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TfOH mediated intermolecular electrocyclization for the synthesis of pyrazolines and application in alkaloid synthesis

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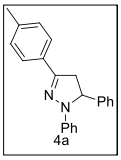
General Procedure for the synthesis of pyrazoline

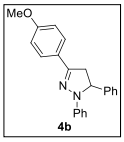
Into the reaction mixture of phenylhydrazine (1.0 mmol) and acetonitrile (10 V) were added aldehyde (1.0 mmol). The reaction mixture then was stirred for 10 min. at 30 ^{o}C followed by TfOH (1.0 mmol) and styrene (1.0 mmol) were added. The mixture was stirred at the same temperature till completion of the reaction which was monitored by TLC. After completion of the reaction, the crude was quenched by sat. solution of sodiumbicarbonate and extracted with ethylacetate. The organic layer was separated and dried with anhydrous sodium sulphate and then concentrated under reduced pressure to get crude compound. The pyrazoline was purified by 60-120 silica get column chromatography using hexane/ethylacetate as eluents.

1,5-diphenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole (4a)



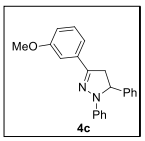
M.P = 159-161 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 7.66-7.64 (2H, m), 7.37-7.36 (4H, m), 7.31-7.28 (1H, m), 7.24-7.19 (4H, m), 7.11-7.09 (2H, m), 6.83-6.79 (1H, m), 5.28 (1H, dd, J = 7.3 Hz & 12.4 Hz), 3.85 (1H, dd, J = 12.4 Hz & J = 17.1 Hz), 3.16 (1H, dd, J = 7.3 Hz & 17.1 Hz), 2.41 (3H, s). The spectral data showed good agreement with the literature data.[1]

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



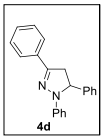
M.P = 148 -150 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 7.71-7.67 (2H, m), 7.36-7.35 (4H, m), 7.30-7.29 (1H, m), 7.22-7.17 (2H, m), 7.09-7.06 (2H, m), 6.96-6.92 (2H, m), 6.78 (1H, tt, J = 1.08 Hz & 7.3Hz), 5.25 (1H, dd, J = 7.3 Hz & 12.4 Hz), 3.88-3.81 (4H, m), 3.14 (1H, dd, J = 7.4 Hz & J = 17.0 Hz).
The spectral data showed good agreement with the literature data.[2]

3-(3-methoxyphenyl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (4c)



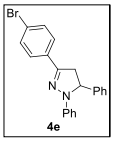
M.P = 108-110 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.33-7.22 (8H, m), 7.20-7.15 (2H, m), 7.08-7.06 (2H, m), 6.90-6.86 (1H, m), 6.78 (1H, t, J = 7.2 Hz), 5.27 (1H, dd, J = 7.2 Hz & 12.4 Hz), 3.88 – 3.76 (4H, m), 3.13 (1H, dd, J = 7.2 Hz & J = 17.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 159.8, 146.6, 144.8, 142.6, 134.1, 129.6, 129.2, 128.9, 127.6, 125.9, 119.2, 118.5, 114.8, 113.4, 110.6, 64.6, 55.4, 43.7.

1,3,5-triphenyl-4,5-dihydro-1H-pyrazole (4d)



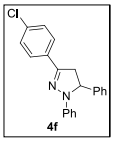
M.P = 138 – 140 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.74-7.71 (2H, m), 7.41-7.22 (8H, m), 7.20-7.15 (2H, m), 7.08-7.06 (2H, m), 6.78 (1H, t, J = 7.2 Hz), 5.27 (1H, dd, J = 7.3 Hz & 12.4 Hz), 3.83 (1H, dd, J = 12.4 Hz & 17.1 Hz), 3.14 (1H, dd, J = 7.3 Hz & J = 17.1 Hz).
The spectral data showed good agreement with the literature data.[1]

3-(4-bromophenyl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (4e)



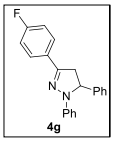
M.P = ^{o}C, ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.61-7.59 (2H, m), 7.53-7.52 (2H, m), 7.38-7.28 (5H, m), 7.23-7.20 (2H, m), 7.11-7.09 (2H, m), 6.85-6.82 (1H, m), 5.31 (1H, dd, J = 5.4 Hz & 10.6 Hz), 3.83 (1H, dd, J = 16.8 Hz & 12.5 Hz), 3.12 (1H, dd, J = 7.3 Hz & J = 17.0 Hz).The spectral data showed good agreement with the literature data.[2]

3-(4-chlorophenyl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (4f)



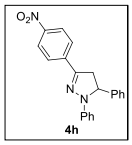
MP – 156-158 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.65 -7.61 (2H, m), 7.36 - 7.25 (7H, m), 7.20-7.15 (2H, m), 7.07-7.04 (2H, m), 6.79 (1H, t, J = 7.2 Hz), 5.28 (1H, dd, J = 7.3 Hz & 12.4 Hz), 3.80 (1H, dd, J = 12.4 Hz & J = 17.1 Hz), 3.10 (1H, dd, J = 7.3 Hz & 17.1 Hz). The spectral data showed good agreement with the literature data.[2]

3-(4-fluorophenyl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (4g)



M.P = 138-140 ^{o}C, ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.74-7.71 (2H, m), 7.37-7.34 (4H, m), 7.32-7.28 (1H, m), 7.23-7.19 (2H, m), 7.12-7.08 (4H, m), 6.83-6.80 (1H, m), 5.30 (1H, dd, J = 4 Hz & 12.4 Hz), 3.84 (1H, dd, J = 12.4 Hz & 17 Hz), 3.15 (1H, dd, J = 7.3 Hz & J = 17.0 Hz). The spectral data showed good agreement with the literature data.[1]

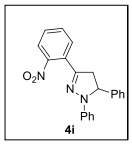
3-(4-nitrophenyl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (4h)



MP – 188-190 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.25 -8.22 (2H, m), 7.83-7.80 (2H, m), 7.38-7.28 (5H, m), 7.23-7.18 (2H, m), 7.12-7.09 (2H, m), 6.85 (1H, t, J = 7.2 Hz); 5.42 (1H, dd, J = 7.0 Hz & 12.3 Hz), 3.87 (1H, dd, J = 12.7 & J = 17.1 Hz), 3.16 (1H, dd, J = 7.0 Hz & 17.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 42.8, 64.9, 113.8, 120.3, 124.0, 125.7, 125.8, 127.9, 129.1, 129.3, 139.0, 141.7, 143.6, 143.9, 147.0.

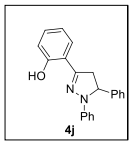
The spectral data showed good agreement with the literature data.[4]

3-(2-nitrophenyl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (4i)



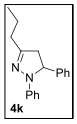
MP – 148-150 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.69-7.66 (1H, m), 7.61-7.52 (2H, m), 7.45-7.39 (1H, m), 7.37-7.24 (5H, m), 7.19-7.14 (2H, m), 7.01-6.90 (2H, m), 6.81 (1H, t, J = 7.3 Hz); 5.32 (1H, dd, J = 7.3 Hz & 12.4 Hz), 3.78 (1H, dd, J = 12.4 & J = 17.0 Hz), 3.05 (1H, dd, J = 7.3 Hz & 17.0 Hz)

2-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)phenol (4j)



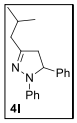
M.P = 178 -180 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 10.83 (1H, S), 7.39-7.35 (4H, m), 7.34-7.28 (2H, m), 7.28-7.21 (2H, m), 7.16-7.08 (2H, m), 7.00-6.98 (2H, m), 6.93-6.85 (2H, m), 5.28-5.23 (1H, dd, J = 12.3 Hz & 7.5 Hz), 4.02-3.94 (1H, dd, J = 12.3 Hz & 17.2 Hz), 3.31-3.25 (1H, dd, 17.2 Hz & 7.56 Hz)
The spectral data showed good agreement with the literature data.[1]

1,5-diphenyl-3-propyl-4,5-dihydro-1H-pyrazole (4k)



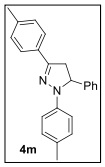
Viscous Liquid, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.36 -7.25 (5H, m), 7.18 - 7.11 (2H, m), 6.94-6.91 (2H, m), 6.73 (1H, t, J = 7.3 Hz), 4.99 (1H, dd, J = 8.0 Hz & 11.9 Hz), 3.40 (1H, dd, J = 11.9 Hz & J = 17.4 Hz), 2.70 (1H, dd, J = 8.0 Hz & 17.4 Hz), 2.37 (2H, t, J = 7.4 Hz), 1.68-1.56 (2H, m), 0.98 (3H, t, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 152.1, 146.2, 143.2, 129.1, 128.9, 127.4, 125.9, 118.6, 113.2, 77.5, 77.1, 76.7, 64.5, 46.2, 32.2, 20.2, 13.9.

3-isobutyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole (4l)



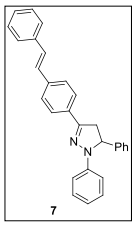
Viscous liquid, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.36 -7.27 (5H, m), 7.16 - 7.11 (2H, m), 6.94-6.91 (2H, m), 6.73 (1H, t, J = 7.3 Hz), 5.00 (1H, dd, J = 7.8 Hz & 11.9 Hz), 3.39 (1H, dd, J = 11.9 Hz & J = 17.5 Hz), 2.69 (1H, dd, J = 7.8 Hz & 17.5 Hz), 2.28 (2H, d, J = 7.3 Hz), 1.99-1.85 (1H, m), 0.98-0.95 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 151.4, 146.1, 143.2, 129.1, 128.9, 127.4, 125.9, 118.6, 113.2, 64.5, 46.6, 39.2, 26.5, 22.7, 22.5.

5-phenyl-1,3-di-p-tolyl-4,5-dihydro-1H-pyrazole (4m)



MP –162-164 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.60 (2H, d, J = 8.1 Hz), 7.33-7.32 (4H, m), 7.29-7.25 (1H, m), 7.18 (2H, d, J = 8.1 Hz), 6.96-6.97 (4H, m), 5.20 (1H, dd, J = 7.7 Hz & 12.3 Hz), 3.80 (1H, dd, J = 12.3 & J = 17.0 Hz), 3.10 (1H, dd, J = 7.7 Hz & 17.0 Hz), 2.37 (3H, s), 2.22 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 143.1, 142.9, 138.5, 130.1, 129.4, 129.3, 129.1, 128.2, 127.5, 126.0, 125.7, 113.5, 64.9, 43.7, 21.4, 20.5.

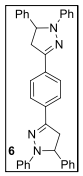
Alkaloid 7



^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.46 -7.43 (2H, m), 7.36 - 7.32 (5H, m), 7.30-7.26 (3H, m), 7.20-7.13 (3H, m), 7.02-6.99 (2H, m), 6.81-6.76 (1H, m), 6.54 (1H, d, J = 16.3 Hz), 5.26 (1H, dd, J = 6.8 Hz & 12.4Hz), 3.72 (1H, dd, J = 12.3 Hz & J = 16.8 Hz), 3.02 (1H, dd, J = 6.8 Hz & 16.8 Hz)

The spectral data showed good agreement with the literature data.[3,4]

1,4-bis(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)benzene (6)



MP – 198-200 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.71 (4H, s), 7.37-7.31 (10H, m), 7.21-7.16 (4H, m), 7.09-7.07 (4H, m), 6.79 (1H, t, J = 7.2 Hz); 5.29 (1H, dd, J = 7.2 Hz & 12.4 Hz), 3.86 (1H, dd, J = 12.4 & J = 17.1 Hz), 3.15 (1H, dd, J = 7.2 Hz & 17.1 Hz). HRMS [M+H] calculated 519.2549. Found 519.2526

Due to poor solubility either in DMSO-d_6 as well as in $CDCl_3$, we were unable to take ^{13}C NMR spectra.

Table 1. Complete optimization for the pyrazoline under metal free conditions

S. No	Reagent	Solvent	Temp. (^{o}C)/Time	Yield (%)
1	I_2 (20 mol%)	CH_3CN	25-30 / 24	25
2	I_2 (1.0 equiv.)	CH_3CN	25-30 / 24	34
3	I_2 (1.0 equiv.)	Toluene	25-30 / 24	47
4	**I_2 (1.0 equiv.)**	**H_2O**	**25-30 / 24**	**35**
5	I_2 (1.0 equiv.)	Ethylacetate	25-30 / 24	Trace
6	$PhI(OAc)_2$ (20 mol%)	CH_3CN	25-30 / 24	ND
7	**TfOH (1.0 equiv.)**	**CH_3CN**	**25-30 / 7**	**82**
8	NaI (1.0 equiv.)	CH_3CN	25-30 / 24	ND
9	NBS (1.0 equiv.)	CH_3CN	25-30 / 24	ND
10	CAN (1.0 equiv.)	CH_3CN	25-30 / 24	ND
11	L-Proline(30 mol%)	CH_3CN	25-30 / 24	ND
12	$CH(OMe)_3$ (1.0 equiv.)	CH_3CN	25-30 / 24	ND
13	TfOH (1.0 equiv.)	H_2O	25-30 / 24	trace
14	TfOH (1.0 equiv.)	DCM	25-30 / 24	trace
15	TfOH (1.0 equiv.)	DMF	25-30 / 24	trace
16	TfOH (1.0 equiv.)	DMSO	25-30 / 24	trace
17	TfOH (1.0 equiv.)	Ethanol	25-30 / 24	ND
18	-	TFA	25-30 / 7	49
19	-	Acetic acid	25-30 / 24	ND

[a] Isolated Yield

Table 2. Complete optimization in DES medium

S.NO	SM 1	SM 2	Eutectic Mixture	Catalyst	Temperature	Yield%
1	$PhNHNH_2$. HCl	$PhCH_3CHO$	Ch.Chloride+ Urea	-	75 – 80 ^{0}C	Trace
2	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Glycerol	-	75 – 80 ^{0}C	Trace
3	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Urea	-	RT	Trace
4	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Urea	I_2(0.2 equiv)	RT	Trace
5	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Urea	NBS	50 ^{0}C	ND
6	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Urea	I_2(2 equiv)	50 ^{0}C	Trace
7	$PhNHNH_2$	$PhCH_3CHO$	Ethylene Glycol	TfOH	RT	Trace
8	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Ethylene Glycol	-	RT	Trace
9	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Ethylene Glycol	-	90 ^{0}C	Trace
10	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Ethylene Glycol	I_2(1 equiv)	RT	Trace
11	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Ethylene Glycol	TfOH(0.2 equiv)	RT	ND
12	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Ethylene Glycol	KOt(Bu) (1 equiv)	50 ^{0}C	Trace
13	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ pTsOH	-	RT	35%
14	$PhNHNH_2$	$PhCH_3CHO$	CH_3CN+ pTsOH	-	RT	62%
15	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ pTsOH(10 V)	-	RT	45%
16	$PhNHNH_2$	$PhCH_3CHO$	Ethanol	Ch.Chloride+ pTsOH(1 equiv)	RT	41%(1g of Silica 60-120 mesh added to the reaction)
17	$PhNHNH_2$	$PhCH_3CHO$	Ethanol	Ch.Chloride+ pTsOH(0.2 equiv)	RT ,70 ^{0}C	Trace
18	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Urea	pTsOH	RT ,70 ^{0}C	Trace
19	$PhNHNH_2$	$PhCH_3CHO$	Ethanol , Ch.Chloride+ pTsOH	-	RT	Trace
20	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ Urea, Ch.Chloride+ pTsOH	-	RT	ND
21	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ TfOH, CH_3CN(0.1 ml)	-	N_2 atm , RT ,70 ^{0}C	54%
22	$PhNHNH_2$	$PhCH_3CHO$	CH_3CN(1 ml)	Ch.Chloride+	N_2 atm ,	30%

				TfOH(1 equiv)	RT	
23	$PhNHNH_2$	$PhCH_3CHO$	Ethanol	TfOH	50 ^0C,70 ^0C	Trace
24	$PhNHNH_2$	$PhCH_3CHO$	Ch.Chloride+ pTsOH	-	RT	55%(Styrene 5 Equiv)

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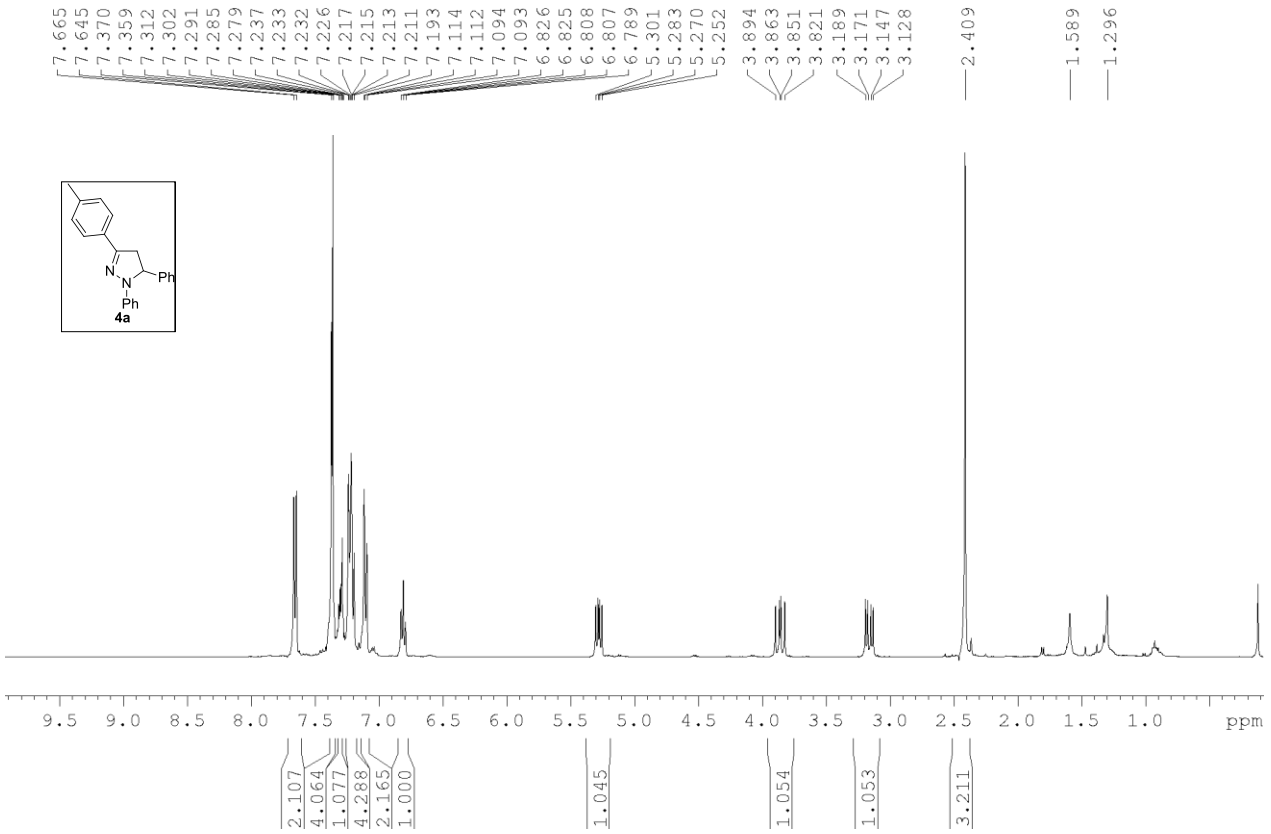
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7.217
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7.213
7.211
7.193
7.114
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7.094
7.093
6.826
6.825
6.808
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6.789
5.301
5.283
5.270
5.252
3.894
3.863
3.851
3.821
3.189
3.171
3.147
3.128
2.409
1.589
1.296
Ph
N
N
Ph
4a
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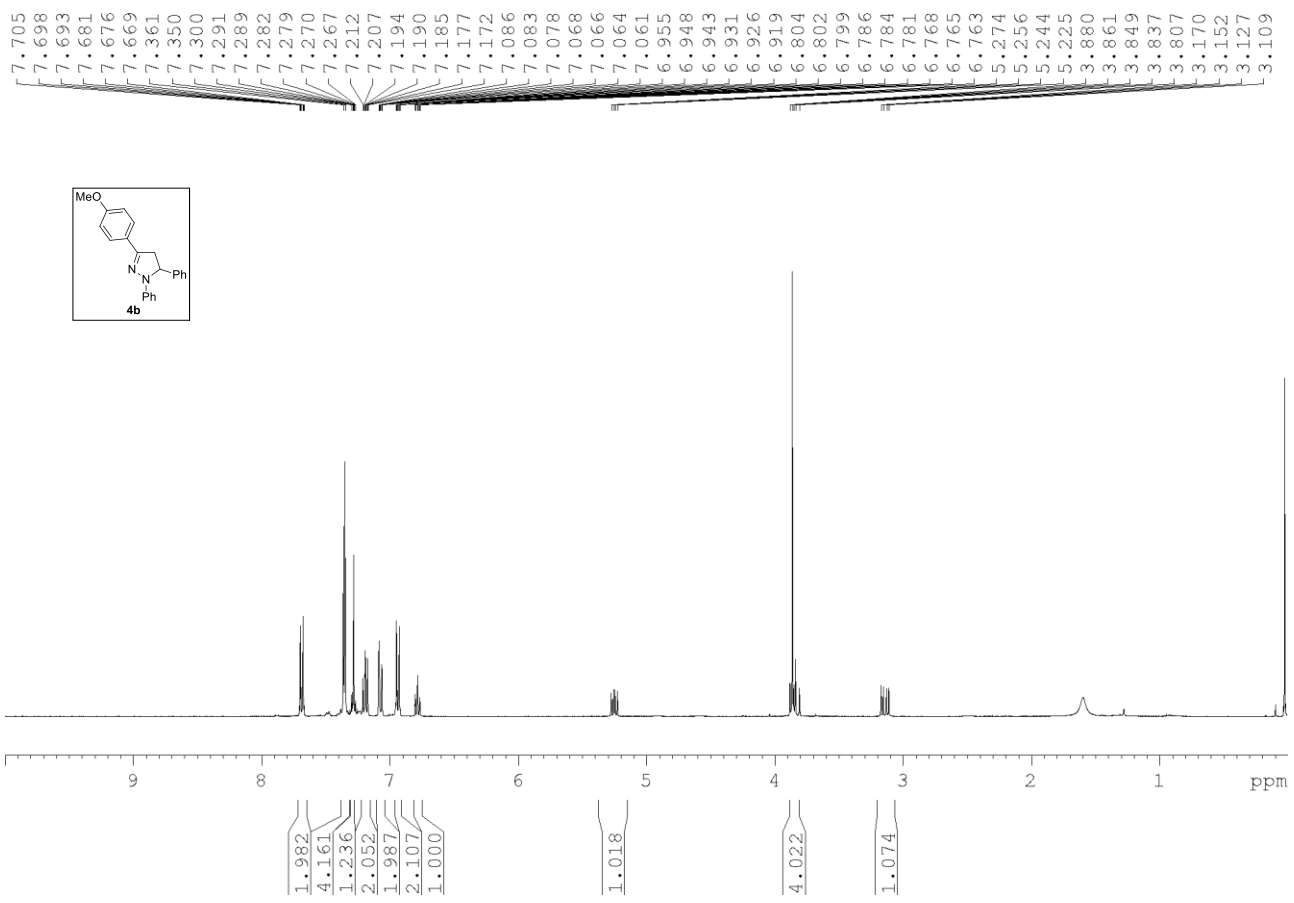
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5.244
5.225
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3.109
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N
Ph
Ph
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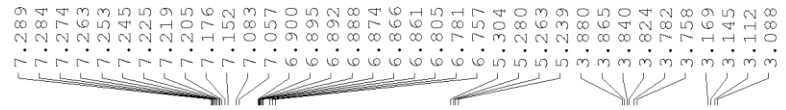
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6.757
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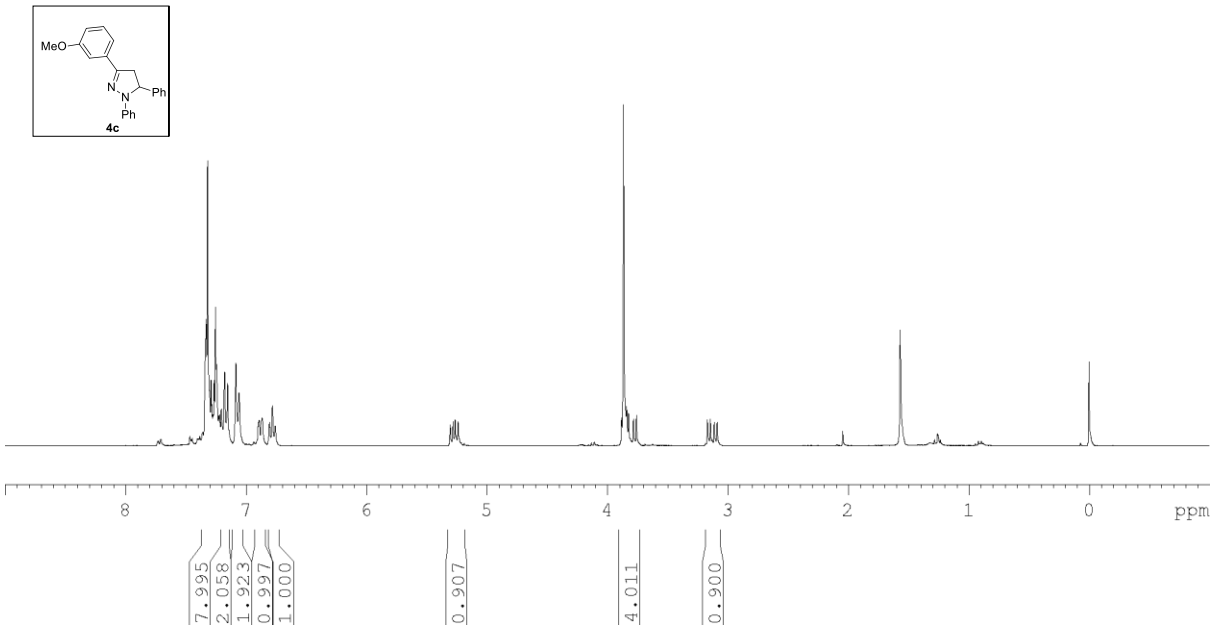
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Ph
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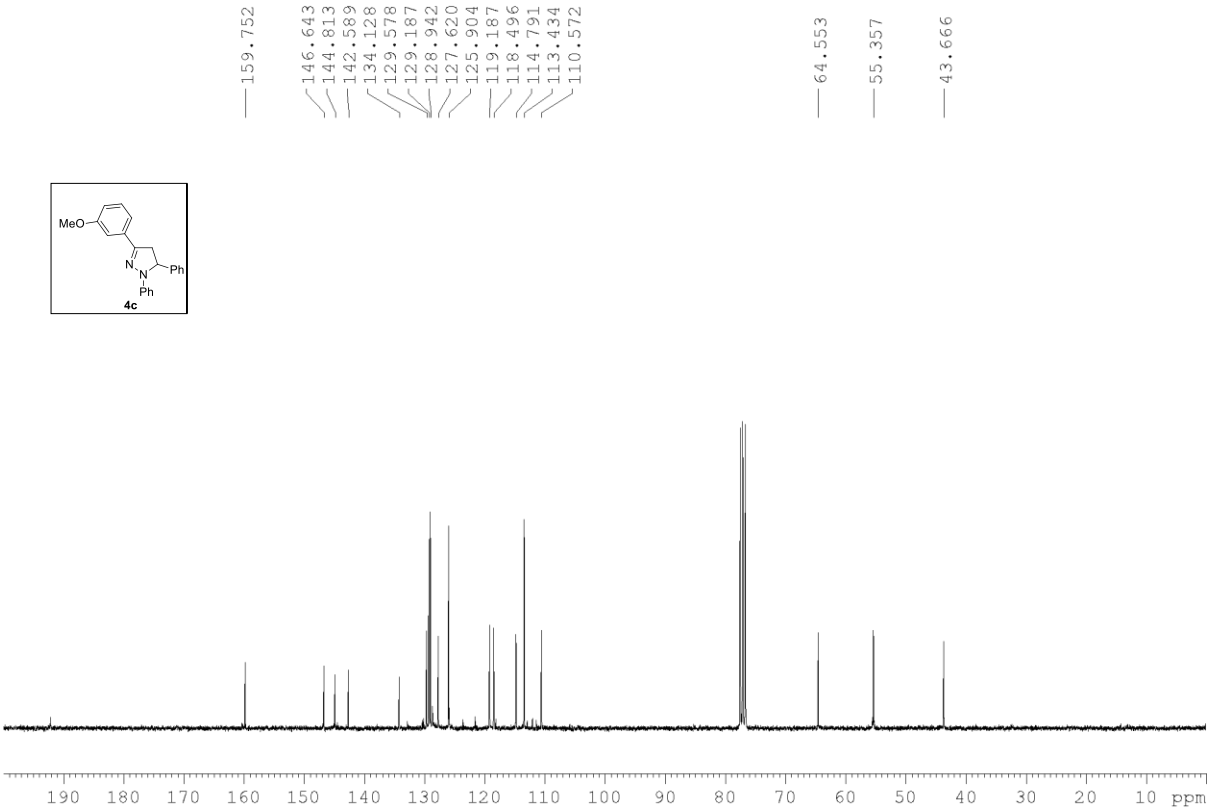
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114.791
113.434
110.572
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55.357
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MeO
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Ph
Ph
4c
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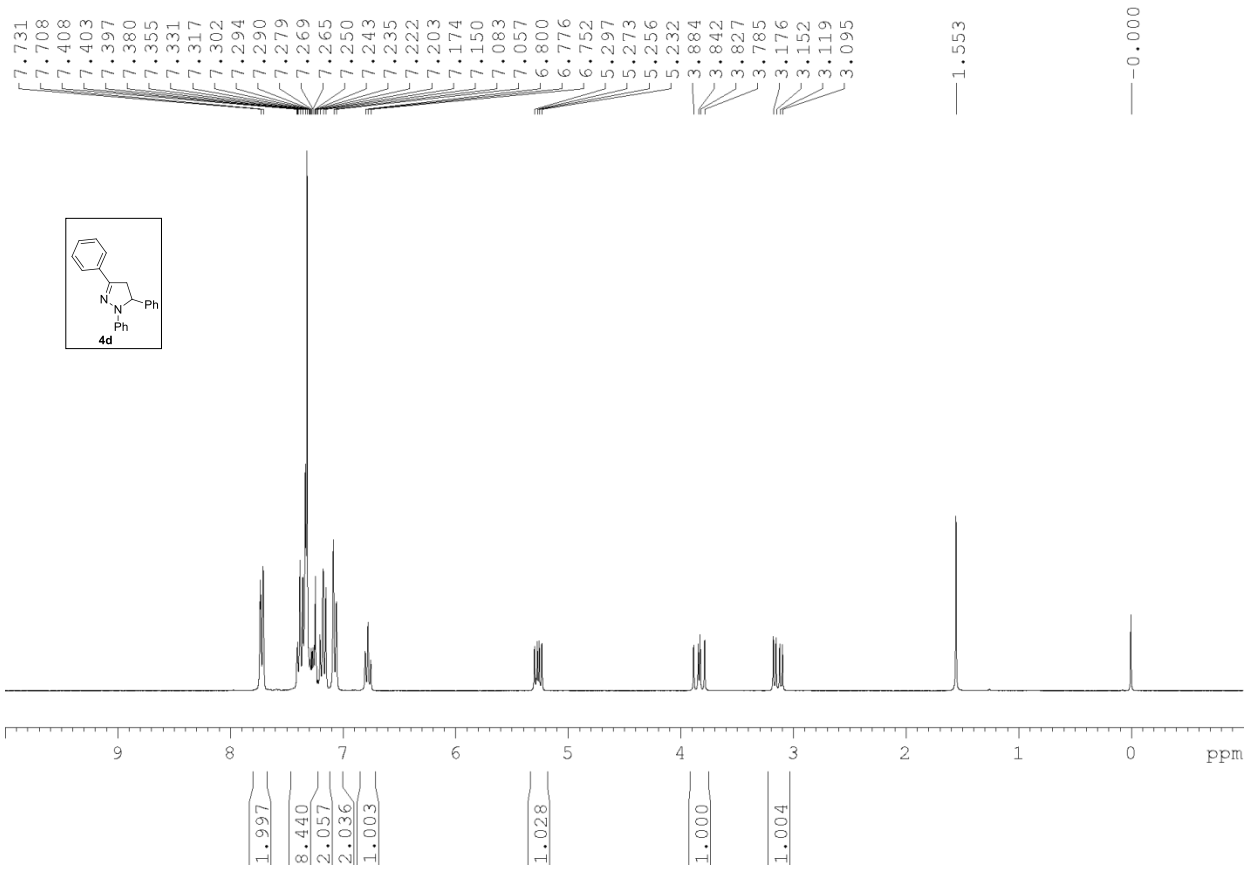
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7.250
7.243
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7.222
7.203
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7.150
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7.057
6.800
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6.752
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5.273
5.256
5.232
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3.842
3.827
3.785
3.176
3.152
3.119
3.095
1.553
0.000
Ph
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N
Ph
4d
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8
7
6
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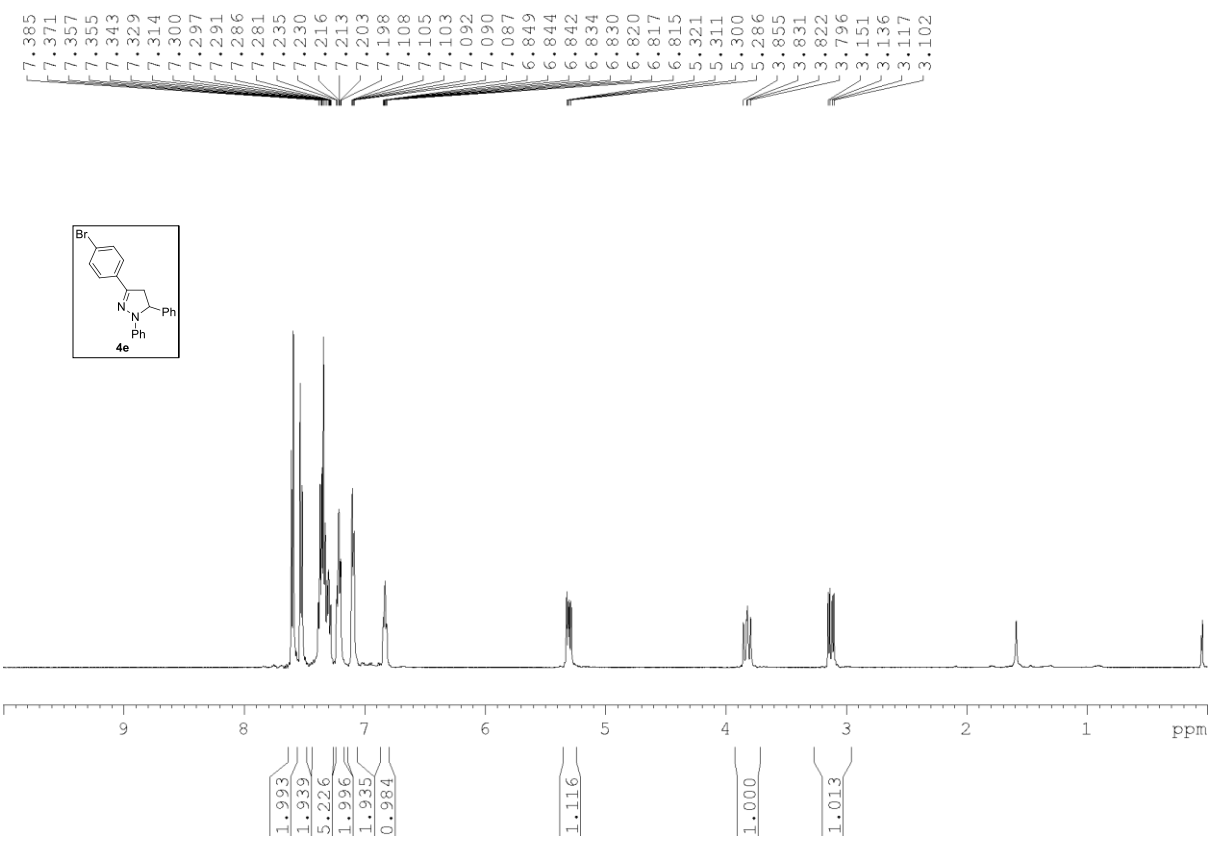
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7.235
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7.216
7.213
7.203
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7.108
7.105
7.103
7.092
7.090
7.087
6.849
6.844
6.842
6.834
6.830
6.820
6.817
6.815
5.321
5.311
5.300
5.286
3.855
3.831
3.822
3.796
3.151
3.136
3.117
3.102
Br
N
N
Ph
Ph
4e
9
8
7
6
5
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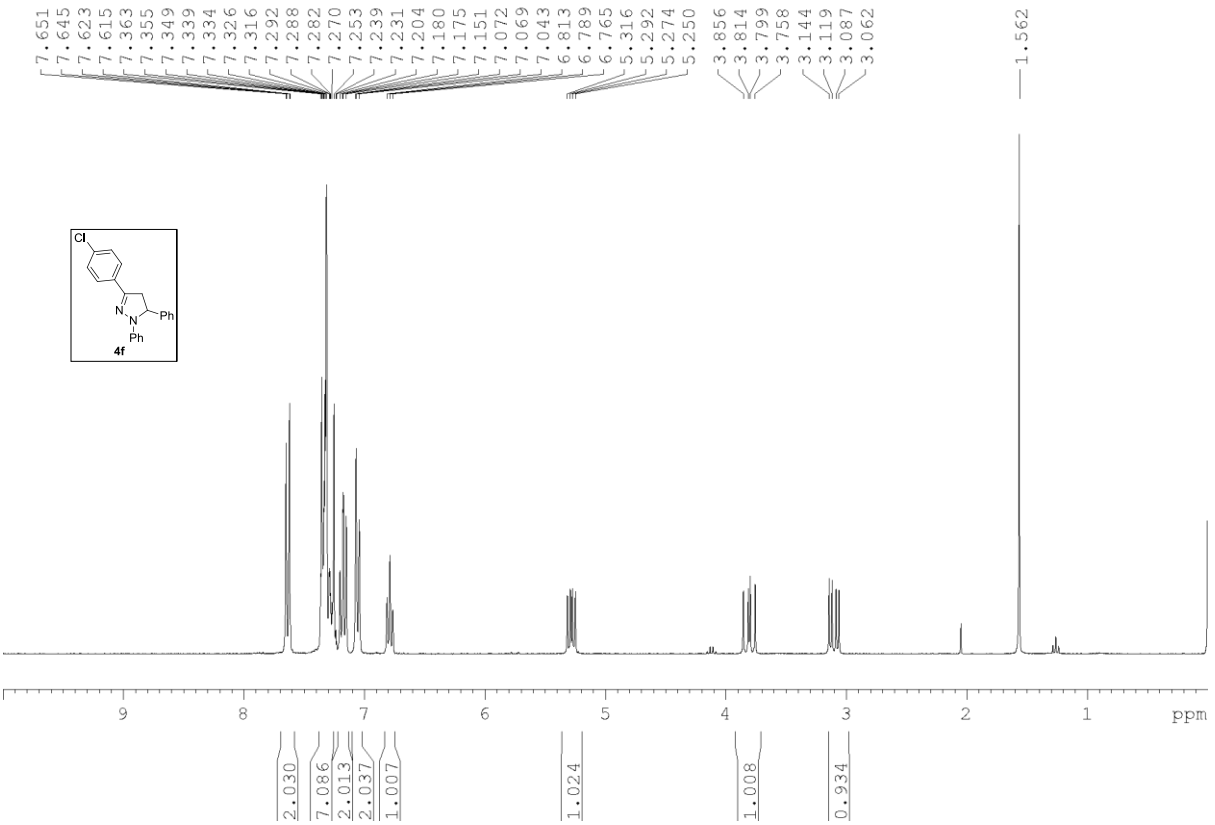
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7.288
7.282
7.270
7.253
7.239
7.231
7.204
7.180
7.175
7.151
7.072
7.069
7.043
6.813
6.789
6.765
5.316
5.292
5.274
5.250
3.856
3.814
3.799
3.758
3.144
3.119
3.087
3.062
1.562
Cl
N
N
Ph
Ph
4f
9
8
7
6
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ppm
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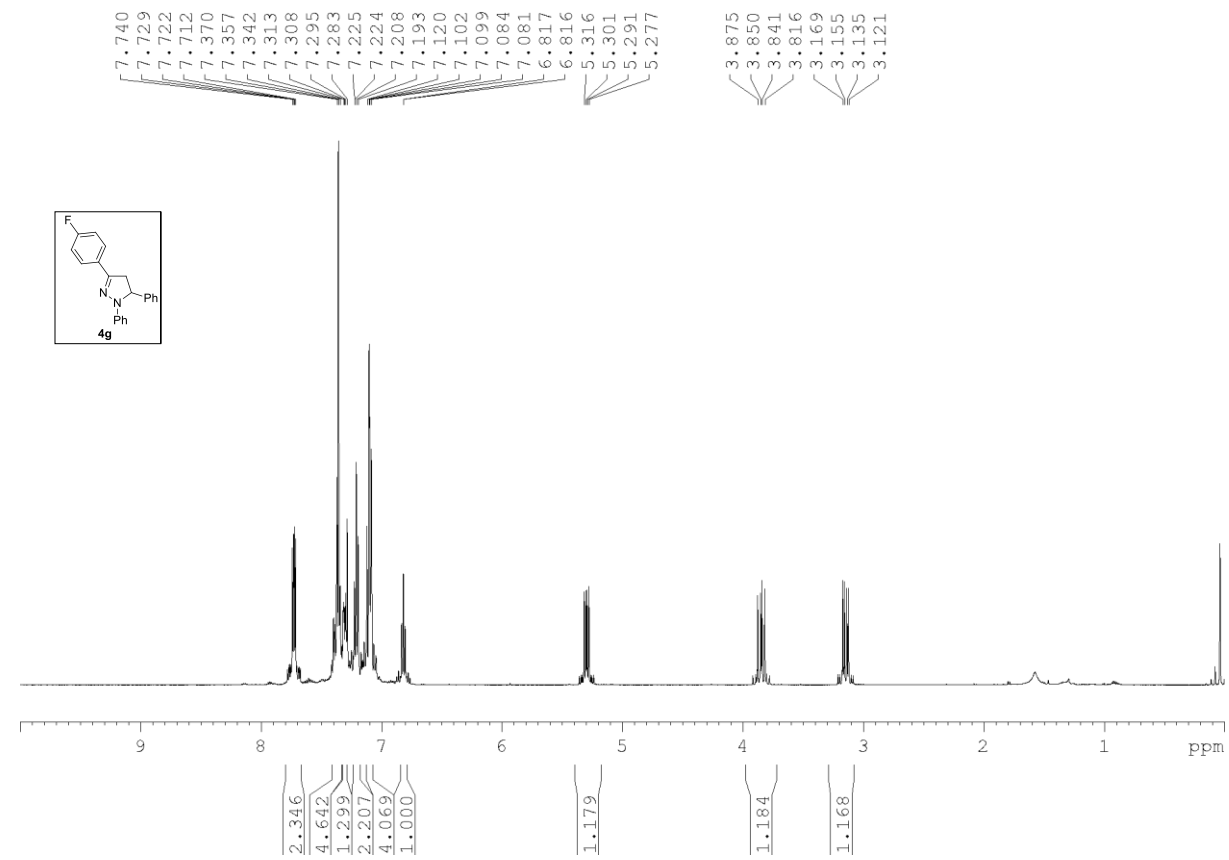
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7.224
7.208
7.193
7.120
7.102
7.099
7.084
7.081
6.817
6.816
5.316
5.301
5.291
5.277
3.875
3.850
3.841
3.816
3.169
3.155
3.135
3.121
F
N
N
Ph
Ph
4g
9
8
7
6
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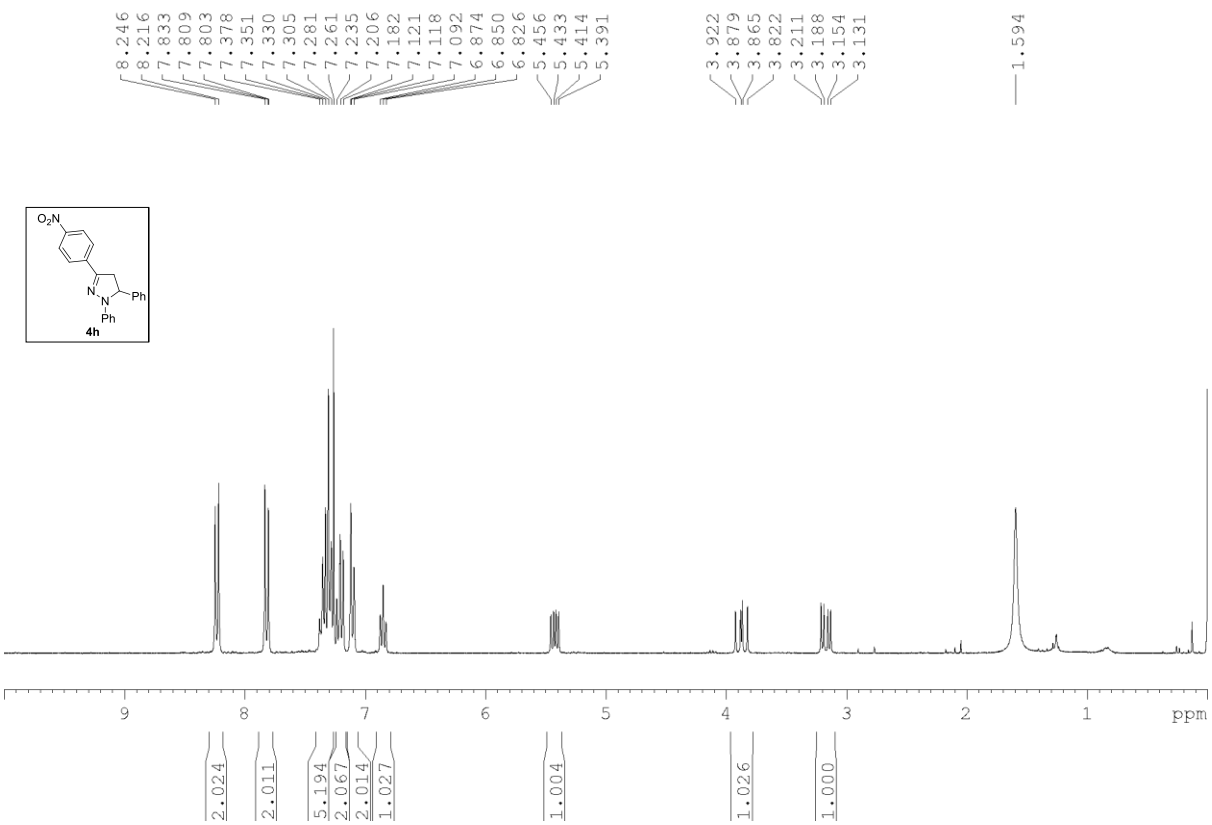
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7.261
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7.206
7.182
7.121
7.118
7.092
6.874
6.850
6.826
5.456
5.433
5.414
5.391
3.922
3.879
3.865
3.822
3.211
3.188
3.154
3.131
1.594
O2N
N
N
Ph
Ph
4h
9
8
7
6
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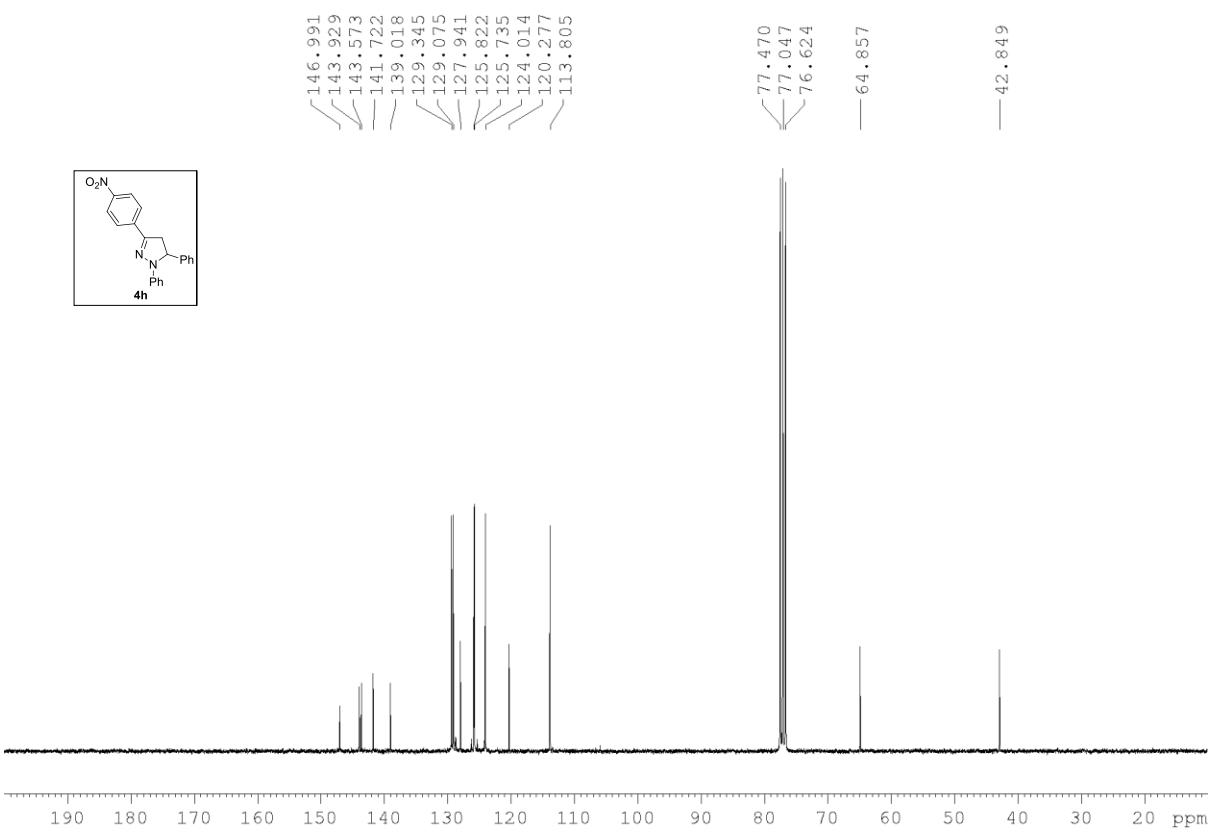
1.000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76.624
64.857
42.849
O2N
N
N
Ph
Ph
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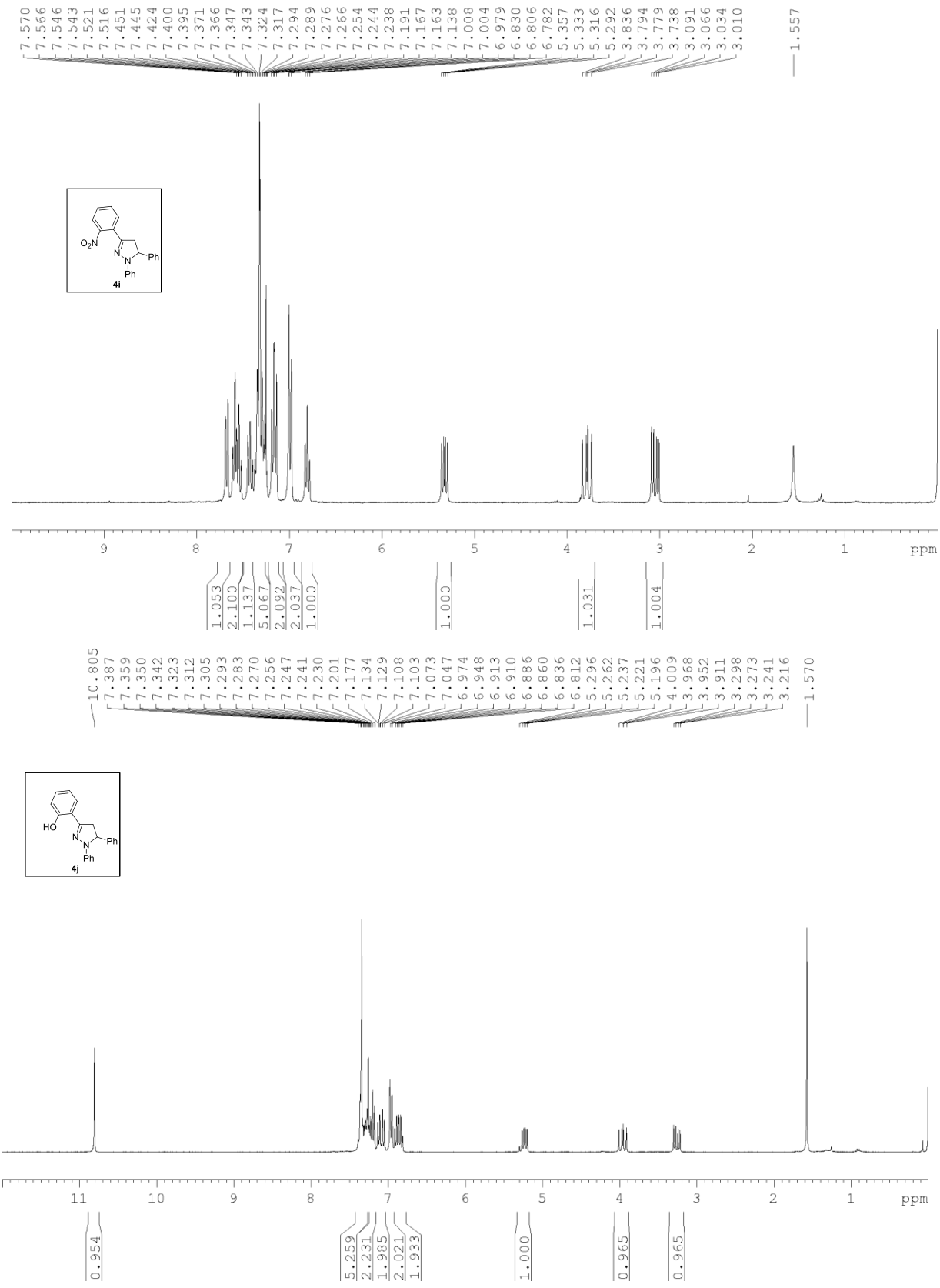
ppm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7.276
7.266
7.254
7.244
7.238
7.191
7.167
7.163
7.138
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6
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7.305
7.293
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7.256
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3.241
3.216
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HO
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N
Ph
Ph
4j
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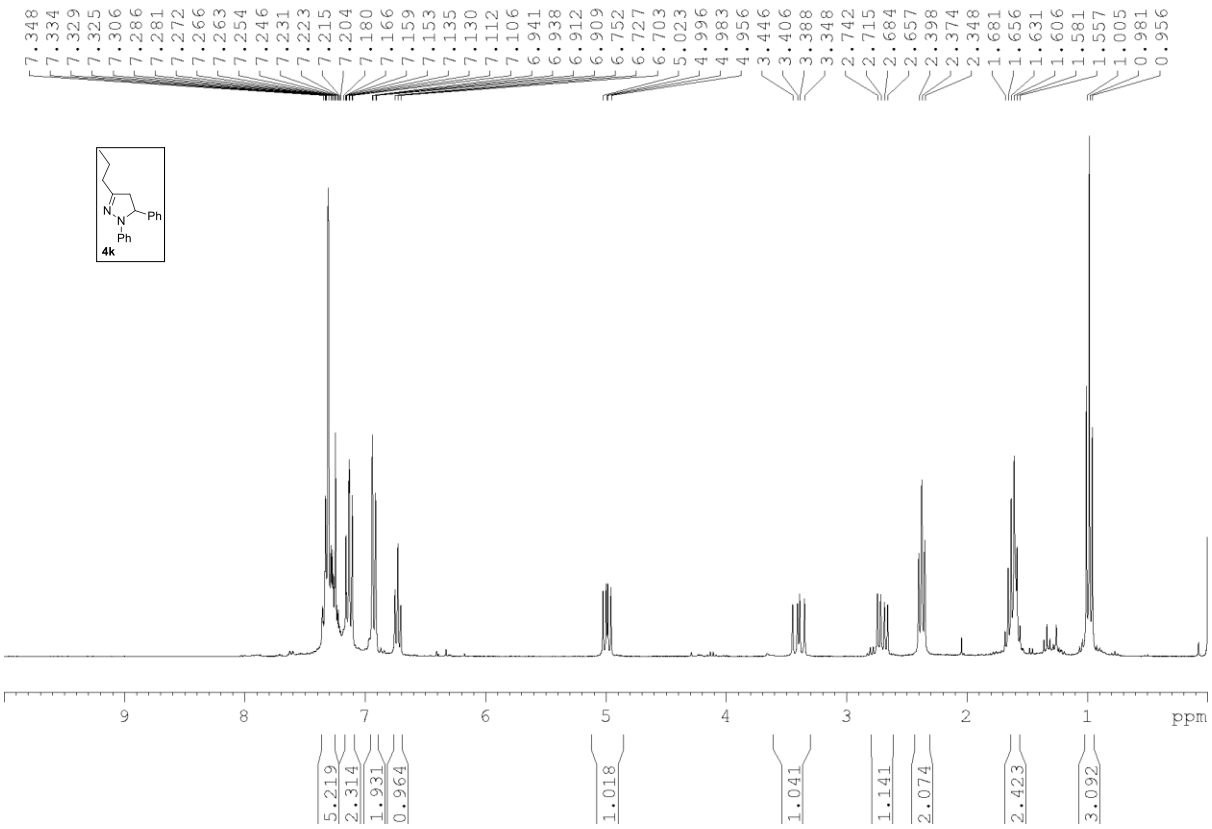
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7.231
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7.215
7.204
7.180
7.166
7.159
7.153
7.135
7.130
7.112
7.106
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6.938
6.912
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6.727
6.703
5.023
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4.983
4.956
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3.406
3.388
3.348
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2.657
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2.374
2.348
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1.656
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1.557
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0.956
Ph
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N
Ph
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8
7
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3
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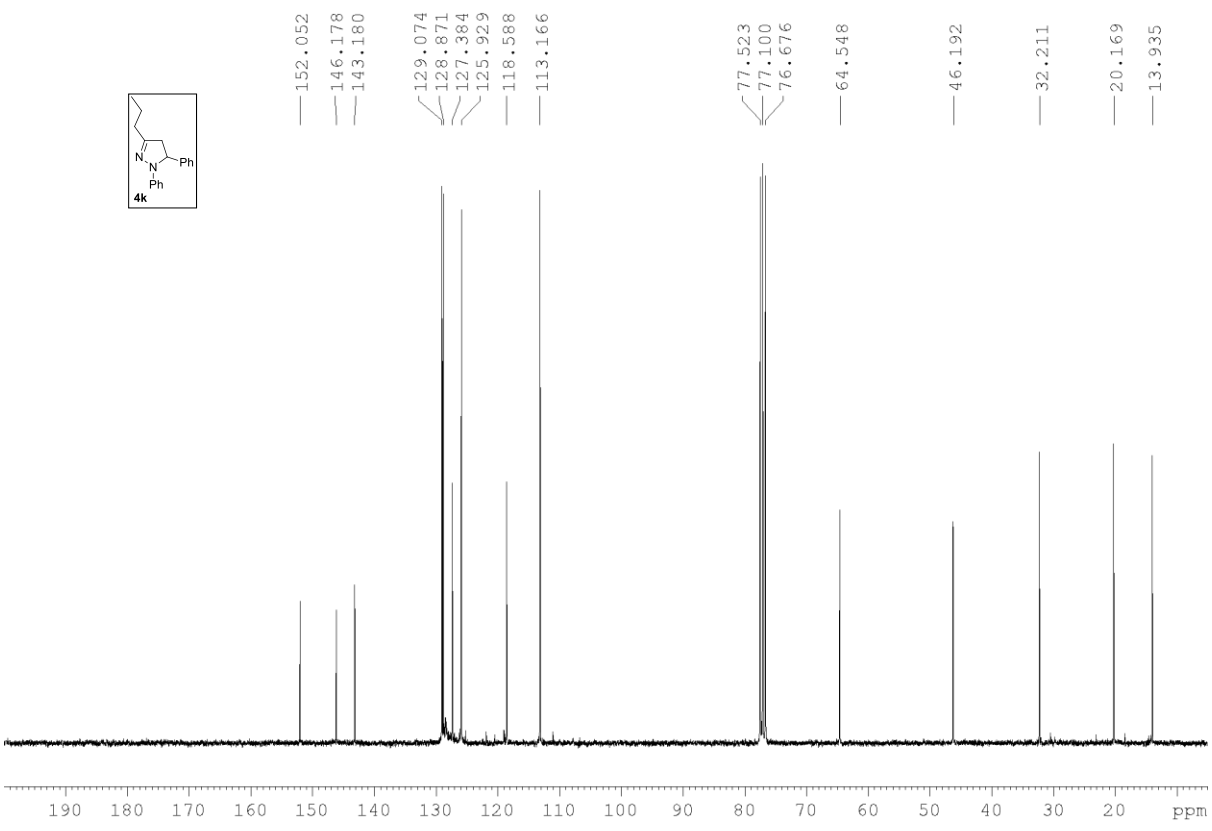
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64.548
46.192
32.211
20.169
13.935
Ph
N
N
Ph
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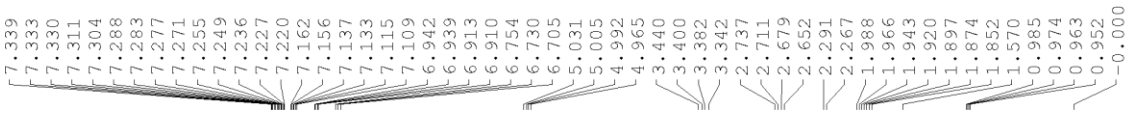
20
ppm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7.220
7.162
7.156
7.137
7.133
7.115
7.109
6.942
6.939
6.913
6.910
6.754
6.730
6.705
5.031
5.005
4.992
4.965
3.440
3.400
3.382
3.342
2.737
2.711
2.679
2.652
2.291
2.267
1.988
1.966
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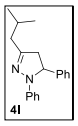
N
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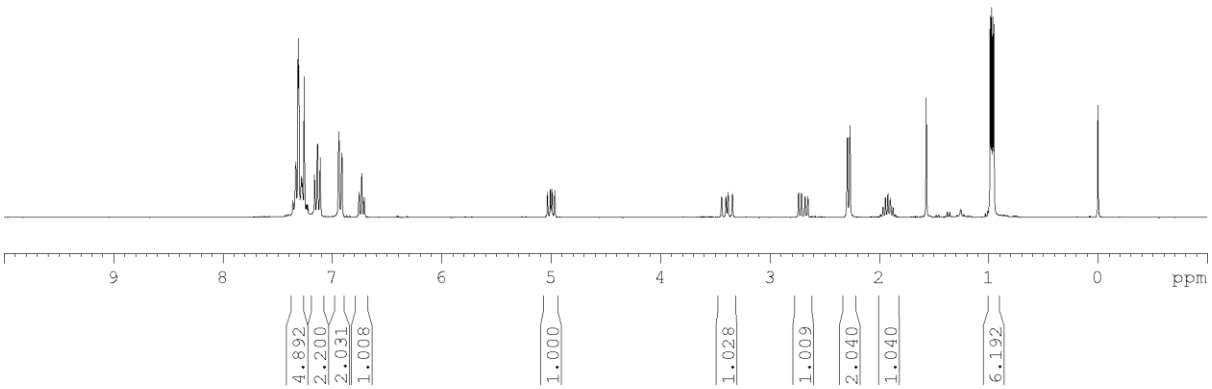
Ph
Ph
4l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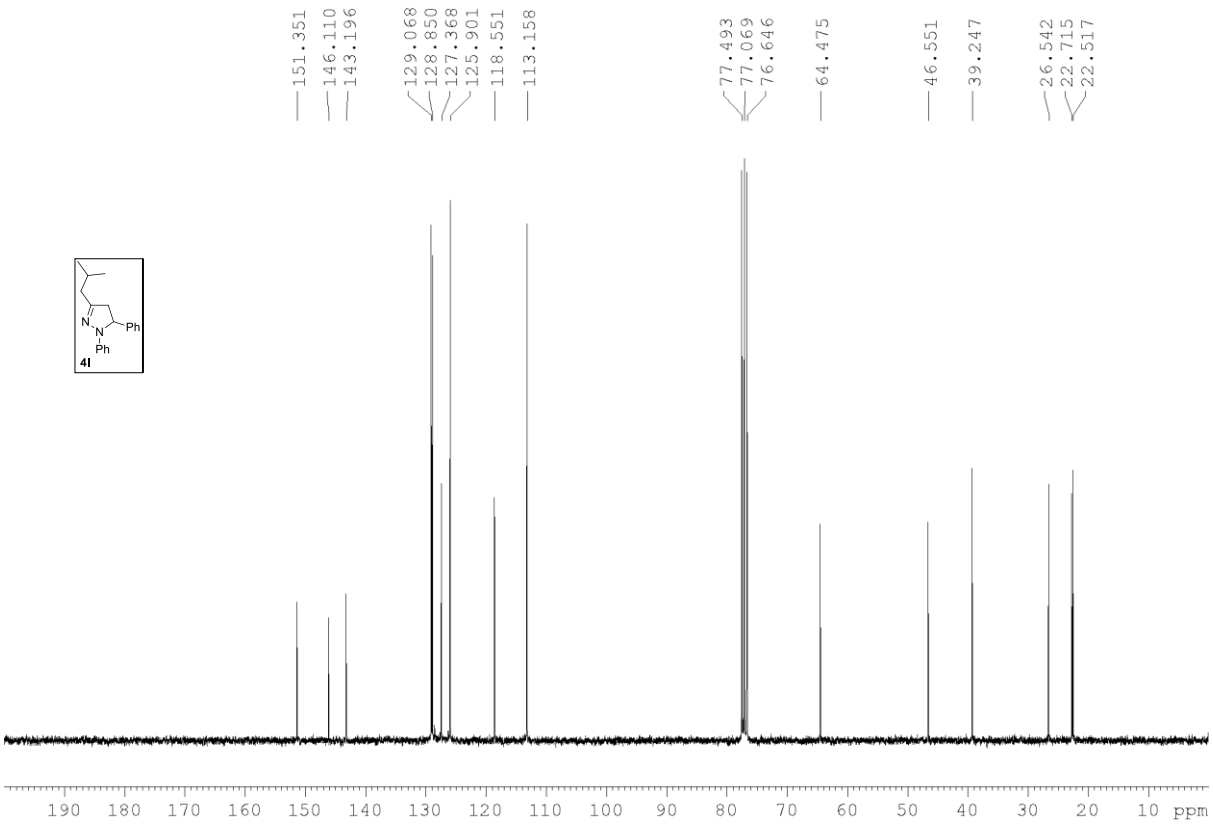
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22.715
22.517
190
180
170
160
150
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10
ppm

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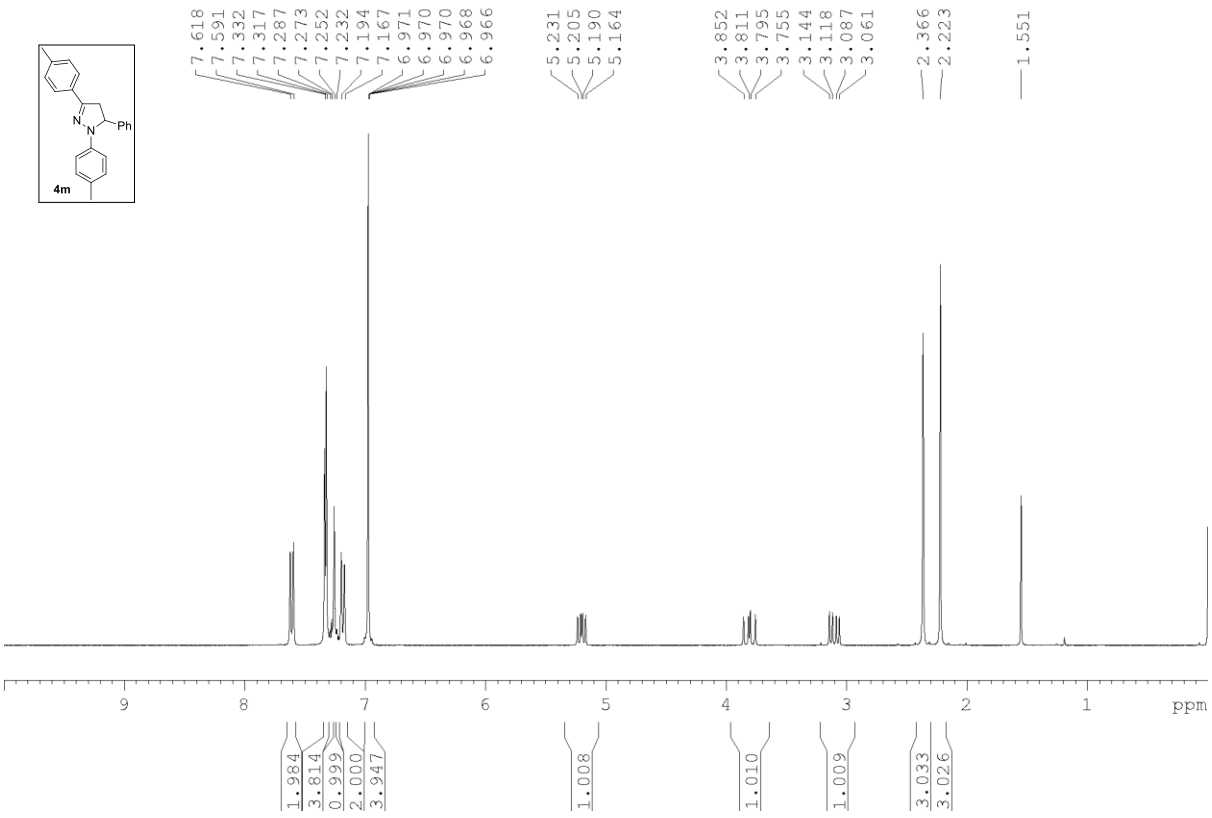
N
Ph
Ph
4l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7.167
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6.970
6.968
6.966
5.231
5.205
5.190
5.164
3.852
3.811
3.795
3.755
3.144
3.118
3.087
3.061
2.366
2.223
1.551
Ph
4m
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8
7
6
5
4
3
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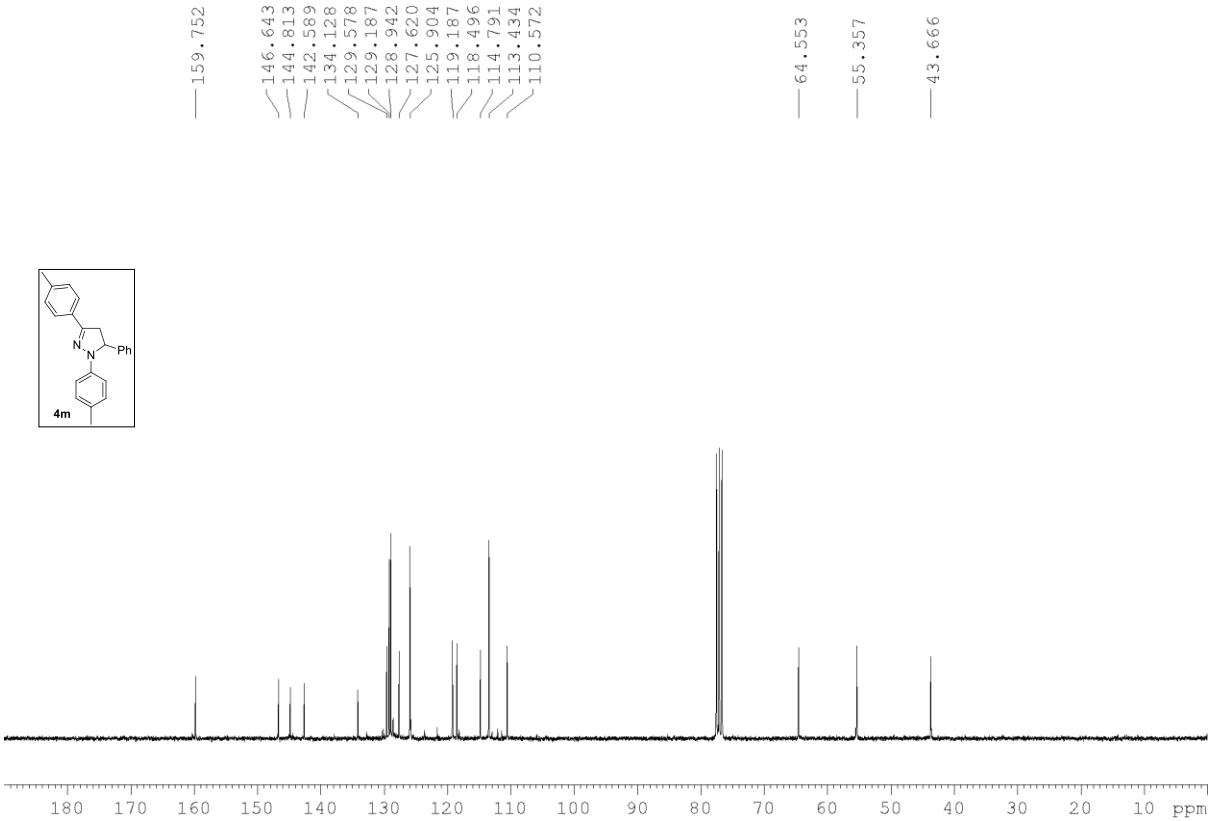
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125.904
119.187
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114.791
113.434
110.572
64.553
55.357
43.666
Ph
4m
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150
140
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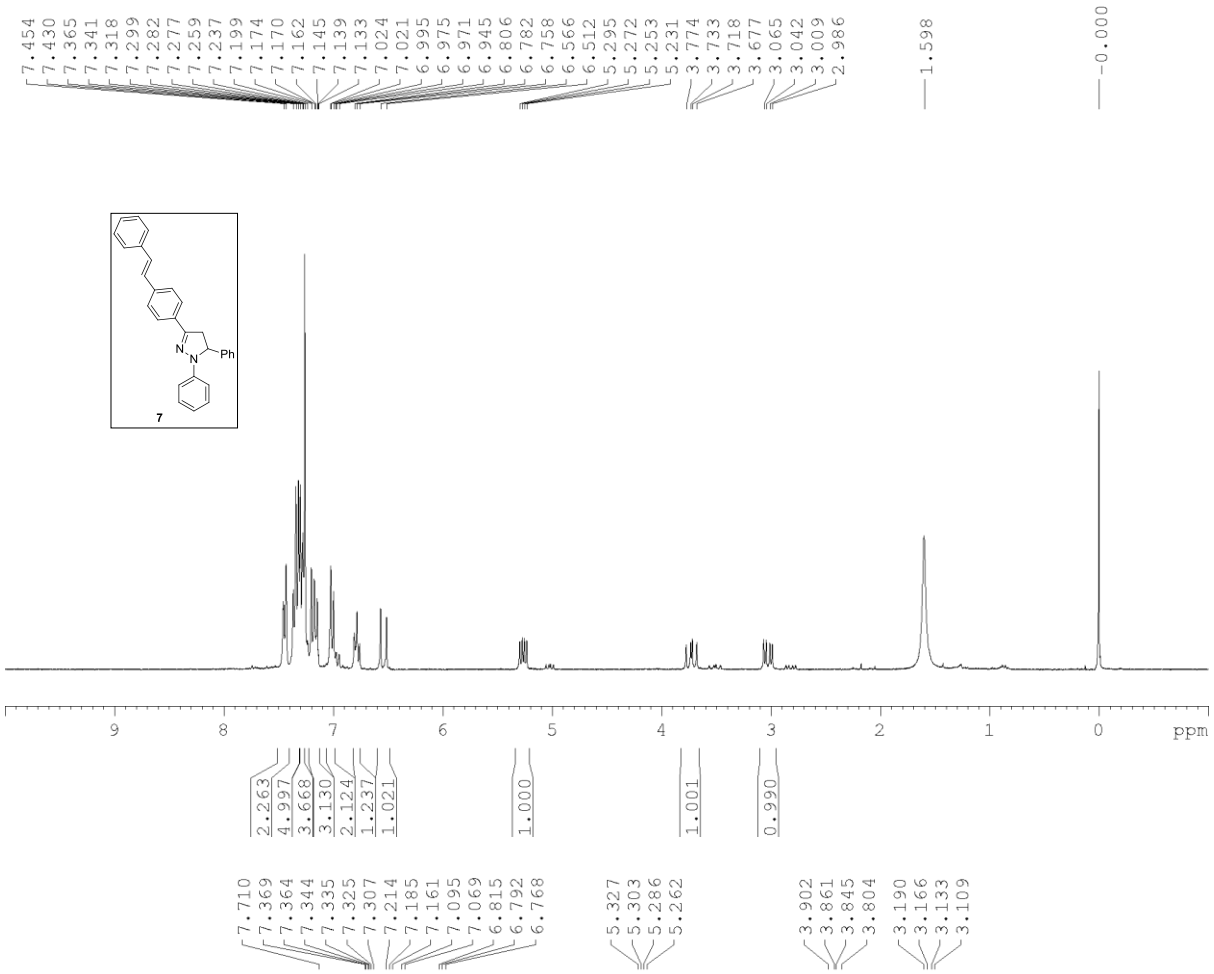
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7.170
7.162
7.145
7.139
7.133
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7.021
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6.971
6.945
6.806
6.782
6.758
6.566
6.512
5.295
5.272
5.253
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3.718
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0.000
Ph
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N
Ph
7
9
8
7
6
5
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3
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1
0
ppm
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7.364
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7.335
7.325
7.307
7.214
7.185
7.161
7.095
7.069
6.815
6.792
6.768
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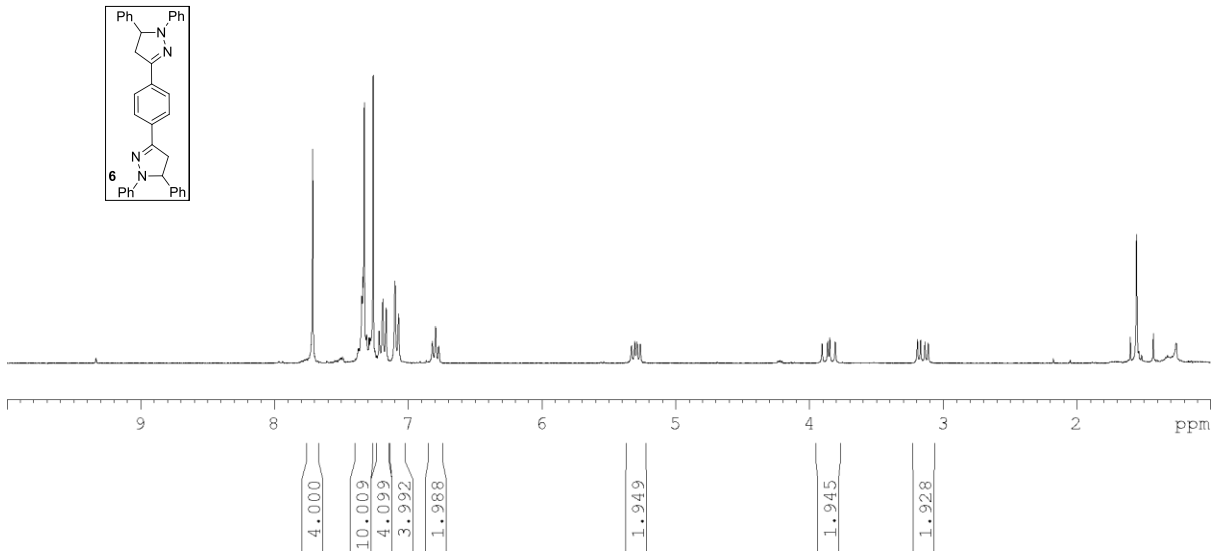
3.133
3.109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Ph
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N
N
N
Ph
Ph
6
9
8
7
6
5
4
3
2
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4.099
3.992
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1.945
1.928