Electronic Supplementary Material (ESI) for Chemical Communications

SUPPLEMENTARY INFORMATION

A novel, efficient synthesis of N-aryl pyrroles via reaction of 1-borodienes with arylnitroso compounds.

Fabien Tripoteau,[a] Ludovic Eberlin,[a] Mark A. Fox,[b] Bertrand Carboni[a]* and Andrew Whiting[b]*

[a]Institut des Sciences Chimiques de Rennes, UMR 6626 CNRS-Université de Rennes 1, Campus de Beaulieu, CS 74205, 35042 Rennes CEDEX, FRANCE
Email bertrand.carboni@univ-rennes1.fr

[b]Centre for Sustainable Chemical Processes, Department of Chemistry, Durham University, South Road, Durham DH1 3LE, U.K.
Email andy.whiting@durham.ac.uk

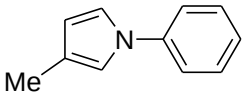
CONTENTS

NMR Spectra were recorded on Bruker apparatus at 300, 400 or 500 MHz for ^{1}H, 75, 101 MHz or 126 MHz for ^{13}C and 96 MHz for ^{11}B. ^{1}H and ^{13}C NMR chemical shifts were referenced to Me_4Si as internal reference, and ^{11}B NMR chemical shifts to external $BF_3.OEt_2$ (0.0 ppm). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration. High-resolution mass spectra (HMRS) were recorded on a Bruker MicrO-Tof-Q II or on a Waters Q-Tof 2 at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest - Rennes - France) using positive ion electrospray. Purifications on silica gel were carried out on Acros silica gel 0.060-0.200 mm, 60 A. Flash chromatography purifications were performed on a Grace RevelerisTM with RevelerisTM flash cartridges. Analytical thin layer chromatography was performed on Merck Silica Gel 60 F254 plates. All solvents were sourced from commercial sources and used without further purification. Arylnitroso compounds were either sourced commercially or prepared according to the literature: A. Defoin, *Synthesis*, **2004**, 706-710.

General procedure for the preparation of pyrroles

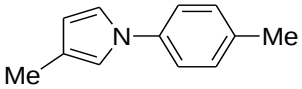
To a solution of diene (1 eq) (pinacol boronate or trifluoroborate) in MeOH was added aryl nitroso (2.5 eq). The reaction mixture was stirred at room temperature. The solvent was evaporated and the crude product was purified by silica gel chromatography.

1-Phenyl-3-methyl-1*H*-pyrrole 8



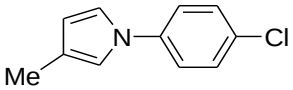
Diene **7** (21 mg, 0.11 mmol) and nitrosobenzene (29 mg, 0.27 mmol) in MeOH (1 mL) gave after silica gel chromatography (hexane/EtOAc, 9/1, R_f = 0.75) the pyrrole **8** (14 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.39-7.24 (m, 4H), 7.16-7.10 (m, 1H), 6.92 (t, *J* = 2.5 Hz, 1H), 6.81-6.79 (m, 1H), 6.11 (t, *J* = 2.5 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 140.8, 129.5, 125.1, 121.1, 120.0, 118.9, 117.1, 112.0, 12.0.
Lit.: U.H. Brinker, M. Boxberger, *J. Chem. Res.*, **1983**, 100-101.

1-(4-Methylphenyl)-3-methyl-1*H*-pyrrole 10



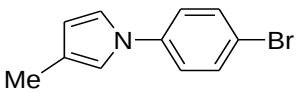
Diene **7** (30 mg, 0.17 mmol) and 4-nitrosotoluene (52 mg, 0.43 mmol) in MeOH (1 mL) gave after silica gel chromatography (hexane/EtOAc 9/1, R_f = 0.8) pyrrole **10** (23 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.19-7.07 (m, 4H), 6.88 (t, *J* = 2.5 Hz, 1H), 6.78-6.76 (m, 1H), 6.08 (dd, *J* = 2.1 and 2.3 Hz, 1H), 2.28 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 138.5, 134.8, 130.0, 120.8, 120.0, 119.0, 117.3, 111.6, 20.8, 12.0. HRMS (ESI) calcd. for $C_{16}H_{22}N$ $[M+H]^+$: 172.11262 found: 172.1127.

1-(4-Chlorophenyl)-3-methyl-1*H*-pyrrole 11



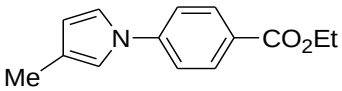
Diene **7** (21 mg, 0.11 mmol) and 4-chloronitrosobenzene (39 mg, 0.27 mmol) in MeOH (2 mL) gave after silica gel chromatography (hexane/EtOAc, 9/1, R_f = 0.9) the pyrrole **11** (14 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28 (d, *J* = 9.0 Hz, 2H), 7.19 (d, *J* = 9.0 Hz, 2H), 6.87 (t, *J* = 2.6 Hz, 1H), 6.74-6.73 (m, 1H), 6.11 (t, *J* = 2.4 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 139.3, 130.4, 129.5, 121.6, 121.0, 118.9, 117.0, 12.4, 11.9. HRMS (ESI) calcd. for $C_{11}H_{11}N^{35}Cl$ $[M+H]^+$: 192.05800 found: 192.0580.
Lit. B. Schmidt , S. Krehl, E. Jablowski *Org. Biomol. Chem.*, **2012**, *10*, 5119-5130.

1-(4-Bromophenyl)-3-methyl-1*H*-pyrrole 12



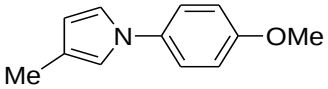
Diene **7** (20 mg, 0.1 mmol) and 4-bromonitrosobenzene (48 mg, 0.25 mmol) in MeOH (2 mL) gave after silica gel chromatography (hexane/EtOAc, 9/1, R_f = 0.9) the pyrrole **12** (16 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.87 (t, *J* = 2.6 Hz, 1H), 6.76-6.73 (m, 1H), 6.11 (t, *J* = 2.2 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) 139.8; 132.5; 121.7; 121.4; 118.8; 118.1; 117.0; 112.5; 11.9. HRMS (ESI) calcd. for $C_{11}H_{11}N^{79}Br$ $[M+H]^+$: 236.00749 found: 236.0074.

1-(4-Ethoxycarbonylphenyl)-3-methyl-1*H*-pyrrole 13



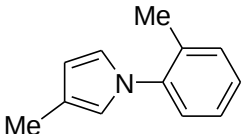
Diene **7** (31 mg, 0.16 mmol) and ethyl 4-nitrosobenzoate (72 mg, 0.40 mmol) in MeOH (1 mL) gave after silica gel chromatography (hexane/EtOAc 9/1, R_f = 0.65) the pyrrole **13** (21 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.09 (d, *J* = 8.9 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.07(t, *J* = 2.6 Hz, 1H), 6.95-6.93 (m, 1H), 6.21 (dd, *J* = 1.8 and 2.4, Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.15 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) 166.0, 143.9, 131.2, 126.7, 122.3, 118.6, 116.7, 113.1, 61.0, 14.3, 12.0. HRMS (ESI) calcd. for $C_{14}H_{15}NO_2Na$ $[M+Na]^+$: 252.10005 found: 252.1001.

1-(4-Methoxyphenyl)-3-methyl-1*H*-pyrrole 14



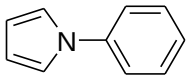
Diene **7** (28 mg, 0.16 mmol) and 4-methoxynitrosobenzene (55 mg, 0.4 mmol) in MeOH (1 mL) gave after silica gel chromatography (hexane/EtOAc, 9/1, R_f = 0.75) pyrrole **14** (23 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.19 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.82 (t, *J* = 2.5 Hz, 1H), 6.71-6.69 (m, 1H), 6.07 (t, *J* = 2.2 Hz, 1H), 3.75 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 157.3, 134.6, 121.7, 120.6, 119.3, 117.6, 114.6, 111.3, 55.6, 12.0. HRMS (ESI) calcd. for $C_{12}H_{14}NO$ $[M+H]^+$: 188.10754 found: 188.1074.

1-(2-Methylphenyl)-3-methyl-1*H*-pyrrole 15



Diene **7** (30 mg, 0.17 mmol) and 2-nitrosotoluene (52 mg, 0.43 mmol), in MeOH (1 mL) gave after silica gel chromatography (hexane/EtOAc, 9/1, R_f = 0.8) pyrrole **15** (20 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.25-7.09 (m, 4H), 6.60 (t, *J* = 2.4 Hz, 1H), 6.50-6.47 (m, 1H), 6.06 (t, *J* = 2.1 Hz, 1H), 2.15 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 140.8, 133.6, 131.1, 127.1, 126.5, 121.9, 120.0, 119.3, 110.2, 18.0, 11.9. HRMS (ESI) calcd. for $C_{12}H_{14}N$ $[M+H]^+$: 172.11262 found: 172.1126.

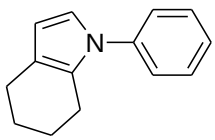
1-Phenyl-1*H*-pyrrole 17



Diene **16** (50 mg, 0.28 mmol) and nitrosobenzene (75 mg, 0.70 mmol) in MeOH (1 mL) gave after silica gel chromatography (hexane/EtOAc, 9/1, R_f = 0. 9) pyrrole **17** (31 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37-7.27 (m, 4H), 7.20-7.09 (m, 1H), 7.10 (t, *J* = 2.1 Hz, 2H), 6.27 (t, *J* = 2.1 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 140.4, 129.2, 125.3, 120.2, 119.0, 110.0.

Lit.: M. Taillefer; N. Xia, A. Ouali, *Angew. Chem., Int. Ed.,* **2007,** *46,* 934.

1-Phenyl-4,5,6,7-tetrahydro-1*H*-indole 19

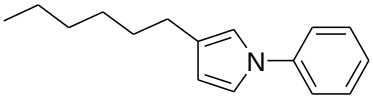


Diene **18** (75 mg, 0.32 mmol) and nitrosobenzene (86 mg, 0.8 mmol) in MeOH (2 mL) gave after silica gel chromatography (hexane/EtOAc, 95/5, R_f = 0.8) pyrrole **19** (30 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm

7.36-7.32 (m, 2H), 7.24-7.21 (m, 3H), 6.79 (d, *J* = 2.7 Hz, 1H), 6.12 (d, *J* = 2.4 Hz, 1H), 2.65-2.55 (m, 4H), 1.84-1.70 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 140.3, 129.2, 129.0; 128.1, 126.1, 124.5, 119.8, 119.0, 108.1, 26.9, 23.6, 23.5, 23.3. HRMS (ESI) calcd. for $C_{14}H_{16}N$ $[M+H]^+$: 198.12827 found: 198.1284.

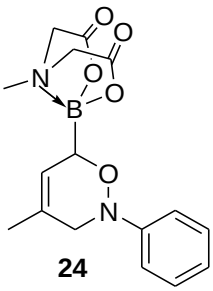
Lit: T. Nishio, N. Okuda, C. Kashima, *J. Chem. Soc., Perkin Trans. I*, **1992**, 899-901.

1-Phenyl-3-n-hexyl-1*H*-pyrrole 21



Diene **20** (58 mg, 0.22 mmol) and nitrosobenzene (59 mg, 0.55 mmol) in MeOH (2 mL) gave after silica gel chromatography (hexane/EtOAc, 95/5, R_f = 0.8) pyrrole **21** (17 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44-7.36 (m, 4H), 7.24-7.16 (m, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.92-6.89 (m, 1H), 6.21 (t *J* = 2.1 Hz, 1H), 2.53 (t, *J* = 7.5 Hz, 2H), 1.70-1.56 (m, 2H), 1.46-1.28 (m, 6H), 0.91 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 140.8, 129.4, 127.1; 125.0, 120.0, 118.8, 116.3, 110.8, 31.8, 31.0, 29.2, 27.1, 22.6, 14.1. HRMS (ESI) calcd. for $C_{16}H_{22}N$ $[M+H]^+$: 228.17522 found: 228.1754.

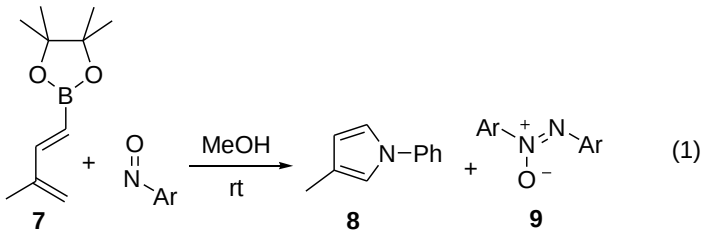
Synthesis of 6-Methyl-2-(4-methyl-2-phenyl-3,6-dihydro-2*H*-1,2-oxazin-6-yl)-1,3,6,2-dioxazaborocane-4,8-dione 24



24

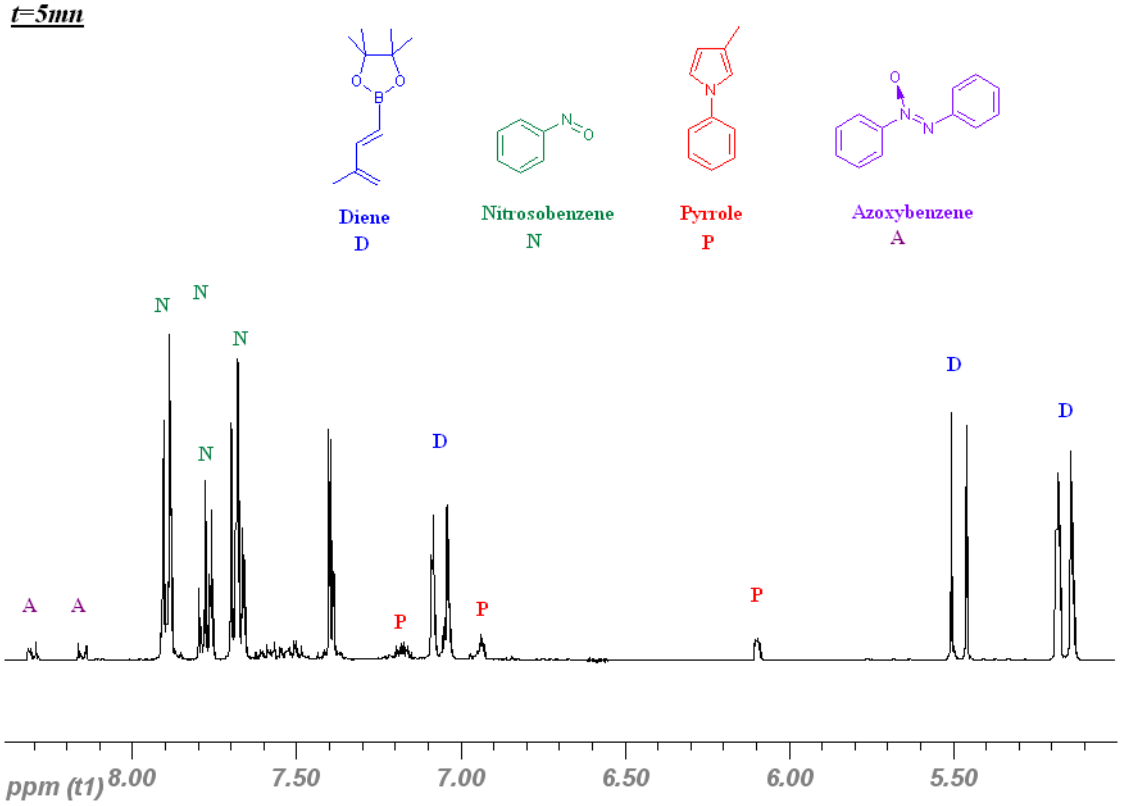
To a solution of diene **23** (20 mg, 0.09 mmol) in MeOH (1 mL) was added nitrosobenzene (15 mg, 0.13 mmol). The reaction mixture was stirred at room temperature overnight. The solvent was evaporated and the residue was purified by silica gel chromatography (Et_2O/acetone 8/2, R_f = 0.5) to give **24** (19 mg, 64%). ^{1}H NMR (400 MHz, Acetone-d6) δ ppm 7.28-7.22 (m, 2H), 7.11-7.08 (m, 2H), 6.93 (tt, *J* = 7.3, 1.1 Hz, 1H), 5.75-5.72 (m, 1H), 4.53-4.48 (m, 1H), 4.29 (d, *J* = 16.9 Hz, 2H), 4.07 (d, *J* = 14.9 Hz, 1H), 4.02 (d, *J* = 16.8 Hz, 1H), 3.90 (dm, *J* = 15.8 Hz, 1H), 3.57 (dm, *J* = 15.7 Hz, 1H), 3.30 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (400 MHz, Acetone-d_6) δ ppm 169.8, 167.6, 152.9, 130.6, 130.4, 123.5, 123.3, 117.5, 64.2, 57.1, 47.9, 21.5, boron-bound carbon was not visible; ^{11}B NMR (400 MHz, Acetone-d_6) δ ppm 10.1. HRMS (ESI) calcd. for $[M+Na]^+$($C_{16}H_{19}N_2O_5{}^{11}BNa$): 353.1284 found: 353.1285.

In situ ^{1}H NMR study of the reaction of diene 7 with nitrosobenzene (1 equiv.)

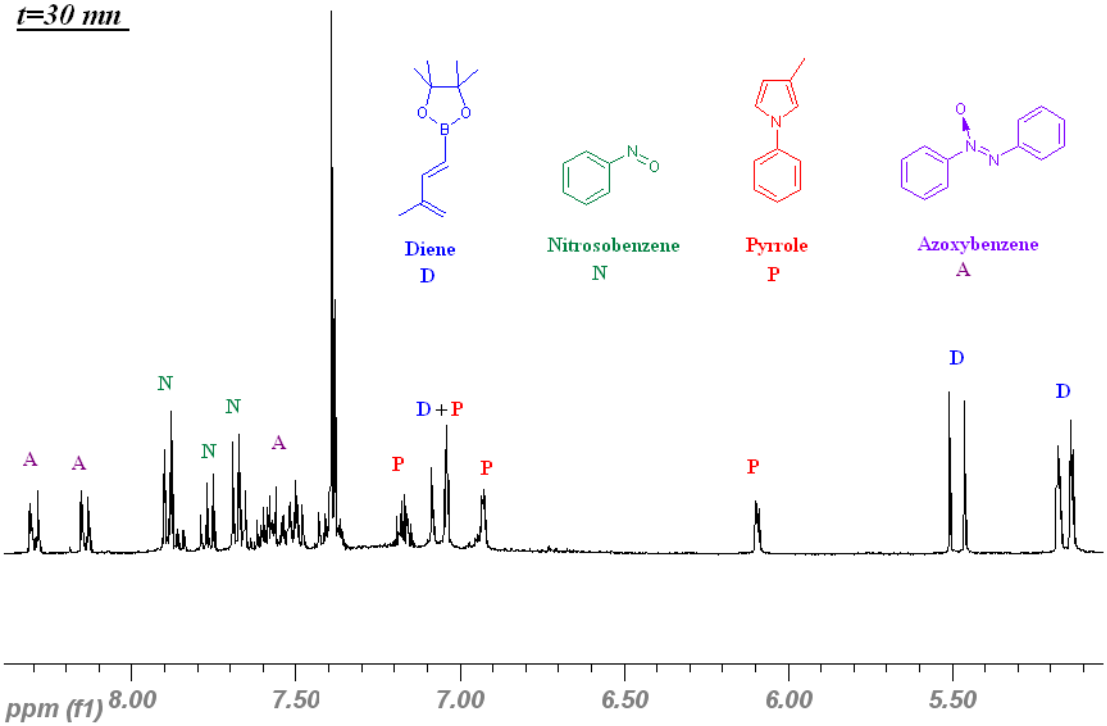


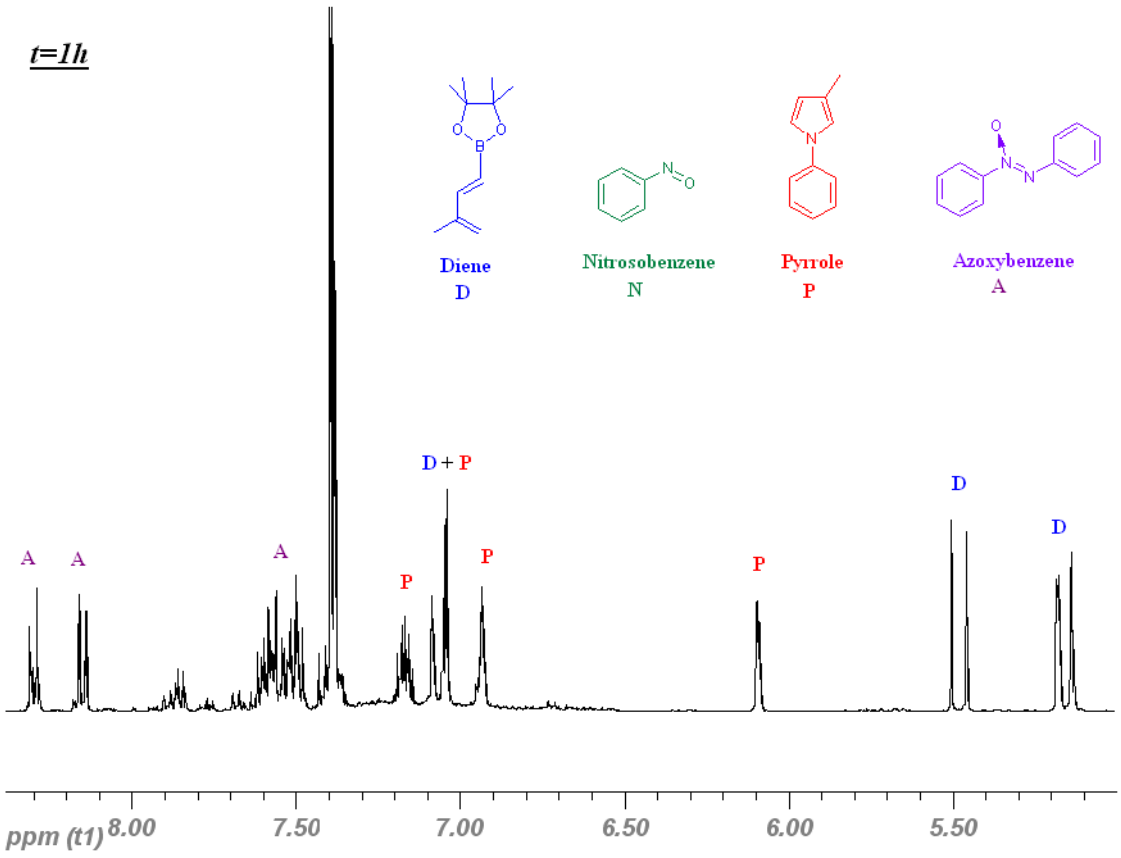
7 **8** **9**

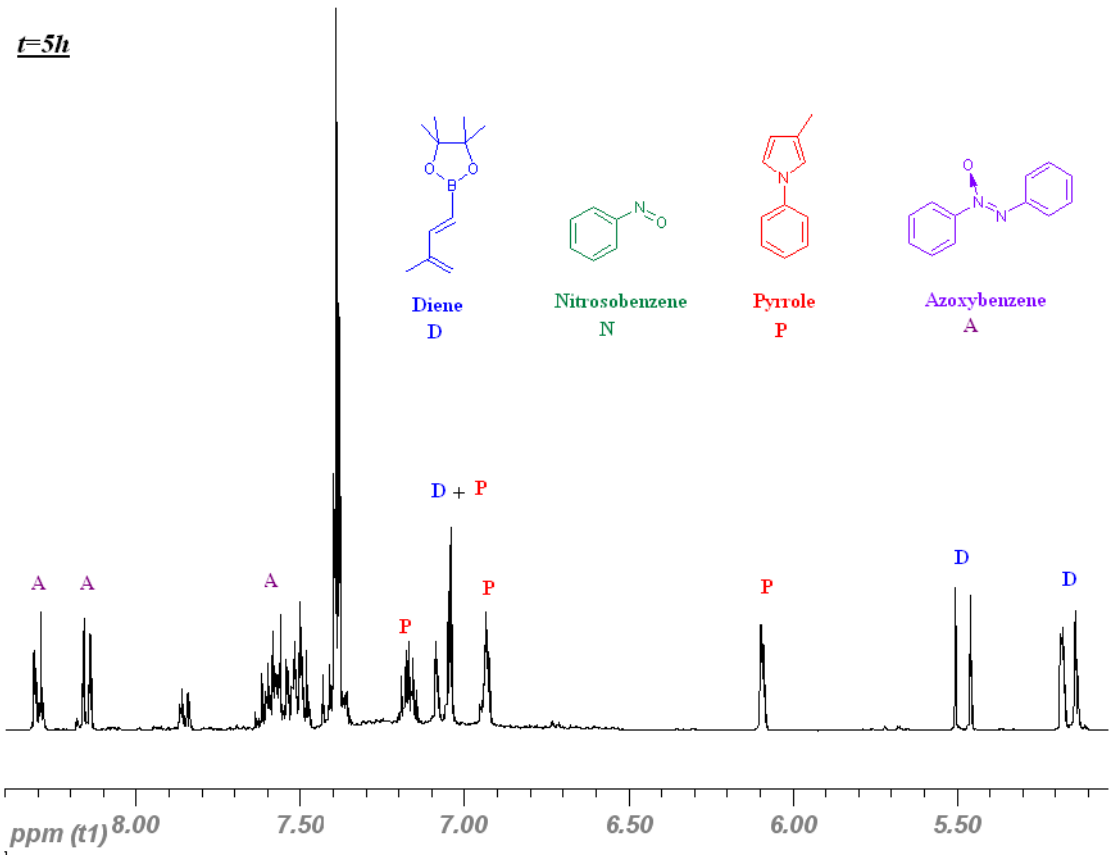
t=5mn



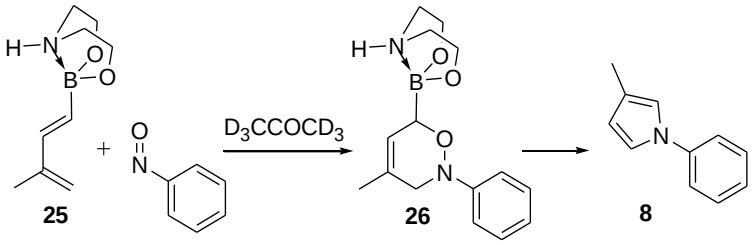
t=30 mn

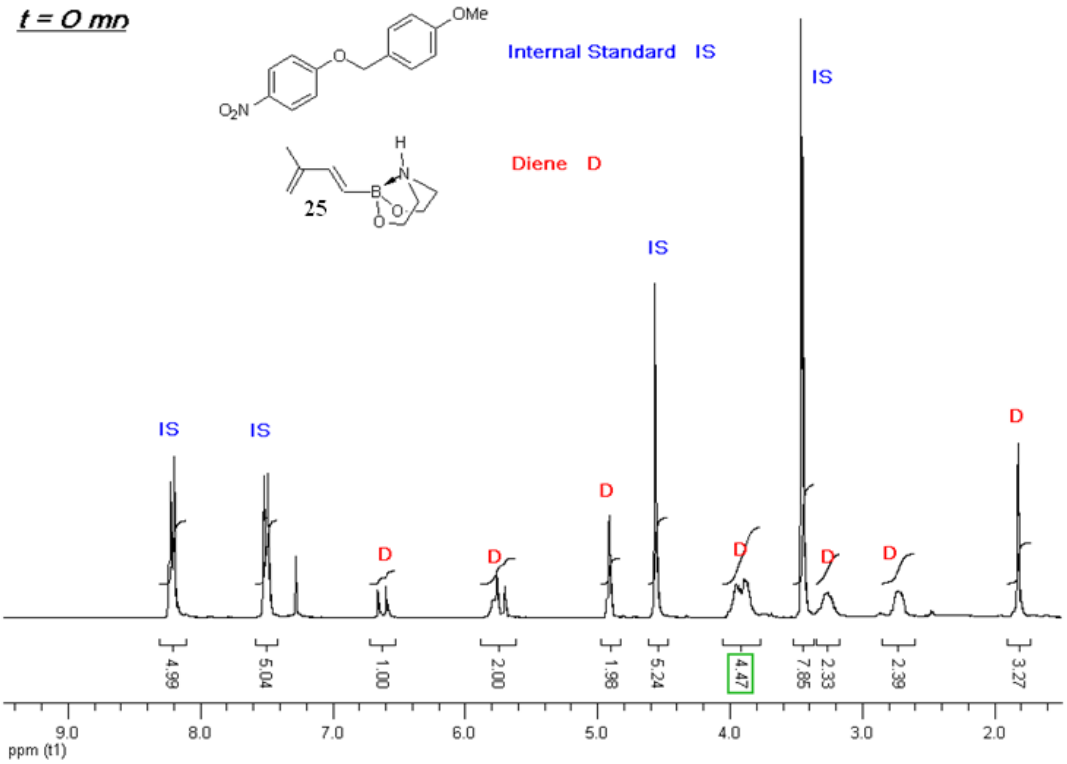


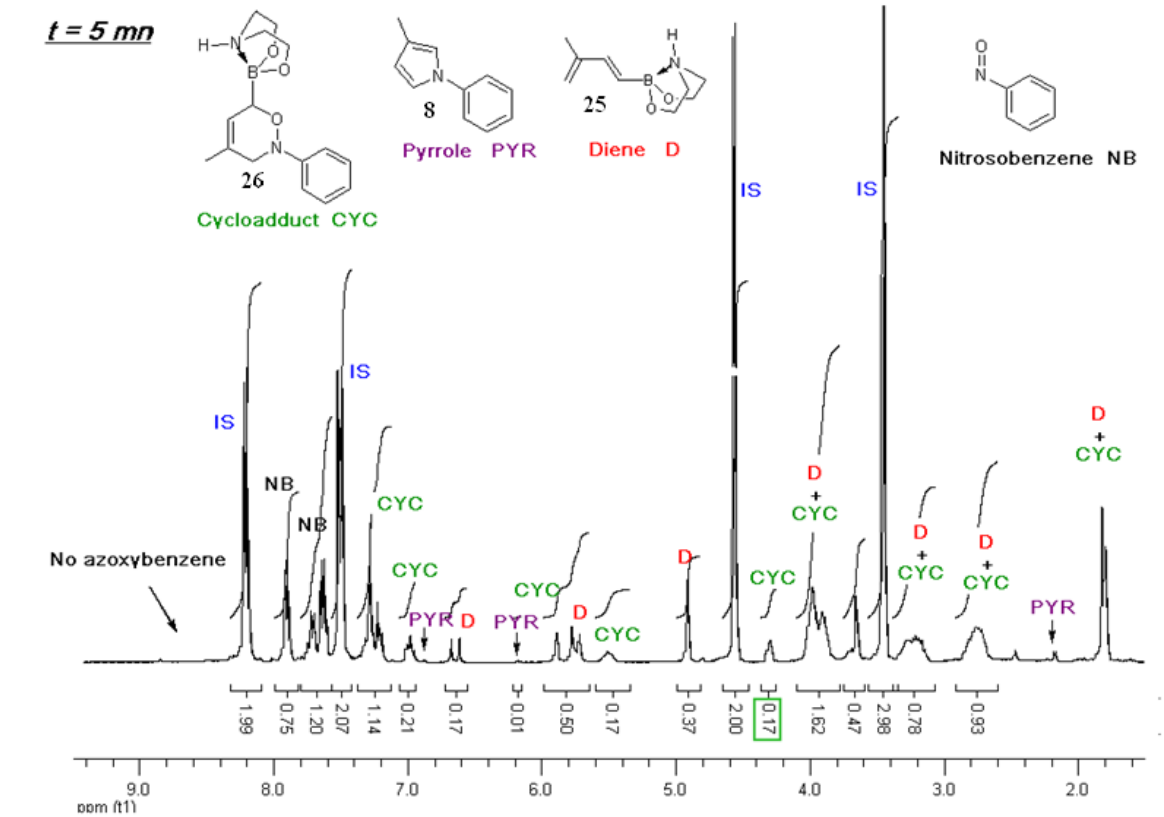

t=1h
Diene
D
Nitrosobenzene
N
Pyrrole
P
Azoxybenzene
A
D + P
A
A
A
P
P
P
D
D
ppm (t1)
8.00
7.50
7.00
6.50
6.00
5.50


t=5h
Diene
D
Nitrosobenzene
N
Pyrrole
P
Azoxybenzene
A
D + P
A
A
A
P
P
P
D
D
ppm (t1)
8.00
7.50
7.00
6.50
6.00
5.50

In situ ^{1}H NMR study of the reaction of diene 25 with nitrosobenzene



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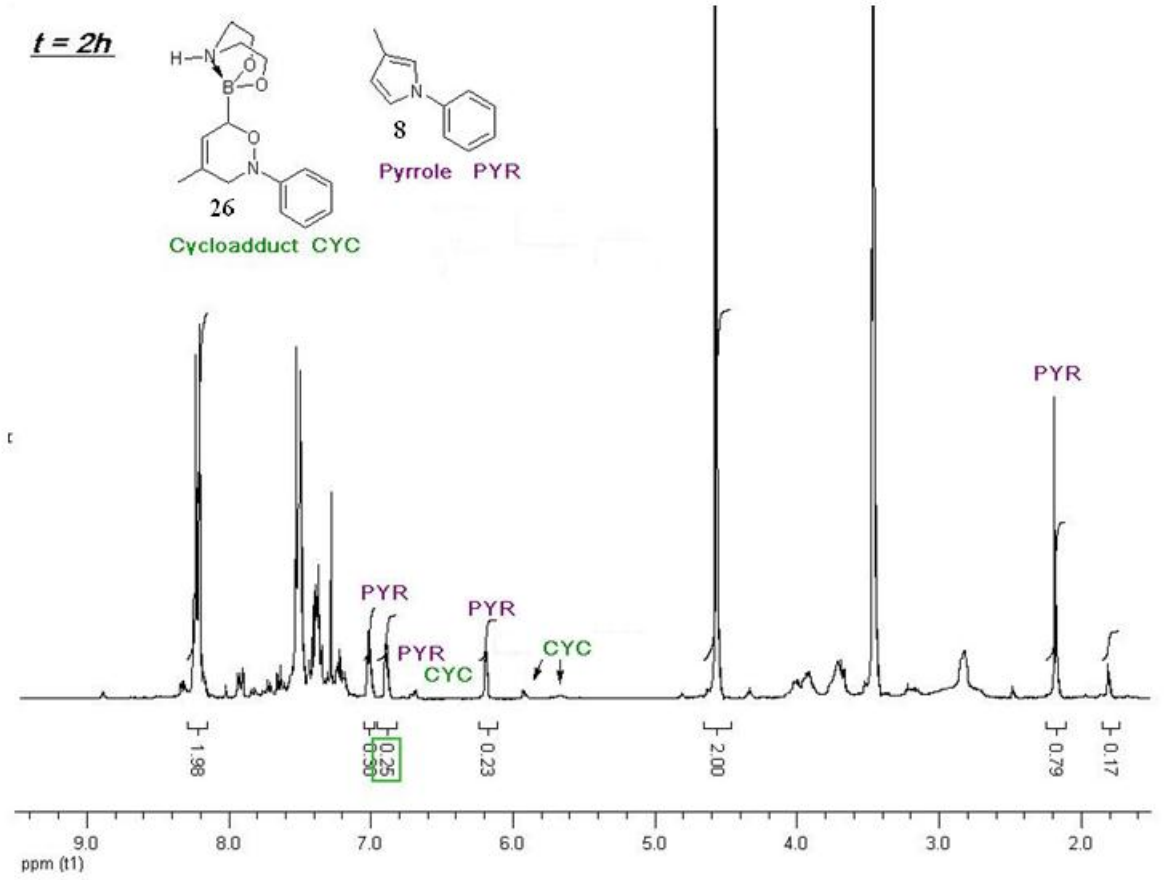
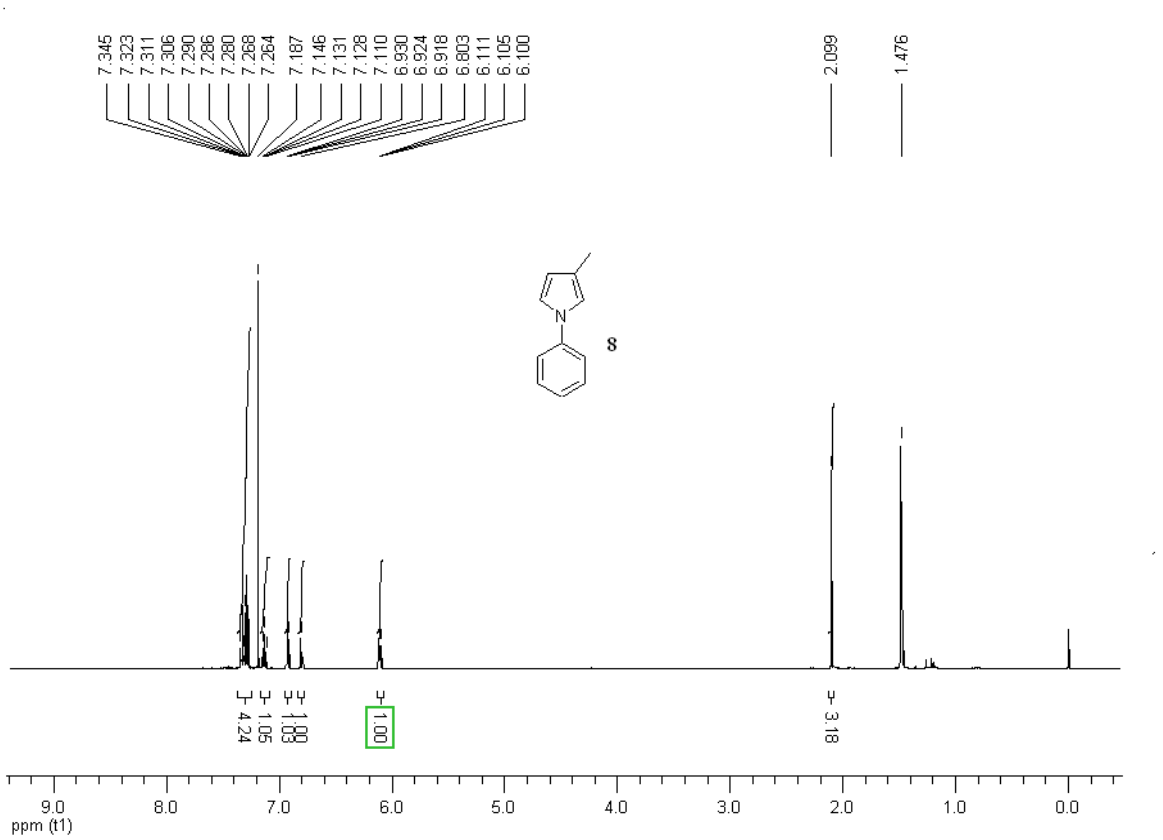
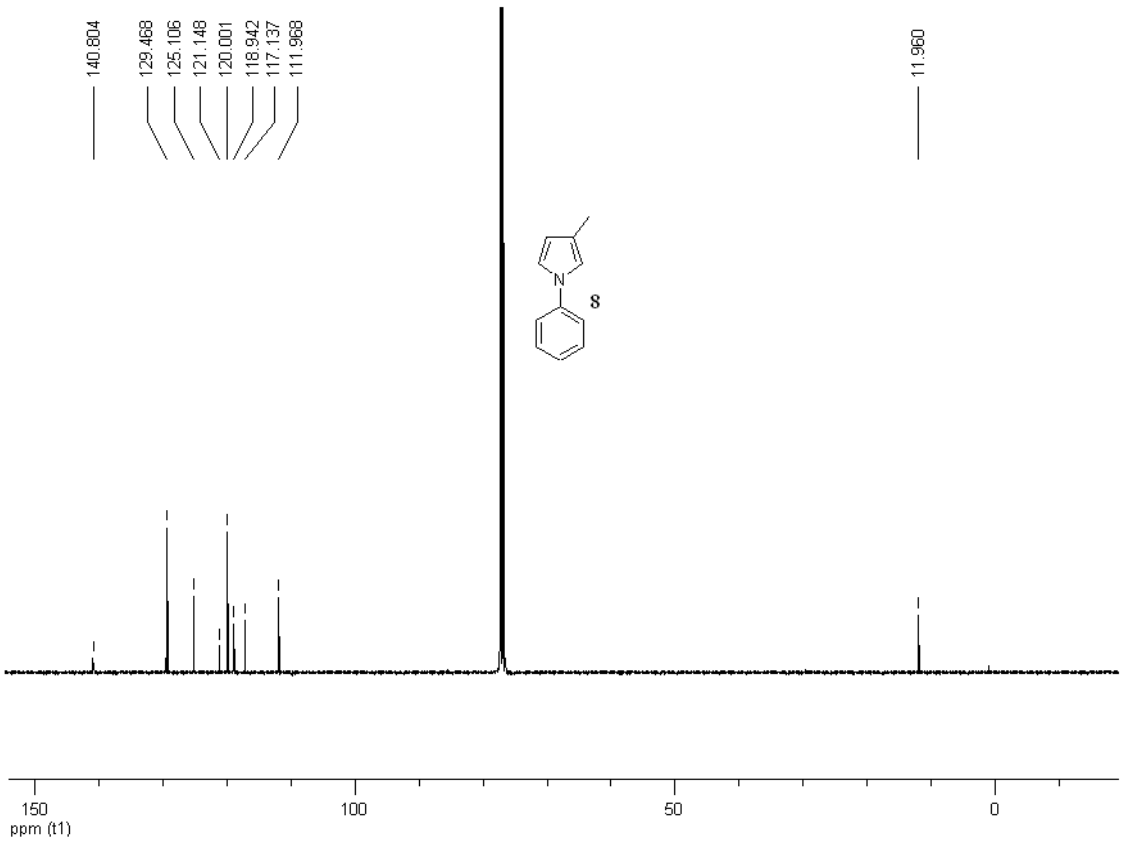
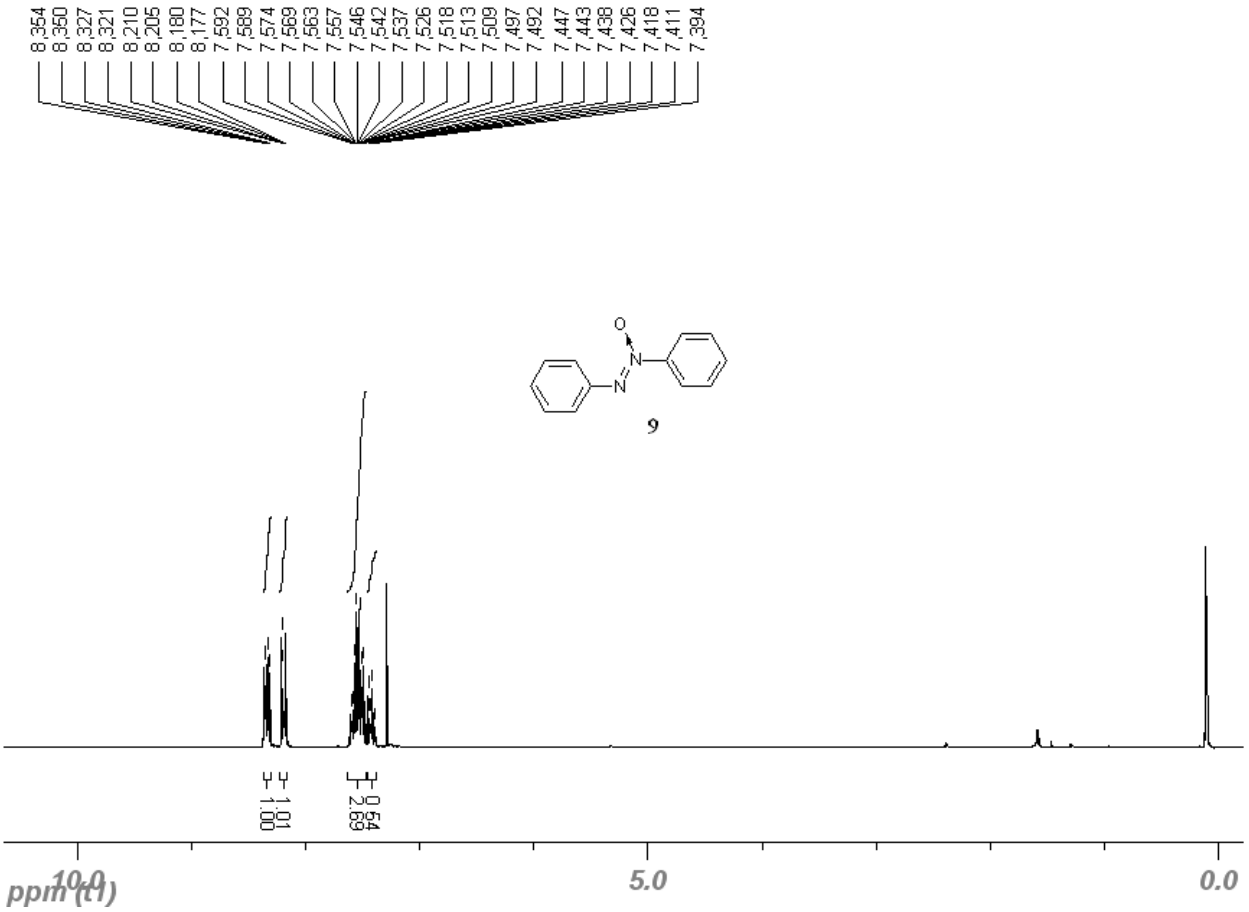
26
Cycloadduct CYC
8
Pyrrole PYR
25
Diene D
Nitrosobenzene NB
IS
NB
CYC
D
PYR
No azoxybenzene
ppm (t1)


t = 2h
26
Cycloadduct CYC
8
Pyrrole PYR
PYR
CYC
ppm (t1)

^{1}H and ^{13}C NMR spectra of pyrroles, azoxybenzene and 3,6-dihydro-2*H*-1,2-oxazine 24



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7,418
7,411
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9
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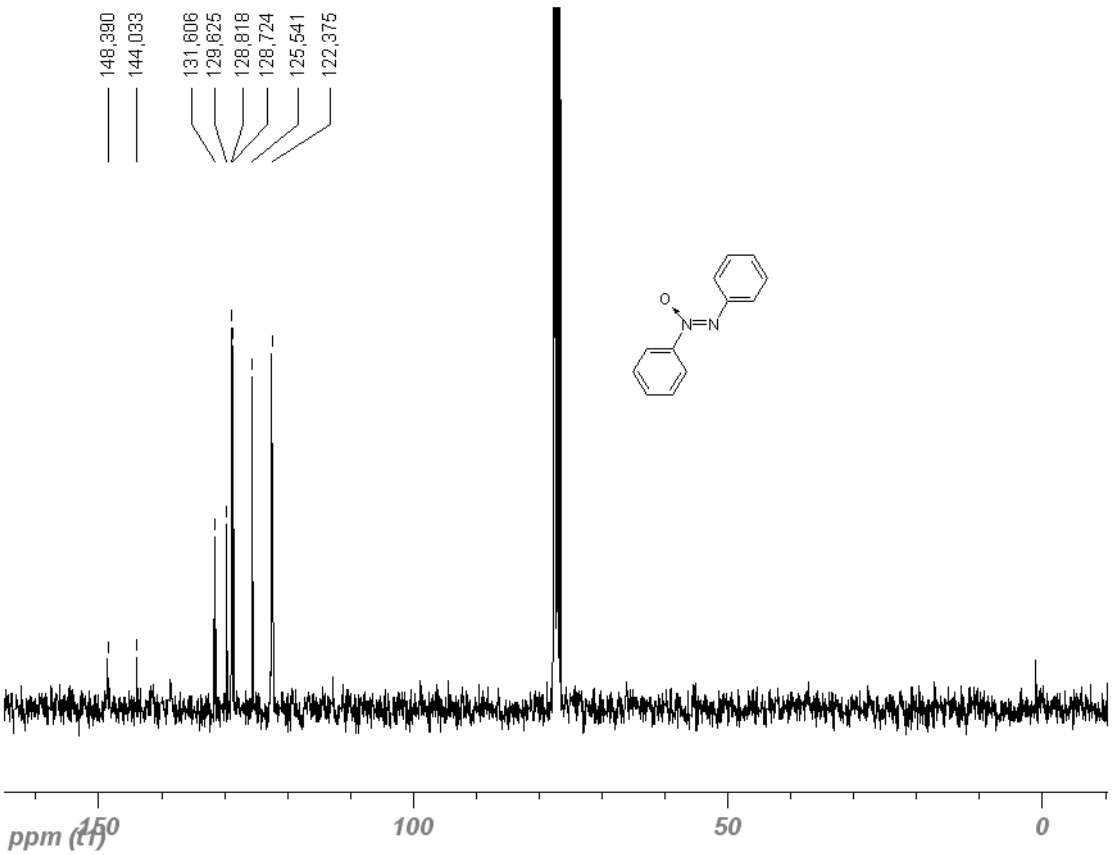
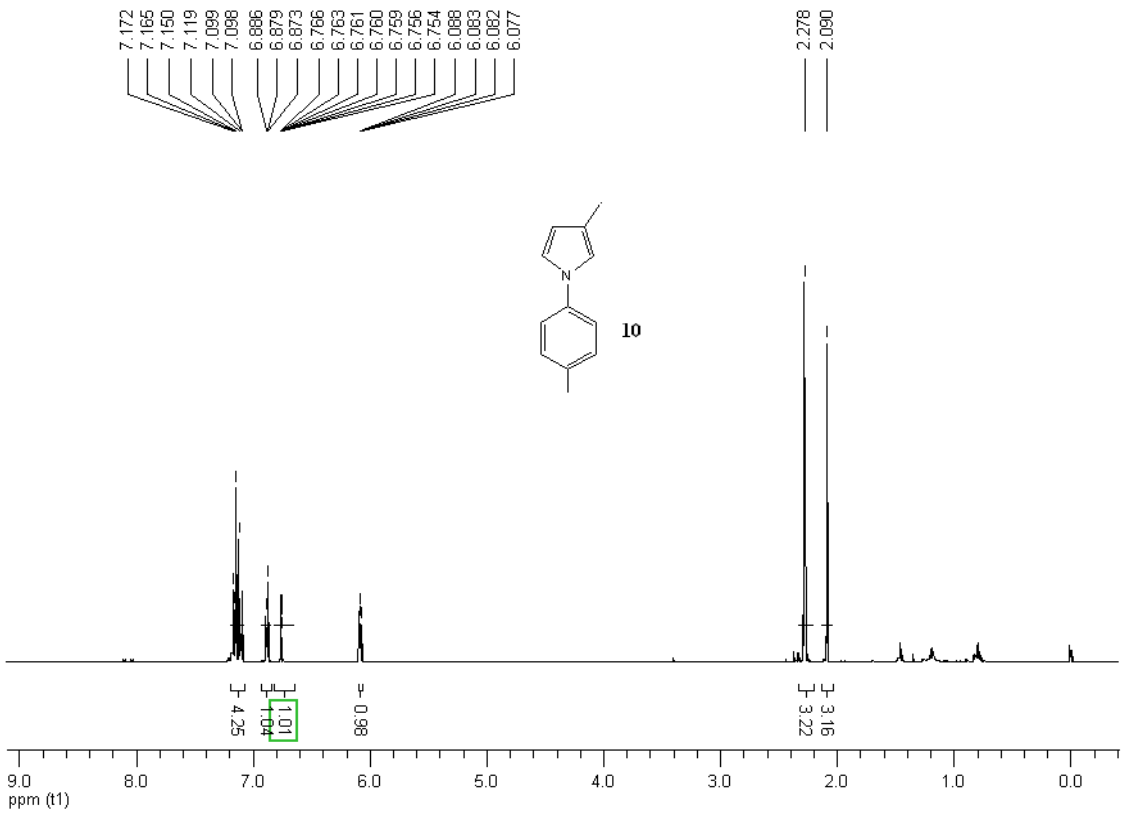
ppm (t1)


148,390
144,033
131,606
129,625
128,818
128,724
125,541
122,375
O
N=N
150
100
50
0
ppm (t1)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7.150
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7.098
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6.879
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6.766
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6.761
6.760
6.759
6.756
6.754
6.088
6.083
6.082
6.077
2.278
2.090
N
10
4.25
1.04
1.01
0.98
3.22
3.16
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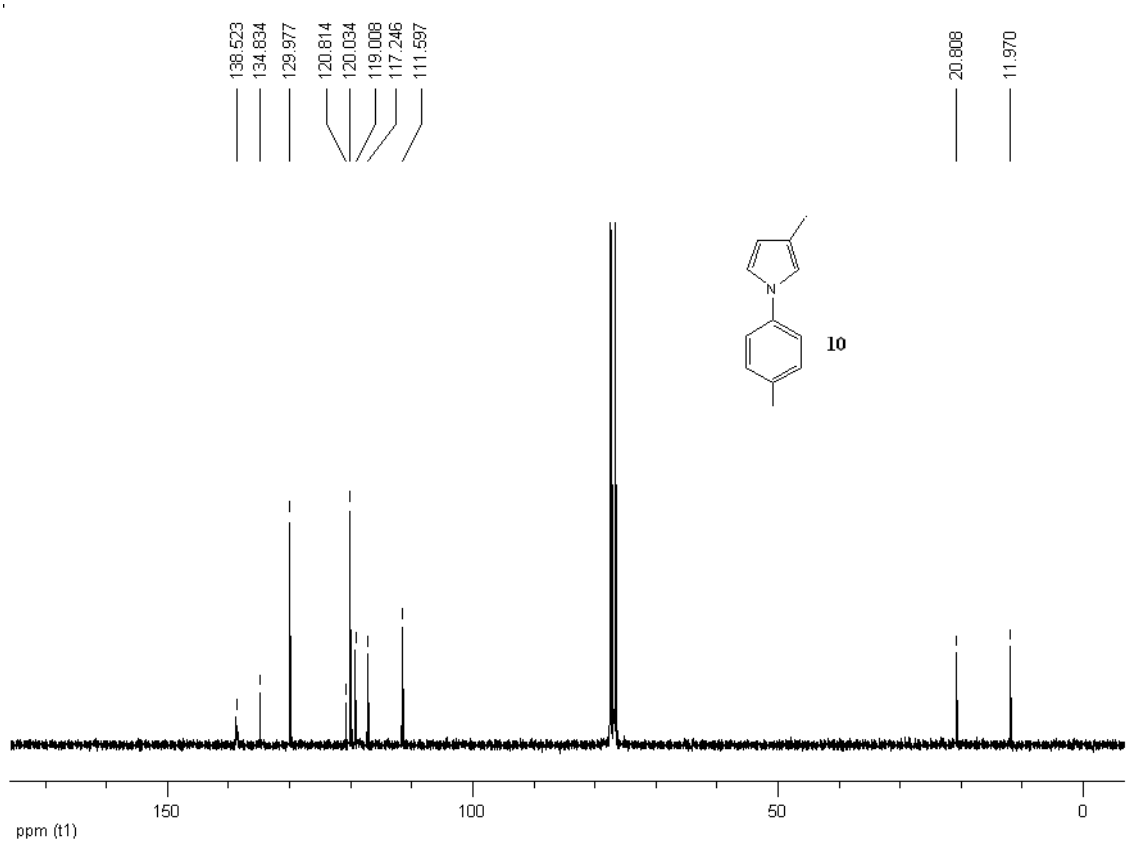
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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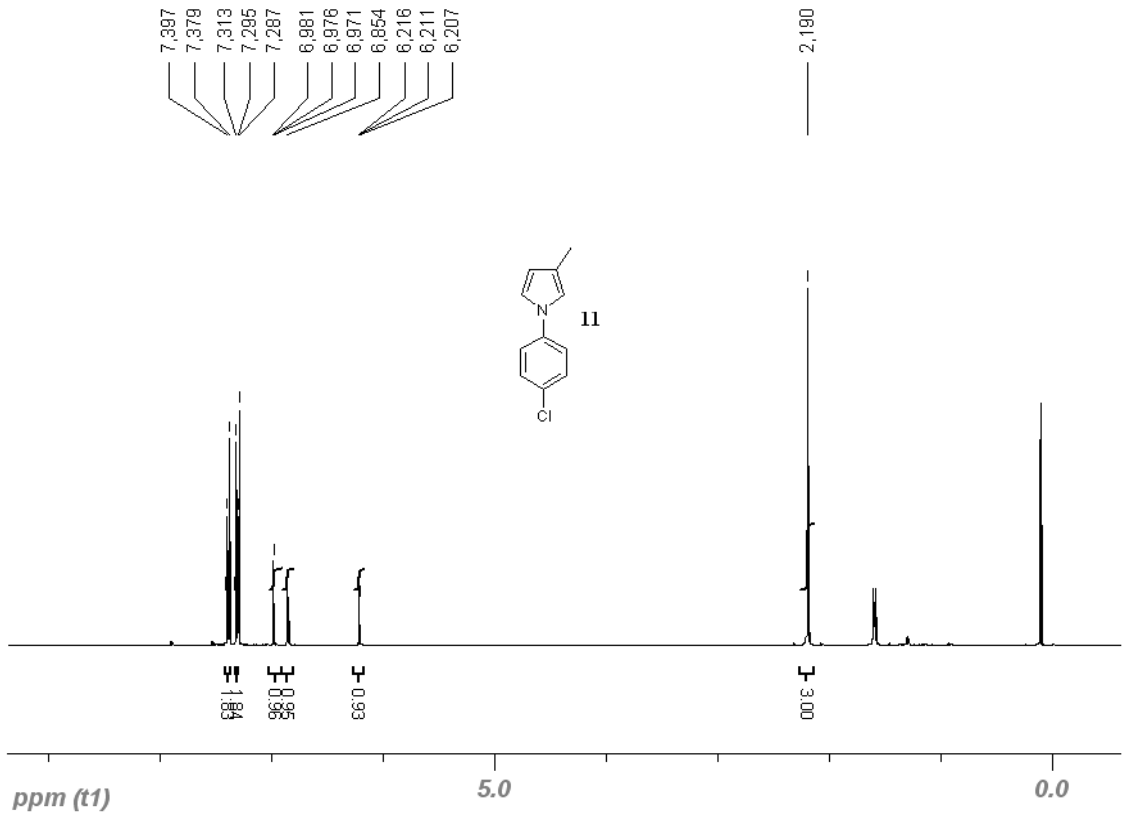
134.834
129.977
120.814
120.034
119.008
117.246
111.597
20.808
11.970
N
10
150
100
50
0
ppm (t1)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7,287
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6,976
6,971
6,854
6,216
6,211
6,207
2,190
11
Cl
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0,96
0,93
3,00
ppm (t1)
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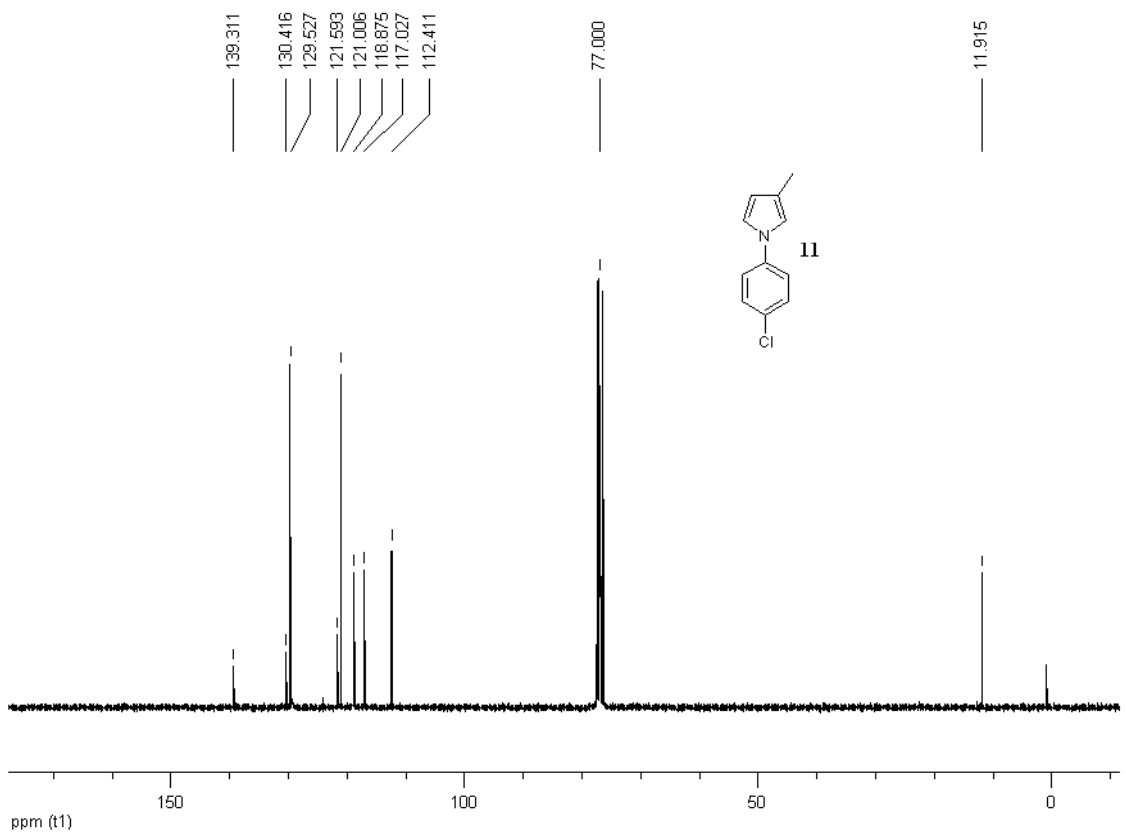
0.0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121.006
118.875
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112.411
77.000
11.915
11
Cl
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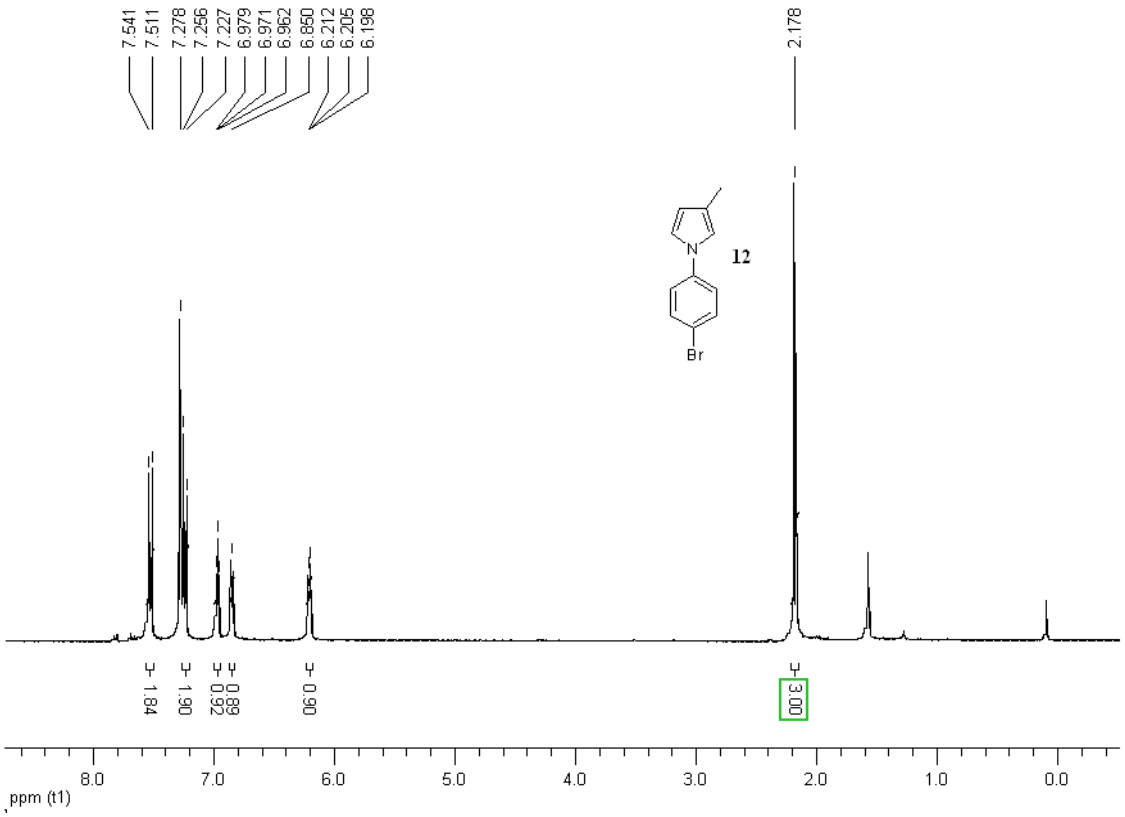
100
50
0
ppm (t1)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6.198
2.178
12
Br
1.84
1.90
0.92
0.88
0.90
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7.0
6.0
5.0
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3.0
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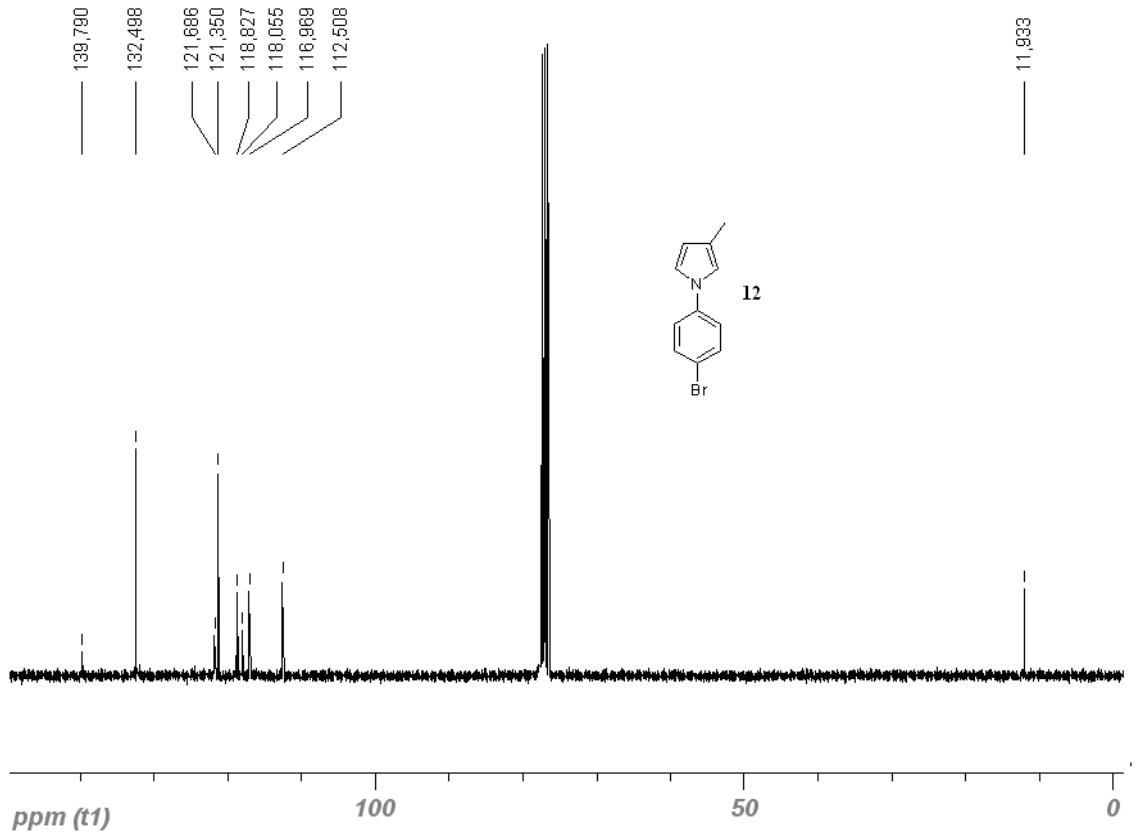
1.0
0.0
ppm (t1)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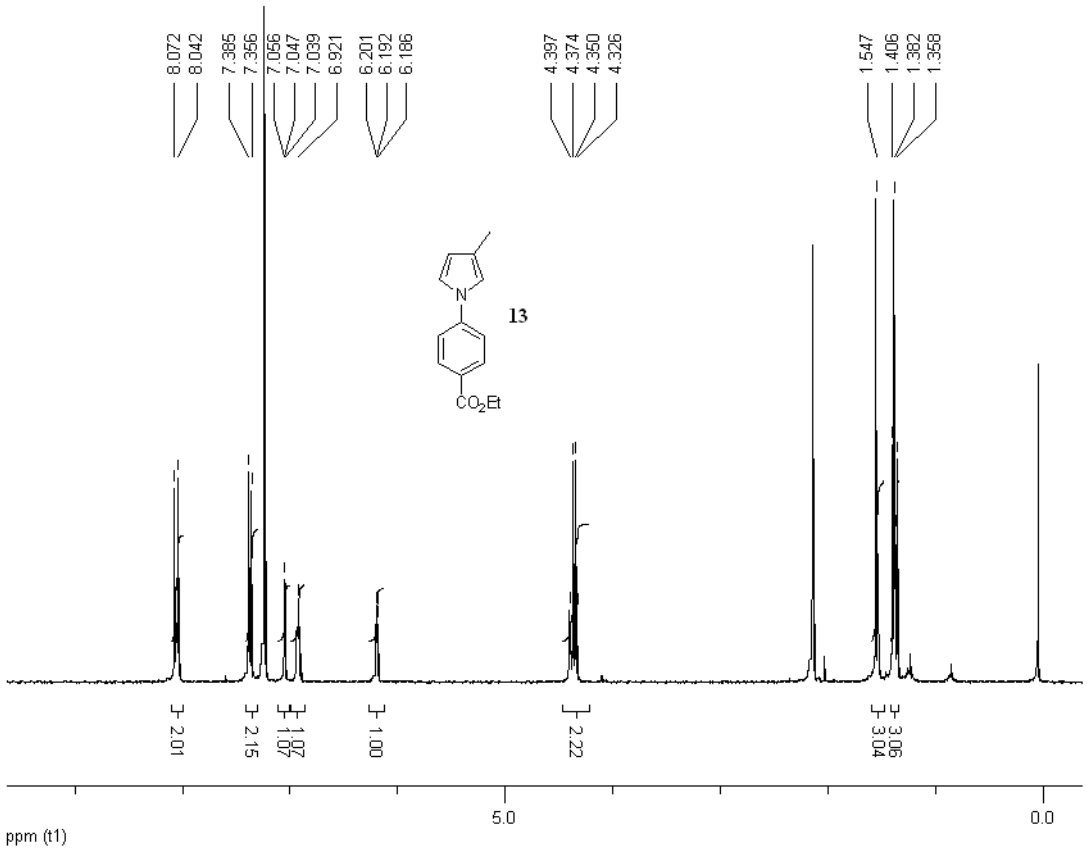
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8.042
7.385
7.356
7.066
7.047
7.039
6.921
6.201
6.192
6.186
4.397
4.374
4.350
4.326
1.547
1.406
1.382
1.358
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CO2Et
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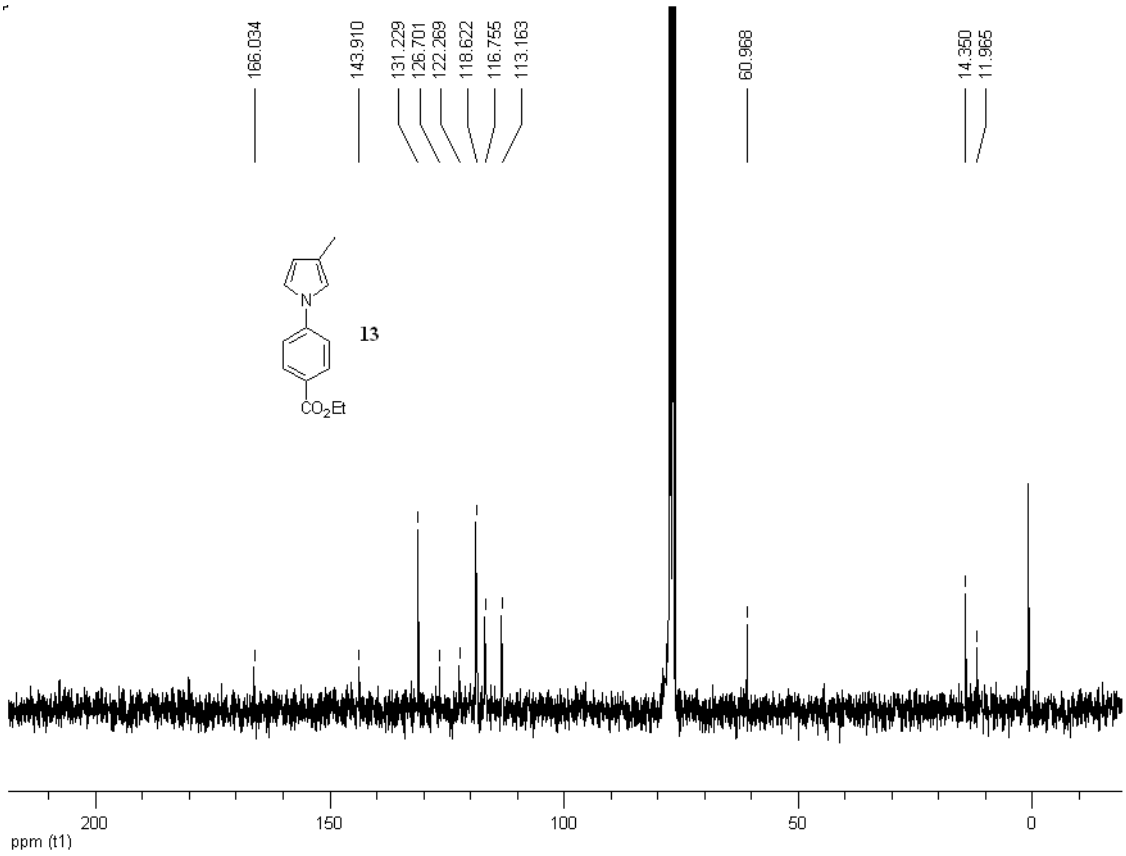
2.15
1.07
1.00
2.22
3.04
3.06
5.0
0.0
ppm (t1)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122.269
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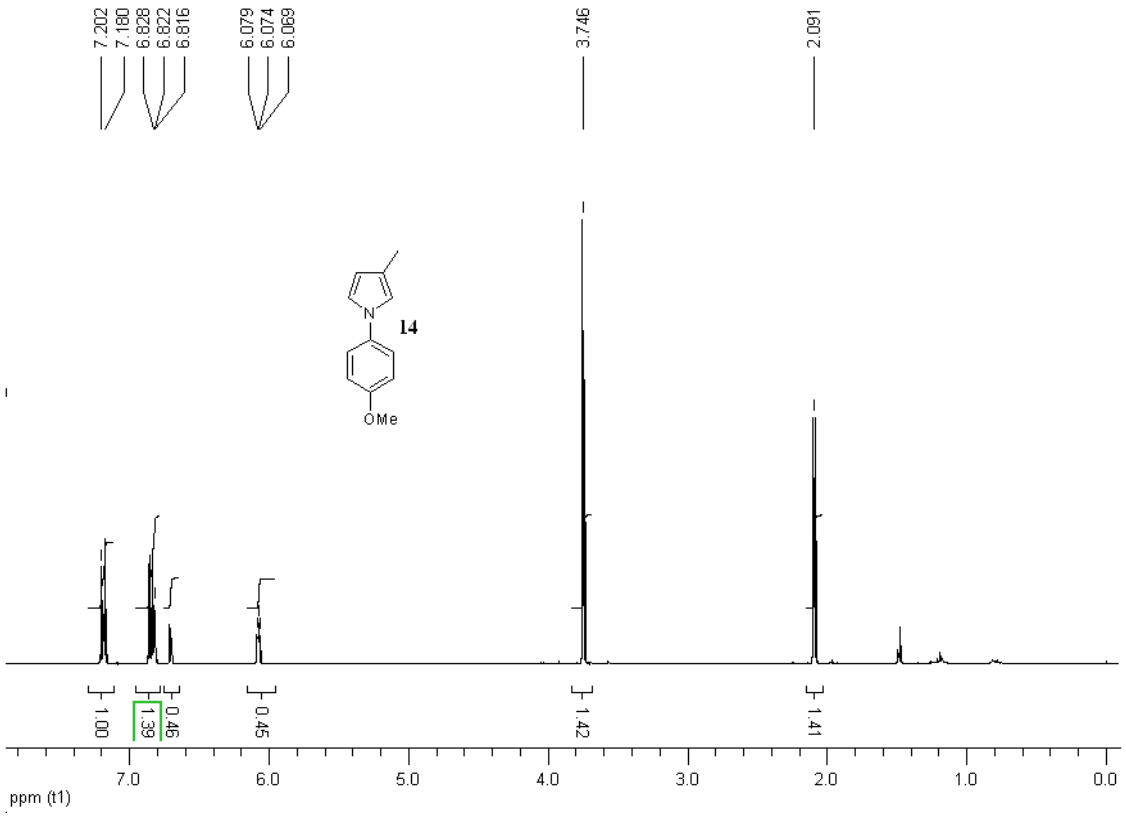
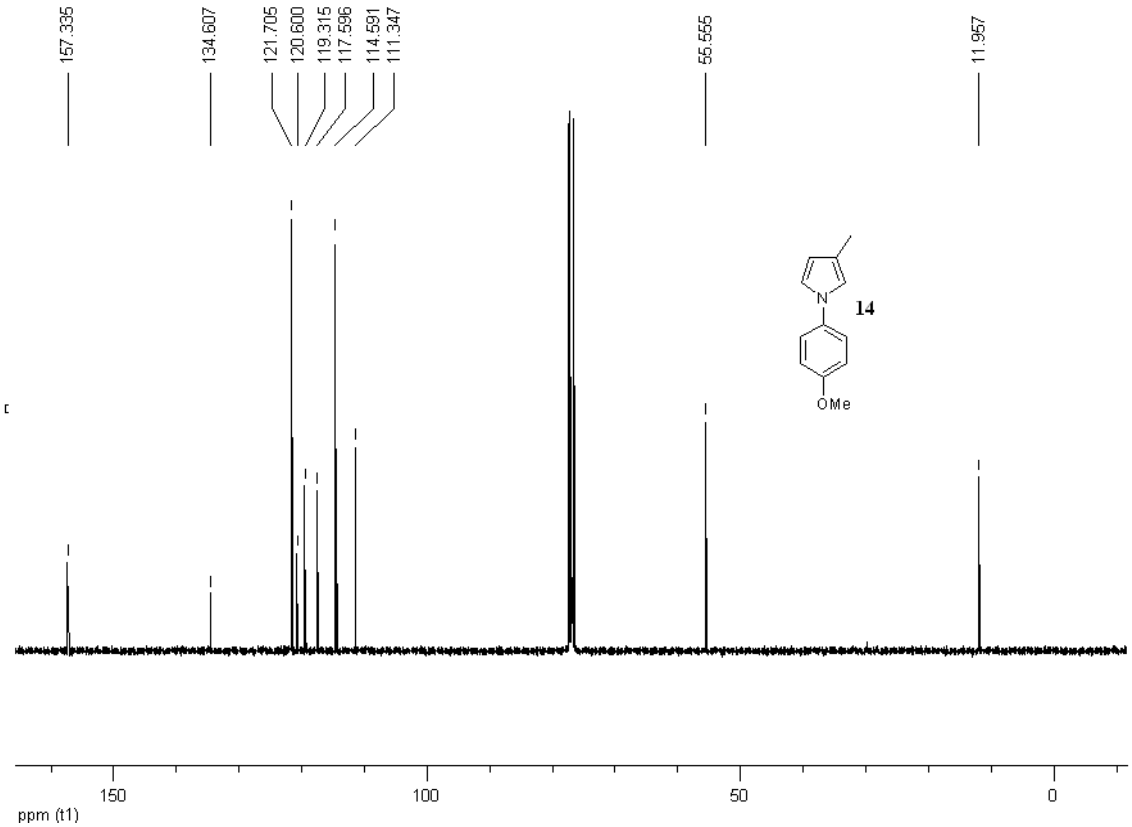
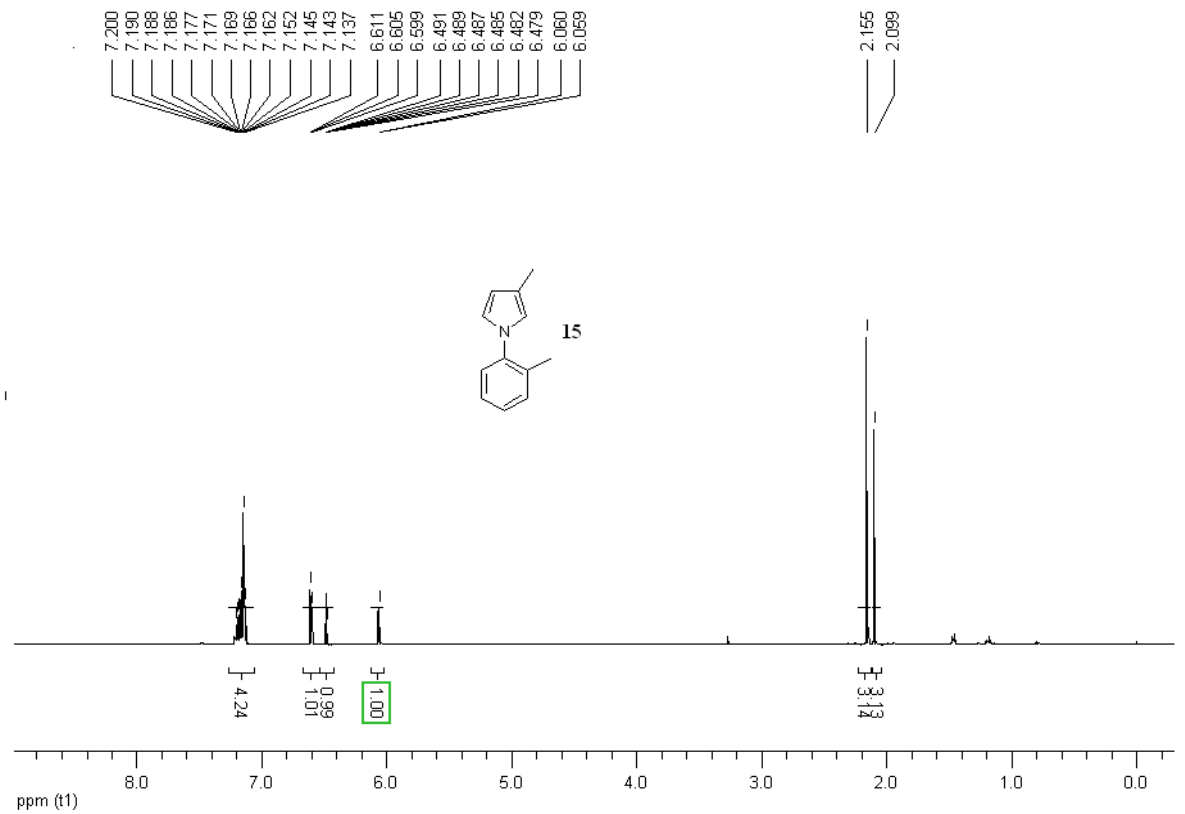
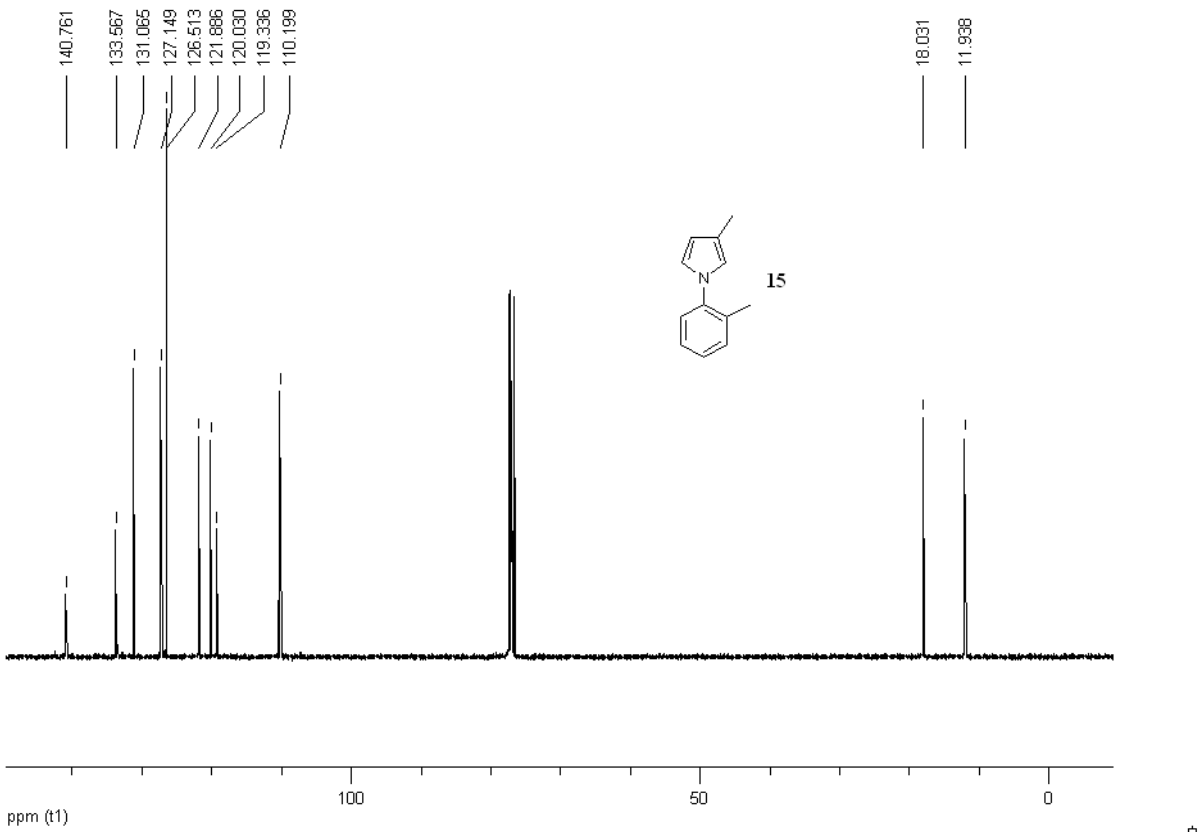
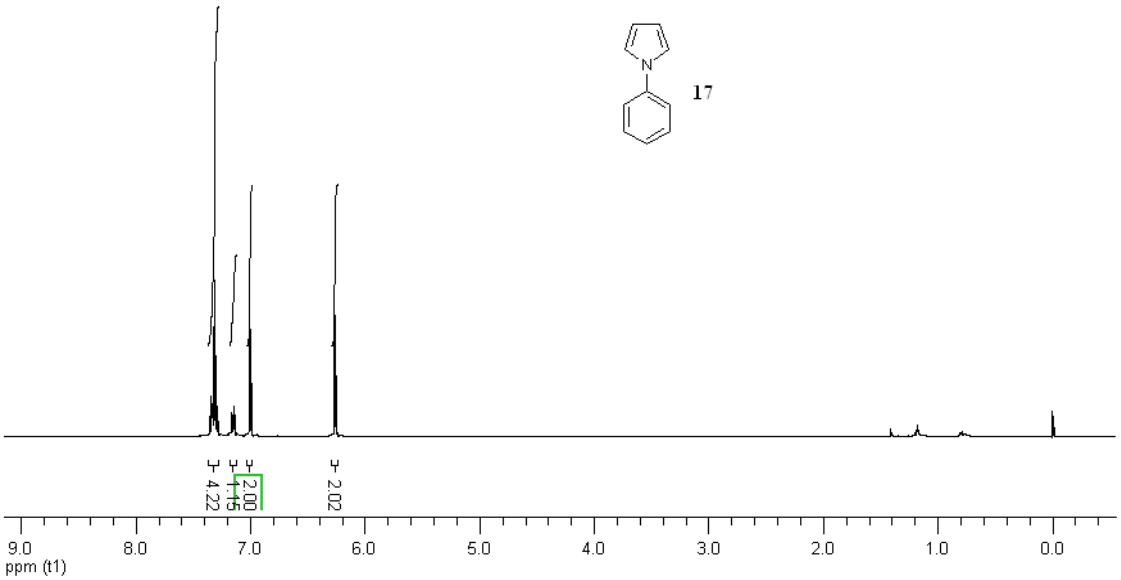
14.350
11.965
13
CO2Et
200
150
100
50
0
ppm (t1)

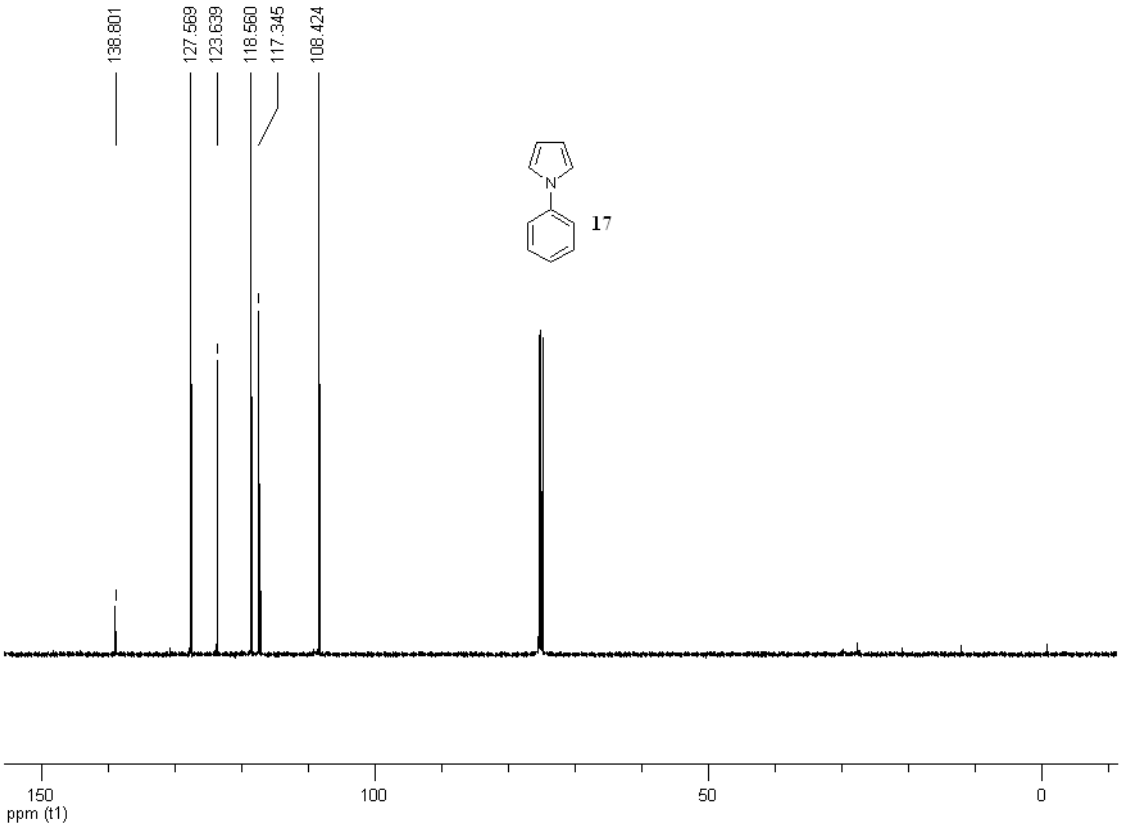


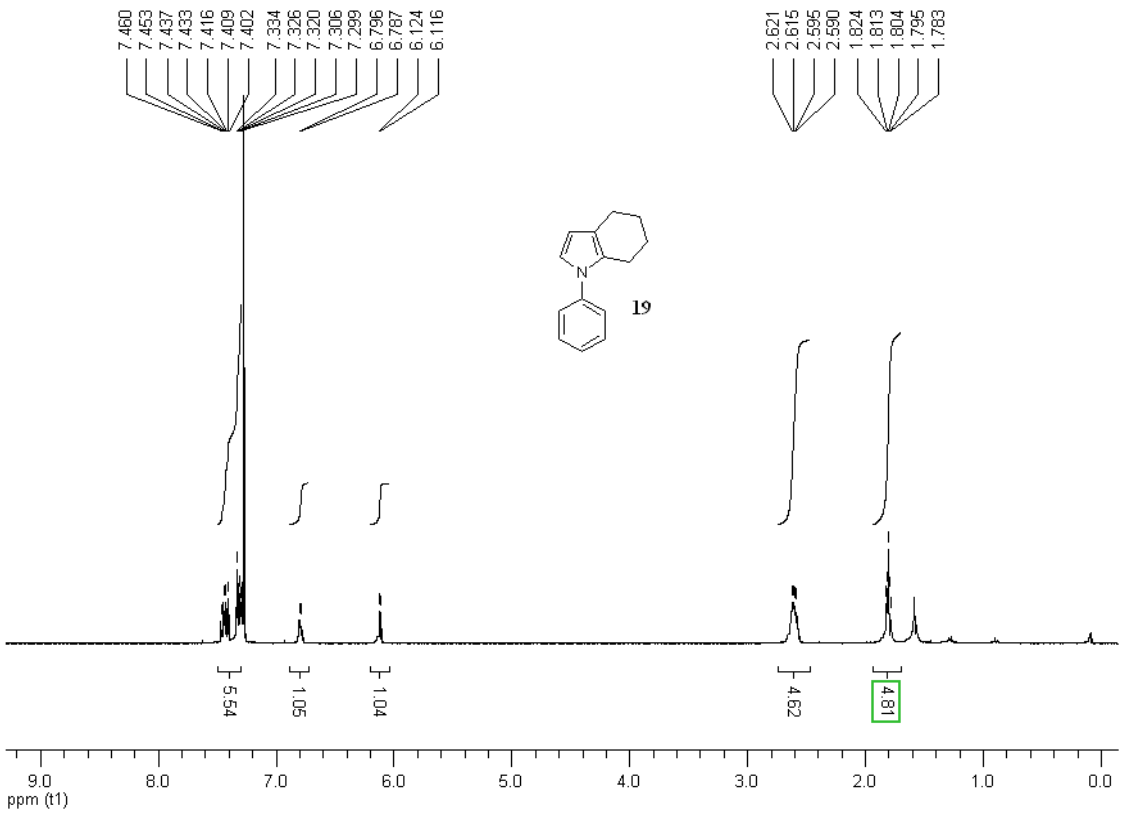








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6.124
6.116
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2.595
2.590
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1.813
1.804
1.795
1.783
19
5.54
1.05
1.04
4.62
4.81
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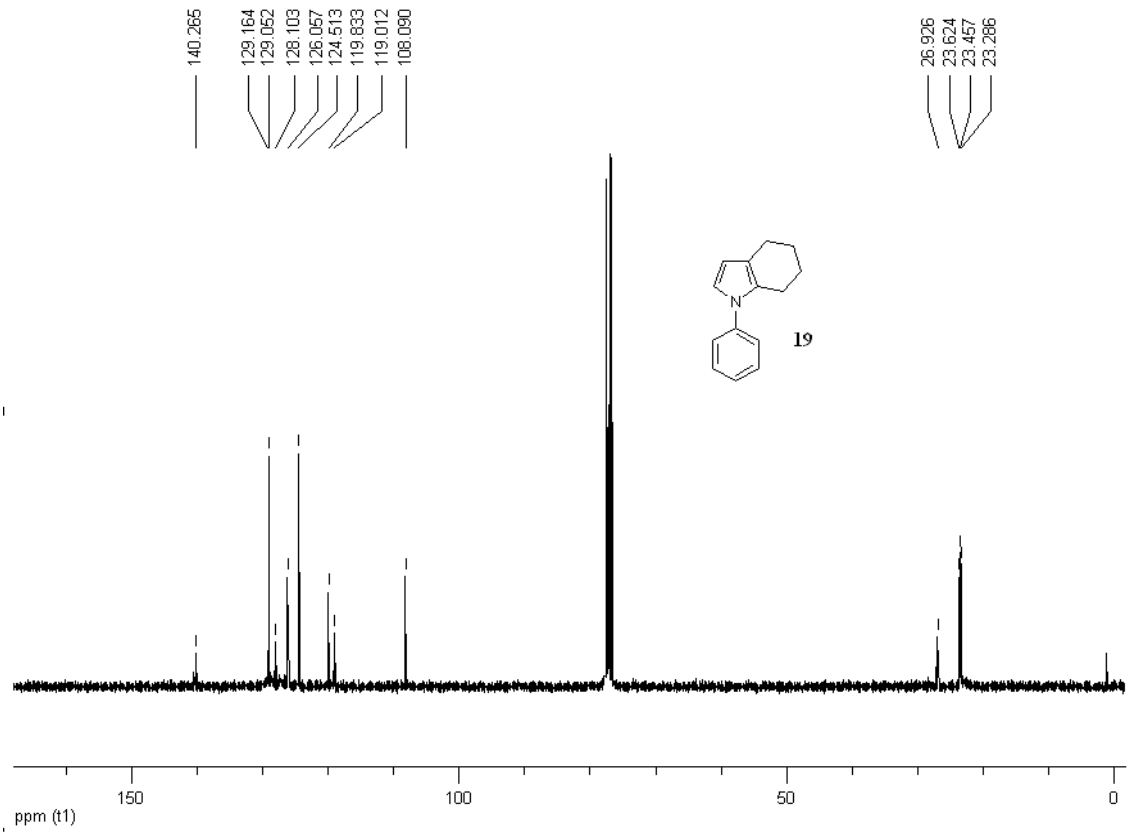
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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129.052
128.103
126.057
124.513
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108.090
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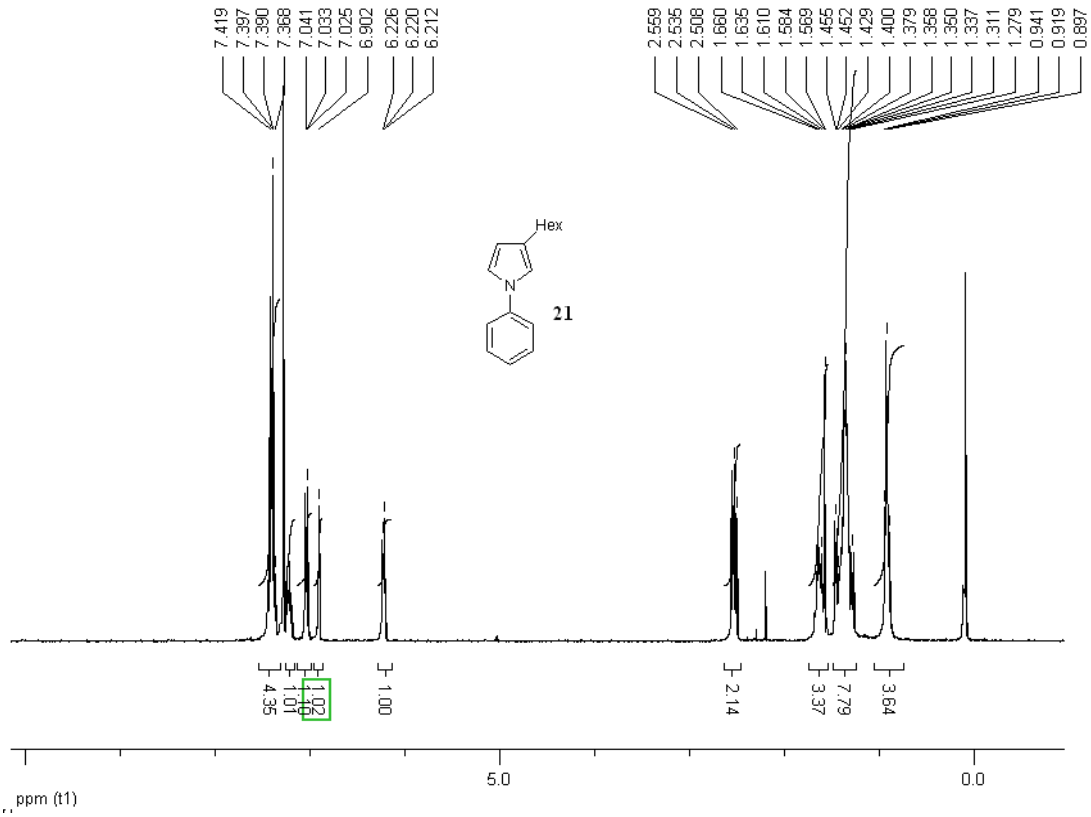
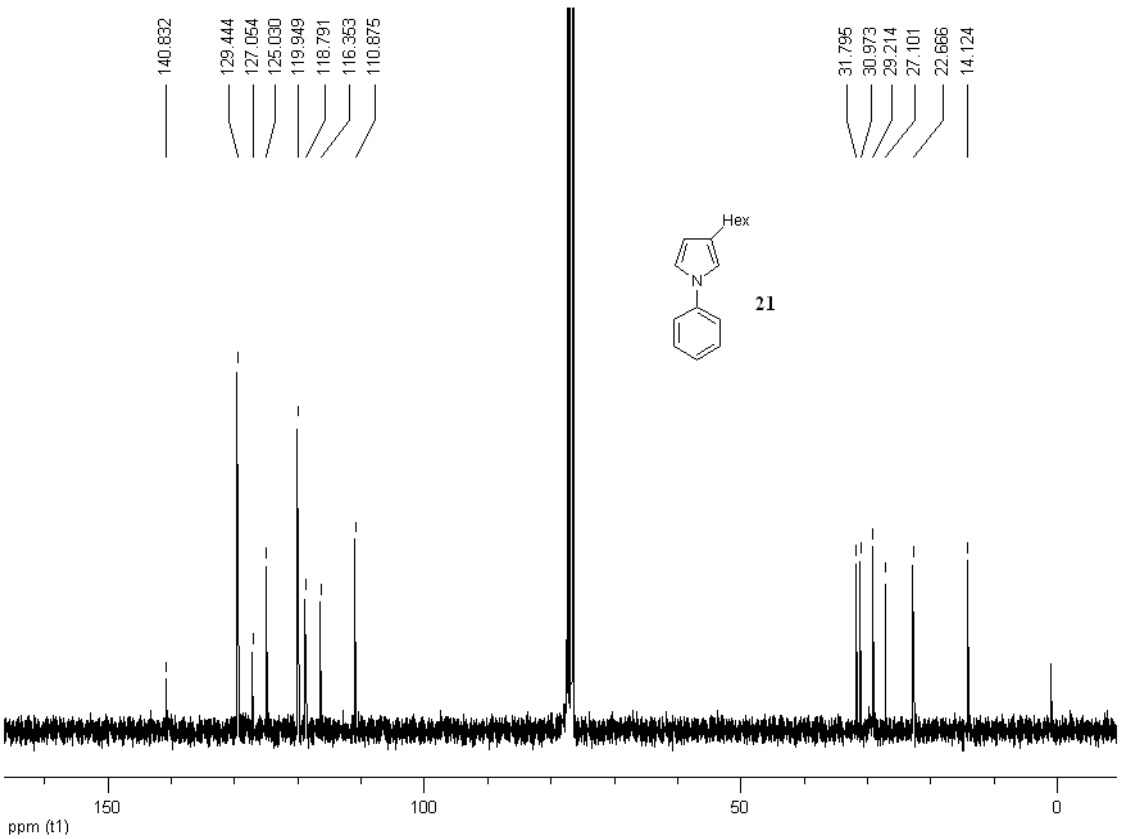
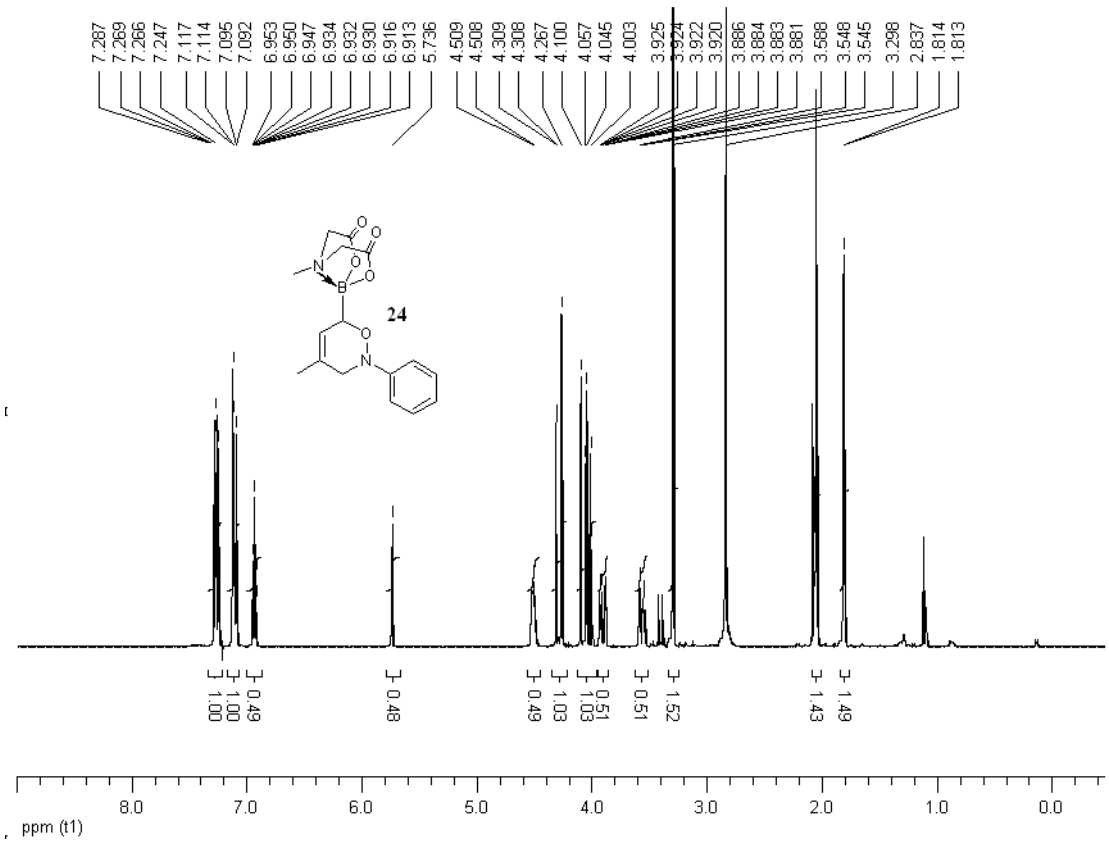
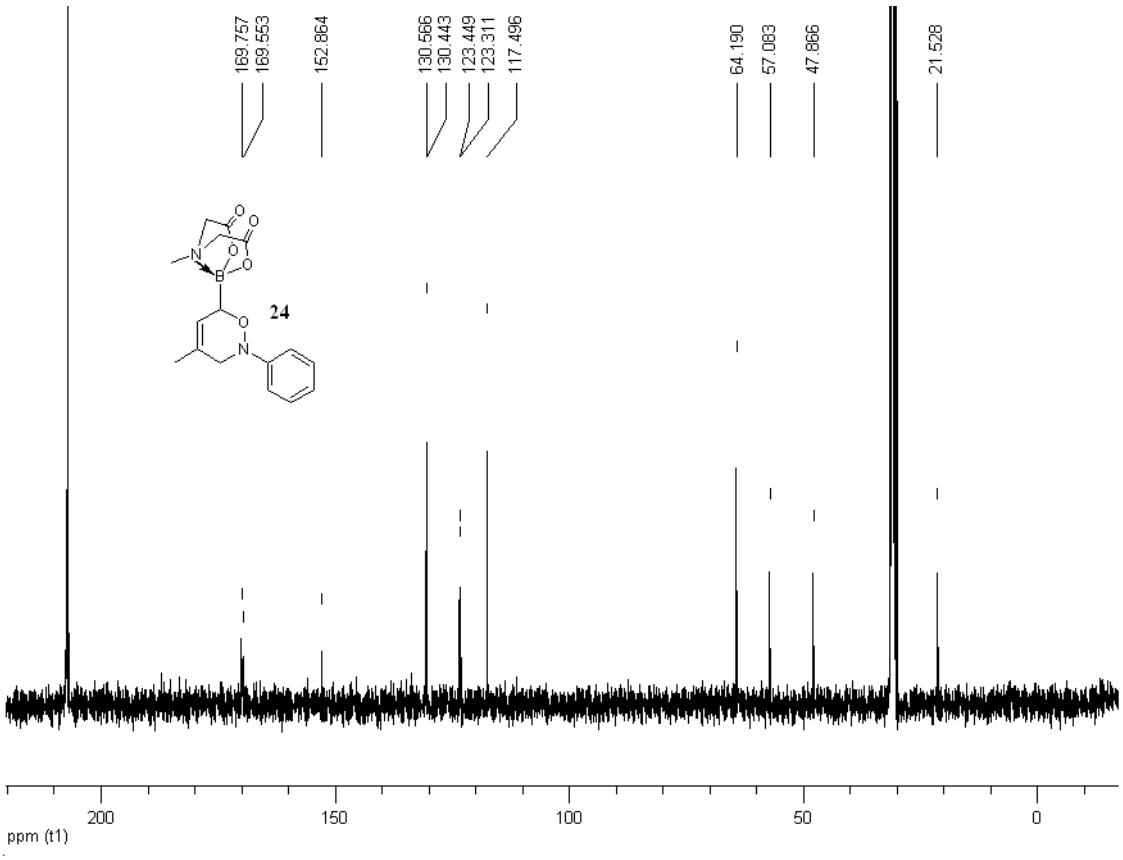
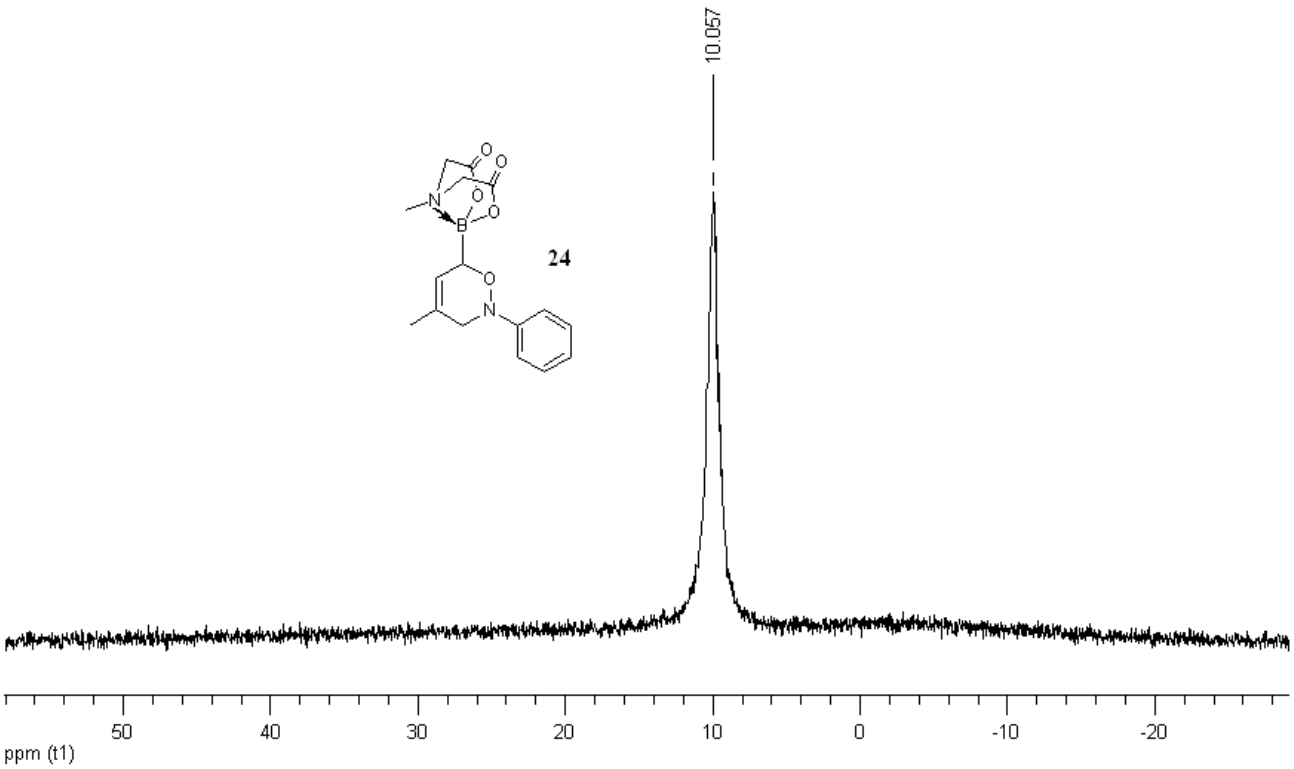
23.624
23.457
23.286
19
150
100
50
0
ppm (t1)







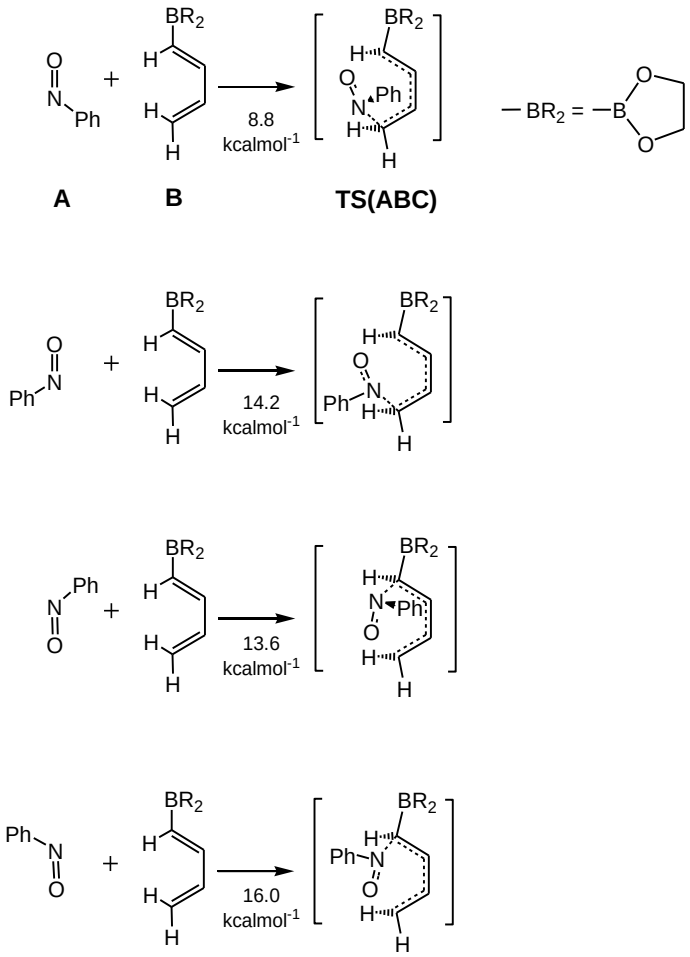




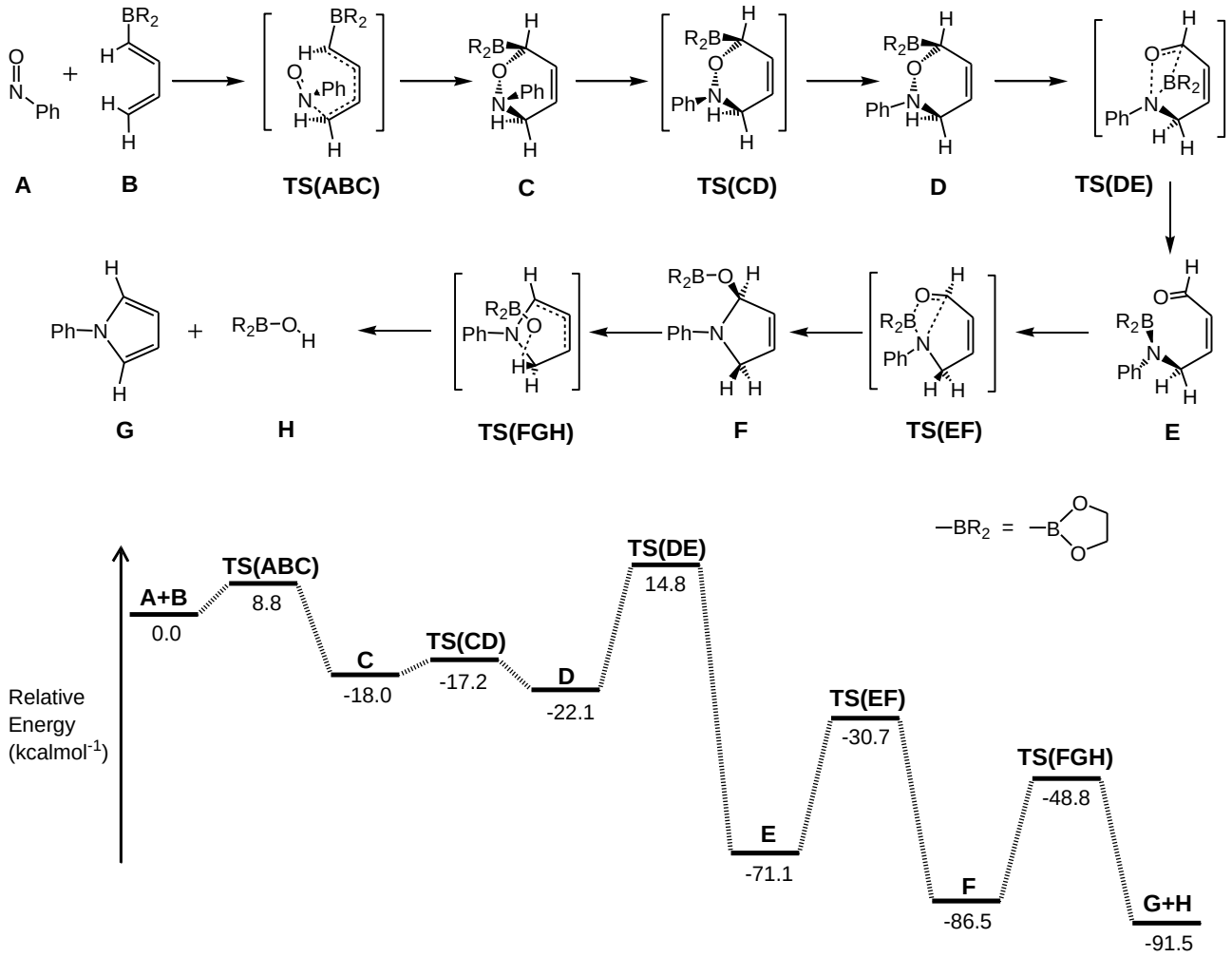
Computations

All computations were carried out with the Gaussian 09 package.[Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr., J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian, Inc.*, Wallingford CT, **2009**.] The geometries discussed in Schemes 1 and 2 were optimised at the B3LYP/6-31G* level [(a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648-5652; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* **1988***, 37*, 785-789 ; (c) G. A. Petersson and M. A. Al-Laham, *J. Chem. Phys.* 1991, **94**, 6081-6090; (d) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. Mantzaris, *J. Chem. Phys.,* **1988**, *89*, 2193-

2218.] with no symmetry constraints. The optimised geometries were found to be true minima based on no imaginary frequencies obtained from frequency calculations. The transition-state (TS) geometries were located using the OPT=QST3 method. Frequency calculations on TS geometries revealed one imaginary frequency for each geometry. All intrinstic reaction pathways shown in Schemes 1 and 2 were determined from transition state geometries using the IRC command.



Scheme 1. Four different pathways and their TS energies determined by computations in the Diels-Alder reaction of nitrosobenzene and the 1-boronodiene model molecule. Computations on simpler systems have been reported elsewhere. [A. G. Leach and K. N. Houk, *J. Org. Chem.*, **2001**, *66*, 5192-5200.]



Scheme 2. Likely reaction steps in the formation of 1-phenyl-1*H*-pyrrole from a 1-boronodiene model and nitrosobenzene.

For animations of these steps, see http://www.dur.ac.uk/m.a.fox/Tripoteau.ppt

There are eight possible conformers of the oxazine where a) the boryl group occupy either the axial or equatorial positions, b) the phenyl group is *exo* or *endo* and c) the oxazine ring is a boat or chair conformation. While **C** and **D** are likely products from the favourable Diels-Alder pathway via **TS(ABC)** with **D** as the most stable conformer of all possible conformers of the oxazine, the next most stable conformer **I** has the boryl group at the equatorial position instead of the axial position in **D**. An alternative pathway to **E** from oxazine **I** is found via boryl migration to the oxygen atom. A direct step from the oxazine **I** (or **D**) to **F** via the migration of boron from carbon to oxygen with simultaneous migration of nitrogen to carbon from oxygen could not be determined.

The rate limiting step in the reaction pathway is likely to be the hetero-Diels-Alder step or the ring cleavage step via boryl group rearrangement. This important point will be examined in detail elsewhere by exploring more boronodiene - nitrosobenzene reactions experimentally and computationally.

The formation of pyrrole **G** from **F** is not necessarily concerted as it could be viewed as R_2BO^- elimination followed by loss of proton from the iminium cation. The calculated Mulliken charges in the **TS(FGH)** geometry are -0.72 a.u. for the R_2BO moiety and +0.72 a.u. for the $PhNC_4H_5$ part. This suggests that the R_2BO anion could dissociate from the iminium cation in a polar solvent and thus the path would be stepwise rather than concerted. The calculations here are based on a solvent-free 'gas-phase' environment.