Supporting Information

Solvent-Dependent Copper-Catalyzed Synthesis of Pyrazoles Under Aerobic Conditions

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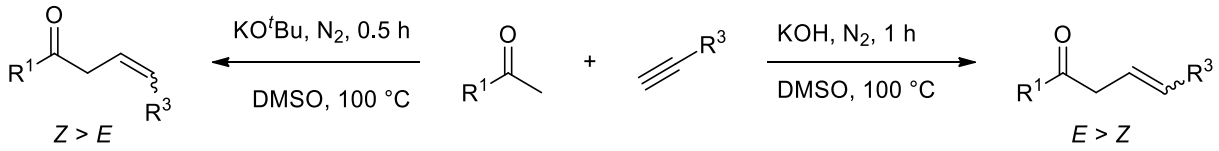
(A) General

NMR spectra were recorded at 400 MHz for ^{1}H-NMR, 100.4 MHz for ^{13}C-NMR and 377.6 MHz for ^{19}F-NMR. Chemical shifts were reported downfield from TMS (= 0) for ^{1}H-NMR. For ^{13}C-NMR, chemical shifts were reported in the scale relative to $CDCl_3$ as an internal reference. Infrared spectra (IR) were measured on a Thermo Nicolet iS5. HRMS (ESI) spectra were measured on a Bruker micrOTOF-QII-RSL. The samples were diluted with MeOH for the measurement. Flash column chromatography was performed with silica gel N 60 (40-100 μm). In some case, purification was carried out using precoated thin layer chromatography (PTLC) plates (silica gel 60 F_{254}, 0.50 mm). Precoated TLC plates (silica gel 60 F_{254}, 0.25 mm) were used for the TLC analysis. Dehydrated solvents were used

directly as purchased. Commercially available reagents were purified by usual methods, if necessary. Copper(II) acetate (98%; Sigma Aldrich), EtOH (>99.5%; Wako Pure Chemical Industries) and HFIP (>99%; TCI) were used as received.

(B) General procedure for the synthesis of β,γ-unsaturated ketones[1,2]



Although the *E*-isomer is reported to be formed exclusively or at least in high excess in both literature procedures, formation of both isomers was usually observed in our hands. The selectivity could be changed in favor of the *Z*-isomer by utilizing dry DMSO and KO^{t}Bu, while with KOH in undried DMSO the *E*-isomer was the major product.

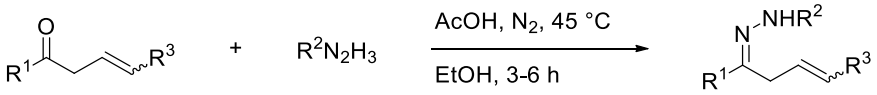
A mixture of 1.0 eq. of ketone, 1.0 eq. of alkyne and 1.1 eq. of base was vigorously stirred under N_2 in DMSO (0.4 M) at 100 ^{O}C for 0.5 h (with KO^{t}Bu) or 1 h (with KOH). The mixture was cooled to room temperature, quenched with H_2O, neutralized with NH_4Cl, and extracted with Et_2O. The organic phases were combined, washed with brine, dried over Na_2SO_4, and evaporated. The major impurities in the crude product were removed by fast column chromatography to give the desired β,γ-unsaturated ketones as isomeric mixtures (in most cases ≥90:10), which often still contained small amounts of unidentified impurities. Those ketones were used directly for the next step.

Note: it is possible with some effort to completely separate the isomeric mixtures in some cases by careful column chromatography and/or crystallization, which leads to lower yields but higher purity, and is not necessary for the next step. It was difficult to obtain highly reproducible results in terms of both selectivity and yield.

1) B. A. Trofimov, E. Yu. Schmidt, I. A. Ushakov, N. V. Zorina, E. V. Skital'tseva, N. I. Protsuk, A. I. Mikhaleva, *Chem. Eur. J.* **2010**, *16*, 8516.

2) B. A. Trofimov, E. Yu. Schmidt, N. V. Zorina, E. V. Ivanova, I. A. Ushakov, *J. Org. Chem.* **2012**, *77*, 6880.

(C) General procedure for the synthesis of hydrazones 1[3]



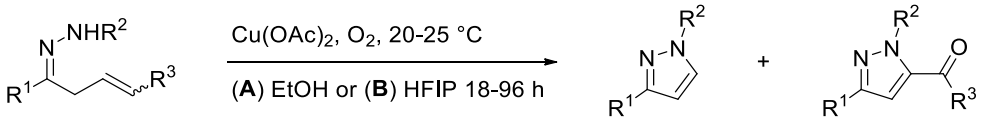
A mixture of ketone (1.0 eq.), AcOH (~1.0 eq.) and hydrazine (~1.2-1.3 eq.) in EtOH (0.5-1.0 M) was stirred for 3-6 h at 45 ^{o}C and then cooled to room temperature. If the product crystallized from the mixture, it was collected by filtration and washed with cold EtOH or MeOH to ensure high purity, even though the yields were often lower than those obtained after purification by column chromatography. If crystallization from the crude mixture did not occur, the solvent was removed under reduced pressure and the crude product was purified by column chromatography. The isolated hydrazones were stored under N_2 in a freezer to prevent autoxidation.[4] All hydrazones but **1m** were obtained as a single isomer in respect to the N-N bond.

The yields over the two steps were not optimized.

3) X. Zhu, S. Chiba, *Org. Biomol. Chem.* **2014**, *12*, 4567.

4) a) M. Harej, D. Dolenc, *J. Org. Chem.* **2007**, *72*, 7214; b) T. Tezuka, S. Ando, *Chem. Lett.* **1985**, 1621; c) A. L. Baumstark, M. Dotrong, P.C. Vasquez, *Tetrahedron Lett.* **1987**, *28*, 1963; d) J. Yu, J. W. Lim, S. Y. Kim, J. Kim, J. N. Kim, *Tetrahedron Lett.* **2015**, *56*, 1432.

(D) General procedure for the synthesis of pyrazoles 2 and 3



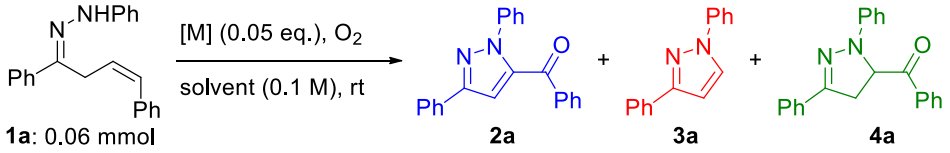
Hydrazone (0.20 mmol; 1.0 eq.) and $Cu(OAc)_2$ (0.004 mmol; 0.02 eq.) were combined under air and dissolved in (**A**) EtOH or (**B**) HFIP (2.0 mL; 0.1 M). An O_2-balloon was applied and the mixture stirred at room temperature overnight. If the room temperature was not in the range of 20-25 ^{o}C, the reactions were run with temperature control at 22 ^{o}C. Progress of the reaction was monitored by TLC and the mixture was passed through a pad of silica after complete consumption of the starting material. The NMR spectrum of the crude material was taken before purification by column chromatography. Toluene or mesitylene was used as an internal standard.

Note: Most reactions, especially in HFIP (**B**), were completed within a far shorter reaction time than indicated, but no negative effects on yield or selectivity were observed when the reactions were run for

longer periods.

Comment on the substrate scope: these reaction conditions were not successful for substrates with allylic substitution. For R^2 = CO_2Me no conversion of the starting material occurred in EtOH, while unselective decomposition was observed in HFIP. In the case of R^2 = 4-$MeC_6H_4SO_2$ (Tos) conversion occurred, but both reaction conditions led to low yield and selectivity.

(E) Screening of reaction conditions



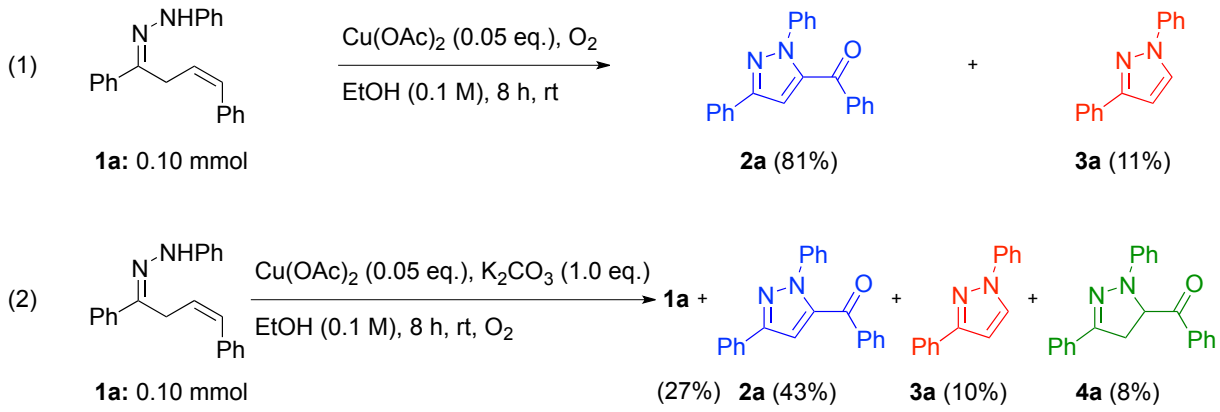
1a: 0.06 mmol

2a **3a** **4a**

Entry	[M]	Solvent	Time [h]	1a [%]	2a [%]	3a [%]	4a [%]
1	$Cu(OAc)_2$	EtOH	18	-	83[a)]	<10	-
2	$Cu(OAc)_2$	EtOH	48	-	79	<13	-
3	$Cu(OAc)_2$	HFIP	18	-	-	quant.[a)]	-
4	$Cu(OAc)_2$	IPA	18	26	64	9	-
5	$Cu(OAc)_2$	DCM	24	-	18	57	trace
6	$Cu(OAc)_2$	THF	18	51	<20	<25	trace
7	CuI	EtOH	18	80	-	-	18[a)]
8	$CuBr_2$	EtOH	10	-	6	54	12
9	$Cu(NO_3)_2{\cdot}3H_2O$	EtOH	20	-	48[a)]	26[a)]	-
10	$CuSO_4{\cdot}5H_2O$	EtOH	20	-	47	14	8
11	$[Cu(MeCN)_4]PF_6$	EtOH	20	-	34	60	-
12	Cu(tartrate)$\cdot 3H_2O$	EtOH	20	23	20	8	47

13	-	HFIP	19	-	-	70	-
14[b)]	-	HFIP	18	-	-	46	-
15[b)]	$Cu(OAc)_2$	HFIP	18	-	-	98[a)]	-
16	-	EtOH	20	≥95		trace	
17	$Mn(OAc)_2$	EtOH	20	≥95		trace	
18	$Fe(OAc)_2$	EtOH	20	≥95		trace	
19	$Co(OAc)_2$	EtOH	20	≥95		trace	
20	$Ni(OAc)_2{\cdot}4H_2O$	EtOH	20	≥95		trace	
21[b)]	$Cu(OAc)_2$	EtOH	20	-	74[a)]	12[a)]	-
22[c)]	$Cu(OAc)_2$	EtOH	20	-	51	<38	-
23[d)]	$Cu(OAc)_2$	EtOH	20	-	77	19	-
24[e)]	$Cu(OAc)_2$	EtOH	21	-	79[a)]	<12	-
25[e,f)]	$Cu(OAc)_2$	EtOH	24	-	84[a)]	<15	-

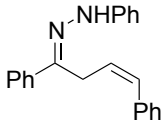
NMR yields based on internal standard; a) isolated yields b); under air; c) + 5 eq. H_2O; d) in dry EtOH with 50 mg MS3Å; e) on 0.20 mmol scale; f) 2 mol% $Cu(OAc)_2$.



Although Brønsted base often accelerates the photocatalytic oxidative cyclization of hydrazones,[5] addition of K_2CO_3 was less effective in the Cu-catalyzed oxidative cyclization of **1a** under aerobic conditions (equation 1: in the absence of K_2CO_3 *vs.* equation 2: in the presence of K_2CO_3). TLC monitoring (every 2 h) suggested that the addition of K_2CO_3 slightly reduced the consumption rate of **1a**. While the reaction was completed in 8 h in the absence of K_2CO_3 (equation 1), unconsumed starting material (27%) was found along with lower product selectivity (**2a**: 42%, **3a**: 10%, **4a**: 8%) in the presence of K_2CO_3 (equation 2). Conversion and yields were determined from crude NMR based on internal standard. Addition of base is therefore not an option to decrease the reaction time.

5) a) X.-Q. Hu, J.-R. Chen, Q. Wei, F.-L. Liu, Q.-H. Deng, A. M. Beauchemin, W.-J. Xiao, *Angew. Chem. Int. Ed.,* 2014, **53**, 12163; b) Q. Wei, J.-R. Chen, X.-Q. Hu, X.-C. Yang, B. Lu, W.-J. Xiao, *Org. Lett.,* 2015, **17**, 4464; c) X.-Q. Hu, X. Qi, Q.-Q. Zhao, Q. Wei, Y. Lan, W.-J, Xiao, *Nature Commun*. 2016, **7**, 11188; d) X.-Q. Hu, J. Chen, J.-R. Chen, D.-M. Yan, W.-J, Xiao, *Chem. Eur. J.,* 2016, **22**, 14141.

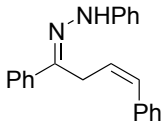
(F) Control experiments

(3) 

1a: 0.06 mmol

$Cu(OAc)_2$ (1.0 eq.), N_2
EtOH (0.1 M), 22 °C, 18 h

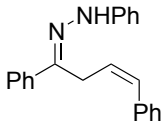
complete conversion/ decomposition of **1a**

(4) 

1a: 0.06 mmol

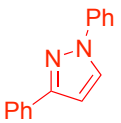
CuOAc (1.0 eq.; 93%), N_2
EtOH (0.1 M), 22 °C, 18 h

~50% conversion/ decomposition of **1a**

(5) 

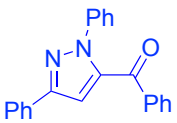
1a: 0.06 mmol

CuOAc (0.05 eq.), O_2
EtOH (0.1 M), 22 °C, 18 h

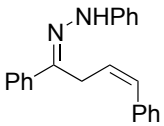


3a (<22%)

+



2a (70%)

(6) 

1a: 0.06 mmol

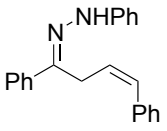
CuI (1.0 eq.; 99.999%), NaOAc (1.0 eq.)
EtOH (0.1 M), N_2, 22 °C, 18 h

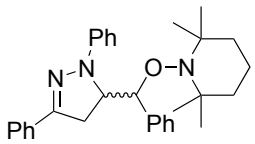
no conversion/ 100% recovery of **1a**

When 1 eq. of $Cu(OAc)_2$ was applied under N_2 the blue suspension turned yellow within ≤2 h, and

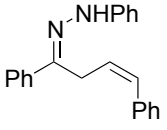
subsequently changed only slightly (equation 3). **1a** was completely consumed and several unidentified compounds were formed. This indicates oxidation of **1a** by Cu(II). When 1 eq. Cu(I)OAc was used, only partial conversion occurred, and several decomposition products were formed (equation 4). If Cu(II) is required for single-electron oxidation of the starting material to a radical, no reaction should occur with Cu(I)OAc. The reason is most likely the insufficient purity of the commercially available copper(I) acetate and its propensity to disproportionate to Cu(0) and Cu(II) in polar solvents.[6] When sub-stoichiometric amounts of $Cu(OAc)_2$ were used (5-20 mol%) under N_2, partial conversion always occurred to a somewhat greater extent than the corresponding 5-20% value. However, when CuI of high purity (99.999%) was used under N_2 no conversion at all was observed (equation 6). With 5 mol% CuI under O_2, approximately 20% of the starting material was converted in the same time. Furthermore, catalytic amounts of Cu(I)OAc under O_2 led to conversion comparable to that obtained with $Cu(OAc)_2$ under the same conditions, with only a slightly less good ratio of **2a**:**3a** (equation 5).

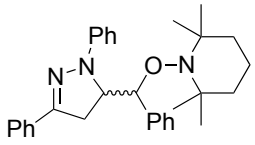
6) a) B. M. Rosen, X. Jiang, C. J. Wilson, N. H. Nguyen, M. J. Monteiro, V. Percec, *J. Polym. Sci. A Polym. Chem.,* 2009, **47**, 5606; b) G. Christou, S. P. Perlepes, E. Libby, K. Folting, J. C. Huffman, R. J. Webb, D. N. Hendrickson, *Inorg. Chem.,* 1990, **29**, 3657; c) A. E. King, T. C. Brunold, S. S. Stahl, *J. Am. Chem. Soc.,* 2009, **131**, 5044; d) Z. Mao, Z. Wang, Z. Xu, F. Huang, Z. Yu, R. Wang, *Org. Lett.,* 2012, **14**, 3854; e) B. Cheng, H. Yi, C. He, C. Liu, A. Lei, *Organometallics,* 2015, **34**, 206.

(7) 

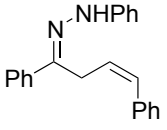
TEMPO (2.2 eq.), N_2
EtOH (0.1 M), 6 h, rt


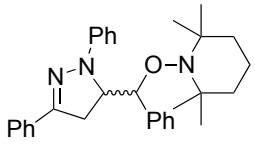
1a: 0.10 mmol — **5: 86%** (72:28 d.r.)

(8) 

TEMPO (1.0 eq.), $Cu(OAc)_2$ (1.0 eq.)
EtOH (0.1 M), 6 h, rt, N_2


1a: 0.10 mmol — **5: 94%** (82:18 d.r.)

(9) 

TEMPO (2.2 eq.), $Cu(OAc)_2$ (1.0 eq.)
EtOH (0.1 M), 6 h, rt, N_2


1a: 0.10 mmol — **5: quant.** (80:20 d.r.)

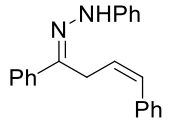
In equations 7-9, control experiments using TEMPO as a radical trapping reagent under nitrogen are shown. The reaction conditions using TEMPO (2.2 eq.) in the absence of Cu(II) (equation 7) gave the

corresponding oxyamination product **5** in 86% with 72:28 diastereomeric ratio (d.r.). In this reaction, TEMPO should oxidize hydrazone **1a** to the corresponding hydrazone radical by hydrogen abstraction (HAT).[7] The oxyamination reaction using TEMPO proceeded smoothly even in the presence of $Cu(OAc)_2$ to give **5** (equations 8 and 9). This circumstantial evidence supports the idea that the proposed radical intermediate (**II** in the main text) participates in the oxidative cyclization of **1** both in the Cu(II)-catalyzed- (Scheme 3 in the main text) and Cu-free conditions (Scheme 4 in the main text). The yields are isolated yields and the diastereomeric ratios are determined from the isolated products.

Further efforts to trap the proposed benzylic radical (**II** in the main text) with other trapping reagents were unsuccessful in our conditions. When we added 1,4-cyclohexadiene, complex mixtures of the products were generated in low yields, and it made the analysis difficult. Ph_2Se_2 completely suppressed any reaction, likely due to formation of Cu(I).[8]

7) a) X.-Y. Duan, N.-N. Zhou, R. Fang, X.-L. Yang, W. Yu, B. Han, *Angew. Chem. Int. Ed.*, 2014, **53**, 3158; b) M.-K. Zhu, Y.-C. Chen, T.-P. Loh, *Chem. Eur. J.,* 2013, **19**, 5250; c) X.-Y. Duan, X.-L. Yang, R. Fang, X.-X. Peng, W. Yu, B. Han, *J. Org. Chem.,* 2013, **78**, 10692; d) X. Zhu, S. Chiba, *Org. Biomol. Chem.,* 2014, **12**, 4567; e) X.-Q. Hu, G. Feng, J.-R. Chen, D.-M. Yan, Q.-Q. Zhao, Q. Wei, W.-J. Xiao, *Org. Biomol. Chem.,* 2015, **13**, 3457; f) X. Zhu, Y.-F. Wang, W. Ren, F.-L. Zhang, S. Chiba, *Org. Lett.,* 2013, **15**, 3214.

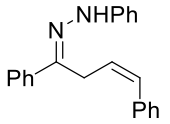
8) N. Miyoshi, Y. Ohno, K. Kondo, S. Murai, N. Sonoda, *Chem. Lett.* 1979, 1309.

(10) 

1a: 0.10 mmol + PPh_3 0.15 mmol

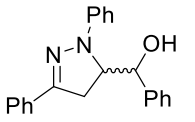
$Cu(OAc)_2$ (0.05 eq.), O_2
EtOH (0.1 M), 16 h, rt

no conversion

(11) 

1a: 0.10 mmol + PPh_3 0.15 mmol

$Cu(OAc)_2$ (0.05 eq.), O_2
HFIP (0.1 M), 16 h, rt



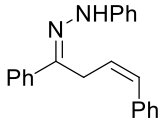
6 (64%; 78:22 d.r)

Our investigations using triphenylphosphine (1.5 eq.) also highlight the mechanistic differences between $Cu(OAc)_2$-catalyzed oxidative cyclization (Scheme 3 in the main text) and HFIP-mediated oxidative cyclization (Scheme 4 in the main text). When triphenylphosphine was added under $Cu(OAc)_2$-catalyzed conditions in EtOH, the reaction was suppressed (equation 10). The active Cu catalyst might be poisoned by triphenylphosphine. On the other hand, alcohol **6** was formed in 64% (crude NMR yield) in HFIP

(equation 11). This result indicates that the proposed hydrogen peroxide species (**V** in Scheme 4, main text) can be reduced to the alcohol **6**. We believe that the preliminary result described in equation 11 may serve to broaden the concept of product switching in the aerobic oxidation by simply changing reaction conditions. In this case the usual product **3a** was only formed in small amounts (≤7%; crude NMR).

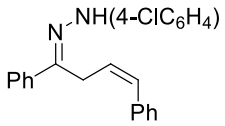
(G) Characterization of hydrazones 1

(*E*)-1-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)-2-phenylhydrazine (1a)



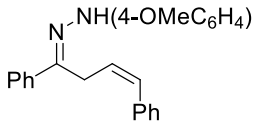
White solid, purified by crystallization; 57% yield (two steps). IR (neat) ν 1600, 1584, 1510, 1492, 1444, 1254, 1157, 1144, 939, 790, 771, 760, 745, 719, 701, 689, 644 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.53-7.36 (m, 7H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.10 (bs, 1H), 6.85-6.78 (m, 3H), 6.74 (d, *J* = 10.8 Hz, 1H), 5.67 (dt, *J* = 11.3, 7.5 Hz, 1H), 3.78 (dd, *J* = 7.8, 1.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.8, 141.6, 138.1, 136.0, 132.0, 129.0, 128.8 (2 C), 128.4, 127.9, 127.8, 125.5, 124.9, 120.0, 113.0, 26.3; HRMS (ESI+) calcd for $C_{22}H_{22}N_2$+Na^+: 335.1519, found: 335.1520.

(*E*)-1-(4-chlorophenyl)-2-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)hydrazine (1b)



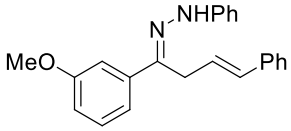
The condensation was performed at 60 ^{o}C. Off-white solid, purified by crystallization; 27% yield (two steps). IR (neat) ν 1599, 1505, 1491, 1445, 1250, 1086, 822, 760, 701, 693, 668 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.47-7.38 (m, 5H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 9.2 Hz, 2H), 7.04 (bs, 1H), 6.77-6.68 (m, 3H), 5.66 (dt, *J* = 11.5, 7.6 Hz, 1H), 3.77 (dd, *J* = 7.6, 1.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.4, 142.3, 137.8, 135.9, 132.0, 128.91, 128.89, 128.8, 128.5, 128.1, 127.9, 125.5, 124.7, 124.5, 114.1, 26.3; HRMS (ESI+) calcd for $C_{22}H_{19}ClN_2$+Na^+: 369.1129 found: 369.1115.

(*E*)-1-(4-methoxyphenyl)-2-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)hydrazine (1c)



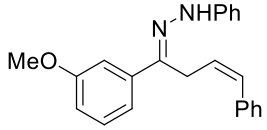
Pale yellow solid, purified by crystallization; 30% yield (two steps). IR (neat) ν 1512, 1445, 1232, 1142, 1036, 823, 763, 693, 668, 614 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.50-7.39 (m, 5H), 7.34 (t, *J* = 6.8 Hz, 1H), 7.01 (bs, 1H), 6.87-6.79 (m, 4H), 6.75 (d, *J* = 11.2, 2H), 5.69 (dt, *J* = 11.2, 7.2 Hz, 1H), 3.82-3.75 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.6, 140.9, 139.0, 138.2, 136.1, 131.8, 128.79, 128.75, 128.4, 127.7, 127.6, 125.3, 125.0, 114.5, 114.0, 55.6, 26.2; HRMS (ESI+) calcd for $C_{23}H_{22}N_2O+Na^+$: 365.1624, found: 365.1612.

(*E*)-1-((*E*)-1-(3-methoxyphenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (1d)



In this case both isomers were obtained in sufficient amount and purity for further conversion from the ketone synthesis with KOH. Yellow oil, purified by column chromatography (hexane/EtOAc 7:1); 48% yield (two steps). The product contained ~0.1 eq. of Et_2O that could not be removed by drying under vacuum overnight. IR (neat) ν 1601, 1507, 1494, 1286, 1256, 1221, 1166, 1136, 1033, 971, 782, 748, 733, 693 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.67 (bs, 1H), 7.48 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.38-7.21 (m, 8H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.94-6.87 (m, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.35 (dt, *J* = 16.0, 5.4 Hz, 1H), 3.89 (s, 3H), 3.66 (dd, *J* = 5.2, 2.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.7, 145.0, 141.8, 140.1, 136.5, 132.2, 129.4, 129.2, 128.6, 127.7, 126.2, 122.2, 120.4, 118.2, 113.6, 113.3, 111.1, 55.3, 30.3; HRMS (ESI+) calcd for $C_{23}H_{22}N_2O+Na^+$: 365.1624, found: 365.1625.

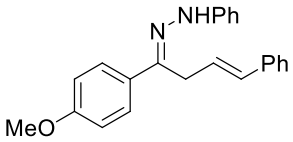
(*E*)-1-((*Z*)-1-(3-methoxyphenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (1e)



In this case both isomers were obtained in sufficient amount and purity for further conversion from the ketone synthesis with KOH. Yellow oil, purified by column chromatography (hexane/EtOAc 7:1); 52%

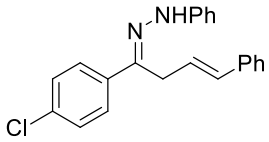
yield (two steps). The product contained ~0.2 eq. of Et_2O that could not be removed by drying under vacuum overnight. IR (neat) ν 1601, 1506, 1494, 1254, 1225, 1165, 1138, 1038, 774, 750, 691 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.4 Hz, 2H), 7.47-7.35 (m, 5H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.11 (bs, 1H), 6.91-6.78 (m, 4H), 6.74 (d, *J* = 11.2 Hz, 1H), 5.67 (dt, *J* = 11.3, 7.4 Hz, 1H), 3.86 (s, 3H), 3.77 (dd, *J* = 7.2, 2.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.7, 144.7, 141.3, 139.6, 136.0, 131.9, 129.3, 129.0, 128.8 (2C), 127.8, 124.9, 120.0, 118.1, 113.6, 113.0, 110.9, 55.2, 26.4; HRMS (ESI+) calcd for $C_{23}H_{22}N_2O+Na^+$: 365.1624, found: 365.1625.

(*E*)-1-((*E*)-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (1f)



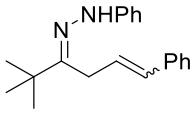
The condensation was performed at 60 ^{o}C. White solid, purified by crystallization; 26% yield (two steps). IR (neat) ν 1600, 1500, 1248, 1178, 1136, 1027, 969, 833, 750, 736, 692 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.54 (bs, 1H), 7.36-7.20 (m, 7H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 16.0, 5.4 Hz, 1H), 3.85 (s, 3H), 3.65 (dd, *J* = 5.6, 2.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.7, 145.3, 142.3, 136.5, 132.2, 131.3, 129.2, 128.6, 127.7, 126.9, 126.2, 122.4., 120.1, 113.8, 113.2, 55.3, 30.2; HRMS (ESI+) calcd for $C_{23}H_{22}N_2O+Na^+$: 365.1624, found: 365.1626.

(*E*)-1-((*E*)-1-(4-chlorophenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (1g)



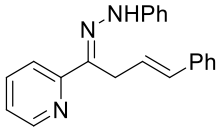
White solid, purified by crystallization; 23% yield (two steps). IR (neat) ν 1601, 1507, 1490, 1248, 1145, 1093, 1009, 963, 832, 749, 692, 668 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.64 (bs, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.34-7.20 (m, 7H), 7.17-7.13 (m, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.50 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.32 (dt, *J* = 16.0, 5.6 Hz, 1H), 3.64 (dd, *J* = 5.5, 1.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.8, 140.8, 137.0, 136.3, 133.8, 132.3, 129.3, 128.62, 128.57, 127.8, 126.7, 126.2, 121.8, 120.5, 113.3, 29.9; HRMS (ESI+) calcd for $C_{22}H_{19}ClN_2+Na^+$: 369.1129, found: 369.1121.

(*E*)-1-((*E*)-2,2-dimethyl-6-phenylhex-5-en-3-ylidene)-2-phenylhydrazine (1h)



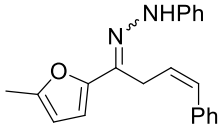
Yellow oil, purified by column chromatography (hexane/EtOAc 12:1); 71% yield (two steps). The product contained ~0.15 eq. of Et_2O that could not be removed by drying under vacuum overnight; inseparable *E*/*Z*-mixture (~13:1); NMR given for the major isomer only. IR (neat) ν 1601, 1502, 1249, 1135, 1086, 1064, 970, 749, 736, 692 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 7.25-7.18 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.81 (t, *J* = 7.4, Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.19 (dt *J* = 15.9, 5.8 Hz, 1H), 3.28 (dd, *J* = 5.8, 1.8 Hz, 2H), 1.24 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.3, 146.1, 136.6, 132.5, 129.1, 128.6, 127.6, 126.1, 123.8, 119.5, 113.0, 38.7, 29.7, 28.0; HRMS (ESI+) calcd for $C_{20}H_{24}N_2$+Na^+: 315.1832, found: 315.1832.

2-((1*E*,3*E*)-4-phenyl-1-(2-phenylhydrazono)but-3-en-1-yl)pyridine (1i)



The condensation was performed at 50 ^{o}C without AcOH. White solid, purified by column chromatography (hexane/EtOAc 8:1 to 6:1); 21% yield (two steps). IR (neat) ν 1601, 1567, 1507, 1494, 1465, 1429, 1248, 1156, 968, 792, 772, 749, 691 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H), 7.71 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.36-7.25 (m, 6H), 7.24-7.15 (m, 4H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 16.1, 5.9 Hz, 1H), 4.00 (dd, *J* = 6.0, 2.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.7, 148.4, 144.5, 142.6, 136.8, 136.0, 132.0, 129.3, 128.5, 127.5, 126.2, 123.4, 122.4, 120.7, 120.0, 113.3, 28.0; HRMS (ESI+) calcd for $C_{21}H_{19}N_3$+Na^+: 336.1471, found 336.1472.

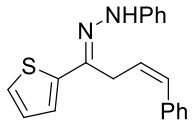
1-((*Z*)-1-(5-methylfuran-2-yl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (1j)



Yellow solid, purified by column chromatography (hexane/EtOAc 10:1); 7% yield (two steps). This is the only substrate obtained as a ~1:1.5 mixture of isomers at the *N*-*N* bond. The exact geometry was not

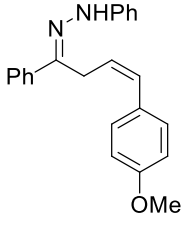
determined, but the major isomer is assumed to be the *Z*-isomer based on the *N*-*H*-proton signal at 9.53 ppm (the *N*-*H*-proton signals of all other compounds are found at 7~8 ppm). The product contained ~0.15 eq. of Et_2O that could not be removed by drying under vacuum overnight. IR (neat) ν 1600, 1521, 1500, 1302, 1255, 1137, 1100, 1070, 1027, 776, 748, 692 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) major: δ 9.53 (s, 1H), 7.52-7.13 (m, 8H), 6.83-6.75 (m, 2H), 6.57 (d, *J* = 12.0 Hz, 1H), 6.35 (d, *J* = 3.2 Hz, 1H), 6.10-6.04 (m, 1H), 5.95 (dt, *J* = 11.5, 7.1 Hz, 1H), 3.61 (dd, *J* = 7.4, 1.8 Hz, 2H), 2.43 (s, 3H); minor: δ 7.52-7.13 (m, 8H), 6.99 (s, 1H), 6.89-6.83 (m, 2H), 6.73 (d, *J* = 11.5 Hz, 1H), 6.51 (d, *J* = 3.2 Hz, 1H), 6.10-6.04 (m, 1H), 5.65 (dt, *J* = 11.5, 7.6 Hz, 1H), 3.66 (dd, *J* = 7.8, 1.8 Hz, 2H), 2.38 (s, 3H); ^{13}C-NMR (mixture of isomers; 100 MHz, $CDCl_3$) δ 153.0, 152.7, 150.7, 148.7, 145.3, 144.6, 137.2, 136.0, 135.3, 131.9, 131.0, 129.9, 129.2, 129.1, 129.0, 128.85, 128.81, 128.77, 128.2, 127.8, 126.8, 125.1, 119.8, 119.7, 112.9, 112.7, 112.6, 108.8, 107.7, 107.5, 34.0, 26.2, 15.3, 13.9; HRMS (ESI+) calcd for $C_{21}H_{20}N_2O+Na^+$: 339.1468, found: 339.1471.

(*E*)-1-phenyl-2-((*Z*)-4-phenyl-1-(thiophen-2-yl)but-3-en-1-ylidene)hydrazine (1k)



White solid, purified by crystallization; 35% yield (two steps). IR (neat) ν 1598, 1502, 1493, 1251, 1234, 1133, 807, 780, 754, 746, 721, 707, 692, 668 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.54-7.47 (m, 2H), 7.45-7.39 (m, 3H), 7.25 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.19 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.15 (dd, *J* = 3.7, 0.9 Hz, 1H), 7.01 (dt, *J* = 5.1, 3.7 Hz, 1H), 6.96 (bs, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.79-6.71 (m, 3H), 5.68 (dt, *J* = 11.7, 7.6 Hz, 1H), 3.74 (dd, *J* = 7.4, 1.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.4, 138.4, 135.9, 132.1, 129.0, 128.9, 128.8, 127.9, 127.1, 126.1, 124.6, 123.6, 120.0, 112.9, 27.1, (2C are overlapping); HRMS (ESI+) calcd for $C_{20}H_{18}N_2S+Na^+$: 341.1083, found: 341.1077.

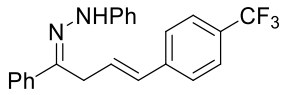
(*E*)-1-((*Z*)-4-(4-methoxyphenyl)-1-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (1l)



White solid, purified by crystallization; 40% yield (two steps). IR (neat) ν 1601, 1509, 1493, 1442, 1252, 1177, 1141, 1033, 844, 765, 749, 691, 612 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H),

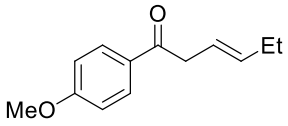
7.42-7.36 (m, 4H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.24-7.15 (m, 3H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.88-6.79 (m, 3H), 6.67 (d, *J* = 10.8 Hz, 1H), 5.57 (dt, *J* = 11.2, 7.5 Hz, 1H), 3.89 (s, 3H), 3.77 (dd, *J* = 7.8, 1.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.2, 144.9, 142.0, 138.2, 131.5, 130.2, 129.1, 128.5, 128.4, 127.9, 125.5, 123.5, 119.9, 114.2, 113.0, 55.4, 26.4; HRMS (ESI+) calcd for $C_{23}H_{22}N_2O+Na^+$: 365.1624, found: 365.1603.

(*E*)-1-phenyl-2-((*E*)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-ylidene)hydrazine (1m)



Although the KO^{t}Bu method was utilized for the ketone formation, the *E*-isomer was formed as the major product. Pale yellow solid, purified by column chromatography (hexane/EtOAc 12:1); 33% yield (two steps). IR (neat) ν 1602, 1507, 1493, 1326, 1248, 1163, 1121, 1067, 1016, 750, 691 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.00 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.46-7.40 (m, 4H), 7.39-7.28 (m, 3H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 16.1 Hz, 1H), 6.47 (dt, *J* = 16.1, 5.1 Hz, 1H), 3.70 (dd, *J* = 5.1, 1.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.9, 141.3, 139.9, 138.4, 130.9, 129.5 (q, *J* = 32.4 Hz), 129.3, 128.5, 128.1, 126.4, 125.53 (q, *J* = 3.4 Hz), 125.47, 125.1, 124.1 (q, *J* = 272.6 Hz), 120.5, 113.3, 29.9; ^{19}F-NMR (378 MHz, $CDCl_3$) δ -62.5; HRMS (ESI+) calcd for $C_{23}H_{19}F_3N_2+Na^+$: 403.1393, found: 403.1364.

(*E*)-1-(4-methoxyphenyl)hex-3-en-1-one (7)

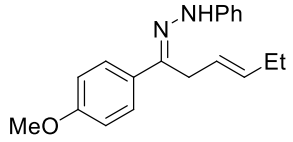


To (*E*)-*N*-methoxy-*N*-methylhex-3-enamide[9] (529 mg; 3.36 mmol; 1.0 eq.) in abs. Et_2O under N_2 was slowly added (4-methoxyphenyl)magnesium bromide (0.5 M in THF; 10.0 mL; 5.0 mmol; 1.5 eq.) at 0 ºC and the mixture was slowly warmed to rt over 1 h. Stirring was continued for another 5 h at rt, and then the reaction was quenched with sat. NH_4Cl_{aq}. The layers were separated and the aqueous layer was extracted with Et_2O. The combined organic phase was dried over Na_2SO_4, the solvent was evaporated, and the crude product was purified by column chromatography (*n*-hexane/EtOAc 5:1) to give the product as a colorless oil (575 mg, 2.81 mmol, 84%). IR (neat) ν 1676, 1601, 1576, 1510, 1317, 1259, 1213, 1168, 1030, 967, 837, 668, 652, 632 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.71-5.59 (m, 2H), 3.86 (s, 3H), 3.63 (d, *J* = 4.8 Hz, 2H), 2.11-2.02 (m, 2H), 0.98 (t, *J* = 7.6

Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 197.3, 163.4, 136.2, 130.6, 129.7, 121.6, 113.7, 55.4, 42.2, 25.7, 13.5; HRMS (ESI+) calcd for $C_{13}H_{16}O_2$+Na^+: 227.1043, found: 227.1020.

9) S. M. Smith, M. Uteuliyeva, J. M. Takacs, *Chem. Commun.*, **2011**, *47*, 7812.

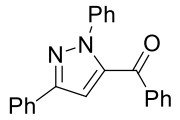
(*E*)-1-((*E*)-1-(4-methoxyphenyl)hex-3-en-1-ylidene)-2-phenylhydrazine (1n)



Yellow oil, purified by column chromatography (hexane/EtOAc 5:1); 91% yield (one step). IR (neat) ν 1601, 1501, 1303, 1248, 1175, 1138, 1029, 835, 750, 693, 668 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.58 (bs, 1H), 7.30-7.25 (m, 2H), 7.16-7.11 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 5.74-5.65 (m, 1H), 5.58-5.50 (m, 1H), 3.84 (s, 3H), 3.45-3.41 (m, 2H), 2.11-2.01 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.6, 145.5, 143.2, 135.4, 131.5, 129.2, 126.9, 121.4, 119.9, 113.7, 113.1, 55.3, 30.2, 25.5, 13.6; HRMS (ESI+) calcd for $C_{19}H_{22}N_2O$+Na^+: 317.1624, found: 317.1605.

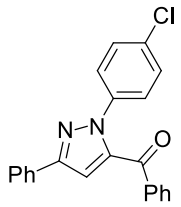
(H) Characterization of pyrazoles 2 and 3

(1,3-diphenyl-1*H*-pyrazol-5-yl)(phenyl)methanone (2a): Table 2, entry 1



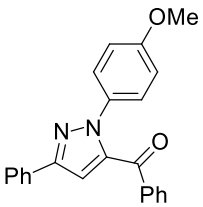
The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1a**) and purified after 24 h by column chromatography (*n*-hexane/ethyl acetate = 11:1) to give **2a** in 84% yield as a white foam. IR (neat) ν 1658, 1598, 1498, 1448, 1425, 1282, 1237, 956, 899, 766, 736, 720, 690, 680 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54-7.34 (m, 10H), 7.09 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.6, 151.4, 140.4, 140.1, 137.2, 133.6, 132.1, 129.8, 128.9, 128.8, 128.6, 128.4, 128.2, 125.8, 124.9, 110.7; HRMS (ESI+) calcd for $C_{22}H_{16}N_2O$+Na^+: 347.1155, found: 347.1157.

(1-(4-chlorophenyl)-3-phenyl-1*H*-pyrazol-5-yl)(phenyl)methanone (2b): Table 2, entry 3



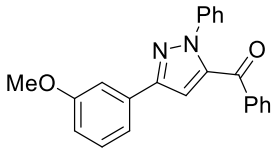
The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-(4-chlorophenyl)-2-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)hydrazine (**1b**) and purified after 24 h by column chromatography (*n*-hexane/ethyl acetate = 10:1) to give **2b** in 49% yield as a white solid. IR (neat) ν 1658, 1494, 1448, 1428, 1289, 1234, 1091, 1012, 956, 899, 831, 768, 727, 701, 693, 676 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 6.8 Hz, 2H), 7.89 (d, *J* = 6.8 Hz, 2H), 7.66 (tt, *J* = 7.2, 1.5 Hz, 1H), 7.53 (t, *J* = 7.6, Hz, 2H), 7.48-7.35 (m, 7H), 7.09 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.3, 151.6, 140.4, 138.6, 137.1, 133.9, 133.8, 131.8, 129.8, 129.1, 128.8, 128.7, 128.6, 126.1, 125.8, 111.1; HRMS (ESI+) calcd for $C_{22}H_{15}ClN_2O+Na^+$: 381.0765, found: 381.0769.

(1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazol-5-yl)(phenyl)methanone (2c): Table 2, entry 5



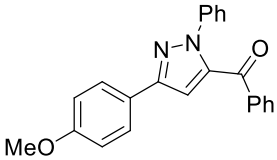
The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-(4-methoxyphenyl)-2-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)hydrazine (**1c**) and purified after 24 h by column chromatography (*n*-hexane/ethyl acetate = 6:1) to give **2c** in 60% yield as a yellow solid. IR (neat) ν 1659, 1514, 1448, 1300, 1281, 1250, 1029, 957, 900, 833, 768, 733, 710, 693, 678, 613 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 2H), 7.93-787 (m, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8, Hz, 2H), 7.47-7.39 (m, 4H), 7.36 (t, *J* = 6.6, Hz, 1H), 7.07 (s, 1H), 6.94 (d, *J* = 7.2, Hz, 2H), 3.83 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.5, 159.3, 151.0, 140.3, 137.4, 133.4, 133.5, 132.2, 129.8, 128.7, 128.6, 128.3, 126.3, 125.8, 114.1, 110.3, 55.5; HRMS (ESI+) calcd for $C_{23}H_{18}N_2O_2+Na^+$: 377.1260, found: 377.1260.

(3-(3-methoxyphenyl)-1-phenyl-1*H*-pyrazol-5-yl)(phenyl)methanone (2d): Table 2, entries 7 and 9



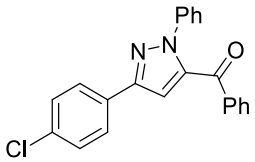
The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-((*E*)-1-(3-methoxyphenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1d**) and purified after 20 h by column chromatography (*n*-hexane/ethyl acetate = 7:1) to give **2d** in 73% yield as a yellow foam. Preparation from (*E*)-1-((*Z*)-1-(3-methoxyphenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1e**) and purification after 20 h by column chromatography (*n*-hexane/ethyl acetate = 7:1) gave **2d** in 76% yield. IR (neat) ν 1659, 1597, 1498, 1474, 1421, 1286, 1233, 1171, 1043, 901, 787, 763, 732, 718, 691, 680 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.4, Hz, 1H), 7.55-7.32 (m, 10H), 7.09 (s, 1H), 6.93 (dd, *J* = 8.3, 2.3 Hz, 1H), 3.88 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.5, 160.0, 151.2, 140.4, 140.0, 137.2, 133.6, 133.4, 129.8 (2C), 128.9, 128.6, 128.2, 124.9, 118.4, 114.4, 110.9, 110.8, 55.3; HRMS (ESI+) calcd for $C_{23}H_{18}N_2O_2$+Na^+: 377.1260, found: 377.1258.

(3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-5-yl)(phenyl)methanone (2e): Table 2, entry 11



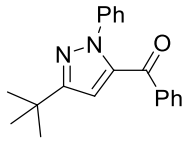
The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-((*E*)-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1f**) and purified after 96 h (1.0 mL of Et_2O was added after 48 h, because the starting material had a very low solubility) by column chromatography (*n*-hexane/ethyl acetate = 6:1) to give **2e** in 63% yield as an off-white solid. IR (neat) ν 1658, 1613, 1597, 1507, 1499, 1459, 1449, 1425, 1292, 1250, 1175, 1030, 956, 898, 837, 762, 717, 692, 678 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.6 Hz, 2H), 7.83 (d, *J* = 8.3, Hz, 2H), 7.63 (t, *J* = 7.4, Hz, 1H), 7.53-7.46 (m, 4H), 7.42 (t, *J* = 7.6, Hz, 2H), 7.36 (t, *J* = 7.1, Hz, 1H), 7.02 (s, 1H), 6.97 (d, *J* = 8.3, Hz, 2H), 3.85 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.6, 159.9, 151.1, 140.3, 140.1, 137.3, 133.5, 129.8, 128.9, 128.6, 128.0, 127.1, 124.81, 124.77, 114.1, 110.2, 55.3; HRMS (ESI+) calcd for $C_{23}H_{18}N_2O_2$+Na^+: 377.1260, found: 377.1258.

(3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl)(phenyl)methanone (2f): Table 2, entry 13



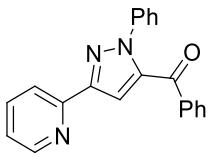
The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-((*E*)-1-(4-chlorophenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1g**) and purified after 24 h by column chromatography (*n*-hexane/ethyl acetate = 12:1) to give **2f** in 81% yield as a white solid. IR (neat) ν 1658, 1597, 1496, 1448, 1424, 1285, 1236, 1092, 1014, 956, 899, 837, 820, 762, 724, 709, 692, 678 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.7, Hz, 2H), 7.64 (t, *J* = 7.4, Hz, 1H), 7.54-7.46 (m, 4H), 7.46-7.35 (m, 5H), 7.06 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.4, 150.3, 140.6, 140.0, 137.1, 134.2, 133.7, 130.6, 129.8, 128.9 (2C), 128.6, 128.3, 127.1, 124.8, 110.4; HRMS (ESI+) calcd for $C_{22}H_{15}ClN_2O+Na^+$: 381.0765, found: 381.0756.

(3-(tert-butyl)-1-phenyl-1*H*-pyrazol-5-yl)(phenyl)methanone (2g): Table 2, entry 15



The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-((*E*)-2,2-dimethyl-6-phenylhex-5-en-3-ylidene)-2-phenylhydrazine (**1h**) and purified after 24 h by column chromatography (*n*-hexane/ethyl acetate = 15:1 to 12:1) to give **2g** in 63% yield as a white solid. IR (neat) ν 1657, 1597, 1500, 1448, 1364, 1286, 1236, 989, 899, 761, 734, 717, 691, 679 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.44-7.35 (m, 4H), 7.31 (t, *J* = 7.1 Hz, 1H), 6.65 (s, 1H), 1.40 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.8, 162.0, 140.3, 139.4, 137.4, 133.3, 129.7, 128.8, 128.5, 127.7, 124.8, 110.6, 32.2, 30.5; HRMS (ESI+) calcd for $C_{20}H_{20}N_2O+Na^+$: 327.1468, found: 327.1461.

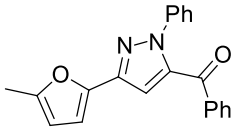
Phenyl(1-phenyl-3-(pyridin-2-yl)-1*H*-pyrazol-5-yl)methanone (2h): Table 2, entry 17



The title compound was prepared according to experimental procedure (**A**) from

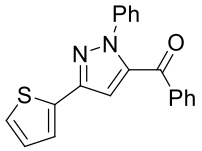
2-((1*E*,3*E*)-4-phenyl-1-(2-phenylhydrazono)but-3-en-1-yl)pyridine (**1i**) and purified after 18 h by column chromatography (*n*-hexane/ethyl acetate = 3:1) to give **2h** in 20% yield together with **3h** in 66% yield as inseparable mixture (yellow oil). IR (neat) ν 1659, 1593, 1568, 1529, 1501, 1484, 1458, 1422, 1387, 1370, 1279, 1267, 1148, 1049, 993, 960, 945, 900, 756, 716, 687, 621 cm^{-1}; ^{1}H-NMR (only **2k**; 400 MHz, $CDCl_3$) δ 8.66-8.62 (m, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.03-7.99 (m, 2H), 7.77-7.72 (m, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53-7.37 (m, 8H), 7.27-7.23 (m, 1H); ^{13}C-NMR (only **2k**; 100 MHz, $CDCl_3$) δ 185.3, 151.6, 151.1, 149.4, 140.5, 140.1, 137.1, 136.7, 133.6, 129.8, 128.9, 128.6, 128.3, 125.0, 123.1, 120.3, 112.2; HRMS (ESI+) calcd for (**2k**) $C_{21}H_{15}N_3O+Na^+$: 348.1107, found: 348.1101 and calcd for (**3l**) $C_{14}H_{11}N_3+Na^+$: 244.0845, found: 244.0847.

(3-(5-methylfuran-2-yl)-1-phenyl-1*H*-pyrazol-5-yl)(phenyl)methanone (2i): Table 2, entry 19



The title compound was prepared according to experimental procedure (**A**) on a 0.10 mmol scale from 1-((*Z*)-1-(5-methylfuran-2-yl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1j**) and purified after 23 h by column chromatography (*n*-hexane/ethyl acetate = 10:1) to give **2i** in 38% yield as an off-white solid. IR (neat) ν 1661, 1597, 1578, 1499, 1448, 1285, 1238, 1020, 910, 893, 789, 762, 730, 715, 691, 679 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99-7.94 (m, 2H), 7.63 (t, *J* = 7.6, Hz, 1H), 7.54-7.33 (m, 7H), , 6.96 (s, 1H), 6.69 (d, *J* = 3.2 Hz, 1H), 6.09 (dd, *J* = 3.2, 0.9 Hz, 1H), 2.38 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.3, 152.6, 145.8, 144.2, 140.0, 139.9, 137.1, 133.6, 129.8, 128.9, 128.6, 128.2, 125.1, 110.0, 108.0, 107.6, 13.7; HRMS (ESI+) calcd for $C_{21}H_{16}N_2O_2+Na^+$: 351.1104, found: 351.1093.

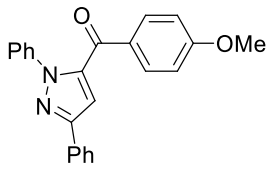
Phenyl(1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazol-5-yl)methanone (2j): Table 2, entry 21



The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-phenyl-2-((*Z*)-4-phenyl-1-(thiophen-2-yl)but-3-en-1-ylidene)hydrazine (**1k**) and purified after 23 h by column chromatography (once with *n*-hexane/ethyl acetate = 11:1 and a second time with *n*-hexane/DCM = 1:1) to give **2j** in 17% as a pale yellow solid. IR (neat) ν 1659, 1597, 1498, 1464, 1284, 1239, 921, 897, 848, 762, 715, 691, 678 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.3, 1.4 Hz,

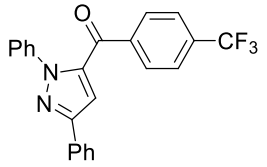
2H), 7.64 (t, *J* = 7.4, Hz, 1H), 7.54-7.33 (m, 8H), 7.32 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.97 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.4, 146.8, 140.4, 139.8, 137.1, 135.1, 133.7, 129.8, 128.9, 128.6, 128.2, 127.6, 125.5, 124.9, 124.7, 110.3; HRMS (ESI+) calcd for $C_{20}H_{14}N_2OS+Na^+$: 353.0719, found: 353.0710.

(1,3-diphenyl-1*H*-pyrazol-5-yl)(4-methoxyphenyl)methanone (2k): Table 2, entry 23



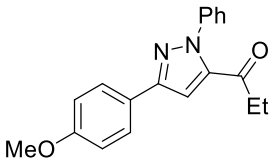
The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-((*Z*)-4-(4-methoxyphenyl)-1-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1l**) and purified after 27 h by column chromatography (*n*-hexane/ethyl acetate = 6:1 to 3:1) to give **2m** in 80% yield as a highly viscous yellow oil. IR (neat) ν 1653, 1597, 1498, 1428, 1288, 1263, 1170, 1028, 957, 902, 846, 764, 736, 694, 668, 621 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 7.2, Hz, 2H), 7.52-7.33 (m, 8H), 7.06 (s, 1H), 6.98 (d, *J* = 9.0, Hz, 2H), 3.89 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.4, 164.1, 151.3, 140.7, 140.0, 132.3, 132.2, 129.9, 128.9, 128.7, 128.3, 128.0, 125.8, 124.6, 113.9, 109.8, 55.5; HRMS (ESI+) calcd for $C_{23}H_{18}N_2O_2+Na^+$: 377.1260, found: 377.1257.

(1,3-diphenyl-1H-pyrazol-5-yl)(4-(trifluoromethyl)phenyl)methanone (2l): Table 2, entry 25



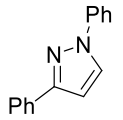
The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-phenyl-2-((*E*)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-ylidene)hydrazine (**1m**) and purified after 21 h by column chromatography (*n*-hexane/ethyl acetate = 9:1), followed by PTLC (*n*-hexane/DCM = 1:1) to give **2l** in 56% yield as a highly viscous yellow oil, which slowly solidified to an off-white solid after several days. IR (neat) ν 1664, 1499, 1426, 1323, 1286, 1169, 1130, 1109, 1066, 1016, 956, 902, 857, 765, 736, 714, 691 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 7.8, Hz, 2H), 7.78 (d, *J* = 8.3, Hz, 2H), 7.52-7.35 (m, 8H), 7.10 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.2, 151.6, 140.2, 140.0, 139.8, 134.7 (q, *J* = 32.8 Hz), 131.8, 129.9, 129.0, 128.8, 128.6, 128.4, 125.8, 125.6 (q, *J* = 3.9 Hz), 125.0, 123.5 (q, *J* = 272.9 Hz), 111.1; ^{19}F-NMR (378 MHz, $CDCl_3$) δ -63.0; HRMS (ESI+) calcd for $C_{23}H_{15}F_3N_2O+Na^+$: 415.1029, found: 415.1024.

1-(3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-5-yl)propan-1-one (2m): Table 2, entry 27



The title compound was prepared according to experimental procedure (**A**) from (*E*)-1-((*E*)-1-(4-methoxyphenyl)hex-3-en-1-ylidene)-2-phenylhydrazine (**1n**) and purified after 28 h by column chromatography (*n*-hexane/ethyl acetate = 6:1 to 5:1) to give **2m** in 33% yield as a yellow solid. IR (neat) ν 1689, 1614, 1597, 1508, 1499, 1458, 1424, 1304, 1290, 1250, 1174, 1030, 956, 927, 836, 797, 767, 695 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.51-7.40 (m, 5H) 7.20 (s, 1H), 6.96 (d, *J* = 8.7, Hz, 2H), 3.85 (s, 3H), 2.92 (d, *J* = 7.2, Hz, 2H), 1.17 (t, *J* = 7.4, Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.2, 159.8, 151.2, 140.8, 140.6, 128.7, 128.5, 127.1, 126.0, 124.8, 114.1, 108.3, 55.3, 34.1, 7.9; HRMS (ESI+) calcd for $C_{19}H_{18}N_2O_2$+Na^+: 329.1260, found: 329.1266.

1,3-diphenyl-1*H*-pyrazole (3a)[10]: Table 2, entries 2, 24 and 26

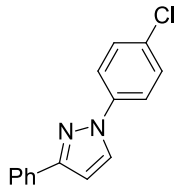


The title compound was prepared according to experimental procedure (**B**) from (*E*)-1-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1a**) and purified after 19 h by column chromatography (*n*-hexane/ethyl acetate = 11:1) to give **3a** in 99% yield as a white solid.

Preparation from (*E*)-1-((*Z*)-4-(4-methoxyphenyl)-1-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1m**) or (*E*)-1-phenyl-2-((*E*)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-ylidene)hydrazine (**1n**) led to lower yields (see paper; Table 2). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98-7.93 (m, 3H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.51-7.43 (m, 4H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 2.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.9, 140.2, 133.1, 129.4, 128.6, 128.0, 127.9, 126.3, 125.8, 119.0, 105.0.

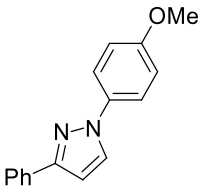
10) X. Tang, L. Huang, J. Yang, Y. Xu, W. Wu, H. Jiang, *Chem. Commun.*, **2014**, *50*, 14793.

1-(4-chlorophenyl)-3-phenyl-1*H*-pyrazole (3b)[10]: Table 2, entry 4



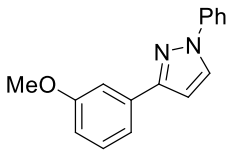
The title compound was prepared according to experimental procedure (**B**) from (*E*)-1-(4-chlorophenyl)-2-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)hydrazine (**1b**) and purified after 20 h by column chromatography (*n*-hexane/ethyl acetate = 10:1) to give **3b** in 99% yield as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 2.8 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.49-7.40 (m, 4H), 7.37 (t, *J* = 6.7 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.1, 138.7, 132.8, 131.6, 129.4, 128.6, 128.2, 127.8, 125.8, 120.0, 105.3.

1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazole (3c)[10]: Table 2, entry 6



The title compound was prepared according to experimental procedure (**B**) from (*E*)-1-(4-methoxyphenyl)-2-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)hydrazine (**1c**) and purified after 22 h by column chromatography (*n*-hexane/ethyl acetate = 5:1) to give **3c** in 100% yield as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.3, 0.9 Hz, 2H), 7.85 (d, *J* = 2.3 Hz, 1H), 7.67 (d, *J* = 9.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 2.3 Hz, 1H), 3.84 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.1, 152.4, 134.0, 133.2, 128.6, 128.0, 127.8, 125.7, 120.7, 114.4, 104.5, 55.5.

3-(3-methoxyphenyl)-1-phenyl-1*H*-pyrazole (3d): Table 2, entries 8 and 10

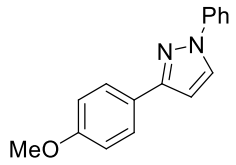


The title compound was prepared according to experimental procedure (**B**) from (*E*)-1-((*E*)-1-(3-methoxyphenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1d**) and purified after 20 h by column chromatography (*n*-hexane/ethyl acetate = 8:1) to give **3d** in 91% yield as a highly

viscous yellow oil.

Preparation from (*E*)-1-((*Z*)-1-(3-methoxyphenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1e**) and purification after 20 h by column chromatography (*n*-hexane/ethyl acetate = 8:1) gave **3d** in 93% yield. IR (neat) ν 1600, 1529, 1505, 1471, 1437, 1355, 1284, 1217, 1045, 948, 839, 753, 689 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.3 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.55-7.44 (m, 4H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.92 (dd, *J* = 8.3, 2.8 Hz, 1H), 6.77 (d, *J* = 2.3 Hz, 1H), 3.90 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.9, 152.7, 140.1, 134.4, 129.6, 129.4, 127.9, 126.3, 119.0, 118.4, 113.9, 110.9, 105.1, 55.3; HRMS (ESI+) calcd for $C_{16}H_{14}N_2O+Na^+$: 273.0998, found: 273.0997.

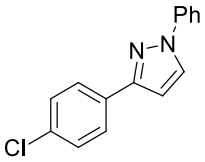
3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (3e)[10]: Table 2, entries 12 and 28



The title compound was prepared according to experimental procedure (**B**) from (*E*)-1-((*E*)-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1f**) and purified after 20 h by column chromatography (*n*-hexane/ethyl acetate = 6:1) to give **3e** in 95% yield as an off-white solid.

Preparation from (*E*)-1-((*E*)-1-(4-methoxyphenyl)hex-3-en-1-ylidene)-2-phenylhydrazine (**1l**) and purification after 22 h by column chromatography (*n*-hexane/ethyl acetate = 8:1) gave **3e** in 72% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.8 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 2.8 Hz, 1H), 3.86 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.5, 152.7, 140.2, 129.3, 127.8, 127.0, 126.1, 125.9, 118.9, 114.0, 104.5, 55.3.

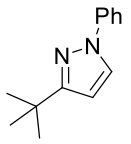
3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole (3f)[10]: Table 2, entry 14



The title compound was prepared according to experimental procedure (**B**) from (*E*)-1-((*E*)-1-(4-chlorophenyl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1g**) and purified after 20 h by column chromatography (*n*-hexane/ethyl acetate = 12:1) to give **3f** in 100% yield as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.3 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.77 (dd, *J* = 8.7, 0.9 Hz,

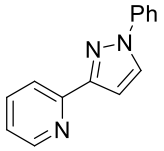
2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 151.7, 140.0, 133.7, 131.6, 129.4, 128.8, 128.1, 127.0, 126.5, 119.0, 104.9.

3-(*tert*-butyl)-1-phenyl-1*H*-pyrazole (3g): Table 2, entry 16



The title compound was prepared according to experimental procedure (**B**) from (*E*)-1-((*E*)-2,2-dimethyl-6-phenylhex-5-en-3-ylidene)-2-phenylhydrazine (**1h**) and purified after 24 h by column chromatography (*n*-hexane/ethyl acetate = 15:1) to give **3g** in 93% yield as a colorless oil. IR (neat) ν 1602, 1529, 1502, 1367, 1269, 1169, 1045, 981, 949, 901, 753, 723, 689 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.8 Hz, 1H), 7.71-7.67 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.33 (d, *J* = 2.3 Hz, 1H), 1.40 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.6, 140.4, 129.3, 126.8, 125.7, 118.9, 104.1, 32.3, 30.5; HRMS (ESI+) calcd for $C_{13}H_{16}N_2$+Na^+: 223.1206, found: 223.1206.

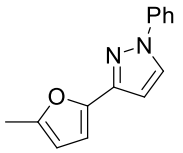
2-(1-phenyl-1*H*-pyrazol-3-yl)pyridine (3h)[11]: Table 2, entry 18



The title compound was prepared according to experimental procedure (**B**) from 2-((1*E*,3*E*)-4-phenyl-1-(2-phenylhydrazono)but-3-en-1-yl)pyridine (**1i**) and purified after 22 h by column chromatography (*n*-hexane/ethyl acetate = 3:1; deactivated silica) to give **3h** in 95% yield as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.6 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 2.3 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.74 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.22 (dd, *J* = 6.7, 5.3 Hz, 1H), 7.13 (d, *J* = 2.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.2, 151.9, 149.3, 140.1, 136.5, 129.4, 128.2, 126.5, 122.6, 120.3, 119.2, 106.4.

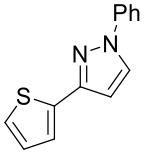
11) L. He, L. Duan, J. Qiao, D. Zhang, L. Wang, Y. Qiu, *Chem. Commun.*, **2011**, *47*, 6467.

3-(5-methylfuran-2-yl)-1-phenyl-1*H*-pyrazole (3i): Table 2, entry 20



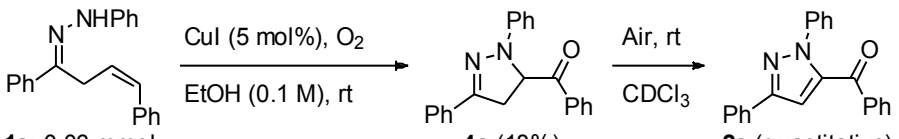
The title compound was prepared according to experimental procedure (**B**) on a 0.10 mmol scale from 1-((*Z*)-1-(5-methylfuran-2-yl)-4-phenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1j**) and purified after 23 h by column chromatography (*n*-hexane/ethyl acetate = 10:1) to give **3i** in 68% yield as a yellow oil. IR (neat) ν 1600, 1577, 1518, 1508, 1374, 1330, 1261, 1045, 1020, 947, 898, 786, 752, 690, 647 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.8 Hz, 1H), 7.74 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 3.2 Hz, 1H), 6.65 (d, *J* = 2.3 Hz, 1H), 6.08 (dd, *J* = 3.2, 0.9 Hz, 1H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.2, 146.7, 145.6, 139.9, 129.3, 127.8, 126.4, 119.2, 107.5, 107.4, 104.6, 13.7; HRMS (ESI+) calcd for $C_{14}H_{12}N_2O$+Na^+: 247.0842, found: 247.0840.

1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazole (3j)[10]: Table 2, entry 22



The title compound was prepared according to experimental procedure (**B**) from ((*E*)-1-phenyl-2-((*Z*)-4-phenyl-1-(thiophen-2-yl)but-3-en-1-ylidene)hydrazine (**1k**) and purified after 23 h by column chromatography (*n*-hexane/ethyl acetate = 10:1) to give **3j** in 100% yield as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.8 Hz, 1H), 7.75 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.42 (dd, *J* = 3.7, 1.4 Hz, 1H), 7.32-7.26 (m, 2H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.68 (d, *J* = 2.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.2, 139.9, 136.3, 129.4, 128.0, 127.4, 126.3, 124.9, 124.2, 119.0, 105.0.

(I) Formation and isolation of 4a, 5, and 6

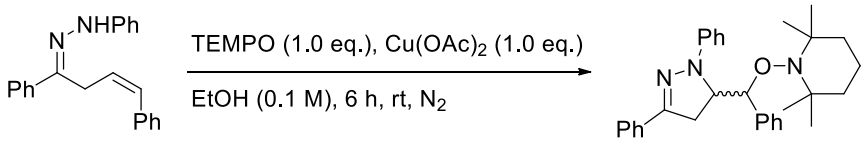


1a: 0.06 mmol **4a** (18%) **2a** (quantitative)

(*E*)-1-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1a**) (18.7 mg; 0.06 mmol; 1.0 eq.) was converted under the standard conditions (**A**) in EtOH, but with CuI (0.6 mg; 0.003 mmol; 0.05 eq.)

instead of $Cu(OAc)_2$ for 18 h. The crude product was purified by column chromatography (*n*-hexane/ethyl acetate = 11:1) to give (1,3-diphenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (**4a**) in 18% (3.6 mg; 0.011 mmol) as a white solid. The ^{1}H NMR spectrum was measured directly after ~15 h and after ~2.5 days, by which time **4a** had been quantitatively converted to **2a** in the absence of any catalyst.

1-((1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)(phenyl)methoxy)-2,2,6,6-tetramethylpiperidine (5)

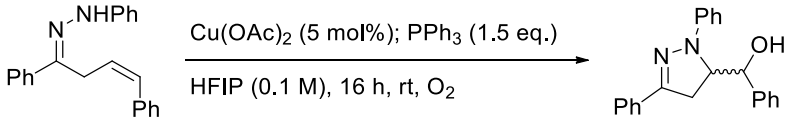


1a: 0.10 mmol

5: 94% (82:18 d.r.)

(*E*)-1-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1a**) (31.2 mg; 0.10 mmol; 1.0 eq.) was stirred in the presence of $Cu(OAc)_2$ (18.2 mg; 0.10 mmol; 1.0 eq.) and TEMPO (15.6 mg; 0.10 mmol; 1.0 eq.) in freshly degassed EtOH (1.0mL) for 6 h under N_2. The mixture was then passed through a short pad of silica with EtOAc and the crude product purified by column chromatography (*n*-hexane/ethyl acetate = 15:1) to give the diastereomeric mixture (82:18) of 1-((1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)(phenyl)methoxy)-2,2,6,6-tetramethylpiperidine (**5**) as a slightly yellow oil, containing traces of other impurities. A second column chromatography (*n*-hexane/ethyl acetate = 20:1) provided the minor compound in 14% (6.7 mg; 0.014 mmol; single diastereomer) as a pale yellow solid and the major compound in 80% (96:4 d.r.), which was further purified by crystallization from Et_2O/*n*-hexane to give a white solid in 47% (21.9 mg; 0.047 mmol; single diastereomer). The isolated products seem to be stable, but color change was observed after prolonged time on silica under air. Major: IR (neat) ν 1597, 1504, 1494, 1395, 1339, 1130, 954, 754, 691 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74-7.69 (m, 2H), 7.42-7.22 (m, 12H), 6.84 (t, *J* = 6.9 Hz, 1H), 5.13 (m, 1H), 4.72 (dd, *J* = 12.9, 6.0 Hz, 1H), 3.80 (dd, *J* = 16.6, 6.0 Hz, 1H), 3.56 (dd, *J* = 16.8, 12.6 Hz, 1H), 1.55-0.80 (m, 15H), 0.25 (bs, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.1, 144.9, 140.0, 133.0, 129.3, 129.0, 128.4, 128.3, 128.0, 127.9, 125.7, 118.7, 113.4, 86.0, 64.7, 61.0, 59.1, 40.6, 35.1, 33.8, 33.4, 20.6, 17.1; HRMS (ESI+) calcd for $C_{31}H_{37}N_3O+Na^+$: 490.2829, found: 490.2842. Minor: IR (neat) ν 1597, 1504, 1494, 1398, 1131, 1033, 745, 704, 690 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 7.38-7.21 (m, 7H), 7.17-7.05 (m, 5H), 6.85 (t, *J* = 7.1 Hz, 1H), 5.29-5.20 (m, 2H), 3.26 (s, 1H), 3.24 (s, 1H), 1.70-0.75 (m, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.9, 144.8, 138.0, 132.7, 129.3, 128.1 (2C), 127.6, 127.3, 127.2, 125.5, 118.4, 112.7, 82.2, 61.5, 60.7, 59.8, 40.5, 35.3, 34.1, 33.8, 29.7, 20.8, 20.4, 17.1; HRMS (ESI+) calcd for $C_{31}H_{37}N_3O+Na^+$: 490.2829, found: 490.2853.

(1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)(phenyl)methanol (6)

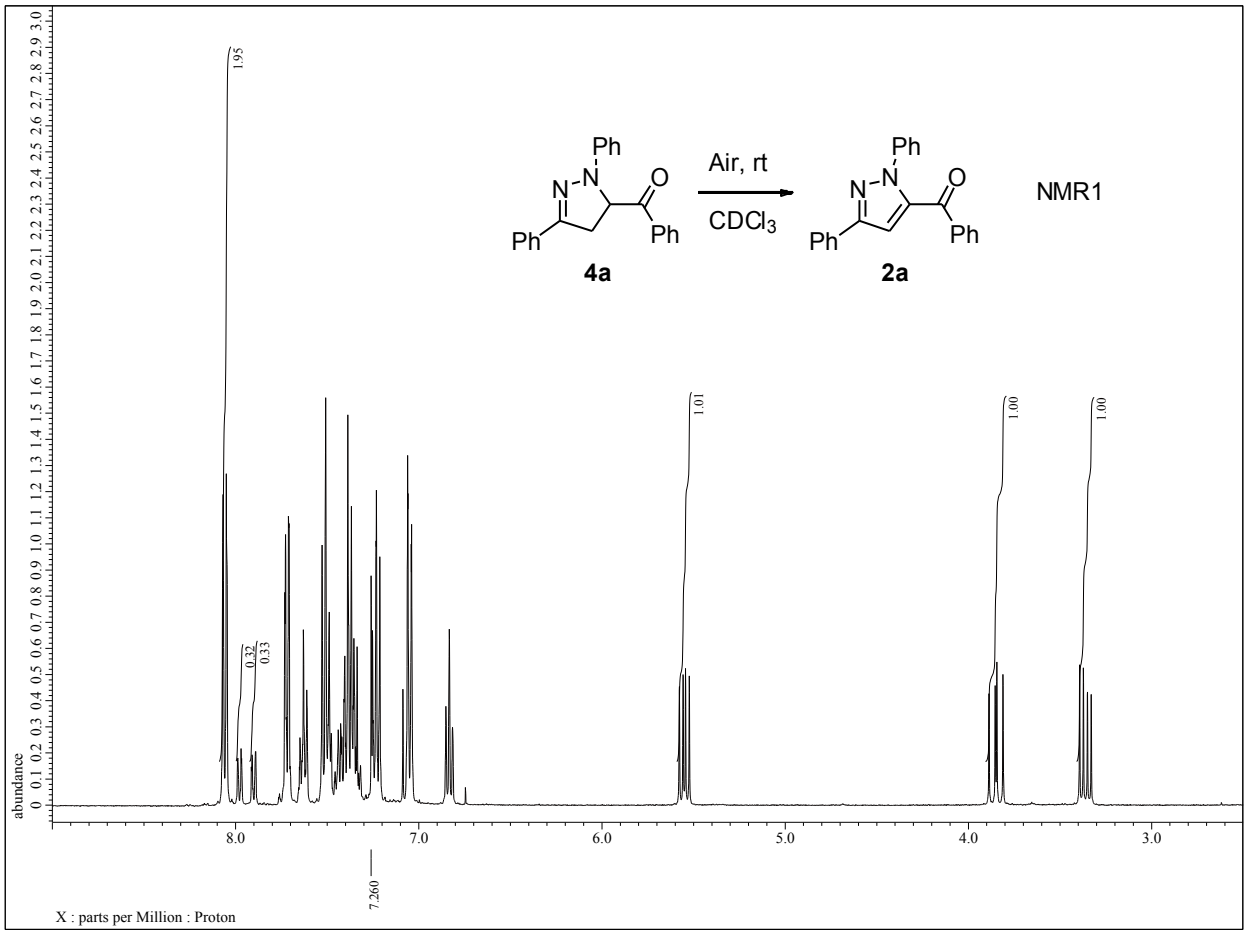


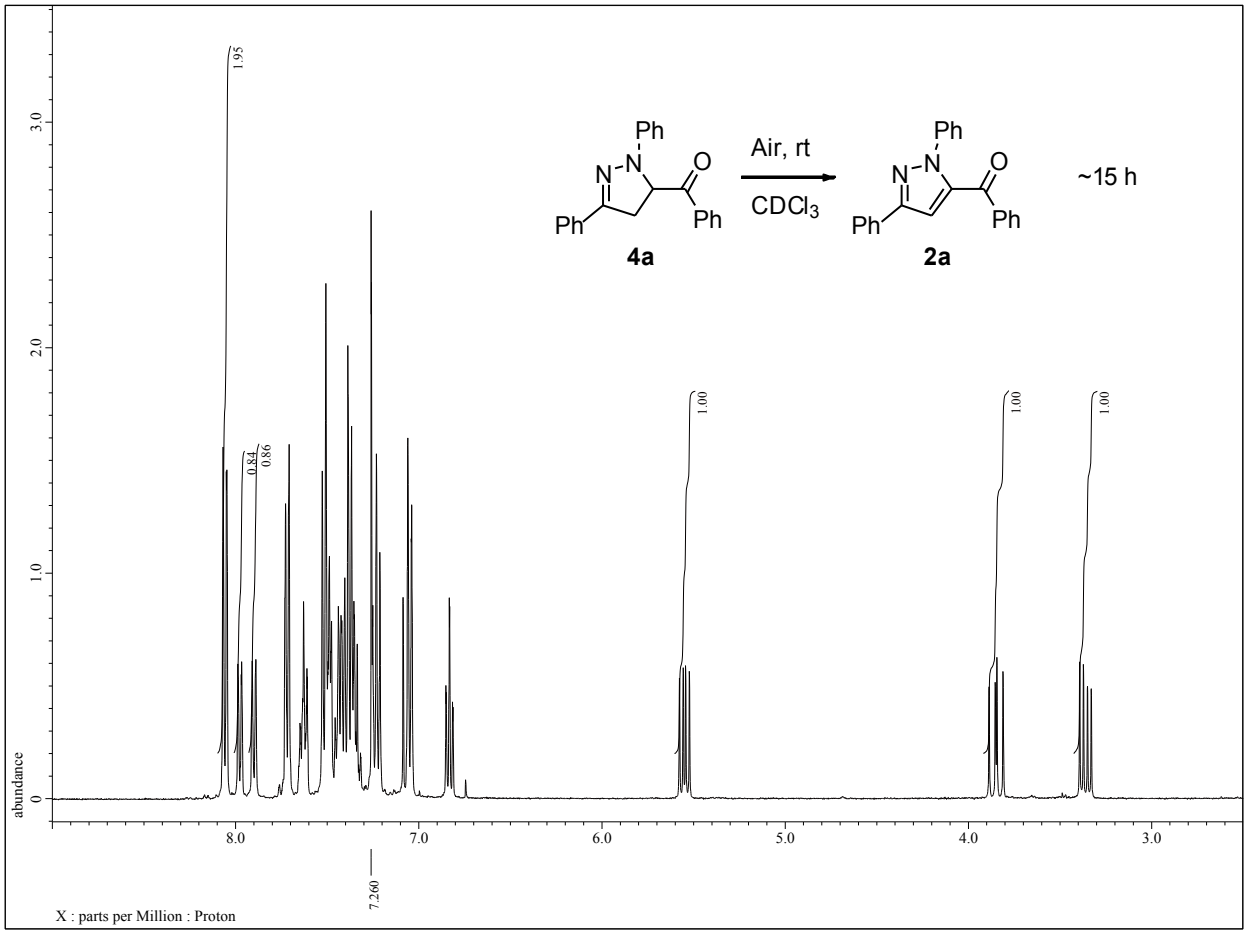
1a: 0.10 mmol

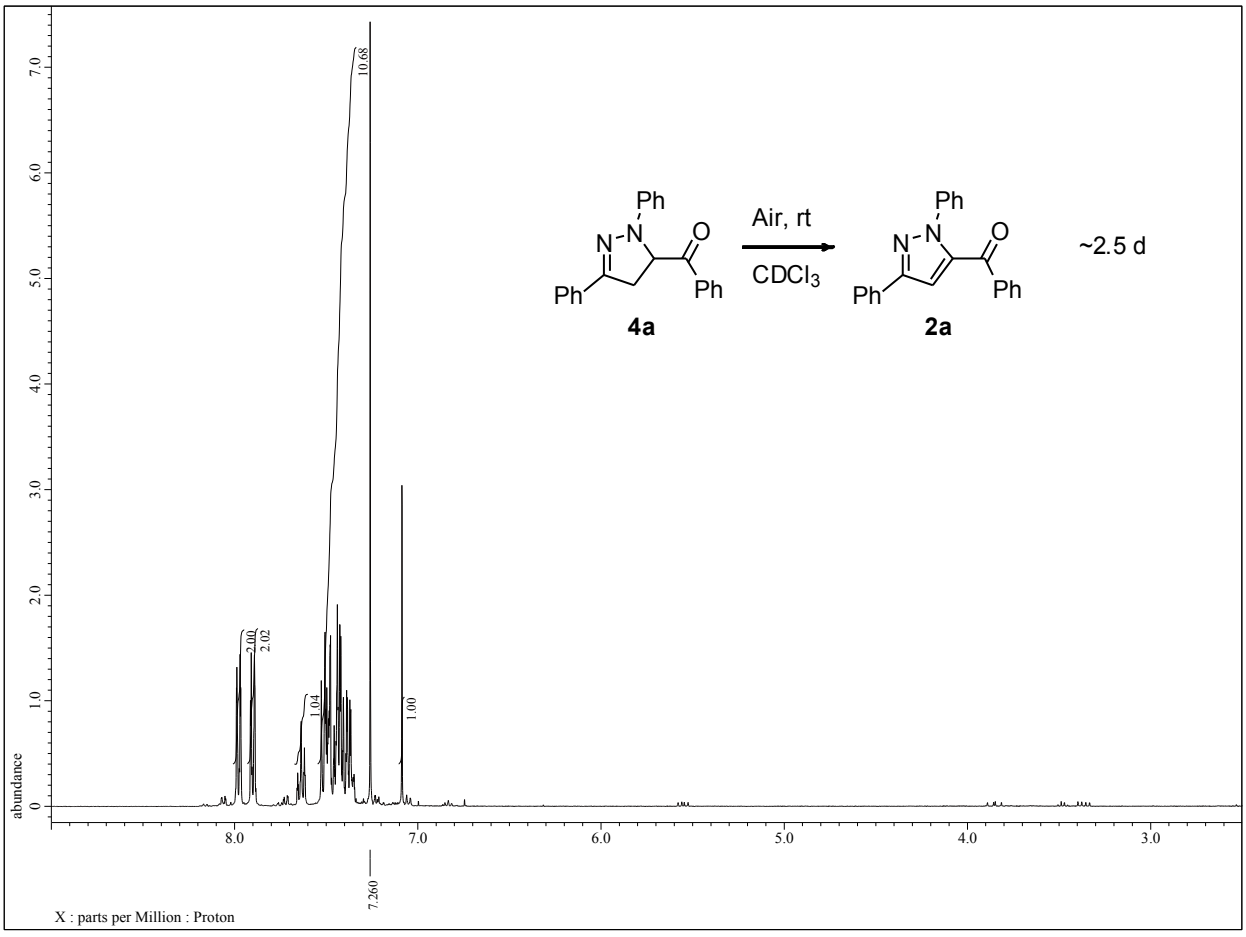
6 (64%; 78:22 d.r.)

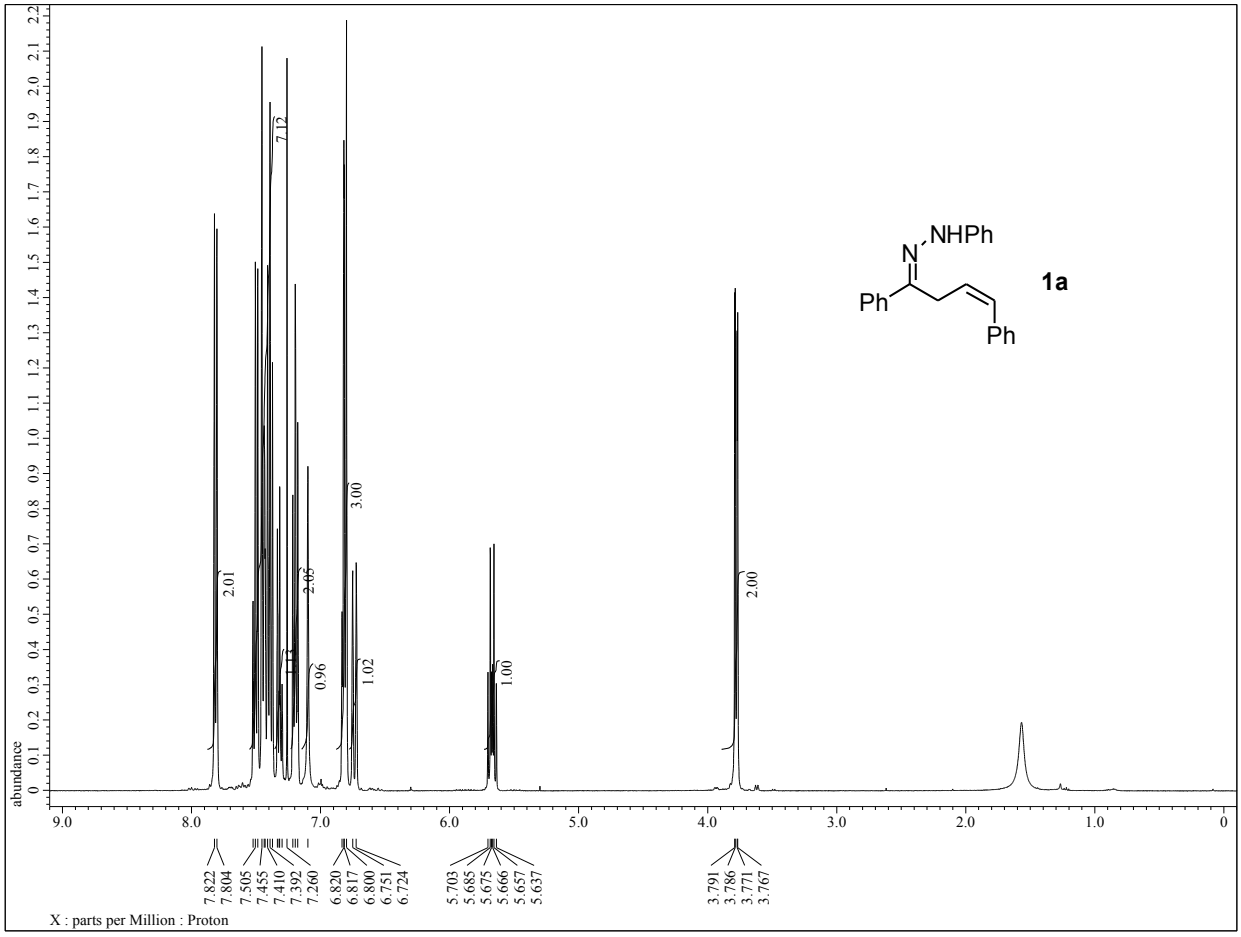
(*E*)-1-((*Z*)-1,4-diphenylbut-3-en-1-ylidene)-2-phenylhydrazine (**1a**) (31.2 mg; 0.10 mmol; 1.0 eq.) was stirred in the presence of $Cu(OAc)_2$ (0.9 mg; 0.005 mmol; 0.05 eq.) and PPh_3 (15.6 mg; 0.10 mmol; 1.0 eq.) in HFIP (1.0mL) for 16 h under O_2. The mixture was then passed through a short pad of silica with EtOAc and the crude product purified by PTLC (*n*-hexane/ethyl acetate = 3:1) to give the minor diastereomer in <16% (slightly impure) as yellow oil and the major diastereomer of (1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)(phenyl)methanol (**6**) as an impure pale yellow solid that was further purified by crystallization from Et_2O/*n*-hexane, providing the pure product as white solid in 23%. The isolated solid product seems to be stable, but slowly decomposes in solution under air. Major only: IR (neat) ν 1596, 1503, 1493, 1447, 1392, 1126, 1069, 1033, 745, 691 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.4 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.41-7.31 (m, 8H), 6.94 (t, *J* = 6.7 Hz, 1H), 5.48 (bs, 1H), 4.65 (ddd, *J* = 12.0, 6.9, 2.3 Hz, 1H), 3.35 (dd, *J* = 17.0, 6.9 Hz, 1H), 3.05 (dd, *J* = 17.2, 12.2 Hz, 1H), 2.24 (d, *J* = 1.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.8, 145.2, 139.6, 132.4, 129.4, 128.9, 128.6, 128.5, 127.6, 126.0, 125.6, 120.0, 113.9, 70.5, 66.8, 32.5; HRMS (ESI+) calcd for $C_{22}H_{20}N_2O+Na^+$: 351.1468, found: 351.1497.

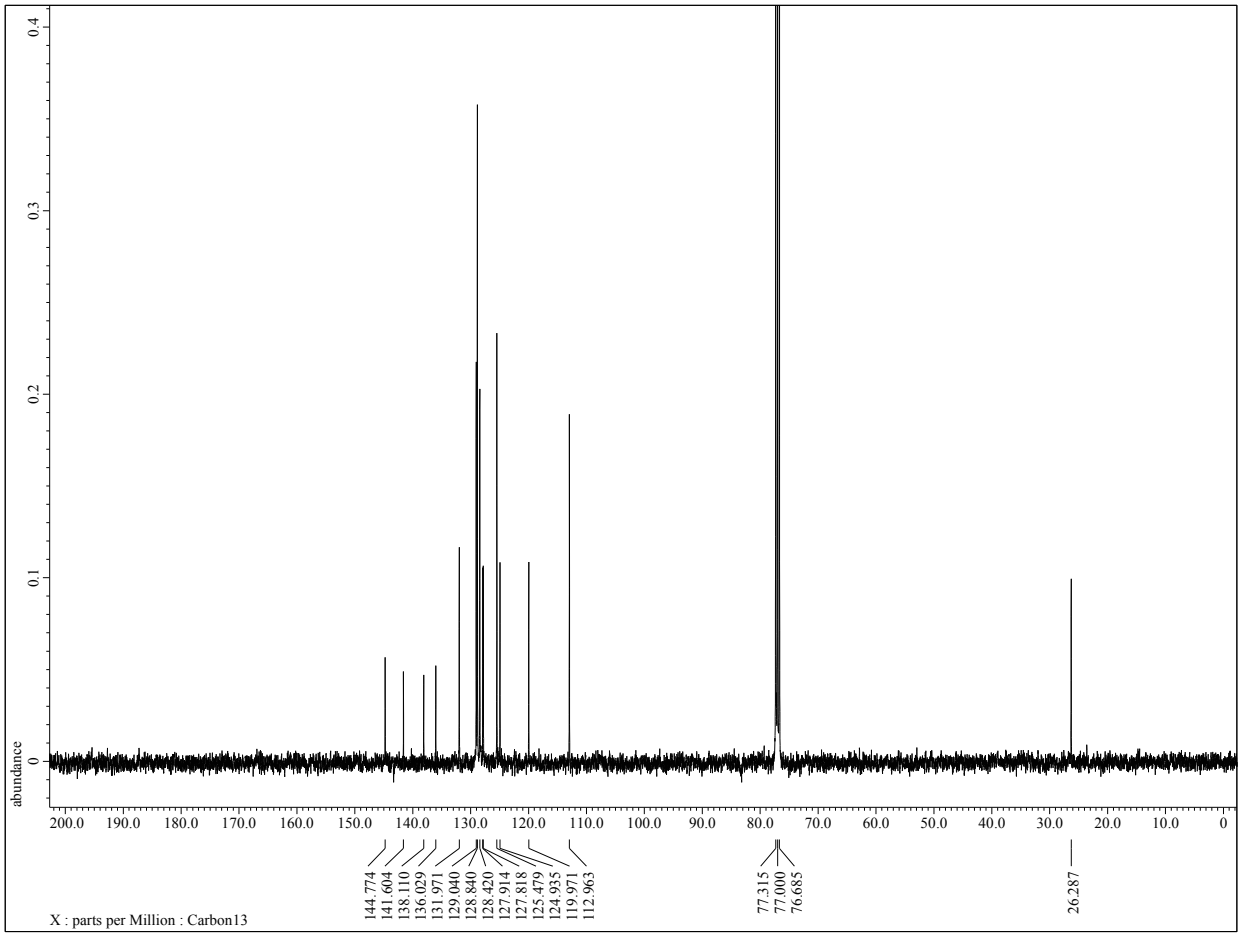
(J) NMR Spectra

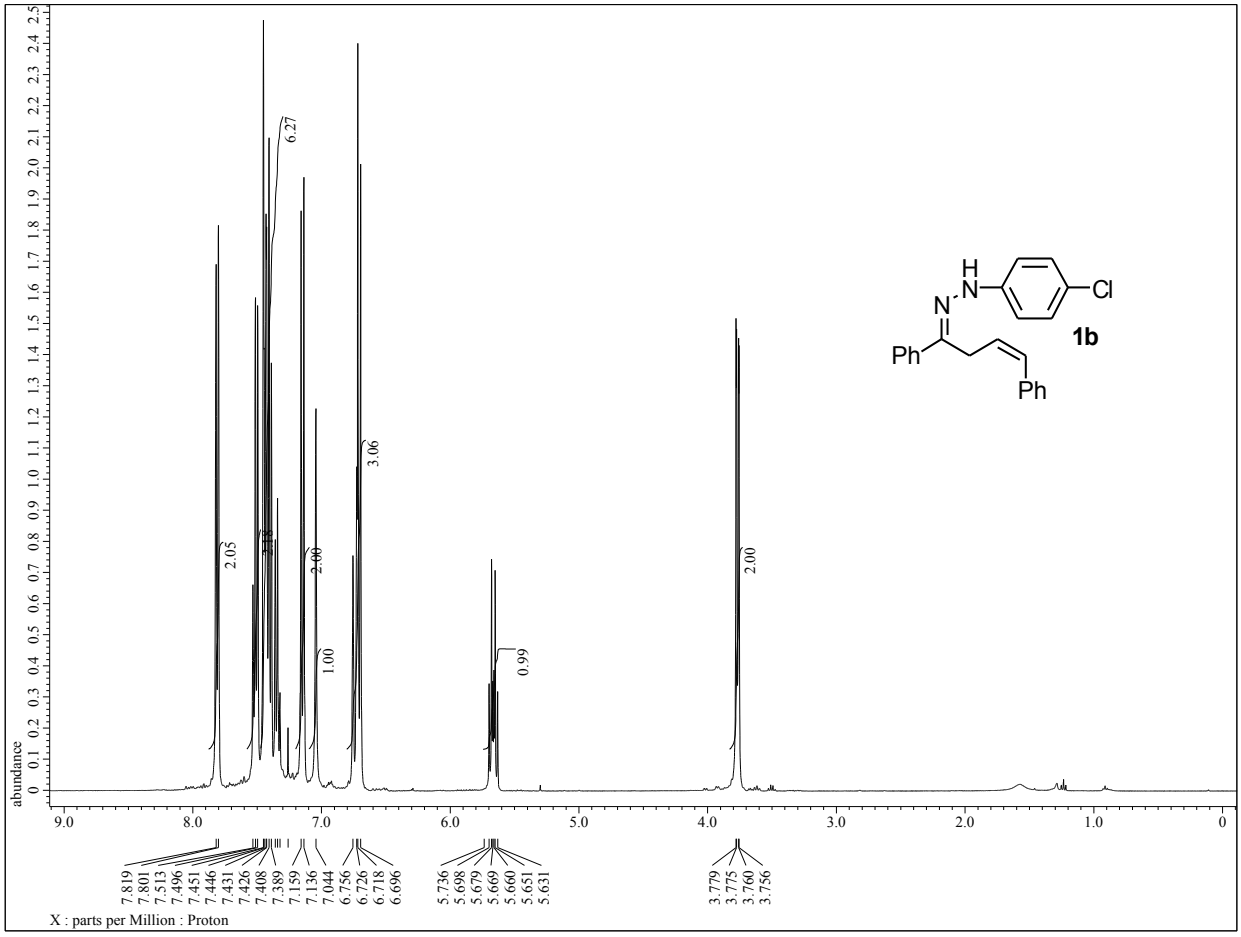


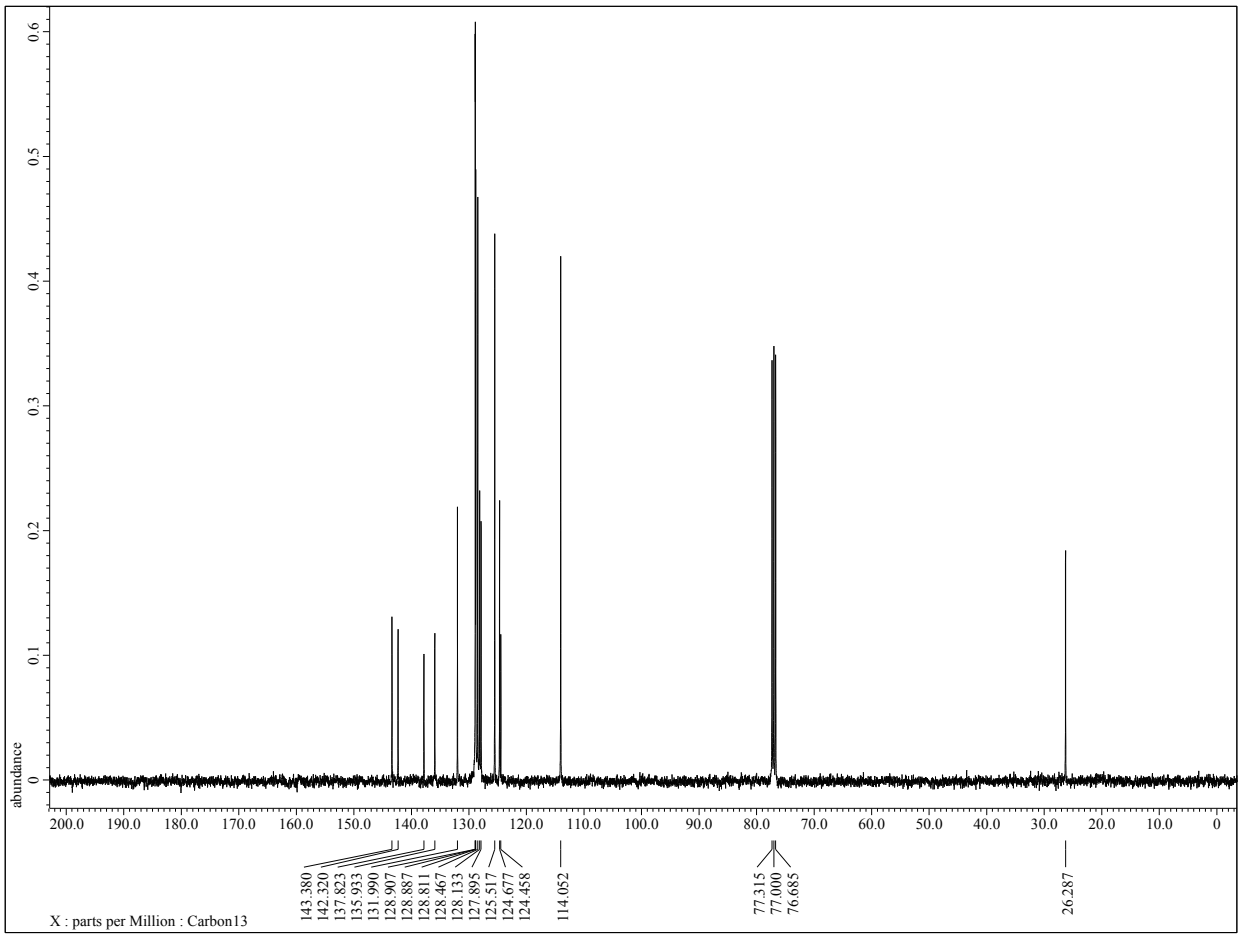

Ph
N-N
O
Ph
Ph
4a
Air, rt
CDCl3
Ph
N-N
O
Ph
Ph
2a
~15 h
1.95
0.83
0.86
1.00
1.00
1.00
abundance
8.0
7.0
6.0
5.0
4.0
3.0
7.260
X : parts per Million : Proton

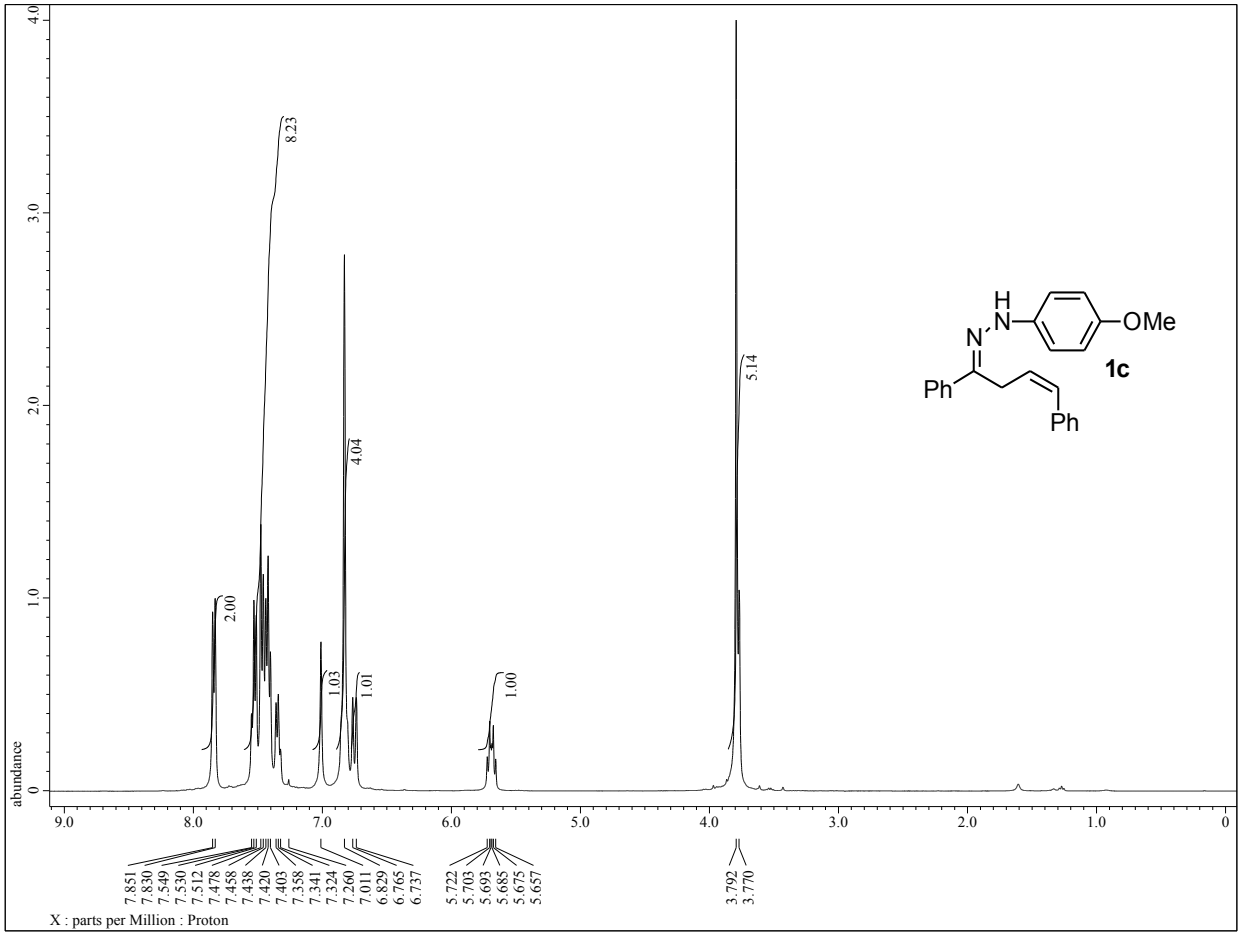

Ph
N-N
O
Ph
Ph
4a
Air, rt
CDCl3
Ph
N-N
O
Ph
Ph
2a
~2.5 d
10.68
2.00
2.02
1.04
1.00
abundance
8.0
7.0
6.0
5.0
4.0
3.0
7.260
X : parts per Million : Proton

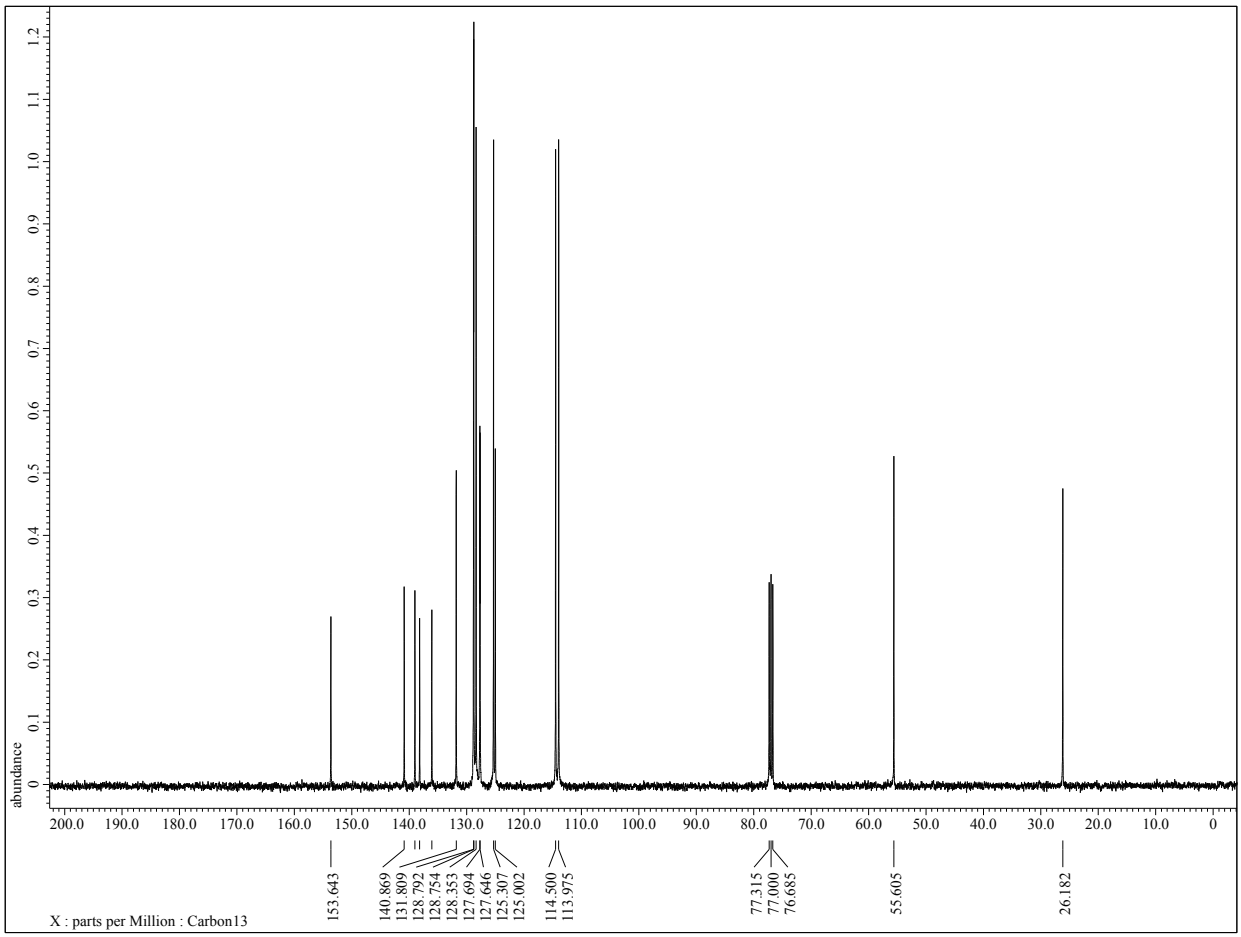

NHPh
N
Ph
Ph
1a
abundance
2.01
7.12
2.05
3.00
0.96
1.02
1.00
2.00
7.822
7.804
7.505
7.455
7.410
7.392
7.260
6.820
6.817
6.800
6.751
6.724
5.703
5.685
5.675
5.666
5.657
5.637
3.791
3.786
3.771
3.767
X : parts per Million : Proton

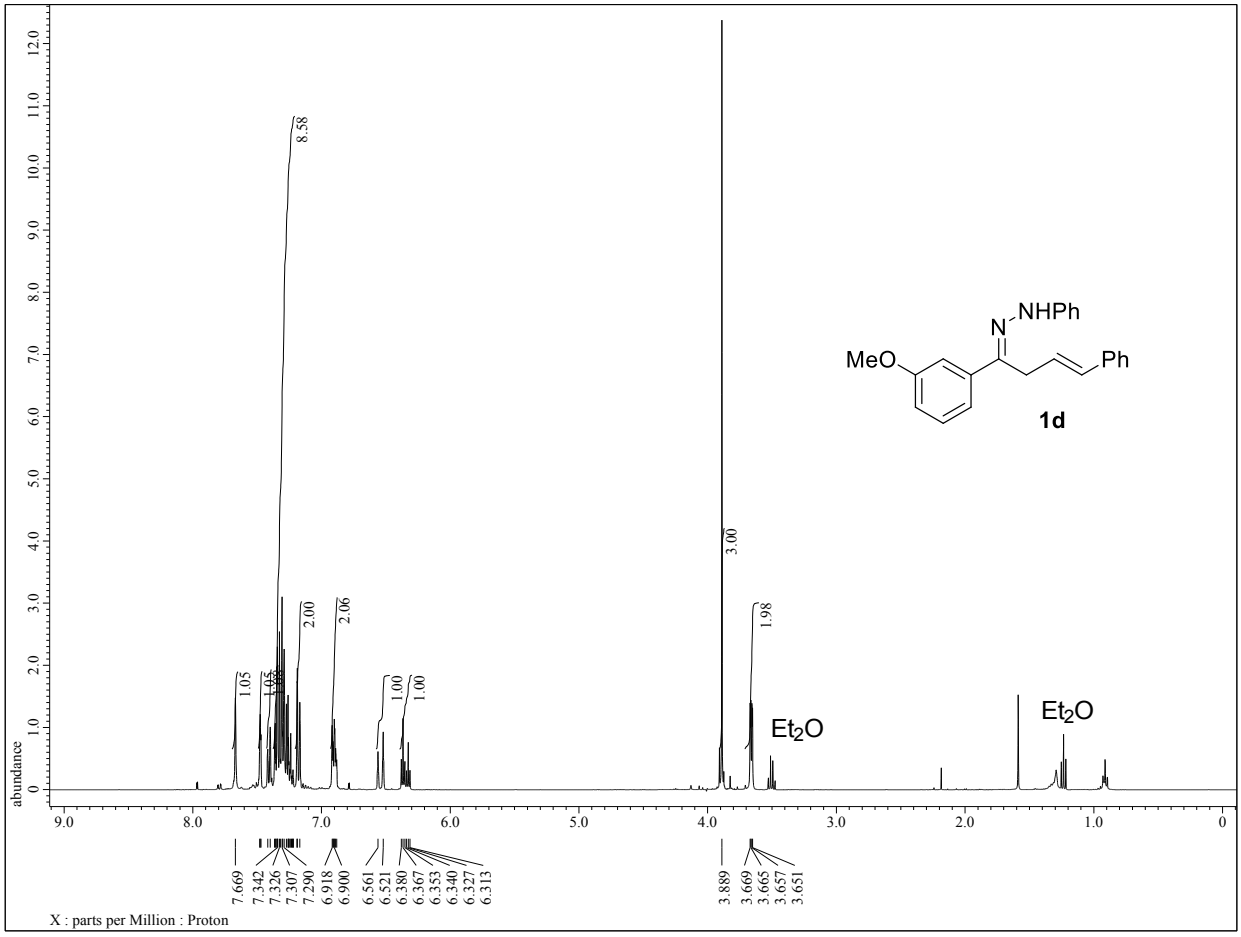

abundance
144.774
141.604
138.110
136.029
131.971
129.040
128.840
128.420
127.914
127.818
125.479
124.935
119.971
112.963
77.315
77.000
76.685
26.287
X : parts per Million : Carbon13

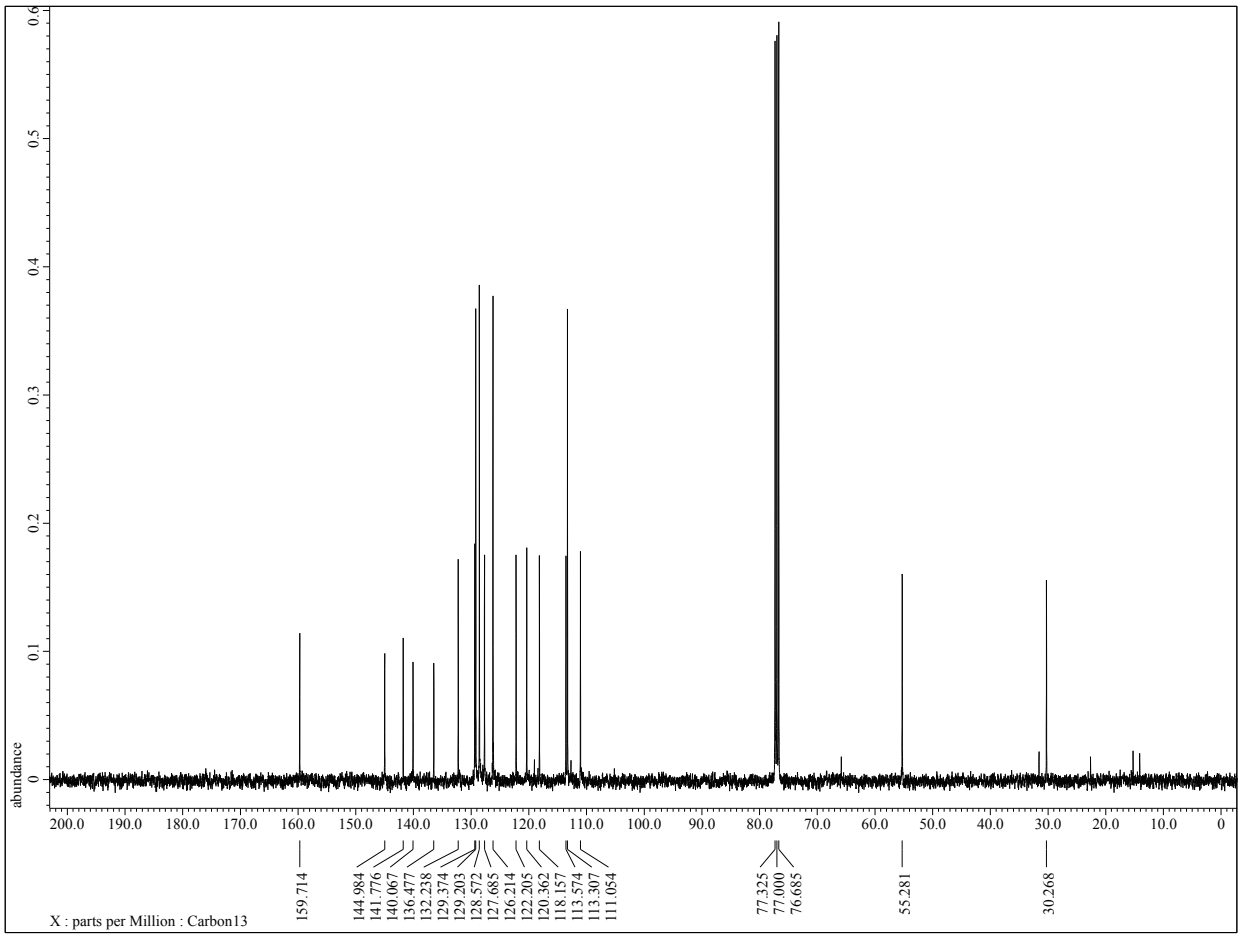

abundance
6.27
3.06
2.05
2.00
1.00
0.99
2.00
7.819
7.801
7.513
7.496
7.451
7.446
7.431
7.426
7.408
7.389
7.159
7.136
7.044
6.756
6.726
6.718
6.696
5.736
5.698
5.679
5.669
5.660
5.651
5.631
3.779
3.775
3.760
3.756
X : parts per Million : Proton
H
N
N
Cl
Ph
Ph
1b

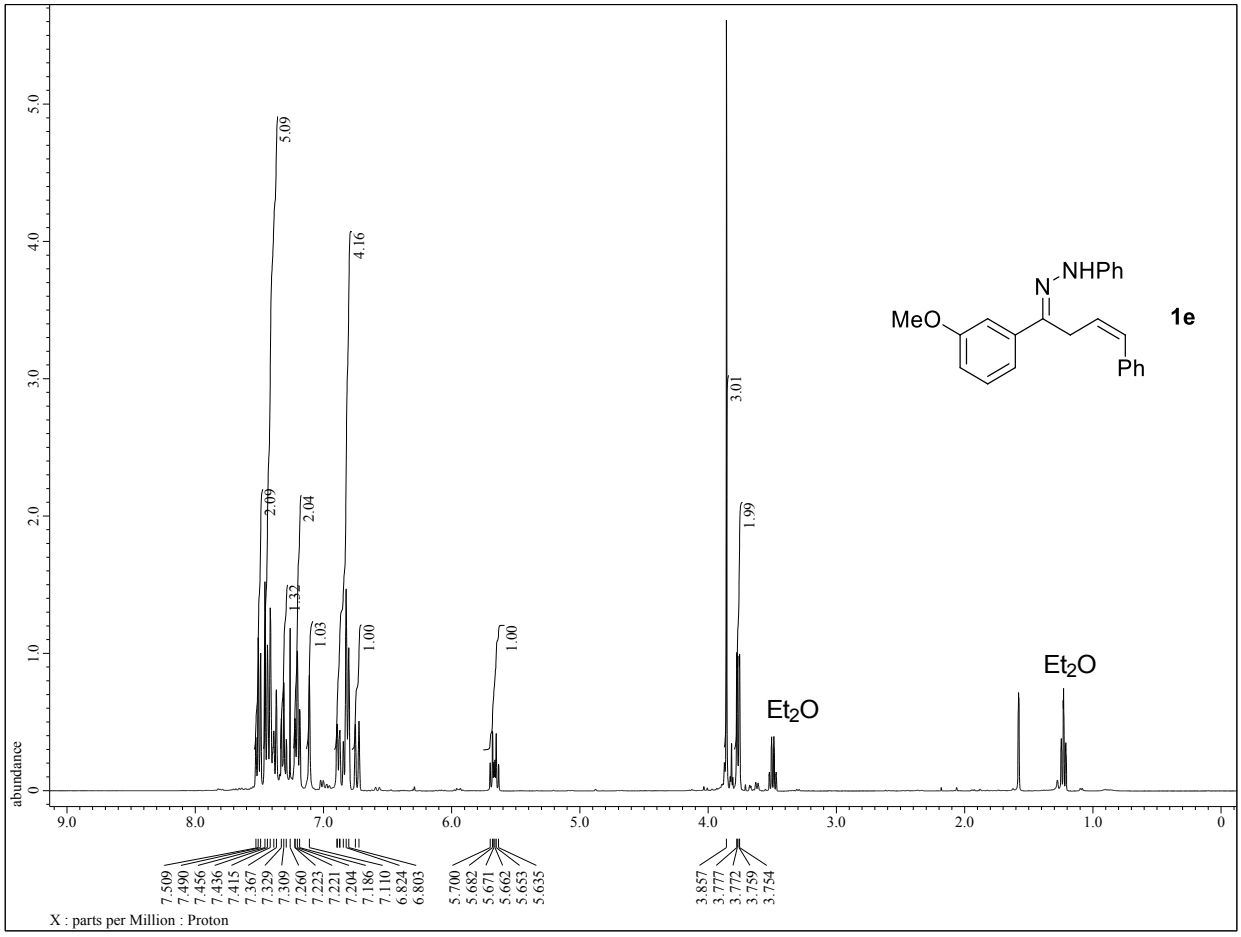

abundance
143.380
142.320
137.823
135.933
131.990
128.907
128.887
128.811
128.467
128.133
127.895
125.517
124.677
124.458
114.052
77.315
77.000
76.685
26.287
X : parts per Million : Carbon13

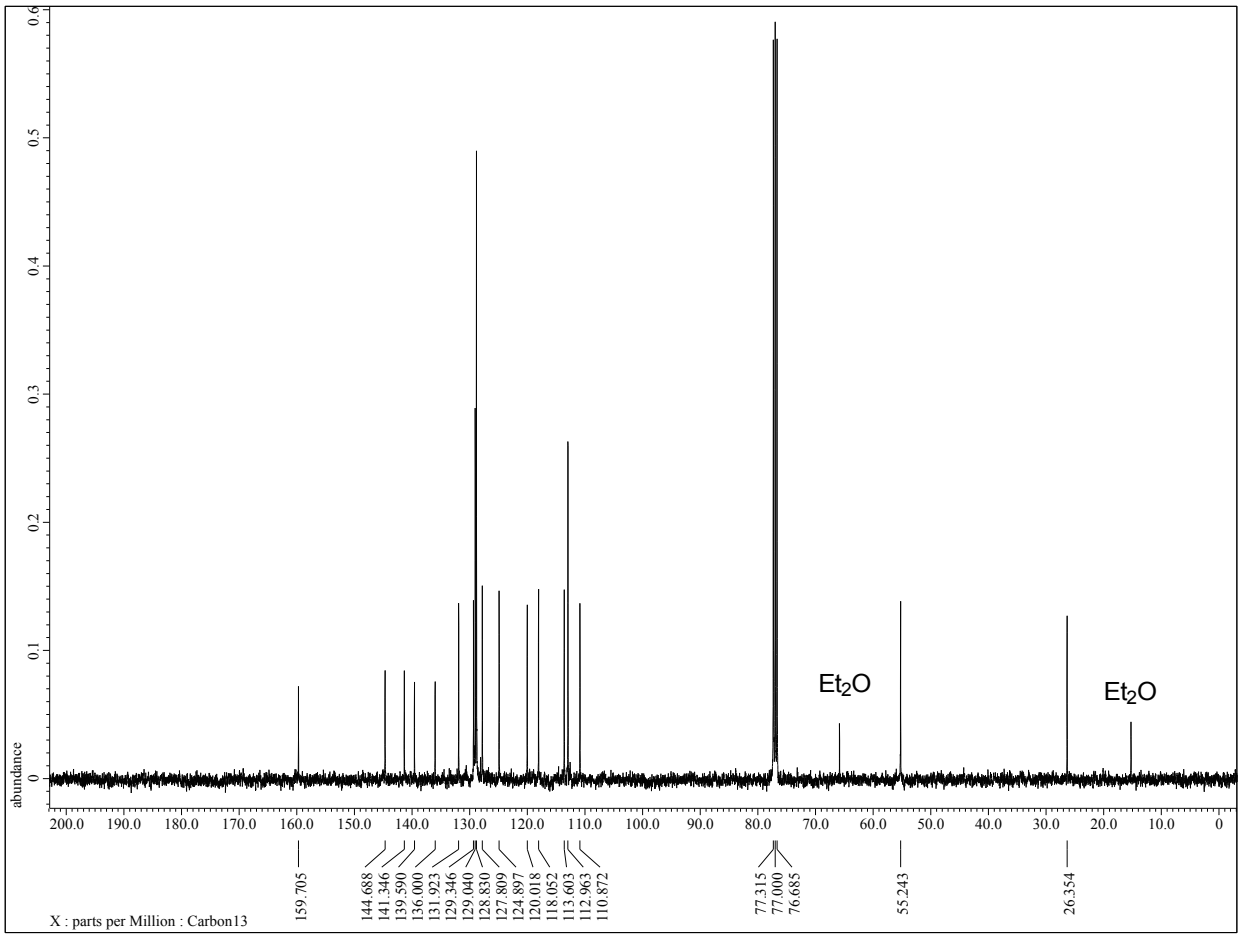

abundance
8.23
2.00
1.03
4.04
1.01
1.00
5.14
H
N
N
OMe
1c
Ph
Ph
7.851
7.830
7.549
7.530
7.512
7.478
7.458
7.438
7.420
7.403
7.358
7.341
7.324
7.260
7.011
6.829
6.765
6.737
5.722
5.703
5.693
5.685
5.675
5.657
3.792
3.770
X : parts per Million : Proton

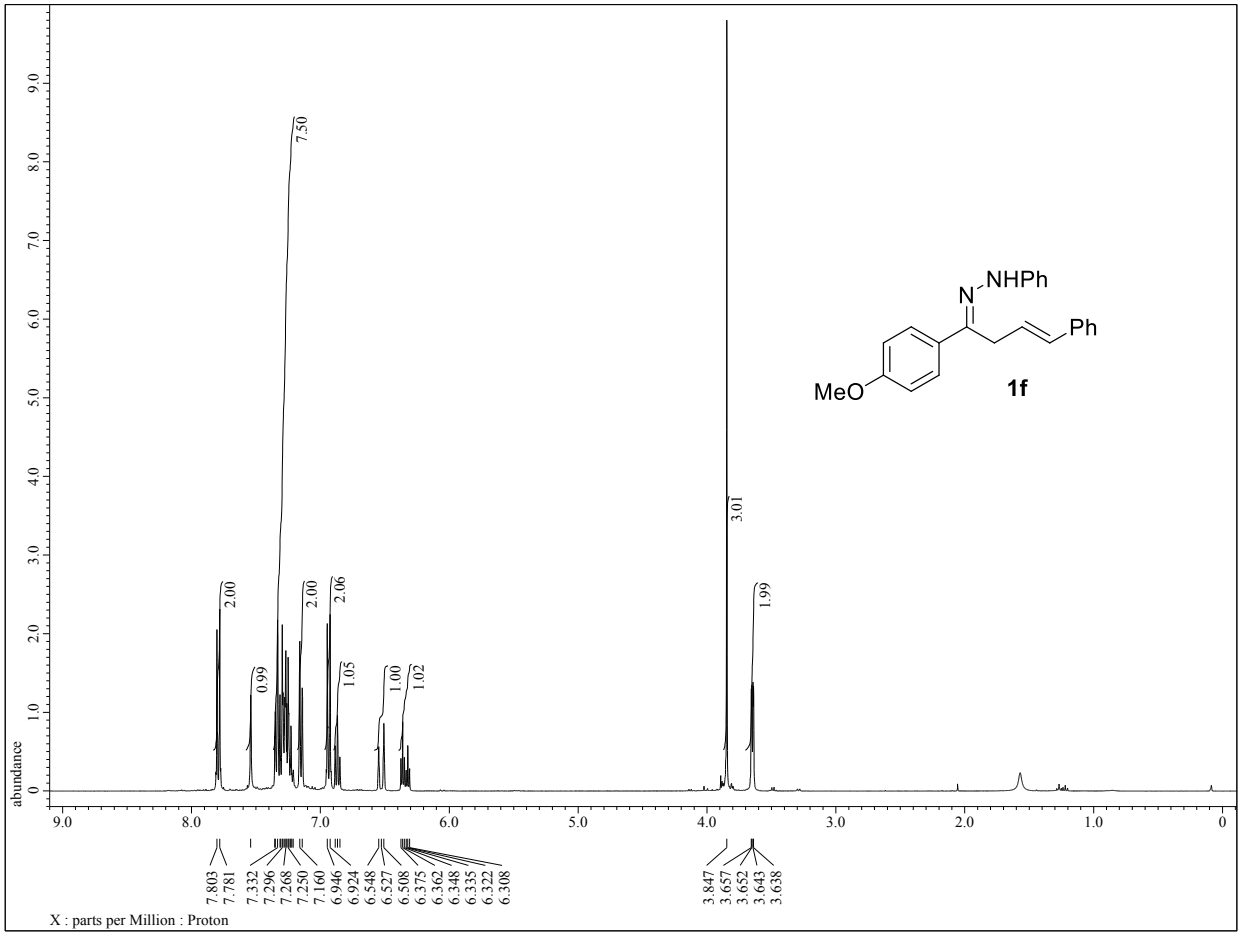

abundance
153.643
140.869
131.809
128.792
128.754
128.353
127.694
127.646
125.307
125.002
114.500
113.975
77.315
77.000
76.685
55.605
26.182
X : parts per Million : Carbon13

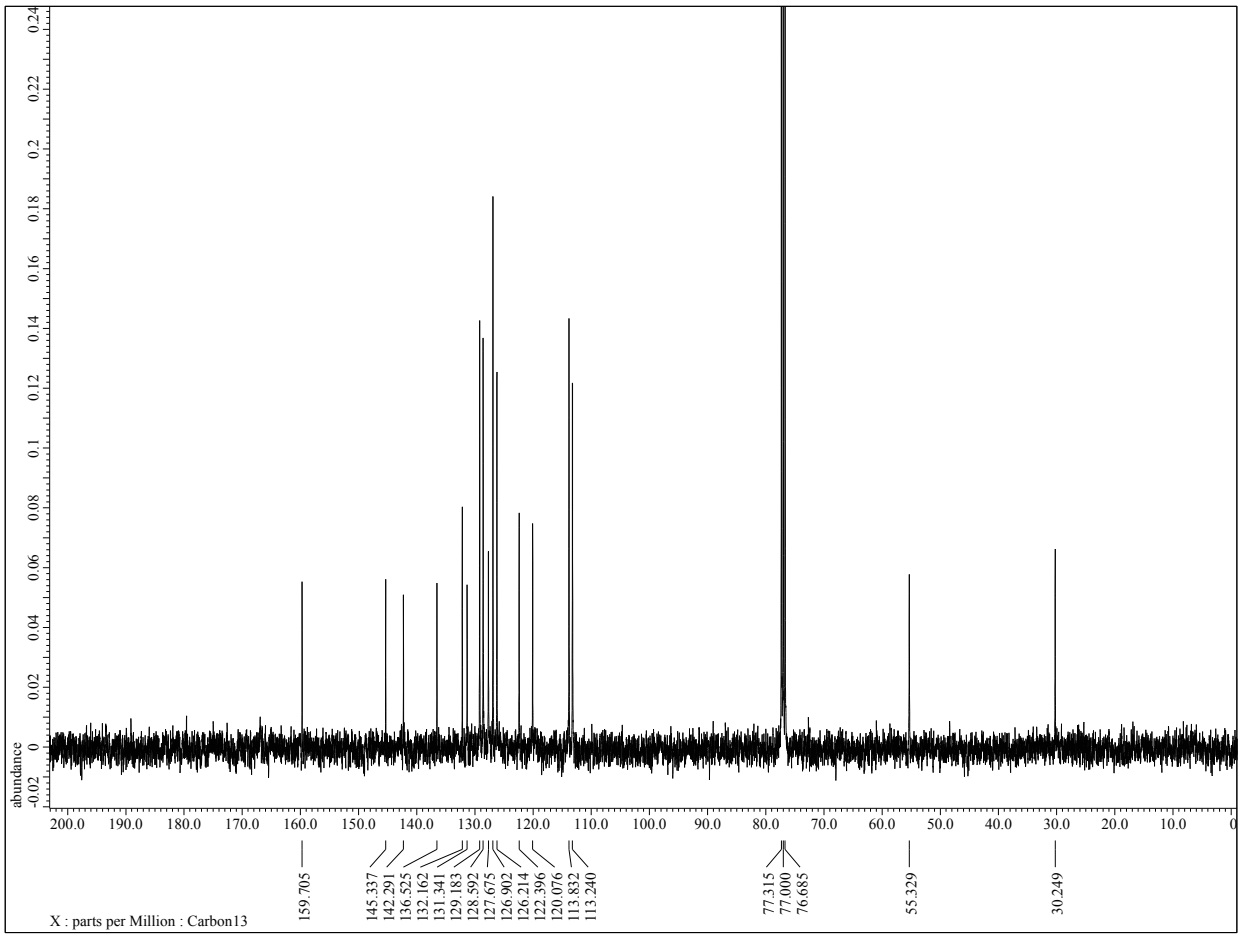

NHPh
N
MeO
Ph
1d
8.58
3.00
2.00
2.06
1.98
1.05
1.00
1.00
Et2O
Et2O
abundance
X : parts per Million : Proton

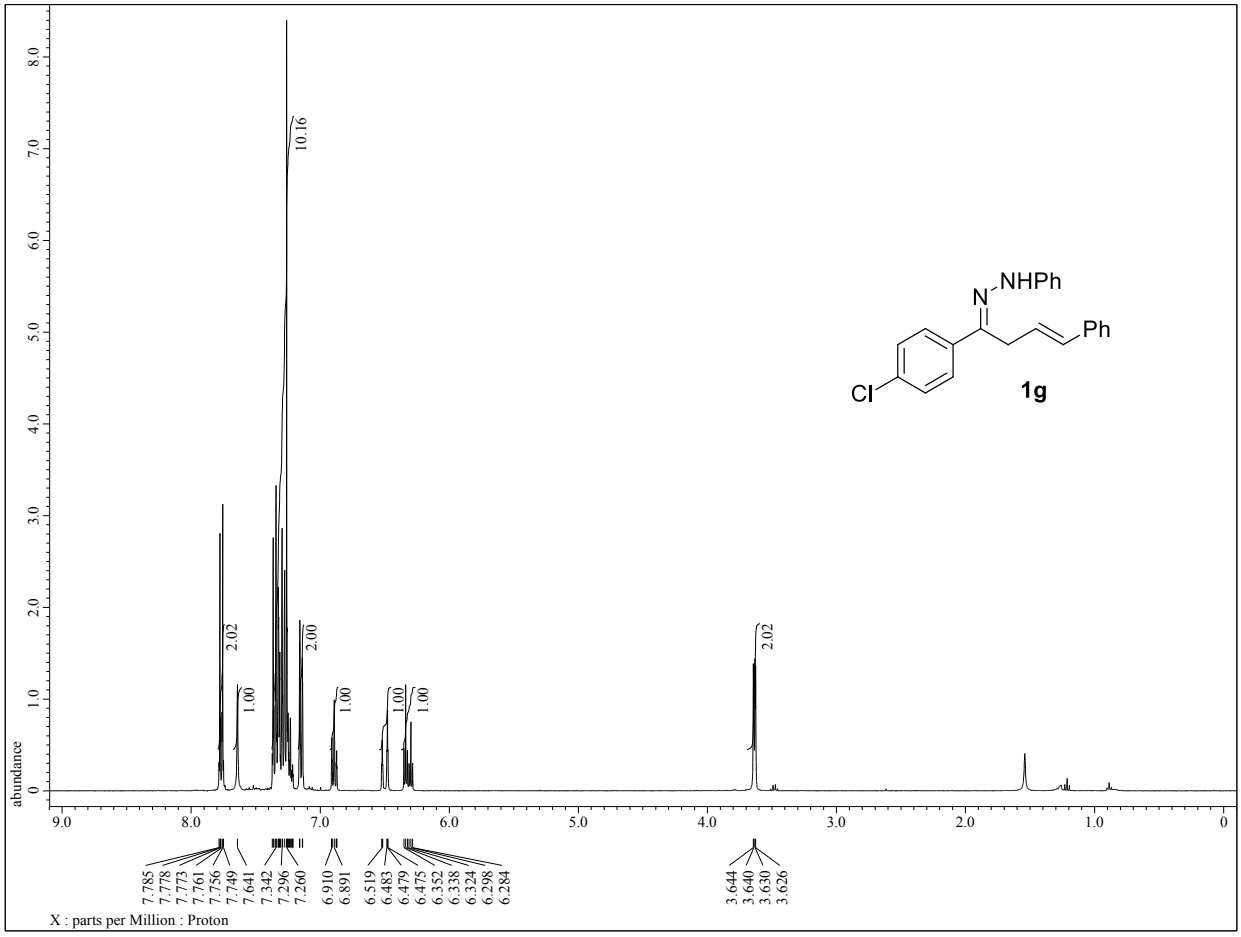

abundance
X : parts per Million : Carbon13

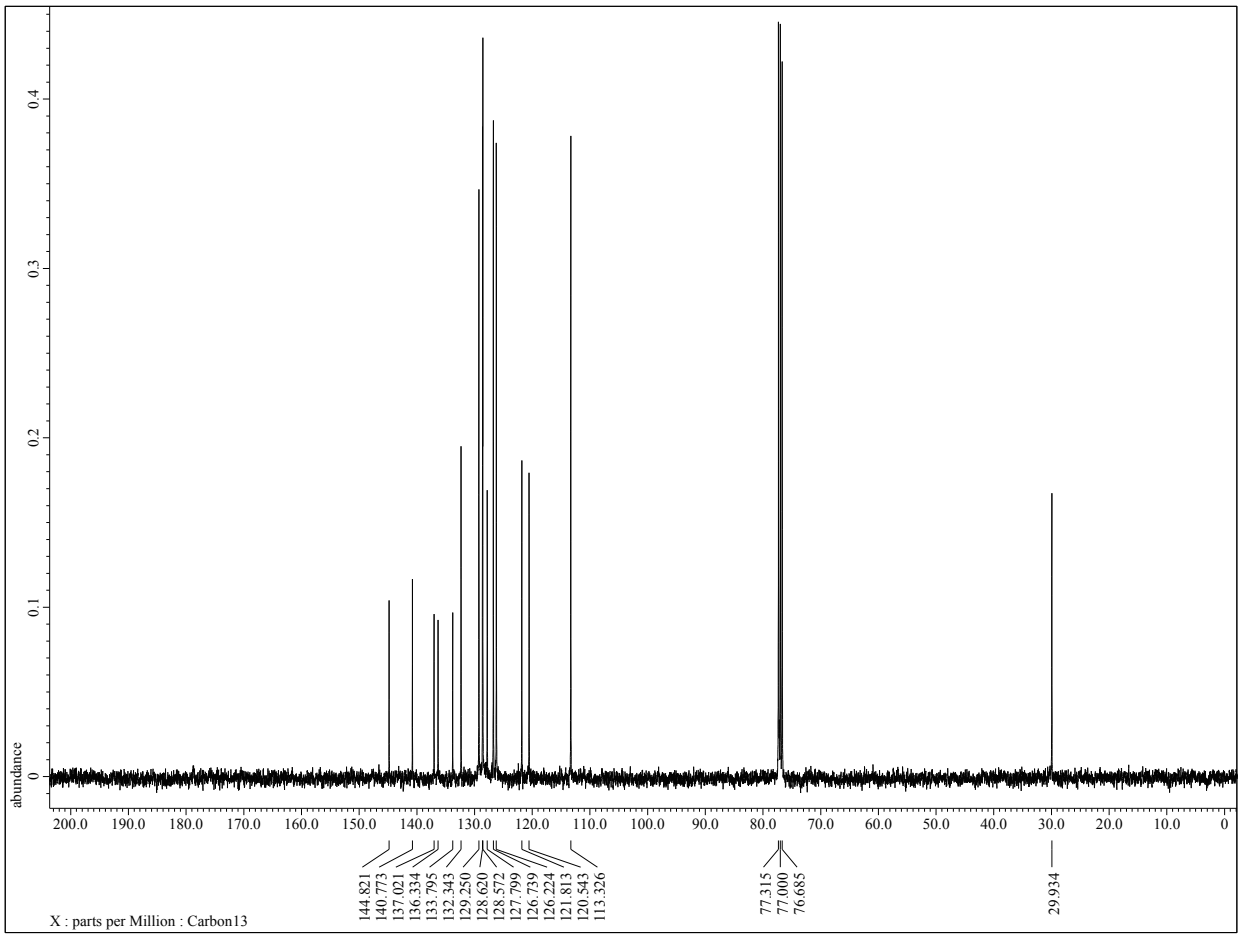

NHPh
N
MeO
Ph
1e
Et2O
Et2O
abundance
X : parts per Million : Proton

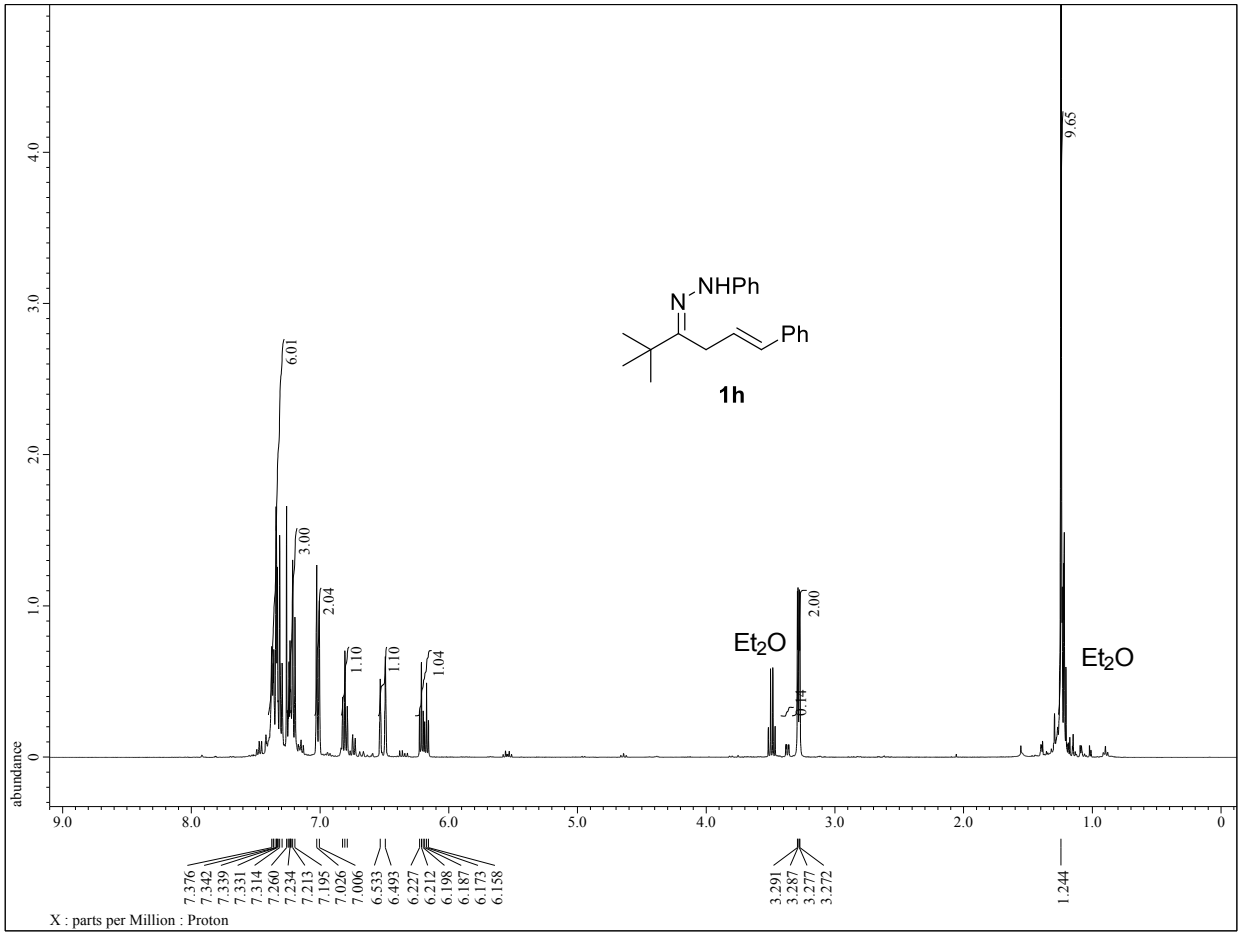

Et2O
Et2O
abundance
X : parts per Million : Carbon13

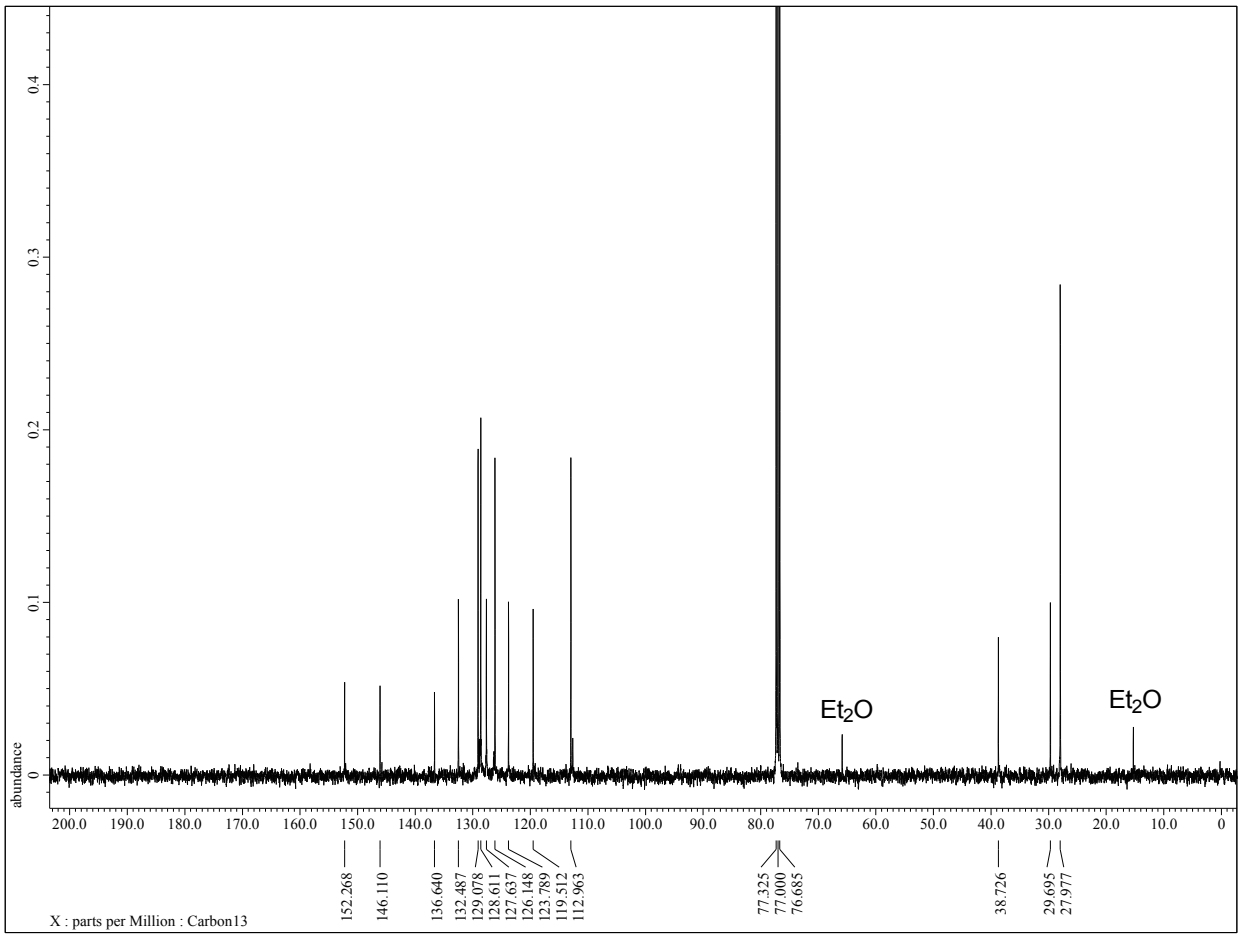

NHPh
N
Ph
MeO
1f
abundance
X : parts per Million : Proton

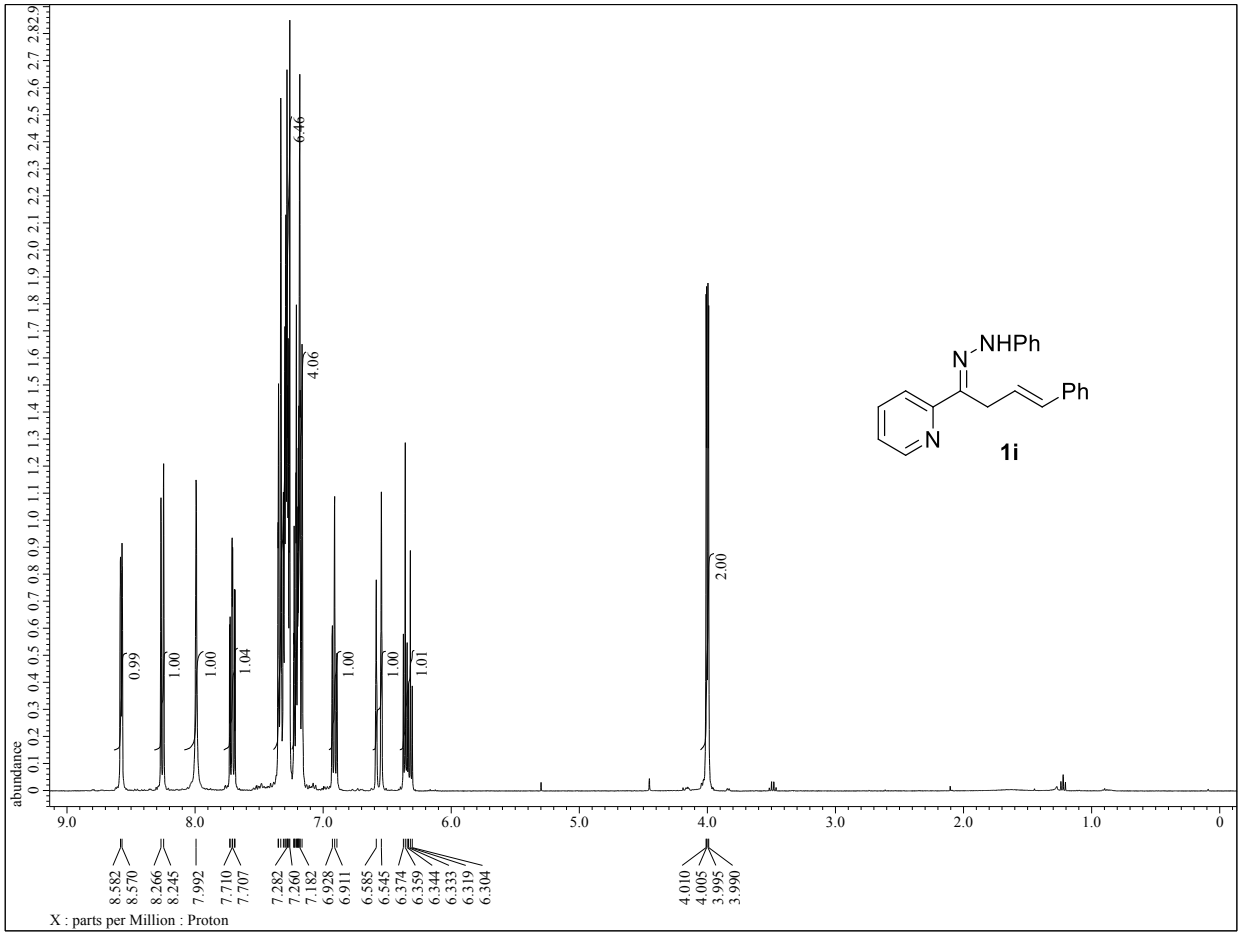

abundance
X : parts per Million : Carbon13

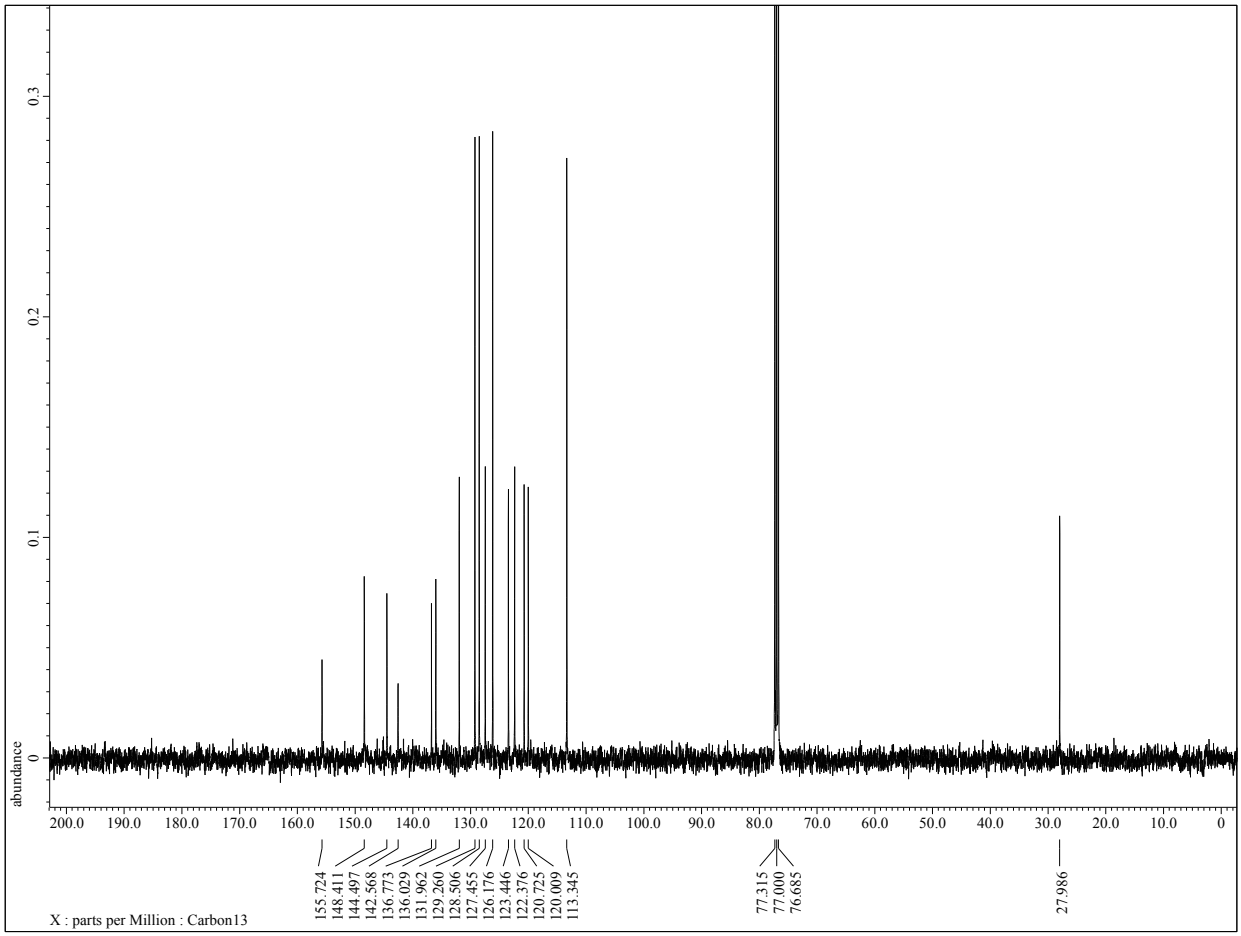

NHPh
N
Ph
Cl
1g
abundance
10.16
2.02
1.00
2.00
1.00
1.00
1.00
2.02
7.785
7.778
7.773
7.761
7.756
7.749
7.641
7.342
7.296
7.260
6.910
6.891
6.519
6.483
6.479
6.475
6.352
6.338
6.324
6.298
6.284
3.644
3.640
3.630
3.626
X : parts per Million : Proton

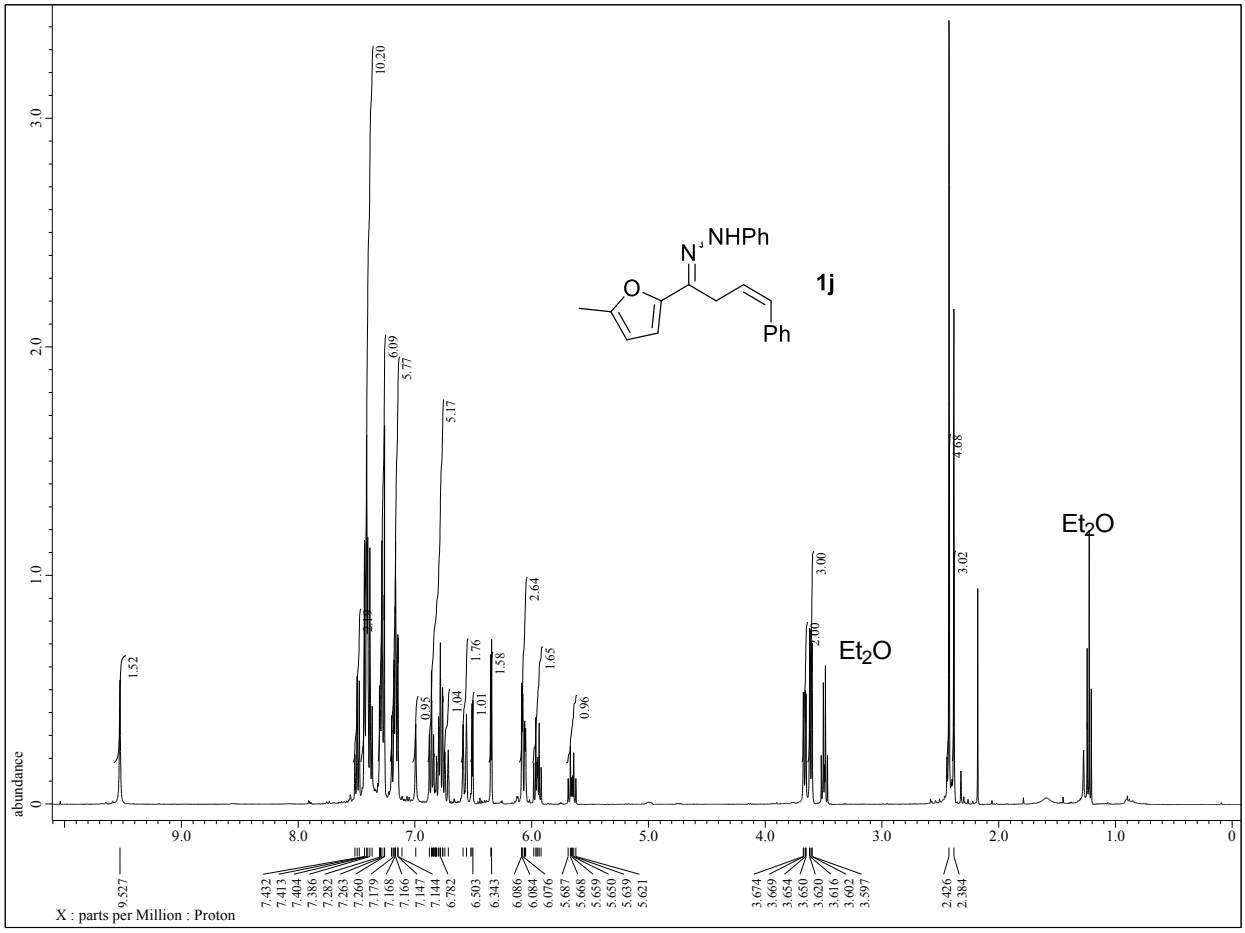

abundance
144.821
140.773
137.021
136.334
133.795
132.343
129.250
128.620
128.572
127.799
126.739
126.224
121.813
120.543
113.326
77.315
77.000
76.685
29.934
X : parts per Million : Carbon13

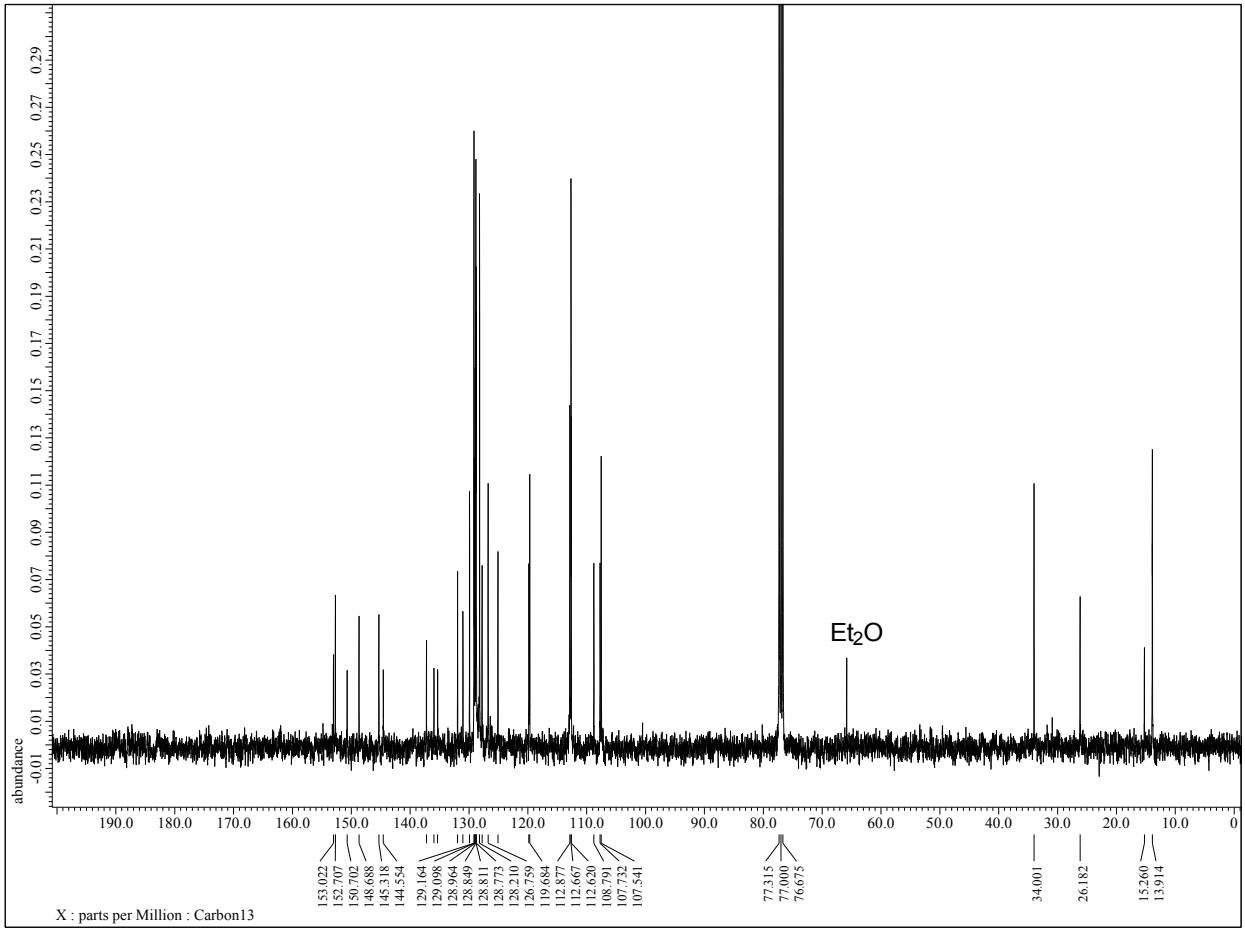

NHPh
N
Ph
1h
6.01
3.00
2.04
1.10
1.10
1.04
2.00
0.14
9.65
Et2O
Et2O
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.376
7.342
7.339
7.331
7.314
7.260
7.234
7.213
7.195
7.026
7.006
6.533
6.493
6.227
6.212
6.198
6.187
6.173
6.158
3.291
3.287
3.277
3.272
1.244
X : parts per Million : Proton

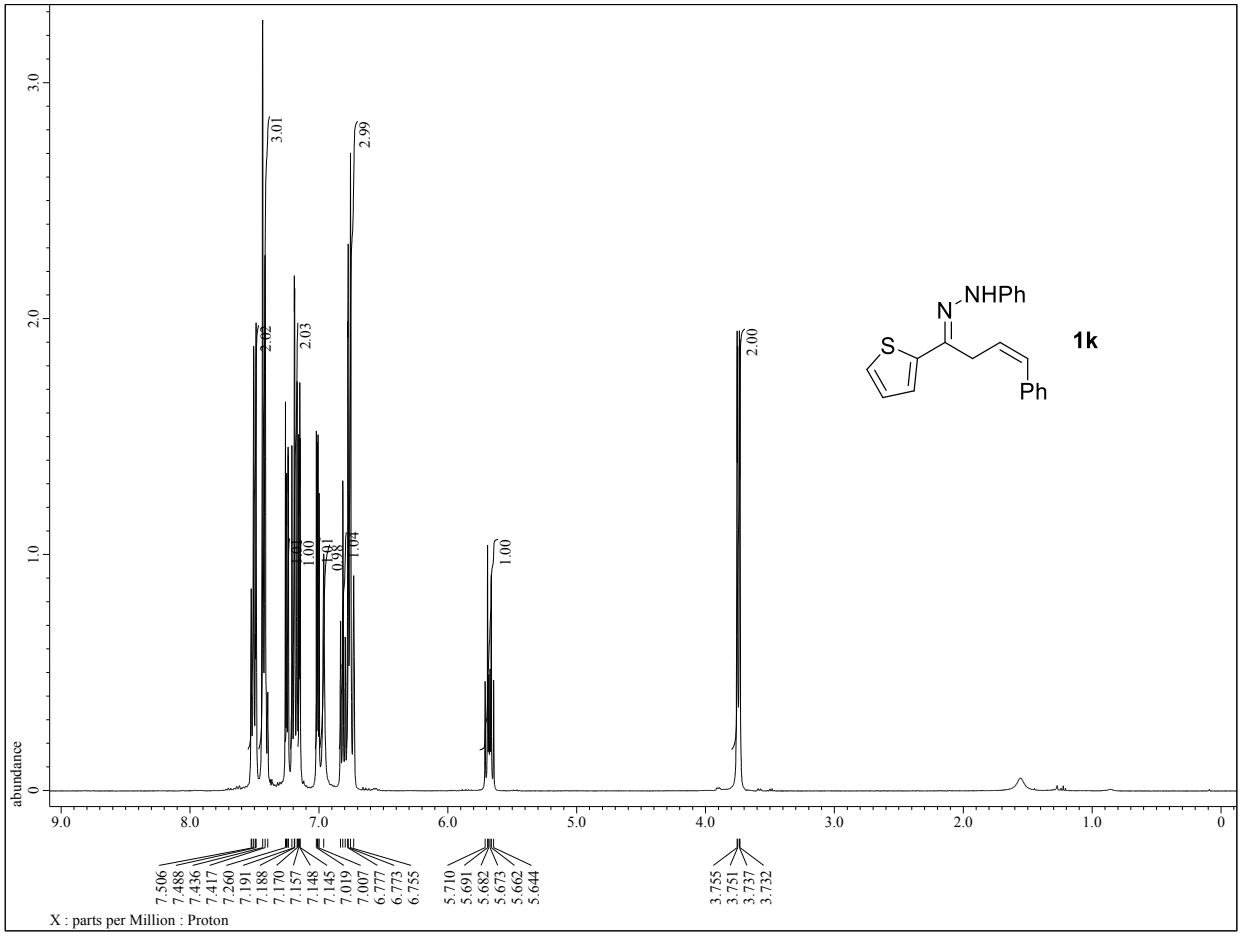

Et2O
Et2O
abundance
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
152.268
146.110
136.640
132.487
129.078
128.611
127.637
126.148
123.789
119.512
112.963
77.325
77.000
76.685
38.726
29.695
27.977
X : parts per Million : Carbon13


NHPh
N
Ph
N
1i
abundance
X : parts per Million : Proton

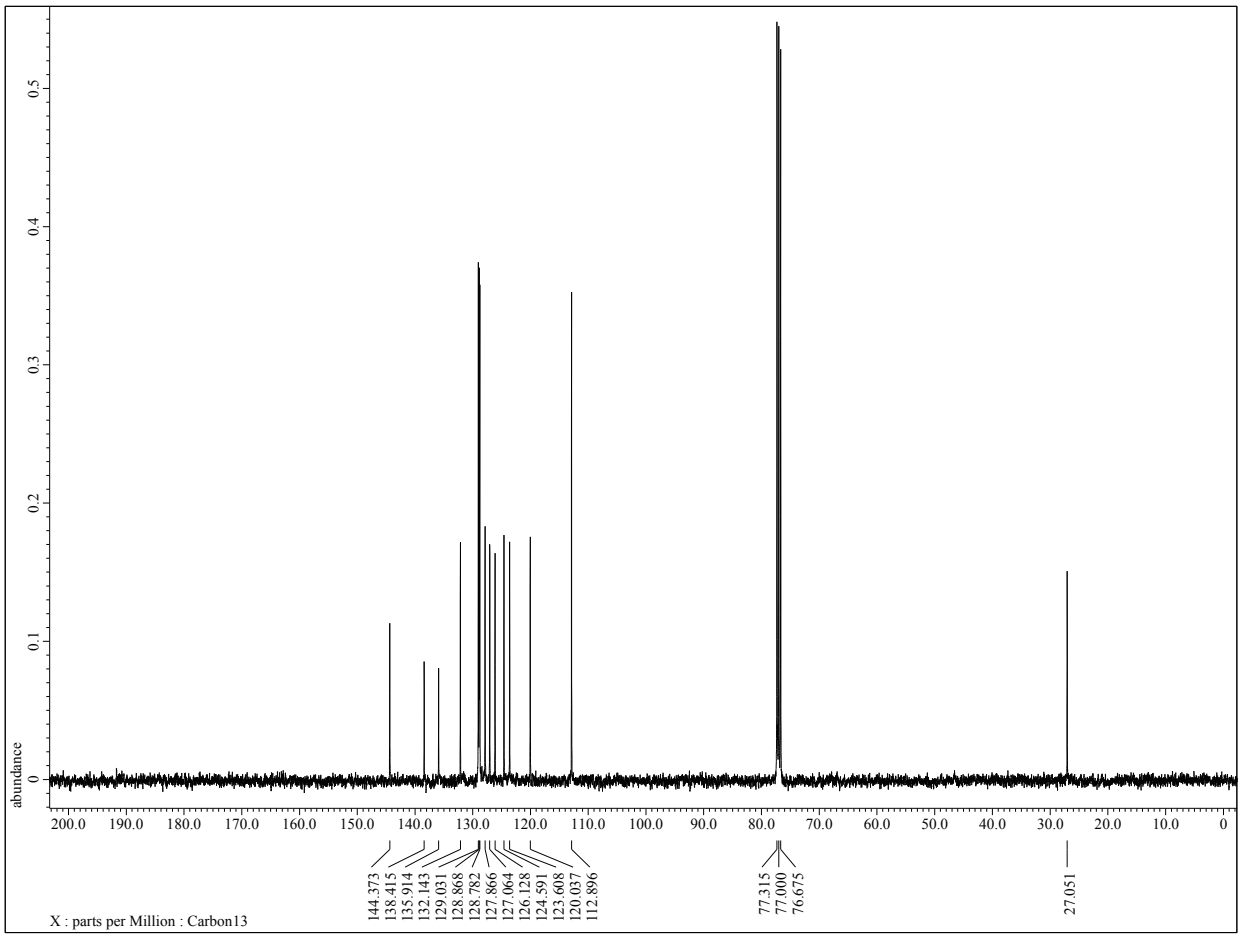

abundance
X : parts per Million : Carbon13

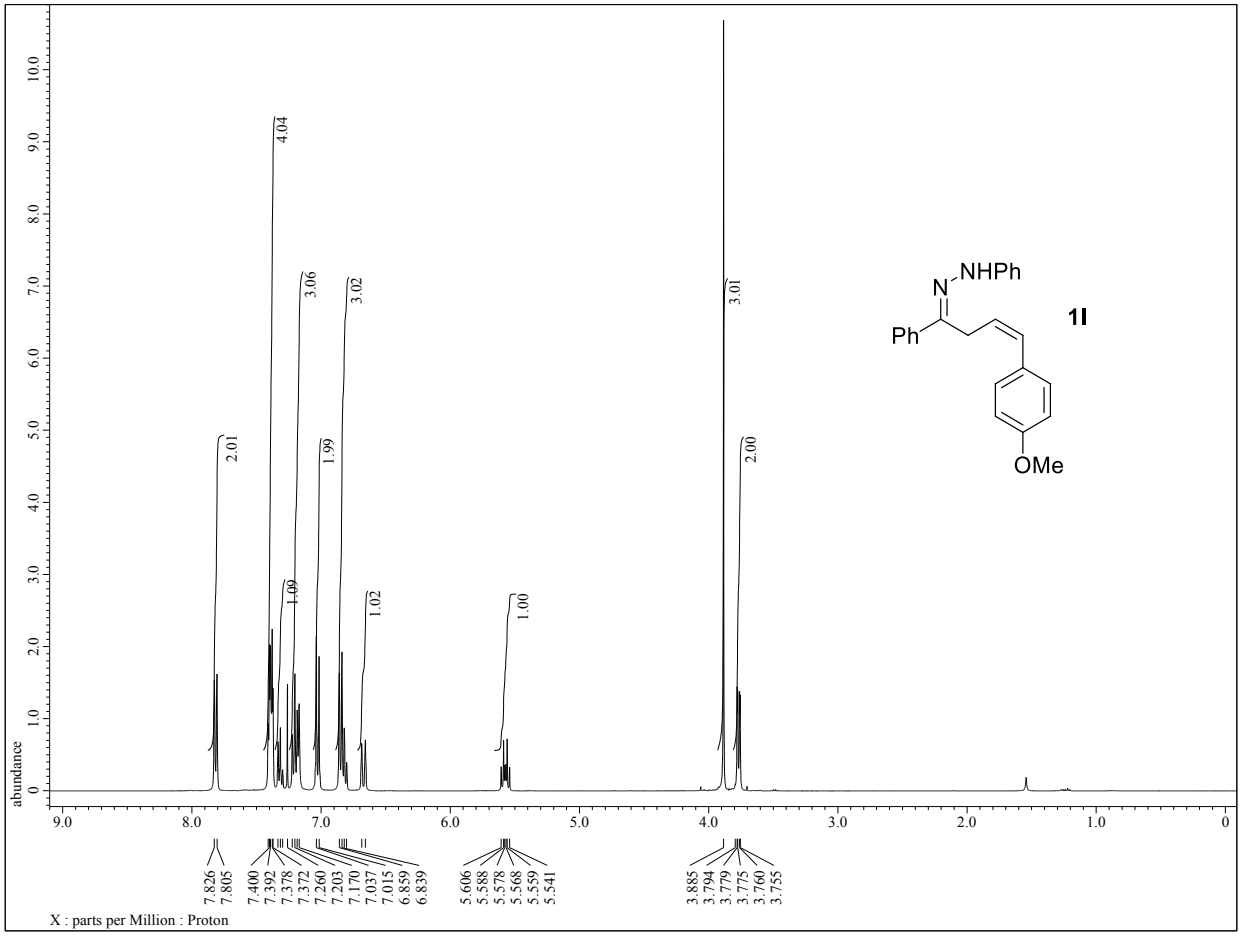

NHPh
O
Ph
1j
Et2O
Et2O
abundance
X : parts per Million : Proton


Et2O
abundance
X : parts per Million : Carbon13


abundance
3.01
2.99
2.02
2.03
2.00
1.00
1.00
0.98
1.04
7.506
7.488
7.436
7.417
7.260
7.191
7.188
7.170
7.157
7.148
7.145
7.019
7.007
6.777
6.773
6.755
5.710
5.691
5.682
5.673
5.662
5.644
3.755
3.751
3.737
3.732
X : parts per Million : Proton

N
NHPh
S
Ph
1k


abundance
144.373
138.415
135.914
132.143
129.031
128.868
128.782
127.866
127.064
126.128
124.591
123.608
120.037
112.896
77.315
77.000
76.675
27.051
X : parts per Million : Carbon13


NHPh
N
Ph
OMe
1l
abundance
X : parts per Million : Proton
2.01
4.04
3.06
3.02
1.99
1.09
1.02
1.00
3.01
2.00
7.826
7.805
7.400
7.392
7.378
7.372
7.260
7.203
7.170
7.037
7.015
6.859
6.839
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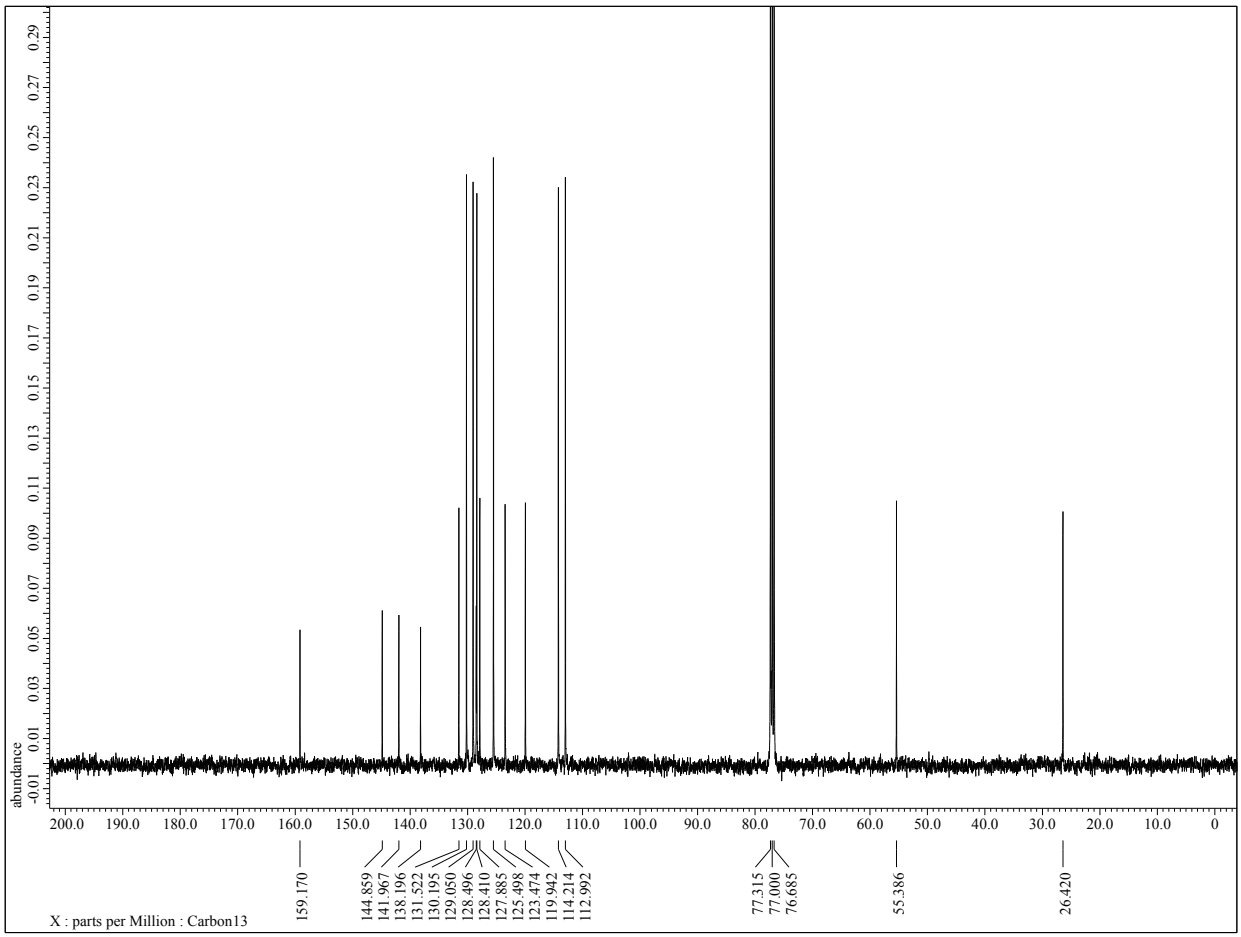
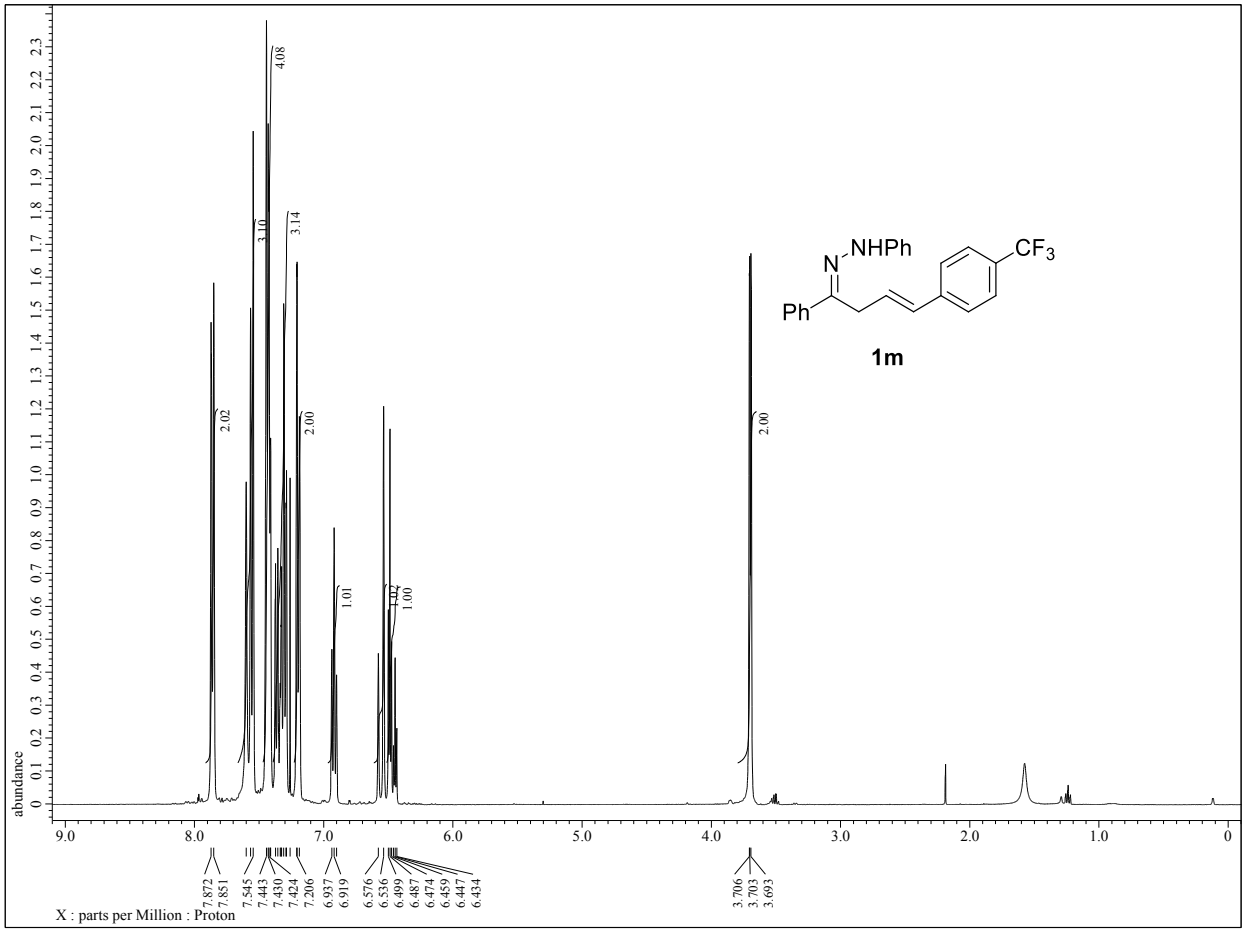
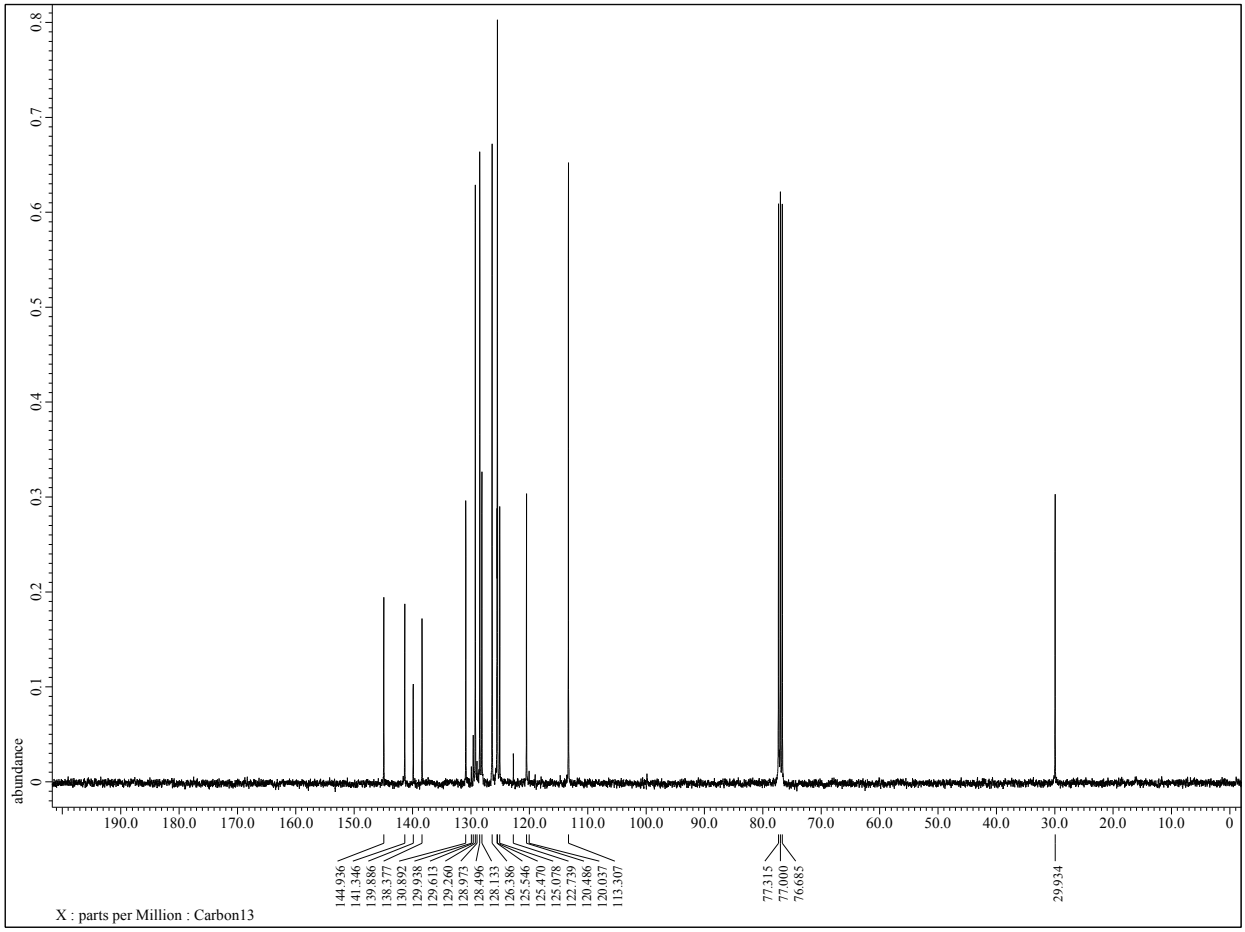
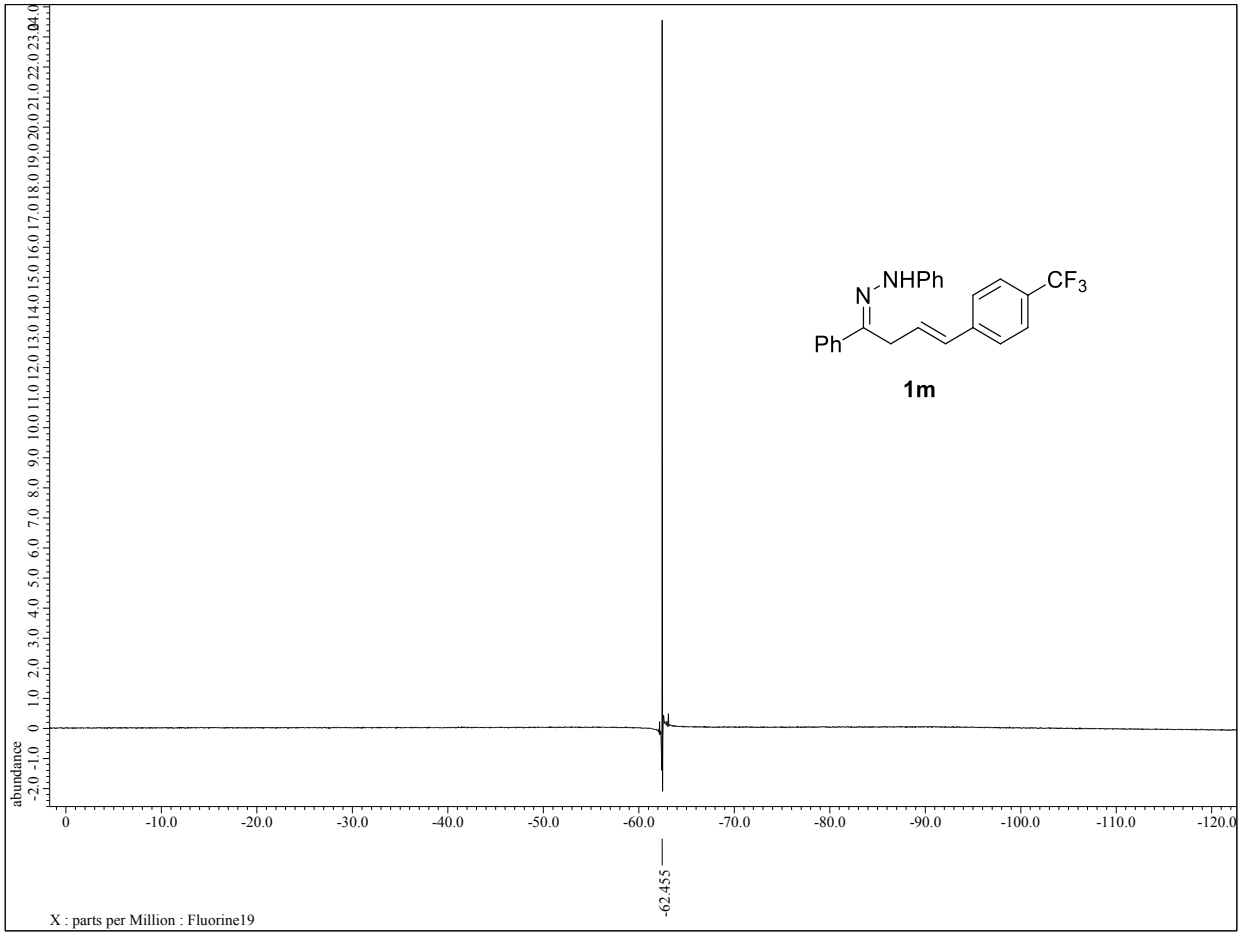
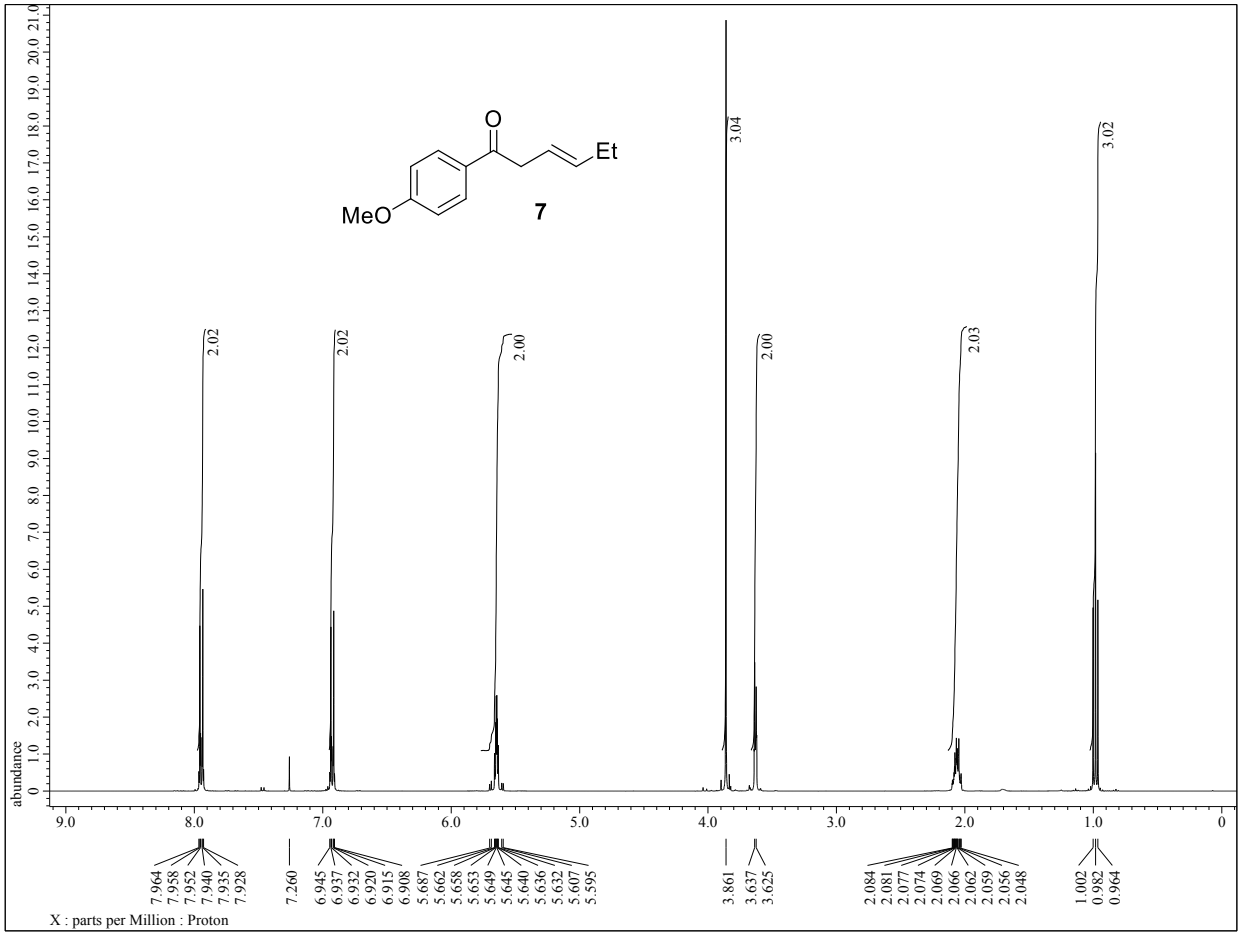
3.885
3.794
3.779
3.775
3.760
3.755

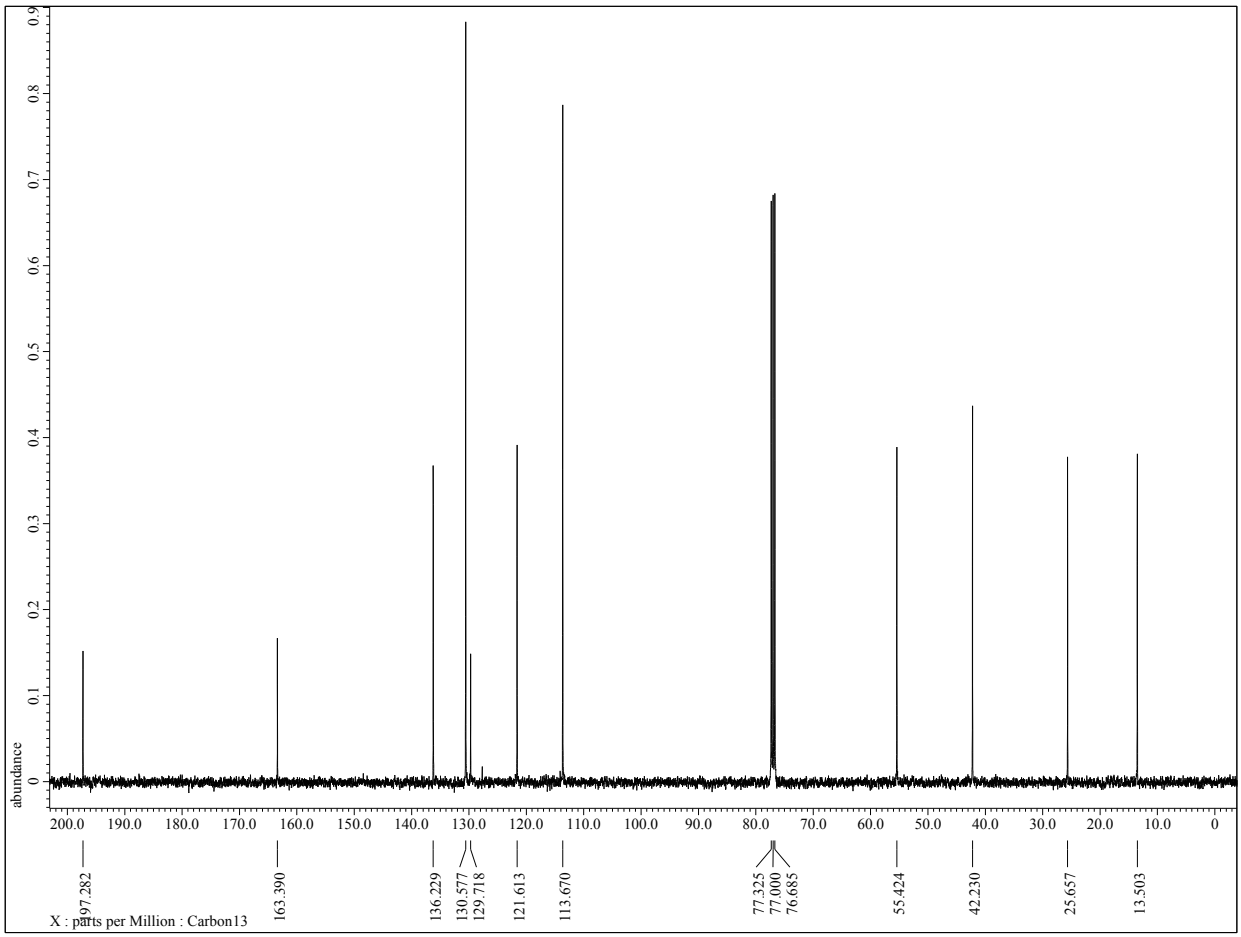

abundance
X : parts per Million : Carbon13
159.170
144.859
141.967
138.196
131.522
130.195
129.050
128.496
128.410
127.885
125.498
123.474
119.942
114.214
112.992
77.315
77.000
76.685
55.386
26.420

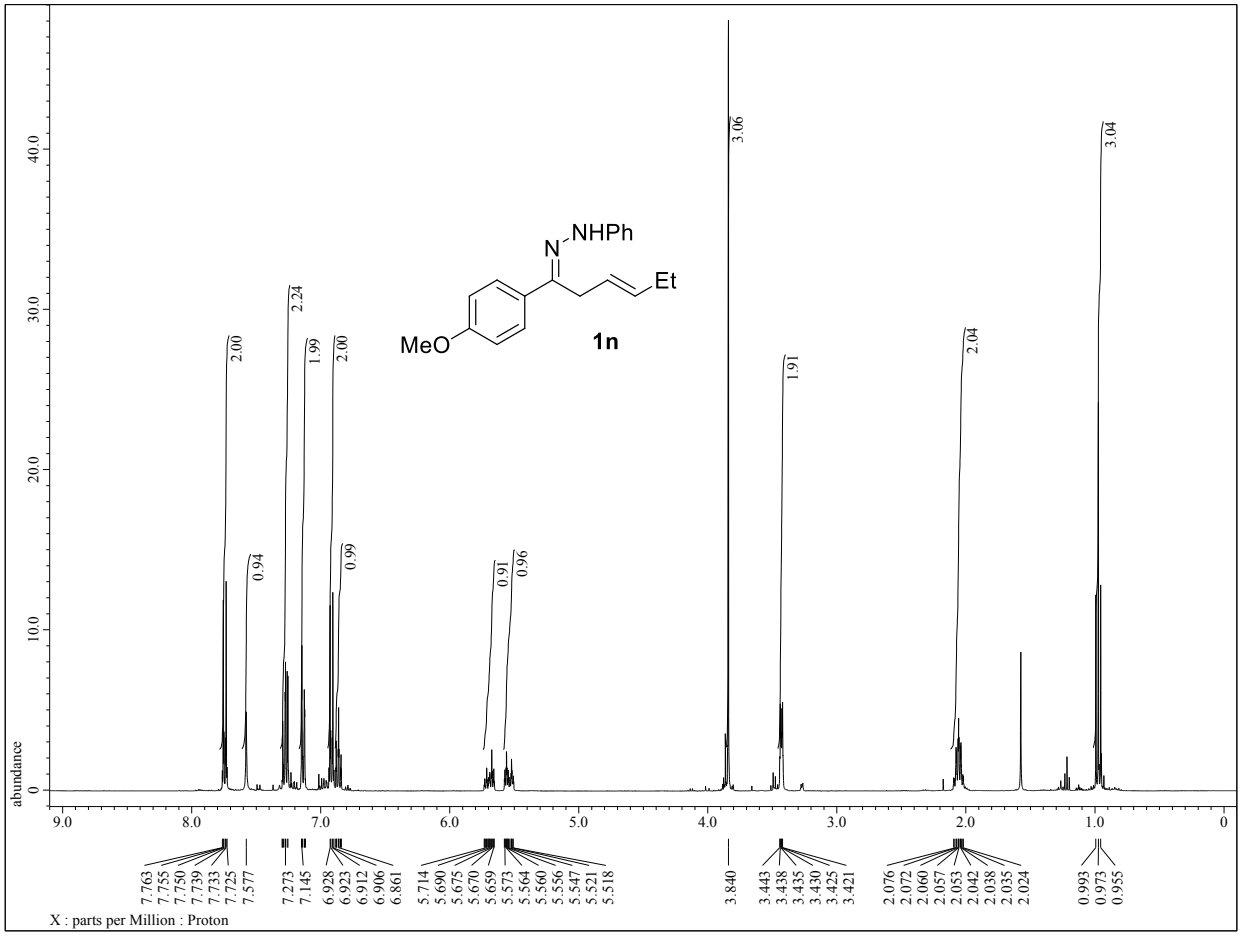

abundance
4.08
3.10
3.14
2.02
2.00
1.01
1.02
1.00
2.00
NHPh
N
Ph
CF3
1m
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.872
7.851
7.545
7.443
7.430
7.424
7.206
6.937
6.919
6.576
6.536
6.499
6.487
6.474
6.459
6.447
6.434
3.706
3.703
3.693
X : parts per Million : Proton

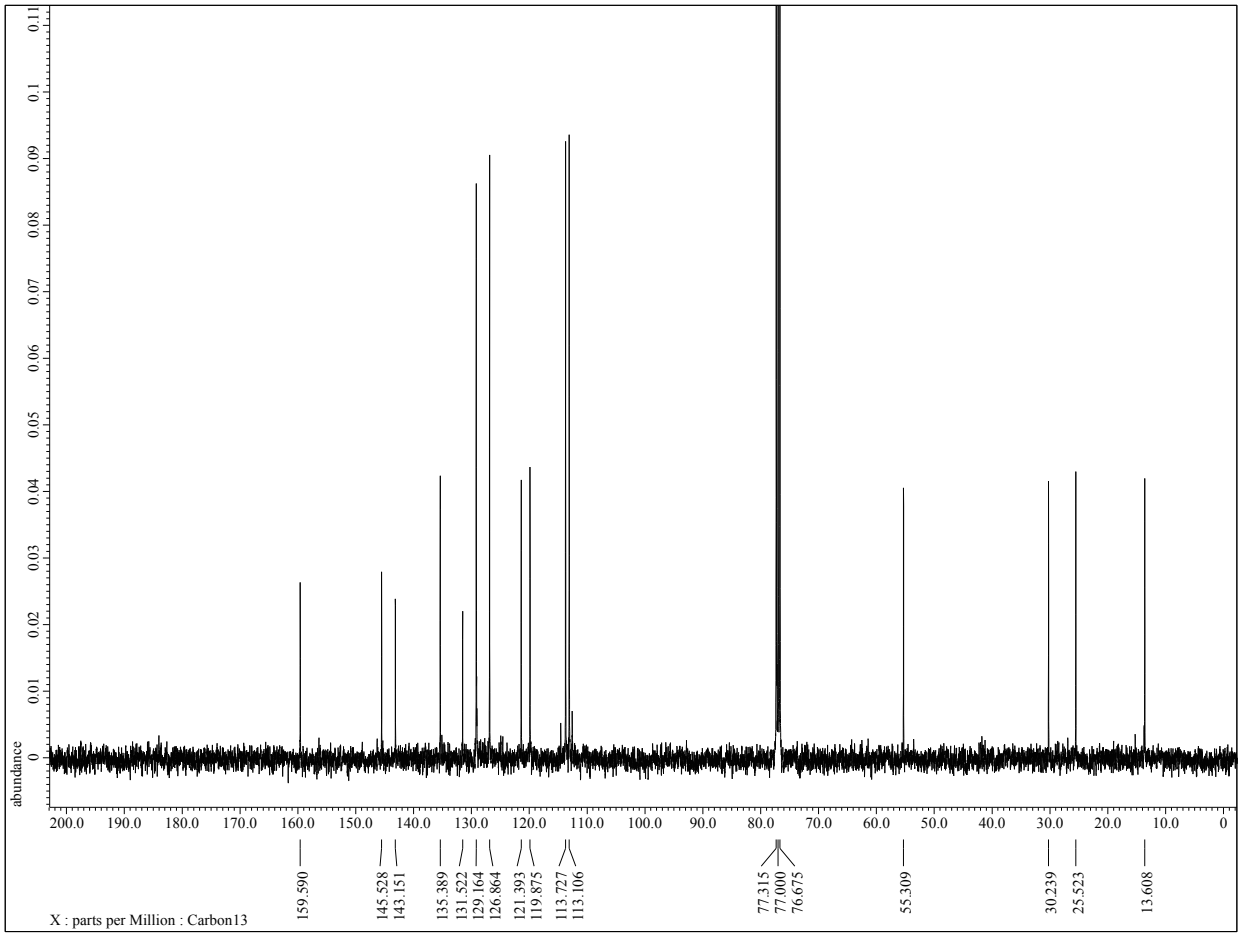

abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
144.936
141.346
139.886
138.377
130.892
129.938
129.613
129.260
128.973
128.496
128.133
126.386
125.546
125.470
125.078
122.739
120.486
120.037
113.307
77.315
77.000
76.685
29.934
X : parts per Million : Carbon13

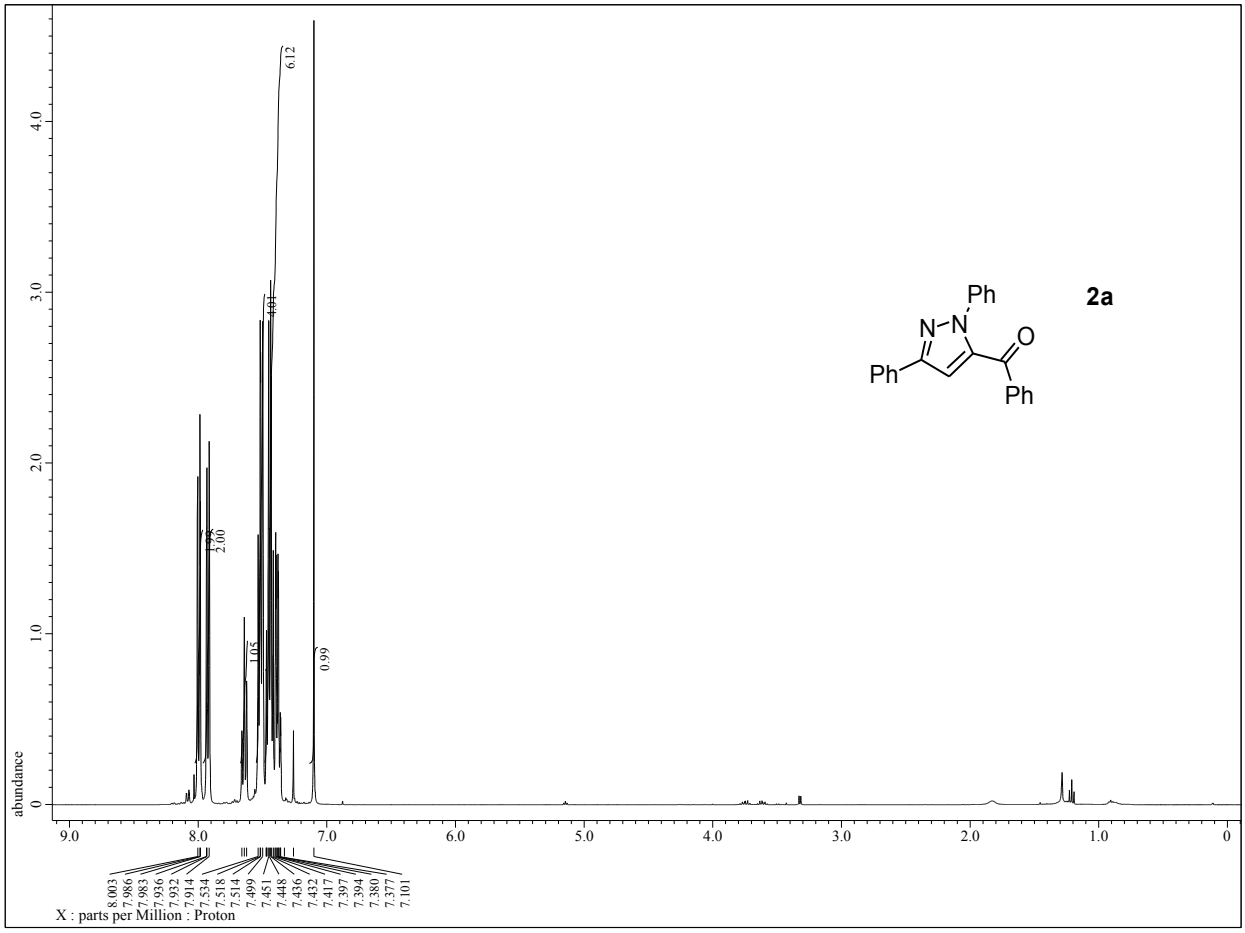

NHPh
N
Ph
CF3
1m
abundance
-62.455
X : parts per Million : Fluorine19

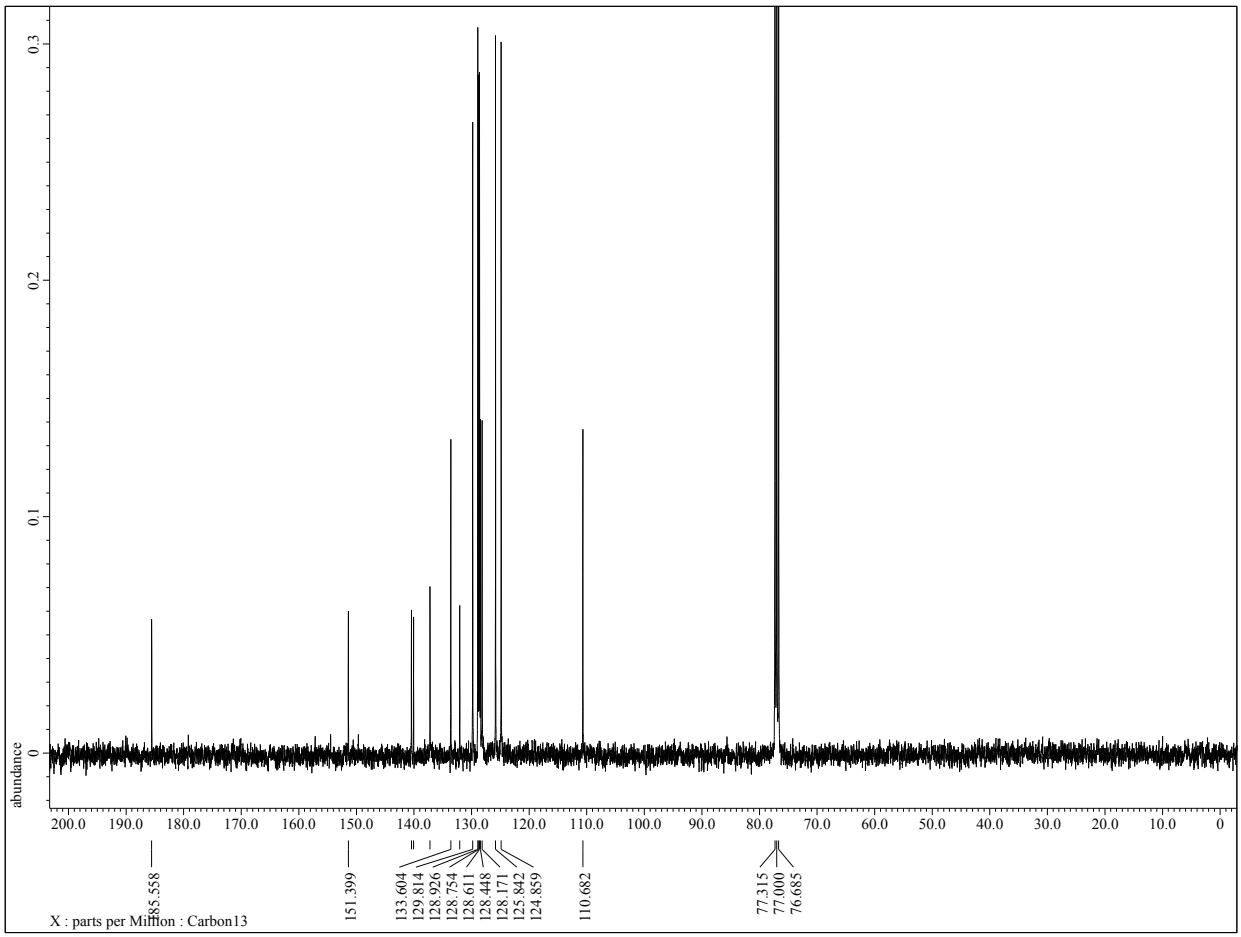

O
Et
MeO
7
abundance
X : parts per Million : Proton
2.02
2.02
2.00
3.04
2.00
2.03
3.02
7.964
7.958
7.952
7.940
7.935
7.928
7.260
6.945
6.937
6.932
6.920
6.915
6.908
5.687
5.662
5.658
5.653
5.649
5.645
5.640
5.636
5.632
5.607
5.595
3.861
3.637
3.625
2.084
2.081
2.077
2.074
2.069
2.066
2.062
2.059
2.056
2.048
1.002
0.982
0.964

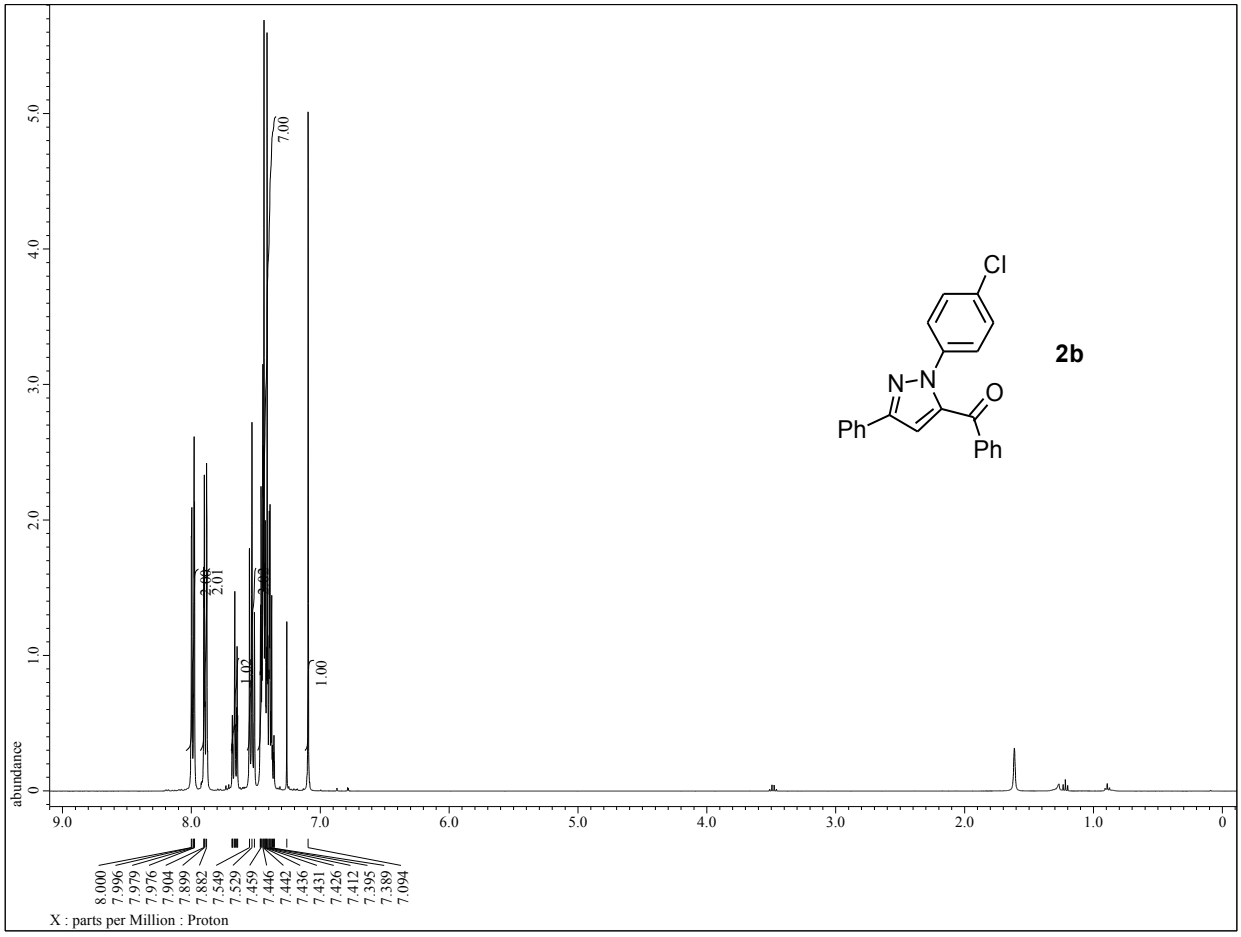

abundance
X : parts per Million : Carbon13
197.282
163.390
136.229
130.577
129.718
121.613
113.670
77.325
77.000
76.685
55.424
42.230
25.657
13.503

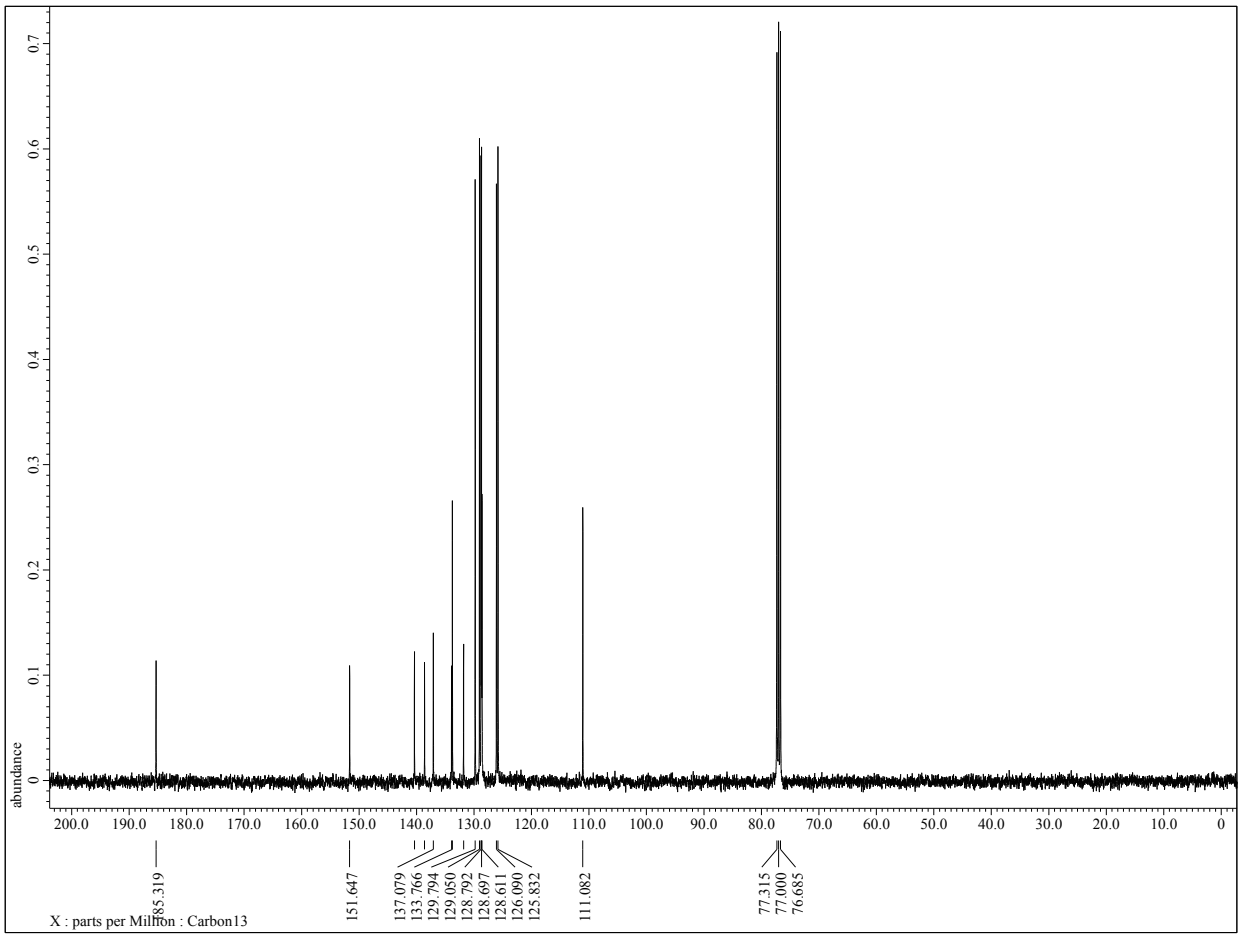

NHPh
N
Et
MeO
1n
abundance
X : parts per Million : Proton

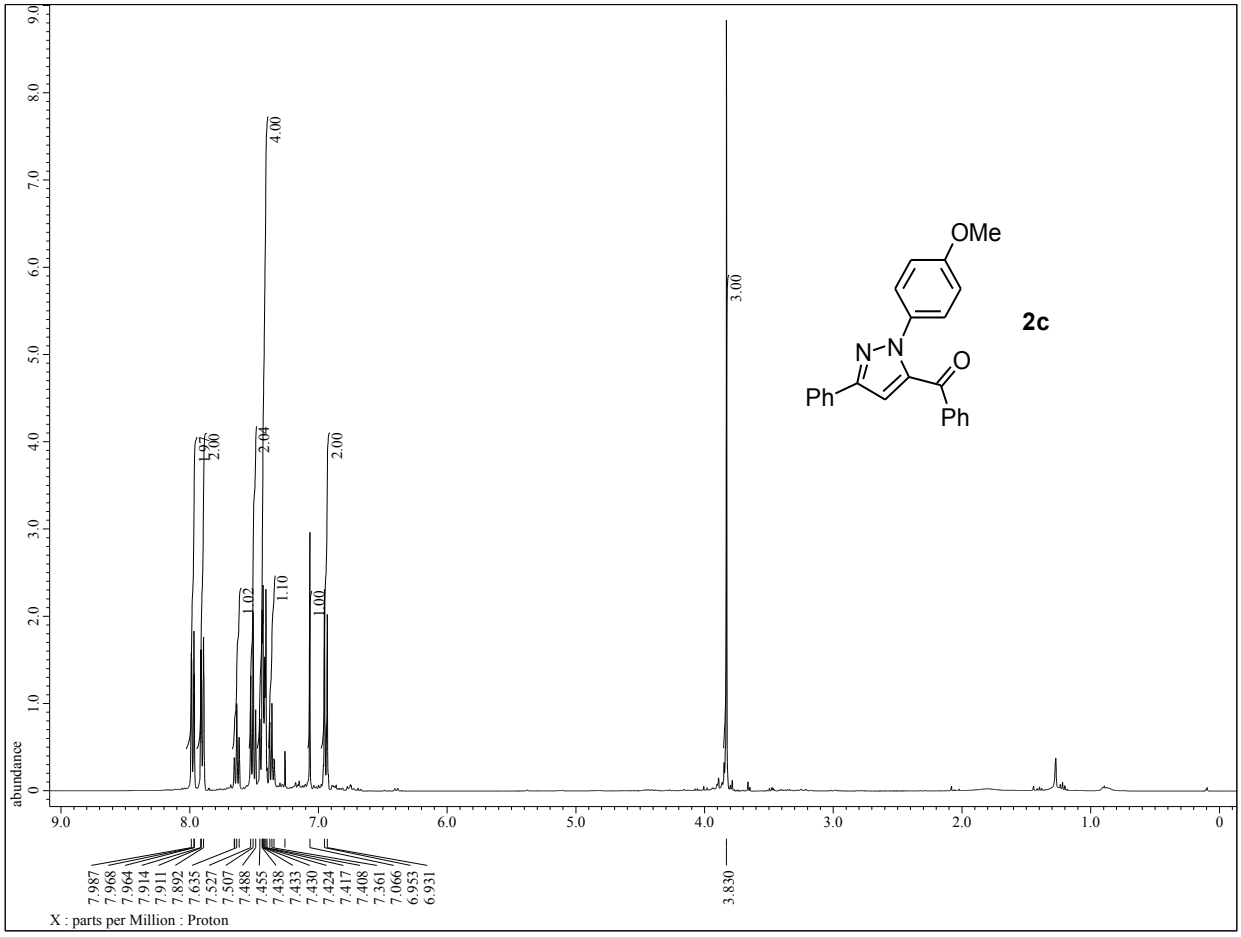

abundance
X : parts per Million : Carbon13

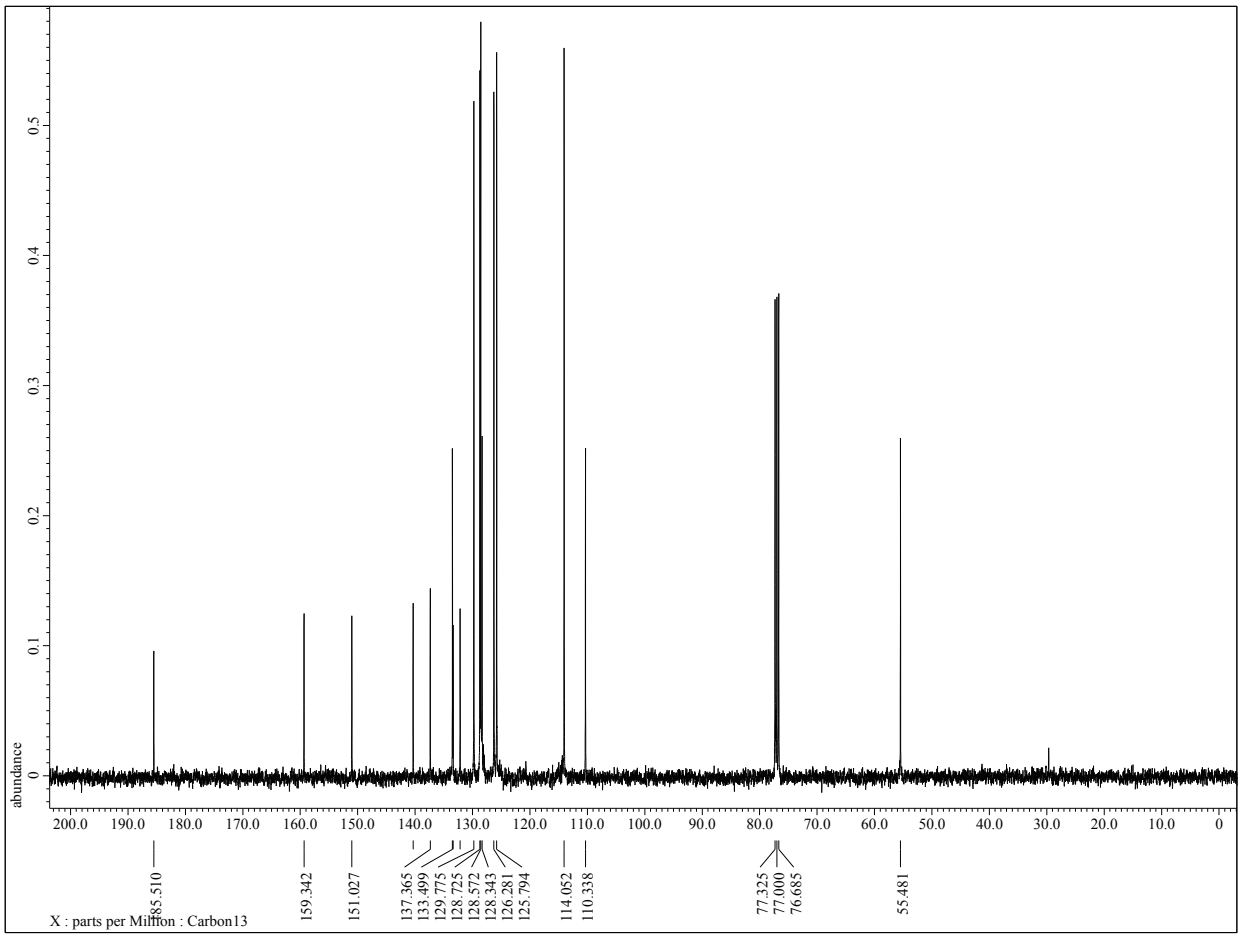

6.12
4.01
2.00
1.95
1.05
0.99
abundance
X : parts per Million : Proton
8.003
7.986
7.983
7.936
7.932
7.914
7.534
7.518
7.514
7.499
7.451
7.448
7.436
7.432
7.417
7.397
7.394
7.380
7.377
7.101
Ph
N
N
O
Ph
Ph
2a

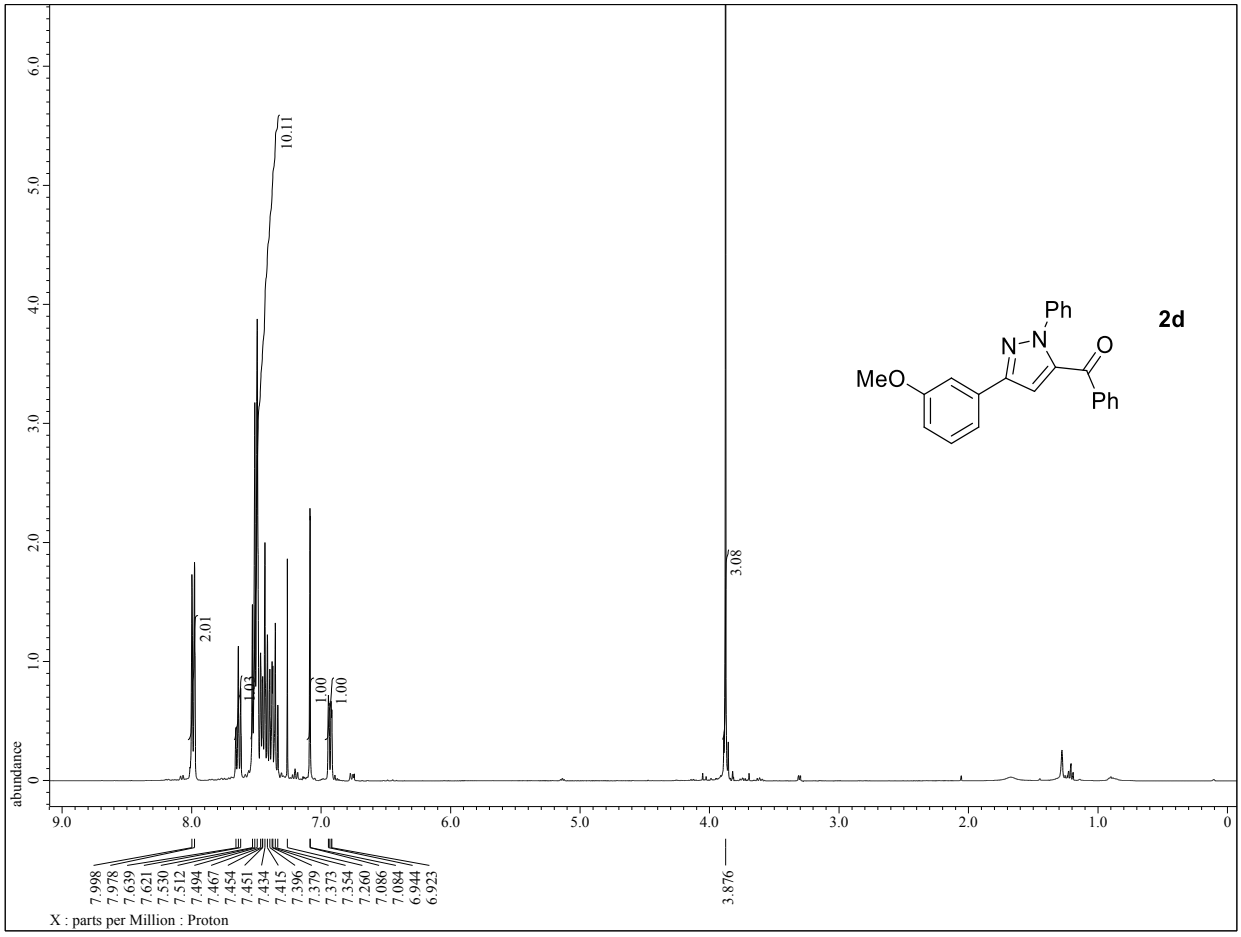

abundance
X : parts per Million : Carbon13
185.558
151.399
133.604
129.814
128.926
128.754
128.611
128.448
128.171
125.842
124.859
110.682
77.315
77.000
76.685

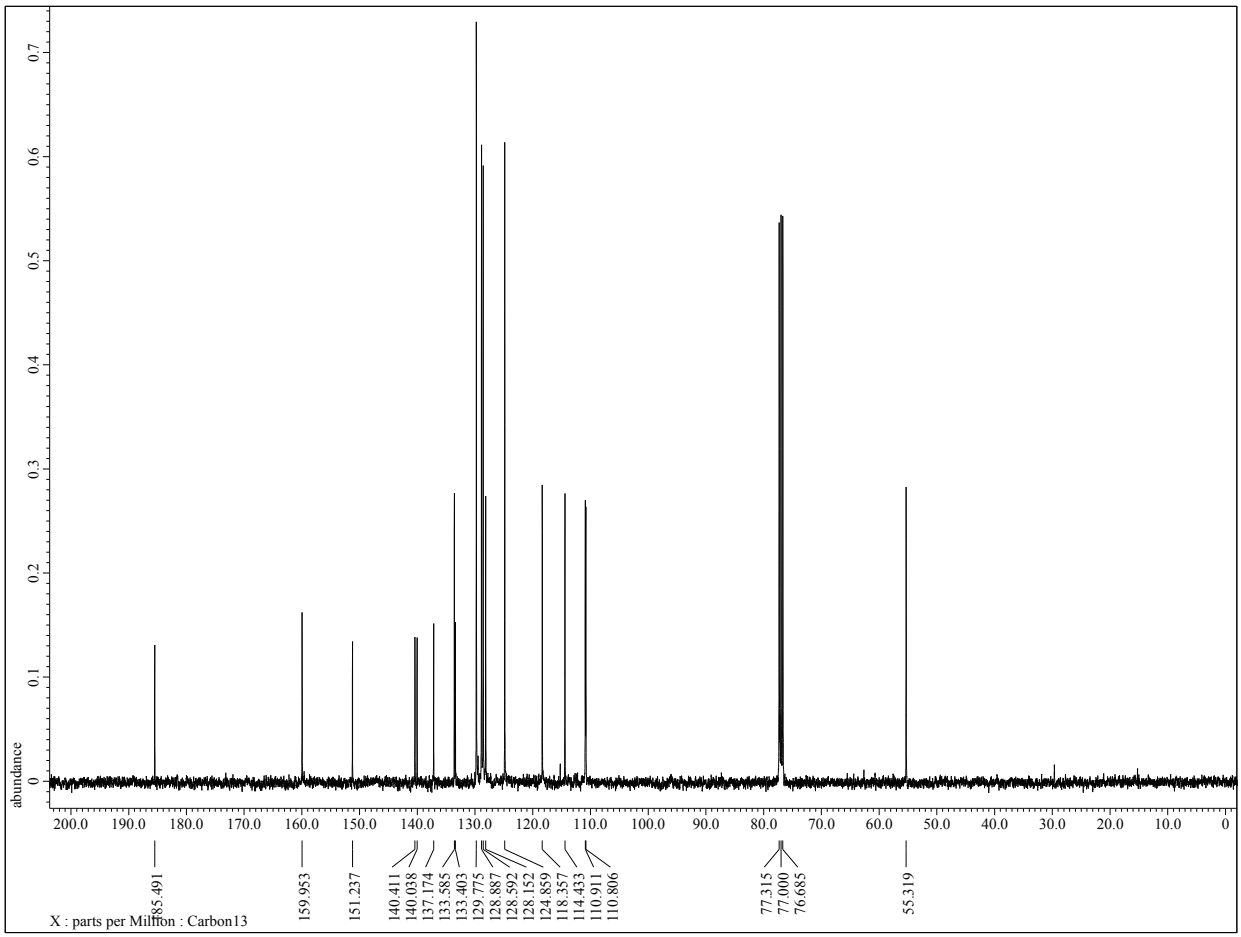

Cl
N
N
O
Ph
Ph
2b
abundance
X : parts per Million : Proton
8.000
7.996
7.979
7.976
7.904
7.899
7.882
7.549
7.529
7.459
7.446
7.442
7.436
7.431
7.426
7.412
7.395
7.389
7.094

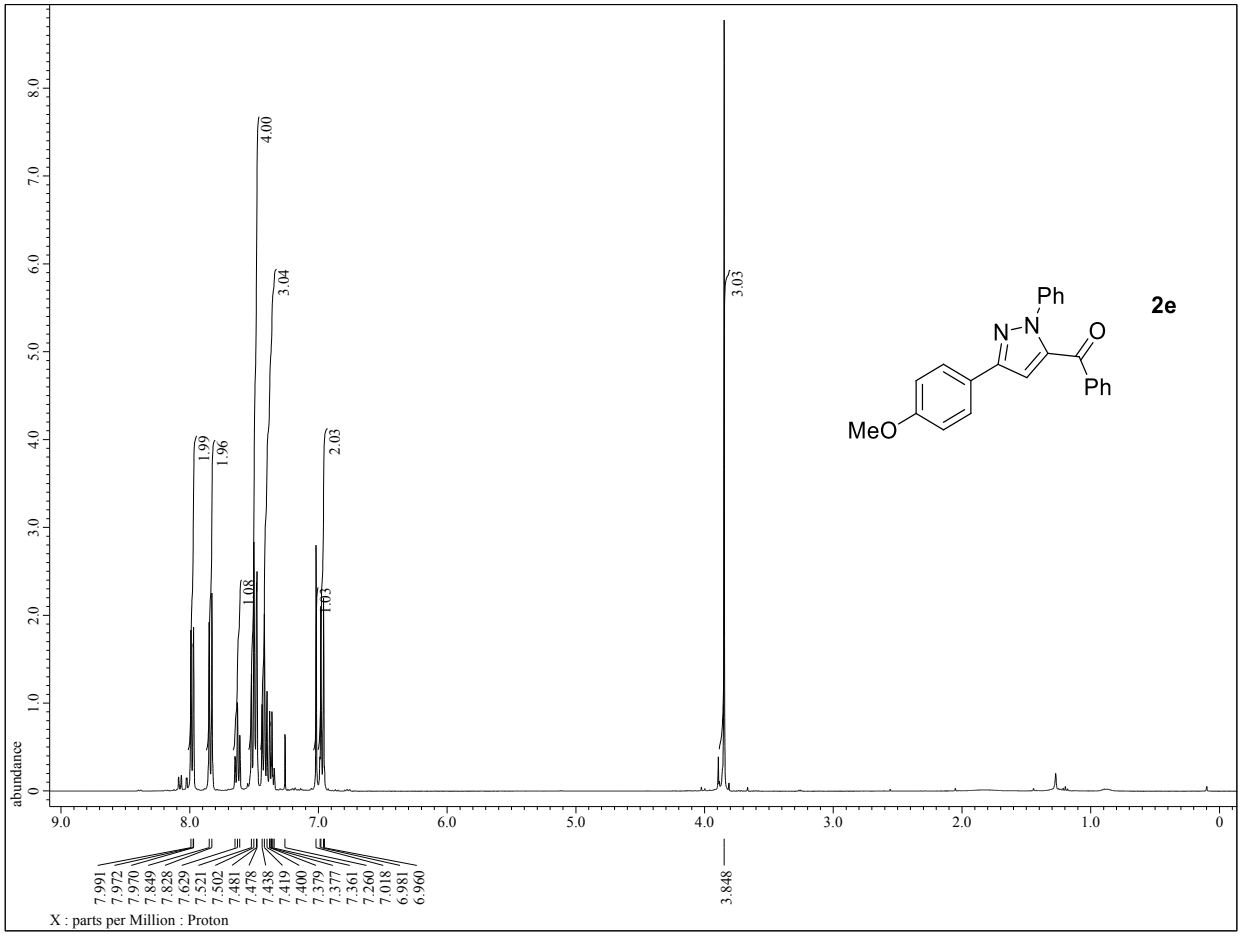

abundance
X : parts per Million : Carbon13
185.319
151.647
137.079
133.766
129.794
129.050
128.792
128.697
128.611
126.090
125.832
111.082
77.315
77.000
76.685

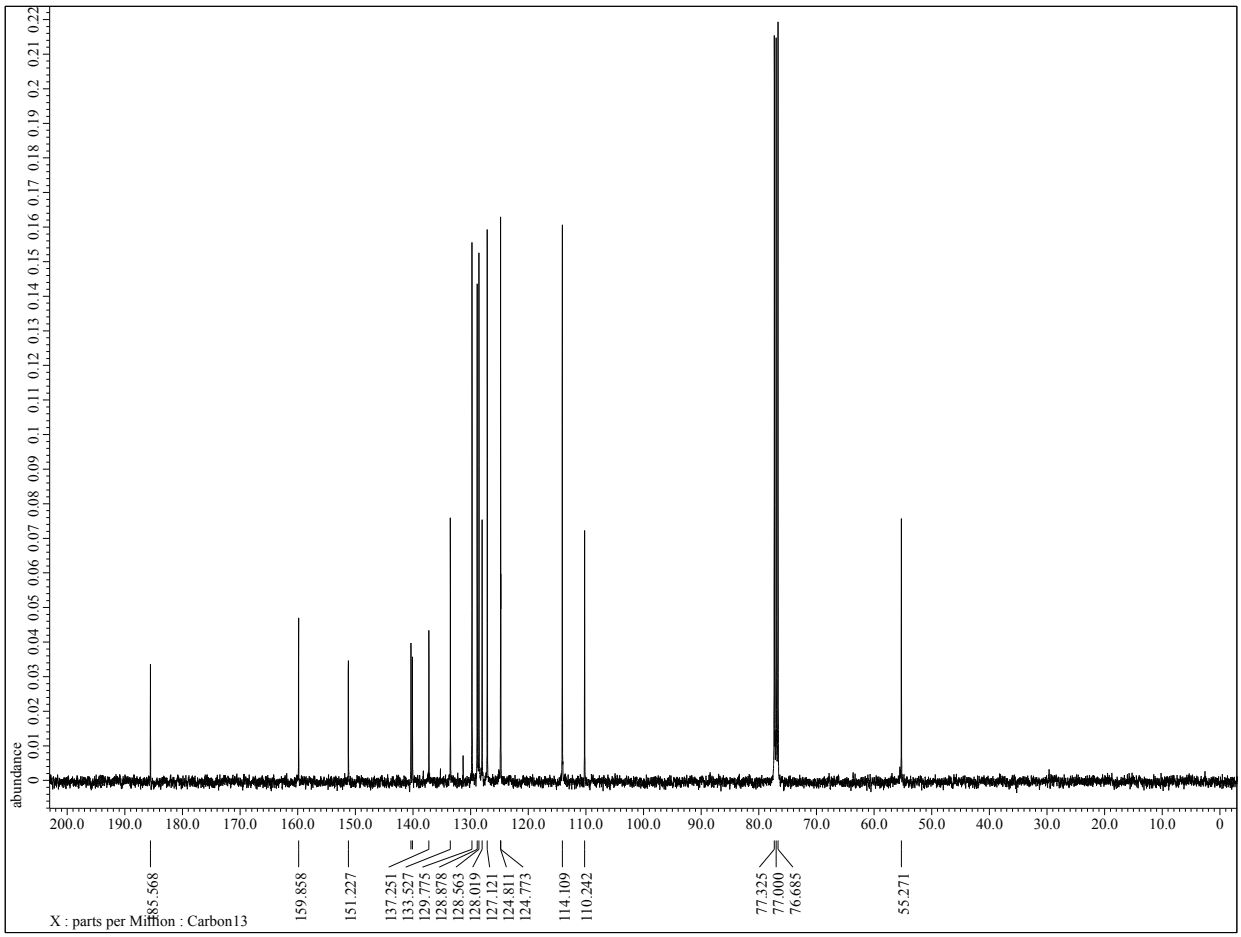

OMe
N
N
O
Ph
Ph
2c
abundance
X : parts per Million : Proton
7.987
7.968
7.964
7.914
7.911
7.892
7.635
7.527
7.507
7.488
7.455
7.438
7.433
7.430
7.424
7.417
7.408
7.361
7.066
6.953
6.931
3.830

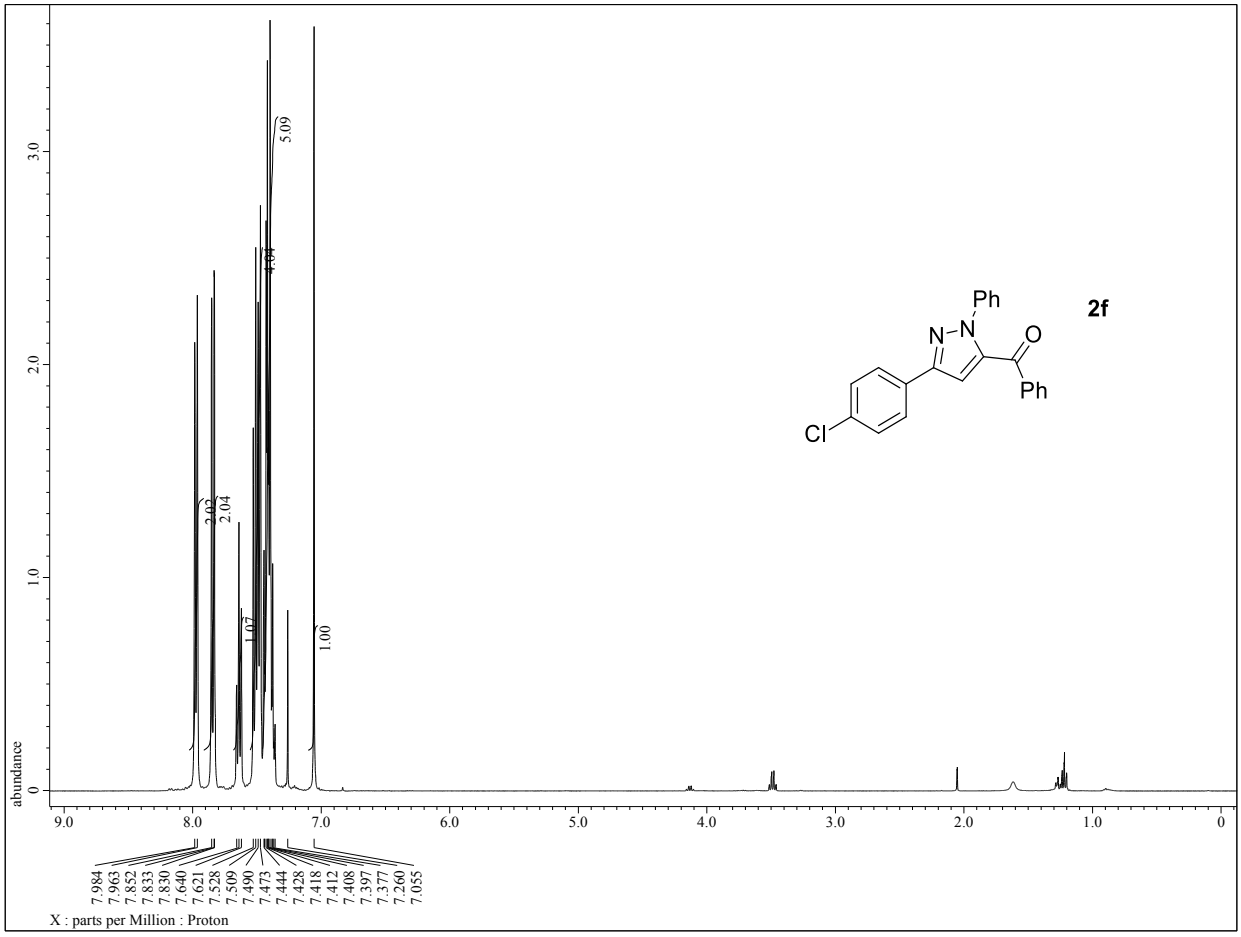

abundance
X : parts per Million : Carbon13
185.510
159.342
151.027
137.365
133.499
129.775
128.725
128.572
128.343
126.281
125.794
114.052
110.338
77.325
77.000
76.685
55.481

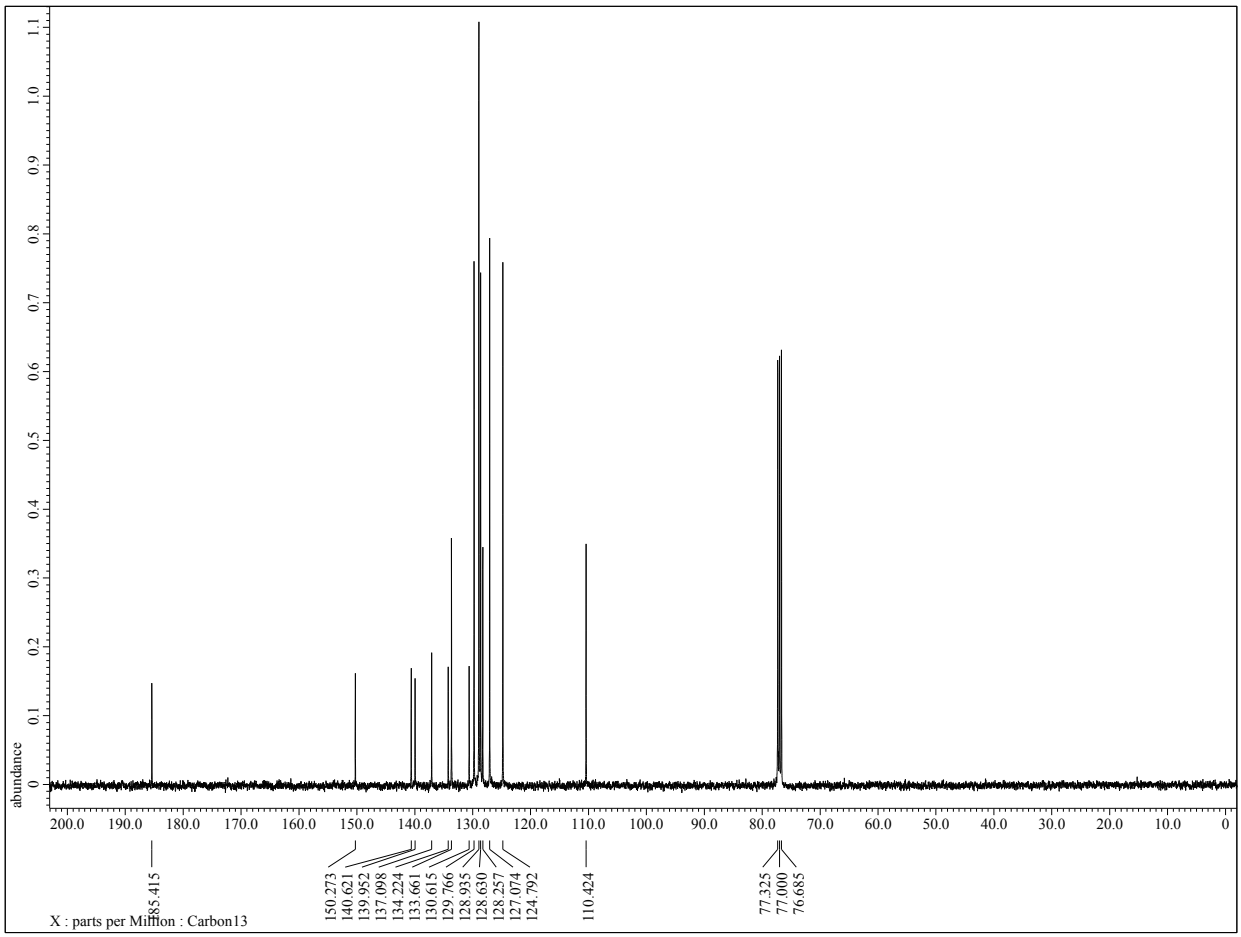

2d
Ph
N
N
O
MeO
Ph
abundance
10.11
2.01
1.03
1.00
1.00
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.998
7.978
7.639
7.621
7.530
7.512
7.494
7.467
7.454
7.451
7.434
7.415
7.396
7.379
7.373
7.354
7.260
7.086
7.084
6.944
6.923
3.876
X : parts per Million : Proton

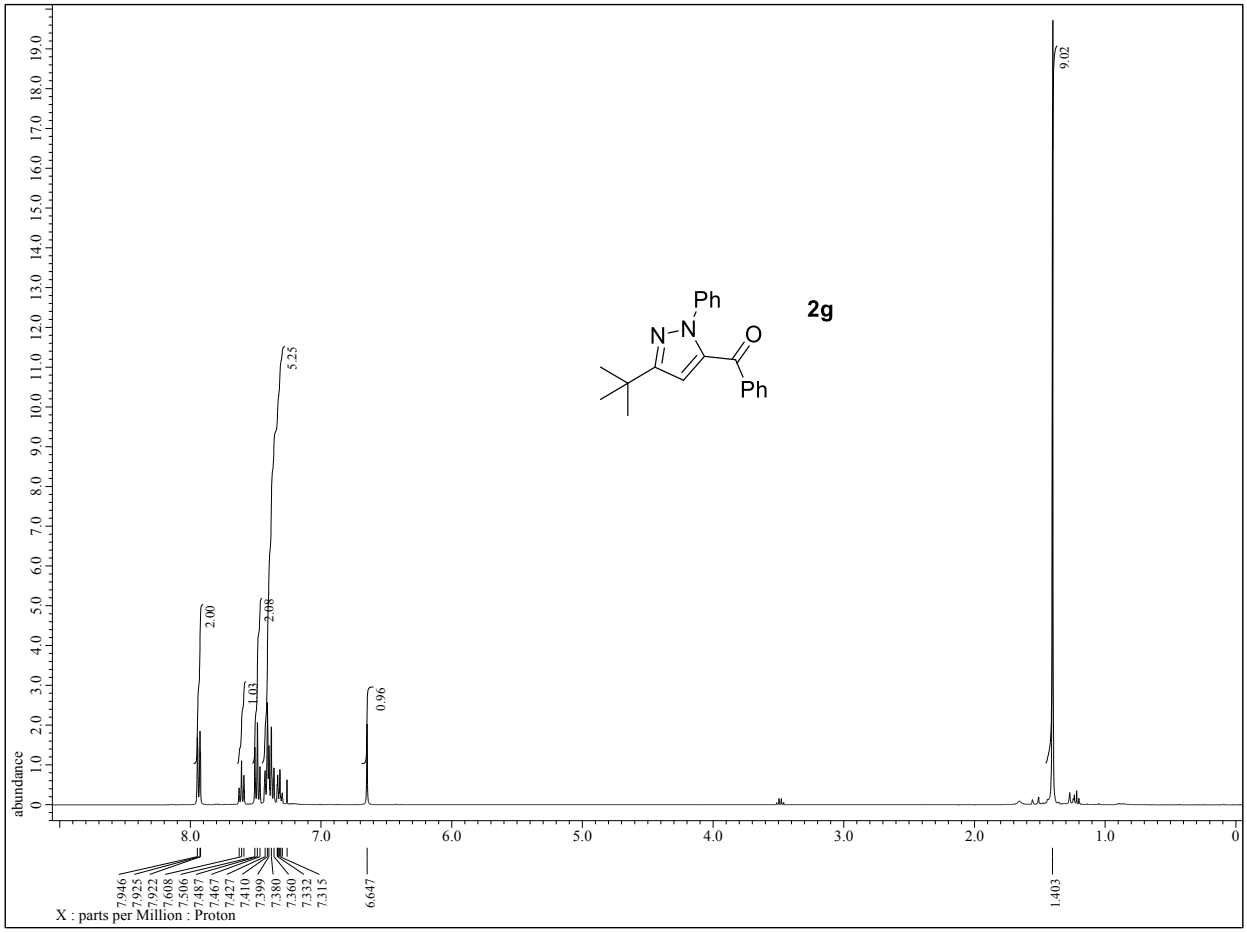

abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
185.491
159.953
151.237
140.411
140.038
137.174
133.585
133.403
129.775
128.887
128.592
128.152
124.859
118.357
114.433
110.911
110.806
77.315
77.000
76.685
55.319
X : parts per Million : Carbon13

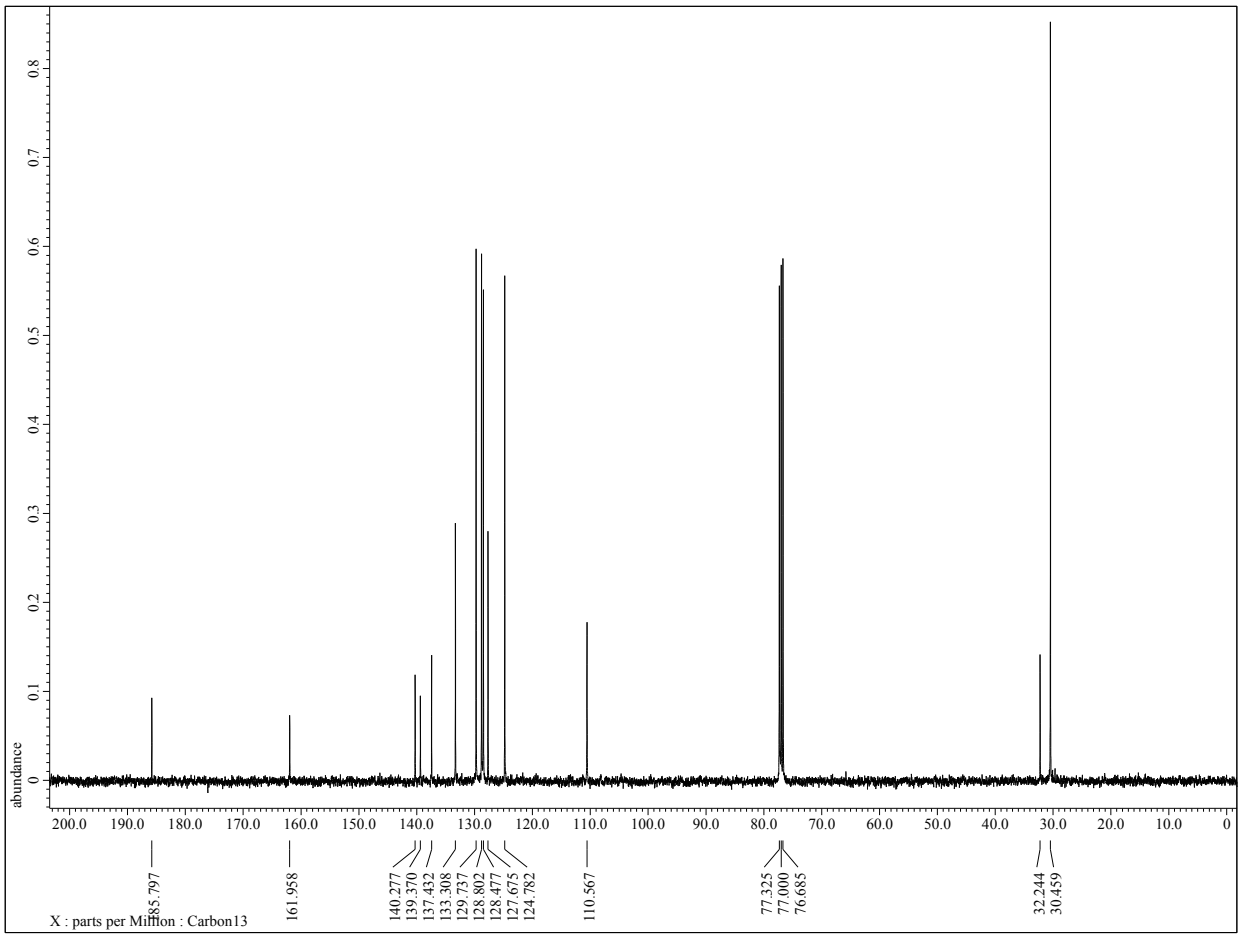

2e
Ph
N
N
O
Ph
MeO
4.00
3.04
3.03
2.03
1.99
1.96
1.08
1.03
abundance
7.991
7.972
7.970
7.849
7.828
7.629
7.521
7.502
7.481
7.478
7.438
7.419
7.400
7.379
7.377
7.361
7.260
7.018
6.981
6.960
3.848
X : parts per Million : Proton

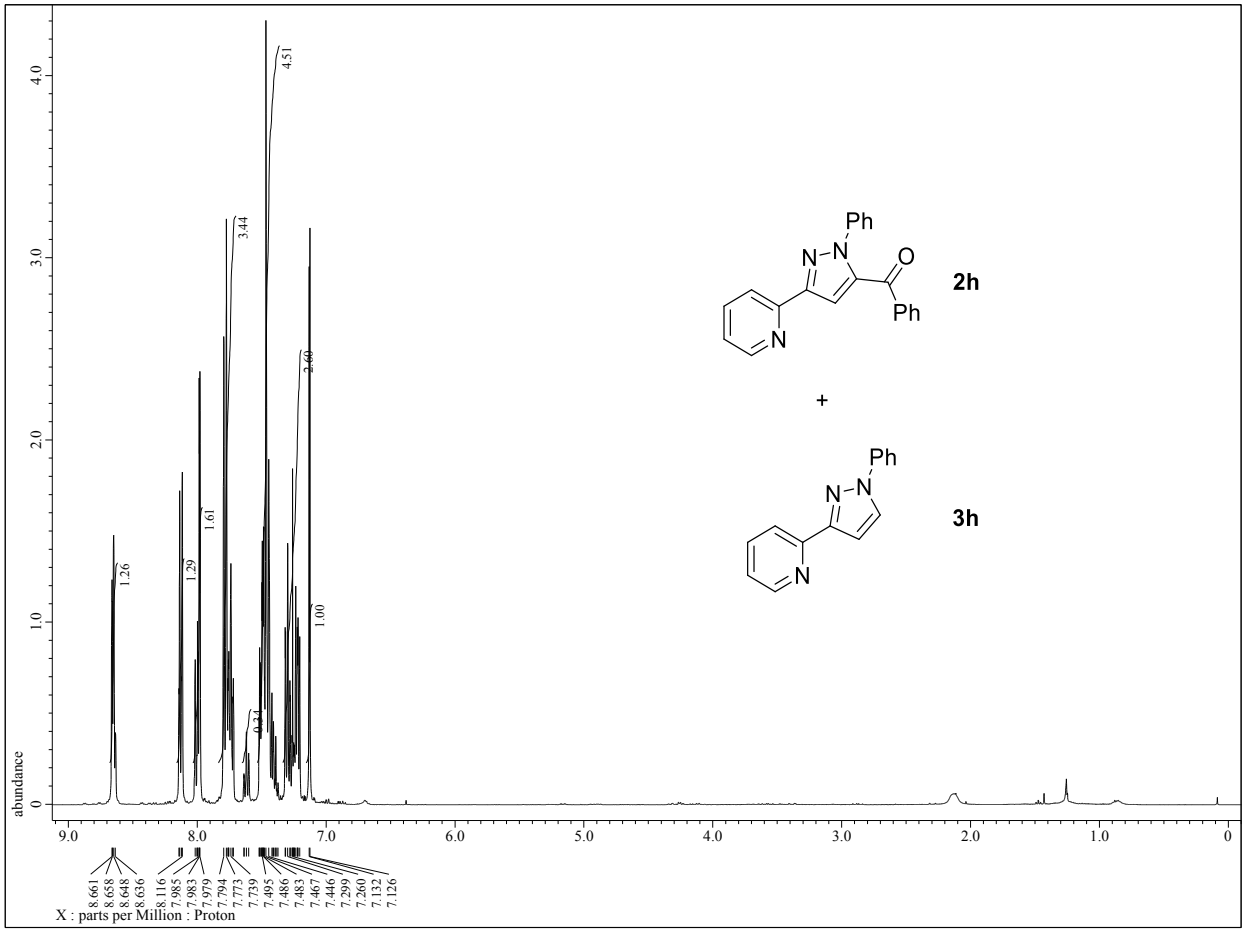

abundance
185.568
159.858
151.227
137.251
133.527
129.775
128.878
128.563
128.019
127.121
124.811
124.773
114.109
110.242
77.325
77.000
76.685
55.271
X : parts per Million : Carbon13

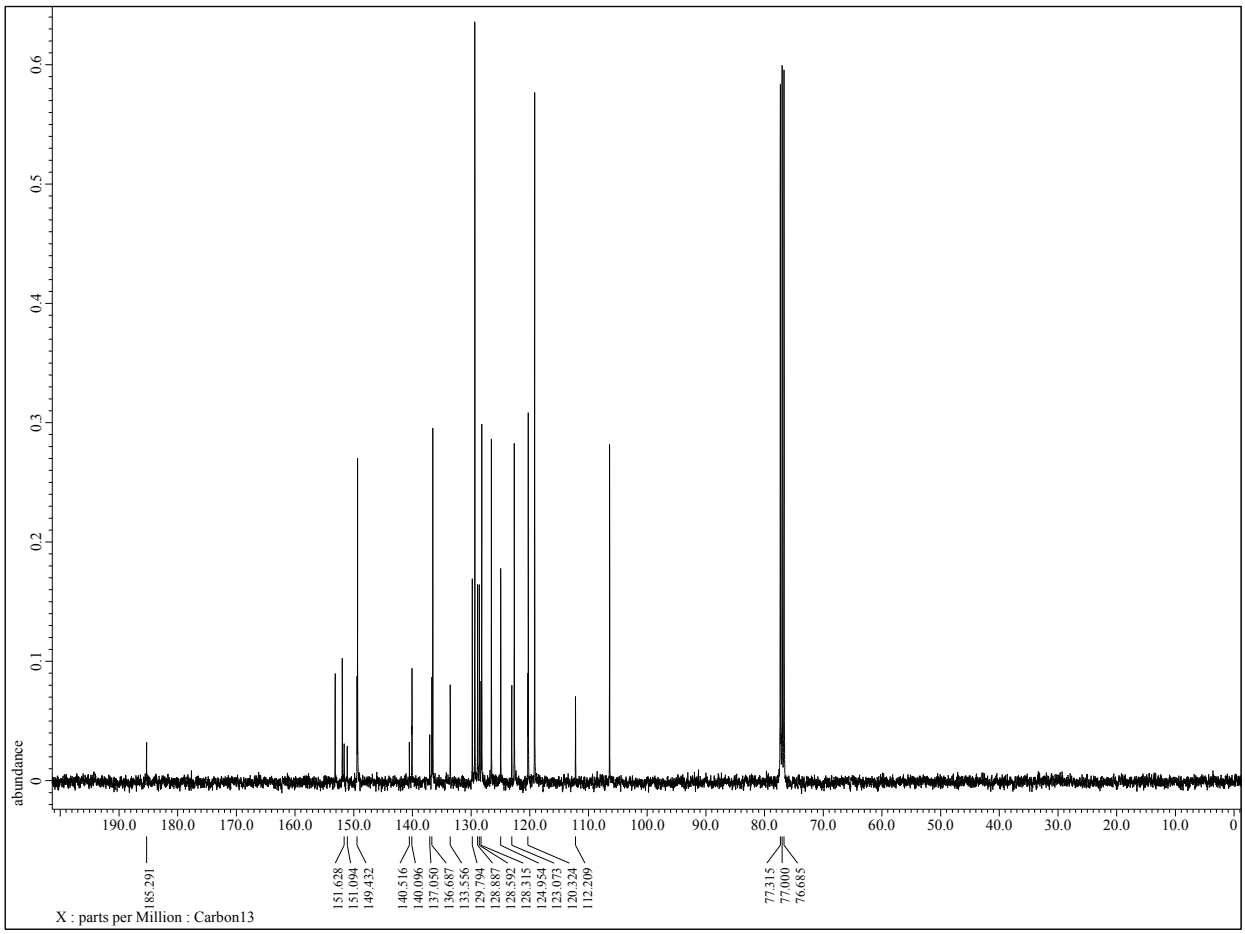

2f
Ph
N
N
O
Ph
Cl
abundance
5.09
4.84
2.03
2.04
1.07
1.00
7.984
7.963
7.852
7.833
7.830
7.640
7.621
7.528
7.509
7.490
7.473
7.444
7.428
7.418
7.412
7.408
7.397
7.377
7.260
7.055
X : parts per Million : Proton

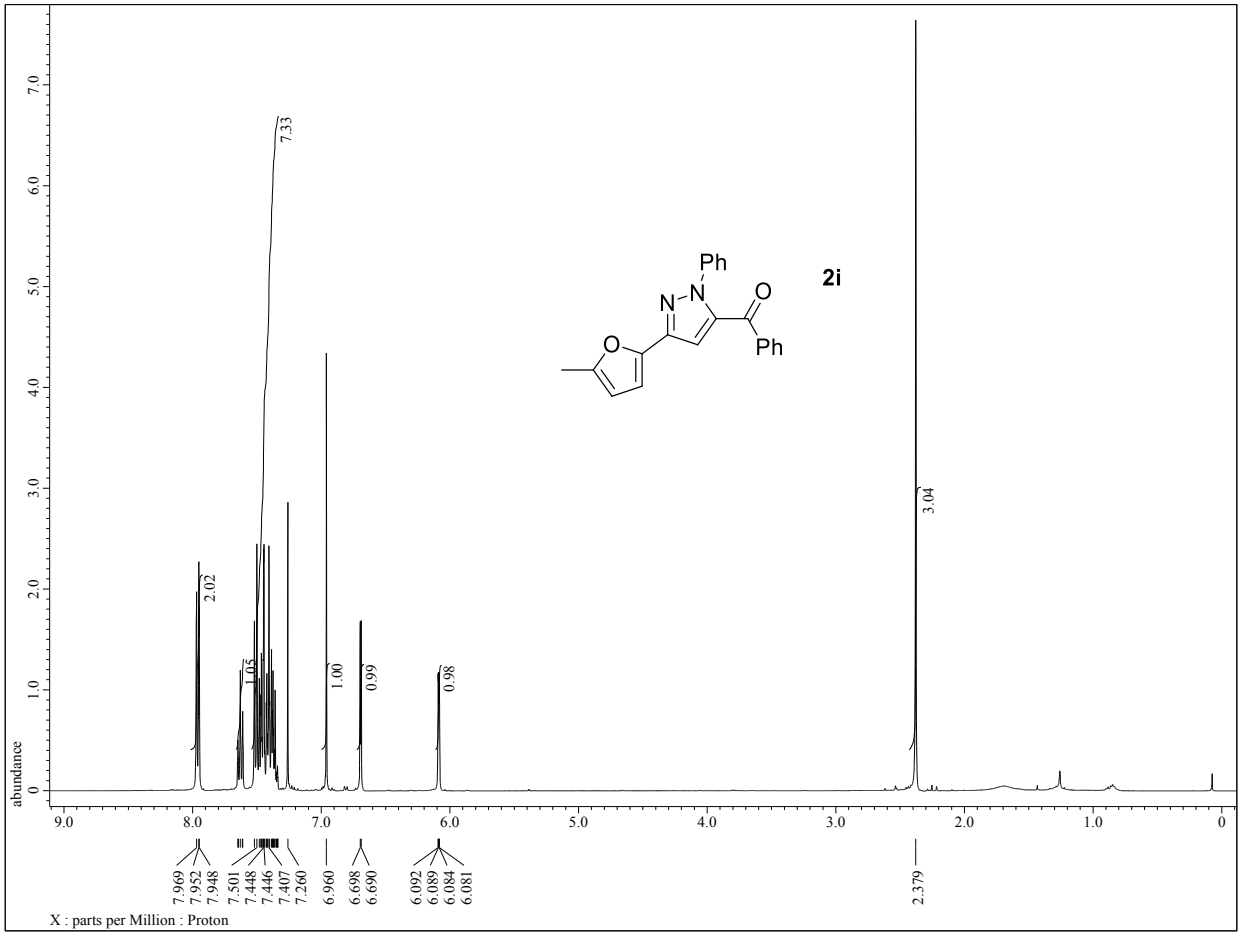

abundance
185.415
150.273
140.621
139.952
137.098
134.224
133.661
130.615
129.766
128.935
128.630
128.257
127.074
124.792
110.424
77.325
77.000
76.685
X : parts per Million : Carbon13

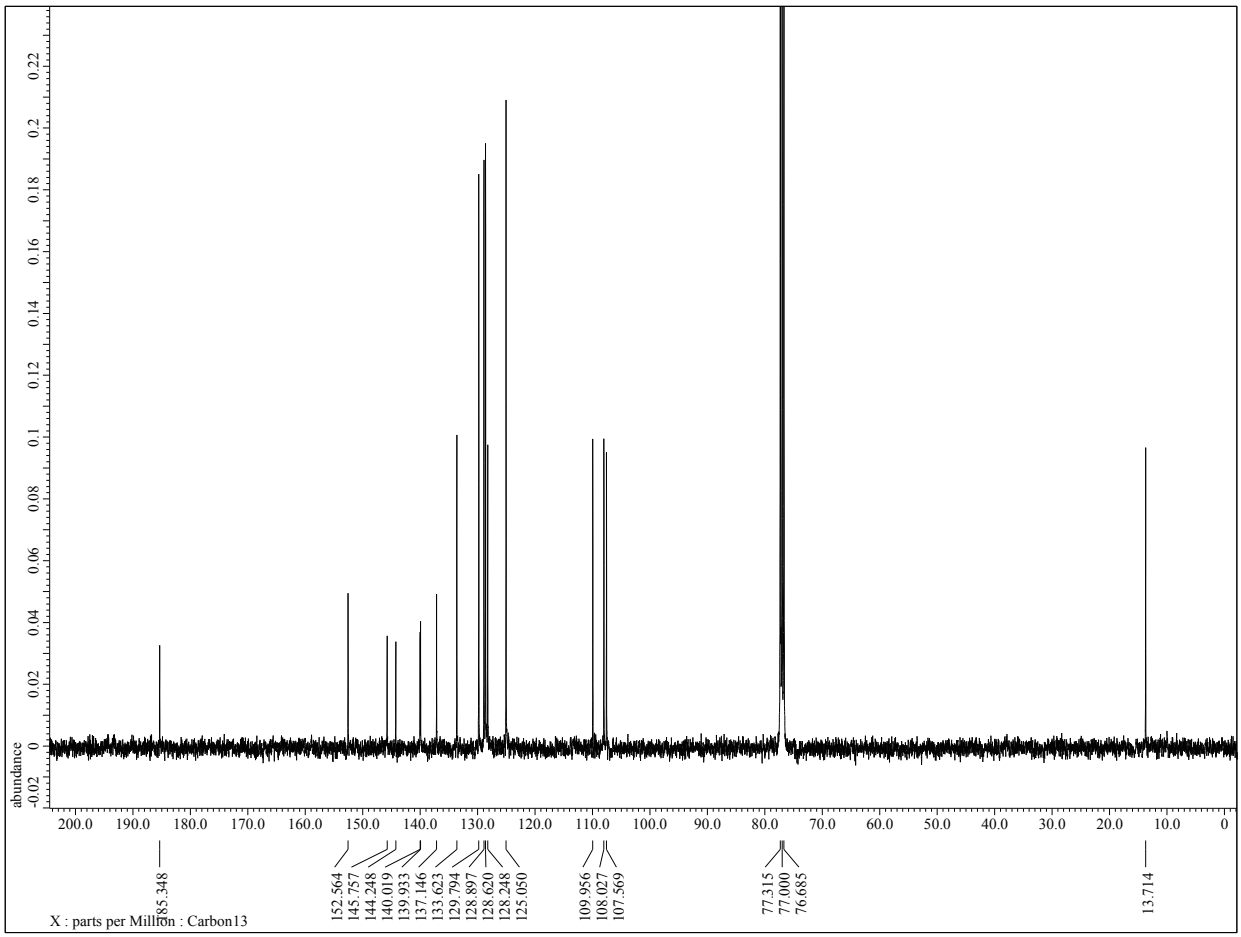

Ph
N
N
O
Ph
2g
abundance
9.02
5.25
2.00
2.08
1.03
0.96
7.946
7.925
7.922
7.608
7.506
7.487
7.467
7.427
7.410
7.399
7.380
7.360
7.332
7.315
6.647
1.403
X : parts per Million : Proton

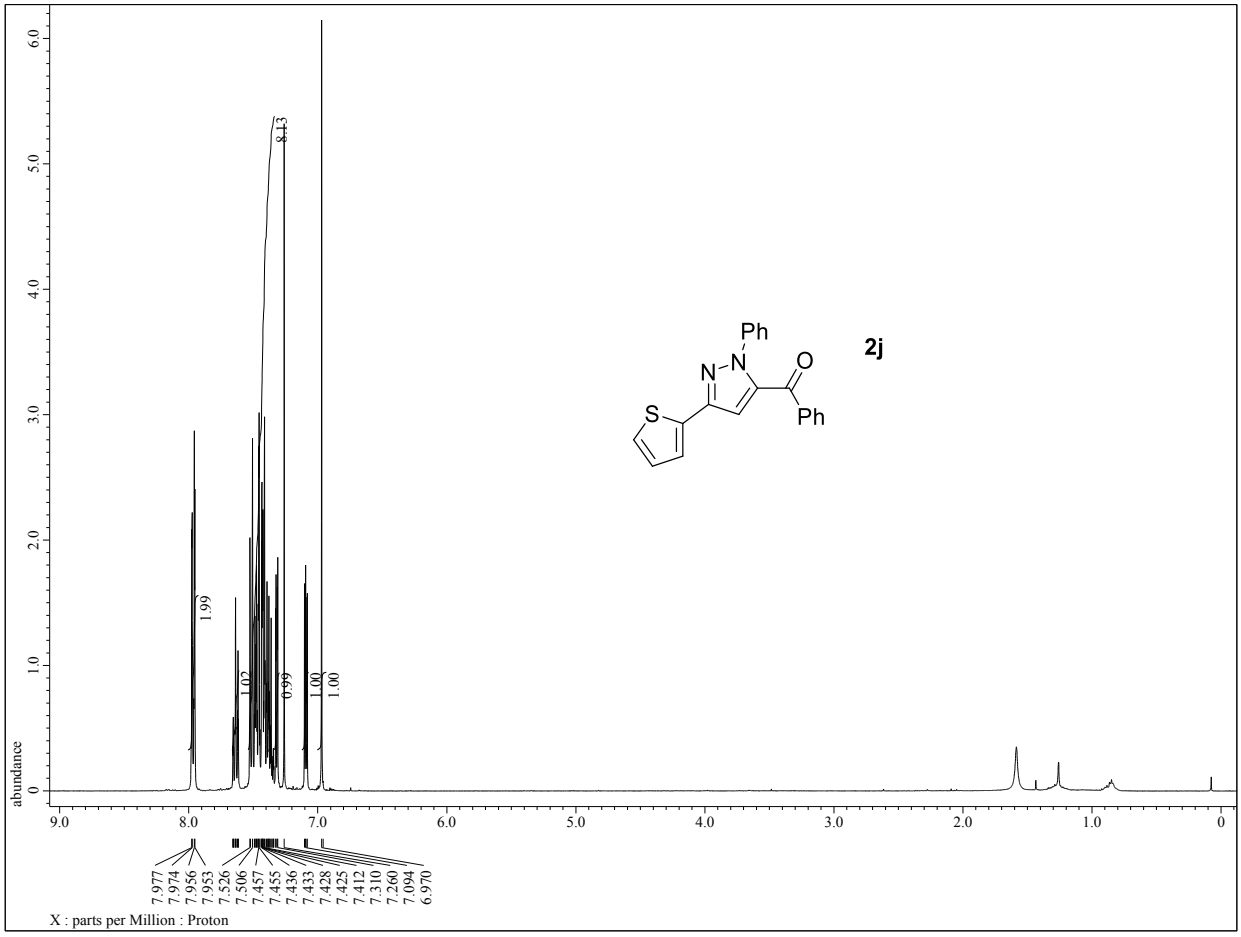

abundance
185.797
161.958
140.277
139.370
137.432
133.308
129.737
128.802
128.477
127.675
124.782
110.567
77.325
77.000
76.685
32.244
30.459
X : parts per Million : Carbon13

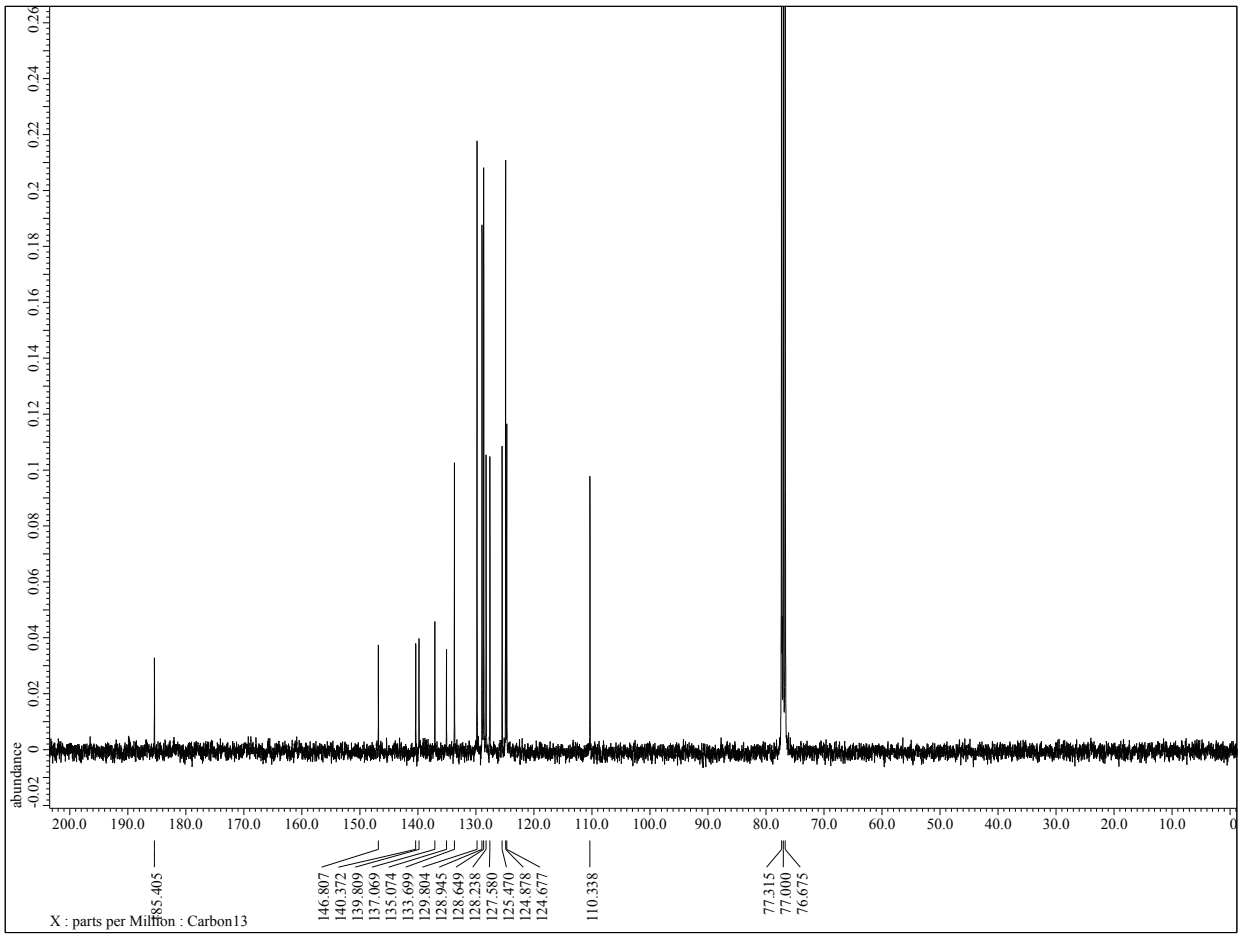

Ph
N
N
O
Ph
N
2h
+
Ph
N
N
N
3h
abundance
4.51
3.44
2.60
1.61
1.29
1.26
1.00
0.34
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.661
8.658
8.648
8.636
8.116
7.985
7.983
7.979
7.794
7.773
7.739
7.495
7.486
7.483
7.467
7.446
7.299
7.260
7.132
7.126
X : parts per Million : Proton

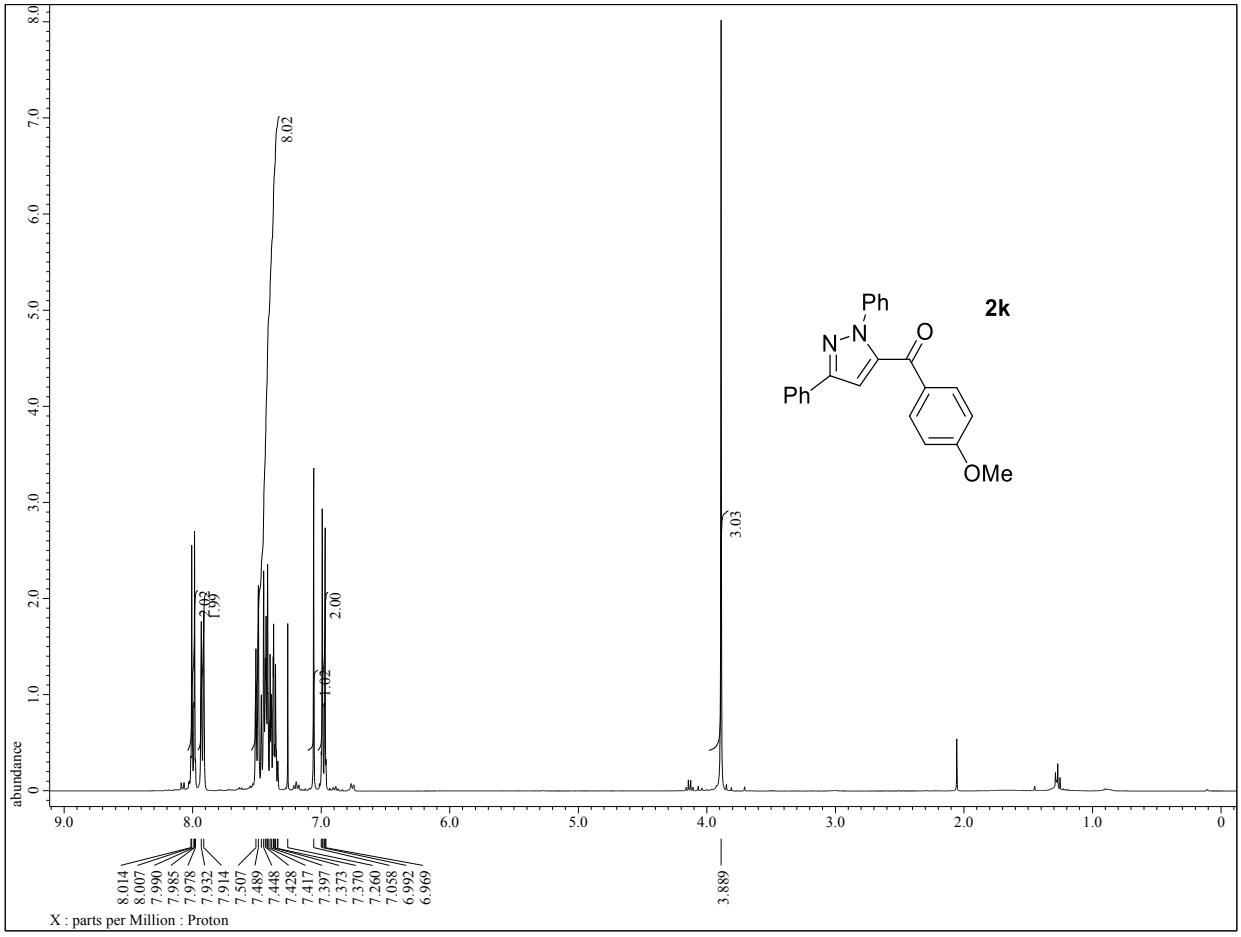

abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
185.291
151.628
151.094
149.432
140.516
140.096
137.050
136.687
133.556
129.794
128.887
128.592
128.315
124.954
123.073
120.324
112.209
77.315
77.000
76.685
X : parts per Million : Carbon13

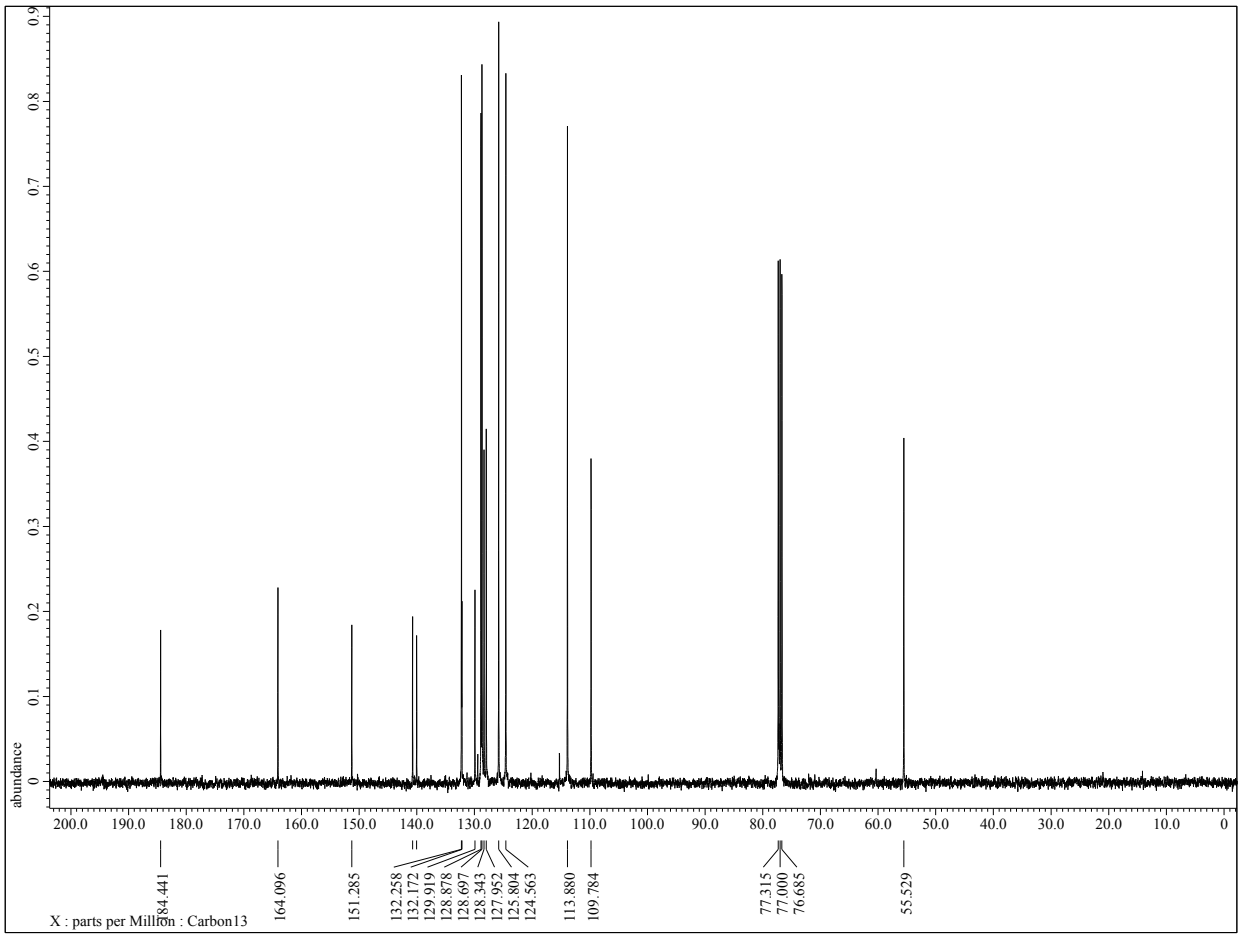

2i
Ph
N
N
O
O
Ph
abundance
7.33
2.02
1.05
1.00
0.99
0.98
3.04
7.969
7.952
7.948
7.501
7.448
7.446
7.407
7.260
6.960
6.698
6.690
6.092
6.089
6.084
6.081
2.379
X : parts per Million : Proton

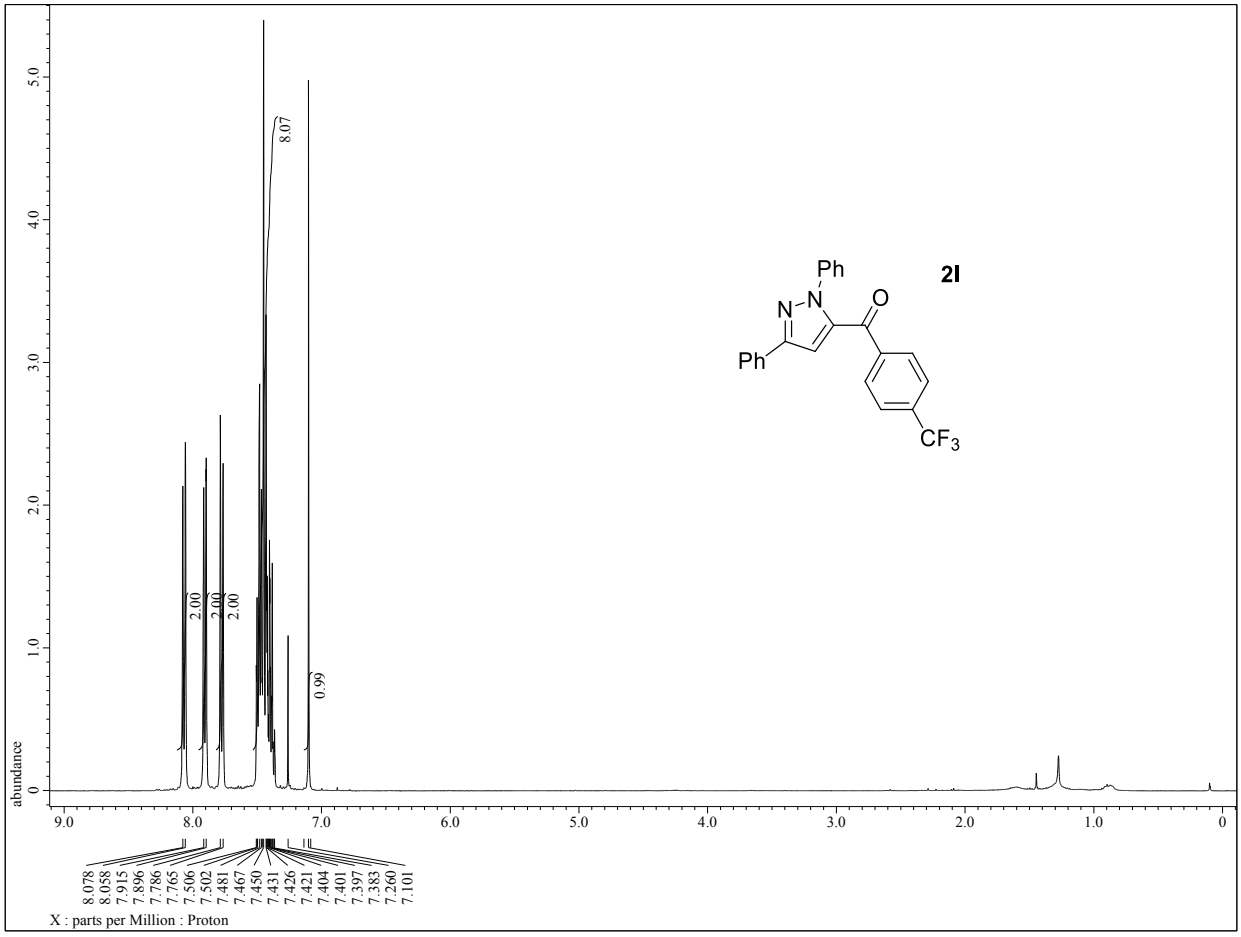

abundance
185.348
152.564
145.757
144.248
140.019
139.933
137.146
133.623
129.794
128.897
128.620
128.248
125.050
109.956
108.027
107.569
77.315
77.000
76.685
13.714
X : parts per Million : Carbon13

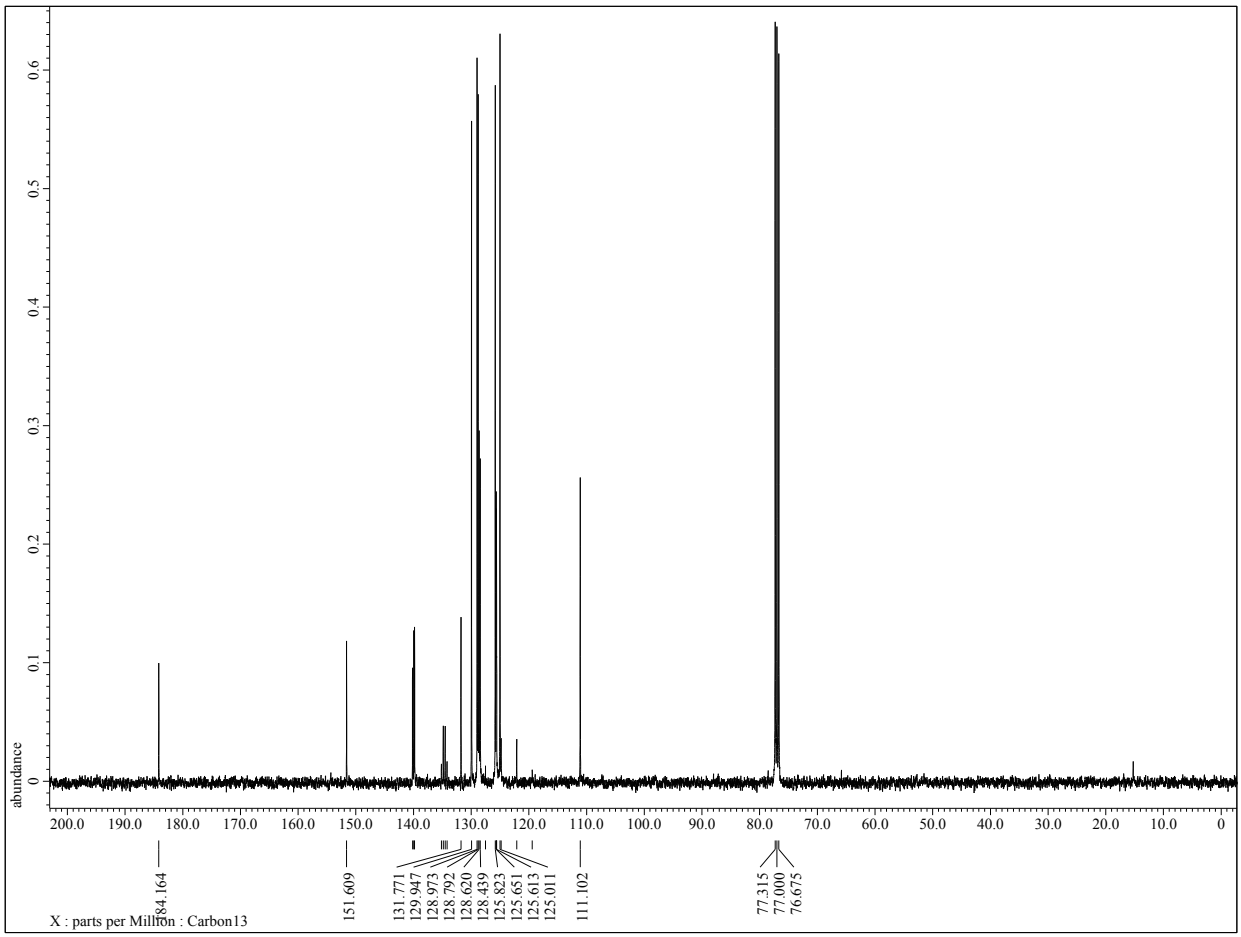

Ph
N
N
O
S
Ph
2j
abundance
1.99
1.02
0.99
1.00
1.00
8.13
7.977
7.974
7.956
7.953
7.526
7.506
7.457
7.455
7.436
7.433
7.428
7.425
7.412
7.310
7.260
7.094
6.970
X : parts per Million : Proton

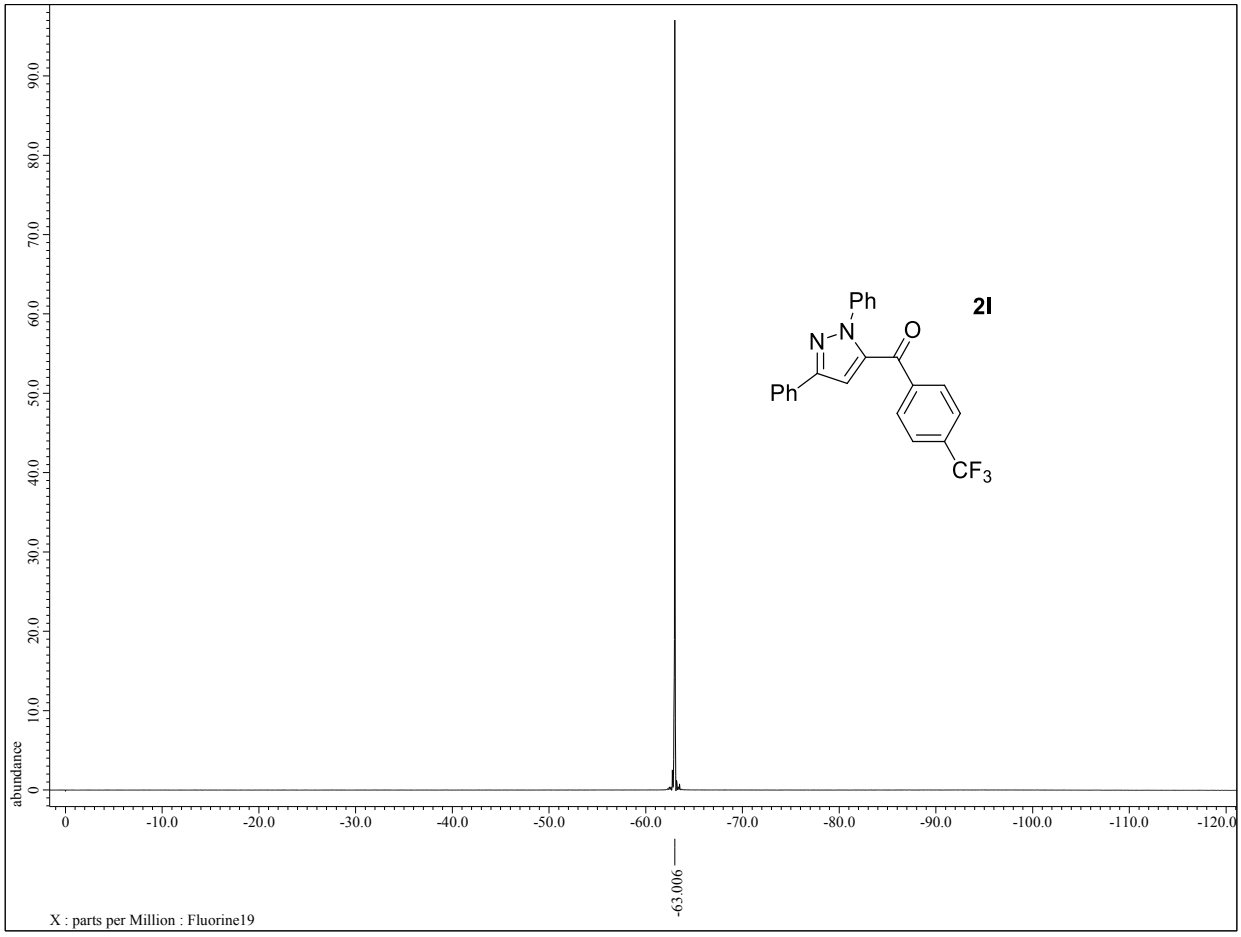

abundance
185.405
146.807
140.372
139.809
137.069
135.074
133.699
129.804
128.945
128.649
128.238
127.580
125.470
124.878
124.677
110.338
77.315
77.000
76.675
X : parts per Million : Carbon13

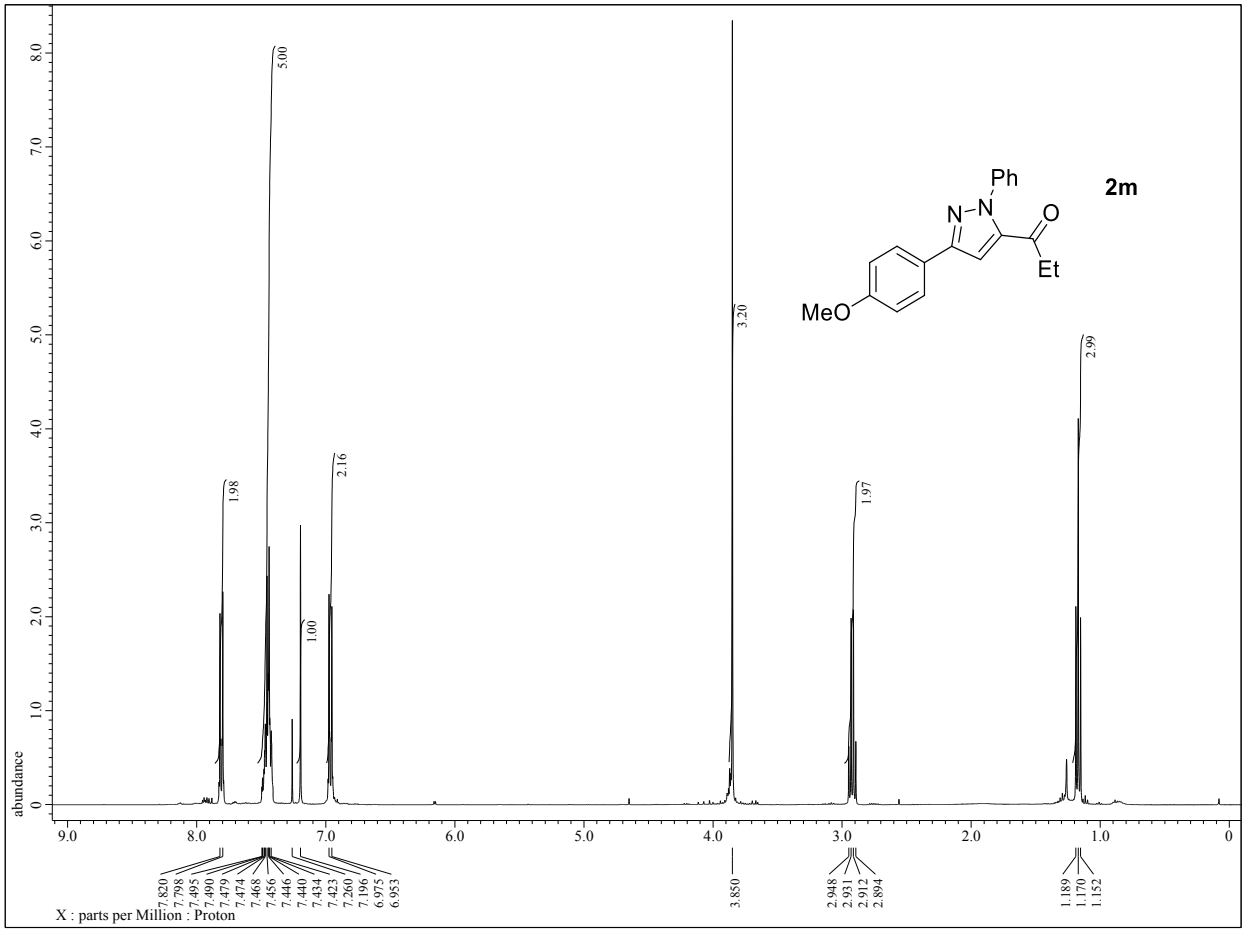

2k
Ph
N
N
O
Ph
OMe
abundance
8.02
3.03
2.00
1.02
2.03
1.99
8.014
8.007
7.990
7.985
7.978
7.932
7.914
7.507
7.489
7.448
7.428
7.417
7.397
7.373
7.370
7.260
7.058
6.992
6.969
3.889
X : parts per Million : Proton

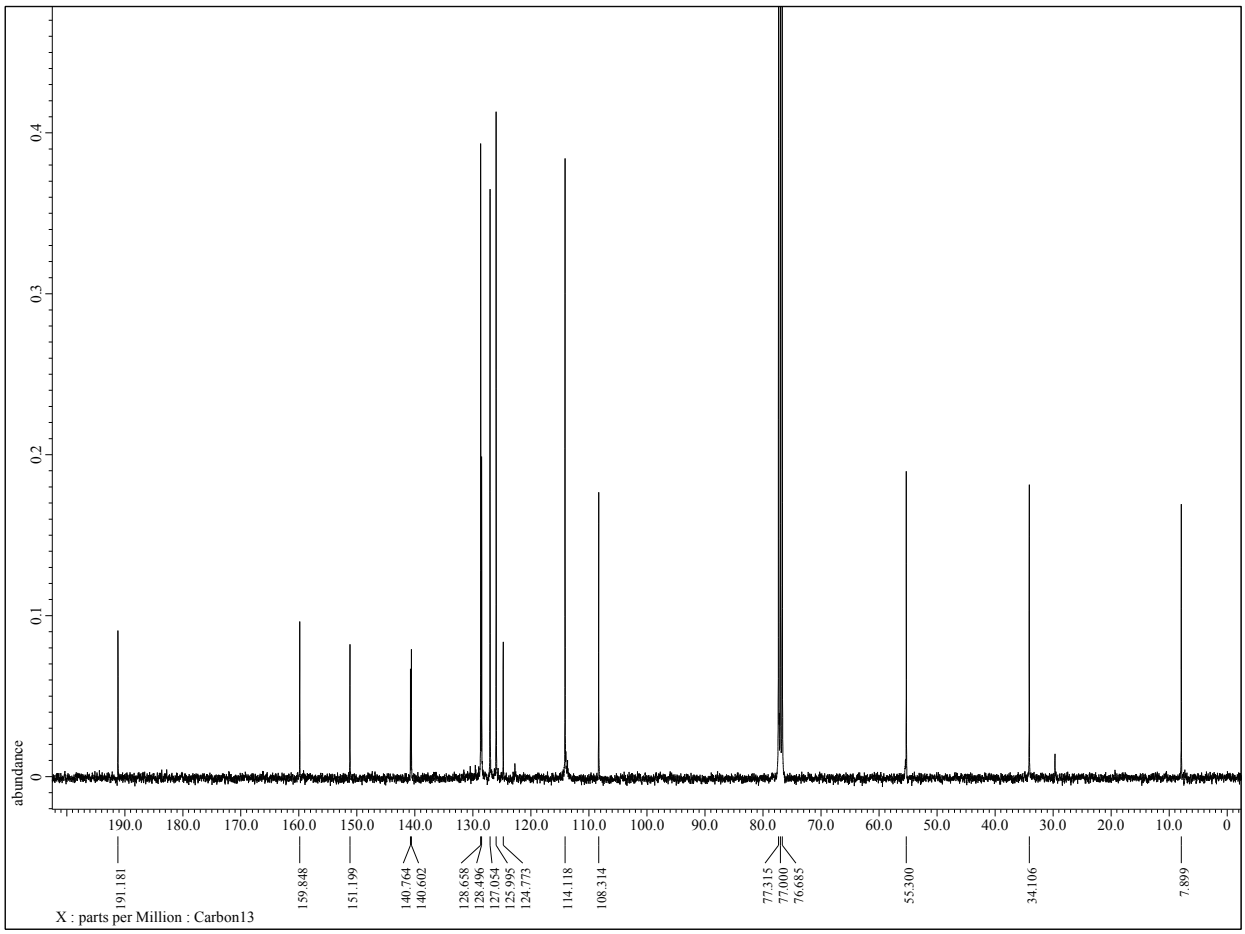

abundance
184.441
164.096
151.285
132.258
132.172
129.919
128.878
128.697
128.343
127.952
125.804
124.563
113.880
109.784
77.315
77.000
76.685
55.529
X : parts per Million : Carbon13

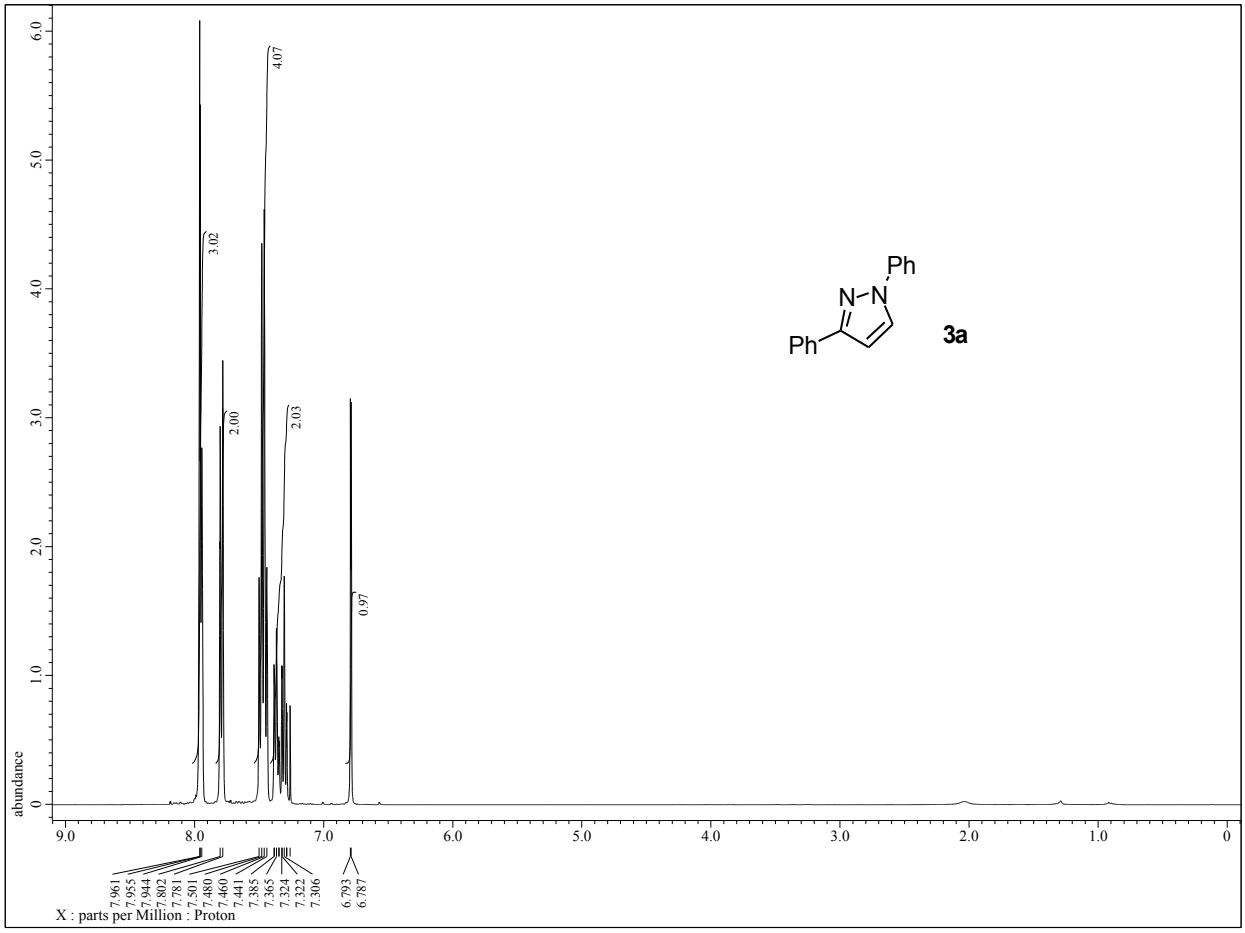

2l
Ph
N
N
O
Ph
CF3
abundance
8.07
2.00
2.00
2.00
0.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.078
8.058
7.915
7.896
7.786
7.765
7.506
7.502
7.481
7.467
7.450
7.431
7.426
7.421
7.404
7.401
7.397
7.383
7.260
7.101
X : parts per Million : Proton

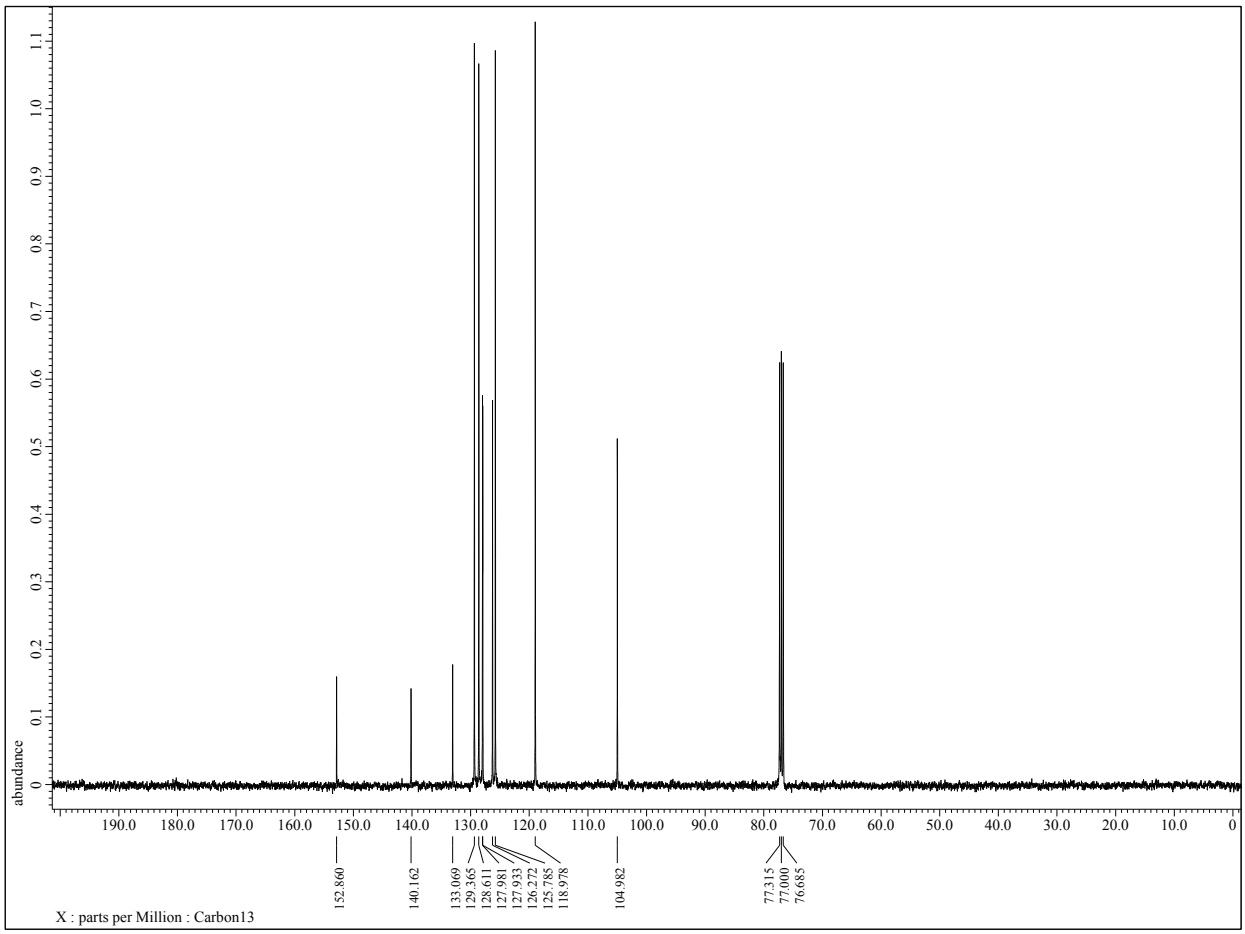

abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
184.164
151.609
131.771
129.947
128.973
128.792
128.620
128.439
125.823
125.651
125.613
125.011
111.102
77.315
77.000
76.675
X : parts per Million : Carbon13

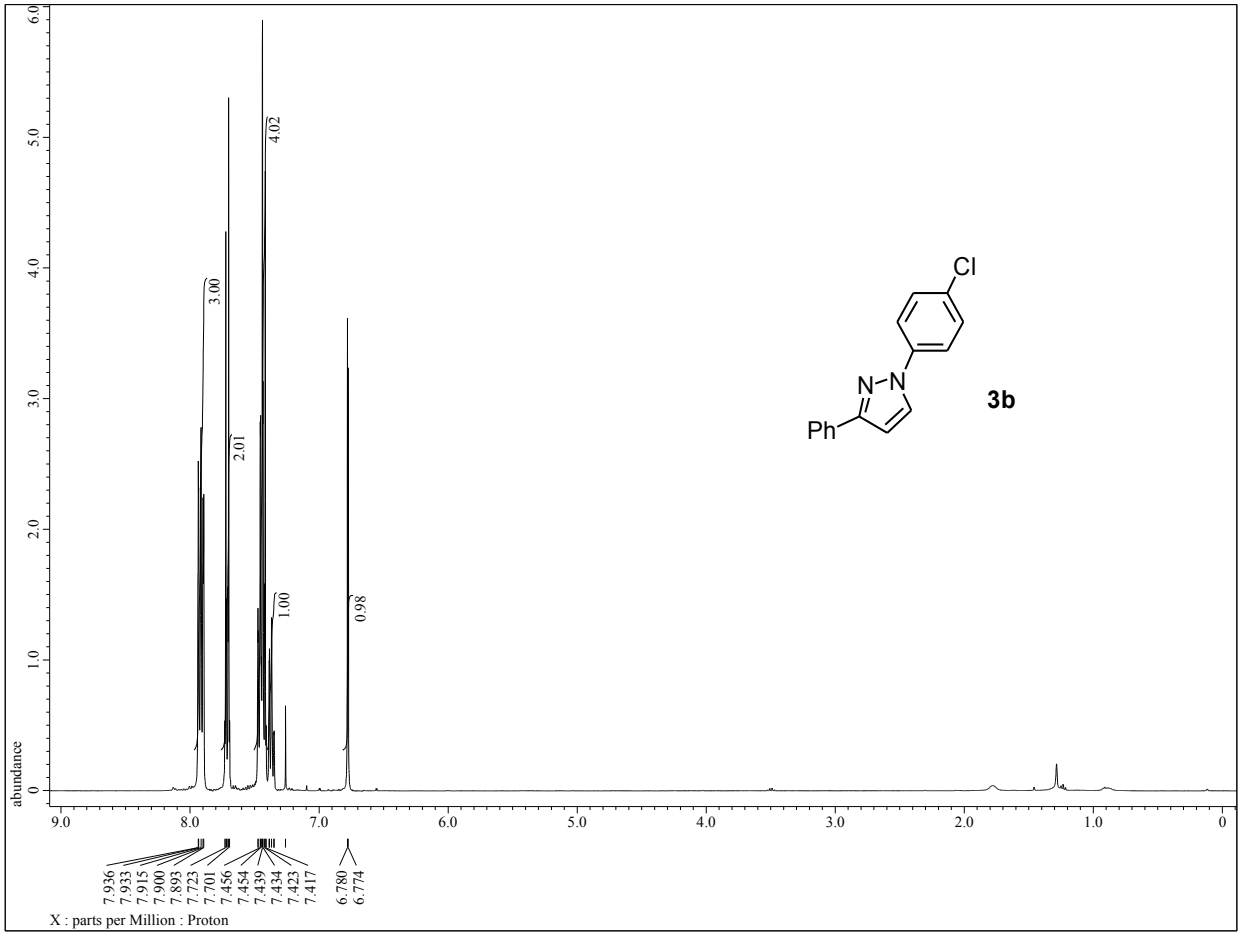

2l
Ph
N
N
O
Ph
CF3
abundance
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
-70.0
-80.0
-90.0
-100.0
-110.0
-120.0
-63.006
X : parts per Million : Fluorine19

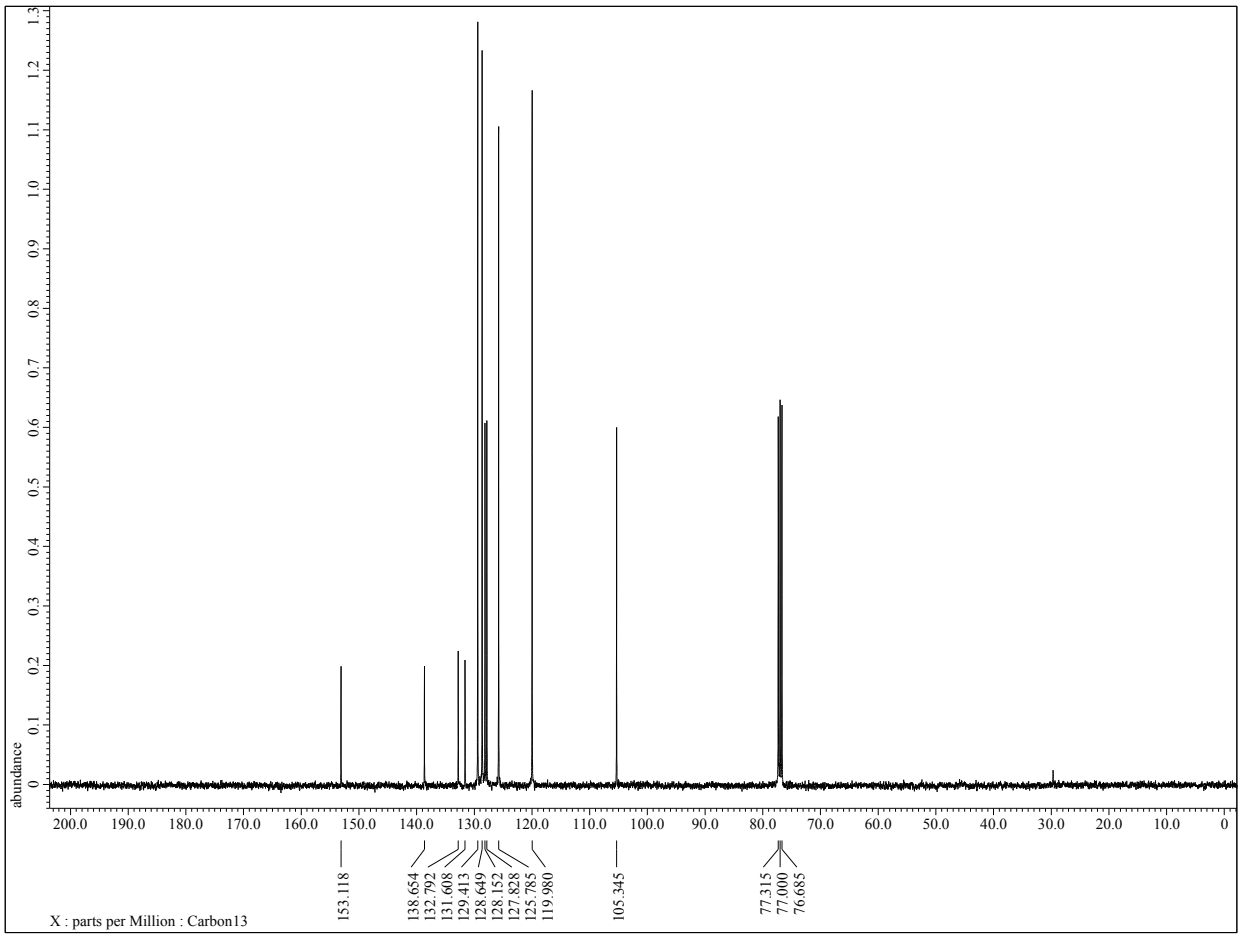

2m
Ph
N
N
O
Et
MeO
abundance
X : parts per Million : Proton
5.00
3.20
2.99
1.98
2.16
1.97
1.00
7.820
7.798
7.495
7.490
7.479
7.474
7.468
7.456
7.446
7.440
7.434
7.423
7.260
7.196
6.975
6.953
3.850
2.948
2.931
2.912
2.894
1.189
1.170
1.152

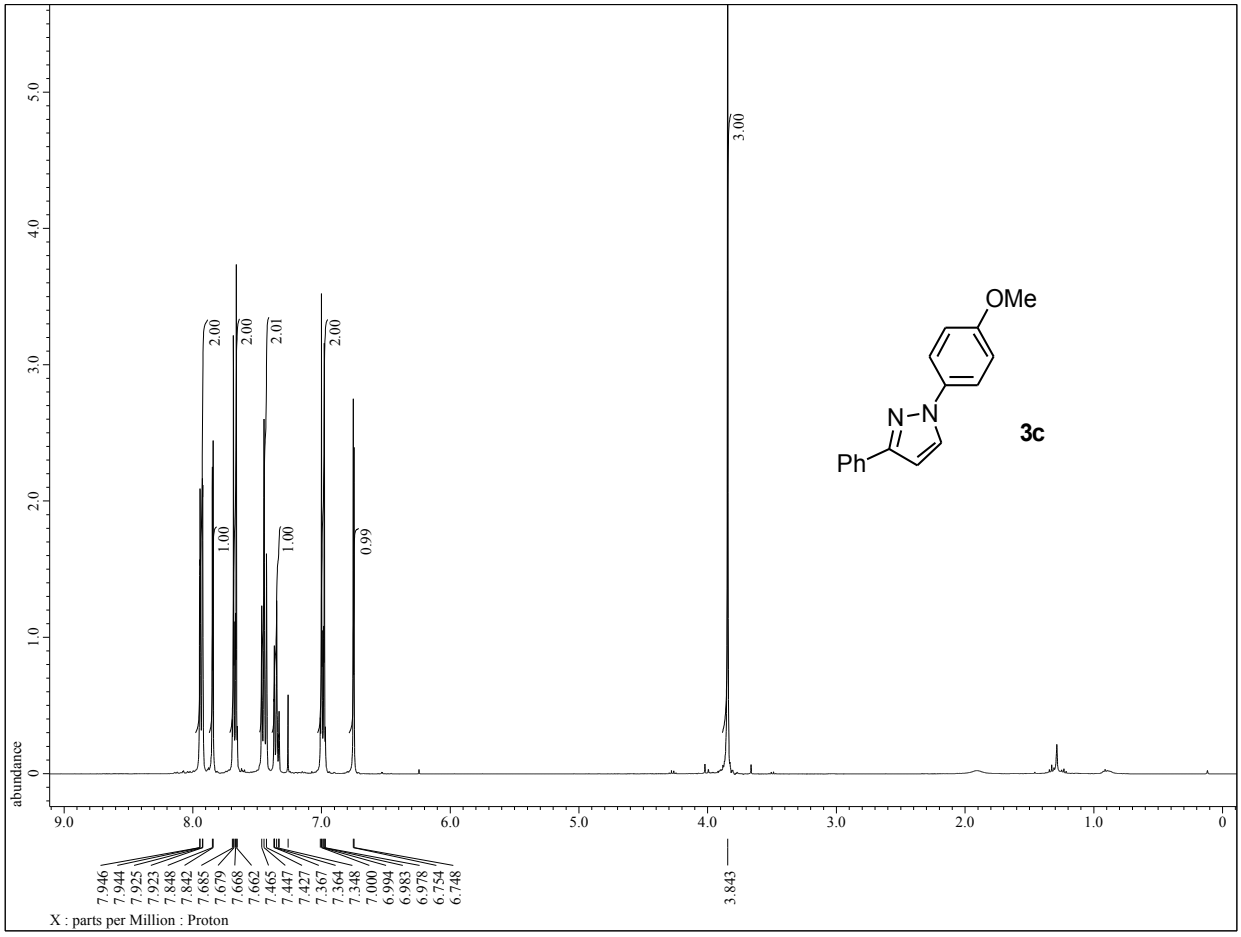

abundance
X : parts per Million : Carbon13
191.181
159.848
151.199
140.764
140.602
128.658
128.496
127.054
125.995
124.773
114.118
108.314
77.315
77.000
76.685
55.300
34.106
7.899

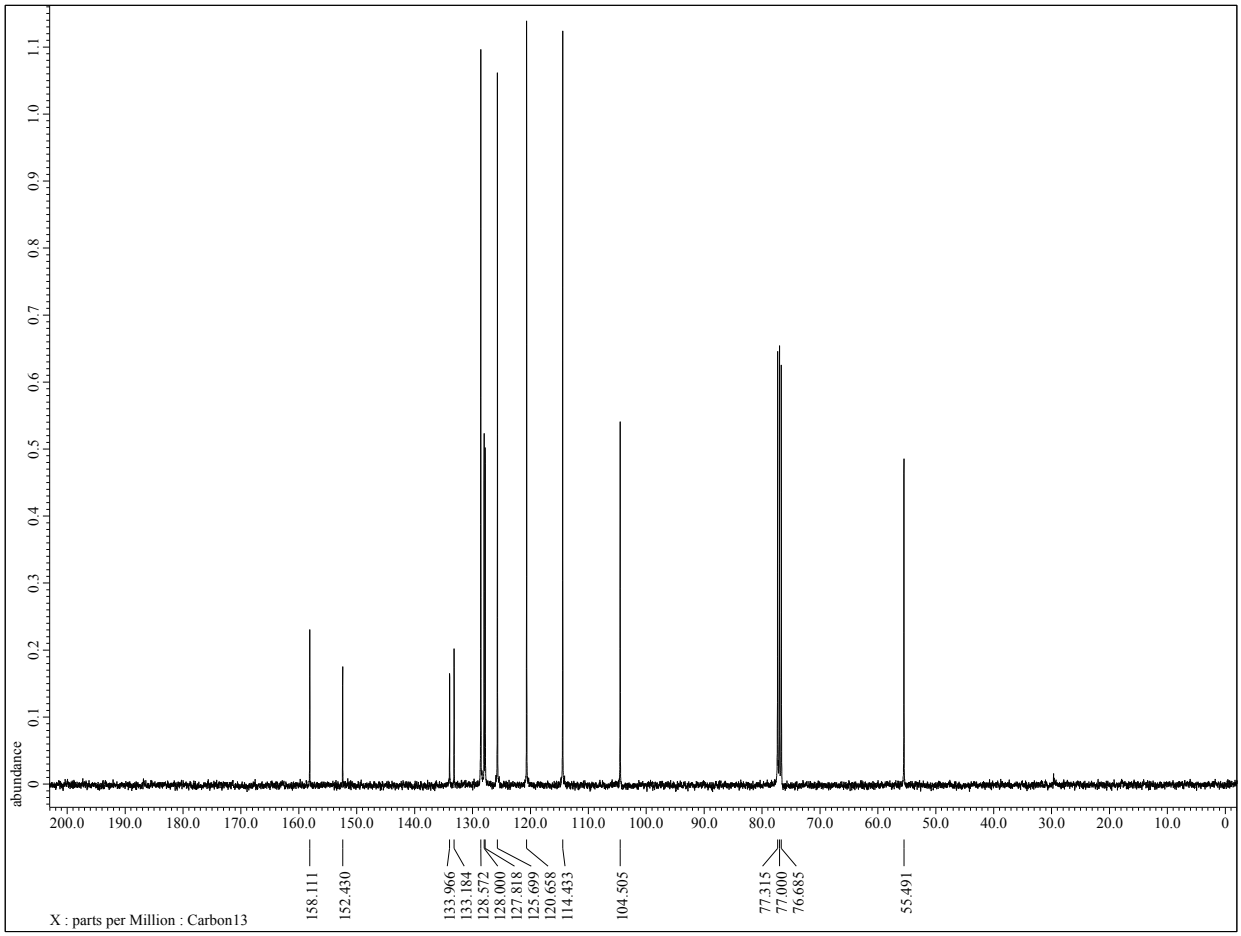

Ph
N-N
Ph
3a
4.07
3.02
2.00
2.03
0.97
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.961
7.955
7.944
7.802
7.781
7.501
7.480
7.460
7.441
7.385
7.365
7.324
7.322
7.306
6.793
6.787
X : parts per Million : Proton

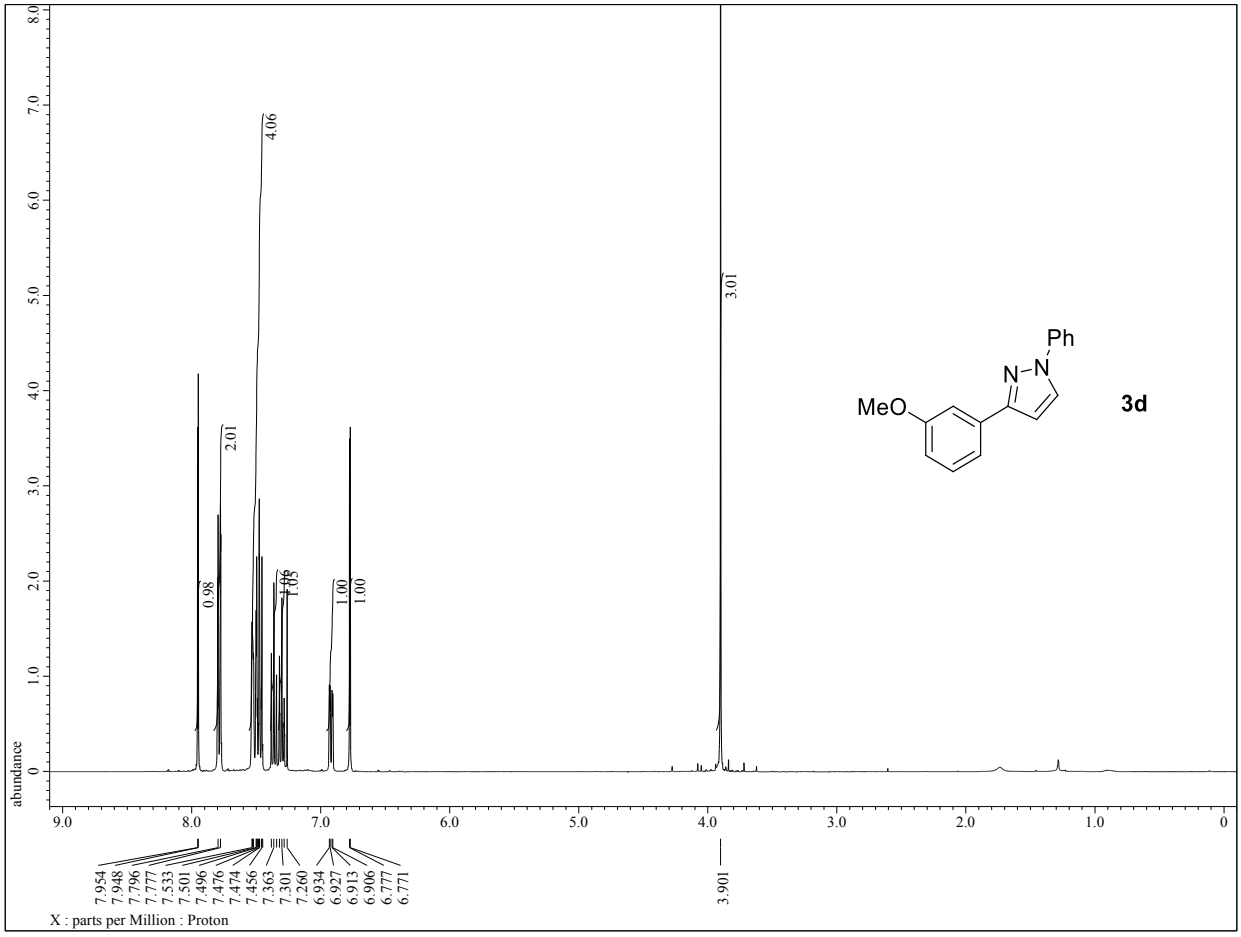

abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
152.860
140.162
133.069
129.365
128.611
127.981
127.933
126.272
125.785
118.978
104.982
77.315
77.000
76.685
X : parts per Million : Carbon13

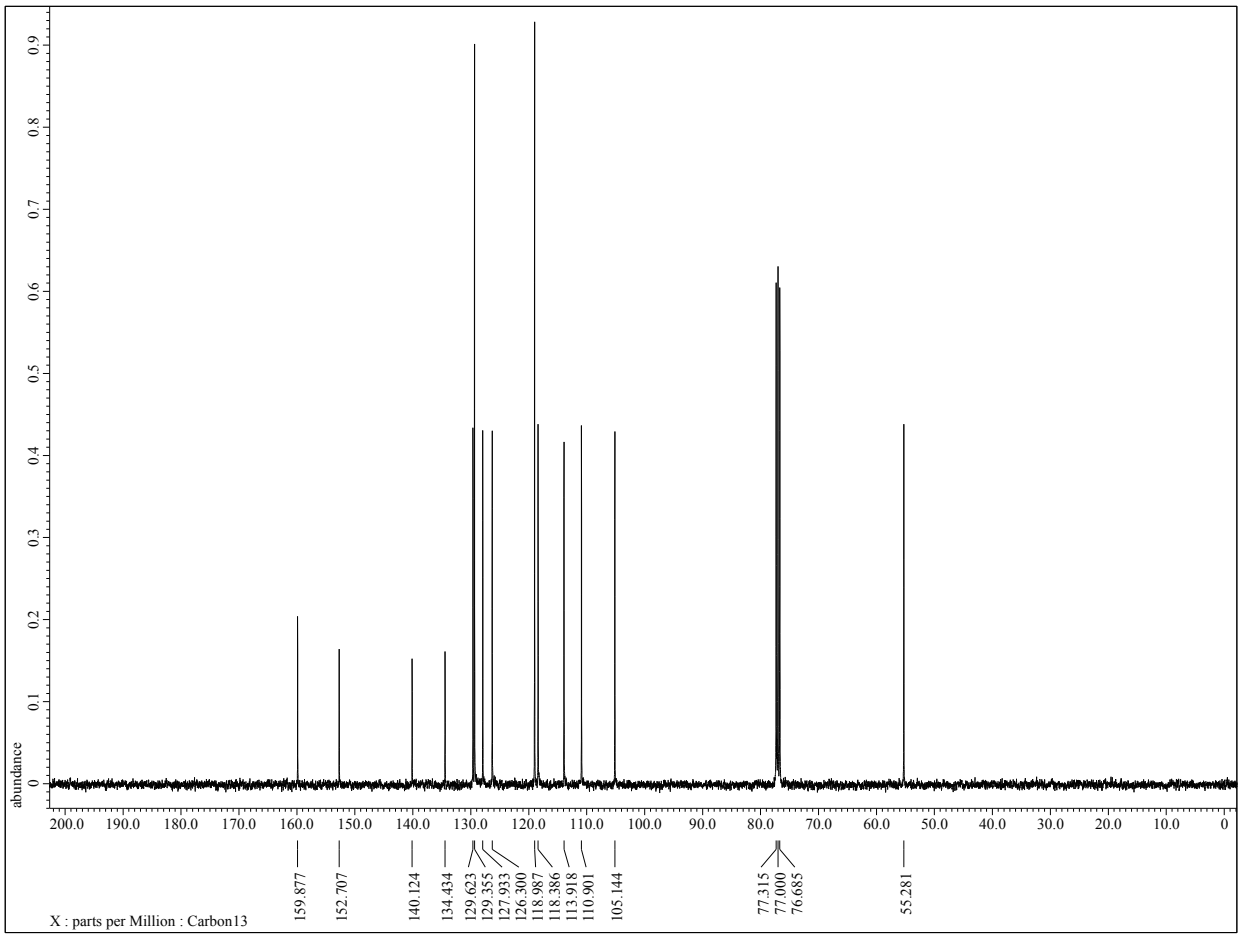

Cl
N
N
Ph
3b
3.00
2.01
4.02
1.00
0.98
abundance
X : parts per Million : Proton

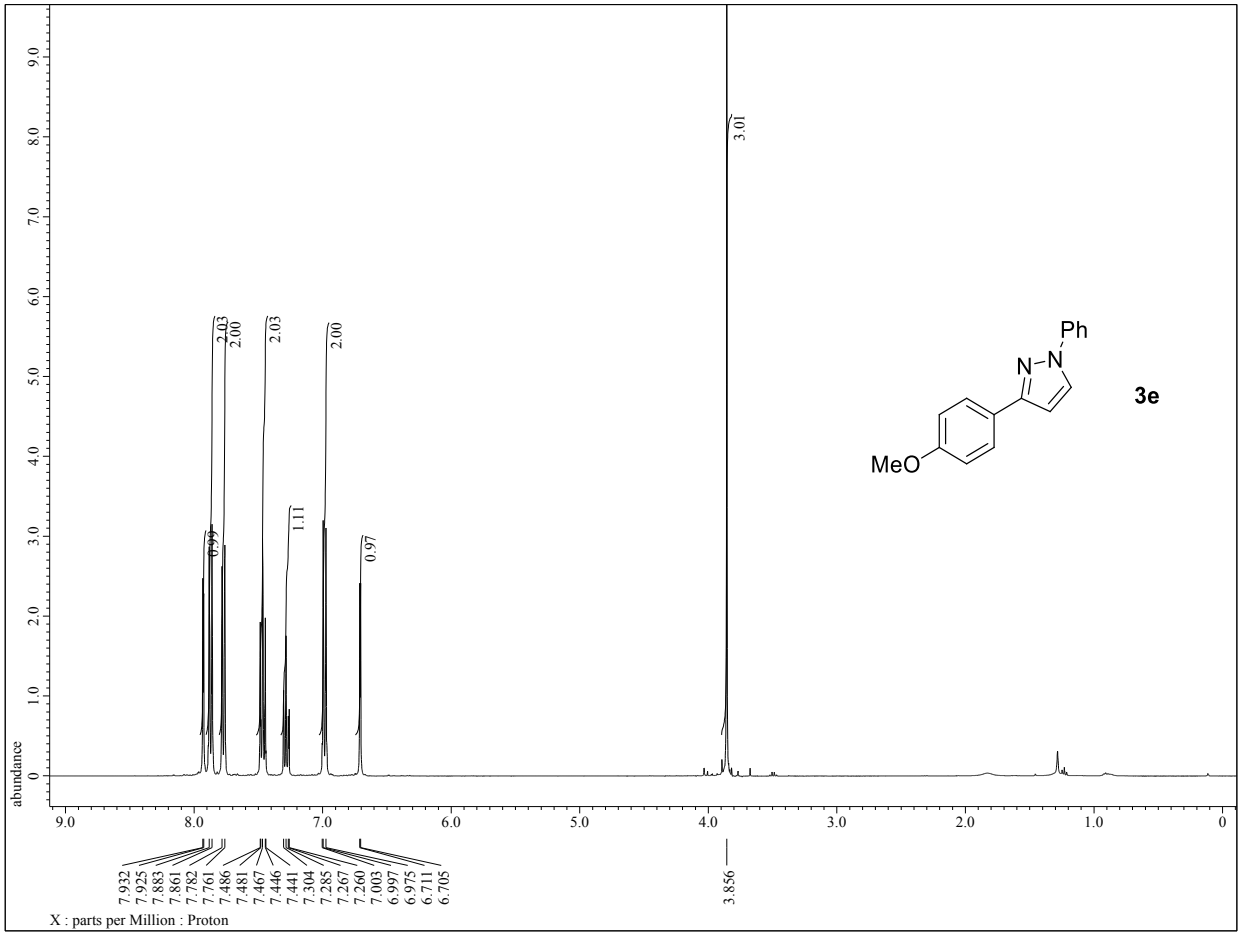

abundance
153.118
138.654
132.792
131.608
129.413
128.649
128.152
127.828
125.785
119.980
105.345
77.315
77.000
76.685
X : parts per Million : Carbon13

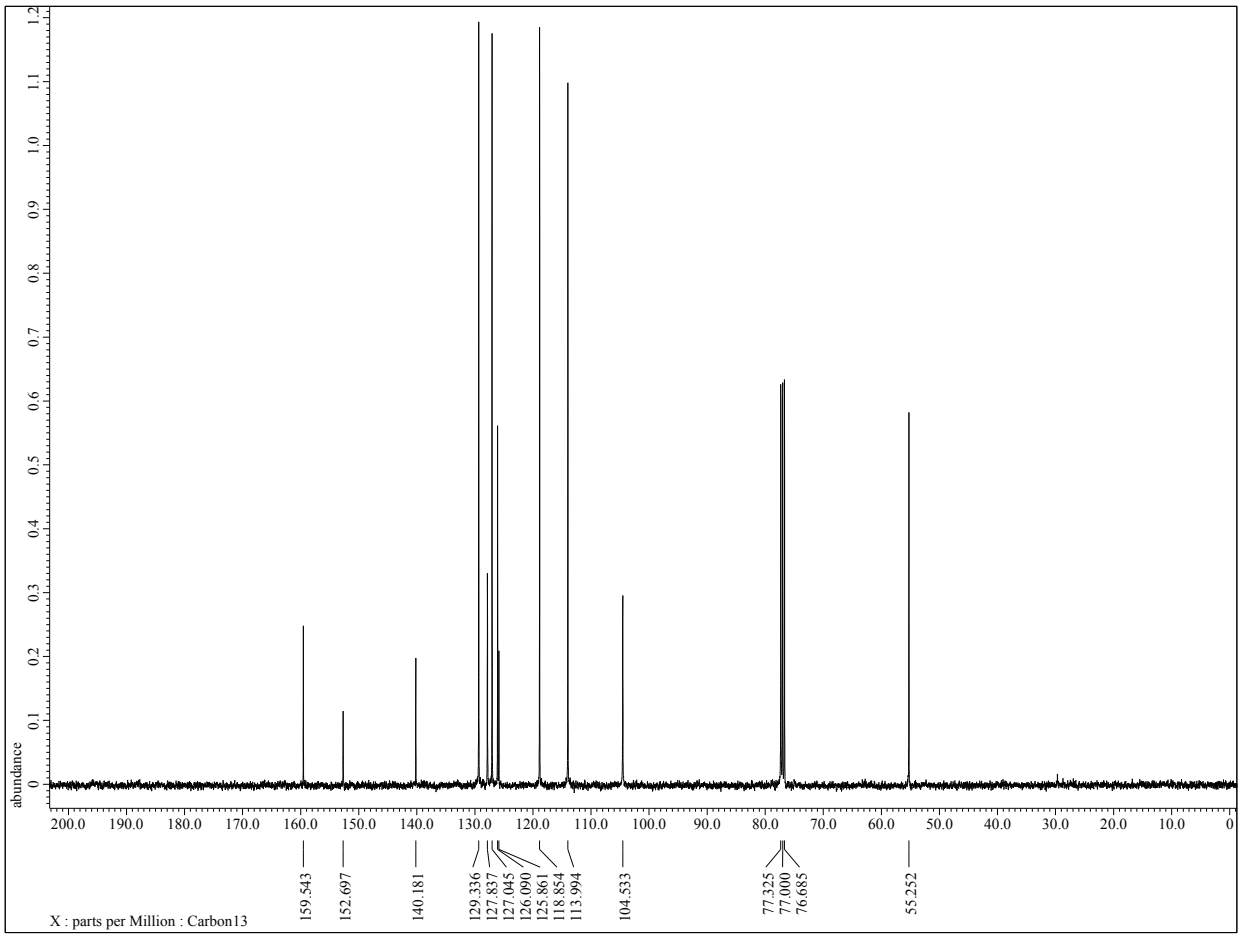

OMe
N-N
Ph
3c
abundance
X : parts per Million : Proton

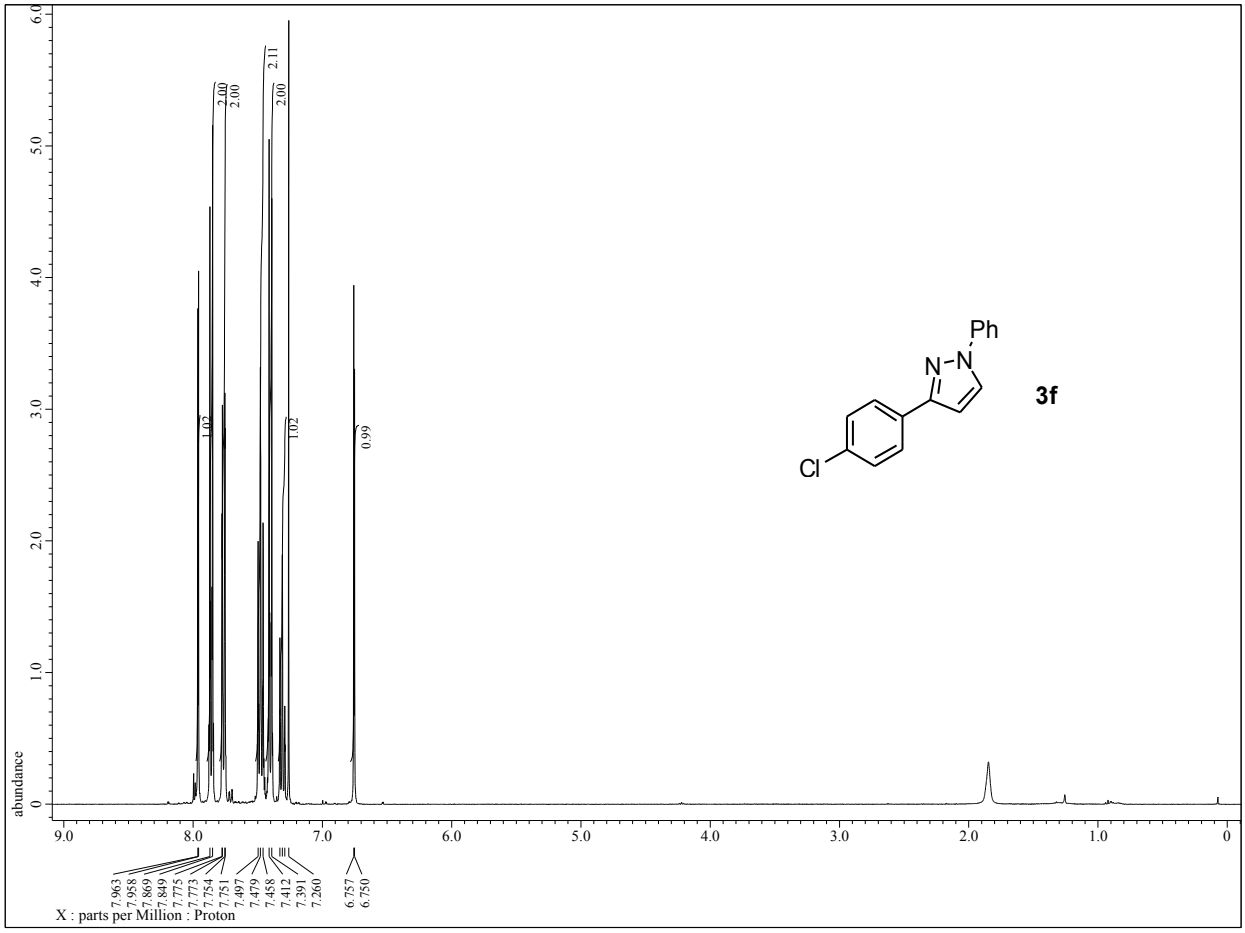

abundance
X : parts per Million : Carbon13

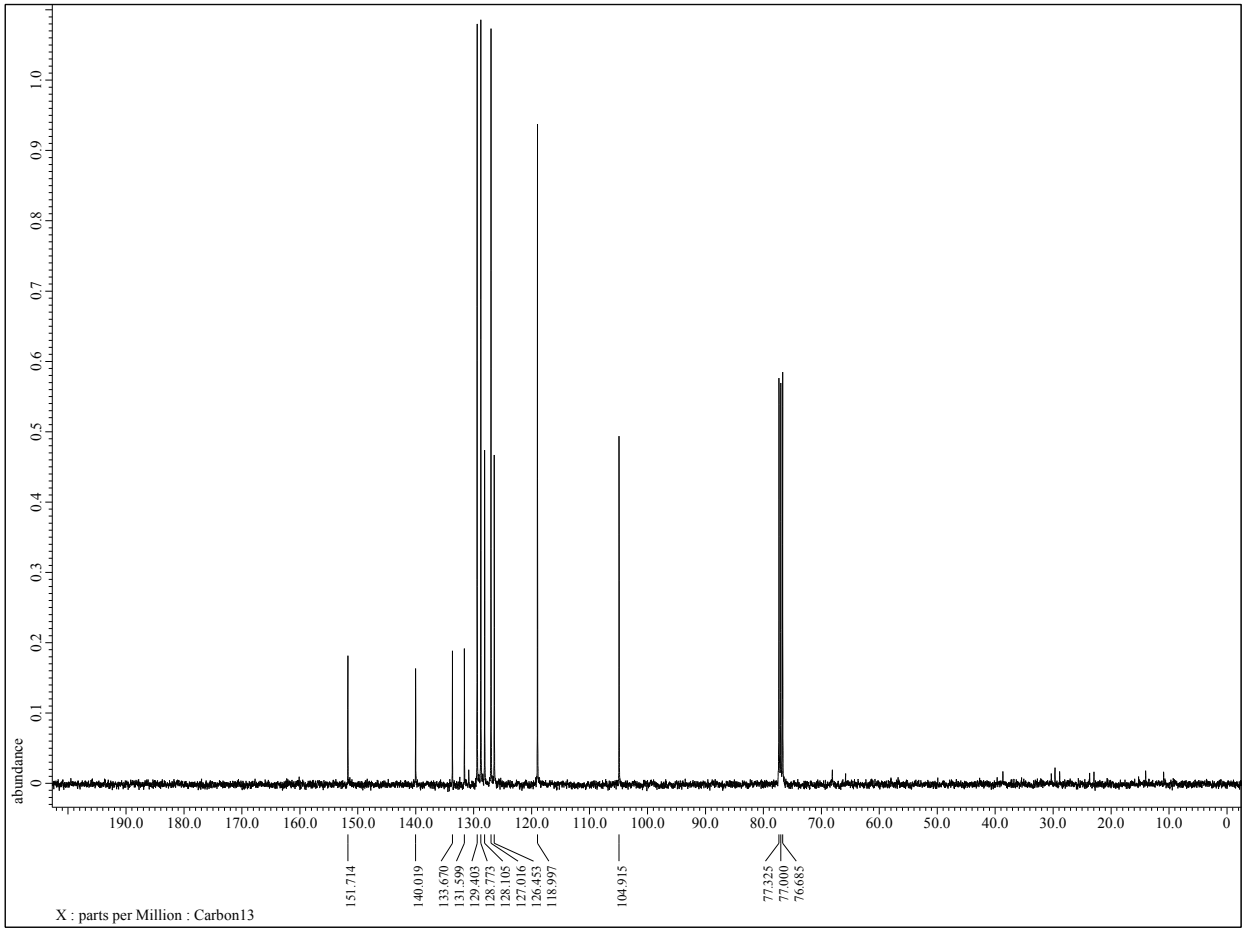

Ph
N
N
MeO
3d
4.06
3.01
2.01
0.98
1.00
1.00
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.954
7.948
7.796
7.777
7.533
7.501
7.496
7.476
7.474
7.456
7.363
7.301
7.260
6.934
6.927
6.913
6.906
6.777
6.771
3.901
X : parts per Million : Proton

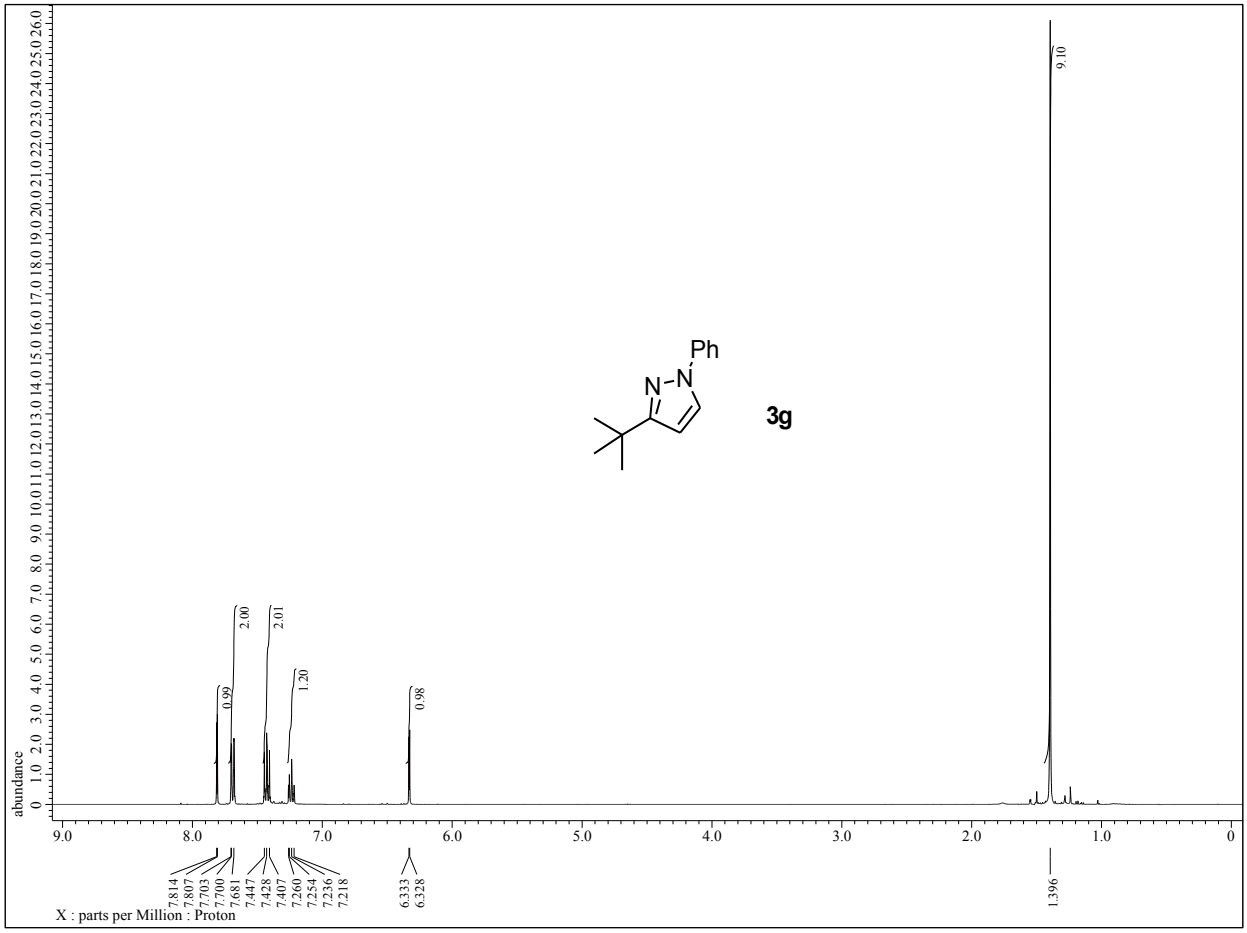

abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.877
152.707
140.124
134.434
129.623
129.355
127.933
126.300
118.987
118.386
113.918
110.901
105.144
77.315
77.000
76.685
55.281
X : parts per Million : Carbon13

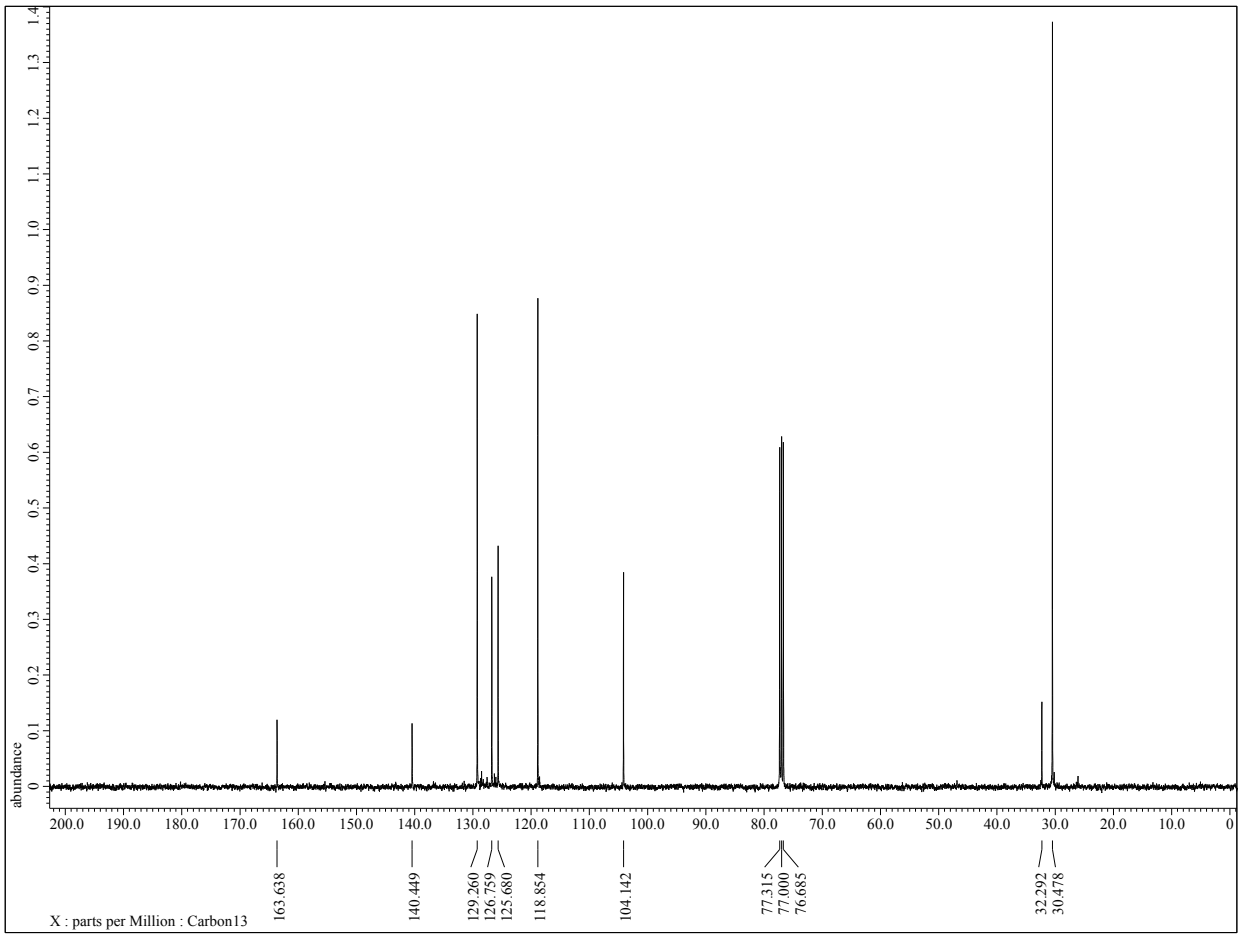

Ph
N–N
MeO
3e
abundance
X : parts per Million : Proton
7.932
7.925
7.883
7.861
7.782
7.761
7.486
7.481
7.467
7.446
7.441
7.304
7.285
7.267
7.260
7.003
6.997
6.975
6.711
6.705
3.856
3.01
2.03
2.00
2.03
2.00
1.11
0.99
0.97

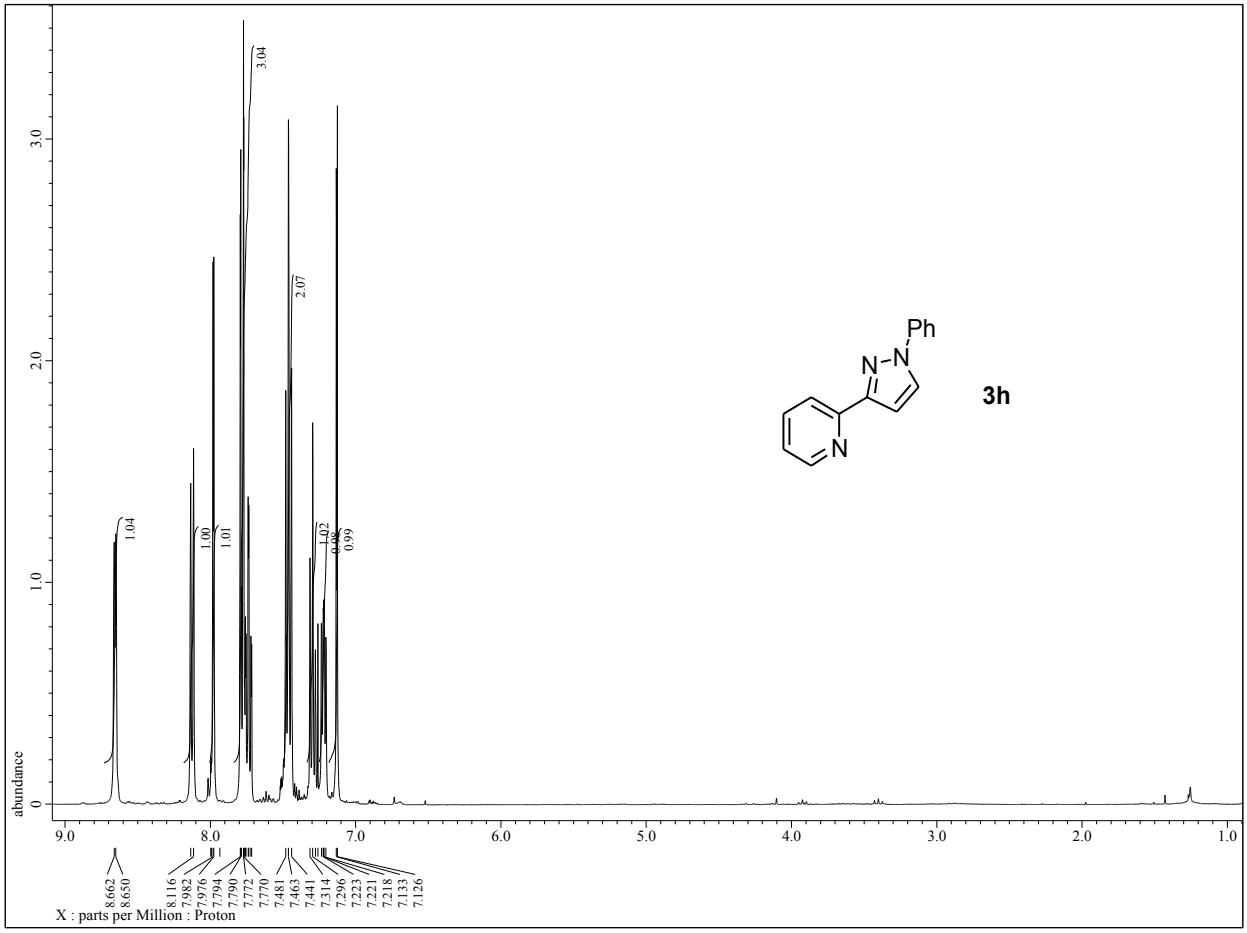

abundance
X : parts per Million : Carbon13
159.543
152.697
140.181
129.336
127.837
127.045
126.090
125.861
118.854
113.994
104.533
77.325
77.000
76.685
55.252

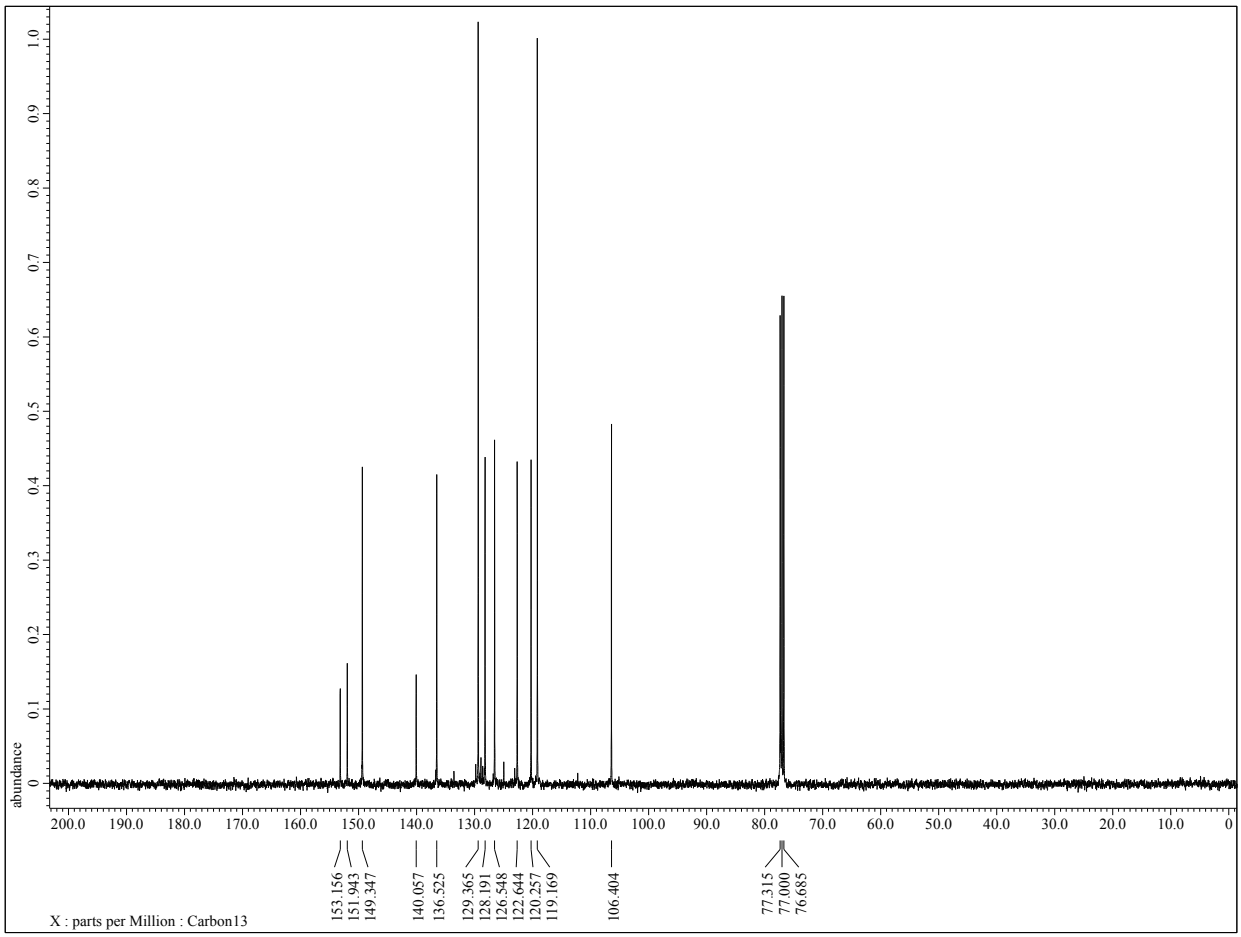

Ph
N
N
Cl
3f
abundance
X : parts per Million : Proton
7.963
7.958
7.869
7.849
7.775
7.773
7.754
7.751
7.497
7.479
7.458
7.412
7.391
7.260
6.757
6.750

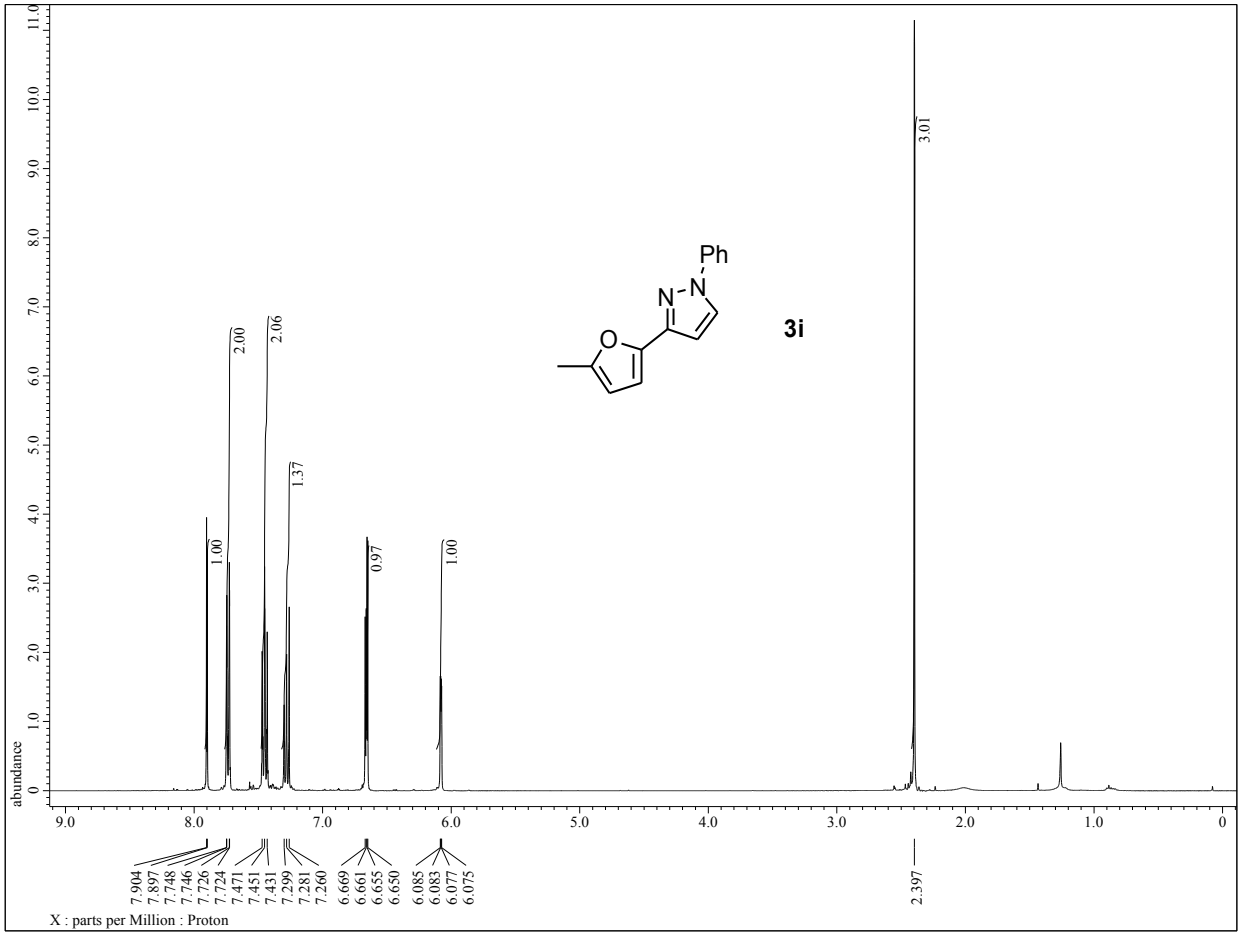

abundance
X : parts per Million : Carbon13
151.714
140.019
133.670
131.599
129.403
128.773
128.105
127.016
126.453
118.997
104.915
77.325
77.000
76.685

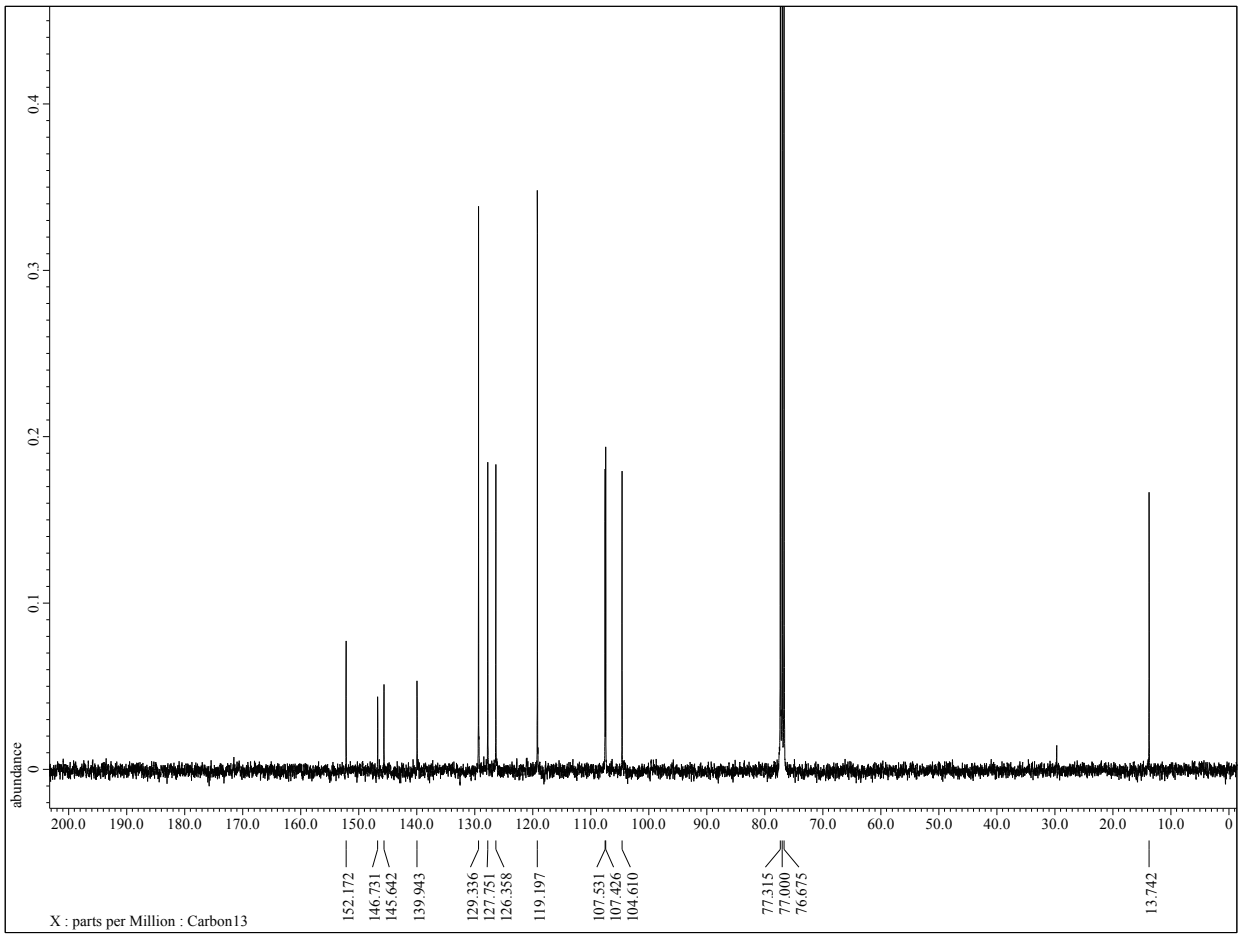

Ph
N
N
3g
abundance
9.10
2.00
2.01
1.20
0.99
0.98
7.814
7.807
7.703
7.700
7.681
7.447
7.428
7.407
7.260
7.254
7.236
7.218
6.333
6.328
1.396
X : parts per Million : Proton

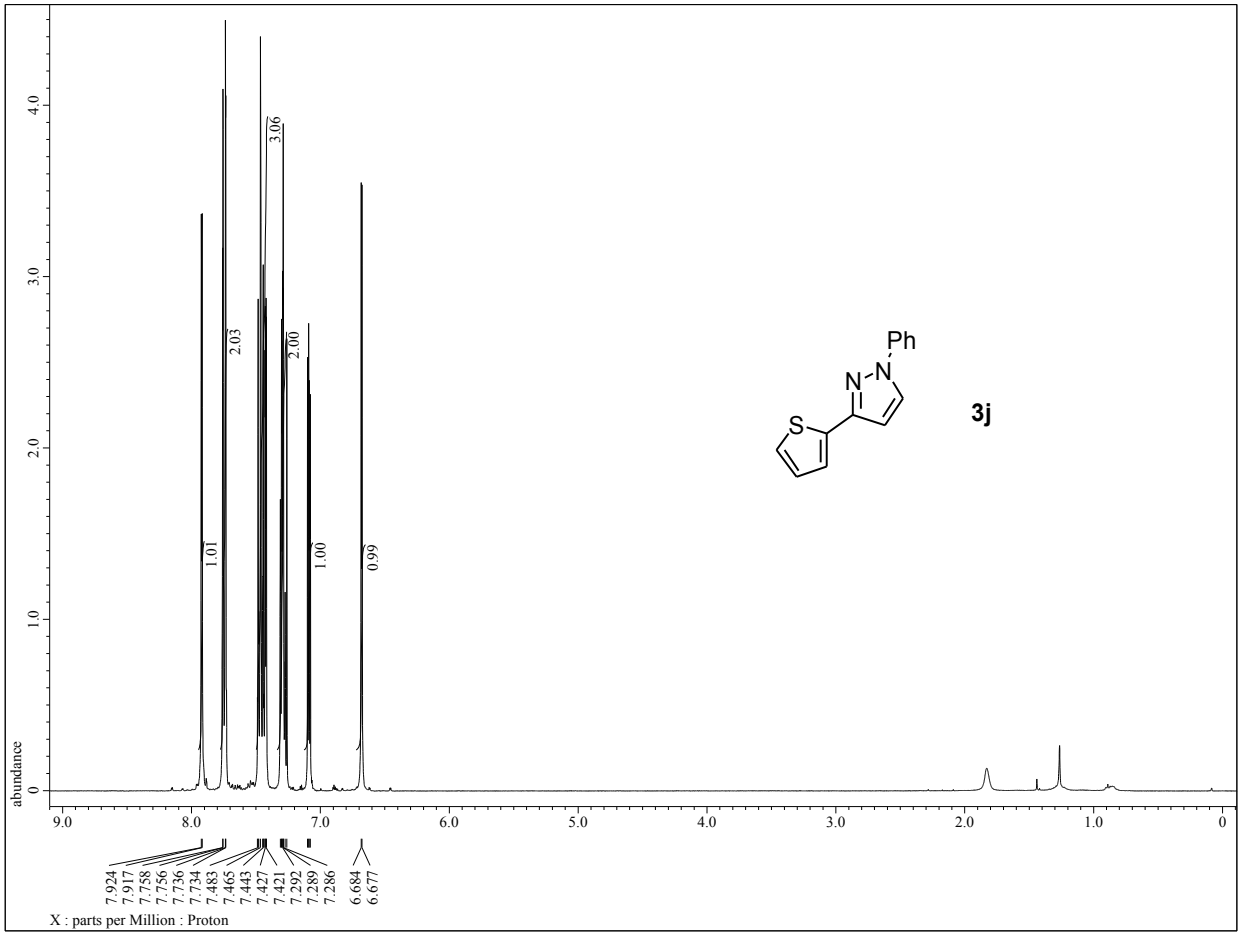

abundance
163.638
140.449
129.260
126.759
125.680
118.854
104.142
77.315
77.000
76.685
32.292
30.478
X : parts per Million : Carbon13

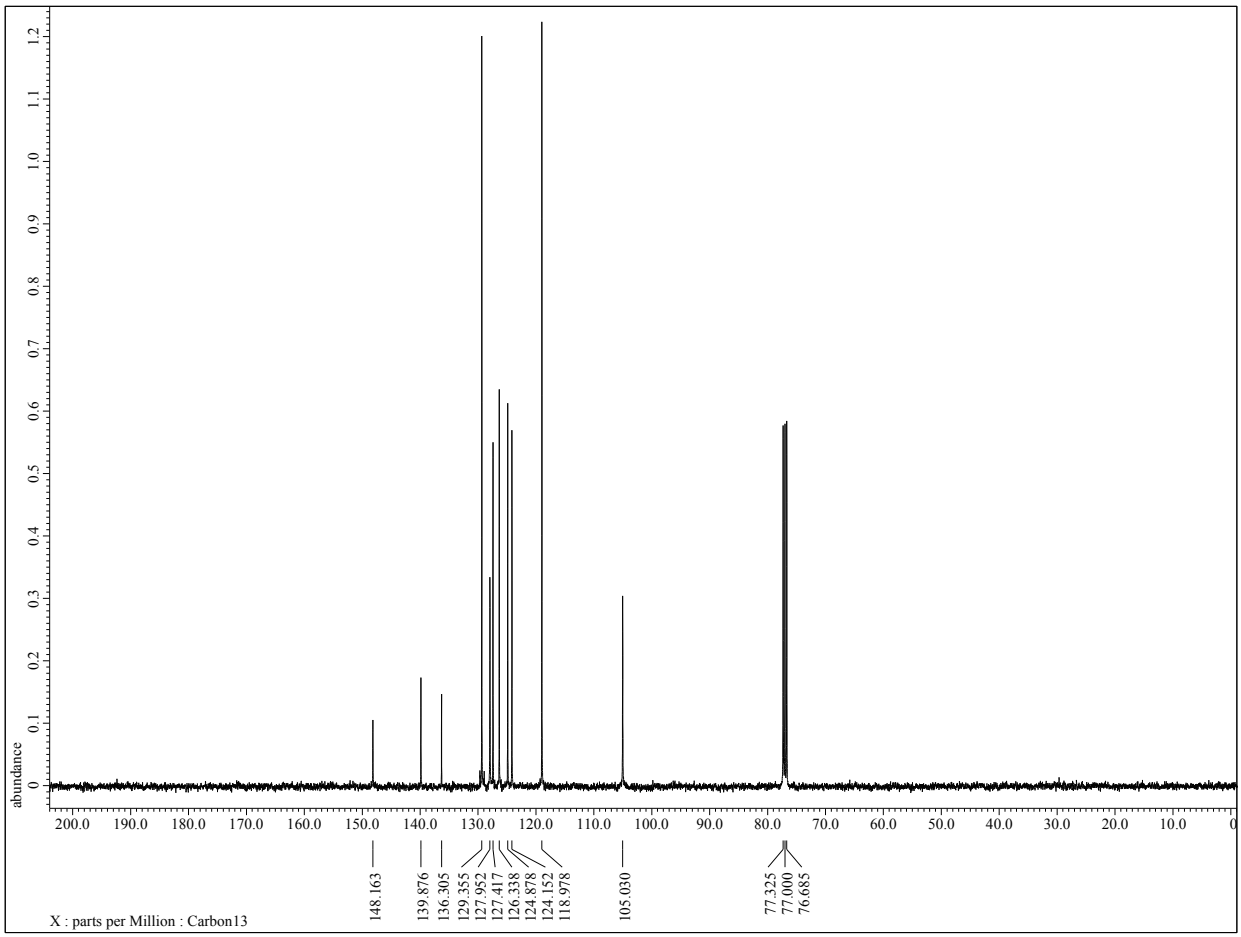

Ph
N
N
N
3h
abundance
X : parts per Million : Proton
8.662
8.650
8.116
7.982
7.976
7.794
7.790
7.772
7.770
7.481
7.463
7.441
7.314
7.296
7.223
7.221
7.218
7.133
7.126

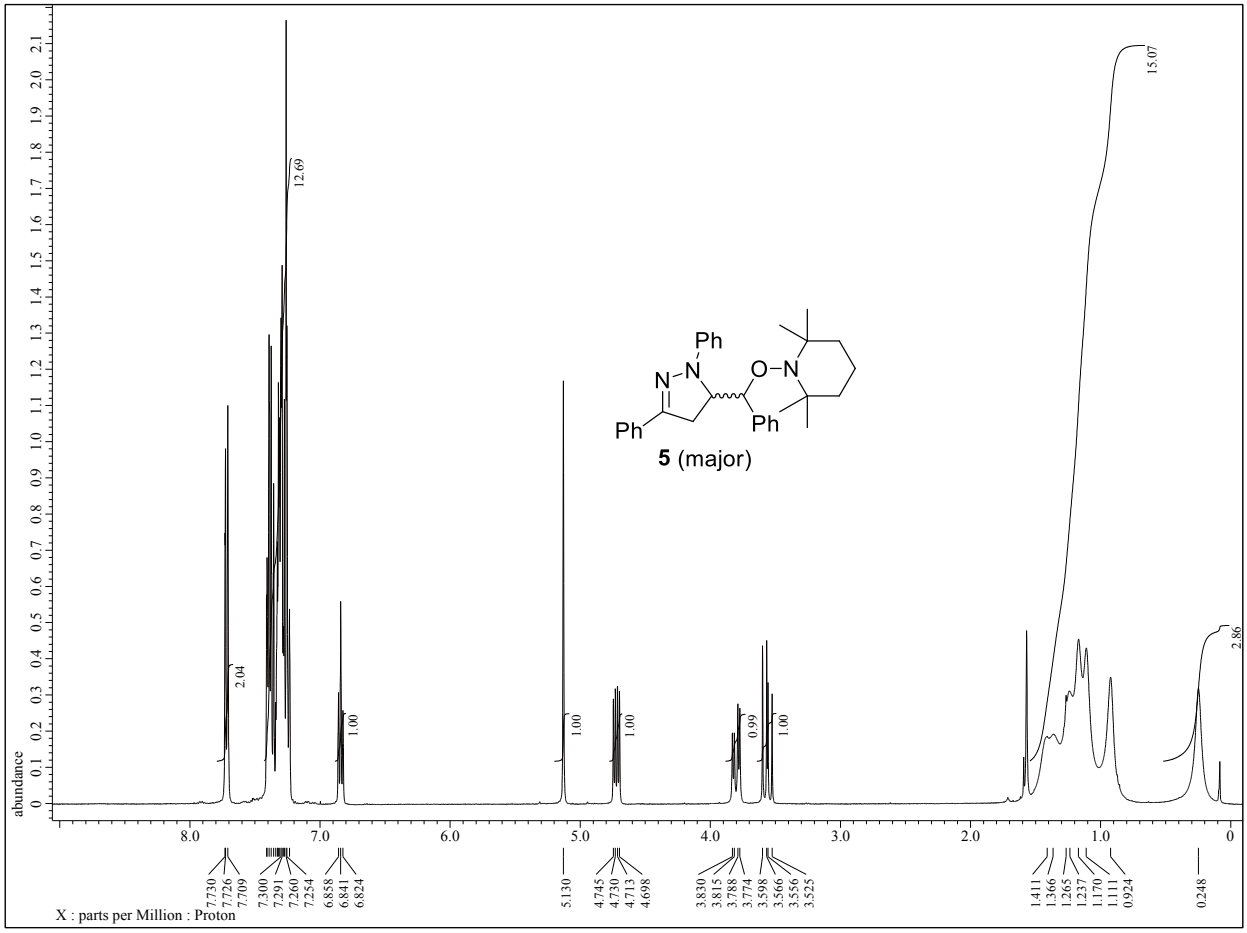

abundance
X : parts per Million : Carbon13
153.156
151.943
149.347
140.057
136.525
129.365
128.191
126.548
122.644
120.257
119.169
106.404
77.315
77.000
76.685

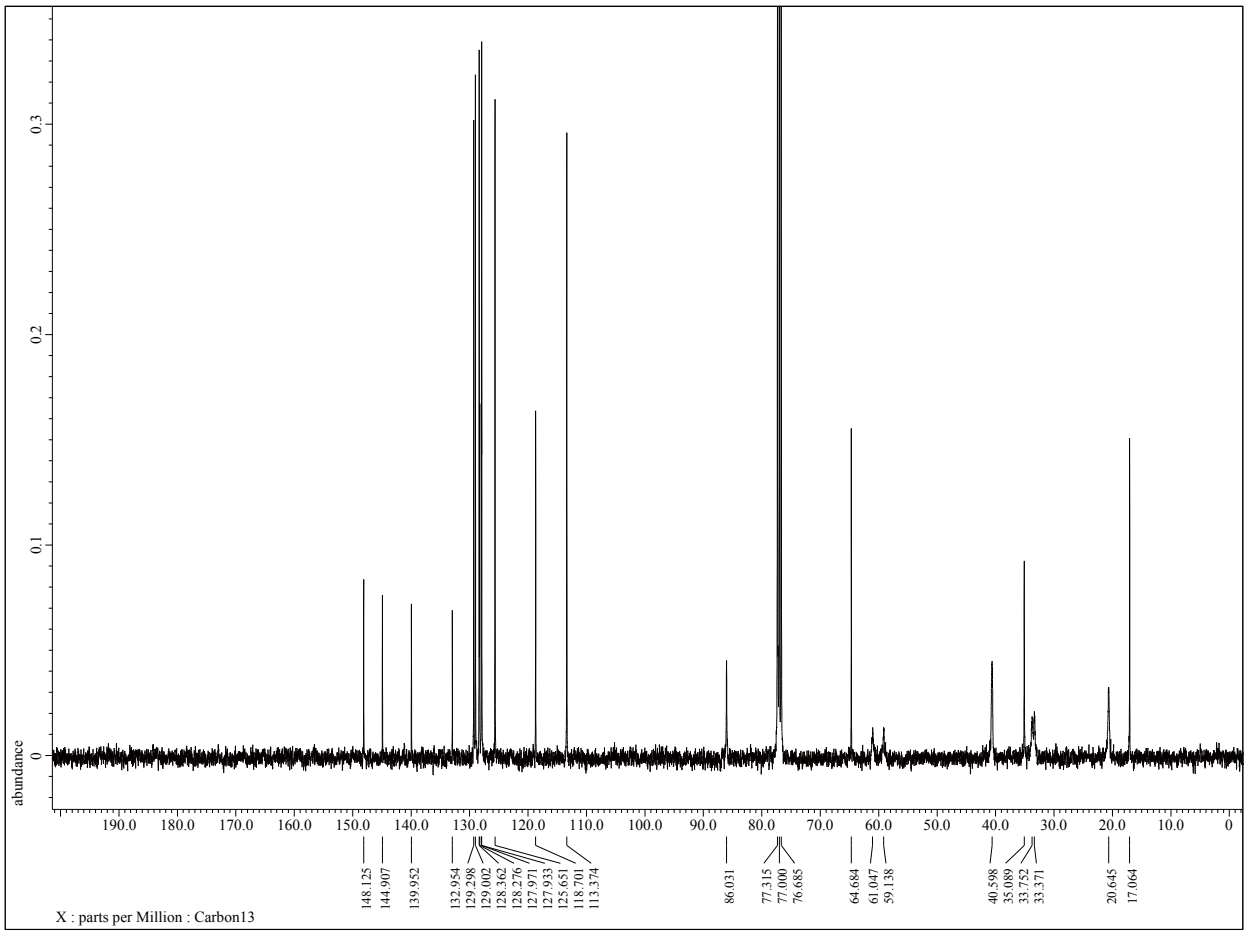

Ph
N
N
O
3i
abundance
X : parts per Million : Proton
7.904
7.897
7.748
7.746
7.726
7.724
7.471
7.451
7.431
7.299
7.281
7.260
6.669
6.661
6.655
6.650
6.085
6.083
6.077
6.075
2.397
1.00
2.00
2.06
1.37
0.97
1.00
3.01

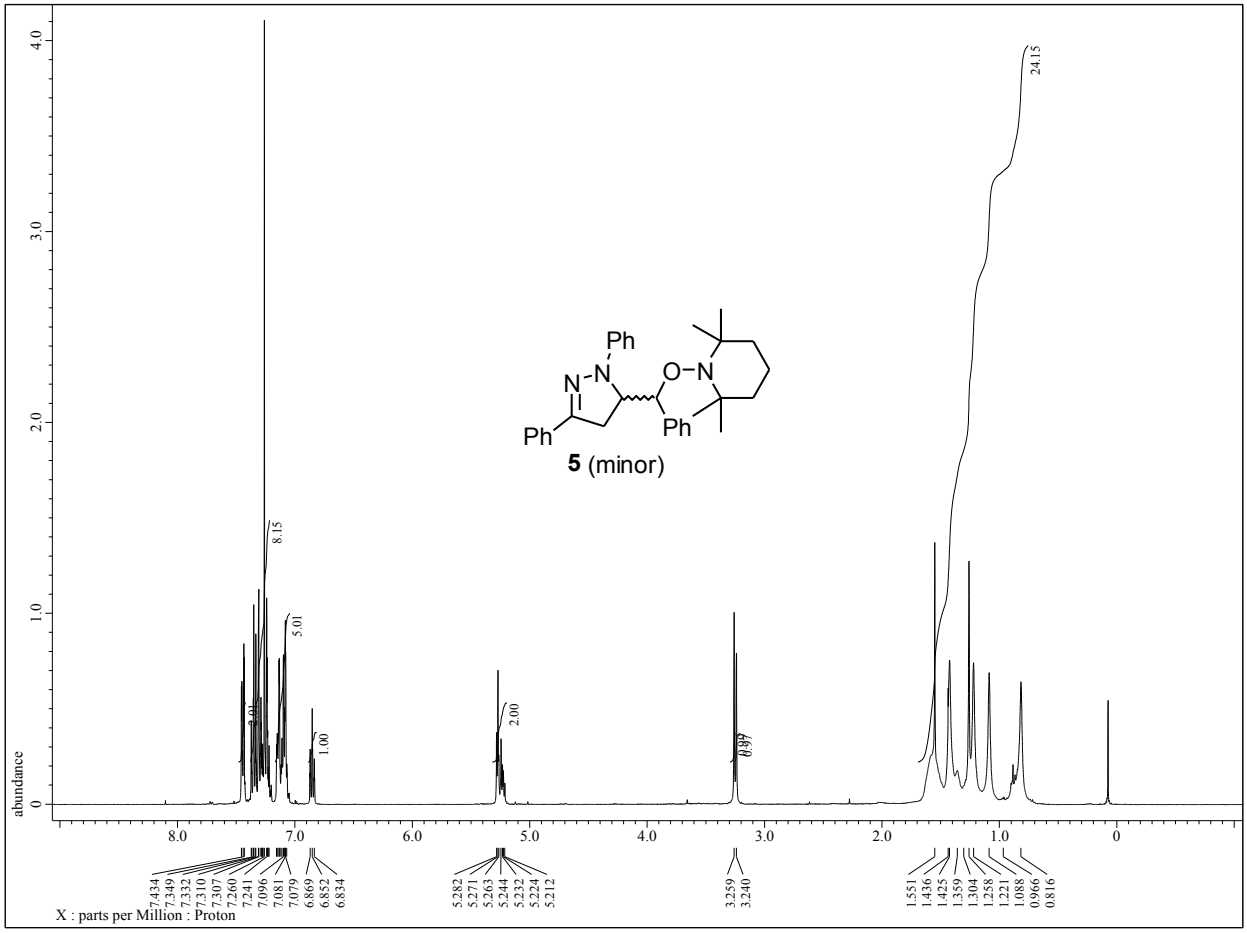

abundance
X : parts per Million : Carbon13
152.172
146.731
145.642
139.943
129.336
127.751
126.358
119.197
107.531
107.426
104.610
77.315
77.000
76.675
13.742

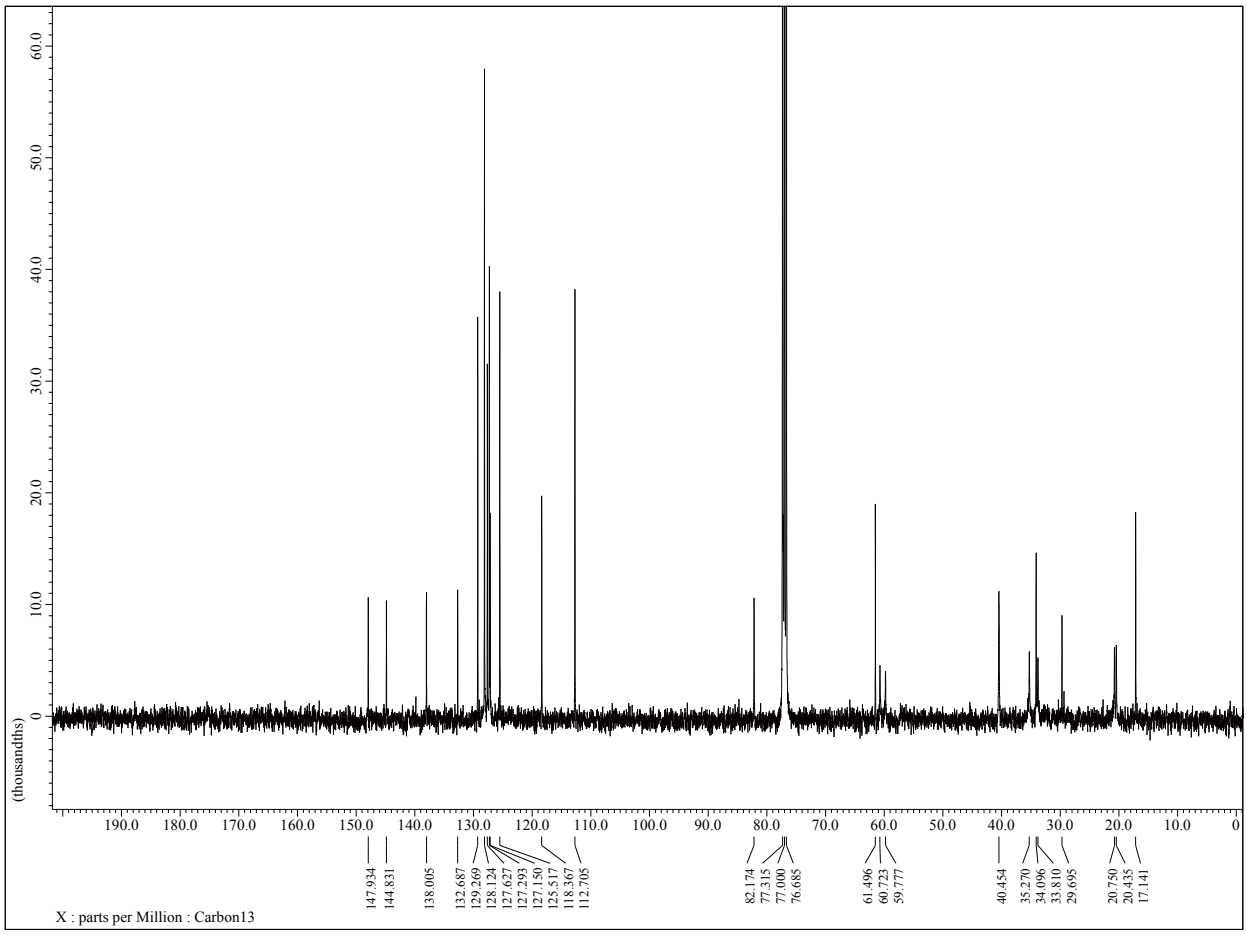

Ph
N
N
S
3j
abundance
1.01
2.03
3.06
2.00
1.00
0.99
7.924
7.917
7.758
7.756
7.736
7.734
7.483
7.465
7.443
7.427
7.421
7.292
7.289
7.286
6.684
6.677
X : parts per Million : Proton

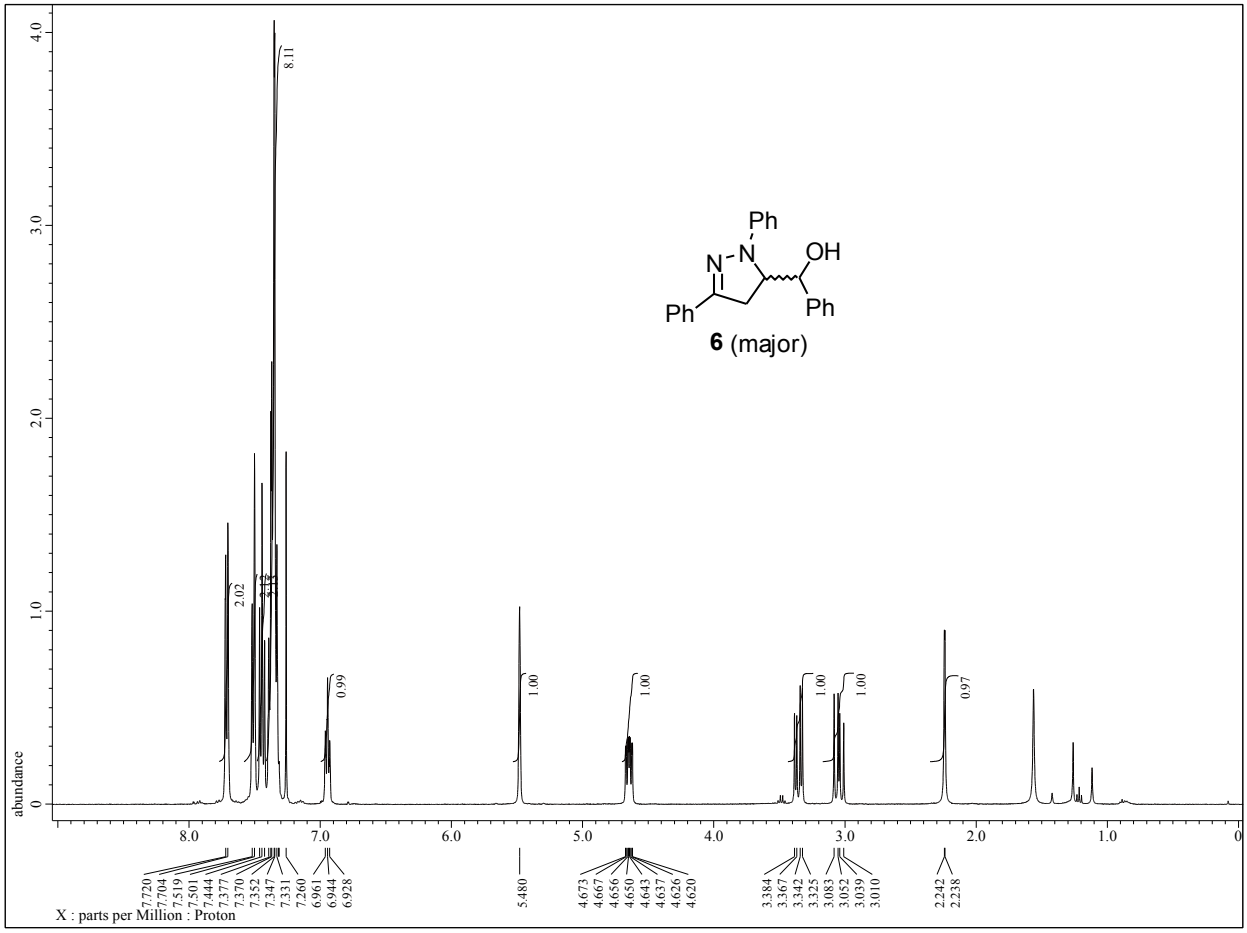

abundance
148.163
139.876
136.305
129.355
127.952
127.417
126.338
124.878
124.152
118.978
105.030
77.325
77.000
76.685
X : parts per Million : Carbon13

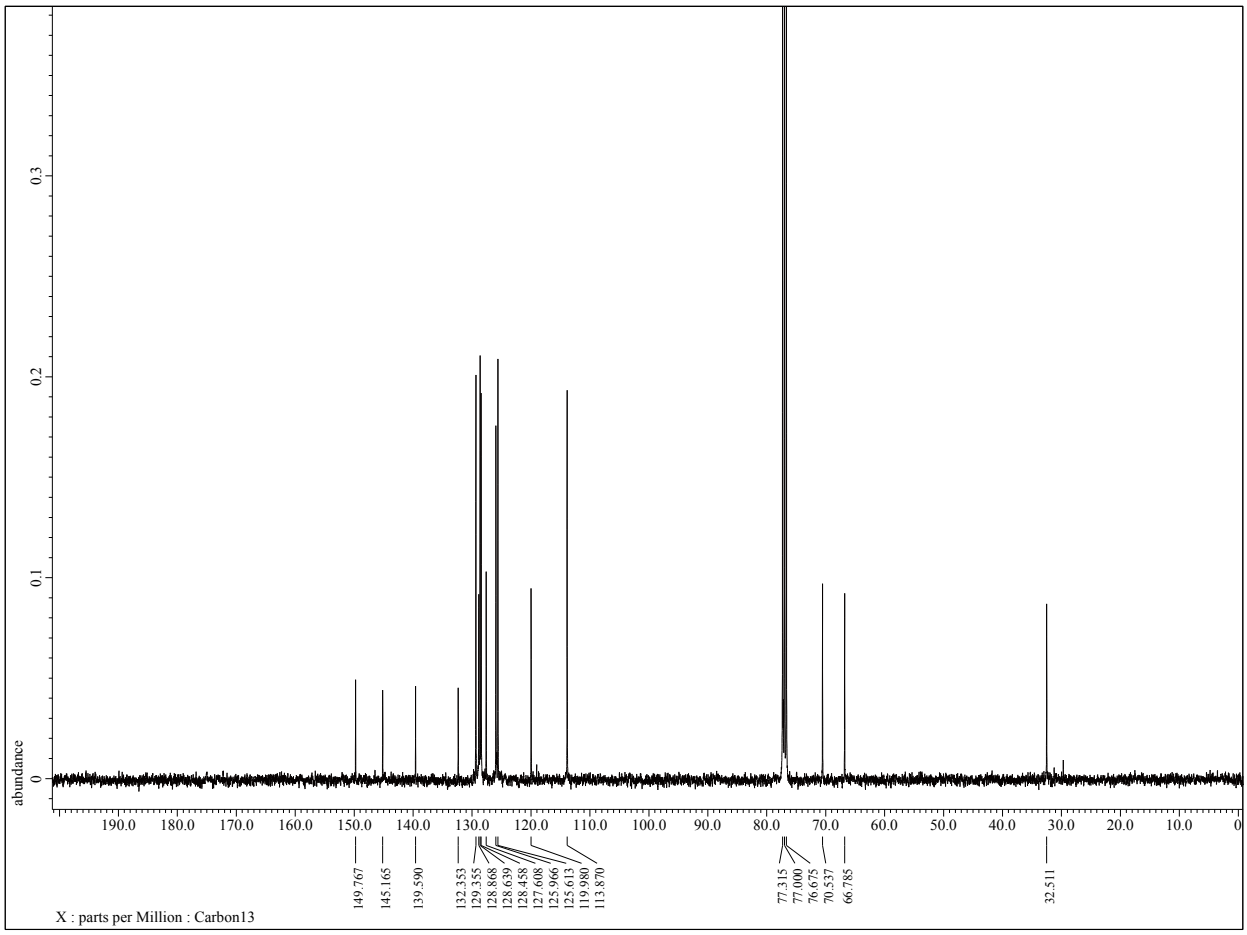

Ph
N
N
O
N
Ph
Ph
5 (major)
abundance
X : parts per Million : Proton
12.69
15.07
2.86
2.04
1.00
1.00
1.00
0.99
1.00
7.730
7.726
7.709
7.300
7.291
7.260
7.254
6.858
6.841
6.824
5.130
4.745
4.730
4.713
4.698
3.830
3.815
3.788
3.774
3.598
3.566
3.556
3.525
1.411
1.366
1.265
1.237
1.170
1.111
0.924
0.248


abundance
X : parts per Million : Carbon13
148.125
144.907
139.952
132.954
129.298
129.002
128.362
128.276
127.971
127.933
125.651
118.701
113.374
86.031
77.315
77.000
76.685
64.684
61.047
59.138
40.598
35.089
33.752
33.371
20.645
17.064


Ph
N-N
O-N
Ph
Ph
5 (minor)
abundance
X : parts per Million : Proton


(thousandths)
X : parts per Million : Carbon13


Ph
N
N
OH
Ph
Ph
6 (major)
abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13