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Supporting Information

Fe-Catalyzed Cycloaddition of Indoles and *o*-Phthalaldehyde for the Synthesis of Benzo[*b*]carbazoles with TMSCl- or Acid-responsive Properties

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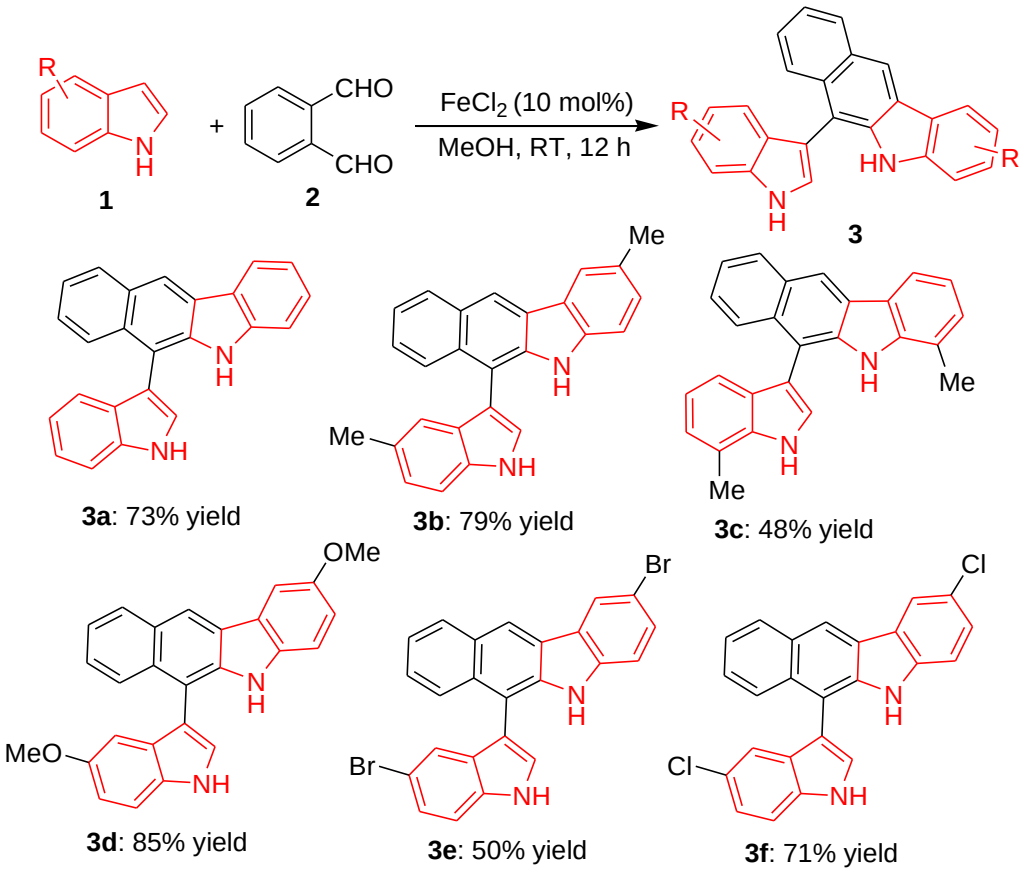
1. General information

All reagents and solvents were used directly without purification. Flash column chromatography was performed over silica (200-300 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 and 100 MHz, respectively on Advance (Brucker) 400 MHz Nuclear Magnetic Resonance Spectromer. Chemical shifts are reported in parts permillion (ppm), using the residual solvent signal as an internal standard: DMSO-D6 (^{1}H-NMR: δ 2.50, singlet; ^{13}C-NMR: δ 39.56, singlet). Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed on VERTEX70 IR (Bruker). The data were collected over 32 scans with a resolution of 4 cm^{-1} at room temperature. HRMS (Analyzer: TOF) was reported in units of mass of charge ratio (m/z).

2. Preparation of indolyl benzo[*b*]carbazoles

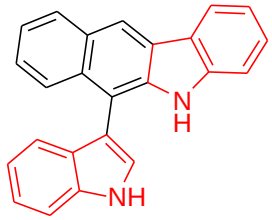


In a typical experiment, to a mixture of phthalaldehyde (5 mmol) and Indoles (15

equiv), $FeCl_2$ (10 mol%) was added to methanol (10 ml), and the resulting solution was stirred at room temperature for 12 h (monitored by TLC). The crude mixture was directly purified by column chromatography (silica gel, petroleum ethyl acetate mixtures) to obtain pure products.

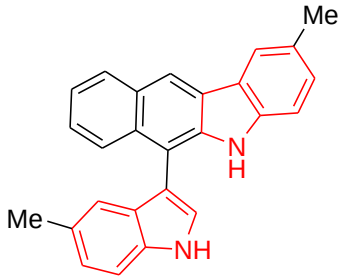
3. The analytical and spectral characterization data of reaction products

1) **3a**: 6-(1H-indol-3-yl)-5H-benzo[b]carbazole



A pale green solid, 88% total yield ($\mathbf{S}_{3/4}$ = 83:17). ^{1}H-NMR (400 MHz, DMSO-D6) δ (ppm) 11.60 (s, 1H), 10.52 (s, 1H), 8.71 (s, 1H), 8.28 (d, J = 7.2, 1H), 8.13-8.05 (m, 1H), 7.94-7.61 (m, 3H), 7.45-7.32 (m, 4H), 7.22-7.17 (m, 2H), 7.04-6.90 (m, 2H); ^{13}C-NMR (100 MHz, DMSO-D6) δ (ppm) 142.66, 139.15, 136.63, 131.33, 128.65, 128.04, 127.59, 127.05, 125.81, 125.06, 124.75, 124.37, 122.51, 122.05, 121.38, 120.88, 119.44, 119.11, 118.50, 117.44, 111.91, 111.37, 111.07,109.47; IR (ν_{max}/cm^{-1}): 3932.3, 3406.4, 3238.2, 2068.1, 1617.1, 1400.4, 1129.9, 743.1, 623.2, 488.0, 419.9; HRMS (MALDI-TOF) Calcd for $C_{24}H_{16}N_2$ $[M+H]^+$: 333.1313; found: 333.1323.

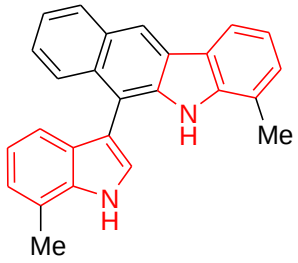
2) **3b**: 2-methyl-6-(5-methyl-1H-indol-3-yl)-5H-benzo[b]carbazole



A yellow solid, 79% total yield ($\mathbf{S}_{3/4}$ = 98:2). ^{1}H-NMR (400 MHz, DMSO-D6) δ (ppm)

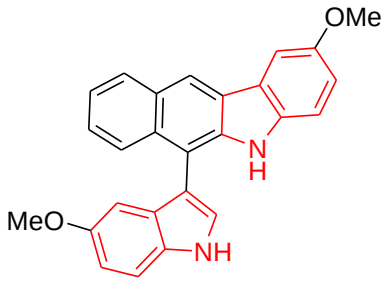
11.45 (s, 1H), 10.35 (s, 1H), 8.65 (s, 1H), 8.11-8.08 (m, 2H), 7.78 (d, J = 8, 1H), 7.64 (d, J = 2.4, 1H), 7.50 (d, J = 8.4, 1H), 7.40-7.24 (m, 4H), 7.02 (d, J = 9.2, 1H), 6.83 (s, 1H), 2.50 (s, 3H), 2.25 (s, 3H); ^{13}C-NMR (100 MHz, DMSO-D6) δ (ppm) 140.79, 139.44, 134.94, 131.31, 128.58, 128.21, 127.87, 127.84, 127.48, 127.06, 125.71, 125.02, 124.59, 124.21, 122.96, 122.59, 121.87, 120.73, 118.86, 117.19, 111.56, 111.33, 110.79, 108.94, 21.18, 21.08; IR (ν_{max}/cm^{-1}): 3930.2, 3413.3, 3237.9, 2067.9, 1617.4, 1399.2, 1131.3, 798.7, 619.8, 484.9, 417.1; HRMS (MALDI-TOF) Calcd for $C_{26}H_{20}N_2$ [M+H]$^+$: 361.1626; found: 361.1702.

3) **3c**: 4-methyl-6-(7-methyl-1H-indol-3-yl)-5H-benzo[b]carbazole



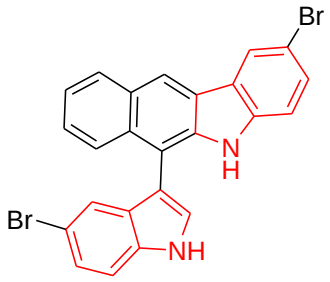
A white solid, 64% total yield (**S**$_{3/4}$ = 73:27). ^{1}H-NMR (400 MHz, DMSO-D6) δ (ppm) 1.45 (s, 1H), 9.93 (s, 1H), 8.63 (s, 1H), 8.07-7.89 (m, 2H), 7.72-7.50 (m, 2H), 7.31-7.04 (m, 4H), 6.93-6.81 (m, 3H), 2.58 (s, 3H), 2.42 (s, 3H); ^{13}C-NMR (100 MHz, DMSO-D6) δ (ppm) 140.79, 139.95, 131.32, 128.58, 128.20, 127.87, 127.84, 127.48, 127.06, 125.71, 125.03, 124.60, 124.20, 122.96, 122.59, 121.86, 120.73, 118.86, 117.18, 111.56, 111.33, 110.79, 108.95, 21.18, 21.08; IR (ν_{max}/cm^{-1}): 3418.5, 2067.4, 1615.2, 1400.1, 1131.3, 775.5, 746.2, 616.1, 418.8; HRMS (MALDI-TOF) Calcd for $C_{26}H_{20}N_2$ [M+Na]$^+$: 361.1626; found: 361.1702.

4) **3d**: 2-methoxy-6-(5-methoxy-1H-indol-3-yl)-5H-benzo[b]carbazole



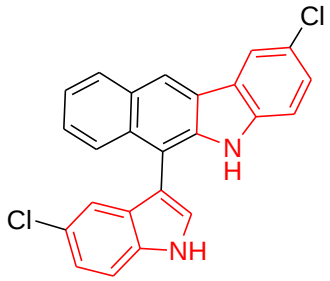
A yellow solid, 85% total yield (**S**$_{3/4}$ = >99:1). ^{1}H-NMR (400 MHz, DMSO-D6) δ (ppm) 11.42 (s, 1H), 10.26 (s, 1H), 8.71 (s, 1H), 8.11-8.09 (m, 1H), 7.88-7.78 (m, 2H), 7.65 (d, J = 2.4, 1H), 7.49 (d, J = 8.8, 1H), 7.38-7.33 (m, 3H), 7.09-7.06 (m, 1H), 6.86-6.84 (m, 1H), 6.46 (d, J = 2, 1H), 3.89 (s, 3H), 3.52 (s, 3H); ^{13}C-NMR (100 MHz, DMSO-D6) δ (ppm) 153.53, 153.01, 139.67, 137.34, 131.72, 131.06, 128.67, 127.80, 127.75, 126.39, 125.05, 124.86, 124.24, 122.88, 121.90, 117.49, 115.87, 112.58, 111.76, 111.62, 111.34, 109.28, 104.20, 101.07, 55.71, 55.19; IR (ν_{max}/cm^{-1}): 3411.3, 2943.9, 2829.6, 2067.1, 1621.7, 1485.6, 1396.4, 1158.9, 783.9, 746.2, 615.5; HRMS (MALDI-TOF) Calcd for $C_{26}H_{20}N_2O_2$ [M]$^{+}$: 392.1525; found: 392.1537.

5) **3e**: 2-bromo-6-(5-bromo-1H-indol-3-yl)-5H-benzo[b]carbazole



A yellow solid, 65% total yield (**S**$_{3/4}$ = >99:1). ^{1}H-NMR (400 MHz, DMSO-D6) δ (ppm) 10.84 (s, 1H), 10.72 (s, 1H), 8.81 (s, 1H), 8.53 (d, J = 1.6, 1H), 8.13-8.10 (m, 1H), 7.80-7.73 (m, 2H), 7.60-7.55 (m, 2H), 7.41-7.30 (m, 4H), 7.10 (d, J = 1.2, 1H); ^{13}C-NMR (100 MHz, DMSO-D6) δ (ppm) 141.33, 139.31, 135.29, 131.53, 129.47, 129.30, 128.82, 128.01, 127.61, 125.04, 124.70, 124.54, 123.92, 123.58, 123.51, 122.41, 121.70, 118.62, 113.98, 112.86, 111.74, 110.65, 110.39, 108.80; IR (ν_{max}/cm^{-1}): 3414.9, 3237.9, 2067.2, 1617.4, 1398.4, 1279.1, 1131.6, 616.5, 473.9, 419.2; HRMS (MALDI-TOF) Calcd for $C_{24}H_{14}Br_2N_2$ [M]$^{+}$: 488.9599; found: 488.9591.

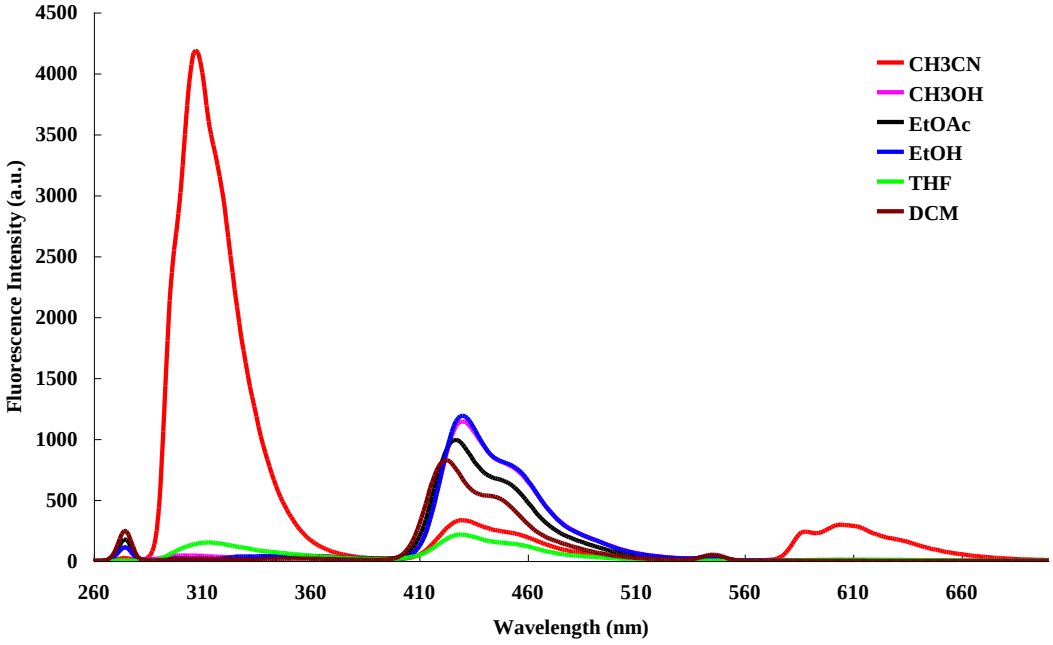
6) **3f**: 2-chloro-6-(5-chloro-1H-indol-3-yl)-5H-benzo[b]carbazole



A pale green solid, 71% total yield ($\mathbf{S}_{3/4}$ = >99:1). ^{1}H-NMR (400 MHz, DMSO-D6) δ (ppm) 11.84 (s, 1H), 10.71 (s, 1H), 8.80 (s, 1H), 8.39 (s, 1H), 8.12-8.10 (m, 1H), 7.82-7.74 (m, 2H), 7.63 (d, J = 8.4, 1H), 7.45-7.37 (m, 4H), 7.22-7.19 (m, 1H), 7.70 (s, 1H); ^{13}C-NMR (100 MHz, DMSO-D6) δ (ppm) 141.05, 139.47, 135.07, 131.51, 128.82, 128.61, 128.00, 127.77,126.85, 125.01, 124.72, 123.91, 123.84, 123.72, 122.77, 122.38, 121.41, 120.57, 118.57, 118.18, 113.51, 112.36, 110.72, 108.94; IR (ν_{max}/cm^{-1}): 3410.1, 2918.3, 2067.5, 1618.0, 1484.3, 1396.8, 1292.4, 1131.5, 797.4, 615.0.

4. FL analysis of indolyl benzo[*b*]carbazoles

(a) Solvent Effect



(b) FL of 3a-3f

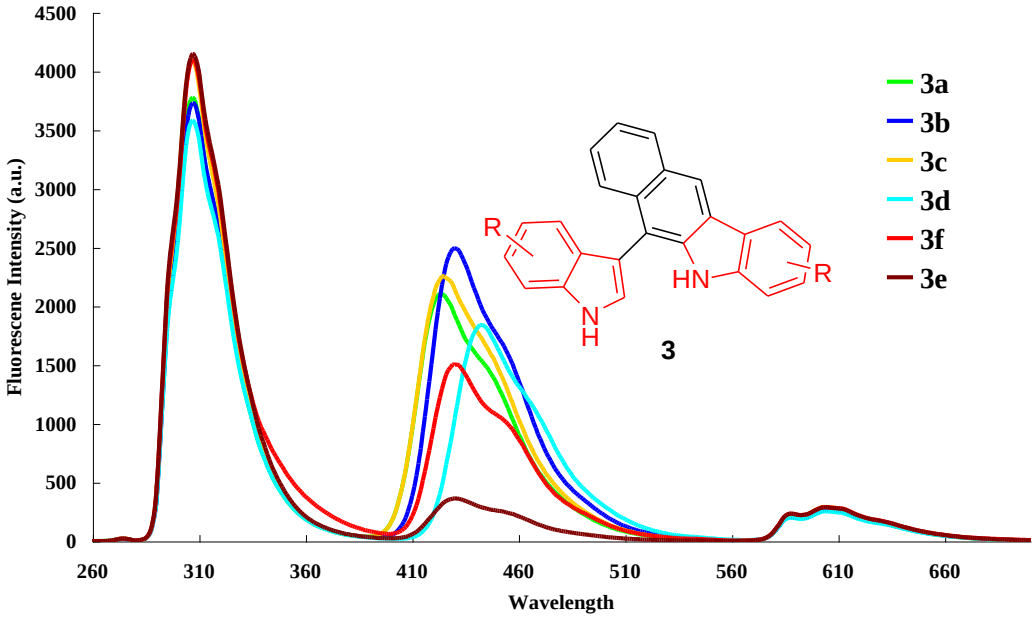
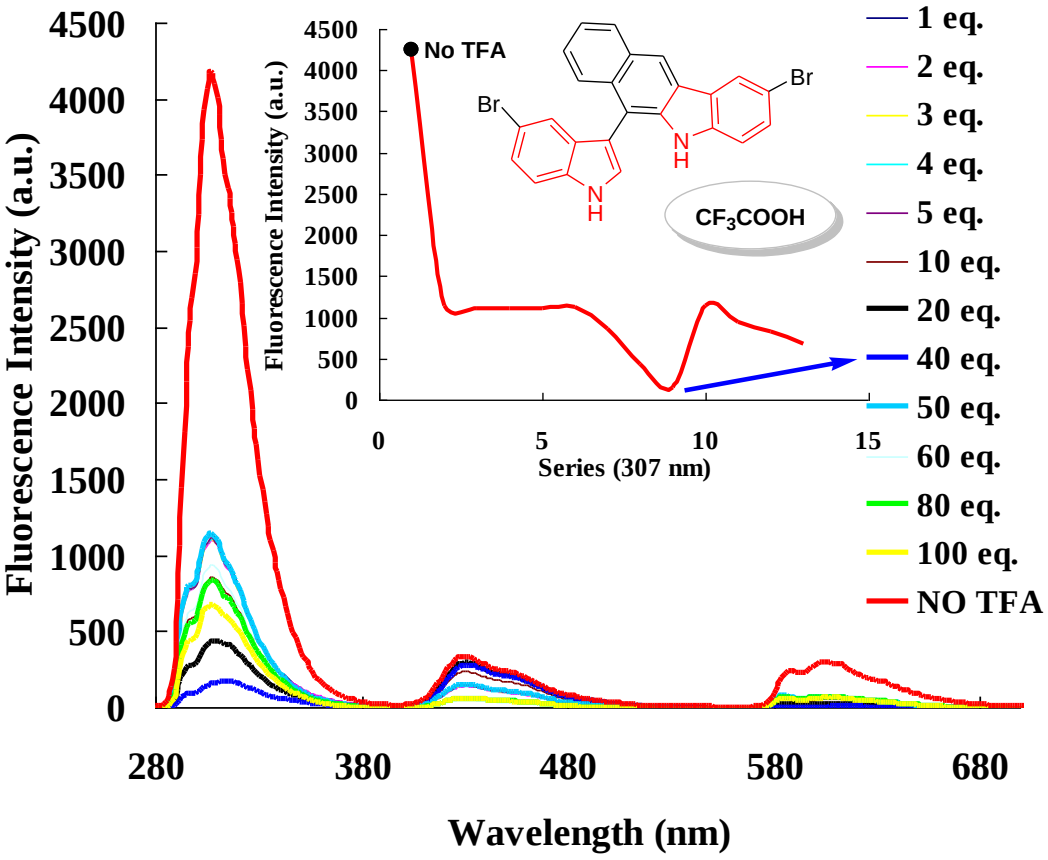


Figure S1. Solvents effect on the fluorescence emission spectrum of **3e** (5×10^{-6} M) in various solvents.



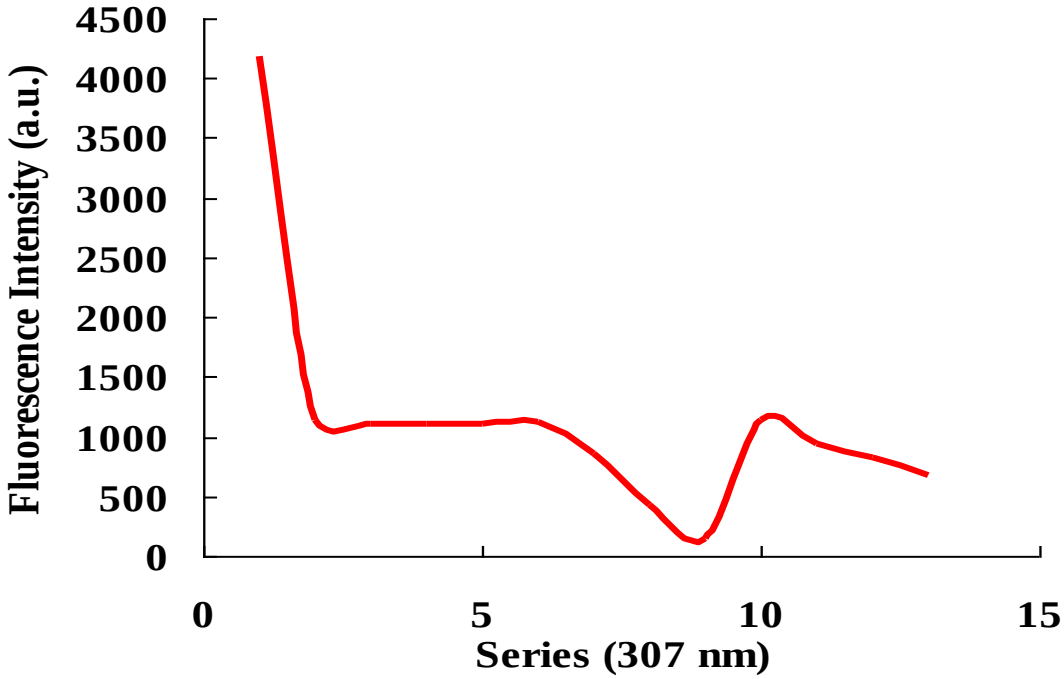


Figure S2. Changes observed in the fluorescence emission spectrum of **3e** (5×10^{-6} M) upon addition of TFA (1 ~ 100 eq.) in CH_3CN.

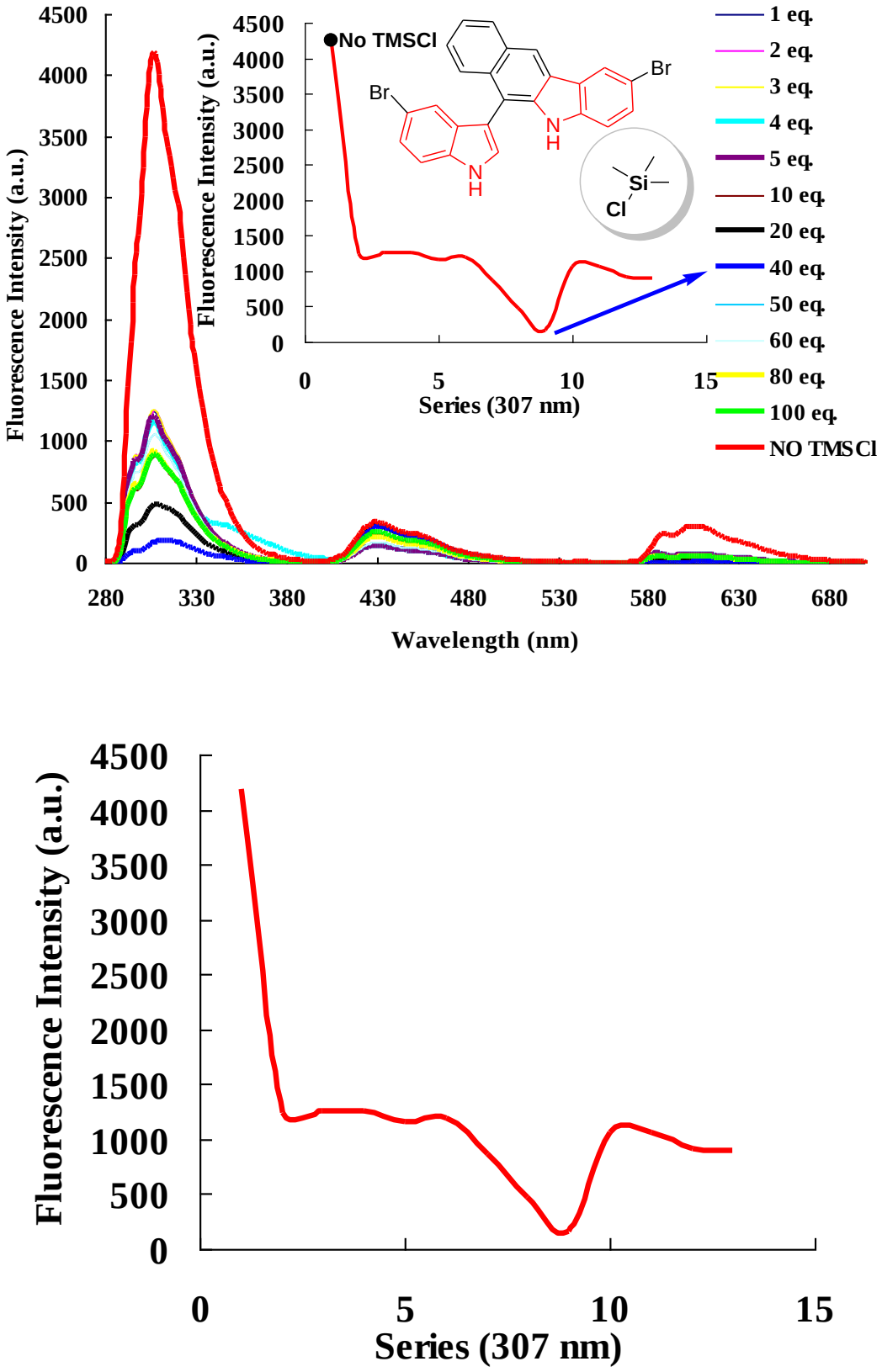


Figure S3. Changes observed in the fluorescence emission spectrum of **3e** (5×10^{-6} M) upon addition of TMSCl (1 ~ 100 eq.) in CH_3CN.

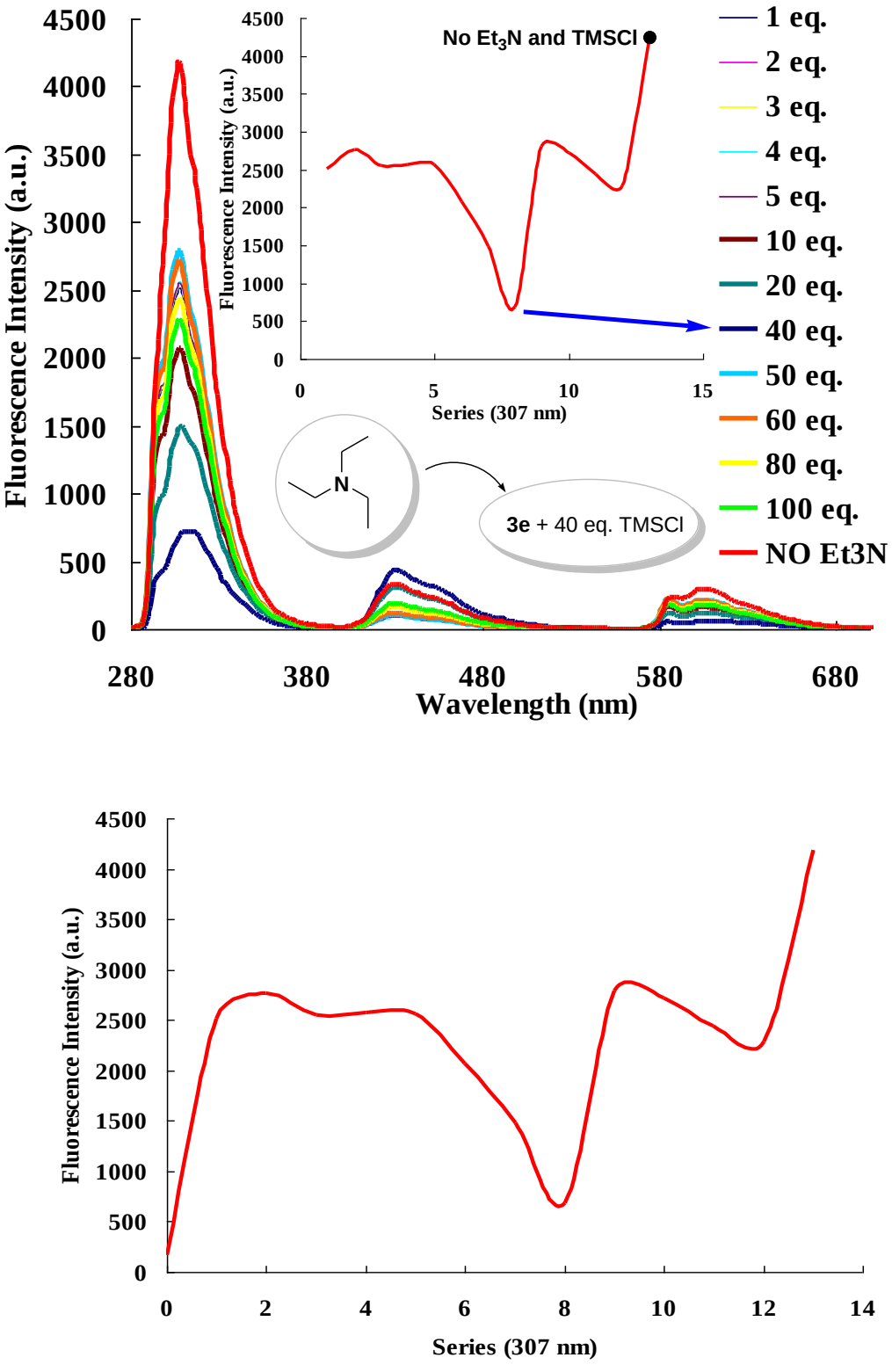
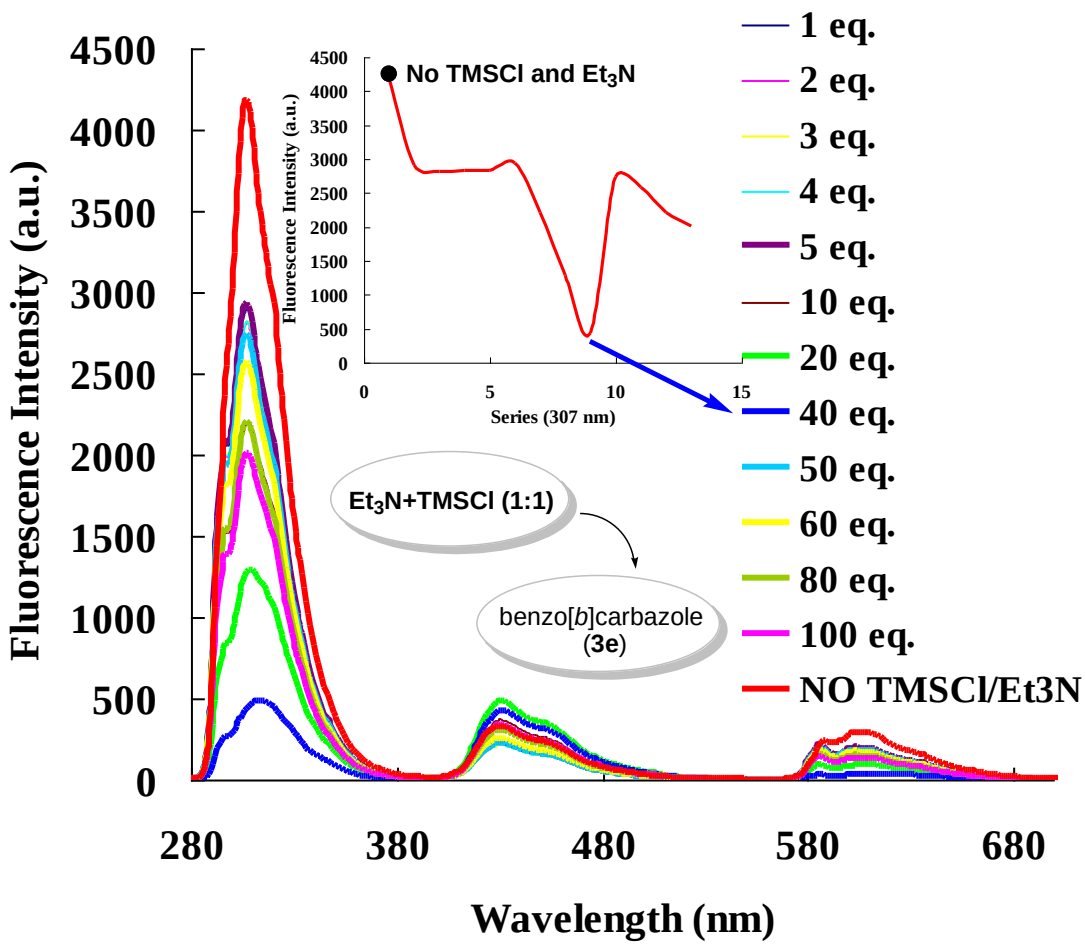


Figure S4. Changes observed in the fluorescence emission spectrum of the mixture of **3e** (5×10^{-6} M) with TMSCl (40 eq.) upon addition of Et_3N (1-100 eq.) in CH_3CN.



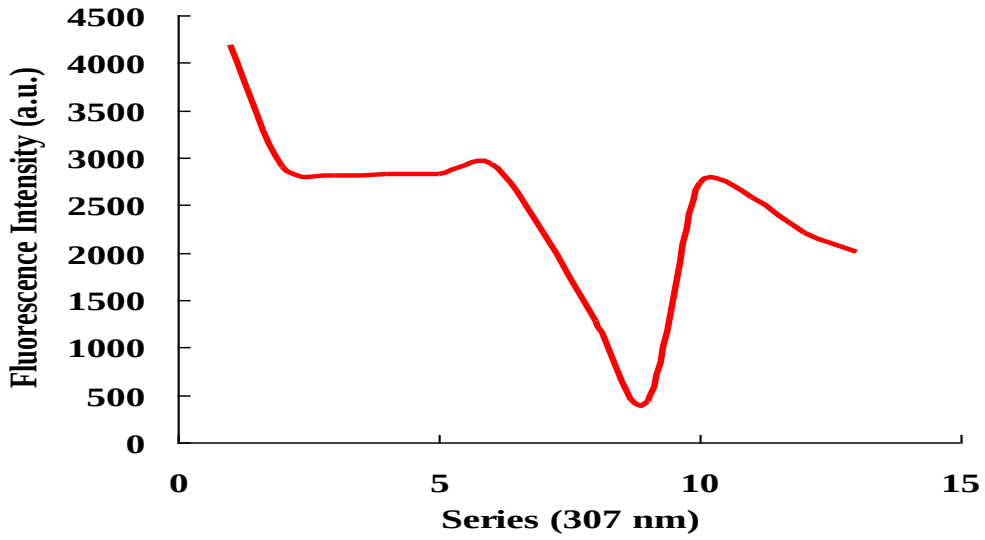


Figure S5. Changes observed in the fluorescence emission spectrum of the mixture of **3e** (5×10^{-6} M) upon addition of Et_3N and TMSCl (1:1, 1-100 eq.) in CH_3CN.

5. $^{1}H/^{13}C$ NMR analysis

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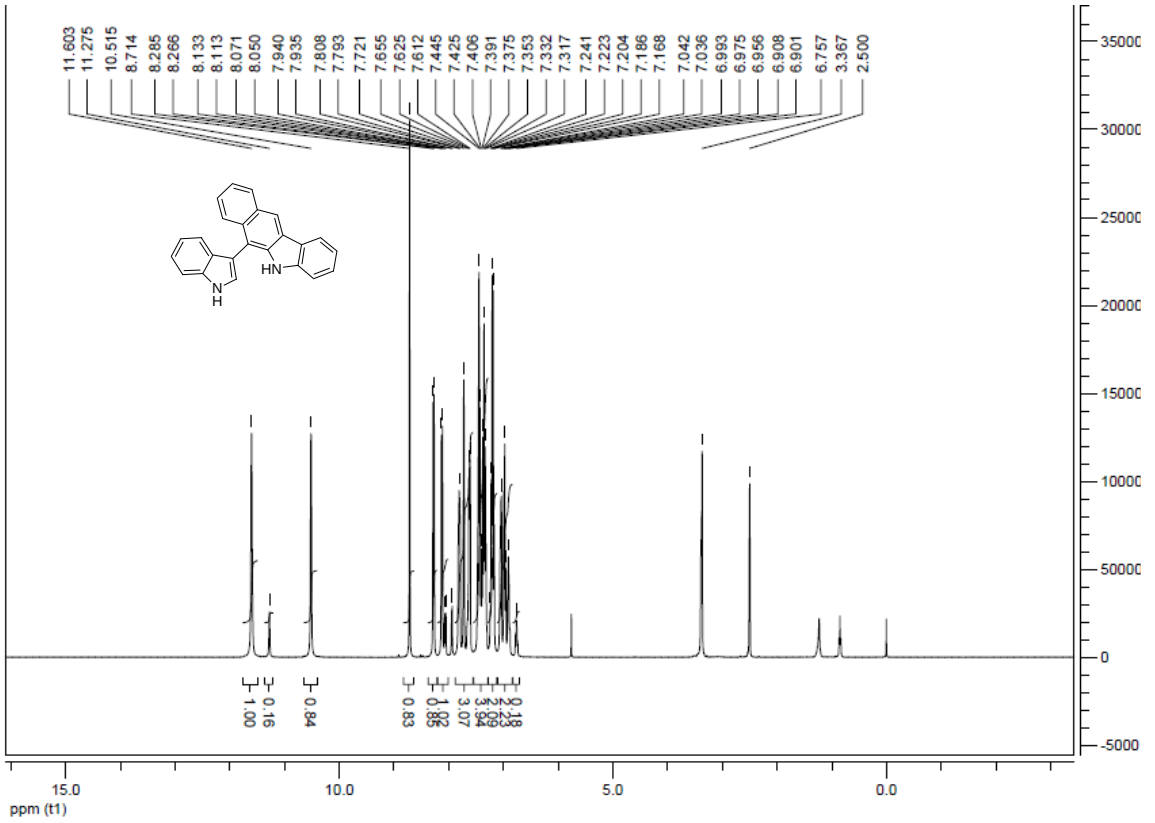

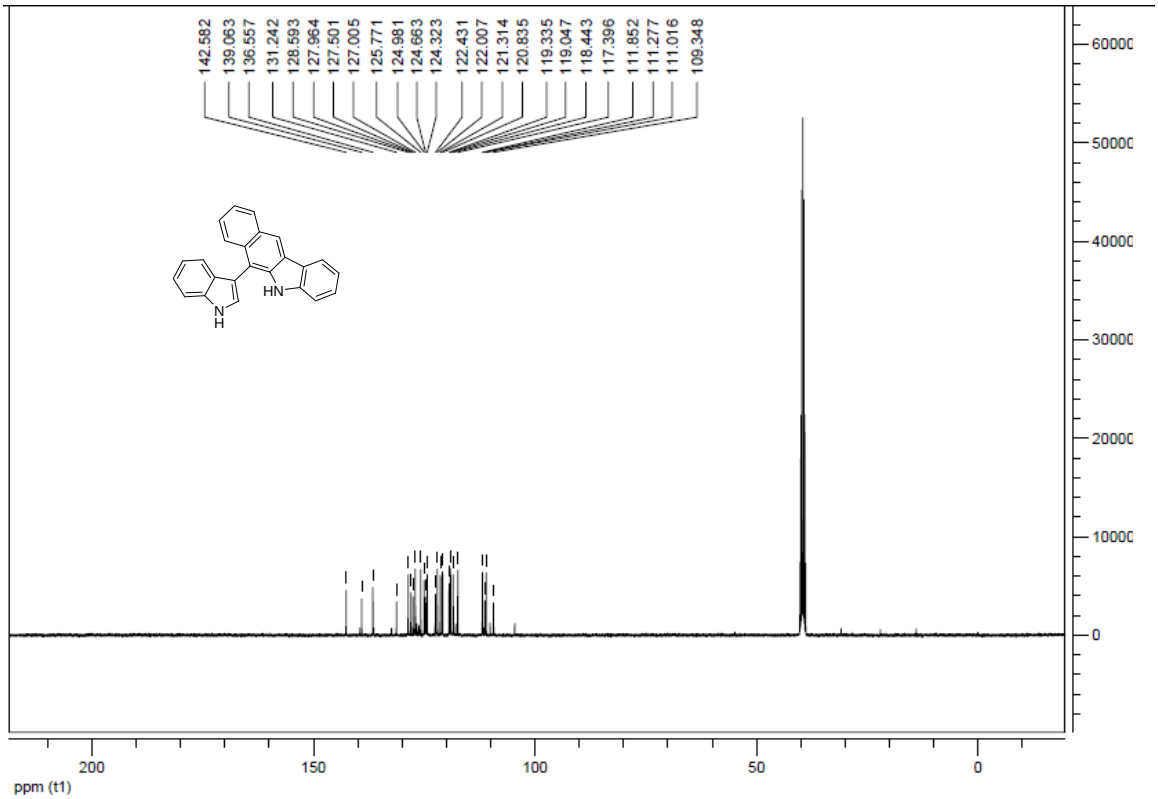

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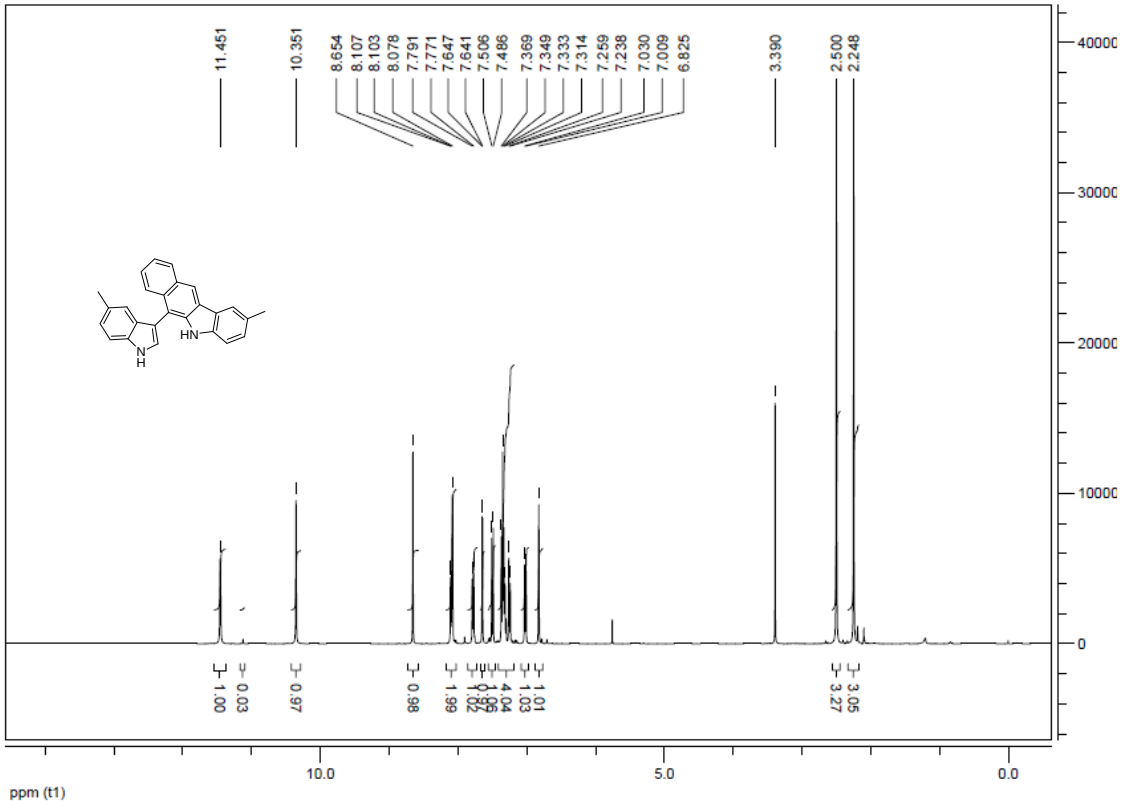
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7.349
7.333
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2.500
2.248
HN
N
H
1.00
0.03
0.97
0.98
1.99
4.04
1.03
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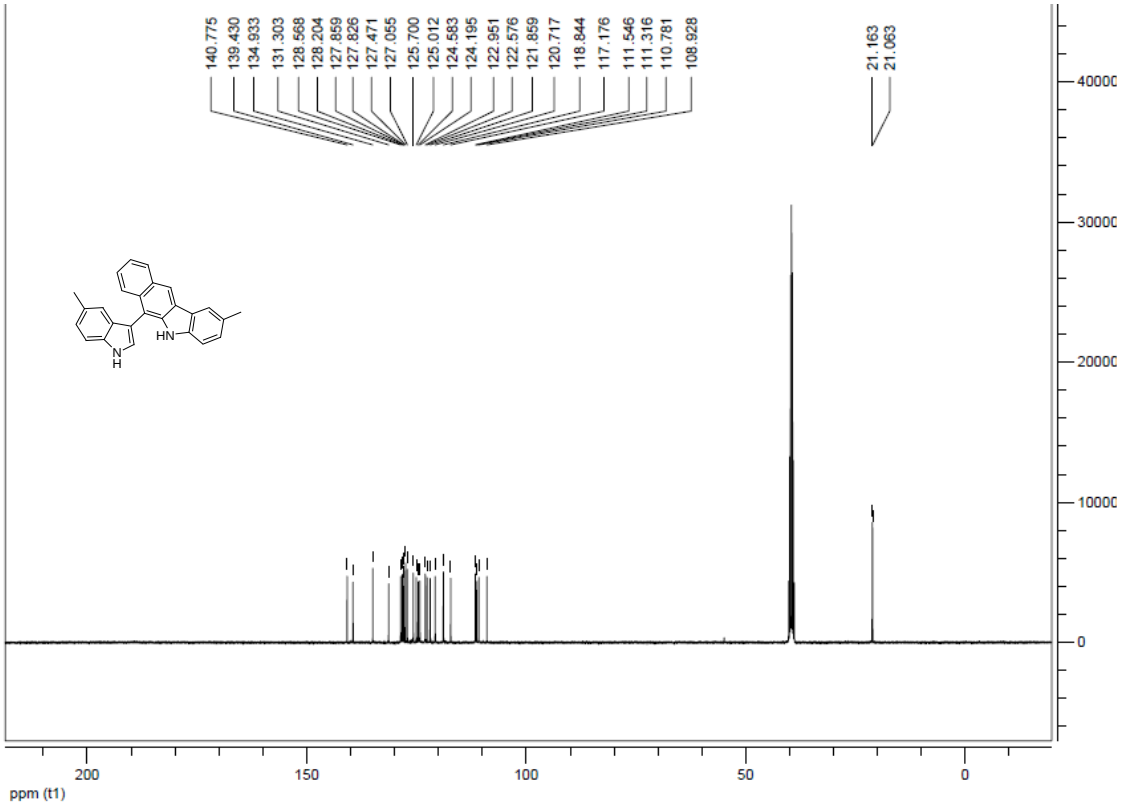
ppm (t1)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124.195
122.951
122.576
121.859
120.717
118.844
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111.546
111.316
110.781
108.928
21.163
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150
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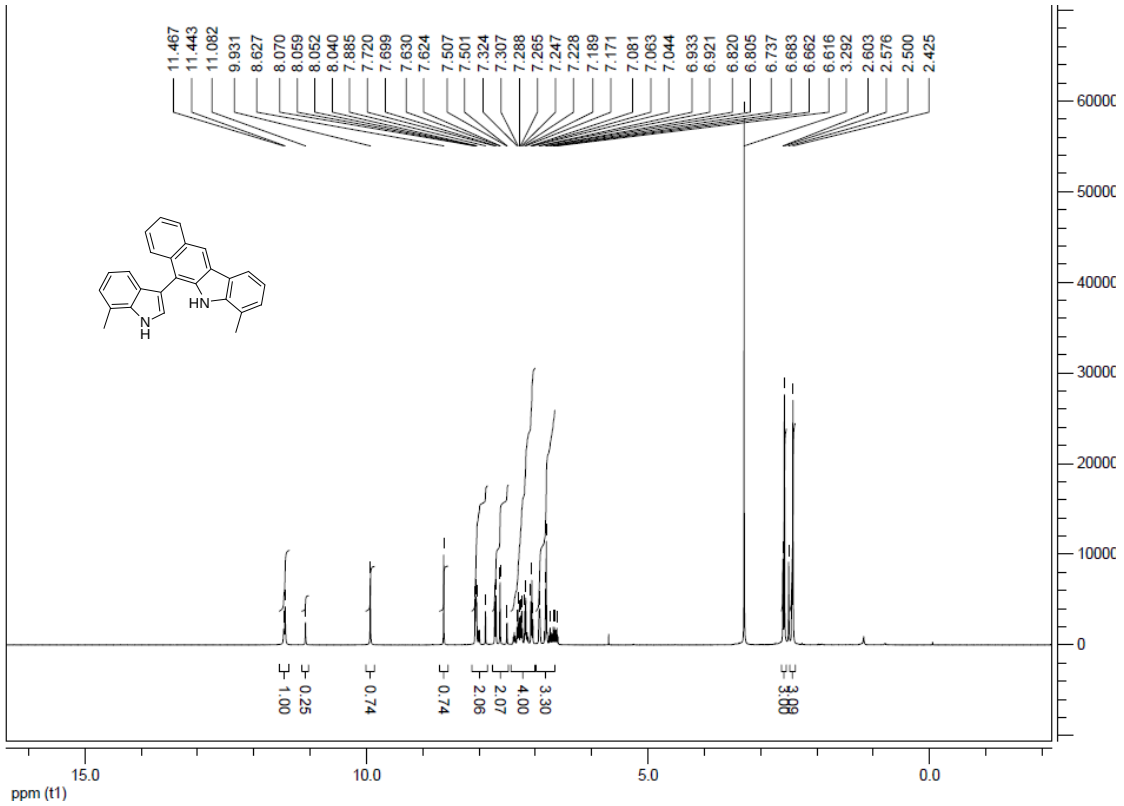
ppm (t1)

Product 3c: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7.624
7.507
7.501
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7.307
7.288
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7.247
7.228
7.189
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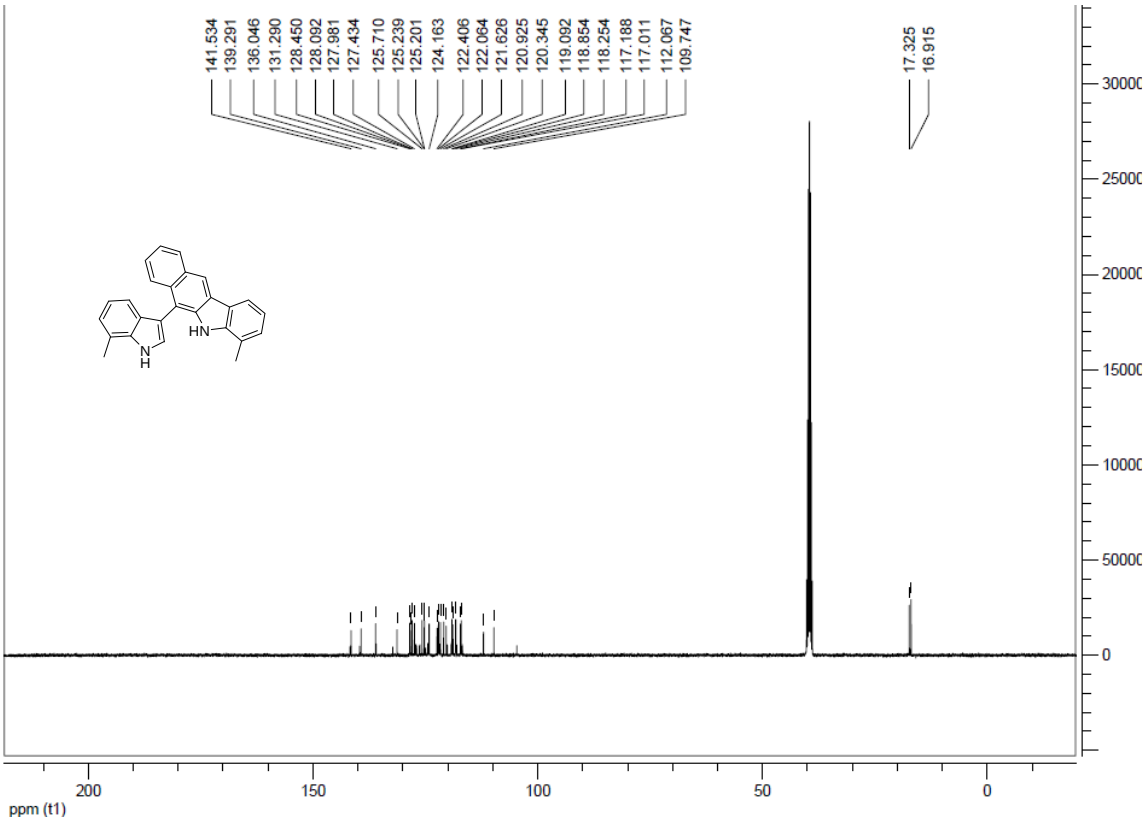
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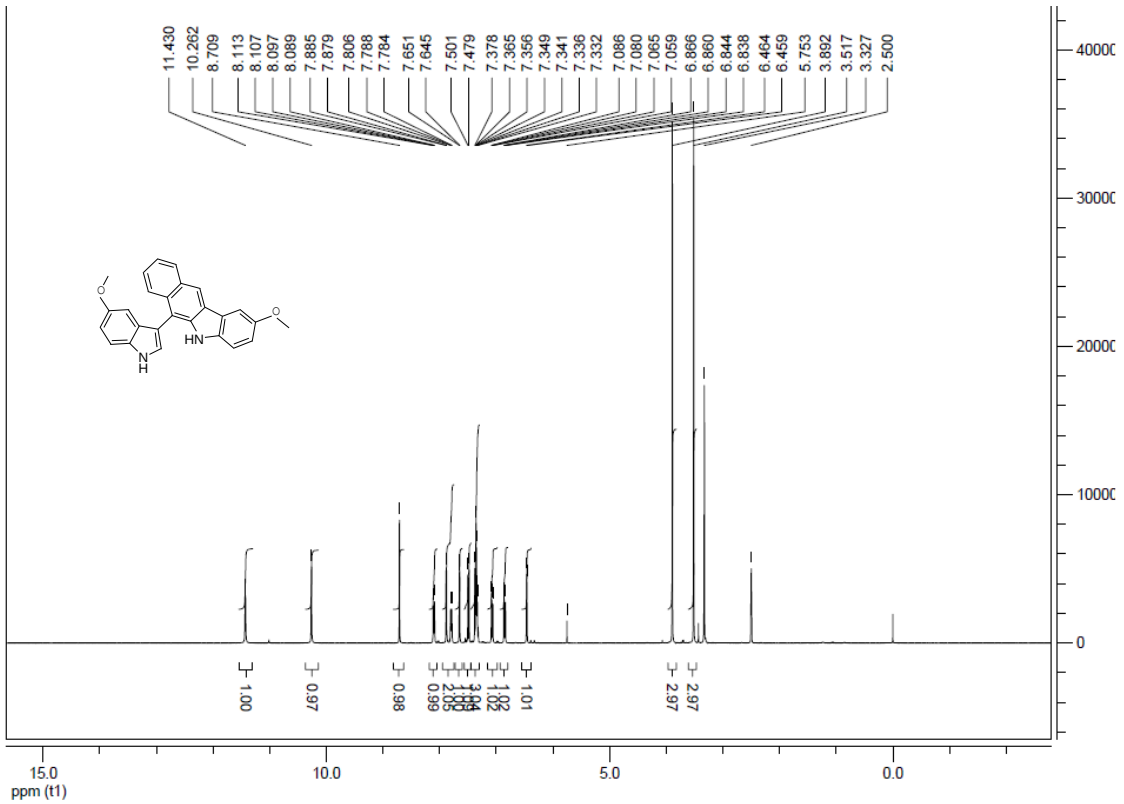
ppm (t1)

Product 3d: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7.336
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6.459
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3.517
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H
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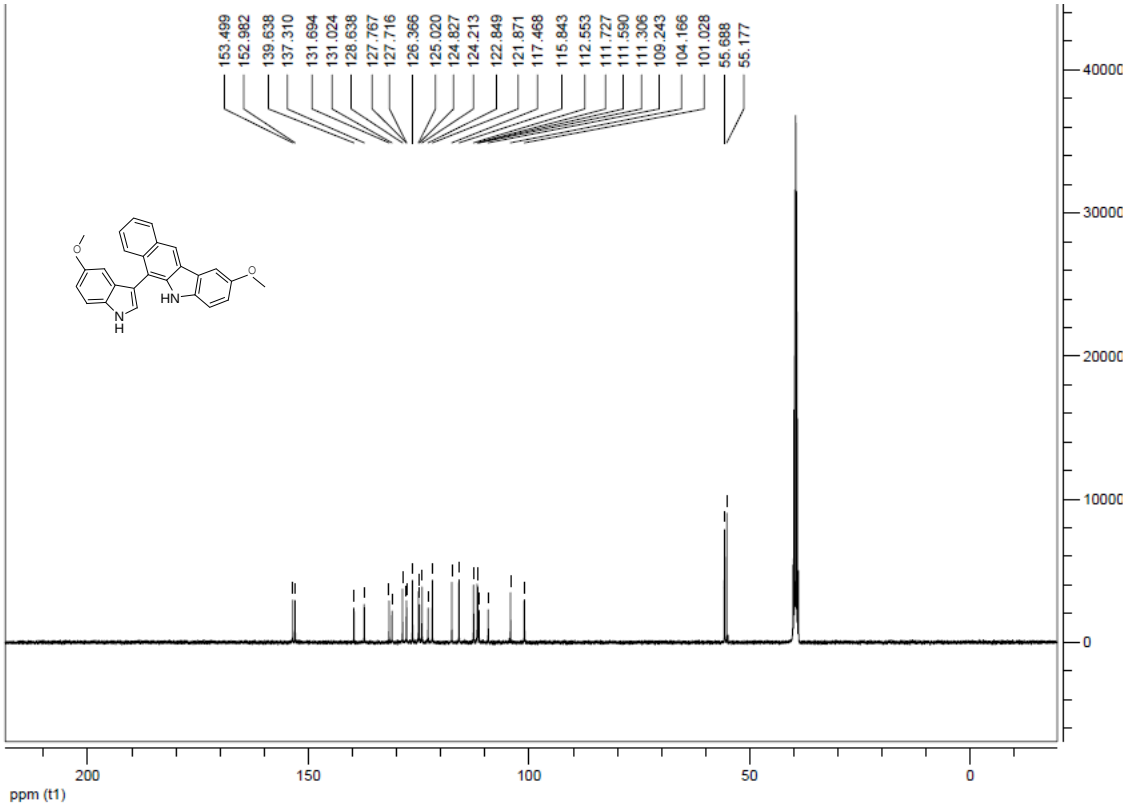
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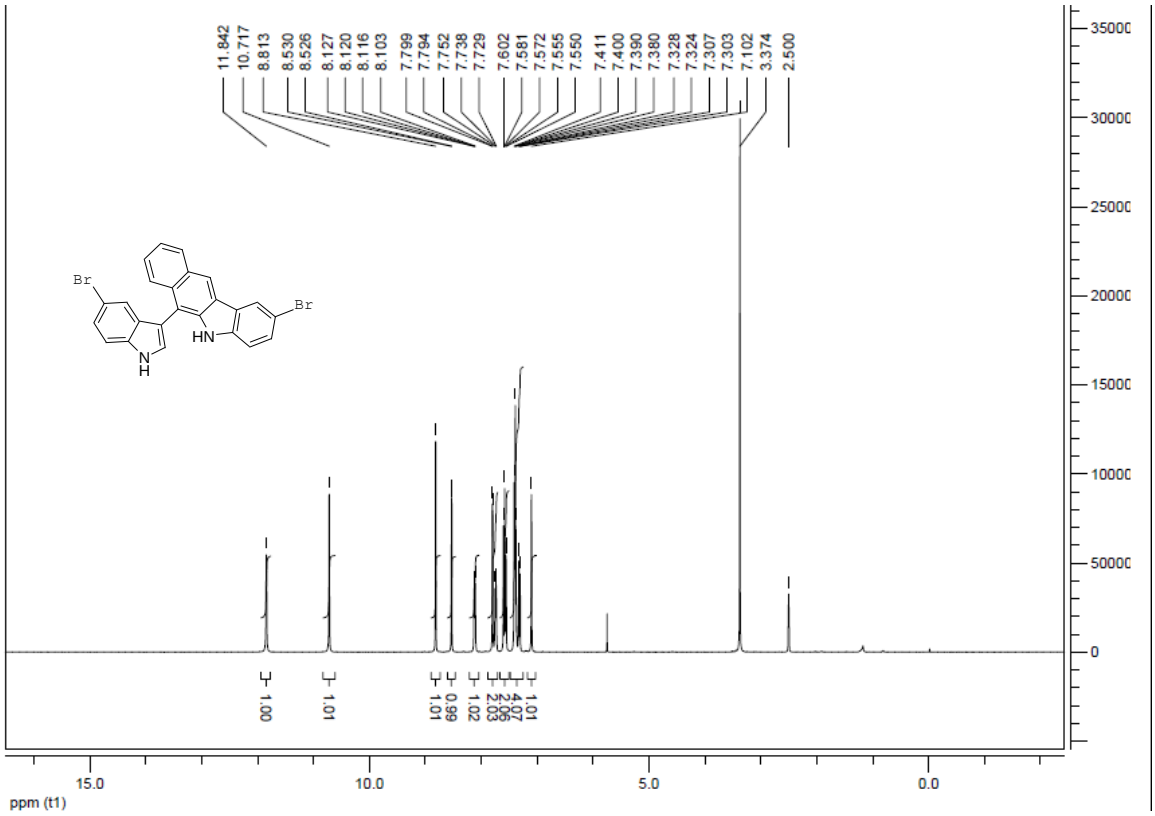
Product 3e: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7.324
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7.303
7.102
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Br
HN
N
H
1.00
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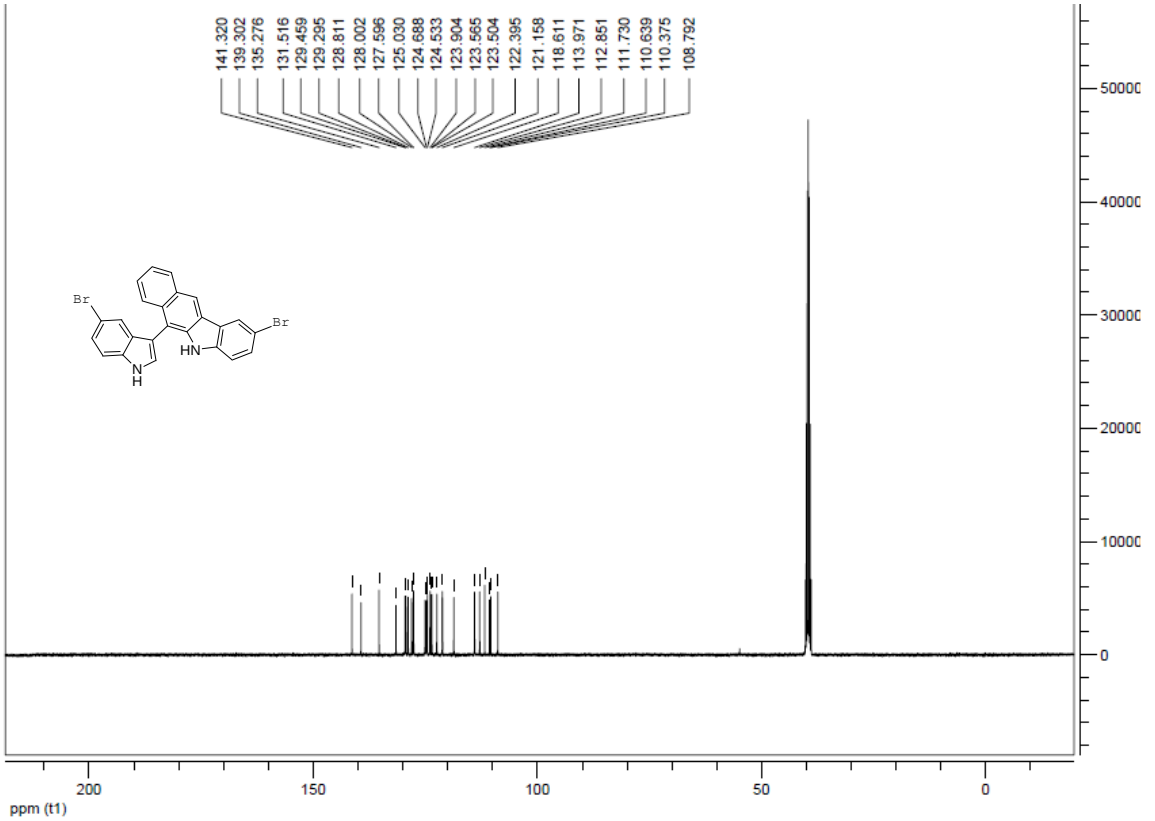
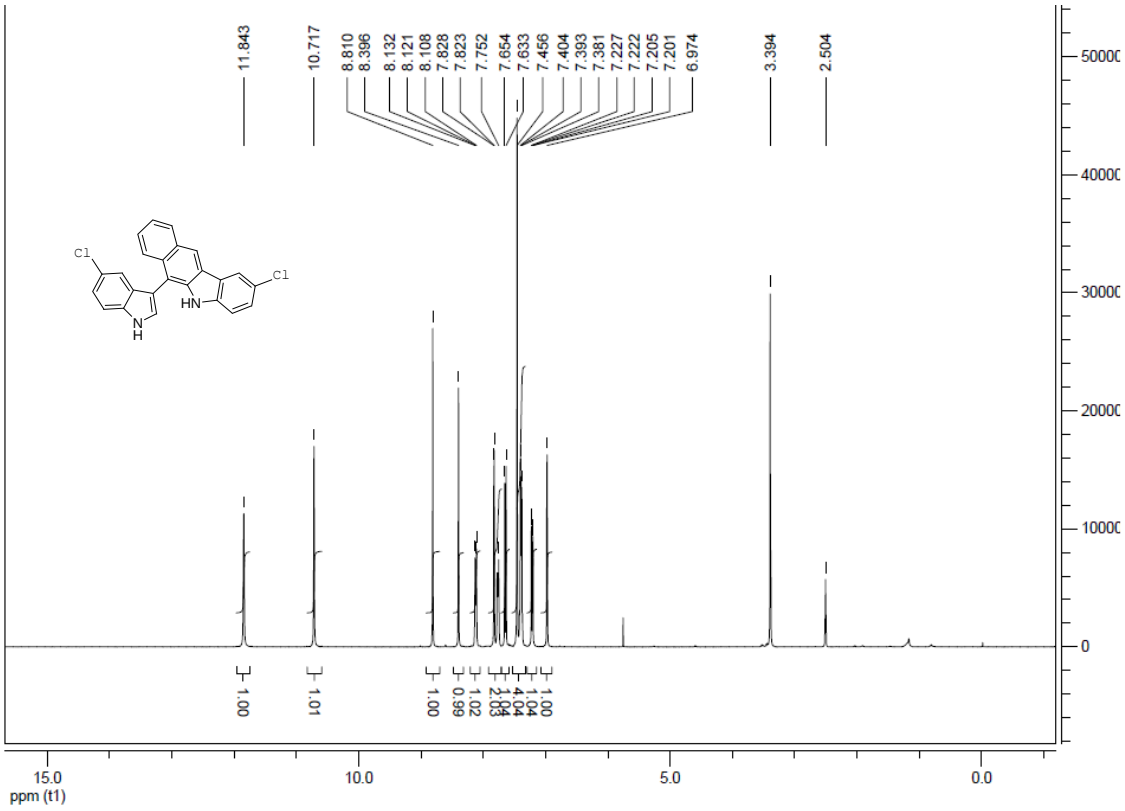
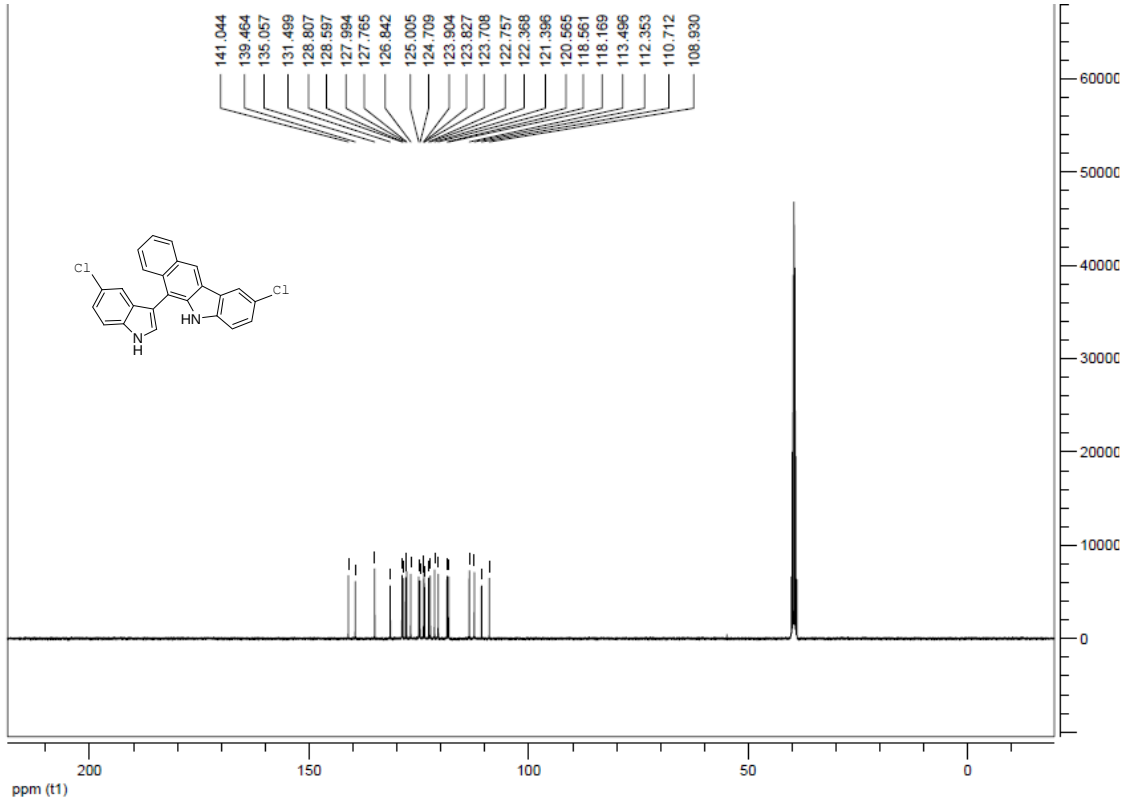
1.01
0.99
1.01
1.02
2.03
2.96
4.07
1.01
35000
30000
25000
20000
15000
10000
5000
0
15.0
10.0
5.0
0.0
ppm (t1)


141.320
139.302
135.276
131.516
129.459
129.295
128.811
128.002
127.596
125.030
124.688
124.533
123.904
123.565
123.504
122.395
121.158
118.611
113.971
112.851
111.730
110.639
110.375
108.792
Br
Br
HN
N
H
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

Product 3f:


11.843
10.717
8.810
8.396
8.132
8.121
8.108
7.828
7.823
7.752
7.654
7.633
7.456
7.404
7.393
7.381
7.227
7.222
7.205
7.201
6.974
3.394
2.504
Cl
Cl
HN
N
H
1.00
1.01
1.00
0.99
1.02
1.00
1.04
1.04
1.00
15.0
10.0
5.0
0.0
ppm (t1)


141.044
139.464
135.057
131.499
128.807
128.597
127.994
127.765
126.842
125.005
124.709
123.904
123.827
123.708
122.757
122.368
121.396
120.565
118.561
118.169
113.496
112.353
110.712
108.930
Cl
Cl
HN
N
H
200
150
100
50
0
ppm (t1)