Supporting Information

Selective Synthesis of 4-(Sulfonyl)-Methyl-1H-Pyrazoles and (*E*)-4,5-Dihydro-1H-Pyrazoles from *N*-Allenic Sulfonylhydrazones

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1. General Information

Tetrahydrofuran was freshly distilled from Na prior to use. Triethylamine was freshly distilled from P_2O_5 prior to use. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Propargylic acetates were prepared according to literature procedures. All reaction mixtures were stirred with a magnetic bar in flame-dried glassware.

Chromatography

Thin layer chromatography (TLC) was performed on Huanghai pre-coated glass-backed TLC plates and visualized by UV lamp (254 nm). Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 ^{o}C petroleum ether (distillated prior to use) and analytical grade EtOAc (without furth er purification). Concentration under reduced pressure was performed by rotary evaporation. Purified compounds were further addressed under high vacuum (3-5 mmHg). Yields refer to chromatographically purified compounds.

Nuclear magnetic resonance spectra

^{1}H and **^{13}C** spectra were recorded on a Bruker AV-500 spectrometer. Chemical shifts were reported in ppm. ^{1}H-NMR spectra were referenced to TMS in $CDCl_3$ (0 ppm) and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm). All ^{13}C-NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz.

IR spectra, Mass spectroscopy and HPLC

IR spectra were recorded on a Nicolet AVATER FTIR360 spectrometer as thin film. Absorptions were given in wavenumbers (cm^{-1}). Mass spectroscopy: We were grateful to the assistance of the Department of Chemistry, Xiamen University in obtaining the MS data. HPLC: HPLC was performed on Shimadzu Prominence LC-20A series (Kyoto, Japan) equipped with a binary high pressure pump, a manual sample injector, a UV-Vis detector and SHIMADZU Shim-pack VP-ODS(4.6×150 mm, 5 μm) column (CH_3OH/H_2O = 85/15, v/v, as an eluent).

2. X-Ray Analysis of 3l

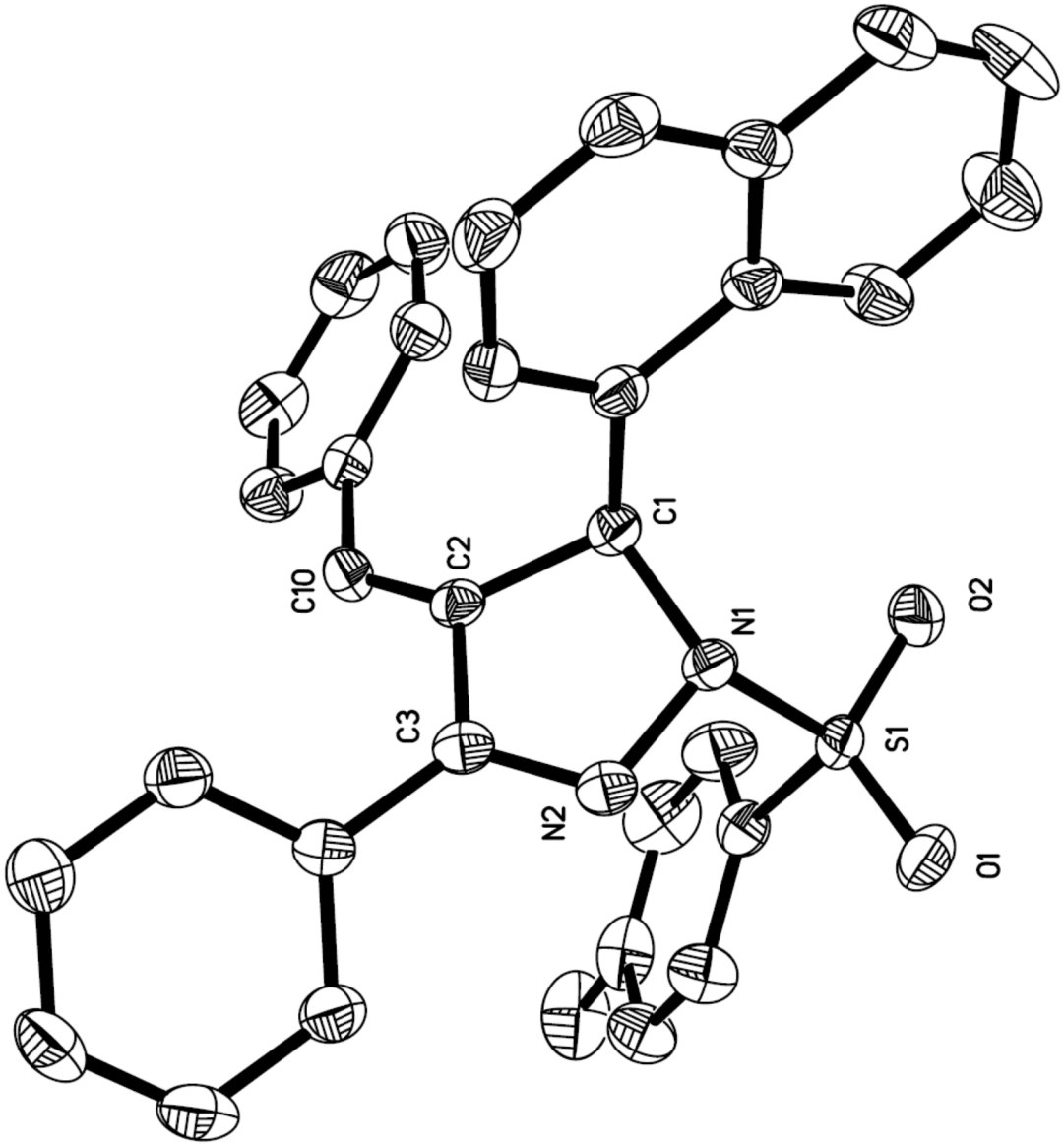


Table 1. Crystal data and structure refinement for mon.

Identification code	mon	
Empirical formula	C33 H26 N2 O2 S	
Formula weight	514.62	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.8941(17) Å	α= 90°.
	b = 19.167(3) Å	β= 102.800(3)°.
	c = 14.200(2) Å	γ = 90°.
Volume	2625.9(8) $Å^3$	
Z	4	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	0.157 mm^{-1}	
F(000)	1080	
Crystal size	0.4 x 0.4 x 0.4 mm^3	
Theta range for data collection	1.81 to 26.00°.	
Index ranges	-11<=h<=12, -17<=k<=23, -17<=l<=16	
Reflections collected	14078	
Independent reflections	5150 [R(int) = 0.0334]	
Completeness to theta = 26.00°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000000 and 0.782460	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5150 / 0 / 343	
Goodness-of-fit on F^2	1.142	
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1466	
R indices (all data)	R1 = 0.0679, wR2 = 0.1512	
Largest diff. peak and hole	0.479 and -0.382 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mon. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5016(1)	1525(1)	10617(1)	24(1)
O(1)	4643(2)	908(1)	11062(1)	33(1)
O(2)	5336(2)	2149(1)	11170(1)	36(1)
N(1)	3636(2)	1725(1)	9739(1)	23(1)
N(2)	3325(2)	1154(1)	9074(1)	23(1)
C(1)	3630(2)	2399(1)	9185(2)	23(1)
C(2)	3730(2)	2124(1)	8207(2)	21(1)
C(17)	2260(2)	2782(1)	9177(2)	23(1)
C(21)	758(2)	3509(1)	9939(2)	28(1)
C(3)	3321(2)	1388(1)	8220(2)	22(1)
C(26)	2071(2)	3190(1)	9980(2)	25(1)
C(18)	1183(2)	2721(1)	8389(2)	29(1)
C(4)	2955(2)	928(1)	7367(2)	24(1)
C(10)	4284(2)	2408(1)	7518(2)	25(1)
C(27)	6425(2)	1337(1)	10097(2)	24(1)
C(9)	3447(3)	248(1)	7407(2)	30(1)
C(32)	6639(2)	668(1)	9811(2)	32(1)
C(12)	4621(3)	3667(1)	8009(2)	34(1)
C(15)	6676(3)	3778(2)	6979(2)	39(1)
C(11)	4947(2)	3091(1)	7511(2)	25(1)
C(5)	2089(2)	1169(1)	6514(2)	30(1)
C(19)	-105(3)	3045(1)	8349(2)	35(1)
C(28)	7362(3)	1860(1)	10030(2)	40(1)
C(30)	8773(3)	1031(2)	9414(2)	38(1)
C(31)	7805(3)	519(2)	9462(2)	38(1)
C(6)	1742(3)	734(1)	5720(2)	36(1)
C(16)	5971(3)	3161(1)	6980(2)	33(1)
C(22)	551(3)	3905(1)	10734(2)	38(1)
C(25)	3127(3)	3309(1)	10815(2)	35(1)
C(13)	5327(3)	4289(1)	8000(2)	41(1)
C(14)	6365(3)	4340(2)	7494(2)	42(1)
C(20)	-318(3)	3425(1)	9104(2)	34(1)
C(8)	3106(3)	-179(1)	6603(2)	38(1)

C(24)	2885(3)	3695(2)	11570(2)	48(1)
C(23)	1578(3)	3993(2)	11531(2)	46(1)
C(29)	8528(3)	1701(2)	9691(2)	47(1)
C(7)	2261(3)	63(1)	5763(2)	38(1)
C(33)	10101(3)	868(2)	9106(2)	54(1)

Table 3. Bond lengths [Å] and angles [°] for mon.

S(1)-O(1)	1.4257(18)
S(1)-O(2)	1.4273(18)
S(1)-N(1)	1.6774(19)
S(1)-C(27)	1.754(2)
N(1)-N(2)	1.433(3)
N(1)-C(1)	1.511(3)
N(2)-C(3)	1.293(3)
C(1)-C(2)	1.510(3)
C(1)-C(17)	1.539(3)
C(2)-C(10)	1.338(3)
C(2)-C(3)	1.468(3)
C(17)-C(18)	1.369(3)
C(17)-C(26)	1.430(3)
C(21)-C(22)	1.413(3)
C(21)-C(20)	1.416(4)
C(21)-C(26)	1.425(3)
C(3)-C(4)	1.477(3)
C(26)-C(25)	1.414(3)
C(18)-C(19)	1.407(3)
C(4)-C(9)	1.387(3)
C(4)-C(5)	1.399(3)
C(10)-C(11)	1.465(3)
C(27)-C(32)	1.376(3)
C(27)-C(28)	1.383(3)
C(9)-C(8)	1.385(4)
C(32)-C(31)	1.383(3)
C(12)-C(13)	1.384(4)
C(12)-C(11)	1.387(3)
C(15)-C(16)	1.374(4)

C(15)-C(14)	1.374(4)
C(11)-C(16)	1.398(3)
C(5)-C(6)	1.384(3)
C(19)-C(20)	1.351(4)
C(28)-C(29)	1.379(4)
C(30)-C(29)	1.380(4)
C(30)-C(31)	1.383(4)
C(30)-C(33)	1.507(4)
C(6)-C(7)	1.380(4)
C(22)-C(23)	1.354(4)
C(25)-C(24)	1.367(4)
C(13)-C(14)	1.381(4)
C(8)-C(7)	1.377(4)
C(24)-C(23)	1.402(4)

O(1)-S(1)-O(2)	119.92(11)
O(1)-S(1)-N(1)	105.70(10)
O(2)-S(1)-N(1)	105.17(10)
O(1)-S(1)-C(27)	108.92(11)
O(2)-S(1)-C(27)	107.68(11)
N(1)-S(1)-C(27)	109.03(10)
N(2)-N(1)-C(1)	109.56(16)
N(2)-N(1)-S(1)	109.63(13)
C(1)-N(1)-S(1)	119.42(14)
C(3)-N(2)-N(1)	107.95(18)
C(2)-C(1)-N(1)	100.77(17)
C(2)-C(1)-C(17)	113.38(17)
N(1)-C(1)-C(17)	108.32(17)
C(10)-C(2)-C(3)	123.9(2)
C(10)-C(2)-C(1)	130.7(2)
C(3)-C(2)-C(1)	104.41(18)
C(18)-C(17)-C(26)	118.9(2)
C(18)-C(17)-C(1)	119.4(2)
C(26)-C(17)-C(1)	121.72(19)
C(22)-C(21)-C(20)	121.0(2)
C(22)-C(21)-C(26)	119.3(2)
C(20)-C(21)-C(26)	119.7(2)
N(2)-C(3)-C(2)	113.7(2)

N(2)-C(3)-C(4)	120.7(2)
C(2)-C(3)-C(4)	125.58(19)
C(25)-C(26)-C(21)	117.6(2)
C(25)-C(26)-C(17)	123.6(2)
C(21)-C(26)-C(17)	118.7(2)
C(17)-C(18)-C(19)	122.0(2)
C(9)-C(4)-C(5)	119.2(2)
C(9)-C(4)-C(3)	120.5(2)
C(5)-C(4)-C(3)	120.3(2)
C(2)-C(10)-C(11)	128.7(2)
C(32)-C(27)-C(28)	120.4(2)
C(32)-C(27)-S(1)	120.30(18)
C(28)-C(27)-S(1)	119.2(2)
C(8)-C(9)-C(4)	120.2(2)
C(27)-C(32)-C(31)	119.5(2)
C(13)-C(12)-C(11)	120.5(2)
C(16)-C(15)-C(14)	120.0(2)
C(12)-C(11)-C(16)	118.4(2)
C(12)-C(11)-C(10)	123.6(2)
C(16)-C(11)-C(10)	118.0(2)
C(6)-C(5)-C(4)	120.0(2)
C(20)-C(19)-C(18)	120.4(2)
C(29)-C(28)-C(27)	119.3(3)
C(29)-C(30)-C(31)	118.6(2)
C(29)-C(30)-C(33)	119.7(3)
C(31)-C(30)-C(33)	121.7(3)
C(32)-C(31)-C(30)	120.9(3)
C(7)-C(6)-C(5)	120.2(2)
C(15)-C(16)-C(11)	120.9(2)
C(23)-C(22)-C(21)	121.4(2)
C(24)-C(25)-C(26)	121.3(2)
C(14)-C(13)-C(12)	120.1(3)
C(15)-C(14)-C(13)	120.1(2)
C(19)-C(20)-C(21)	120.3(2)
C(7)-C(8)-C(9)	120.4(2)
C(25)-C(24)-C(23)	120.6(3)
C(22)-C(23)-C(24)	119.8(2)
C(28)-C(29)-C(30)	121.2(3)

C(8)-C(7)-C(6)	120.0(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mon. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	28(1)	26(1)	18(1)	3(1)	3(1)	6(1)
O(1)	36(1)	37(1)	28(1)	13(1)	11(1)	10(1)
O(2)	46(1)	36(1)	22(1)	-5(1)	-2(1)	9(1)
N(1)	24(1)	21(1)	23(1)	2(1)	5(1)	3(1)
N(2)	20(1)	22(1)	27(1)	1(1)	5(1)	0(1)
C(1)	22(1)	22(1)	23(1)	2(1)	3(1)	2(1)
C(2)	18(1)	21(1)	24(1)	2(1)	3(1)	4(1)
C(17)	25(1)	20(1)	24(1)	4(1)	6(1)	2(1)
C(21)	31(1)	23(1)	35(1)	2(1)	15(1)	0(1)
C(3)	16(1)	23(1)	28(1)	1(1)	4(1)	2(1)
C(26)	29(1)	19(1)	28(1)	2(1)	8(1)	0(1)
C(18)	32(1)	33(1)	22(1)	2(1)	5(1)	8(1)
C(4)	21(1)	23(1)	28(1)	-1(1)	6(1)	-3(1)
C(10)	28(1)	27(1)	21(1)	-3(1)	6(1)	2(1)
C(27)	19(1)	28(1)	24(1)	1(1)	0(1)	1(1)
C(9)	33(1)	24(1)	32(1)	3(1)	8(1)	2(1)
C(32)	27(1)	29(1)	43(1)	-2(1)	12(1)	-4(1)
C(12)	45(2)	28(1)	32(1)	2(1)	17(1)	-1(1)
C(15)	28(1)	44(2)	47(2)	12(1)	14(1)	1(1)
C(11)	26(1)	27(1)	22(1)	4(1)	5(1)	1(1)
C(5)	29(1)	26(1)	33(1)	0(1)	4(1)	2(1)
C(19)	31(1)	44(2)	29(1)	7(1)	4(1)	11(1)
C(28)	37(2)	29(1)	52(2)	2(1)	7(1)	-6(1)
C(30)	24(1)	56(2)	32(1)	5(1)	6(1)	-1(1)
C(31)	35(1)	37(2)	44(2)	-5(1)	13(1)	4(1)
C(6)	34(1)	38(2)	34(1)	-3(1)	1(1)	-3(1)
C(16)	32(1)	31(1)	37(1)	3(1)	13(1)	4(1)
C(22)	39(1)	30(1)	49(2)	-7(1)	22(1)	2(1)
C(25)	33(1)	33(1)	38(1)	-10(1)	3(1)	3(1)

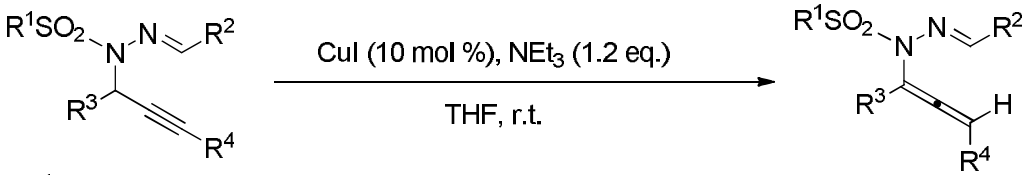
C(13)	61(2)	27(1)	39(1)	-1(1)	15(1)	-6(1)
C(14)	46(2)	33(2)	46(2)	8(1)	7(1)	-13(1)
C(20)	26(1)	34(1)	42(1)	8(1)	10(1)	10(1)
C(8)	46(2)	22(1)	48(2)	-4(1)	15(1)	0(1)
C(24)	45(2)	52(2)	42(2)	-21(1)	2(1)	1(1)
C(23)	51(2)	43(2)	50(2)	-27(1)	22(1)	-3(1)
C(29)	34(2)	47(2)	61(2)	6(2)	11(1)	-13(1)
C(7)	47(2)	34(1)	35(1)	-14(1)	12(1)	-10(1)
C(33)	27(1)	88(3)	50(2)	3(2)	13(1)	4(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mon.

	x	y	z	U(eq)
H(1B)	4432	2689	9468	27
H(7A)	1305	2457	7864	35
H(9A)	4244	2135	6971	30
H(11A)	4007	79	7975	35
H(12A)	6003	318	9852	39
H(13A)	3924	3635	8351	40
H(14A)	7364	3816	6629	47
H(16A)	1747	1622	6480	35
H(17A)	-812	2998	7799	42
H(18A)	7208	2314	10211	48
H(20A)	7940	69	9256	45
H(21A)	1158	893	5155	44
H(22A)	6178	2785	6622	39
H(23A)	-309	4109	10710	45
H(24A)	4003	3121	10851	42
H(25A)	5102	4673	8334	50
H(26A)	6855	4755	7502	51
H(27A)	-1176	3632	9075	40
H(28A)	3450	-632	6630	45
H(29A)	3593	3761	12115	57
H(30A)	1418	4249	12052	56

H(31A)	9161	2052	9647	57
H(32A)	2039	-225	5224	46
H(33A)	10115	383	8940	81
H(33B)	10876	969	9627	81
H(33C)	10159	1147	8556	81

3. Procedures for Synthesis of 1a-1q.

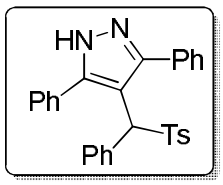


R^1 = aryl, methyl;
R^2, R^3 = aryl;
R^4 = aryl, H, TMS and alkyl

To a solution of *N*-propargylic sulfonylhydrazone (2 mmol) in THF (10 mL), CuI (38 mg, 0.2 mmol) and NEt_3 (243mg, 2.4 mmol) were added and the mixture was stirred at room temperature. When the reaction was completed (5min-30min, monitored by TLC), the solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford *N*-allenic sulfonylhydrazones **1a-1q** greater than 99% yields.

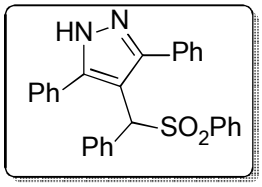
4. ^{1}H, ^{13}C-NMR, IR, MP, MS Datas and Synthesis Procedures of 2a-2p, 3a-3m, 4aa-ac and 5a.

3,5-Diphenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2a**)



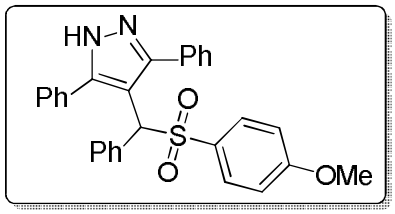
To a solution of *N*-allenic sulfonylhydrazone **1a** (232 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (4 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2a** in 87% yields. A yellow solid (mp: 174-175 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.70 (s, 1H), 7.00-7.04 (m, 2H), 7.06-7.12 (m, 2H), 7.16-7.21 (m, 3H), 7.26-7.30 (m, 6H), 7.32-7.37 (m, 4H), 7.38-7.44 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 66.8, 109.0, 127.8, 128.0, 128.1, 128.5, 128.7, 129.3, 129.6, 129.7, 133.4, 135.8, 144.1; **IR** (film): 3201, 3120, 1601, 1559 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{24}N_2NaO_2S$ $[M+Na]^+$ 487.1456, found: 487.1459.

4-(Benzenesulfonyl-phenyl-methyl)-3,5-diphenyl-1H-pyrazole (**2b**)



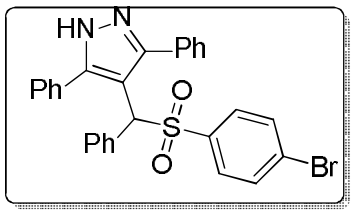
To a solution of *N*-allenic sulfonylhydrazone **1b** (225 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (3 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2b** in 71% yields. A yellow solid (mp: 169-170 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.71 (s, 1H), 7.01-7.13 (m, 2H), 7.15-7.21 (m, 3H), 7.24-7.28 (m, 2H), 7.30-7.35 (m, 4H), 7.35-7.41 (m, 4H), 7.41-7.51 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 66.9, 108.7, 127.9, 128.1, 128.5, 128.6, 128.8, 129.6, 129.7, 131.0, 133.3, 138.8; **IR** (film): 3301, 3100, 1636 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{28}H_{22}N_2NaO_2S$ $[M+Na]^+$ 473.1300, found: 473.1294.

4-[(4-Methoxy-benzenesulfonyl)-phenyl-methyl]-3,5-diphenyl-1H-pyrazole (**2c**)



To a solution of *N*-allenic sulfonylhydrazone **1c** (240 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (3 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2c** in 67% yields. A yellow solid (mp: 174-175 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 5.81 (s, 1H), 6.65-6.73 (m, 2H), 7.06-7.13 (m, 2H), 7.17-7.23 (m, 3H), 7.29-7.47 (m, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.5, 66.9, 109.1, 113.8, 127.7, 128.1, 128.1, 128.7, 129.6, 129.7, 130.2, 130.6, 133.5, 164.4; **IR** (film): 3310, 3100, 1616 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{24}N_2NaO_3S$ $[M+Na]^+$ 503.1405, found: 503.1402.

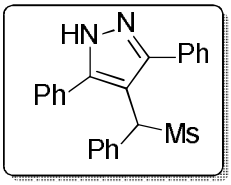
4-[(4-Bromo-benzenesulfonyl)-phenyl-methyl]-3,5-diphenyl-1H-pyrazole (**2d**)



To a solution of *N*-allenic sulfonylhydrazone **1d** (265mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (4 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v,

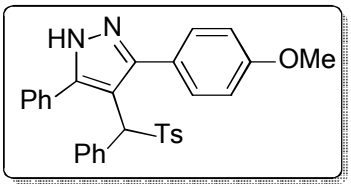
3:1) to afford pyrazoles **2d** in 85% yields. A yellow solid (mp: 178-179 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.74 (s, 1H), 7.08-7.15 (m, 2H), 7.16-7.25 (m, 9H), 7.29-7.37 (m, 6H), 7.38-7.45 (m, 2H), 10.79 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 66.7, 108.5, 128.0, 128.2, 128.2, 129.6, 129.9, 131.9, 132.8, 137.6; **IR** (film): 3313, 3100, 1606 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{28}H_{21}BrN_2NaO_2S$ $[M+Na]^+$ 551.0405 and 553.0384, found: 551.0409 and 553.0374.

4-(Methanesulfonyl-phenyl-methyl)-3,5-diphenyl-1H-pyrazole (**2e**)



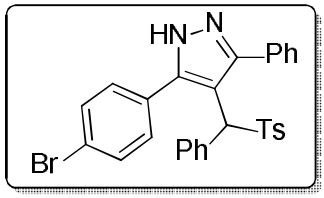
To a solution of *N*-allenic sulfonylhydrazone **1e** (194 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (4 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2e** in 96% yields. A yellow solid (mp: 162-163 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.62 (s, 3H), 5.30 (s, 1H), 6.98-7.07 (m, 2H), 7.07-7.14 (m, 2H), 7.20-7.25 (m, 1H), 7.31-7.64 (m, 10H), 10.76 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 40.1, 65.8, 110.9, 126.7, 128.3, 128.7, 128.7, 128.8, 129.8, 130.1, 130.6, 131.0, 132.0, 135.3, 153.6; **IR** (film): 3210, 3090, 1610 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{23}H_{20}N_2NaO_2S$ $[M+Na]^+$ 411.1143, found: 411.1145.

3-(4-Methoxy-phenyl)-5-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2f**)



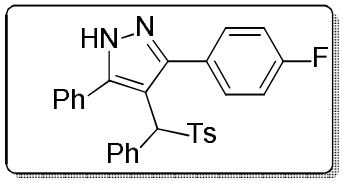
To a solution of *N*-allenic sulfonylhydrazone **1f** (246 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (3 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2f** in 94% yields. A yellow solid (mp: 160-161 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.85 (s, 3H), 5.65 (s, 1H), 6.76-6.84 (m, 2H), 6.95-7.02 (m, 2H), 7.06-7.12 (m, 2H), 7.13-7.20 (m, 5H), 7.20-7.33 (m, 6H), 7.34-7.41 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 55.3, 67.1, 108.7, 113.4, 127.8, 127.9, 128.1, 128.5, 129.2, 129.6, 129.6, 131.0, 133.5, 135.8, 144.1, 159.9; **IR** (film): 3210, 3111, 1611 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{30}H_{26}N_2NaO_3S$ $[M+Na]^+$ 517.1562, found: 517.1566.

5-(4-Bromo-phenyl)-3-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2g**)



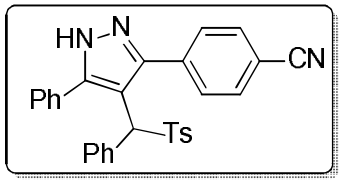
To a solution of *N*-allenic sulfonylhydrazone **1g** (271 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (3 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2g** in 83% yields. A yellow solid (mp: 192-193 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.65 (s, 1H), 7.02-7.06 (m, 2H), 7.06-7.12 (m, 2H), 7.14-7.23 (m, 5H), 7.28-7.32 (m, 4H), 7.34-7.41 (m, 2H), 7.41-7.46 (m, 1H), 7.47-7.53 (m, 2H), 10.27 (s, 1H); **^{13}C NMR** (125 MHz, d^6-DMSO) δ 21.5, 66.4, 128.2, 128.4, 128.5, 129.7, 129.9, 131.2, 133.8, 135.7, 144.9; **IR** (film): 3100, 1606, 1580 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{23}BrN_2NaO_2S$ $[M+Na]^+$ 565.0651 and 567.0451, found: 565.0655 and 567.0448.

3-(4-Fluoro-phenyl)-5-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2h**)



To a solution of *N*-allenic sulfonylhydrazone **1h** (241 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (4 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2h** in 89% yields. A yellow solid (mp: 180-181 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.64 (s, 1H), 6.95-7.06 (m, 4H), 7.04-7.11 (m, 2H), 7.12-7.21 (m, 3H), 7.23-7.32 (m, 6H), 7.32-7.39 (m, 2H), 7.40-7.46 (m, 1H), 10.54 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 66.8, 109.2, 114.9, 115.0, 127.9, 128.1, 128.19, 128.5, 128.9, 129.3, 129.5, 129.5, 131.7, 131.8, 133.3, 135.7, 144.3; **IR** (film): 3217, 3100, 1610 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{23}FN_2NaO_2S$ $[M+Na]^+$ 505.1362, found: 505.1365.

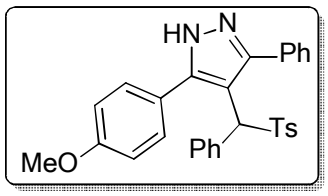
4-{5-Phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazol-3-yl}-benzonitrile (**2i**)



To a solution of *N*-allenic sulfonylhydrazone **1i** (245 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (5 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v,

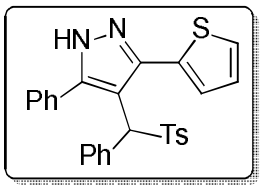
3:1) to afford pyrazoles **2i** in 84% yields. A yellow solid (mp: 207-208 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 5.80 (s, 1H), 7.07-7.19 (m, 6H), 7.19-7.30 (m, 5H), 7.30-7.50 (m, 5H), 7.68-7.93 (m, 2H), 13.42 (s, 1H); **^{13}C NMR** (125 MHz, d^{6}-DMSO) δ 21.5, 66.0, 128.2, 128.4, 128.5, 129.3, 129.7, 129.8, 129.9, 130.3, 132.1, 133.7, 135.5, 144.9; **IR** (film): 3210, 3111, 2226, 1610 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{30}H_{23}N_3NaO_2S$ $[M+Na]^+$ 512.1409, found: 512.1405.

5-(4-Methoxy-phenyl)-3-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2j**)



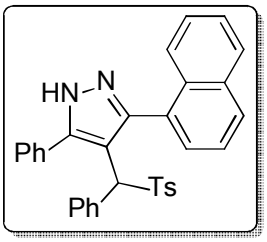
To a solution of *N*-allenic sulfonylhydrazone **1j** (247 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (1 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2j** in 97% yields. A yellow solid (mp: 110-111 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.83 (s, 3H), 5.63 (s, 1H), 6.72-6.83 (m, 2H), 6.92-7.00 (m, 2H), 7.05-7.12 (m, 4H), 7.13-7.21 (m, 5H), 7.21-7.29 (m, 4H), 7.32-7.40 (m, 1H), 11.65 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 55.2, 67.1, 108.4, 113.3, 127.7, 127.9, 128.1, 128.4, 128.5, 129.2, 129.6, 129.6, 131.0, 133.5, 135.8, 144.1, 159.8; **IR** (film): 3211, 3102, 1608 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{30}H_{26}N_2NaO_3S$ $[M+Na]^+$ 517.1562, found: 517.1563.

5-Phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-3-thiophen-2-yl-1H-pyrazole (**2k**)



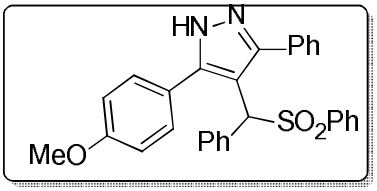
To a solution of *N*-allenic sulfonylhydrazone **1k** (235 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (3 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2k** in 94% yields. A yellow solid (mp: 160-161 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 5.83 (s, 1H), 6.95-7.04 (m, 3H), 7.08-7.15 (m, 5H), 7.18-7.22 (m, 1H), 7.23-7.88 (m, 8H), 11.39 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.6, 66.9, 109.1, 126.5, 127.2, 127.9, 128.0, 128.2, 128.5, 128.9, 129.3, 129.5, 129.6, 133.0, 135.7, 144.2; **IR** (film): 3310, 3100, 1610 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{27}H_{22}N_2NaO_2S_2$ $[M+Na]^+$ 493.1020, found: 493.1023.

3-Naphthalen-1-yl-5-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2l**)



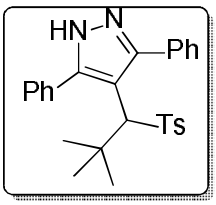
To a solution of *N*-allenic sulfonylhydrazone **1l** (257 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (5 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2l** in 73% yields. A yellow solid (mp: 191-192 ^oC); **^{1}H NMR** (500 MHz, d^6-DMSO) δ 2.16-2.38 (m, 3H), 5.38-5.87 (m, 2H), 6.44-7.28 (s, 12H), 7.30-7.81 (m, 9H), 7.87-8.12 (m, 2H), 13.15-13.46 (m, 1H); **^{13}C NMR** (125 MHz, d^6-DMSO) δ 21.5, 66.9, 109.2, 125.2, 125.9, 126.4, 127.9, 128.1, 128.4, 128.7, 129.3, 129.8, 129.9, 133.2, 135.8, 144.7; **IR** (film): 3300, 3101, 1610 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{33}H_{26}N_2NaO_2S$ $[M+Na]^+$ 537.1613, found: 537.1617.

4-(Benzenesulfonyl-phenyl-methyl)-5-(4-methoxy-phenyl)-3-phenyl-1H-pyrazole (**2m**)



To a solution of *N*-allenic sulfonylhydrazone **1m** (240 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (2 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2m** in 85% yields. A yellow solid (mp: 148-149 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.84 (s, 3H), 5.54 (s, 1H), 6.76-6.91 (m, 2H), 7.04-7.13 (m, 4H), 7.16-7.29 (m, 7H), 7.32-7.37 (m, 2H), 7.39-7.49 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.3, 66.9, 113.6, 128.1, 128.2, 128.4, 128.7, 129.1, 129.6, 129.9, 131.3, 132.9, 133.4, 138.7, 160.3; **IR** (film): 3310, 3100, 1611 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{24}N_2NaO_3S$ $[M+Na]^+$ 503.1405, found: 503.1409.

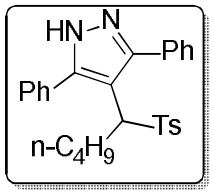
4-[2,2-Dimethyl-1-(toluene-4-sulfonyl)-propyl]-3,5-diphenyl-1H-pyrazole (**2n**)



To a solution of *N*-allenic sulfonylhydrazone **1n** (222 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction

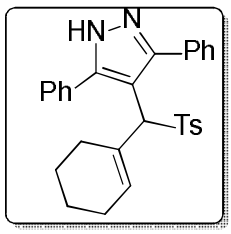
was completed (48 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2n** in 82% yields. A yellow solid (mp: 183-184 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.06 (s, 9H), 2.38 (s, 3H), 4.54 (s, 1H), 6.77-6.88 (m, 2H), 6.92-7.00 (m, 2H), 7.18-7.27 (m, 4H), 7.29-7.36 (m, 1H), 7.39-7.48 (m, 3H), 7.73-7.84 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 30.5, 36.3, 70.9, 108.7, 127.9, 128.1, 128.7, 129.1, 131.2, 138.3, 143.5; **IR** (film): 3310, 3101, 1611 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{27}H_{28}N_2NaO_2S$ $[M+Na]^+$ 467.1769, found: 467.1766.

3,5-Diphenyl-4-[1-(toluene-4-sulfonyl)-pentyl]-1H-pyrazole (**2o**)



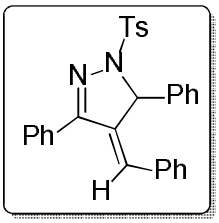
To a solution of *N*-allenic sulfonylhydrazone **1o** (222 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (13 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (2 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2o** in 50% yields. A yellow solid (mp: 183-184 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.67 (t, 3H, *J* = 6.9 Hz), 0.95-1.20 (m, 4H), 1.80-2.06 (m, 2H), 2.34 (s, 3H), 4.47 (dd, 2H, *J* = 12.5 Hz, 3.5Hz), 6.79-7.04 (m, 4H), 7.13-7.26 (m, 4H), 7.28-7.35 (m, 3H), 7.38-7.45 (m, 1H), 7.57-7.74 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.4, 21.5, 22.2, 24.3, 29.0, 62.8, 106.3, 127.9, 128.2, 128.5, 128.9, 129.3, 130.1, 135.2, 143.9; **IR** (film): 3211, 3101, 1610 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{27}H_{28}N_2NaO_2S$ $[M+Na]^+$ 467.1769, found: 467.1761.

4-[Cyclohex-1-enyl-(toluene-4-sulfonyl)-methyl]-3,5-diphenyl-1H-pyrazole (**2p**)



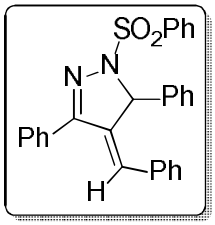
To a solution of *N*-allenic sulfonylhydrazone **1p** (234 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $ZnBr_2$ (123 mg, 0.55 mmol) was added and it was stirred at room temperature until the reaction was completed (3 h). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 3:1) to afford pyrazoles **2p** in 72% yields. A yellow solid (mp: 221-222 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.75-0.92 (m, 1H), 1.37-1.56 (m, 2H), 1.66-1.76 (m, 1H), 1.81-1.97 (m, 2H), 2.14-2.16 (m, 2H), 2.44 (s, 3H), 3.87-3.95 (m, 2H), 6.37 (s, 1H), 7.29-7.34 (m, 2H), 7.34-7.49 (m, 6H), 7.60-7.72 (m, 4H), 7.73-7.84 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 20.7, 21.6, 25.2, 27.2, 27.2, 69.5, 111.8, 123.9, 127.6, 128.2, 128.6, 128.7, 129.7, 134.1, 136.06, 144.3; **IR** (film): 3330, 3100, 1636, 1611 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{28}N_2NaO_2S$ $[M+Na]^+$ 491.1769, found: 491.1767.

4-Benzylidene-3,5-diphenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3a**)



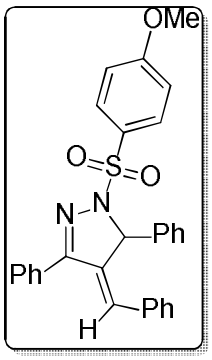
To a solution of *N*-allenic sulfonylhydrazone **1a** (242 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (5 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3a** in 83% yields. A yellow solid (mp: 181-182 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 6.15 (s, 1H), 6.92 (s, 1H), 7.11-716 (m, 3H), 7.20-7.25 (m, 5H), 7.26-7.31 (m, 3H), 7.32-7.41 (m, 2H), 7.50-7.58 (m, 4H), 7.67-7.75 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 67.6, 128.6, 128.8, 127.8, 128.5, 128.5, 128.7, 128.9, 129.2, 129.3, 129.7, 129.9, 130.2, 134.4, 137.4, 138.6, 143.7, 159.8; **IR** (film): 3054, 2846, 1636 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{24}N_2NaO_2S$ $[M+Na]^+$ 487.1456, found: 487.1451.

1-Benzenesulfonyl-4-benzylidene-3,5-diphenyl-4,5-dihydro-1H-pyrazole (**3b**)



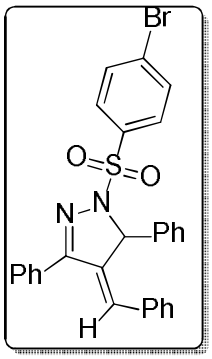
To a solution of *N*-allenic sulfonylhydrazone **1b** (225 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (5 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3b** in 81% yields. A yellow solid (mp: 167-168 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.18 (d, 1H, J = 2.7 Hz), 6.93 (d, 1H, J = 2.8 Hz), 7.12-7.16 (m, 2H), 7.19-7.26 (m, 6H), 7.29-7.35 (m, 4H), 7.44-7.48 (m, 1H), 7.50-7.56 (m, 3H), 7.63-7.67 (m, 2H), 7.68-7.74 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 67.7, 127.6, 128.5, 128.5, 128.6, 126.6, 128.6, 128.8, 128.9, 128.9, 129.2, 129.7, 129.9, 130.2, 132.7, 134.3, 137.2, 137.5, 138.5, 159.7; **IR** (film): 3050, 2917, 1633 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{28}H_{22}N_2NaO_2S$ $[M+Na]^+$ 473.1300, found: 473.1309.

4-Benzylidene-1-(4-methoxy-benzenesulfonyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (**3c**)



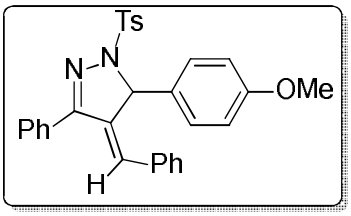
To a solution of *N*-allenic sulfonylhydrazone **1c** (240 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (40 mg, 0.25 mmol) was added and it was stirred at room temperature until the reaction was completed (5 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3c** in 63% yields. A yellow solid (mp: 71-73 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.15 (d, 1H, *J* = 2.8 Hz), 6.77-6.83 (m, 2H), 6.92-6.95 (m, 1H), 7.11-7.19 (m, 3H), 7.20-7.26 (m, 6H), 7.32-7.40 (m, 3H), 7.50-7.55 (m, 3H), 7.59-7.63 (m, 2H), 7.68-7.73 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.5, 67.6, 113.8, 128.4, 128.6, 128.8, 128.8, 128.9, 129.1, 129.6, 129.9, 129.9, 130.2, 134.4, 137.4, 138.7, 159.7, 163.1; **IR** (film): 3054, 2847, 1636 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{24}N_2NaO_3S$ $[M+Na]^+$ 503.1405, found: 503.1409.

4-Benzylidene-1-(4-bromo-benzenesulfonyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (**3d**)



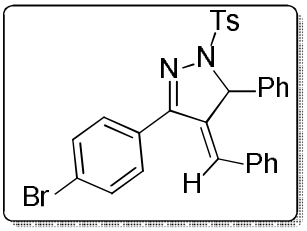
To a solution of *N*-allenic sulfonylhydrazone **1d** (265 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (10 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3d** in 72% yields. A yellow solid (mp: 186-187 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.20 (d, 1H, *J* = 2.7 Hz), 6.99 (d, 1H, *J* = 2.7 Hz), 7.13-7.19 (m, 2H), 7.20-7.29 (m, 6H), 7.30-7.35 (m, 2H), 7.38-7.48 (m, 4H), 7.51-7.59 (m, 3H), 7.70-7.79 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 67.9, 127.7, 128.5, 128.7, 128.9, 128.9, 128.9, 129.0, 129.2, 129.7, 129.9, 130.4, 131.8, 134.3, 136.9, 136.9, 138.2, 159.5; **IR** (film): 3053, 2920, 1616 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{28}H_{21}BrN_2NaO_2S$ $[M+Na]^+$ 551.0405 and 553.0384, found: 551.0403 and 553.0388.

4-Benzylidene-5-(4-methoxy-phenyl)-3-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3f**)



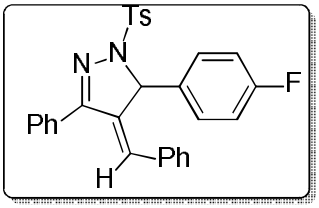
To a solution of *N*-allenic sulfonylhydrazone **1f** (247 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (5 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3f** in 82% yields. A yellow solid (mp: 90-91 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.78 (s, 3H), 6.13 (d, 1H, J = 2.7 Hz), 6.71-6.78 (m, 1H), 6.90-6.94 (m, 1H), 7.10-7.15 (m, 2H), 7.15-7.19 (m, 2H), 7.21-7.26 (m, 3H), 7.26-7.31 (m, 2H), 7.50-7.55 (m, 3H), 7.55-7.60 (m, 2H), 7.68-7.44 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 55.2, 67.3, 113.9, 127.7, 128.5, 128.8, 128.8, 128.9, 129.2, 129.2, 129.4, 129.6, 129.8, 130.1, 130.1, 134.5, 134.6, 138.6, 143.5, 159.5, 159.6; **IR** (film): 3106, 2910, 1616 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{30}H_{26}N_2NaO_3S$ $[M+Na]^+$ 517.1562, found: 517.1562.

4-Benzylidene-3-(4-bromo-phenyl)-5-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3g**)



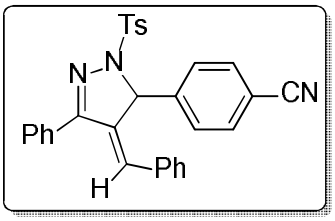
To a solution of *N*-allenic sulfonylhydrazone **1g** (271 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (10 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3g** in 76% yields. A yellow solid (mp: 188-189 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.37 (s, 3H), 6.89 (d, 1H, J = 2.7 Hz), 6.86-6.92 (m, 1H), 7.10-7.17 (m, 4H), 7.19-7.27 (m, 6H), 7.31-7.36 (m, 2H), 7.49-7.56 (m, 2H), 7.52-7.63 (m, 2H), 7.63-7.69 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.6, 67.8, 124.7, 127.8, 128.5, 128.6, 128.6, 128.9, 129.0, 129.2, 129.3, 129.4, 130.4, 132.1, 134.2, 134.6, 137.2, 143.7, 158.1; **IR** (film): 3054, 2926, 1616 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{23}BrN_2NaO_2S$ $[M+Na]^+$ 565.0561 and 567.0541, found: 565.0560 and 567.0531.

4-Benzylidene-5-(4-fluoro-phenyl)-3-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3h**)



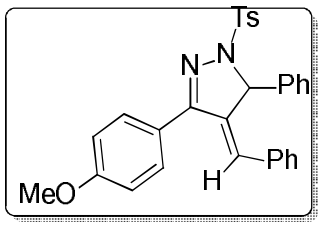
To a solution of *N*-allenic sulfonylhydrazone **1h** (241 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (10 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3h** in 63% yields. A yellow solid (mp: 158-159 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 6.15 (d, 1H, J = 2.8 Hz), 6.88-6.97 (m, 3H), 7.10-7.14 (m, 2H), 7.15-7.20 (m, 2H), 7.21-7.27 (m, 3H), 7.30-7.38 (m, 2H), 7.50-7.57 (m, 3H), 7.59-7.65 (m, 2H), 7.66-7.33 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 66.8, 111.5 (d, ^2J_F = 21.7 Hz), 127.8, 128.3, 128.5, 128.8, 128.9, 128.9, 129.1, 129.3, 129.8, 129.9, 130.3, 130.4, 133.3, 134.2, 138.4, 143.9, 159.6, 162.6 (d, ^1J_F = 247.8 Hz); **IR** (film): 3055, 2916, 1636 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{23}FN_2NaO_2S$ $[M+Na]^+$ 505.1360, found: 505.1355.

4-[4-Benzylidene-5-phenyl-2-(toluene-4-sulfonyl)-3,4-dihydro-2H-pyrazol-3-yl]-benzonitrile (**3i**)



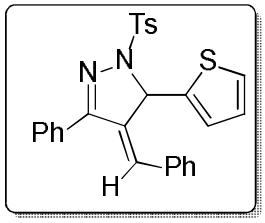
To a solution of *N*-allenic sulfonylhydrazone **1i** (245 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (10 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3i** in 53-95% yields. A yellow solid (mp: 96-98 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 6.16 (d, 1H, J = 2.9 Hz), 6.93-6.99 (m, 1H), 7.04-7.09 (m, 2H), 7.19-7.26 (m, 5H), 7.42-7.48 (m, 2H), 7.48-7.57 (m, 5H), 7.63-7.71 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.6, 66.8, 112.1, 118.4, 128.0, 128.6, 128.8, 128.8, 128.9, 129.2, 133.5, 133.9, 138.1, 142.4, 144.5, 159.8; **IR** (film): 3055, 2228, 1636 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{30}H_{23}N_3NaO_2S$ $[M+Na]^+$ 512.1409, found: 512.1407.

4-Benzylidene-3-(4-methoxy-phenyl)-5-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3j**)



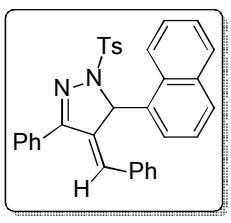
To a solution of *N*-allenic sulfonylhydrazone **1j** (247 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (5 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3j** in 83% yields. A yellow solid (mp: 182-183 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.90 (s, 3H), 5.12 (s, 2H), 6.11 (d, 1H, J = 2.6 Hz), 6.90-6.95 (m, 1H), 6.99-7.07 (m, 2H), 7.10-7.18 (m, 4H), 7.19-7.28 (m, 6H), 7.32-7.41 (m, 2H), 7.52-7.60 (m, 2H), 7.63-7.71 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 55.4, 67.5, 114.3, 122.2, 127.8, 128.4, 128.5, 128.6, 128.6, 128.84, 129.1, 129.2, 129.7, 130.3, 134.2, 134.5, 137.5, 138.7, 143.7, 157.7, 161.7; **IR** (film): 3060, 2905, 1636 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{30}H_{26}N_2NaO_3S$ $[M+Na]^+$ 517.1563, found: 517.1568.

4-Benzylidene-3-phenyl-5-thiophen-2-yl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3k**)



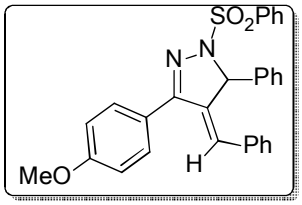
To a solution of *N*-allenic sulfonylhydrazone **1k** (235 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (10 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3k** in 90% yields. A yellow solid (mp: 149-150 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 6.53 (d, 1H, J = 1.8 Hz), 6.88-6.98 (m, 2H), 7.13-7.20 (m, 3H), 7.22-7.33 (m, 6H), 7.49-7.57 (m, 3H), 7.60-7.68 (m, 2H), 7.68-7.76 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ21.7, 62.5, 126.49, 126.6, 127.8, 128.4, 128.6, 128.8, 128.9, 129.2, 129.3, 129.4, 129.9, 130.1, 130.2, 134.3, 134.5, 137.8, 139.6, 143.7, 159.1; **IR** (film): 3106, 2846, 1635 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{27}H_{22}N_2NaO_2S_2$ $[M+Na]^+$ 493.1020, found: 493.1027.

4-Benzylidene-5-naphthalen-1-yl-3-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3l**)



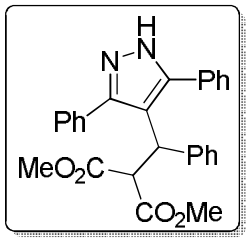
To a solution of *N*-allenic sulfonylhydrazone **1l** (257 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (10 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3l** in 95% yields. A yellow solid (mp: 177-178 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 6.75 (s, 1H), 6.89-6.94 (s, 3H), 6.94-6.99 (m, 2H), 7.01-7.07 (m, 3H), 7.15-7.22 (m, 1H), 7.30-7.36 (m, 1H), 7.39-7.45 (m, 2H), 7.49-7.53 (m, 1H), 7.54-7.61 (m, 4H), 7.68-7.73 (m, 1H), 7.78-7.86 (m, 3H), 8.15-8.32 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.5, 65.5, 123.8, 125.0, 125.7, 126.4, 127.7, 128.0, 128.4, 128.7, 128.8, 128.9, 128.9, 129.1, 129.3, 129.4, 130.1, 130.2, 131.0, 133.8, 134.7, 134.3, 140.2, 143.6, 159.1; **IR** (film): 3055, 3017, 1635 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{33}H_{26}N_2NaO_2S$ $[M+Na]^+$ 537.1613, found: 537.1617.

1-Benzenesulfonyl-4-benzylidene-3-(4-methoxy-phenyl)-5-phenyl-4,5-dihydro-1H-pyrazole (**3m**)



To a solution of *N*-allenic sulfonylhydrazone **1m** (240 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL), $FeCl_3$ (16 mg, 0.1 mmol) was added and it was stirred at room temperature until the reaction was completed (5 min). The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford (*E*)-4,5-dihydro-1H-pyrazole **3m** in 73% yields. A yellow solid (mp: 195-197 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.90 (s, 3H), 6.14 (d, 1H, *J* = 2.7 Hz), 6.94 (d, 1H, *J* = 2.7 Hz), 7.02-7.07 (m, 2H), 7.12-7.17 (m, 2H), 7.20-7.27 (m, 6H), 7.29-7.36 (m, 4H), 7.43-7.48 (m, 1H), 7.63-7.71 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.4, 67.5, 114.3, 122.1, 127.6, 128.7, 128.5, 128.6, 128.6, 128.8, 129.1, 129.7, 130.3, 132.6, 134.7, 137.3, 137.5, 138.6, 159.5, 161.3; **IR** (film): 3064, 2906, 1606 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{24}N_2NaO_3S$ $[M+Na]^+$ 503.1405, found: 503.1401.

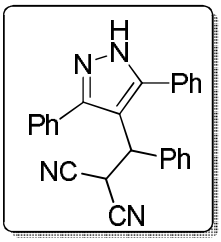
dimethyl 2-((3,5-diphenyl-1H-pyrazol-4-yl)(phenyl)methyl)malonate (**4aa**)



To a solution of 1H-pyrazole **2a** (232 mg, 0.5 mmol) and KF/Al_2O_3 (200 mg) in anhydrous DCM (5 mL) under nitrogen, dimethyl malonate (132 mg, 1 mmol) was added and it was stirred at room temperature for 6 hours. The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v,

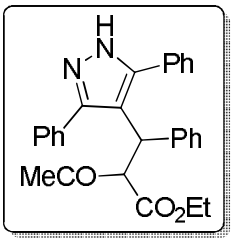
5:1) to afford **5a** in 75% yield. A white solid (mp: 125-126 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.51 (s, 6H), 4.15 (d, 1H, *J* = 12.3 Hz), 5.13 (d, 1H, *J* = 12.3 Hz), 6.80-6.85 (m, 2H), 7.10-7.15 (m, 3H), 7.36-7.42 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 39.6, 52.4, 52.5, 55.2, 115.9, 126.4, 127.3, 128.1, 128.4, 128.5, 129.4, 141.5, 168.1, 168.3; **IR** (film): 3210, 3030, 1600 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{27}H_{24}N_2NaO_4$ $[M+Na]^+$ 463.4802, found: 463.4805.

2-((3,5-diphenyl-1H-pyrazol-4-yl)(phenyl)methyl)malononitrile (**4ab**)



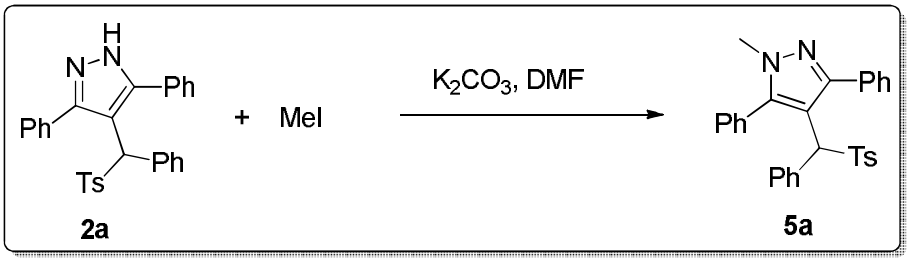
To a solution of 1H-pyrazole **2a** (232 mg, 0.5 mmol) and KF/Al_2O_3 (200 mg) in anhydrous DCM (5 mL) under nitrogen, malononitrile (66 mg, 1 mmol) was added and it was stirred at room temperature for 6 hours. The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 5:1) to afford **4ab** in 78% yield. A white solid (mp: 104-105 ^{o}C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.17 (d, 1H, *J* = 11.8 Hz), 4.78 (d, 1H, *J* = 11.8 Hz), 7.00-7.06 (m, 2H), 7.27-7.32 (m, 3H), 7.34-7.39 (m, 4H), 7.41-7.46 (m, 4H), 7.47-7.52 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 27.6, 42.6, 112.1, 112.2, 113.2, 127.5, 128.2, 128.9, 129.0, 129.3, 129.4, 131.0, 137.4; **IR** (film): 3310, 3030, 2260, 1620 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{25}H_{18}N_4Na$ $[M+Na]^+$ 397.1429, found: 397.1433.

ethyl 2-((3,5-diphenyl-1H-pyrazol-4-yl)(phenyl)methyl)-3-oxobutanoate (**4ac**)



To a solution of 1H-pyrazole **2a** (232 mg, 0.5 mmol) and KF/Al_2O_3 (200 mg) in anhydrous DCM (5 mL) under nitrogen, ethyl acetylacetate (129 mg, 1 mmol) was added and it was stirred at room temperature for 4 hours. The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 5:1) to afford **4ac** in 82% yield. A colorless liquid, d.r. = 4:3; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 093-1.07 (m, 3H), 1.80 (s, 1.63H), 2.01 (s, 1.26H), 3.85-4.08 (m, 2H), 4.19-4.35 (m, 1H), 5.06-5.22 (m, 1H), 6.69-6.80 (m, 1H), 6.93-6.98 (m, 1H), 7.08-7.19 (m, 3H), 7.31-7.44 (m, 10H), 11.13-11.88 (brs, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.6, 13.7, 29.1, 29.2, 39.1, 61.4, 61.5, 63.0, 63.2, 116.0, 116.2, 126.4, 127.5, 127.7, 128.2, 128.3, 128.4, 129.5, 141.6, 142.2, 167.9 168.1, 201.2, 201.9; **IR** (film): 3300, 3010, 1680, 1620 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{28}H_{26}N_2NaO_3$ $[M+Na]^+$ 461.1841, found: 461.1838.

1-Methyl-3,5-diphenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**5a**)

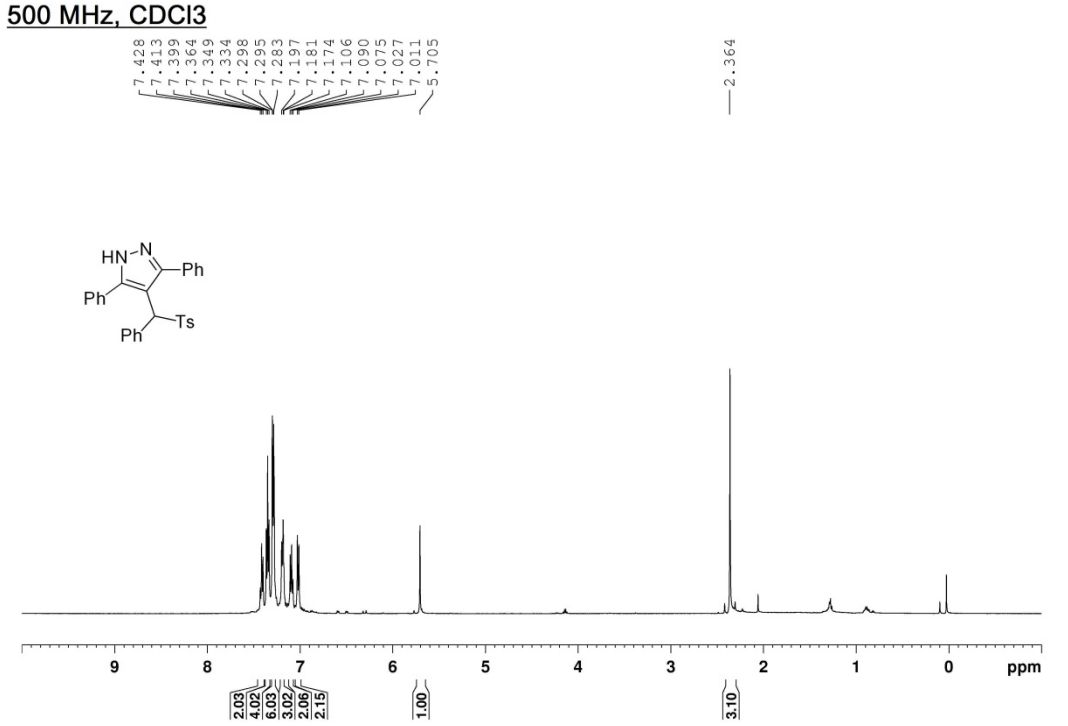


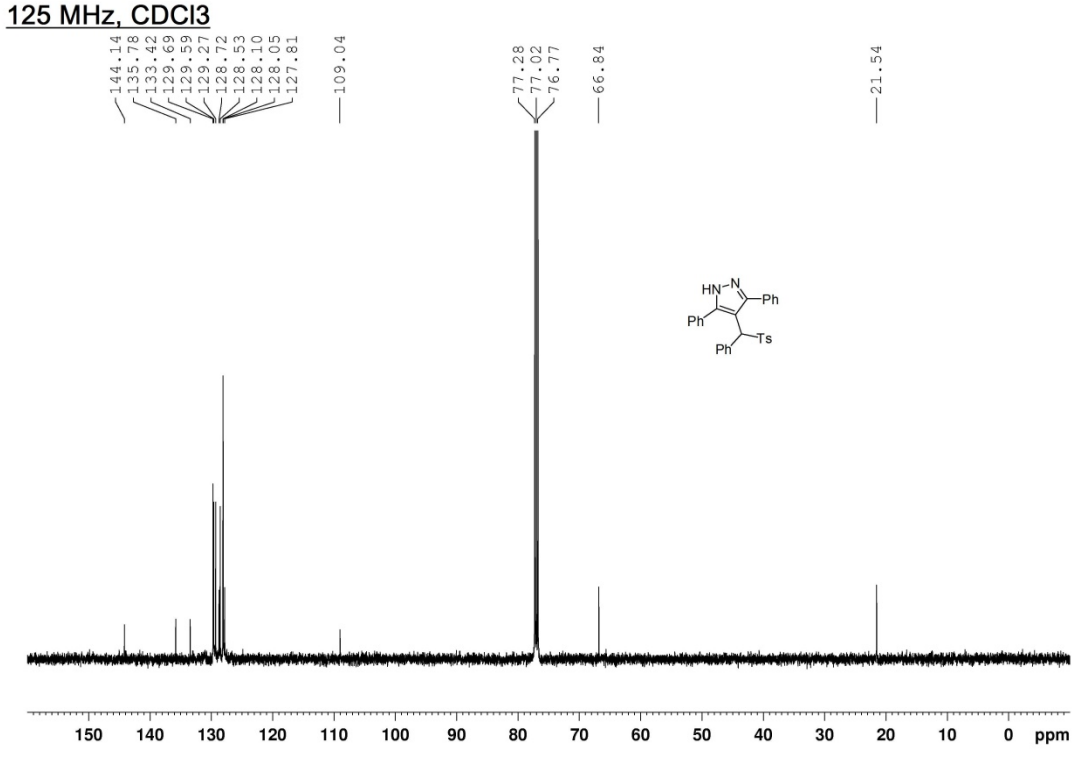
Because of the dynamic tautomeric forms of the NH-pyrazoles **2**, their ^{13}C NMR spectra are unusual as normal organic compounds show. To circumvent this issue, alkylation of **2a** has been adopted to generate the corresponding product **5a** and gave clear ^{13}C NMR spectra.

To a solution of 1H-pyrazole **2a** (232 mg, 0.5 mmol) in anhydrous DMF (5 mL), K_2CO_3 (83 mg, 0.6 mmol) and iodomethane (83 mg, 0.6 mmol) were added and it was stirred at room temperature for 0.5 hour. The mixture was filtered off and water (20 mL) was added. The aqueous phase was extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$. The solvent was removed under vacuum, and then the residue was further purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (v/v, 15:1) to afford **5a** in 95% yield. A yellow solid (mp: 176-177 ^oC); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.60 (s, 3H), 5.60 (s, 1H), 6.99-7.07 (m, 6H), 7.11-7.26 (m, 3H), 7.29-7.34 (m, 2H), 7.34-7.44 (m, 7H), 7.46-7.51 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ21.5, 37.2, 67.2, 109.5, 127.6, 127.9, 127.9, 128.0, 1289.5, 129.8, 131.0, 132.9, 133.3, 135.9, 144.0, 144.2, 151.8; **IR** (film): 3050, 3030, 1636 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{30}H_{26}N_2NaO_2S$ $[M+Na]^+$ 501.1613, found: 501.1622.

5. ^{1}H, ^{13}C-NMR Spectra of 2a-2p, 3a-3m, 4aa-ac and 5a.

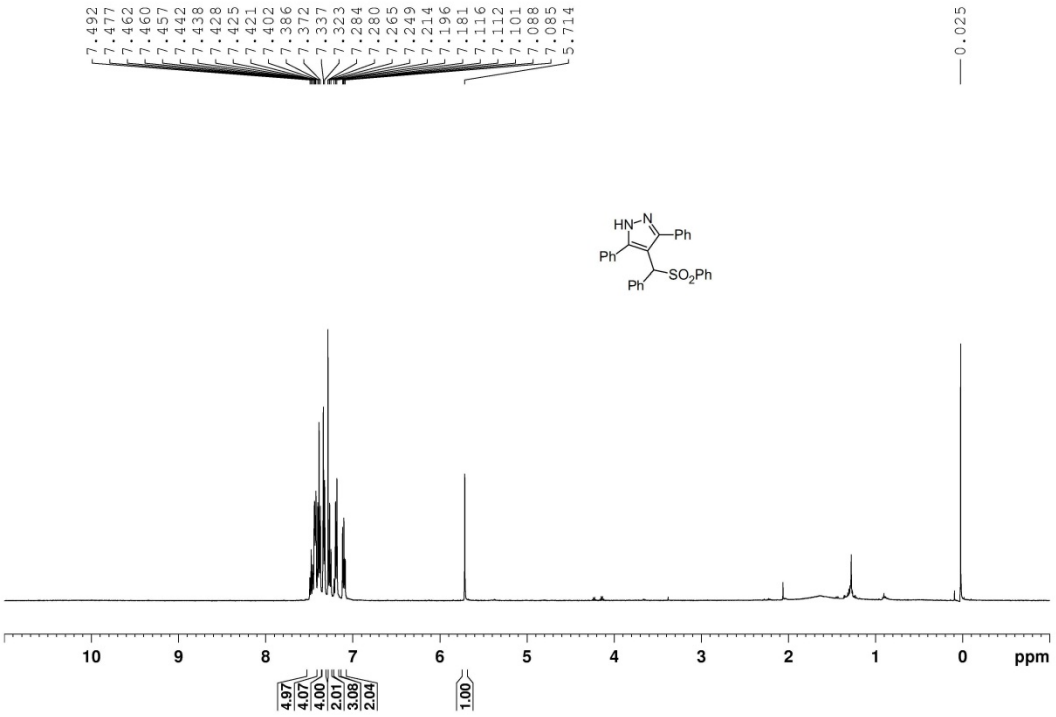
3,5-Diphenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2a**)



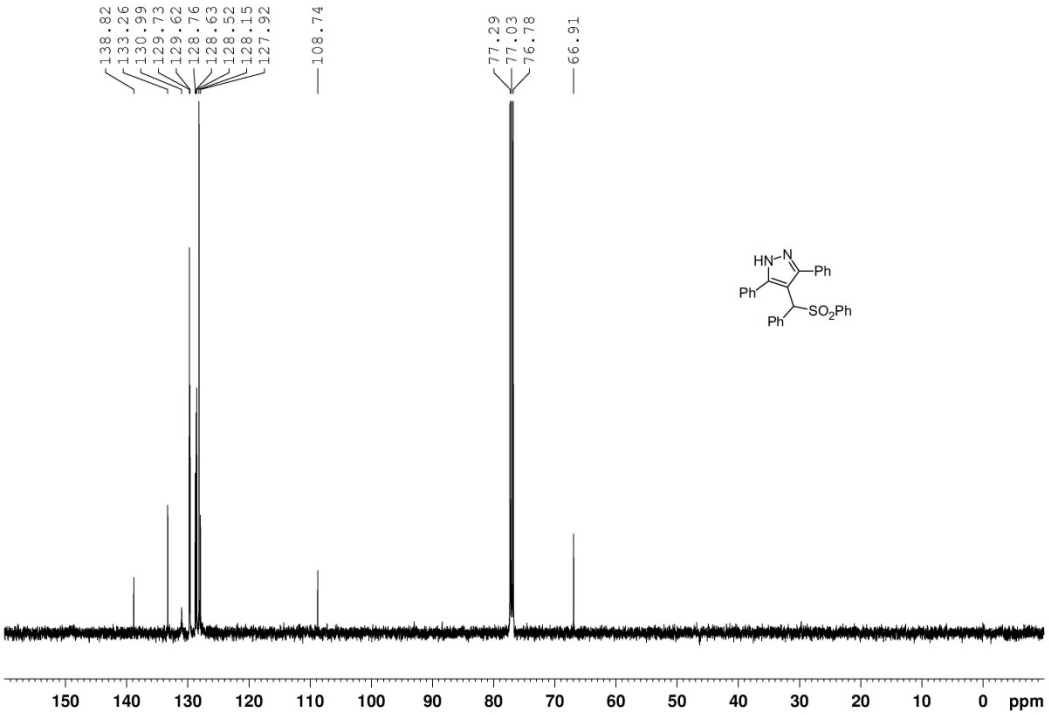


4-(Benzenesulfonyl-phenyl-methyl)-3,5-diphenyl-1H-pyrazole (**2b**)

500 MHz, CDCl3

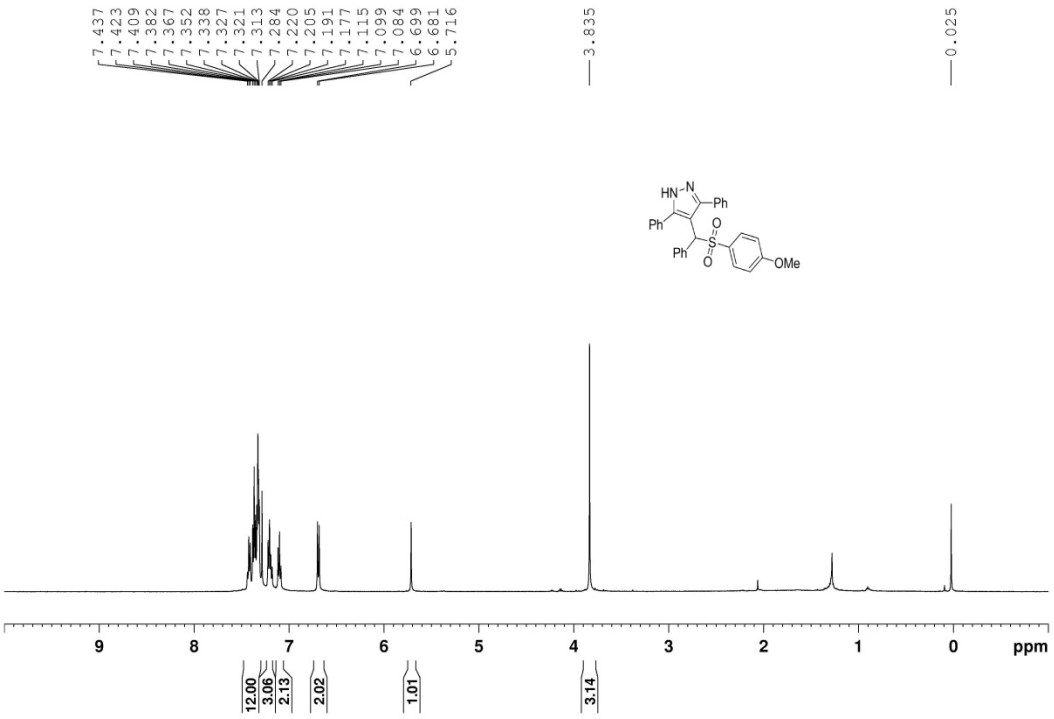


125 MHz, CDCl3

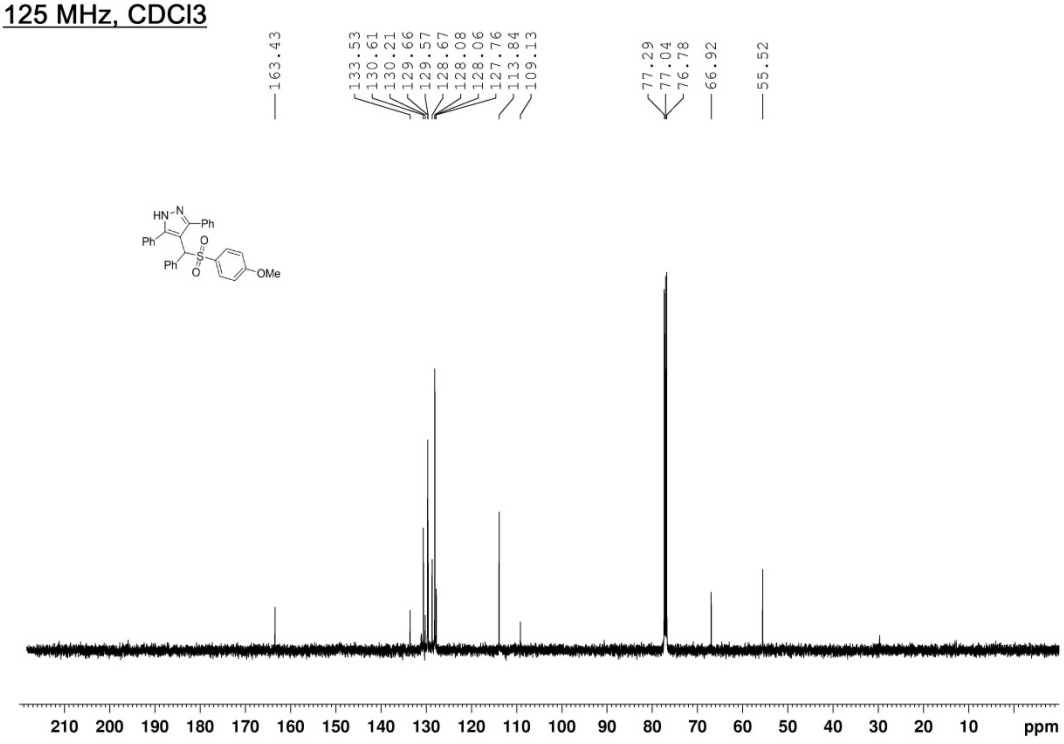


4-[(4-Methoxy-benzenesulfonyl)-phenyl-methyl]-3,5-diphenyl-1H-pyrazole (**2c**)

500 MHz, CDCl3

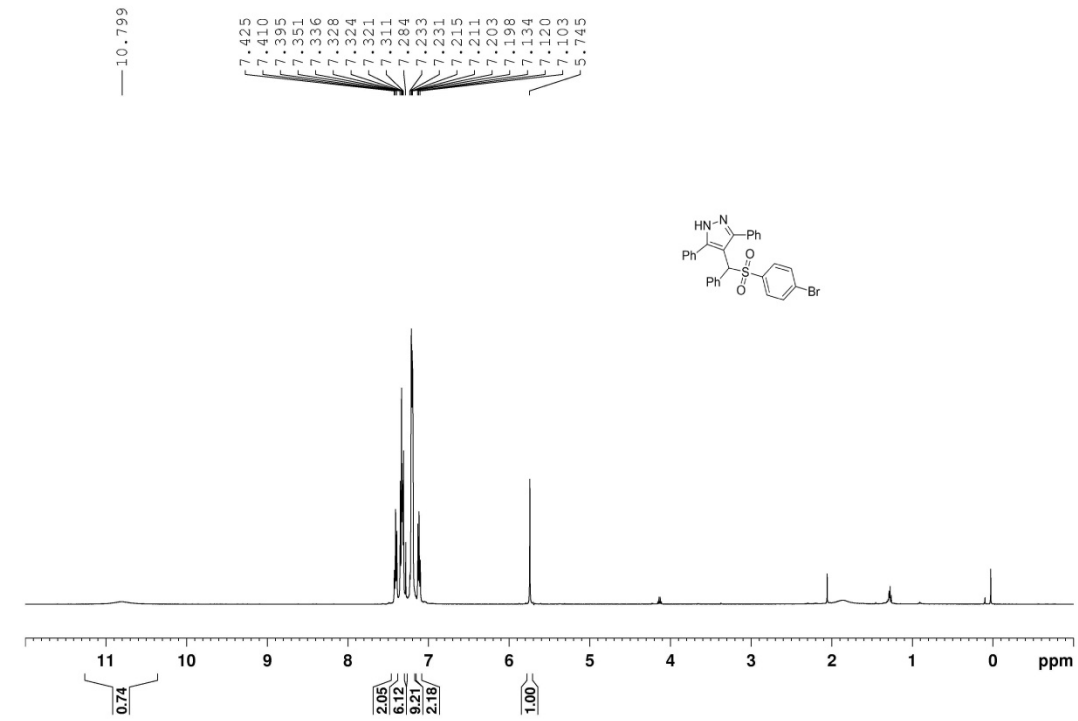


125 MHz, CDCl3

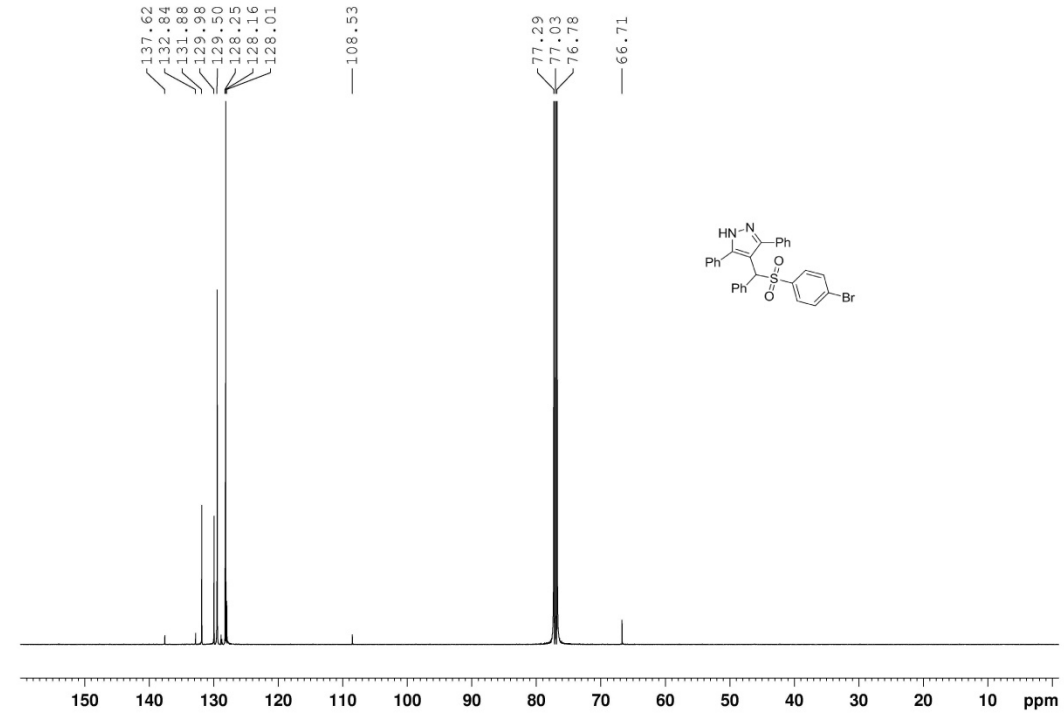


4-[(4-Bromo-benzenesulfonyl)-phenyl-methyl]-3,5-diphenyl-1H-pyrazole (**2d**)

500 MHz, CDCl3

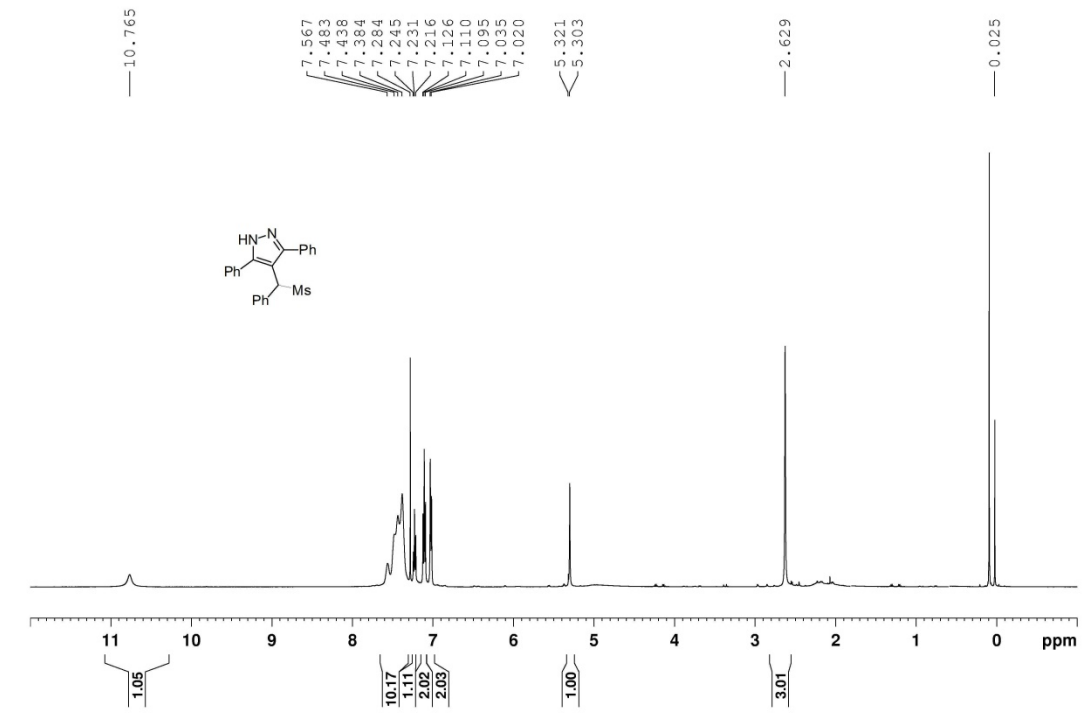


125 MHz, CDCl3

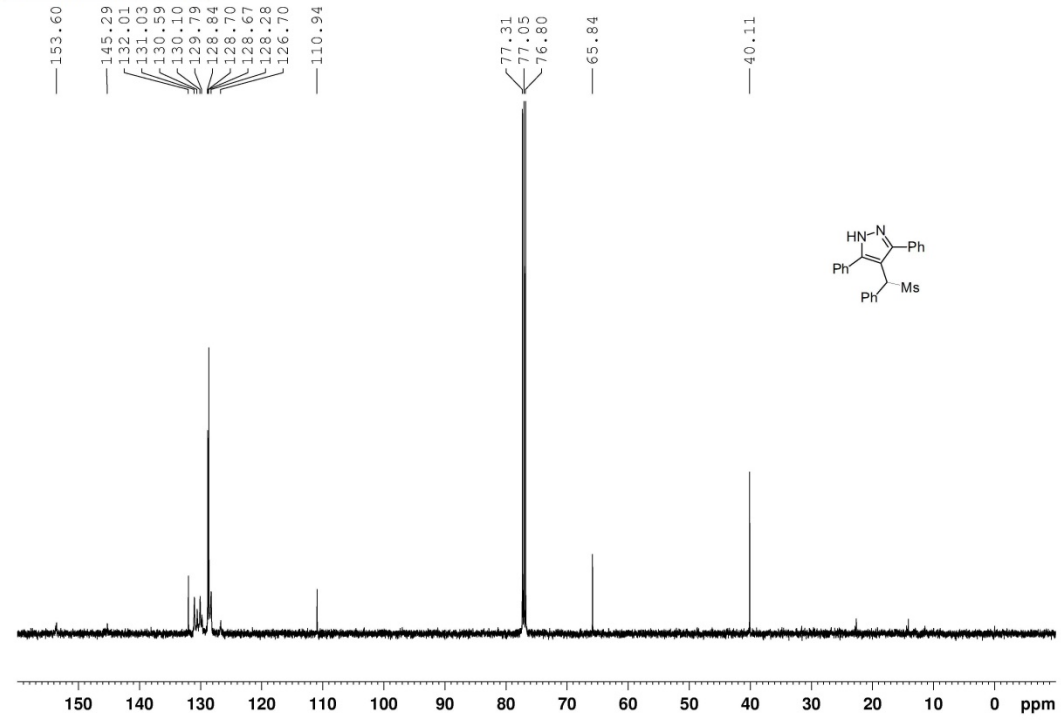


4-(Methanesulfonyl-phenyl-methyl)-3,5-diphenyl-1H-pyrazole (**2e**)

500 MHz, CDCl3

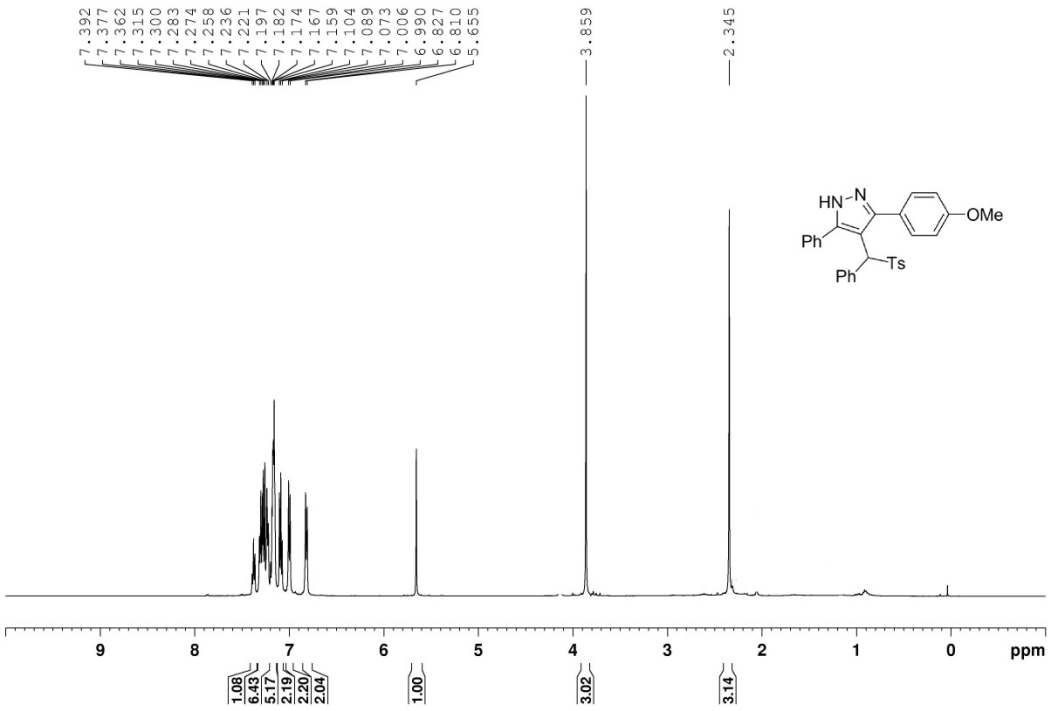


125 MHz, CDCl3

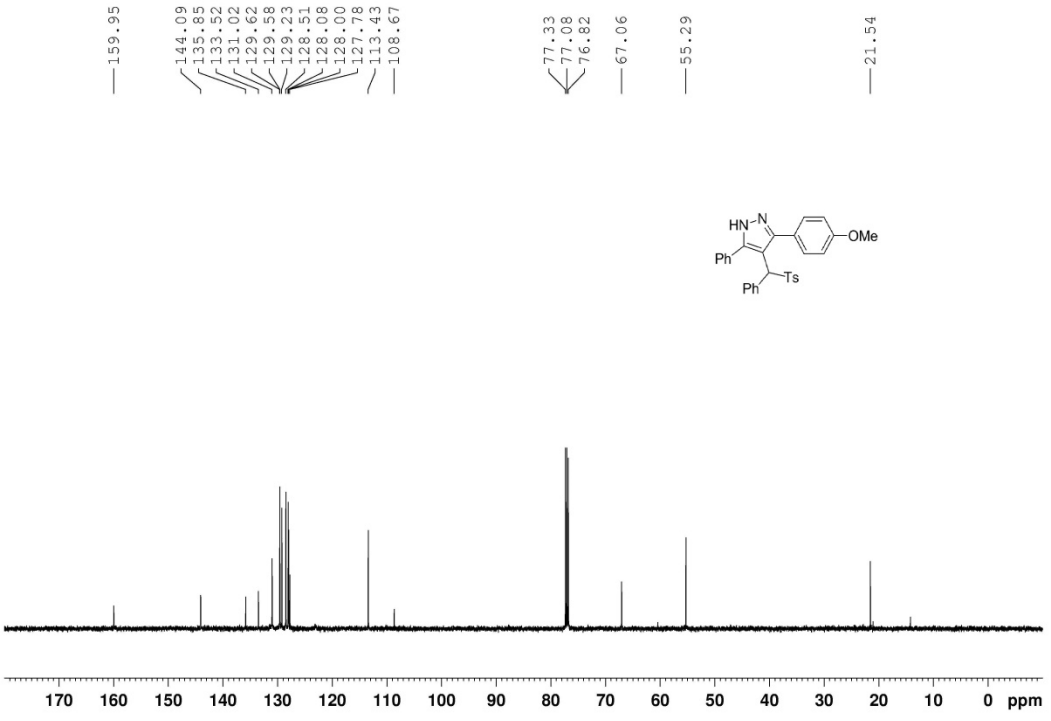


3-(4-Methoxy-phenyl)-5-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2f**)

500 MHz, CDCl3

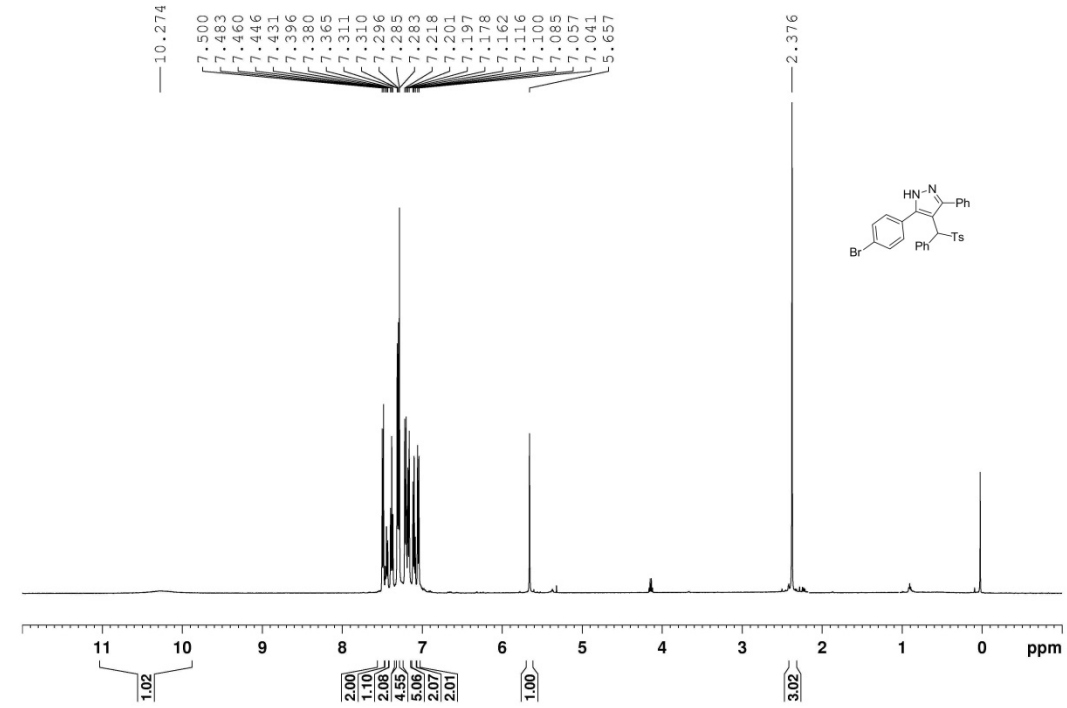


125 MHz, CDCl3

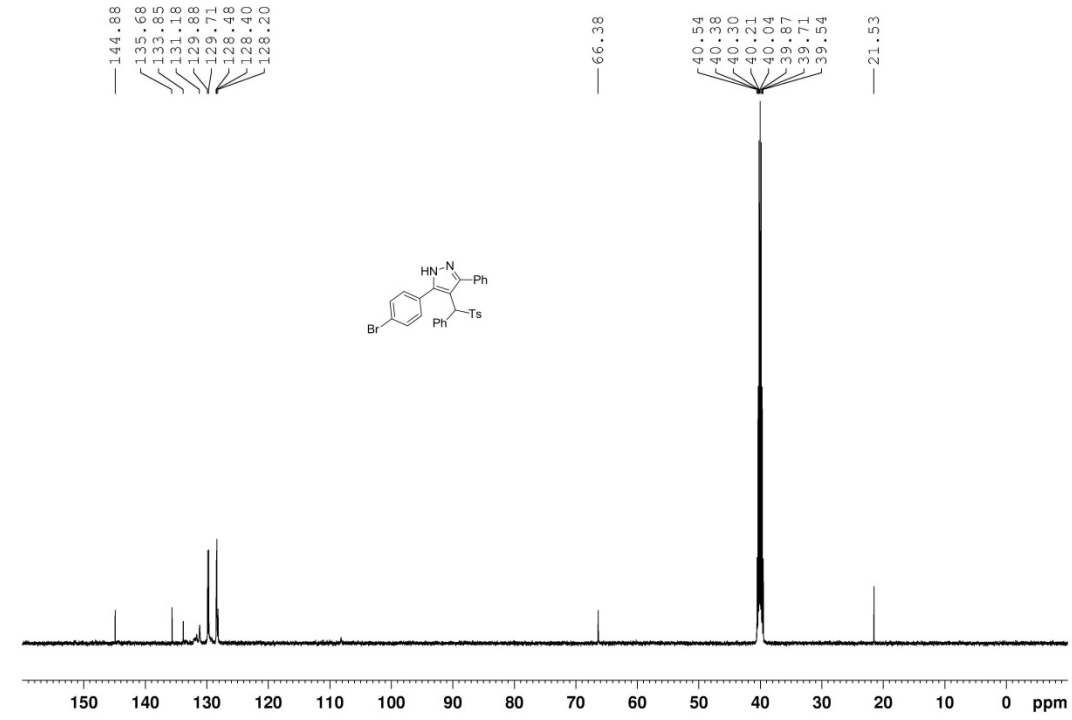


5-(4-Bromo-phenyl)-3-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2g**)

500 MHz, CDCl3

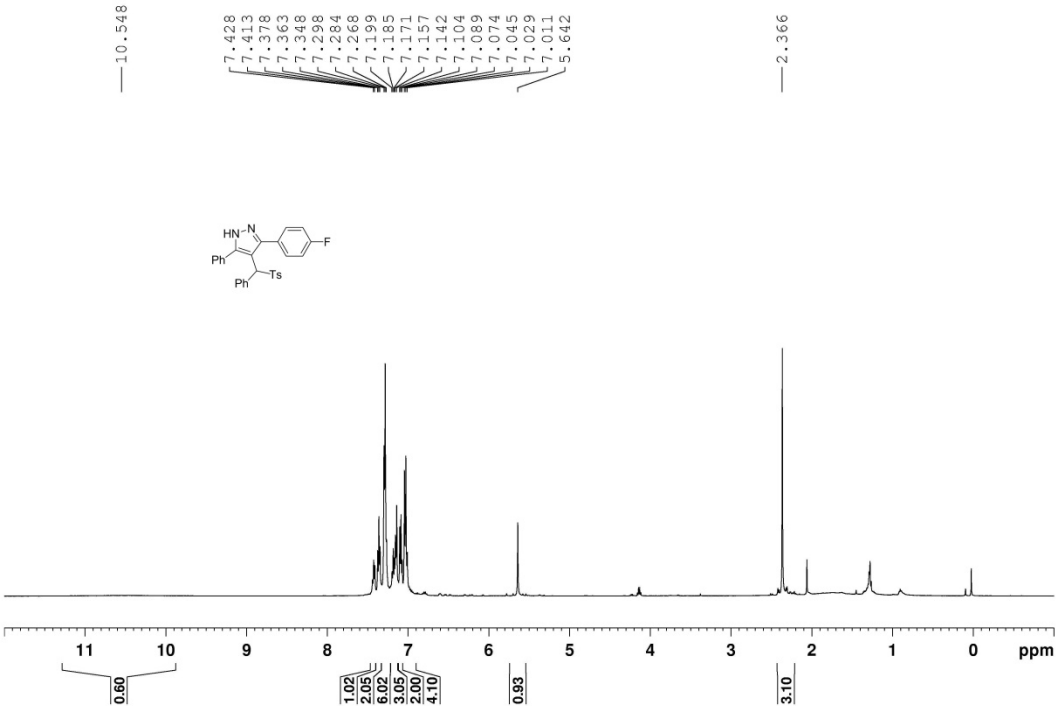


125 MHz, d6-DMSO

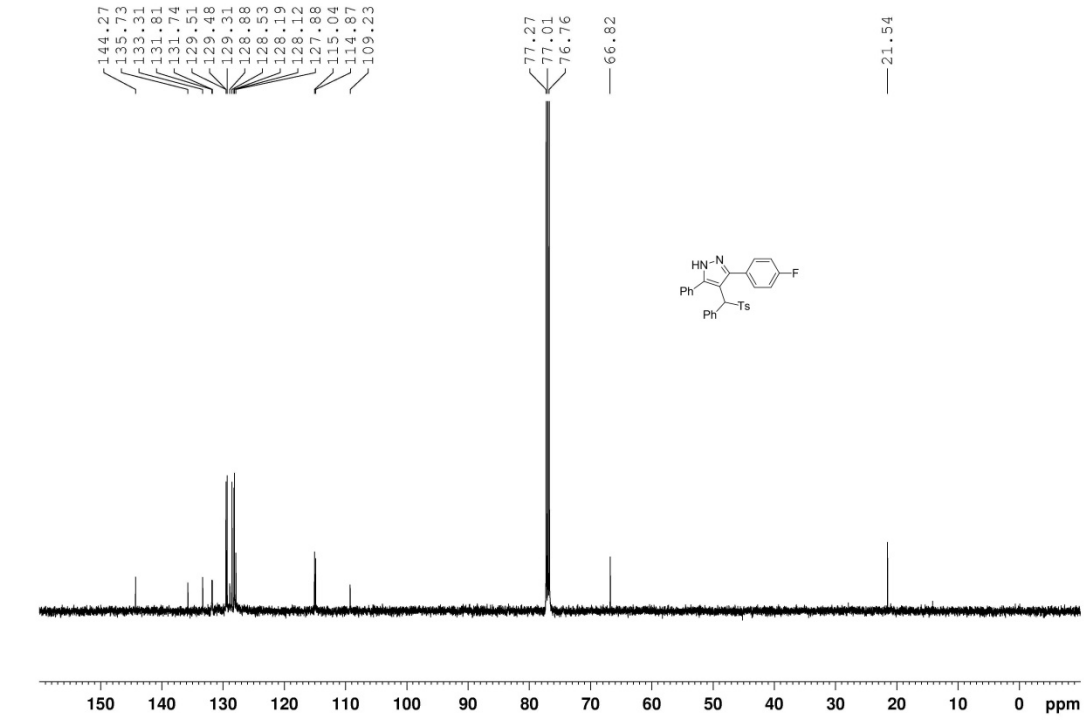


3-(4-Fluoro-phenyl)-5-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2h**)

500 MHz, CDCl3

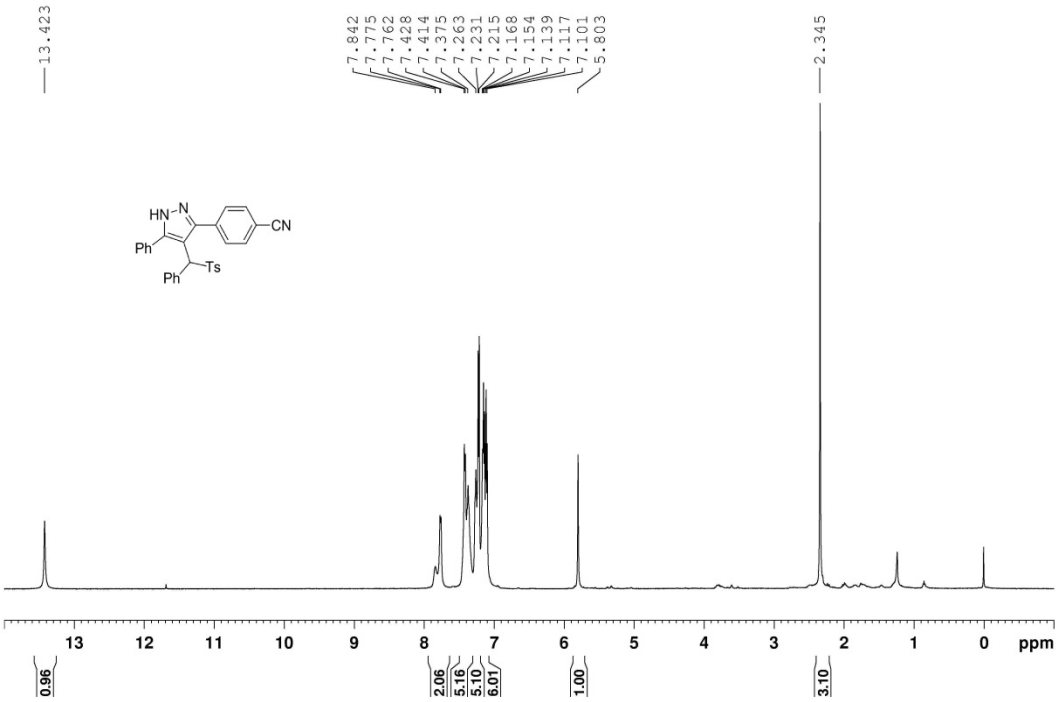


125 MHz, CDCl3

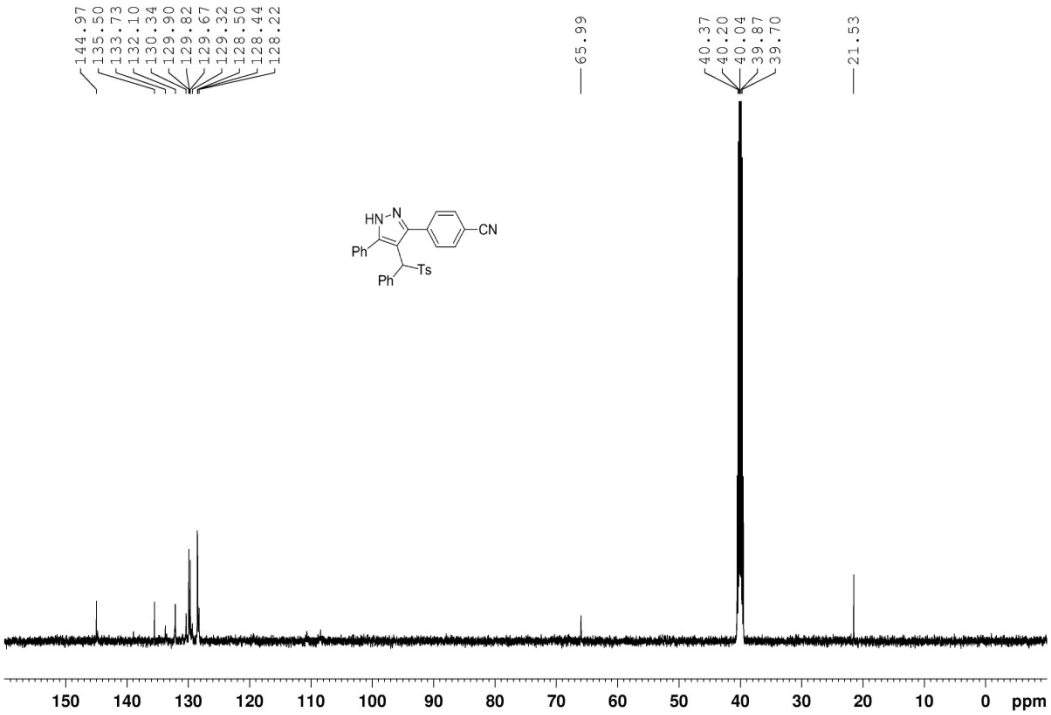


4-{5-Phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazol-3-yl}-benzonitrile (**2i**)

500 MHz, d6-DMSO

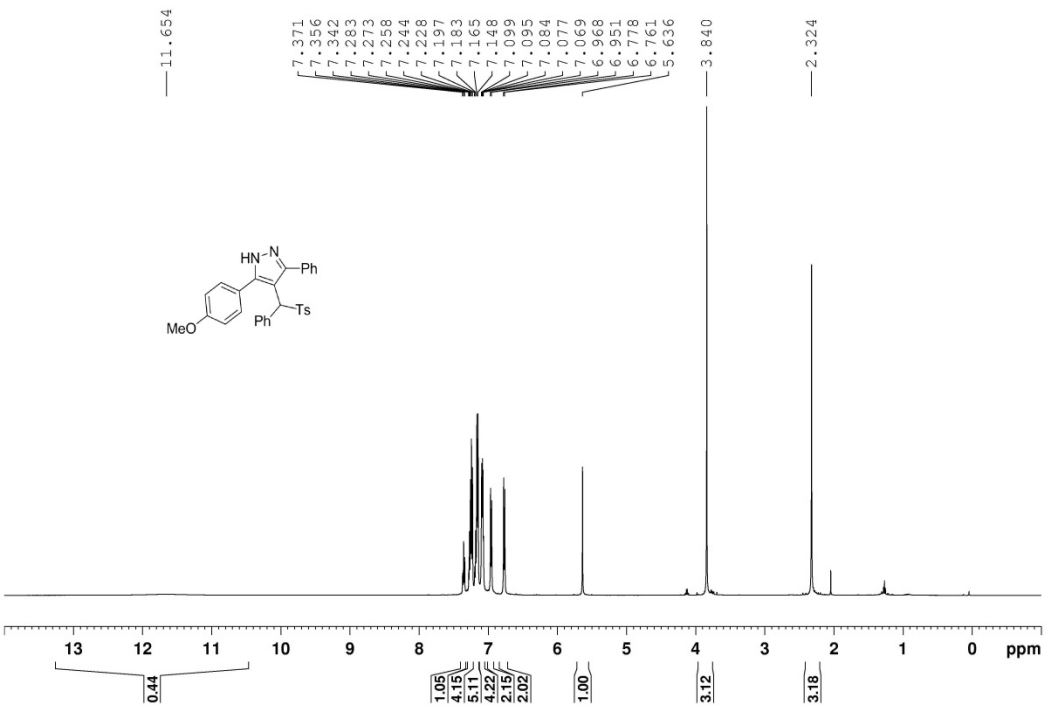


125 MHz, d6-DMSO

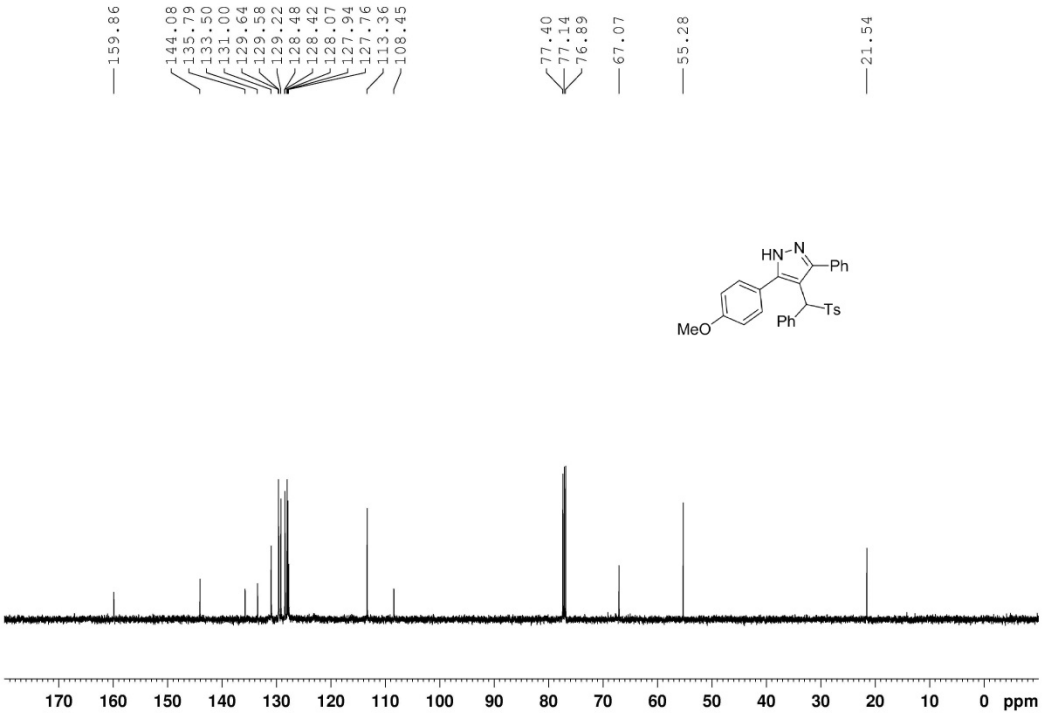


5-(4-Methoxy-phenyl)-3-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2j**)

500 MHz, CDCl3

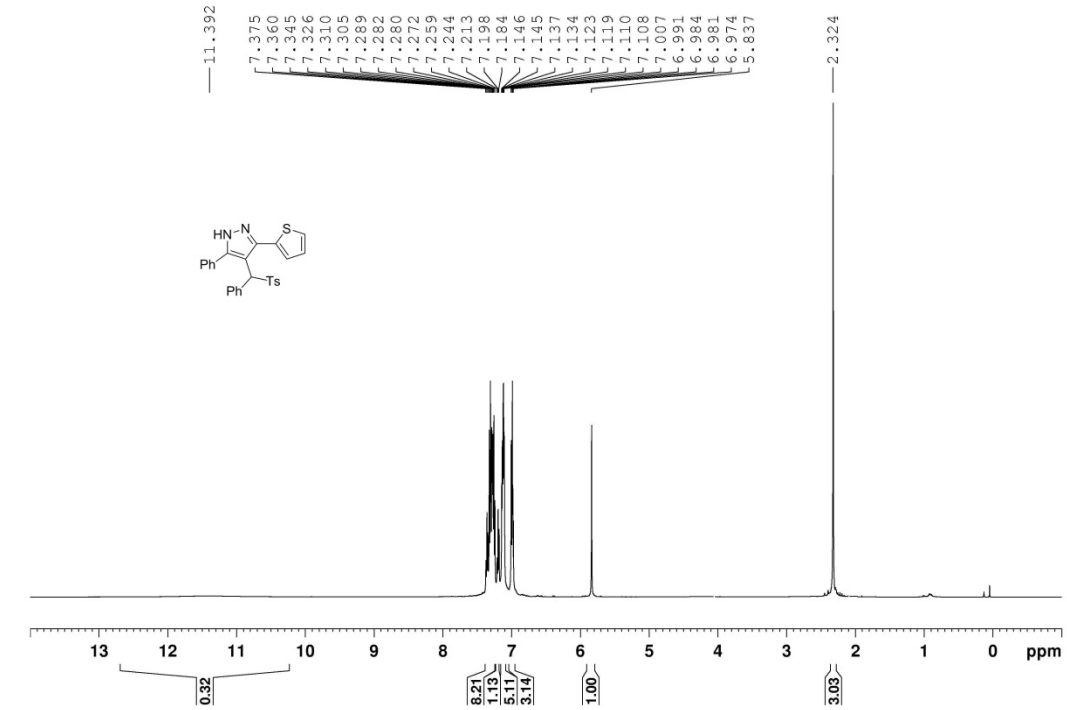


125 MHz, CDCl3

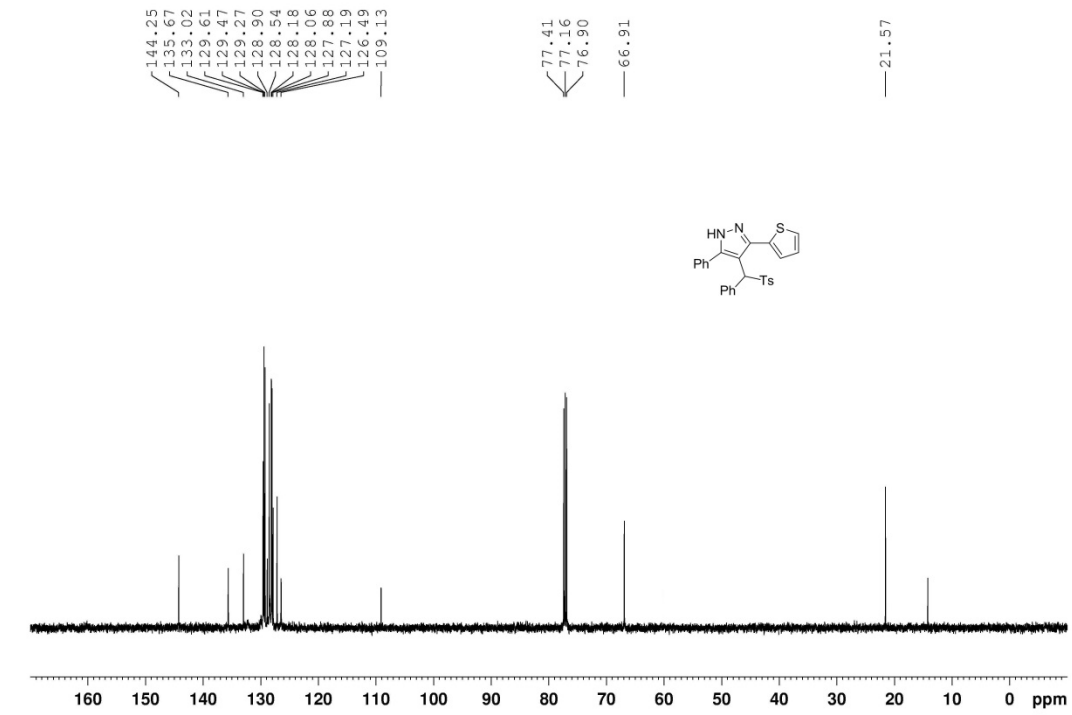


5-Phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-3-thiophen-2-yl-1H-pyrazole (**2k**)

500 MHz, CDCl3

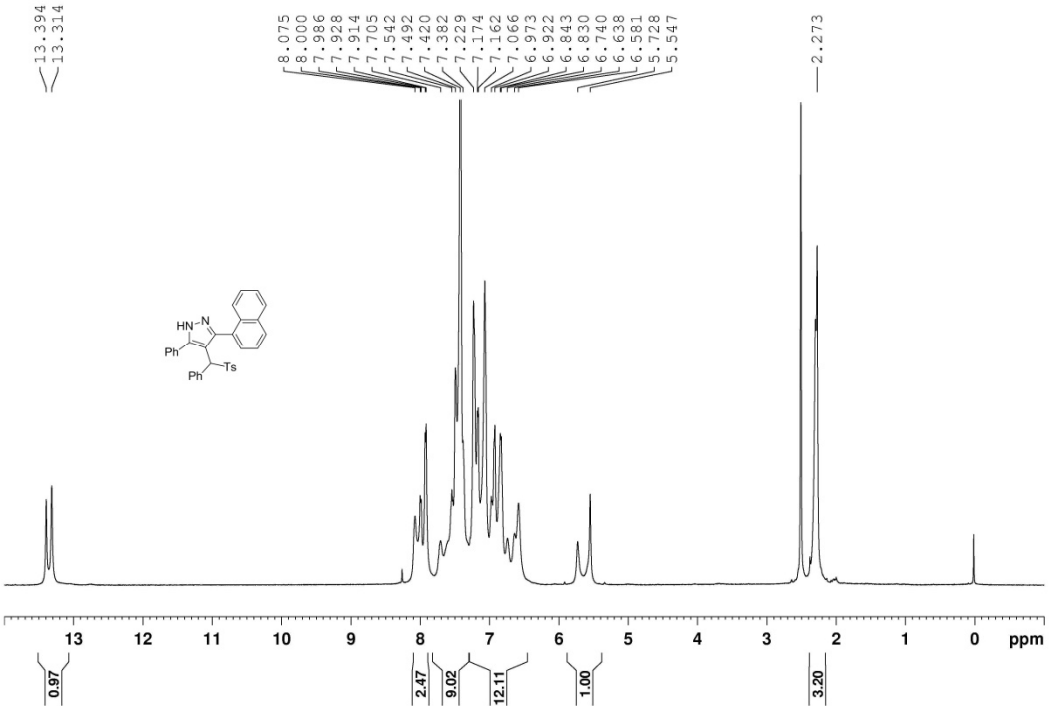


125 MHz, CDCl3

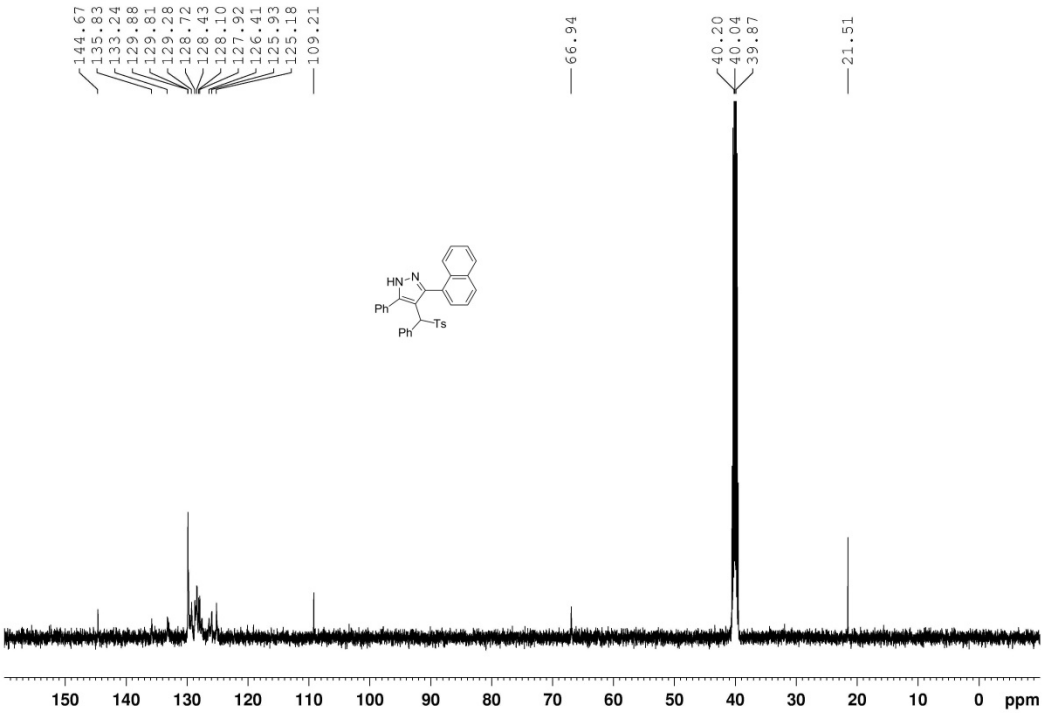


3-Naphthalen-1-yl-5-phenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**2l**)

500 MHz, d6-DMSO

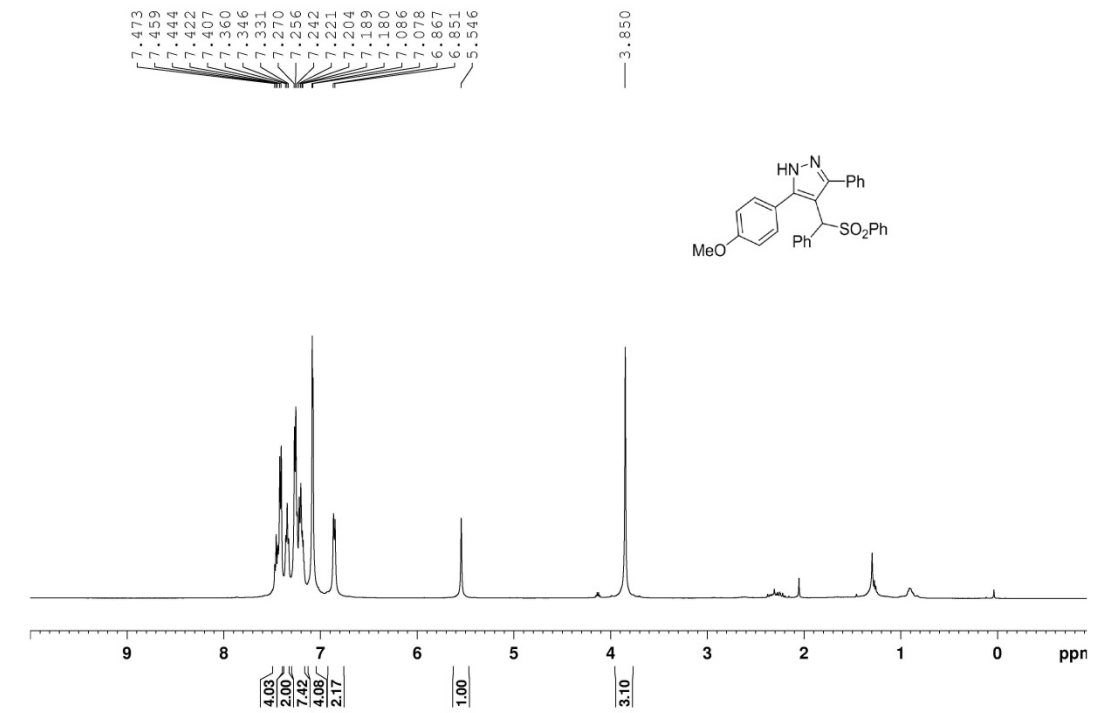


125 MHz, d6-DMSO

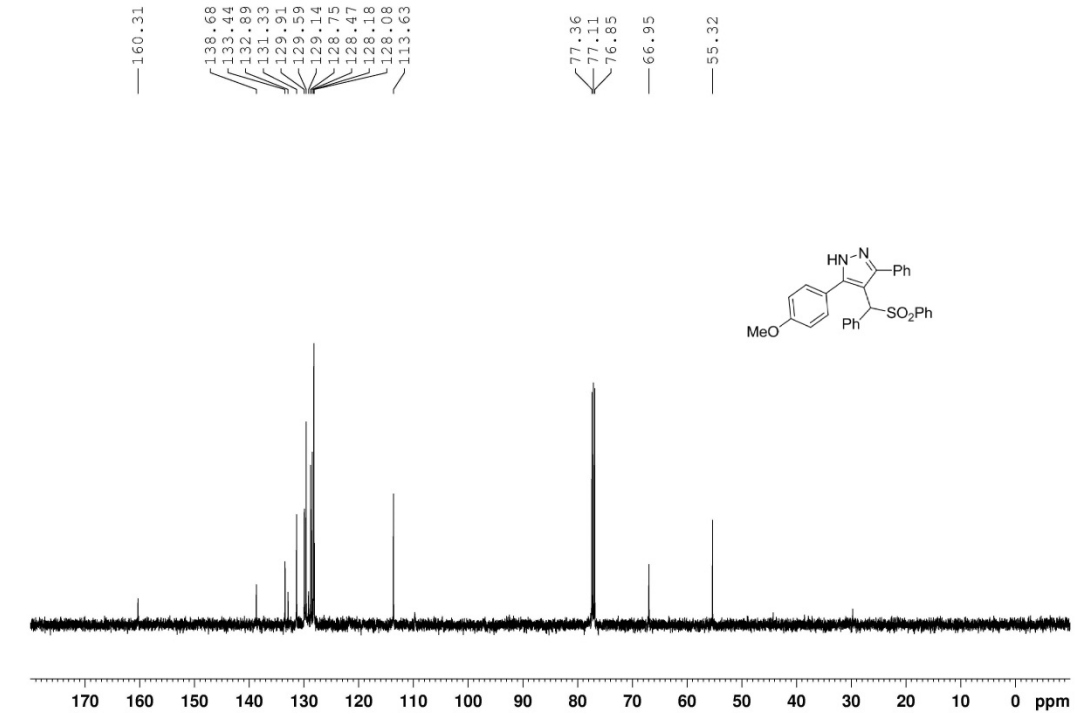


4-(Benzenesulfonyl-phenyl-methyl)-5-(4-methoxy-phenyl)-3-phenyl-1H-pyrazole (**2m**)

500 MHz, CDCl3

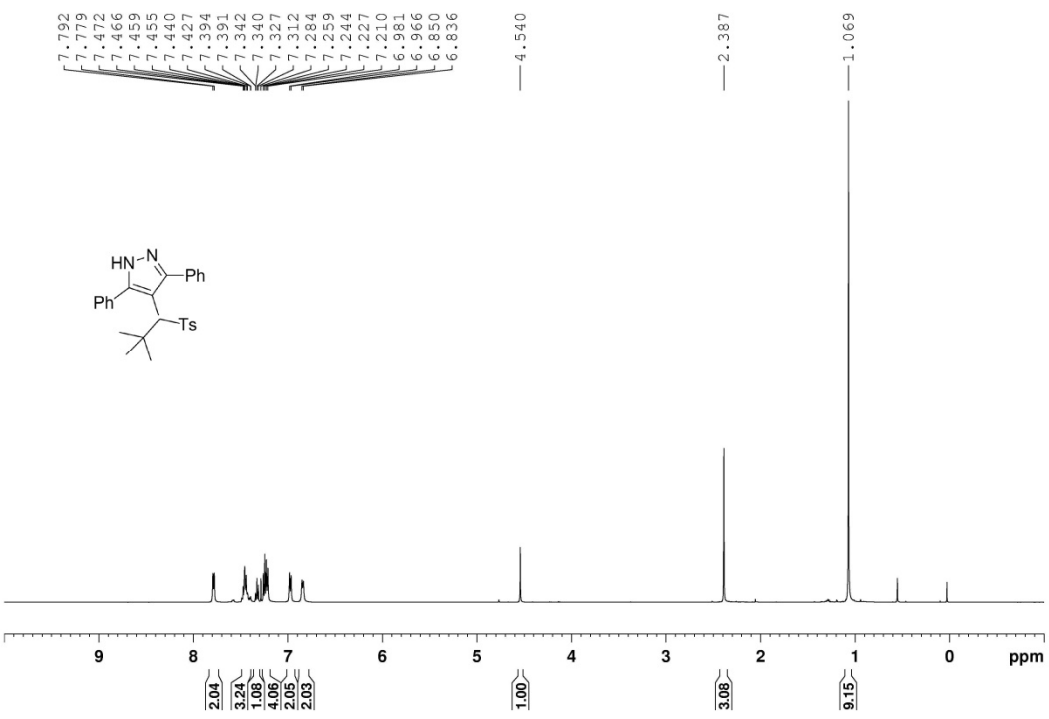


125 MHz, CDCl3



4-[2,2-Dimethyl-1-(toluene-4-sulfonyl)-propyl]-3,5-diphenyl-1H-pyrazole (**2n**)

500 MHz, CDCl3



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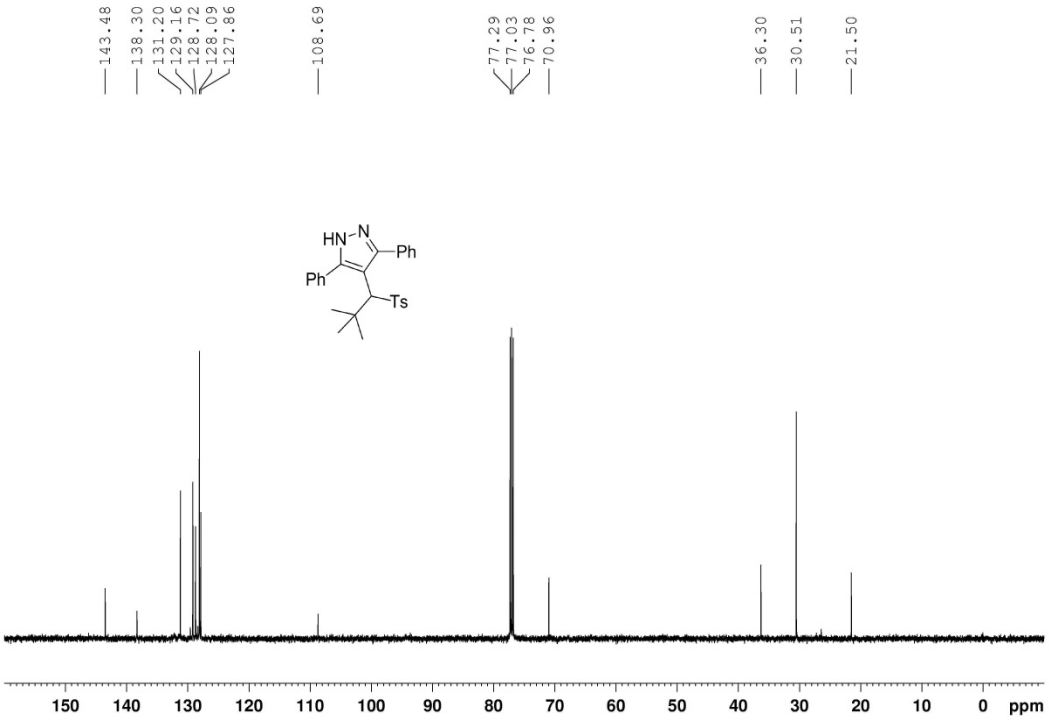
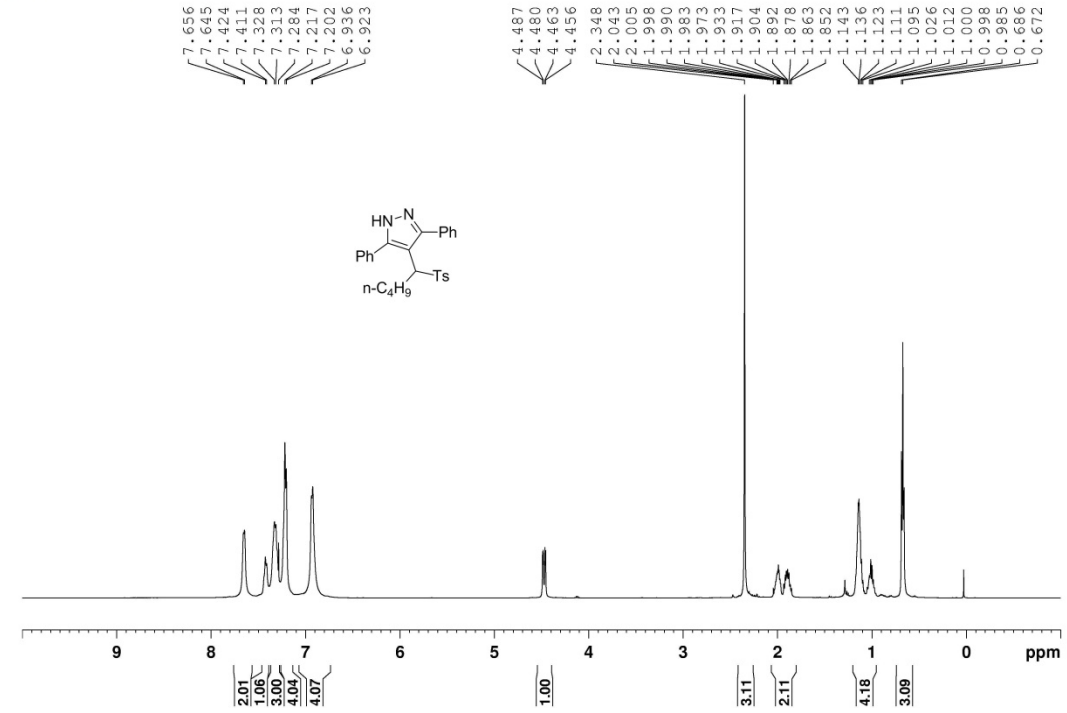


3,5-Diphenyl-4-[1-(toluene-4-sulfonyl)-pentyl]-1H-pyrazole (**2o**)

500 MHz, CDCl3



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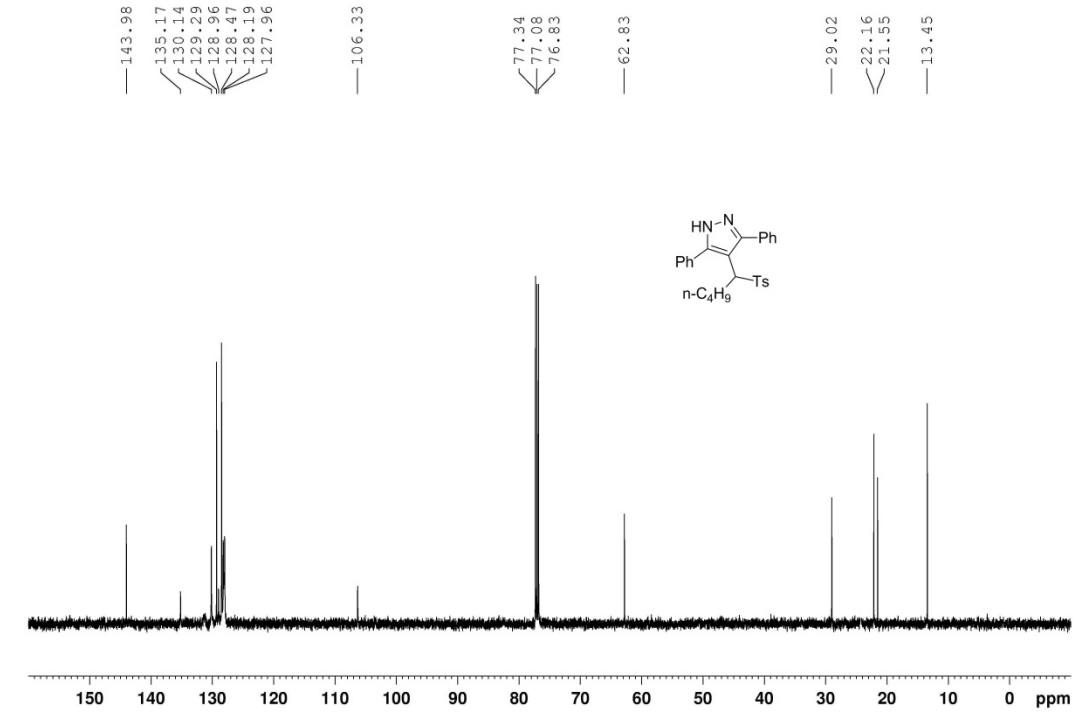
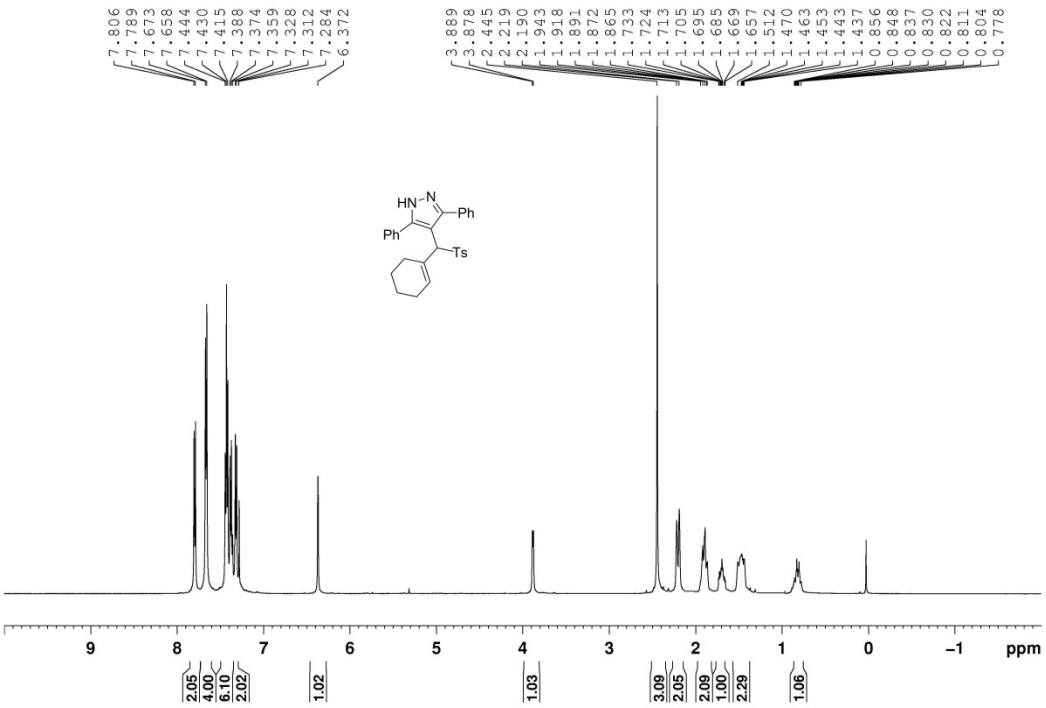


4-[Cyclohex-1-enyl-(toluene-4-sulfonyl)-methyl]-3,5-diphenyl-1H-pyrazole (**2p**)

500 MHz, CDCl3



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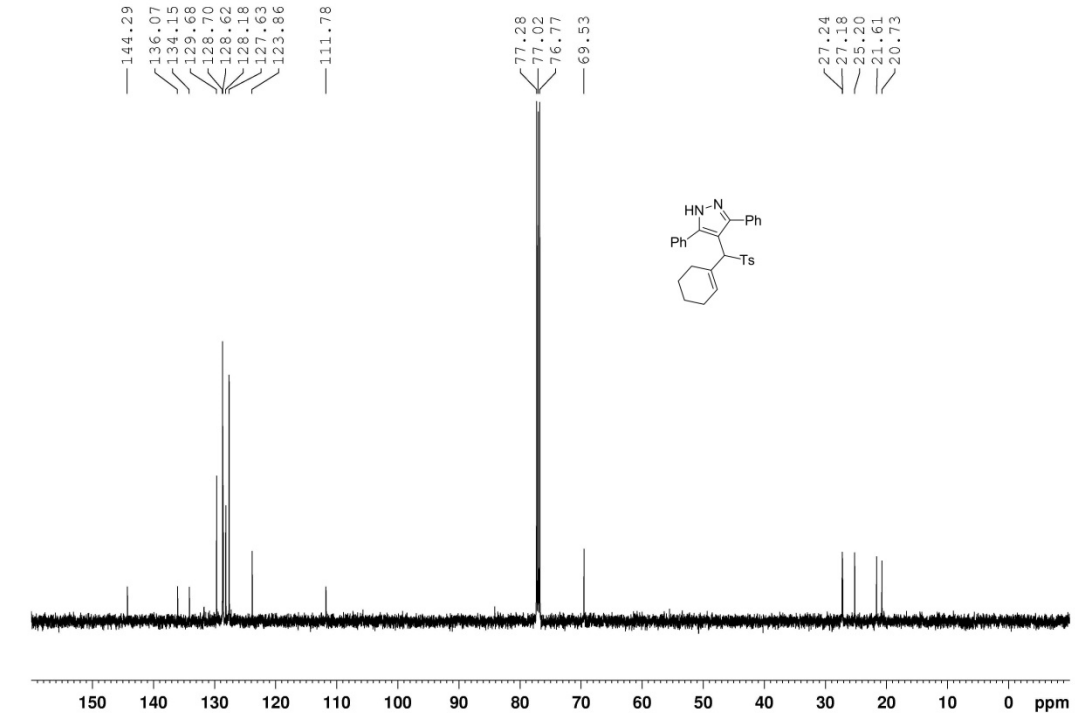
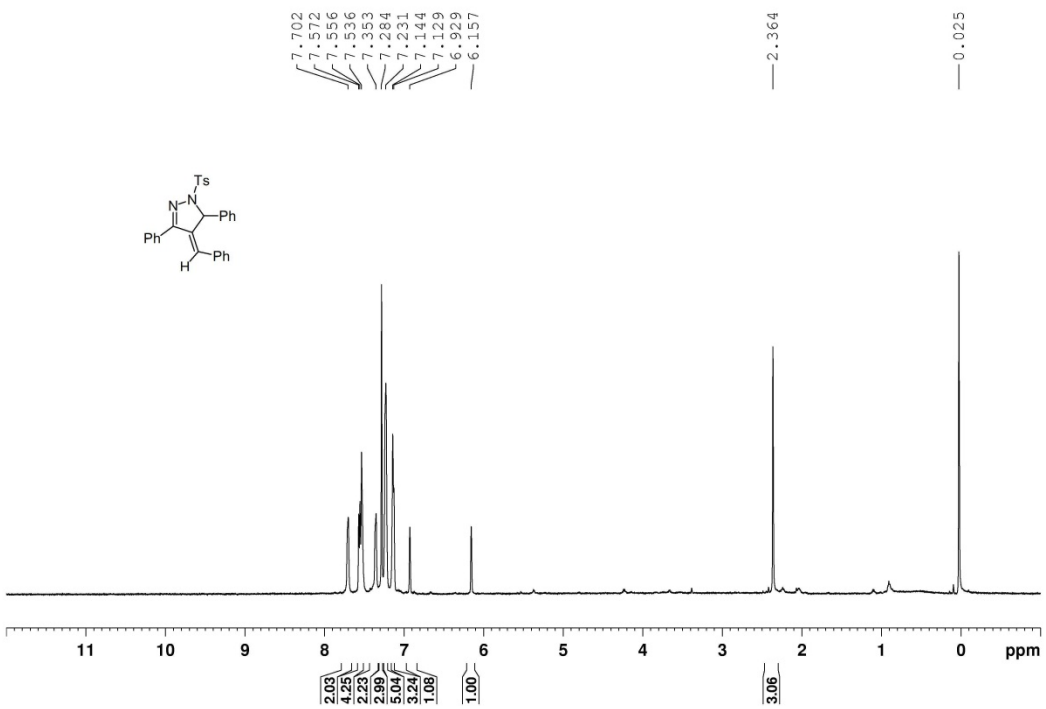
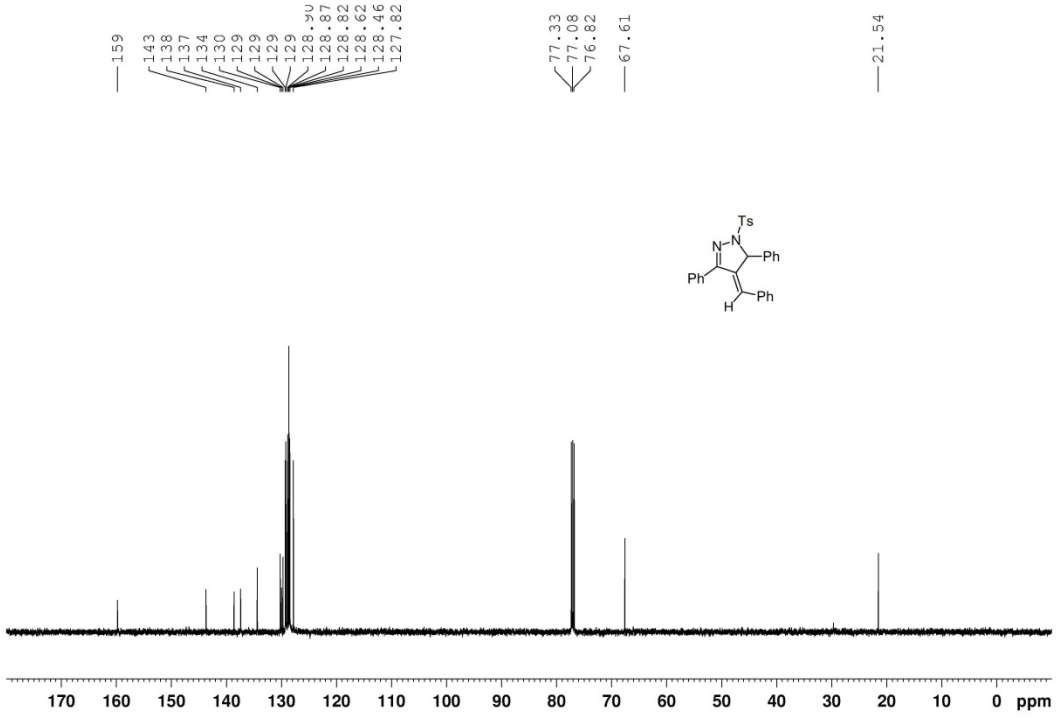


4-Benzylidene-3,5-diphenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3a**)

500 MHz, CDCl3

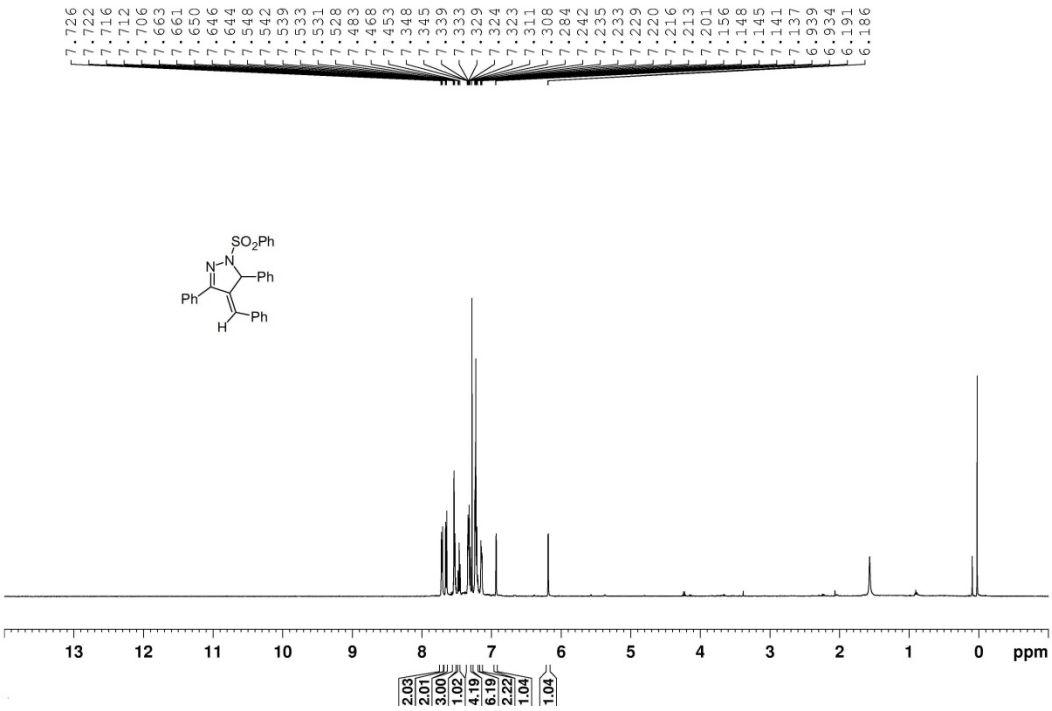


125 MHz, CDCl3

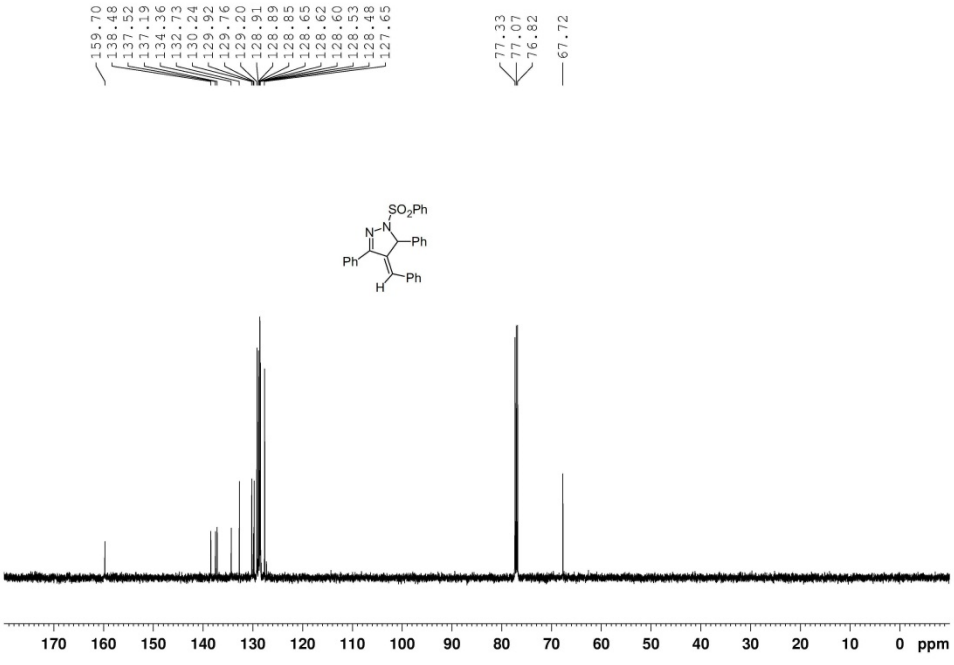


1-Benzenesulfonyl-4-benzylidene-3,5-diphenyl-4,5-dihydro-1H-pyrazole (**3b**)

500 MHz, CDCl3

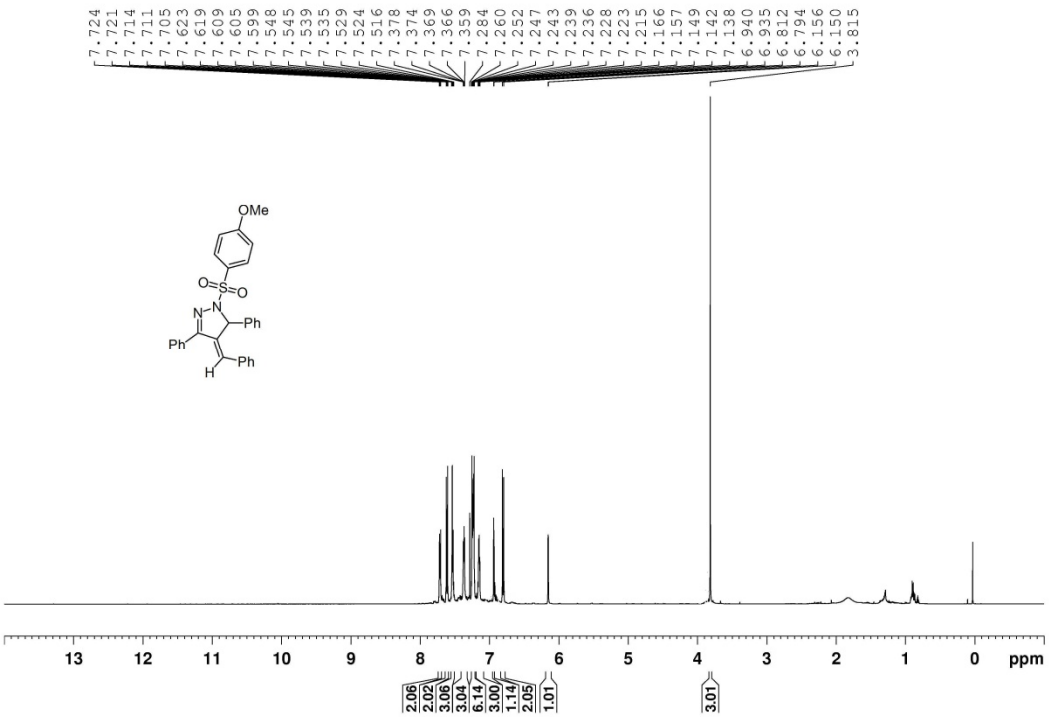


125 MHz, CDCl3

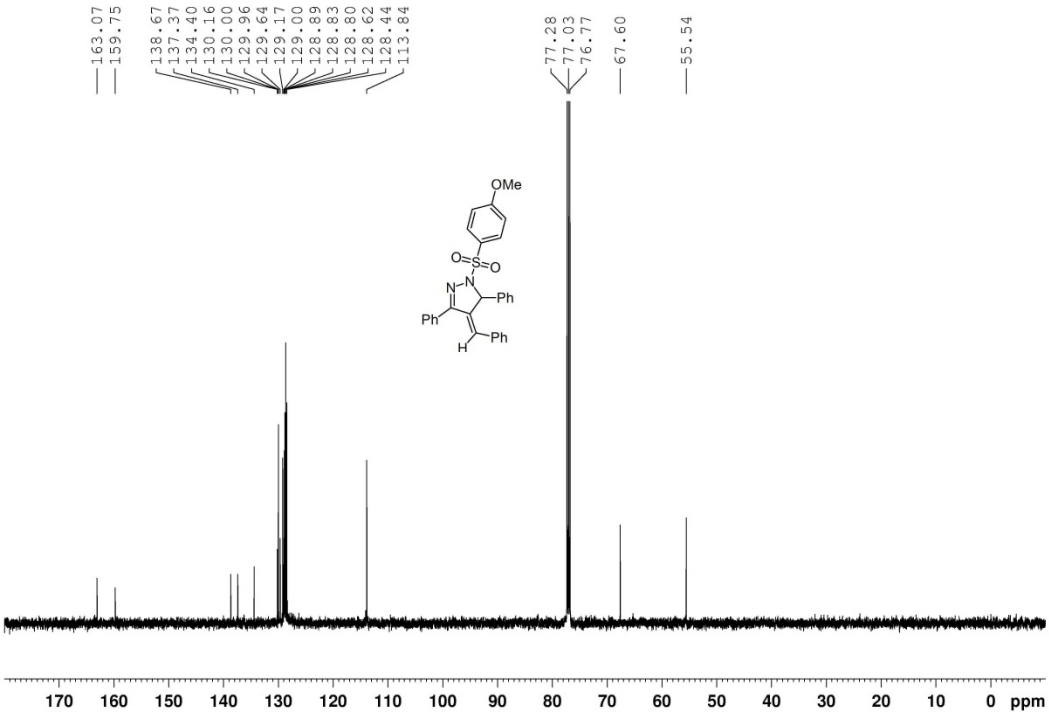


4-Benzylidene-1-(4-methoxy-benzenesulfonyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (**3c**)

500 MHz, CDCl3

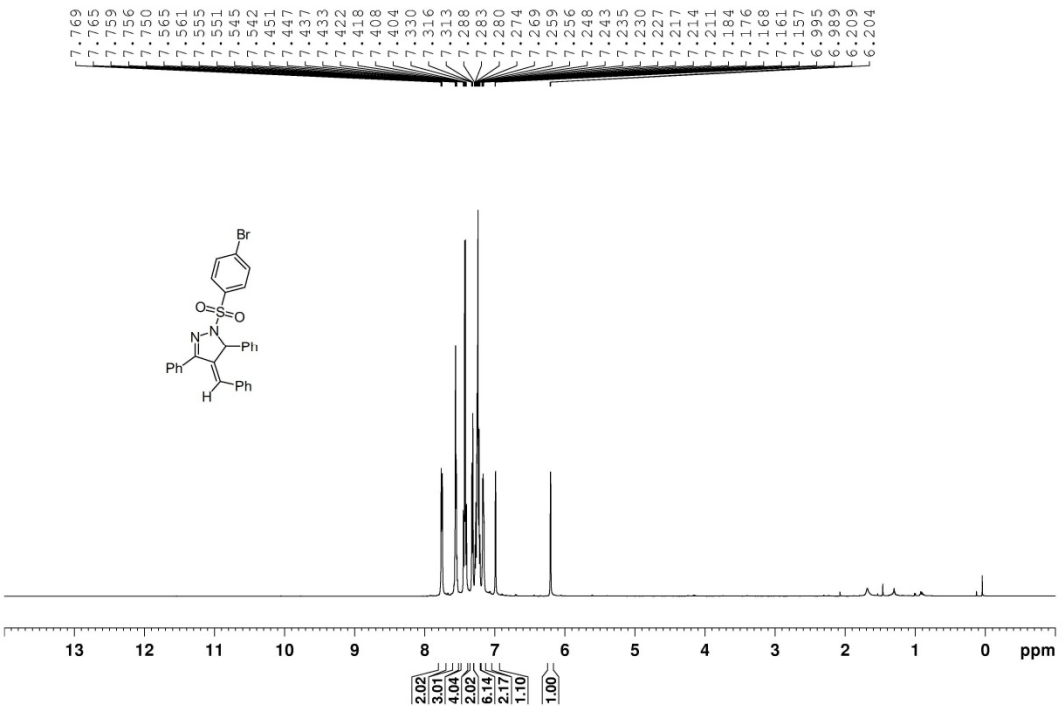


125 MHz, CDCl3

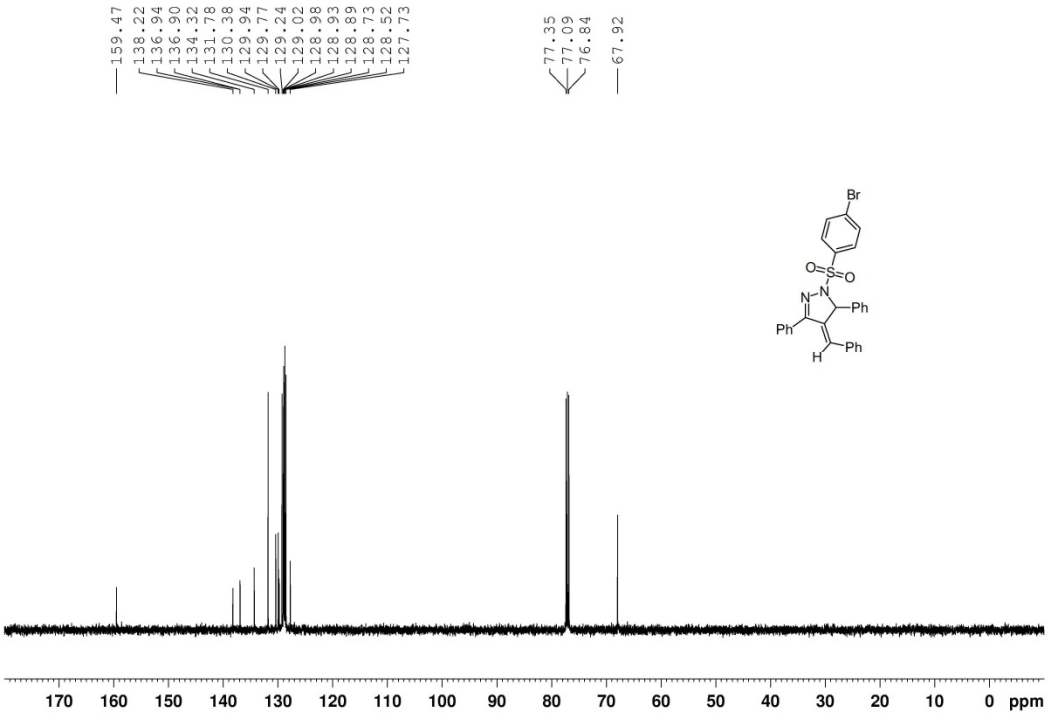


4-Benzylidene-1-(4-bromo-benzenesulfonyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (**3d**)

500 MHz, CDCl3

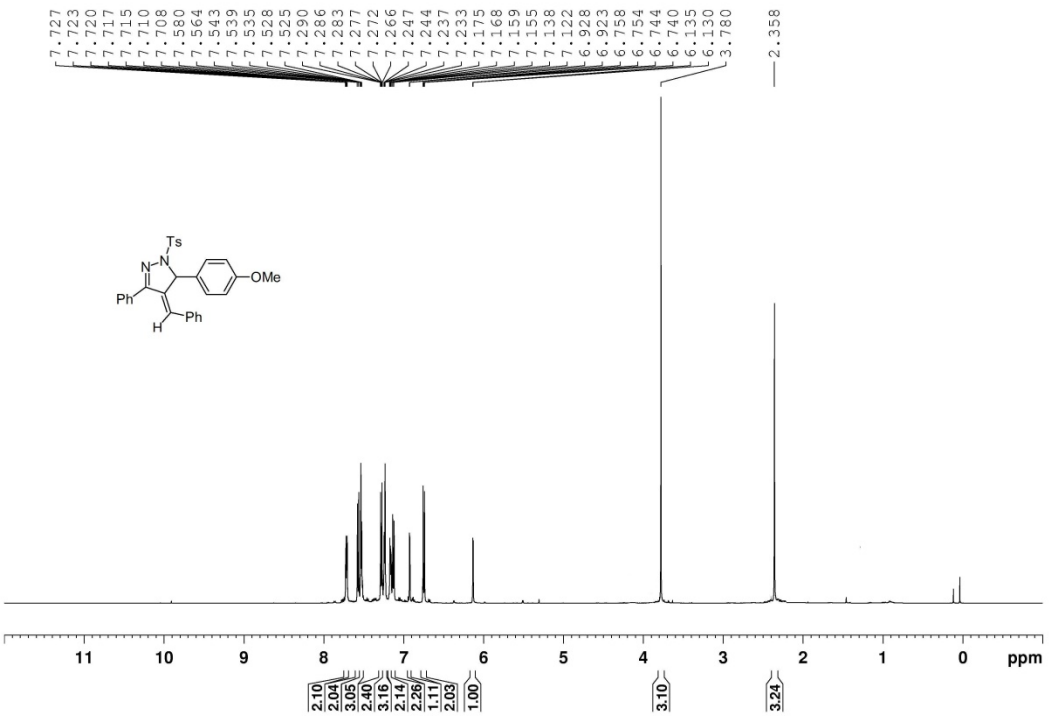


125 MHz, CDCl3

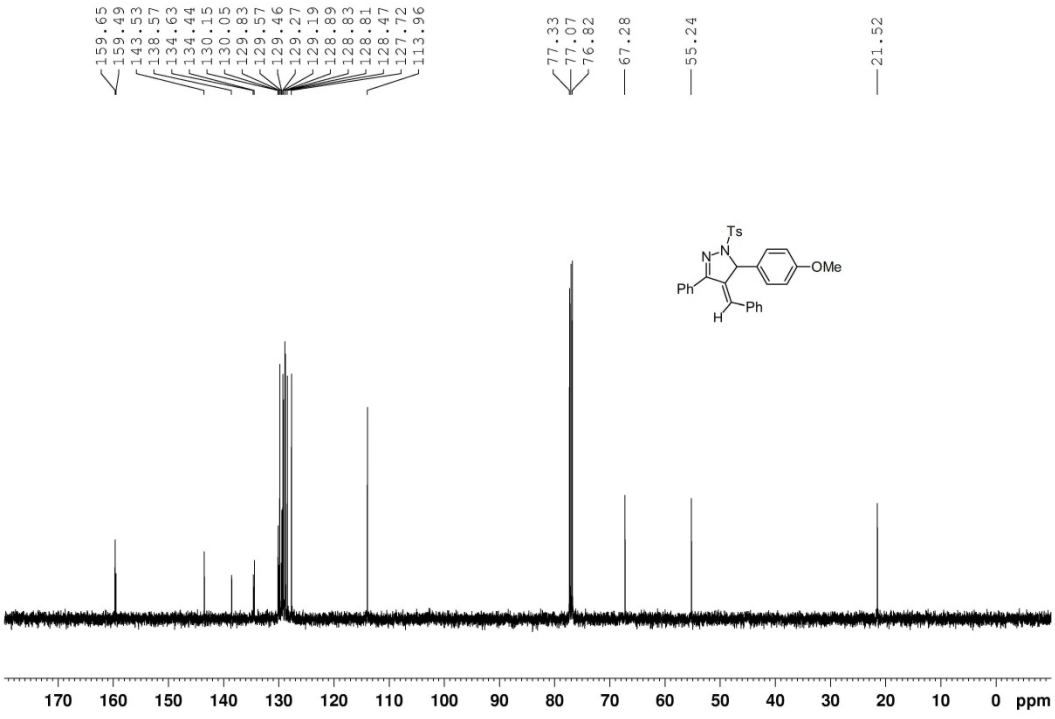


4-Benzylidene-5-(4-methoxy-phenyl)-3-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3f**)

500 MHz, CDCl3

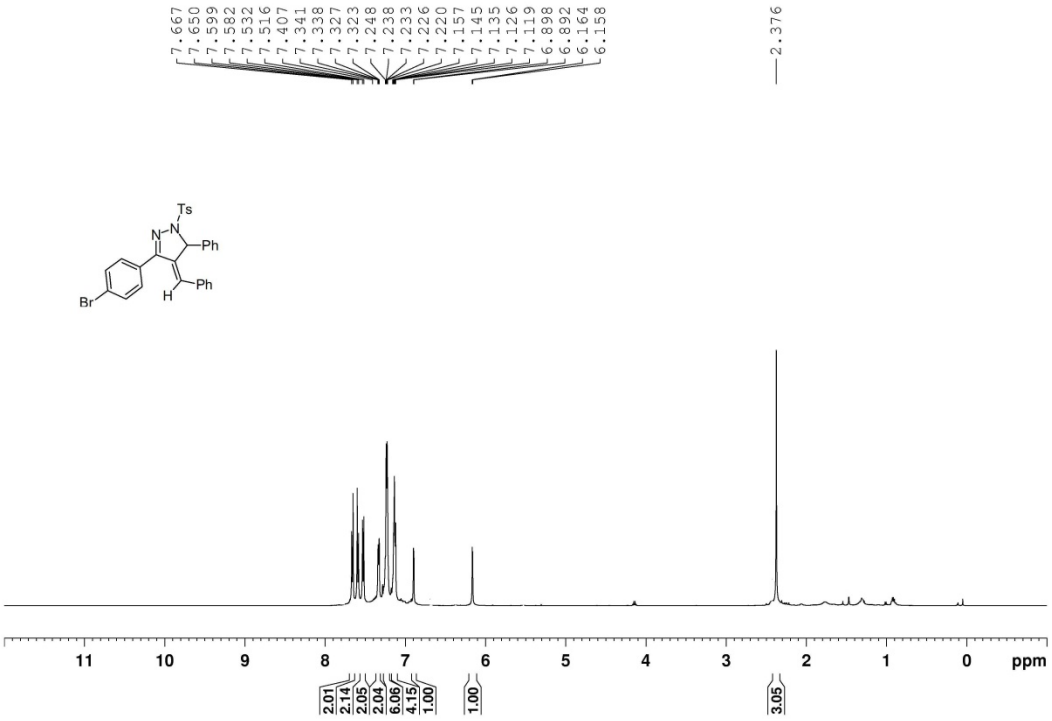


125 MHz, CDCl3

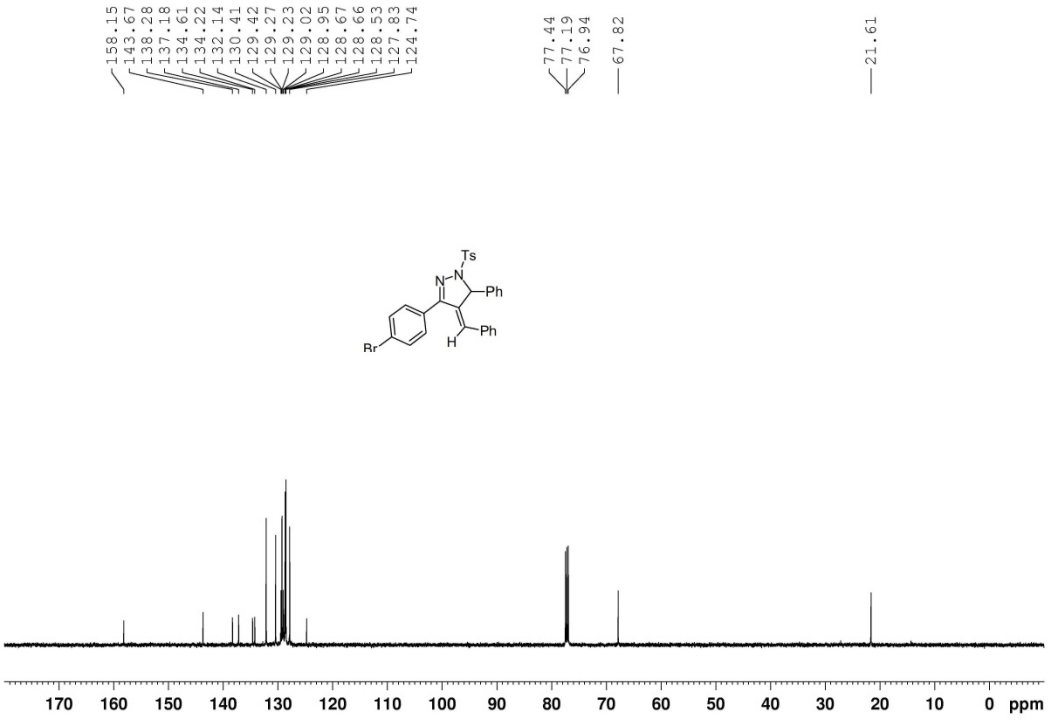


4-Benzylidene-3-(4-bromo-phenyl)-5-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3g**)

500 MHz, CDCl3

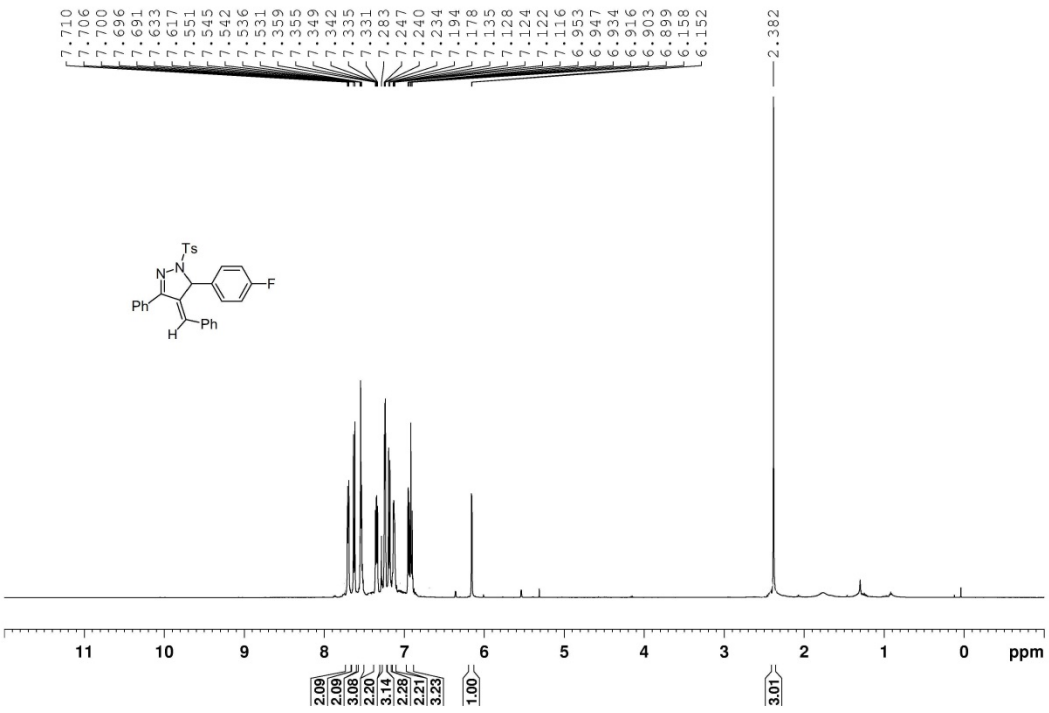


125 MHz, CDCl3

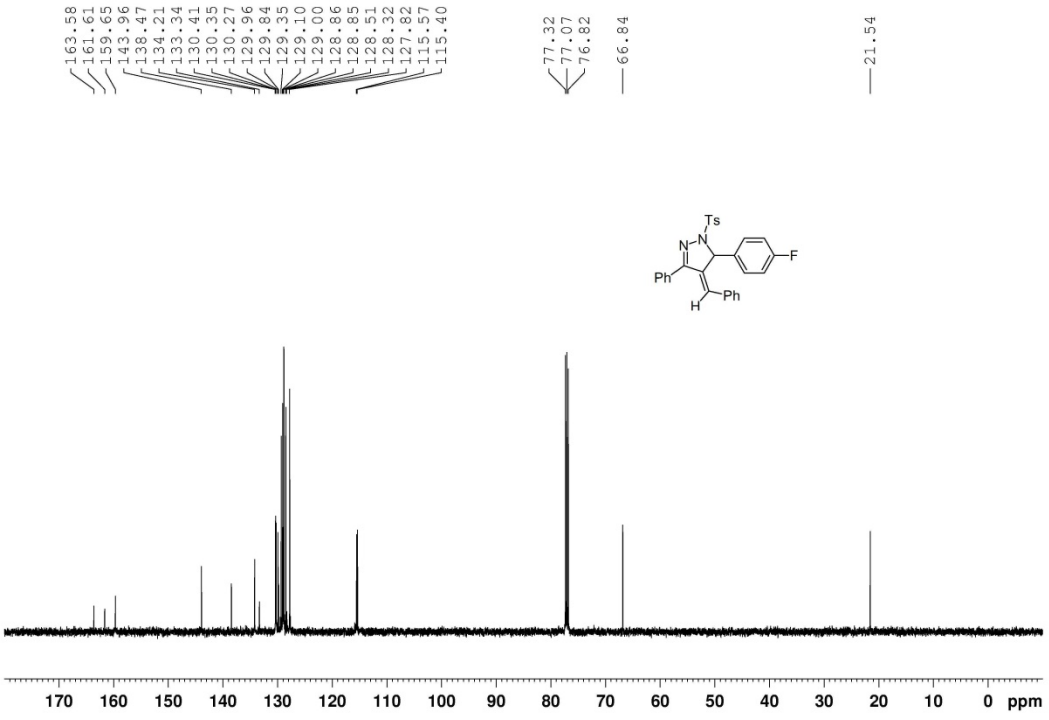


4-Benzylidene-5-(4-fluoro-phenyl)-3-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3h**)

500 MHz, CDCl3

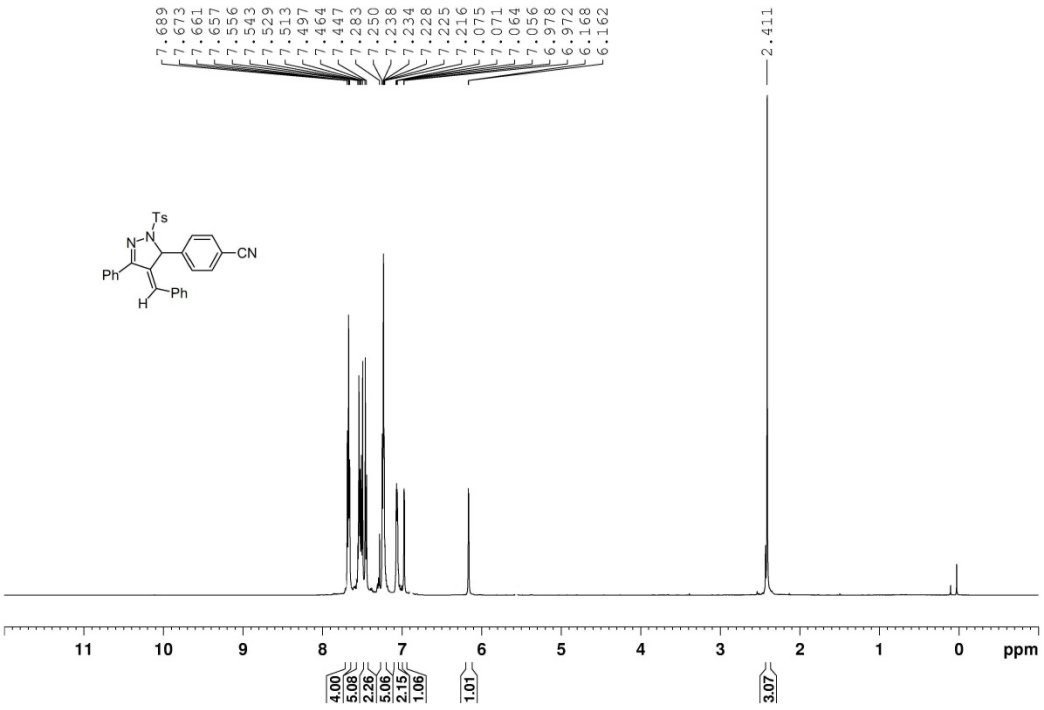


125 MHz, CDCl3

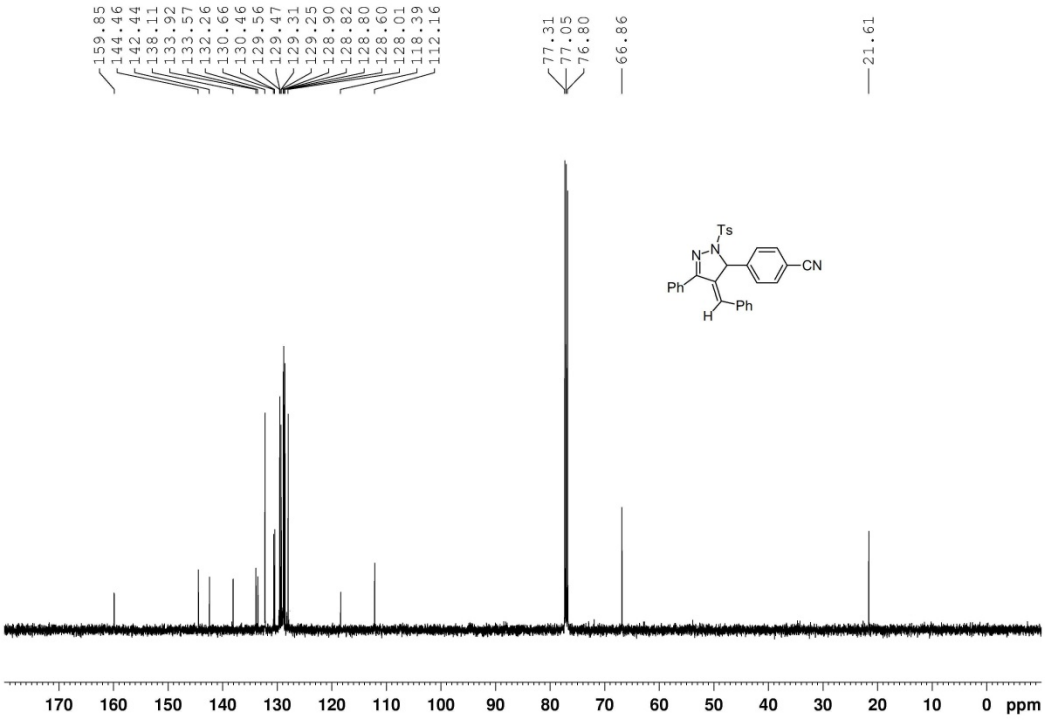


4-[4-Benzylidene-5-phenyl-2-(toluene-4-sulfonyl)-3,4-dihydro-2H-pyrazol-3-yl]-benzonitrile (**3i**)

500 MHz, CDCl3

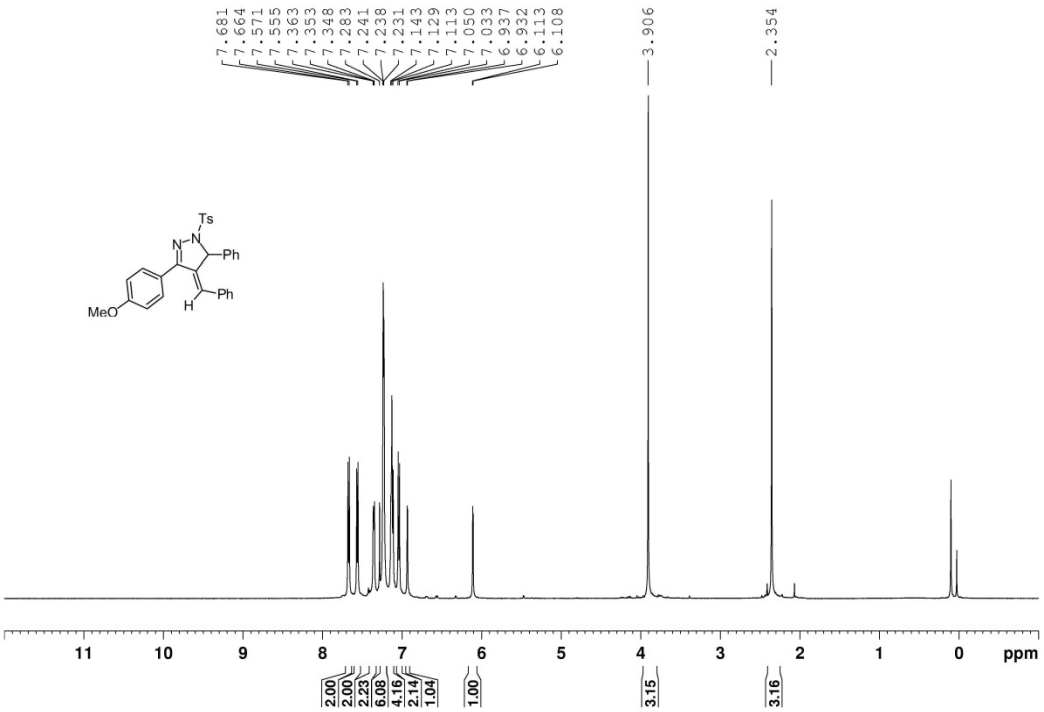


125 MHz, CDCl3

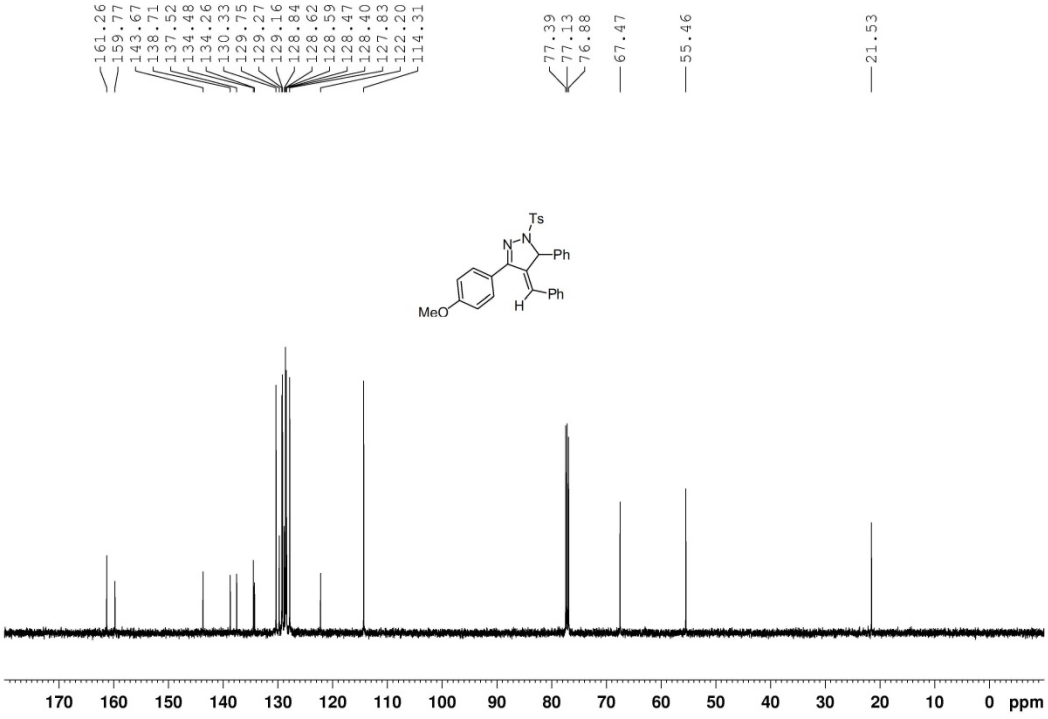


4-Benzylidene-3-(4-methoxy-phenyl)-5-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3j**)

500 MHz, CDCl3

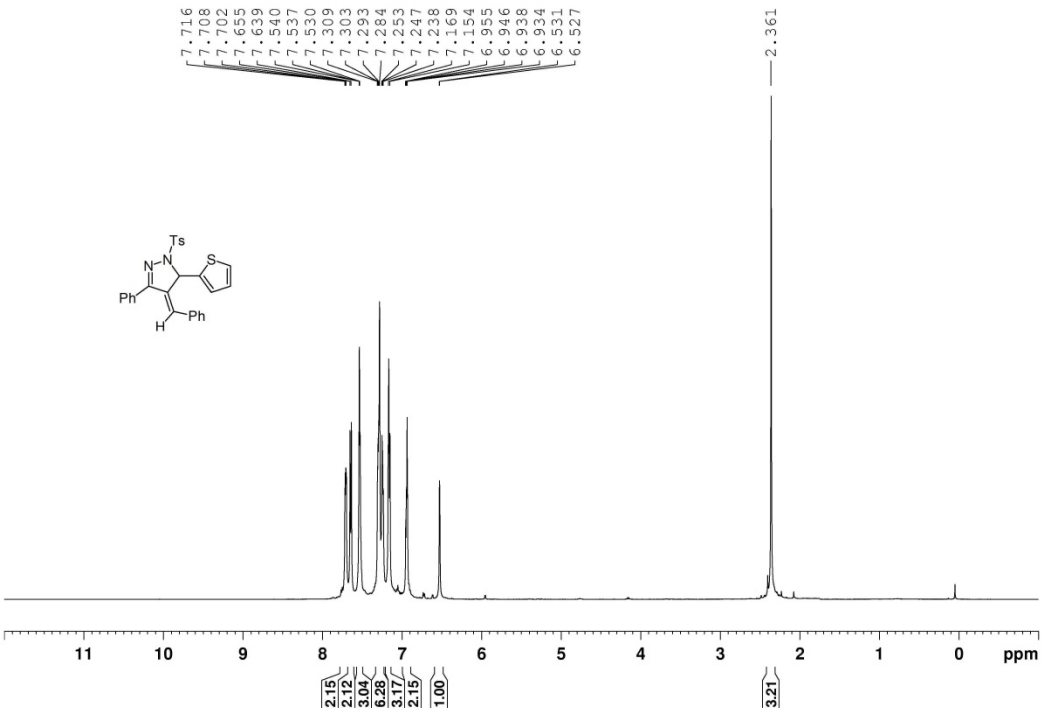


125 MHz, CDCl3

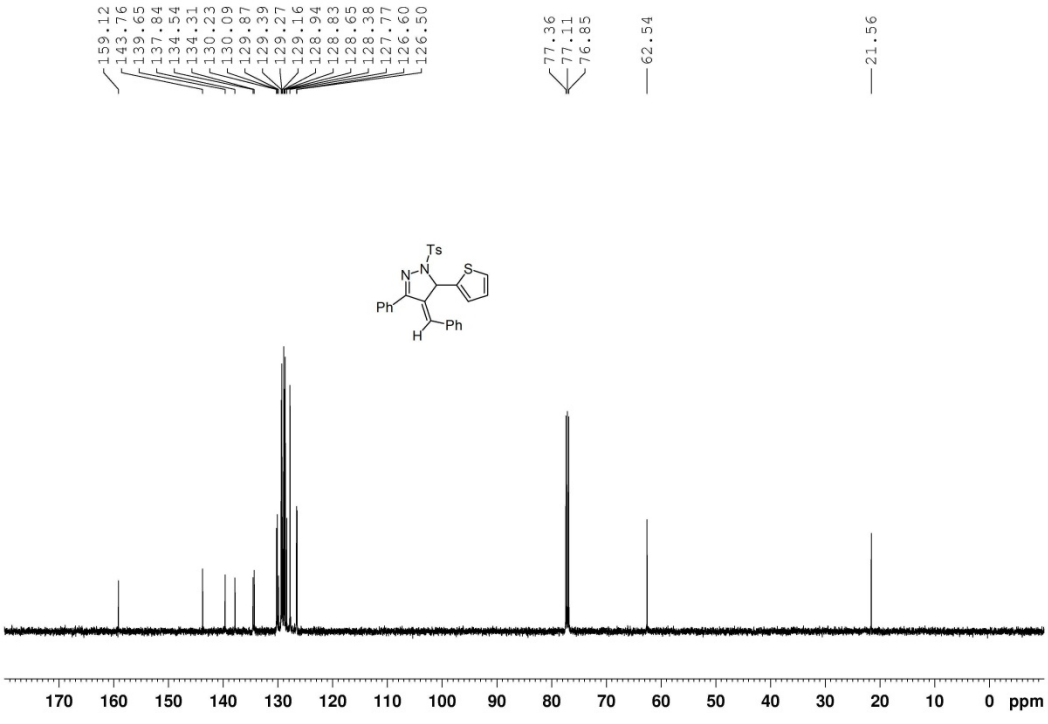


4-Benzylidene-3-phenyl-5-thiophen-2-yl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3k**)

500 MHz, CDCl3

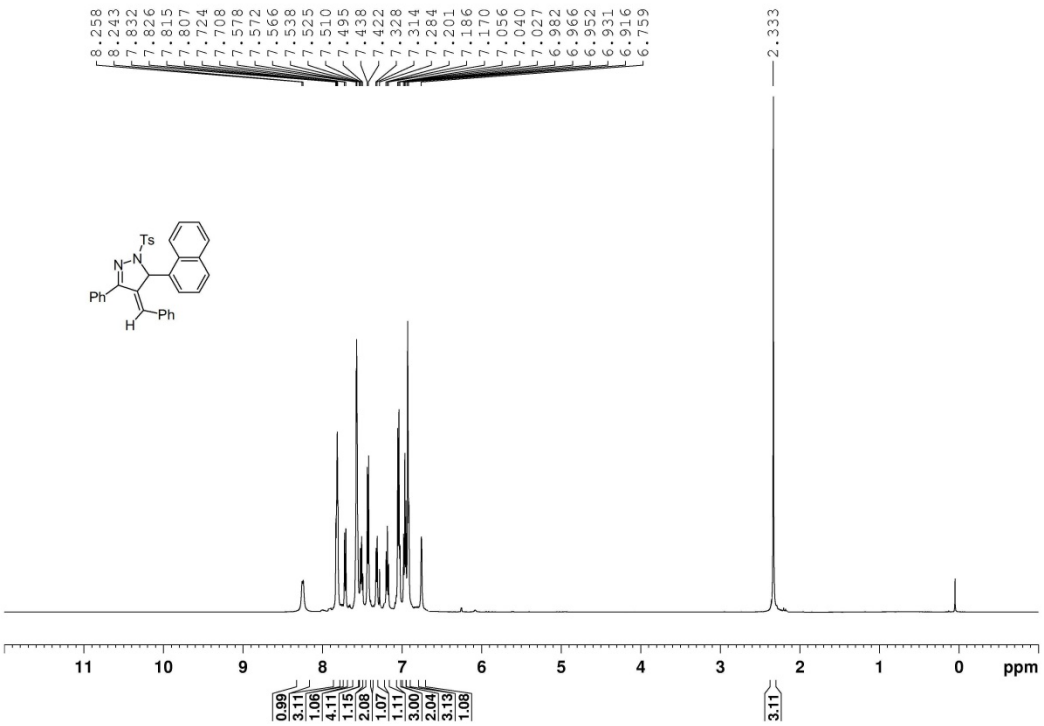


125 MHz, CDCl3



4-Benzylidene-5-naphthalen-1-yl-3-phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1H-pyrazole (**3l**)

500 MHz, CDCl3



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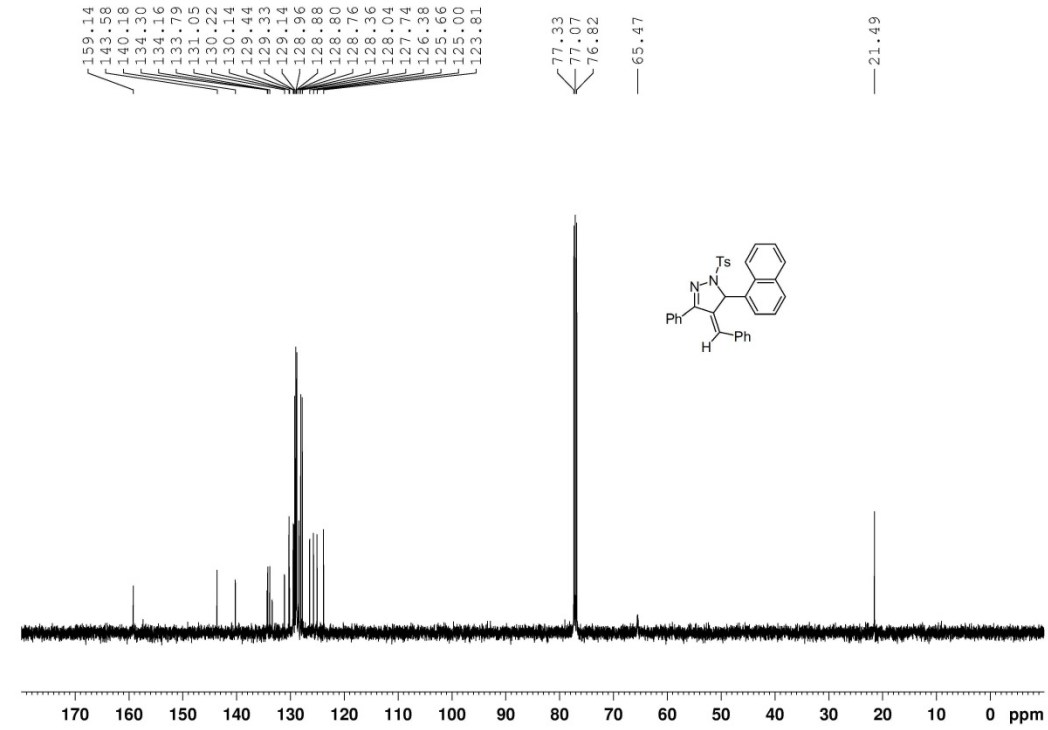
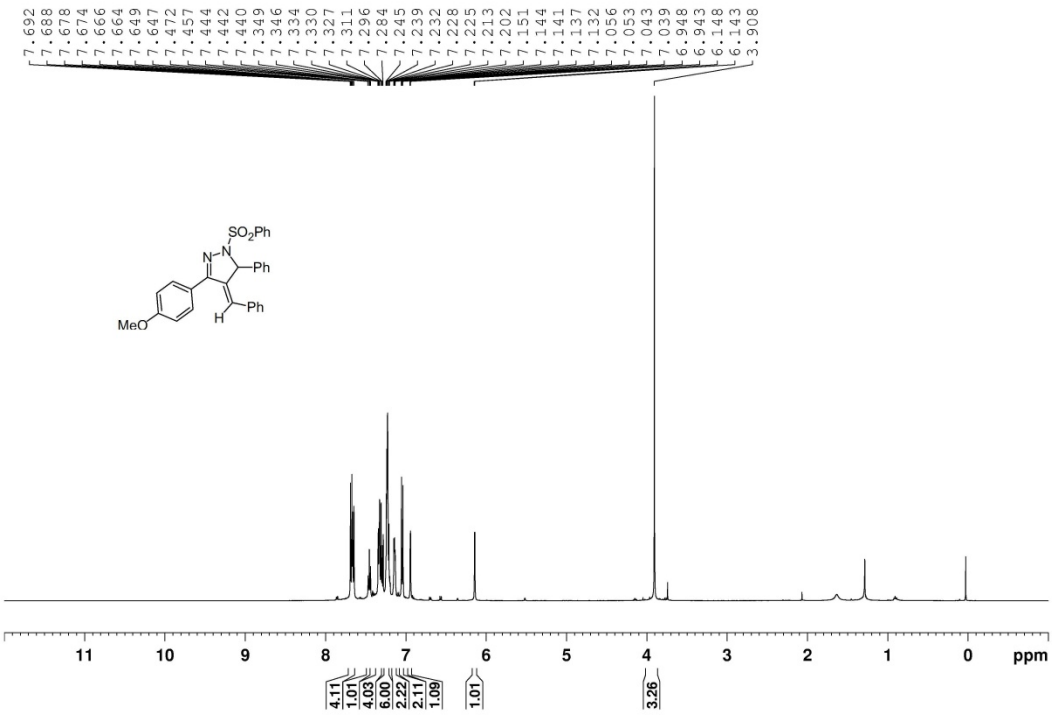


1-Benzenesulfonyl-4-benzylidene-3-(4-methoxy-phenyl)-5-phenyl-4,5-dihydro-1H-pyrazole (**3m**)

500 MHz, CDCl3



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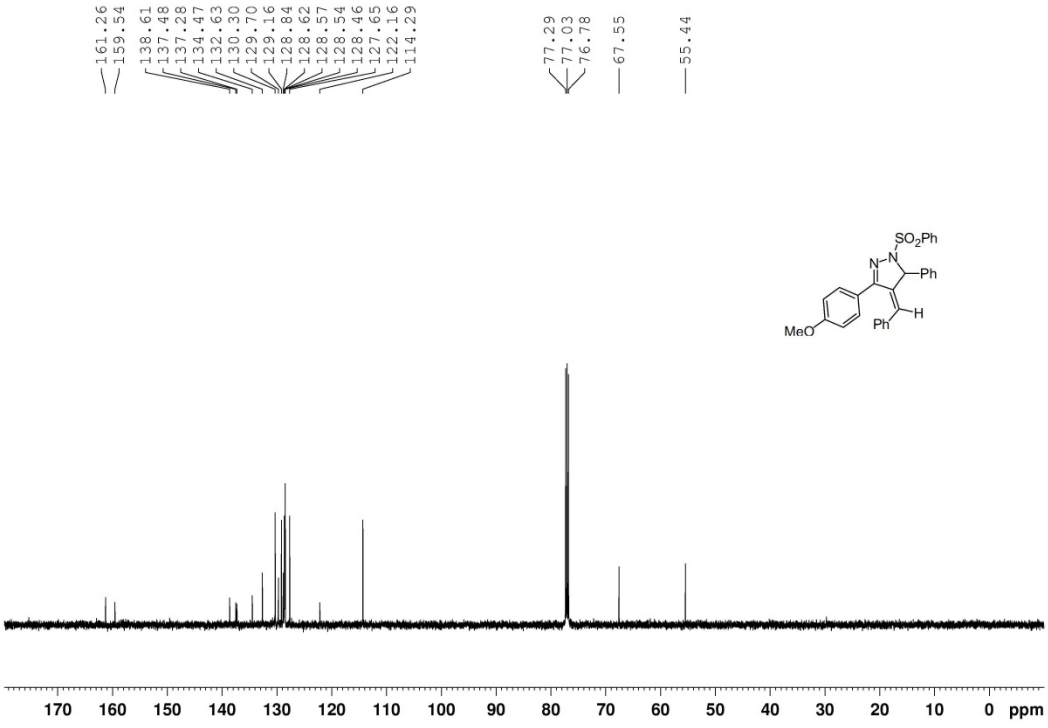
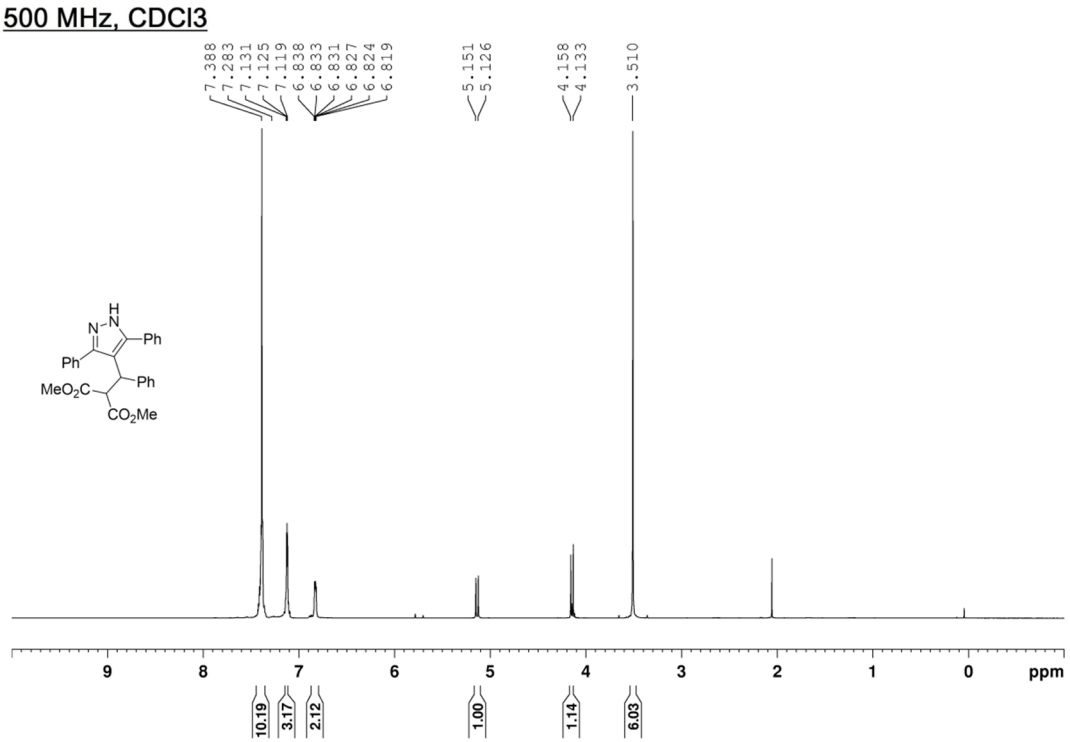
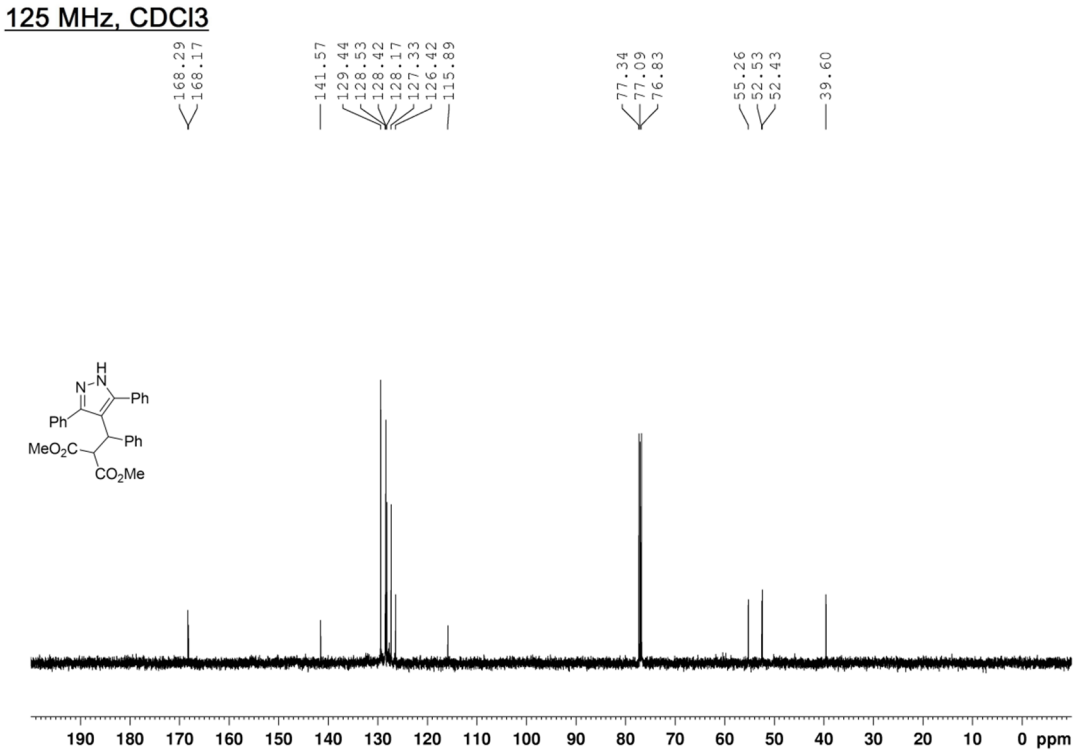


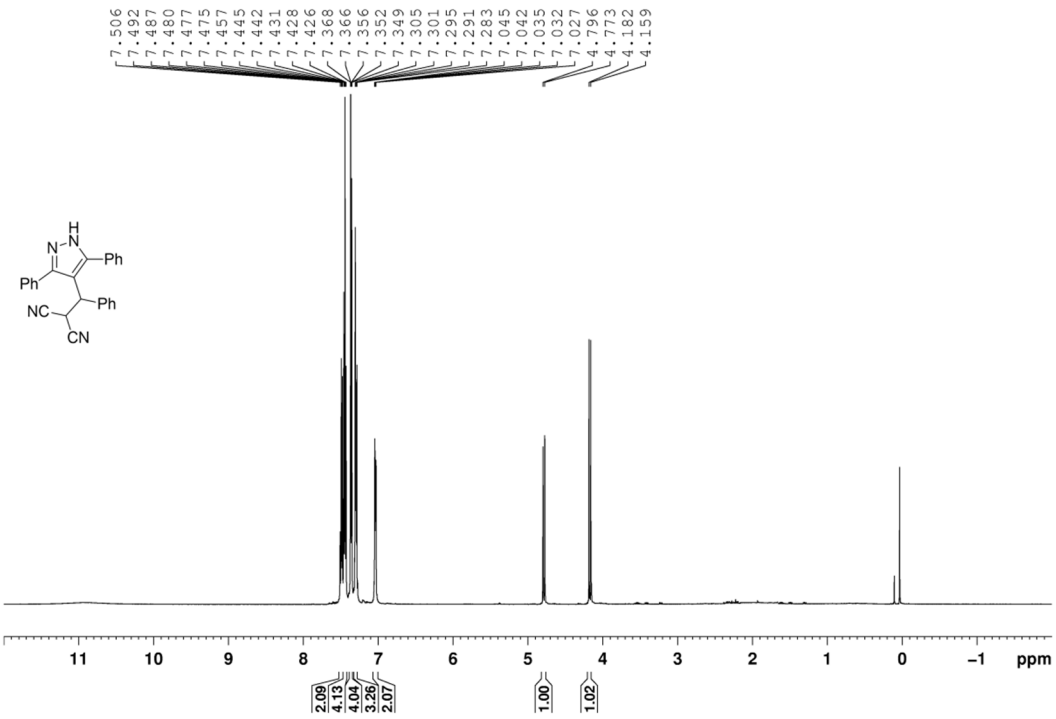
dimethyl 2-((3,5-diphenyl-1H-pyrazol-4-yl)(phenyl)methyl)malonate (**4aa**)



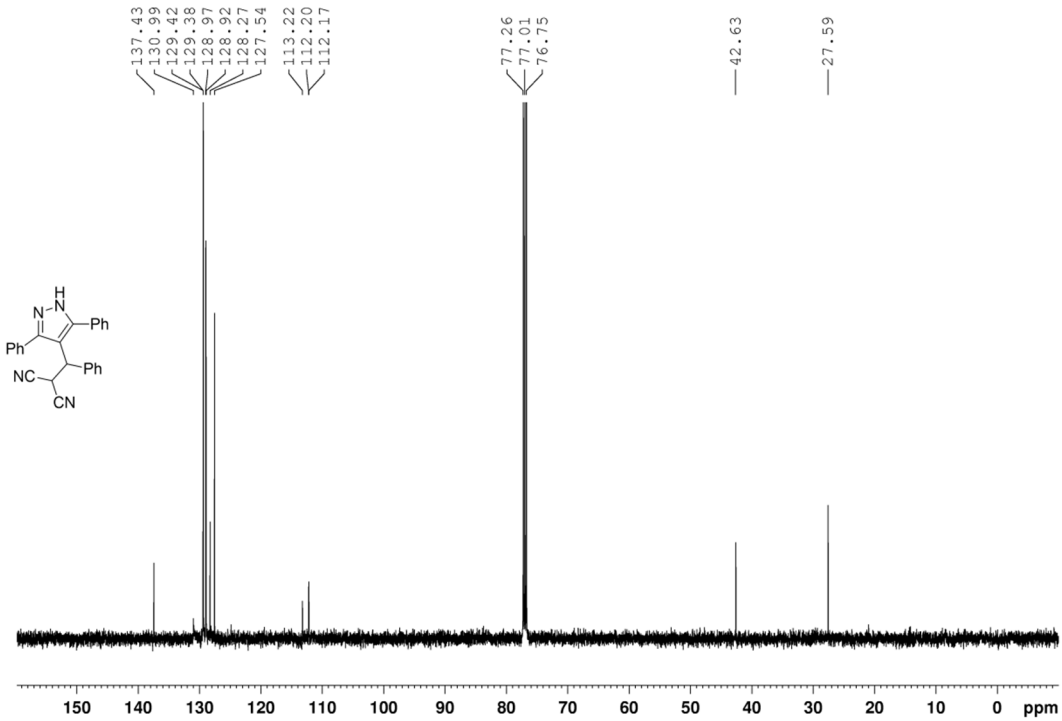


2-((3,5-diphenyl-1H-pyrazol-4-yl)(phenyl)methyl)malononitrile (**4ab**)

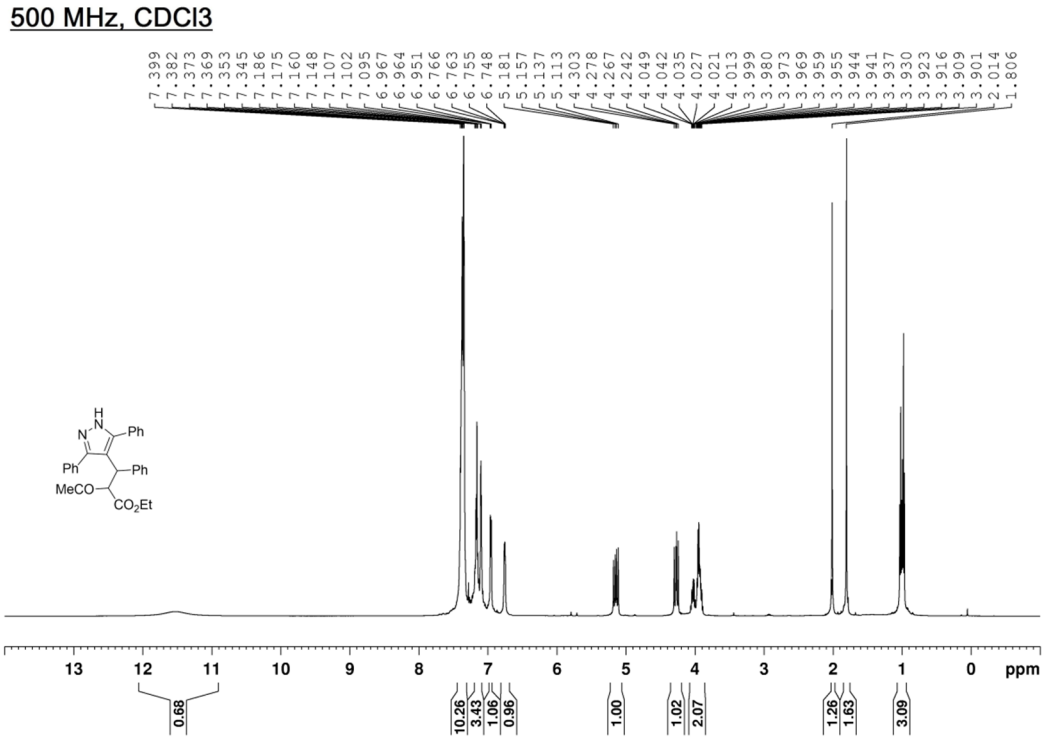
500 MHz, CDCl3

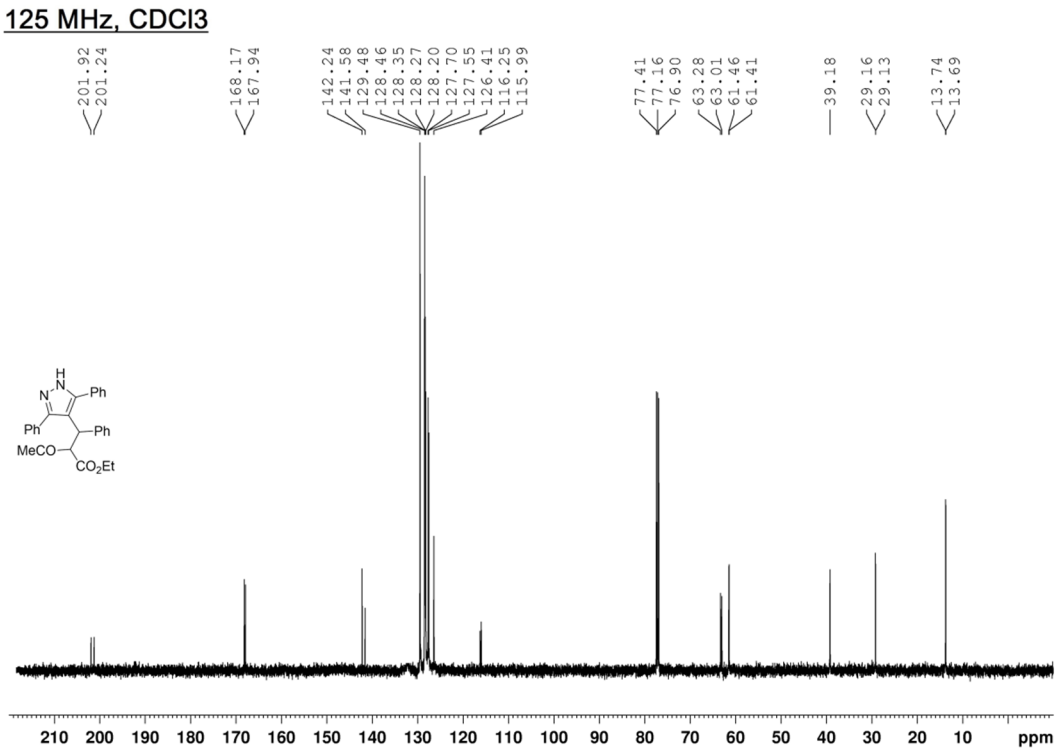


125 MHz, CDCl3



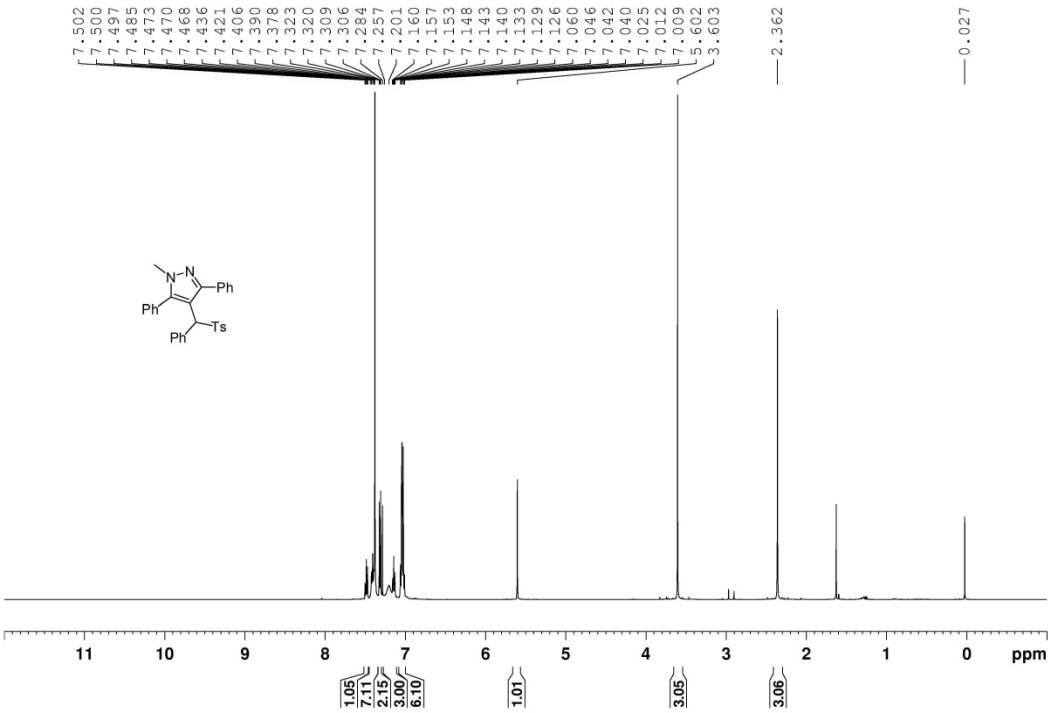
ethyl 2-((3,5-diphenyl-1H-pyrazol-4-yl)(phenyl)methyl)-3-oxobutanoate (**4ac**)





1-Methyl-3,5-diphenyl-4-[phenyl-(toluene-4-sulfonyl)-methyl]-1H-pyrazole (**5a**)

500 MHz, CDCl3



125 MHz, CDCl3