Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Mild and ambient annulations for pyrrole synthesis from amines and arylacetaldehydes

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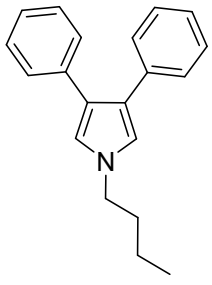
A. General method

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. High-resolution mass spectra were obtained with Shimadazu LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. All the other chemicals were purchased without further purification.

B. General procedure

Procedure for the synthesis of pyrrole from corresponding alkylamines and arylacetaldehydes. To the mixture of alkylamine (0.3 mmol, 0.6 equiv) and arylacetaldehyde (0.5 mmol, 1.0 equiv), $Cu(OTf)_2$ (5 mol%), and DMF (1 mL) were added successively. The mixture was stirred under air at 40 ^{o}C for 24 h. Upon completion, the crude product was flushed through a short column of silica gel with ethyl acetate, and, after rotary evaporation, the residue was separated by flash column chromatography on silica gel to give the pure product.

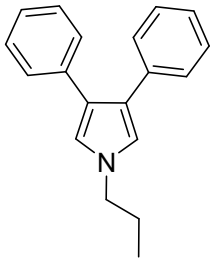
C. Analytical data for the products prepared



1-butyl-3,4-diphenyl-1H-pyrrole (3a)

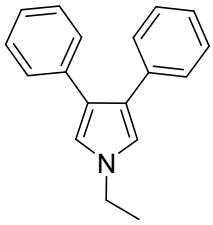
Light yellow oil. IR (KBr, cm^{-1}) ν 2956, 2927, 1698, 1538, 1176, 758, 695. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.20 (m, 8H), 7.18–7.13 (m, 2H), 6.75 (s, 2H), 3.89 (t, J = 7.2 Hz, 2H),

1.87–1.75 (m, 2H), 1.44–1.35 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 128.3, 128.1, 125.4, 122.9, 120.2, 49.5, 33.4, 20.0, 13.7. HRMS (ESI), calcd for $C_{20}H_{21}N$ $[M+H]^+$ 276.1747, found 276.1736.



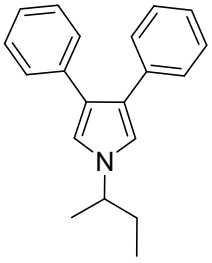
3,4-diphenyl-1-propyl-1H-pyrrole (3b)

Light yellow oil. IR (KBr, cm^{-1}) v 2964, 2931, 1539, 1399, 1179, 760, 698. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.12 (m, 10H), 6.74 (s, 2H), 3.83 (t, J = 7.0 Hz, 2H), 1.92–1.76 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 128.3, 128.1, 125.4, 123.0, 120.2, 51.5, 24.6, 11.4. HRMS (ESI), calcd for $C_{19}H_{19}N$ $[M+H]^+$ 262.1590, found 262.1582.



1-ethyl-3,4-diphenyl-1H-pyrrole (3c)

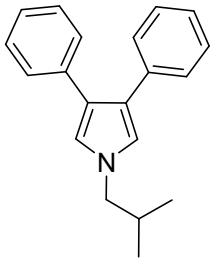
Light yellow oil. IR (KBr, cm^{-1}) v 2976, 2931, 1601, 1539, 1178, 760, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.15 (m, 10H), 6.78 (s, 2H), 3.98–3.93 (m, 2H), 1.49 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 128.4, 128.1, 125.5, 123.1, 119.7, 44.3, 16.4. HRMS (ESI), calcd for $C_{18}H_{17}N$ $[M+H]^+$ 248.1434, found 248.1425.



1-sec-butyl-3,4-diphenyl-1H-pyrrole (3d)

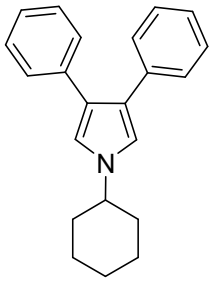
Light yellow oil. IR (KBr, cm^{-1}) v 2959, 2927, 1602, 1539, 1179, 759, 698. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.11 (m, 10H), 6.79 (s, 2H), 4.01–3.84 (m, 1H), 1.86–1.71 (m, 2H),

1.49 (d, J = 6.8 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 128.3, 128.1, 125.3, 122.6, 118.3, 57.3, 31.1, 21.7, 10.9. HRMS (ESI), calcd for $C_{20}H_{21}N$ $[M+H]^+$ 276.1747, found 276.1741.



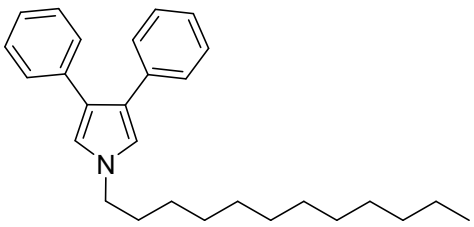
1-isobutyl-3,4-diphenyl-1H-pyrrole (3e)

Light yellow oil. IR (KBr, cm^{-1}) v 2968, 2929, 1601, 1536, 1179, 760, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.12 (m, 10H), 6.72 (s, 2H), 3.66 (d, J = 7.2 Hz, 2H), 2.10–2.03 (m, 1H), 0.95 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 128.3, 128.1, 125.4, 122.9, 120.7, 57.6, 30.4, 20.1. HRMS (ESI), calcd for $C_{20}H_{21}N$ $[M+H]^+$ 276.1747, found 276.1741.



1-cyclohexyl-3,4-diphenyl-1H-pyrrole (3f)[1]

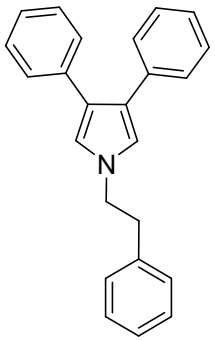
Light yellow oil. IR (KBr, cm^{-1}) v 2932, 2855, 1601, 1536, 1172, 759, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.13 (m, 10H), 6.83 (s, 2H), 3.84–3.76 (m, 1H), 2.25–2.11 (m, 2H), 1.96–1.88 (m, 2H), 1.75–1.63 (m, 3H), 1.47–1.34 (m, 2H), 1.29–1.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 128.3, 128.1, 125.3, 122.5, 118.3, 58.8, 34.6, 25.7, 25.4. HRMS (ESI), calcd for $C_{22}H_{23}N$ $[M+H]^+$ 302.1903, found 302.1896.



1-dodecyl-3,4-diphenyl-1H-pyrrole (3g)

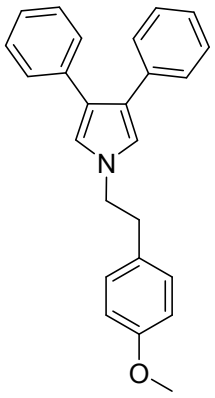
Light yellow oil. IR (KBr, cm^{-1}) v 2925, 2853, 1602, 1540, 1178, 759, 697. ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.30–7.12 (m, 10H), 6.75 (s, 2H), 3.88 (t, *J* = 7.2 Hz, 2H), 1.86–1.79 (m, 2H), 1.37–1.23 (m, 19H), 0.89–0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 128.4, 128.1, 125.4, 123.0, 120.2, 49.9, 31.9, 31.4, 29.6, 29.6, 29.6, 29.5, 29.3, 29.2, 26.8, 22.7, 14.1. HRMS (ESI), calcd for $C_{28}H_{37}N$ $[M+H]^+$ 388.2999, found 388.2987.



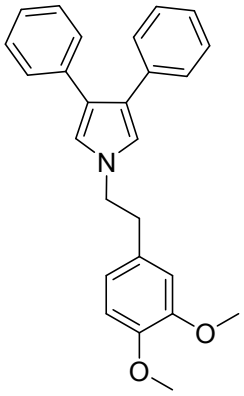
1-phenethyl-3,4-diphenyl-1H-pyrrole (3h)[1]

Light yellow oil. IR (KBr, cm^{-1}) *v* 3027, 2928, 1538, 1397, 1177, 759, 697. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.12 (m, 15H), 6.68 (s, 2H), 4.08 (t, *J* = 7.4 Hz, 2H), 3.09 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 135.9, 128.7, 128.6, 128.4, 128.1, 126.7, 125.5, 123.2, 120.1, 51.3, 38.2. HRMS (ESI), calcd for $C_{24}H_{21}N$ $[M+H]^+$ 324.1747, found 324.1736.



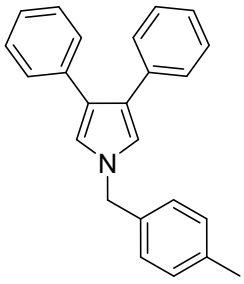
1-(4-methoxyphenethyl)-3,4-diphenyl-1H-pyrrole (3i)[1]

Light yellow oil. IR (KBr, cm^{-1}) *v* 3028, 2928, 1511, 1245, 1176, 761, 698. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.13 (m, 10H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.69 (s, 2H), 4.08 (t, *J* = 7.4 Hz, 2H), 3.79 (s, 3H), 3.06 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 136.0, 130.3, 129.7, 128.4, 128.1, 125.5, 123.2, 120.2, 114.0, 55.3, 51.6, 37.33. HRMS (ESI), calcd for $C_{25}H_{23}NO$ $[M+H]^+$ 354.1852, found 354.1842.



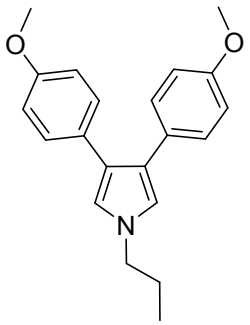
1-(3,4-dimethoxyphenethyl)-3,4-diphenyl-1H-pyrrole (3j)[2]

Light yellow oil. IR (KBr, cm^{-1}) *v* 2933, 2834, 1514, 1263, 1027, 762, 699. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27–7.12 (m, 10H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 6.45 (s, 1H), 4.09–4.05 (m, 2H), 3.85 (s, 3H), 3.75 (s, 3H), 3.03 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 147.8, 135.9, 130.8, 128.3, 128.1, 125.5, 123.2, 120.6, 120.3, 111.9, 111.3, 55.9, 55.7, 51.6, 37.7. HRMS (ESI), calcd for $C_{26}H_{25}NO_2$ $[M+H]^+$ 384.1958, found 384.1952.



1-(4-methylbenzyl)-3,4-diphenyl-1H-pyrrole (3k)

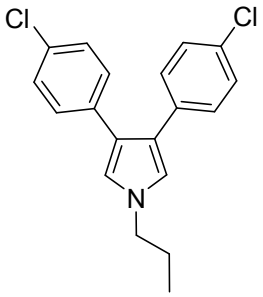
Light yellow oil. IR (KBr, cm^{-1}) *v* 3025, 2921, 1699, 1537, 1169, 758, 697. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.12 (m, 14H), 6.77 (s, 2H), 5.02 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 135.9, 134.3, 129.5, 128.4, 128.1, 127.5, 125.5, 123.5, 120.6, 53.4, 21.1. HRMS (ESI), calcd for $C_{24}H_{21}N$ $[M+H]^+$ 324.1747, found 324.1739.



3,4-bis(4-methoxyphenyl)-1-propyl-1H-pyrrole (3l)

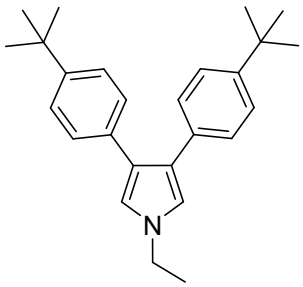
Light yellow oil. IR (KBr, cm^{-1}) *v* 3012, 2938, 1641, 1422, 1154, 770, 699. ^1H NMR (400

MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.8 Hz, 4H), 6.79 (d, *J* = 8.8 Hz, 4H), 6.68 (s, 2H), 3.81 (d, *J* = 7.4 Hz, 2H), 3.78 (s, 6H), 1.90–1.76 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 129.4, 128.7, 122.4, 119.5, 113.6, 55.1, 51.5, 24.6, 11.4. HRMS (ESI), calcd for $C_{21}H_{23}NO_2$ $[M+H]^+$ 322.1802, found 322.1794.



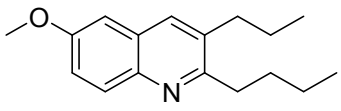
3,4-bis(4-chlorophenyl)-1-propyl-1H-pyrrole (3m)

Light yellow oil. IR (KBr, cm^{-1}) *v* 2992, 2943, 1589, 1384, 1201, 795, 701. ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 4H), 7.14 (d, *J* = 8.4 Hz, 4H), 6.72 (s, 2H), 3.84 (t, *J* = 7.2 Hz, 2H), 1.91–1.78 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 131.4, 129.5, 128.4, 121.8, 120.4, 51.6, 24.6, 11.4. HRMS (ESI), calcd for $C_{19}H_{17}Cl_2N$ $[M+H]^+$ 330.0811, found 330.0817.



3,4-bis(4-tert-butylphenyl)-1-ethyl-1H-pyrrole (3n)

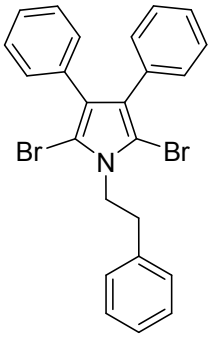
Light yellow oil. IR (KBr, cm^{-1}) *v* 3047, 2967, 1643, 1424, 1204, 779, 699. ^1H NMR (400 MHz, $CDCl_3$) δ 7.18–7.12 (m, 8H), 6.64 (s, 2H), 3.81 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.23 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 133.2, 127.8, 124.9, 122.8, 119.5, 44.2, 34.4, 31.4, 16.4. HRMS (ESI), calcd for $C_{26}H_{33}N$ $[M+H]^+$ 360.2686, found 360.2689.



2-butyl-6-methoxy-3-propylquinoline (4)[3]

^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.2 Hz, 1H), 7.73 (s, 1H), 7.30–7.22 (m, 1H), 6.99

(d, J = 2.6 Hz, 1H), 3.89 (s, 3H), 2.98–2.91 (m, 2H), 2.78–2.69 (m, 2H), 1.80–1.65 (m, 4H), 1.53–1.43 (m, 2H), 1.054–0.958 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 157.1, 142.5, 134.0, 133.9, 129.8, 128.0, 120.8, 104.6, 55.4, 35.3, 34.4, 31.9, 23.6, 23.0, 14.0, 14.0.



2,5-dibromo-1-phenethyl-3,4-diphenyl-1H-pyrrole (5)

Light yellow oil. IR (KBr, cm^{-1}) v 3044, 2940, 1641, 1454, 1134, 762, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.14 (m, 15H), 4.40–4.28 (m, 2H), 3.11–3.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 133.8, 130.2, 129.0, 128.7, 127.9, 126.9, 126.6, 124.7, 101.7, 49.4, 36.7. HRMS (ESI), calcd for $C_{24}H_{19}Br_2N$ $[M+H]^+$ 479.9957, found 479.9954.

Reference

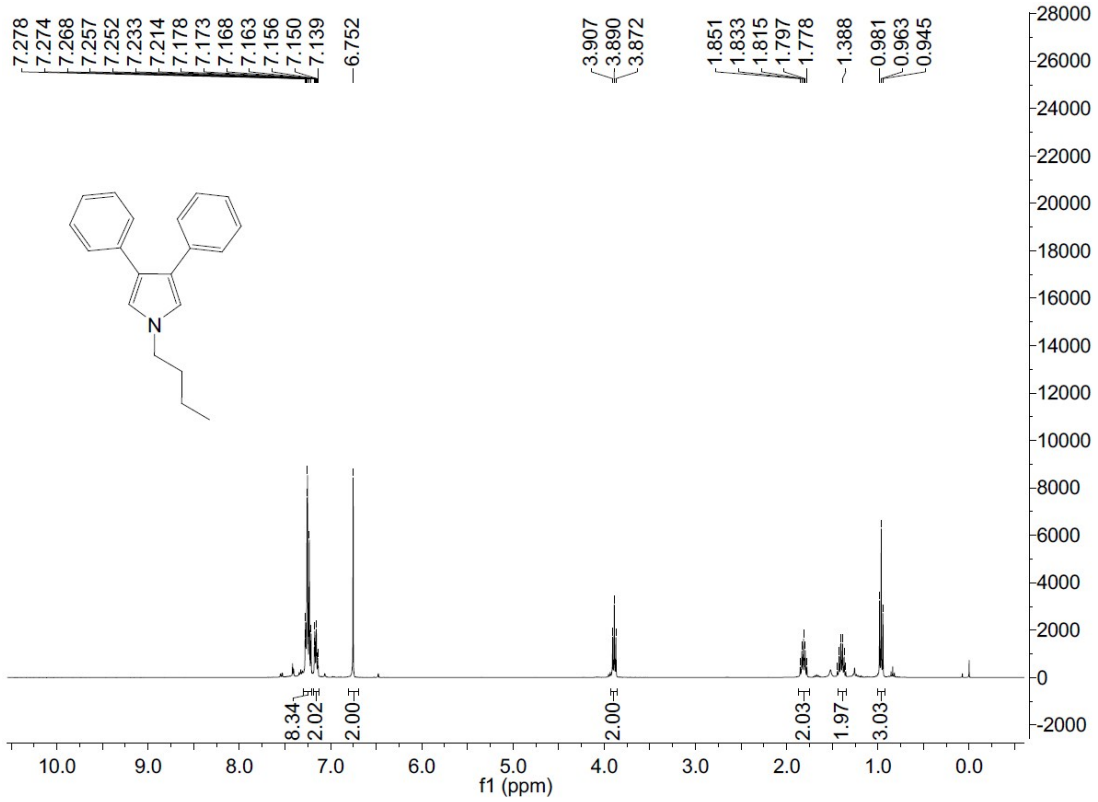
1 Q. Li, A. Fan, Z. Lu, Y. Cui, W. Lin, Y. Jia, *Org. Lett.*, 2010, **12**, 4066.

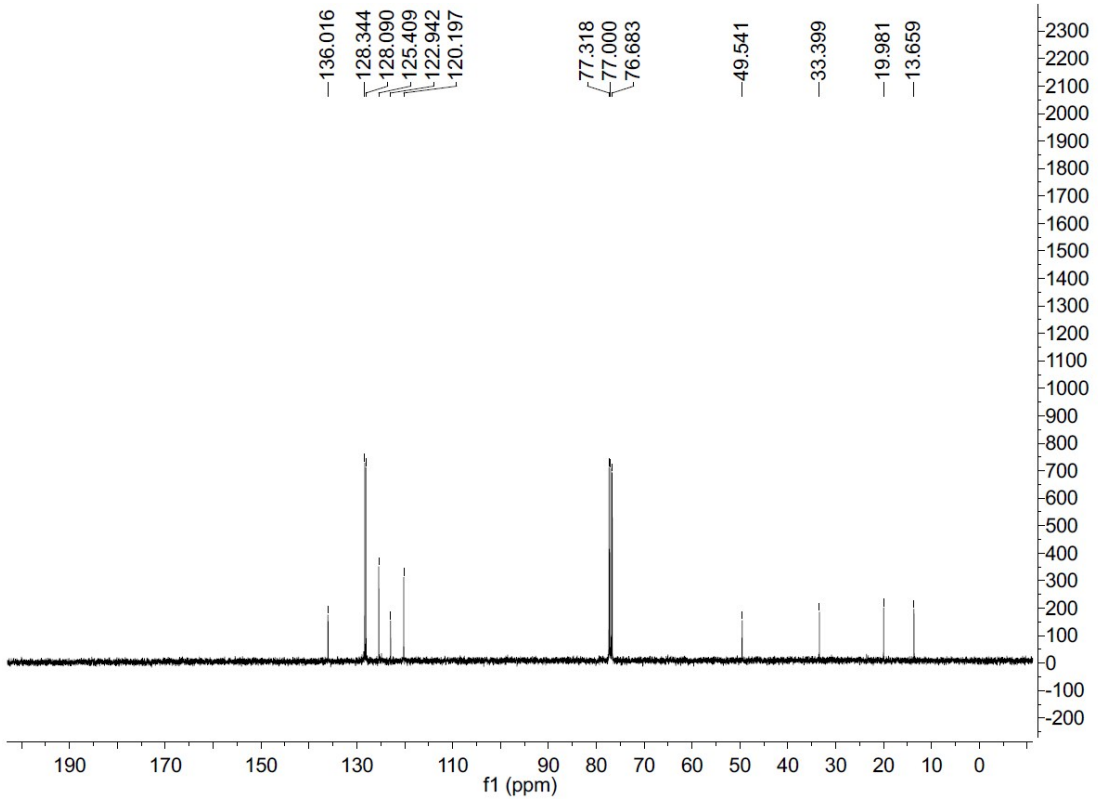
2 F. Dagorn, L. H. Yan, E. Gravel, K. Leblanc, A. MacIuk, E. Poupon, *Tetrahedron Lett.,* 2011, **52**, 3523.

3 C. E. Meyet, C. H. Larsen, *J. Org. Chem.*, 2014, **79**, 9835.

D. ^{1}H and ^{13}C NMR spectra

3a





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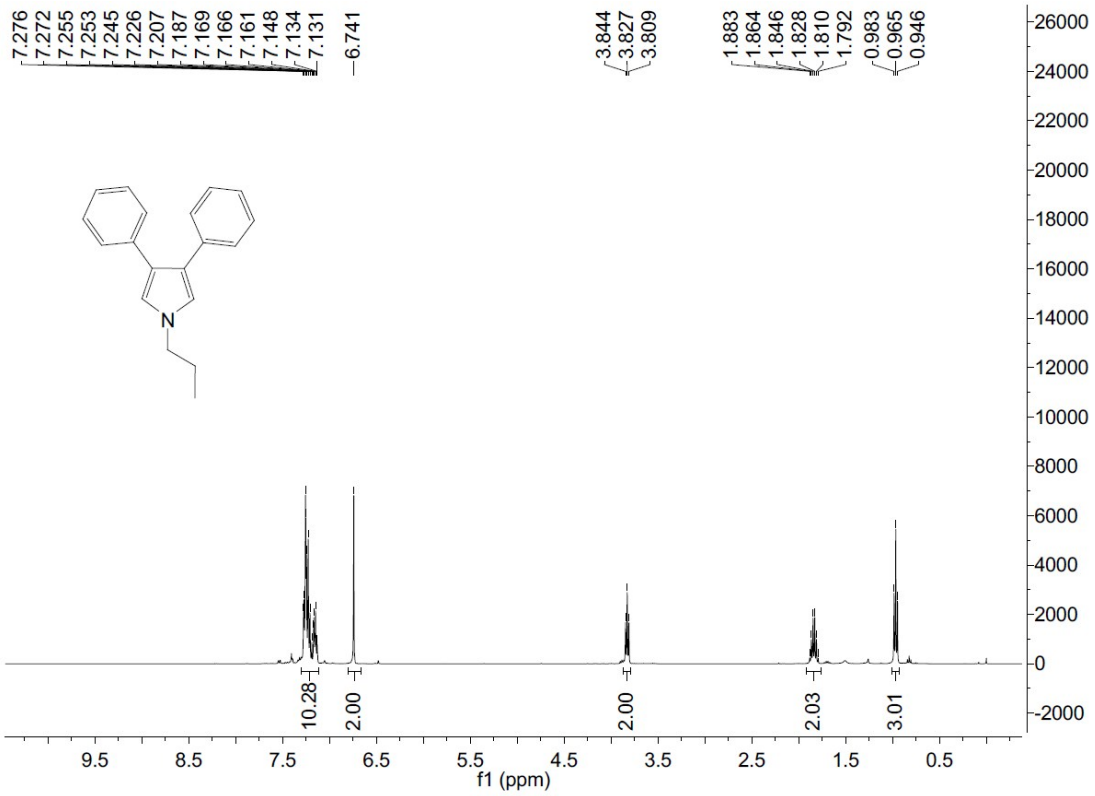
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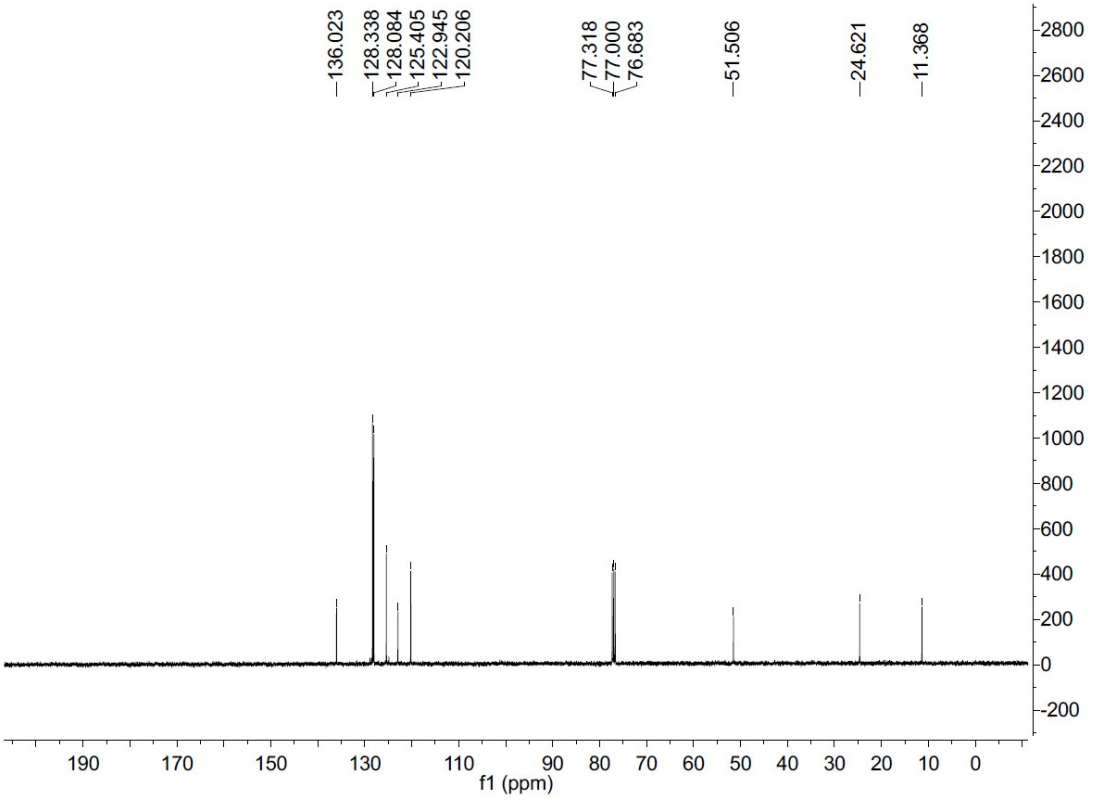
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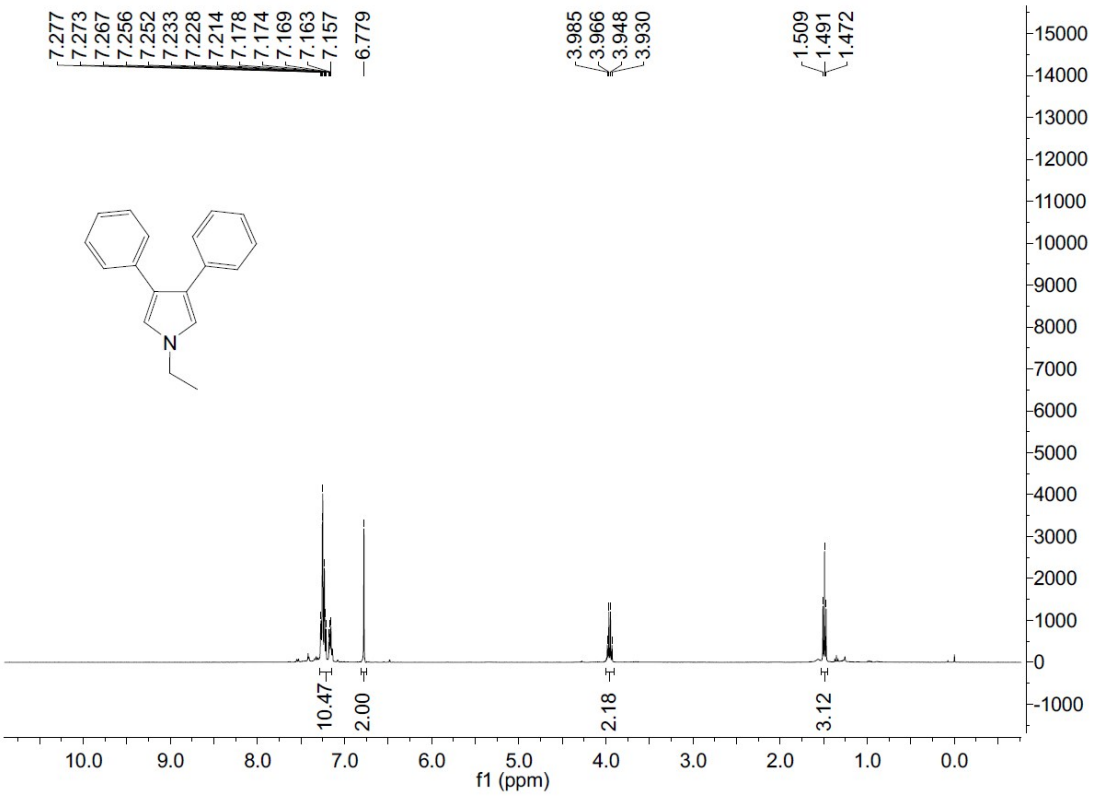
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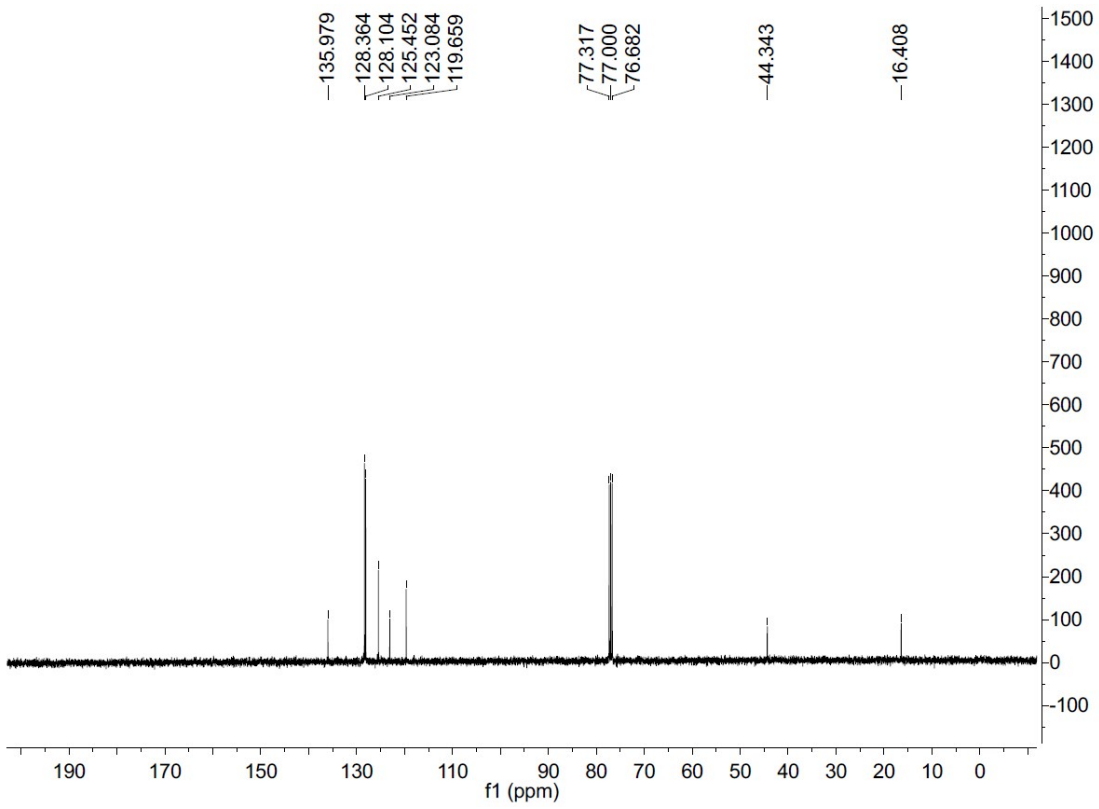
f1 (ppm)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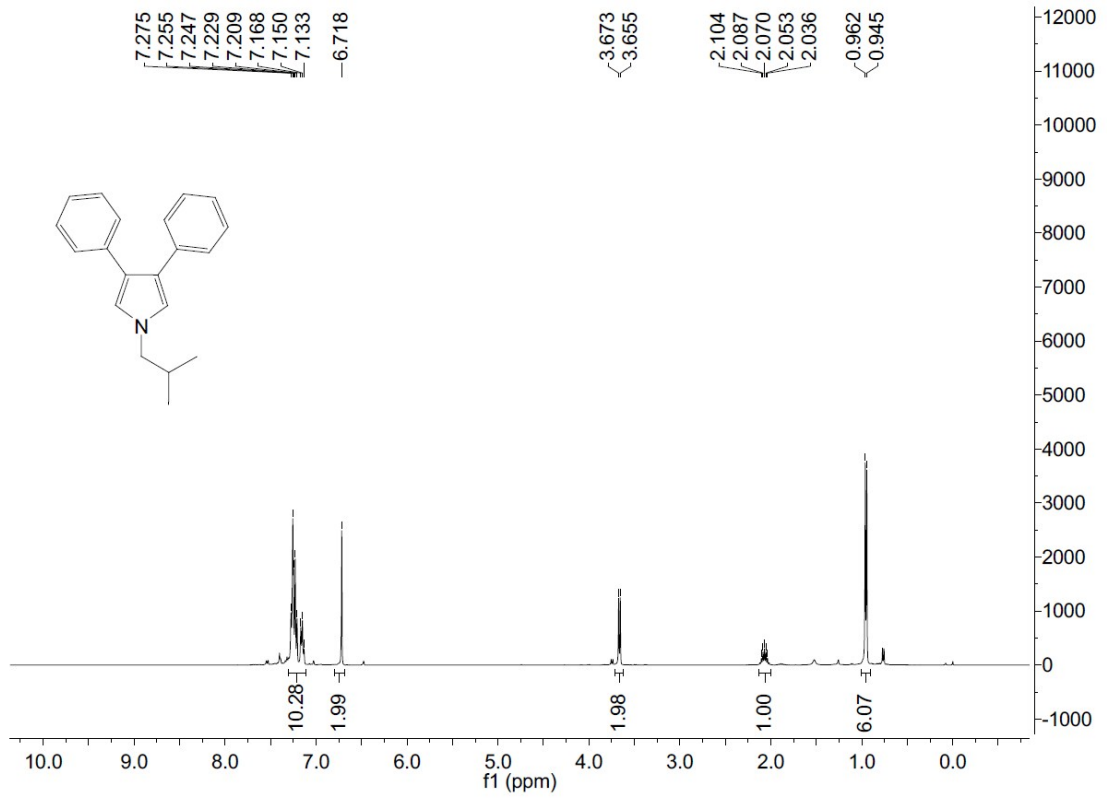
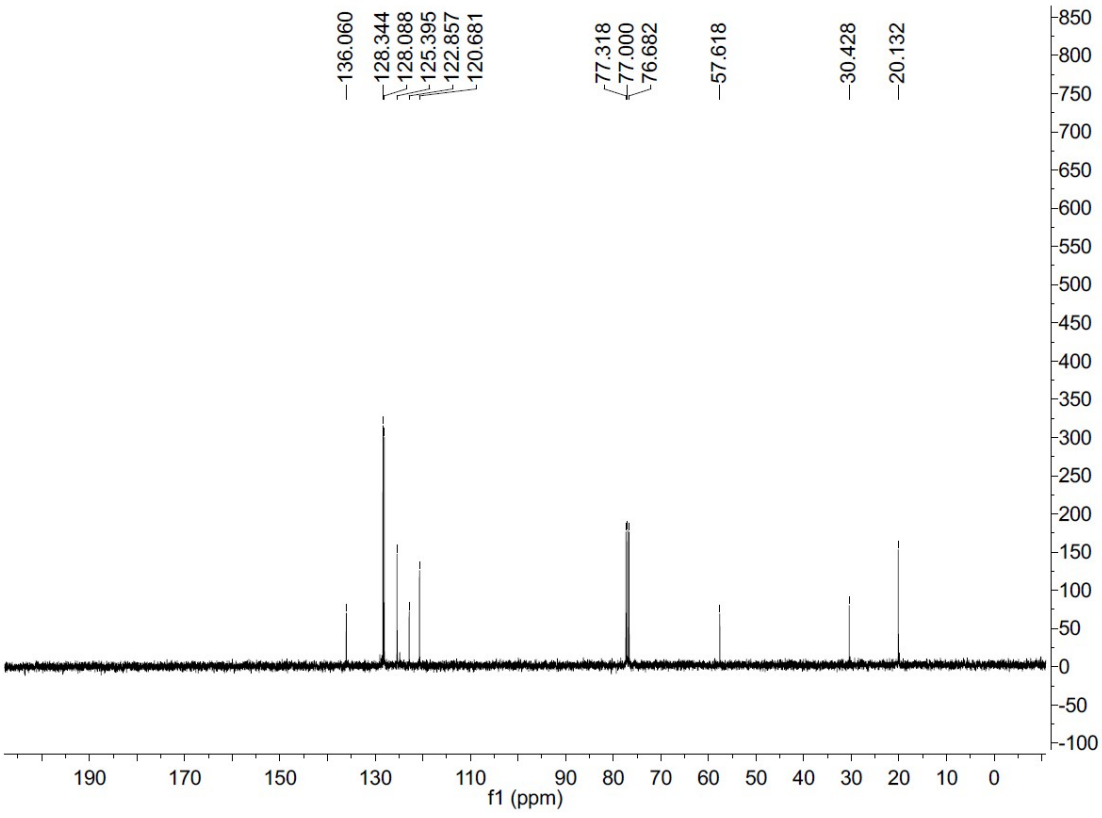
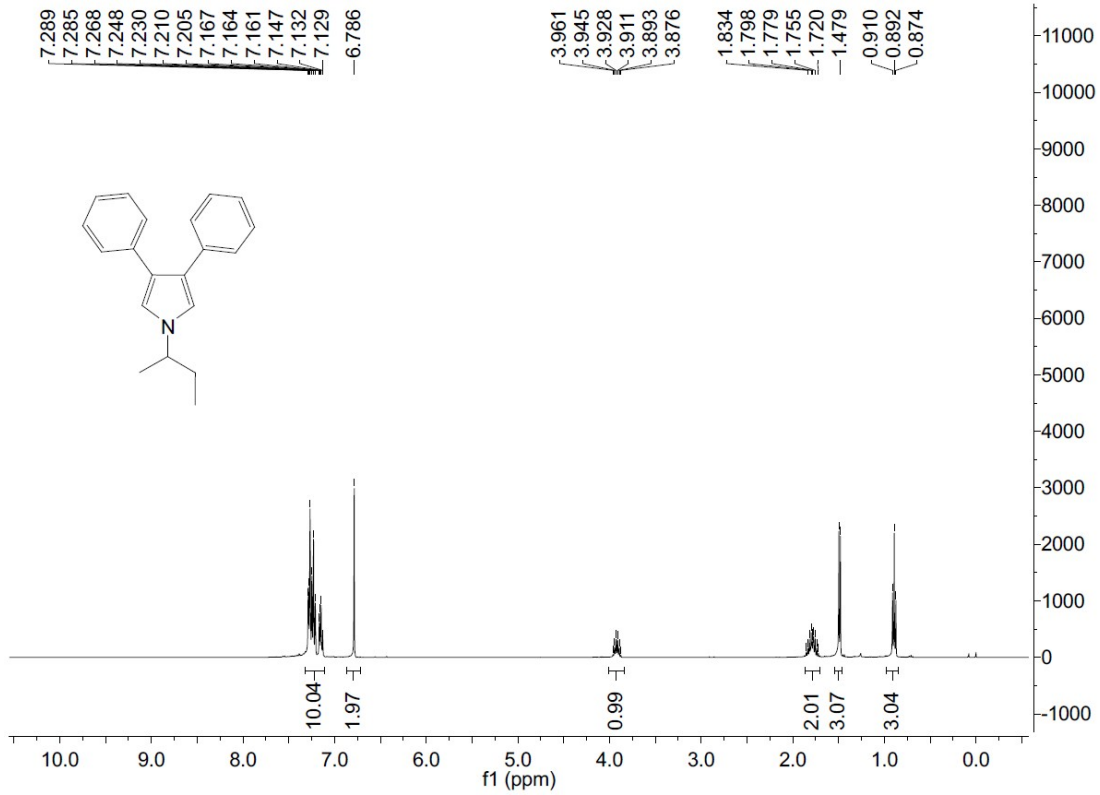
f1 (ppm)

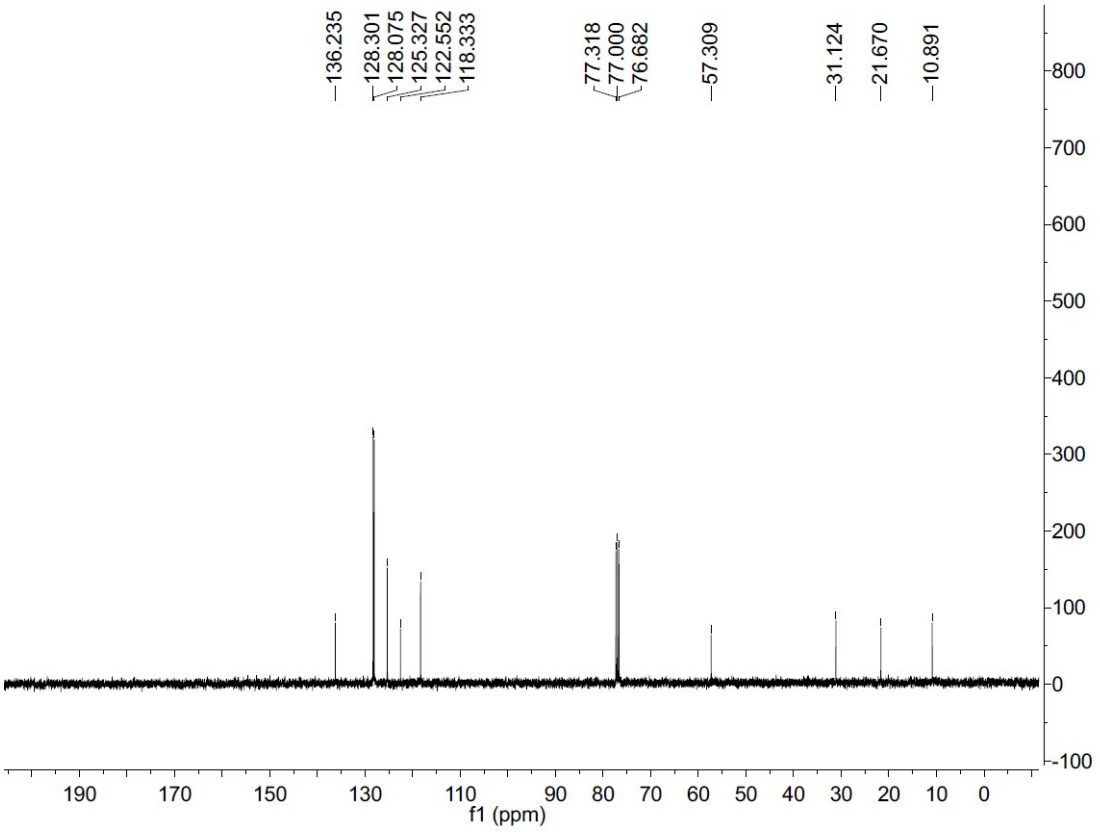
3d


7.275
7.255
7.247
7.229
7.209
7.168
7.150
7.133
6.718
3.673
3.655
2.104
2.087
2.070
2.053
2.036
0.962
0.945
N
10.28
1.99
1.98
1.00
6.07
f1 (ppm)

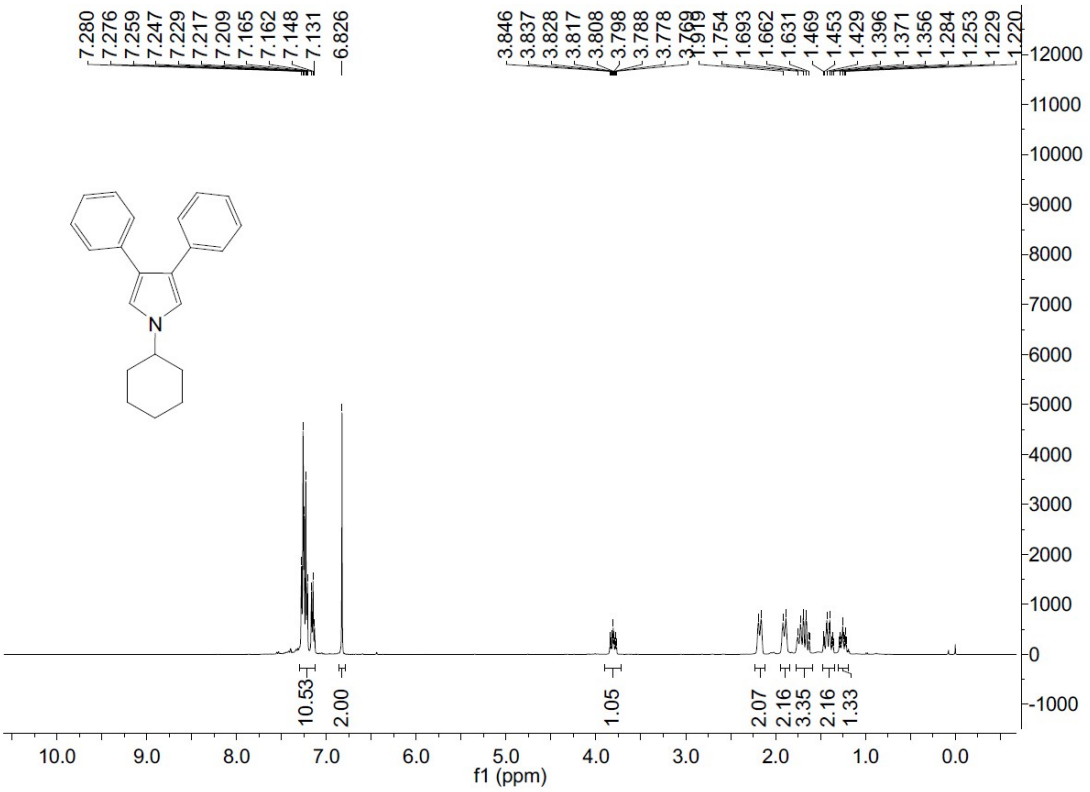

136.060
128.344
128.088
125.395
122.857
120.681
77.318
77.000
76.682
57.618
30.428
20.132
f1 (ppm)

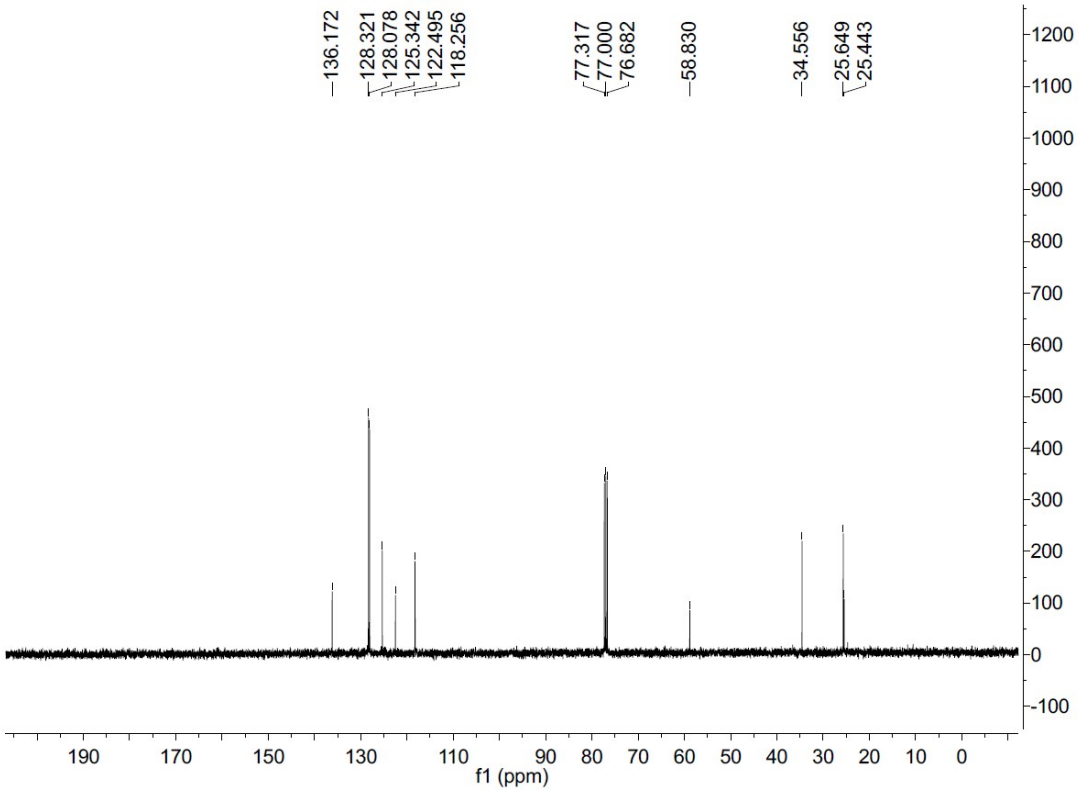
3e


7.289
7.285
7.268
7.248
7.230
7.210
7.205
7.167
7.164
7.161
7.147
7.132
7.129
6.786
3.961
3.945
3.928
3.911
3.893
3.876
1.834
1.798
1.779
1.755
1.720
1.479
0.910
0.892
0.874
N
10.04
1.97
0.99
2.01
3.07
3.04
f1 (ppm)

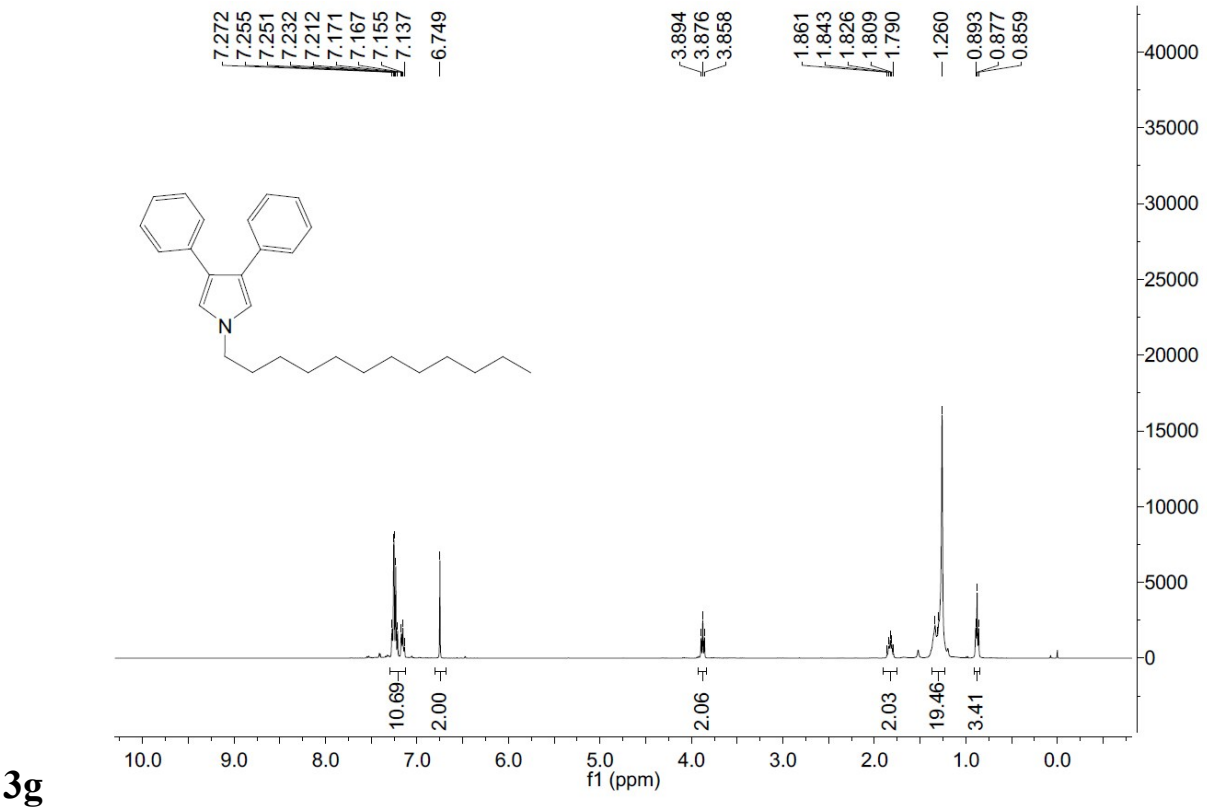

136.235
128.301
128.075
125.327
122.552
118.333
77.318
77.000
76.682
57.309
31.124
21.670
10.891
f1 (ppm)

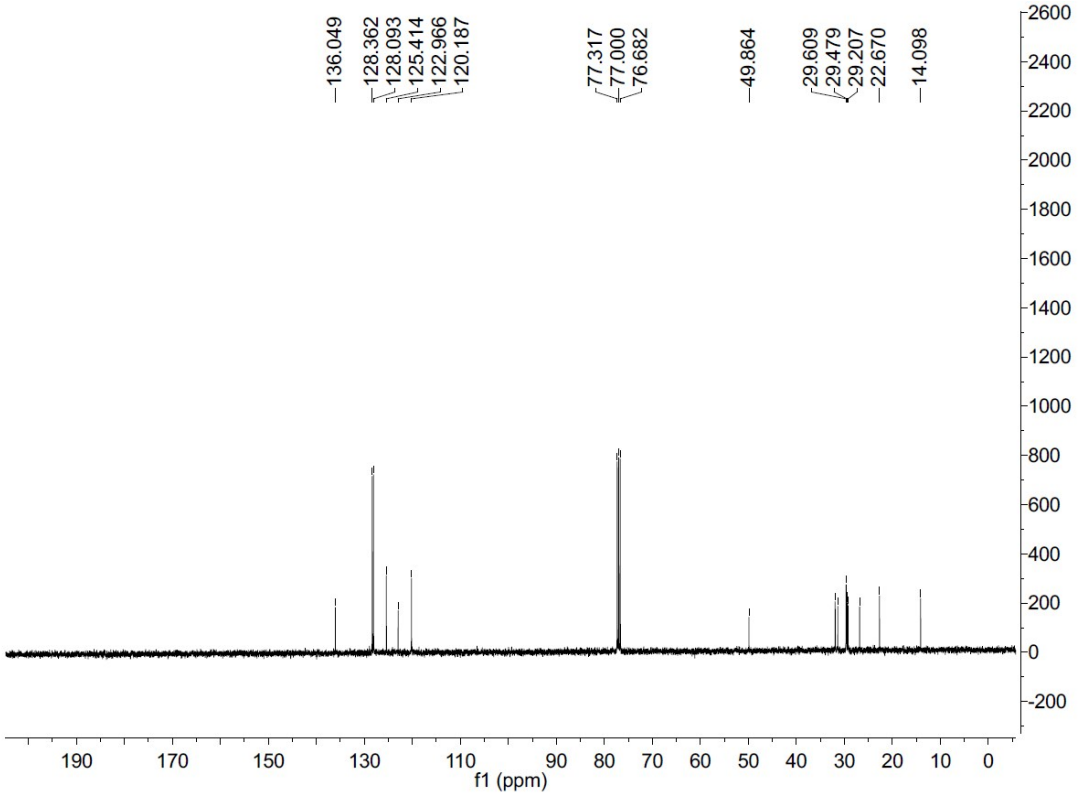
3f


7.280
7.276
7.259
7.247
7.229
7.217
7.209
7.165
7.162
7.148
7.131
6.826
3.846
3.837
3.828
3.817
3.808
3.798
3.788
3.778
3.769
1.754
1.693
1.662
1.631
1.469
1.453
1.429
1.396
1.371
1.356
1.284
1.253
1.229
1.220
N
10.53
2.00
1.05
2.07
2.16
3.35
2.16
1.33
f1 (ppm)

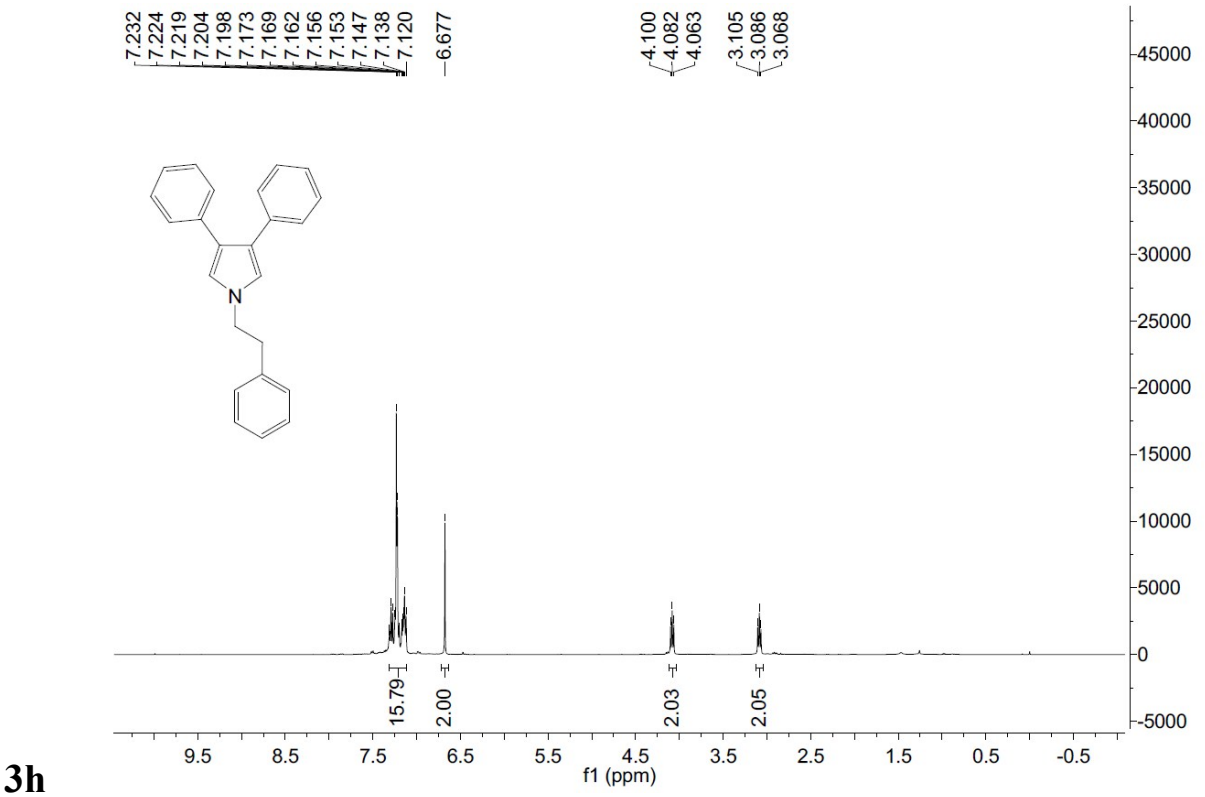

136.172
128.321
128.078
125.342
122.495
118.256
77.317
77.000
76.682
58.830
34.556
25.649
25.443
f1 (ppm)

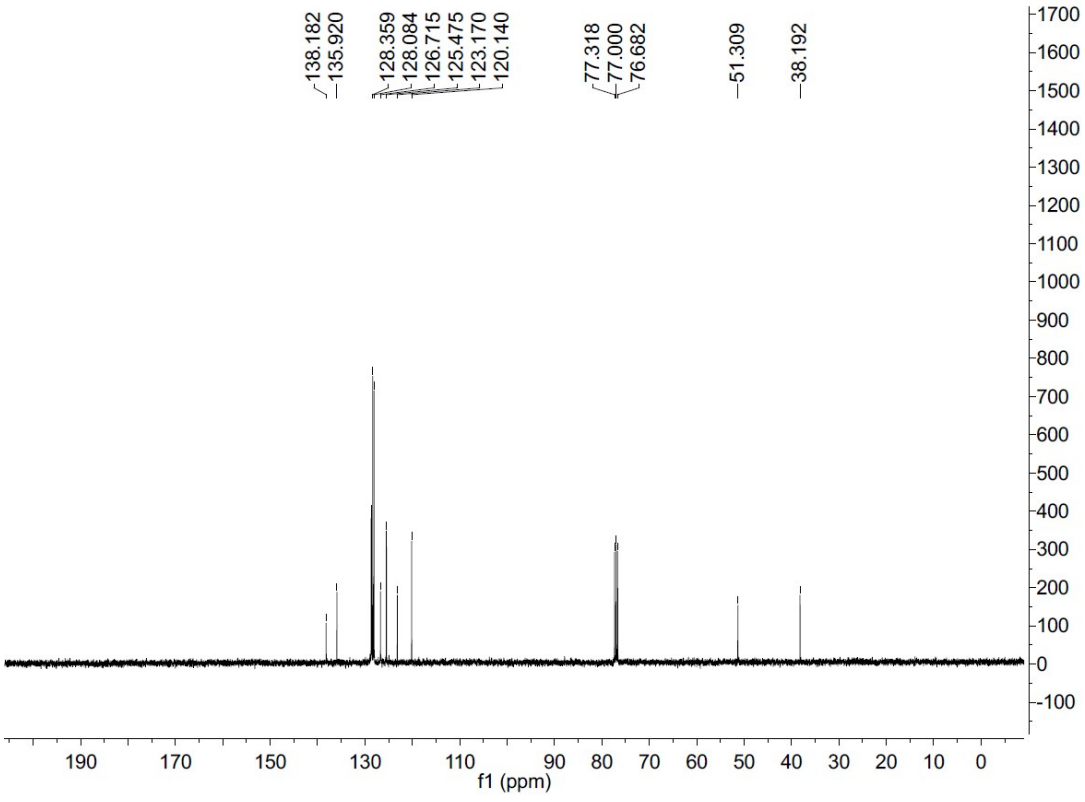
3g


7.272
7.255
7.251
7.232
7.212
7.171
7.167
7.155
7.137
6.749
3.894
3.876
3.858
1.861
1.843
1.826
1.809
1.790
1.260
0.893
0.877
0.859
N
10.69
2.00
2.06
2.03
19.46
3.41
f1 (ppm)

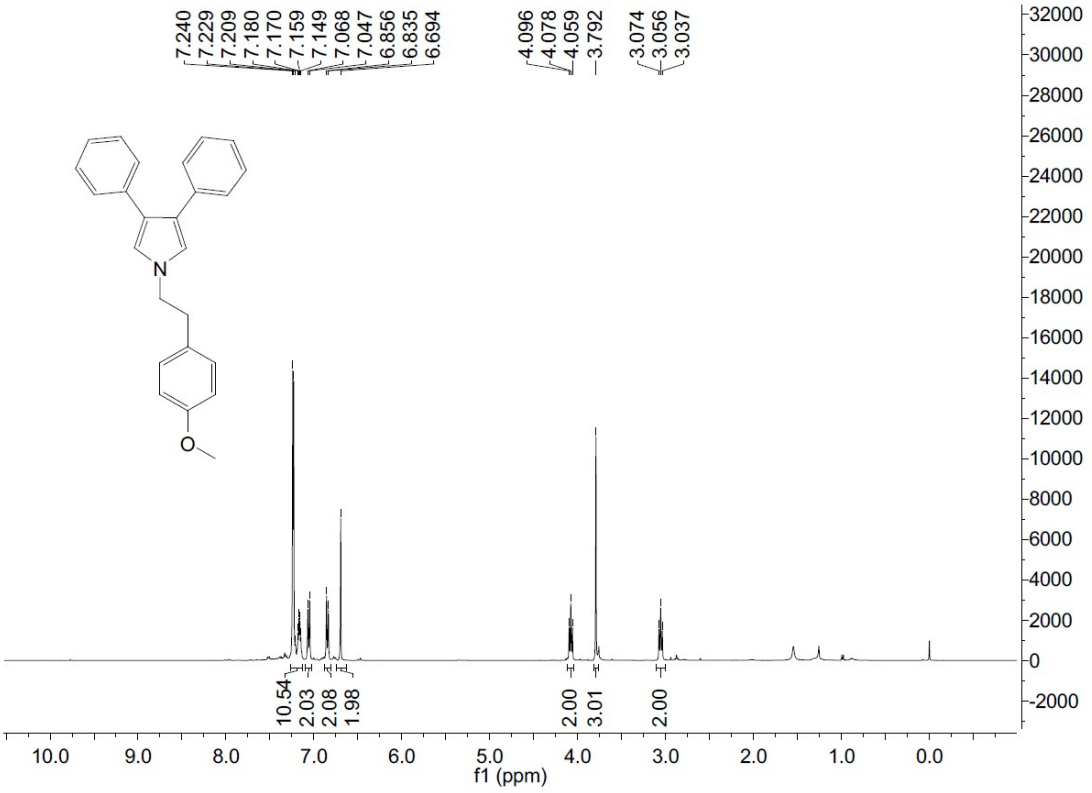

136.049
128.362
128.093
125.414
122.966
120.187
77.317
77.000
76.682
49.864
29.609
29.479
29.207
22.670
14.098
f1 (ppm)

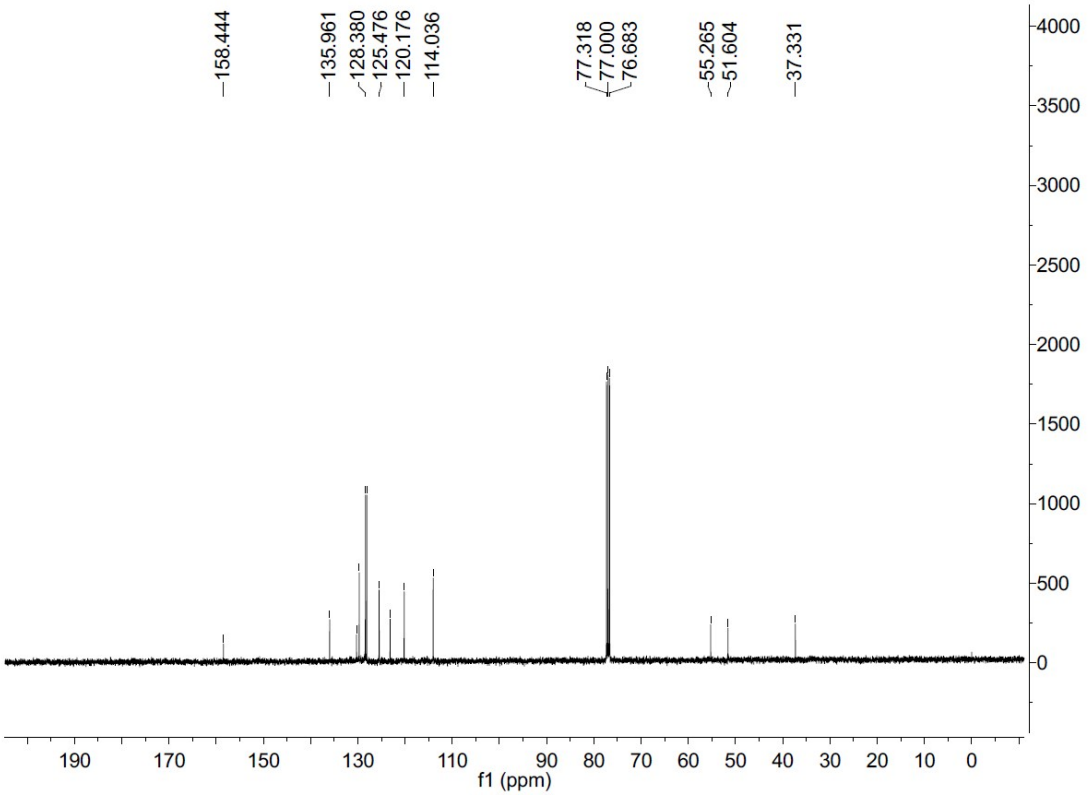
3h


7.232
7.224
7.219
7.204
7.198
7.173
7.169
7.162
7.156
7.153
7.147
7.138
7.120
6.677
4.100
4.082
4.063
3.105
3.086
3.068
N
15.79
2.00
2.03
2.05
f1 (ppm)

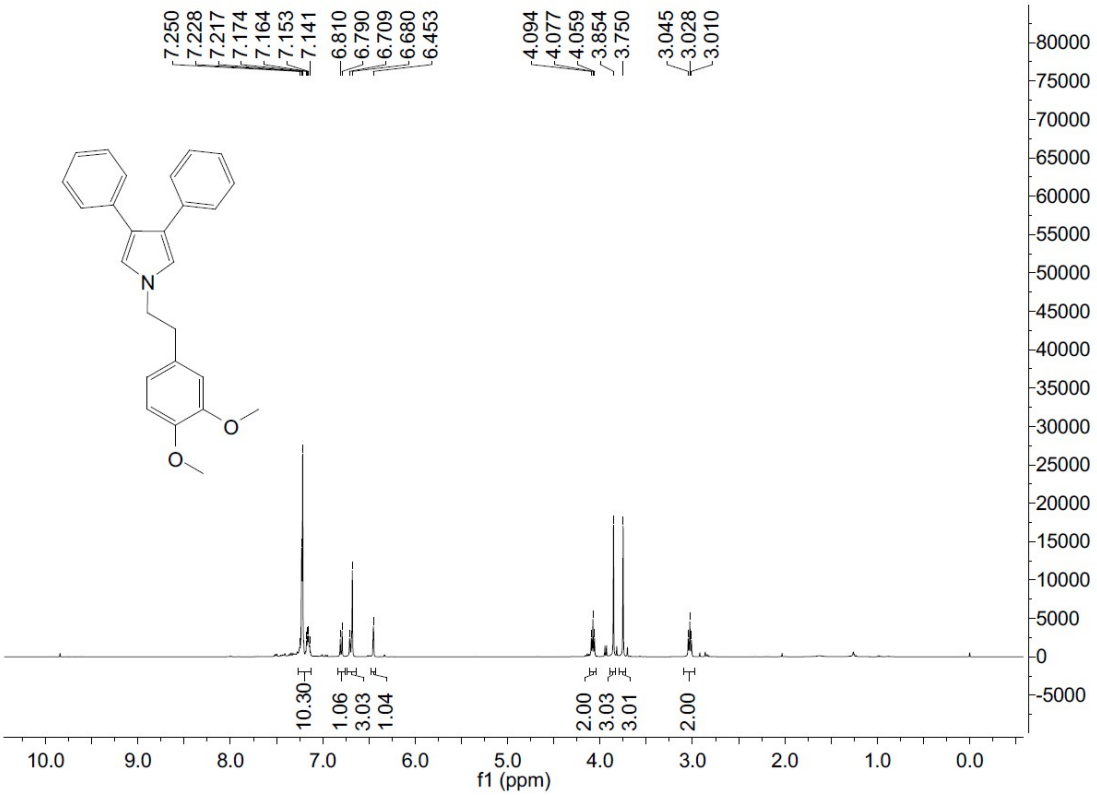

138.182
135.920
128.359
128.084
126.715
125.475
123.170
120.140
77.318
77.000
76.682
51.309
38.192
f1 (ppm)

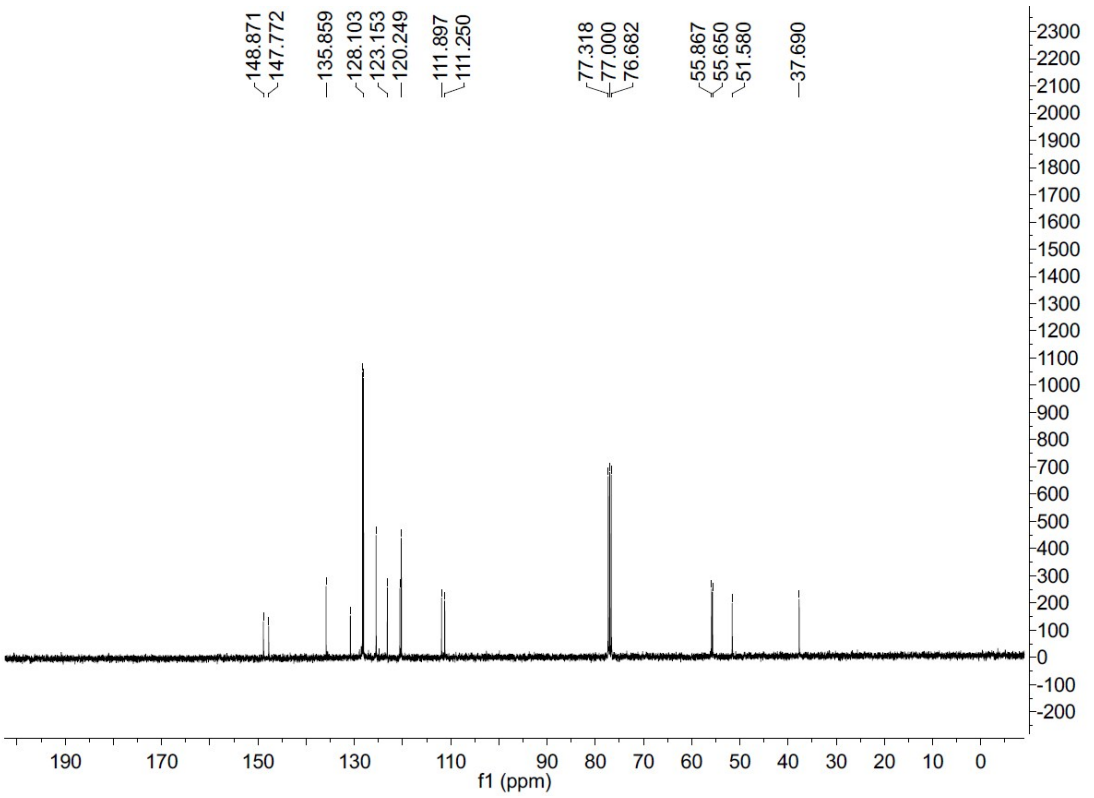
3i


7.240
7.229
7.209
7.180
7.170
7.159
7.149
7.068
7.047
6.856
6.835
6.694
4.096
4.078
4.059
3.792
3.074
3.056
3.037
N
O
10.54
2.03
2.08
1.98
2.00
3.01
2.00
f1 (ppm)

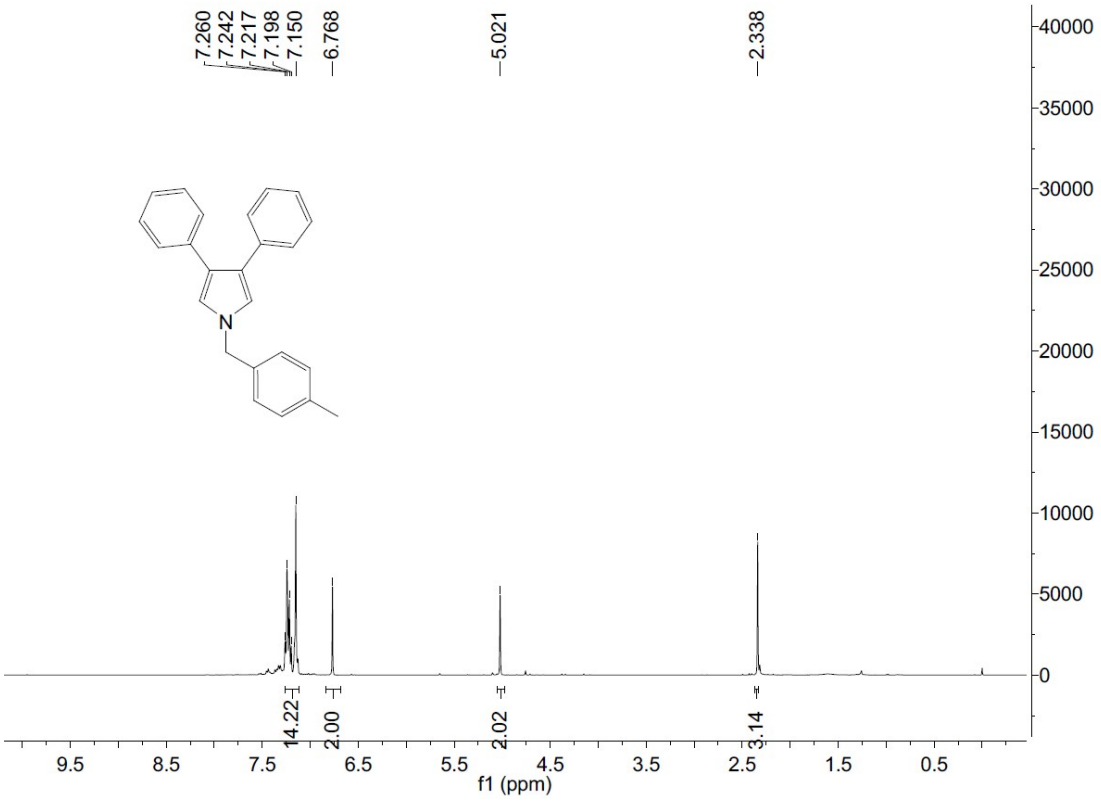

158.444
135.961
128.380
125.476
120.176
114.036
77.318
77.000
76.683
55.265
51.604
37.331
f1 (ppm)

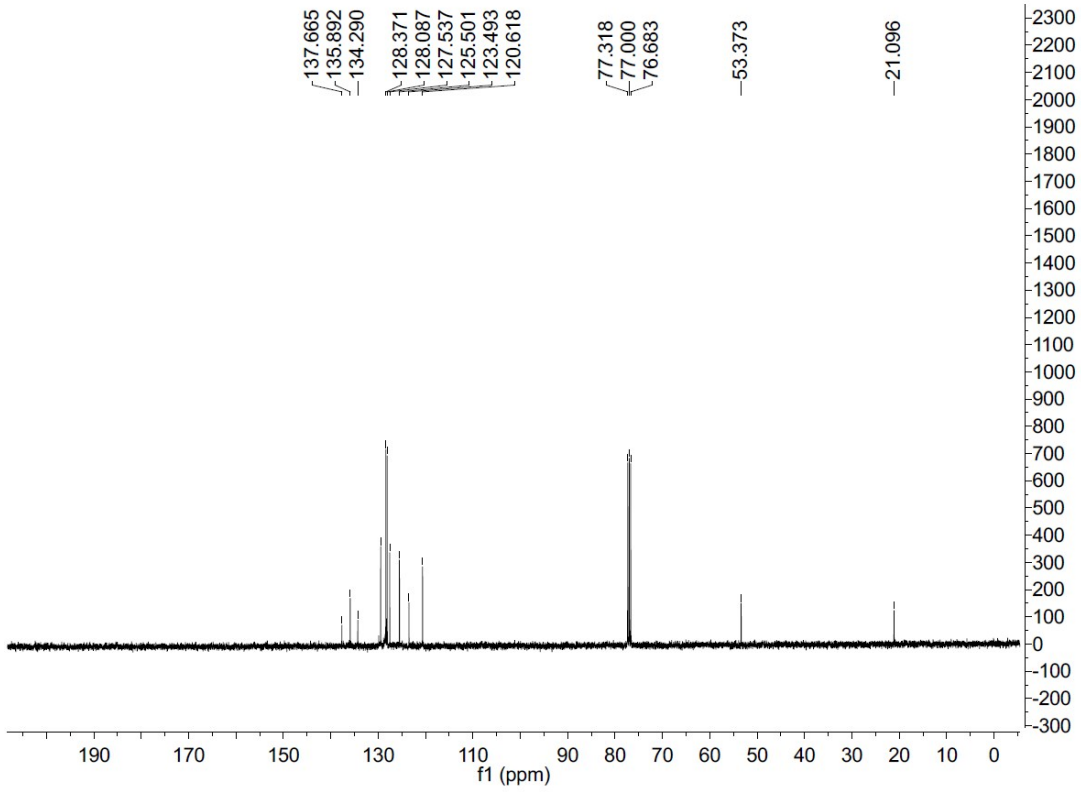
3j


7.250
7.228
7.217
7.174
7.164
7.153
7.141
6.810
6.790
6.709
6.680
6.453
4.094
4.077
4.059
3.854
3.750
3.045
3.028
3.010
N
O
O
10.30
1.06
3.03
1.04
2.00
3.03
3.01
2.00
f1 (ppm)

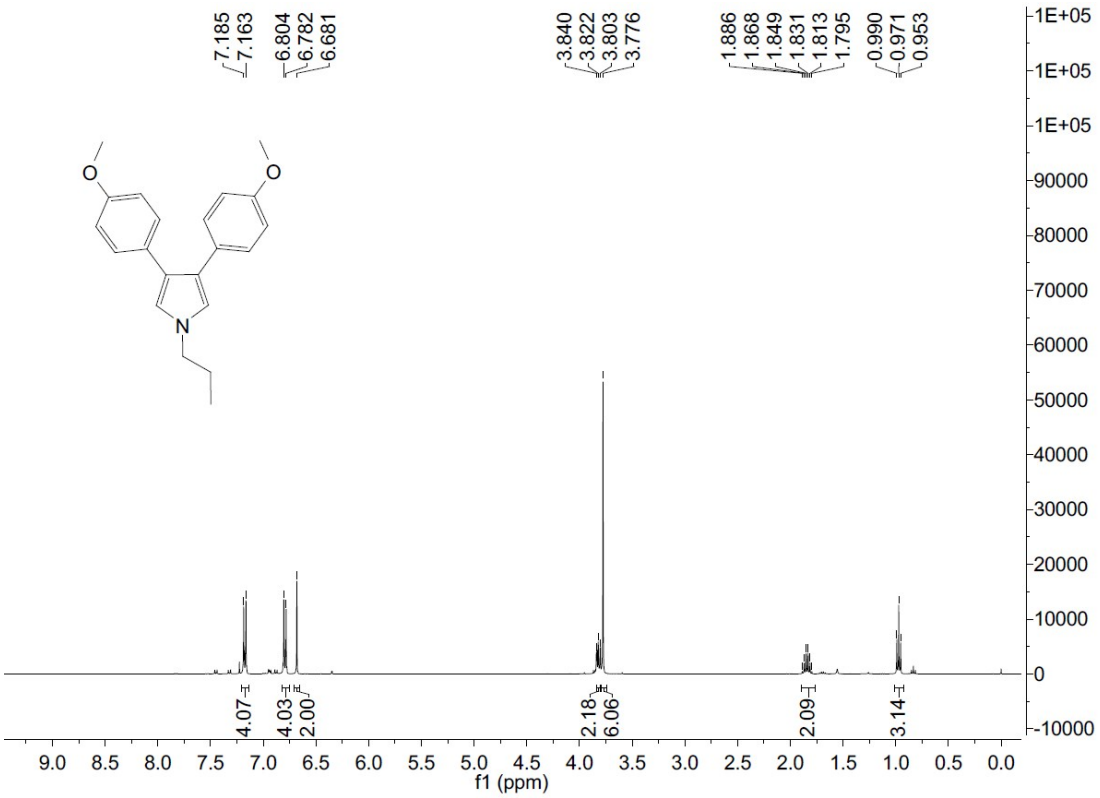

148.871
147.772
135.859
128.103
123.153
120.249
111.897
111.250
77.318
77.000
76.682
55.867
55.650
51.580
37.690
f1 (ppm)

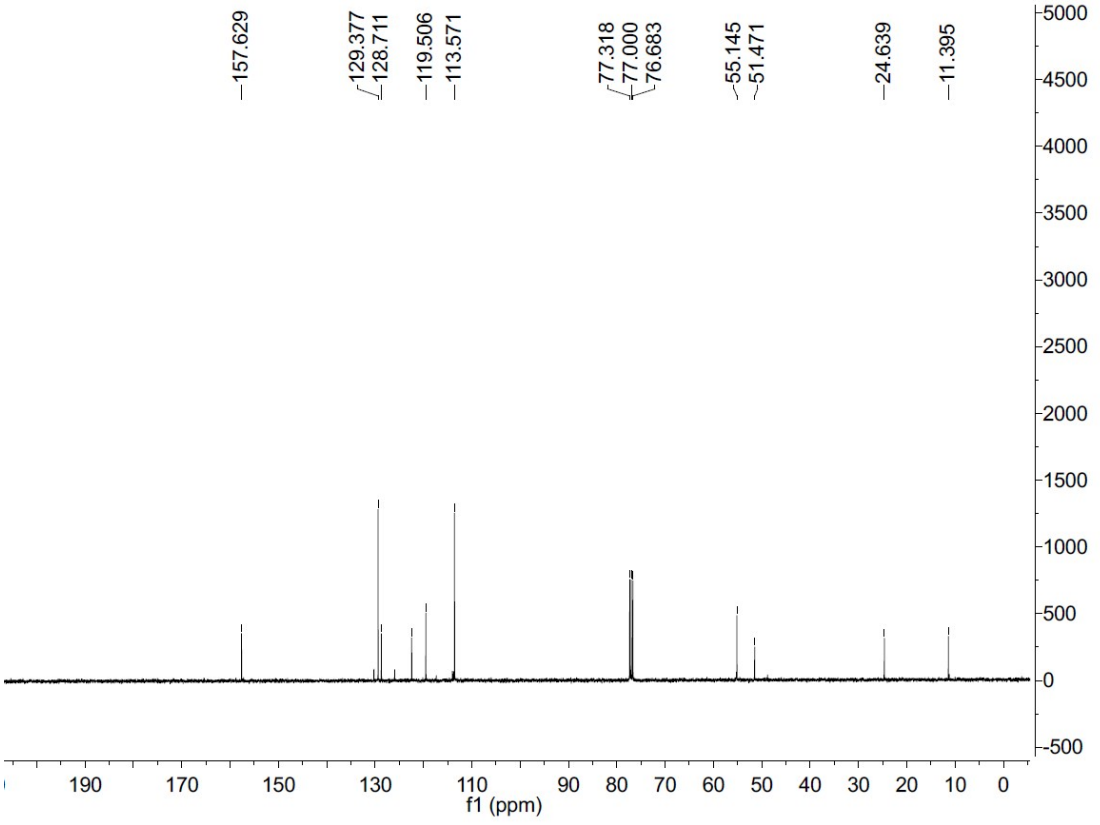
3k


7.260
7.242
7.217
7.198
7.150
6.768
5.021
2.338
N
14.22
2.00
2.02
3.14
f1 (ppm)

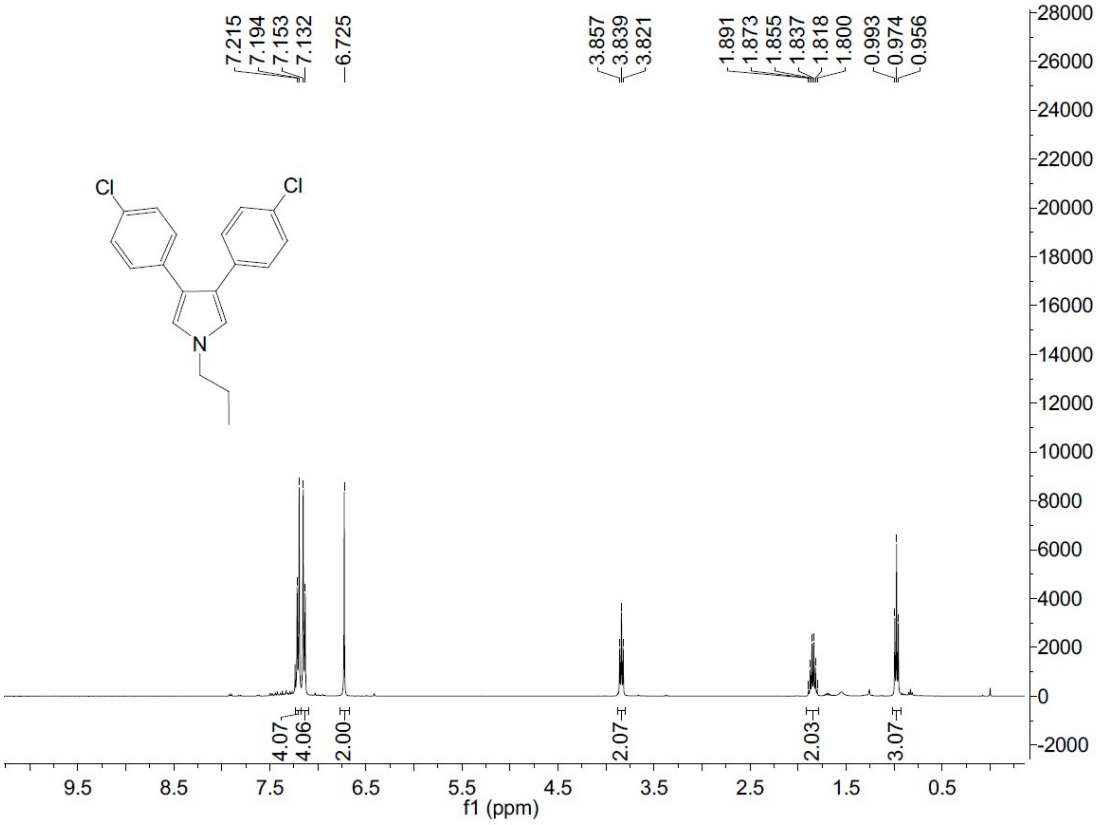

137.665
135.892
134.290
128.371
128.087
127.537
125.501
123.493
120.618
77.318
77.000
76.683
53.373
21.096
f1 (ppm)

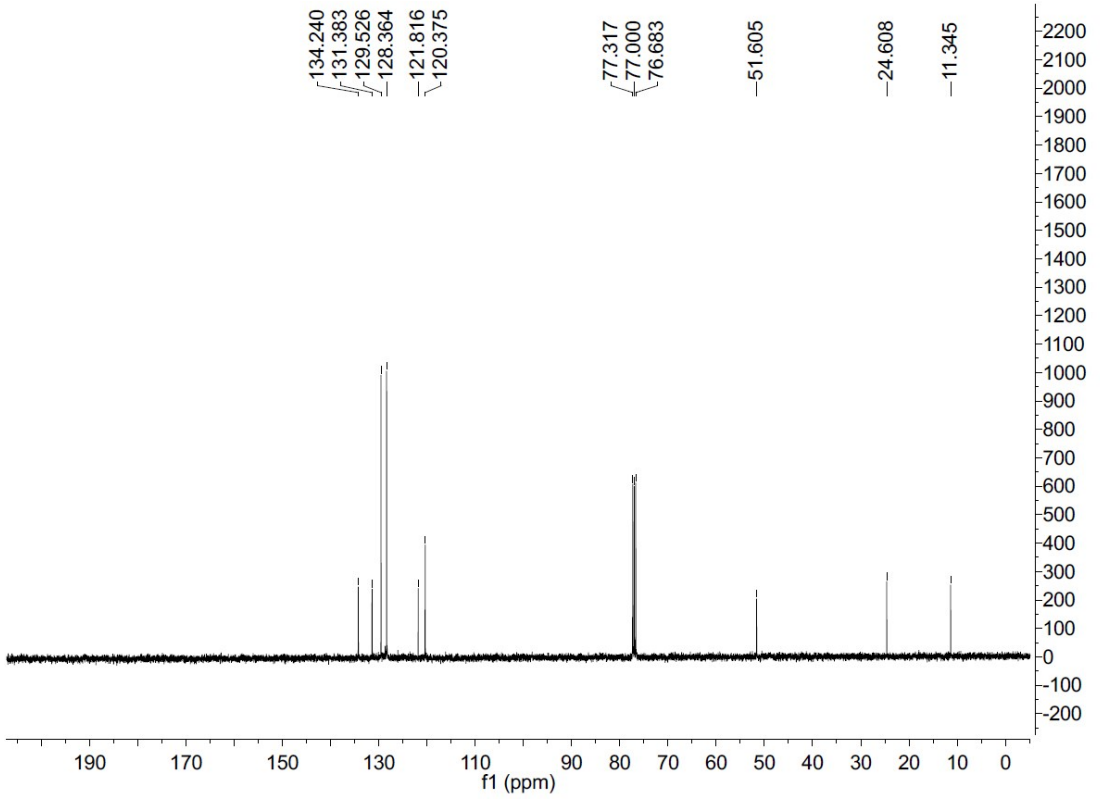
3l


7.185
7.163
6.804
6.782
6.681
3.840
3.822
3.803
3.776
1.886
1.868
1.849
1.831
1.813
1.795
0.990
0.971
0.953
O
O
N
4.07
4.03
2.00
2.18
6.06
2.09
3.14
f1 (ppm)

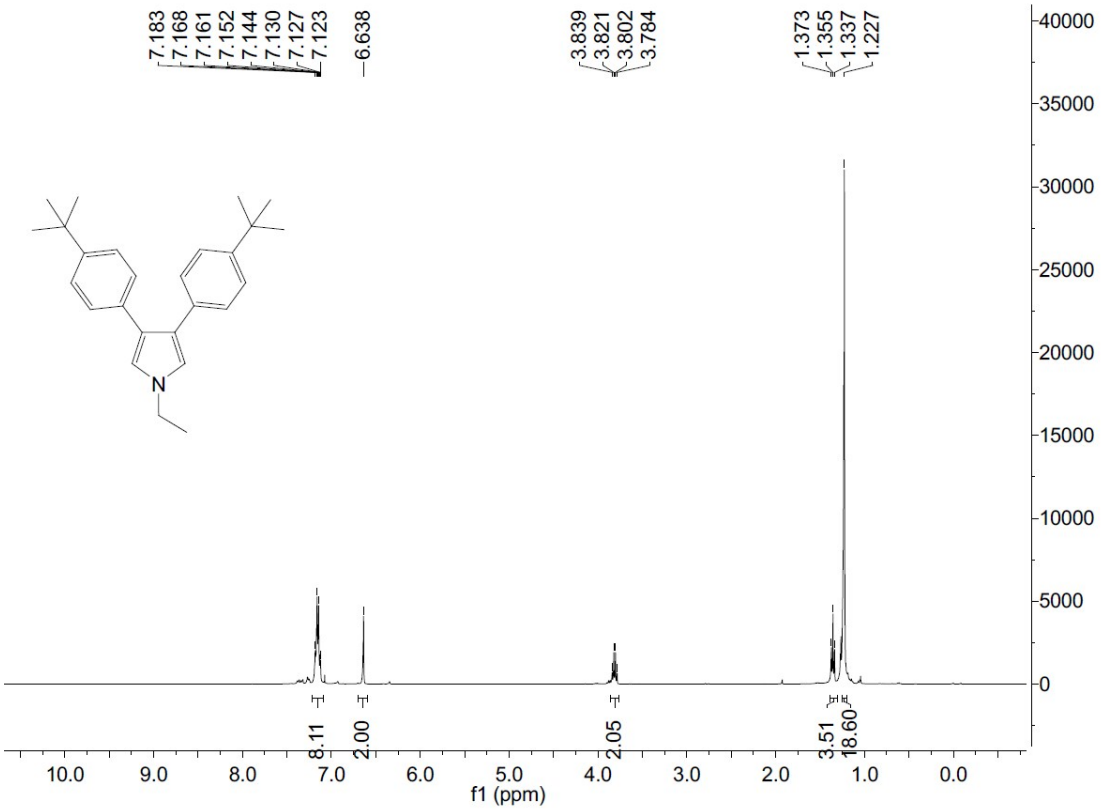

157.629
129.377
128.711
119.506
113.571
77.318
77.000
76.683
55.145
51.471
24.639
11.395
f1 (ppm)

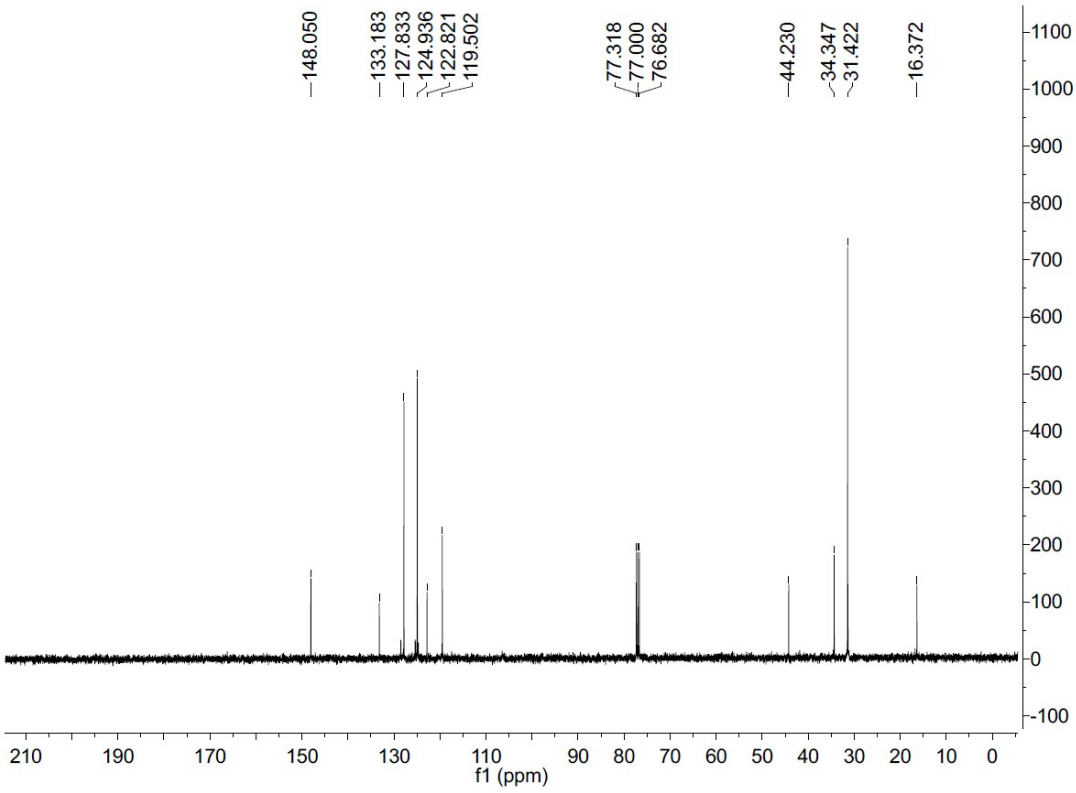
3m


7.215
7.194
7.153
7.132
6.725
3.857
3.839
3.821
1.891
1.873
1.855
1.837
1.818
1.800
0.993
0.974
0.956
Cl
Cl
N
4.07
4.06
2.00
2.07
2.03
3.07
f1 (ppm)

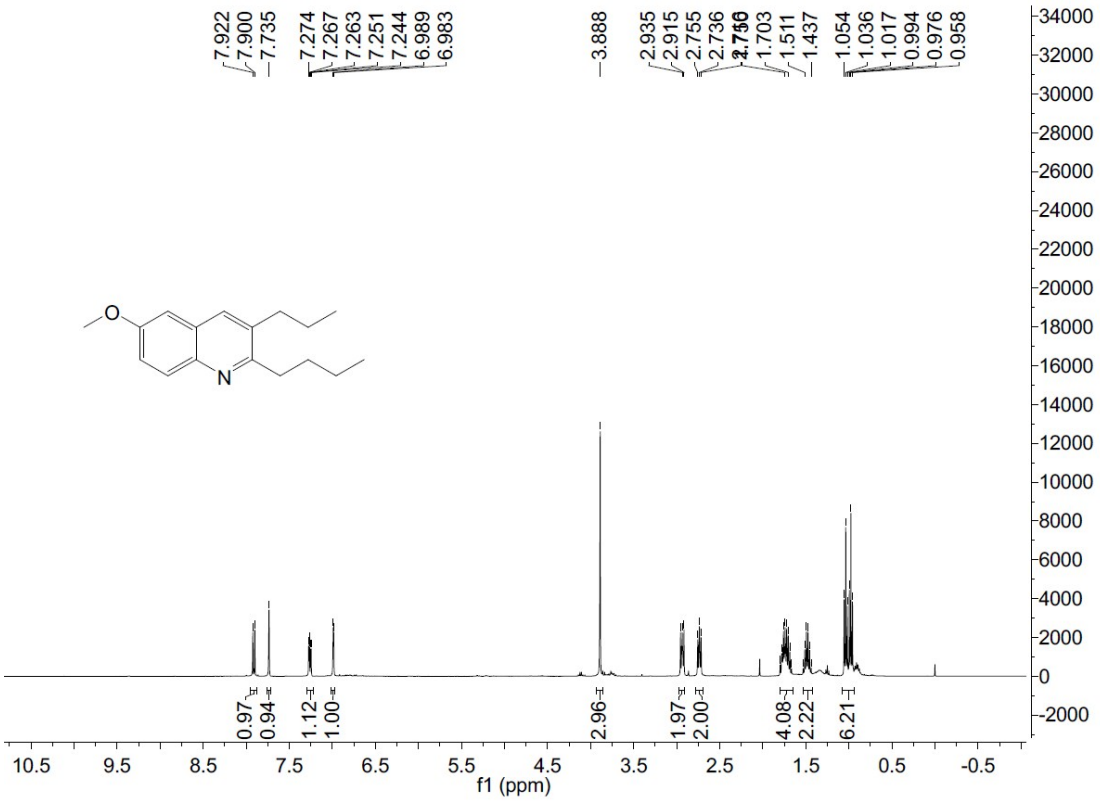

134.240
131.383
129.526
128.364
121.816
120.375
77.317
77.000
76.683
51.605
24.608
11.345
f1 (ppm)

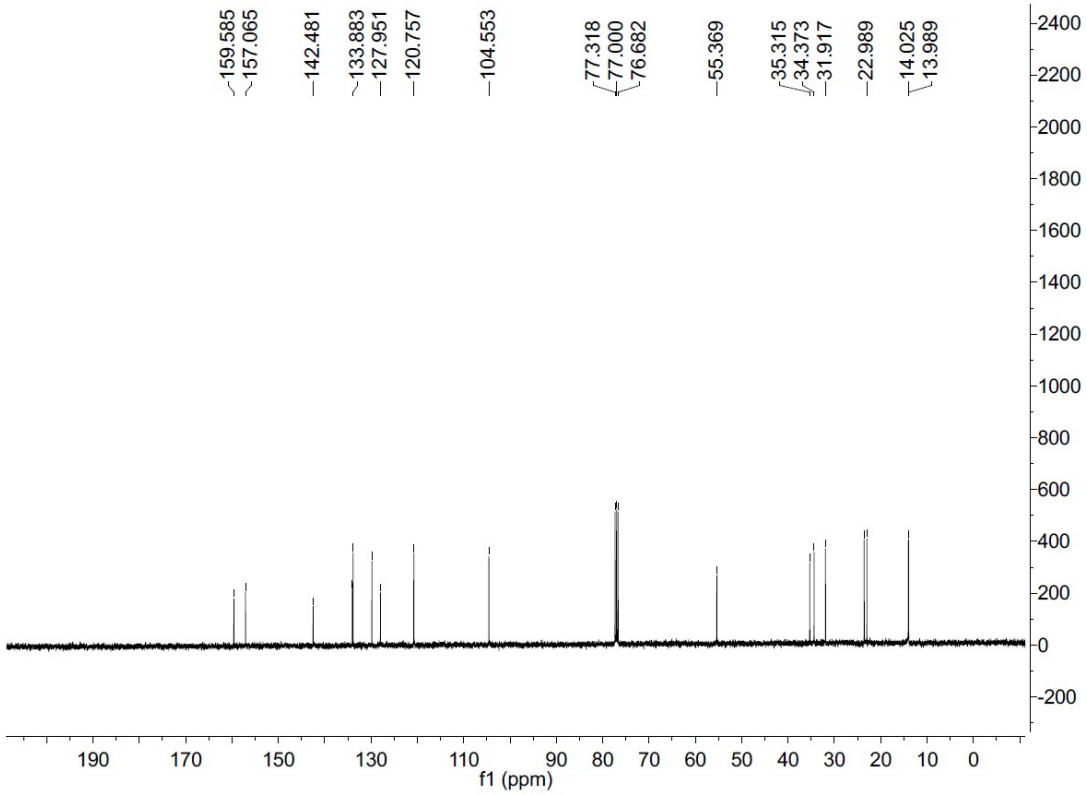
3n


7.183
7.168
7.161
7.152
7.144
7.130
7.127
7.123
6.638
3.839
3.821
3.802
3.784
1.373
1.355
1.337
1.227
N
8.11
2.00
2.05
3.51
18.60
f1 (ppm)

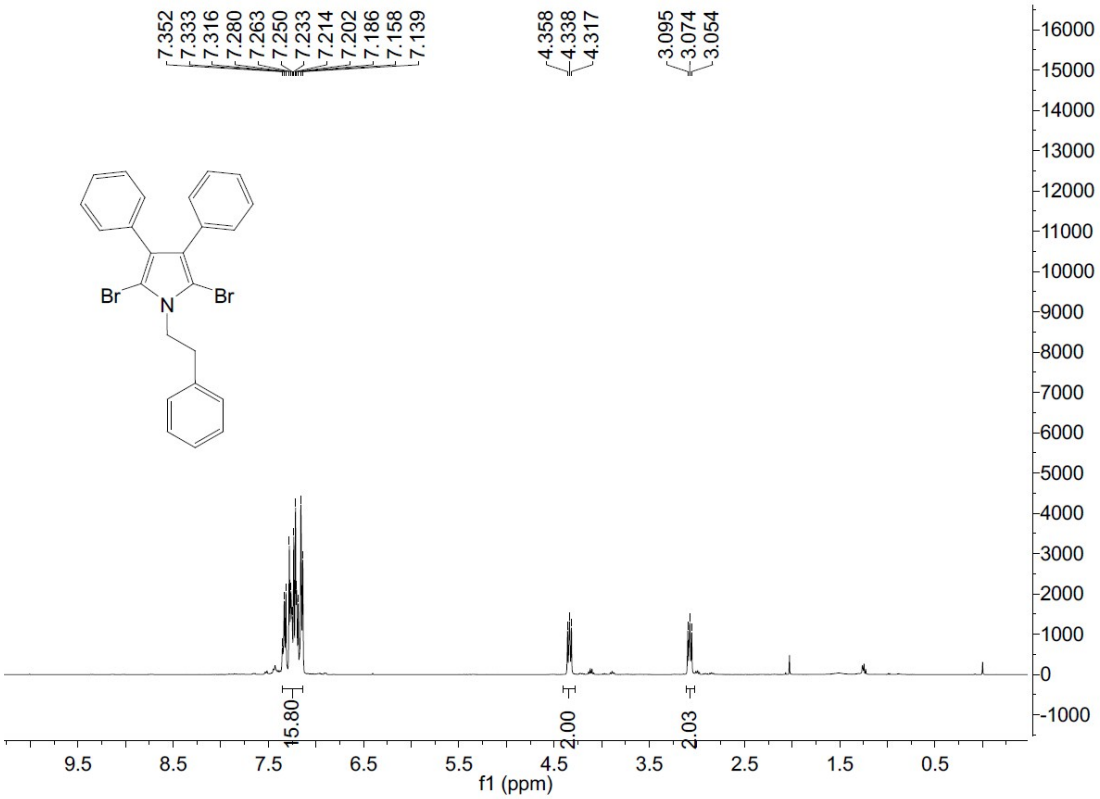

148.050
133.183
127.833
124.936
122.821
119.502
77.318
77.000
76.682
44.230
34.347
31.422
16.372
f1 (ppm)

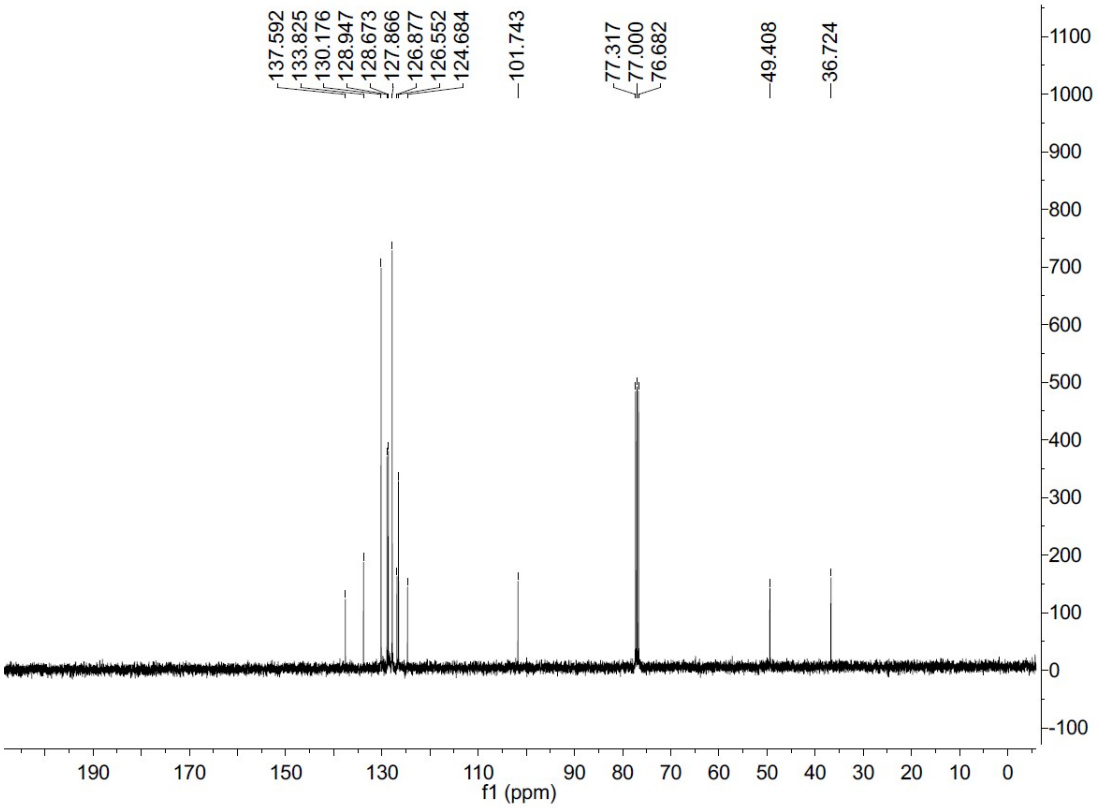
4


7.922
7.900
7.735
7.274
7.267
7.263
7.251
7.244
6.989
6.983
3.888
2.935
2.915
2.755
2.736
1.703
1.511
1.437
1.054
1.036
1.017
0.994
0.976
0.958
O
N
0.97
0.94
1.12
1.00
2.96
1.97
2.00
4.08
2.22
6.21
f1 (ppm)


159.585
157.065
142.481
133.883
127.951
120.757
104.553
77.318
77.000
76.682
55.369
35.315
34.373
31.917
22.989
14.025
13.989
f1 (ppm)

5


7.352
7.333
7.316
7.280
7.263
7.250
7.233
7.214
7.202
7.186
7.158
7.139
4.358
4.338
4.317
3.095
3.074
3.054
Br
N
Br
15.80
2.00
2.03
f1 (ppm)


137.592
133.825
130.176
128.947
128.673
127.866
126.877
126.552
124.684
101.743
77.317
77.000
76.682
49.408
36.724
f1 (ppm)