Supporting Information

Enhancement of N-Heterocyclic Carbenes on Rhodium Catalyzed Olefination of Triazoles

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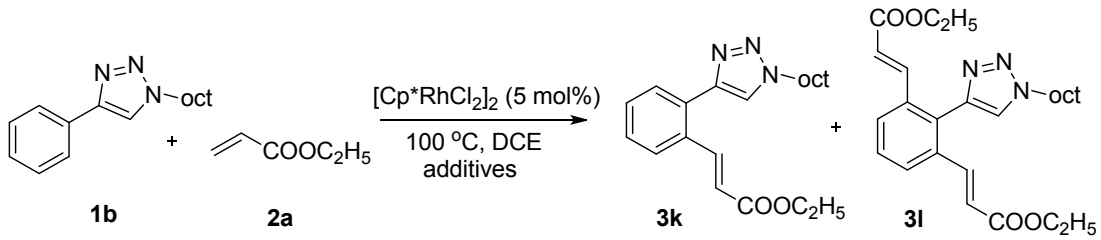
Contents

General Procedure for $[Cp^*RhCl_2]_2$ catalyzed C-H activation of triazoles with ethyl acrylate

1-Octyl-4-phenyl-1*H*-1,2,3-triazole (50 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol%), ethyl acrylate (48 mg, 0.48 mmol, 2.4 equiv) and additives listed in Table S1 in 1,2-dichloroethane (2 mL) were charged into an oven-dried 25 mL tube sealed with a Teflon screw cap.. The sealed tube was heated at 100 °C for 12 h. The products were purified by flash column chromatography eluting with petroleum ether/ethyl acetate (5/1). The results were summarized in Table S1.

Table S1 $[Cp^*RhCl_2]_2$ catalyzed C-H activation of triazoles with ethyl acrylate [a]



Entry	Additives (equiv)	**3k** (%)[b]	**3l** (%)[b]
1	$Cu(OAc)_2 \cdot H_2O$ (1.0), $AgSbF_6$ (0.05)	18	21
2	$Cu(OAc)_2 \cdot H_2O$ (1.0)	10	41
3	$AgSbF_6$ (0.05)	Trace	Trace
4	KOAc (1.0)	10	Trace
5	AgOAc (1.0)	Trace	Trace
6	$AgCO_3$ (1.0)	0	0

7	AgOAc (1.0), KOAc (0.5)	0	0
8	CsOAc (0.5)	Trace	Trace
9	K_2CO_3 (1.0)	0	0
10	$Cu(OAc)_2{\cdot}H_2O$ (1.0), AgOAc (1.0)	20	Trace
11	$Cu(OAc)_2{\cdot}H_2O$(1), KOAc (1.0)	25	44
12	$Cu(OAc)_2{\cdot}H_2O$ (1.0), $AgSbF_6$ (0.05), KOAc(1.0)	38	47

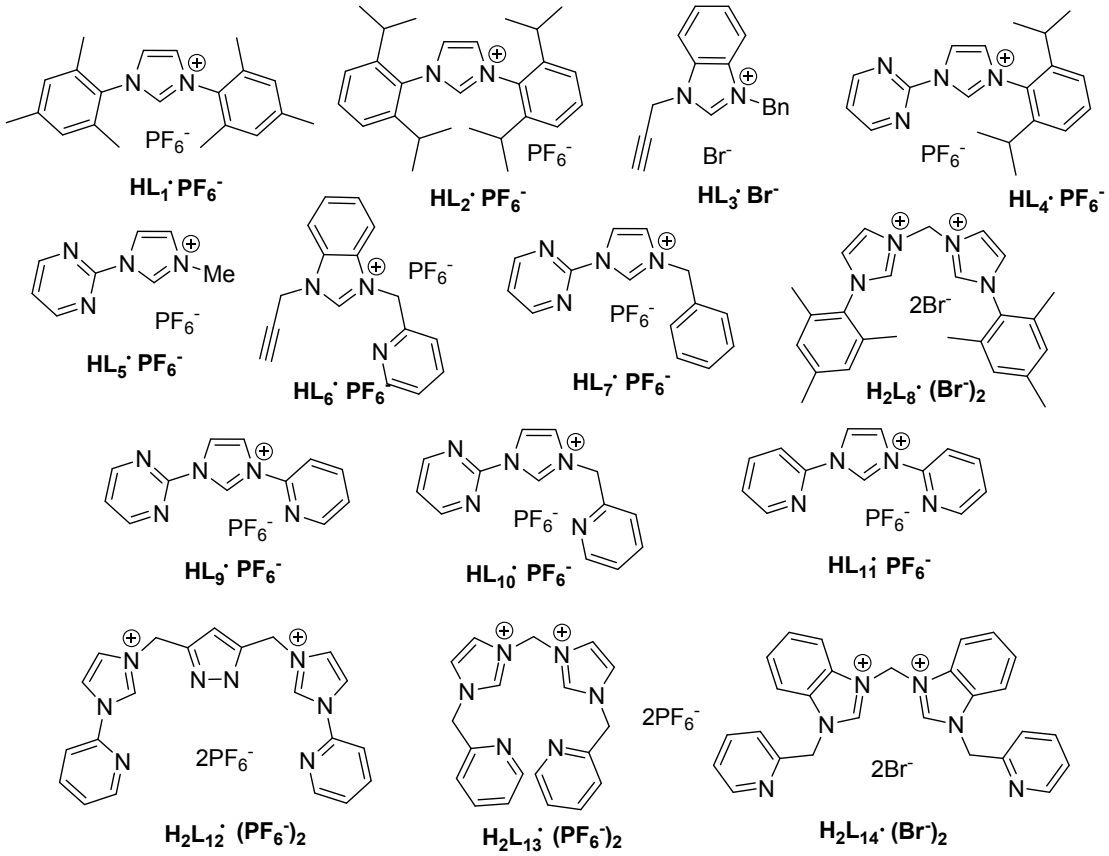
[a] Unless otherwise mentioned, all reactions were carried out using **1k** (0.2 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (5 mol%) at 100 °C in DCE (2 mL) for 14 h. [b] Isolated yields.

The olefination reaction between 1-octyl-4-phenyltriazole **1b** and ethyl acrylate **2a** was chosen as the model reaction for the optimization of reaction conditions, and the results were presented in Table S1. The reaction was initially performed by using $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (1 equiv), and $AgSbF_6$ (5 mol%) as catalyst in DCE at 100 °C in air. Under these conditions, a mixture of mono- and double vinylation products **3k** and **3l** was obtained in 18% and 21% yields (Table S1, entry 1). In the absence of $AgSbF_6$, the reaction could take place giving **3k** and **3l** in 10% and 41% yields, respectively. The combination of $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2{\cdot}H_2O$ can improve the yield of double vinylation product **3l** (entry 2). Without $Cu(OAc)_2{\cdot}H_2O$ the reaction did not occur (entry 3). Other additives such as AgOAc, KOAc, and Ag_2CO_3 are not effective (entries 4-9). However, addition of AgOAc promotes the formation of mono-vinylation product **3k** in low yield (entry 10). The yields of **3k** and **3l** can be reached to 25% and 44%, respectively, when both $Cu(OAc)_2{\cdot}H_2O$ and KOAc were used (entry 11). The addition of $AgSbF_6$ can further increase the total yields of **3k** and **3l** to 85% (entry 12). In all these reactions, even one equivalent of

ethyl acrylate was used, the reactions still gave mixtures of **3k** and **3l**. The employment of more than two equivalent of ethyl acrylate was adopted to increase the conversion and selectivity of double vinylation products.

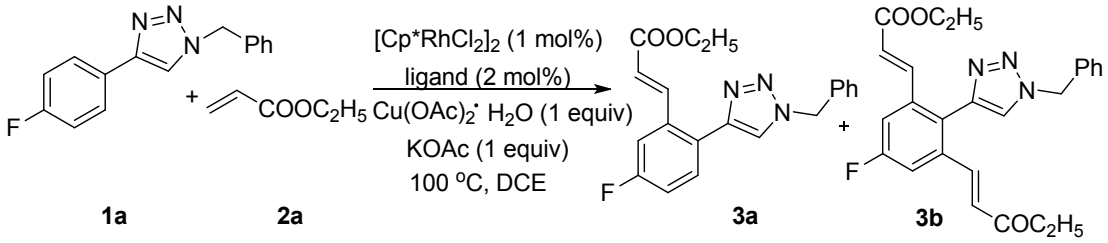
General Procedure for ligand effect on $[Cp^*RhCl_2]_2$ catalyzed C-H activation of triazoles with ethyl acrylate

The reactions between **1a** and **2a** were conducted an oven-dried 25 mL tube sealed with a Teflon screw cap. $[Cp^*RhCl_2]_2$ (1 mol%), $Cu(OAc)_2{\cdot}H_2O$ (0.2 mmol), KOAc (0.2 mmol) and ligand (2 mol%) at 100 ^oC in DCE. The sealed tube was heated at 100 ^oC for 14 h. The products were purified by flash column chromatography eluting with petroleum ether/ethyl acetate (5/1).



Scheme S1 The ligand precursors HL·X and $H_2L·X_2$ (X = Br^-, PF_6^-)

Table S2 The ligand effects on Rh-catalyzed C-H vinylation of triazoles with ethyl acrylate [a]



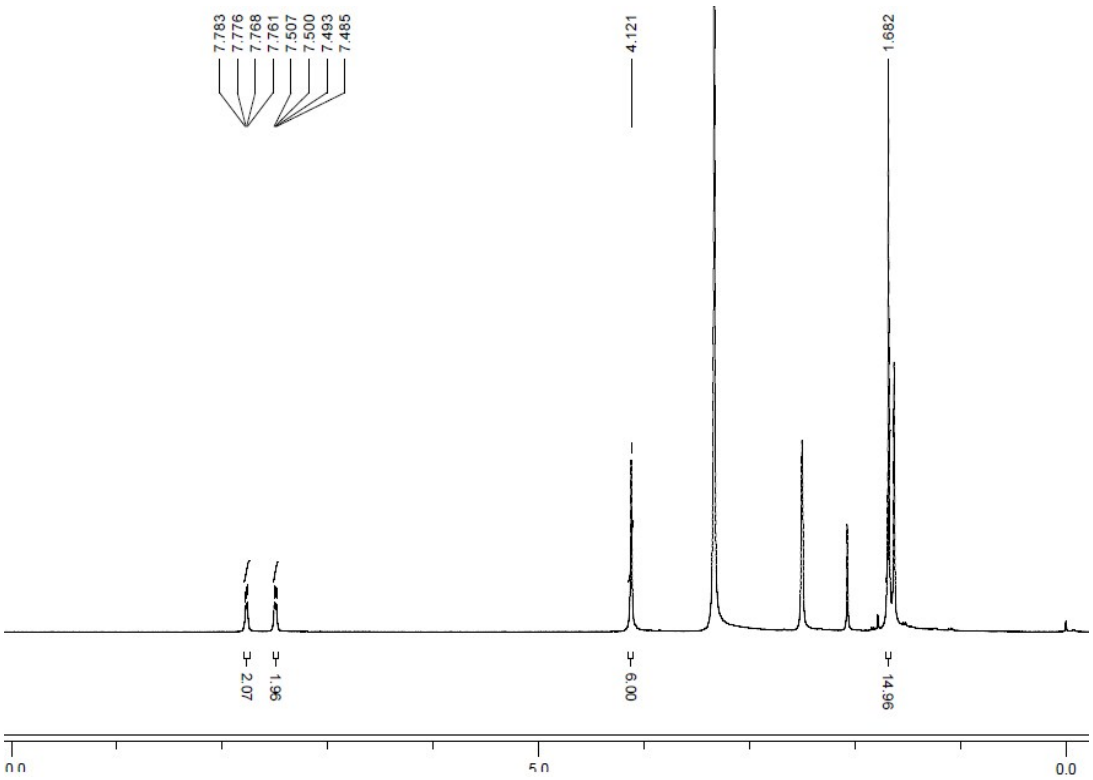
Entry	Ligand	**3a** (%)[b]	**3b** (%)[b]
1	L_1	44	50
2	L_2	41	53
3	L_3	21	50
4	L_4	30	56
5	L_5	49	23
6	L_6	41	38
7	L_7	35	50
8[c]	L_8	61	27
9	L_9	33	46
10	L_{10}	33	51
11	L_{11}	21	50
12[c]	L_{11}	23	65

13[c]	L_{12}	20	69
14[c]	L_{14}	41	Trace

[a] Unless otherwise mentioned, all reactions were carried out using **1a** (0.2 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (1 mol%), $Cu(OAc)_2 \cdot H_2O$ (0.2 mmol), KOAc (0.2 mmol) and ligand (2 mol%) at 100 °C in DCE for 14 h. [b] Isolated yields. [c] 1 mol% was used.

The ligands used were summarized in Scheme S1. The catalysts were generated through reactions of imidazolium salts and $[Cp^*RhCl_2]_2$ under basic conditions without isolation of the rhodium NHC complexes. We examined the NHC ligands with various *N*-substituents, and the results are presented in Table S2. The popularly used L_1 and L_2 are good in these cases, and the total yields of **3a** and **3b** can reach up to 94% (entries 1 and 2). $[Cp^*RhCl_2]_2$ together with L_3 showed lower activity with a yield of 71% because of less steric effect (entry 3). Ligands L_4-L_7 bearing additional pyridyl and pyrimidyl groups may form chelate rhodium complexes with structures similar to **IV**. In the presence of these *C*,*N*-bidentate ligands, the mono- and double vinylated products were obtained in 72-86% yields (entries 4-7). Among these ligands, bulkier NHCs favor the triazole-directed C-H activation and *ortho*-vinylation. L_8 represents a *C*,*C*-bidentate ligand, and it displays slightly better activity than *C*,*N*-bidentate ligands (entry 8). Tridente ligands L_9, L_{10} and L_{11} are also active to give the corresponding vinylation products in 79%, 84% and 71% yields, respectively (entry 9-11). The imidazolium salts L_{12}, L_{13}, and L_{14} are potentially tetradente after deprontonation, and they are also useful for the vinylation reaction of triazole. The combination of $[Cp^*RhCl_2]_2$ and L_{12}, L_{13} behaved similarly affording mixtures of **3a** and **3b** in 88% and 89% yields. However, when 2 mol% of L_{14} was used, only **3a** was isolated in 41% yield.

Spectral data



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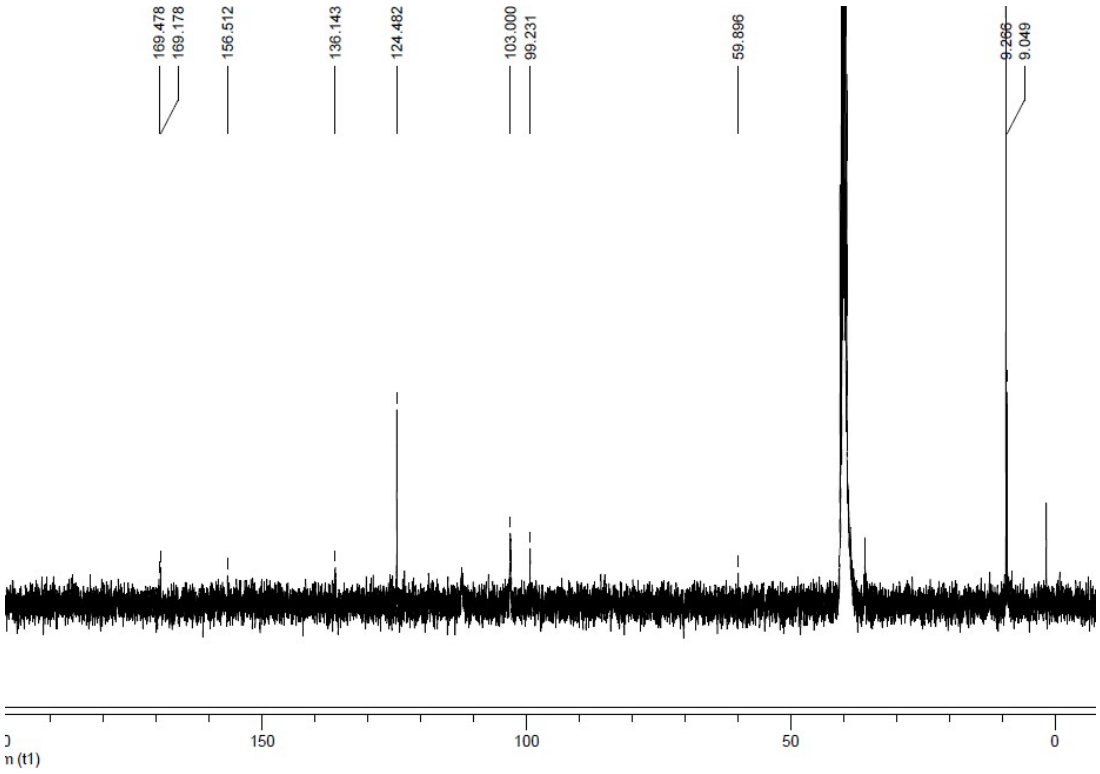
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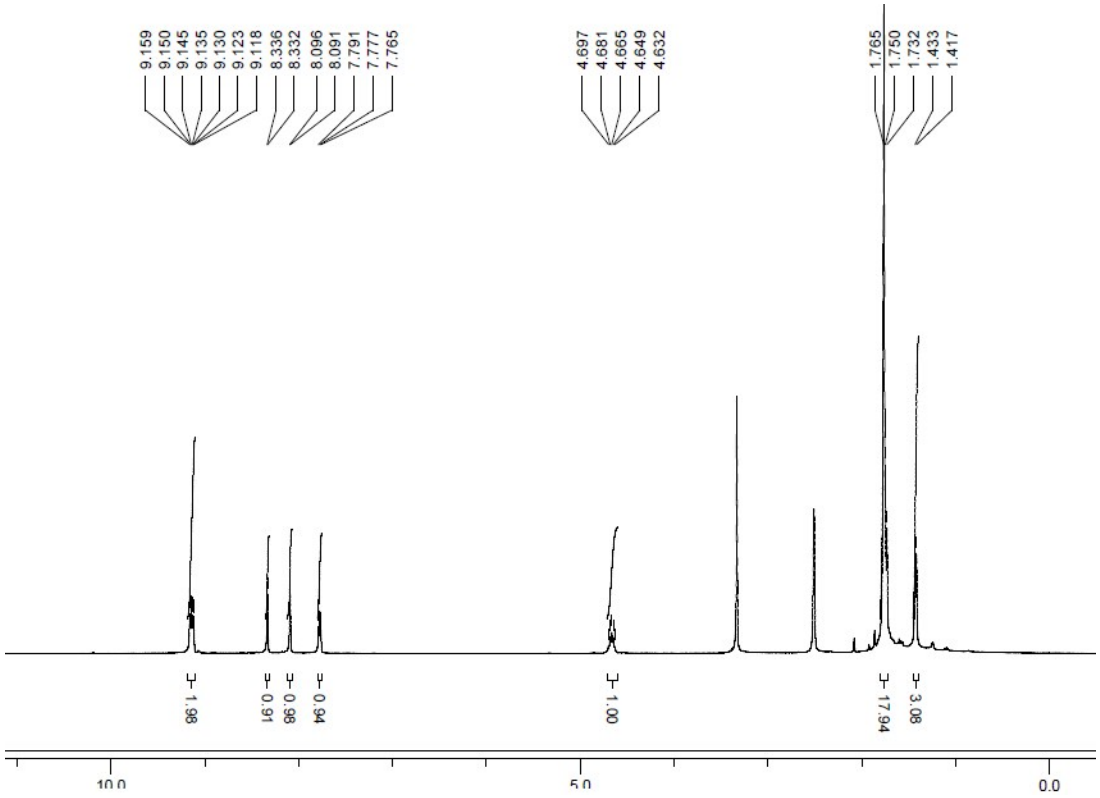
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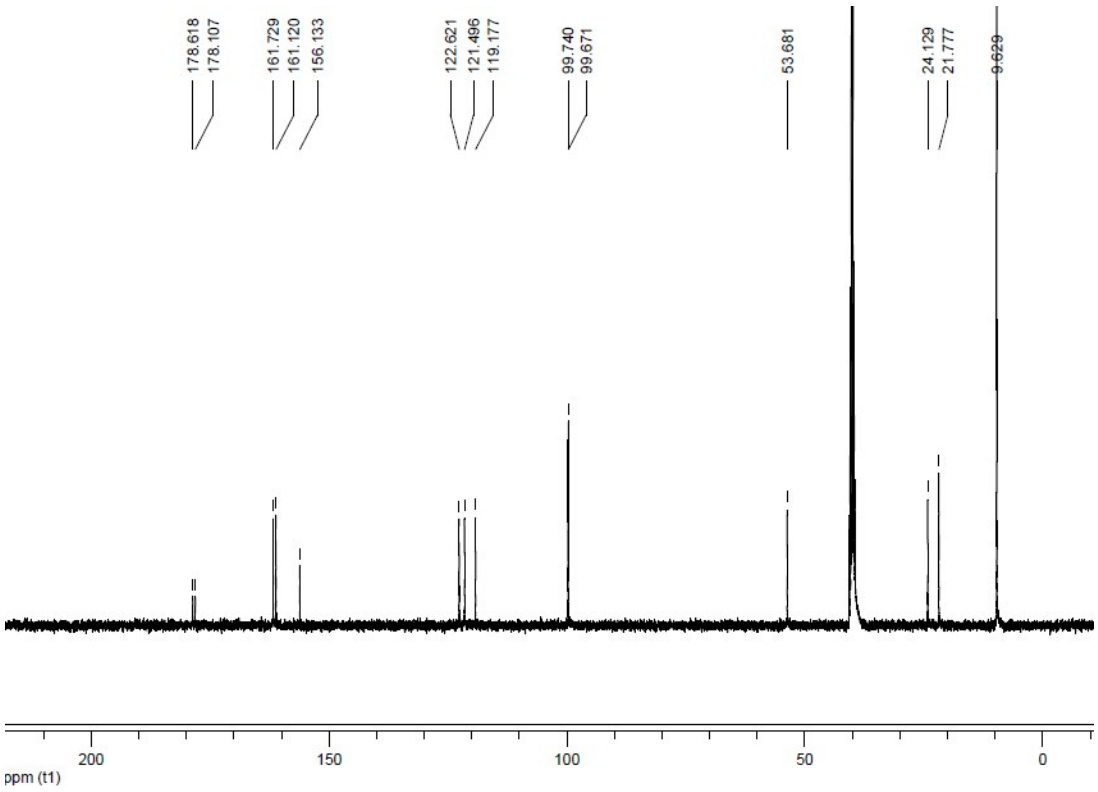

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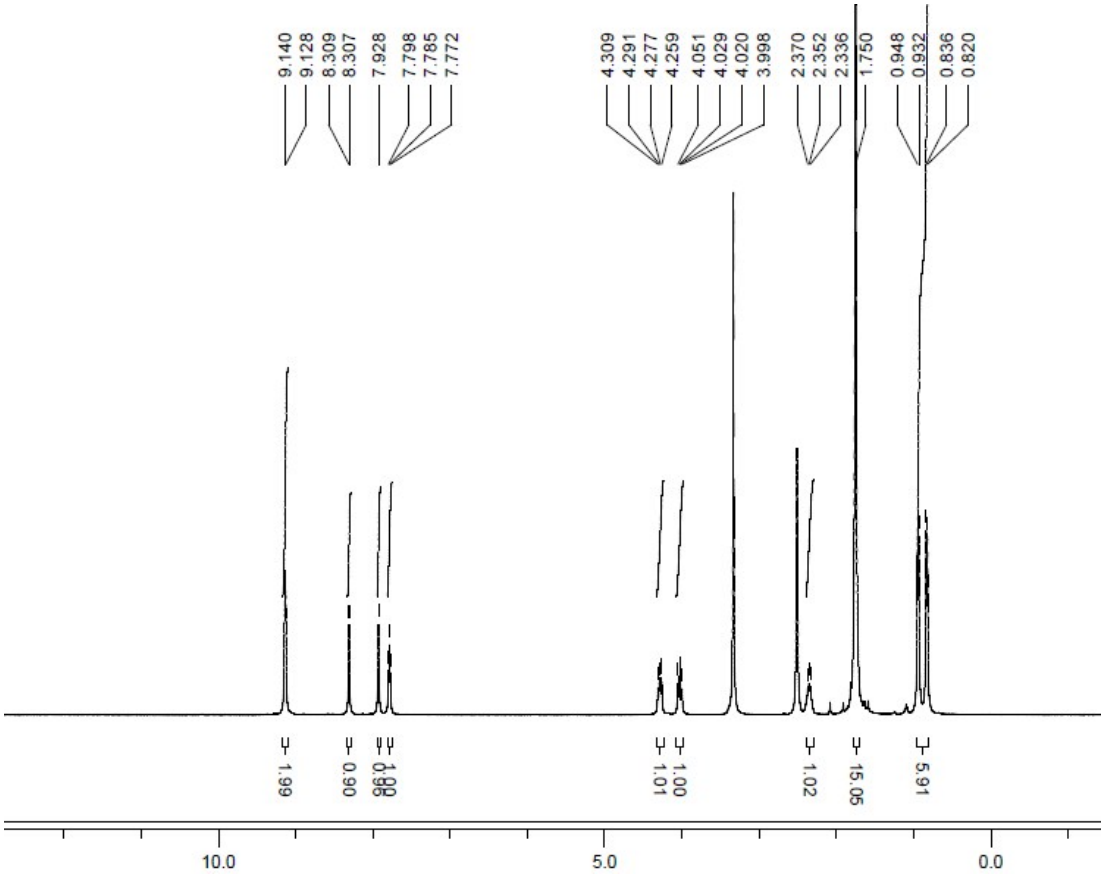
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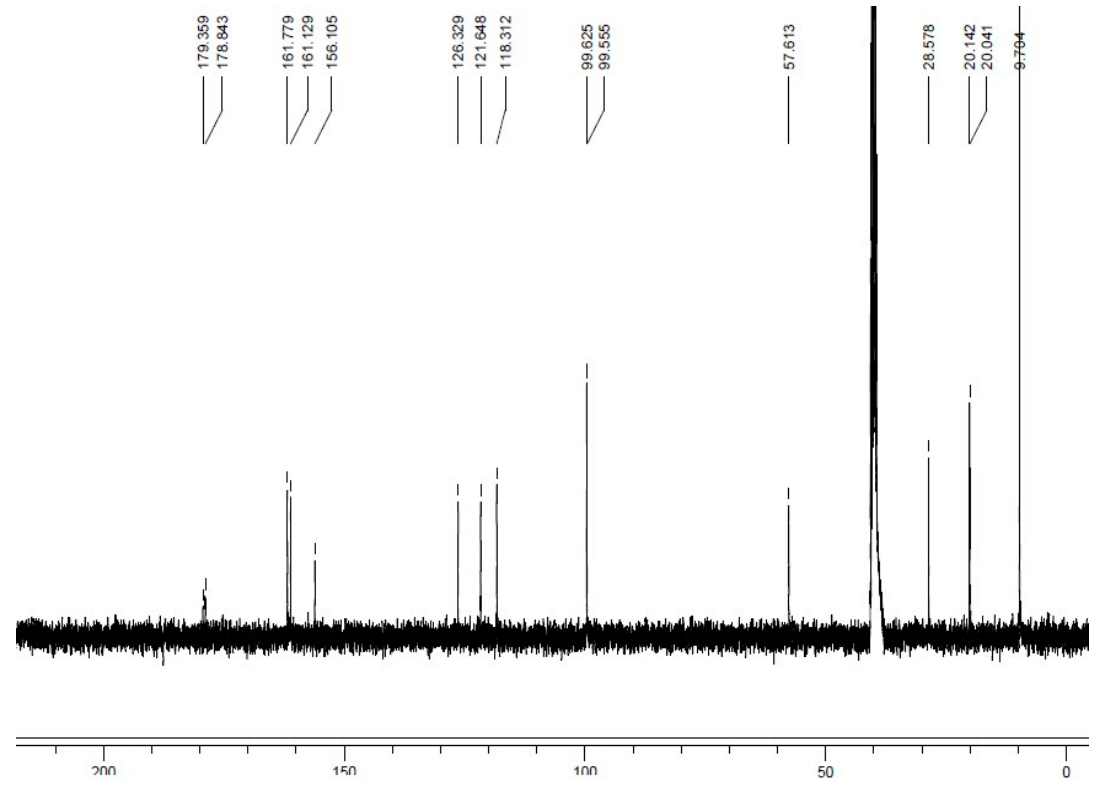
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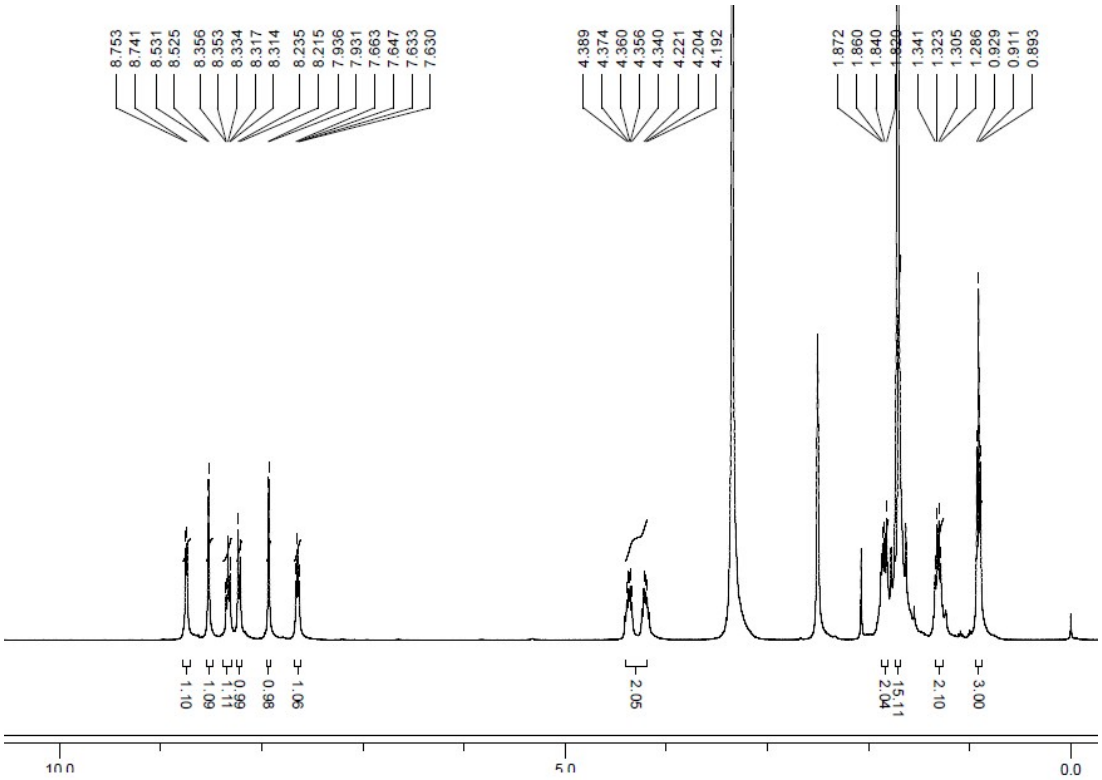

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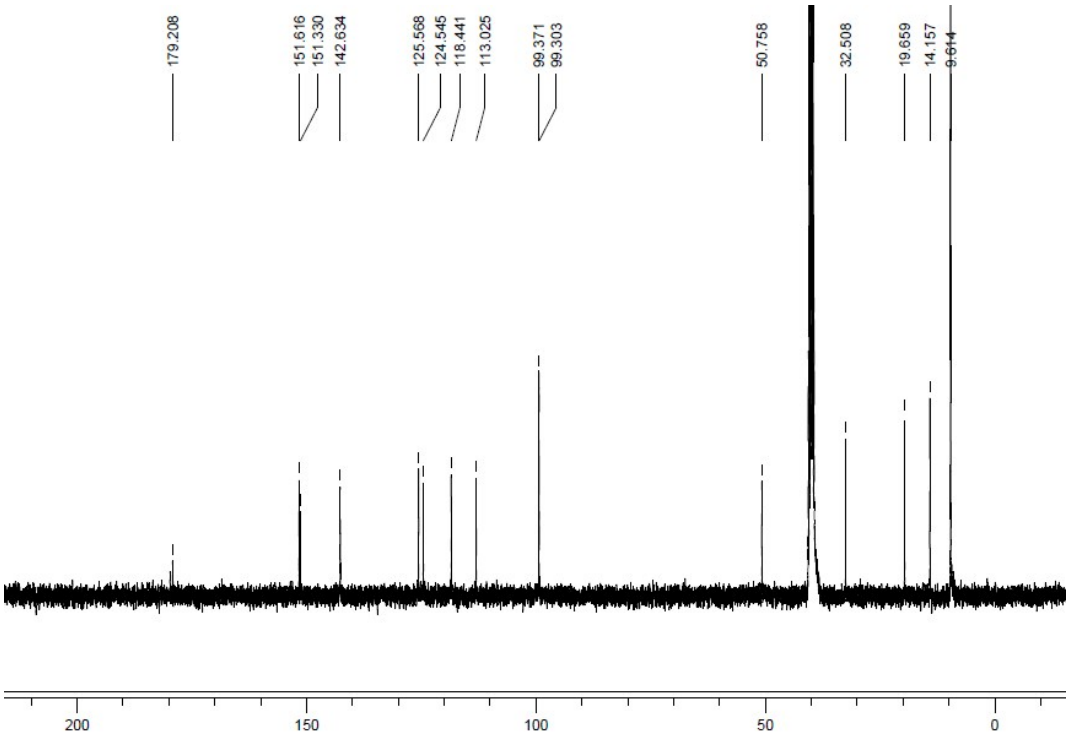
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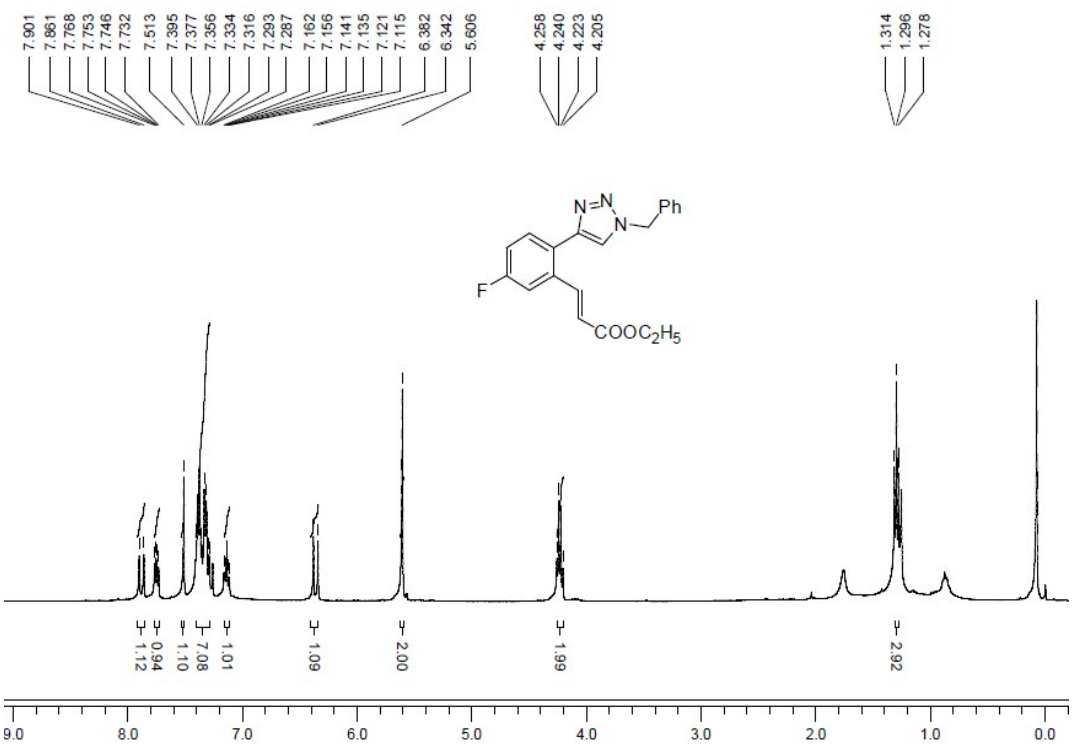
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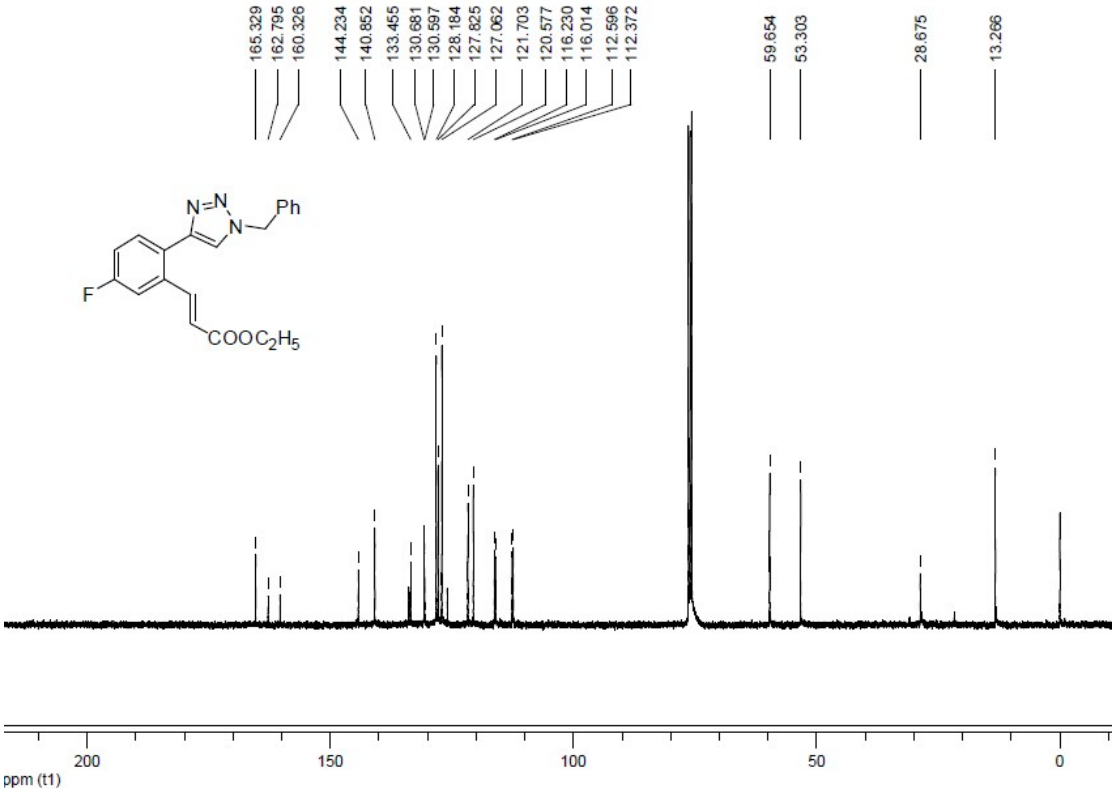
H-3a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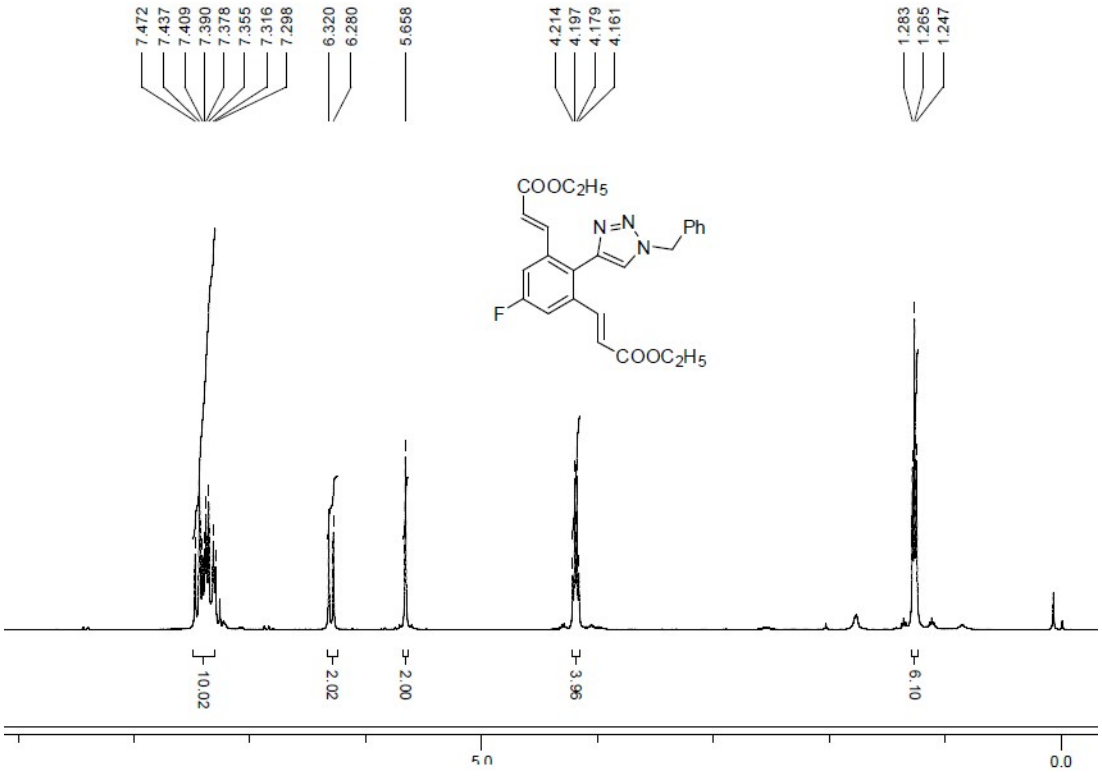
ppm (t1)

C-3a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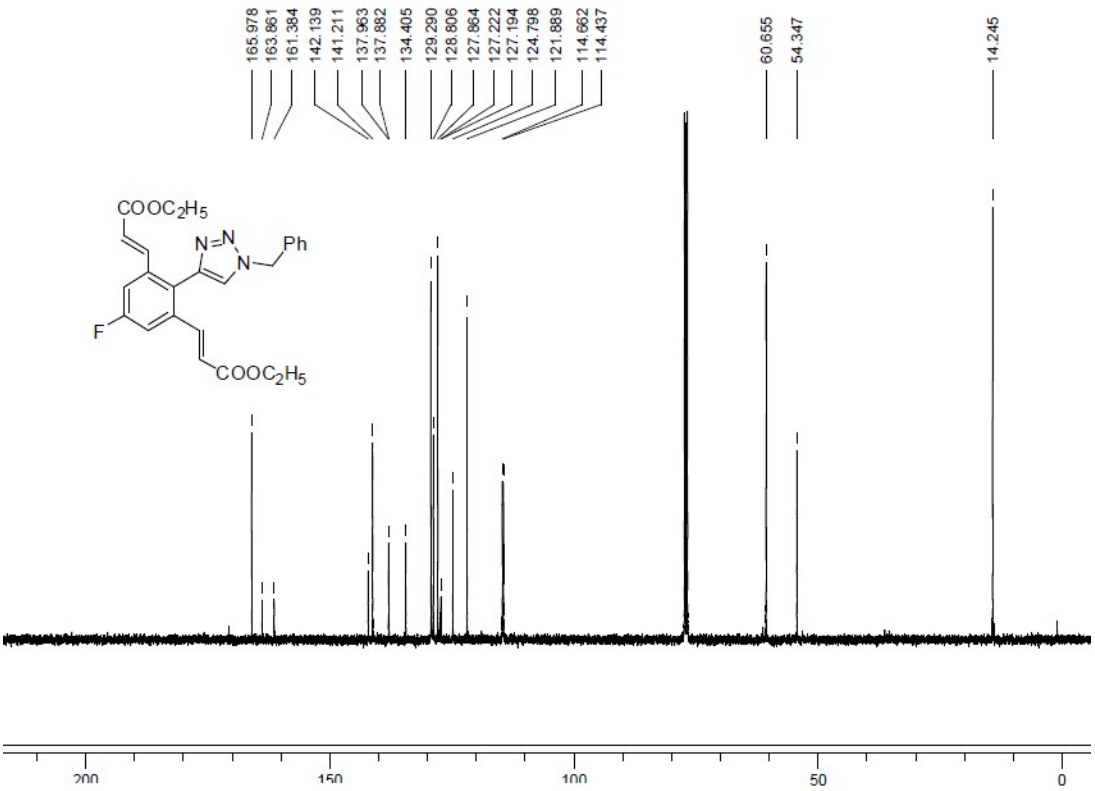
H-3b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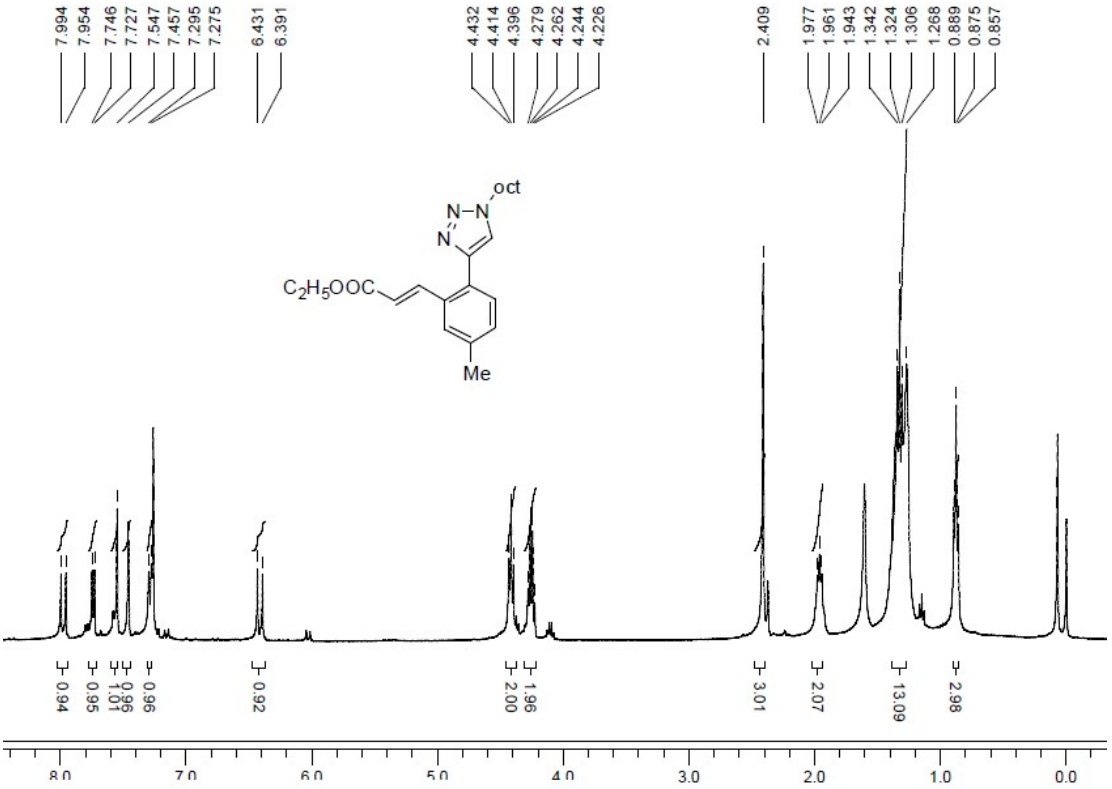
C-3b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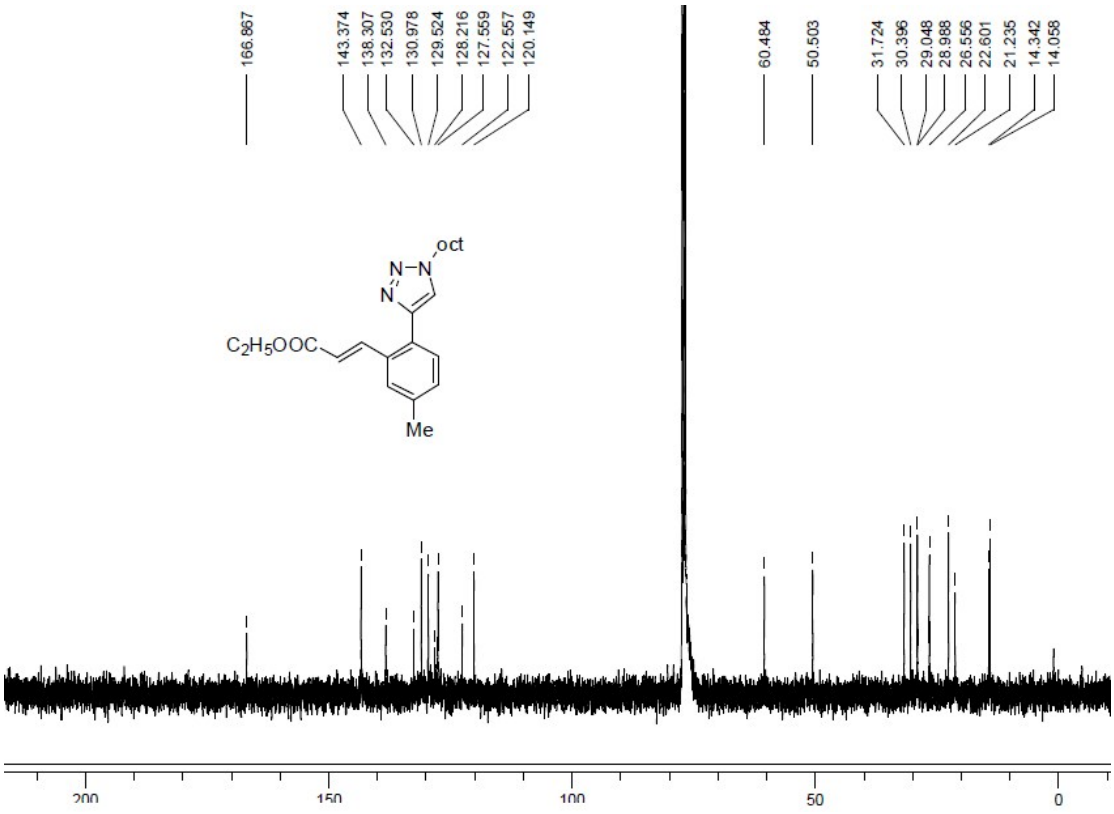
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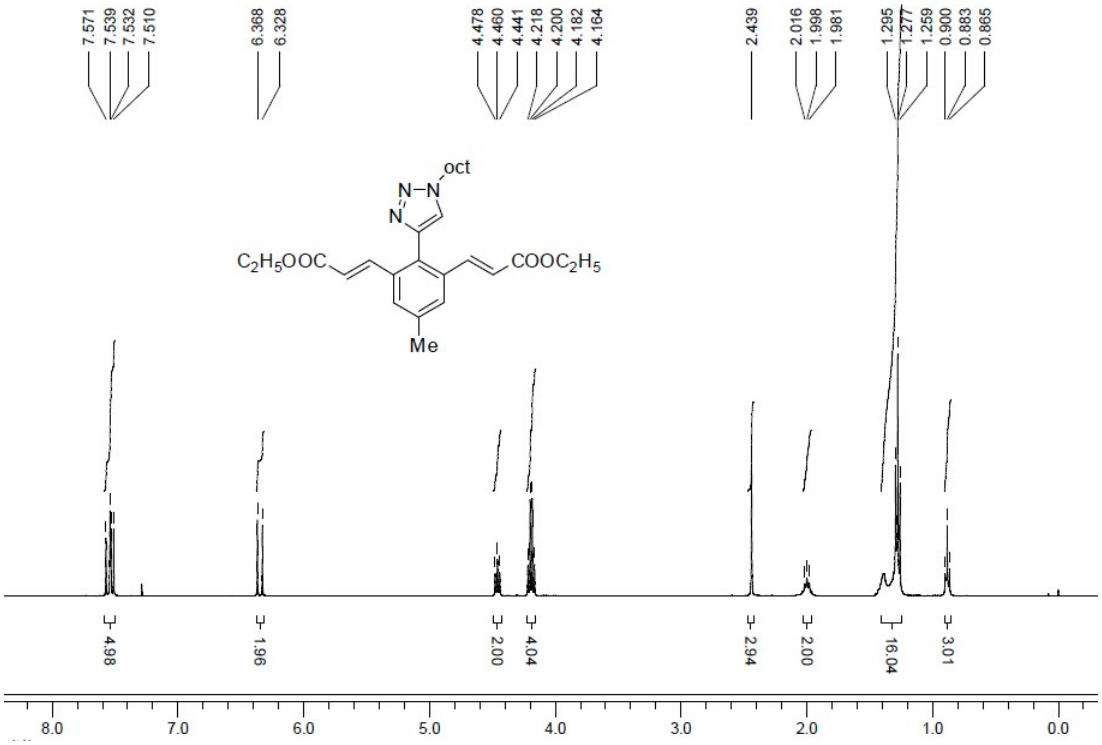
C-3c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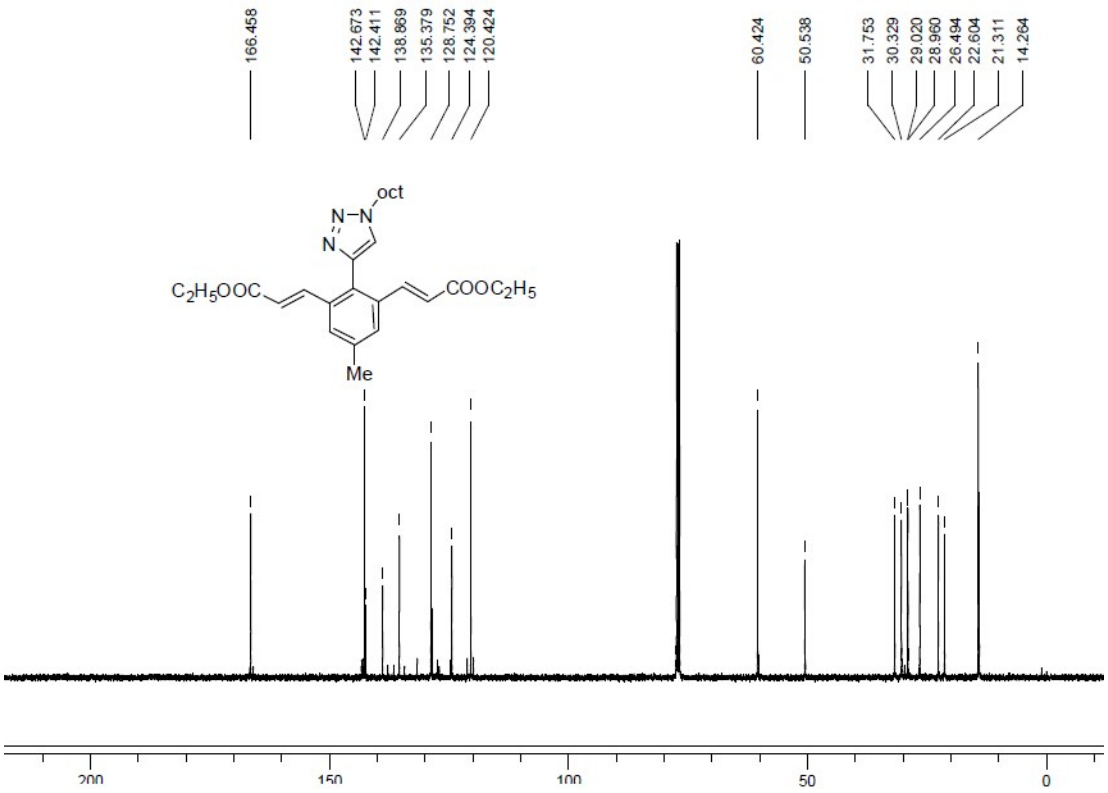
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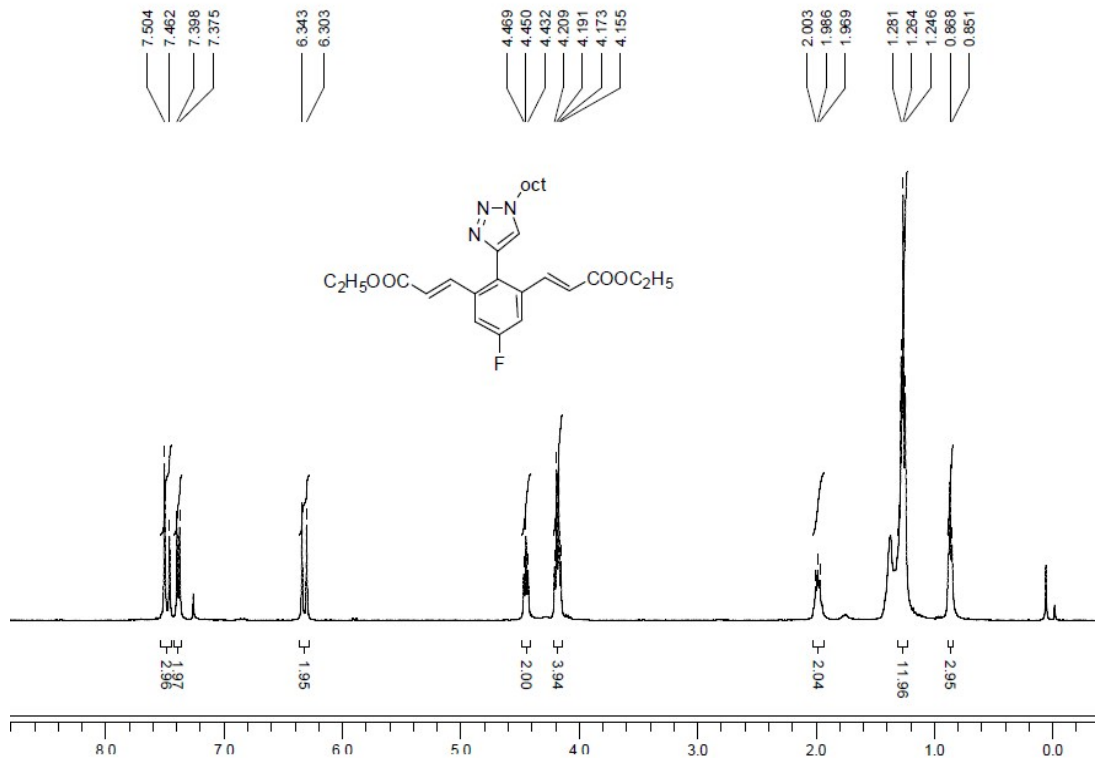
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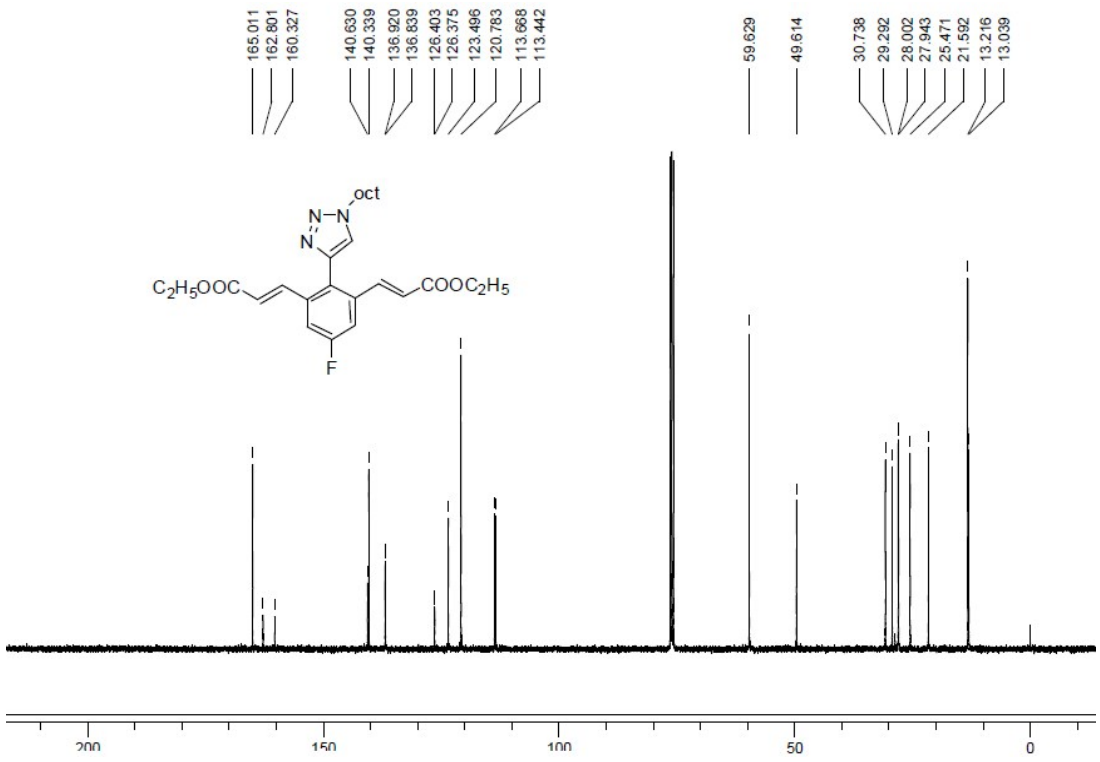
H-3e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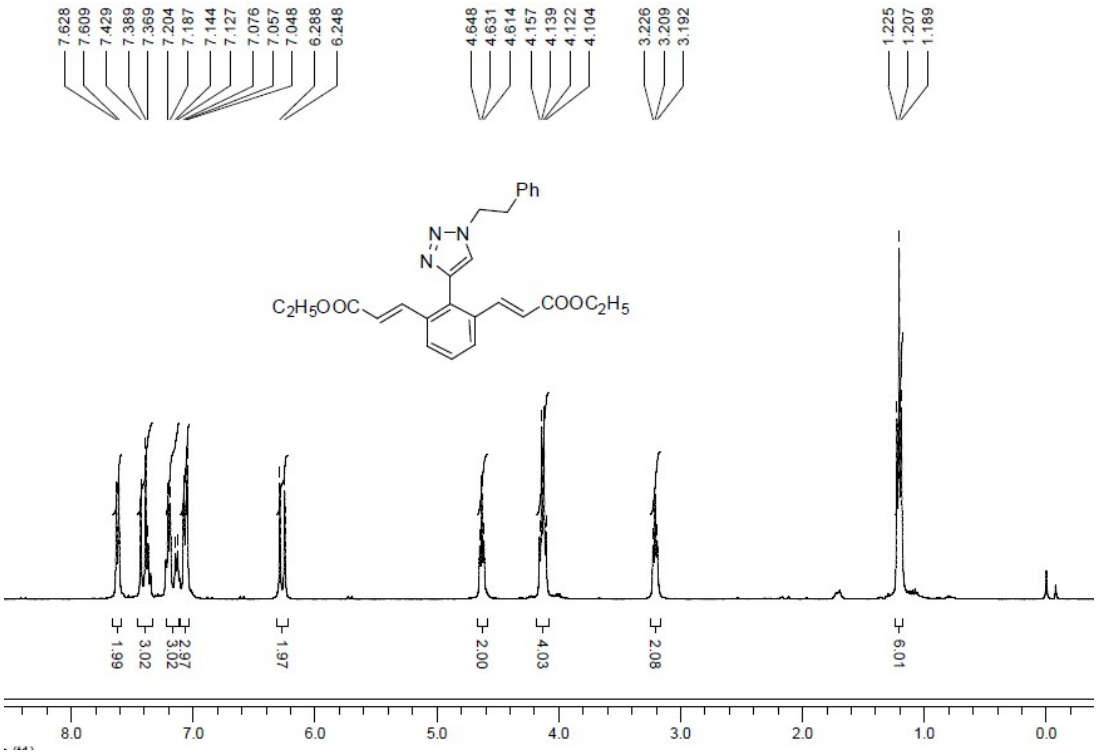
C-3e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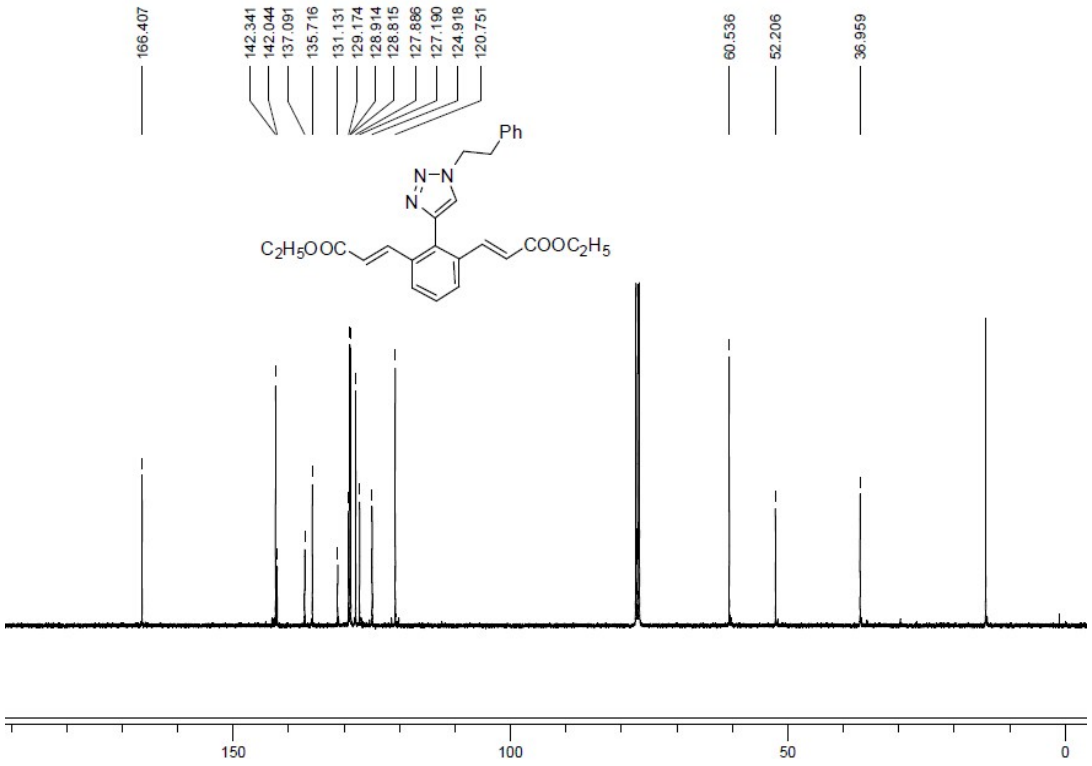
H-3f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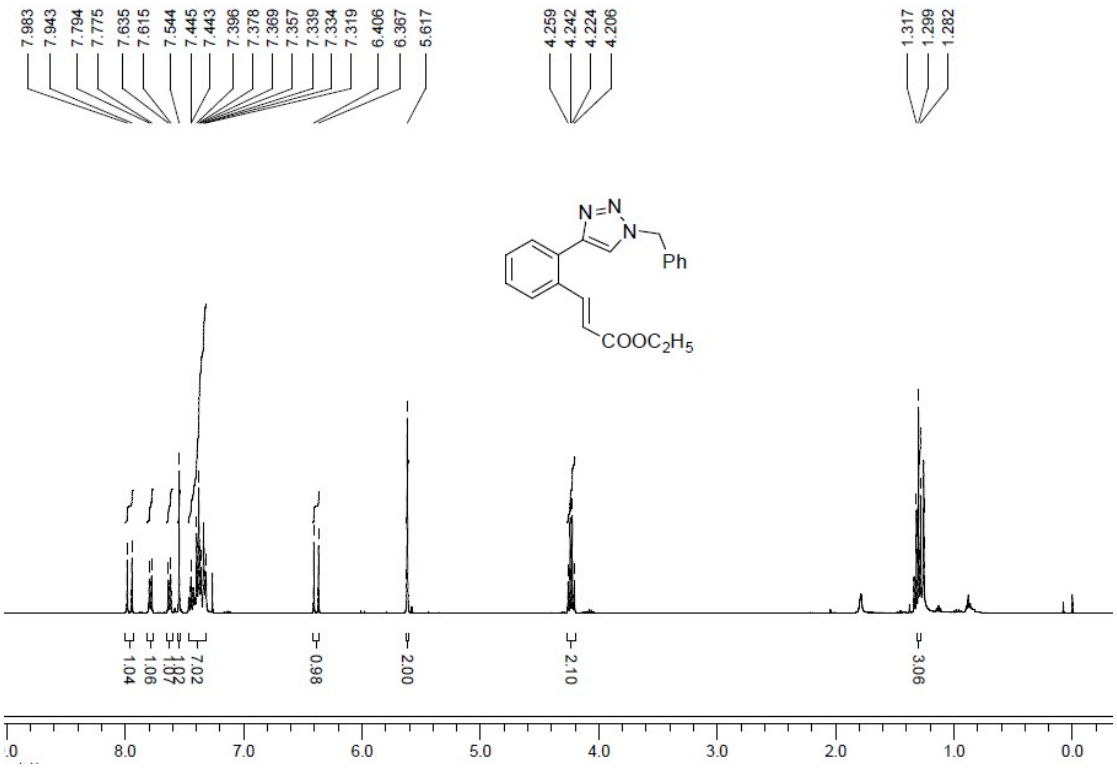
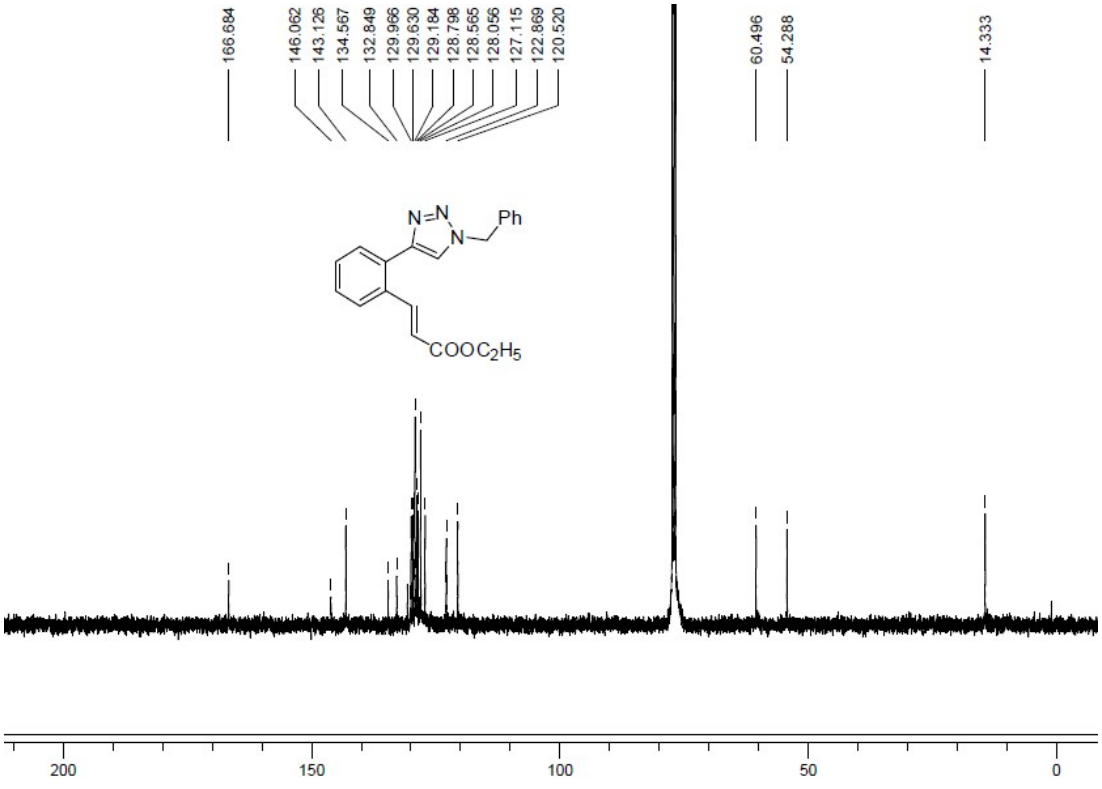
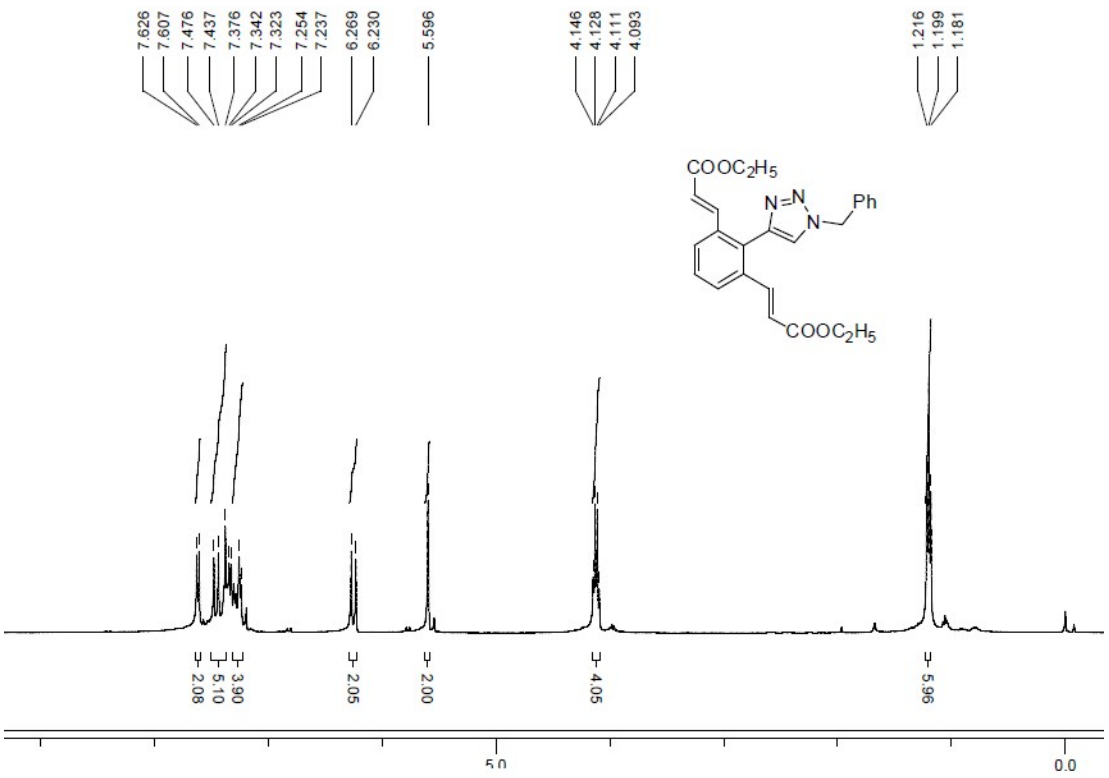
C-3f


7.983
7.943
7.794
7.775
7.635
7.615
7.544
7.445
7.443
7.396
7.378
7.369
7.357
7.339
7.334
7.319
6.406
6.367
5.617
4.259
4.242
4.224
4.206
1.317
1.299
1.282
N=N
N
Ph
COOC2H5
1.04
1.06
7.02
0.98
2.00
2.10
3.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

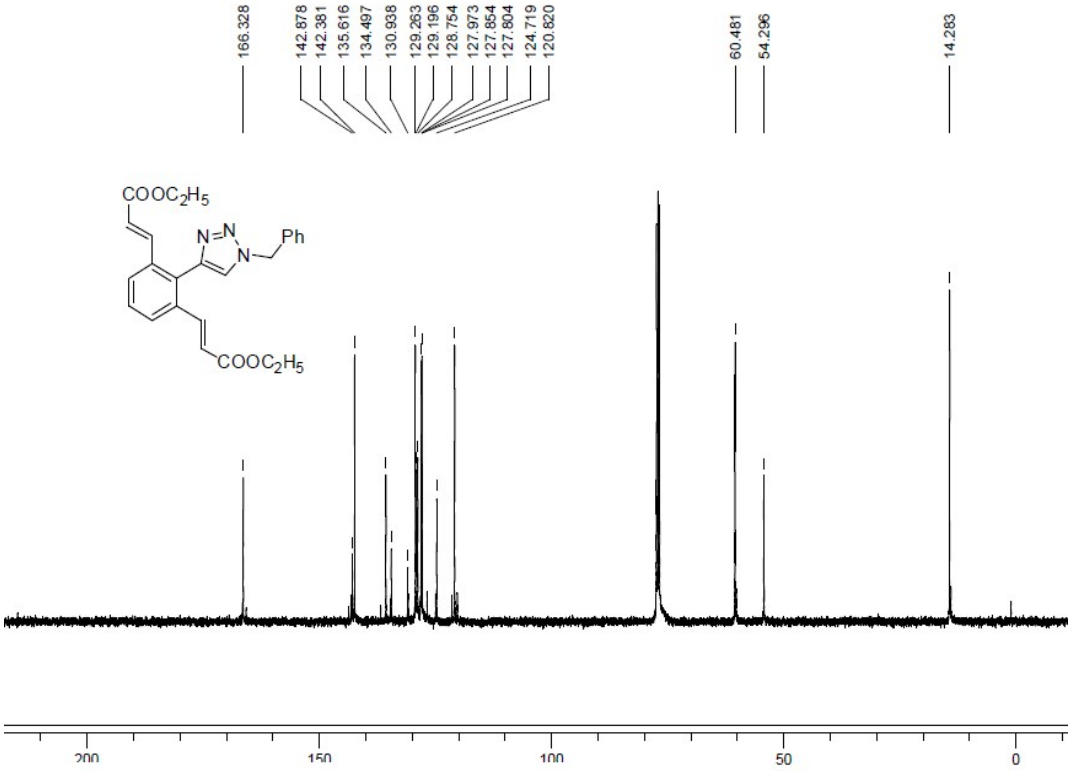
H-3g


166.684
146.062
143.126
134.567
132.849
129.966
129.630
129.184
128.798
128.565
128.056
127.115
122.869
120.520
60.496
54.288
14.333
N=N
N
Ph
COOC2H5
200
150
100
50
0

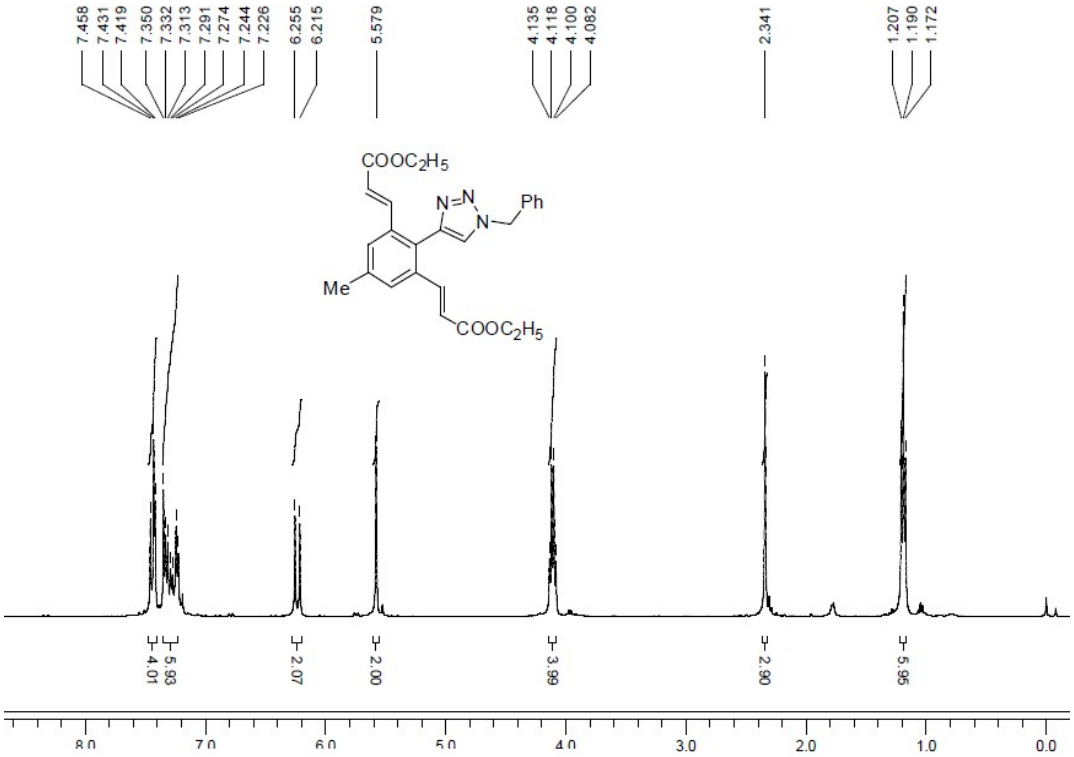
C-3g


7.626
7.607
7.476
7.437
7.376
7.342
7.323
7.254
7.237
6.269
6.230
5.596
4.146
4.128
4.111
4.093
1.216
1.199
1.181
COOC2H5
N=N
N
Ph
COOC2H5
2.08
5.10
3.90
2.05
2.00
4.05
5.96
5.0
0.0

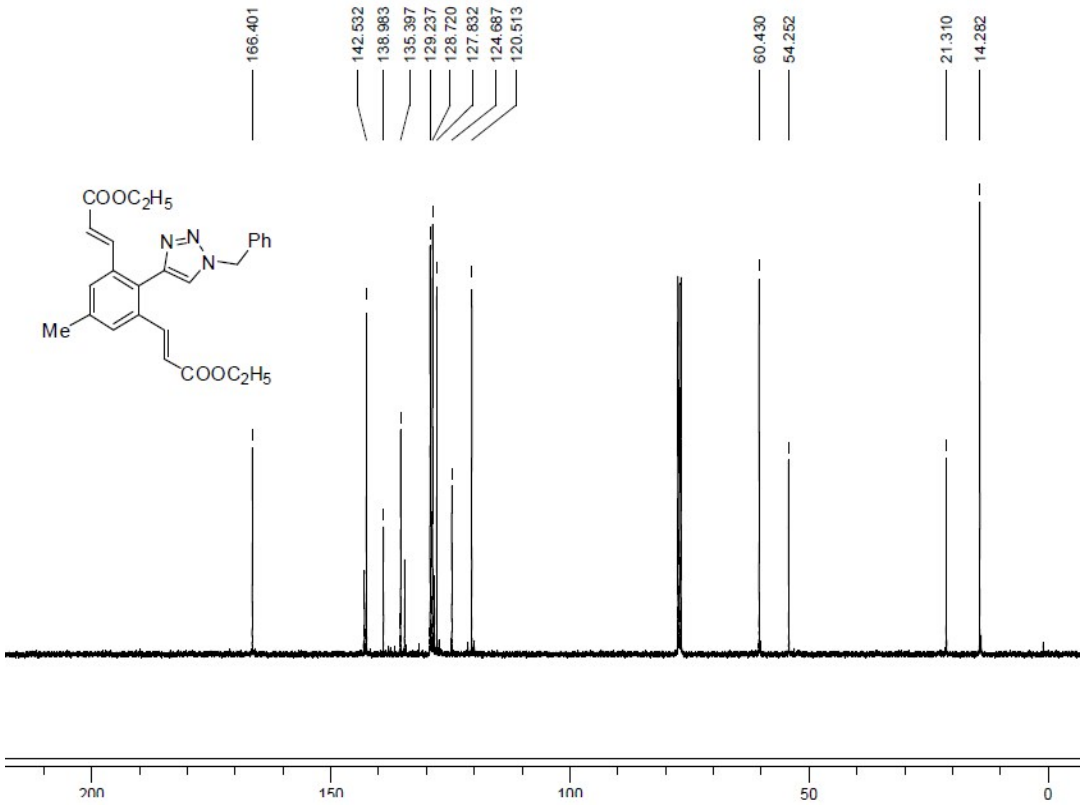
H-3h


166.328
142.878
142.381
135.616
134.497
130.938
129.263
129.196
128.754
127.973
127.854
127.804
124.719
120.820
60.481
54.296
14.283
COOC2H5
N=N
N
Ph
COOC2H5
200
150
100
50
0

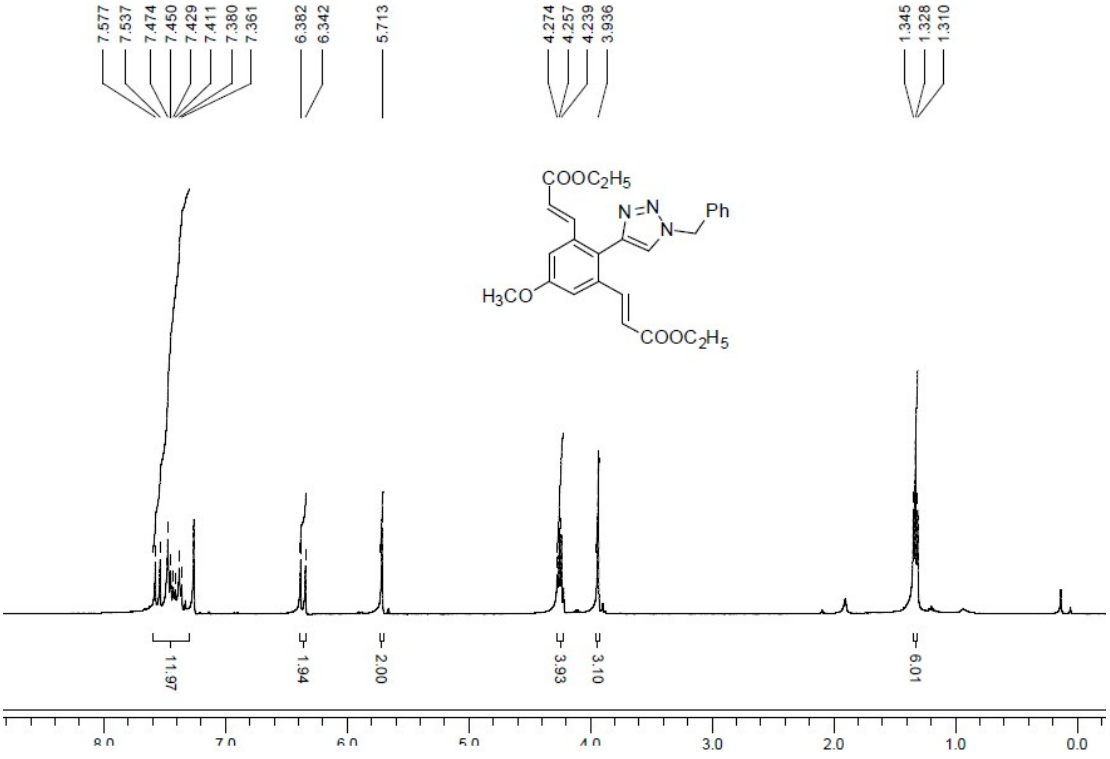
C-3h


7.458
7.431
7.419
7.350
7.332
7.313
7.291
7.274
7.244
7.226
6.255
6.215
5.579
4.135
4.118
4.100
4.082
2.341
1.207
1.190
1.172
COOC2H5
N=N
N
Ph
Me
COOC2H5
4.01
5.93
2.07
2.00
3.99
2.90
5.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

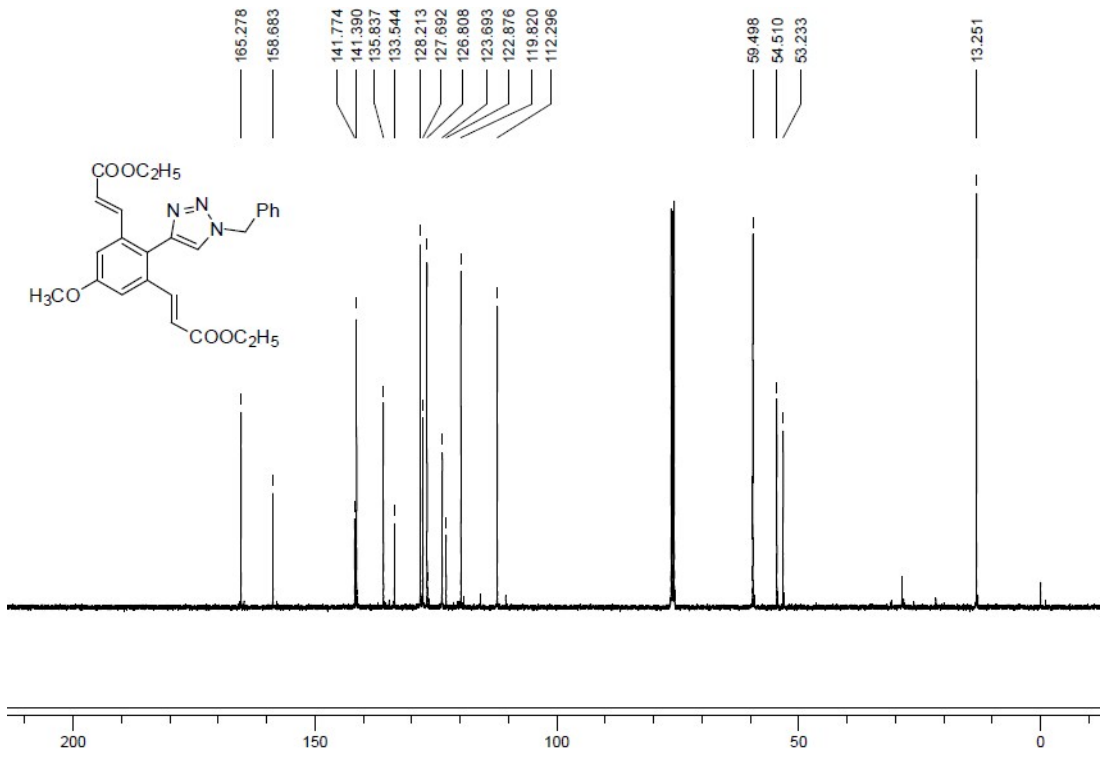
H-3i


166.401
142.532
138.983
135.397
129.237
128.720
127.832
124.687
120.513
60.430
54.252
21.310
14.282
COOC2H5
N=N
N
Ph
Me
COOC2H5
200
150
100
50
0

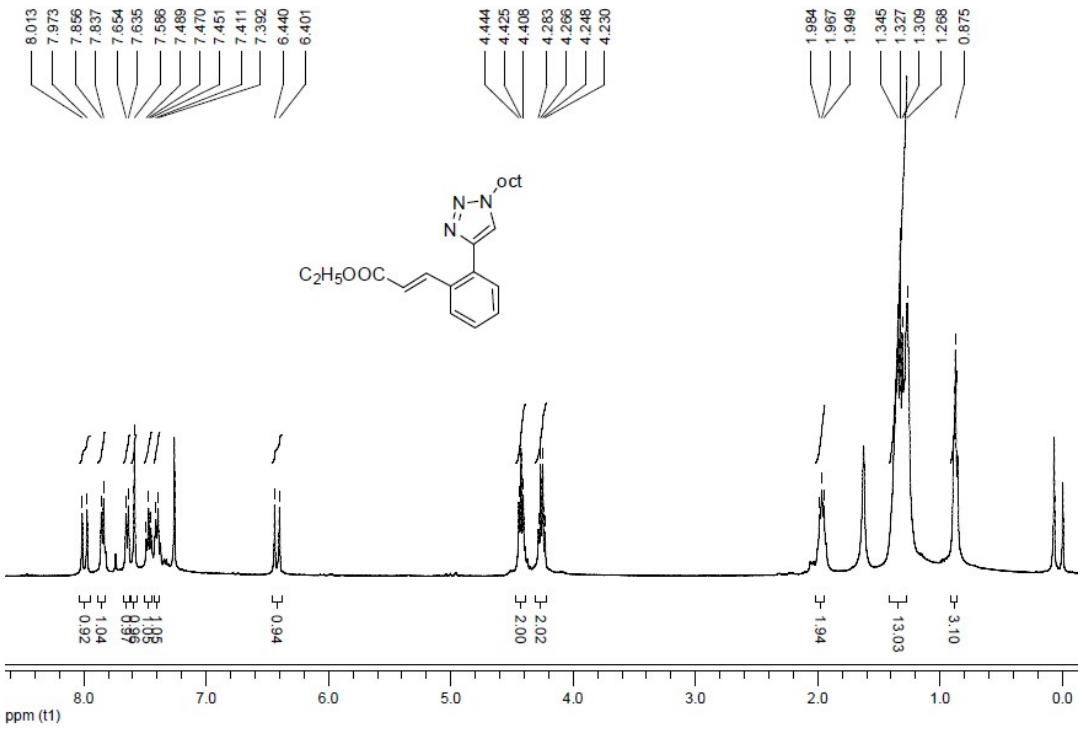
C-3i


7.577
7.537
7.474
7.450
7.429
7.411
7.380
7.361
6.382
6.342
5.713
4.274
4.257
4.239
3.936
1.345
1.328
1.310
COOC2H5
N=N
N
Ph
H3CO
COOC2H5
1.11
1.94
2.00
3.93
3.10
6.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

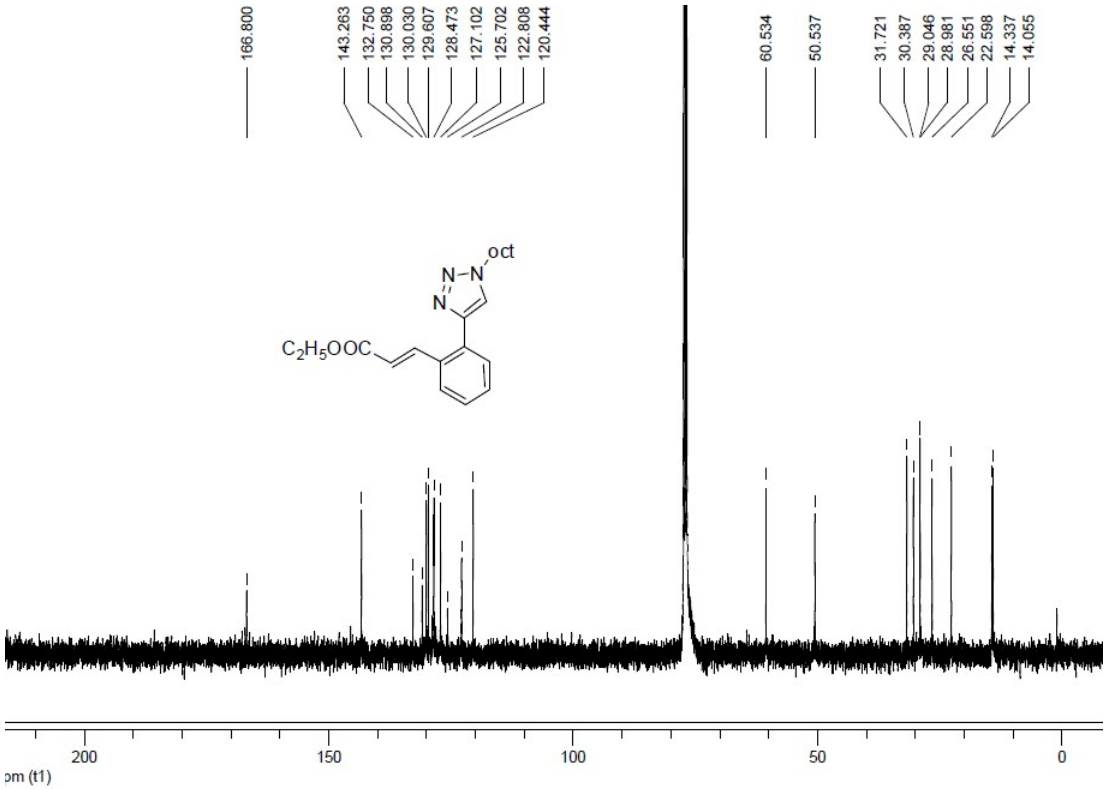
H-3j


165.278
158.683
141.774
141.390
135.837
133.544
128.213
127.692
126.808
123.693
122.876
119.820
112.296
59.498
54.510
53.233
13.251
COOC2H5
N=N
N
Ph
H3CO
COOC2H5
200
150
100
50
0

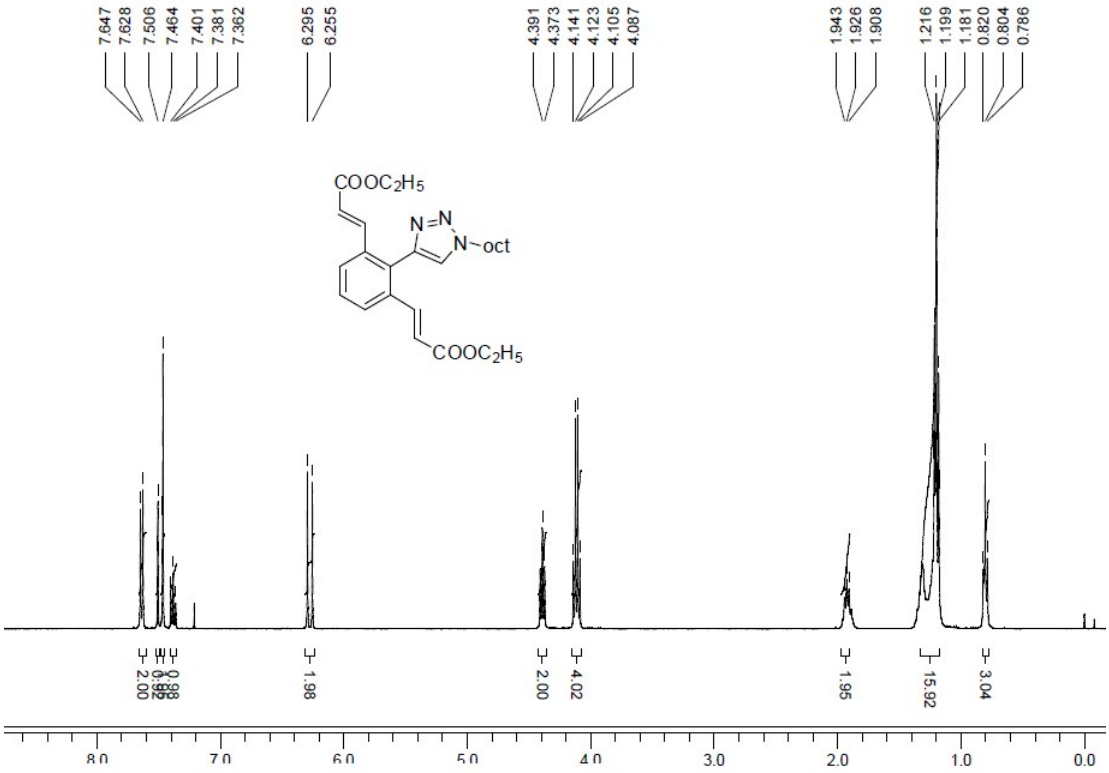
C-3j


8.013
7.973
7.856
7.837
7.654
7.635
7.586
7.489
7.470
7.451
7.411
7.392
6.440
6.401
4.444
4.425
4.408
4.283
4.266
4.248
4.230
1.984
1.967
1.949
1.345
1.327
1.309
1.268
0.875
oct
N
N
N
C2H5OOC
0.92
1.04
0.94
2.00
2.02
1.94
13.03
3.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

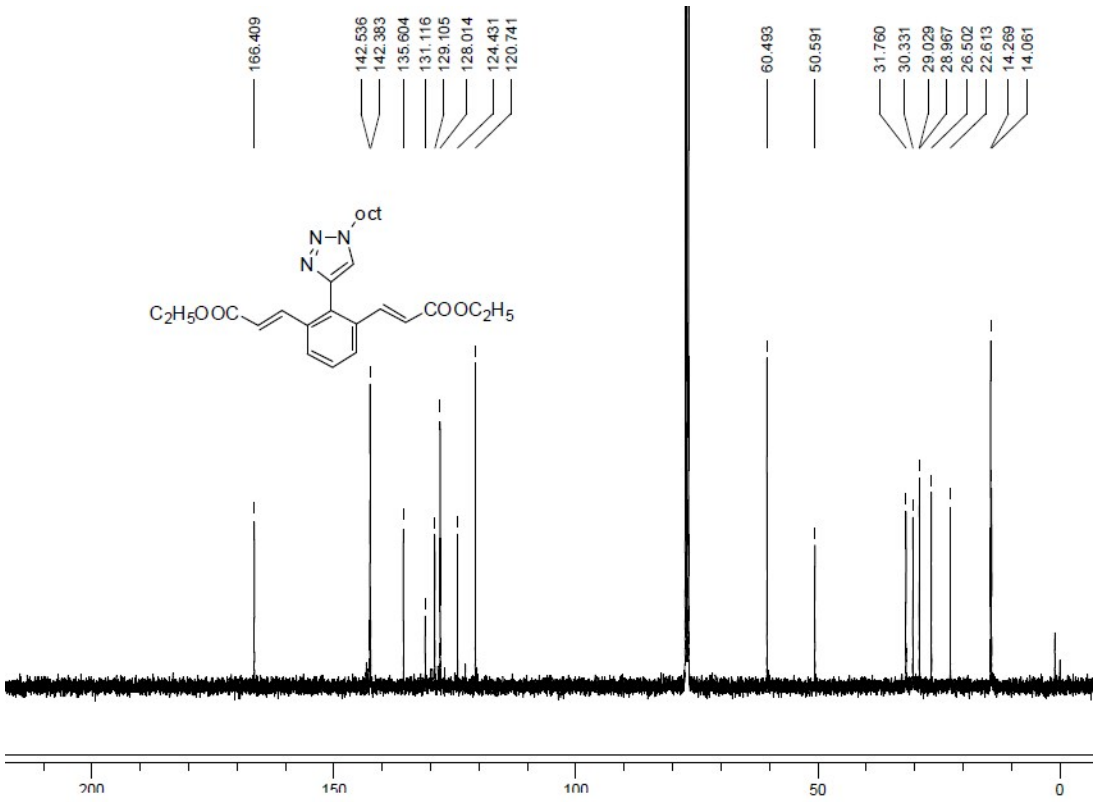
H-3k


166.800
143.263
132.750
130.898
130.030
129.607
128.473
127.102
125.702
122.808
120.444
60.534
50.537
31.721
30.387
29.046
28.981
26.551
22.598
14.337
14.055
oct
N
N
N
C2H5OOC
200
150
100
50
0
pm (t1)

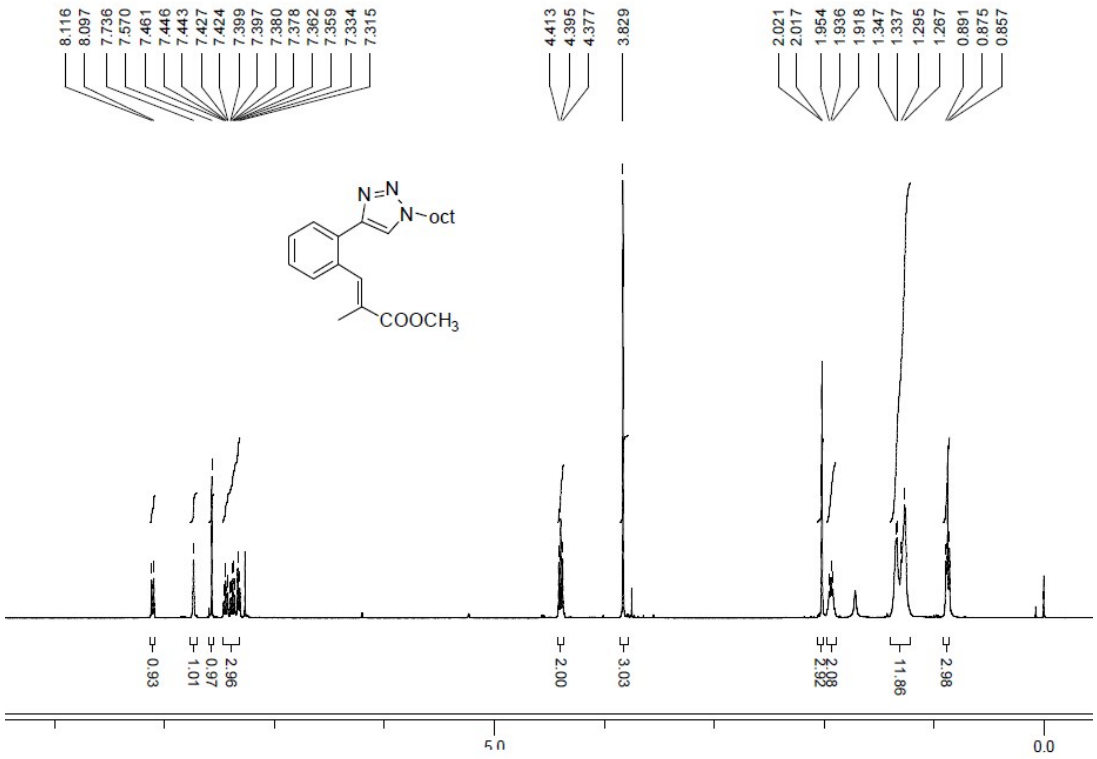
C-3k


7.647
7.628
7.506
7.464
7.401
7.381
7.362
6.295
6.255
4.391
4.373
4.141
4.123
4.105
4.087
1.943
1.926
1.908
1.216
1.199
1.181
0.820
0.804
0.786
COOC2H5
N
N
oct
COOC2H5
2.00
1.98
2.00
4.02
1.95
15.92
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

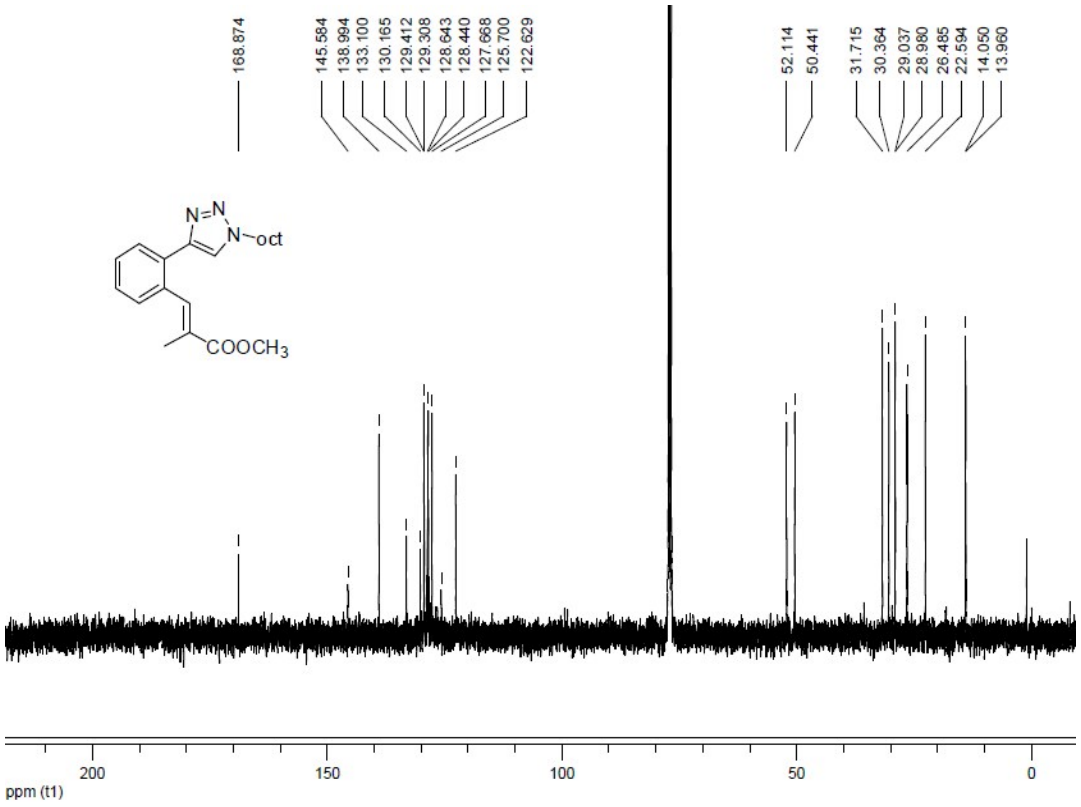
H-3l


166.409
142.536
142.383
135.604
131.116
129.105
128.014
124.431
120.741
60.493
50.591
31.760
30.331
29.029
28.967
26.502
22.613
14.269
14.061
oct
N
N
N
C2H5OOC
COOC2H5
200
150
100
50
0

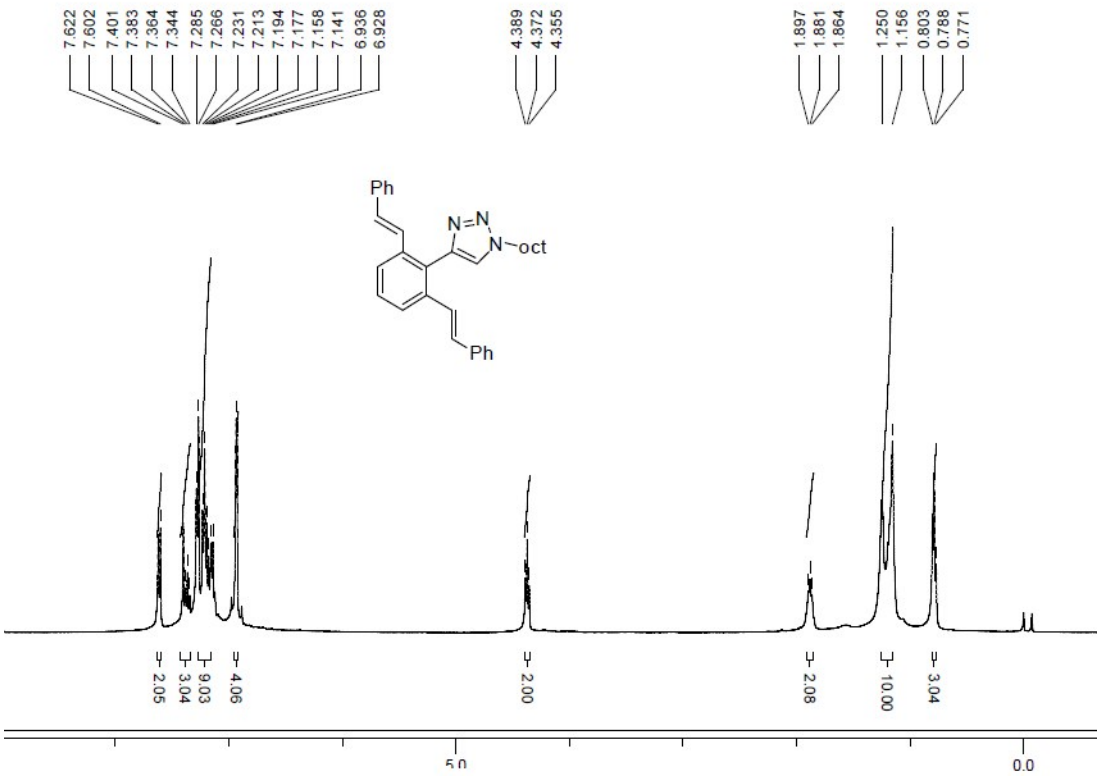
C-3l


8.116
8.097
7.736
7.570
7.461
7.446
7.443
7.427
7.424
7.399
7.397
7.380
7.378
7.362
7.359
7.334
7.315
4.413
4.395
4.377
3.829
2.021
2.017
1.954
1.936
1.918
1.347
1.337
1.295
1.267
0.891
0.875
0.857
N=N
N-oct
COOCH3
0.93
1.01
0.97
2.96
2.00
3.03
2.02
2.08
11.86
2.98
5.0
0.0

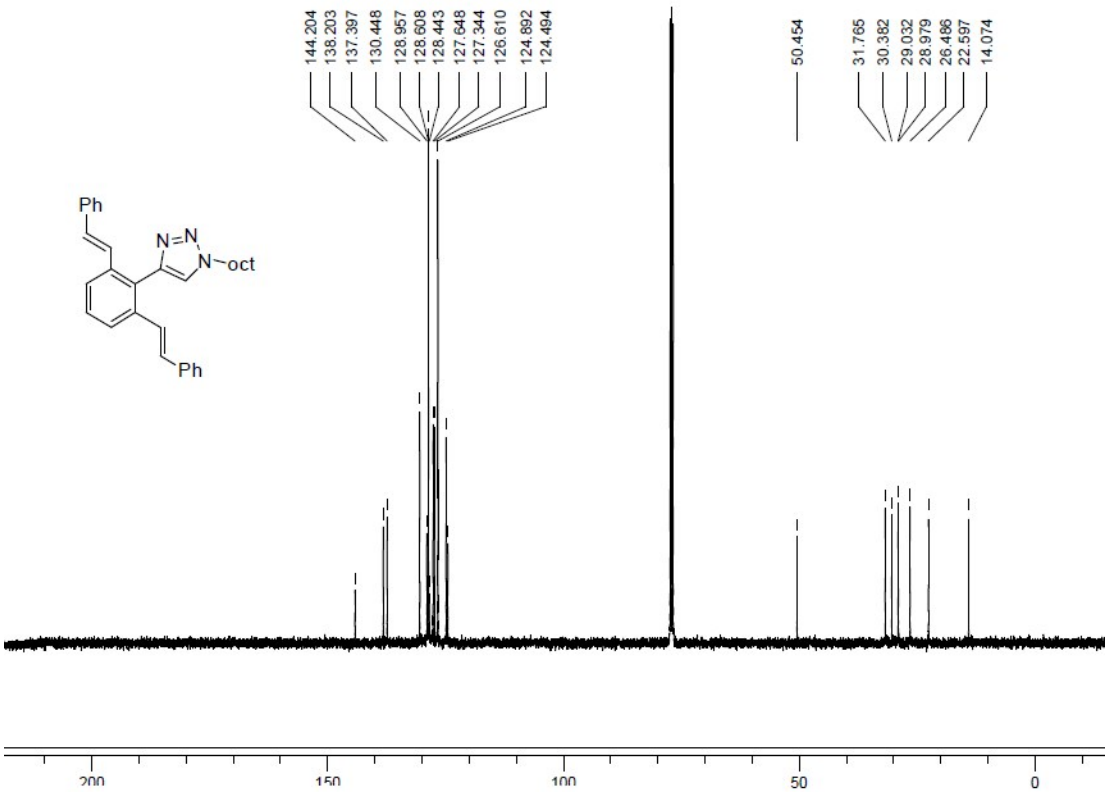
H-3m


168.874
145.584
138.994
133.100
130.165
129.412
129.308
128.643
128.440
127.668
125.700
122.629
52.114
50.441
31.715
30.364
29.037
28.980
26.485
22.594
14.050
13.960
N=N
N-oct
COOCH3
200
150
100
50
0
ppm (t1)

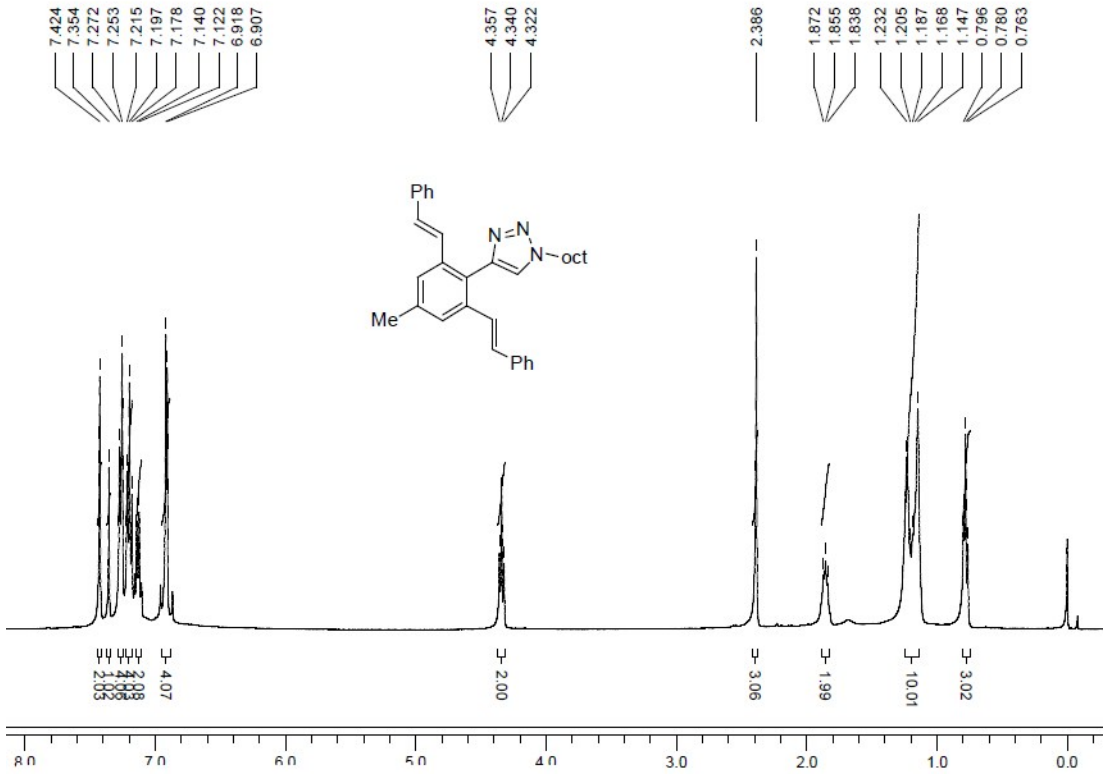
C-3m


7.622
7.602
7.401
7.383
7.364
7.344
7.285
7.266
7.231
7.213
7.194
7.177
7.158
7.141
6.936
6.928
4.389
4.372
4.355
1.897
1.881
1.864
1.250
1.156
0.803
0.788
0.771
Ph
N=N
N
oct
Ph
2.05
3.04
9.03
4.06
2.00
2.08
10.00
3.04
5.0
0.0

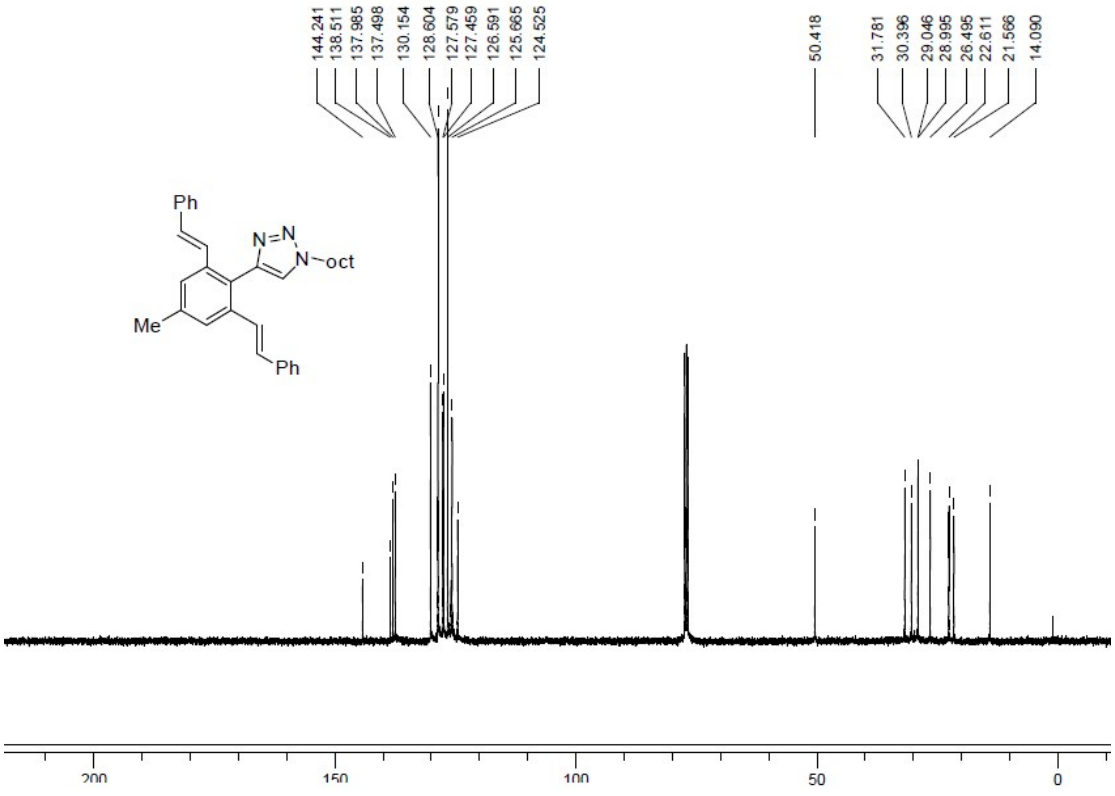
H-3n


144.204
138.203
137.397
130.448
128.957
128.608
128.443
127.648
127.344
126.610
124.892
124.494
50.454
31.765
30.382
29.032
28.979
26.486
22.597
14.074
Ph
N=N
N
oct
Ph
200
150
100
50
0

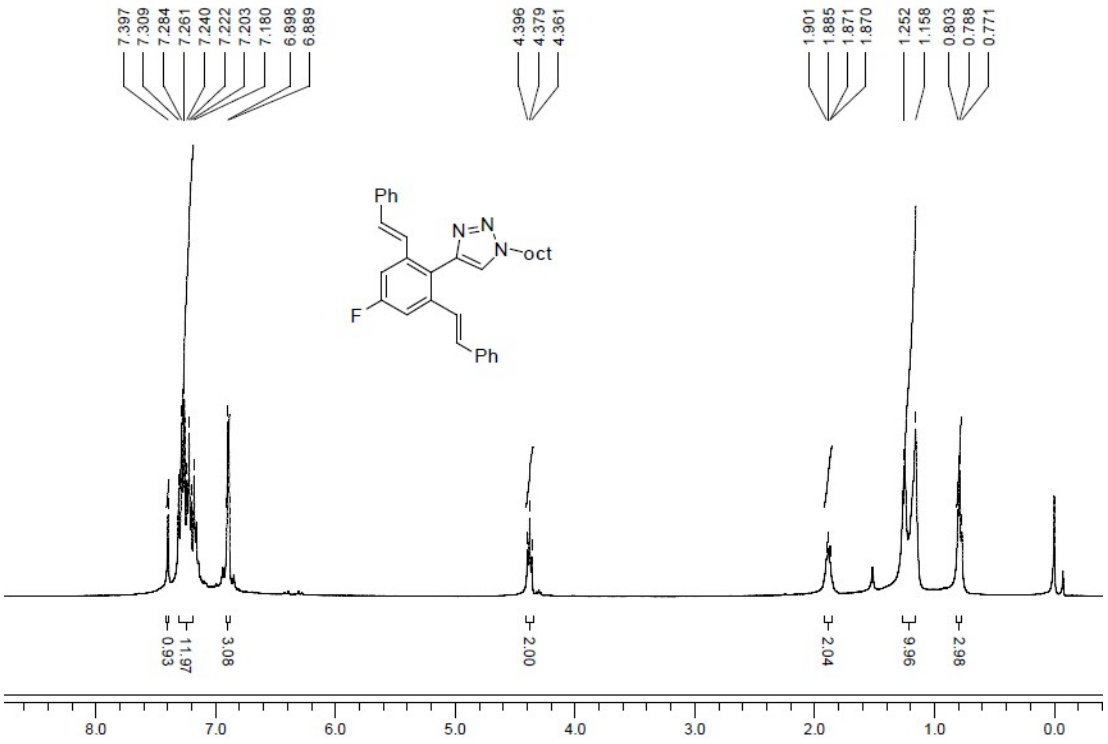
C-3n


7.424
7.354
7.272
7.253
7.215
7.197
7.178
7.140
7.122
6.918
6.907
4.357
4.340
4.322
2.386
1.872
1.855
1.838
1.232
1.205
1.187
1.168
1.147
0.796
0.780
0.763
Ph
N=N
N
oct
Me
Ph
4.07
2.00
3.06
1.99
10.01
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

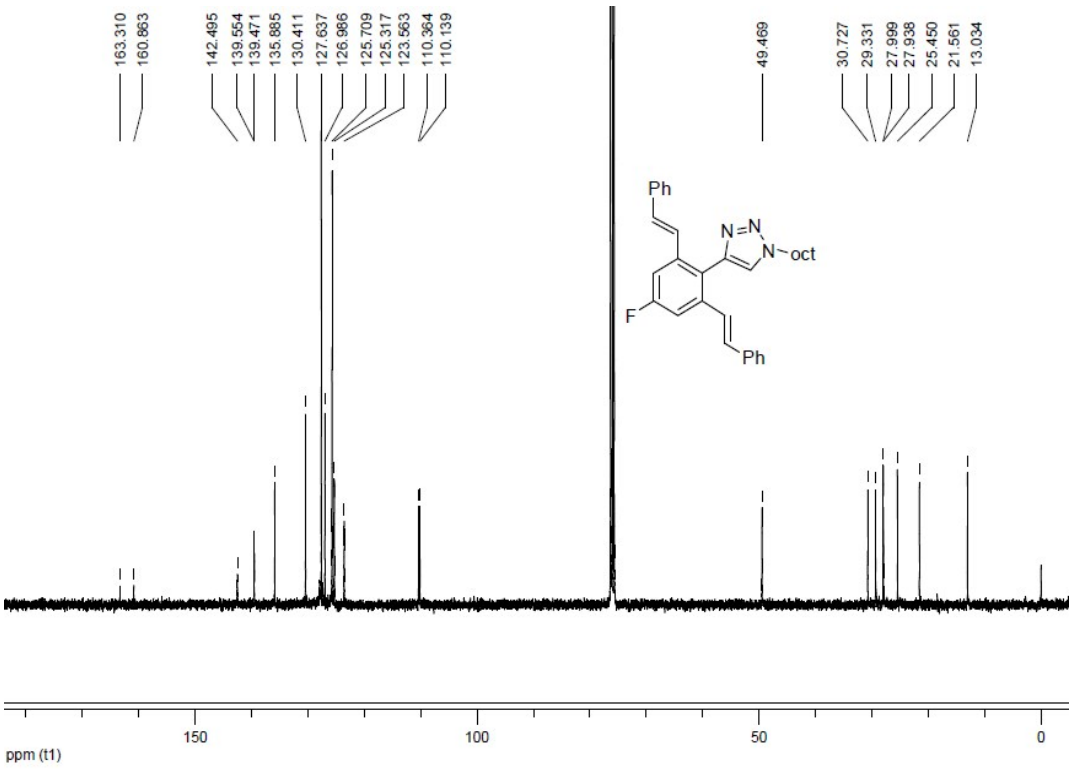
H-3o


144.241
138.511
137.985
137.498
130.154
128.604
127.579
127.459
126.591
125.665
124.525
50.418
31.781
30.396
29.046
28.995
26.495
22.611
21.566
14.090
Ph
N=N
N
oct
Me
Ph
200
150
100
50
0

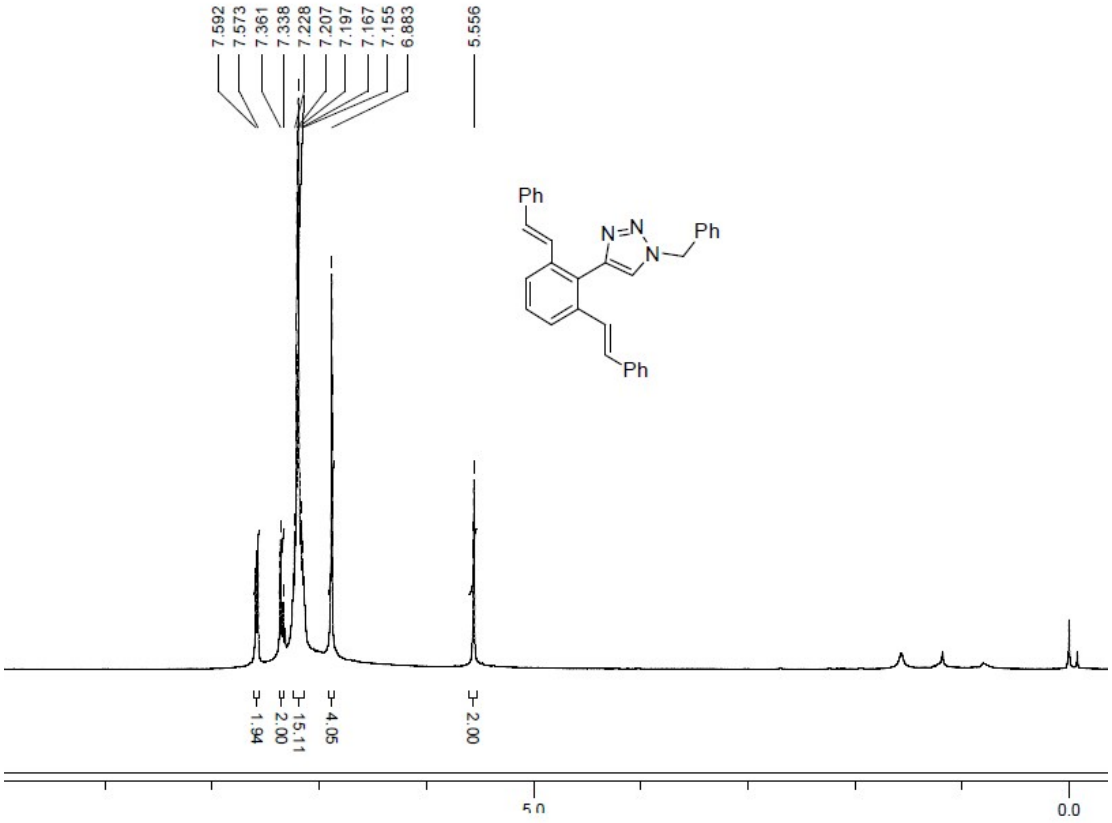
C-3o


7.397
7.309
7.284
7.261
7.240
7.222
7.203
7.180
6.898
6.889
4.396
4.379
4.361
1.901
1.885
1.871
1.870
1.252
1.158
0.803
0.788
0.771
Ph
N=N
N
oct
F
Ph
0.93
11.97
3.08
2.00
2.04
9.96
2.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

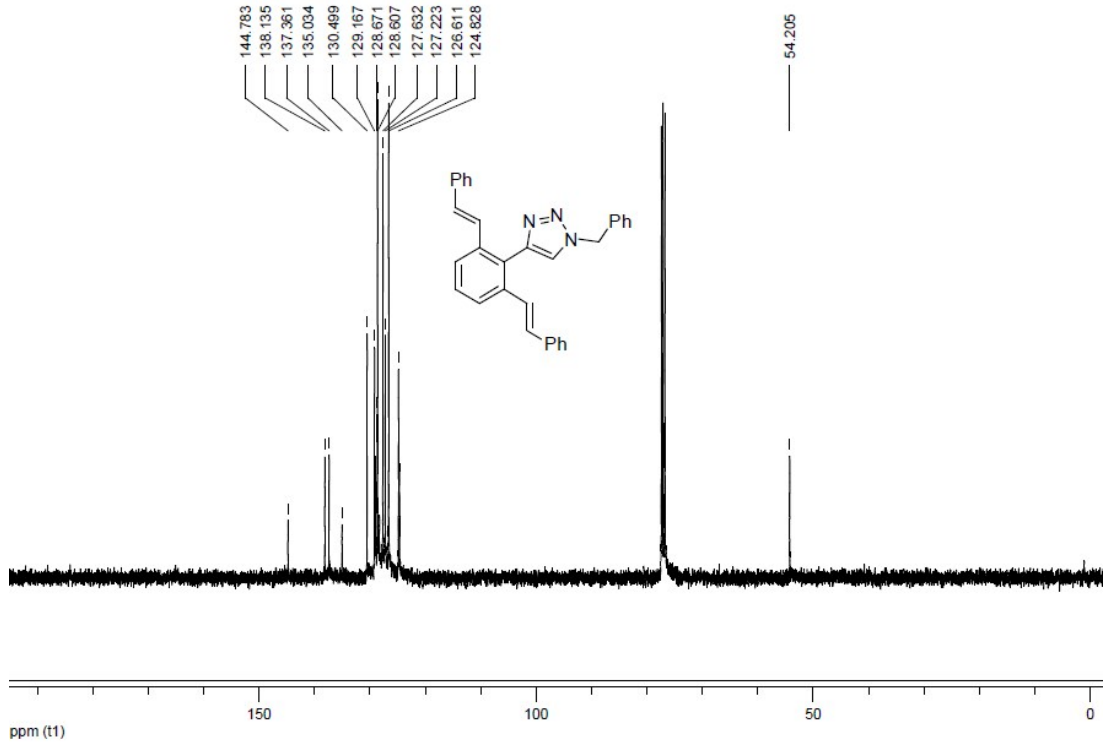
H-3p


163.310
160.863
142.495
139.554
139.471
135.885
130.411
127.637
126.986
125.709
125.317
123.563
110.364
110.139
49.469
30.727
29.331
27.999
27.938
25.450
21.561
13.034
Ph
N=N
N
oct
F
Ph
150
100
50
0
ppm (t1)

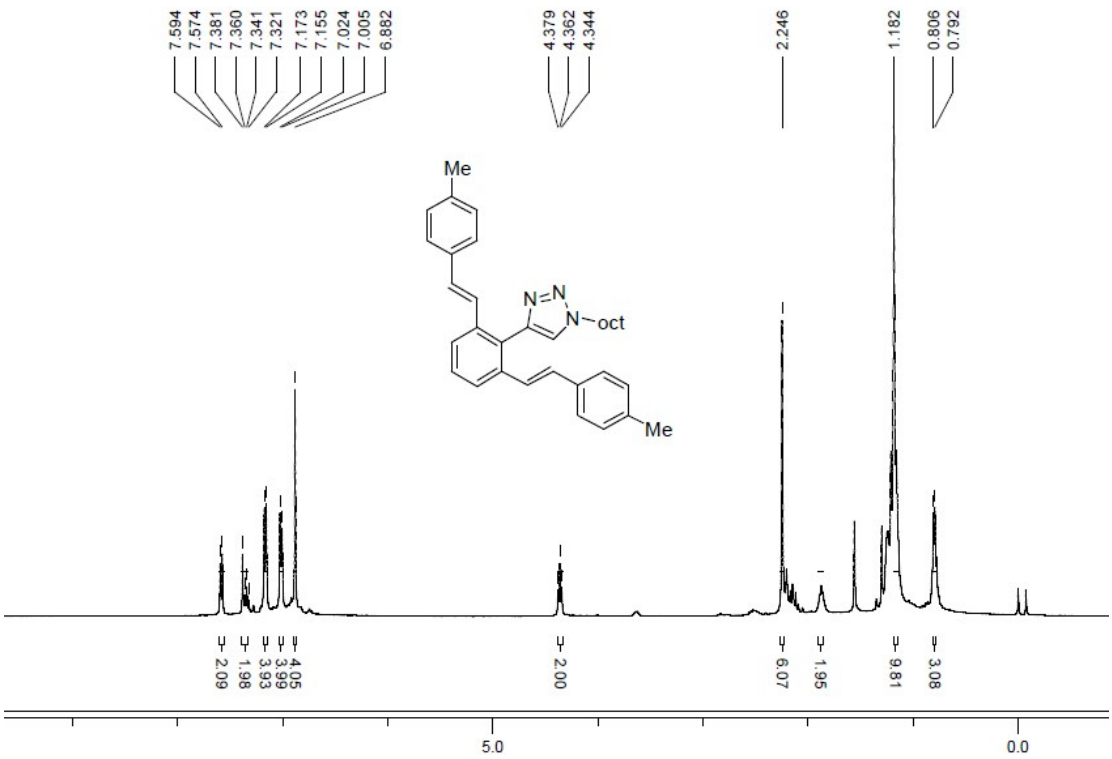
C-3p


7.592
7.573
7.361
7.338
7.228
7.207
7.197
7.167
7.155
6.883
5.556
Ph
N=N
N
Ph
Ph
1.94
2.00
15.11
4.05
2.00
5.0
0.0

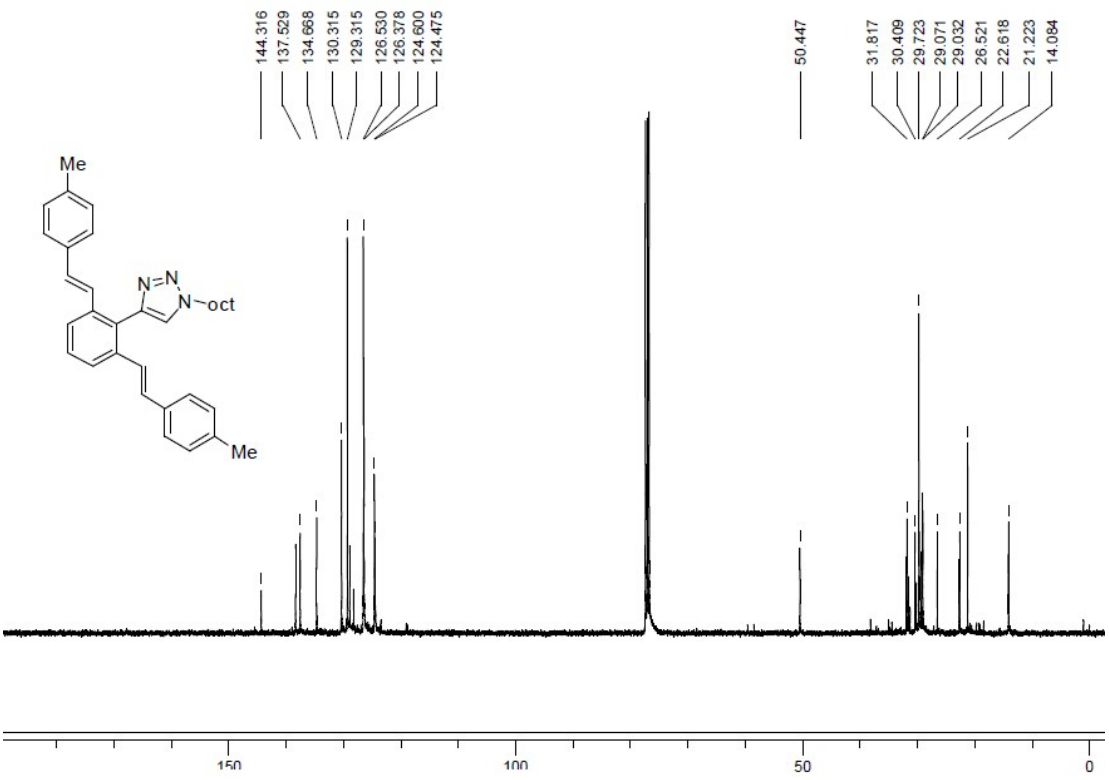
H-3q


144.783
138.135
137.361
135.034
130.499
129.167
128.671
128.607
127.632
127.223
126.611
124.828
54.205
Ph
N=N
N
Ph
Ph
150
100
50
0
ppm (t1)

C-3q


7.594
7.574
7.381
7.360
7.341
7.321
7.173
7.155
7.024
7.005
6.882
4.379
4.362
4.344
2.246
1.182
0.806
0.792
Me
N=N
N
oct
Me
2.09
1.98
3.93
3.69
4.05
2.00
6.07
1.95
9.81
3.08
5.0
0.0

H-3r


144.316
137.529
134.668
130.315
129.315
126.530
126.378
124.600
124.475
50.447
31.817
30.409
29.723
29.071
29.032
26.521
22.618
21.223
14.084
Me
N=N
N-oct
Me
150
100
50
0

C-3r