BINOL-Linked 1,2,3-Triazoles: An Unexpected Fluorescent Sensor with Anion-π Interaction for Iodide Ion

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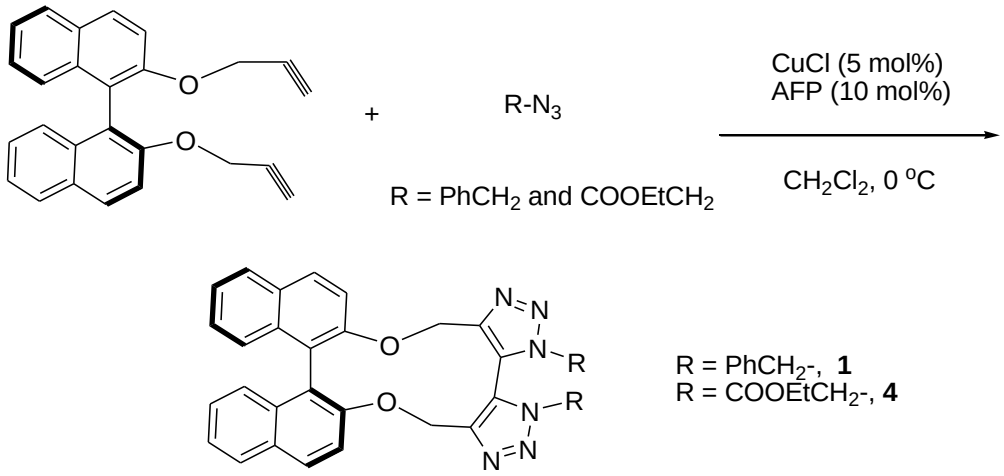
1. General information for synthesis and characterization of compound 1-6

All reagents were used as purchased. Substitued azides were synthesised at room temperature from the corresponding bromides with sodium azide in DMF[2,3], Amino-functional Polysiloxane (AFP) was purchased from Hangzhou Bald Silicone Co., Ltd. (0.55 mmol /g polysiloxane, Mw ~1900). Flash column chromatography was performed over silica (100-200 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recored at 400 and 100 MHz, respectively on Advance (Bruker) 400 MHz Nuuclear Magnetic Resonance Spectromer, and were referenced to the internal solvent signals. GC-MS was performed on TRACE DSQ. High Resolution Mass Spectra (ESI-HRMS) were operated on a microOTOF-Q Ⅱ (Bruker). IR spectra were recorded using a FTIR apparatus (Nicolot 5700). UV/Vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were measured on a Hitachi F-2700 FL spectrophotometer with a xenon arc lamp as light source. Thin layer chromatography was performed using Silica.



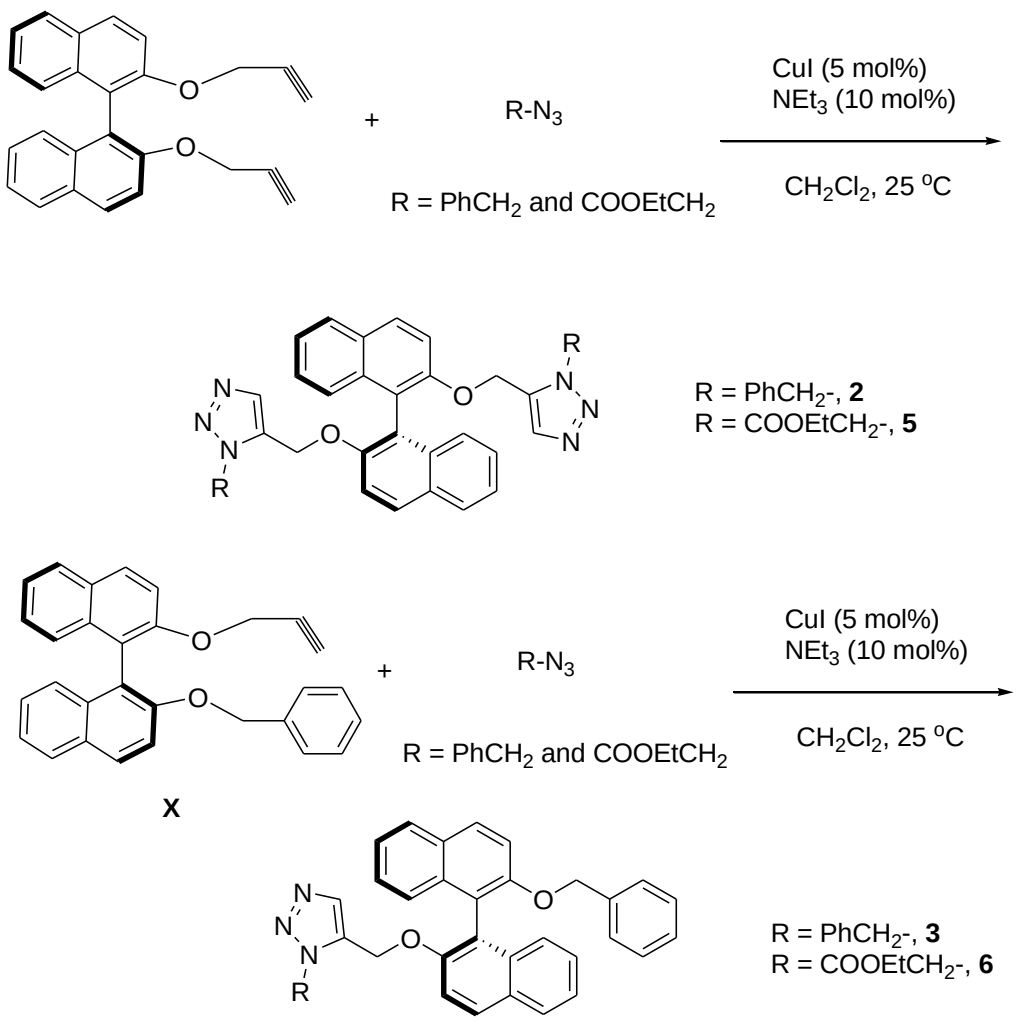
Scheme S1 Synthetic approach to compound **1** and **4**

Synthesis of compound 1 *and* ***4***. Amine-functional polysiloxane **AFP** (0.1 mmol) and CuCl (0.05 mmol) was added into a solution of azide (1.0 mmol) and dipropargyl compound (1.0 mmol) in CH_2Cl_2 (4 mL). The resulting mixture was stirred at 0 ^{o}C for

24h and diluted with MeOH (10 mL), then the solution was passed through a short pad of Celite. The filtrate was dried (Na_2SO_4), concentrated in vacuo, and purified by column chromatograph on silica gel to gain the desired cyclic compound **1** and **4**.

Ligand **1** was obtained as a white solid in 35% yield. ^{1}H-NMR ($CDCl_3$, 400MHz), δ =7.81 (m, Naph-H, 4H), 7.49 (m, Naph-H, 2H), 7.38 (m, Naph-H, 5H), 7.24 (m, Naph-H, 1H), 7.09 (m, Ph-H, 2H), 6.90 (m, Ph-H, 6H), 6.84(d, J= 8.4Hz, Ph-H, 2H), 5.28 (d, J=14.8 Hz, O-*CH_2*, 2H), 4.85 (d, J=10.8 Hz, Ph-*CH_2*, 2H), 4.57 (d, J=14.8 Hz, O-*CH_2*, 2H), 3.64 (d, J=10.8 Hz, Ph-*CH_2*, 2H). ^{13}C-NMR ($CDCl_3$, 100MHz), δ= 171.3, 154.1, 146.9, 134.0, 133.8, 129.4, 129.3, 128.9, 128.1, 127.8, 126.3, 125.9, 123.5, 122.3, 118.0, 113.4, 60.6, 53.2. HRMS calcd. for $C_{40}H_{30}N_6NaO_2$, 649.2322 $[M+Na]^+$, found 649.2347. IR(cm^{-1}), 3055, 2928, 2359, 2323, 1750, 1622, 1593, 1508, 1456, 1322, 1251, 1083, 1036, 1017, 915, 807, 750, 714.

Ligand **4** was obtained as a white solid in 28% yield. ^{1}H-NMR ($CDCl_3$, 400MHz), δ =7.89 (d, J= 9.2 Hz, Naph-H, 2H), 7.83 (d, J= 8.0 Hz, Naph-H, 2H), 7.37 (d, J= 9.2 Hz, Naph-H, 2H), 7.28 (m, Naph-H, 2H), 7.09 (t, J= 7.2 Hz, Naph-H, 2H), 6.94 (d, J= 8.8 Hz, Naph-H, 2H), 5.29 (m, O-*CH_2*, 2H), 4.88 (m, O-*CH_2* and COOEt-*CH_2*, 6H), 4.17 (m, O*CH_2*CH_3, 4H), 1.22 (t, J=7.2 Hz, OCH_2*CH_3*, 6H). ^{13}C-NMR ($CDCl_3$, 100MHz), δ= 166.2, 154.4, 146.5, 134.1, 129.6, 129.1, 127.9, 126.4, 125.9, 123.6, 123.5, 118.2, 114.1, 62.7, 61.5, 49.6, 14.0. HRMS calcd. for $C_{34}H_{30}N_6NaO_6$, 641.2119 $[M+Na]^+$, found 641.2129. IR(cm^{-1}), 3062, 2928, 2854, 2365, 1749, 1624, 1594, 1508, 1458, 1376, 1323, 1229, 1147, 1081, 1017, 915, 806, 747, 667, 582.



Scheme S2 Synthetic approach to compound **2**, **3**, **5** and **6**.

Synthesis of compound X. The compound **X** was preared according to reported method [1] in 92% yield. ^{1}H-NMR ($CDCl_3$, 400MHz), δ =8.02 (d, J=8.8 Hz, Naph-H, 1H), 7.93 (m, Naph-H, 2H), 7.88 (d, J=8.4 Hz, Naph-H, 1H), 7.61 (d, J=8.8 Hz, Naph-H, 1H), 7.44 (d, J=8.8 Hz, Naph-H, 1H), 7.36 (m, Naph-H, 2H), 7.20 (m, Naph-H and Ph-H, 7H), 7.03 (m, Ph-H, 2H), 4.05-5.13 (AB-quartet, J=12.4 Hz, Ph-*CH*$_2$, 2H), 4.60 (dq, J=2.4 Hz, 16.4 Hz, *O*-*CH*$_2$, 2H), 2.36 (t, J=2 Hz, C≡*CH*, 1 H). ^{13}C-NMR ($CDCl_3$, 100MHz), δ= 154.0, 153.2, 137.6, 134.1, 134.0, 129.8, 129.4, 129.3, 128.2, 127.9, 127.3, 126.8, 126.4, 126.3, 125.6, 125.5, 124.0, 123.8, 120.9, 120.3, 116.1, 115.8, 79.3, 76.7, 75.3, 71.2, 57.1. HRMS calcd. for $C_{30}H_{22}NaO_2$, 437.1512 $[M+Na]^+$, found 437.1563. IR(cm^{-1}), 3282, 3057, 2924, 2868, 2363, 2120, 1733, 1621, 1591, 1507, 1453, 1431, 1354, 1328, 1271, 1218, 1146, 1087, 1048, 1017,

805, 746, 695, 637.

Synthesis of compound 2, 3, 5 and 6. NEt_3(0.1 mmol) and CuCl (0.05 mmol) was added into a solution of substituted azide (2.0 or 1.0 mmol) and the alkyne compound (1.0 mmol) in CH_2Cl_2 (4 mL). The resulting mixture was stirred at 25 ^oC for 24h, and then the solvent was removed in vacuo, and the crude product was further purified by column chromatograph on silica gel to give the desired cyclic compound **2**, **3**, **5** and **6**.

Ligand **2** was obtained as a white solid in 66% yield, ^{1}H-NMR ($CDCl_3$, 400MHz), δ =7.86 (m, Naph-H, 4H), 7.43 (d, J=9.2 Hz, Naph-H, 2H), 7.33 (m, Ar-H, 8H), 7.14 (m, Ph-H, 4H), 7.07 (d, J=6.0 Hz, Ph-H, 4H), 6.42 (s, Triazole-H, 2H), 5.20 (s, O-*CH_2*, 4H), 5.15 (d, J=12.8 Hz, Ph-*CH_2*, 2H), 5.04 (d, J=12.8 Hz, Ph-*CH_2*, 2H). ^{13}C-NMR ($CDCl_3$, 100MHz), δ= 153.6, 145.1, 134.6, 133.9, 129.4, 129.0, 128.6, 128.0, 127.9, 126.4, 125.4, 123.9, 122.4, 120.7, 115.9, 64.0, 53.9. HRMS calcd. for $C_{40}H_{33}N_6O_2$, 629.2660 $[M+H]^+$, found 629.2676.. IR(cm^{-1}), 2067, 1625, 1591, 1507, 1458, 1433, 1356, 1329, 1260, 1241, 1208, 1148, 1117, 1087, 1046, 1016, 904, 814, 775, 755, 711, 695, 589.

Ligand **3** was obtained as a white solid in 82% yield, ^{1}H-NMR ($CDCl_3$, 400MHz), δ =7.96 (d, J=9.2 Hz, Naph-H, 1H), 7.90 (d, J=8.0 Hz, Naph-H, 1H), 7.83 (t, J=9.2 Hz, Naph-H, 2H), 7.47 (d, J=9.2 Hz, Naph-H, 1H), 7.33(m, Naph-H, 6H), 7.23(m, Ar-H, 2H), 7.11(m, Ph-H, 5H), 7.00 (d, J=6.44 Hz, Ph-H, 2H), 6.87 (d, J=6.8 Hz, Ph-H, 2H), 6.43 (s, Triazole-H, 1H), 5.16 (m, O-*CH_2*, 4H), 4.91-4.98 (AB-quartet, J= 12.8 Hz, Ph-CH_2, 2H). ^{13}C-NMR ($CDCl_3$, 100MHz), δ =153.9, 153.5, 145.5, 137.3, 134.6, 134.0, 133.9, 129.5, 129.3, 129.2, 128.9, 128.6, 128.2, 128.0, 127.9, 127.8, 127.5, 126.8, 126.5, 126.4, 125.5, 125.4, 123.9, 123.8, 122.4, 120.7, 120.6, 116.0, 115.9, 71.2, 64.1, 53.8. HRMS calcd. for $C_{37}H_{30}N_3O_2$, 548.2333 $[M+H]^+$, found 548.2347. IR(cm^{-1}), 3140, 3057, 3032, 2930, 2872, 2362, 1621, 1590, 1506, 1455, 1431, 1354, 1328, 1221, 1147, 1087, 1046, 1016, 904, 807, 747, 731, 695.

Ligand **5** was obtained as a white solid in 62% yield, ^{1}H-NMR ($CDCl_3$, 400MHz), δ =7.96 (d, J= 8.8 Hz, Naph-H, 2H), 7.88 (d, J= 8.4 Hz, Naph-H, 2H), 7.53 (d, J= 8.8 Hz, Naph-H, 2H), 7.35 (t, J= 7.2 Hz, Naph-H, 2H), 7.22 (m, Naph-H, 2H),

7.15 (d, J= 8.4 Hz, Naph-H, 2H), 6.81 (s, Triazole-H, 2H), 5.27 (d, J= 13.2 Hz, O-*CH*$_2$, 2H), 5.14 (d, J= 13.2 Hz, O-*CH*$_2$, 2H), 4.90 (s, -*CH*$_2$COOEt, 4H), 4.21 (q, J= 7.2 Hz, O*CH*$_2$CH$_3$, 4H), 1.25 (t, J=6.8 Hz, OCH$_2$*CH*$_3$, 6H). ^{13}C-NMR ($CDCl_3$, 100MHz), δ= 166.1, 153.6, 145.0, 134.0, 129.6, 129.5, 127.9, 126.5, 125.5, 124.1, 123.9, 120.7, 115.9, 63.8, 62.3, 50.7, 14.0. HRMS calcd. for $C_{34}H_{32}N_6NaO_6$, 643.2276 $[M+Na]^+$, found 643.2276. IR(cm^{-1}), 3146, 3057, 2929, 2362, 2330, 1750, 1623, 1592, 1507, 1458, 1375, 1262, 1214, 1148, 1086, 1049, 1017, 809, 750.

Ligand **6** was obtained as a white solid in 78% yield, ^{1}H-NMR ($CDCl_3$, 400MHz), δ =7.96 (d, J=8.8 Hz, Naph-H, 2H), 7.88 (m, Naph-H, 2H), 7.46 (d, J=8.8 Hz, Naph-H, 2H), 7.35 (m, Naph-H, 2H), 7.21(m, Naph-H, 4H), 7.11(m, Ph-H, 3H), 6.86 (d, J=7.2 Hz, Ph-H, 2H), 6.78 (s, Triazole-H, 1H), 5.30 (d, J=13.6 Hz, O-*CH*$_2$, 1H), 5.21 (d, J=13.6 Hz, O-*CH*$_2$, 1H), 5.07 (d, J=12.4 Hz, O-*CH*$_2$, 1H), 4.98 (d, J=12.4 Hz, O-*CH*$_2$, 1H), 4.68 (d, J=17.6 Hz, COOEt-*CH*$_2$, 1H), 4.50 (d, J=17.6 Hz, COOEt-*CH*$_2$, 1H), 4.17 (m, O*CH*$_2$CH$_3$, 2H), 1.23 (t, J=7.2 Hz, OCH$_2$*CH*$_3$, 3H). ^{13}C-NMR ($CDCl_3$, 100MHz), δ= 165.9, 154.0, 153.3, 145.4, 137.3, 134.1, 134.0, 129.6, 129.5, 129.4, 129.3, 128.2, 128.0, 127.9, 127.5, 126.8, 126.5, 126.4, 125.5, 125.4, 124.0, 123.9, 123.8, 120.8, 120.6, 116.2, 115.7, 71.4, 63.6, 62.3 , 50.5, 14.1. HRMS calcd. for $C_{34}H_{30}N_3O_4$, 544.2231 $[M+H]^+$, found 544.2257. IR(cm^{-1}), 3144, 3057, 2982, 2938, 2873, 2364, 1751, 1621, 1591, 1455, 1431, 1374, 1354, 1328, 1262, 1215, 1147, 1088, 1047, 1017, 905, 866, 807, 747, 696, 577.

Reference:

1) C. Efe, I. N. Lykakis, M. Stratakis, *Chem. Commun.*, 2011, **47**, 803.

2. Fluorescence emission spectra of Ligand 2 in CH_3CN in the presence of various anions.

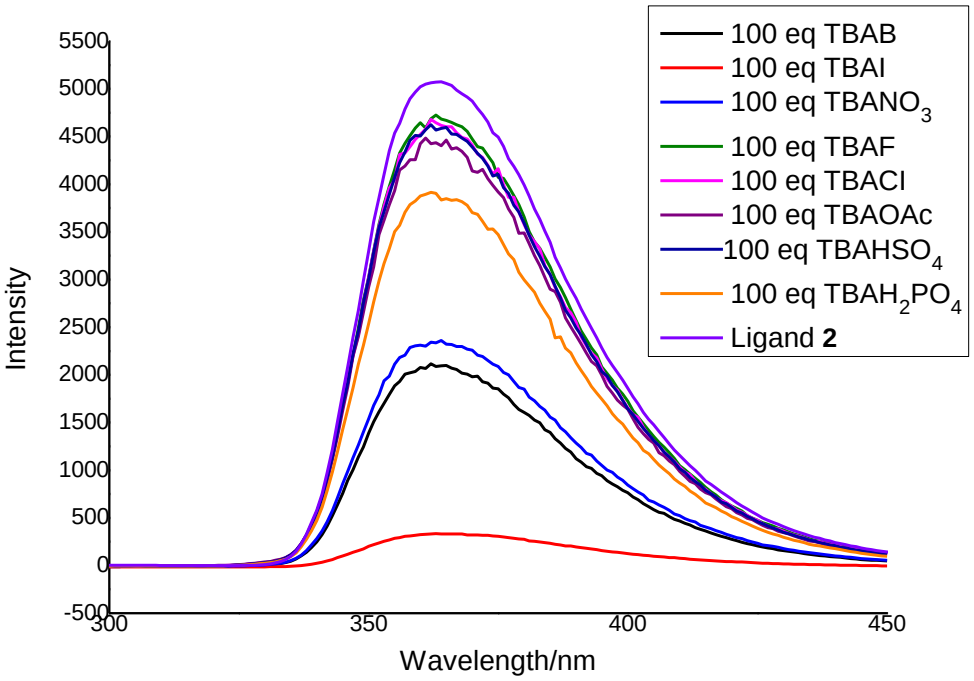


Figure S1 Fluorescence emission spectra of Ligand **2** (6.3 μM) in CH_3CN in the presence of various anions (100eq): F^-, Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, HSO_4^- and $H_2PO_4^-$.

3. Fluorescence spectra of Ligand 2-6 (5 μM) in CH_3CN with increasing concentration of I^-

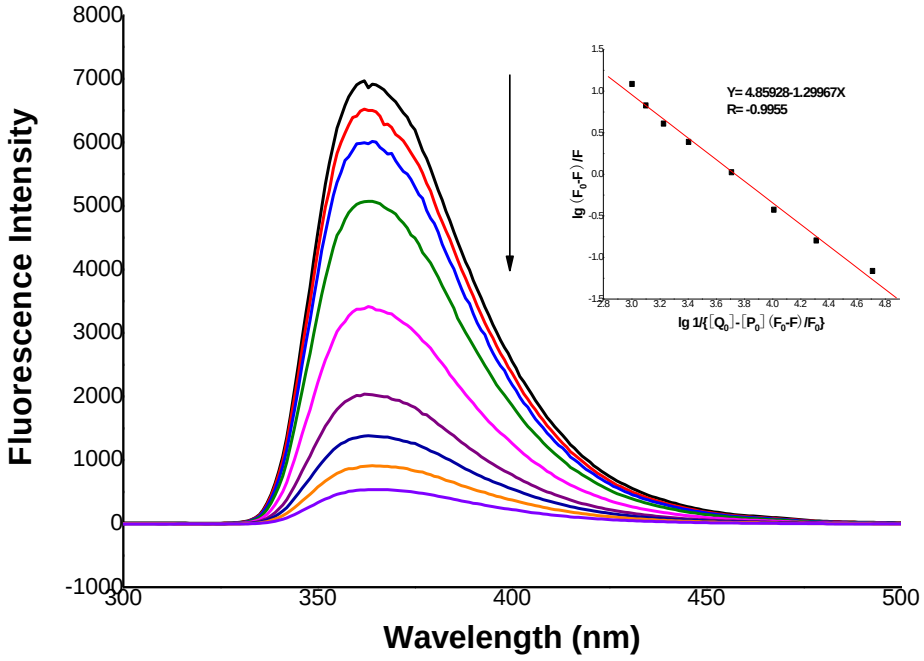


Figure S2 Fluorescence spectra of Ligand **2** (10 μM) in CH_3CN with increasing concentration of I^-, Inset shows a Modified Stern-Volmer plot of Ligand **2** upon the addition of I^- in CH_3CN.

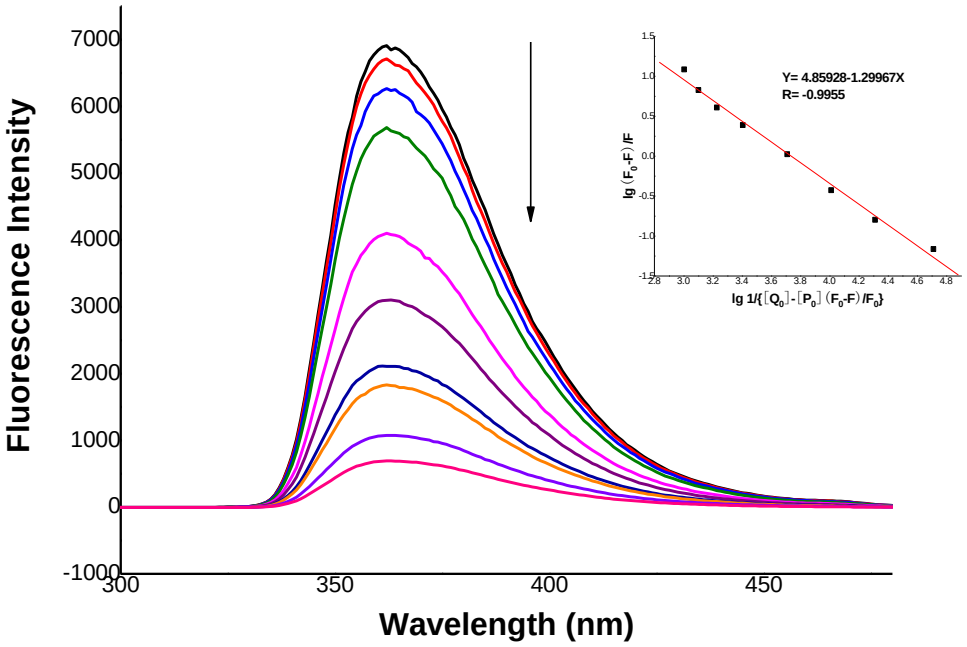


Figure S3 Fluorescence spectra of Ligand **3** (5 μM) in CH_3CN with increasing concentration of I⁻, Inset shows a Modified Stern-Volmer plot of Ligand **3** upon the addition of I⁻ in CH_3CN.

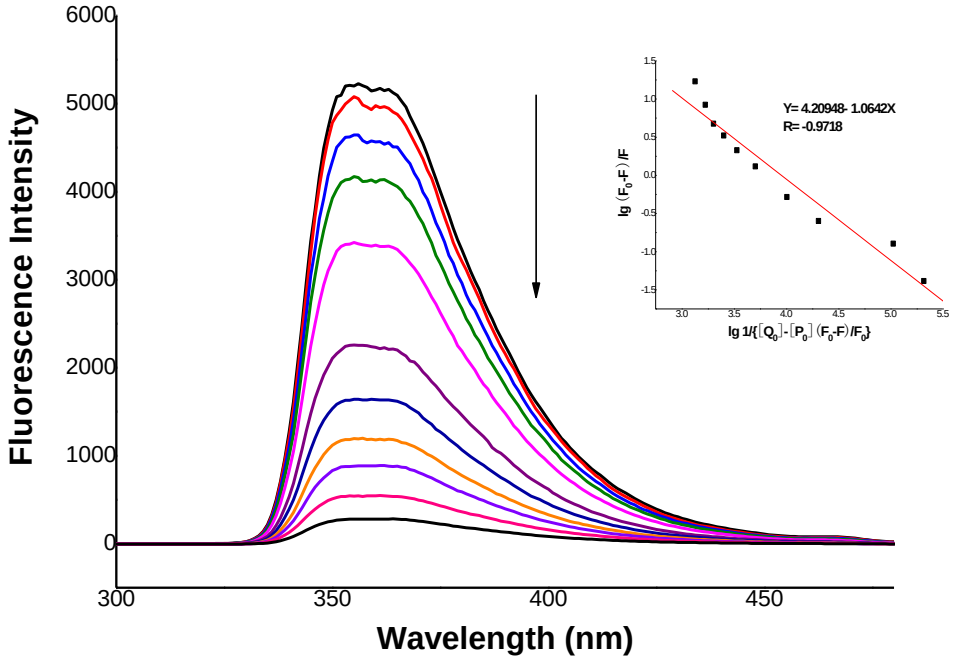


Figure S4 Fluorescence spectra of Ligand **4** (5 μM) in CH_3CN with increasing concentration of I^-, Inset shows a Modified Stern-Volmer plot of Ligand **4** upon the addition of I^- in CH_3CN.

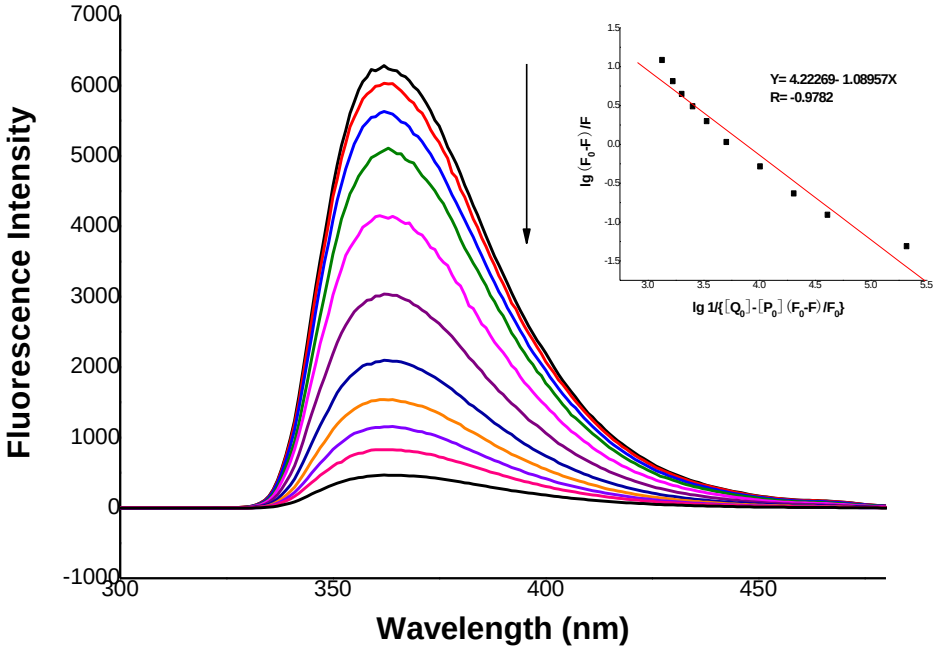


Figure S5 Fluorescence spectra of Ligand **5** (5 μM) in CH_3CN with increasing concentration of I^-, Inset shows a Modified Stern-Volmer plot of Ligand **5** upon the addition of I^- in CH_3CN.

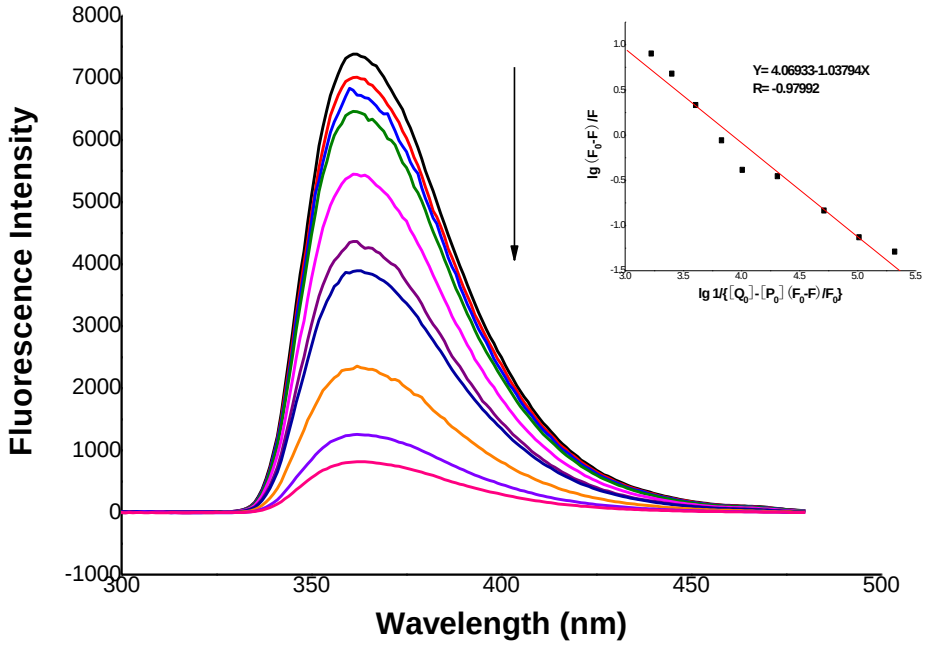


Figure S6 Fluorescence spectra of Ligand **6** (5 μM) in CH_3CN with increasing concentration of I^-, Inset shows a Modified Stern-Volmer plot of Ligand **6** upon the addition of I^- in CH_3CN.

4. UV-Vis titration spectra of Ligand 2-6 (5 μM) in CH_3CN with increasing concentration of I^- in CH_3CN

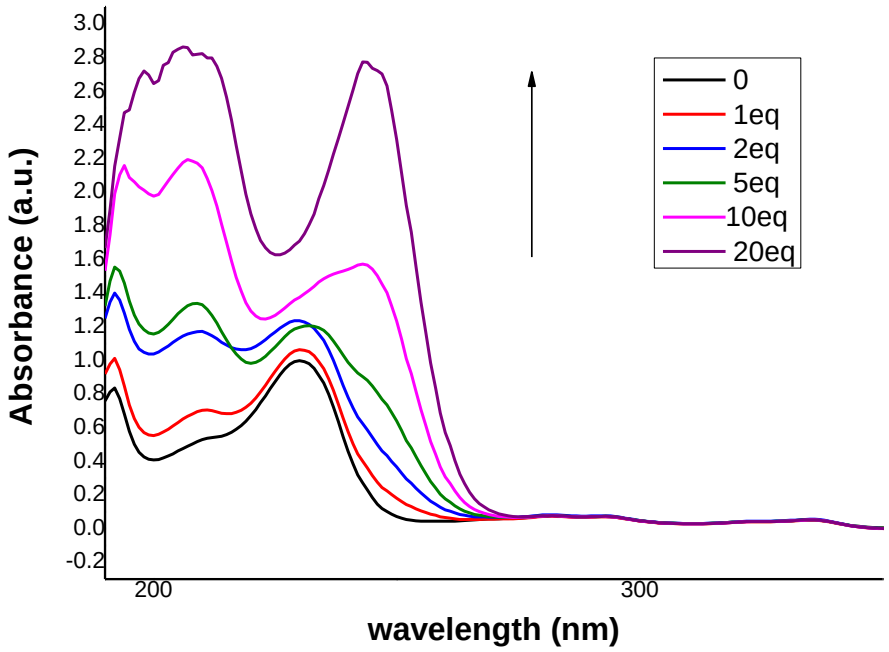


Figure S7 UV-Vis titration spectra of Ligand **2** (10 μM) in CH_3CN with increasing concentration of I^- in CH_3CN.

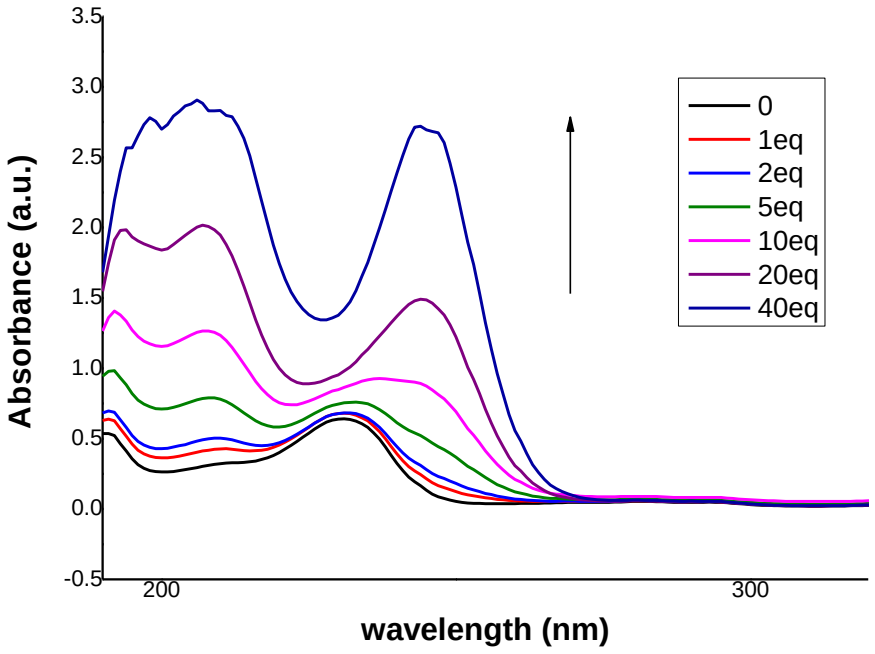


Figure S8 UV-Vis titration spectra of Ligand **3** (5 μM) in CH_3CN with increasing concentration of I^- in CH_3CN.

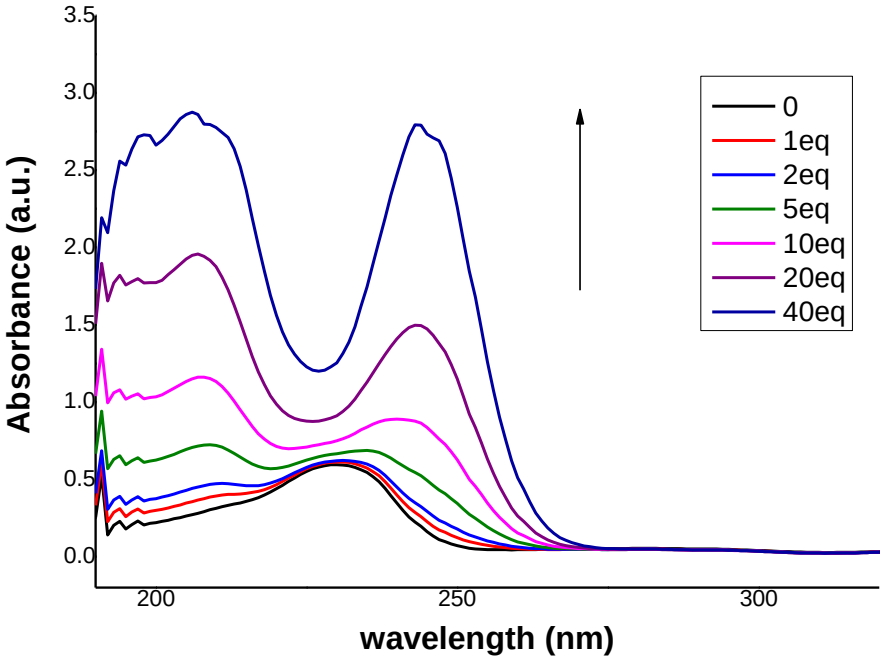


Figure S9 UV-Vis titration spectra of Ligand **4** (5 μM) in CH_3CN with increasing concentration of I^- in CH_3CN.

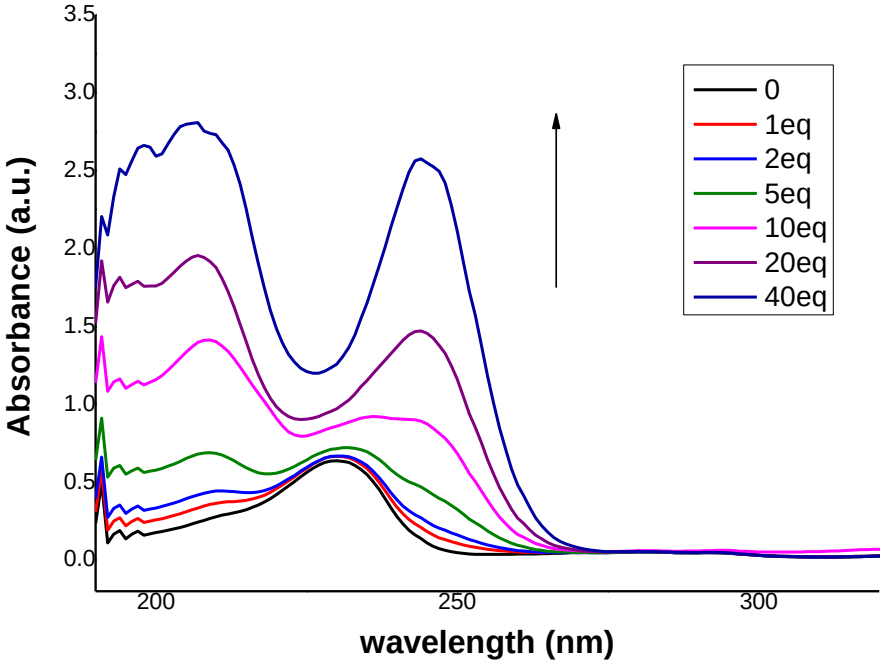


Figure S10 UV-Vis titration spectra of Ligand **5** (5 μM) in CH_3CN with increasing concentration of I^- in CH_3CN.

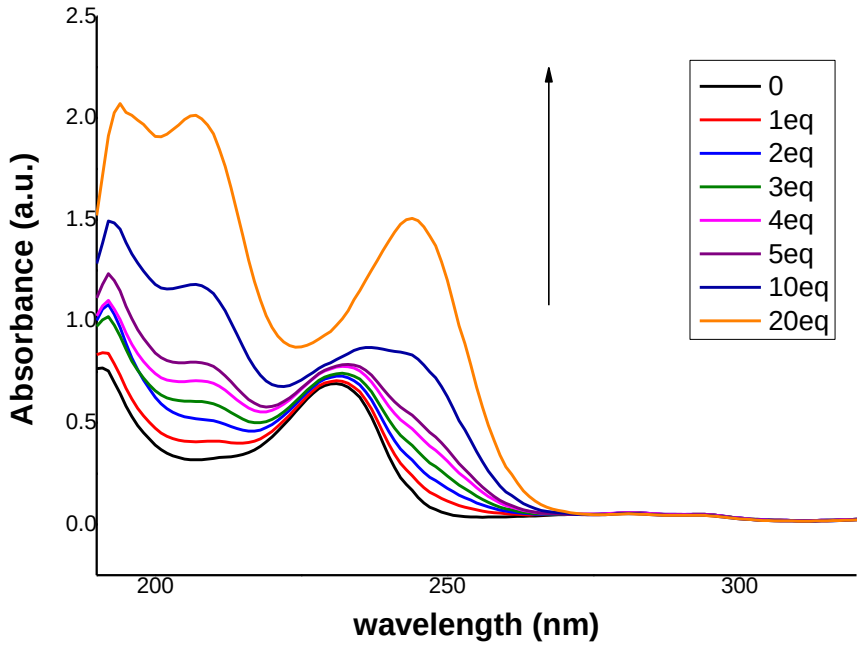


Figure S11 UV-Vis titration spectra of Ligand **6** (5 μM) in CH_3CN with increasing concentration of I^- in CH_3CN.

5. ^{1}HNMR spectrum (500 MHz, $CDCl_3$) of Ligand 1-5 before and after addition of 10 equiv of I^- .

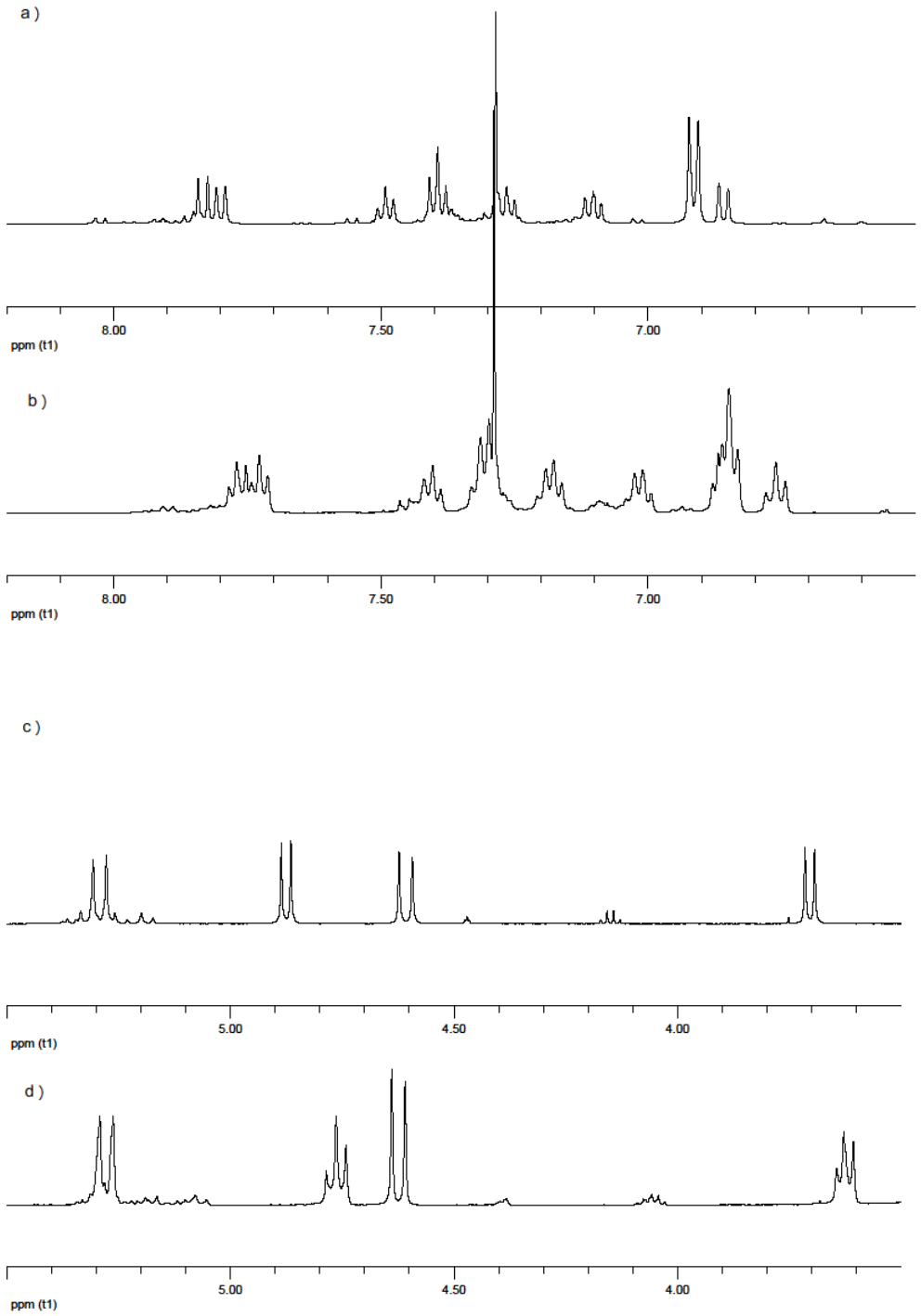


Figure S12 ^{1}HNMR spectrum (500 MHz, $CDCl_3$) of Ligand **1** before (a), (c) and after addition of 10 equiv of I^- (b), (d).

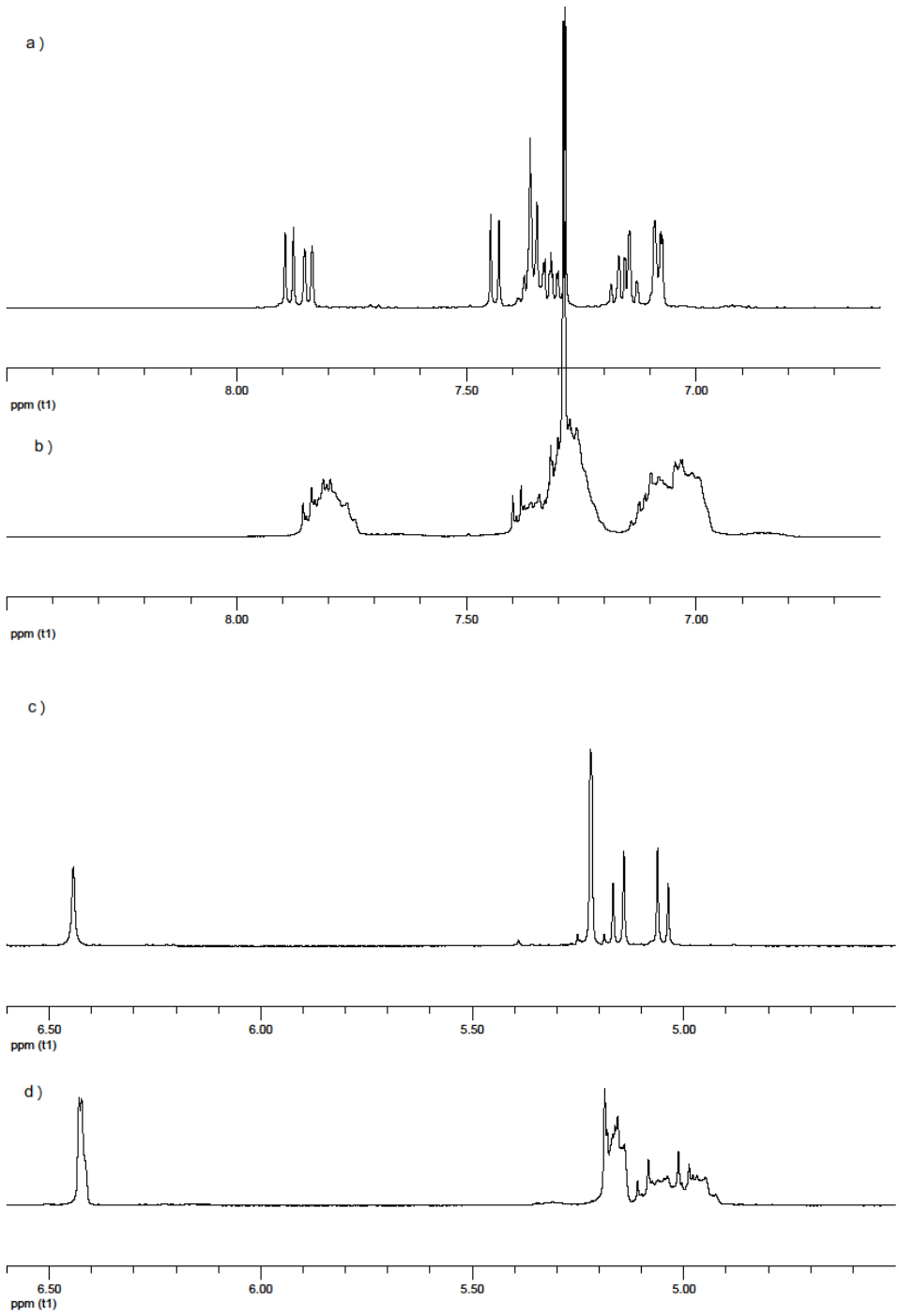


Figure S13 ^{1}HNMR spectrum (500 MHz, $CDCl_3$) of Ligand **2** before (a), (c) and after addition of 10 equiv of I^- (b), (d).

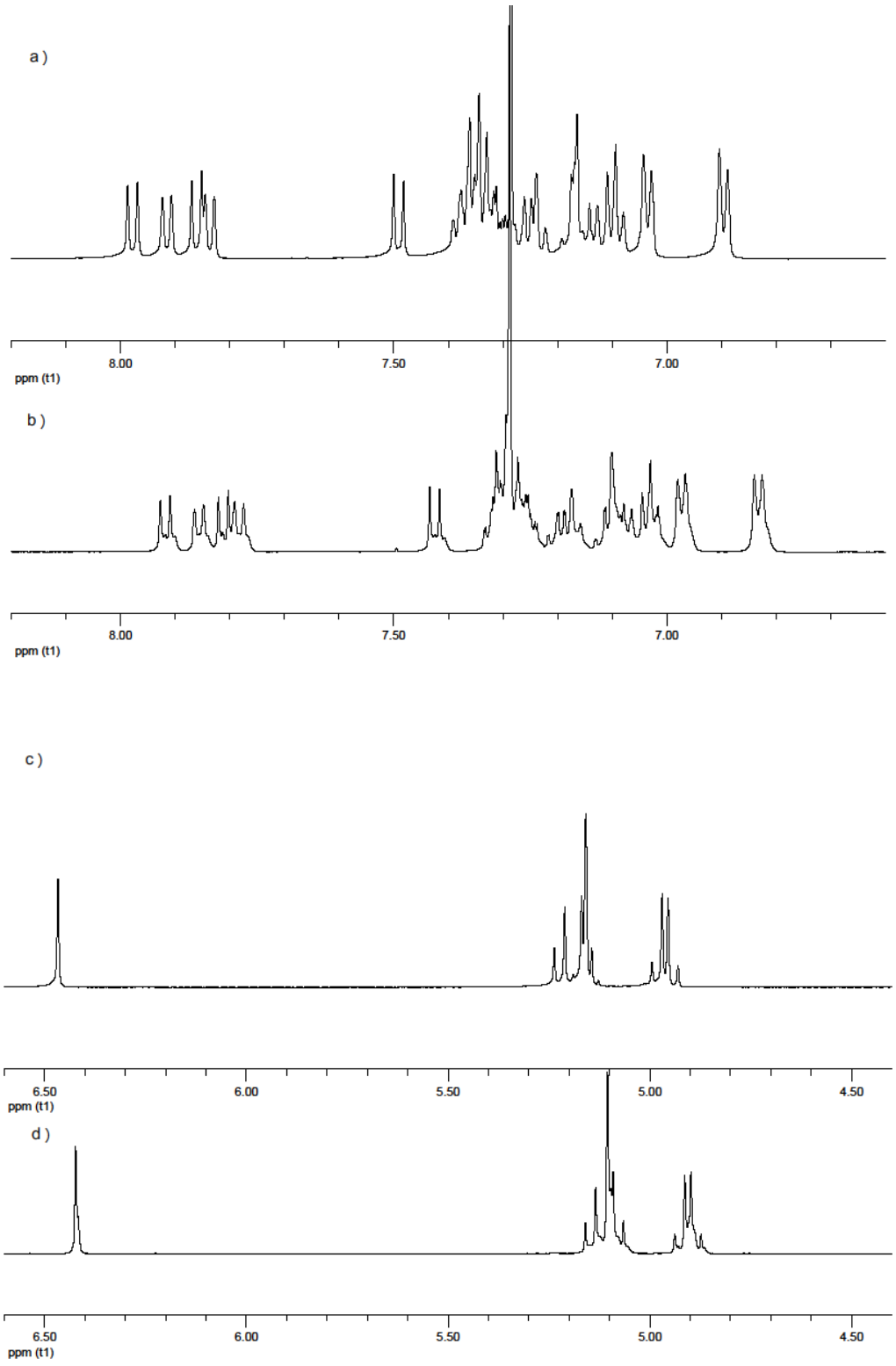


Figure S14 ^{1}HNMR spectrum (500 MHz, $CDCl_3$) of Ligand **3** before (a), (c) and after addition of 10 equiv of I^- (b), (d).

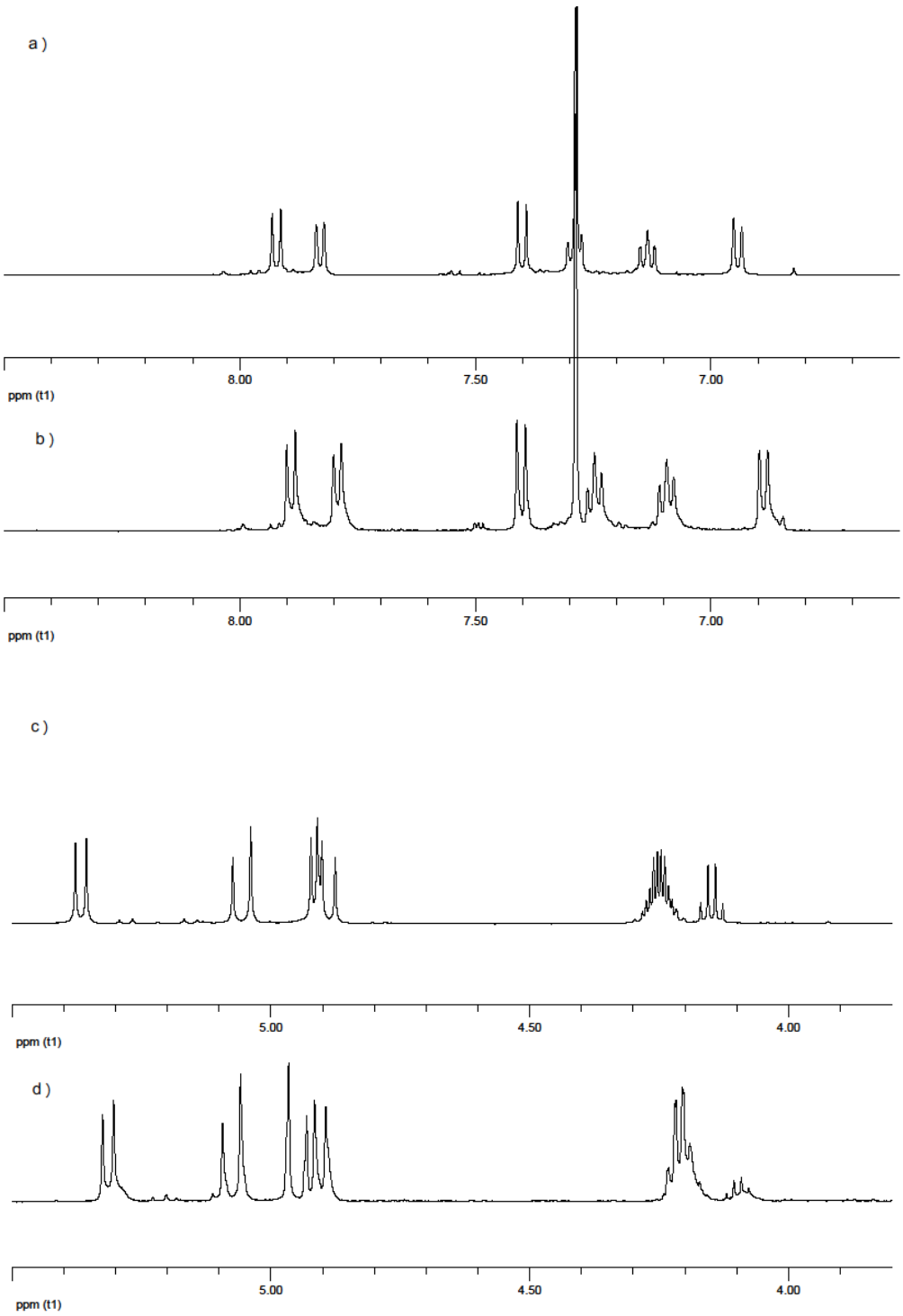


Figure S15 ^{1}HNMR spectrum (500 MHz, $CDCl_3$) of Ligand **4** before (a), (c) and after addition of 10 equiv of I^- (b), (d).

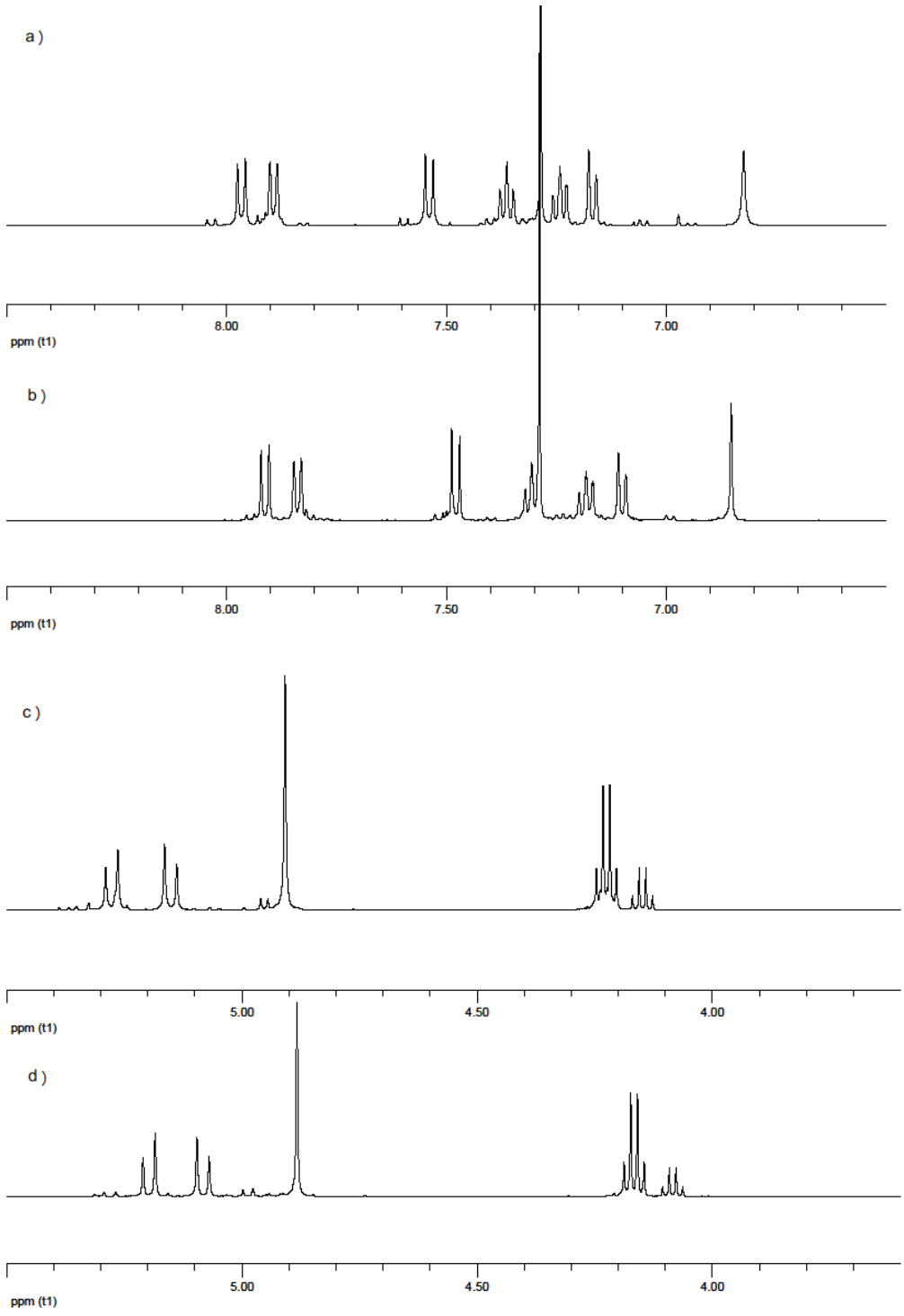
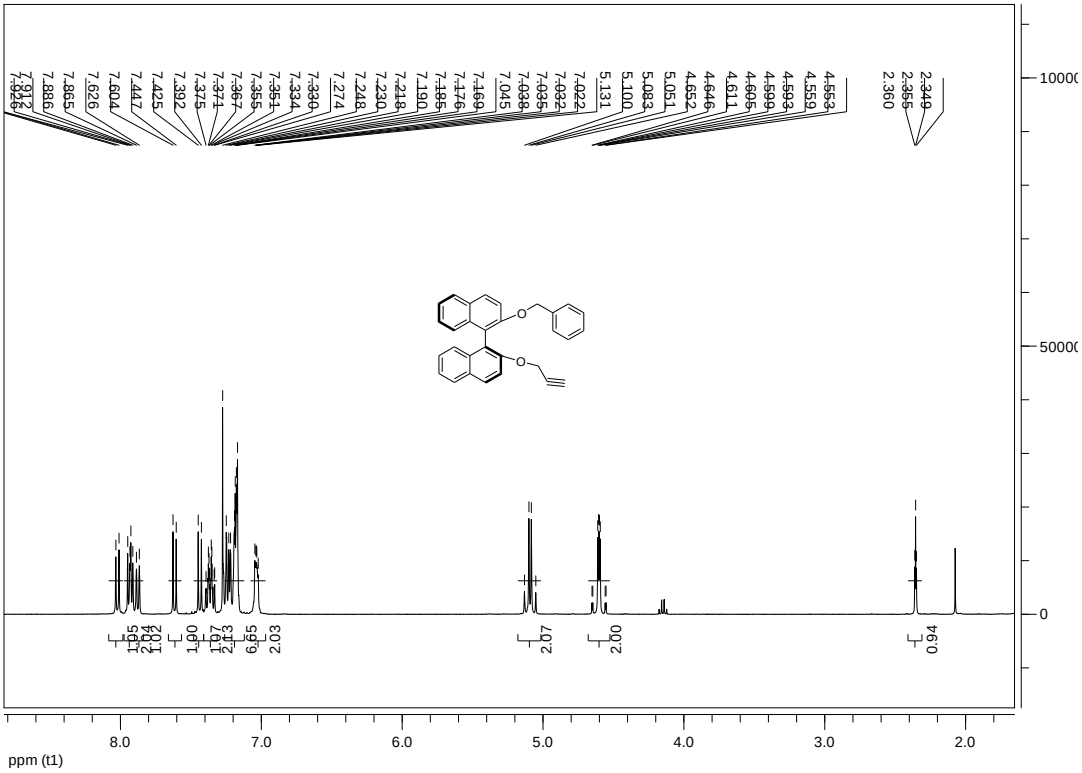
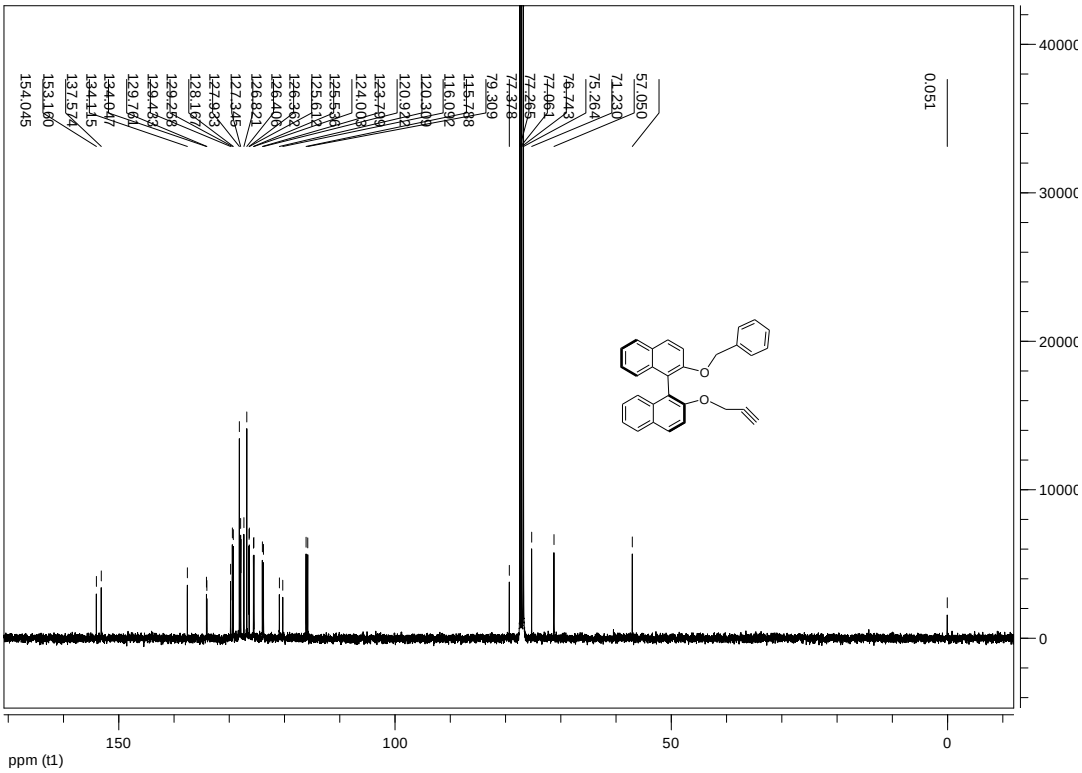
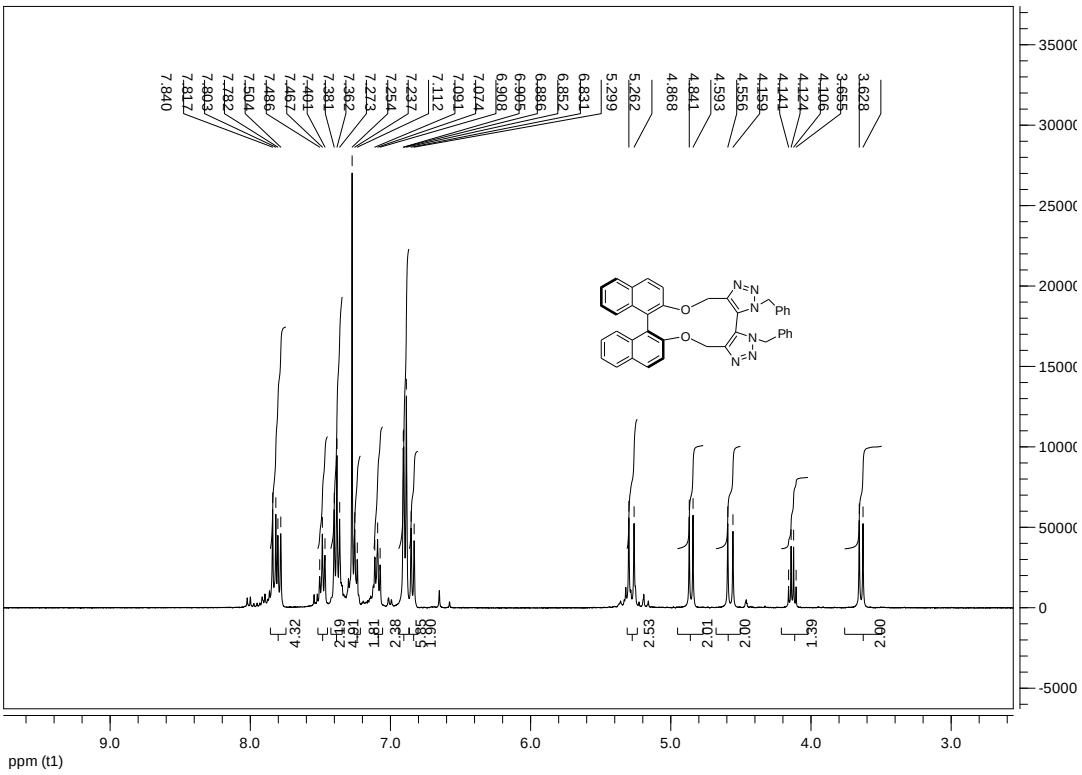


Figure S16 ^{1}HNMR spectrum (500 MHz, $CDCl_3$) of Ligand **5** before (a), (c) and after addition of 10 equiv of I^- (b), (d).

6. ^{1}H-NMR and ^{13}C-NMR spectra of the new compounds






7.840
7.817
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7.782
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7.467
7.401
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7.362
7.273
7.254
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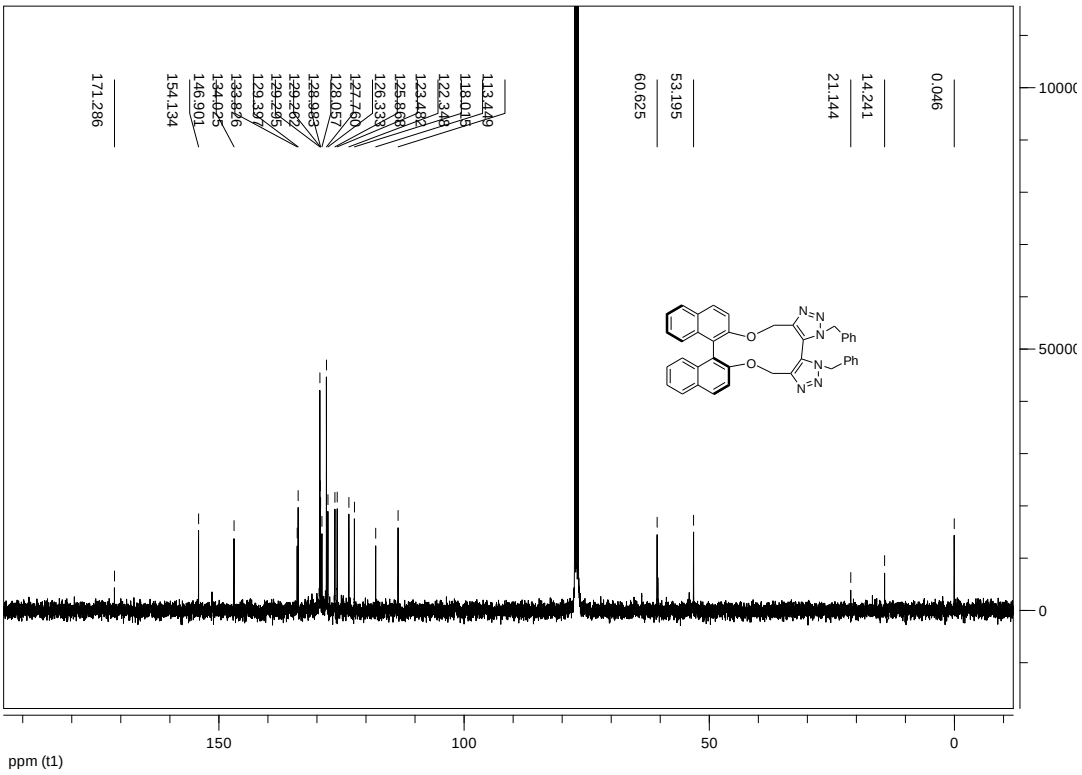
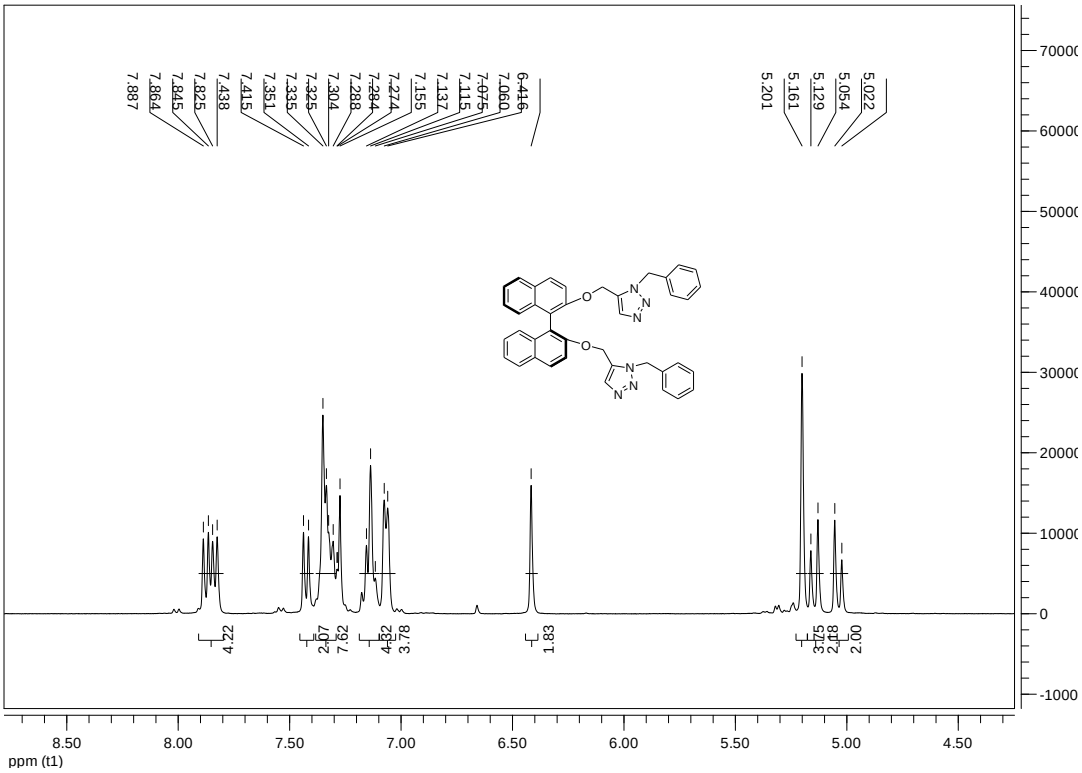
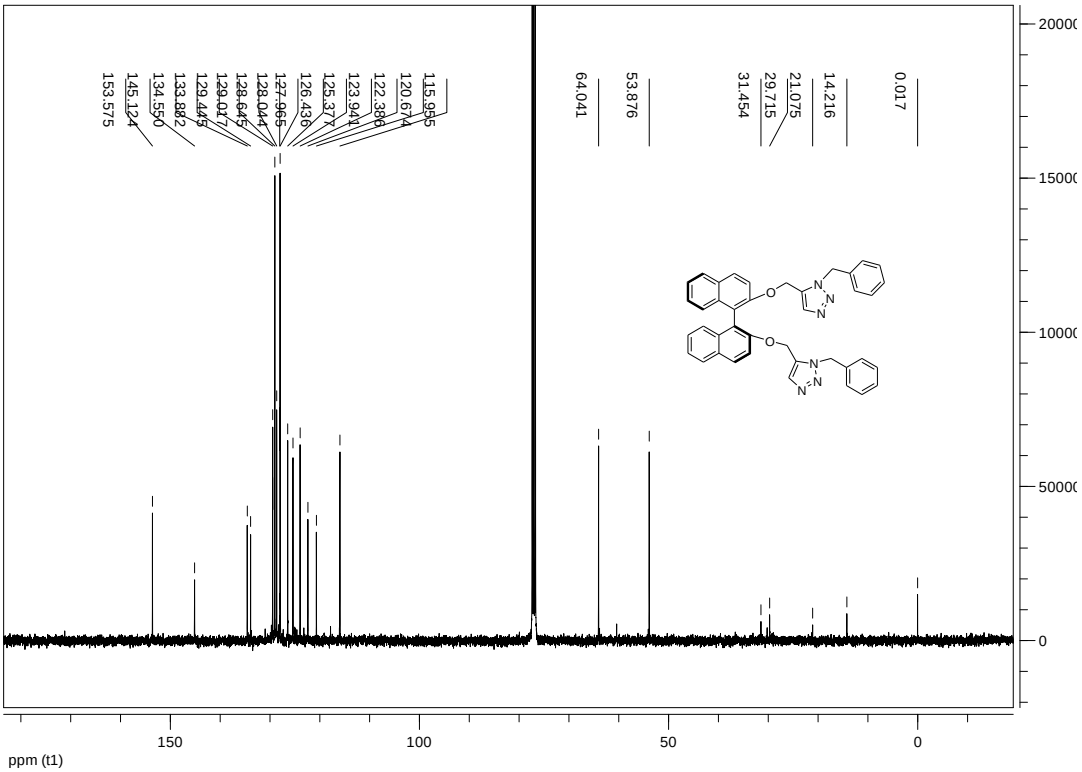
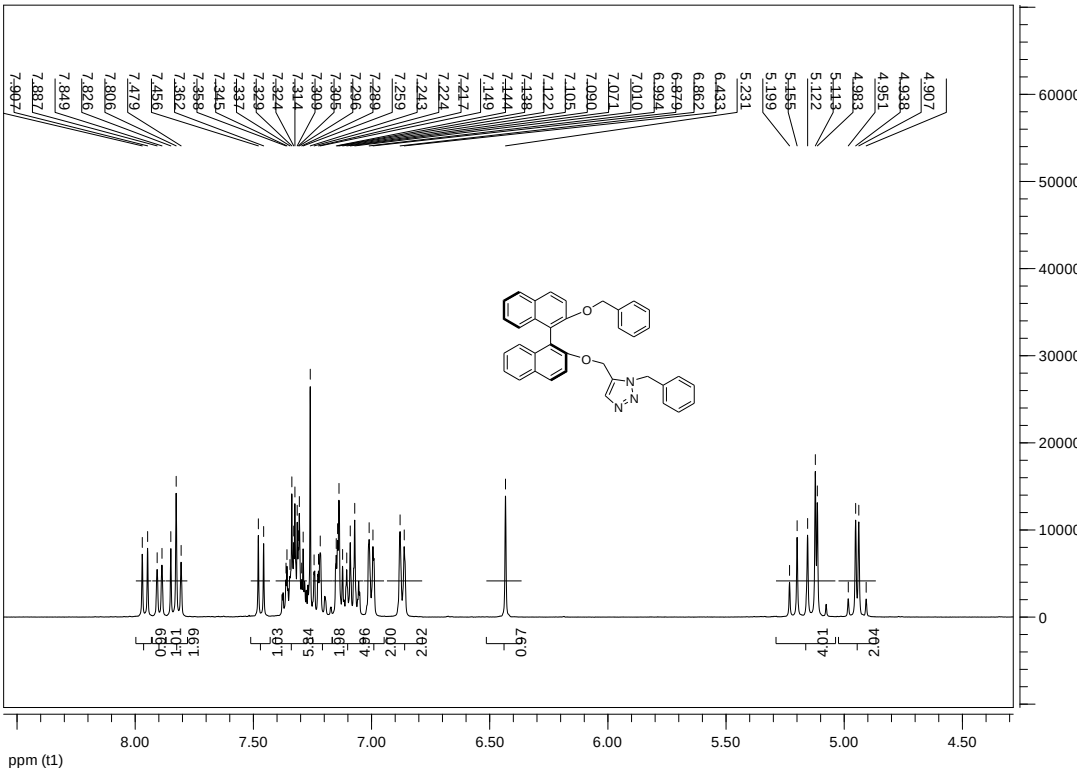
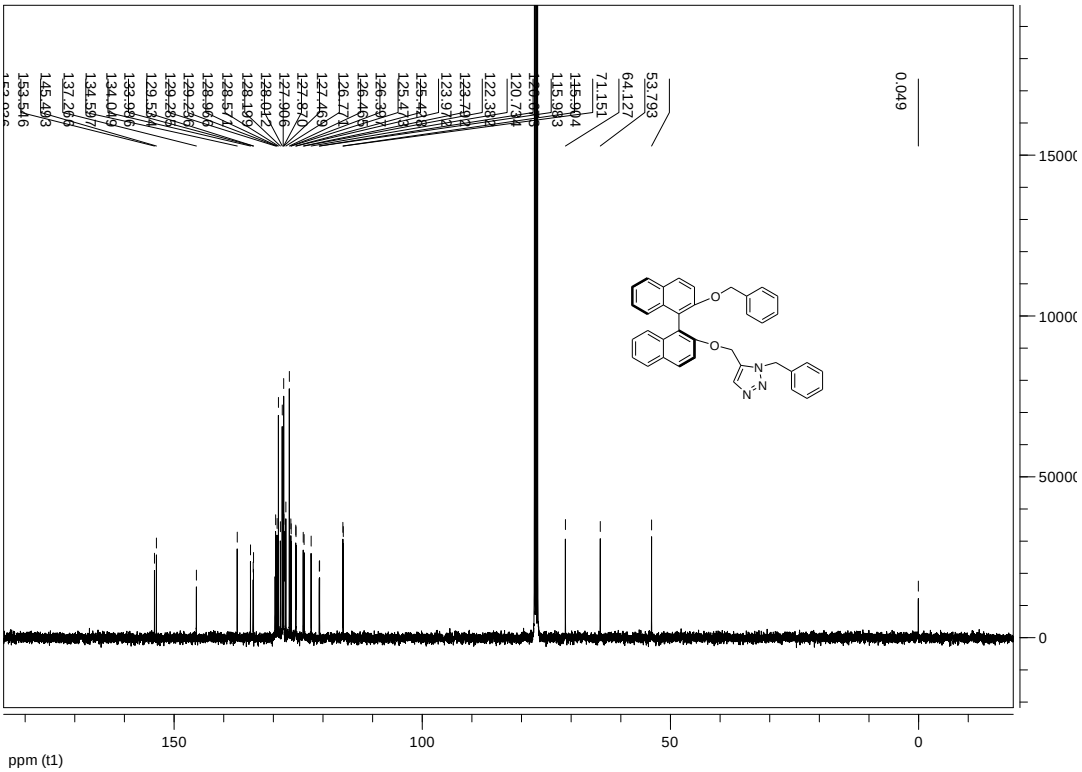
Ph
Ph
ppm (t1)

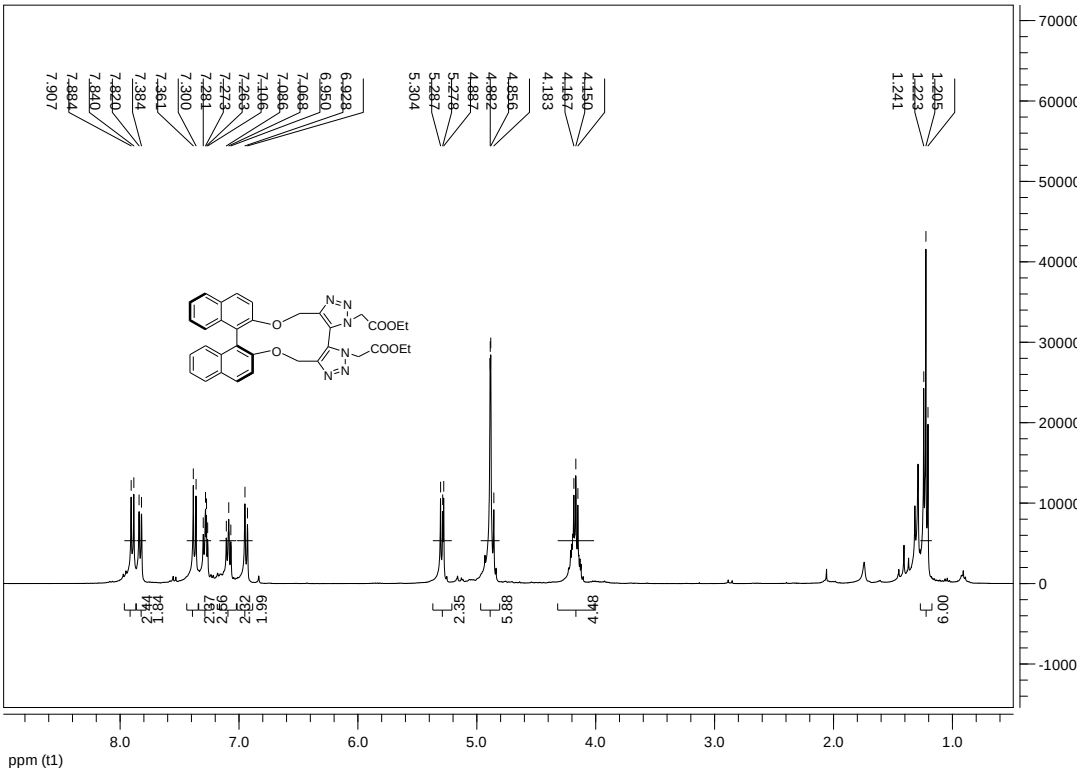

171.286
154.134
146.901
134.025
133.826
129.397
129.295
129.267
128.983
128.057
127.760
126.336
125.808
123.483
122.348
118.015
113.449
60.625
53.195
21.144
14.241
0.046
Ph
Ph
ppm (t1)

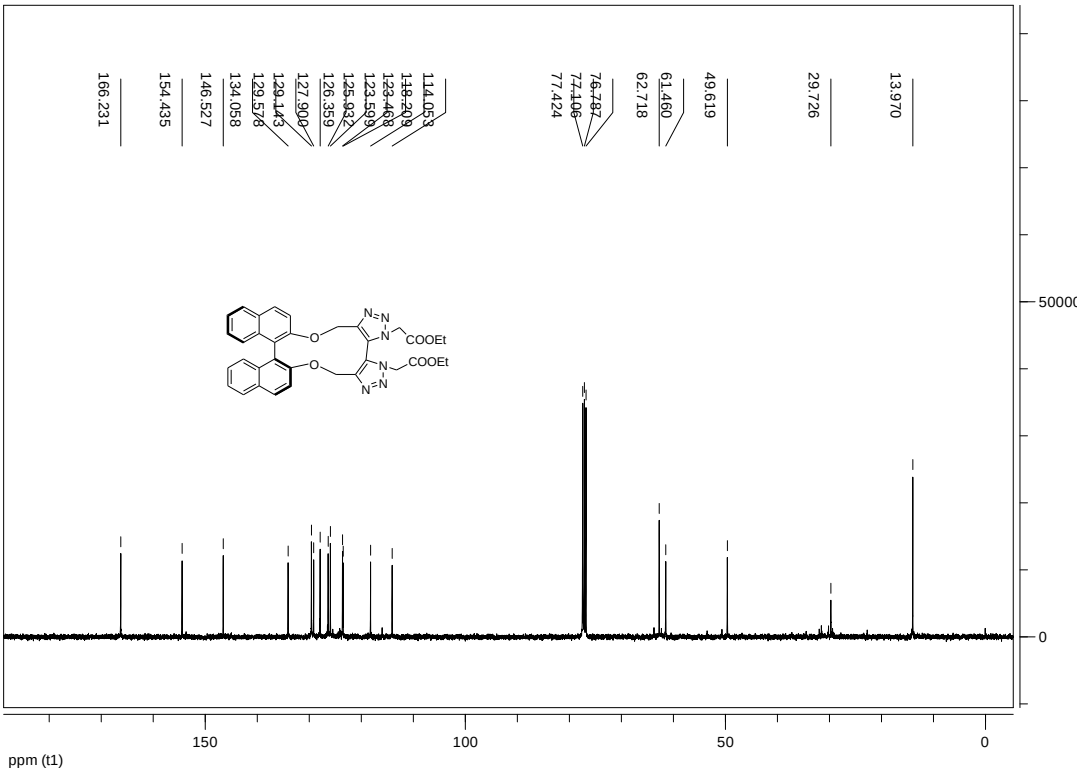

7.887
7.864
7.845
7.825
7.438
7.415
7.351
7.335
7.325
7.304
7.288
7.284
7.274
7.155
7.137
7.115
7.075
7.060
6.416
5.201
5.161
5.129
5.054
5.022
4.22
2.07
2.97
2.25
3.78
1.83
3.52
2.81
2.00
ppm (t1)

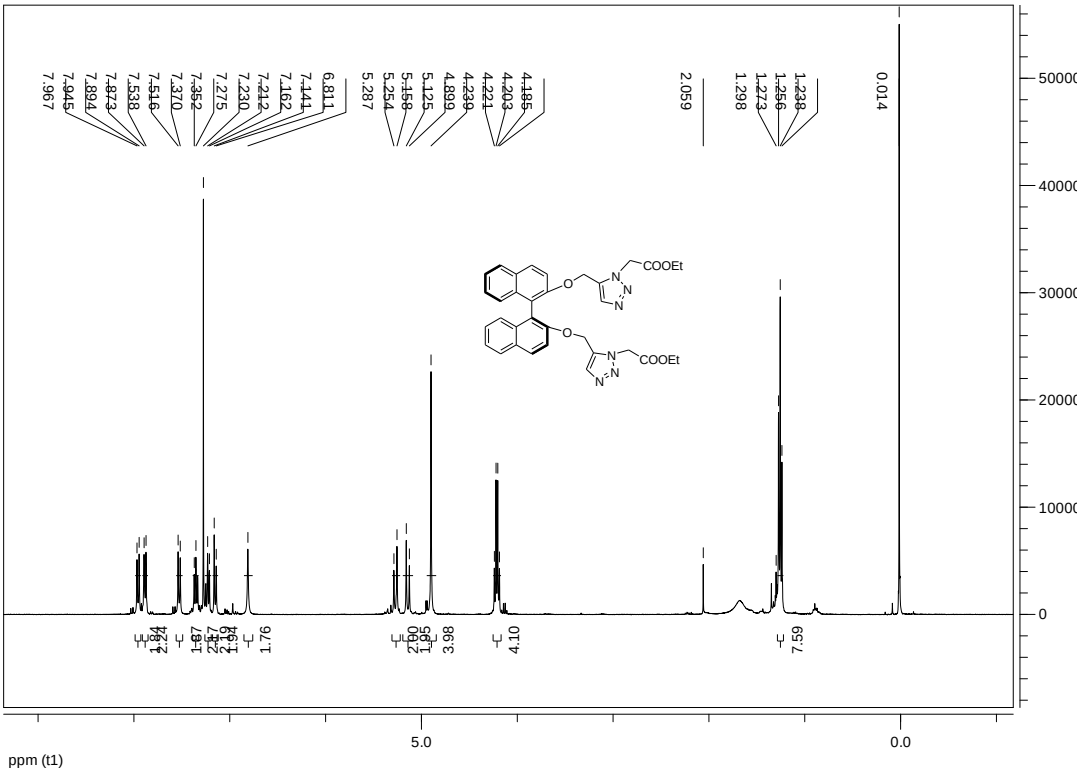

153.575
145.124
134.550
133.882
129.445
129.017
128.645
128.044
127.965
126.436
125.377
123.941
122.386
120.674
115.955
64.041
53.876
31.454
29.715
21.075
14.216
0.017
ppm (t1)

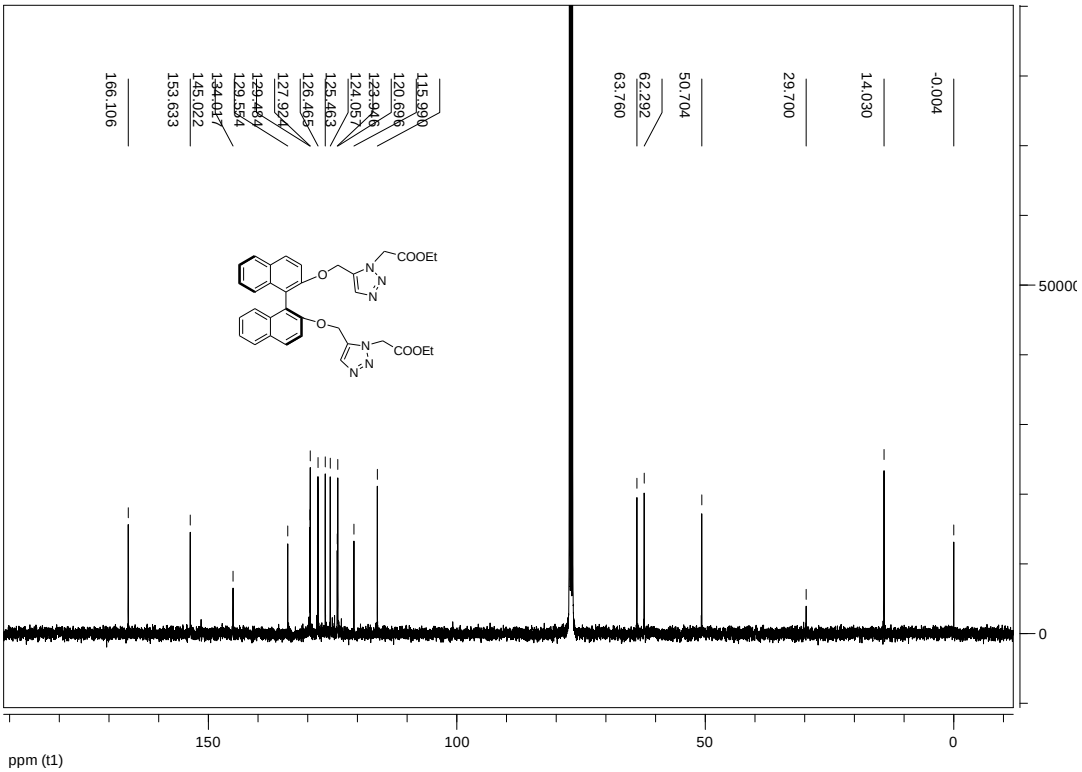

7.907
7.887
7.849
7.826
7.806
7.479
7.456
7.362
7.358
7.345
7.337
7.329
7.324
7.314
7.309
7.305
7.296
7.289
7.259
7.243
7.224
7.217
7.149
7.144
7.138
7.122
7.105
7.090
7.071
7.010
6.994
6.879
6.862
6.433
5.231
5.199
5.155
5.122
5.113
4.983
4.951
4.938
4.907
1.00
1.01
1.01
6.91
1.03
5.84
1.58
4.96
2.00
2.02
0.97
4.01
2.04
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
ppm (t1)

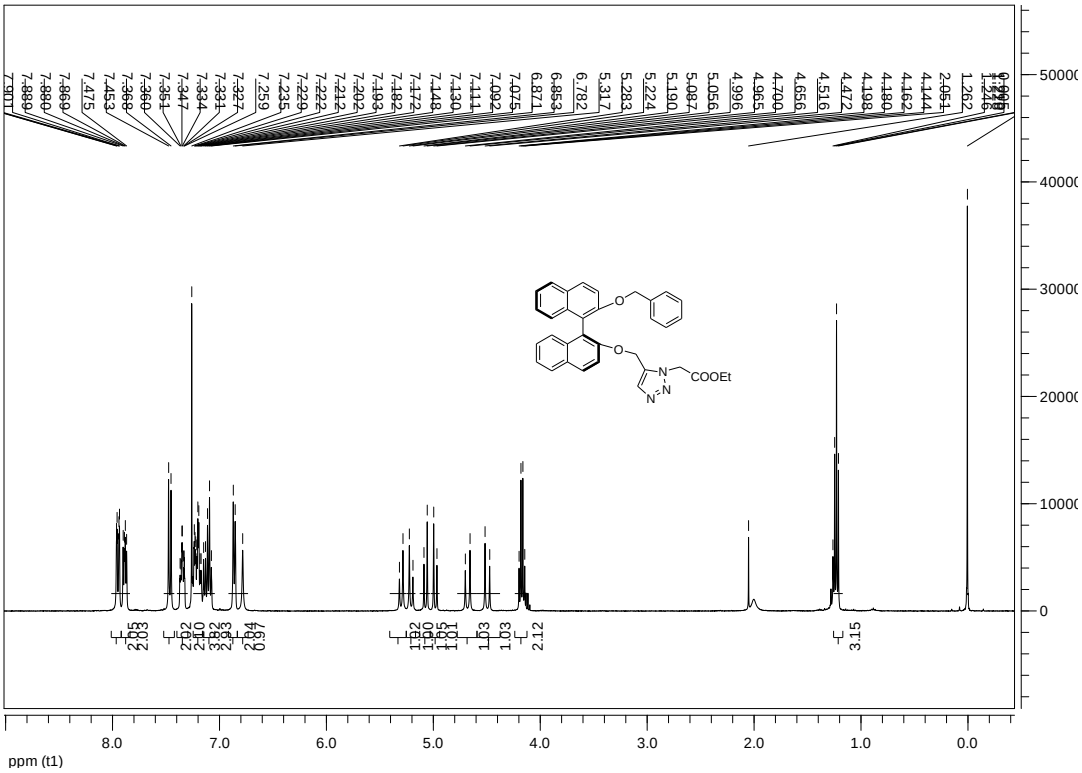

153.546
145.493
137.260
134.597
134.049
133.906
129.534
129.283
129.236
128.966
128.577
128.199
128.012
127.906
127.870
127.469
126.771
126.405
126.390
125.473
125.428
123.970
123.792
122.380
120.734
115.904
115.983
71.151
64.127
53.793
0.049
150
100
50
0
ppm (t1)


7.907
7.884
7.840
7.820
7.384
7.361
7.300
7.281
7.273
7.263
7.106
7.086
7.068
6.950
6.928
5.304
5.287
5.278
4.887
4.882
4.856
4.183
4.167
4.150
1.241
1.223
1.205
COOEt
COOEt
2.44
2.14
1.84
2.27
2.46
2.15
2.32
1.99
2.35
5.88
4.48
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


166.231
154.435
146.527
134.058
129.578
129.143
127.900
126.359
125.932
123.599
123.468
118.209
114.053
77.424
77.106
76.787
62.718
61.460
49.619
29.726
13.970
COOEt
COOEt
150
100
50
0
ppm (t1)


7.967
7.945
7.894
7.873
7.538
7.516
7.370
7.352
7.275
7.230
7.212
7.162
7.141
6.811
5.287
5.254
5.158
5.125
4.899
4.239
4.221
4.203
4.185
2.059
1.298
1.273
1.256
1.238
0.014
COOEt
COOEt
1.76
3.98
4.10
7.69
5.0
0.0
ppm (t1)


166.106
153.633
145.022
134.017
129.574
129.484
127.924
126.465
125.463
124.057
123.946
120.696
115.990
63.760
62.292
50.704
29.700
14.030
-0.004
COOEt
COOEt
150
100
50
0
ppm (t1)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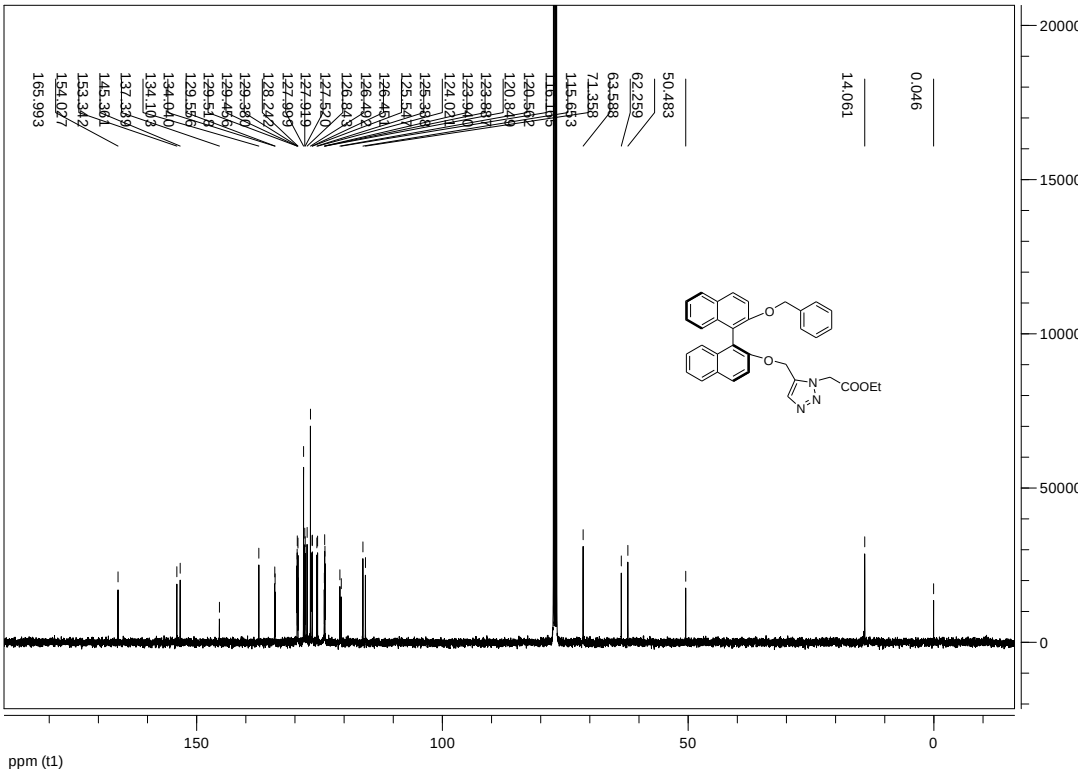
7.880
7.869
7.475
7.453
7.368
7.360
7.351
7.347
7.334
7.331
7.327
7.259
7.235
7.229
7.222
7.212
7.202
7.193
7.182
7.172
7.148
7.130
7.111
7.092
7.075
6.871
6.853
6.782
5.317
5.283
5.224
5.190
5.087
5.056
4.996
4.965
4.700
4.656
4.516
4.472
4.194
4.180
4.162
4.144
2.051
1.262
1.216
COOEt
ppm (t1)


165.993
154.027
153.342
145.361
137.339
134.103
134.040
129.556
129.518
129.456
129.380
128.242
127.999
127.919
127.520
126.843
126.492
126.451
125.541
125.388
124.021
123.940
123.681
120.849
120.562
116.105
115.653
71.358
63.588
62.259
50.483
14.061
0.046
COOEt
ppm (t1)