 138 °C

R_f: 0.26 in 5% ethyl acetate in hexane

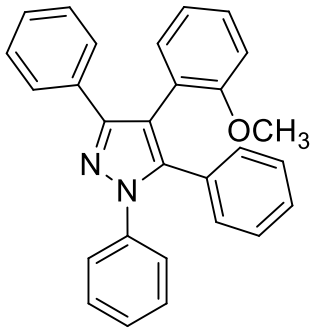
IR (ν cm^{-1}, in KBr): 3050, 3003, 2926, 1595, 1553, 1508, 1496, 1361, 1246, 1174, 1028, 969, 837, 770, 760, 700.

^1H NMR (400 MHz, $CDCl_3$): 7.76 – 7.54 (m, 2H), 7.32 – 7.20 (m, 11H), 7.08 – 7.05 (m, 2H), 7.03 – 7.01 (m, 2H), 6.76 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.50, 150.29, 141.41, 140.09, 133.31, 131.88, 130.57, 130.30, 128.88, 128.50, 128.39, 128.32, 128.21, 127.72, 127.32, 125.45, 125.40, 120.47, 113.83, 55.23.

HR–MS (ESI): Calcd. for $C_{28}H_{22}N_2O$(M+H): 403.1805, found: 403.1853.

4-(2-Methoxyphenyl)-1,3,5-triphenyl-1*H*-pyrazole (2c)



Yield: 0.132 g (73%) as a colourless solid.

Melting point: 116 °C

R_f: 0.23 in 20 % ethyl acetate in hexane

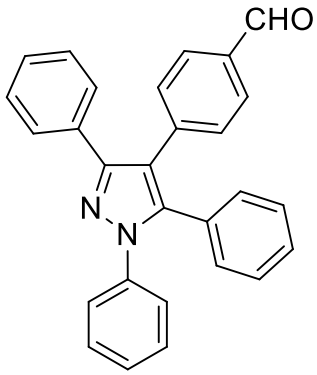
IR (ν cm^{-1}, in KBr): 2373, 2345, 1593, 1495, 1364, 1273, 1249, 1179, 1113, 1074, 1024, 970, 791, 763, 733, 699, 670.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.52 (m, 2H), 7.35 – 7.34 (m, 2H), 7.30 – 7.28 (m, 2H), 7.27 – 7.22 (m, 5H), 7.20 – 7.14 (m, 3H), 7.06 – 7.01 (m, 3H), 6.84–6.81 (m, 2H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.65, 150.76, 141.98, 140.18, 133.91, 132.79, 130.78, 129.95, 128.83(2C), 128.18, 128.17, 127.99, 127.66, 127.54, 127.17, 125.41, 122.47, 120.69, 117.10, 111.33, 55.11.

HR–MS (ESI): Calcd. for $C_{28}H_{22}N_2O$ (M+H): 403.1805, found: 403.1777.

4-(4-Formylphenyl)-1,3,5-triphenyl-1*H*-pyrazole (2d)



Yield: 0.067 g (37%) as a colourless solid.

Melting point: 147–148 °C

R_f: 0.44 in 25 % ethyl acetate in hexane

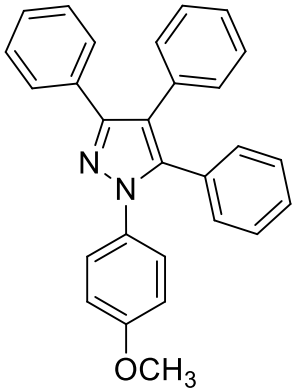
IR (ν cm^{-1}, in KBr): 2925, 2373, 2345, 1718, 1700, 1604, 1496, 1363, 1212, 1172, 1062, 970, 835, 769, 697.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.31 – 7.29 (m, 9H), 7.25 – 7.21 (m, 4H), 7.06– 7.05 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.10, 150.54, 141.96, 140.05, 139.73, 134.71, 132.73, 131.25, 130.52, 129.76, 129.69, 128.99, 128.76, 128.73, 128.70, 128.55, 128.18, 127.68, 125.51, 119.59.

HR–MS (ESI): Calcd. for $C_{28}H_{20}N_2O$ (M+H): 401.1648, found: 401.1594.

1-(4-Methoxyphenyl)-3,4,5-triphenyl-1*H*-pyrazole (2e)



Yield: 0.127 mg (70%) as a colourless solid.

Melting point: 186 °C

R_f: 0.32 in 20% ethyl acetate in hexane

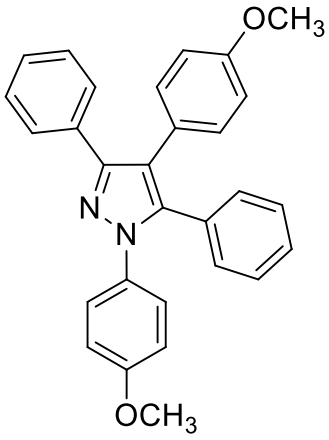
IR (ν cm^{-1}, in KBr): 3807, 2931, 2372, 2345, 1542, 1512, 1298, 1253, 1167, 1066, 1032, 969, 834, 771, 724, 699, 614, 540, 463.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 – 751 (m, 2H), 7.29 – 7.18 (m, 11H), 7.12–7.09 (m, 2H), 7.05 (dd, *J* = 8.2, 1.6 Hz, 2H), 6.85 – 6.81 (m, 2H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.79, 149.96, 141.51, 133.39, 133.37 (2C), 130.85, 130.59, 130.25, 128.54, 128.35, 128.31 (2C), 128.16, 127.67, 126.86, 126.71, 120.39, 114.08, 55.60.

HR–MS (ESI): Calcd. for $C_{28}H_{22}N_2O$ (M+H): 403.1805, found: 403.1803.

1,4-Di(4–methoxyphenyl)-3,5-diphenyl-1*H*-pyrazole (2f)



Yield: 0.136 mg (70%) as a colourless solid.

Melting point: 187–188 °C

R_f: 0.26 in 20% ethyl acetate in hexane

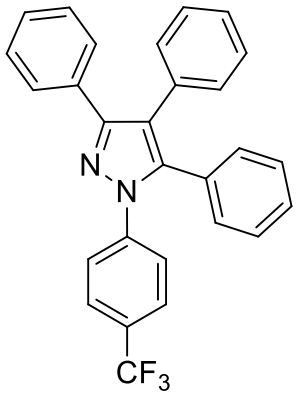
IR (ν cm^{-1}, in KBr): 3456, 2932, 1546, 1515, 1458, 1370, 1291, 1250, 1171, 1035, 971, 838, 771, 702, 680.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.53 (m, 2H), 7.31 – 7.24 (m, 4H), 7.22–7.17 (m, 4H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.03 – 6.99 (m, 2H), 6.85 – 6.79 (m, 2H), 6.77 – 6.73 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 158.47, 149.82, 141.46, 133.28, 133.25, 131.87, 130.58, 130.26, 128.51, 128.35, 128.31, 128.12, 127.68, 126.88, 125.47, 120.00, 114.08, 113.83, 55.59, 55.23.

HR–MS (ESI): Calcd. for $C_{29}H_{24}N_2O_2$ (M+H): 433.1911, found: 433.1856.

1-(4-Trifluoromethylphenyl)-3,4,5-triphenyl-1*H*-pyrazole (2g)



Yield: 0.135 mg (68%) as a colourless solid.

Melting point: 175 °C

R_f: 0.34 in 4% ether in hexane

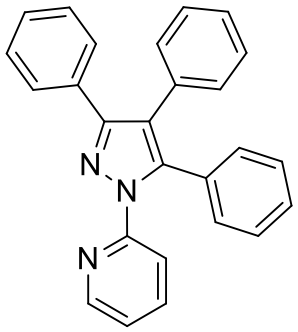
IR (ν cm^{-1}, in KBr): 3057, 2372, 2345, 1609, 1522, 1437, 1366, 1327, 1162, 1123, 1106, 1073, 1058, 1018, 967, 846, 776, 797, 766, 735, 726, 697, 684, 662, 593.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.33–7.28 (m, 5H), 7.24 – 7.20 (m, 4H), 7.11–7.08 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ =151.15, 142.80, 141.66, 132.84, 132.74, 130.76, 130.49, 129.86, 128.93 (q, *J* = 33 Hz), 128.73 (2C), 128.48, 128.41, 128.38, 128.07, 127.04, 126.07 (q, *J* = 4 Hz), 124.93, 124.01 (q, *J* = 270 Hz), 121.83.

HR–MS (ESI): Calcd. for $C_{28}H_{19}F_3N_2$ (M+H): 441.1573, found: 441.1513.

1-(2-Pyridyl)-3,4,5-triphenyl-1*H*-pyrazole (2i)



Yield: 0.114 mg (68%) as a colourless solid (15 mol% of catalyst).

Melting point: 174 °C

R_f: 0.34 in 50% ether in hexane

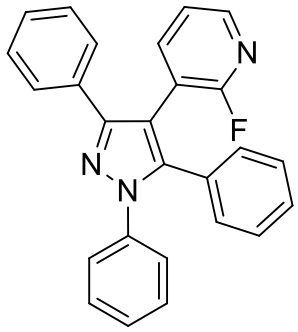
IR (ν cm^{-1}, in KBr): 2372, 2345, 1586, 1458, 1470, 1449, 1361, 1179, 1146, 1074, 991, 971, 800, 787, 770, 742, 701, 651.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (ddd, *J* = 5.0, 1.6, 0.8 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.54 – 7.51 (m, 3H), 7.29 – 7.27 (m, 3H), 7.23 – 7.18 (m, 7H), 7.14 – 7.07 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.58, 151.19, 148.63, 141.92, 138.19, 133.07, 133.01, 130.89, 130.59, 130.39, 128.62, 128.31, 128.27, 128.15, 128.11, 127.92, 126.92, 122.46, 121.81, 119.28.

HR–MS (ESI): Calcd. for $C_{26}H_{19}N_3$ (M+H): 374.1651, found: 374.1674.

4-(2-Fluoro-3-pyridyl)-1,3,5-triphenyl-1*H*-pyrazole (2h)



Yield: 0.132 g (75%) as a colourless solid (15 mol% of catalyst).

Melting point: 225 °C

R_f: 0.25 in 20 % ethyl acetate in hexane

IR (ν cm^{-1}, in KBr): 3448, 2925, 2372, 2345, 1498, 1426, 1365, 1246, 1211, 1111, 1073, 102, 971, 844, 809, 790, 767, 738, 700, 670.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 4.4 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.36 – 7.27 (m, 9H), 7.24 – 7.20 (m, 2H), 7.10 – 7.06 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.43 (d, *J* = 239.0 Hz), 150.84, 146.89 (d, *J* = 14 Hz), 143.57 (d, *J* = 5.0 Hz), 142.86, 139.75, 132.77, 129.93, 129.57, 128.98, 128.77, 128.66, 128.61, 128.18, 127.86, 127.66, 125.36, 121.38 (d, *J* = 5.0 Hz), 116.51 (d, *J* = 31. Hz), 112.73 (d, *J* = 4.0 Hz).

HR–MS (ESI): Calcd. for $C_{26}H_{18}N_3F$(M+H): 392.1558, found: 392.1633.

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1. S. Peruncheralathan, T. A. Khan, H. Ila, H. Junjappa *J. Org. Chem.* **2005**, *70*, 10030.
2. X. Li, L. He, H. Chen, W. Wu, H. Jiang, *J. Org. Chem.*, **2013**, *78*, 3636.
3. R. N. Butler, J. M. Hanniffy, J. C. Stephens, L. A. Burke, *J. Org. Chem.*, **2008**, *73*, 1354.
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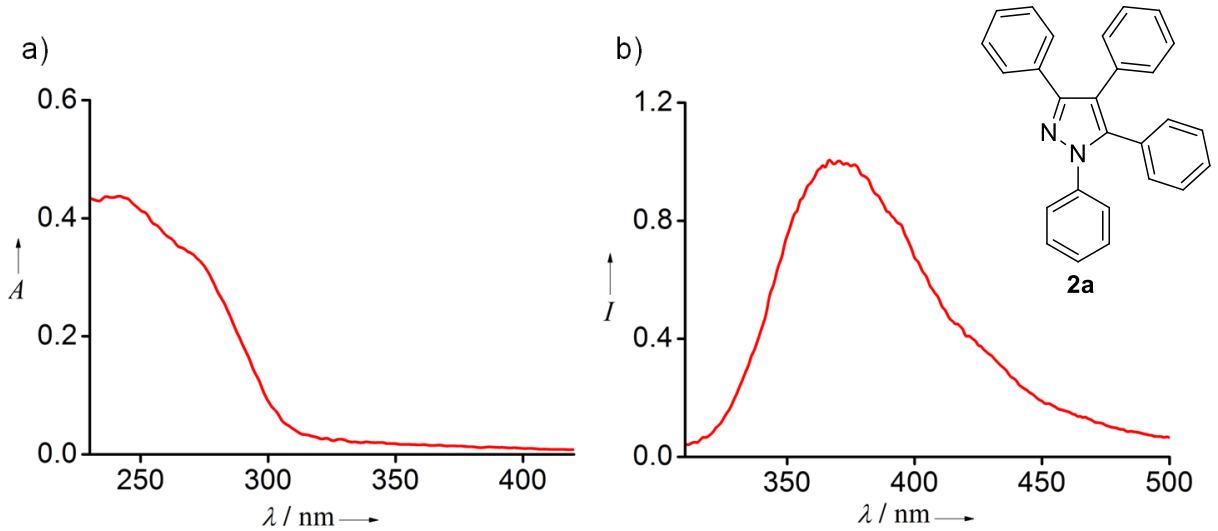


Figure S1: Absorption (a) and emission (b) spectrum of **2a** in acetonitrile

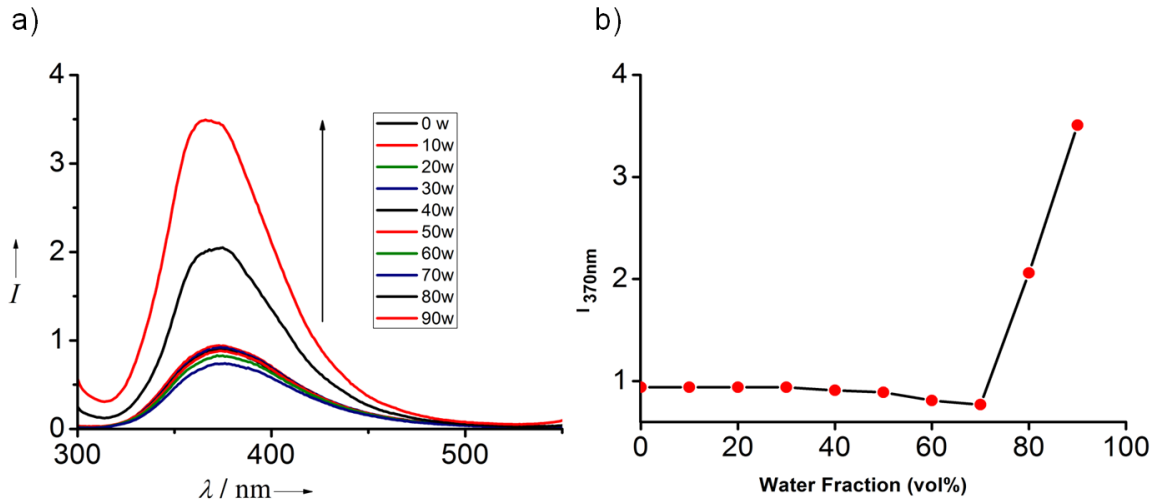


Figure S2: (a) Emission spectra of **2a** in acetonitrile/water mixtures with increasing addition of water (f_w = 0-90 vol%). (b) The changes in the emission intensity of **2a** with the water contents in the acetonitrile/water mixture.

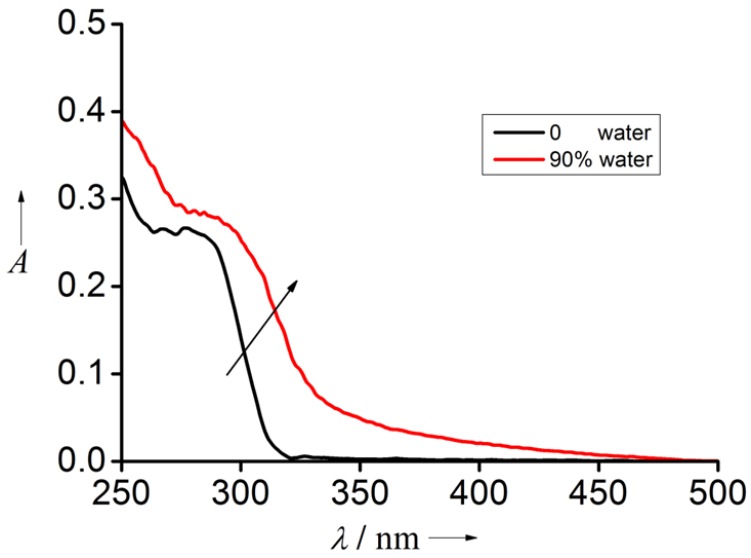


Figure S3: Absorption spectra of **2a** in acetonitrile (f_w = 0 vol%) and acetonitrile/water mixture (f_w = 90 vol%)

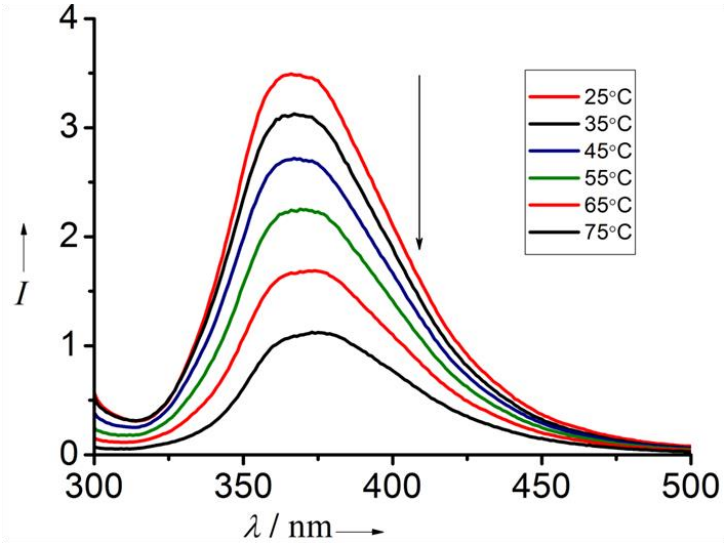


Figure S4: Temperature effect on the emission intensity of **2a** in acetonitrile/water (1:9 v/v), (λ_{ex} = 280 nm)

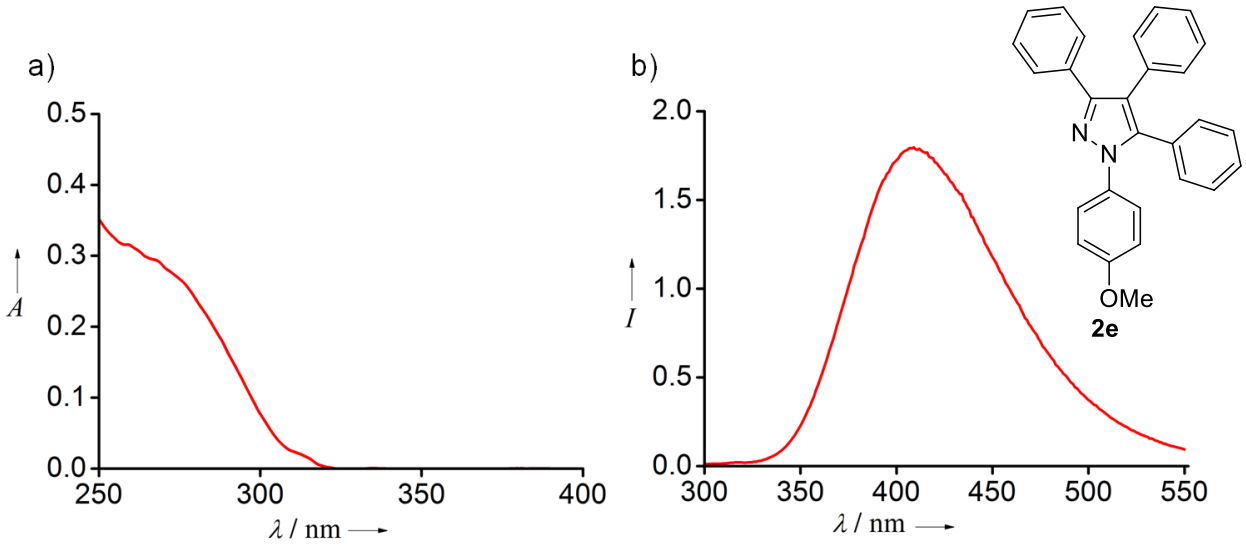


Figure S5: Absorption (a) and emission (b) spectrum of **2e** in acetonitrile

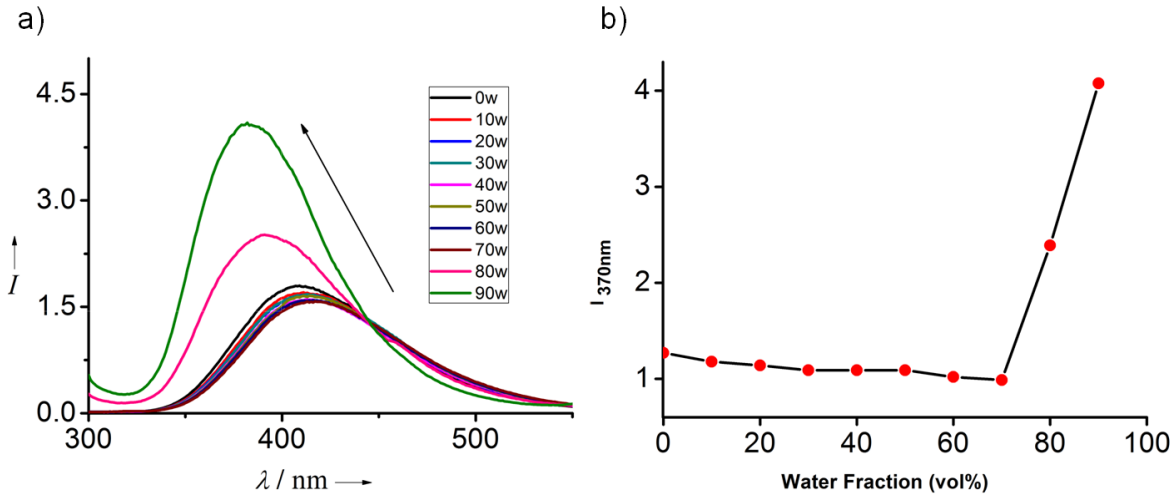


Figure S6: (a) Emission spectra of **2e** in acetonitrile/water mixtures with increasing addition of water (f_w=0-90 vol%). (b) The changes in the emission intensity of **2e** with the water contents in the acetonitrile/water mixture.

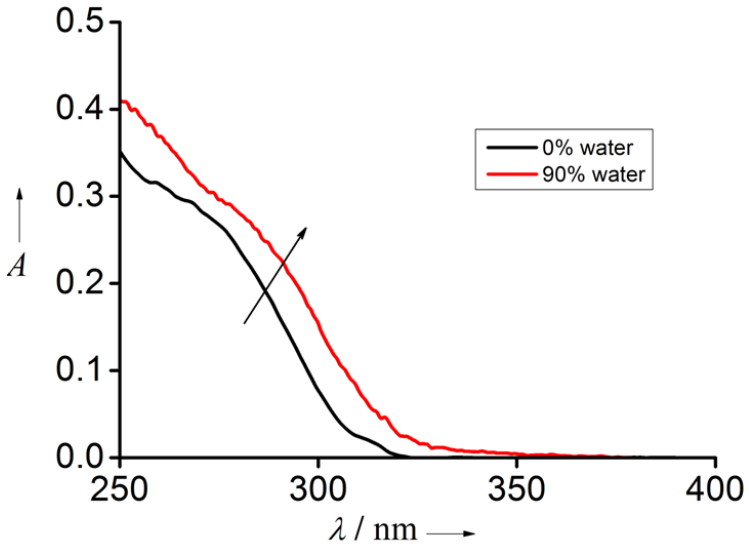


Figure S7: Absorption spectra of **2e** in acetonitrile (f_w= 0 vol%) and acetonitrile/water mixture (f_w= 90 vol%)

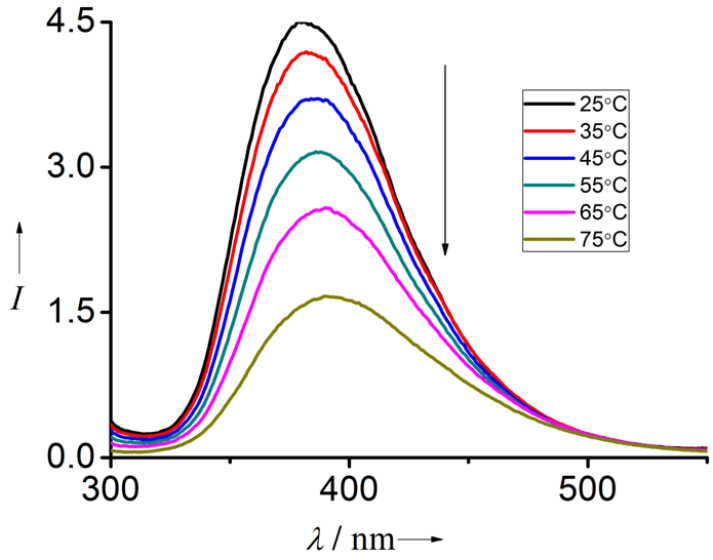


Figure S8: Temperature effect on the emission intensity of **2e** in acetonitrile/water (1:9 v/v), (λ_{ex}=280 nm)

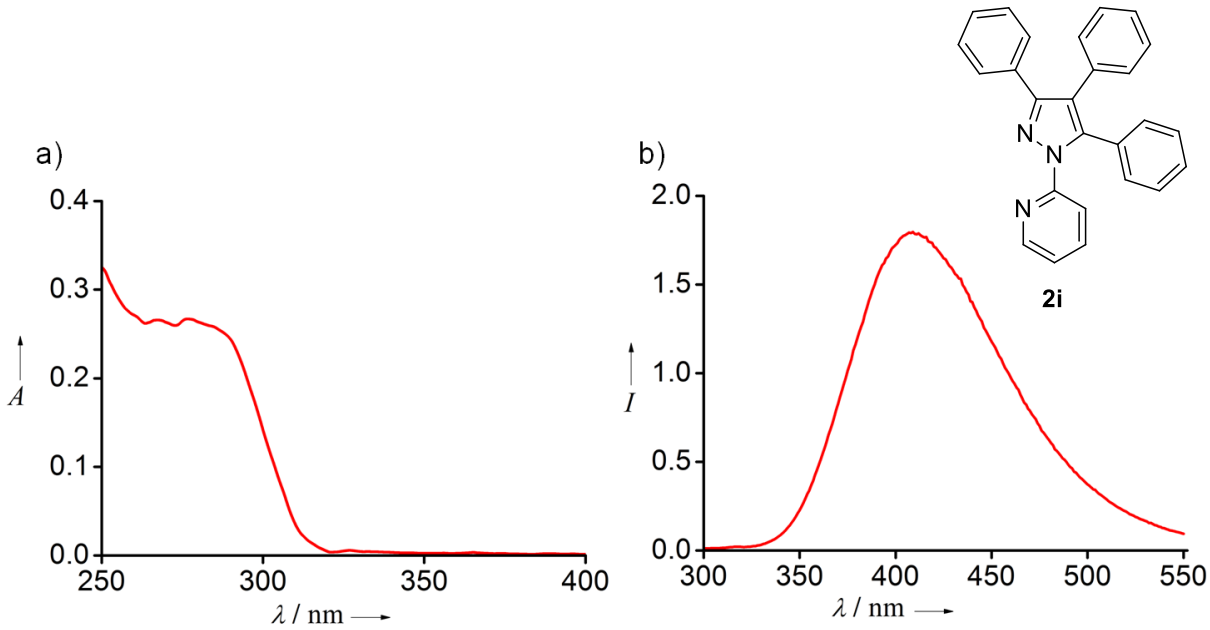


Figure S9: Absorption (a) and emission (b) spectrum of **2i** in acetonitrile

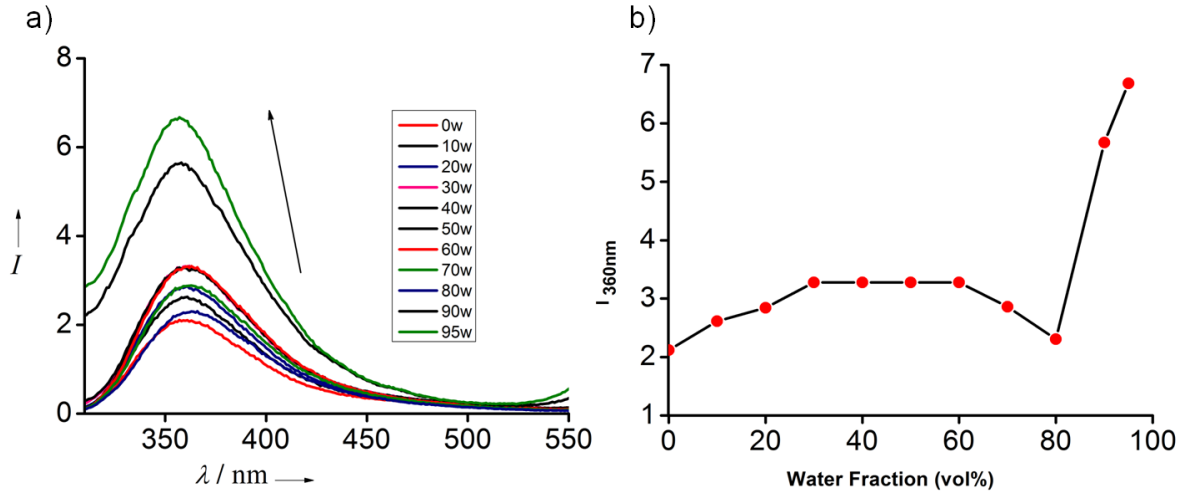


Figure S10: (a) Emission spectra of **2i** in acetonitrile/water mixtures with increasing addition of water (f_w=0-95 vol%). (b) The changes in the emission intensity of **2i** with the water contents in the acetonitrile/water mixture.

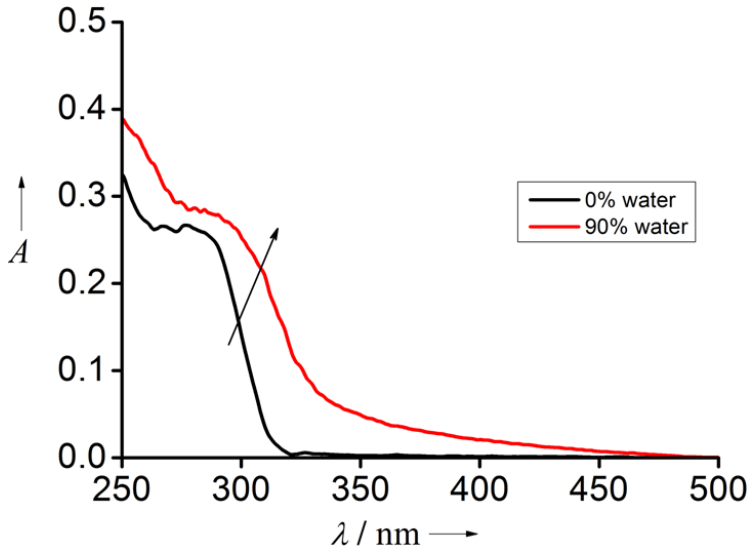


Figure S11: Absorption spectra of **2i** in acetonitrile (f_w= 0 vol%) and acetonitrile/water mixture (f_w= 90 vol%)

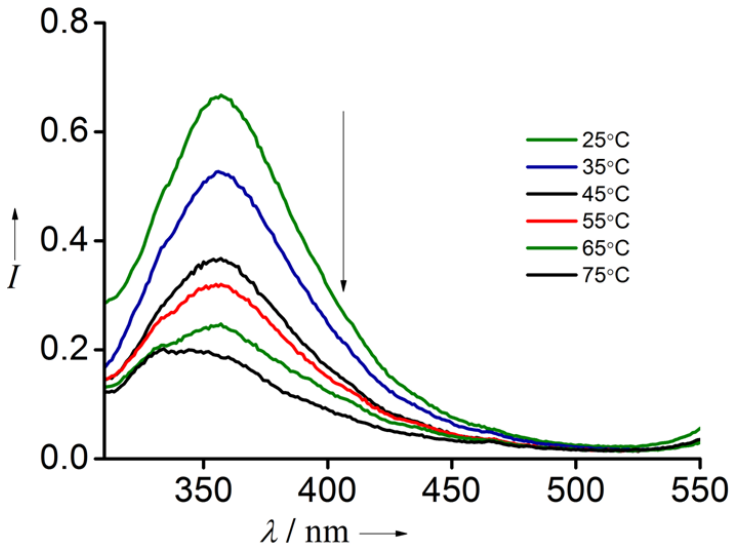


Figure S12: Temperature effect on the emission intensity of **2i** in acetonitrile/water (1:9 v/v), (λ_{ex}=280 nm)

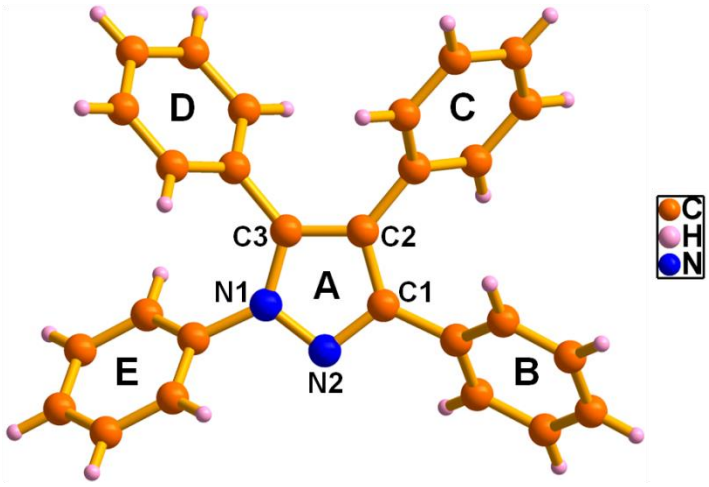


Figure S13: Single crystal X-ray structure of **2a** with the dihedral angle between the planes.

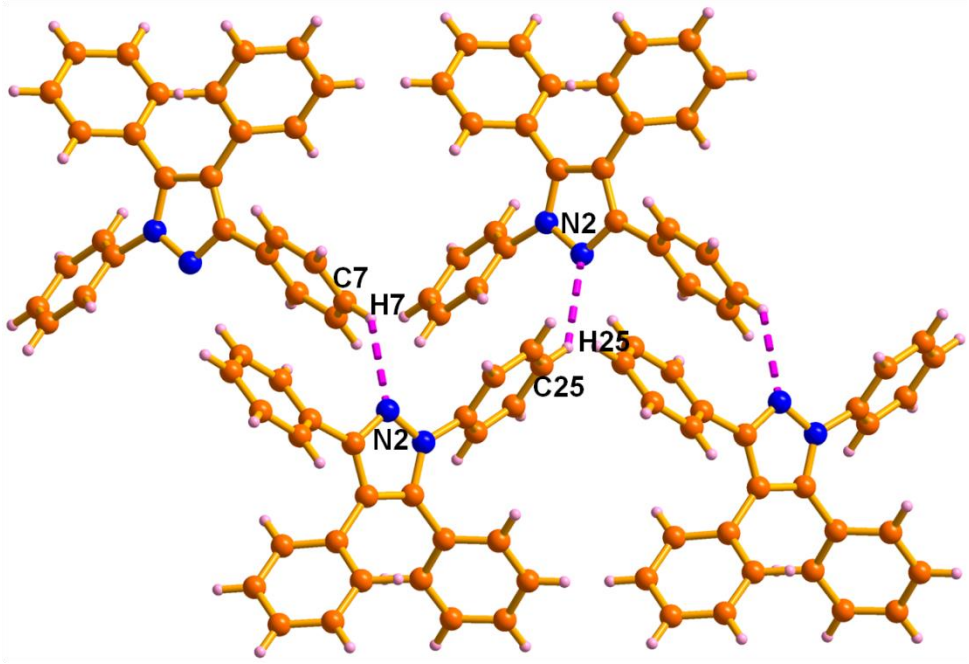


Figure S14: 1-D array in **2a.** The array is formed between one of the phenyl-CHs (C7-H7; C25-H25) with two different units of pyrazole nitrogens (N2) with the bond distances and angles of C7-H7…N2 and C25-H25…N2 are 2.78 Å; 141° and 2.80Å; 140°.

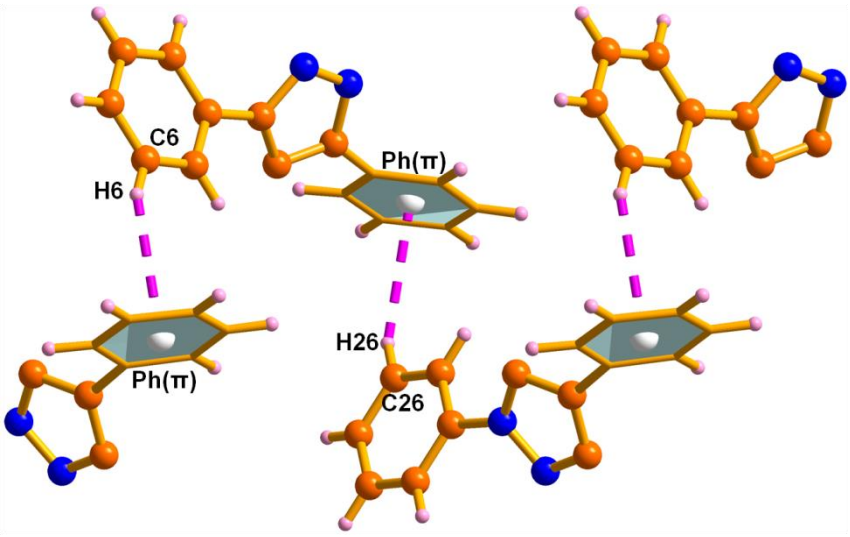


Figure S15: 1-D array in **2a**. The array is formed between one of the phenyl-CHs (C6-H6) and N-phenyl-CH (C26-H26) unit with two different phenyl π-clouds with the bond distances and angles of C6-H6…Ph(π) and C26-H26…Ph(π) are: 3.00 Å and 144°.

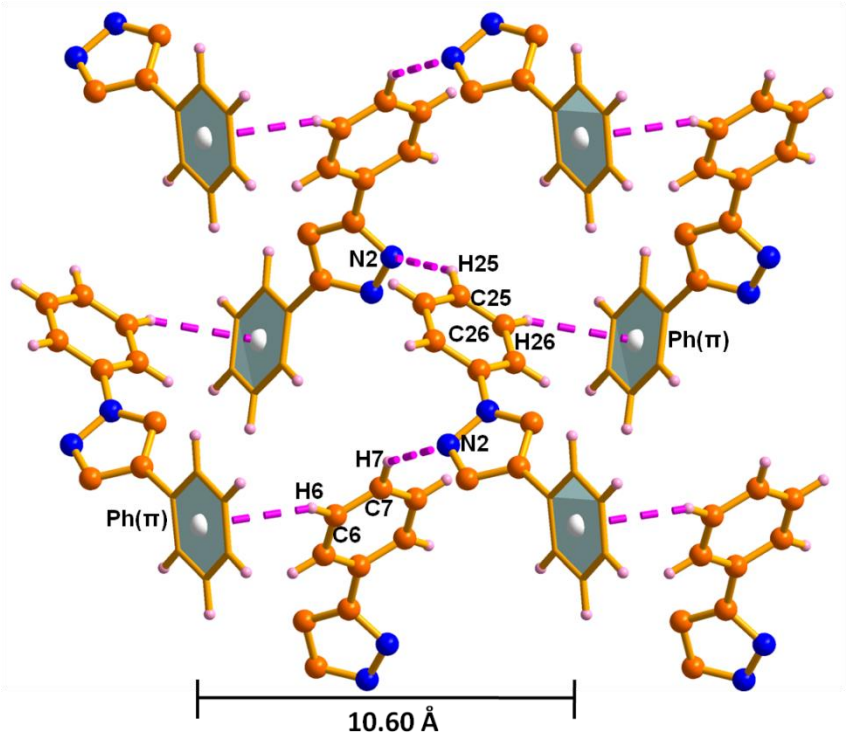


Figure S16: 2-D array in **2a**. The π – π distance between two closely packed molecules is 10.60Å. The bond distance and angles of C7-H7…N2; C25-H25…N2; C6-H6…Ph(π) and C26-H26…Ph(π) are 2.78 Å & 141°; 2.80Å & 140° and 3.00 Å &144°.

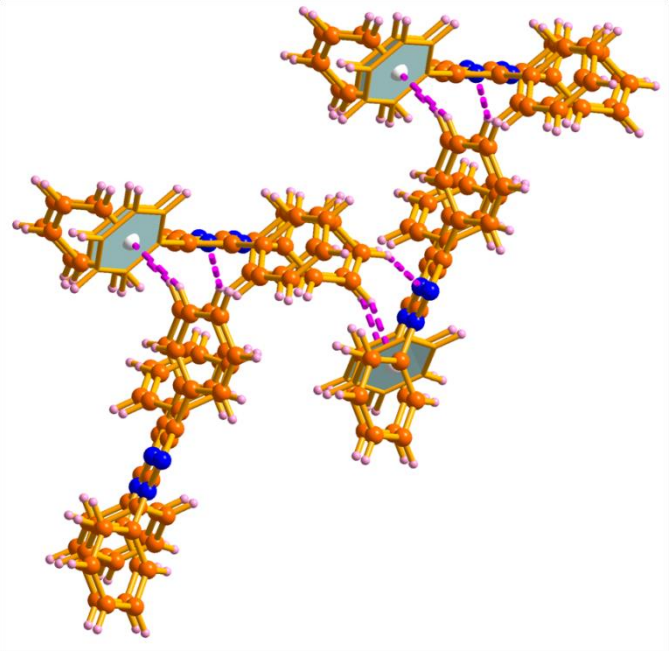


Figure S17: Crystal packing in **2a**.

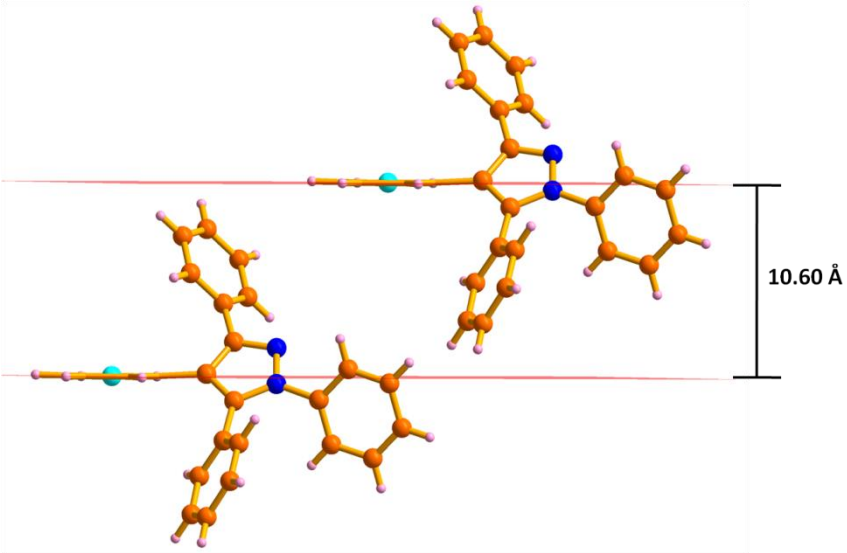


Figure S18: The π – π distance between two closely packed molecules in **2a** is 10.60 Å.

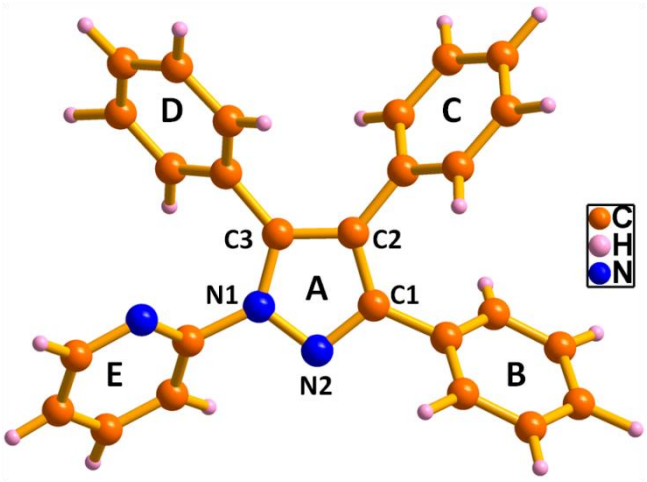


Figure S19: Single crystal X-ray structure of **2i** with the dihedral angle between the planes.

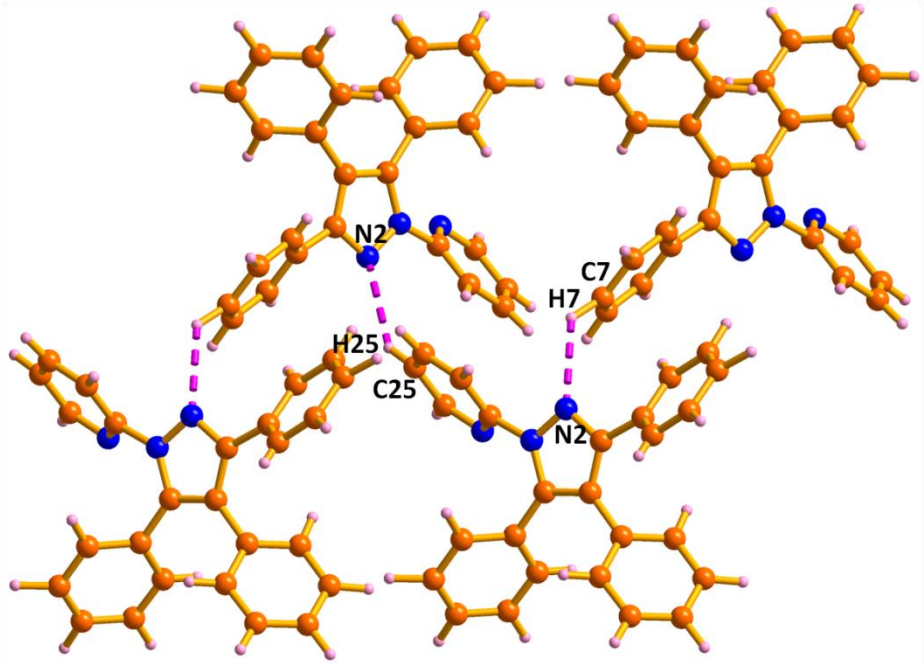


Figure S20: 1-D array in **2i**. The array is formed between one of the phenyl-CHs (C7-H7; C25-H25) with two different units of pyrazole nitrogens (N2) with the bond distances and angles of C7-H7…N2 and C25-H25…N2 are 2.66 Å; 133° and 2.70Å; 145°.

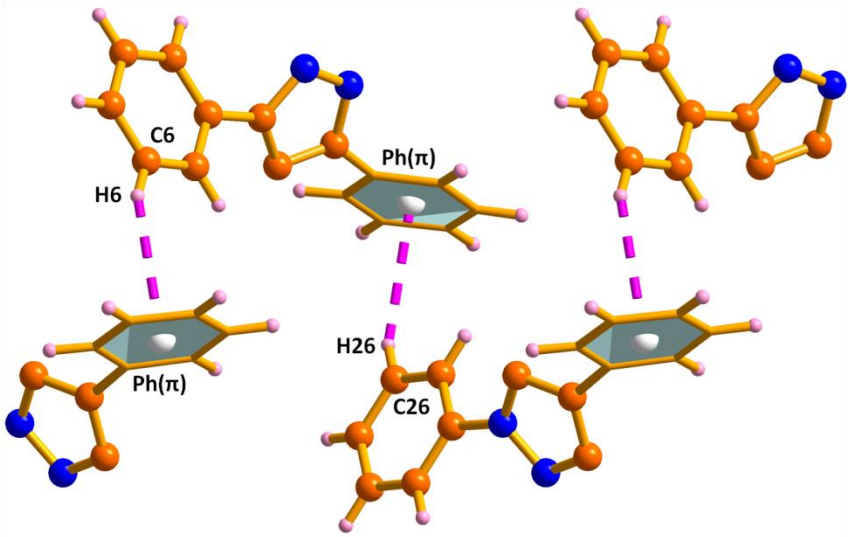


Figure S21: 1-D array in **2i**. The array is formed between one of the phenyl-CHs (C6-H6) and N-phenyl-CH (C26-H26) unit with two different phenyl π-clouds with the bond distances and angles of C6-H6…Ph(π) and C26-H26…Ph(π) are 3.05 Å; 144° and 2.92 Å; 145°.

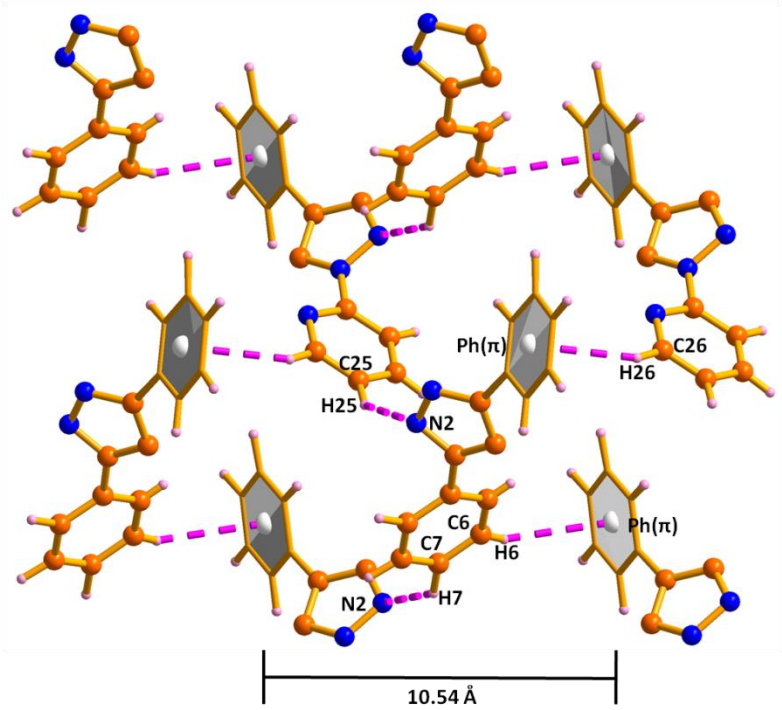


Figure S22: 2-D array in **2i**. The π – π distance between two closely packed molecules is 10.54Å. The bond distances and angles of C7-H7…N2; C25-H25…N2; C6-H6…Ph(π) and C26-H26…Ph(π) are 2.66 Å & 133°; 2.70Å & 145°; 3.05 Å &144° and 2.92 Å & 145°.

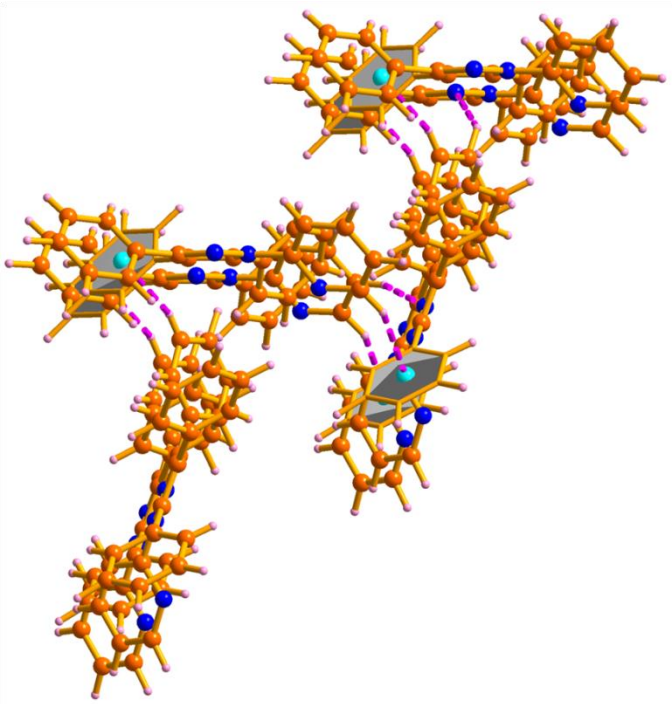


Figure S23: Crystal packing in **2a**.

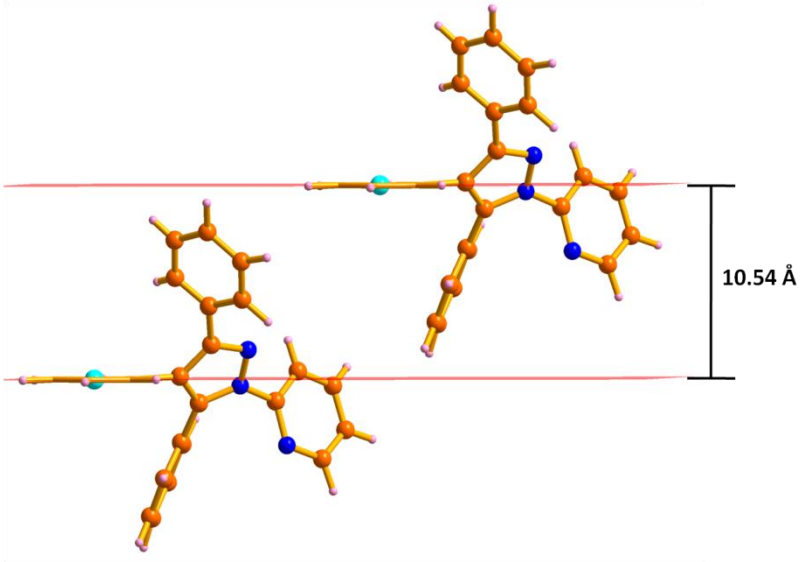


Figure S24: The π – π distance between two closely packed molecules in **2i** is 10.54 Å.

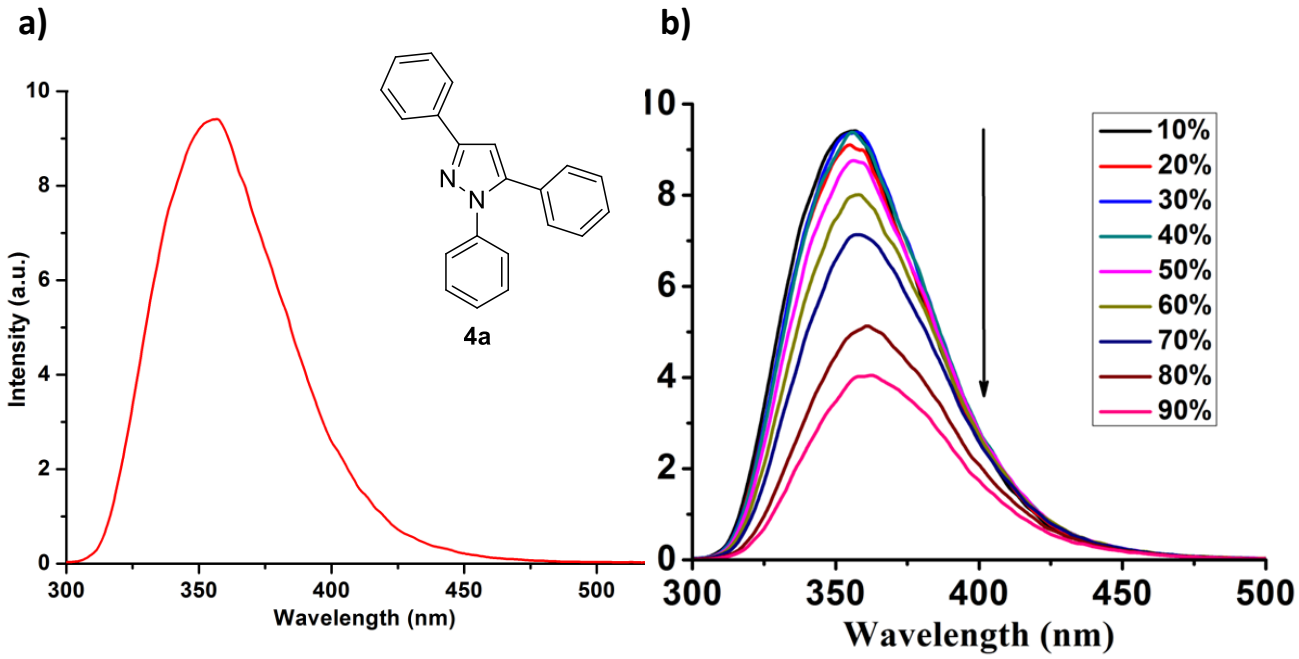
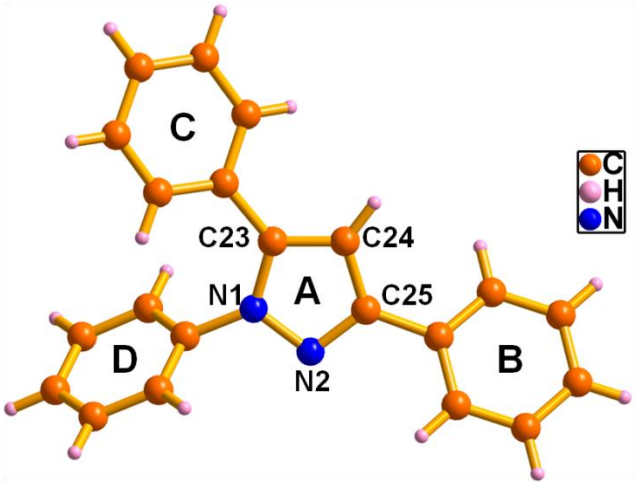


Figure S25: a) Emission spectra of **4a** in acetonitrile, b) Emission spectra of **4a** in acetonitrile /water mixtures with increasing addition of water (f_w=0-90 vol%).



Dihedral Angle (°) between Planes

A and B: 33.6°

A and C: 29.5°

A and D: 64.1°

Figure S26: Single crystal X-ray structure of **4a** with the dihedral angle between the planes.

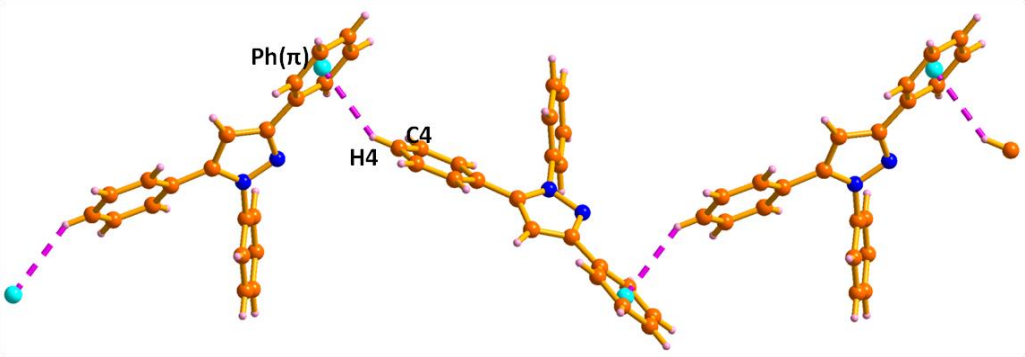


Figure S27 1-D array in **4a**. The array is formed between one of the phenyl-CHs (C4-H4) and second pyrazole unit phenyl π-cloud with the bond distance and angle of C4-H4…Ph(π) is: 2.88 Å and 147°.

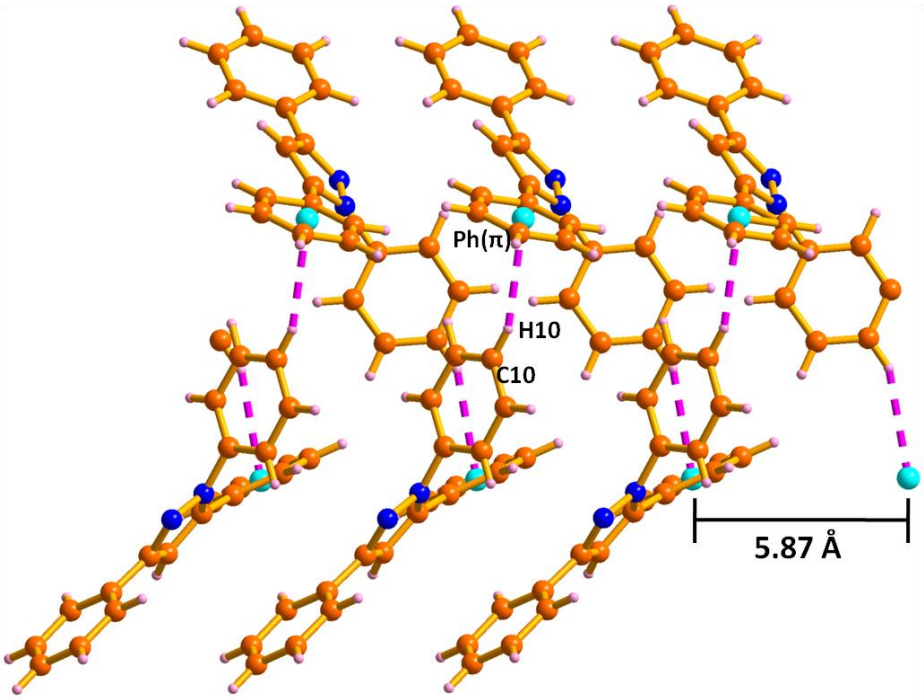


Figure S28: 1-D array in **4a**. The array is formed between one of the pyrazole N-phenyl-CHs (C10-H10) and second pyrazole unit phenyl π-cloud with the bond distance and angle of C10-H10…Ph(π) is: 2.88 Å and 156°. The π – π distance between two closely packed molecules is 5.87 Å.

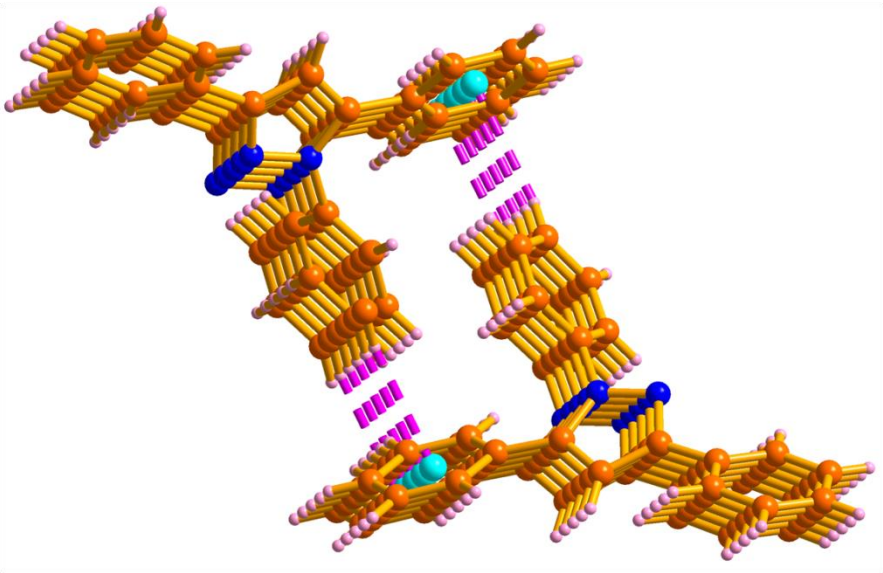


Figure S29: Crystal packing in **4a**.

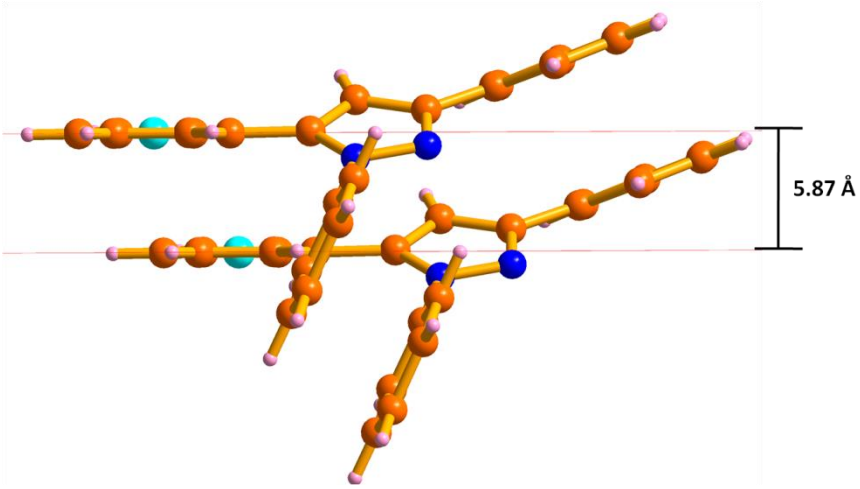


Figure S30: The π – π distance between two closely packed molecules in **4a** is 5.87 Å.

Crystallographic data of 2a, 2i and 4a:

Crystallographic data of **2a** in CH_2Cl_2/*n*-hexane**:** $C_{27}H_{20}N_2$**,** Mw = 372.45, monoclinic, space group $P2_1$, a = 9.9297(3) Å, b = 9.6354(3) Å, c = 10.6037(3) Å, α = 90.00 º, β = 90.080(2) º, γ = 90.00º, *V* = 1014.53(5) $Å^3$, *Z* = 2, *D*calc = 1.219 mg/m3, *T* = 296(2) K, R1 = 0.0443 {I > 2σ (I)}, R2w = 0.1085, GOF = 1.038.

Crystallographic data of **2i** in CH_2Cl_2/*n*-hexane**:** $C_{26}H_{19}N_3$**,** Mw = 373.44, monoclinic, space group $P2_1$, a = 9.7331(3) Å, b = 9.7771(3) Å, c = 10.5392(3) Å, α = 90.00 º, β = 90.204(2) º, γ = 90.00º, *V* = 1002.92(5) $Å^3$, *Z* = 2, *D*calc = 1.237 mg/m3, *T* = 296(2) K, R1 = 0.0431 {I > 2σ (I)}, R2w = 0.1021, GOF = 1.002.

Crystallographic data of **4a** in CH_2Cl_2/*n*-hexane**:** $C_{21}H_{16}N$**,** Mw = 296.36, orthorhombic, space group Fdd2, a = 29.627(10) Å, b = 36.790(12) Å, c = 5.865(2) Å, α = 90.00 º, β = 90.00 º, γ = 90.00º, *V* = 6393(6) $Å^3$, *Z* = 16, *D*calc = 1.232 mg/m3, *T* = 296(2) K, R1 = 0.0401 {I > 2σ (I)}, R2w = 0.0992, GOF = 0.978.

CCDC-1032189, 1032190 & 1032191 contain the supplementary crystallographic data for **2a**, **2i** and **4a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

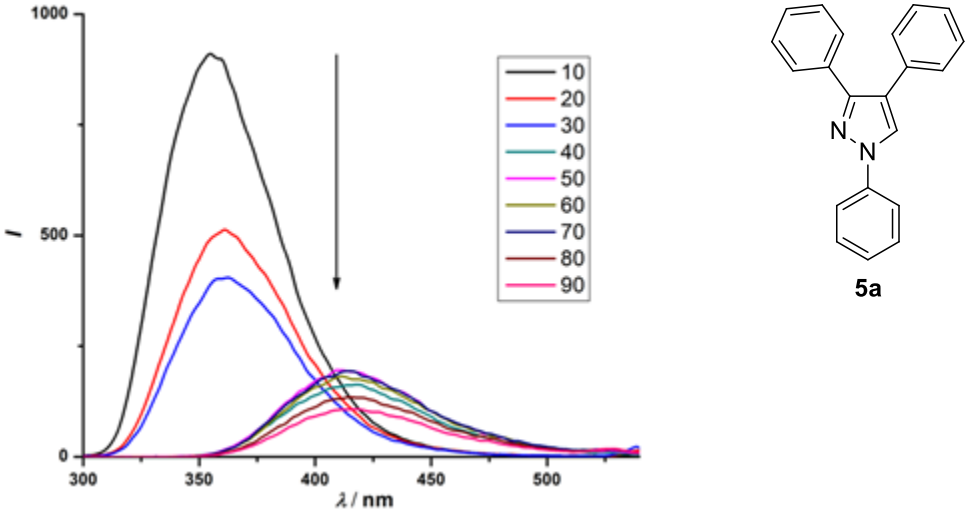
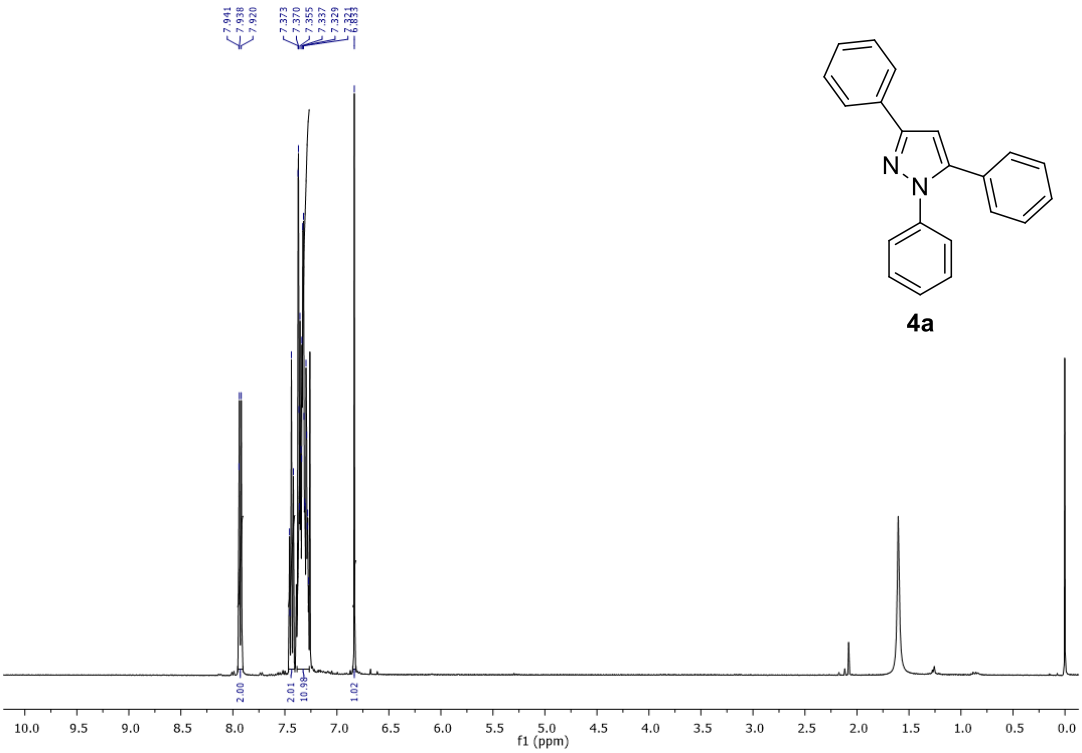
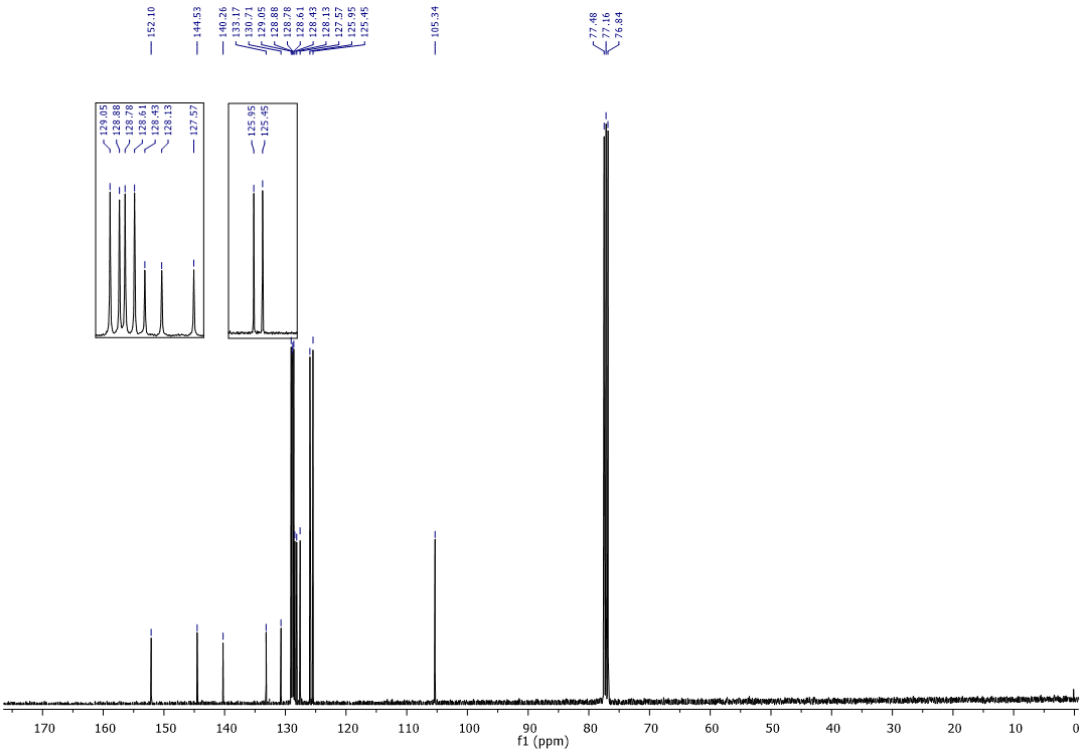


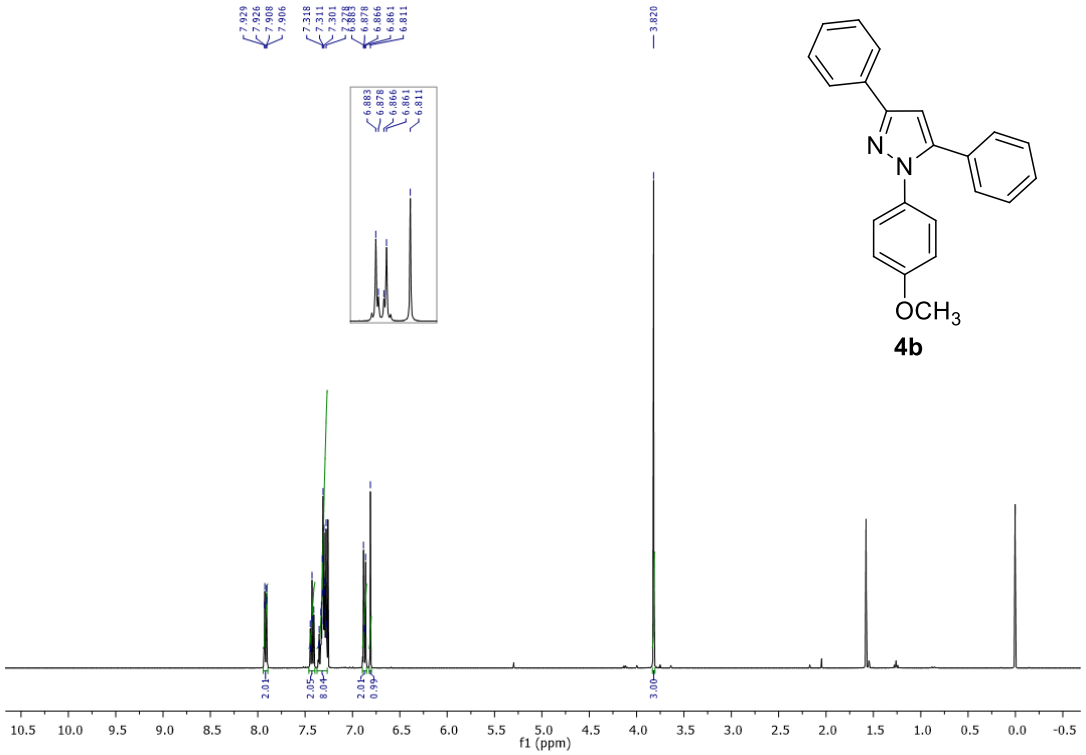
Figure S31: (a) Emission spectra of **1,3,4-triphenyl-1*H*-pyrazole (5a)** in acetonitrile/water mixtures with increasing addition of water (f_w=0-90 vol%).



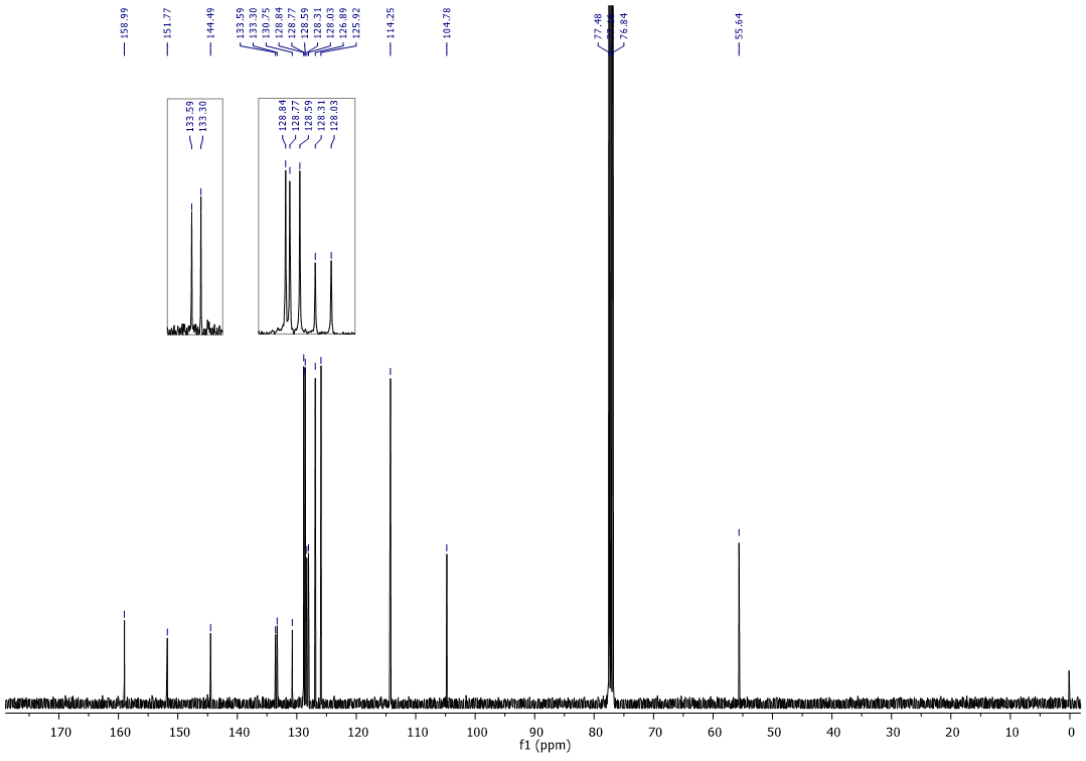
^{1}H NMR Spectra of **4a**



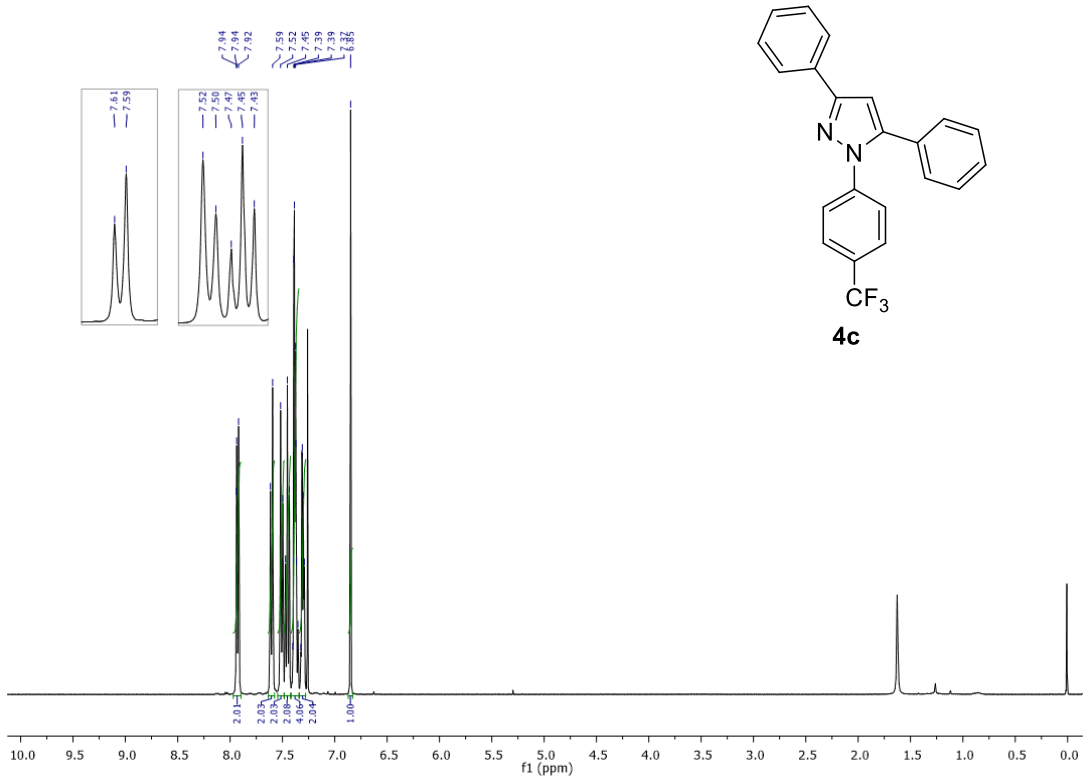
^{13}C NMR Spectra of **4a**



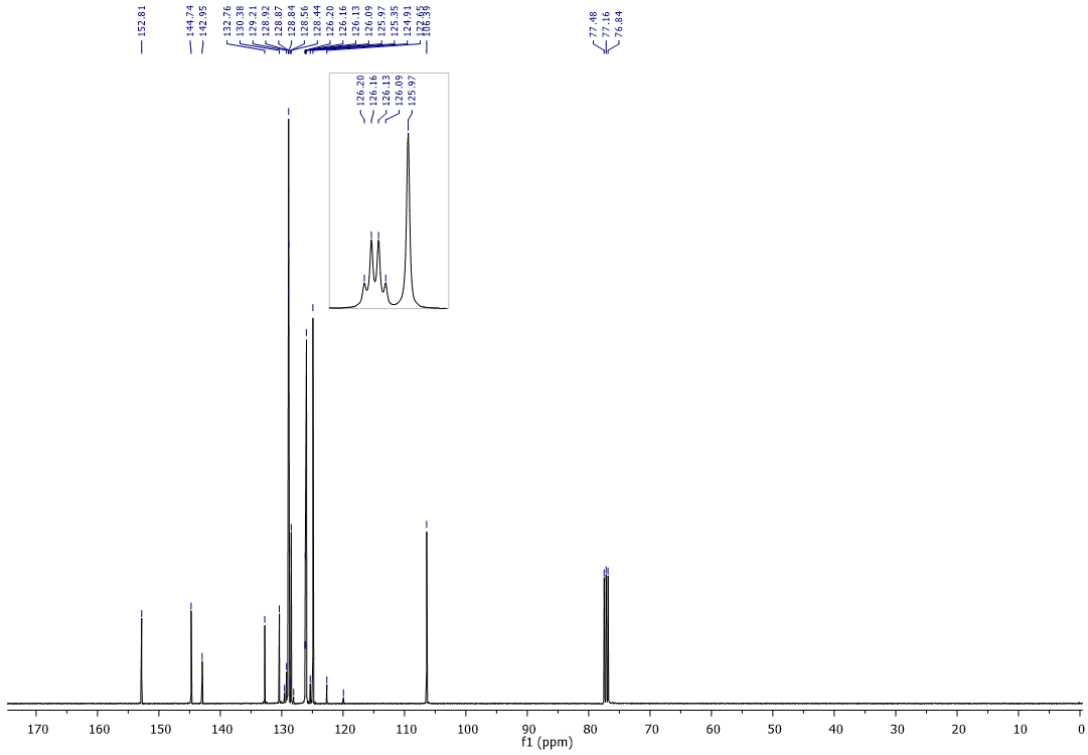
^{1}H NMR Spectra of **4b**



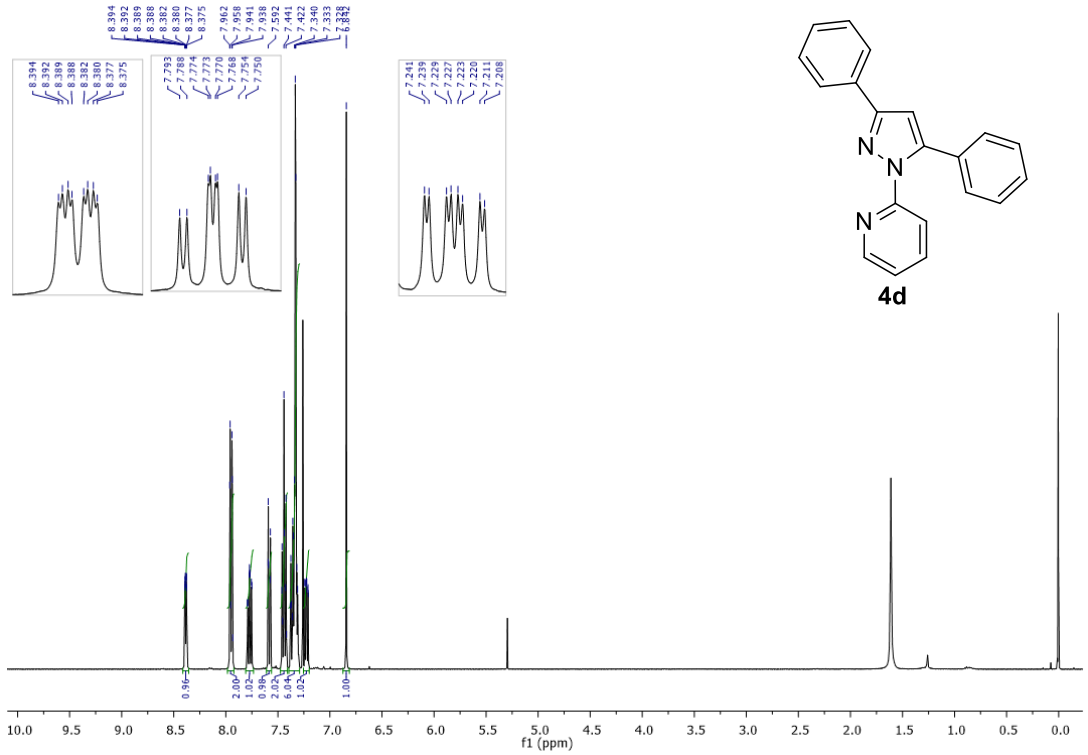
^{13}C NMR Spectra of **4b**



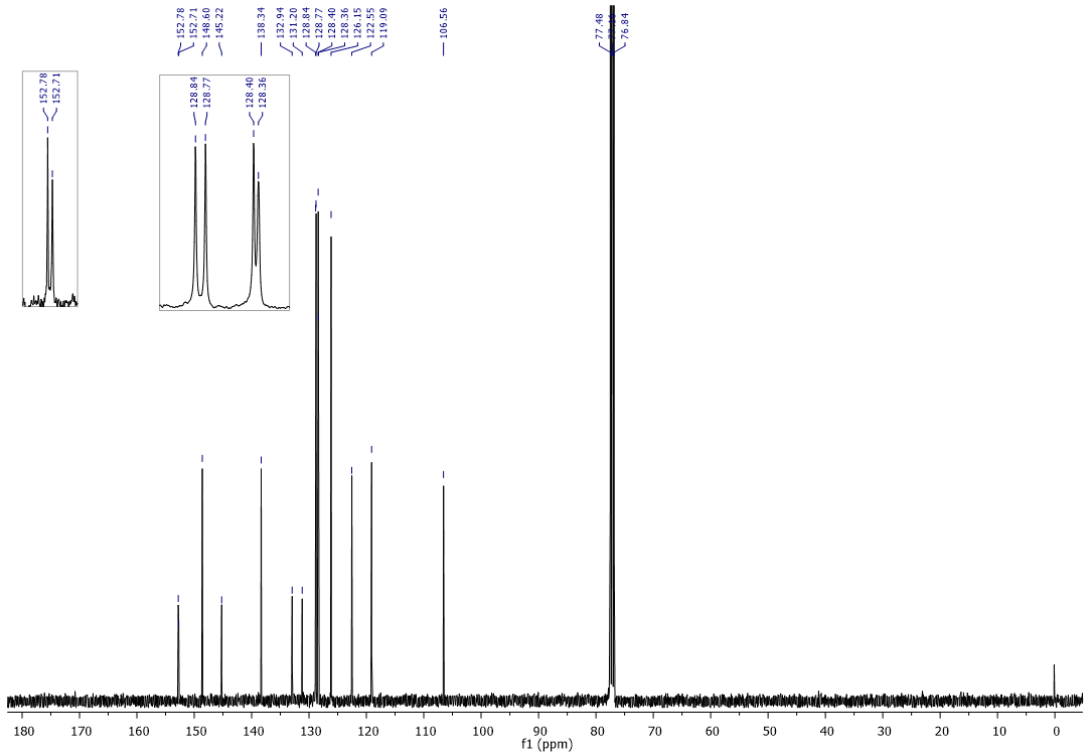
^{1}H NMR Spectra of **4c**



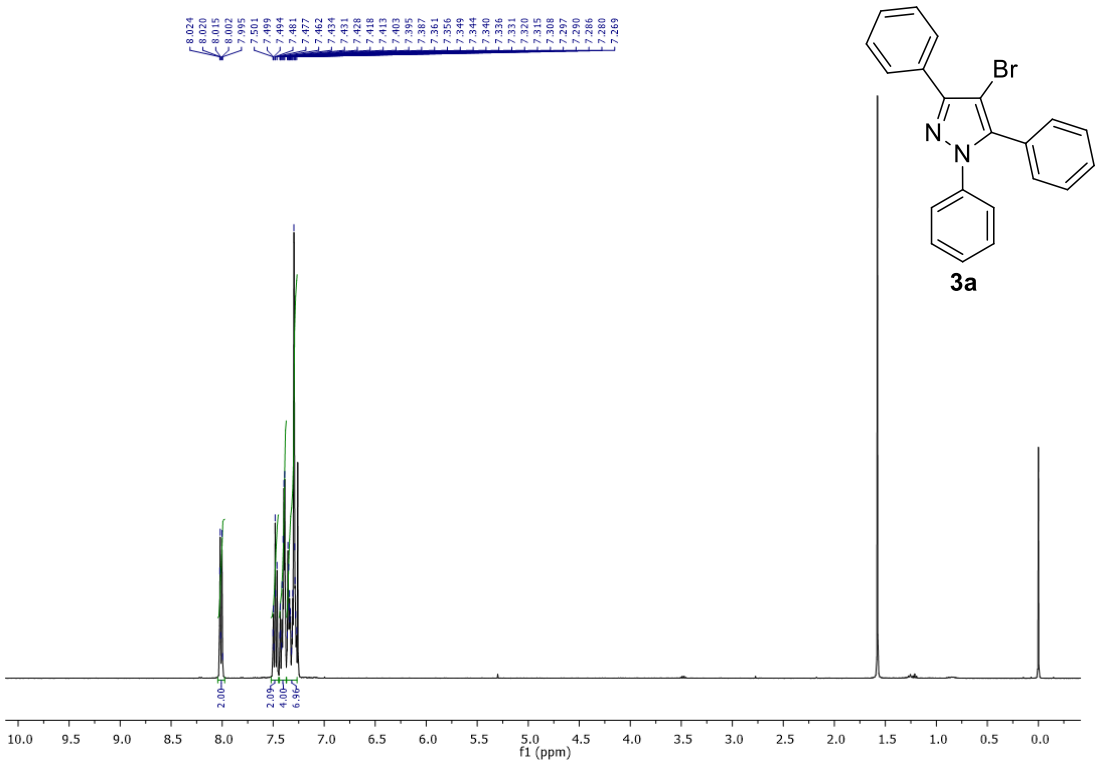
^{13}C NMR Spectra of **4c**



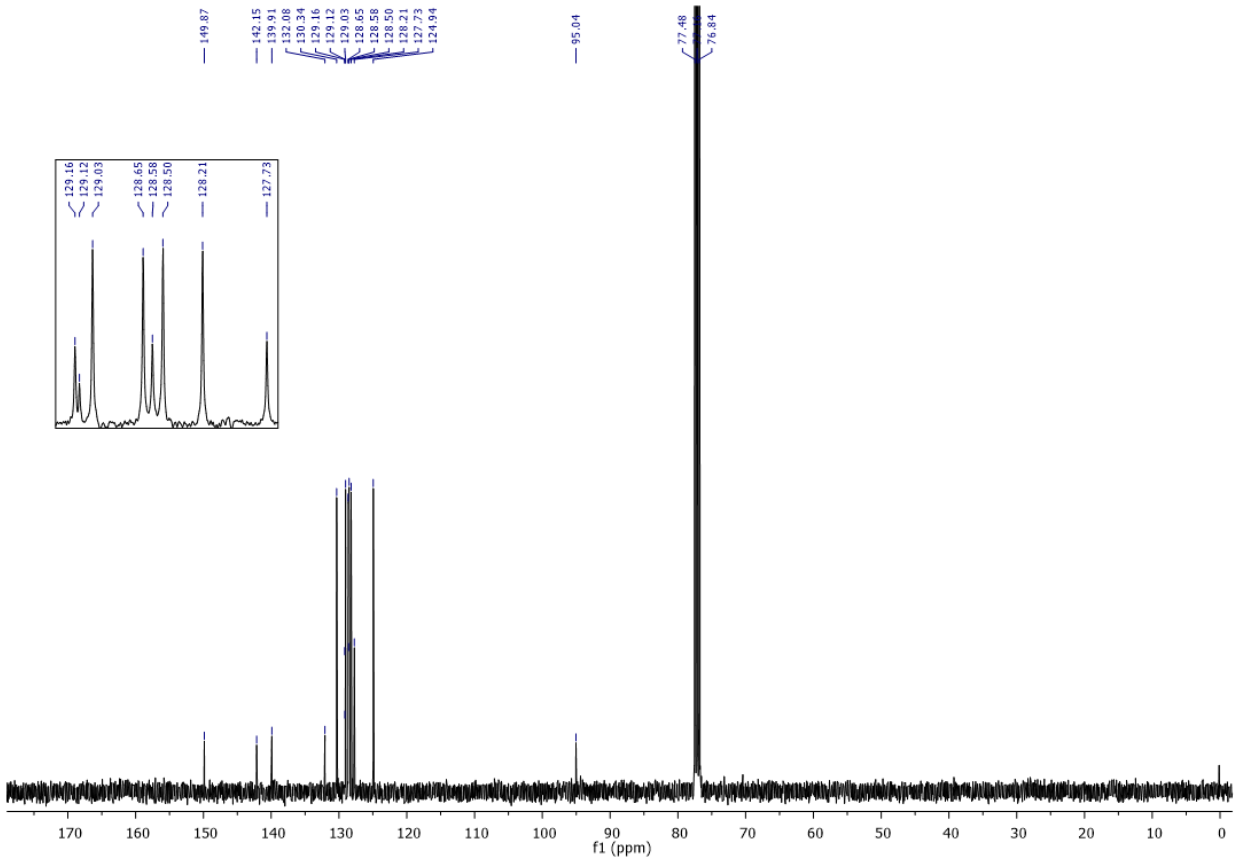
^{1}H NMR Spectra of **4d**



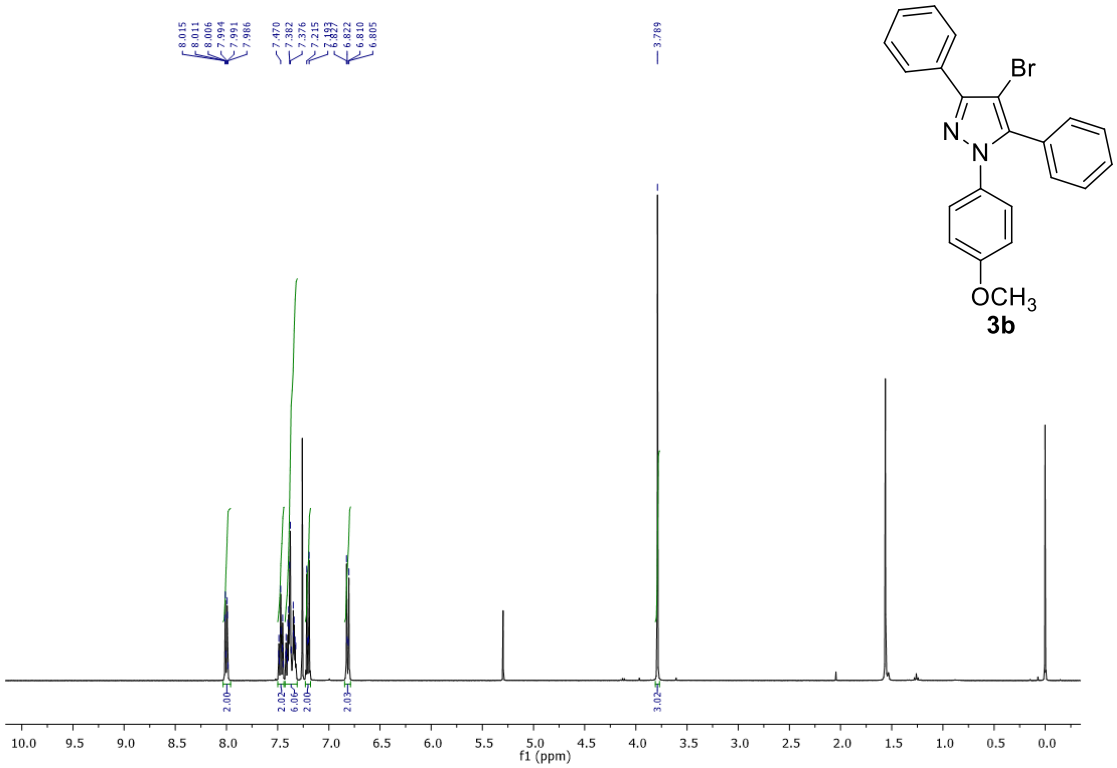
^{13}C NMR Spectra of **4d**



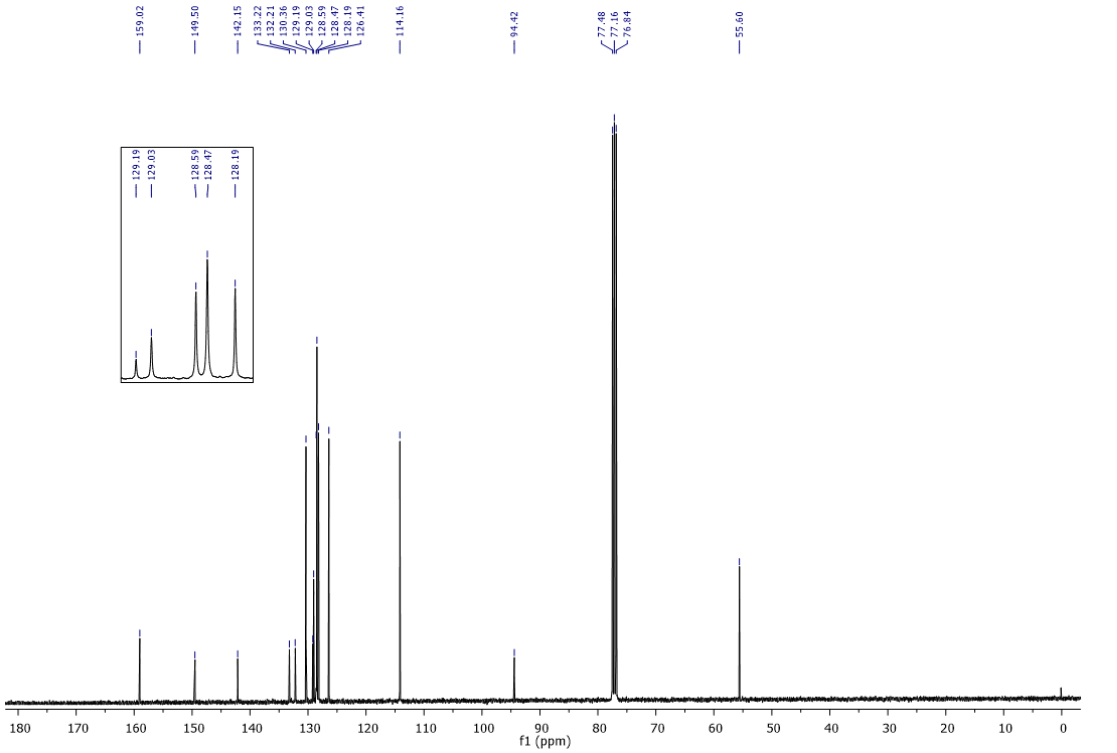
^{1}H NMR Spectra of **3a**



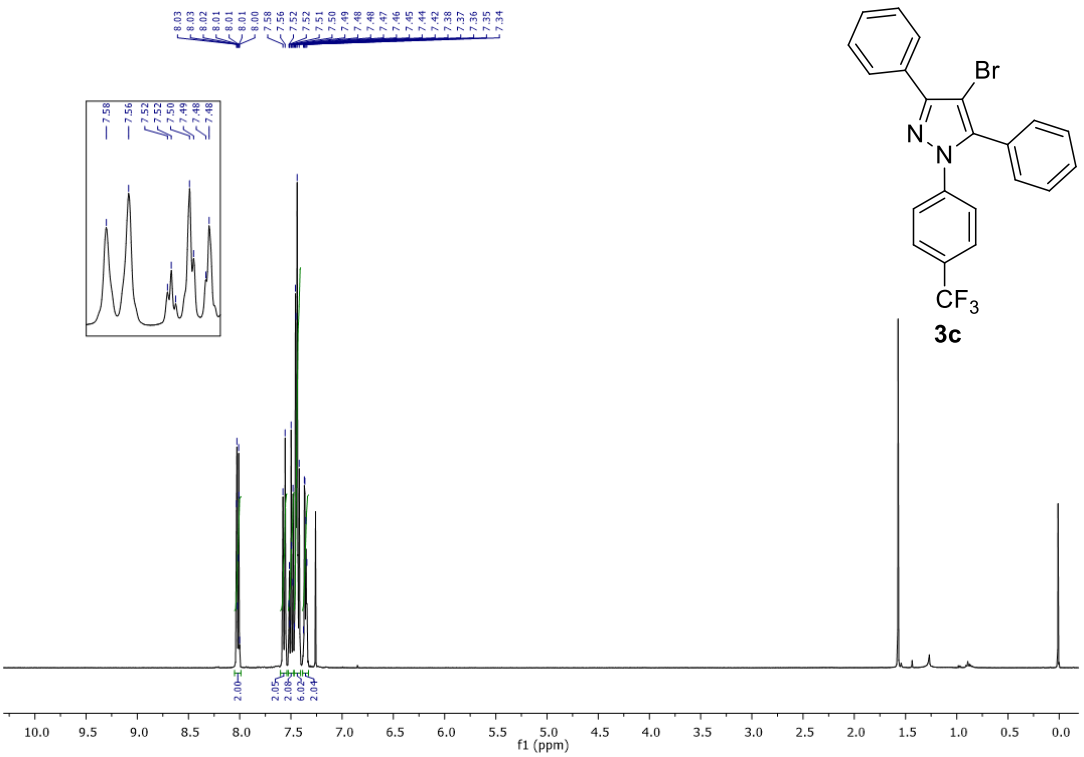
^{13}C NMR Spectra of **3a**



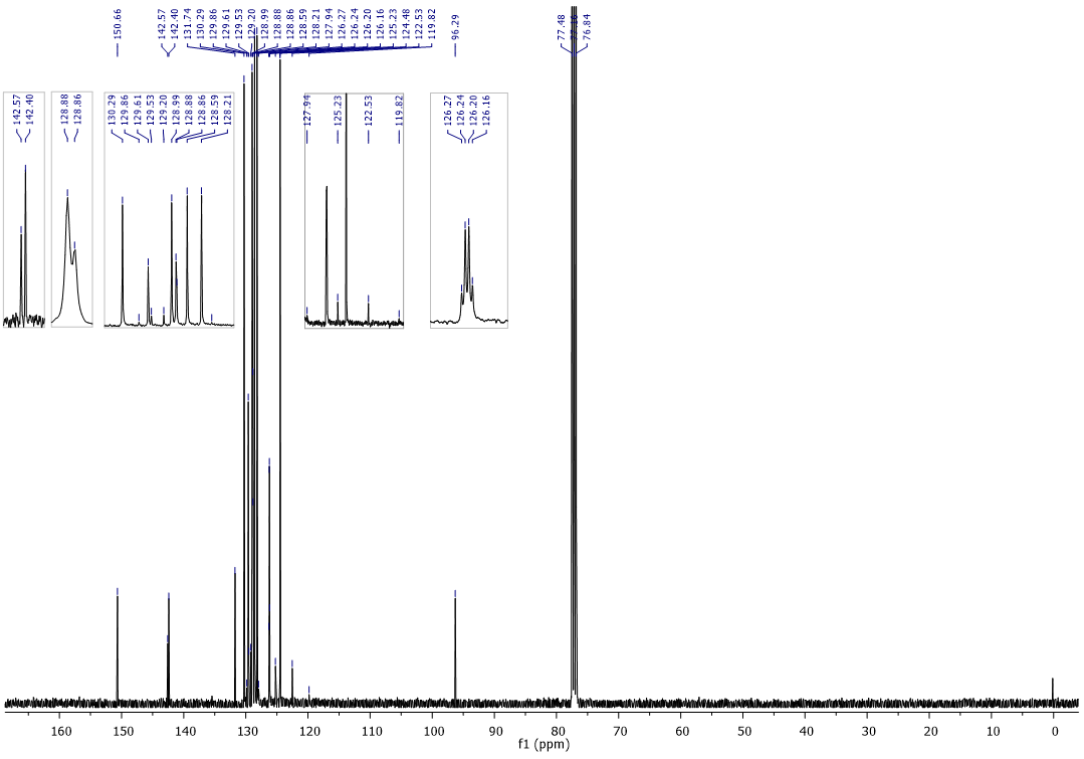
^{1}H NMR Spectra of **3b**



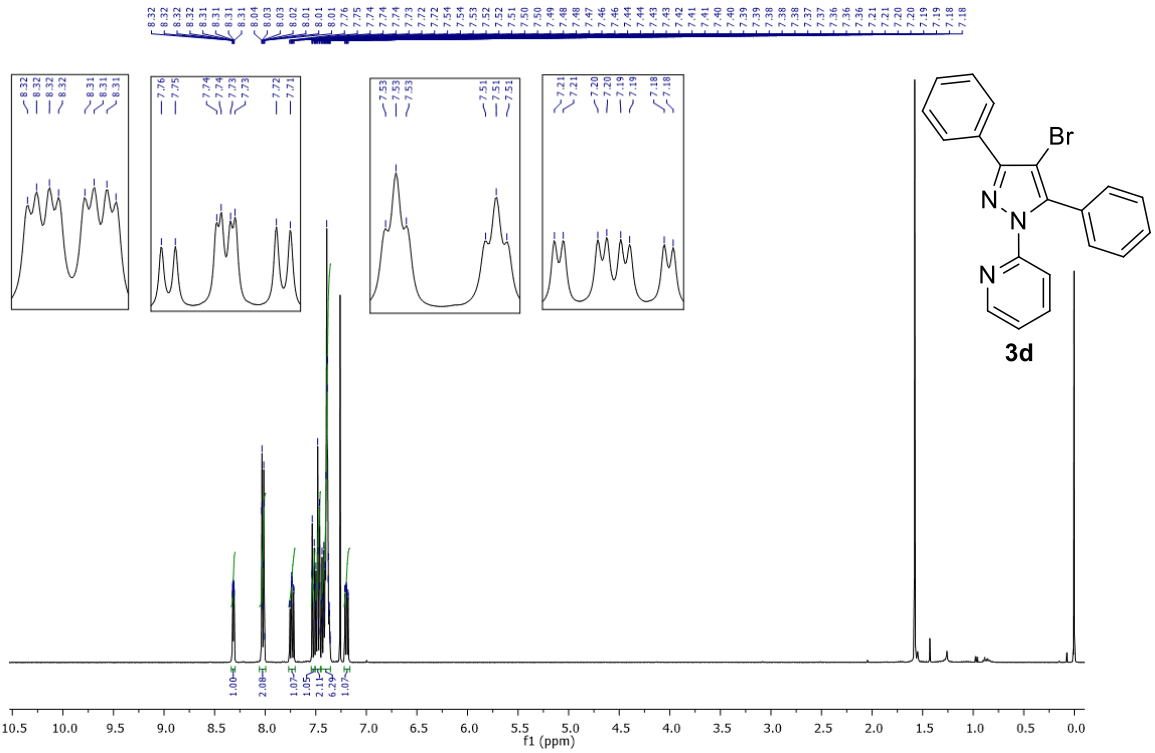
^{13}C NMR Spectra of **3b**



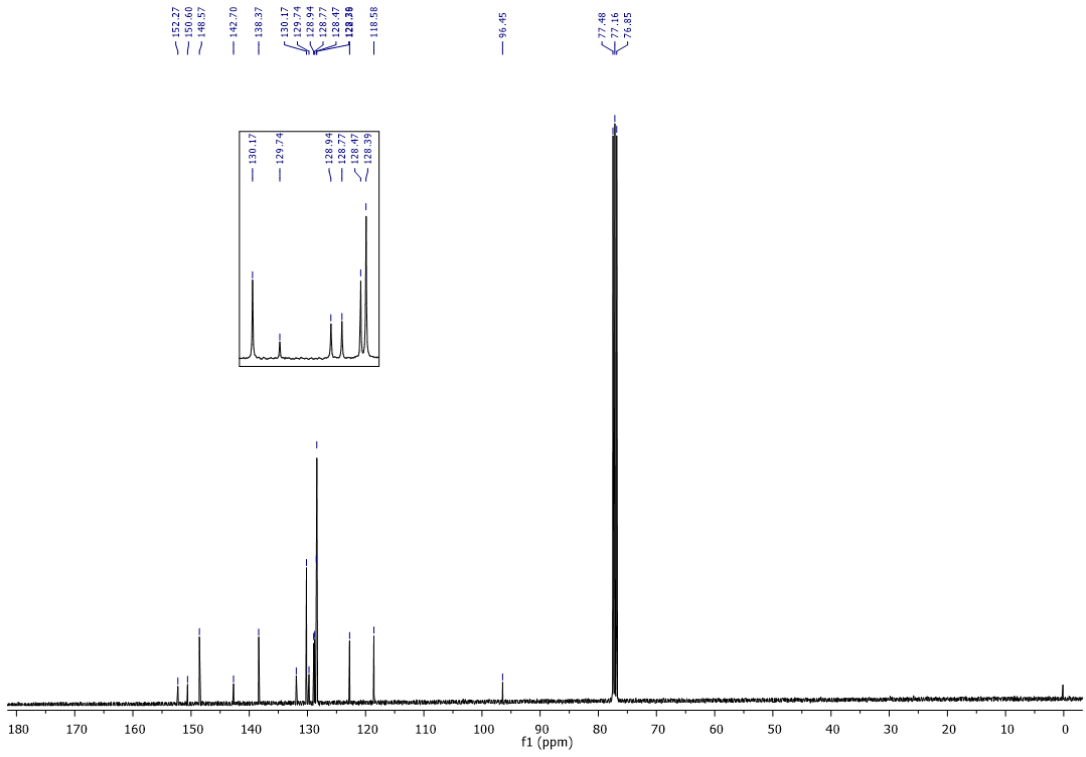
^{1}H NMR Spectra of **3c**



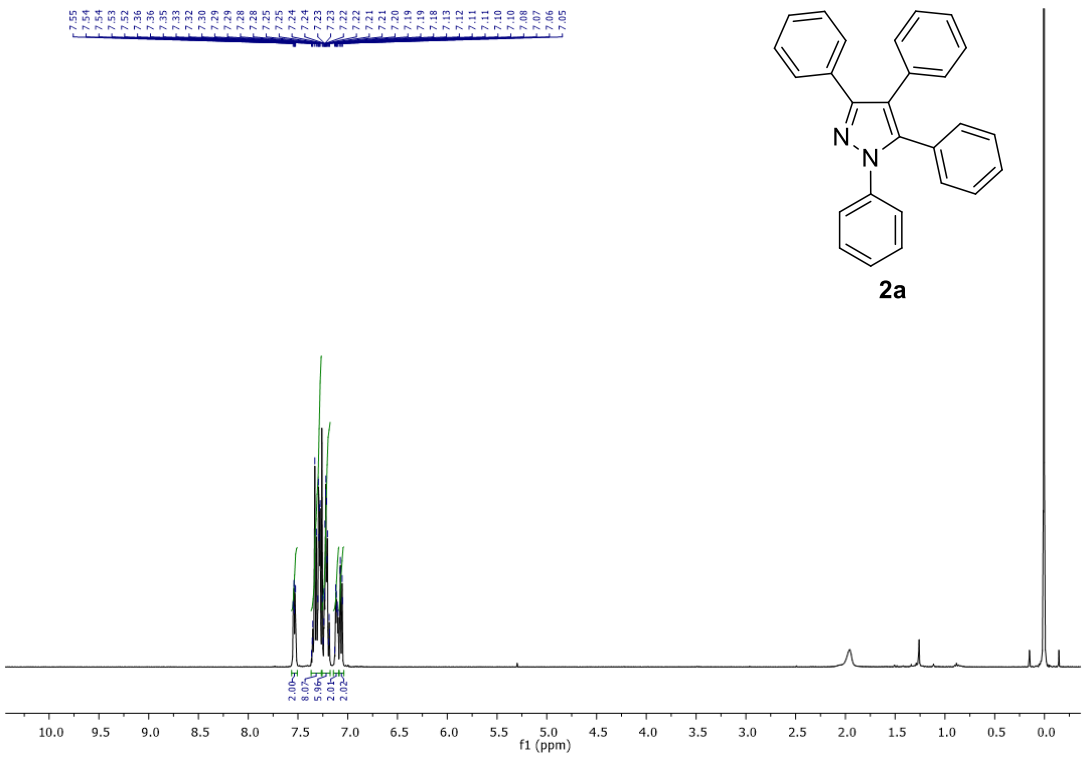
^{13}C NMR Spectra of **3c**



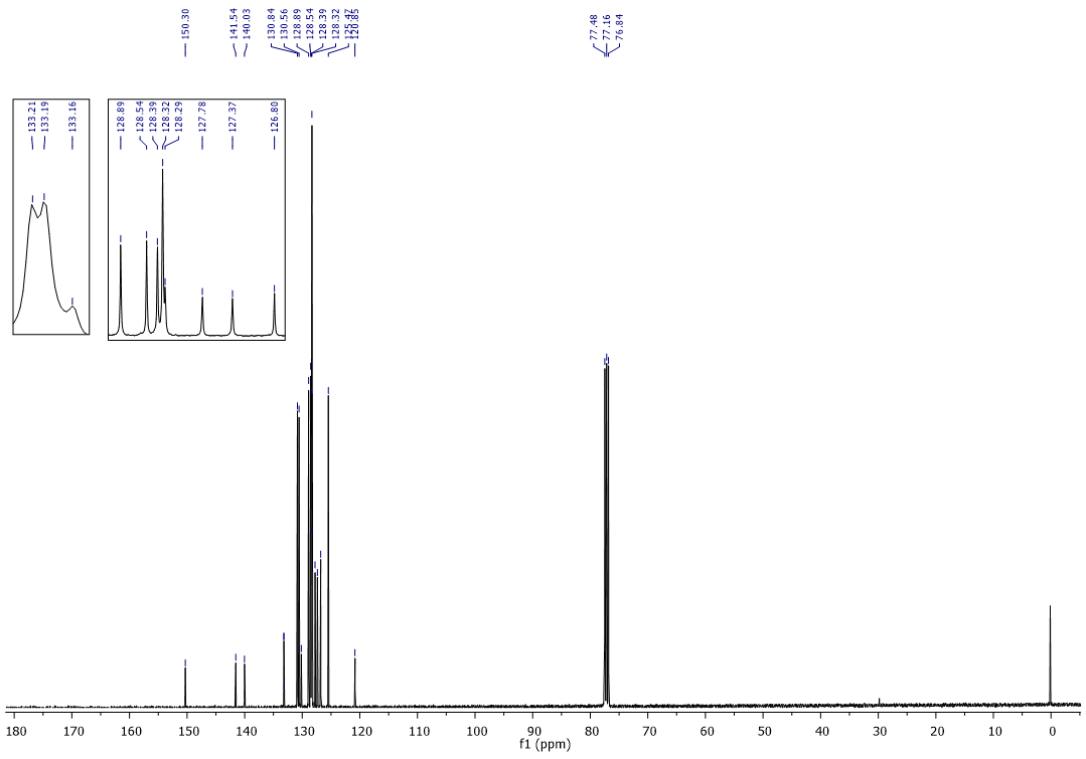
^{1}H NMR Spectra of **3d**



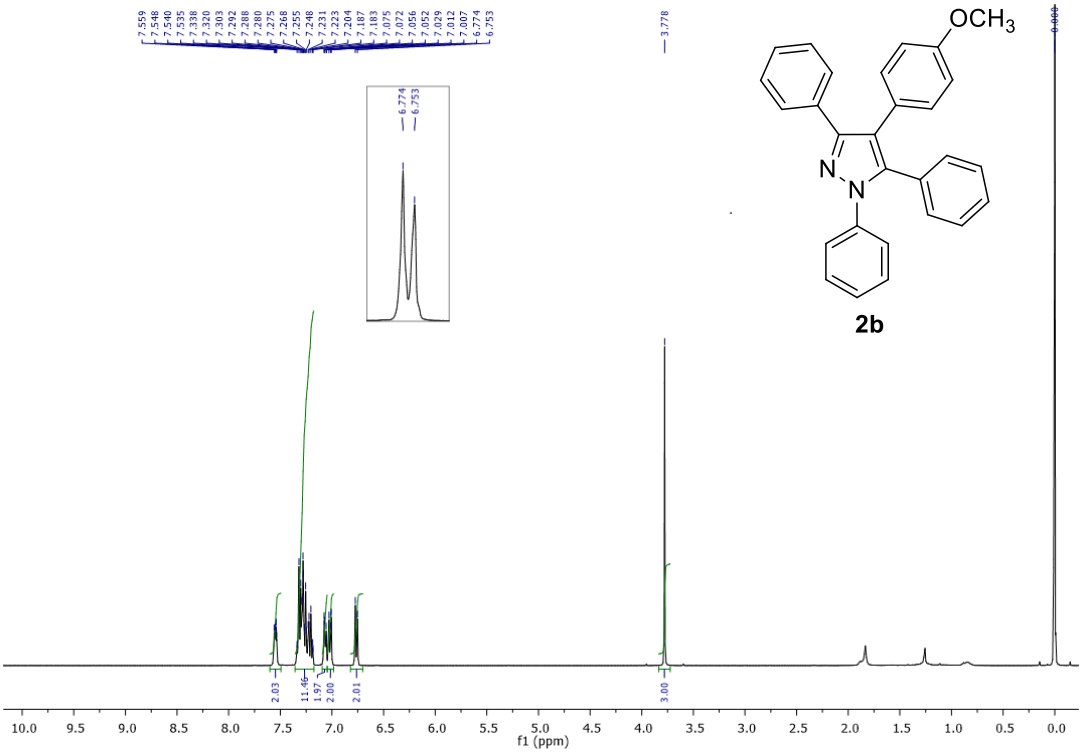
^{13}C NMR Spectra of **3d**



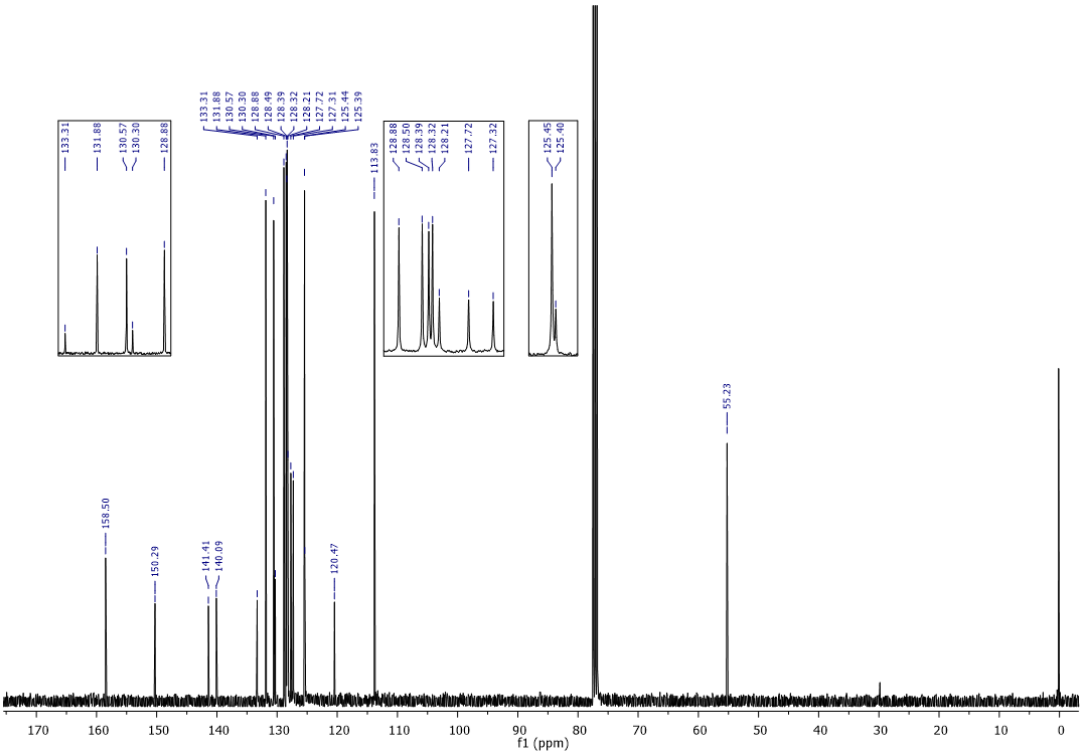
^{1}H NMR Spectra of **2a**



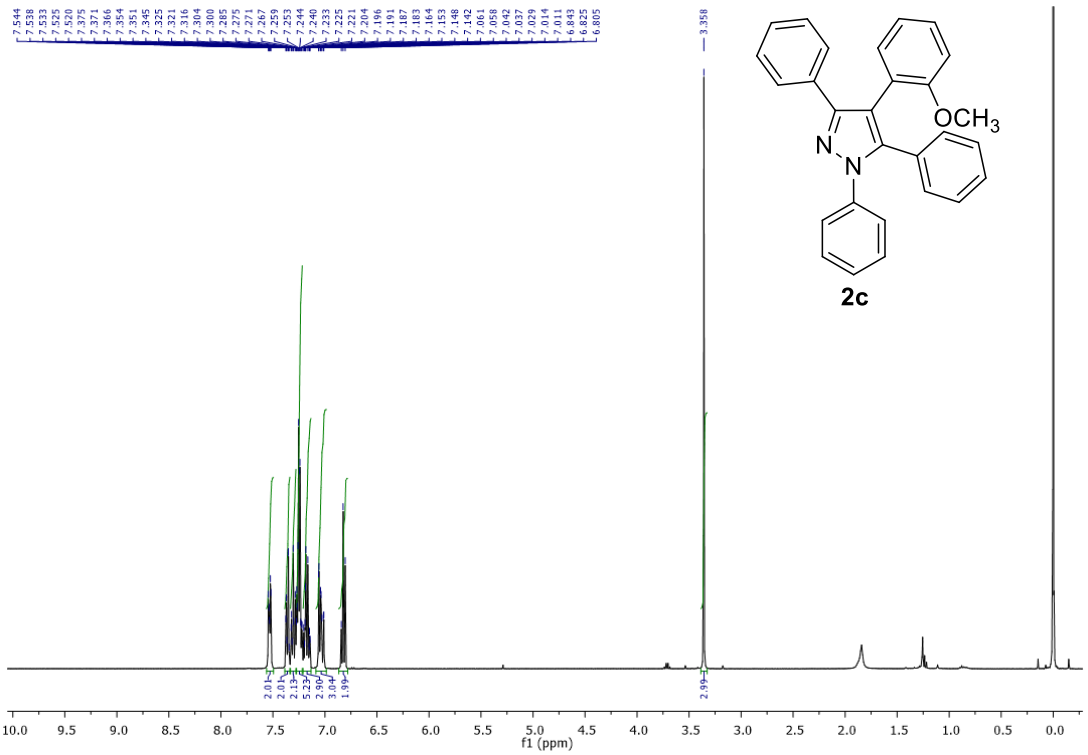
^{13}C NMR Spectra of **2a**



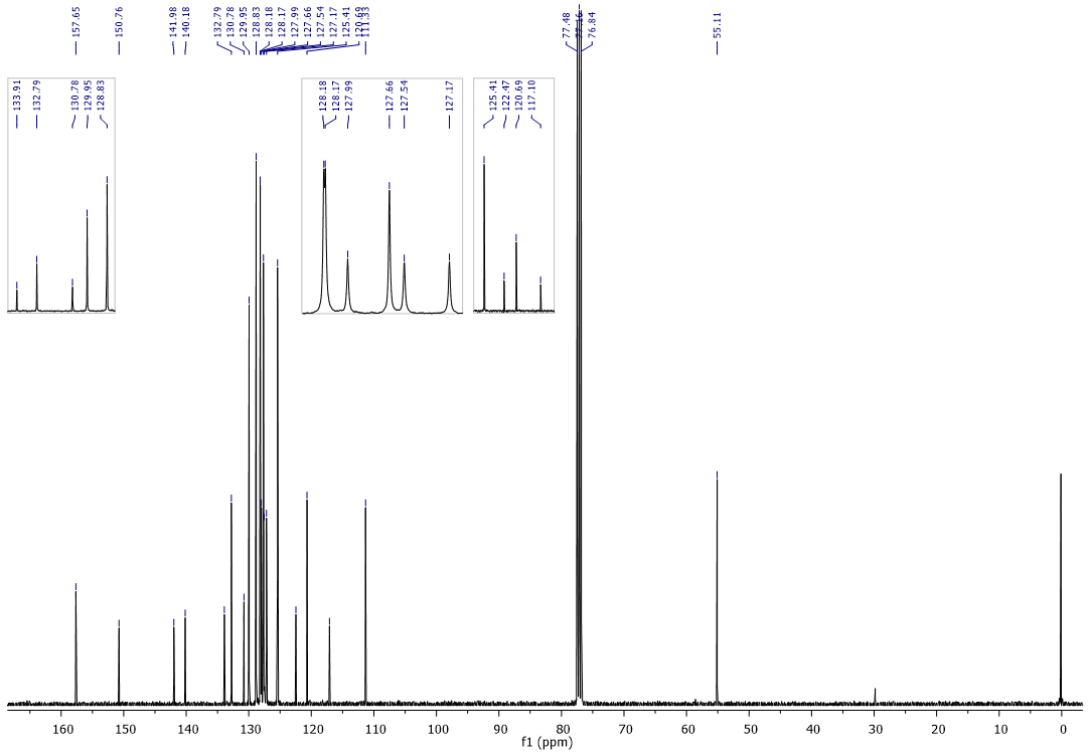
^{1}H NMR Spectra of **2b**



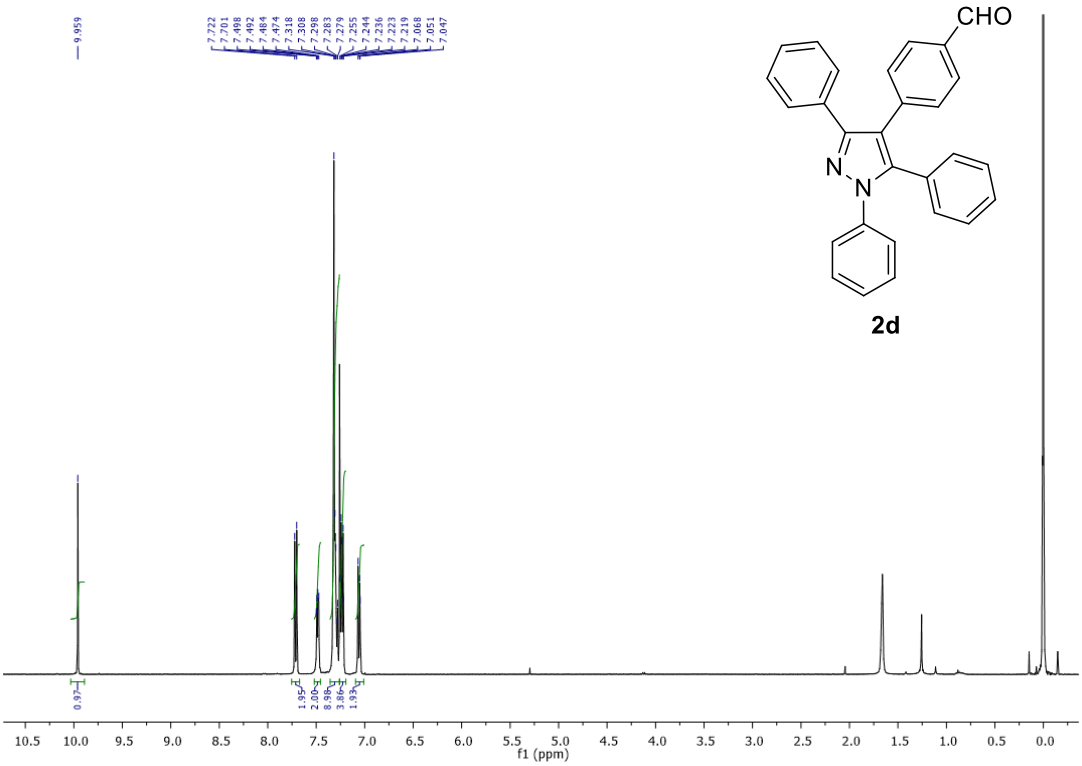
^{13}C NMR Spectra of **2b**



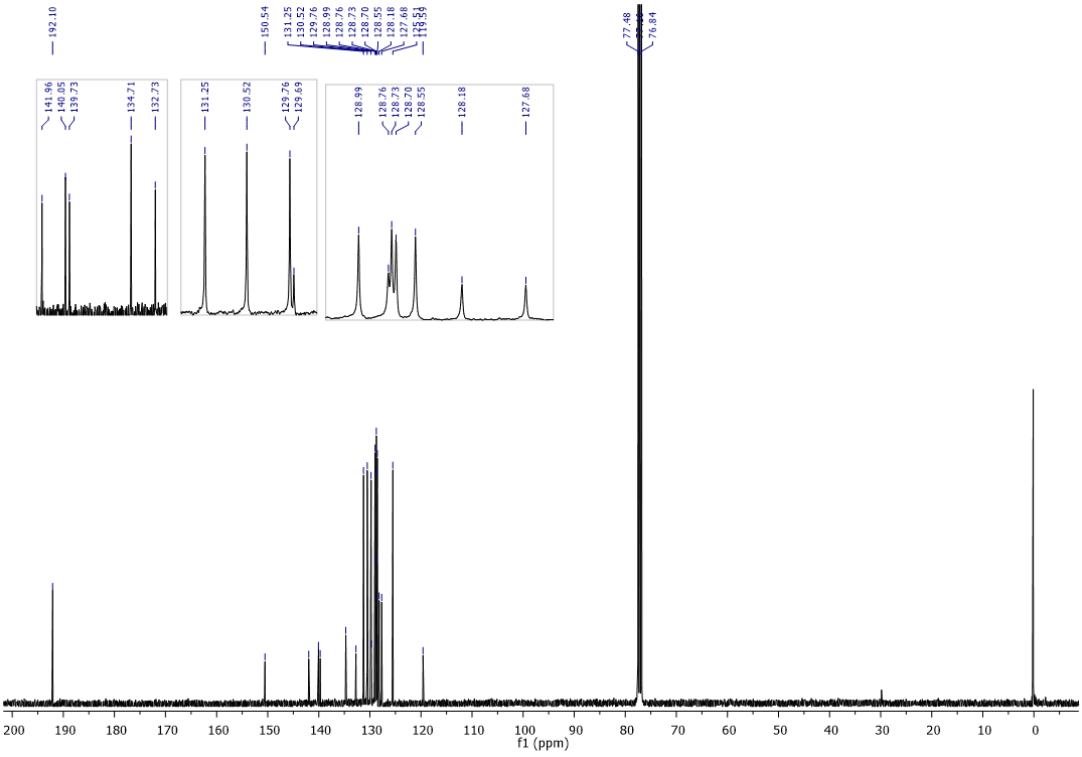
^{1}H NMR Spectra of **2c**



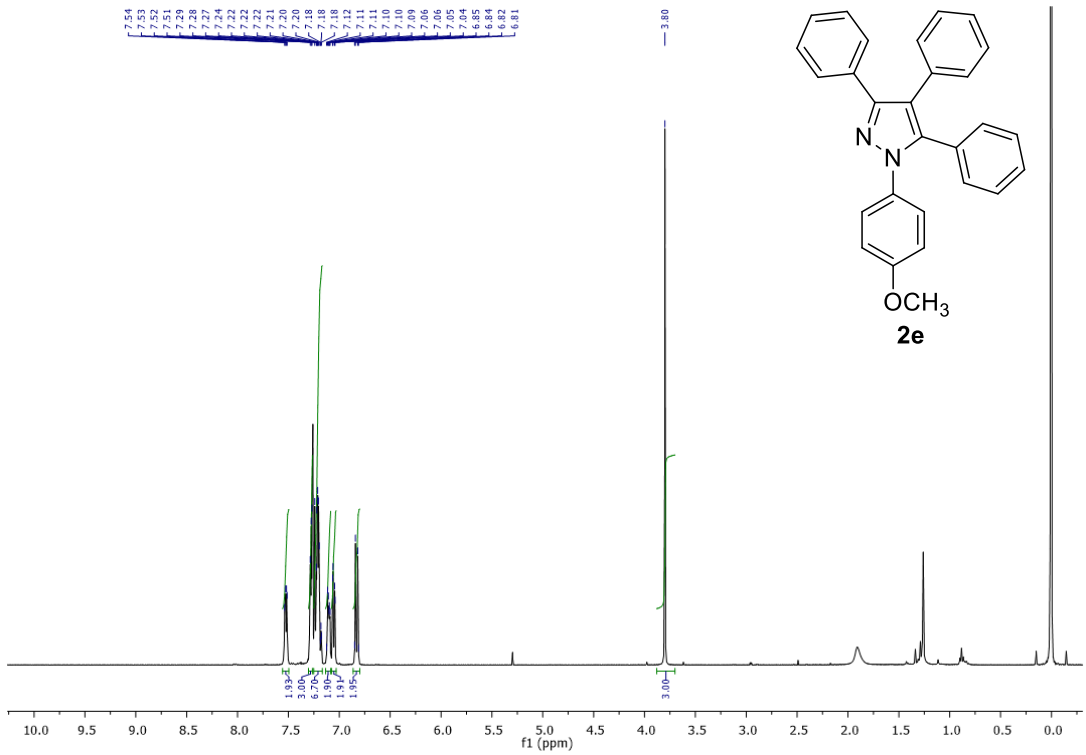
^{13}C NMR Spectra of **2c**



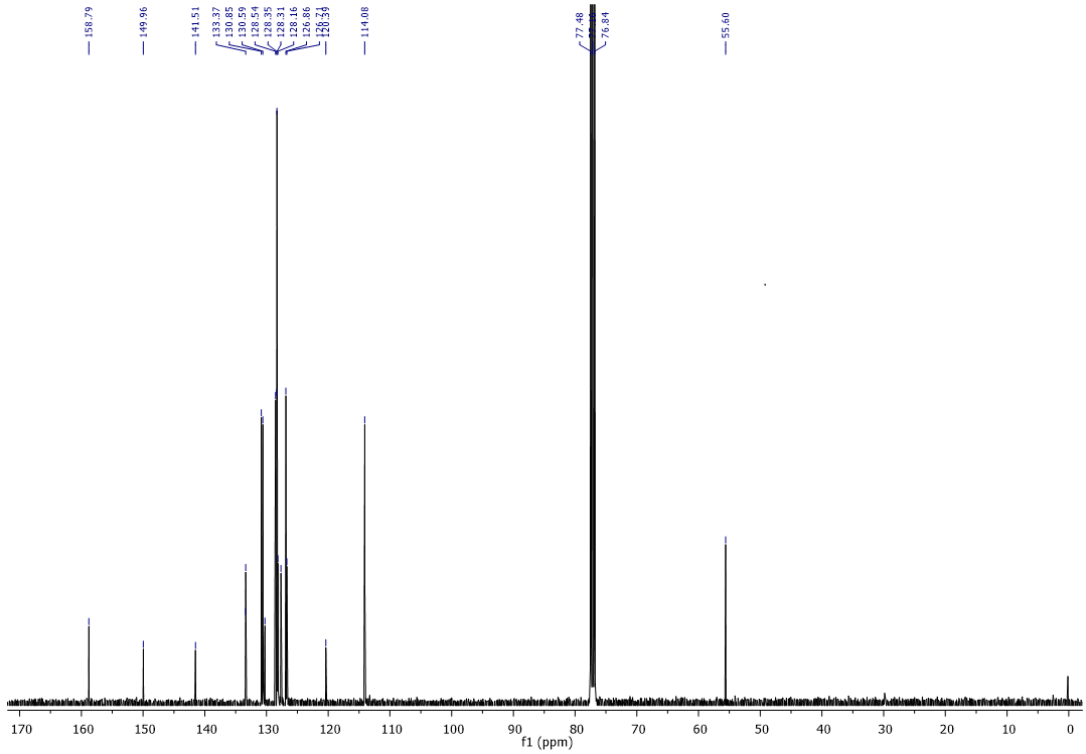
^{1}H NMR Spectra of **2d**



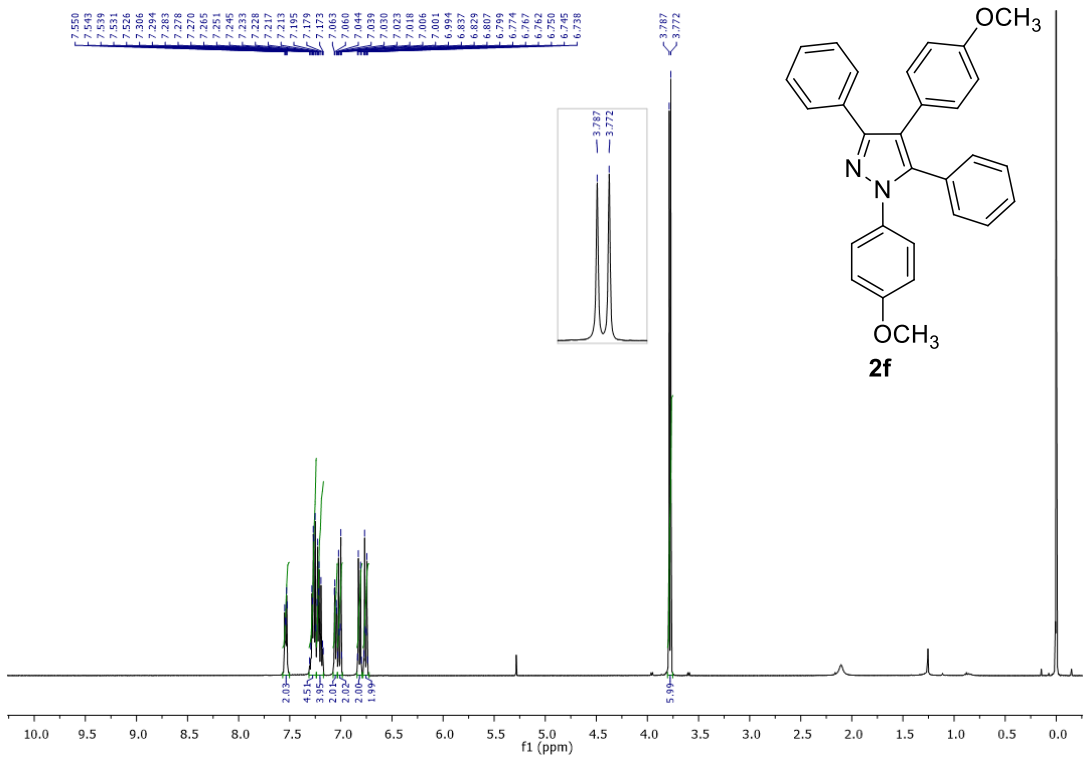
^{13}C NMR Spectra of **2d**



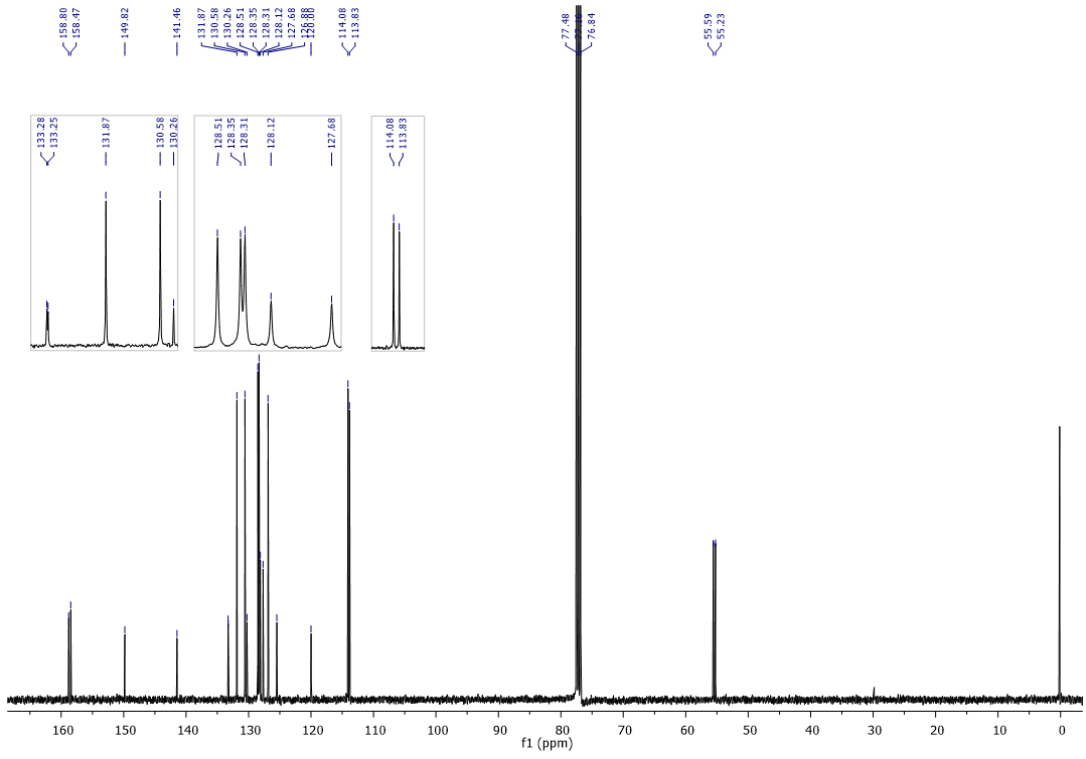
^{1}H NMR Spectra of **2e**



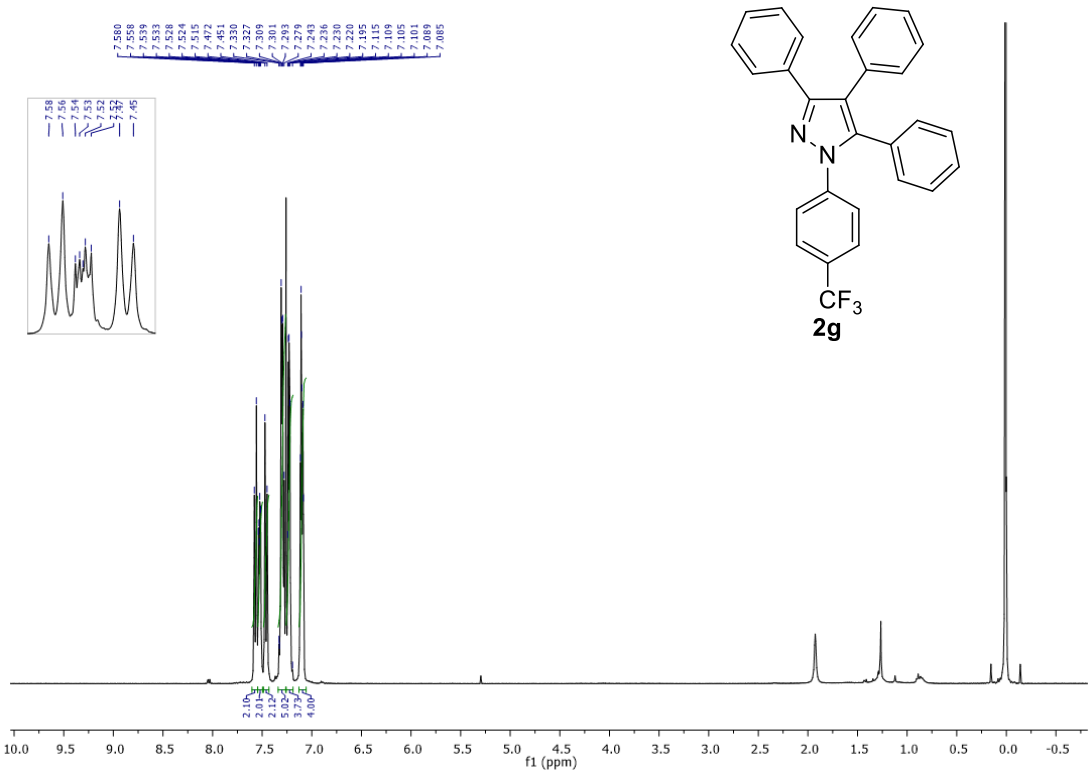
^{13}C NMR Spectra of **2e**



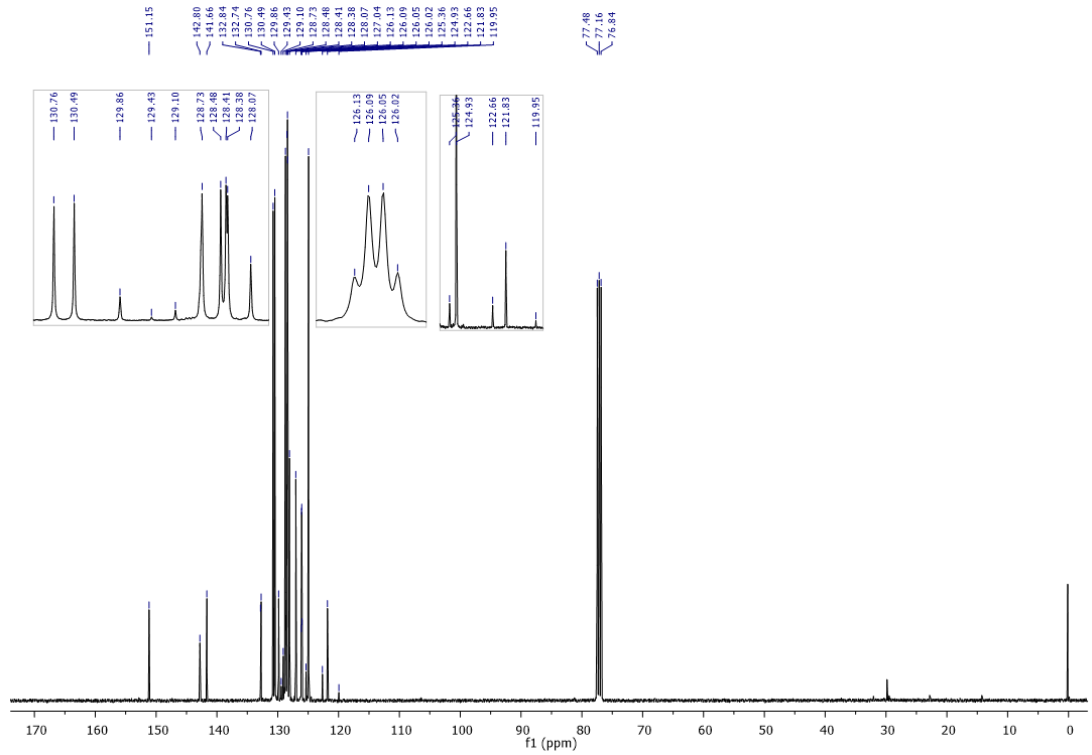
^{1}H NMR Spectra of **2f**



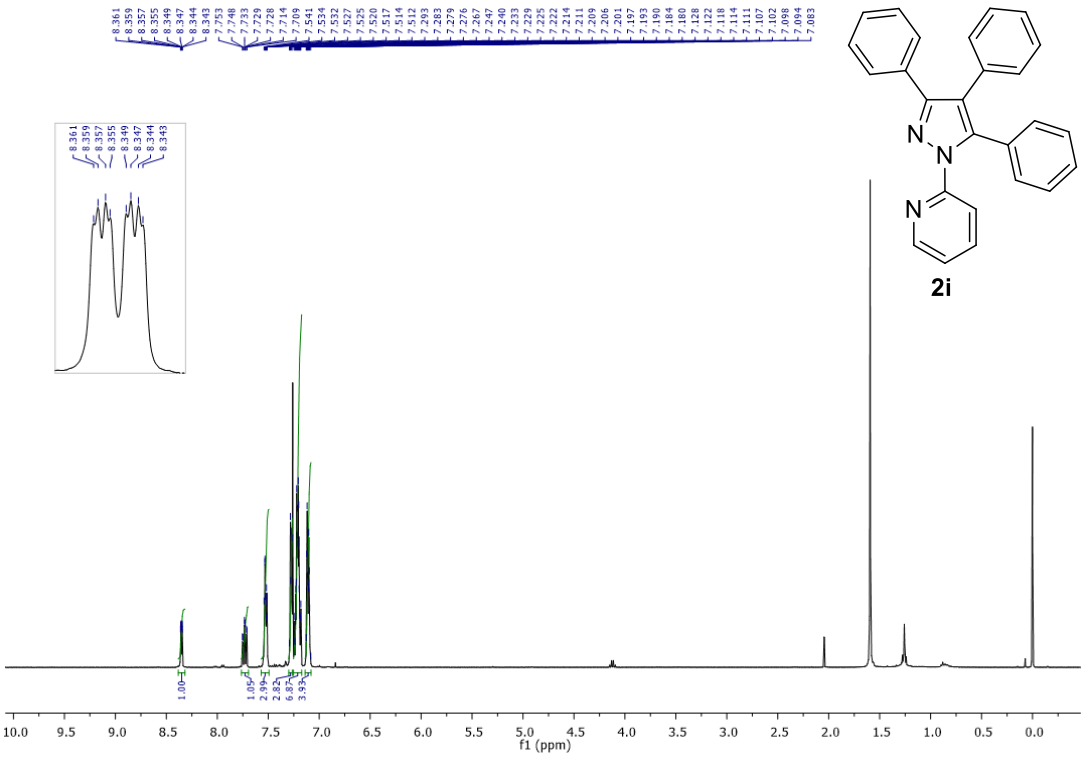
^{13}C NMR Spectra of **2f**



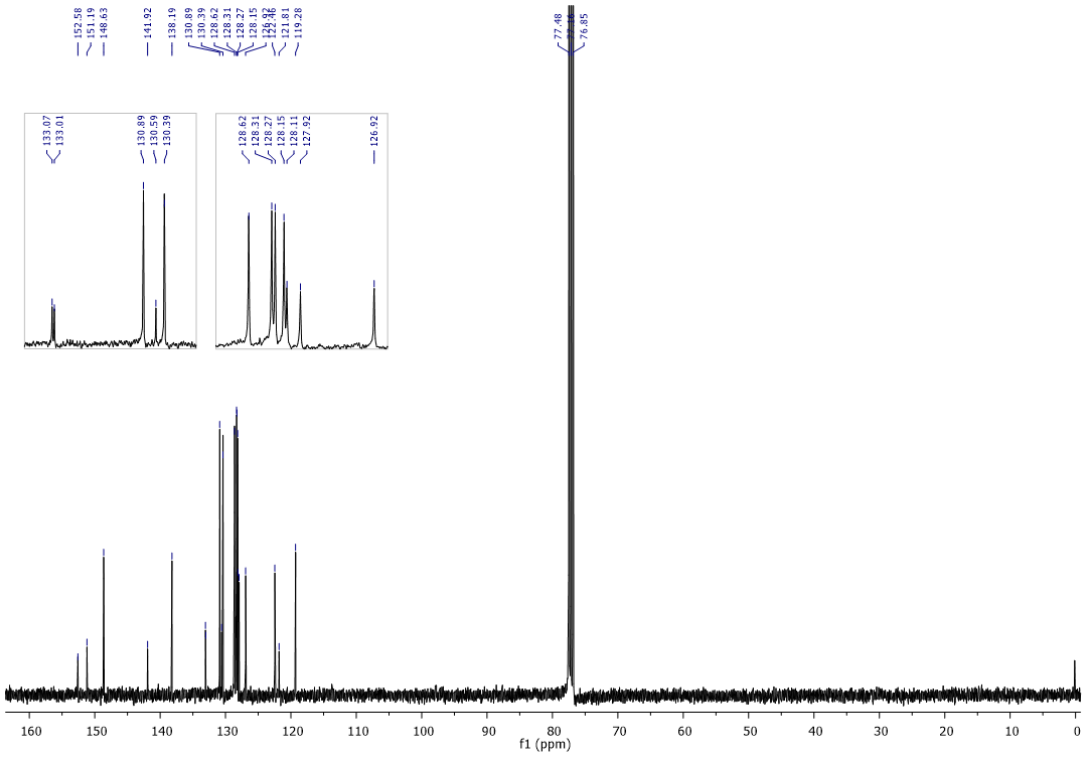
^{1}H NMR Spectra of **2g**



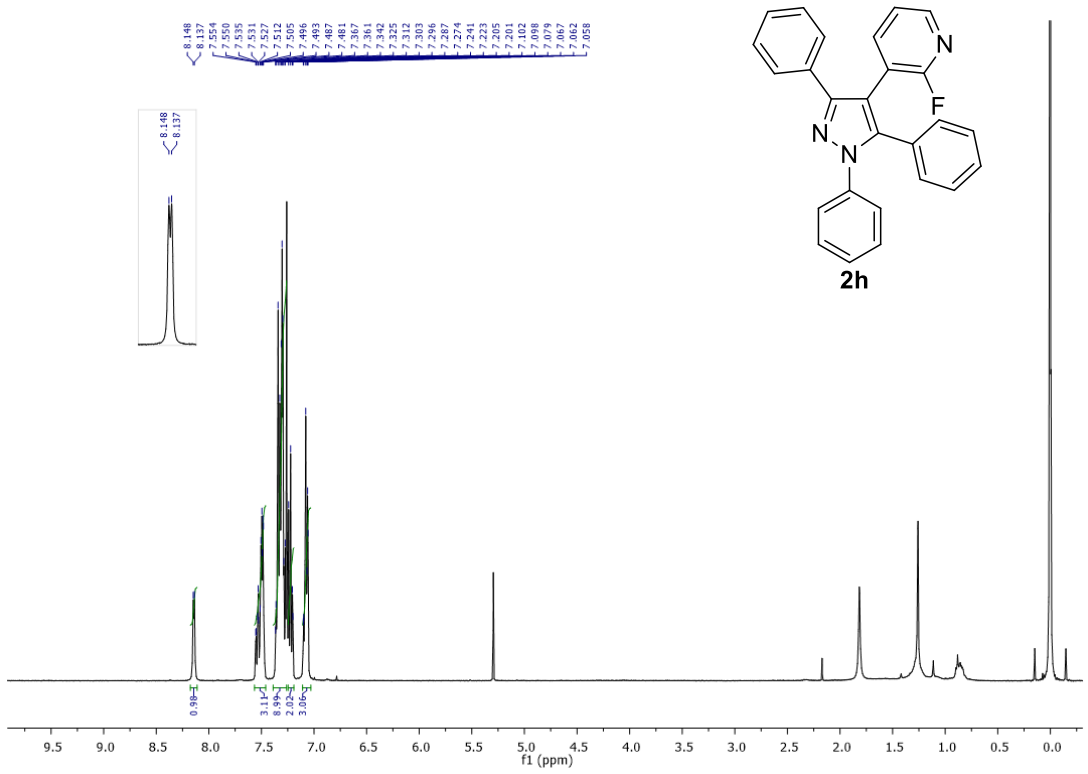
^{13}C NMR Spectra of **2g**



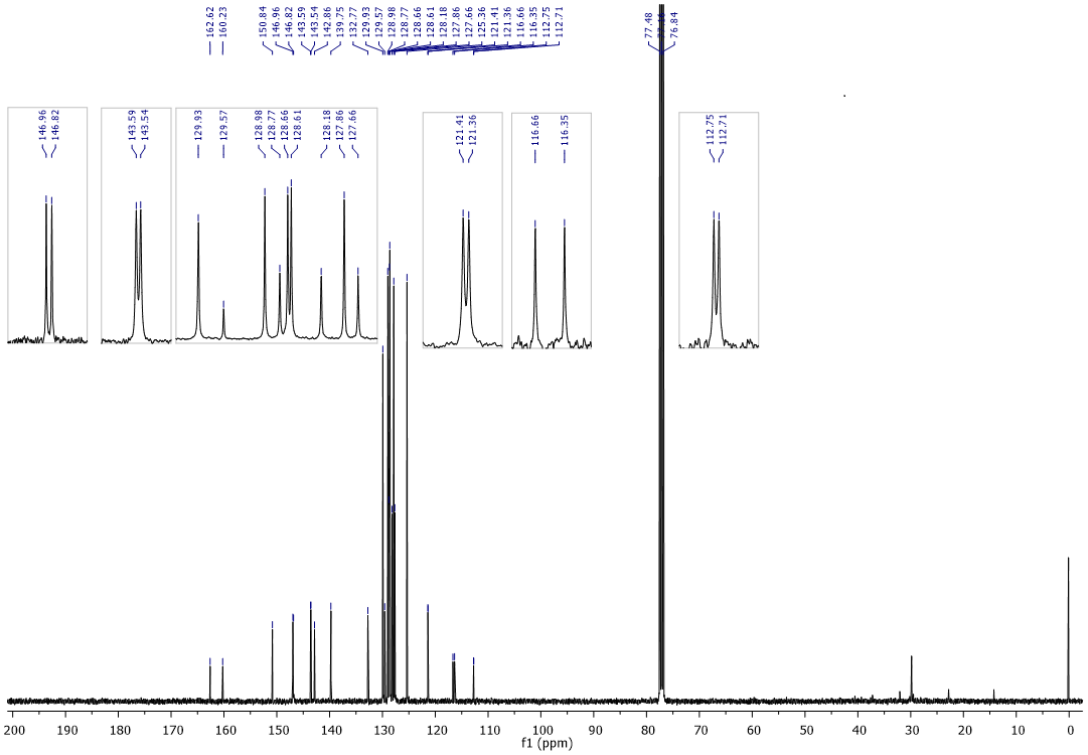
^{1}H NMR Spectra of **2i**



^{13}C NMR Spectra of **2i**



^{1}H NMR Spectra of **2h**



^{13}C NMR Spectra of **2h**