Electronic Supplementary Information

Submillisecond-lived photoinduced charge separation in inclusion complexes composed of $Li^+@C_{60}$ and cyclic porphyrin dimers

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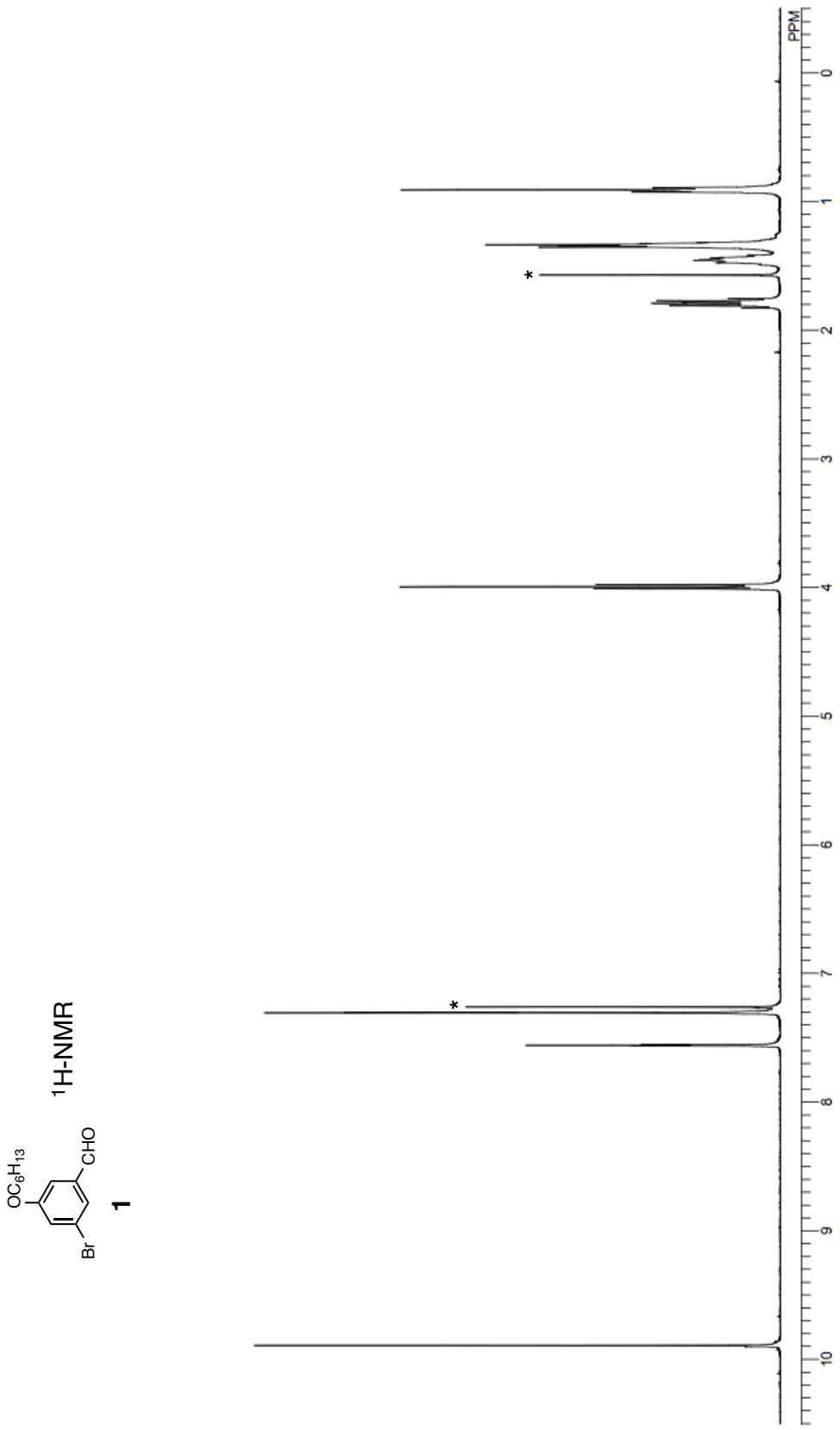

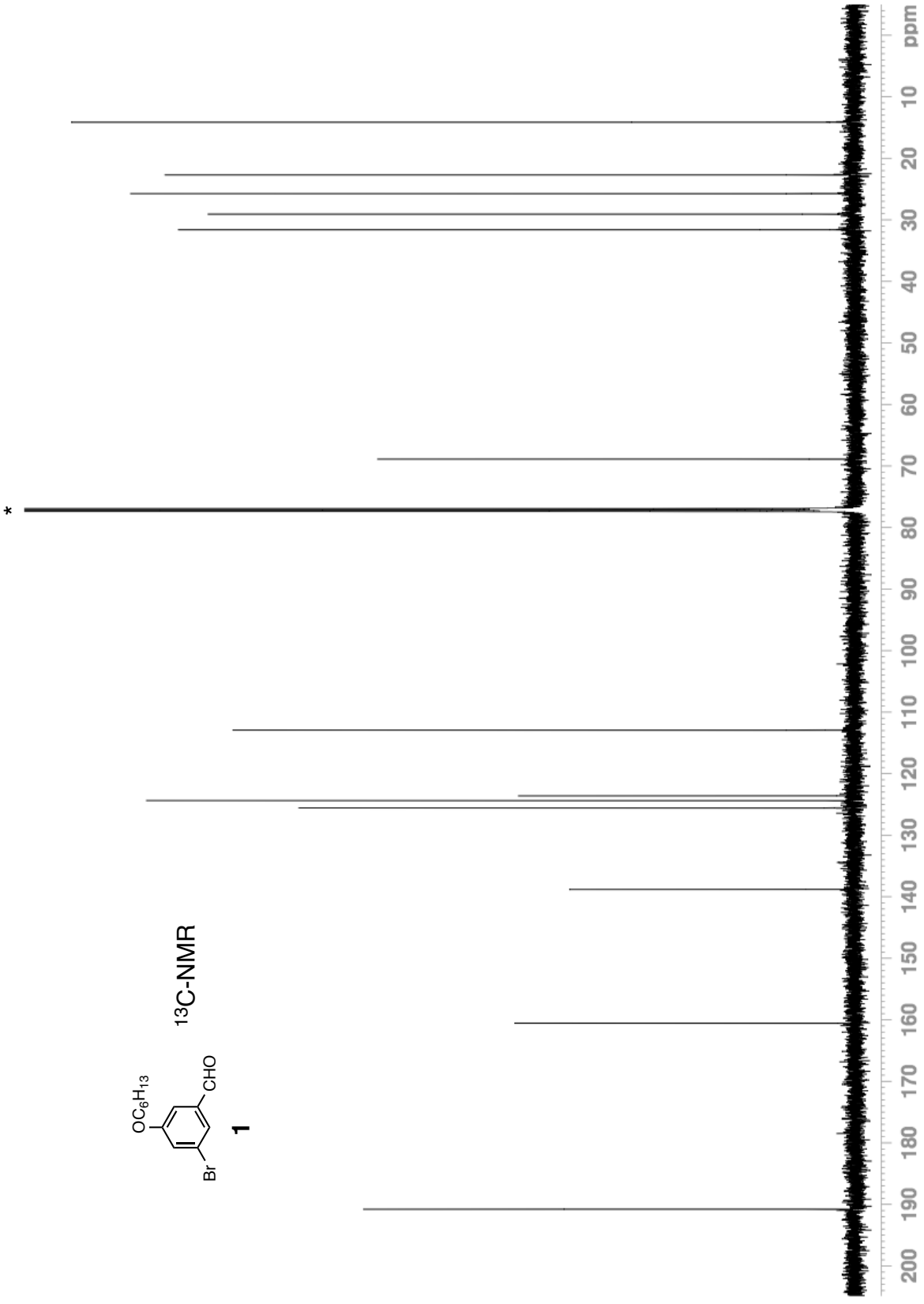
^{13}C-NMR
1
OC$_6$H$_{13}$
CHO
Br
*
ppm
10
20
30
40
50
60
70
80
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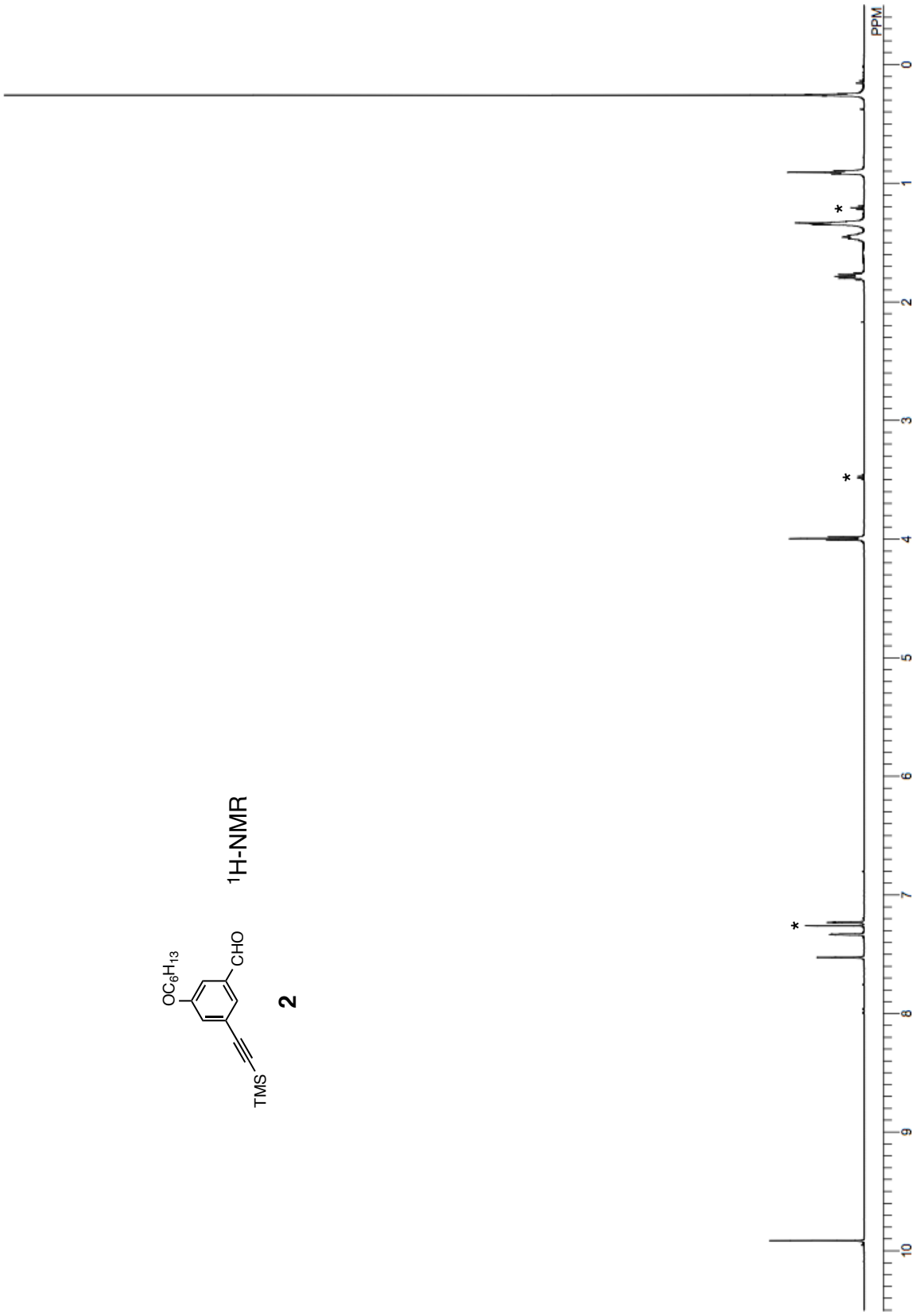
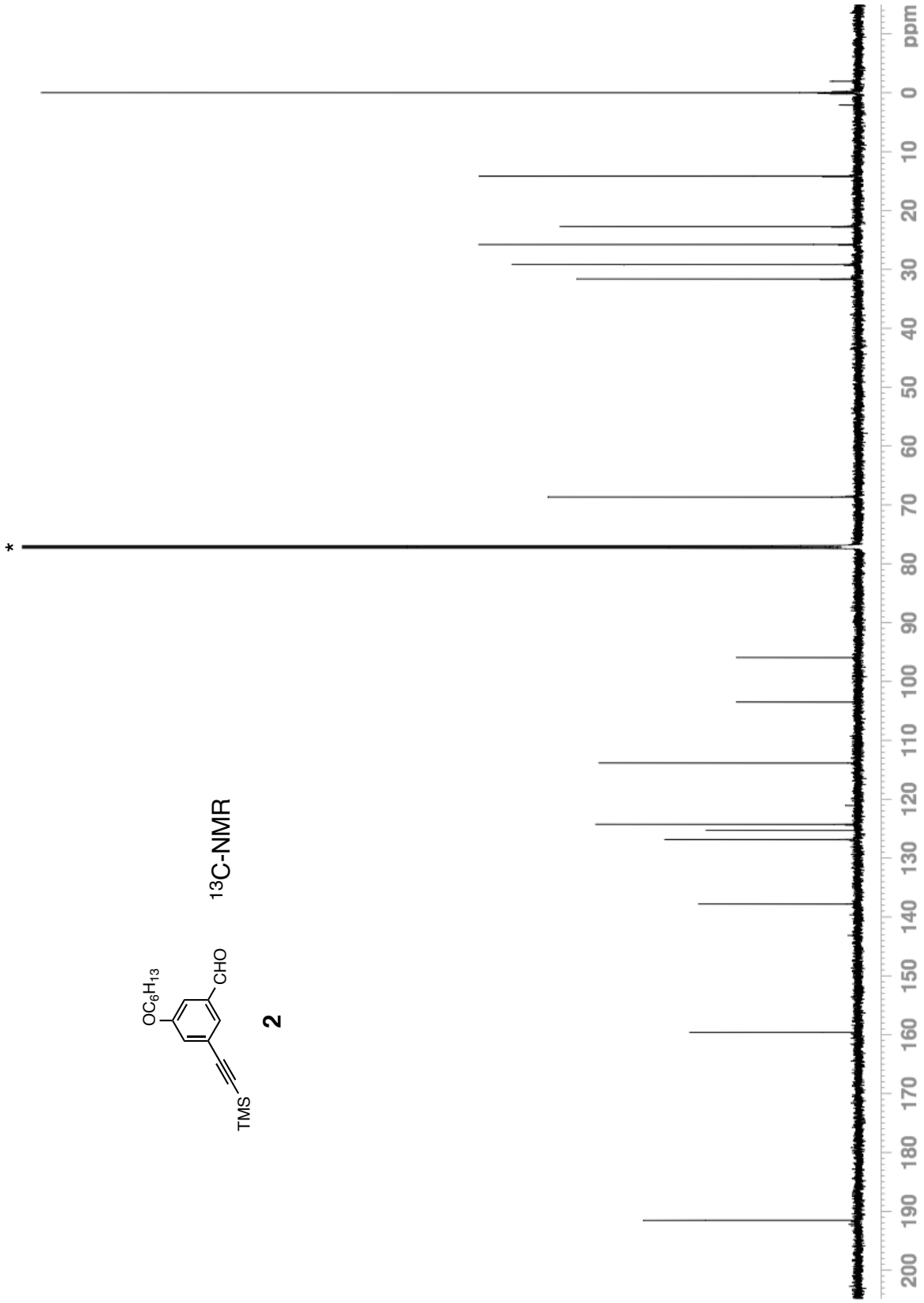
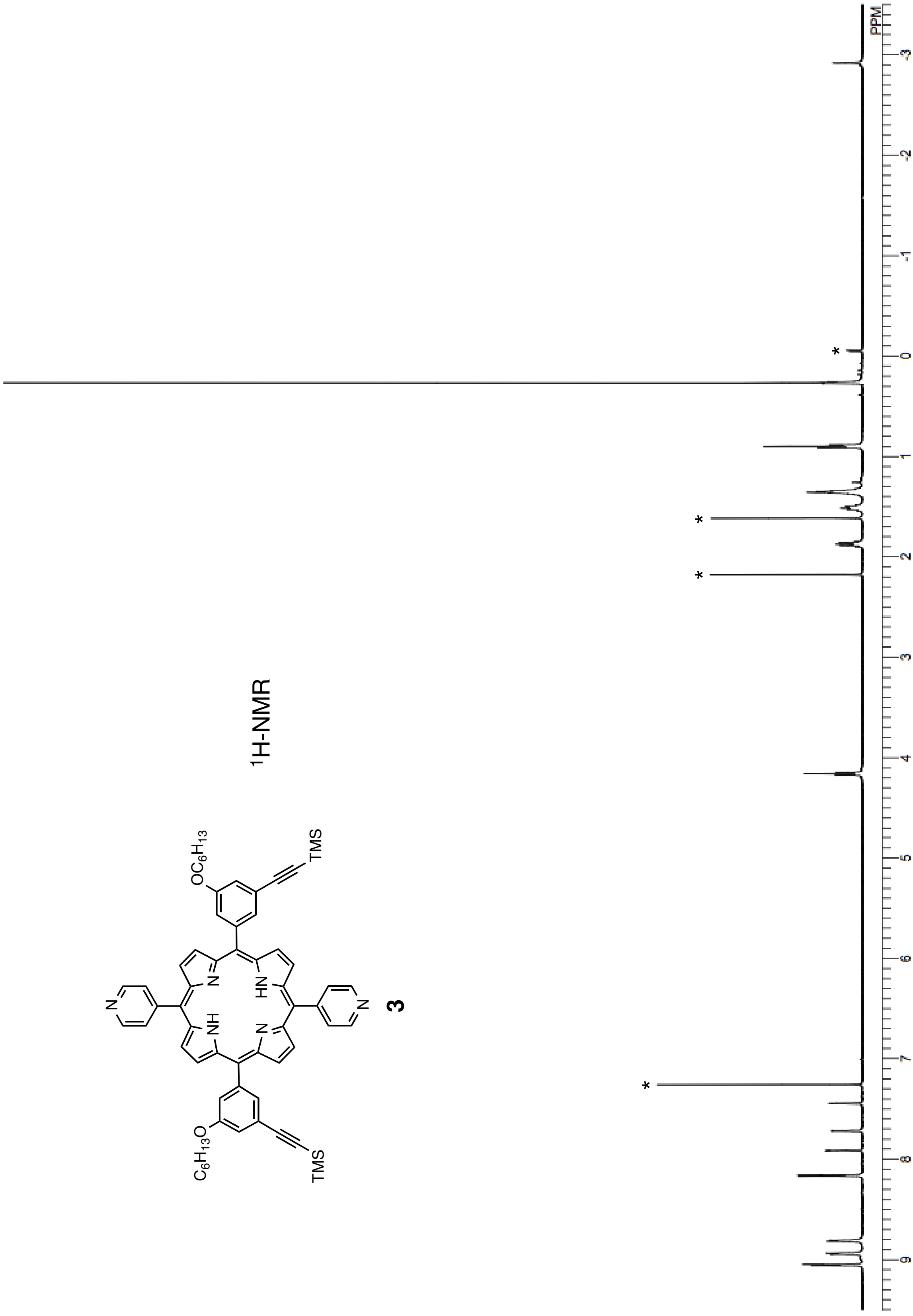
100
110
120
130
140
150
160
170
180
190
200


^{1}H-NMR
2
OC_6H_{13}
CHO
TMS
PPM
0
1
2
3
4
5
6
7
8
9
10
*
*
*

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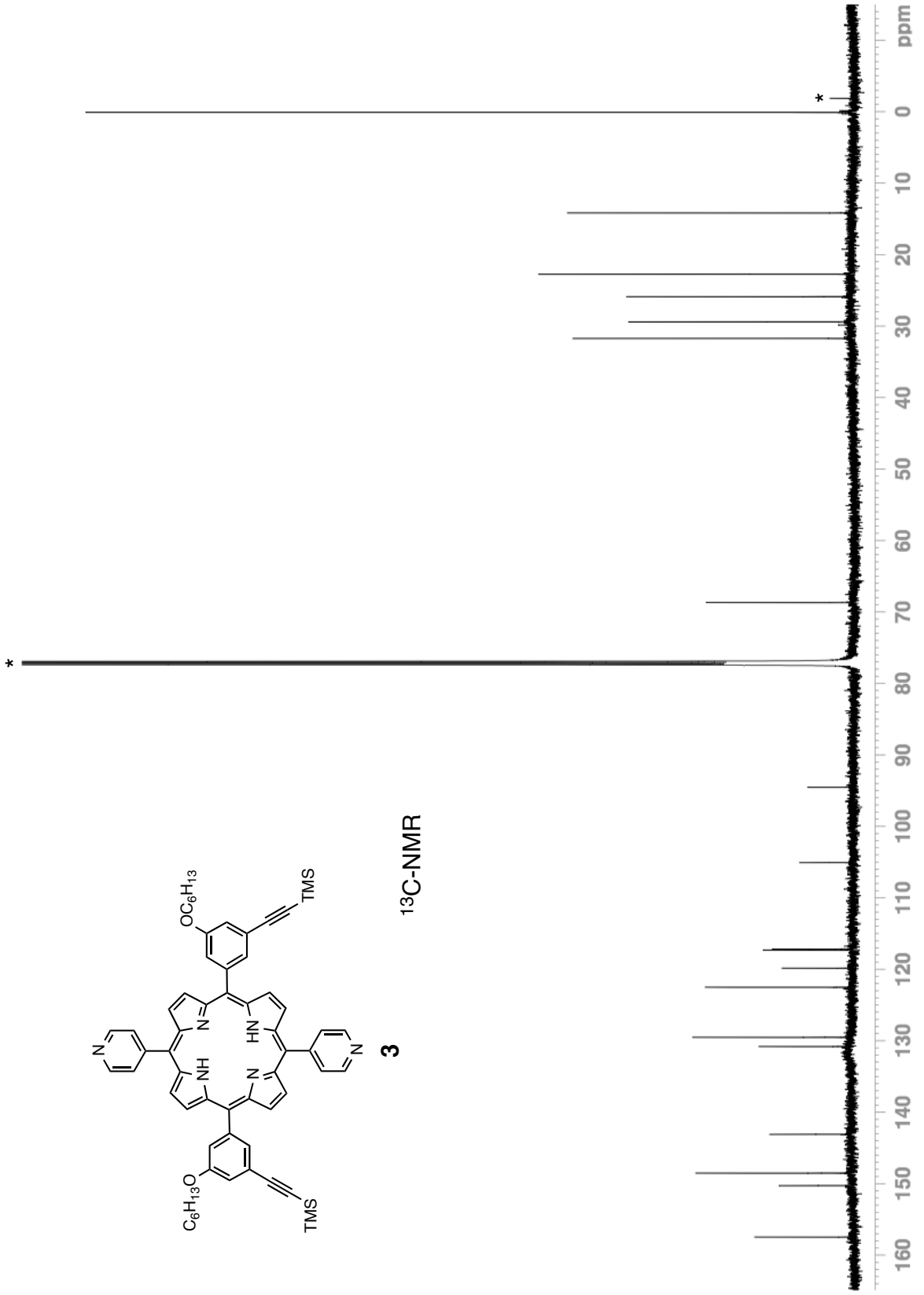
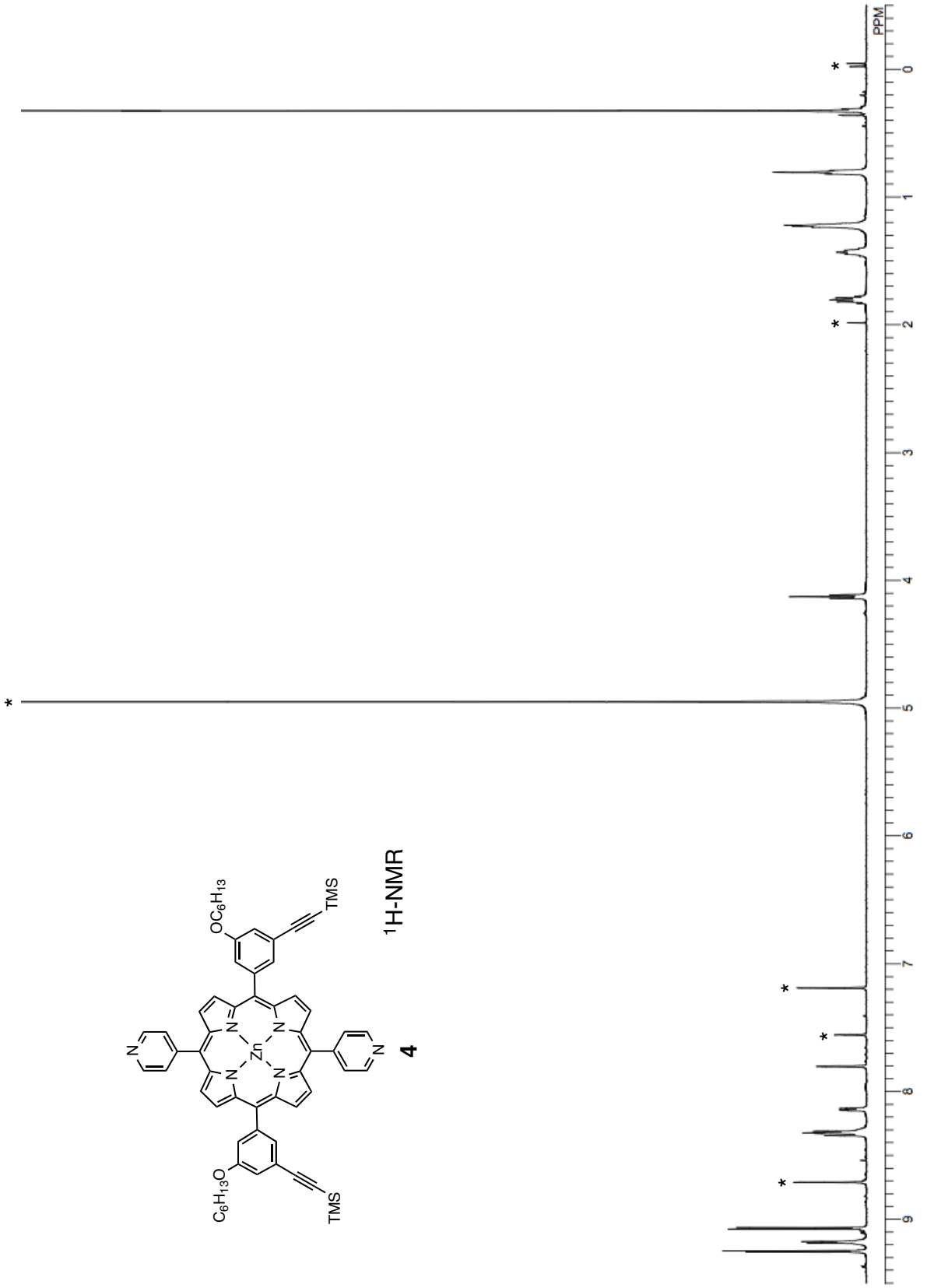
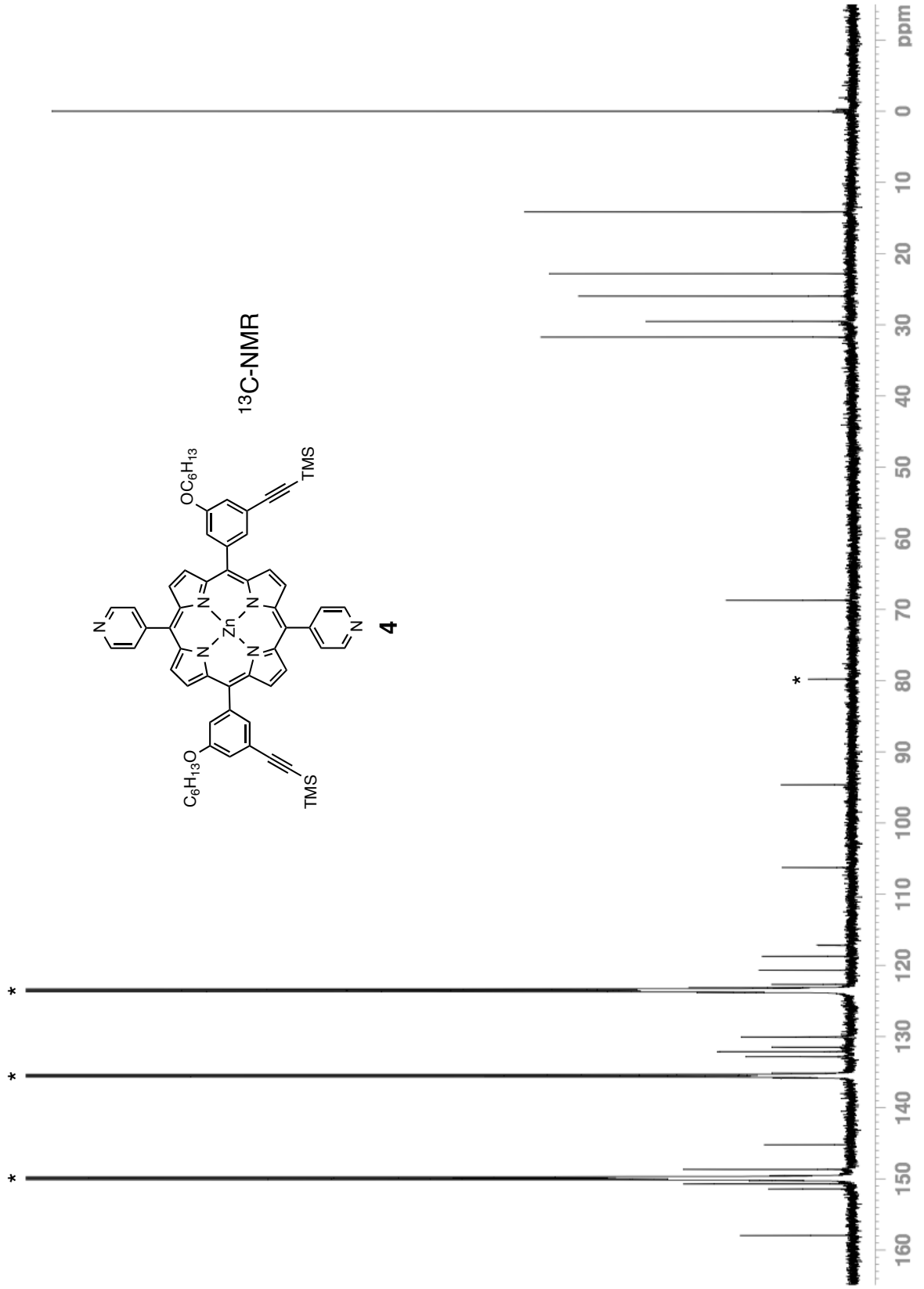
3
OC$_6$H$_{13}$
C$_6$H$_{13}$O
TMS
TMS
PPM

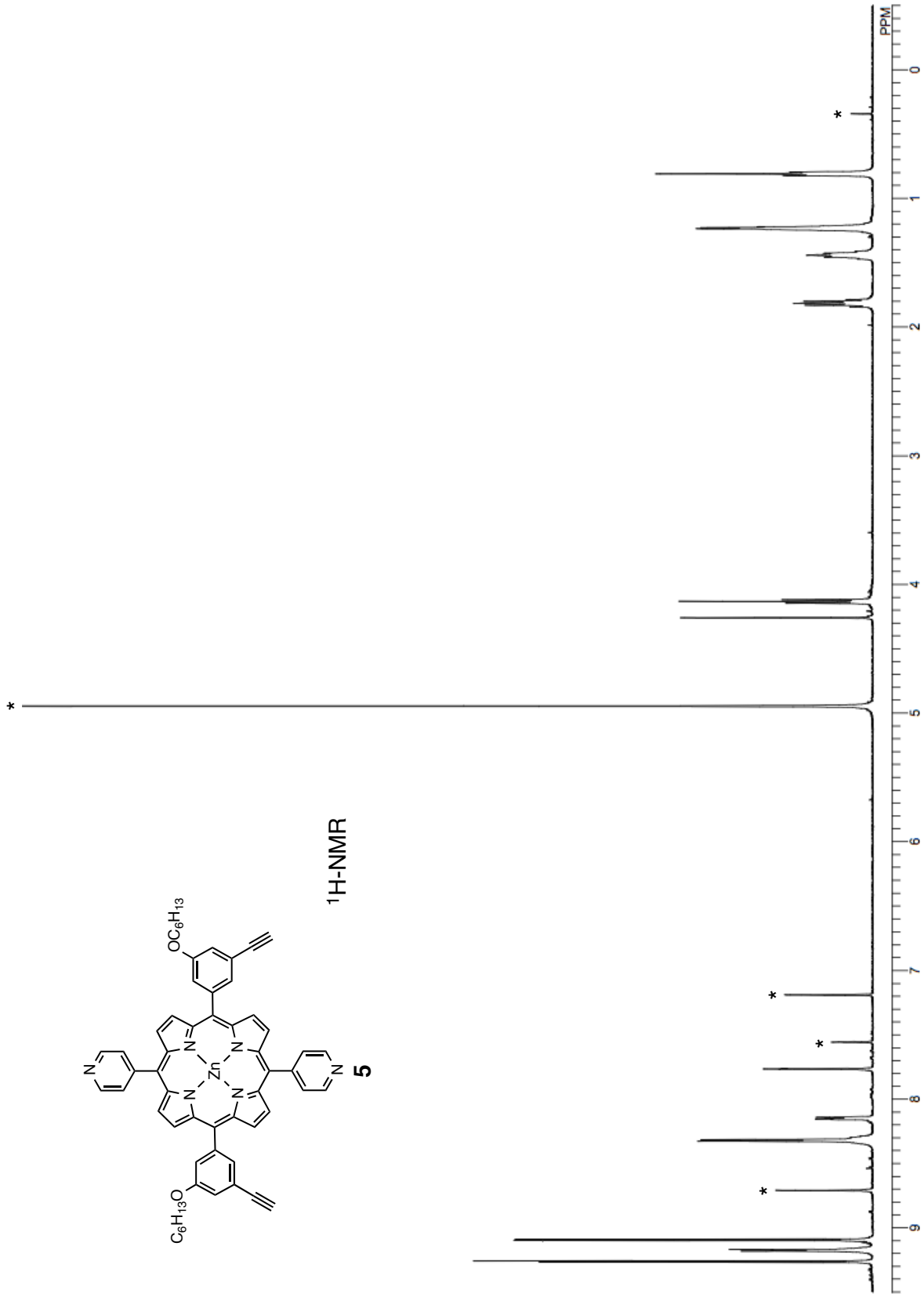

^{13}C-NMR
3
OC6H13
TMS
C6H13O
TMS
N
NH
HN
N
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

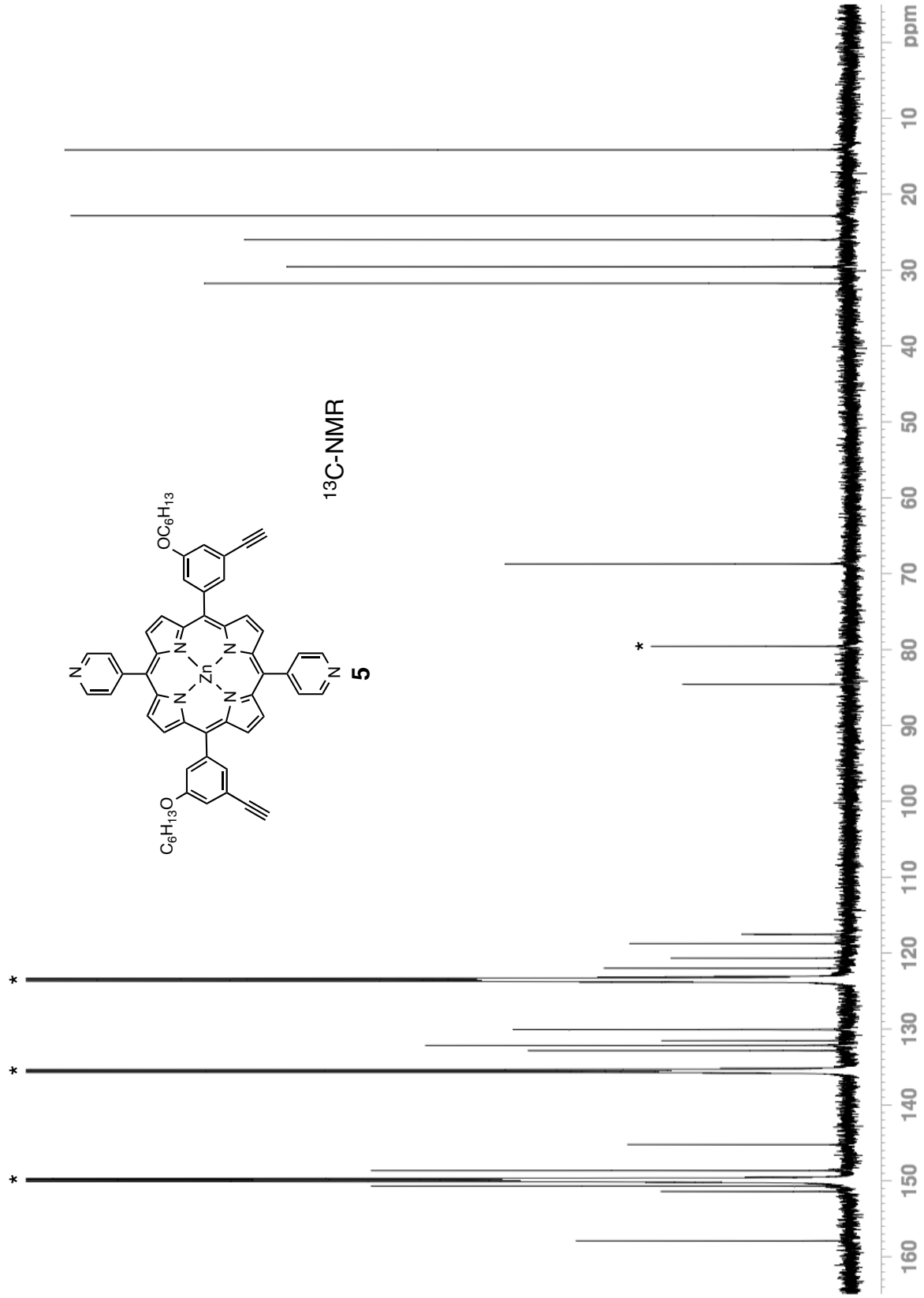


^{1}H-NMR

4


^{13}C-NMR
4
TMS
TMS
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
*
*
*
*


^{1}H-NMR
PPM
0
1
2
3
4
5
6
7
8
9
*
*
*
*
*
OC_6H_{13}
$C_6H_{13}O$
N
N
N
N
Zn
N
N
5


^{13}C-NMR
5
OC_6H_{13}
$C_6H_{13}O$
Zn
N
*
ppm
10
20
30
40
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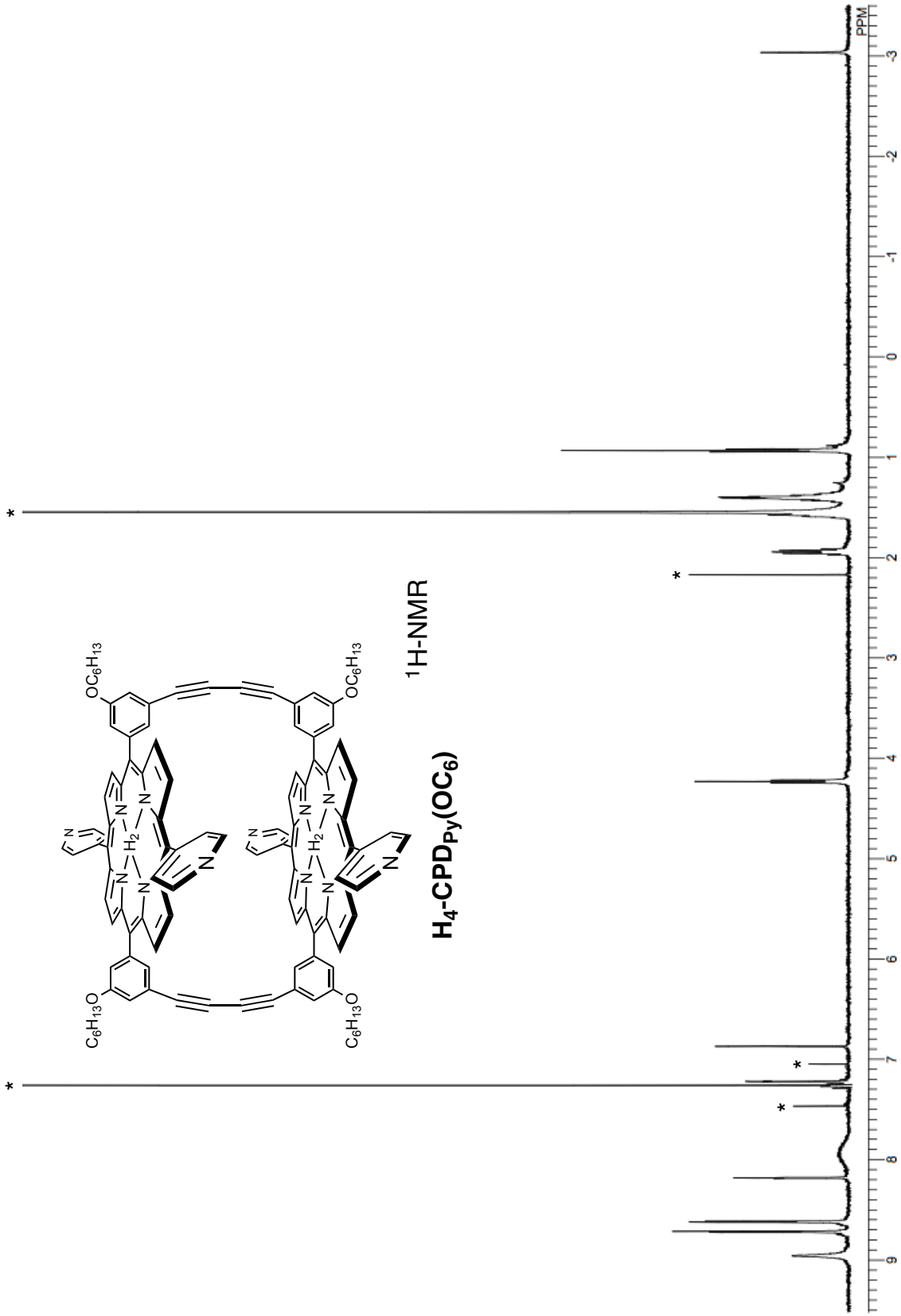
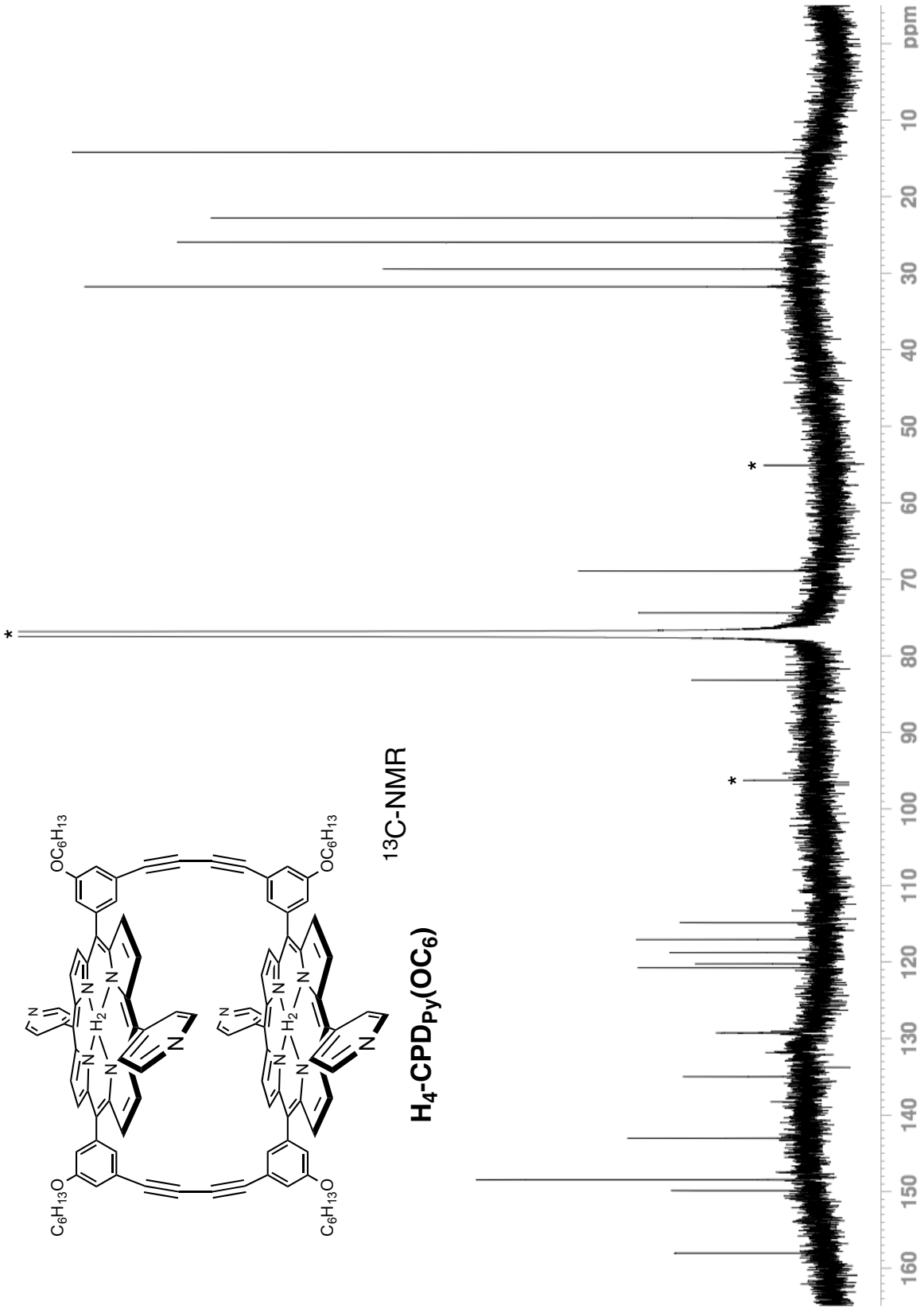
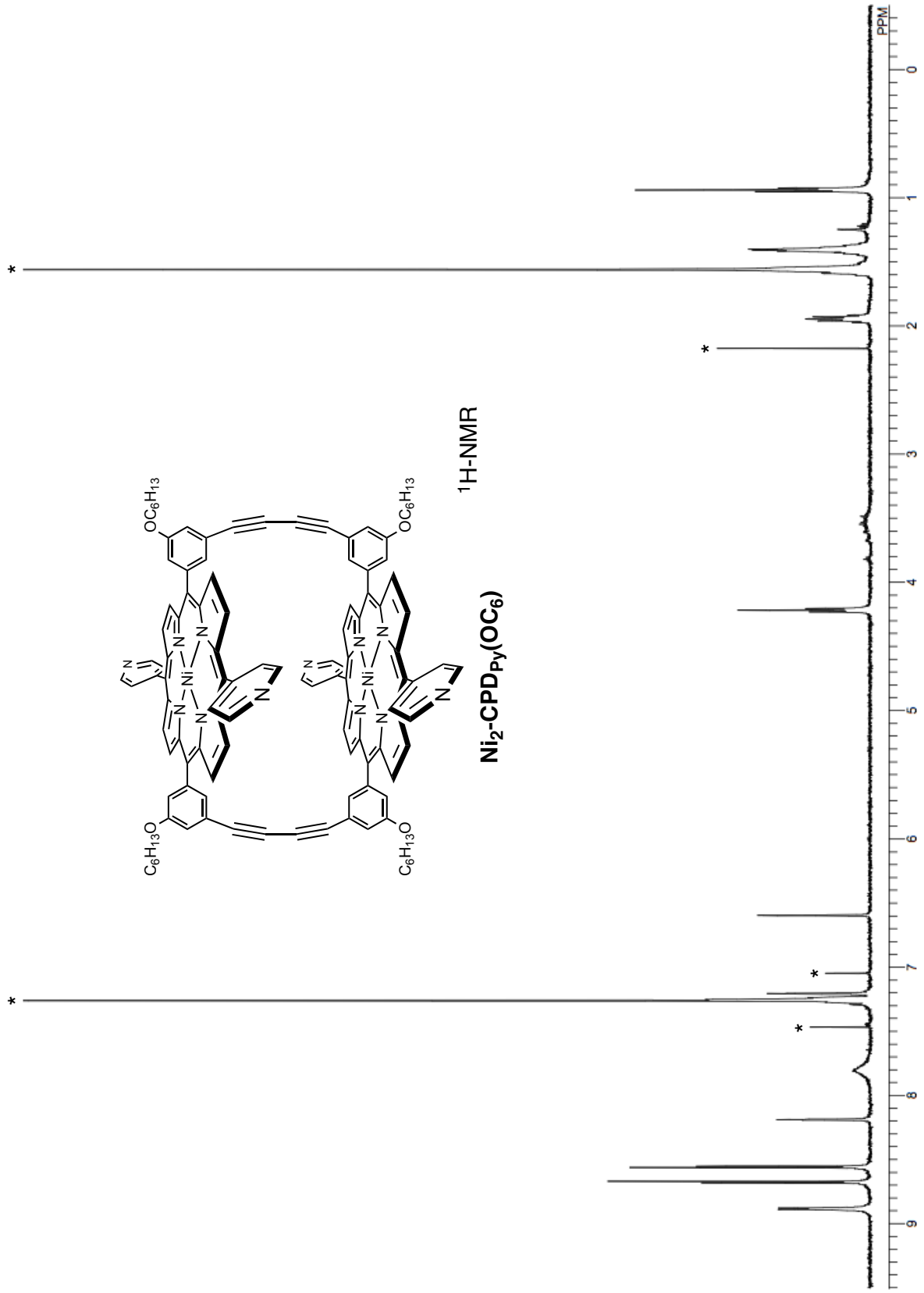
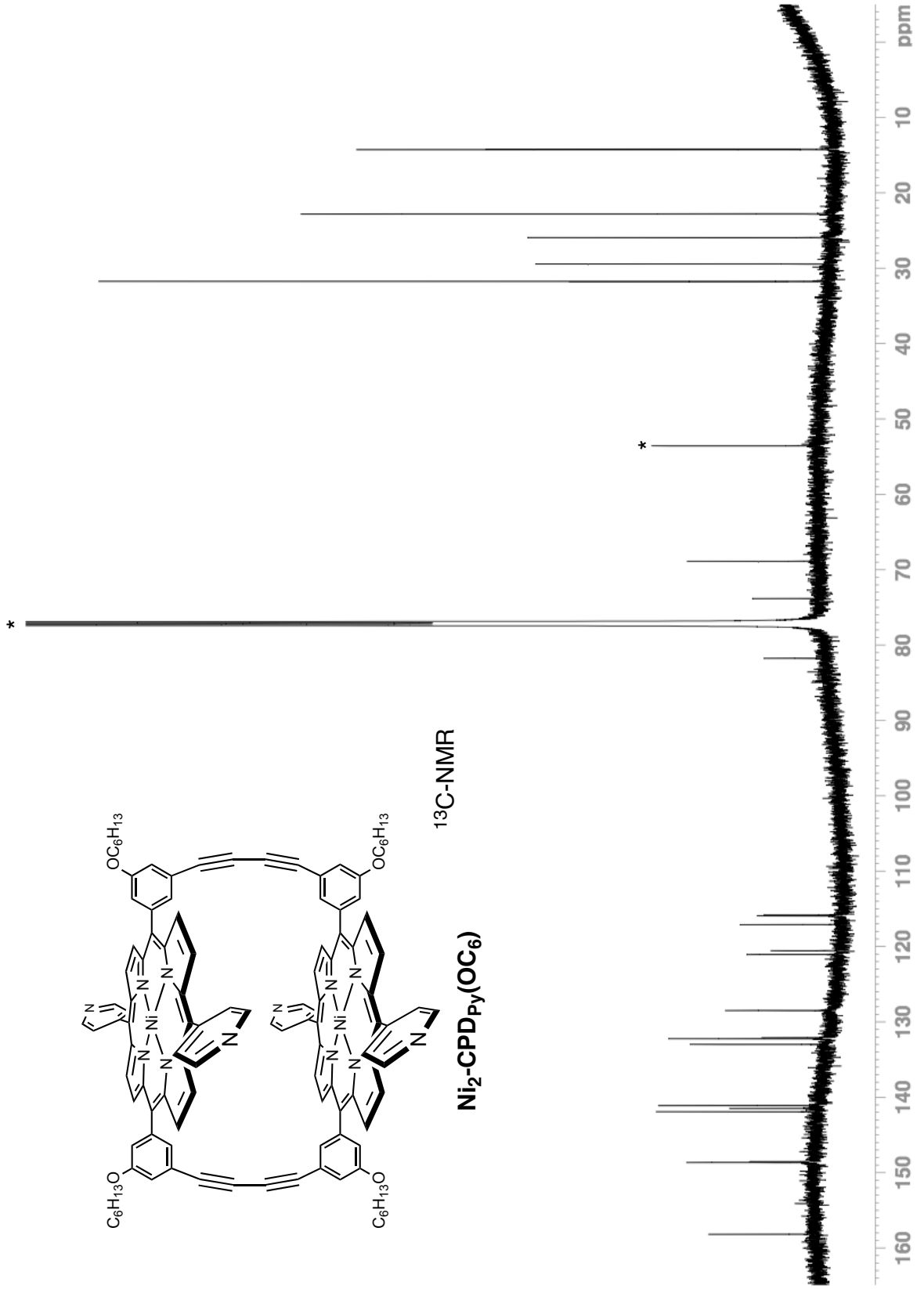
70
80
90
100
110
120
130
140
150
160




^{13}C-NMR
H_4-CPD$_{Py}$(OC_6)
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
*
*
*
OC_6H_{13}
$C_6H_{13}O$




^{13}C-NMR
Ni_2-CPD$_{Py}$(OC_6)
OC_6H_{13}
$C_6H_{13}O$
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
*
*

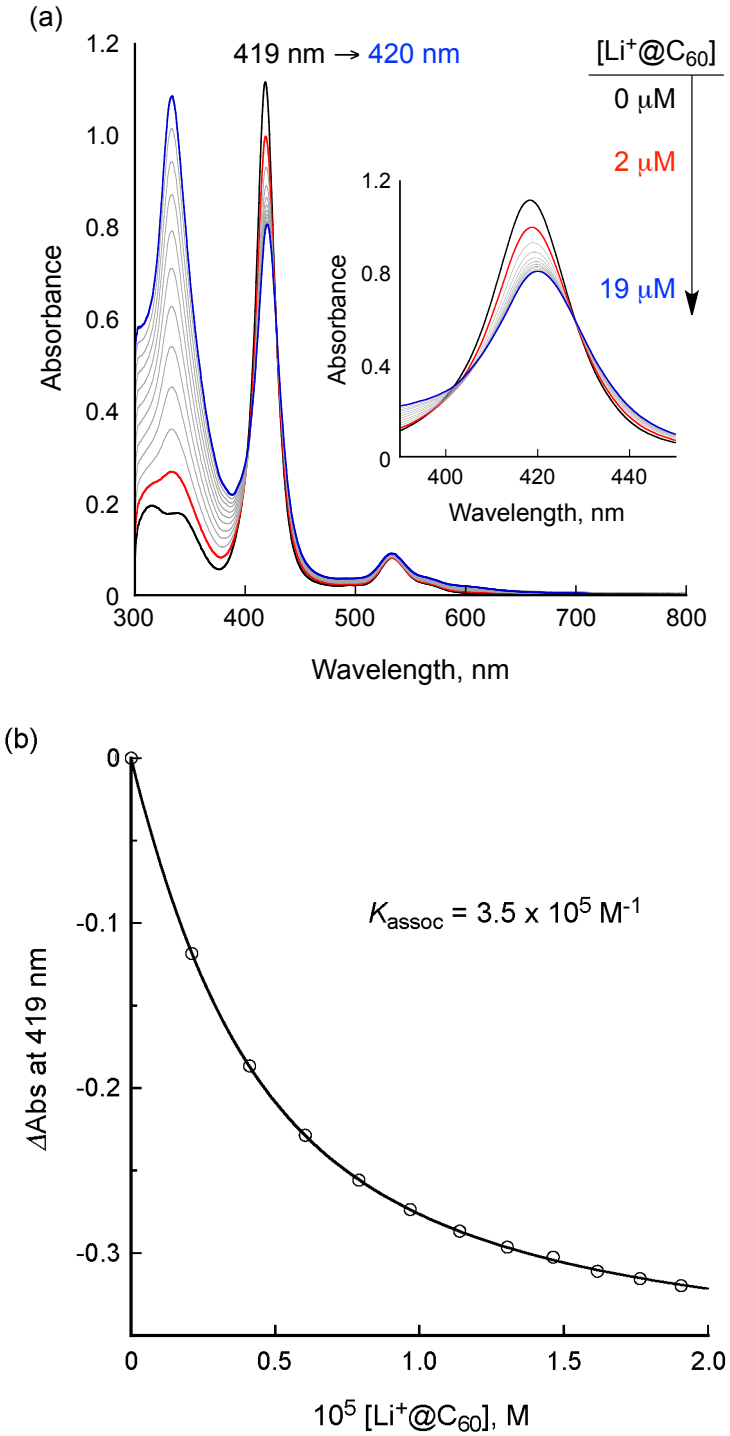


Fig. S15. (a) UV-vis absorption changes of Ni_2-$CPD_{Py}(OC_6)$ in the course of titration with $Li^+@C_{60}$ in PhCN at room temperature. The inset shows the Soret band region. [Ni_2-$CPD_{Py}(OC_6)$] = 2.5 × 10^{-6} M. (b) Change in the UV-Vis absorbance (ΔAbs) at 419 nm.

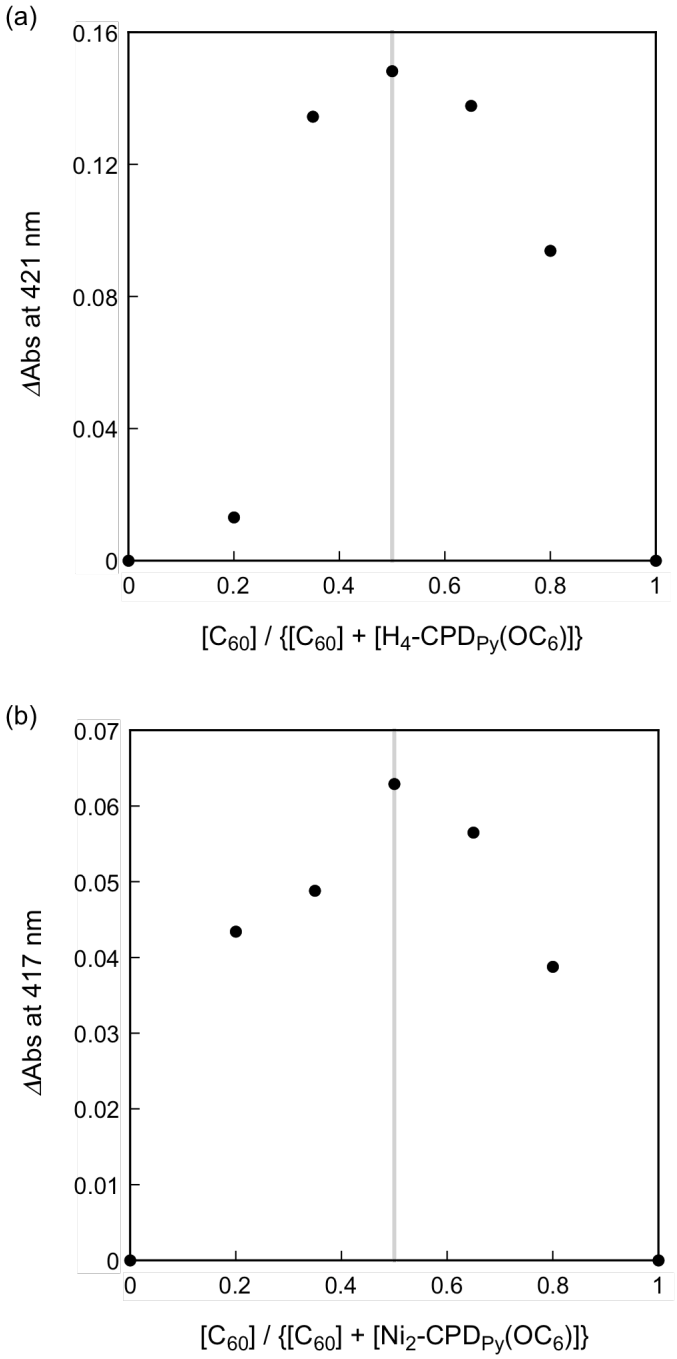


Fig. S16. Job's plots upon mixing (a) H_4-$CPD_{Py}(OC_6)$ or (b) Ni_2-$CPD_{Py}(OC_6)$ with $Li^+@C_{60}$ in $CHCl_3$/PhCN (1/1) at room temperature. $[CPD_{Py}(OC_6)] + [Li^+@C_{60}] = 4.0 \times 10^{-6}$ M.

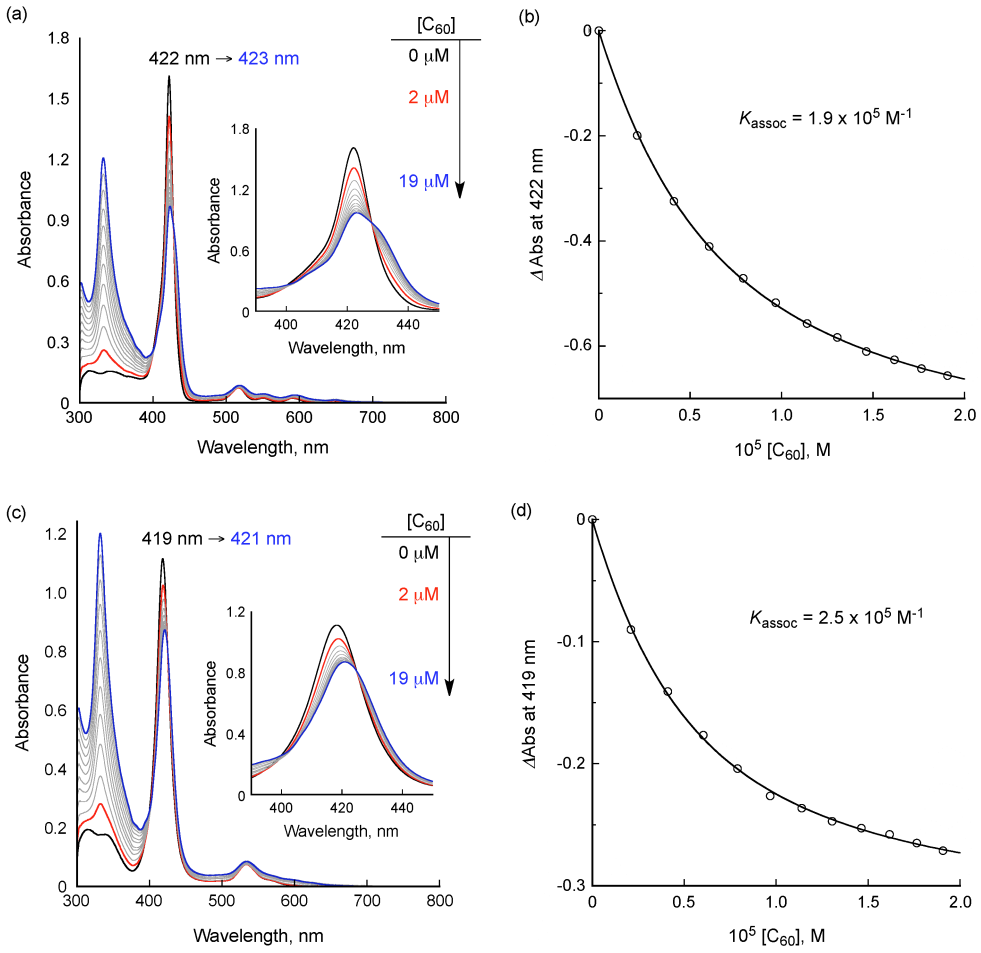


Fig. S17. UV-vis absorption changes of (a) H_4-$CPD_{Py}(OC_6)$ and (c) Ni_2-$CPD_{Py}(OC_6)$ in the course of titration with C_{60} in PhCN at room temperature. The insets show the Soret band region. $[CPD_{Py}(OC_6)] = 2.5 \times 10^{-6}$ M. Changes in the UV-Vis absorbance (ΔAbs) of (b) H_4-$CPD_{Py}(OC_6)$ and (d) Ni_2-$CPD_{Py}(OC_6)$ at 422 nm and 419 nm, respectively, at room temperature.

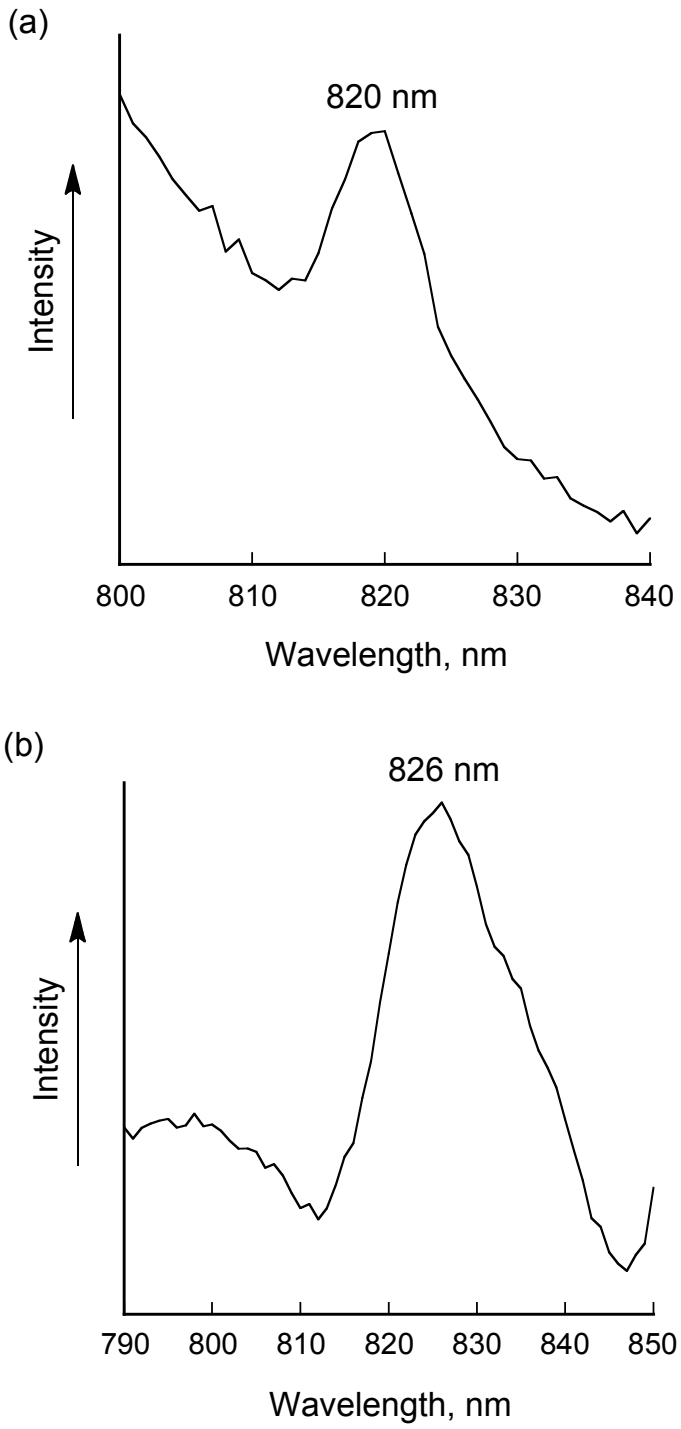


Fig. S18. Phosphorescence spectra of PrCN/CH_3CH_2I (3/1) glasses of (a) H_4-$CPD_{Py}(OC_6)$ and (b) Ni_2-$CPD_{Py}(OC_6)$ at 77 K excited at 440 nm.

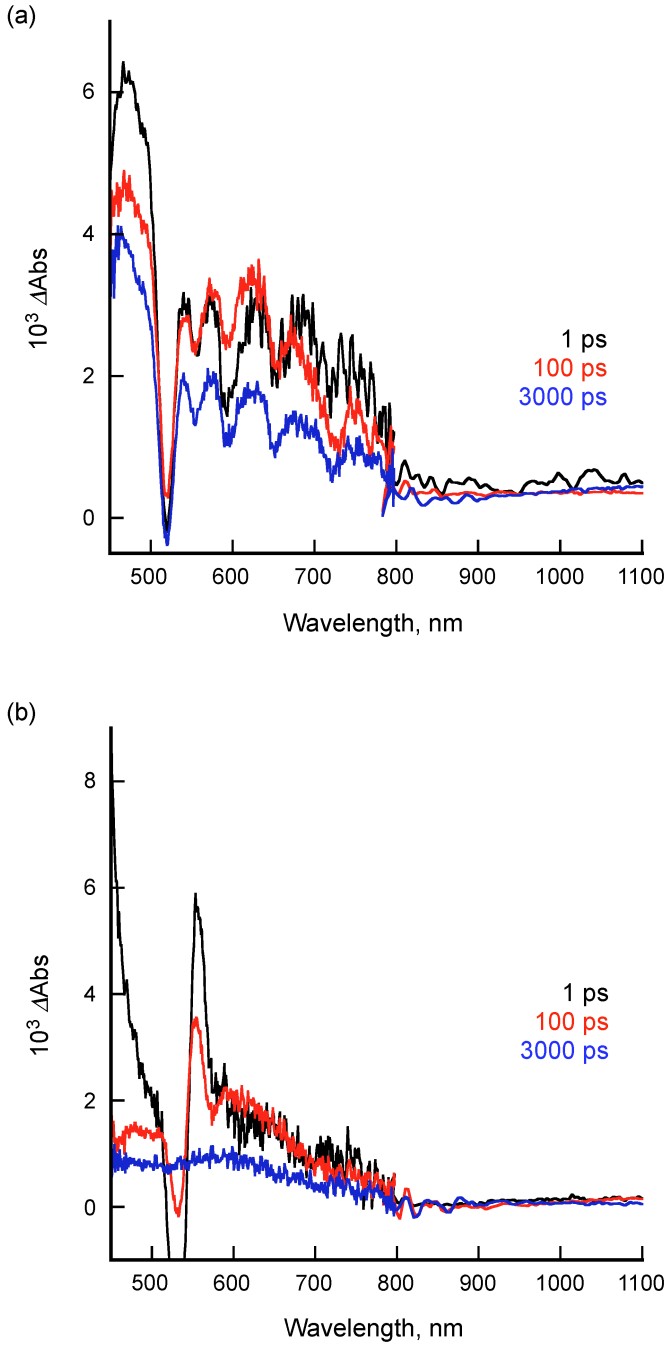


Fig. S19. Transient absorption spectra of (a) H_4-$CPD_{Py}(OC_6)$ and (b) Ni_2-$CPD_{Py}(OC_6)$ in deaerated PhCN at room temperature taken at 1, 100, and 3000 ps after femtosecond laser excitation at 420 nm. [H_4-$CPD_{Py}(OC_6)$] = 7.0×10^{-6} M, [Ni_2-$CPD_{Py}(OC_6)$] = 1.0×10^{-5} M.

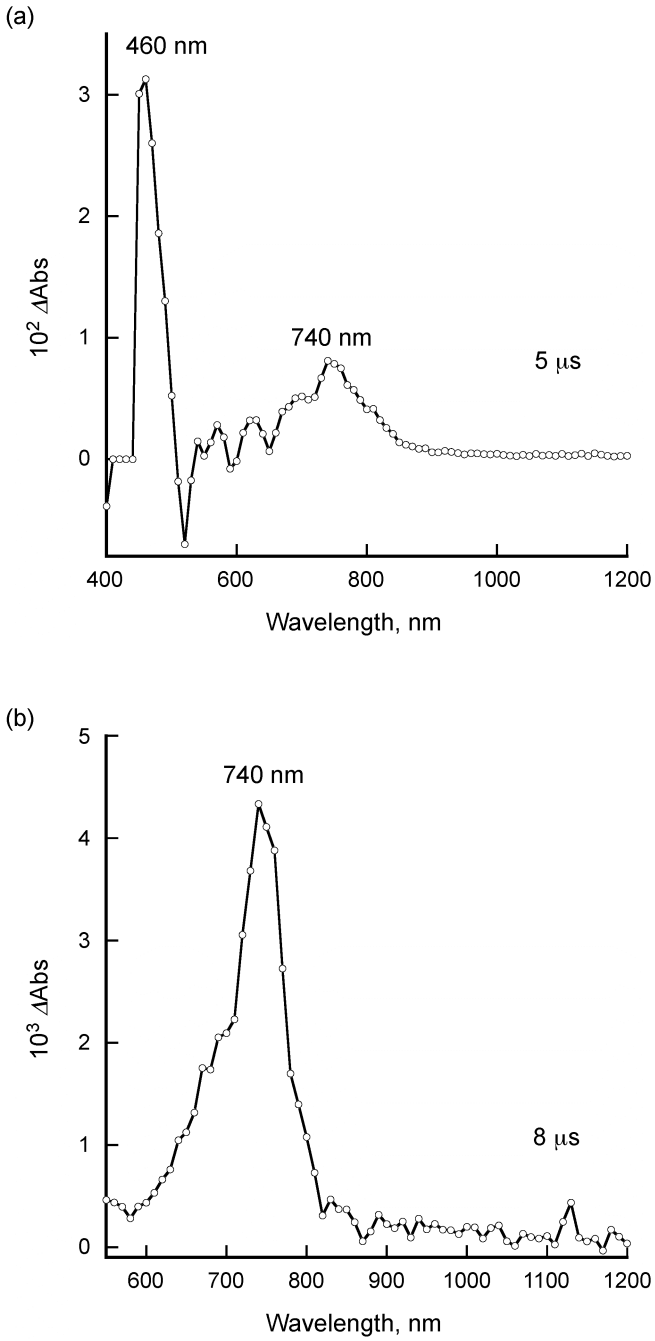


Fig. S20. Transient absorption spectra of (a) H_4-$CPD_{Py}(OC_6)$ with C_{60} and (b) Ni_2-$CPD_{Py}(OC_6)$ with C_{60} in deaerated PhCN at room temperature taken at 5 and 8 μs, respectively, after nanosecond laser excitation at (a) 505 and (b) 520 nm. $[CPD_{Py}(OC_6)] = 2.5 \times 10^{-5}$ M, $[C_{60}] = 5.0 \times 10^{-5}$ M.

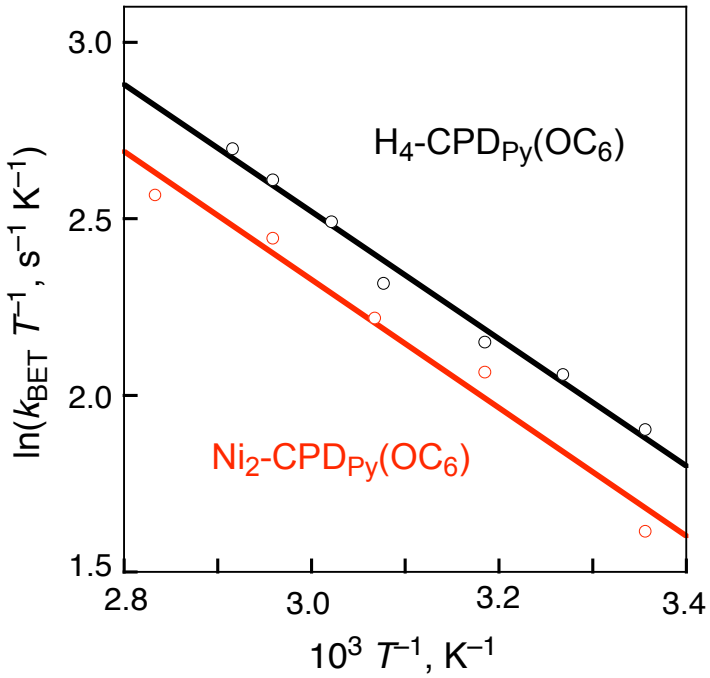


Fig. S21. Plots of $\ln(k_{BET}\ T^{-1})$ *vs.* T^{-1} for charge recombination of $[H_4\text{-}CPD_{Py}(OC_6)^{\bullet+} + Li^+@C_{60}^{\bullet-}]$ (black) and $[Ni_2\text{-}CPD_{Py}(OC_6)^{\bullet+} + Li^+@C_{60}^{\bullet-}]$ (red) in PhCN.