Supplementary Information

Regioisomeric Allene Dimer Formation by the Reaction of Tetraarylbutatrienes with Tetracyanoethene

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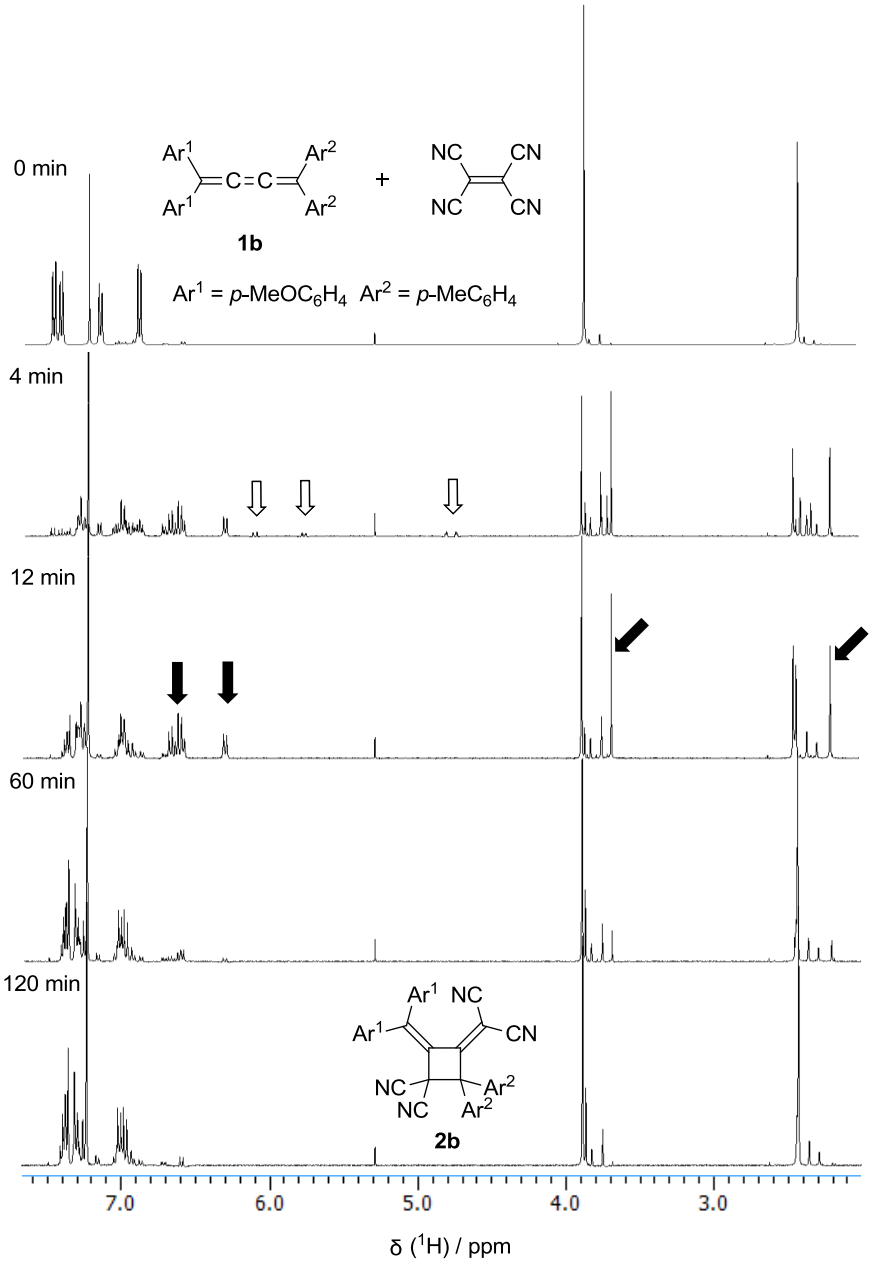
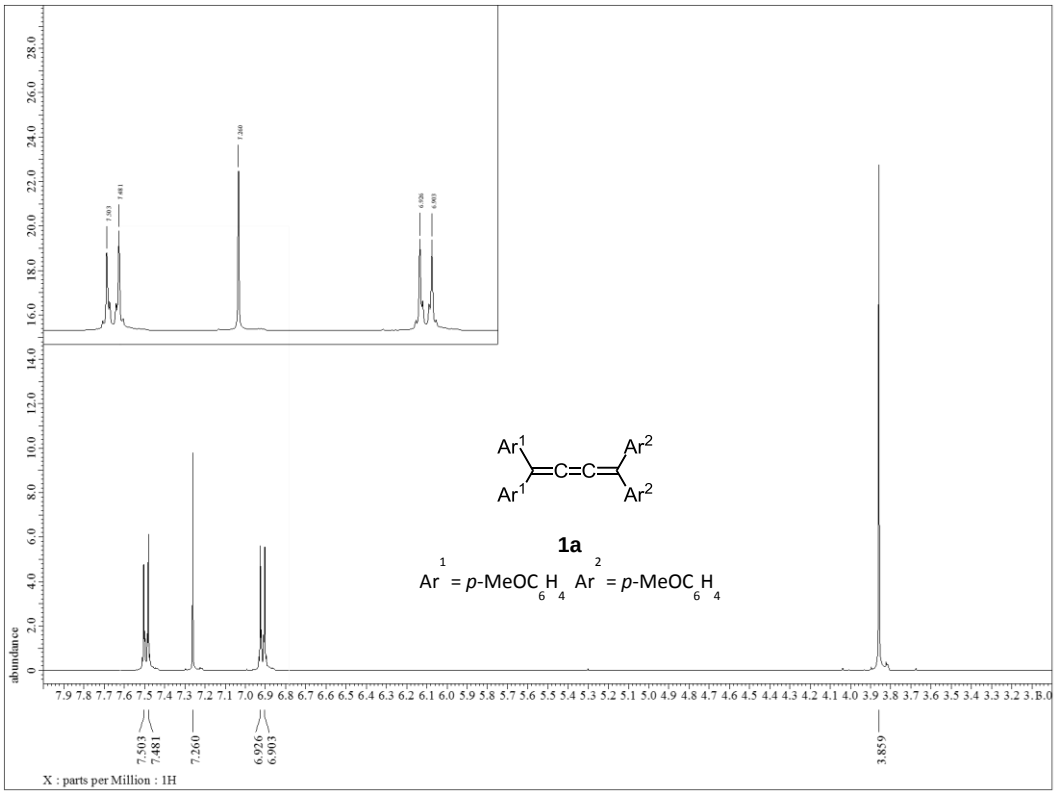
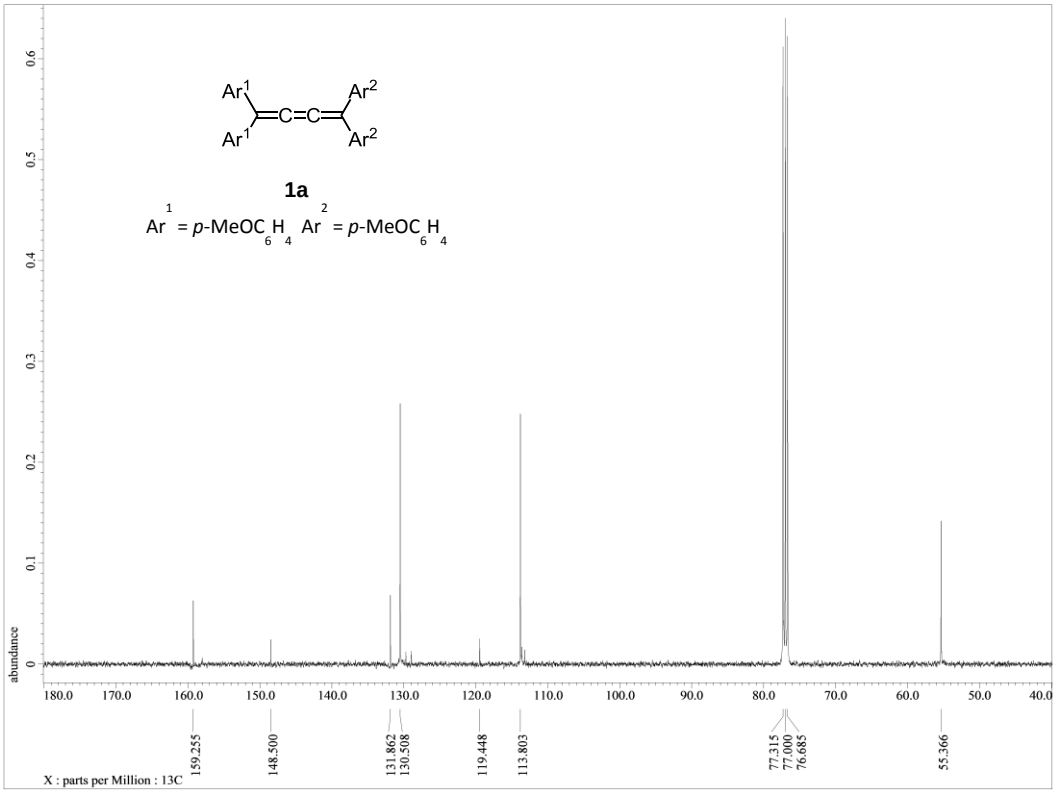
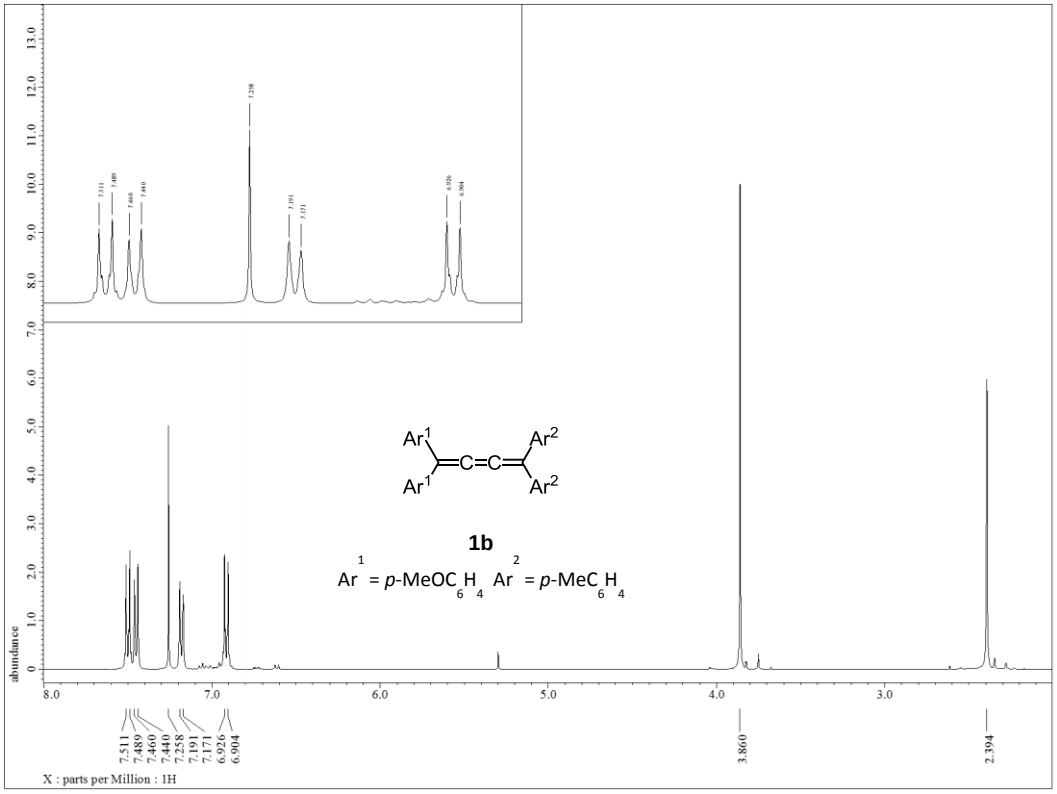
(1) Time dependent ^{1}H-NMR spectra (in $CDCl_3$) of the reaction of tetraarylbutatriene **1b** with TCNE.

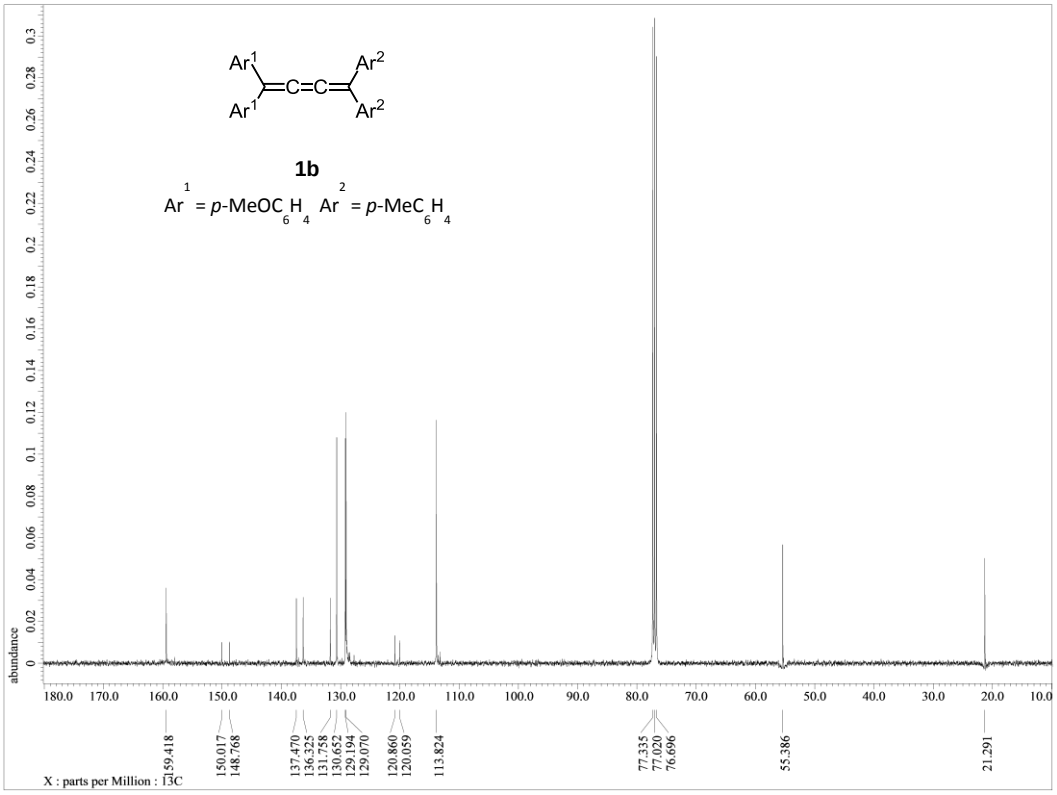


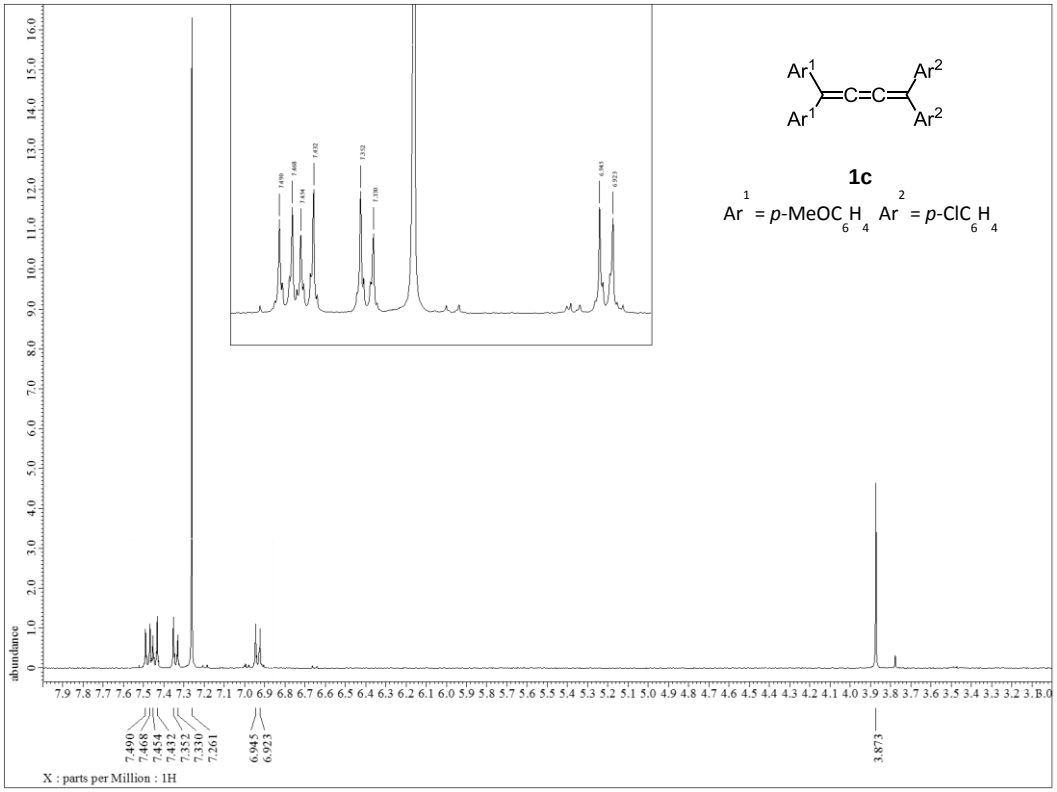
(2) ^{1}H-NMR and ^{13}C-NMR spectra (in $CDCl_3$) of products.

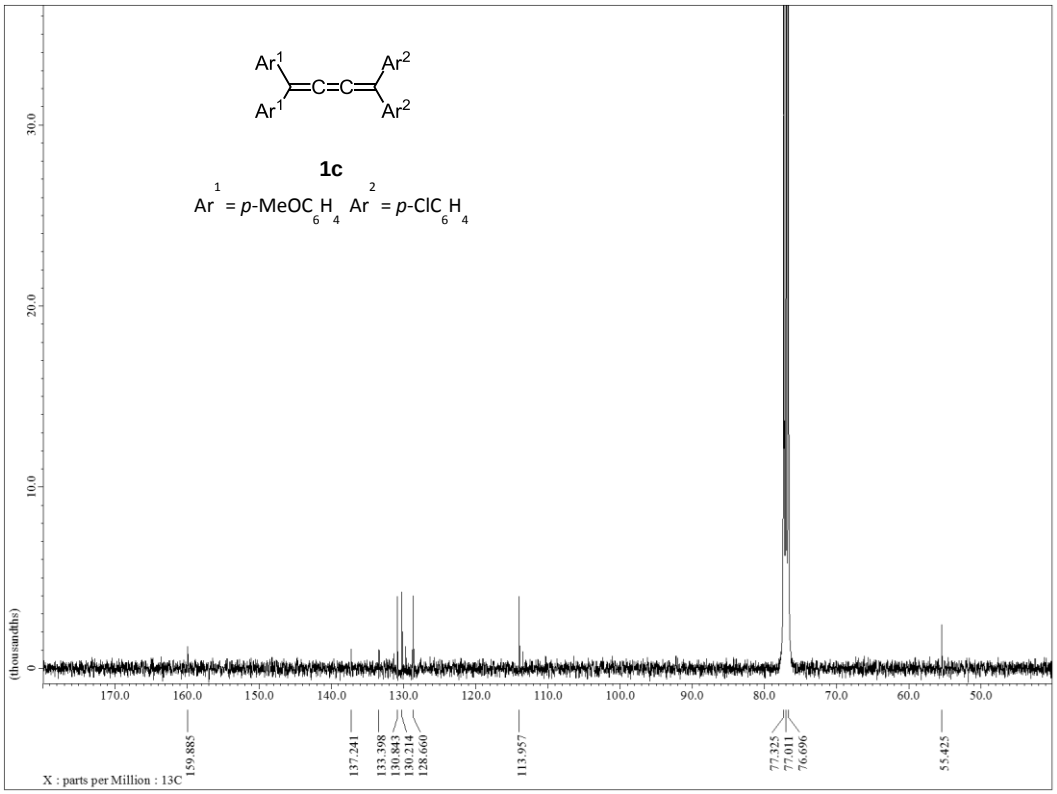


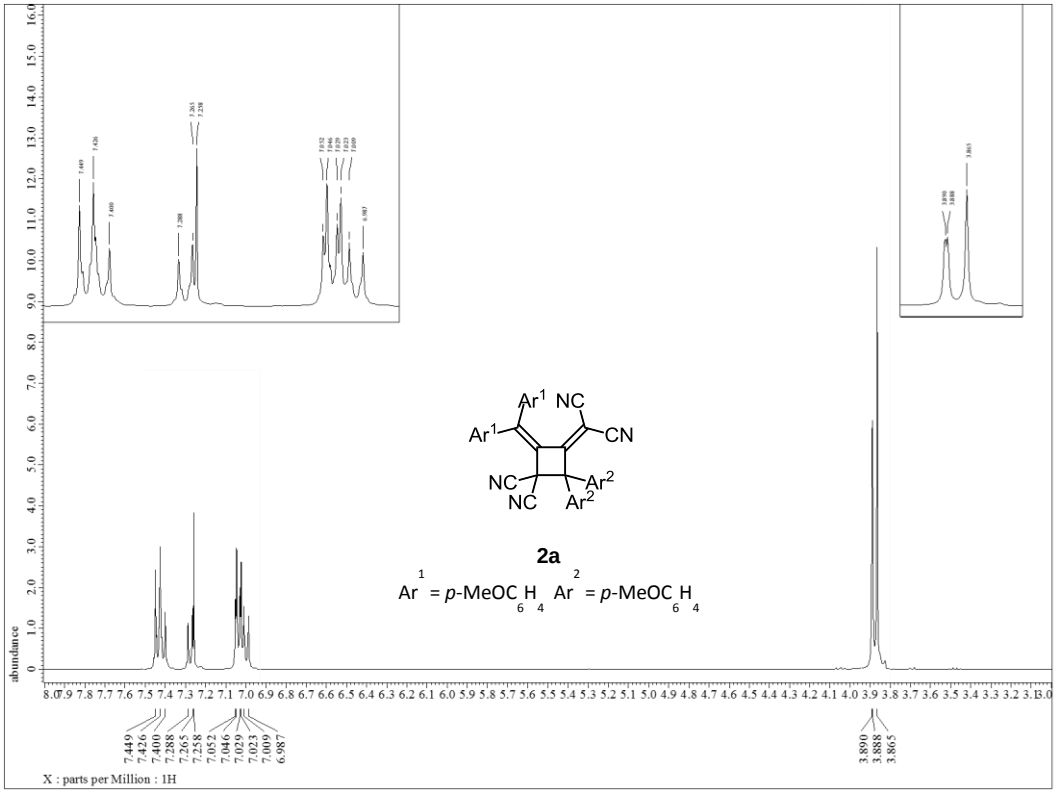


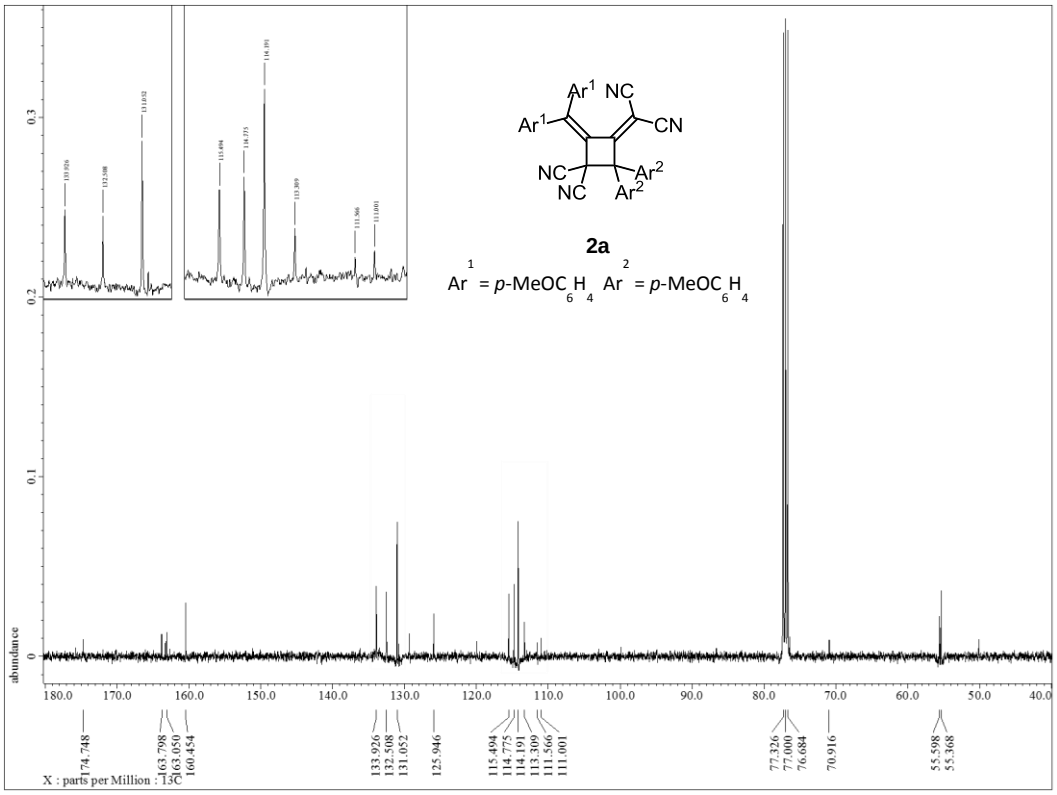

Ar1
Ar2
Ar1
Ar2
1b
Ar1 = p-MeOC6H4 Ar2 = p-MeC6H4
abundance
7.511
7.489
7.460
7.440
7.258
7.191
7.171
6.926
6.904
3.860
2.394
X : parts per Million : 1H

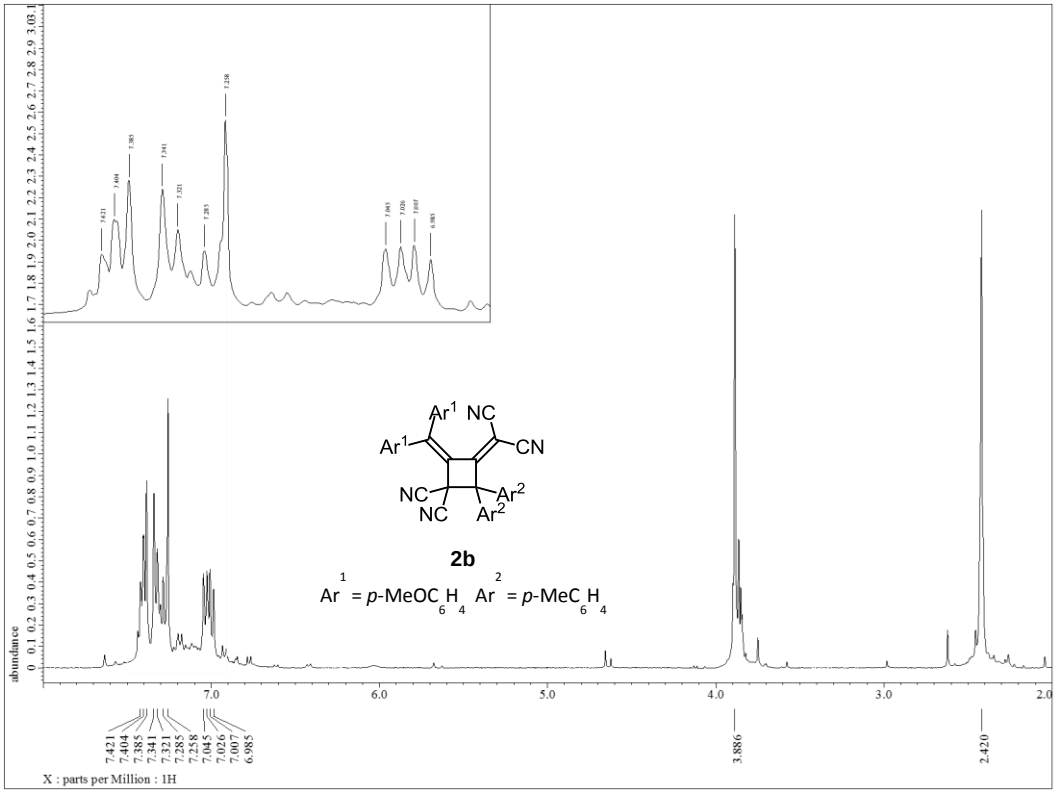

Ar1
Ar2
Ar1
Ar2
1b
Ar1 = p-MeOC6H4 Ar2 = p-MeC6H4
abundance
159.418
150.017
148.768
137.470
136.325
131.758
130.652
129.194
129.070
120.860
120.059
113.824
77.335
77.020
76.696
55.386
21.291
X : parts per Million : 13C

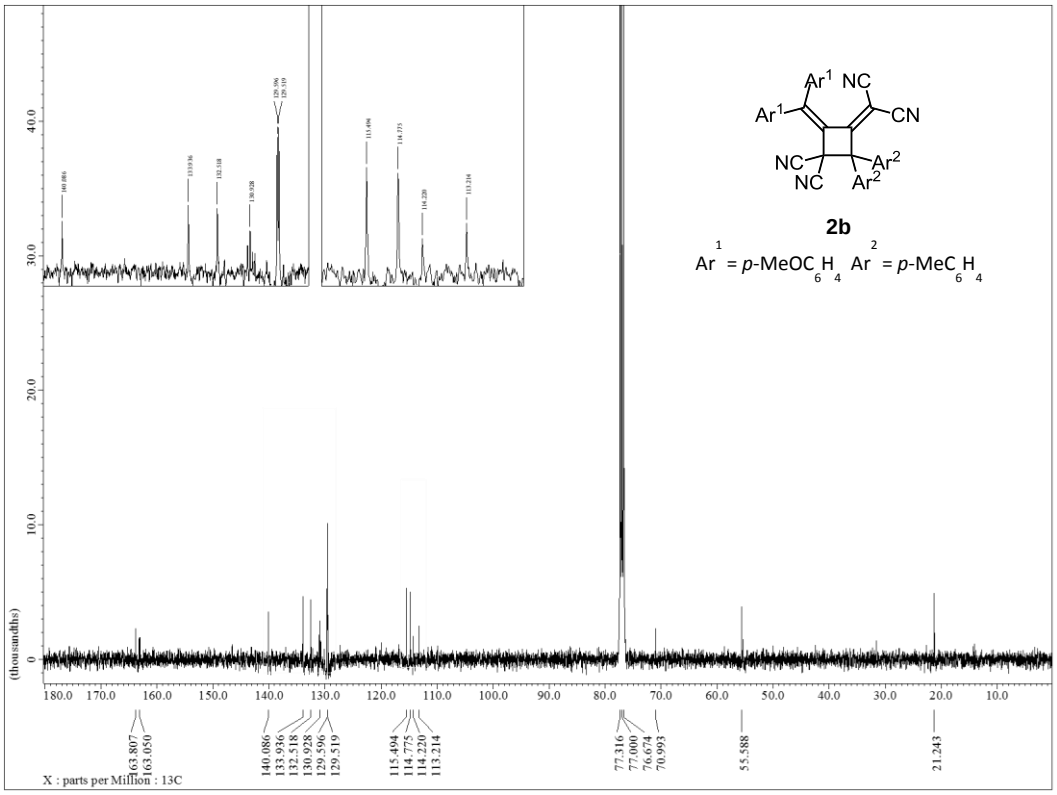

Ar1
Ar2
Ar1
Ar2
1c
Ar1 = p-MeOC6H4 Ar2 = p-ClC6H4
abundance
7.490
7.468
7.454
7.432
7.352
7.330
7.261
6.945
6.923
3.873
X : parts per Million : 1H

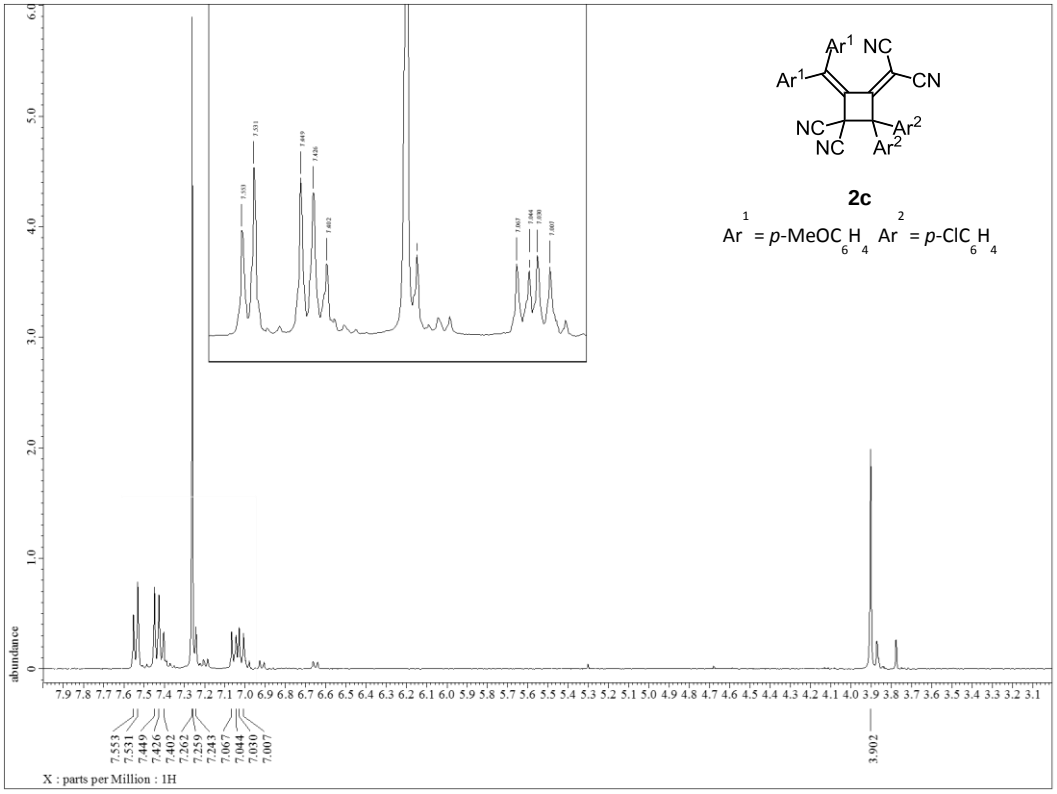

Ar1
Ar2
Ar1
Ar2
1c
Ar1 = p-MeOC6H4 Ar2 = p-ClC6H4
(thousandths)
159.885
137.241
133.398
130.843
130.214
128.660
113.957
77.325
77.011
76.696
55.425
X : parts per Million : 13C

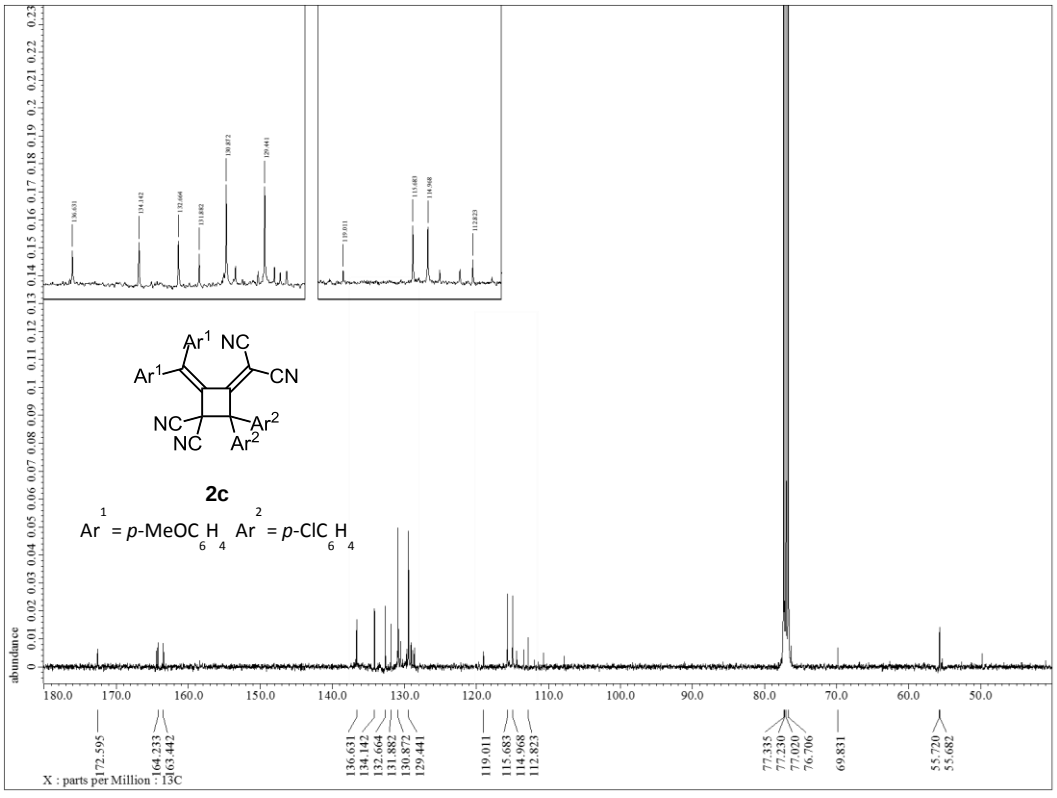

Ar1 NC
Ar1
CN
NC
Ar2
NC
Ar2
2a
Ar1 = p-MeOC6H4 Ar2 = p-MeOC6H4
abundance
7.449
7.426
7.400
7.288
7.265
7.258
7.052
7.046
7.029
7.023
7.009
6.987
3.890
3.888
3.865
X : parts per Million : 1H

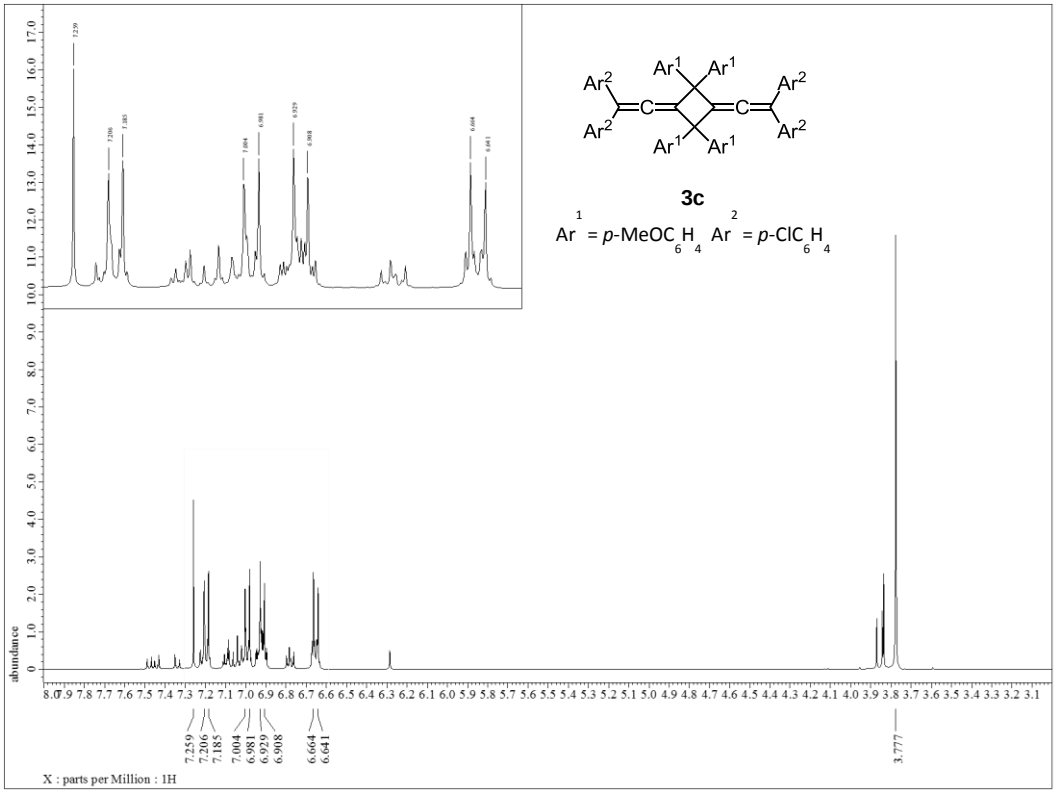

Ar1 NC
Ar1
CN
NC
Ar2
NC
Ar2
2a
Ar1 = p-MeOC6H4 Ar2 = p-MeOC6H4
abundance
174.748
163.798
163.050
160.454
133.926
132.508
131.052
125.946
115.494
114.775
114.191
113.309
111.566
111.001
77.326
77.000
76.684
70.916
55.598
55.368
X : parts per Million : 13C

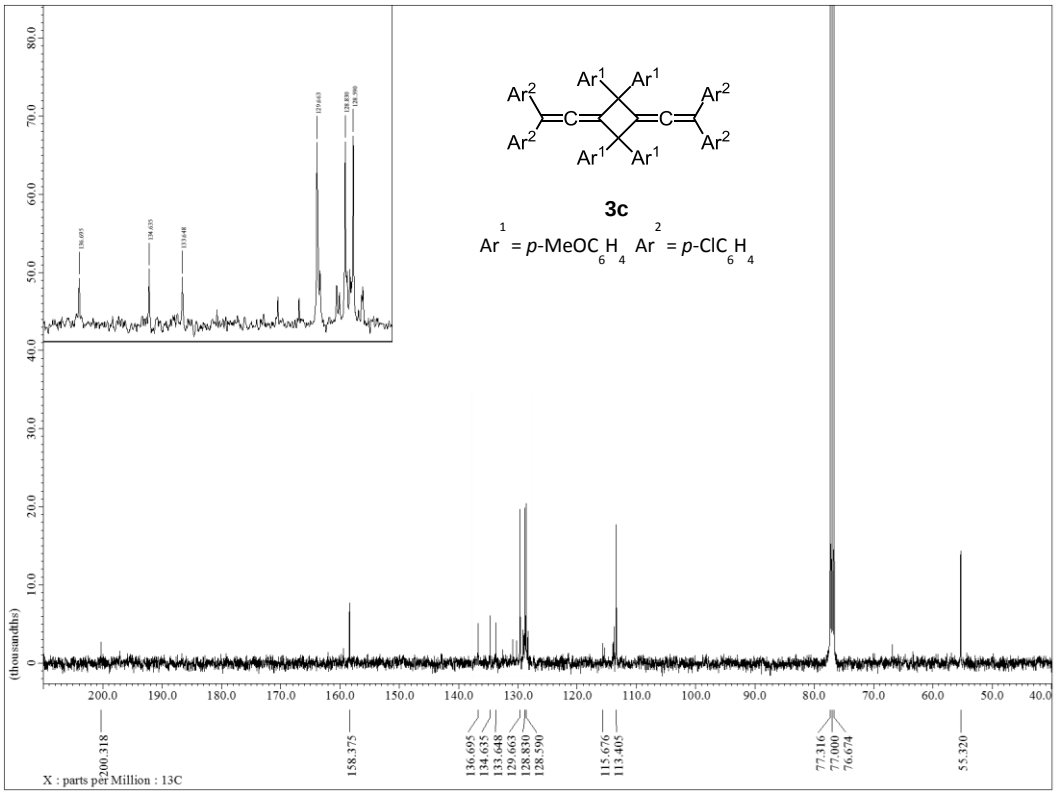

Ar1 NC
Ar1
CN
NC
Ar2
NC
Ar2
2b
Ar1 = p-MeOC6H4 Ar2 = p-MeC6H4
abundance
7.421
7.404
7.385
7.341
7.321
7.285
7.258
7.045
7.026
7.007
6.985
3.886
2.420
X : parts per Million : 1H

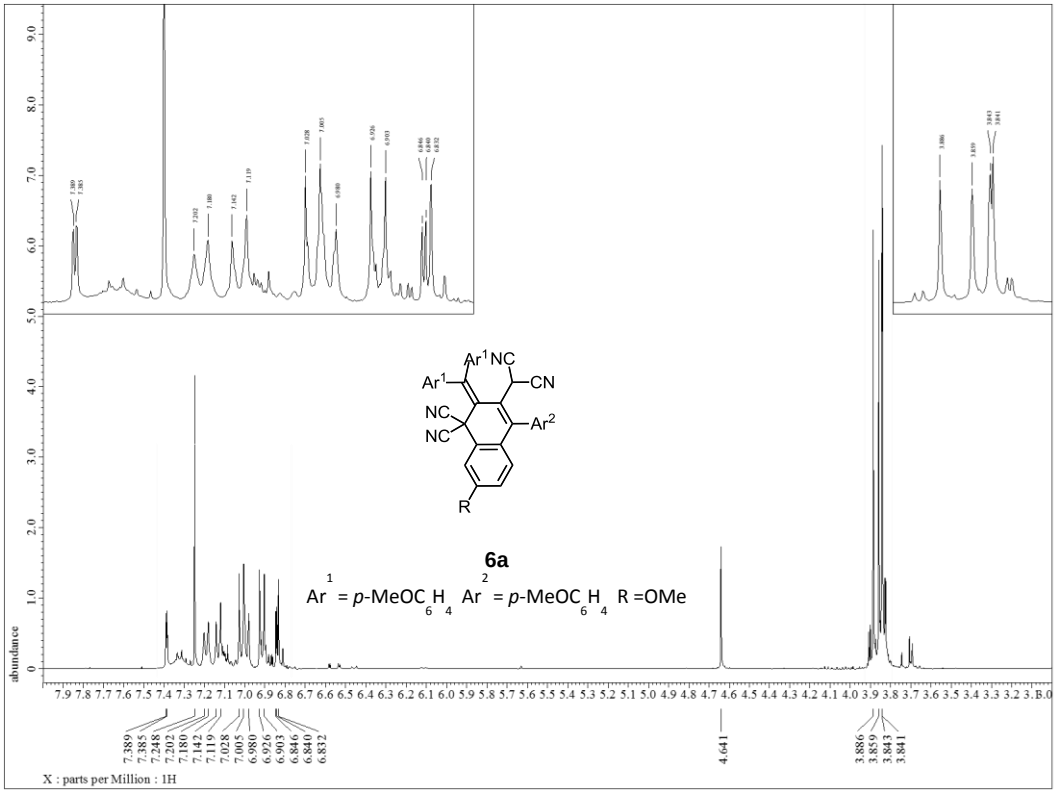

Ar1 NC
Ar1
CN
NC
Ar2
NC
Ar2
2b
Ar1 = p-MeOC6H4 Ar2 = p-MeC6H4
(thousandths)
63.807
63.050
140.086
133.936
132.518
130.928
129.596
129.519
115.494
114.775
114.220
113.214
77.316
77.000
76.674
70.993
55.588
21.243
X : parts per Million : 13C

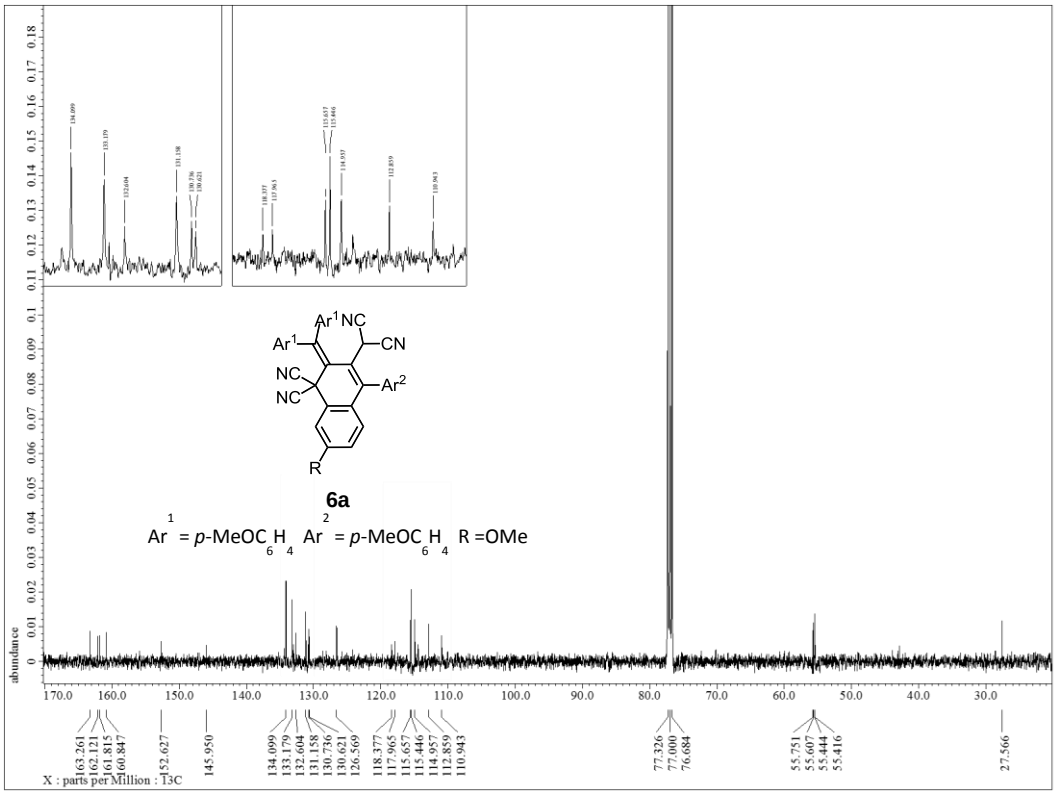

Ar1 NC
Ar1
CN
NC
Ar2
NC
Ar2
2c
Ar1 = p-MeOC6H4 Ar2 = p-ClC6H4
abundance
X : parts per Million : 1H

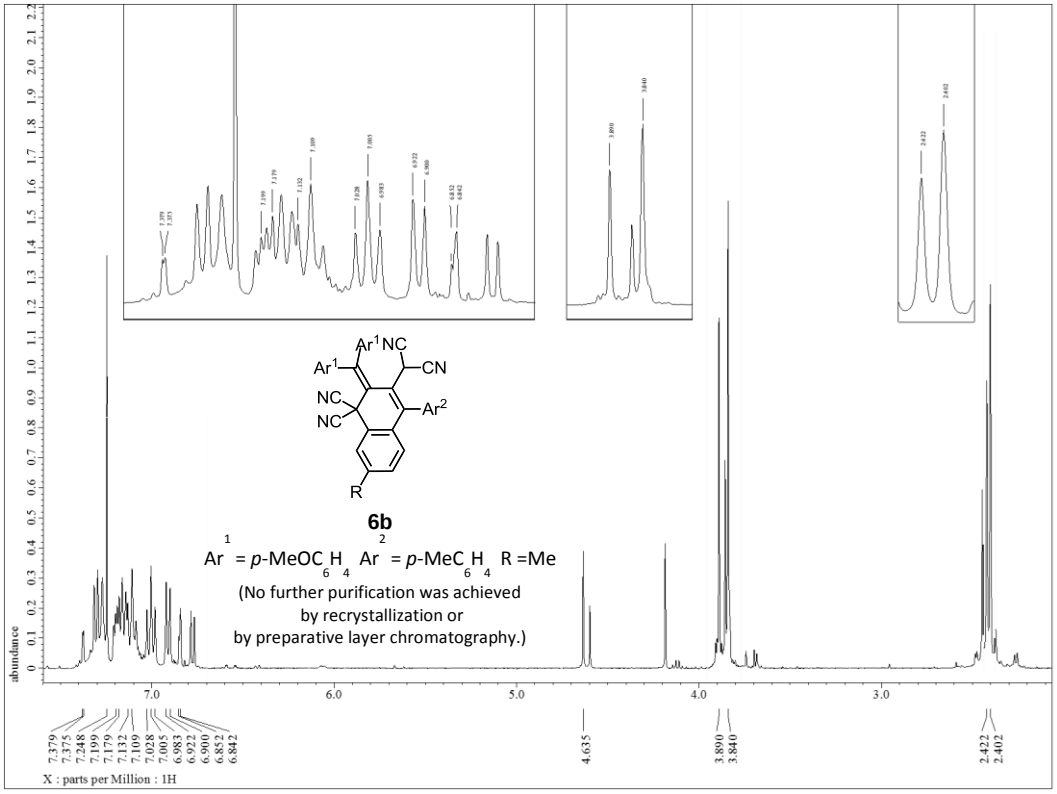

Ar1 NC
Ar1
CN
NC
Ar2
NC
Ar2
2c
Ar1 = p-MeOC6H4 Ar2 = p-ClC6H4
abundance
X : parts per Million : 13C

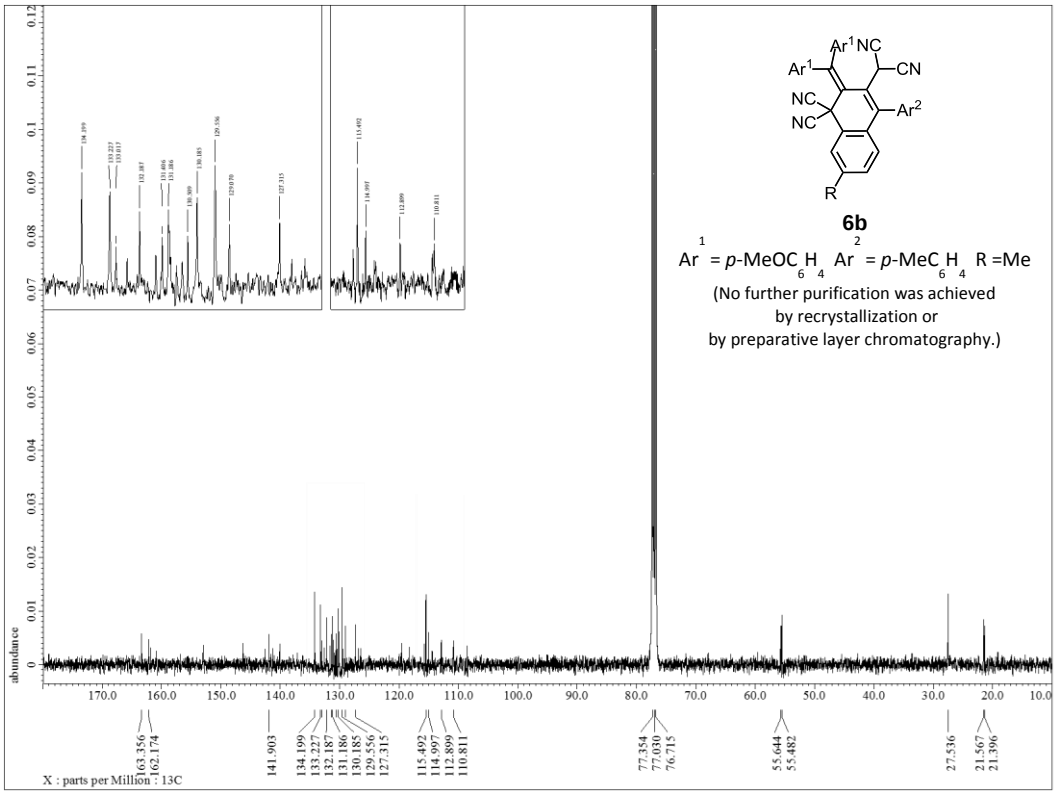

3c
Ar1 = p-MeOC6H4 Ar2 = p-ClC6H4
abundance
X : parts per Million : 1H

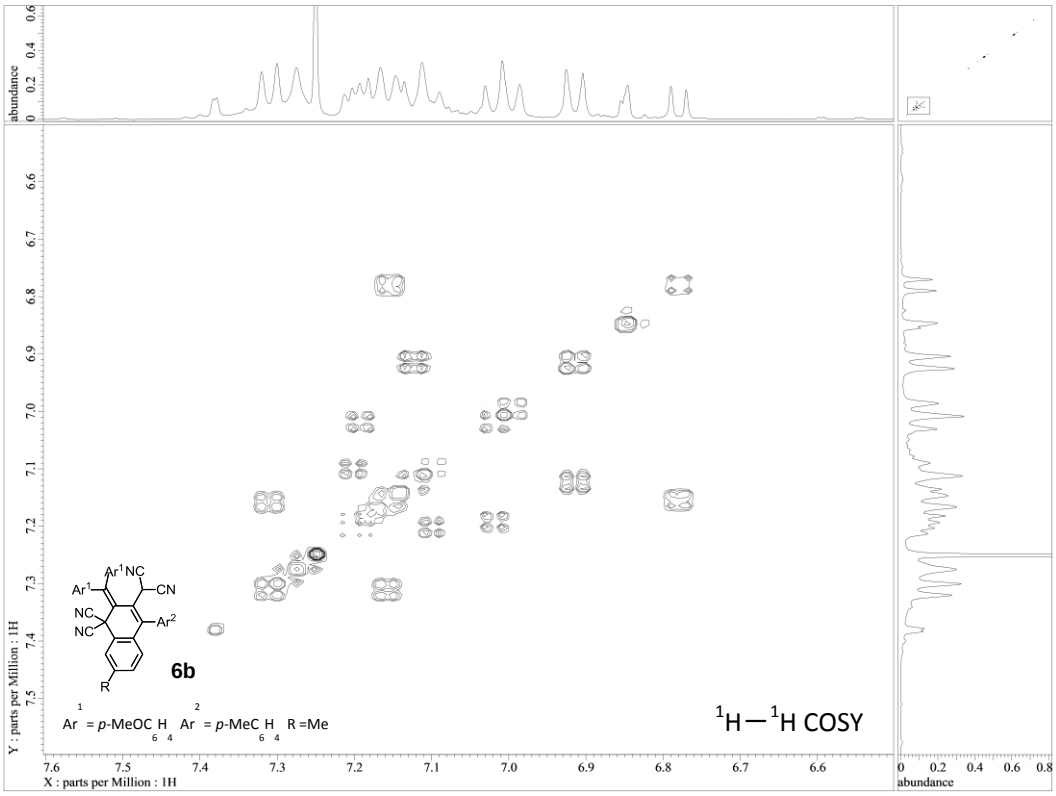

3c
Ar1 = p-MeOC6H4 Ar2 = p-ClC6H4
(thousandths)
X : parts per Million : 13C

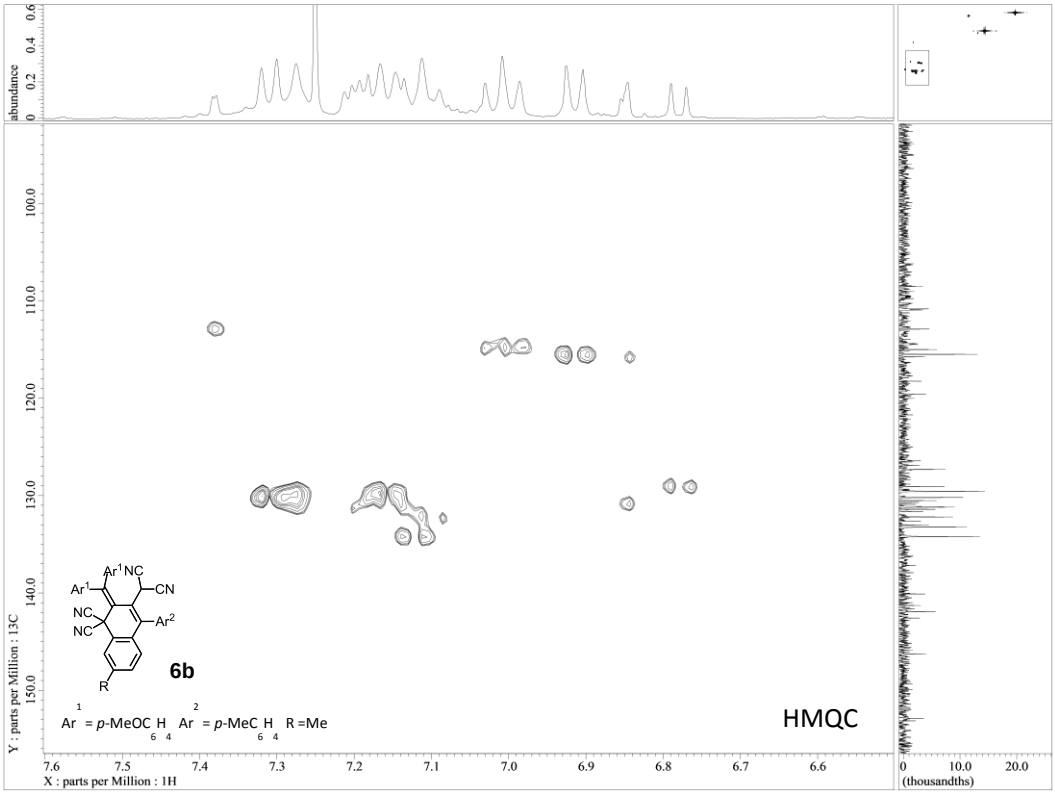

Ar1NC
Ar1
CN
NC
NC
Ar2
R
6a
Ar1 = p-MeOC6H4 Ar2 = p-MeOC6H4 R =OMe
abundance
X : parts per Million : 1H

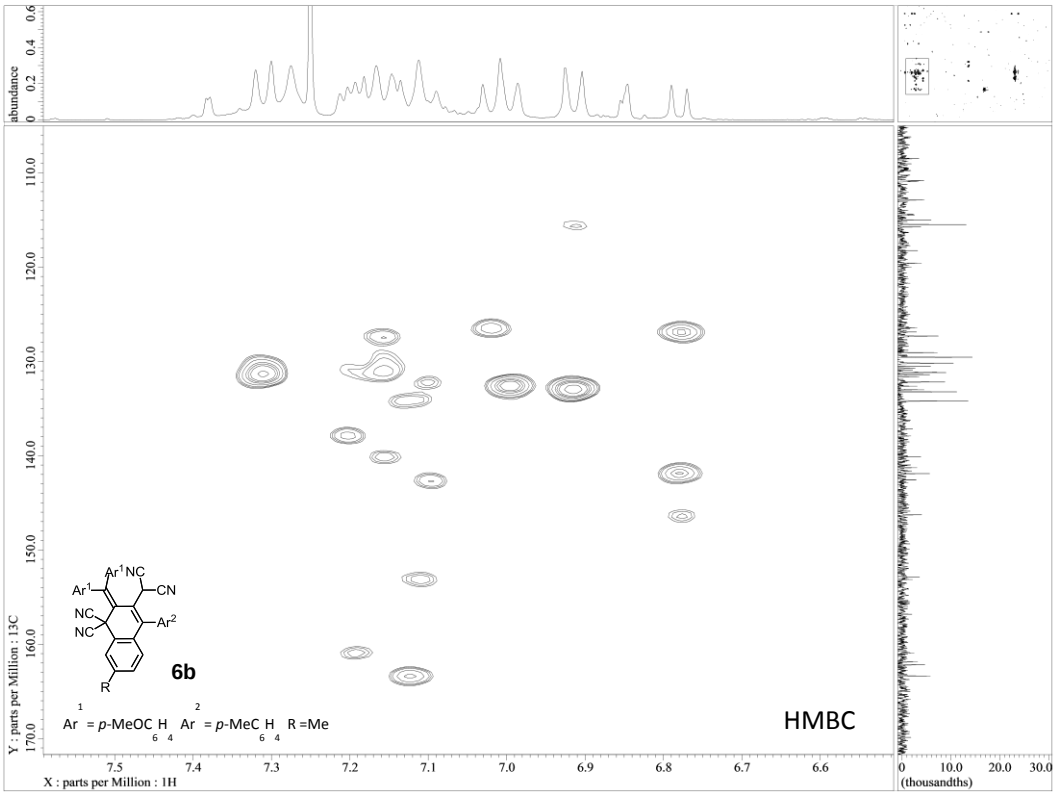

Ar1NC
Ar1
CN
NC
NC
Ar2
R
6a
Ar1 = p-MeOC6H4 Ar2 = p-MeOC6H4 R =OMe
abundance
X : parts per Million : 13C

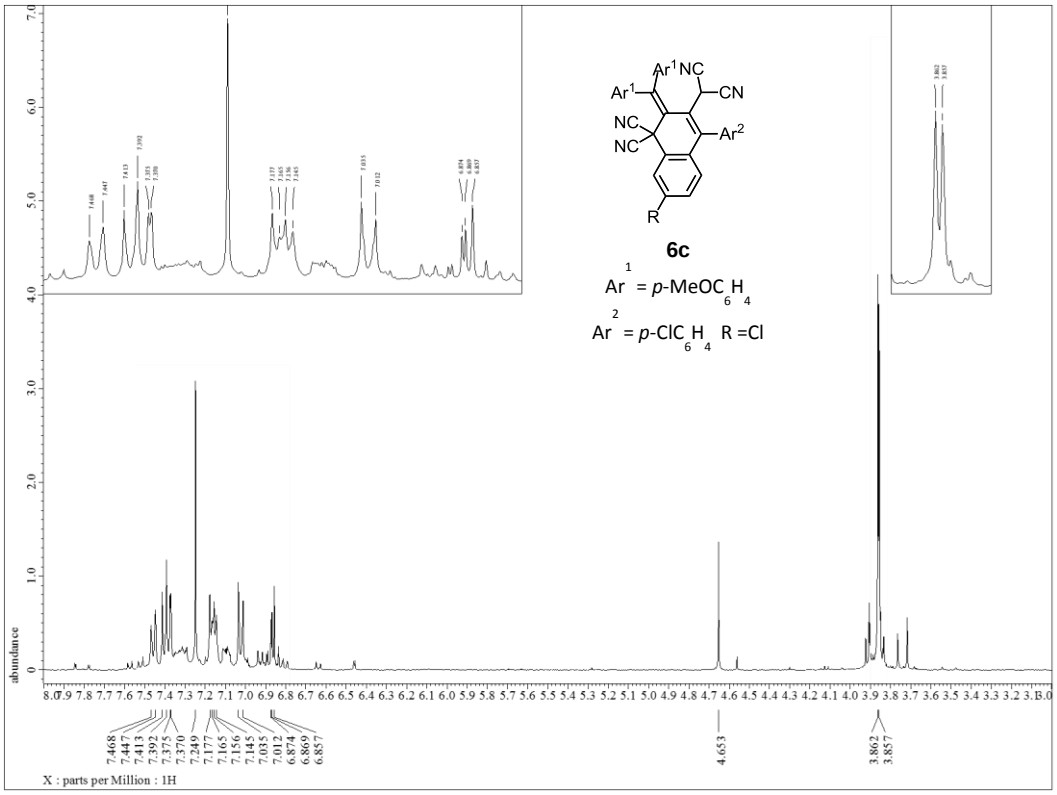

Ar1NC
Ar1
CN
NC
NC
Ar2
R
6b
Ar1 = p-MeOC6H4 Ar2 = p-MeC6H4 R =Me
(No further purification was achieved
by recrystallization or
by preparative layer chromatography.)
abundance
7.379
7.375
7.248
7.199
7.179
7.132
7.109
7.028
7.005
6.983
6.922
6.900
6.852
6.842
4.635
3.890
3.840
2.422
2.402
X : parts per Million : 1H

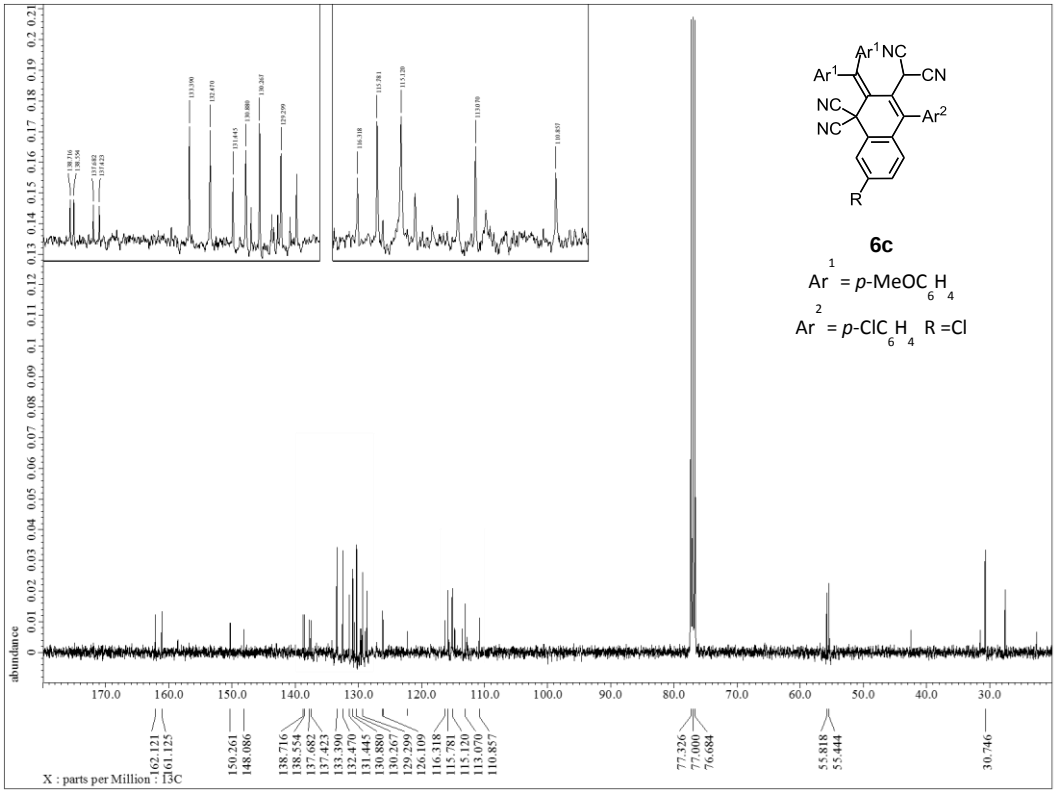

Ar1NC
Ar1
CN
NC
NC
Ar2
R
6b
Ar1 = p-MeOC6H4 Ar2 = p-MeC6H4 R =Me
(No further purification was achieved
by recrystallization or
by preparative layer chromatography.)
abundance
163.356
162.174
141.903
134.199
133.227
132.187
131.186
130.185
129.556
127.315
115.492
114.997
112.899
110.811
77.354
77.030
76.715
55.644
55.482
27.536
21.567
21.396
X : parts per Million : 13C

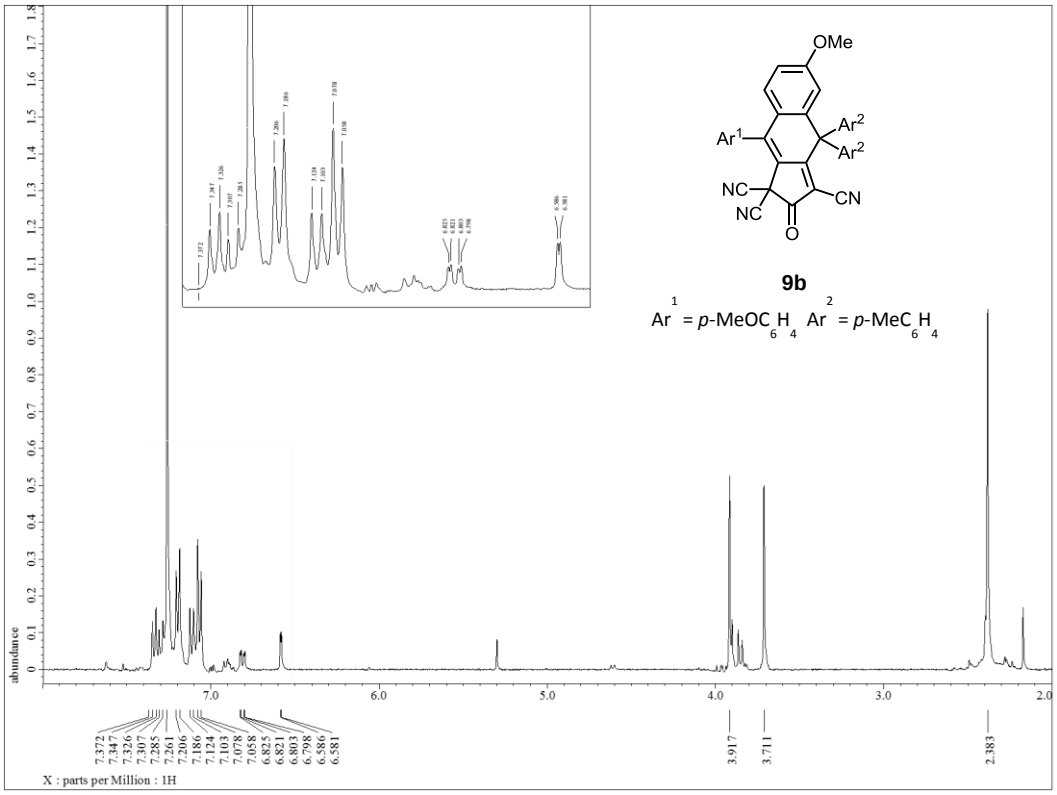

abundance
Y : parts per Million : 1H
X : parts per Million : 1H
abundance
6b
Ar = p-MeOC H Ar = p-MeC H R =Me
1 6 4 2 6 4
1H—1H COSY


abundance
Y : parts per Million : 13C
X : parts per Million : 1H
(thousandths)
6b
Ar = p-MeOC H Ar = p-MeC H R =Me
1 6 4 2 6 4
HMQC

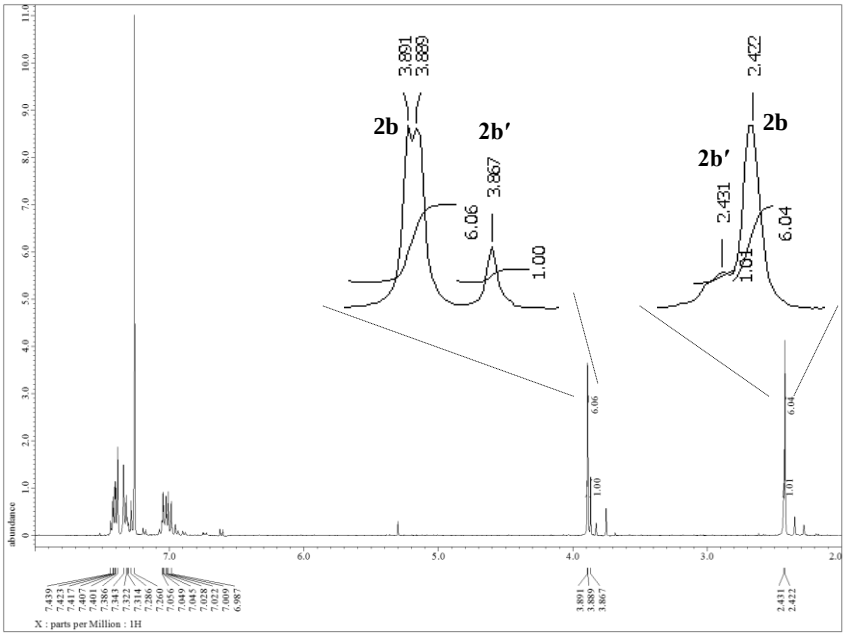

abundance
Y : parts per Million : 13C
X : parts per Million : 1H
(thousandths)
HMBC
6b
Ar = p-MeOC H
6 4
Ar = p-MeC H
6 4
R =Me


6c
Ar = p-MeOC H
6 4
Ar = p-ClC H
6 4
R =Cl
abundance
X : parts per Million : 1H
7.468
7.447
7.413
7.392
7.375
7.370
7.249
7.177
7.165
7.156
7.145
7.035
7.012
6.874
6.869
6.857
4.653
3.862
3.857

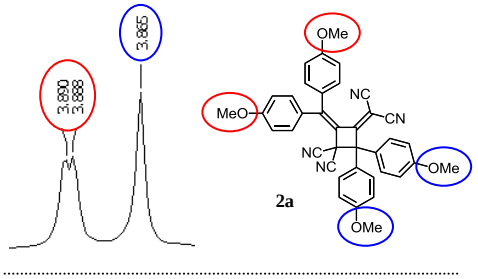

Ar1NC
Ar1
CN
NC
Ar2
NC
R
6c
Ar1 = p-MeOC6H4
Ar2 = p-ClC6H4 R =Cl
abundance
X : parts per Million : 13C


OMe
Ar1
Ar2
Ar2
NC
NC
CN
O
9b
Ar1 = p-MeOC6H4 Ar2 = p-MeC6H4
abundance
X : parts per Million : 1H

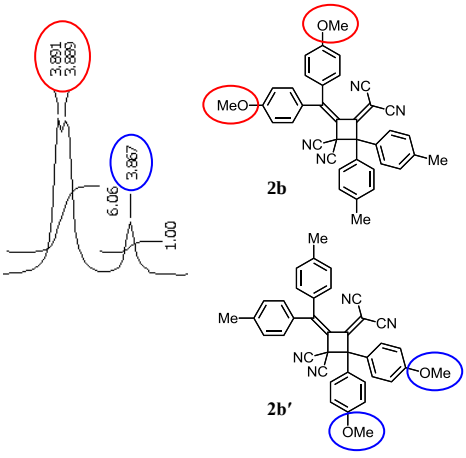
(3) ^{1}H-NMR spectra (in $CDCl_3$) of **2b′** and **2c′**.



From ^{1}H-NMR spectra of crude product **2b** (see the upper figure), three singlets (2.42, 3.88 and 3.89 ppm) derived from the methyl signals of the methylphenyl and methoxyphenyl groups are confirmed. In addition, two singlets (2.43, 3.86 ppm) are also appeared close to signals of **2b** and the integrations of these two signals are equivalent each other. As compared with the methyl signals of the methoxyphenyl group of **2a** and analogous compound Ⅰ (see figure on the right), these signals are presumed to be due to **2b′**, which is a regioisomer of **2b**. From integration of ^{1}H-NMR spectra, the isomer **2b′** was obtained in 1/6 of the yield of **2b**.

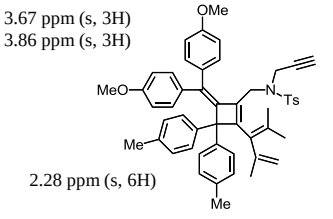


2a



2b

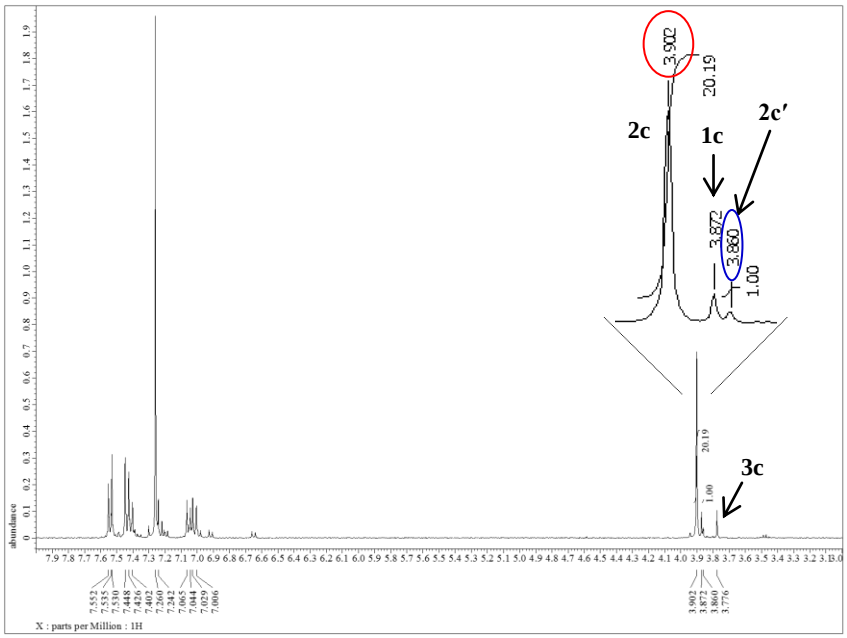
2b′



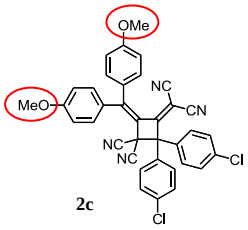
Analogous compound Ⅰ [1]

Reference

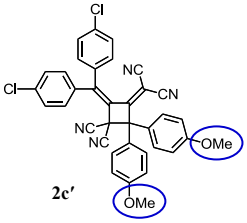
1 L. -F. Yao, M. Shi. *Chem. Eur. J*. 2009, **15**, 3875－3881.



^{1}H-NMR spectra of crude product of the reaction of **1c** and TCNE (see the upper figure) showed that not only the methyl signals of the methoxyphenyl group of **2c** (3.90 ppm) but also two singlets (3.86 and 3.87 ppm) were existed. One singlet 3.87 ppm is confirmed to be derived from material compound **1c** (see S-5). Along with the case of **2b′**, the other singlet 3.86 ppm is assumed to be due to **2c′** which is a regioisomer of **2c**. From integration of ^{1}H-NMR spectra, the isomer **2c′** was obtained in 1/20 of the yield of **2c**. In addition, the methyl signals of the methoxyphenyl group of **3c** could be confirmed (See S-9).

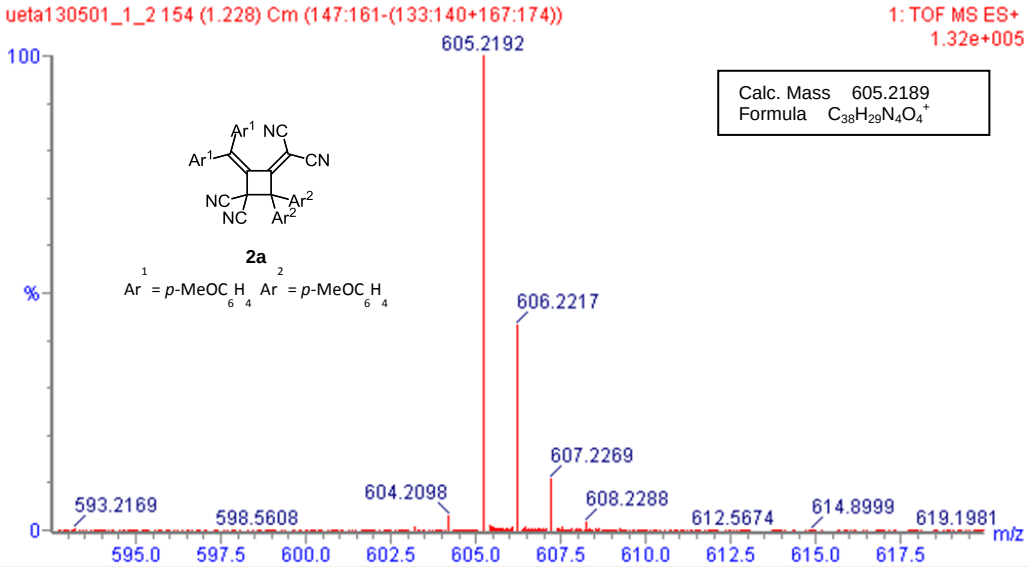


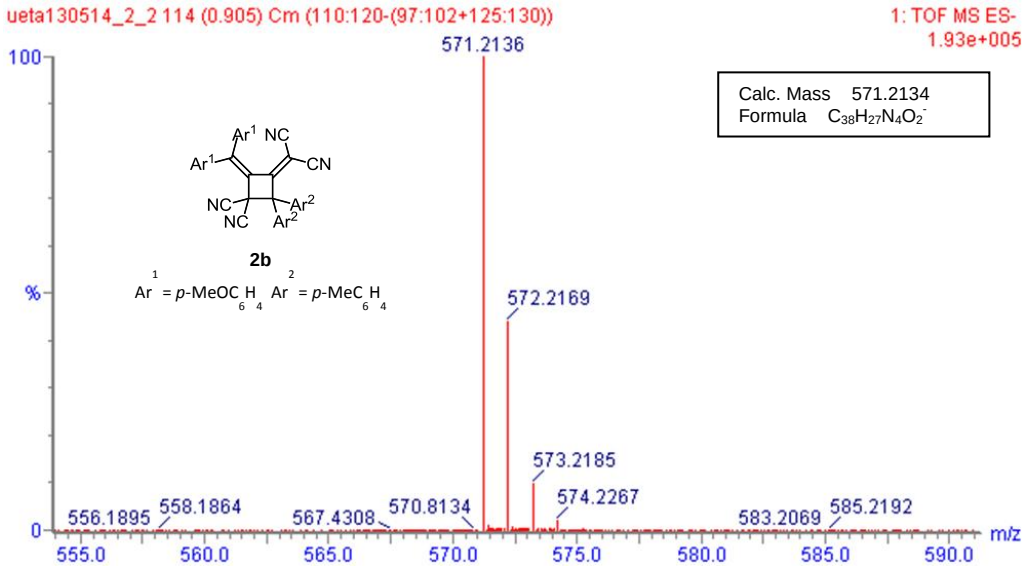
2c

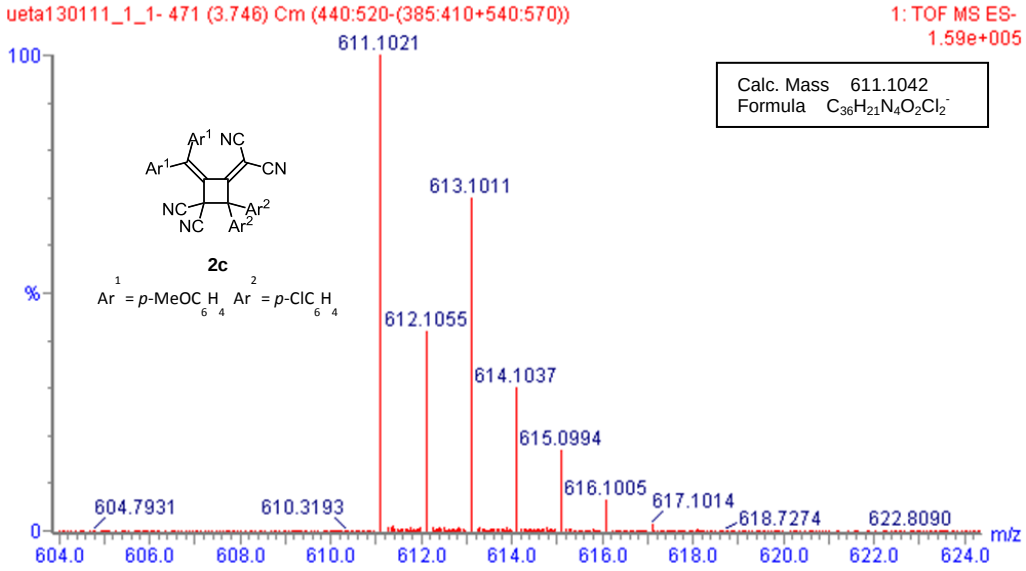


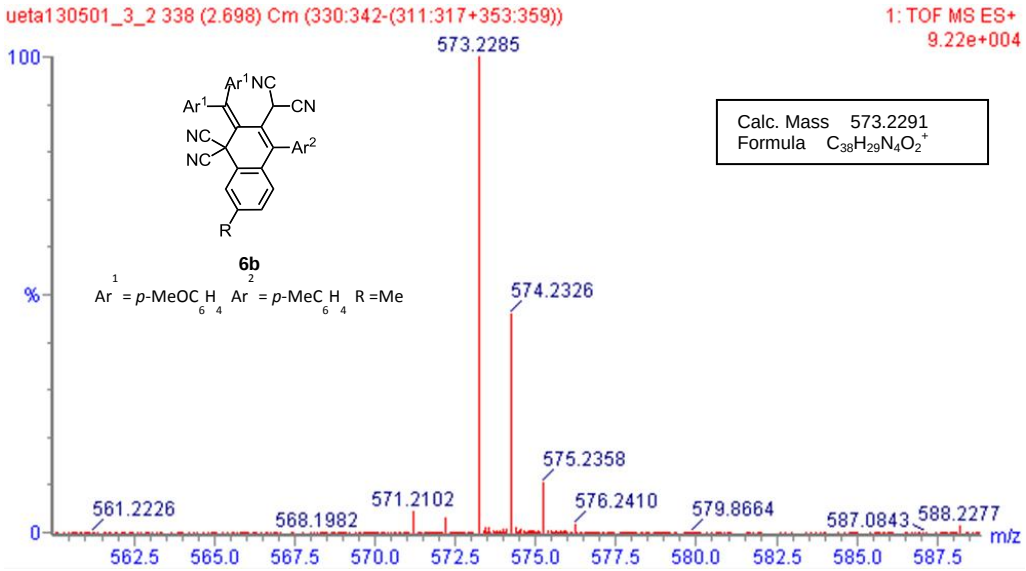
2c′

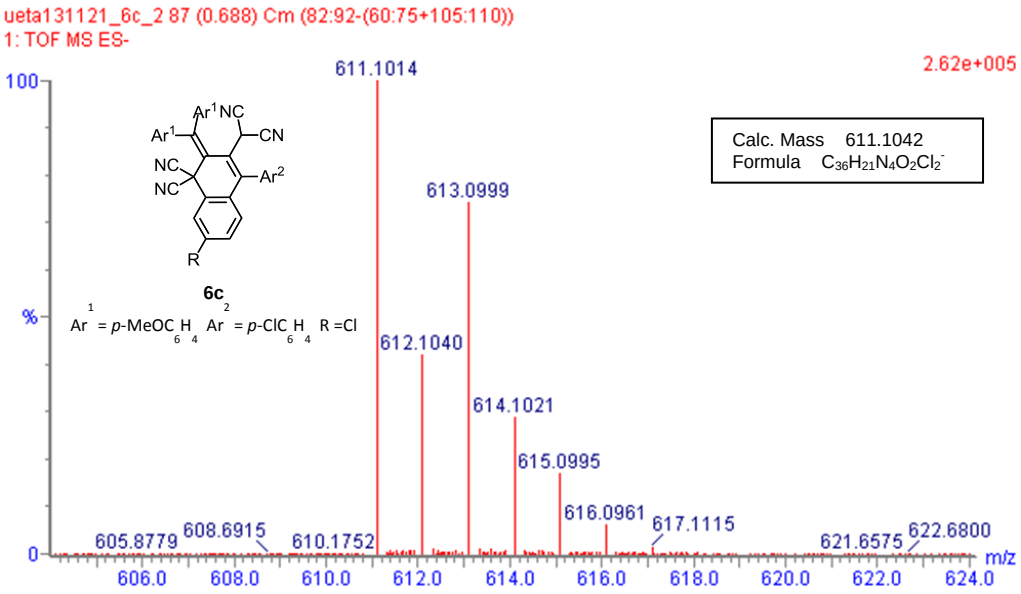
(4) ESI-TOF-MS spectra of products.

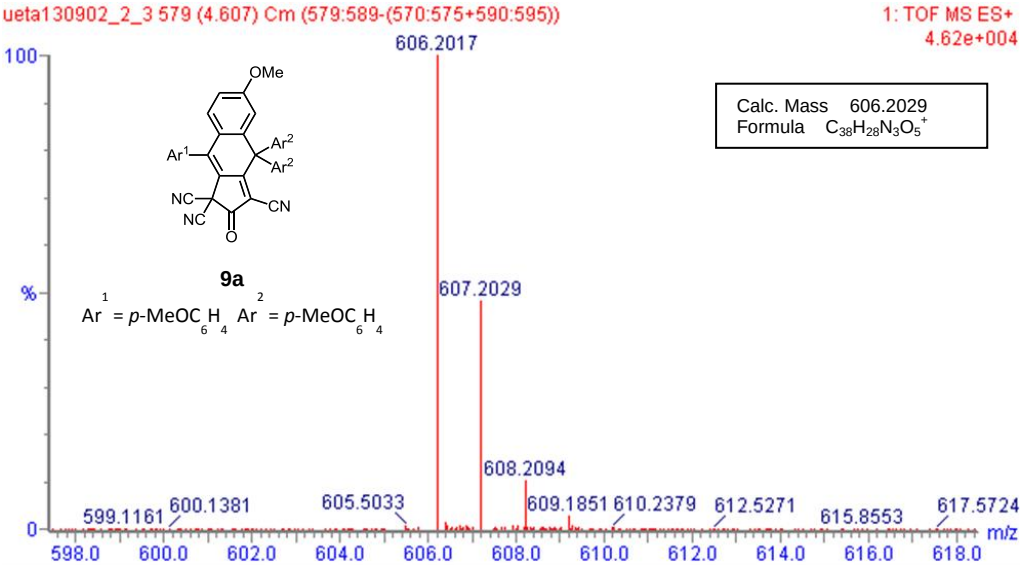


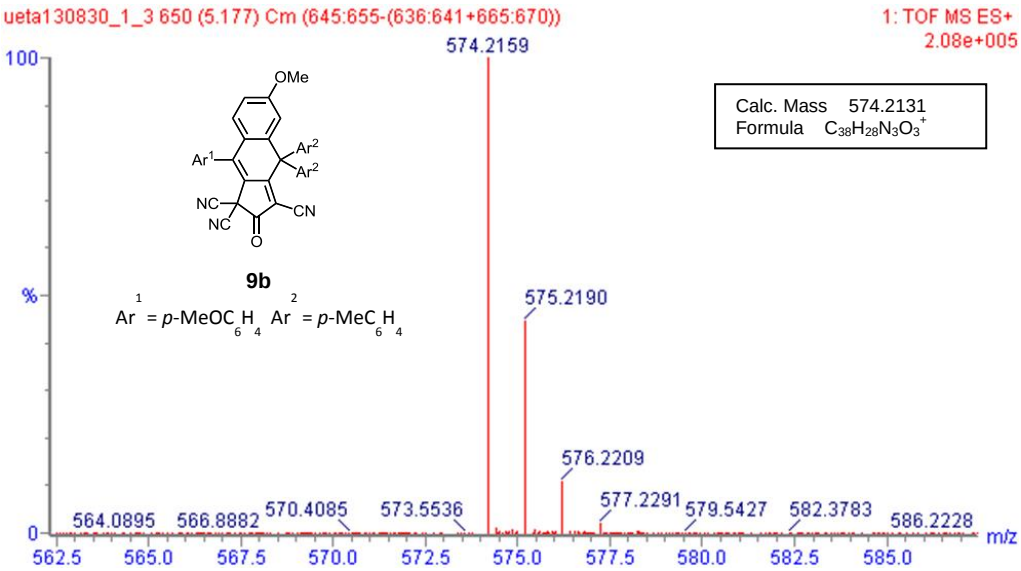


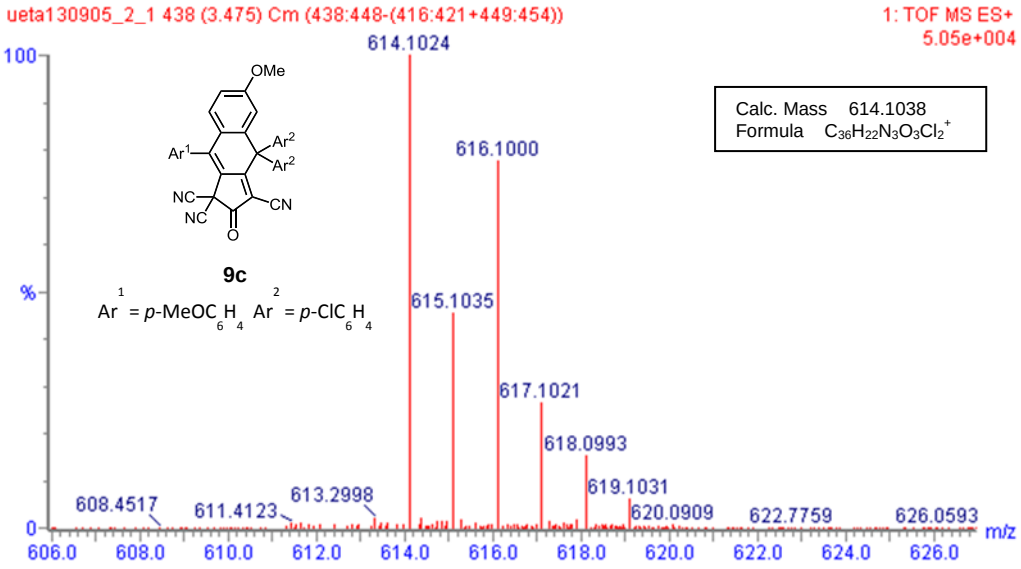

ueta130111_1_1- 471 (3.746) Cm (440:520-(385:410+540:570))
1: TOF MS ES-
1.59e+005
611.1021
Calc. Mass 611.1042
Formula C36H21N4O2Cl2-
613.1011
612.1055
614.1037
615.0994
616.1005
617.1014
604.7931
610.3193
618.7274
622.8090
2c
Ar1 = p-MeOC6H4 Ar2 = p-ClC6H4
m/z


ueta130501_3_2 338 (2.698) Cm (330:342-(311:317+353:359))
1: TOF MS ES+
9.22e+004
573.2285
Calc. Mass 573.2291
Formula C38H29N4O2+
574.2326
575.2358
571.2102
576.2410
561.2226
568.1982
579.8664
587.0843
588.2277
6b
Ar1 = p-MeOC6H4 Ar2 = p-MeC6H4 R =Me
m/z


ueta131121_6c_2 87 (0.688) Cm (82:92-(60:75+105:110))
1: TOF MS ES-
2.62e+005
611.1014
613.0999
612.1040
614.1021
615.0995
616.0961
617.1115
605.8779
608.6915
610.1752
621.6575
622.6800
Calc. Mass 611.1042
Formula C36H21N4O2Cl2-
6c
Ar1 = p-MeOC6H4 Ar2 = p-ClC6H4 R =Cl
m/z


ueta130902_2_3 579 (4.607) Cm (579:589-(570:575+590:595))
1: TOF MS ES+
4.62e+004
606.2017
607.2029
608.2094
599.1161
600.1381
605.5033
609.1851
610.2379
612.5271
615.8553
617.5724
Calc. Mass 606.2029
Formula C38H28N3O5+
9a
Ar1 = p-MeOC6H4 Ar2 = p-MeOC6H4
m/z


ueta130830_1_3 650 (5.177) Cm (645:655-(636:641+665:670))
1: TOF MS ES+
2.08e+005
574.2159
100
%
0
OMe
Ar1
Ar2
Ar2
NC
NC
CN
O
9b
Ar1 = p-MeOC6H4 Ar2 = p-MeC6H4
Calc. Mass 574.2131
Formula C38H28N3O3+
575.2190
576.2209
577.2291
564.0895
566.8882
570.4085
573.5536
579.5427
582.3783
586.2228
562.5
565.0
567.5
570.0
572.5
575.0
577.5
580.0
582.5
585.0
m/z


ueta130905_2_1 438 (3.475) Cm (438:448-(416:421+449:454))
1: TOF MS ES+
5.05e+004
614.1024
100
%
0
OMe
Ar1
Ar2
Ar2
NC
NC
CN
O
9c
Ar1 = p-MeOC6H4 Ar2 = p-ClC6H4
Calc. Mass 614.1038
Formula C36H22N3O3Cl2+
616.1000
615.1035
617.1021
618.0993
619.1031
608.4517
611.4123
613.2998
620.0909
622.7759
626.0593
606.0
608.0
610.0
612.0
614.0
616.0
618.0
620.0
622.0
624.0
626.0
m/z

(5) UPLC-MS analyses of **6b** and **6c**

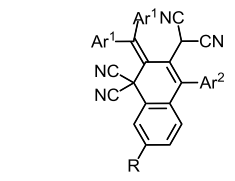
Column : 1.7 μm ACQUITY UPLC BEH C_{18}, 50×2.1 mm

Injection volume: 3 ppm×7 μl

Column temperature: 40℃

Gradient separations

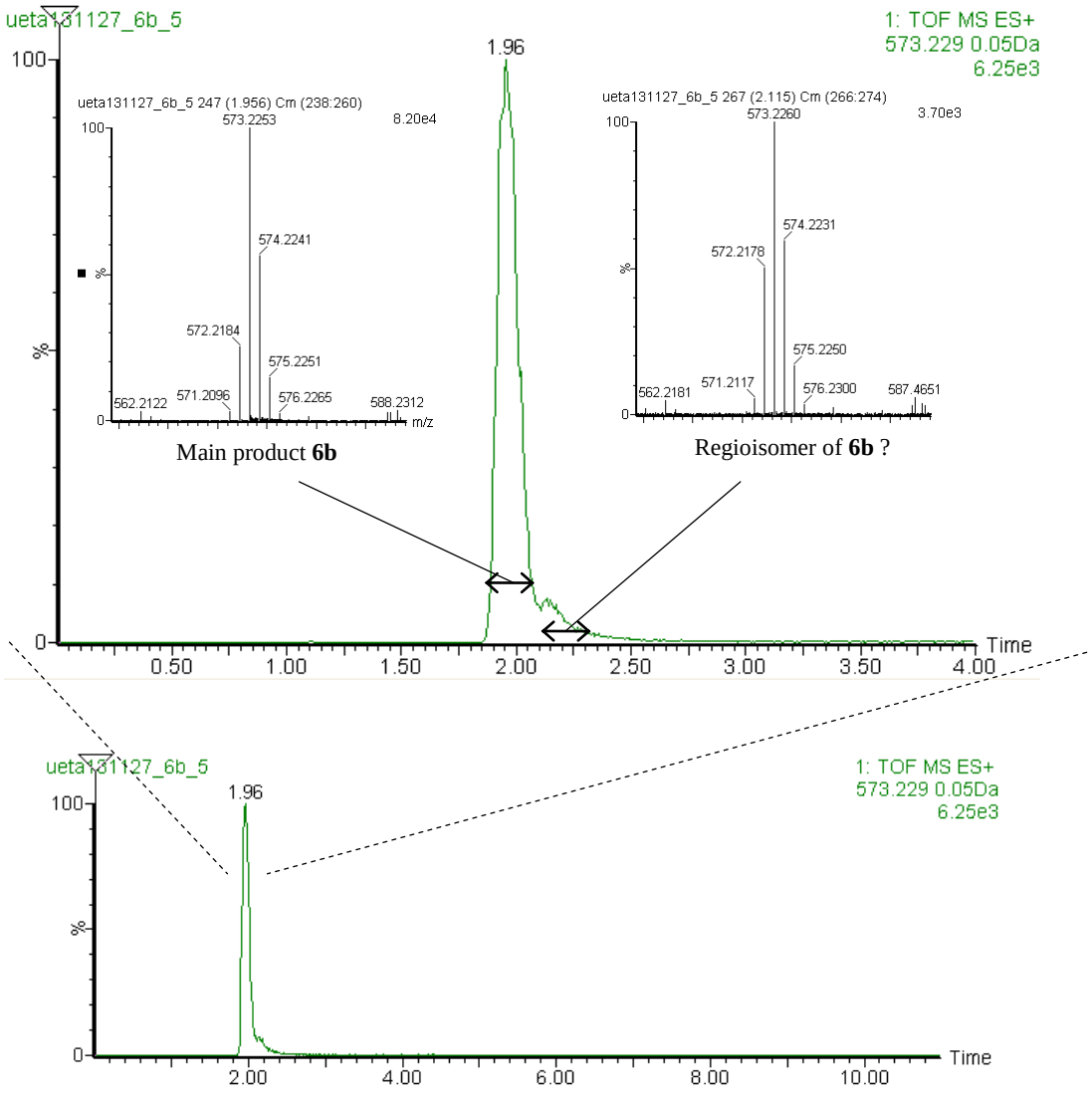
Time	Flow [ml/min]	0.1% Formic acid H_2O [%]	0.1% Formic acid CH_3CN [%]
0 min	0.1	40	60
10 min	0.1	0	100
10.1 min	0.1	40	60
11 min	0.1	40	60



6b

Ar^1 = *p*-MeOC$_6$H$_4$ Ar^2 = *p*-MeC$_6$H$_4$ R =Me

Calc. Mass 573.2291
Formula $C_{38}H_{29}N_4O_2^+$



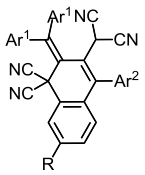
Column : 1.7 μm ACQUITY UPLC BEH C_{18}, 50×2.1 mm

Injection volume: 3 ppm×7 μl

Column temperature: 40℃

Gradient separations

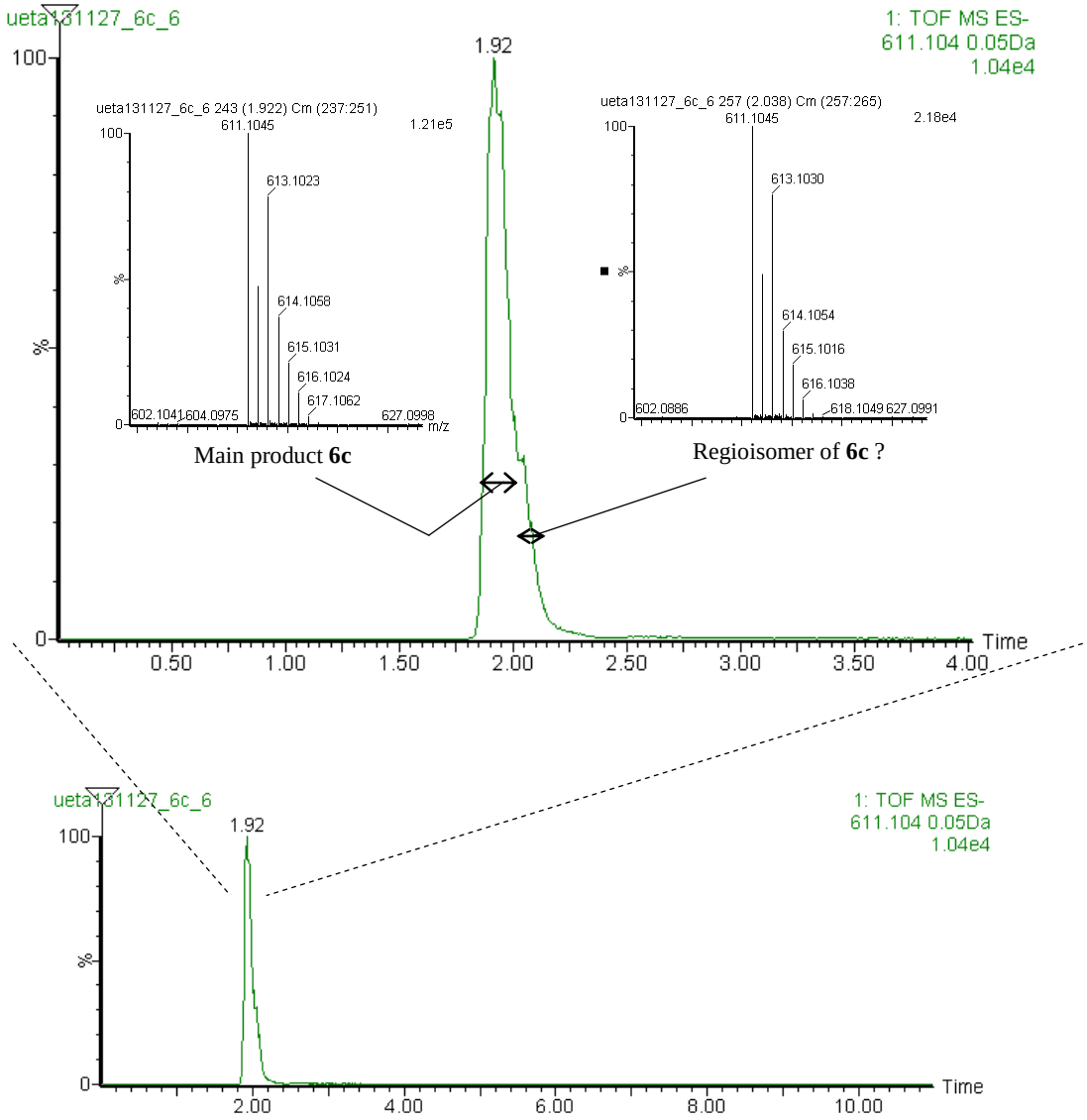
Time	Flow [ml/min]	0.1% Formic acid H_2O [%]	0.1% Formic acid CH_3CN [%]
0 min	0.1	40	60
10 min	0.1	0	100
10.1 min	0.1	40	60
11 min	0.1	40	60



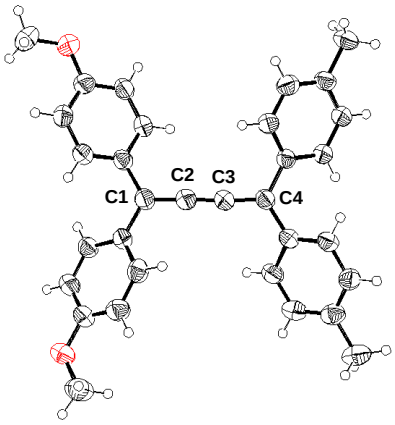
6c

Ar[1] = *p*-MeOC$_6$H$_4$ Ar[2] = *p*-ClC$_6$H$_4$ R =Cl

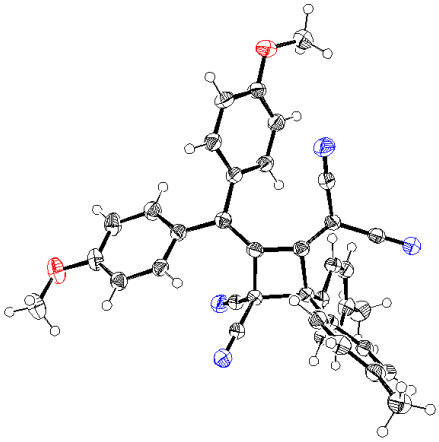
Calc. Mass 611.1042
Formula $C_{36}H_{21}N_4O_2Cl_2^-$



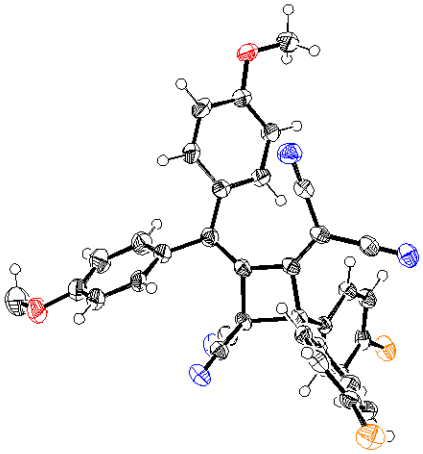
(6) Crystal structures of products.



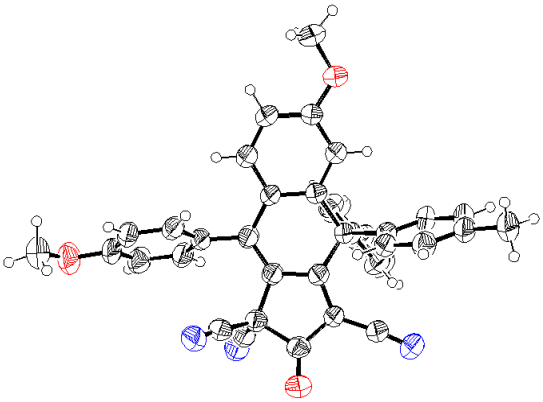
1b (CCDC 937964)
Selected bond length [Å]: C1-C2 1.346(3), C2-C3 1.248(3), C3-C4 1.334(3)



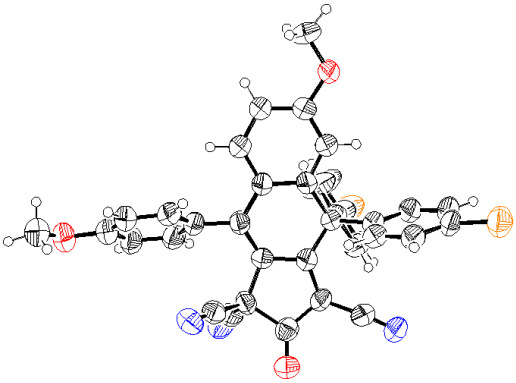
2b (CCDC 937945)



2c (CCDC 937946)



9b (CCDC 958310)



9c (CCDC 937949)