Supporting Information

Sequentially palladium catalyzed coupling-cyclocondensation-coupling (C^3) four-component synthesis of intensively blue luminescent biarylsubstituted pyrazoles

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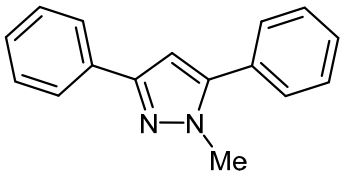
General Considerations

^{1}H, ^{13}C, DEPT and NOESY NMR spectra were recorded in $CDCl_3$, $CDCl_2$ or acetone (d^6) on a 300 MHz (Bruker AVIII) or 600 MHz (Bruker Avance III-600) NMR spectrometer. The assignments of C_{quat}, CH, CH_2 and CH_3 were based on DEPT spectra. Absorption spectra were recorded in CH_2Cl_2 or cyclohexane UVASOL at T = 293 K on a Perkin Elmer UV/VIS/NIR Spectrometer Lambda 19. Emission spectra were recorded in CH_2Cl_2 or cyclohexane UVASOLat T = 293 K on a Perkin Elmer LS55 spectrometer.

One-pot Synthesis of 1-methyl-3,5-diphenyl-1H-pyrazole (9)[1]

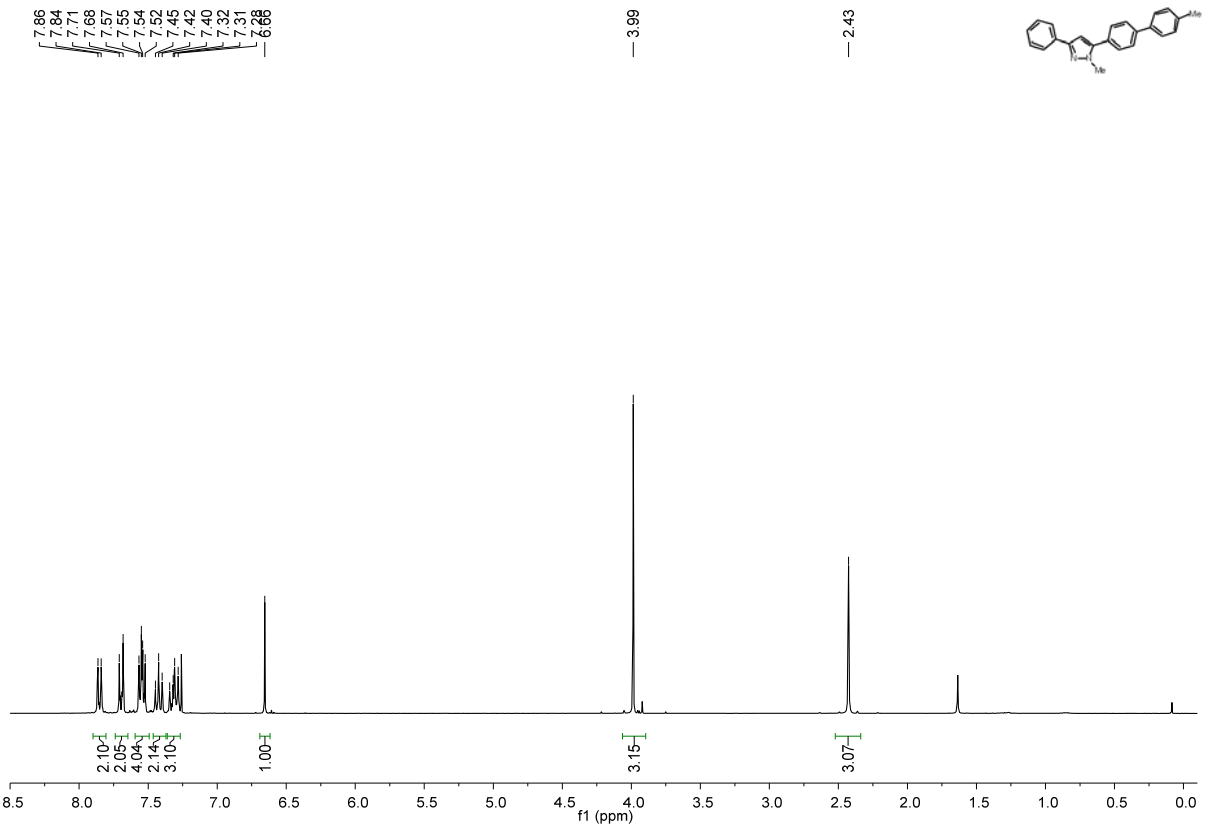


In a 10 mL microwave tube $PdCl_2(PPh_3)_2$ (14.6 mg, 0.02 mmol) and CuI (8.37 mg, 0.04 mmol) were dissolved in THF (4.00 mL) under nitrogen. To the yellow solution acid chloride (**1a**) (141 mg, 1.00 mmol) and alkyne (**2b**) (103 mg, 1.00 mmol) were added. Finally triethylamine (107 mg, 1.05 mmol) was added. The reaction mixture turned from yellow to light brown and was stirred at room temperature for 2 h. Then methyl hydrazine (**3a**) (52.8 mg, 1.14 mmol), 0.5 mL methanol and 0.5 mL concentrated acetic acid were added and the reaction mixture was stirred under continuous microwave irradiation at 150°C for 10 min. After cooling to room temperature the reaction mixture was extracted with dichloromethane (3 x 20 mL) and then washed with a saturated aqueous solution of ammonium chloride and brine. The combined organic layers were dried with anhydrous magnesium sulfate. The crude product was purified by flash chromatography (*n*-hexane/ethyl acetate 4:1, v/v) to give 151 mg (66%) of pyrazole **9** as a yellow to orange solid; Mp 55 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.94 (s, 3 H), 6.62 (s, 1 H), 7.28-7.35 (m, 1 H), 7.38-7.42 (m, 2 H), 7.43-7.51 (m, 5 H), 7.84 (dd, J = 8.3, 1.3 Hz, 2H), ^{13}C NMR (75 MHz, $CDCl_3$) δ = 37.6 (CH_3), 103.3 (CH), 125.54 (2 CH), 128.58, 128.63, 128.7 (2 CH), 128.8 (2 CH), 130.6 (C_{quat}), 133.3 (C_{quat}), 145.1 (C_{quat}), 150.5 (C_{quat}), IR (ATR): $\tilde{\nu}$ [cm^{-1}] 3026 (w), 2962 (w), 1603 (w), 1551 (w), 1485 (m), 1460 (m), 1439 (m), 1362 (w), 1260 (m), 1088 (m), 1074 (m), 1026 (m), 1007 (m), 959 (m), 916 (w), 792 (s), 762 (s), 745 (s), 729 (s), 692 (s), 671 (m). GC-MS (*m/z* (%)): 235 (18), 234 (100), 233 (24), 191 (4), 189 (5), 131 (3), 130 (8), 128 (3), 118 (8), 117 (6), 116 (4), 104 (8), 103 (9), 102 (4), 95 (3), 91 (8), 89 (4), 77 (15), 76 (3), 63 (3), 51 (5). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$Lcm^{-1}mol^{-1}$]) = 254.0 (28800). Emission (CH_2Cl_2): λ_{max} [nm] (Φ_f) = 338.5 (0.40). Stokes shift [cm^{-1}] = 9800.

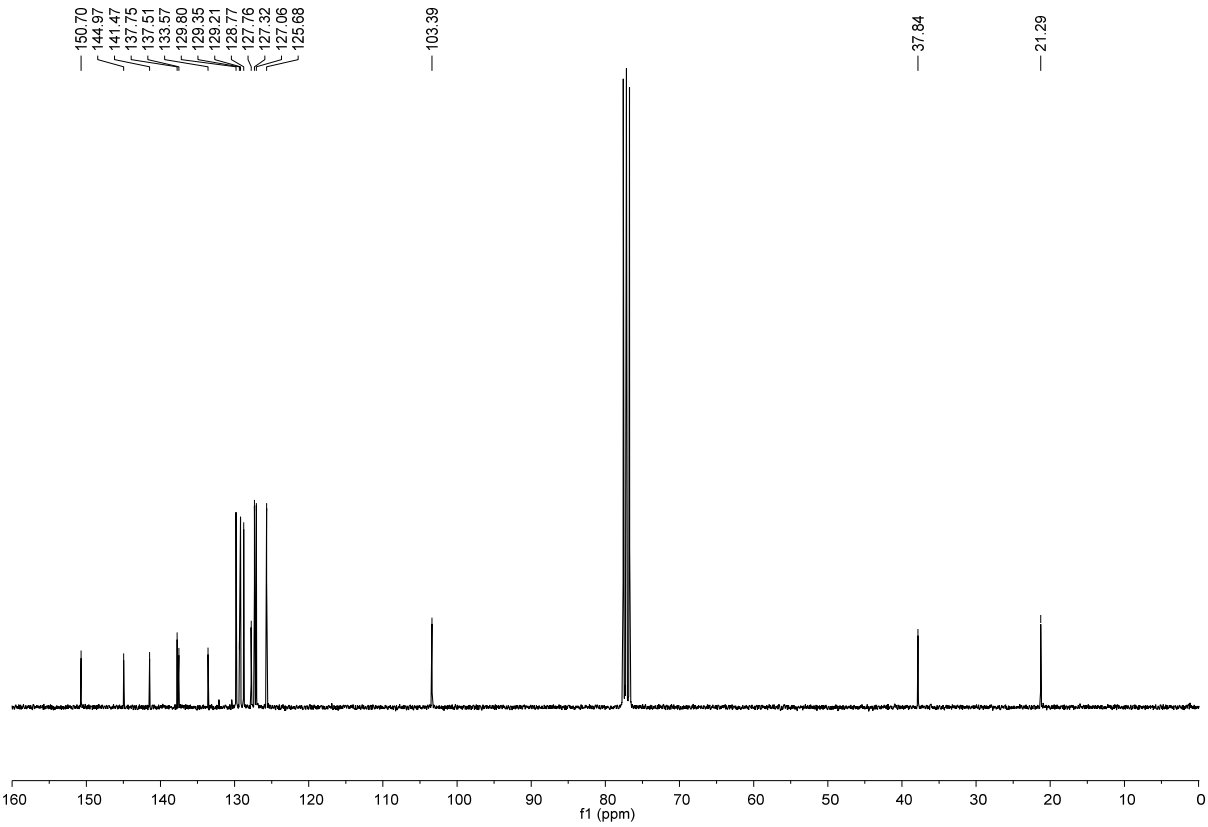
[1] B. Willy and T. J. J. Müller, *Eur. J. Org. Chem.*, 2008, 4157.

Spectra of 5-Biarylsubstituted Pyrazoles 5

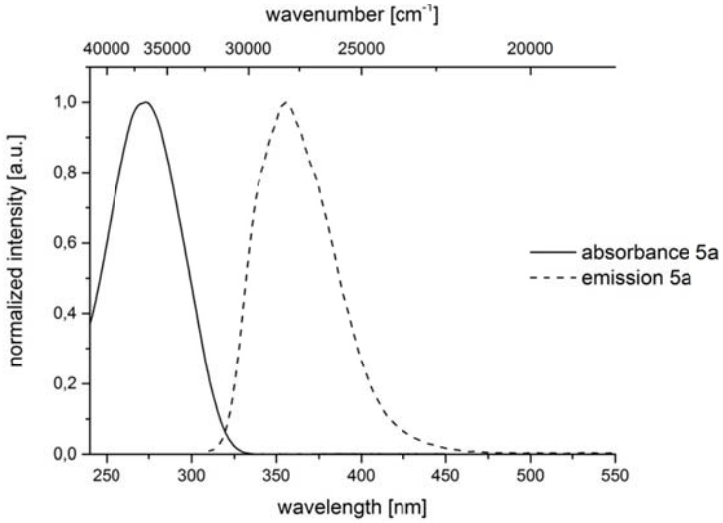
1-Methyl-5-(4'-methyl-[1,1'-biphenyl]-4-yl)-3-phenyl-1*H*-pyrazole (**5a**)



300 MHz ^{1}H NMR spectrum of compound **5a** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

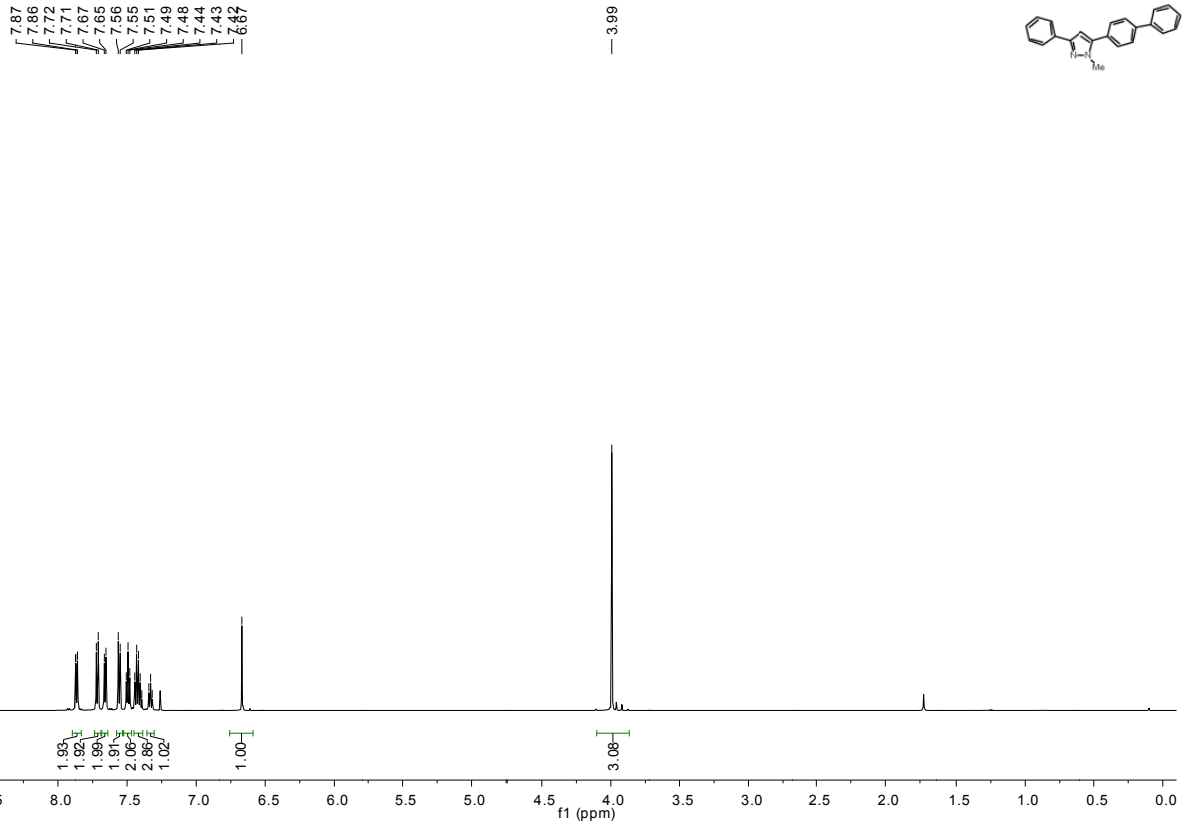


75 MHz ^{13}C NMR spectrum of compound **5a** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

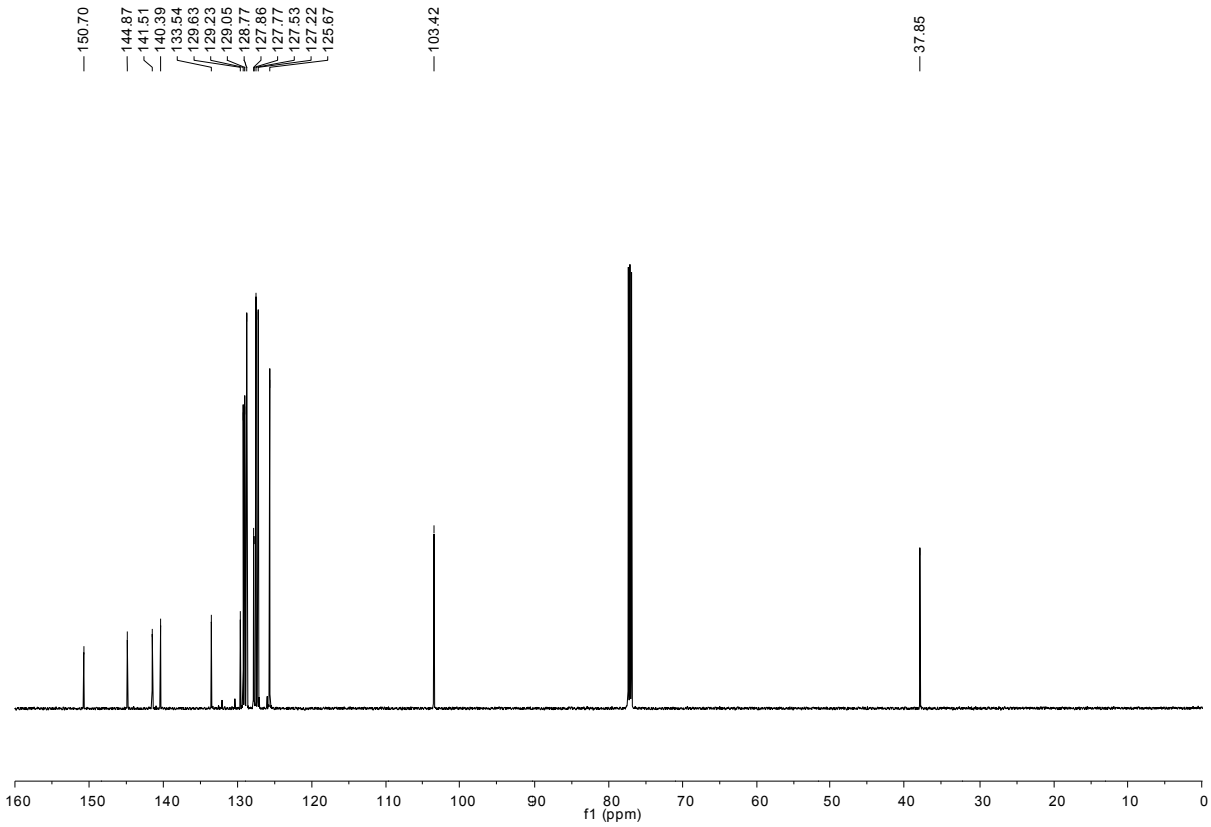


Normalized absorption and emission spectra of compound **5a** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

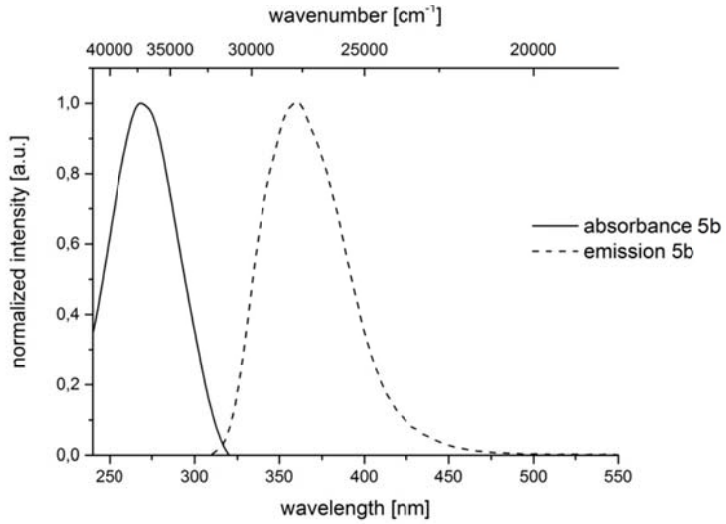
5-([1,1'-Biphenyl]-4-yl)-1-methyl-3-phenyl-1*H*-pyrazole (**5b**)



300 MHz ^{1}H NMR spectrum of compound **5b** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

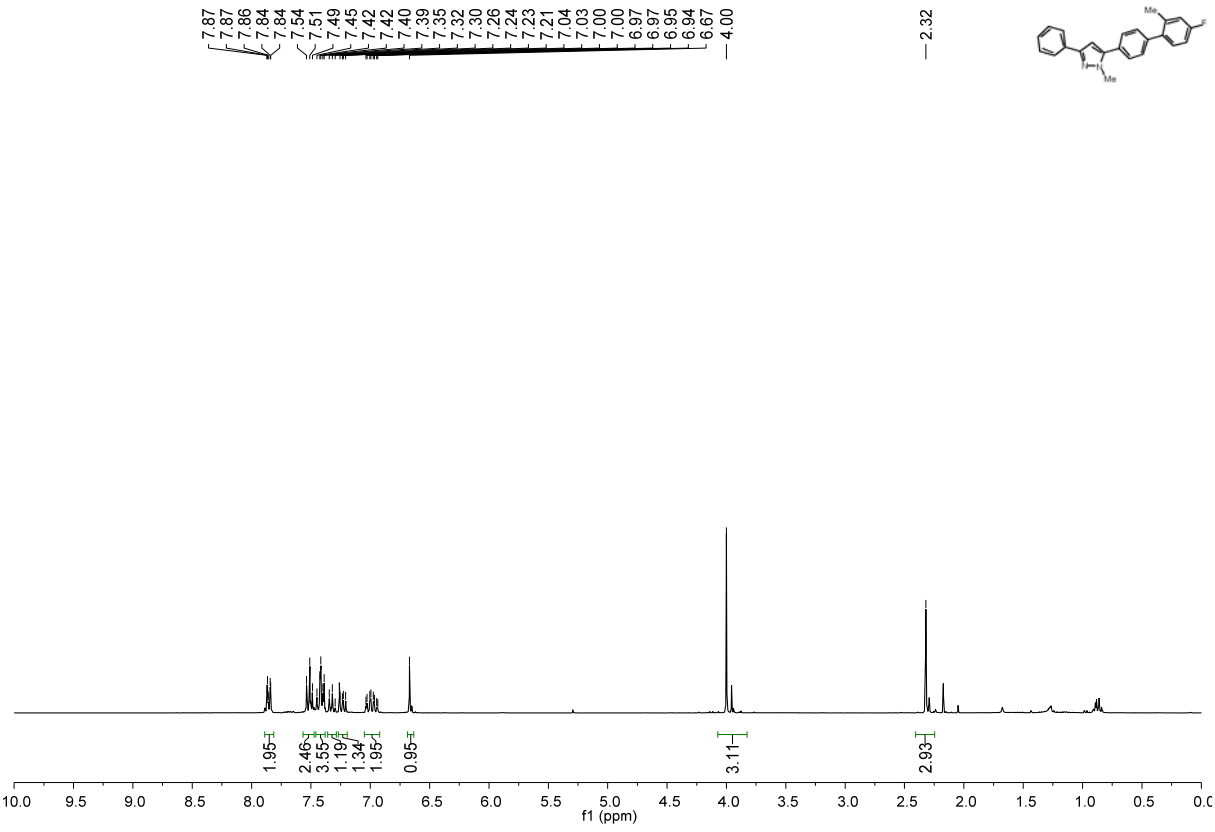


75 MHz ^{13}C NMR spectrum of compound **5b** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

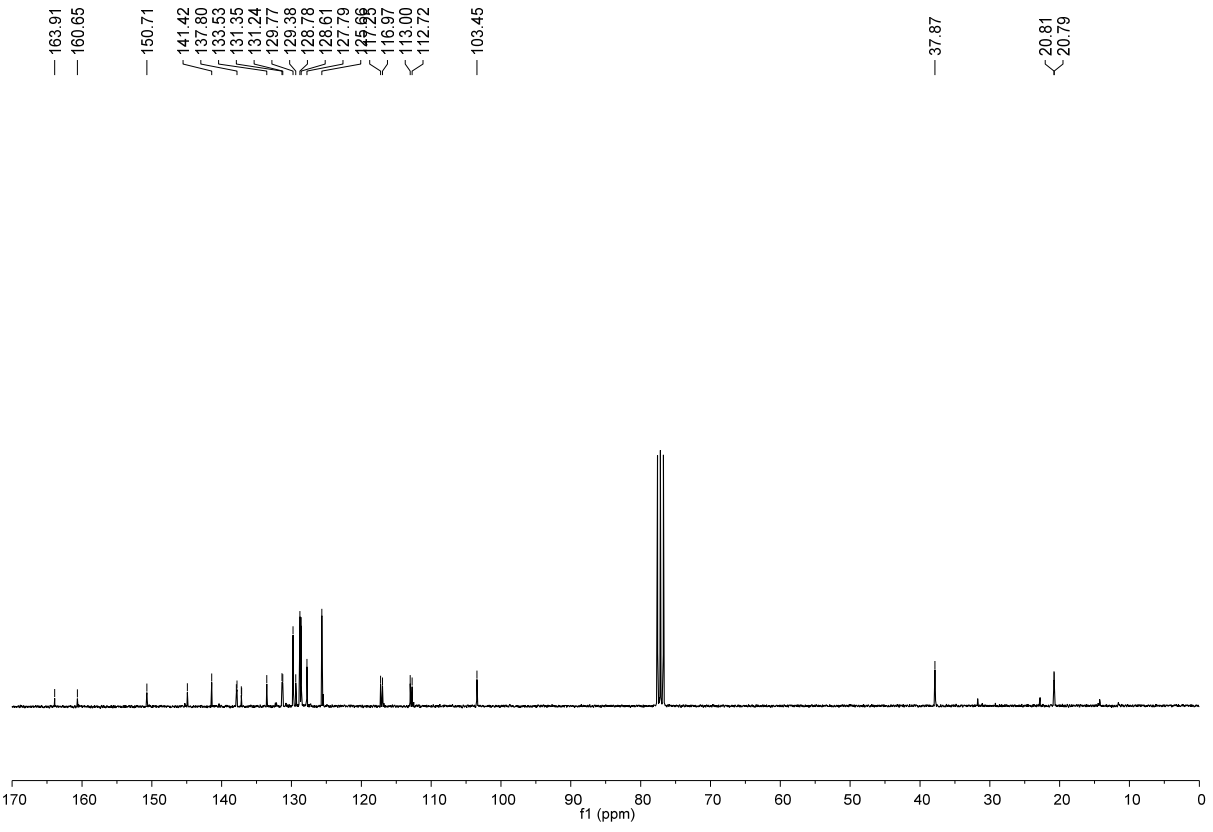


Normalized absorption and emission spectra of compound **5b** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

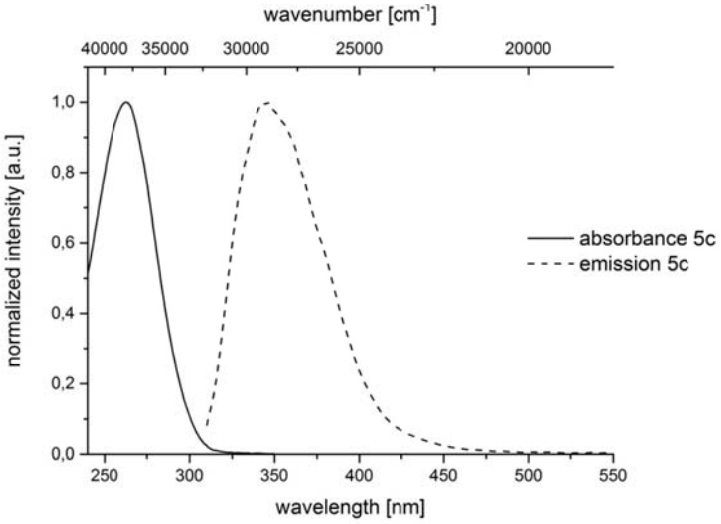
5-(4'-Fluoro-2'-methyl-[1,1'-biphenyl]-4-yl)-1-methyl-3-phenyl-1*H*-pyrazole (**5c**)



300 MHz ^{1}H NMR spectrum of compound **5c**recorded in $CDCl_3$ at T = 298 K (δ in ppm).

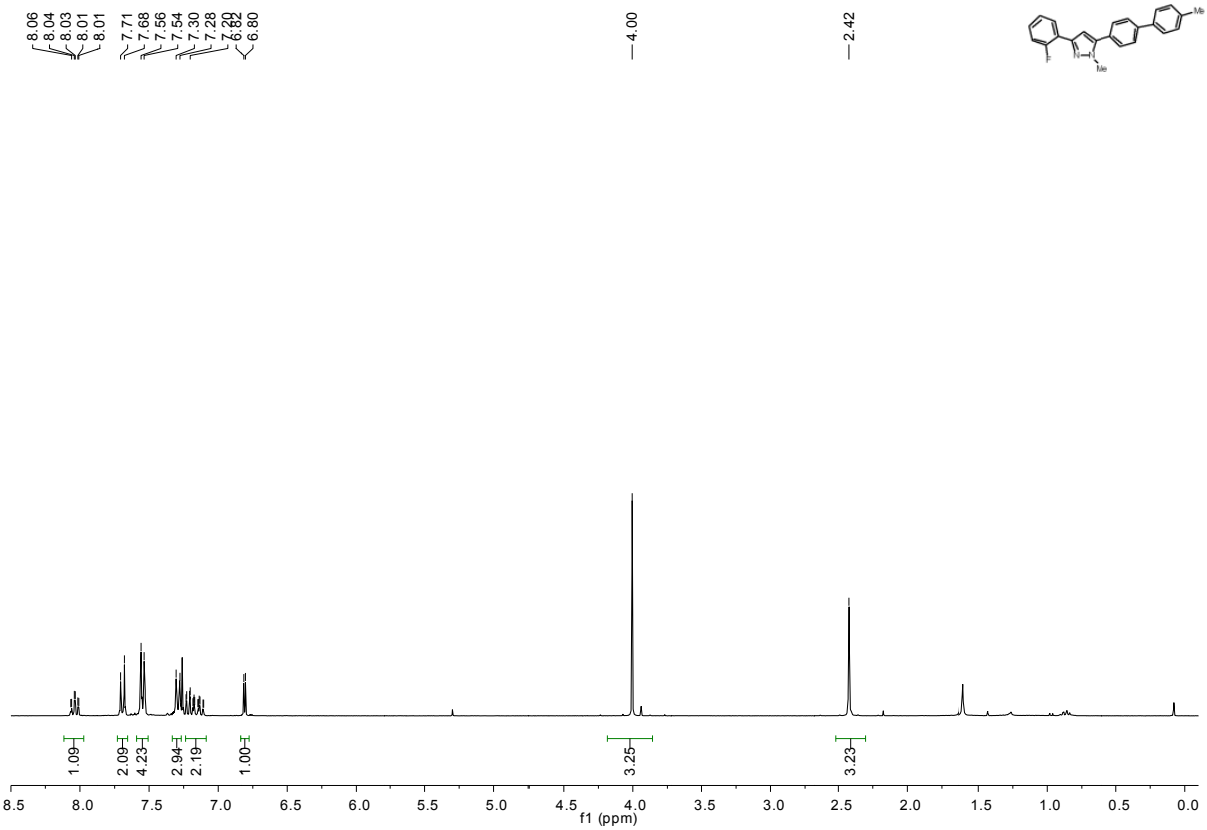


75 MHz ^{13}C NMR spectrum of compound **5c** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

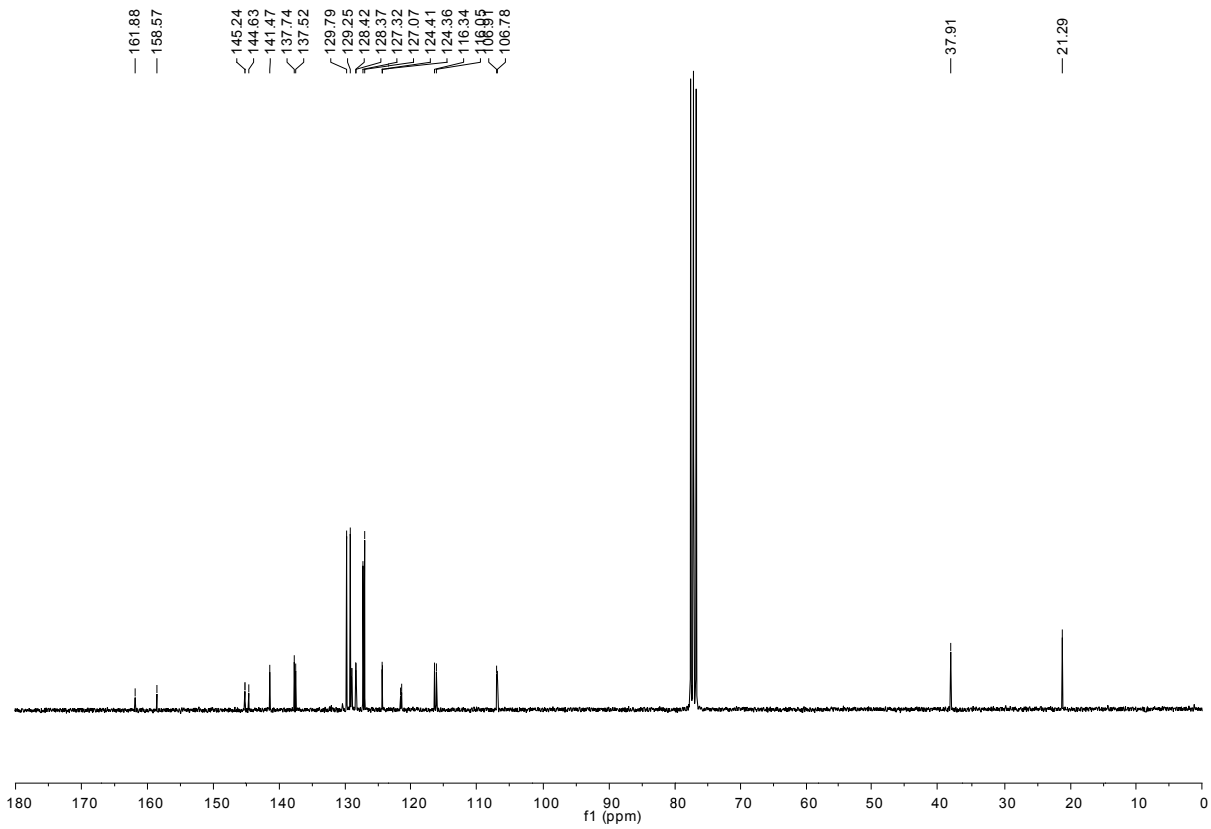


Normalized absorption and emission spectra of compound **5c** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

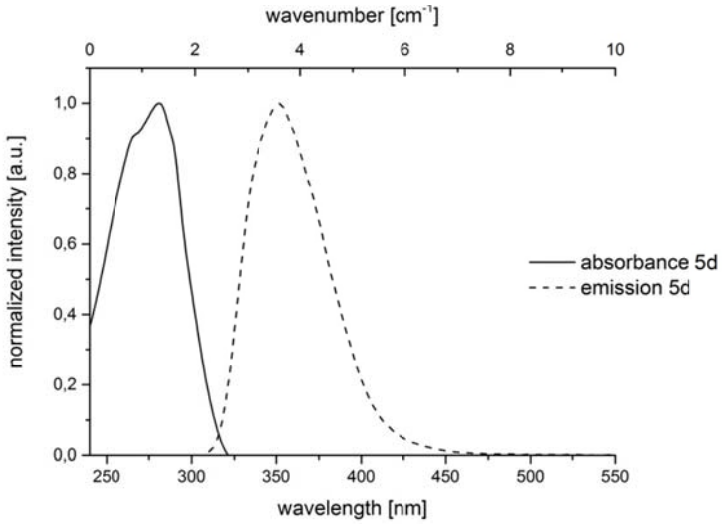
3-(2-Fluorophenyl)-1-methyl-5-(4'-methyl-[1,1'-biphenyl]-4-yl)-1*H*-pyrazole (**5d**)



300 MHz ^{1}H NMR spectrum of compound **5d** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

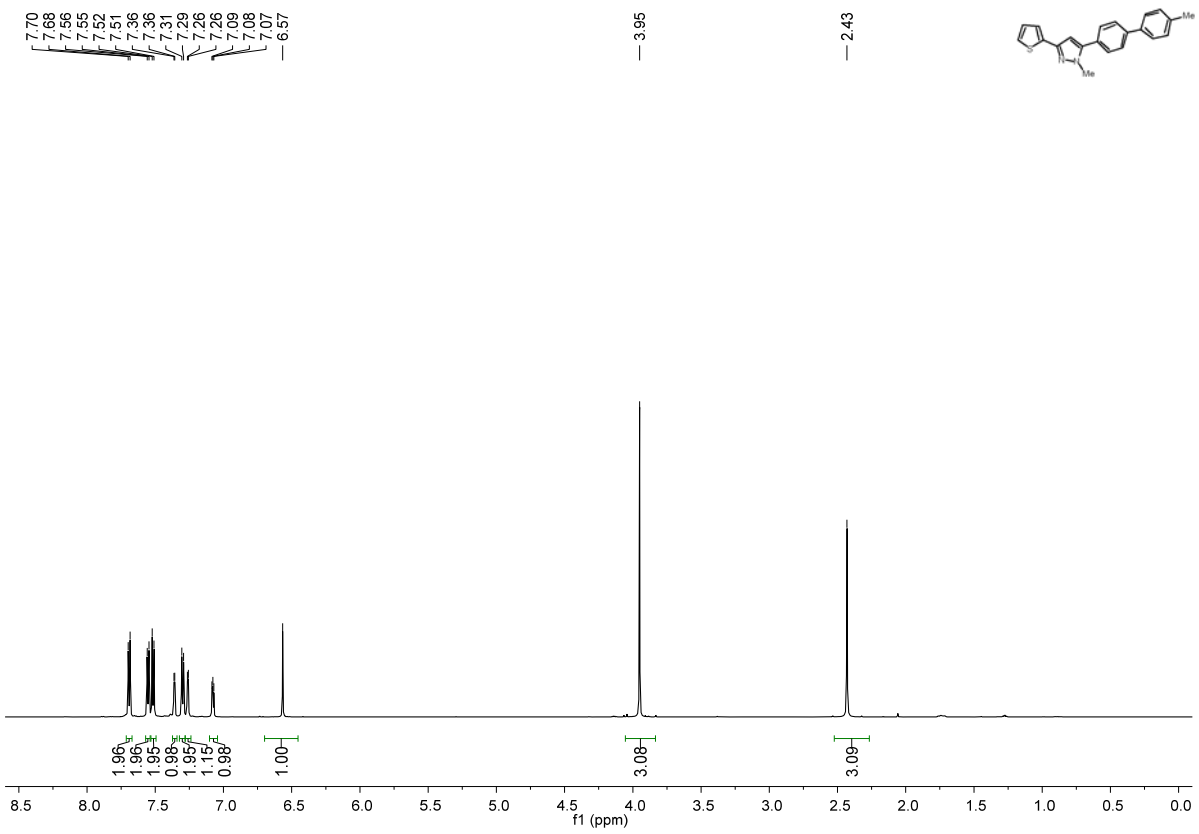


75 MHz ^{13}C NMR spectrum of compound **5d** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

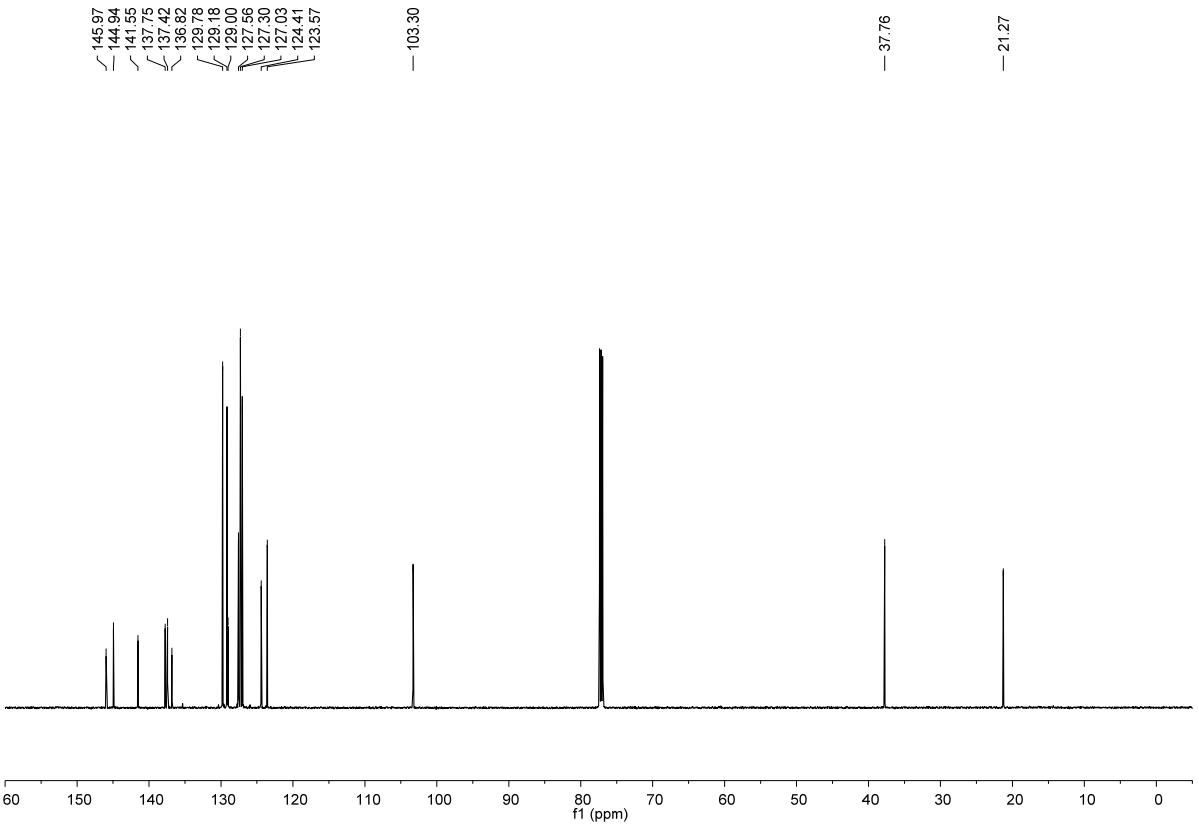


Normalized absorption and emission spectra of compound **5d** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

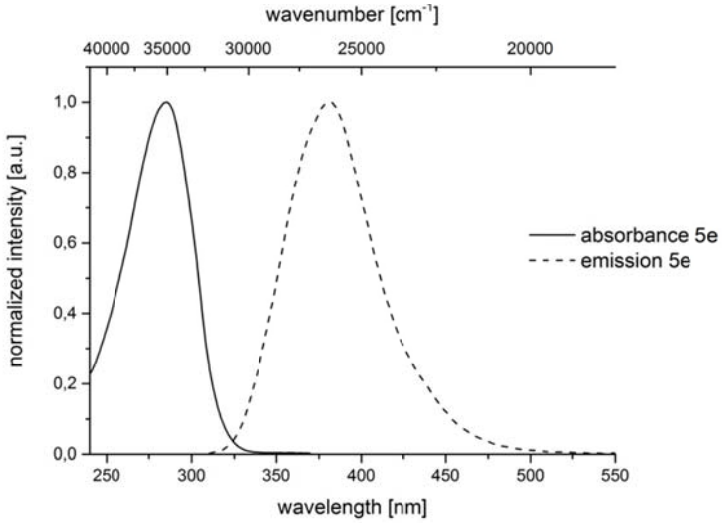
1-Methyl-5-(4'-methyl-[1,1'-biphenyl]-4-yl)-3-(thiophen-2-yl)-1*H*-pyrazole (**5e**)



600 MHz ^{1}H NMR spectrum of compound **5e** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

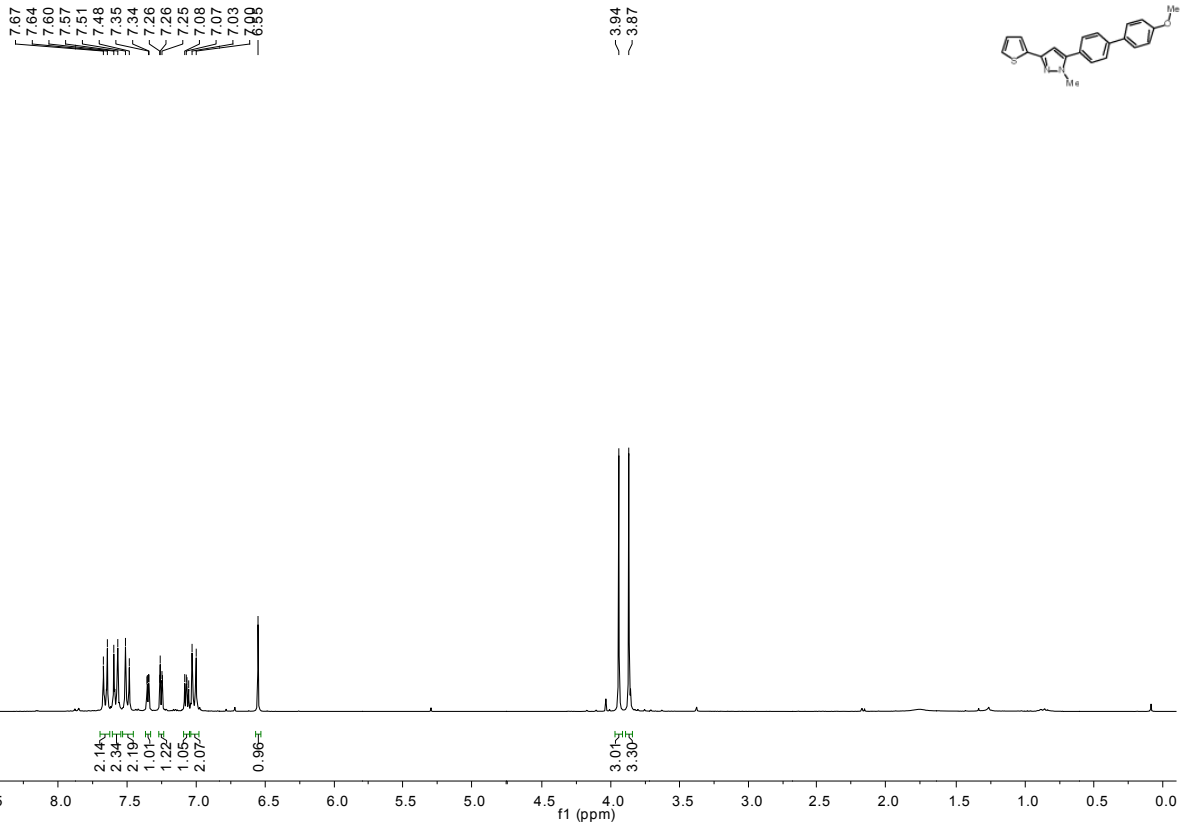


125 MHz ^{13}C NMR spectrum of compound **5e** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

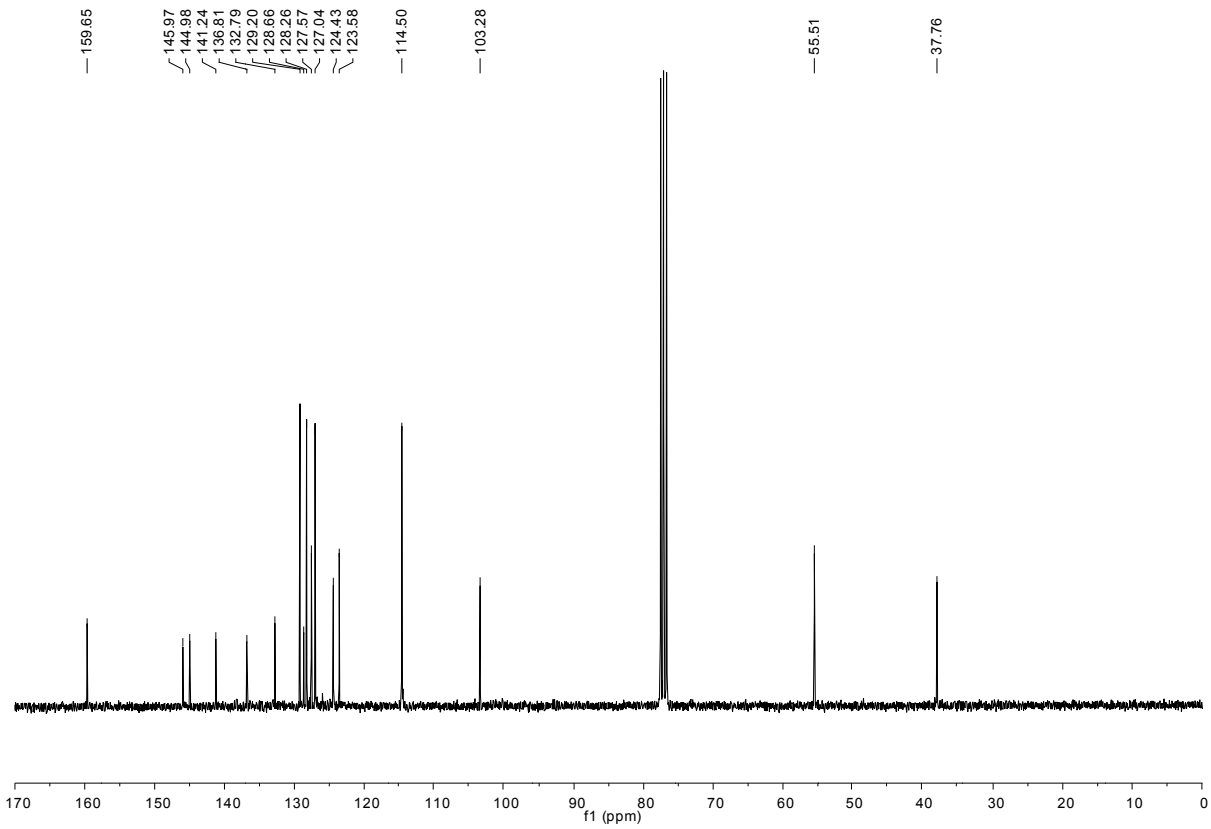


Normalized absorption and emission spectra of compound **5e** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

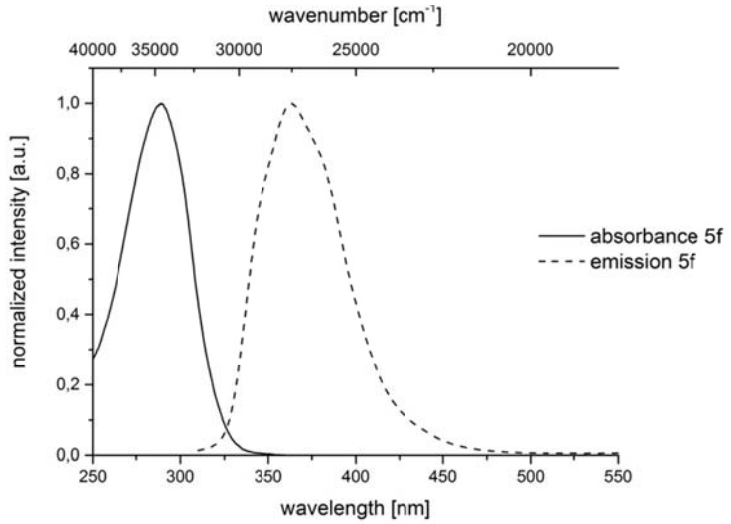
5-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-1-methyl-3-(thiophen-2-yl)-1*H*-pyrazole (**5f**)



300 MHz ^{1}H NMR spectrum of compound **5f** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

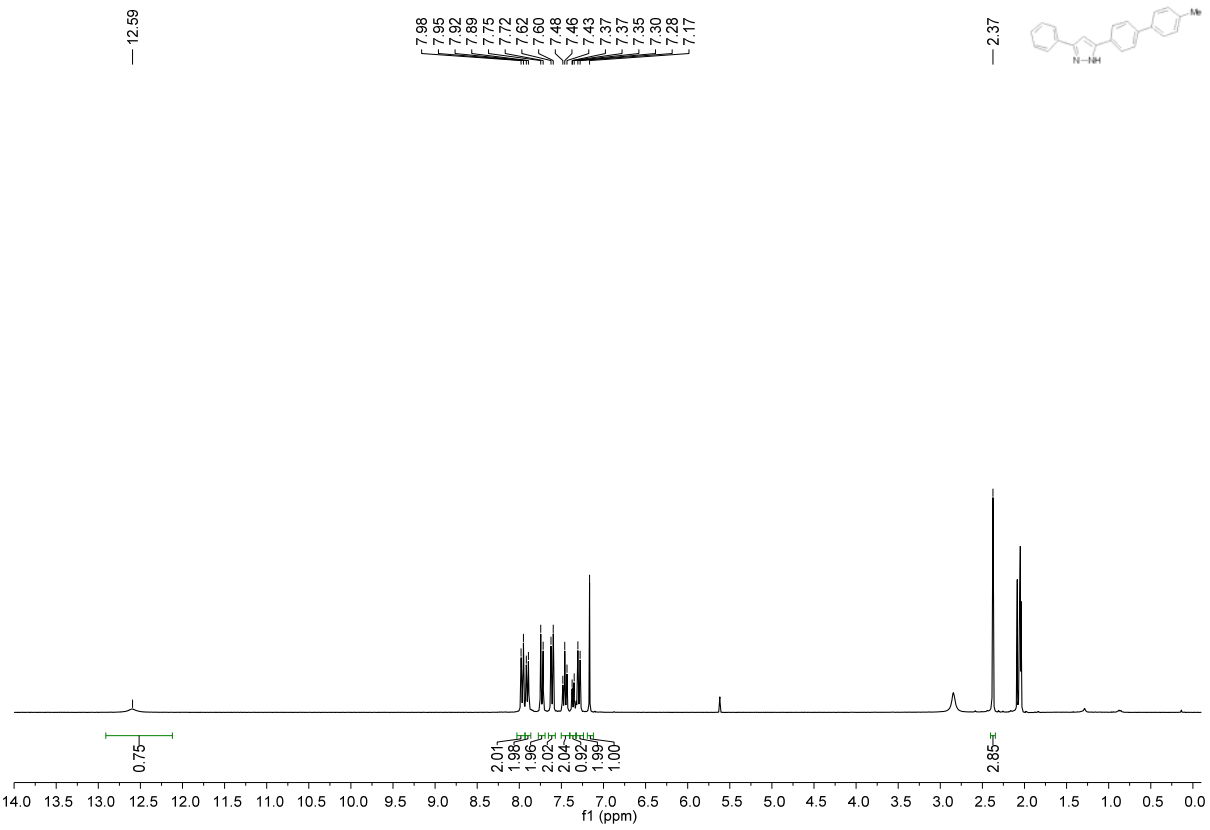


75 MHz ^{13}C NMR spectrum of compound **5f** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

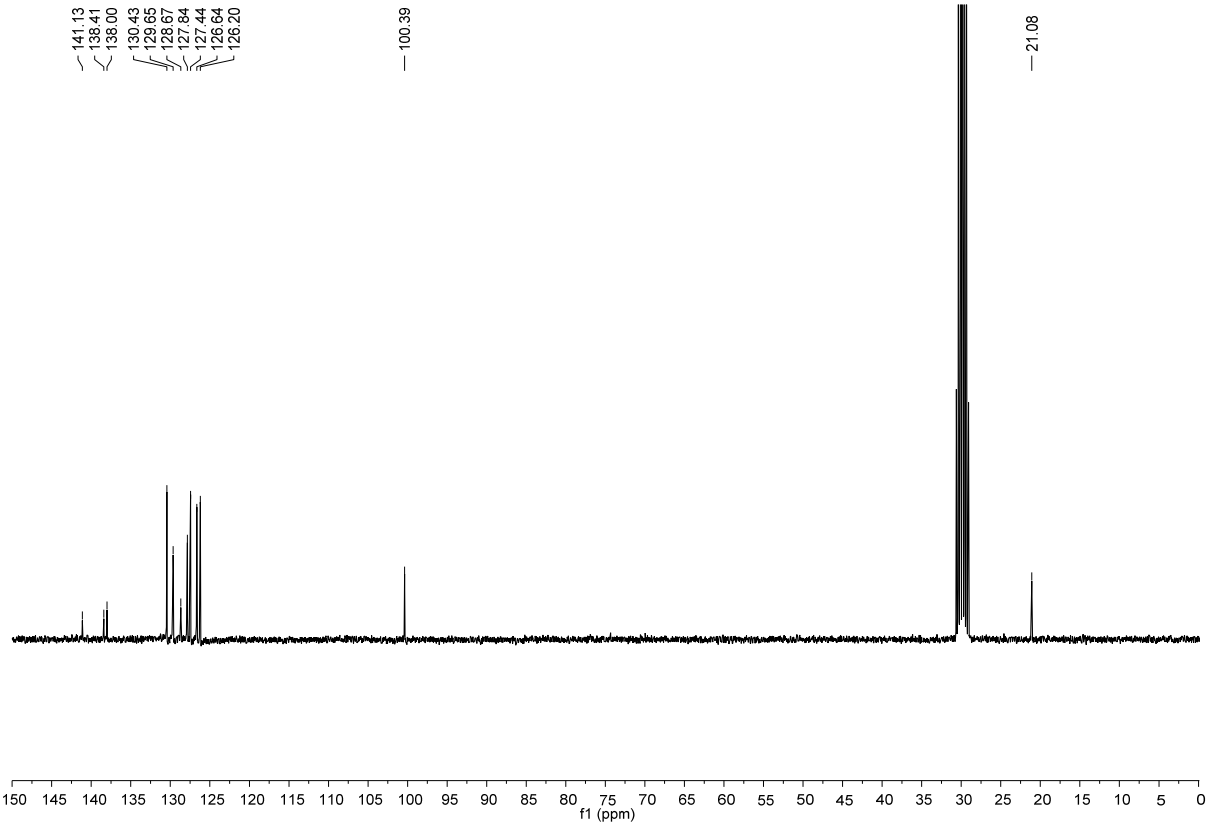


Normalized absorption and emission spectra of compound **5f** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

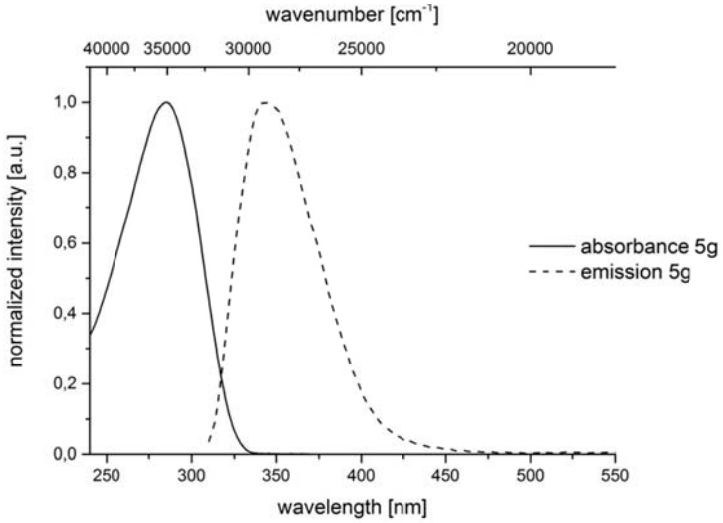
5-(4'-Methyl-[1,1'-biphenyl]-4-yl)-3-phenyl-1*H*-pyrazole (**5g**)



300 MHz ^{1}H NMR spectrum of compound **5g** recorded in d^{6}-acetone at *T* = 298 K (*δ* in ppm).



75 MHz ^{13}C NMR spectrum of compound **5g** recorded in d^{6}-acetone at *T* = 298 K (*δ* in ppm).



Normalized absorption and emission spectra of compound **5g** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

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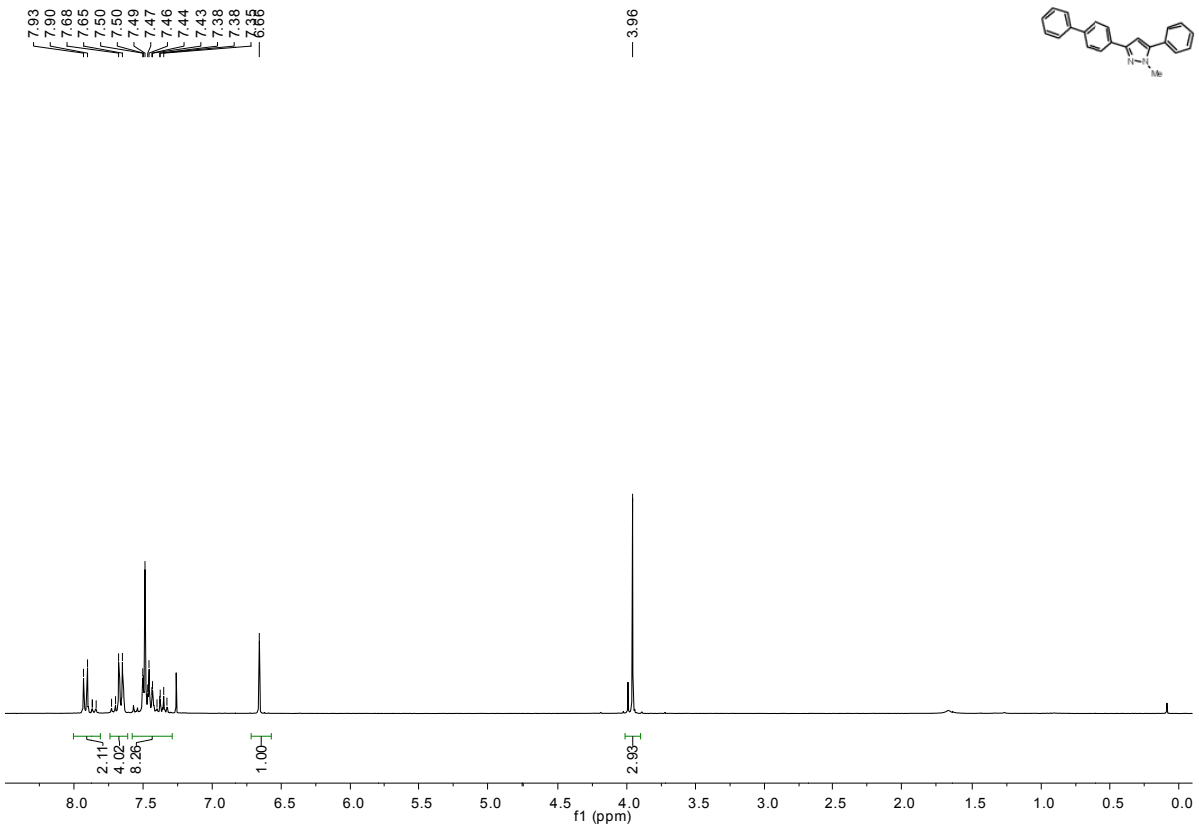
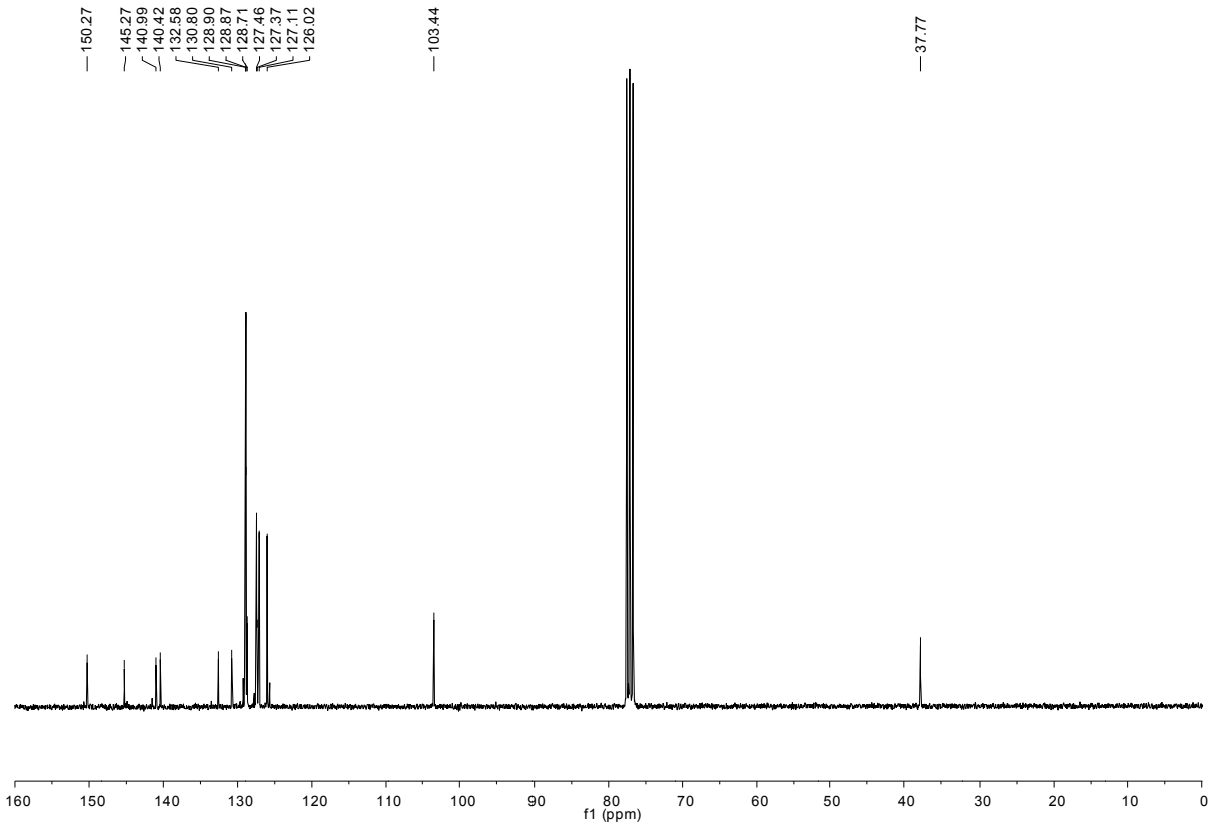
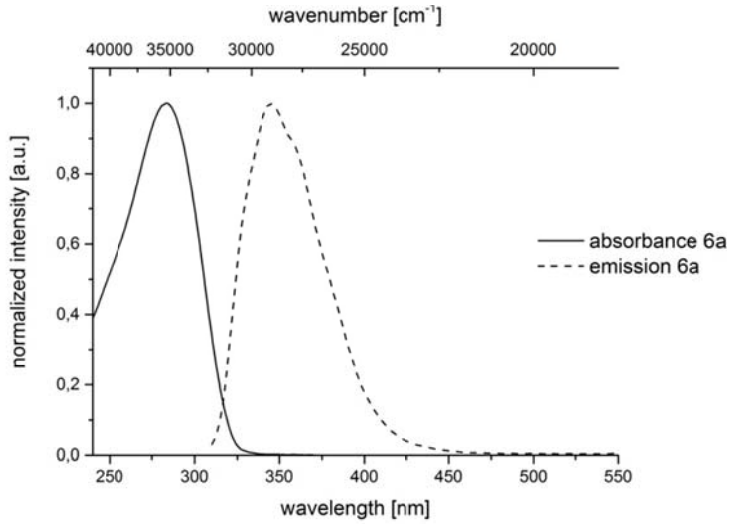
3-([1,1'-Biphenyl]-4-yl)-1-methyl-5-phenyl-1*H*-pyrazole (**6a**)



300 MHz ^{1}H NMR spectrum of compound **6a** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

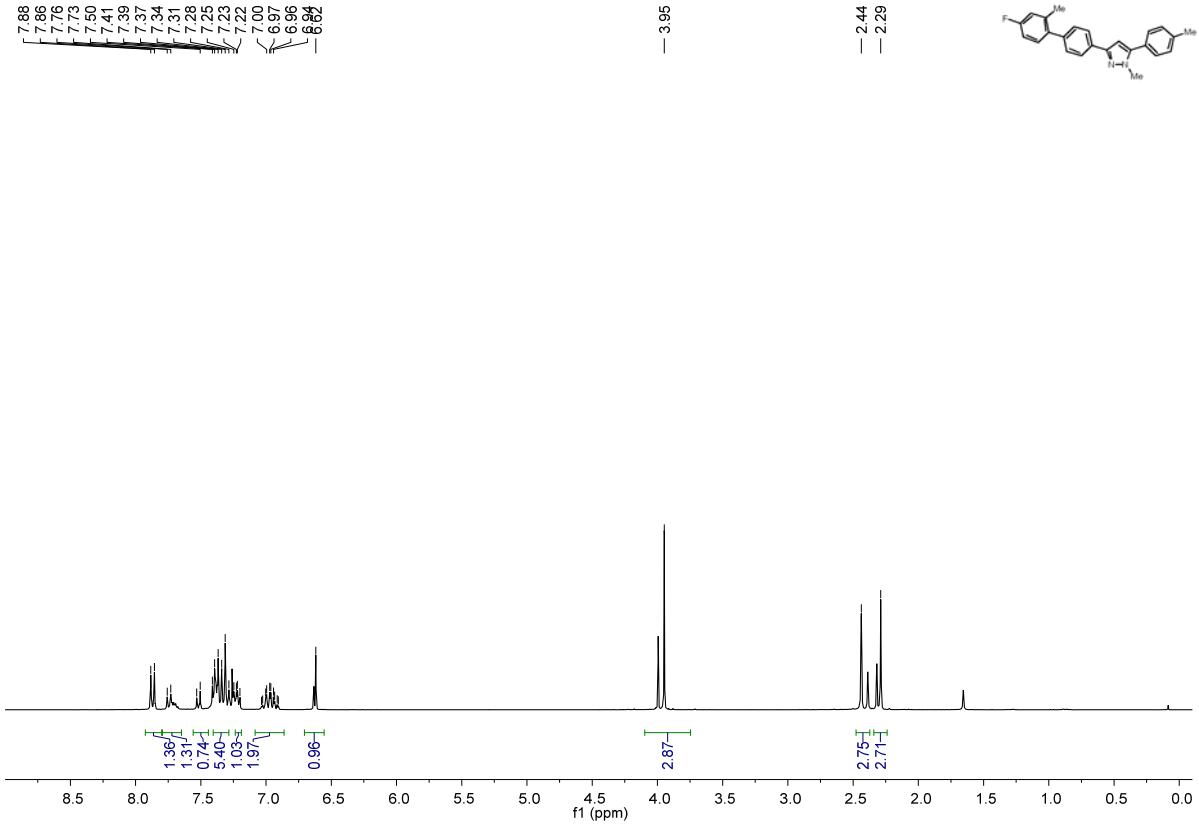


75 MHz ^{13}C NMR spectrum of compound **6a** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

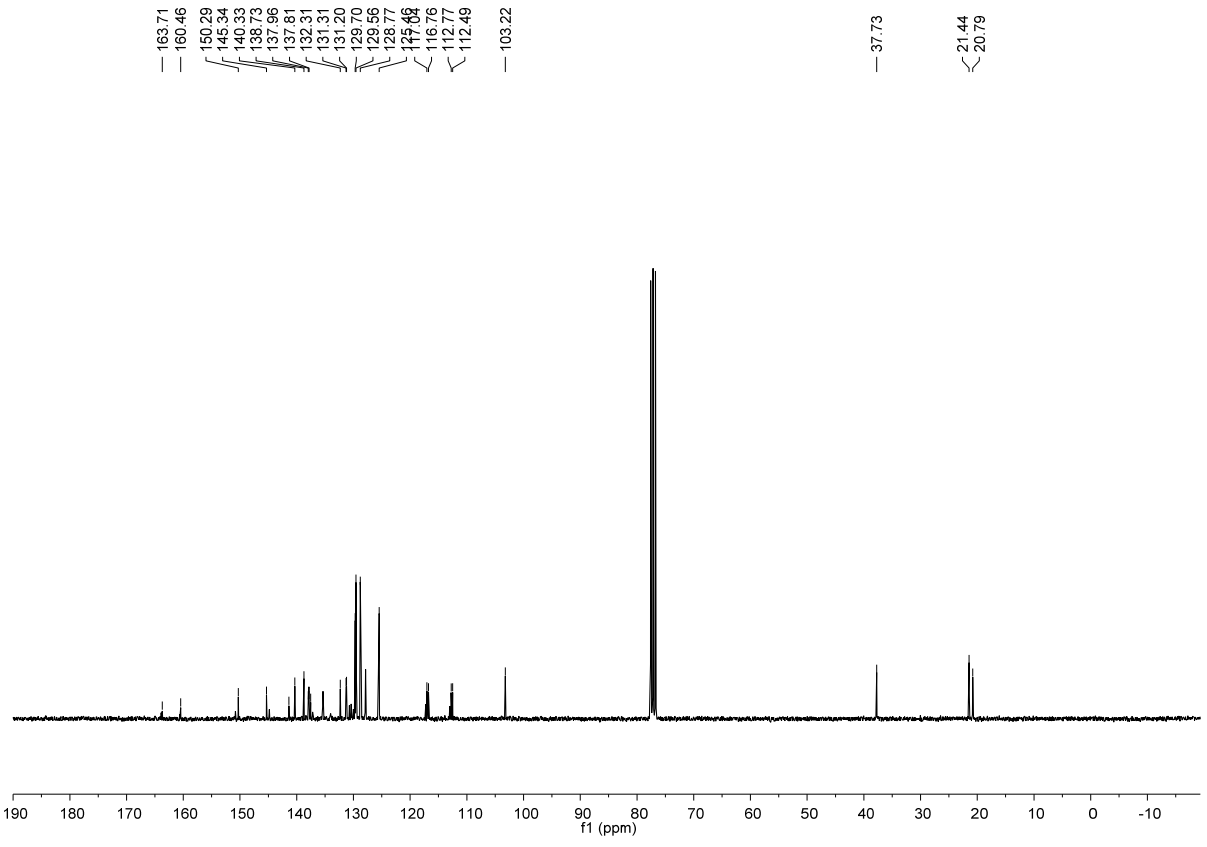


Normalized absorption and emission spectra of compound **6a** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

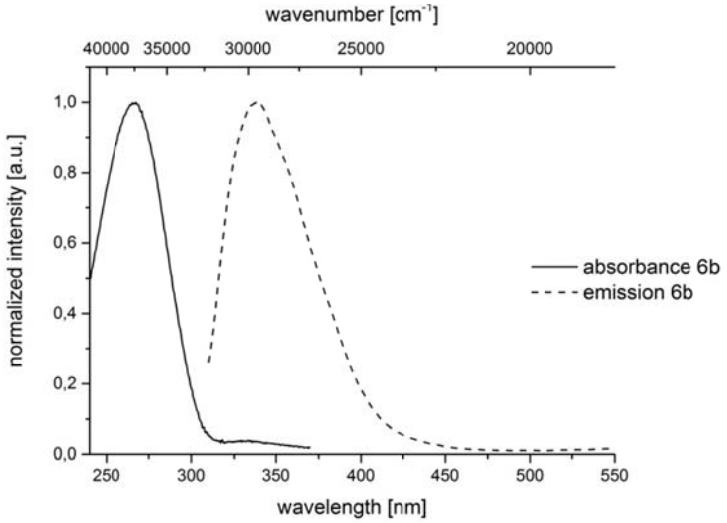
3-(4'-fluoro-2'-methyl-[1,1'-biphenyl]-4-yl)-1-methyl-5-(*p*-tolyl)-1*H*-pyrazole (**6b**)



300 MHz ^{1}H NMR spectrum of compound **6b** recorded in $CDCl_3$at *T* = 298 K (*δ* in ppm).

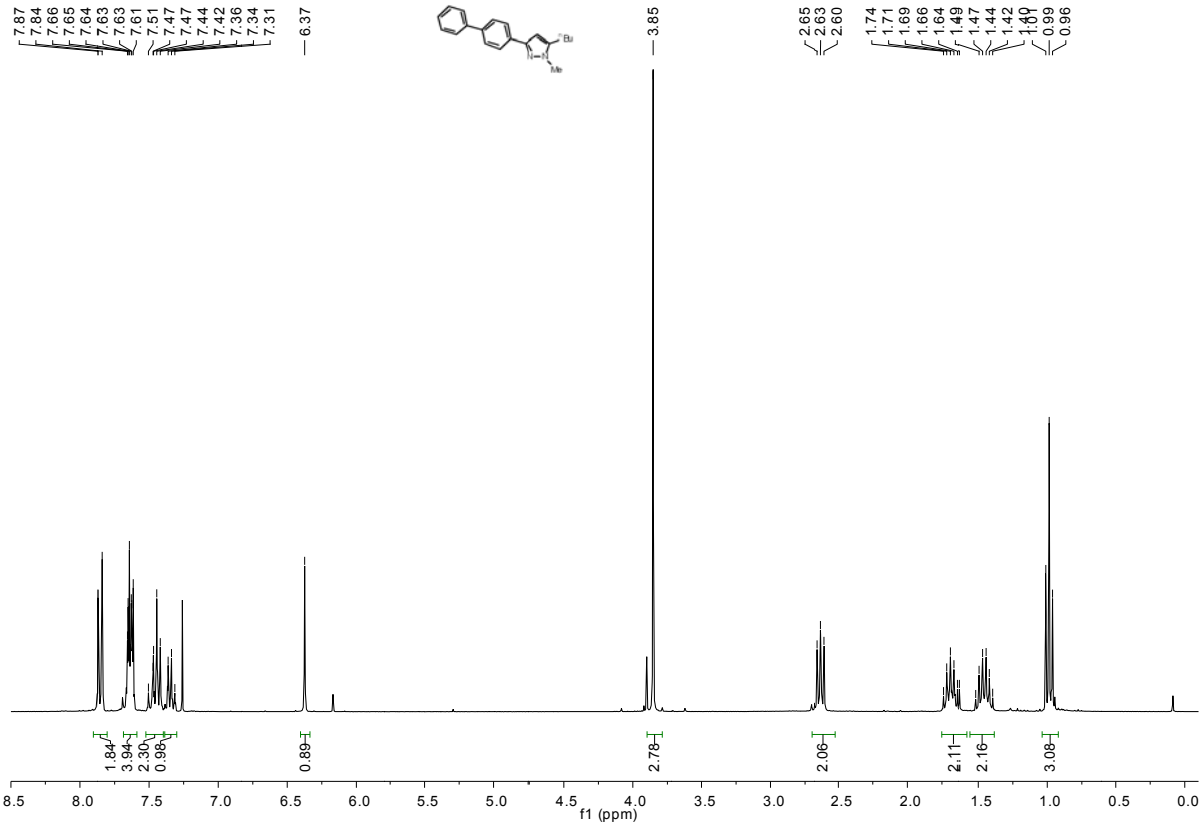


75 MHz ^{13}C NMR spectrum of compound **6b** recorded in $CDCl_3$ at *T* = 298 K (*δ* in ppm).

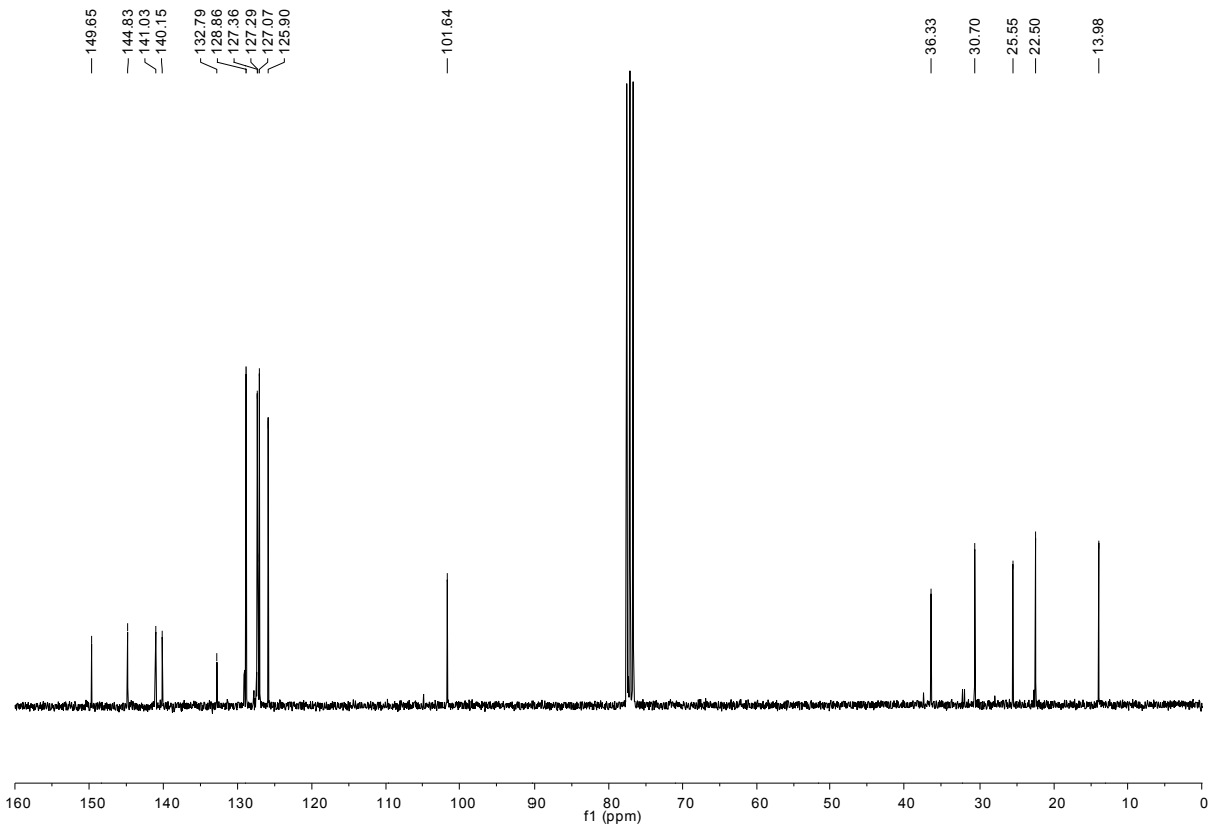


Normalized absorption and emission spectra of compound **6b** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

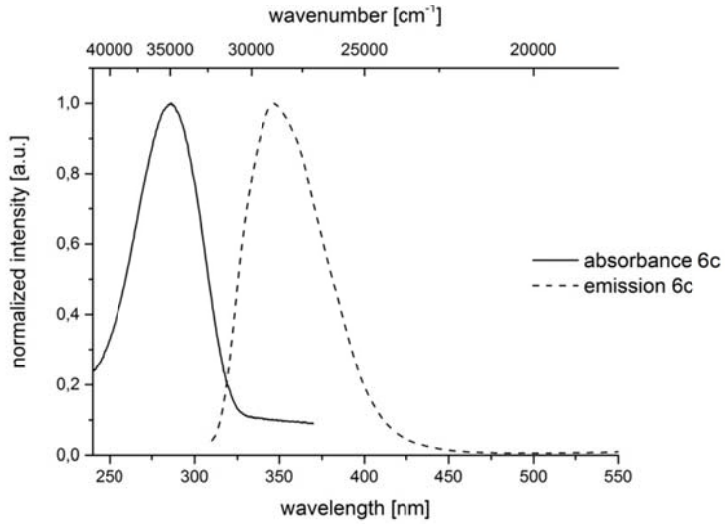
3-([1,1'-biphenyl]-4-yl)-5-butyl-1-methyl-1*H*-pyrazole (**6c**)



300 MHz ^{1}H NMR spectrum of compound **6c** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

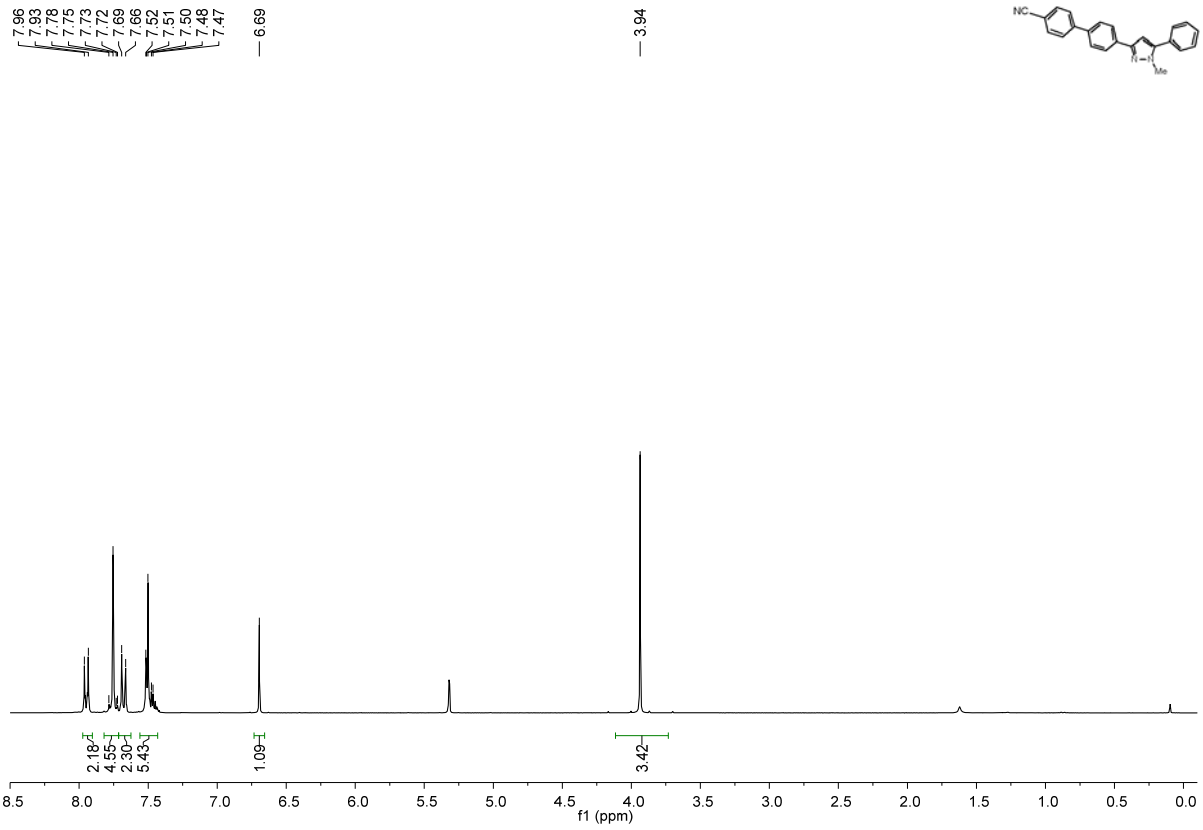


75 MHz ^{13}C NMR spectrum of compound **6c** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

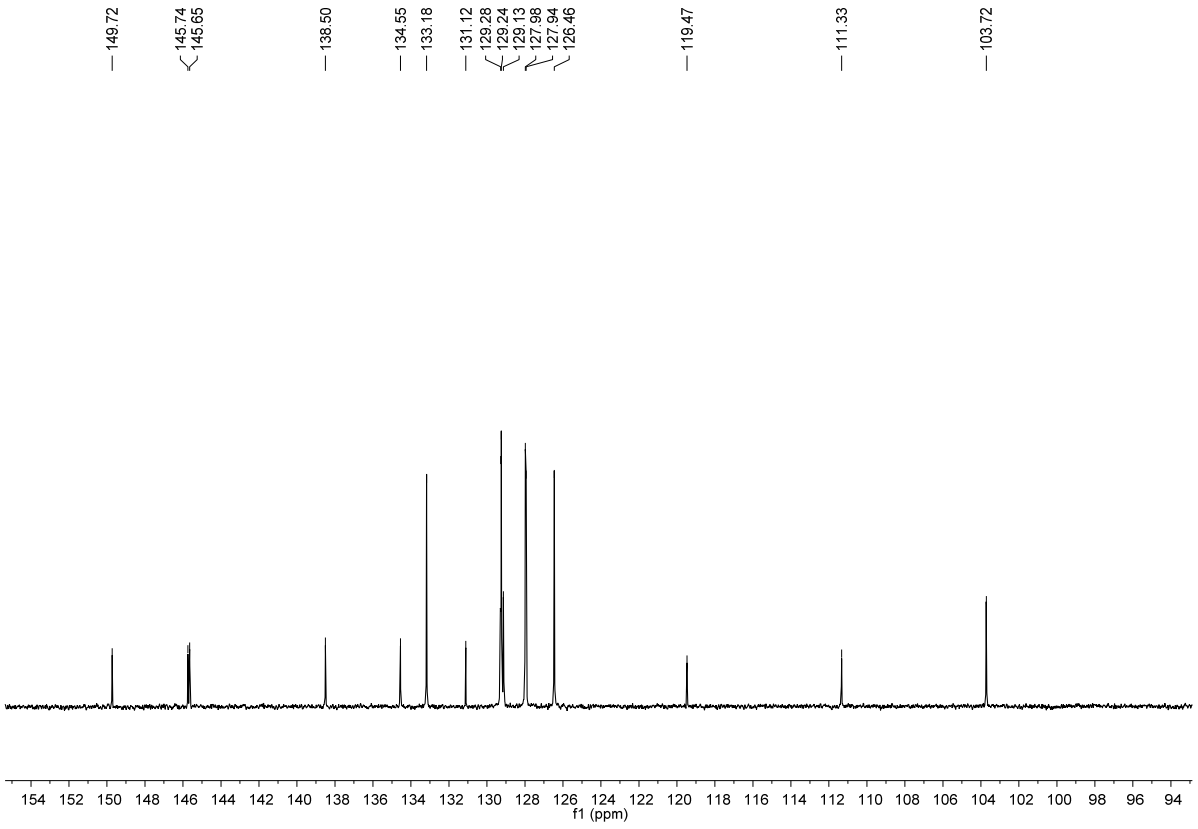


Normalized absorption and emission spectra of compound **6c** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

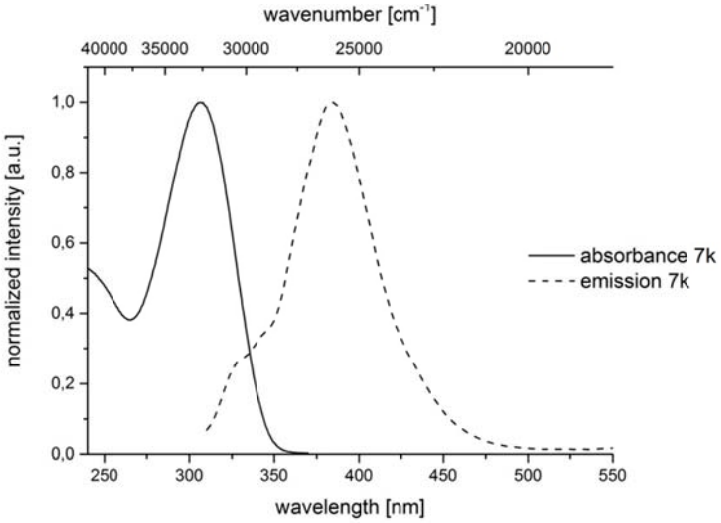
4’-(1-methyl-5-phenyl-1*H*-pyrazol-3-yl)-[1,1’-biphenyl]-4-carbonitrile (**6d**)



300 MHz ^{1}H NMR spectrum of compound **6d** recorded in CD_2Cl_2at *T* = 298 K (*δ* in ppm).

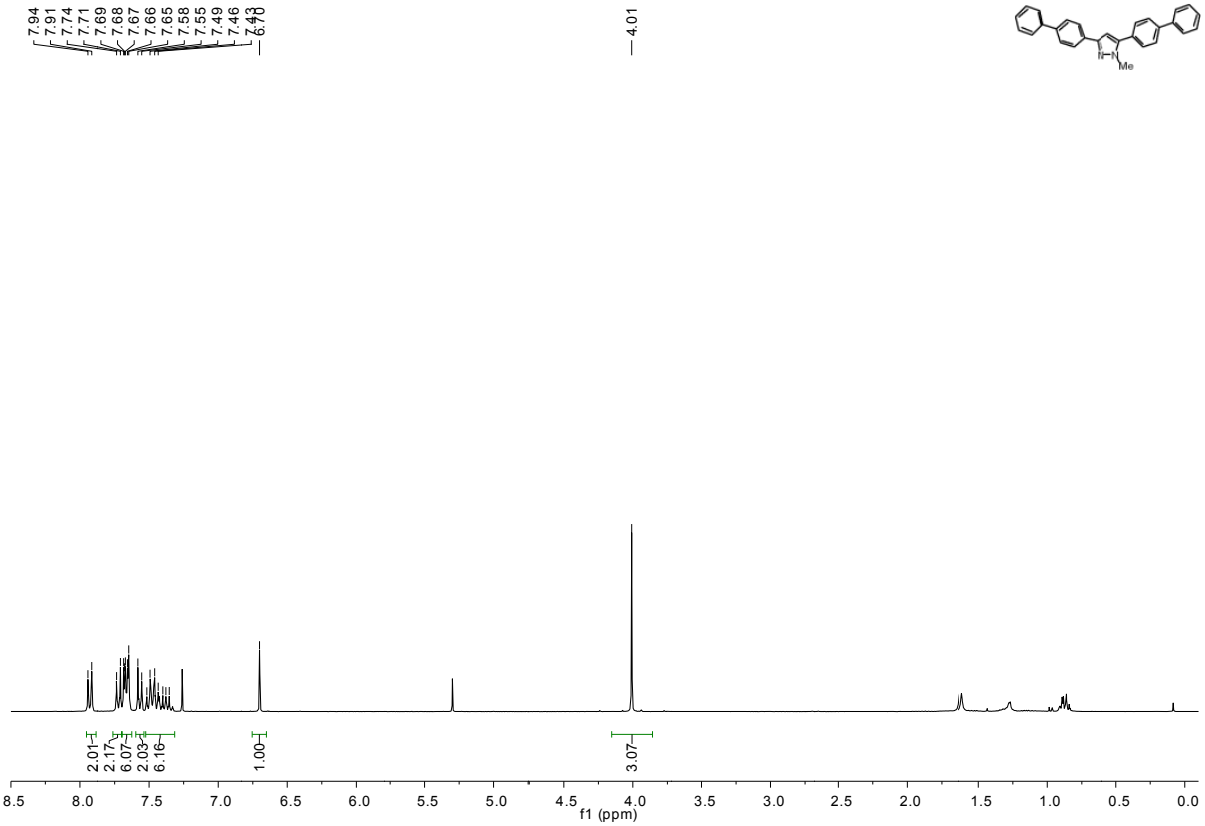


75 MHz ^{13}C NMR spectrum of compound **6d** recorded in CD_2Cl_2at *T* = 298 K (*δ* in ppm).

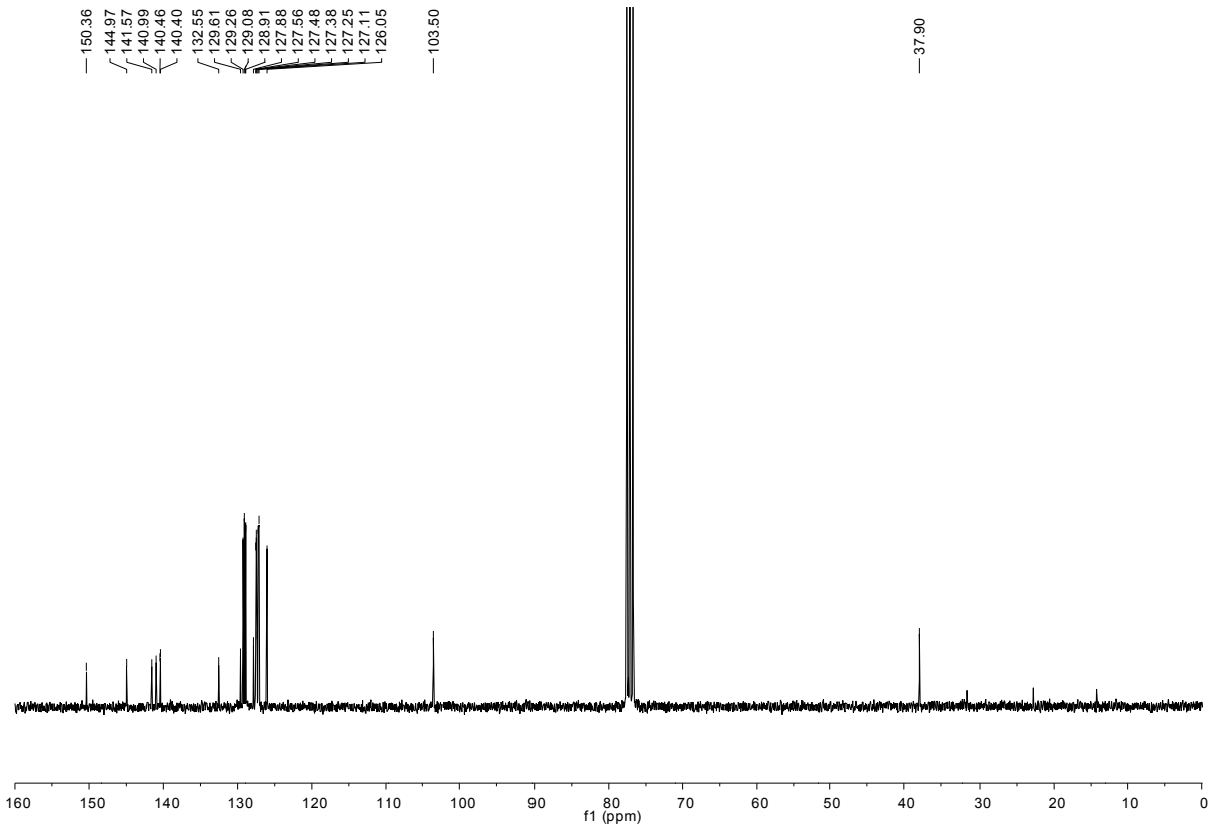


Normalized absorption and emission spectra of compound **6d** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

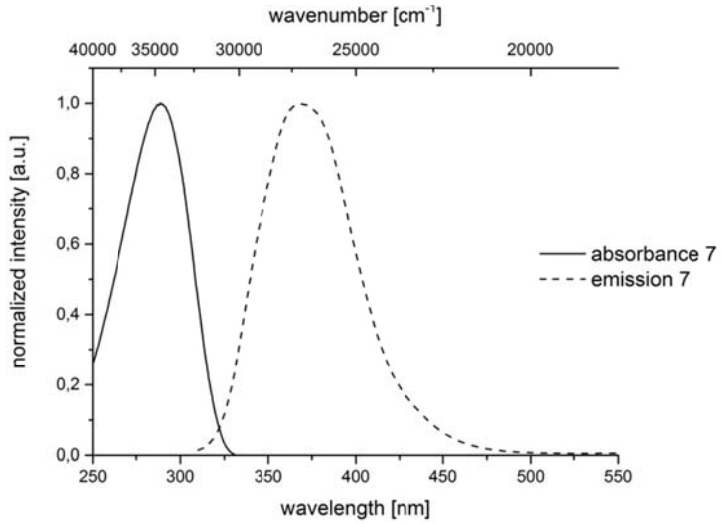
Spectra of the 3,5-Di([1,1'-biphenyl]-4-yl)-1-methyl-1*H*-pyrazole (**7**)



300 MHz ^{1}H NMR spectrum of compound **7** recorded in $CDCl_3$ at T = 298 K (δ in ppm).



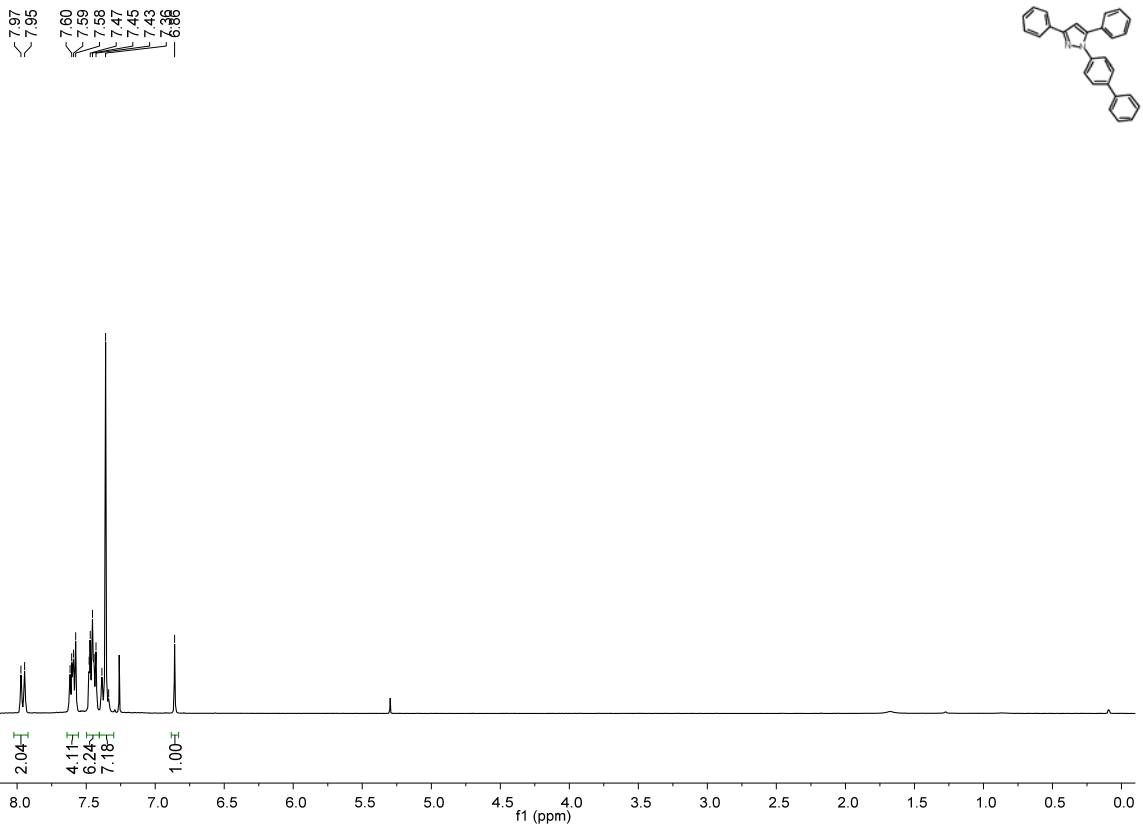
75 MHz ^{13}C NMR spectrum of compound **7** recorded in $CDCl_3$ at T = 298 K (δ in ppm).



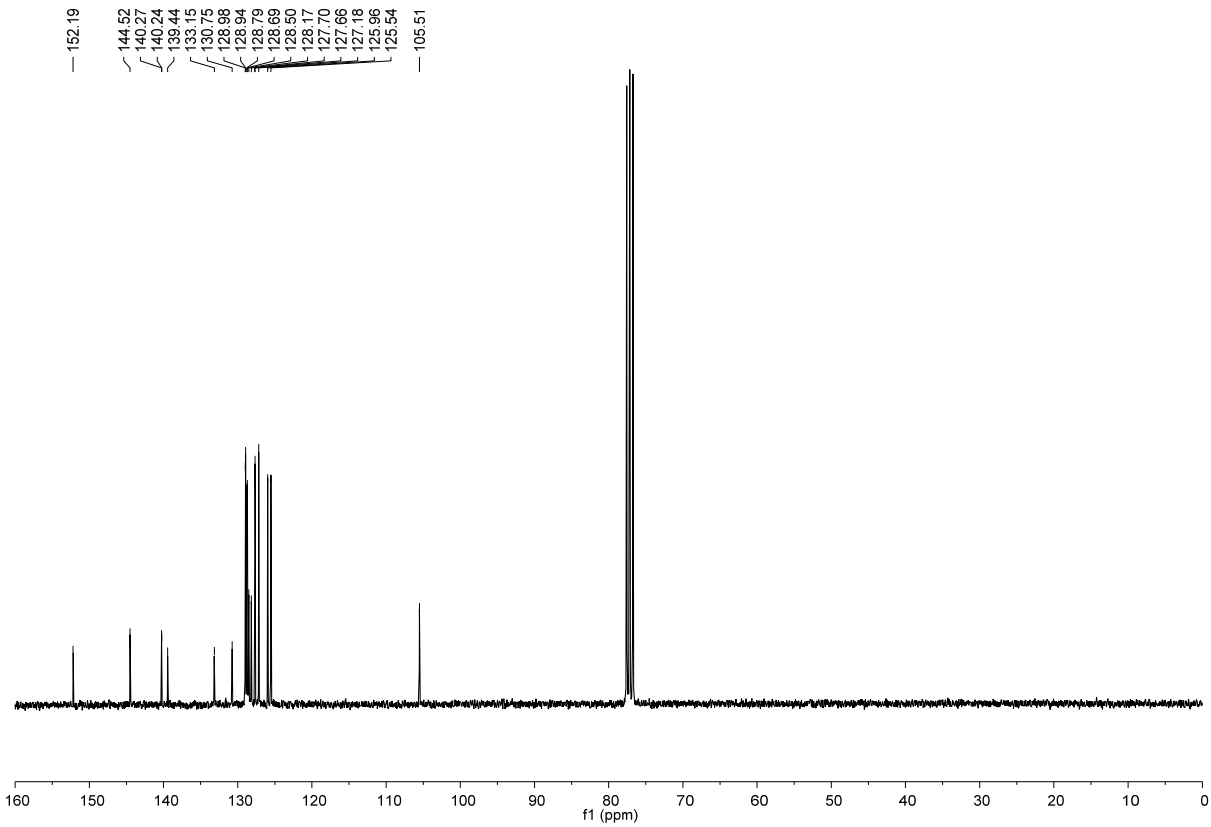
Normalized absorption and emission spectra of compound **7** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

Spectra of 1-Biarylsubstituted Pyrazoles 8

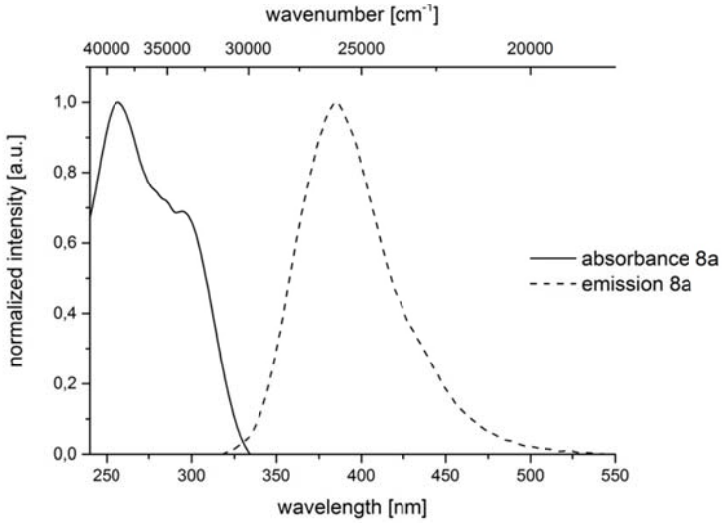
1-([1,1'-biphenyl]-4-yl)-3,5-diphenyl-1*H*-pyrazole (**8a**)



300 MHz ^{1}H NMR spectrum of compound **8a** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

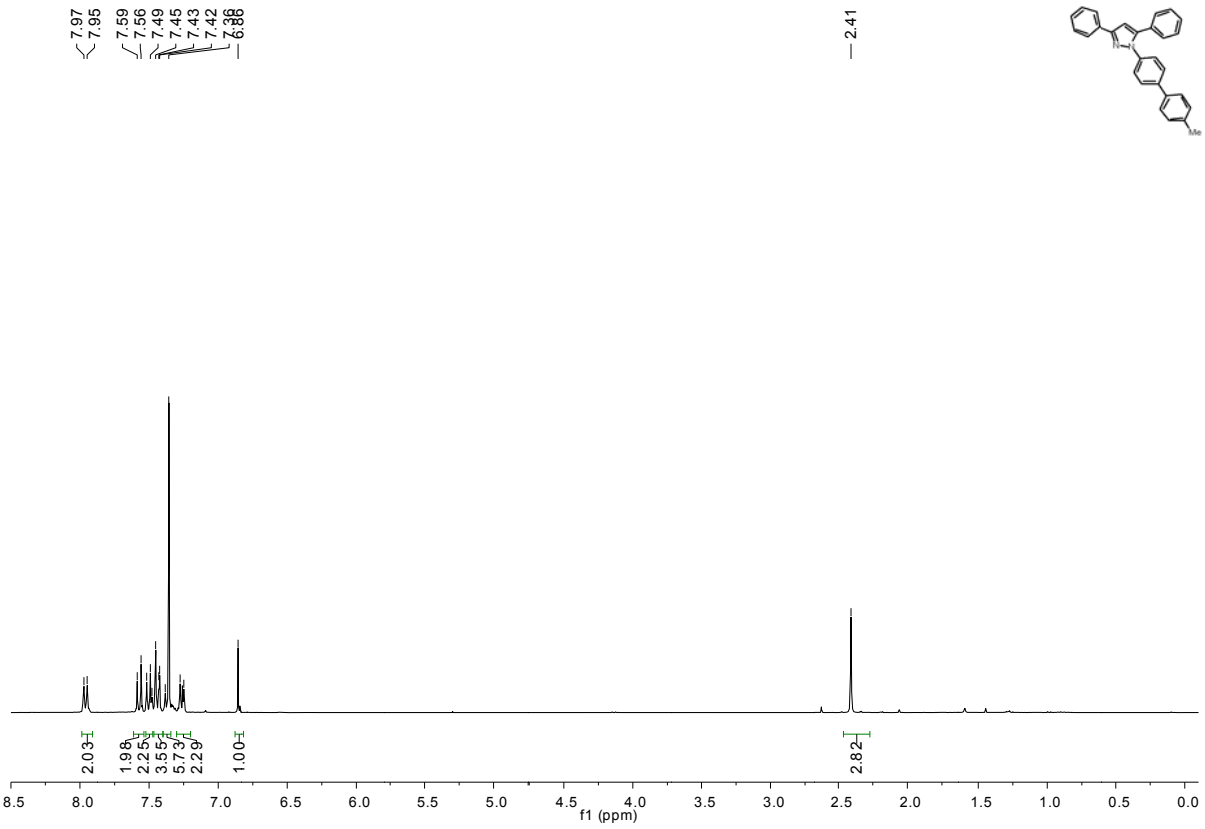


75 MHz ^{13}C NMR spectrum of compound **8a** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

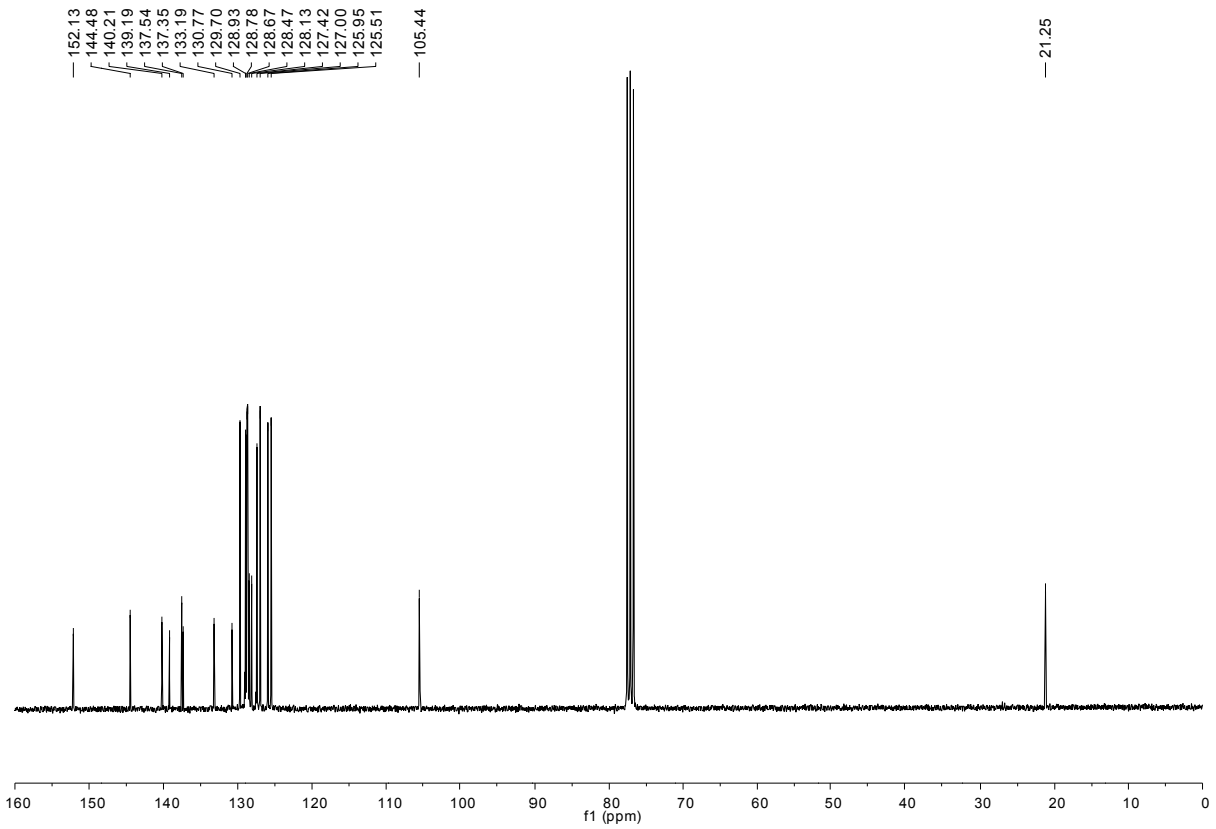


Normalized absorption and emission spectra of compound **8a** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc}= 290 nm).

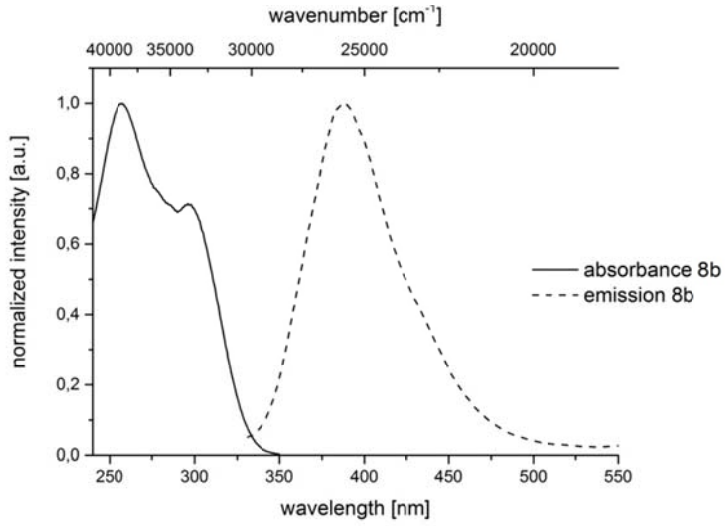
1-(4'-methyl-[1,1'-biphenyl]-4-yl)-3,5-diphenyl-1*H*-pyrazole (**8b**)



300 MHz ^{1}H NMR spectrum of compound **8b** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

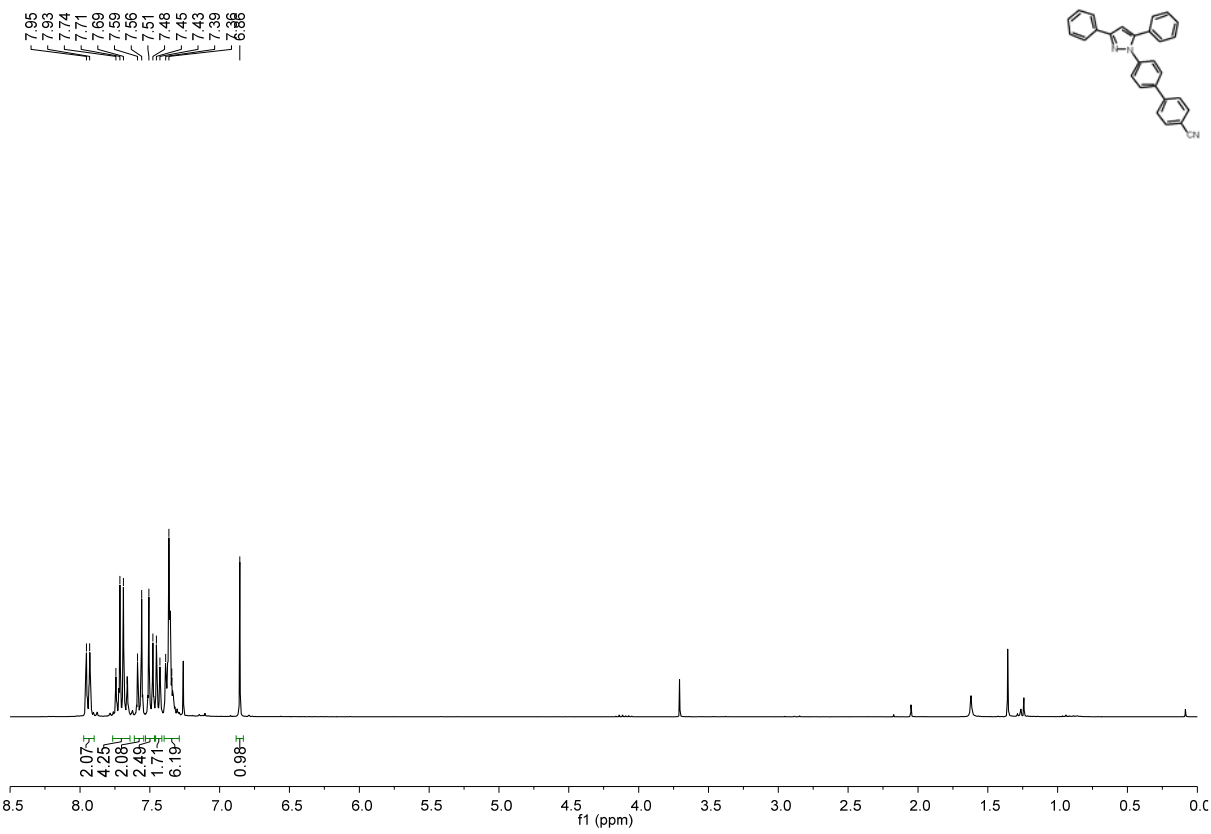


75 MHz ^{13}C NMR spectrum of compound **8b** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

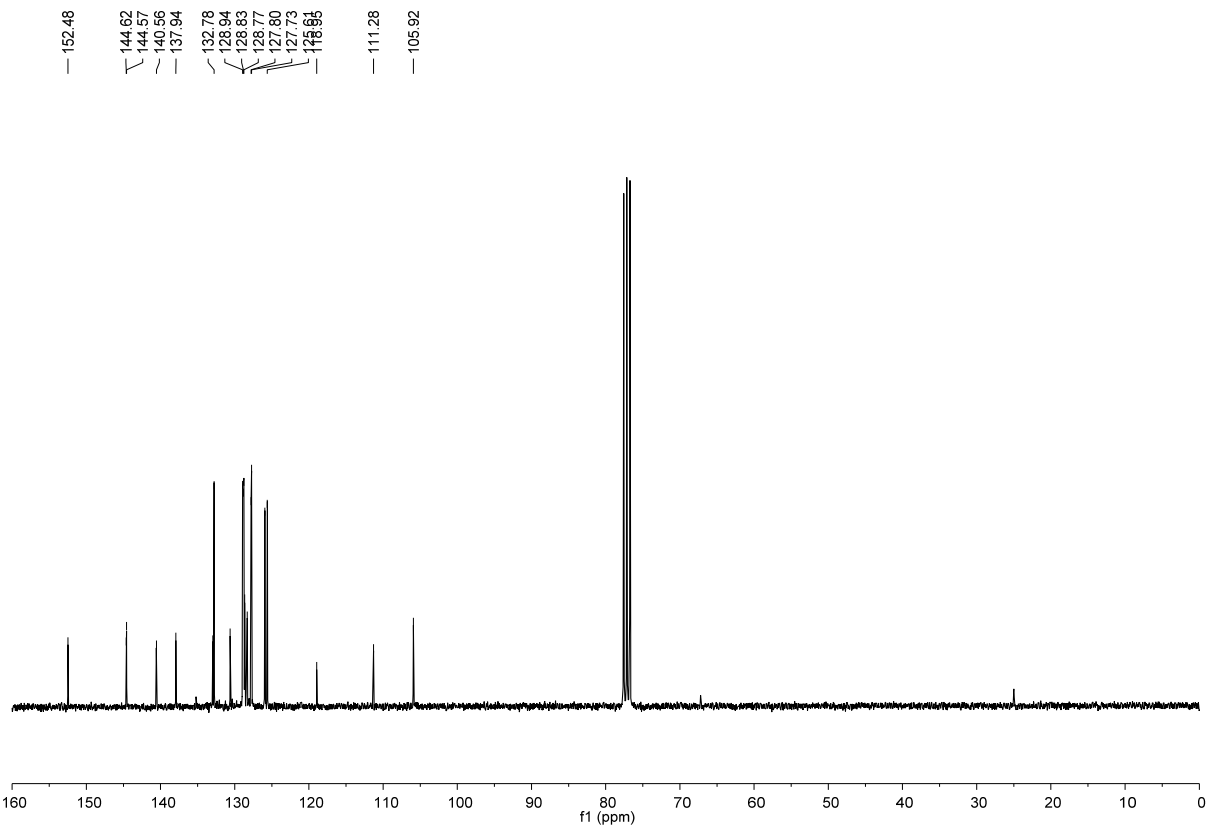


Normalized absorption and emission spectra of compound **8b** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

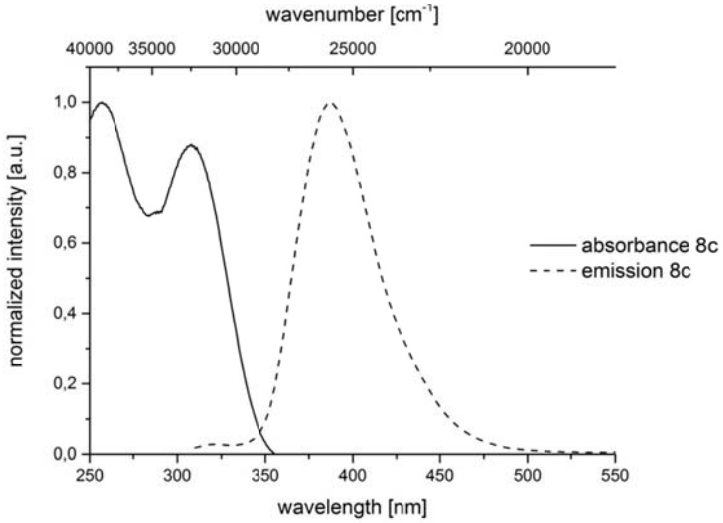
4'-(3,5-diphenyl-1*H*-pyrazol-1-yl)-[1,1'-biphenyl]-4-carbonitrile (**8c**)



300 MHz ^{1}H NMR spectrum of compound **8c** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

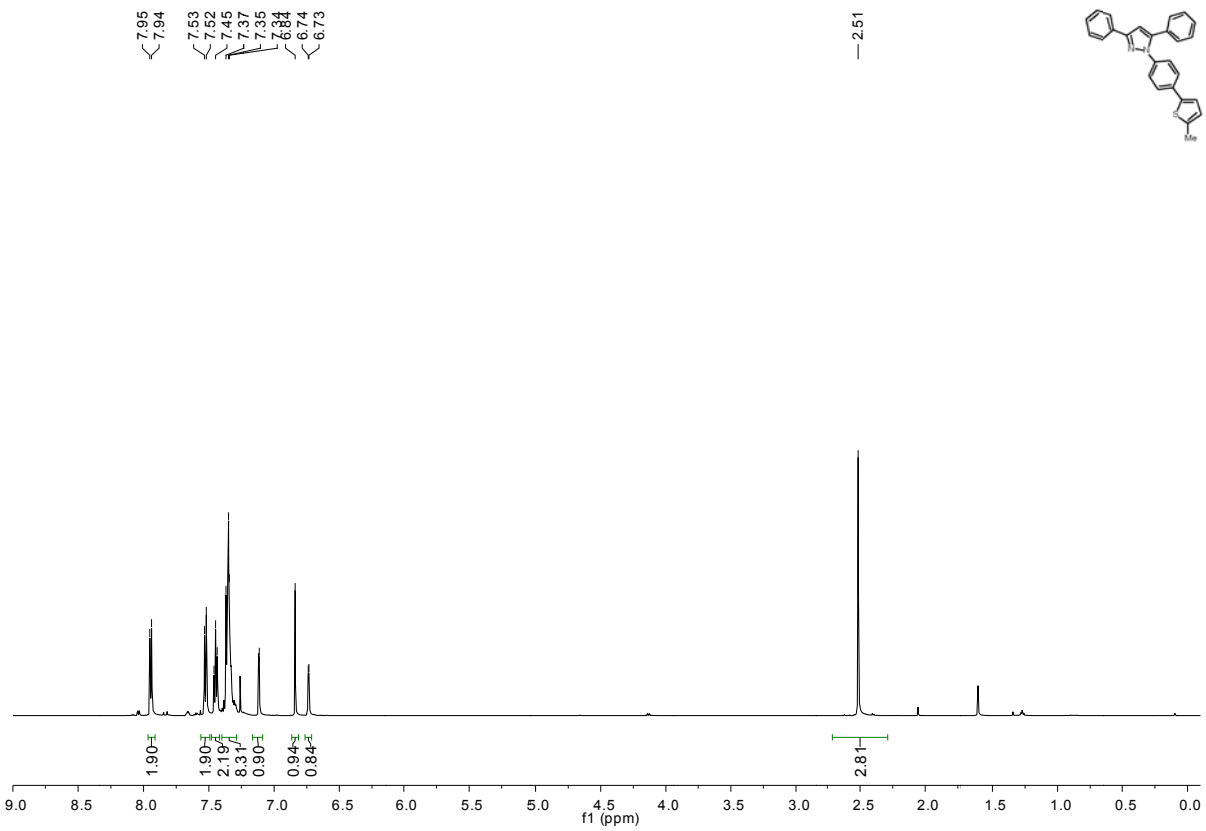


75 MHz ^{13}C NMR spectrum of compound **8c** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

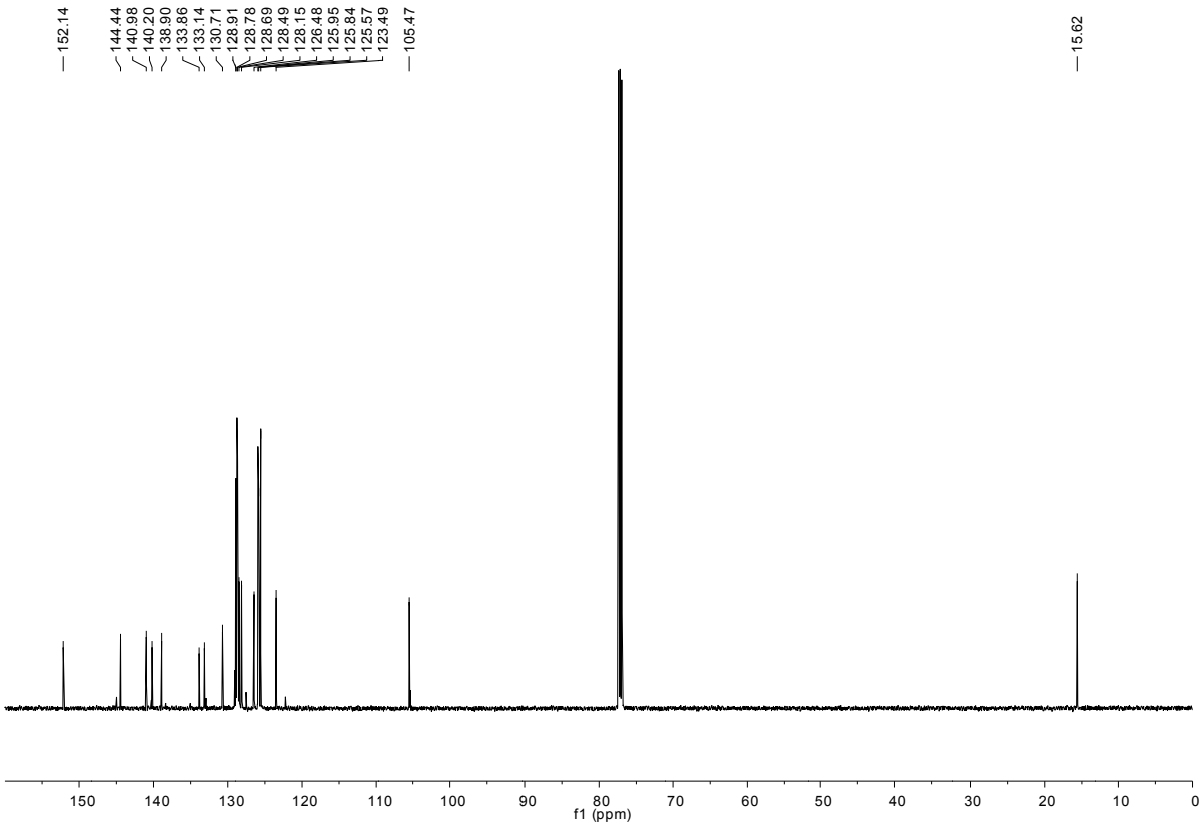


Normalized absorption and emission spectra of compound **8c** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

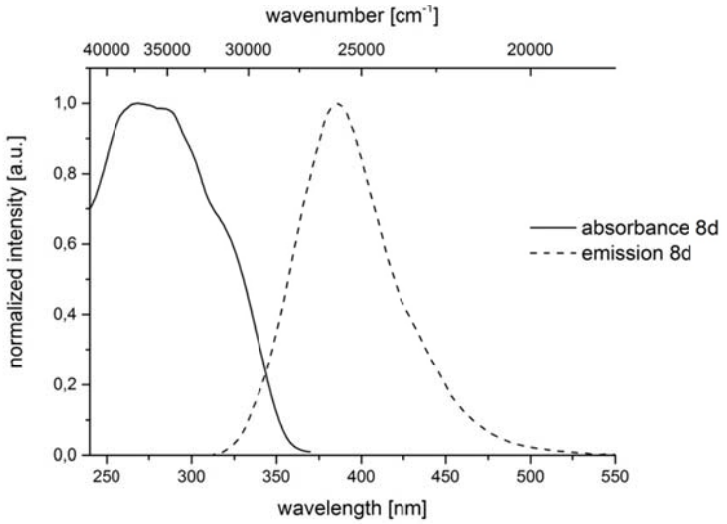
1-(4-(5-methylthiophen-2-yl)phenyl)-3,5-diphenyl-1*H*-pyrazole (**8d**)



600 MHz ^{1}H NMR spectrum of compound **8d** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

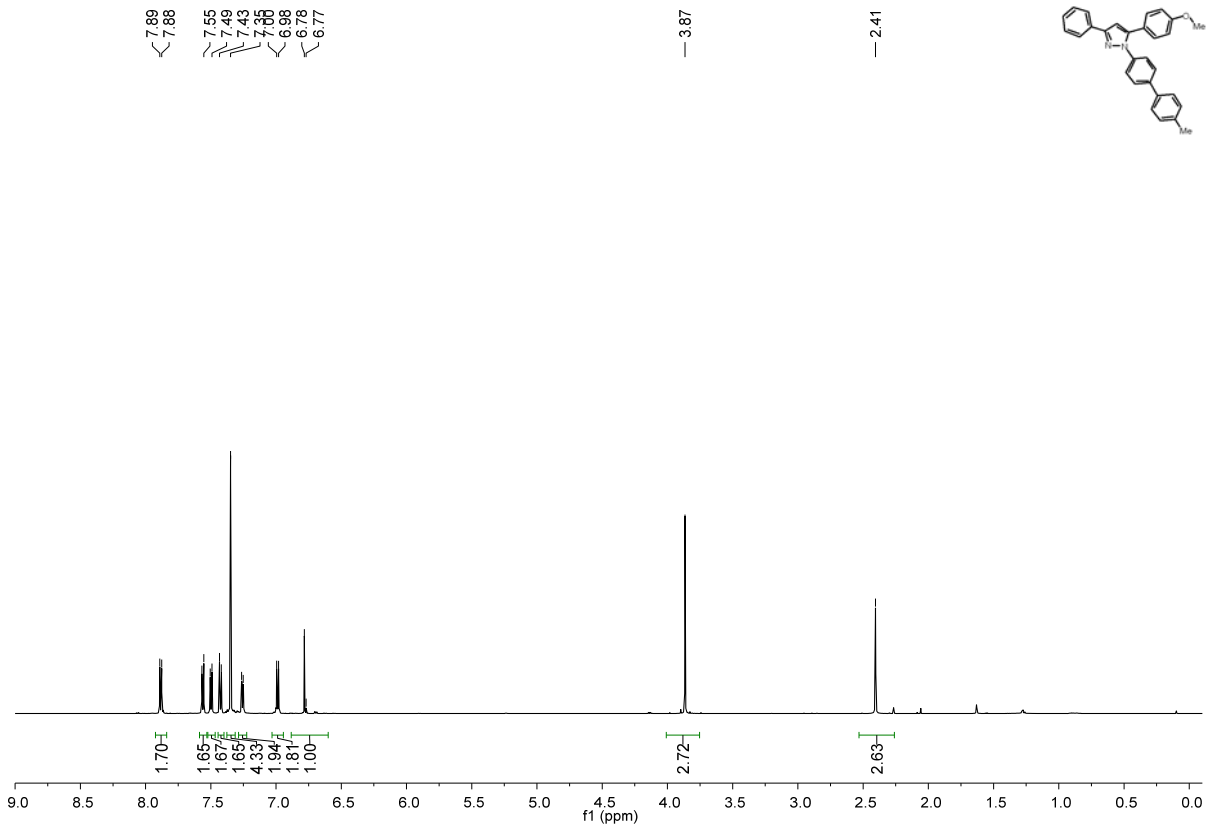


125 MHz ^{13}C NMR spectrum of compound **8d** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

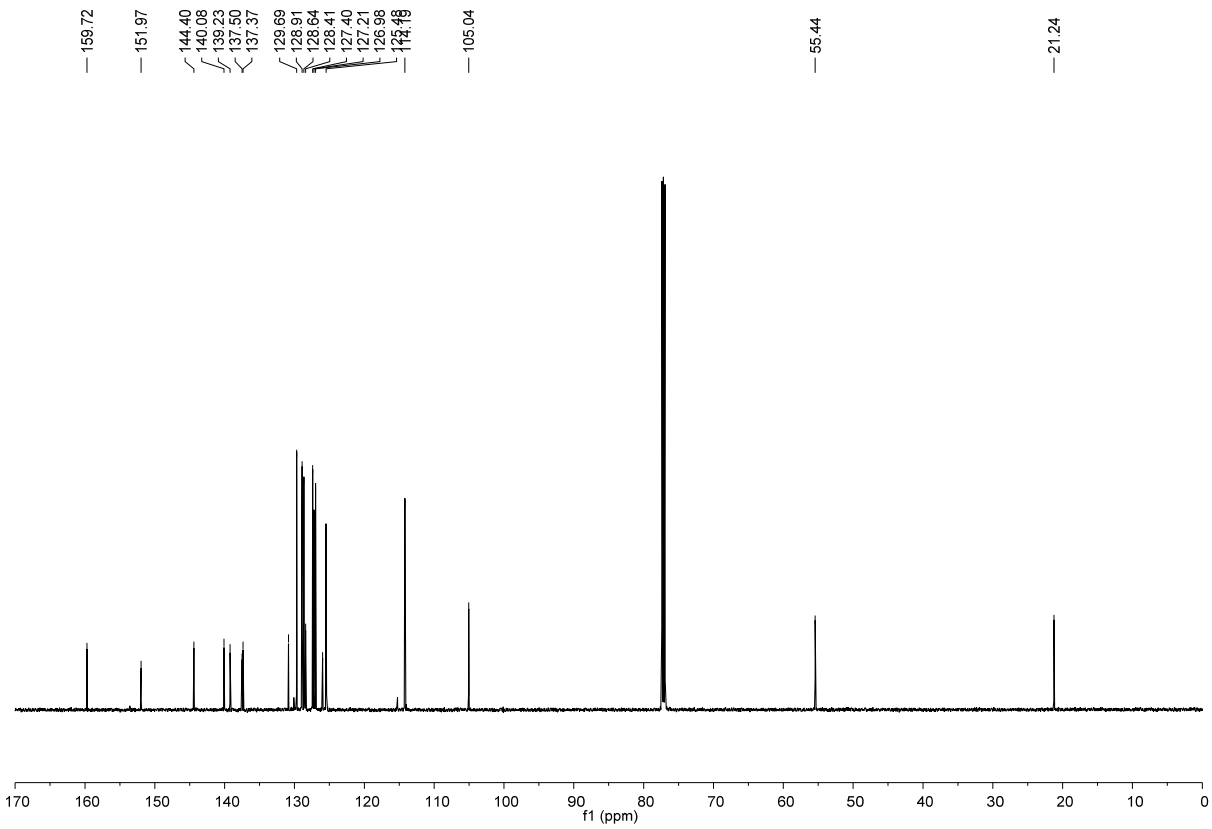


Normalized absorption and emission spectra of compound **8d** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

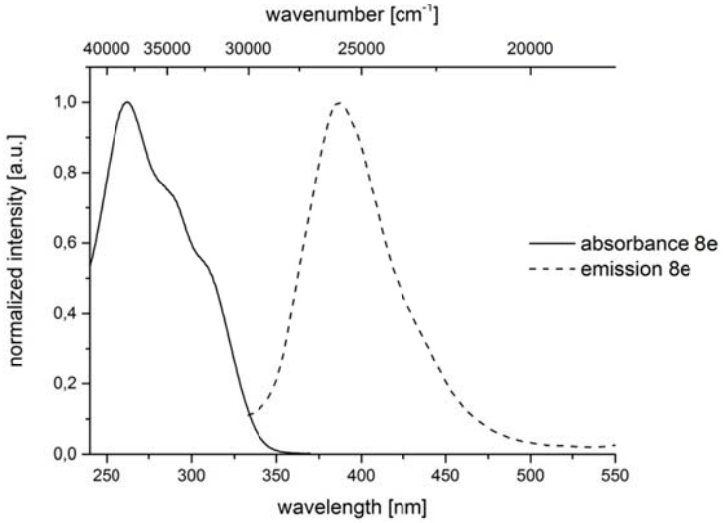
5-(4-methoxyphenyl)-1-(4'-methyl-[1,1'-biphenyl]-4-yl)-3-phenyl-1*H*-pyrazole (**8e**)



600 MHz ^{1}H NMR spectrum of compound **8e** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

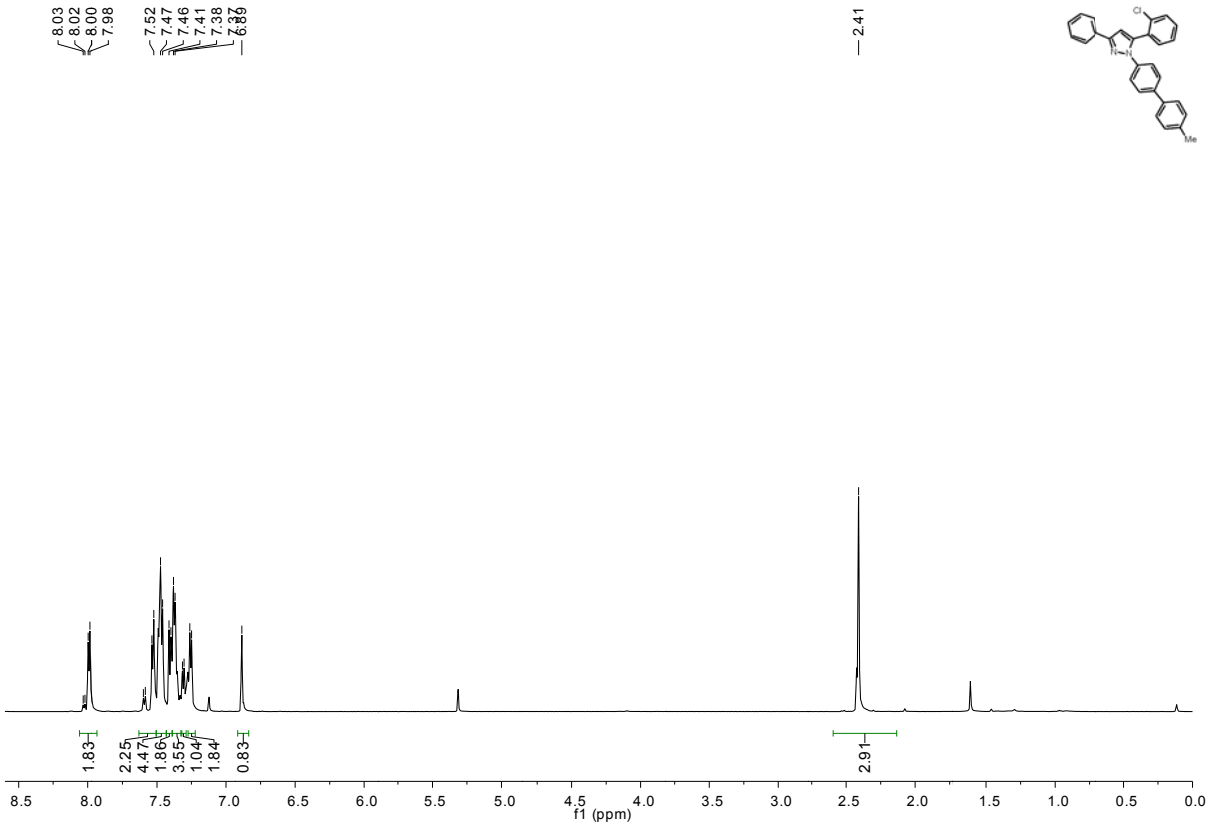


125 MHz ^{13}C NMR spectrum of compound **8e** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

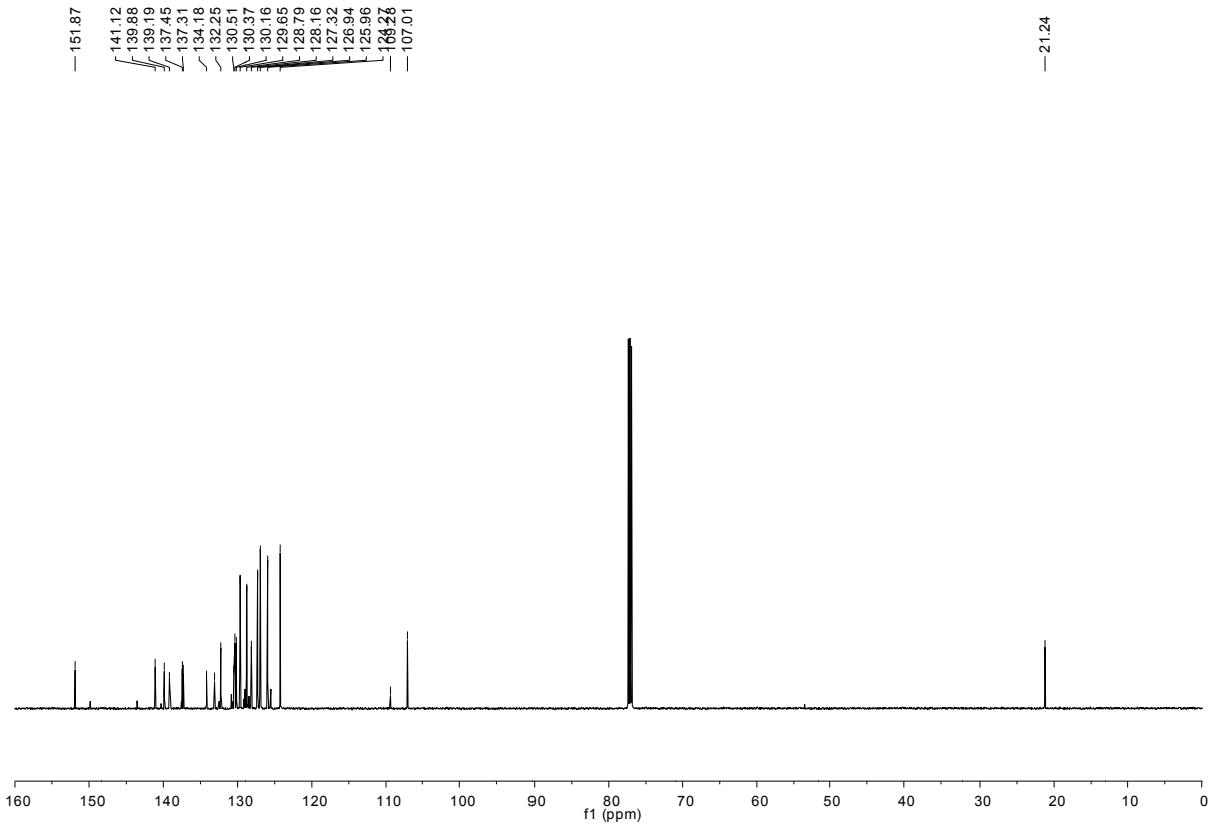


Normalized absorption and emission spectra of compound **8e** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

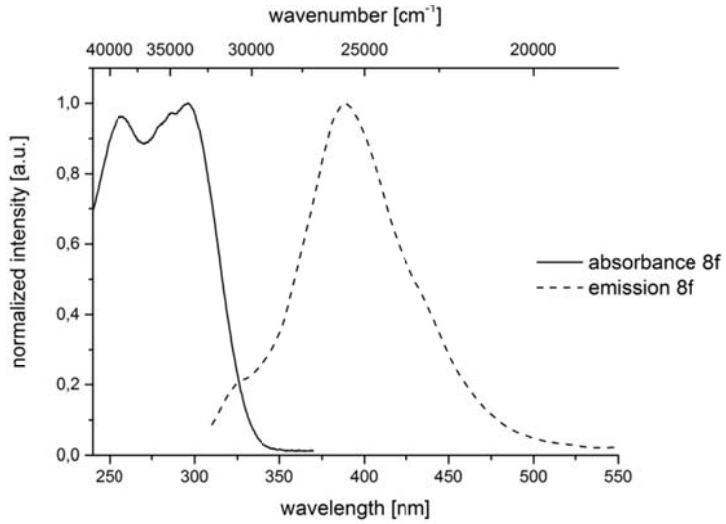
5-(2-chlorophenyl)-1-(4'-methyl-[1,1'-biphenyl]-4-yl)-3-phenyl-1*H*-pyrazole (**8f**)



600 MHz ^{1}H NMR spectrum of compound **8f** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

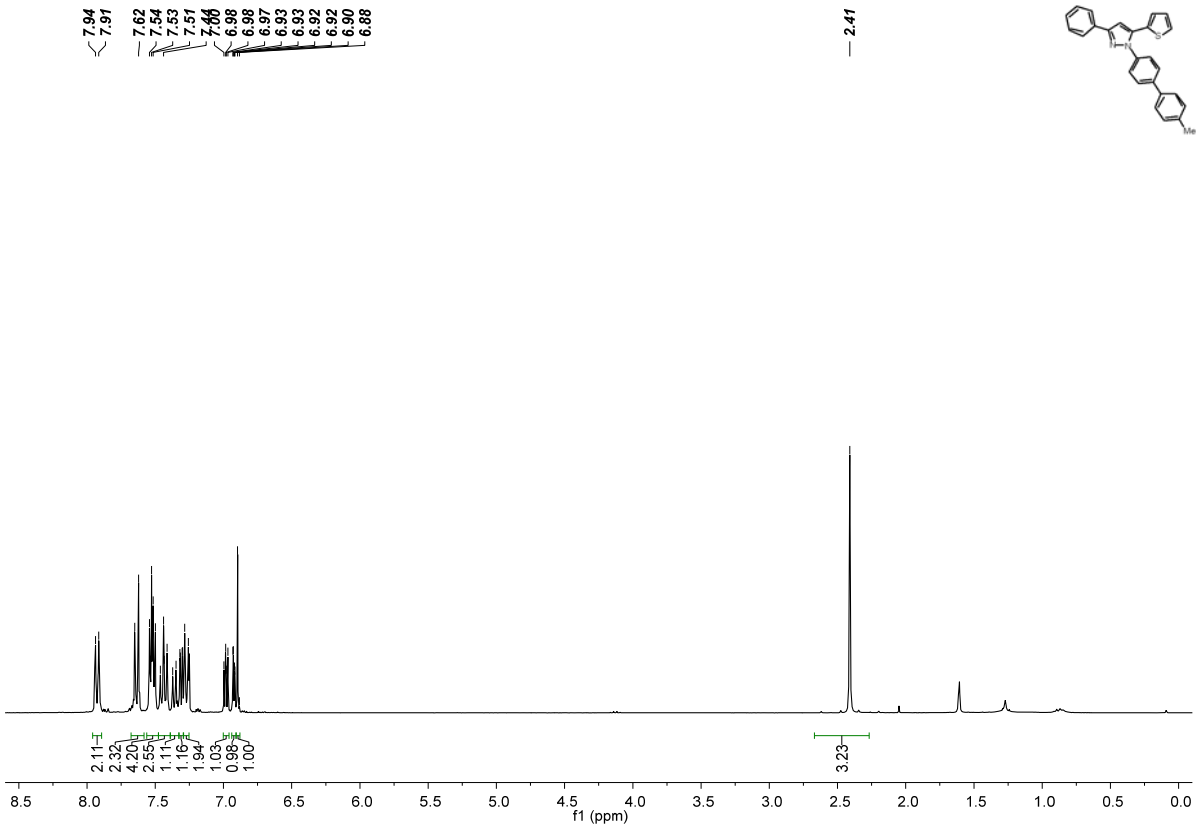


125 MHz ^{13}C NMR spectrum of compound **8f** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

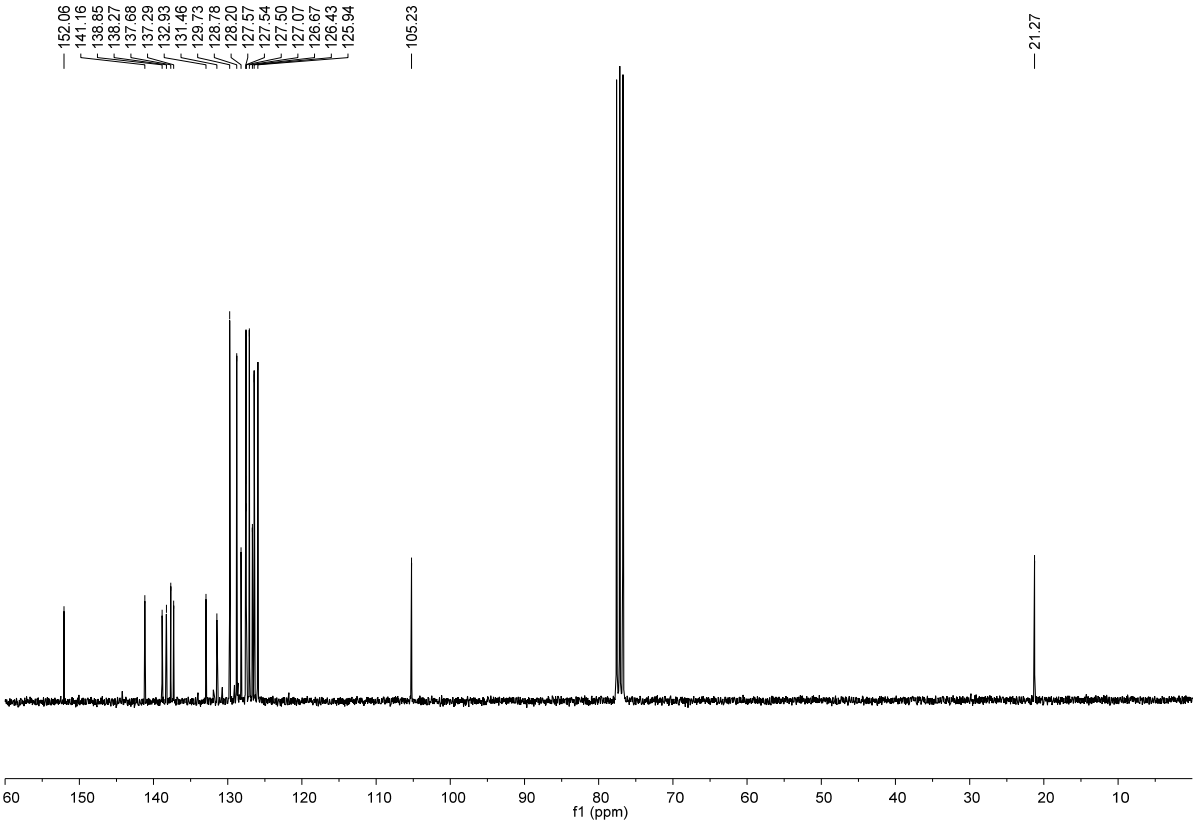


Normalized absorption and emission spectra of compound **8f** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

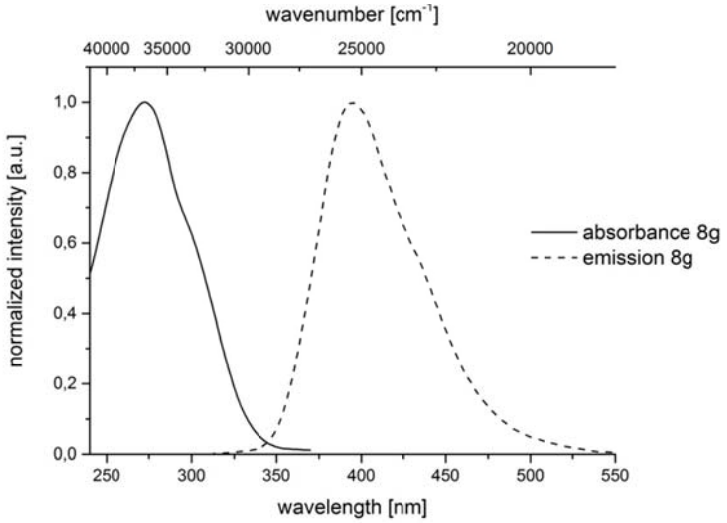
1-(4'-methyl-[1,1'-biphenyl]-4-yl)-3-phenyl-5-(thiophen-2-yl)-1*H*-pyrazole (**8g**)



300 MHz ^{1}H NMR spectrum of compound **8g** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

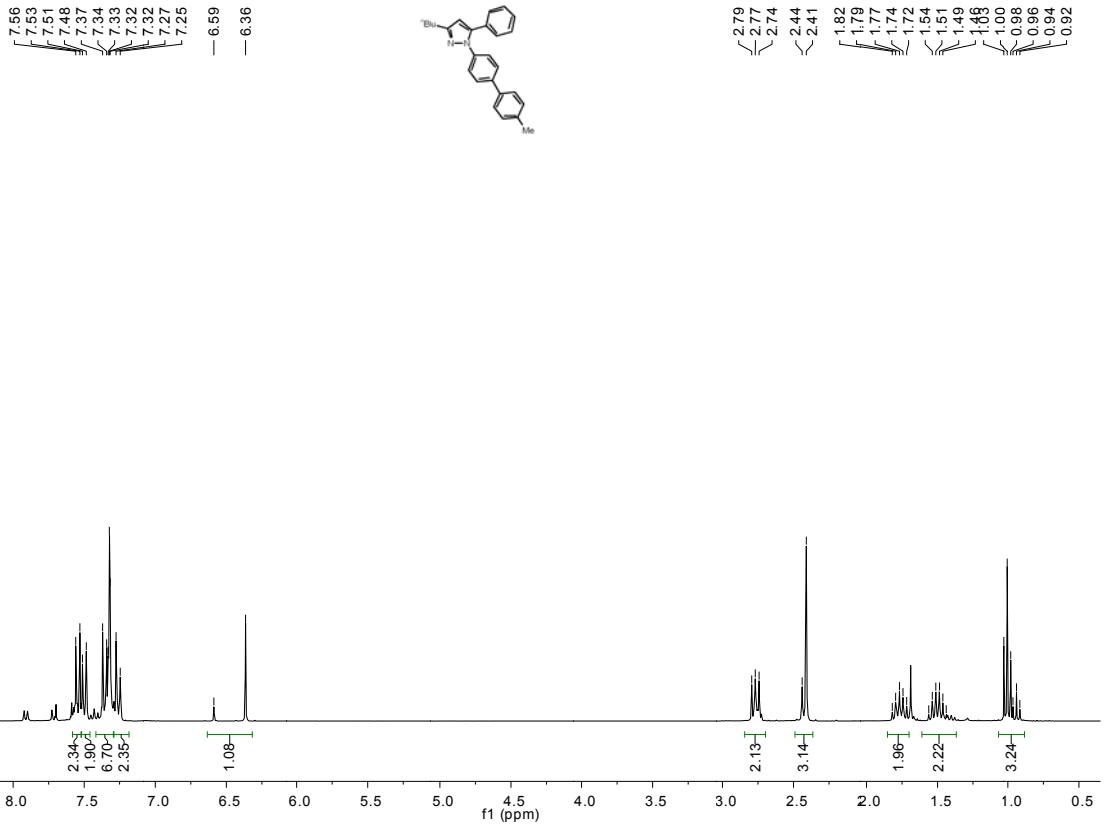


75 MHz ^{13}C NMR spectrum of compound **8g** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

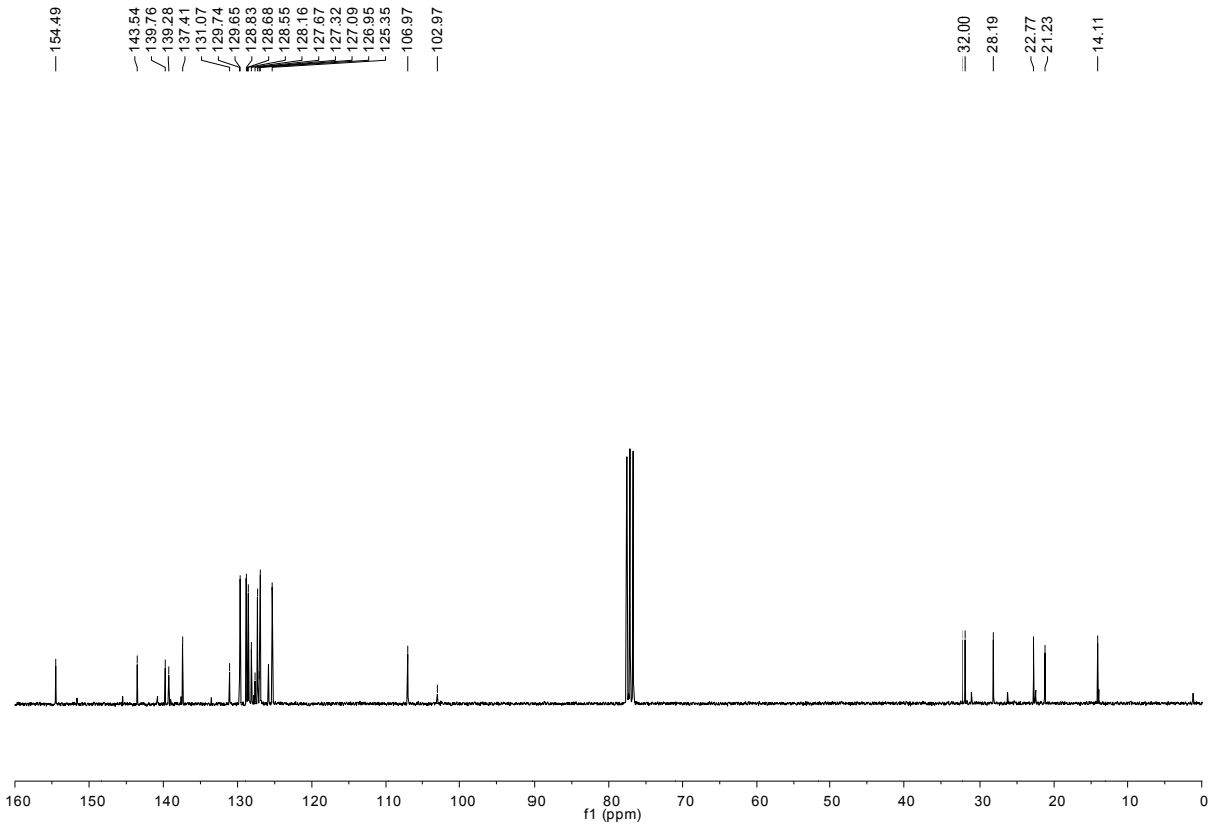


Normalized absorption and emission spectra of compound **8g** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

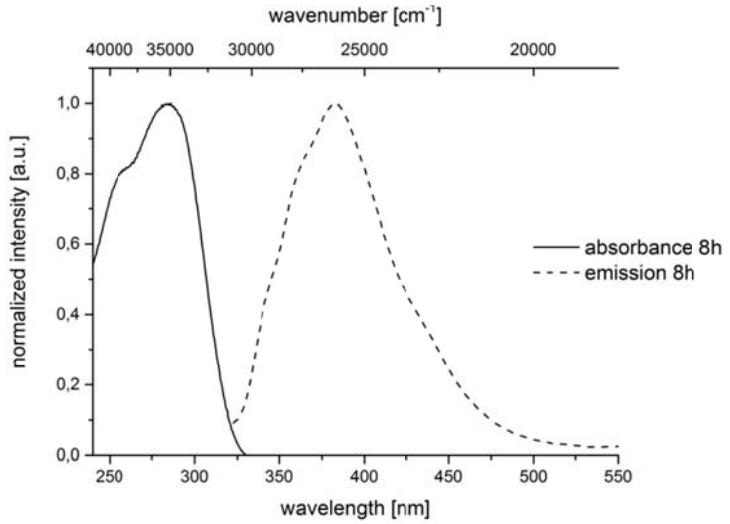
3-butyl-1-(4'-methyl-[1,1'-biphenyl]-4-yl)-5-phenyl-1*H*-pyrazole (**8h**)



300 MHz ^{1}H NMR spectrum of compound **8h** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

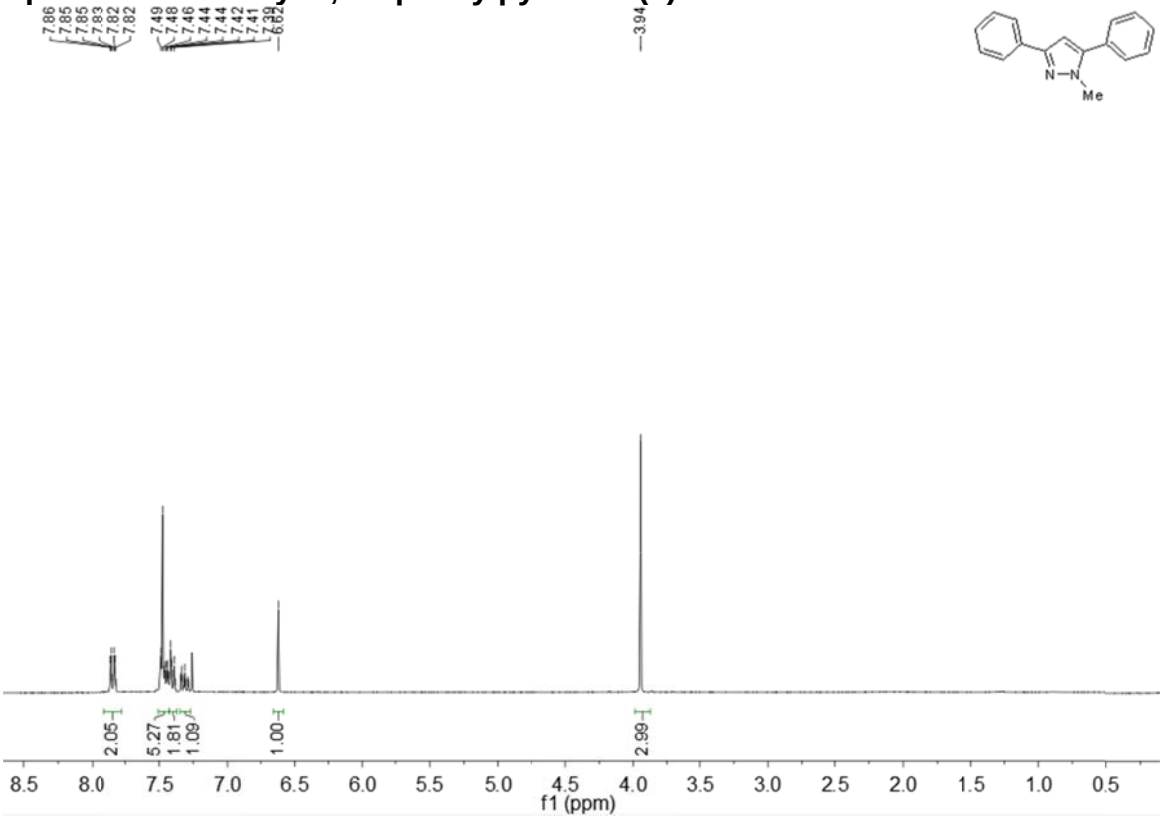


75 MHz ^{13}C NMR spectrum of compound **8h** recorded in $CDCl_3$ at T = 298 K (δ in ppm).

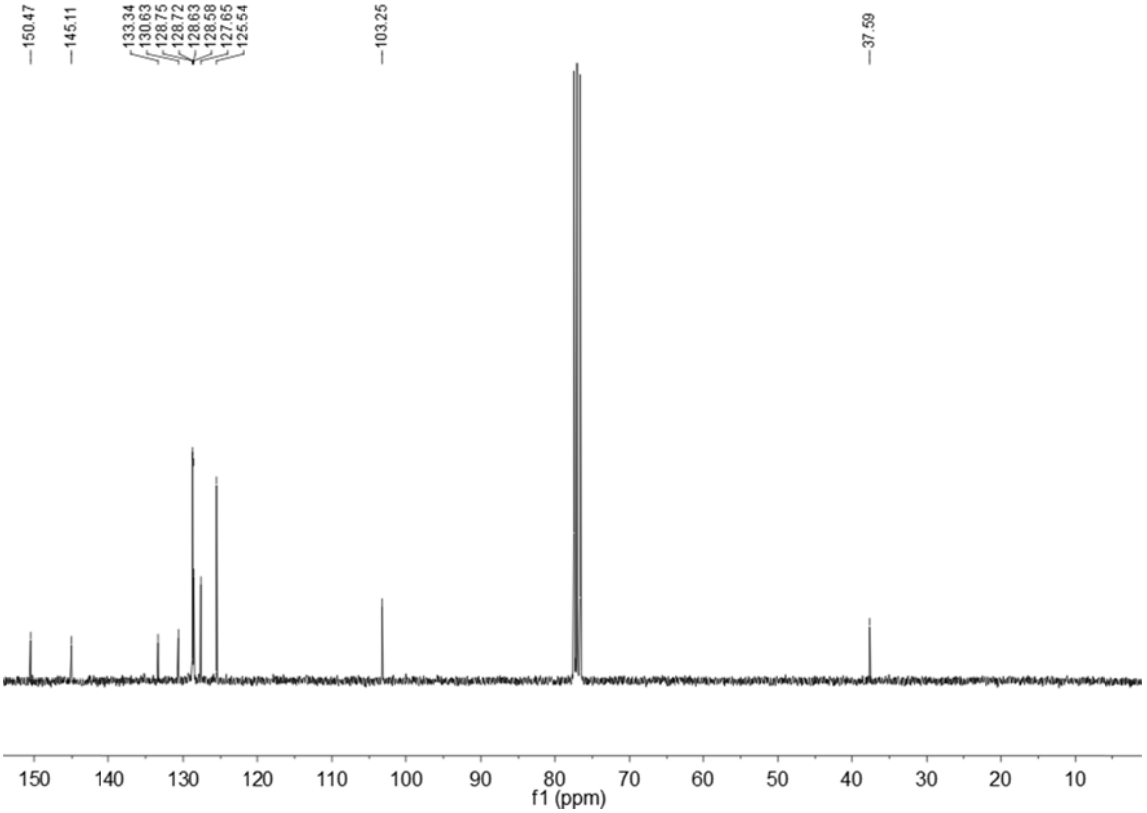


Normalized absorption and emission spectra of compound **8h** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

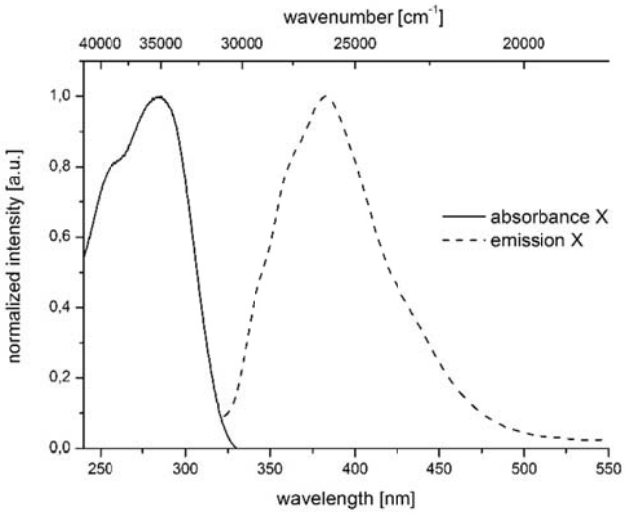
Spectra of 1-methyl-3,5-diphenylpyrazole (9)



300 MHz ^{1}H NMR spectrum of compound **9** recorded in $CDCl_3$ at T = 298 K (δ in ppm).



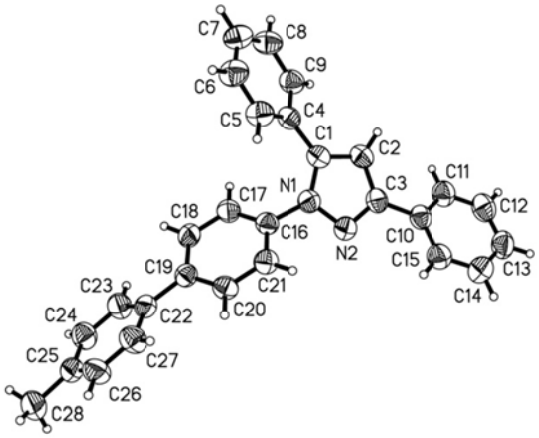
75 MHz ^{13}C NMR spectrum of compound **9** recorded in $CDCl_3$ at T = 298 K (δ in ppm).



Normalized absorption and emission spectra of compound **9** recorded in CH_2Cl_2 UVASOL at T = 293 K (λ_{exc} = 290 nm).

Crystal Data and Structure Refinement for Pyrazole 8b

Empirical formula	$C_{28}H_{22}N_2$	
Formula weight	386.48	
Temperature	291(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	*Pca*2_1	
Unit cell dimensions	a = 9.1521(4) Å	α= 90°.
	b = 11.4375(4) Å	β= 90°.
	c = 19.7882(6) Å	γ= 90°.
Volume	2071.37(13) Å3	
Z	4	
Density (calculated)	1.239 Mg/m^3	
Absorption coefficient	0.072 mm^{-1}	
F(000)	816	
Crystal size	0.5 x 0.5 x 0.5 mm^3	
Theta range for data collection	2.72 to 24.99°.	
Index ranges	-10<=h<=10, -13<=k<=13, -23<=l<=20	
Reflections collected	14730	
Independent reflections	3321 [R(int) = 0.0452]	
Completeness to theta = 24.99°	99.7 %	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	3321 / 1 / 272	
Goodness-of-fit on F2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0324, wR2 = 0.0913	
R indices (all data)	R1 = 0.0338, wR2 = 0.0925	
Absolute structure parameter	0(3)	
Largest diff. peak and hole	0.112 and -0.093 e.Å-3	



ORTEP plot of theX-ray structur of compound **8b**.

Computed xyz-Coordinates of the S_0State for the Pyrazoles **5c**, **5d**, **6d**, and **8**

The ground state geometries of the pyrazoles were optimized in a DFT calculation with the B3LYP functional and the 6-311G(d,p) basis set in the program package Gaussian09. The minima structures were confirmed by analytical frequency analysis. Computational details of the calculated pyrazoles:

XYZ-coordinates for **5c**

C	1.629035	0.581032	-0.048339
C	2.590881	-0.418251	-0.038930
C	3.835553	0.250604	-0.026770
N	3.650604	1.576498	-0.038312
N	2.318087	1.764126	-0.050762
C	1.808956	3.127450	-0.115560
C	0.163227	0.454881	-0.043522
C	5.192260	-0.322129	0.000615
C	-0.651711	1.227875	0.795974

C	-2.032174	1.058353	0.801519
C	-2.650398	0.105163	-0.019229
C	-1.832352	-0.670749	-0.852487
C	-0.453666	-0.498679	-0.867389
C	6.318519	0.509694	0.105054
C	7.600538	-0.028863	0.130738
C	7.787785	-1.409602	0.054585
C	6.677297	-2.245651	-0.049160
C	5.392901	-1.708080	-0.076585
C	-4.134461	-0.038326	-0.023747
C	-4.912993	1.099809	-0.280638
C	-6.302861	1.050519	-0.309145
C	-6.907864	-0.170046	-0.066594
C	-6.177710	-1.313922	0.205669
C	-4.779761	-1.269242	0.231761
F	-8.262662	-0.251043	-0.086592
C	-4.023094	-2.535674	0.561316
H	2.399034	-1.477986	-0.011231
H	2.509894	3.718471	-0.701767
H	0.834329	3.132396	-0.599467
H	1.720855	3.561943	0.882985
H	-0.206018	1.946728	1.472698
H	-2.638163	1.659201	1.470182
H	-2.280793	-1.399067	-1.517528
H	0.153543	-1.095597	-1.537815

H 6.174835 1.581125 0.166763

H 8.457312 0.630961 0.212340

H 8.787490 -1.828279 0.076076

H 6.809634 -3.320165 -0.110171

H 4.542237 -2.374060 -0.162470

H -4.416391 2.042567 -0.478719

H -6.901992 1.928192 -0.515906

H -6.704866 -2.238494 0.409916

H -4.663931 -3.231566 1.105370

H -3.680510 -3.046894 -0.343549

H -3.140823 -2.331455 1.170317

SCF Done: E(RB3LYP) = -1097.51323242 A.U. after 12 cycles

Sum of electronic and zero-point Energies= -1097.153731

Sum of electronic and thermal Energies= -1097.131831

Sum of electronic and thermal Enthalpies= -1097.130887

Sum of electronic and thermal Free Energies= -1097.207530

XYZ-coordinates for **5d**

C -7.263859 -1.657429 0.408842

C -7.090781 -0.299524 0.629079

C -5.841666 0.260279 0.447371

C -4.734583 -0.480364 0.044125

C -4.940231 -1.846388 -0.166307

C	-6.182786	-2.433033	0.012382
C	-3.396209	0.103025	-0.140299
N	-3.213051	1.340613	-0.586468
N	-1.886949	1.512581	-0.646151
C	-1.203958	0.407200	-0.243572
C	-2.159671	-0.531452	0.086207
C	0.261159	0.299804	-0.180666
C	1.054942	1.299332	0.382509
C	2.430034	1.152941	0.459064
C	3.061485	0.002088	-0.015188
C	2.262125	-0.999565	-0.569533
C	0.888209	-0.853724	-0.653018
C	4.533634	-0.154460	0.070360
C	5.253422	-0.768060	-0.955716
C	6.629699	-0.911662	0.874793
C	7.339453	-0.452780	0.232349
C	6.620857	0.162053	1.254965
C	5.244813	0.309333	1.177899
C	8.829374	-0.637867	0.332007
C	-1.373339	2.775014	-1.145576
F	-5.709304	1.577598	0.696544
H	-8.240288	-2.104400	0.547366
H	-7.906838	0.336768	0.946713
H	-4.102889	-2.451984	-0.490498
H	-6.307793	-3.493833	-0.164476

H	-1.980498	-1.518989	0.477516
H	0.596471	2.196339	0.779565
H	3.022619	1.952516	0.886463
H	2.719710	-1.913267	-0.928717
H	0.290147	-1.642963	-1.092096
H	4.734669	-1.117367	-1.840621
H	7.163974	-1.382001	-1.693168
H	7.146230	0.528429	2.130286
H	4.714436	0.776051	1.999487
H	9.295302	-0.643113	-0.654483
H	9.289049	0.154856	0.924064
H	9.071786	-1.589456	0.813861
H	-0.396228	2.620882	-1.596983
H	-2.067661	3.142739	-1.896890
H	-1.291213	3.509506	-0.342903

SCF Done: E(RB3LYP) = -1096.927637 A.U. after cycles

Sum of electronic and zero-point Energies= -1096.563666

Sum of electronic and thermal Energies= -1096.541901

Sum of electronic and thermal Enthalpies= -1096.540956

Sum of electronic and thermal Free Energies= -1096.617934

1 singlet a excitation

Total energy: -1096.927637

Excitation energy: 0.17787862

Excitation energy / eV: 4.840325569

Excitation energy / nm: 256.1485941

Excitation energy / cm^(-1): 39039.83949

XYZ-coordinates for **6d**

C	-3.768107	0.172803	-0.026095
C	-2.556188	-0.500263	-0.042432
C	-1.562761	0.504865	-0.027606
N	-2.128705	1.718580	-0.013184
N	-3.456317	1.506117	-0.012044
C	-4.345056	2.660176	-0.044751
C	-5.134106	-0.377485	-0.013582
C	-0.100154	0.356634	-0.021728
C	-6.112545	0.086865	0.878524
C	-7.385366	-0.477869	0.890380
C	-7.700222	-1.519553	0.019387
C	-6.732656	-1.995546	-0.864743
C	-5.461498	-1.429114	-0.883145
C	0.737780	1.481214	0.040828
C	2.118172	1.344405	0.045888
C	2.723764	0.078064	-0.003741
C	1.884640	-1.044649	-0.064222
C	0.502466	-0.908354	-0.076305
C	4.197780	-0.068117	0.008965

C	5.022820	0.860916	-0.647678
C	6.403135	0.729245	-0.639154
C	6.998820	-0.348040	0.033760
C	6.190201	-1.284857	0.694589
C	4.811306	-1.140470	0.678988
C	8.420184	-0.490184	0.046005
N	9.570551	-0.605640	0.055958
H	-2.429242	-1.570085	-0.035696
H	-3.875504	3.429324	-0.655079
H	-5.297732	2.375361	-0.486174
H	-4.513295	3.052680	0.960695
H	-5.872087	0.873704	1.583392
H	-8.128126	-0.109767	1.588877
H	-8.691018	-1.958877	0.031320
H	-6.969382	-2.804851	-1.545992
H	-4.716815	-1.791709	-1.582038
H	0.292091	2.466300	0.094008
H	2.734580	2.233041	0.117861
H	2.315998	-2.036748	-0.129388
H	-0.111175	-1.799160	-0.137252
H	4.577677	1.684666	-1.191793
H	7.022798	1.449968	-1.157814
H	6.645796	-2.113002	1.222857
H	4.202288	-1.858371	1.214318

SCF Done: E(RB3LYP) = -1051.19477297 A.U. after 13 cycles

Sum of electronic and zero-point Energies= -1050.855532

Sum of electronic and thermal Energies= -1050.834426

Sum of electronic and thermal Enthalpies= -1050.833482

Sum of electronic and thermal Free Energies= -1050.908409

XYZ-coordinates for **8b**

C	4.982028	-0.815130	-1.272503
C	4.268418	-0.812964	-0.064595
C	4.988591	-1.044203	1.116545
C	6.362061	-1.265234	1.088807
C	7.073754	-1.264671	-0.115649
C	6.354933	-1.038186	-1.294833
C	2.802615	-0.579981	-0.037328
C	1.974797	-1.276207	0.857800
C	0.603833	-1.055317	0.894431
C	0.026264	-0.132632	0.021987
C	0.824881	0.558619	-0.888688
C	2.197552	0.339380	-0.907573
N	-1.386357	0.066951	0.051945
C	-2.105377	1.240010	0.006022
C	-3.434711	0.865048	-0.046655
C	-3.440572	-0.550869	-0.016905
N	-2.193360	-1.021673	0.039861

C	-1.539869	2.598137	0.089417
C	-0.563564	2.933655	1.039255
C	-0.086024	4.237532	1.129992
C	-0.577122	5.227952	0.279622
C	-1.552643	4.906359	-0.662602
C	-2.030335	3.601923	-0.758364
C	-4.593865	-1.466892	-0.040854
C	-4.409859	-2.853642	0.077580
C	-5.498306	-3.718773	0.052890
C	-6.793655	-3.219260	-0.089116
C	-6.988373	-1.844293	-0.207817
C	-5.899688	-0.976303	-0.184576
H	-4.276206	1.537737	-0.051686
H	-0.187738	2.176462	1.716568
H	0.665893	4.481807	1.871629
H	-0.203508	6.242827	0.352894
H	-1.939312	5.669700	-1.328131
H	-2.779642	3.352785	-1.500769
H	-3.405416	-3.242570	0.188011
H	-5.336016	-4.786935	0.145520
H	-7.641225	-3.894851	-0.107645
H	-7.989995	-1.444583	-0.320201
H	-6.070332	0.089284	-0.282786
H	-0.026381	-1.601286	1.584183
H	2.405635	-2.012732	1.525426

H 2.807469 0.900692 -1.605121

H 0.377704 1.263902 -1.577064

H 4.473710 -1.032634 2.070604

H 6.890495 -1.436303 2.021235

C 8.567735 -1.476049 -0.140811

H 6.875151 -1.046927 -2.247394

H 4.454715 -0.668228 -2.208301

H 8.883518 -1.975397 -1.059609

H 9.099449 -0.519411 -0.090736

H 8.899065 -2.078364 0.707847

SCF Done: E(RB3LYP) = -1190.03297607 A.U. after 6 cycles

Sum of electronic and zero-point Energies= -1189.613259

Sum of electronic and thermal Energies= -1189.588929

Sum of electronic and thermal Enthalpies= -1189.587985

Sum of electronic and thermal Free Energies= -1189.672006

Computed UV/Vis Spectra of TD-DFT Calculated Structures of 5c, 5d, 6d, and 8b

The optimized structures were used in a TD-DFT calculation using the hybrid exchange-correlation functional CAM-B3LYP.

First four dominant transitions of the first excited state for **5c** regarding to the oscillatory strength:

1) 256 nm, oscillator strength: 1.6126, orbitals involved: HOMO-1 → LUMO, HOMO → LUMO, HOMO → LUMO+1
2) 248 nm, oscillator strength: 0.4607, orbitals involved: HOMO-1 → LUMO+1, HOMO → LUMO, HOMO → LUMO+1
3) 218 nm, oscillator strength: 0.0335, orbitals involved: HOMO-4 → LUMO, HOMO-4 → LUMO+2, HOMO-3 → LUMO, HOMO-2 → LUMO, HOMO-1 → LUMO+1, HOMO-1 → LUMO+5, HOMO → LUMO+5
4) 203 nm, oscillator strength: 0.3949, orbitals involved: HOMO-5 → LUMO, HOMO-4 → LUMO, HOMO-1 → LUMO+2, HOMO-1 → LUMO+3, HOMO → LUMO+2, HOMO-1 → LUMO+3

First four dominant transitions of the first excited state for **5d** regarding to the oscillatory strength:

1) 258 nm, oscillator strength: 1.2547, orbitals involved: HOMO-2 → LUMO+4, HOMO-1 → LUMO, HOMO → LUMO
2) 244 nm, oscillator strength: 0.0006, orbitals involved: HOMO-6 → LUMO+2, HOMO-5 → LUMO, HOMO-2→ LUMO+2, HOMO→ LUMO+2
3) 237 nm, oscillator strength: 0.0007, orbitals involved: HOMO-5 → LUMO, HOMO-4 → LUMO, HOMO-4→ LUMO+4, HOMO-2→ LUMO+2, HOMO-2 → LUMO+3, HOMO-1→ LUMO+3, HOMO→ LUMO+3
4) 236 nm, oscillator strength: 0.0807, orbitals involved: HOMO-7 → LUMO+4, HOMO-6 → LUMO+2, HOMO-3→ LUMO+1, HOMO-1→ LUMO+1, HOMO-1 → LUMO+4, HOMO→ LUMO+1, HOMO→ LUMO+4

First four dominant transitions of the first excited state for **6d** regarding to the oscillatory strength:

5) 298 nm, oscillator strength: 1.6697, orbitals involved: HOMO-1 → LUMO, HOMO → LUMO, HOMO → LUMO+3

6) 237 nm, oscillator strength: 0.5622, orbitals involved: HOMO-1 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+1
7) 213 nm, oscillator strength: 0.0740, orbitals involved: HOMO-5 → LUMO, HOMO-4 → LUMO, HOMO-3 → LUMO, HOMO-1 → LUMO,HOMO-1 → LUMO+1,HOMO-1 → LUMO+3,HOMO → LUMO+1,HOMO → LUMO+2
8) 210 nm, oscillator strength: 0.0784, orbitals involved: HOMO-7 → LUMO, HOMO-4 → LUMO, HOMO-3 → LUMO, HOMO-2 → LUMO, HOMO → LUMO, HOMO → LUMO+3

First four dominant transitions of the first excited state for **8b** regarding to the oscillatory strength:

1) 278 nm, oscillator strength: 1.4044, orbitals involved: HOMO-2 → LUMO+2, HOMO-1 → LUMO+1, HOMO → LUMO
2) 248 nm, oscillator strength: 0.1371, orbitals involved: HOMO-7 → LUMO+3, HOMO-6 → LUMO, HOMO-6 → LUMO+1, HOMO-5 → LUMO, HOMO-2 → LUMO, HOMO-1 → LUMO+3, HOMO-1 → LUMO+4, HOMO → LUMO+2, HOMO → LUMO+3, HOMO → LUMO+4, HOMO → LUMO+5
3) 245 nm, oscillator strength: 0.4253, orbitals involved: HOMO-2 → LUMO, HOMO-2 → LUMO+2, HOMO-1 → LUMO, HOMO-1 → LUMO+1, HOMO-1 → LUMO+2, HOMO → LUMO+1, HOMO → LUMO+2, HOMO → LUMO+3
4) 242 nm, oscillator strength: 0.5791, orbitals involved: HOMO-3 → LUMO, HOMO-3 → LUMO+2, HOMO-2 → LUMO, HOMO-2 → LUMO+1, HOMO-2 → LUMO+6, HOMO-1 → LUMO, HOMO-1 → LUMO+1, HOMO-1 → LUMO+2, HOMO-1 → LUMO+6, HOMO → LUMO+1, HOMO → LUMO+6

Computed xyz-Coordinates of the S_1State of Pyrazole 5d

The excited state geometry of the pyrazole **5d** was optimized in a DFT calculation with the B3LYP functional and the 6-311G(d,p) basis set in the program package Gaussian09.

XYZ-coordinates of the S_1 state for **5d**:

C	-7.191916	-1.799506	0.122896
C	-7.062221	-0.487260	0.551563
C	-5.830716	0.131157	0.469150

C	-4.699625	-0.505457	-0.034246
C	-4.861505	-1.828540	-0.455280
C	-6.085922	-2.471963	-0.379791
C	-3.380093	0.137923	-0.114369
N	-3.243238	1.447440	-0.348074
N	-1.931025	1.690634	-0.376809
C	-1.178350	0.548012	-0.168572
C	-2.136000	-0.476955	-0.004100
C	0.231792	0.436683	-0.114880
C	1.149847	1.531282	0.016225
C	2.492071	1.338800	0.077886
C	3.094255	0.025240	0.008912
C	2.161095	-1.070692	-0.095805
C	0.821238	-0.877619	-0.147440
C	4.494164	-0.168783	0.046728
C	5.089657	-1.473466	0.006399
C	6.448682	-1.648105	0.045583
C	7.334911	-0.560707	0.126403
C	6.774697	0.725064	0.158681
C	5.417583	0.926188	0.122187
C	8.814938	-0.771737	0.203244
C	-1.508743	3.037209	-0.712820
F	-5.739787	1.397155	0.919376
H	-8.154464	-2.291746	0.182370
H	-7.898802	0.067430	0.956612

H	-4.004838	-2.350389	-0.863598
H	-6.177842	-3.495701	-0.719831
H	-1.937723	-1.508558	0.229383
H	0.779208	2.540442	0.105558
H	3.120636	2.208599	0.202287
H	2.529386	-2.085292	-0.144492
H	0.174170	-1.738686	-0.247396
H	4.462718	-2.351362	-0.057240
H	6.852459	-2.654542	0.011779
H	7.433729	1.585180	0.211928
H	5.050308	1.942121	0.143287
H	9.128478	-1.624105	-0.403633
H	9.362397	0.111351	-0.130105
H	9.130042	-0.980409	1.232736
H	-0.746240	3.015238	-1.490185
H	-2.387673	3.555870	-1.084539
H	-1.128232	3.566098	0.162542

1 singlet a excitation

Total energy after PCM correction: -1096.907757

Excitation energy: 0.13392489

Excitation energy / eV: 3.644283216

Excitation energy / nm: 340.2157615

Excitation energy / cm^(-1): 29393.11205

Computed xyz-Coordinates of the S_1State of Pyrazole 6d

The excited state structure of pyrazole **6d** was optimized in a DFT calculation in the gasphase with the B3LYP functional and the def-TZVP basis set in the program package turbomole. The minimum structure was confirmed by a numerical frequency analysis.

XYZ-coordinates of the S_1 state for **6d**:

C	-3.758800	0.146900	-0.017100
C	-2.558200	-0.521200	0.005200
C	-1.545700	0.478500	-0.058400
N	-2.128900	1.710600	-0.131900
N	-3.435400	1.497700	-0.103600
C	-4.326600	2.639900	-0.231200
C	-5.125300	-0.380000	0.023400
C	-0.121300	0.339000	-0.042300
C	-6.112600	0.171500	0.852800
C	-7.387200	-0.379400	0.895700
C	-7.697700	-1.491500	0.118100
C	-6.723100	-2.053200	-0.702600
C	-5.448900	-1.503900	-0.750900
C	0.727800	1.481100	-0.059000
C	2.091900	1.353500	-0.038600
C	2.733400	0.074500	-0.002000
C	1.864000	-1.066600	0.013800
C	0.499700	-0.936500	-0.005600
C	4.169900	-0.061300	0.016200
C	5.034800	1.036400	-0.282700

C	6.401100	0.906300	-0.276700
C	7.010500	-0.335200	0.046700
C	6.169600	-1.436200	0.355500
C	4.803500	-1.303800	0.331700
C	8.415900	-0.470700	0.060700
N	9.572300	-0.581900	0.072600
H	-2.429800	-1.585500	0.099600
H	-3.834900	3.374800	-0.864400
H	-5.264800	2.324100	-0.680400
H	-4.522200	3.086500	0.746600
H	-5.876000	1.012700	1.492000
H	-8.136200	0.053100	1.547800
H	-8.691800	-1.920000	0.154400
H	-6.957900	-2.917600	-1.311600
H	-4.698300	-1.932300	-1.403600
H	0.273900	2.462900	-0.079800
H	2.693900	2.250900	-0.023700
H	2.290300	-2.059300	0.010700
H	-0.112600	-1.830100	-0.003100
H	4.615900	1.994800	-0.558000
H	7.028100	1.753600	-0.524000
H	6.618200	-2.386800	0.614700
H	4.204300	-2.164100	0.598000

ENERGY = -1050.4850749196 a.u.; # of cycles = 32

The emission spectrum of compound **6d** was computed after the numerical frequency analysis using the implementation egrad in the program package turbomole.

1 singlet a excitation

Total energy: -1050.485076059829

Excitation energy: 0.12196734

Excitation energy / eV: 3.3189

Excitation energy / nm: 373.57

Excitation energy / cm^(-1): 26768.7372

Oscillator strength:

velocity representation: 1.256849456584993

length representation: 1.313413816131701

mixed representation: 1.284818722329036

Dominant contributions:

occ. orbital	energy / eV	virt. orbital	energy / eV	|coeff.|^2*100
88 a	-5.73	89 a	-2.20	97.5