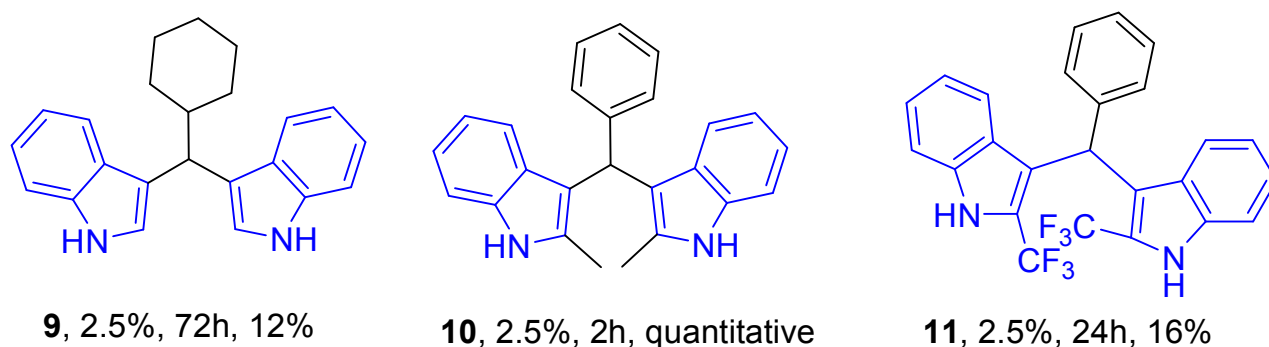




Scheme S1. The schematic representation of products **9,10** and **11**

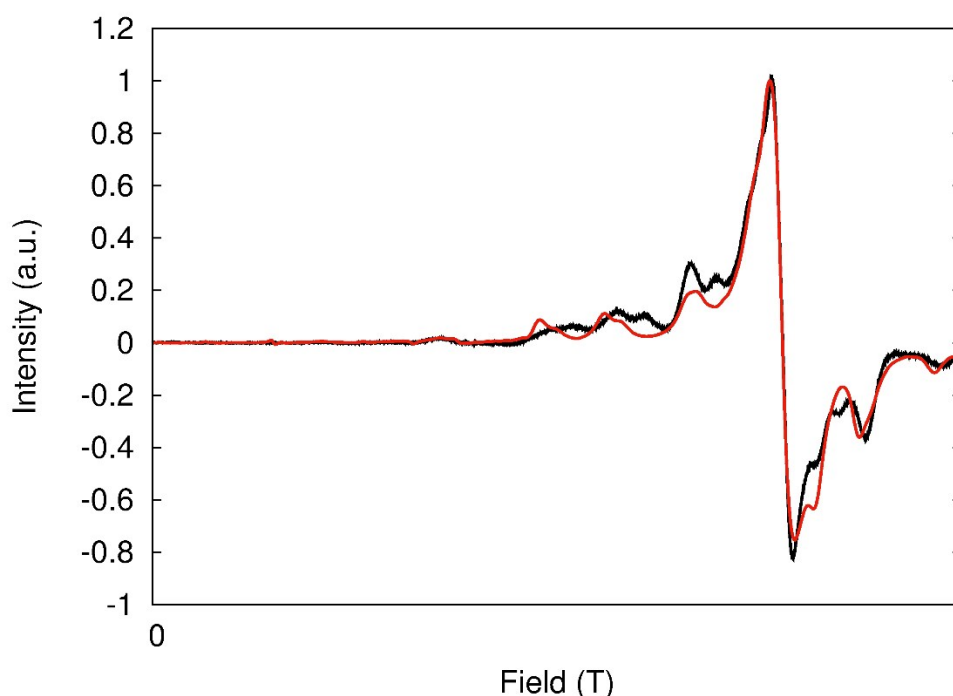


Figure S1. EPR Simulation of solution phase (80% DMF, 20% Et₂O) 1Y at 34.0865 GHz and 7 K.

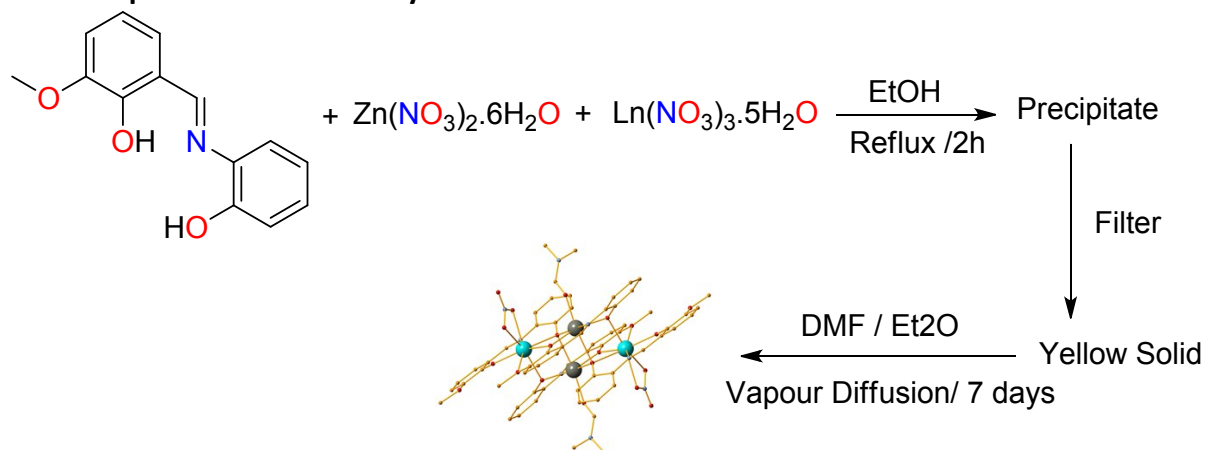
Hamiltonian:

$$\hat{H}$$

$$= B_2^0(3\hat{S}_z^2 - \hat{S}^2) + \frac{B_2^2}{2}(\hat{S}_+^2 + \hat{S}_-^2) + B_4^0(35\hat{S}_z^4 - 30\hat{S}^2\hat{S}_z^2 + 25\hat{S}_z^2 + 3\hat{S}^{22} - 6\hat{S}^2) + \mu_B g \hat{S} \cdot B$$

. Parameters: $g = 1.961(2)$, $B_2^0 = -0.0259(7) \text{ cm}^{-1}$, $B_2^2 = 0.0212(6) \text{ cm}^{-1}$, $B_4^0 = 0.000018(6) \text{ cm}^{-1}$, $B_4^4 = -0.00011(3) \text{ cm}^{-1}$, Lorentzian frequency-space linewidth = 1.13(8) GHz. Given the complexity of the ZFS for the $S = 7/2$ state, this is likely not the only parameter set which can approach agreement with the data. We provide this simulation to show a plausible parameter set for the data.

Visual Representation of the synthesis of 1-Ln



1-Ln Synthetic Protocol.

$\text{H}_2\text{L1}$ (0.2 mmol, 48 mg) and Et_3N (61 μL , 0.4 mmol) were added to EtOH (20 mL) and the resultant solution was stirred for 5 minutes under reflux. Upon completion, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (56, 0.2 mmol) and $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ were added and the solution was refluxed for a further 2 hours. After cooling, the yellow precipitate was filtered, washed with Et_2O and dissolved in DMF (10 mL). The resultant solution underwent vapor diffusion and after 1 week long yellow crystals with the formula $[\text{Zn}^{\text{II}}_2\text{Ln}^{\text{III}}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)_2(\text{DMF})_2]$ had formed. Yield 45-71%.

Compound **1Dy** - $[\text{Zn}^{\text{II}}_2\text{Dy}^{\text{III}}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)_2(\text{DMF})_2]$ CHN (Expected) - C 44.02; H 3.46; N 6.63. (Measured); C 41.90; H 2.84; N 5.61 corresponding to $[\text{Zn}^{\text{II}}_2\text{Dy}^{\text{III}}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$ C 41.58; H 3.24; N 5.19.

Compound **1Y** - $[\text{Zn}^{\text{II}}_2\text{Y}^{\text{III}}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)_2(\text{DMF})_2]$ CHN (Expected) - C 48.31; H 3.80; N 7.27. (Measured); C 45.34; H 3.12; N 5.90 corresponding to a formula $[\text{Zn}^{\text{II}}_2\text{Y}^{\text{III}}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$; C 45.84; H 3.57; N 5.73.

Compound **1Gd** - $[\text{Zn}^{\text{II}}_2\text{Gd}^{\text{III}}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)_2(\text{DMF})_2]$ CHN (Expected) C 44.33; H 3.48; N 6.68. (Measured); C 41.50; H 2.86; N 5.20 corresponding to a formula $[\text{Zn}^{\text{II}}_2\text{Gd}^{\text{III}}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$; C 41.89; H 3.26; N 5.24. CCDC 1452416-1452423

Table S1 Crystallographic Data

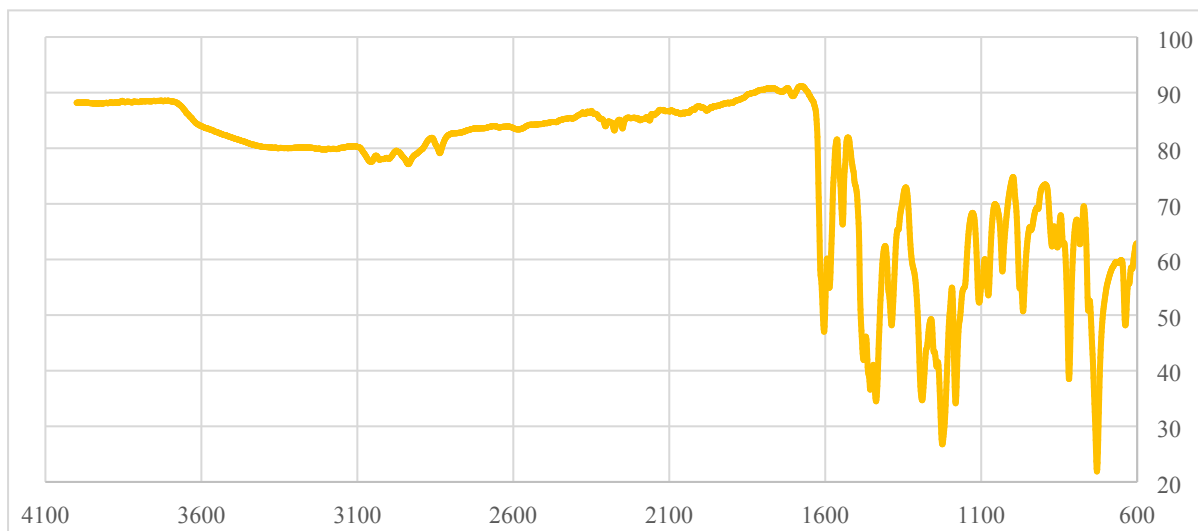
Identification code	1Dy	1Y	1Gd	1Eu
Empirical formula	C ₆₂ H ₅₈ Dy ₂ N ₈ O ₂₀ Zn ₂	C ₆₂ H ₅₈ N ₈ O ₂₀ Y ₂ Zn ₂	C ₆₂ H ₅₈ Gd ₂ N ₈ O ₂₀ Zn ₂	C ₆₂ H ₅₈ Eu ₂ N ₈ O ₂₀ Zn ₂
Formula weight	1690.9	1543.72	1678.1	1669.91
Temperature/K	173	173	173	173
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	13.75033(18)	13.7448(6)	13.8175(6)	13.8125(4)
b/Å	14.3147(2)	14.3133(7)	14.3074(6)	14.3087(5)
c/Å	16.9418(2)	16.9268(7)	16.9999(8)	16.9783(5)
α/°	90	90	90	90
β/°	95.2801(12)	95.068(5)	95.503(4)	95.498(3)
γ/°	90	90	90	90
Volume/Å ³	3320.55(8)	3317.0(3)	3345.3(3)	3340.12(18)
Z	2	2	2	2
ρ _{calc} /g/cm ³	1.691	1.546	1.668	1.6603
μ/mm ¹	3.016	2.525	14.089	14.709
F(000)	1676	1568	1668	1627.8
Crystal size/mm ³	0.32 × 0.20 × 0.18	0.28 × 0.22 × 0.16	0.30 × 0.24 × 0.20	0.34 × 0.22 × 0.20
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.766 to 54.964	6.77 to 58.646	8.092 to 122.2	8.1 to 122.28
Index ranges	-17 ≤ h ≤ 18, -18 ≤ k ≤ 12, -23 ≤ l ≤ 13	-18 ≤ h ≤ 15, -18 ≤ k ≤ 14, -22 ≤ l ≤ 20	-15 ≤ h ≤ 14, -16 ≤ k ≤ 15, -19 ≤ l ≤ 17	-12 ≤ h ≤ 15, -15 ≤ k ≤ 16, -19 ≤ l ≤ 19
Reflections collected	14238	10546	17350	16615
Independent reflections	7145 [R _{int} = 0.0295, R _{sigma} = 0.0479]	6364 [R _{int} = 0.0364, R _{sigma} = 0.0586]	5096 [R _{int} = 0.0723, R _{sigma} = 0.0602]	5100 [R _{int} = 0.0717, R _{sigma} = 0.0651]
Data/restraints/parameters	7145/0/428	6364/0/428	5096/0/428	5100/0/427
Goodness-of-fit on F ²	1.064	1.162	1.053	1.072
Final R indexes [I > 2σ (I)]	R ₁ = 0.0367, wR ₂ = 0.0946	R ₁ = 0.0558, wR ₂ = 0.1467	R ₁ = 0.0644, wR ₂ = 0.1795	R ₁ = 0.0572, wR ₂ = 0.1605
Final R indexes [all data]	R ₁ = 0.0462, wR ₂ = 0.0992	R ₁ = 0.0791, wR ₂ = 0.1627	R ₁ = 0.0701, wR ₂ = 0.1883	R ₁ = 0.0619, wR ₂ = 0.1685
Largest diff. peak/hole / e Å ⁻³	2.51/-0.60	2.25/-0.71	3.02/-1.79	3.06/-1.19

Table S2. Crystallographic Parameters for compounds **1Sm**, **1Yb** and **1Tb**.

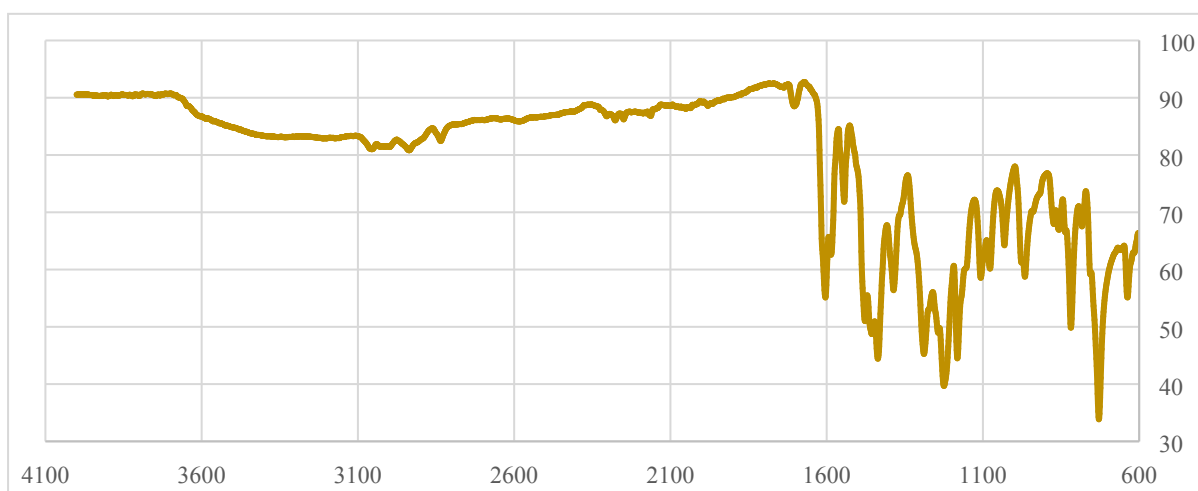
Identification code	1Sm	1Yb	1Tb
Temperature/K	173	173	173
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	13.803(5)	13.53(2)	13.758(13)
b/Å	14.26(4)	14.06(4)	14.344(12)
c/Å	16.98(2)	17.98(6)	16.952(8)
α /°	90.09(17)	90.06(9)	90.02(9)
β /°	95.56(6)	95.21(13)	95.56(6)
γ /°	89.94(8)	90.12(4)	90.21(8)
Volume/Å ³	3326(10)	3329(11)	3333(3)

FT-IR of 1-Ln

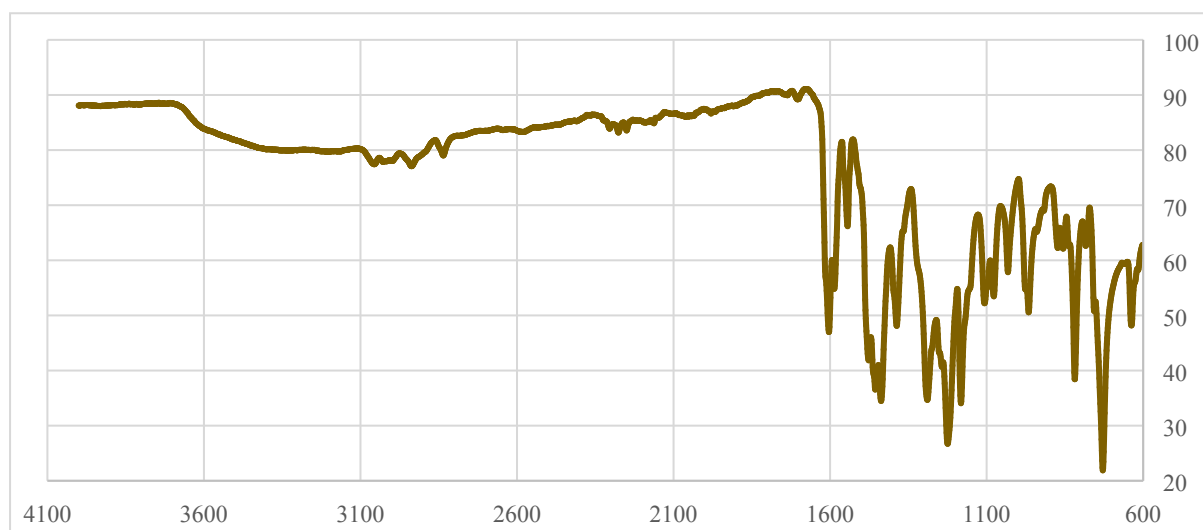
1-Dy



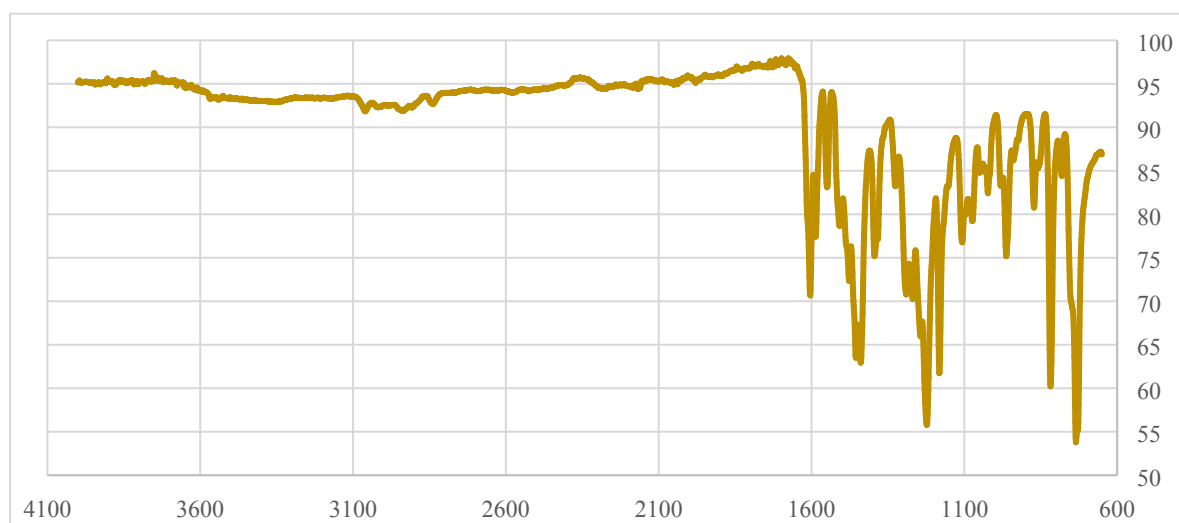
1-Y



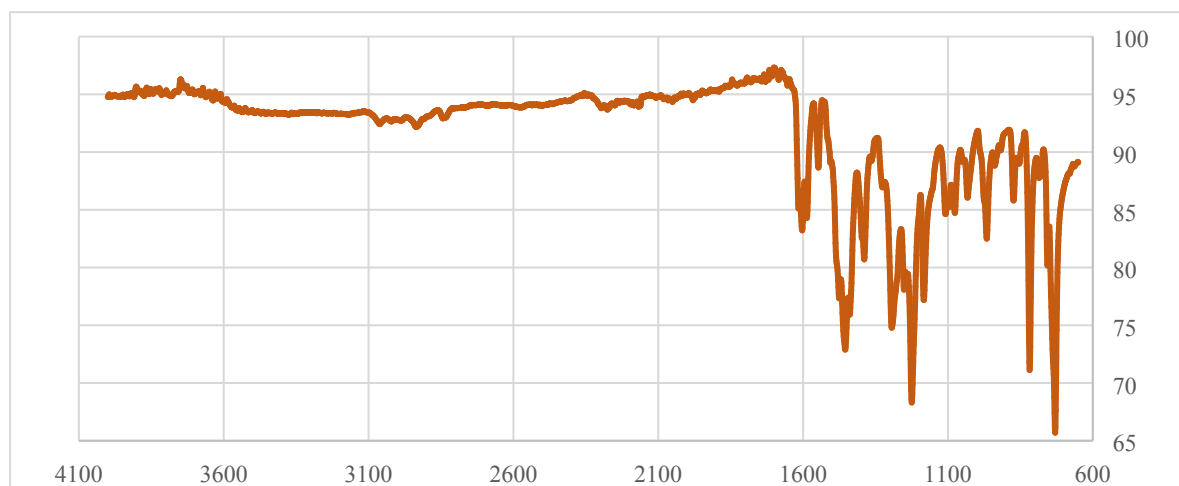
1-Gd



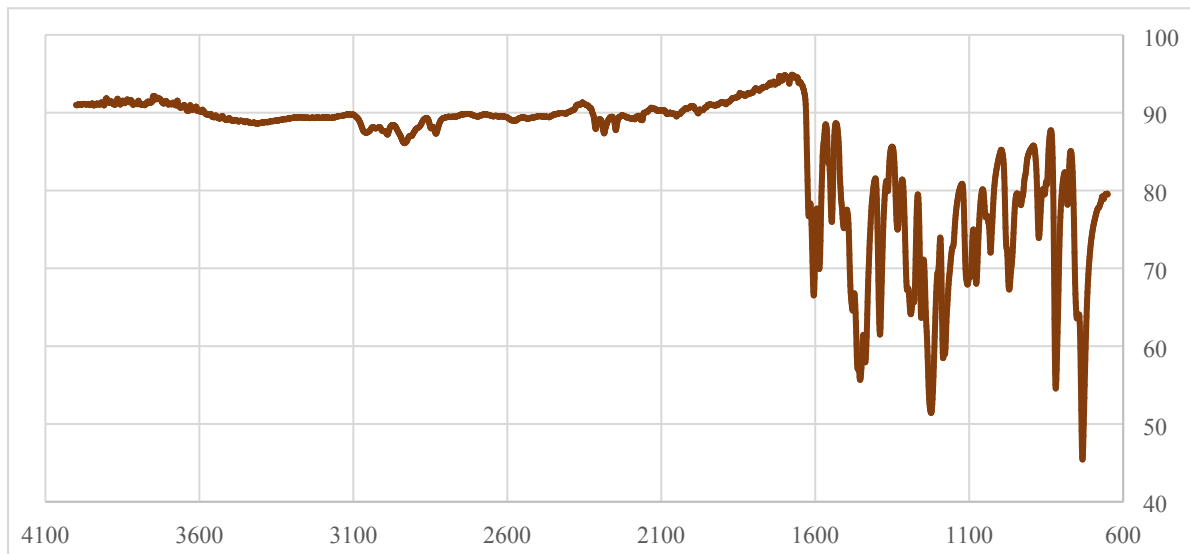
1-Eu



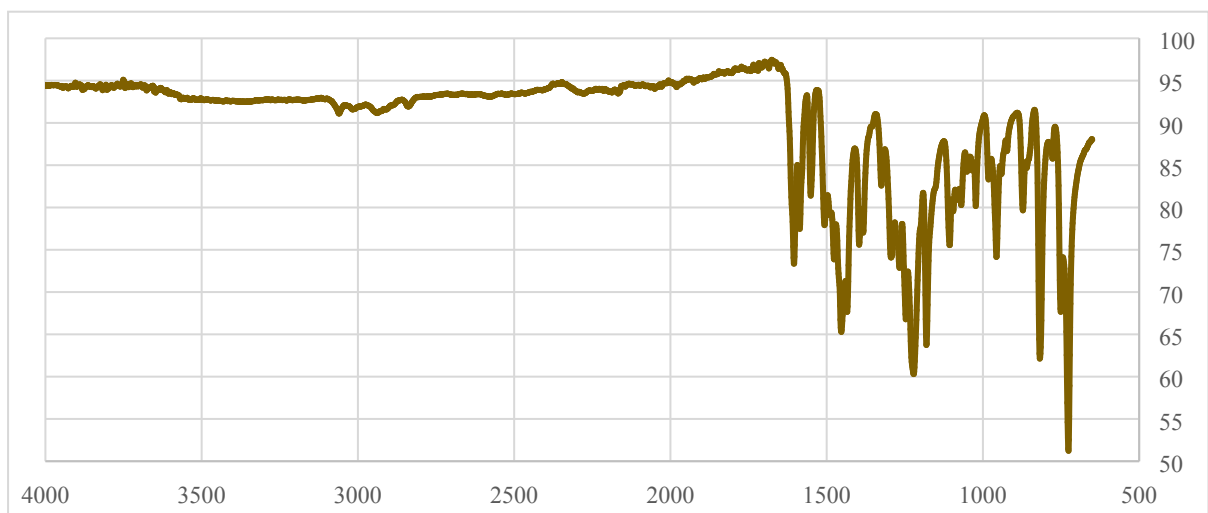
1-Tb



1-Ybs



1-Sm



ESI-MS of 1-Ln

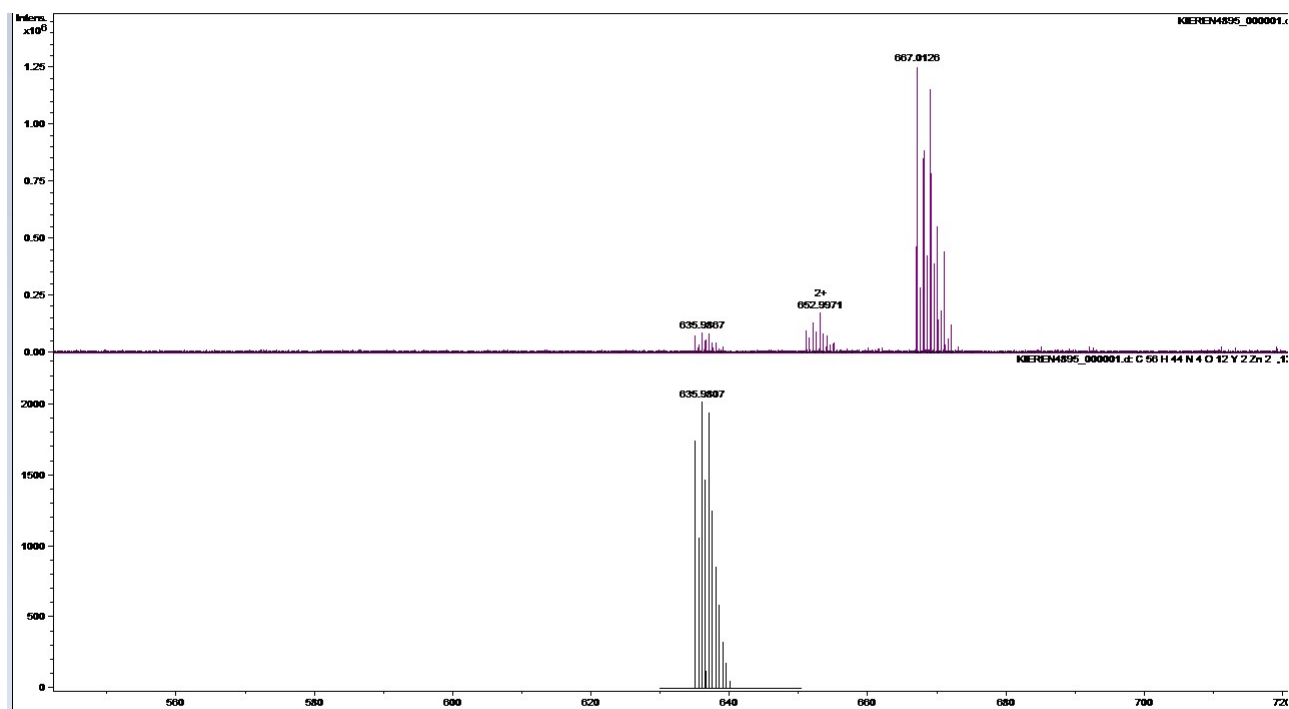


Figure S2. ESI-MS of 1-Y. $[\text{Zn}^{\text{II}}\text{Y}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4]^{2+}$ Fragment – 635.9867, $[\text{Zn}^{\text{II}}\text{Y}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{MeOH})]^{2+}$ Fragment – 652.9971, $[\text{Zn}^{\text{II}}\text{Y}^{\text{II}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{2+}$ Fragment – 667.0126

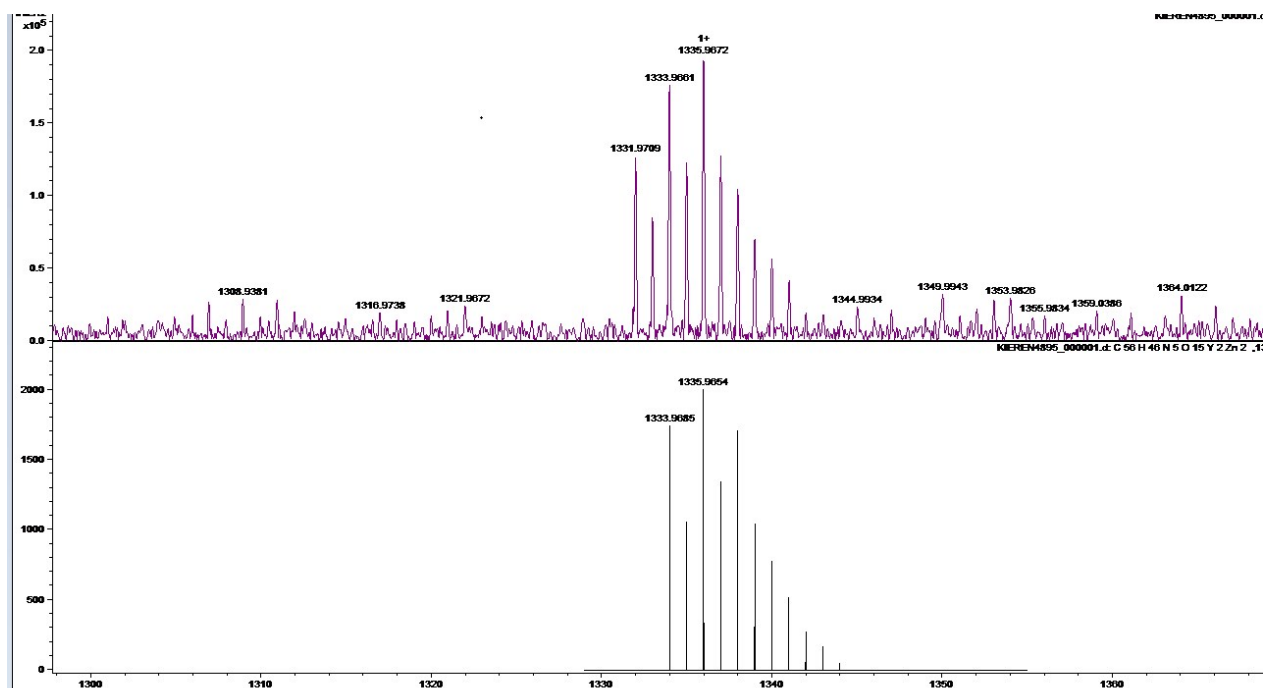


Figure S3. ESI-MS of 1-Y. $[\text{Zn}^{\text{II}}\text{Y}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{1+}$ Fragment -1335.9672

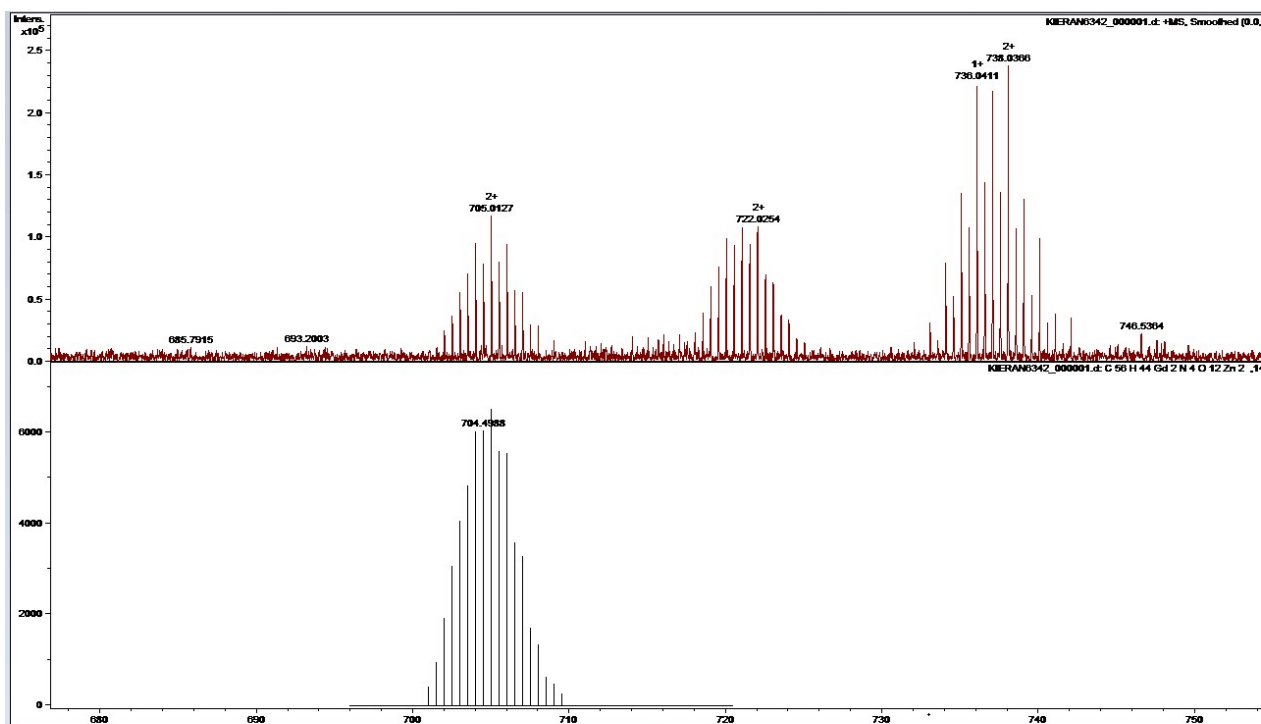


Figure S4. ESI-MS of 1-Gd. $[\text{Zn}^{\text{II}}\text{Gd}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4]^{2+}$ Fragment – 705.0127, $[\text{Zn}^{\text{II}}\text{Gd}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{MeOH})]^{2+}$ Fragment – 722.0254, $[\text{Zn}^{\text{II}}\text{Gd}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{2+}$ Fragment – 738.0366

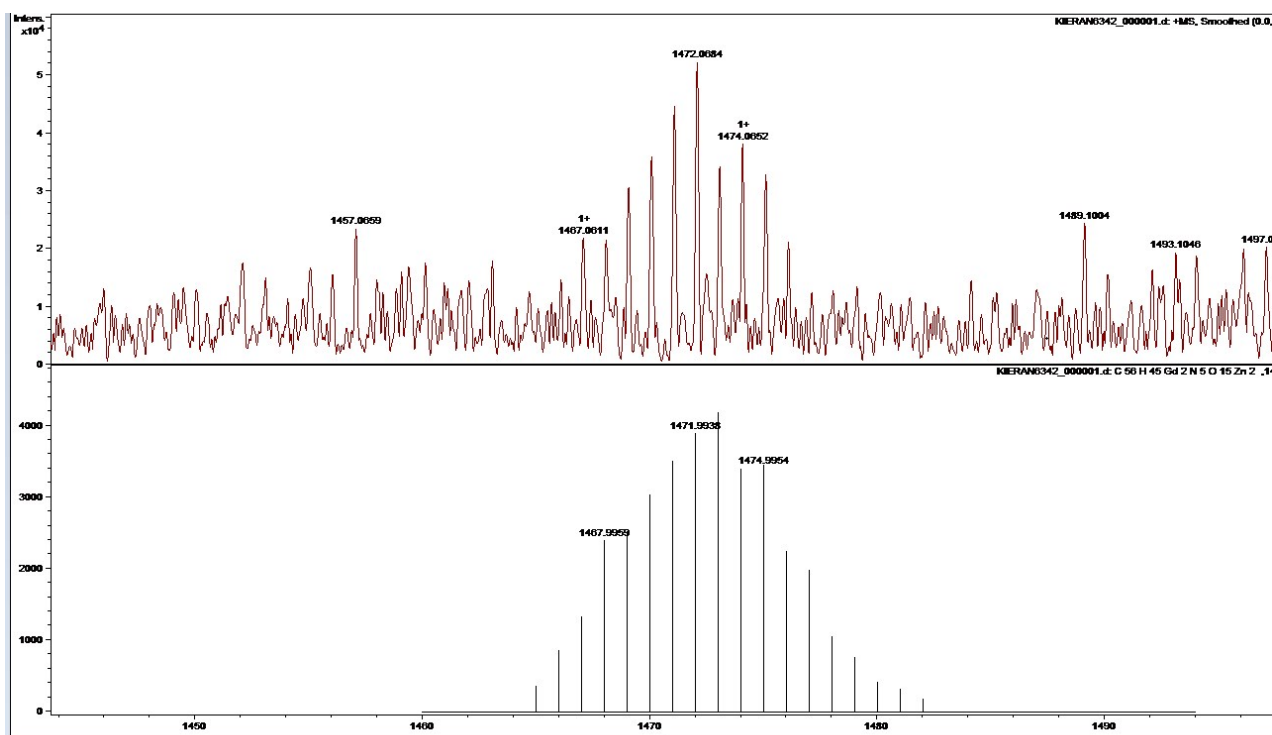


Figure S5. ESI-MS of 1-Gd. $[\text{Zn}^{\text{II}}\text{Gd}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{1+}$ Fragment -1471.9936

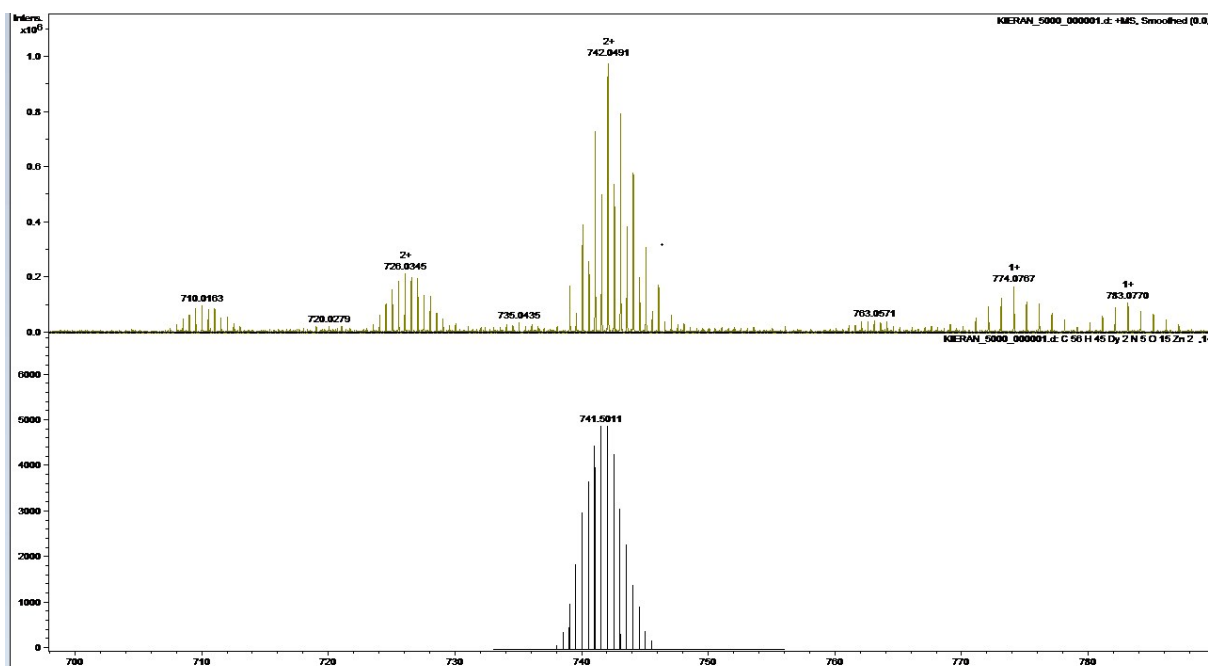


Figure S6. ESI-MS of 1-Dy. $[\text{Zn}^{\text{II}}\text{Dy}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4]^{2+}$ Fragment – 710.0163, $[\text{Zn}^{\text{II}}\text{Dy}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{MeOH})]^{2+}$ Fragment – 726.0345, $[\text{Zn}^{\text{II}}\text{Dy}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{2+}$ Fragment – 742.0491

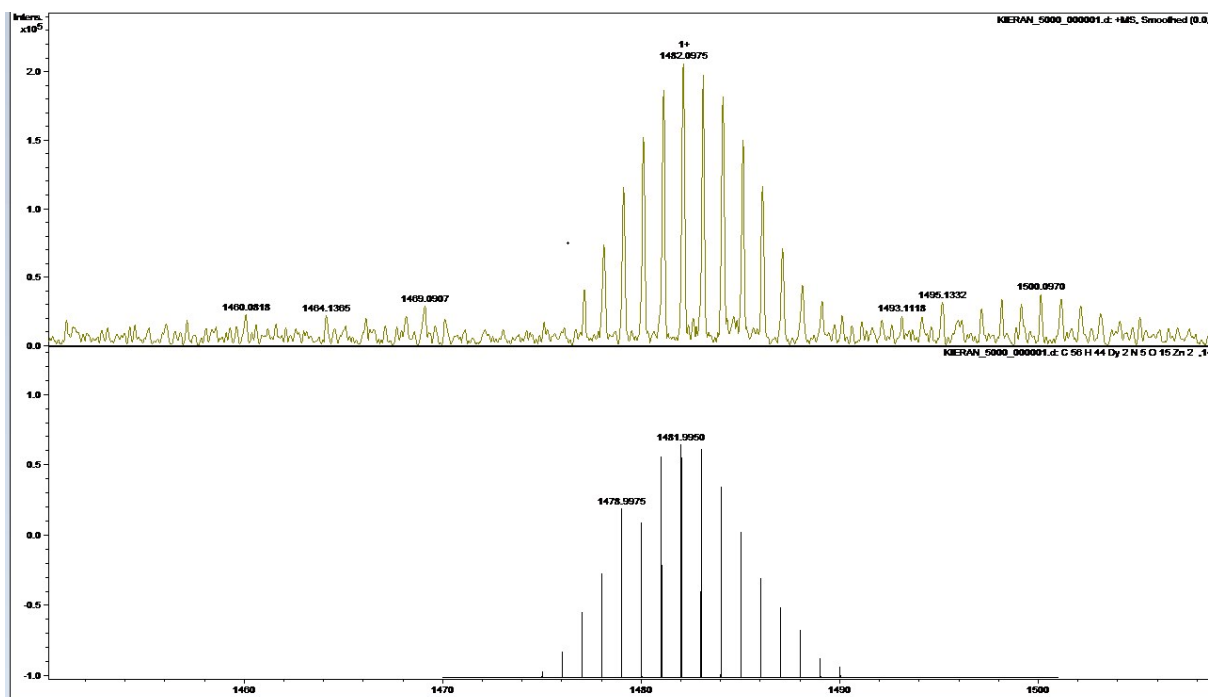


Figure S7. ESI-MS of 1-Dy. $[\text{Zn}^{\text{II}}\text{Dy}^{\text{III}}(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{1+}$ Fragment -1482.0975

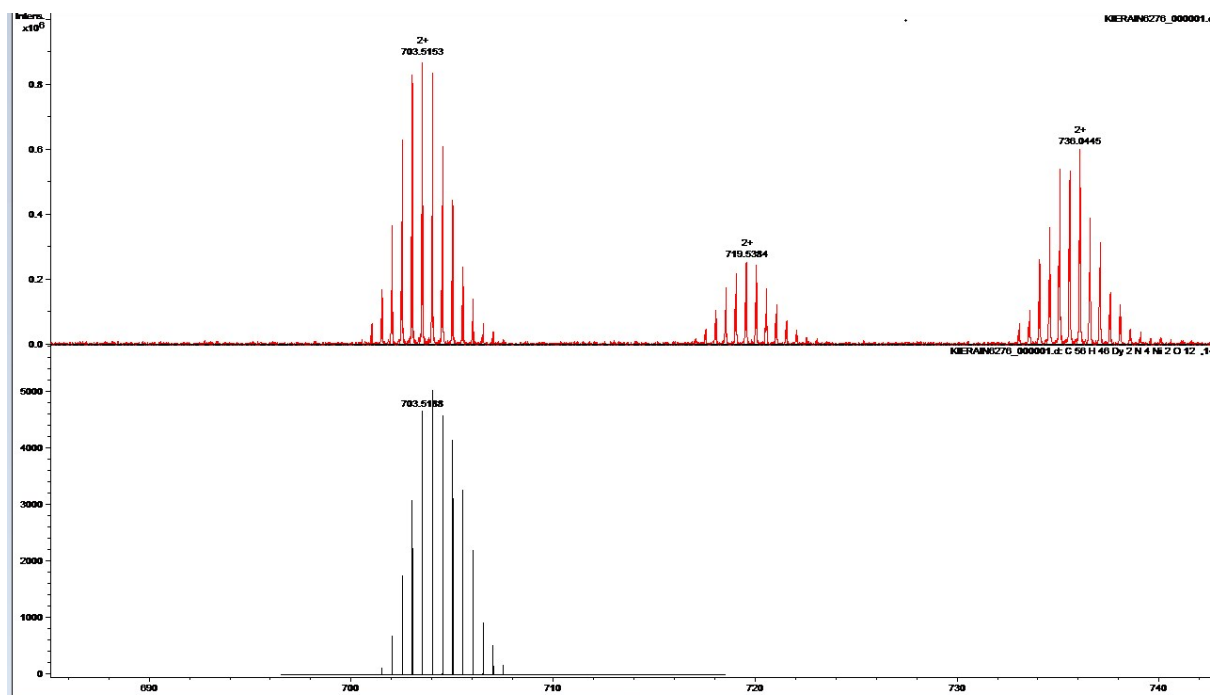


Figure S8. ESI-MS of Dy₂Ni₂. [Ni^{II}Dy^{III}(C₁₄H₁₁NO₃)₄]²⁺ Fragment – 703.5153, [Ni^{II}Dy^{III}(C₁₄H₁₁NO₃)₄(MeOH)]²⁺ Fragment – 719.5384, [Ni^{II}Dy^{II}(C₁₄H₁₁NO₃)₄(NO₃)]²⁺ Fragment – 736.0445

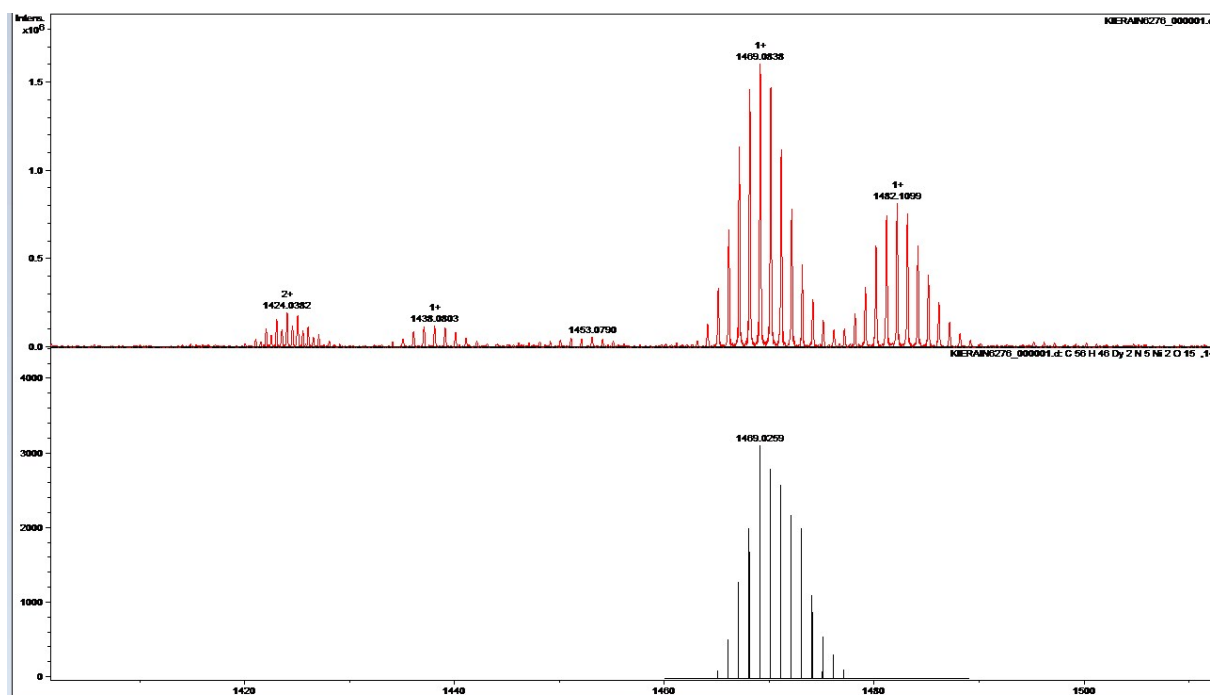


Figure S9. ESI-MS of Y₂Dy₂. [Ni^{II}Dy^{III}(C₁₄H₁₁NO₃)₄(NO₃)]¹⁺ Fragment -1469.0383

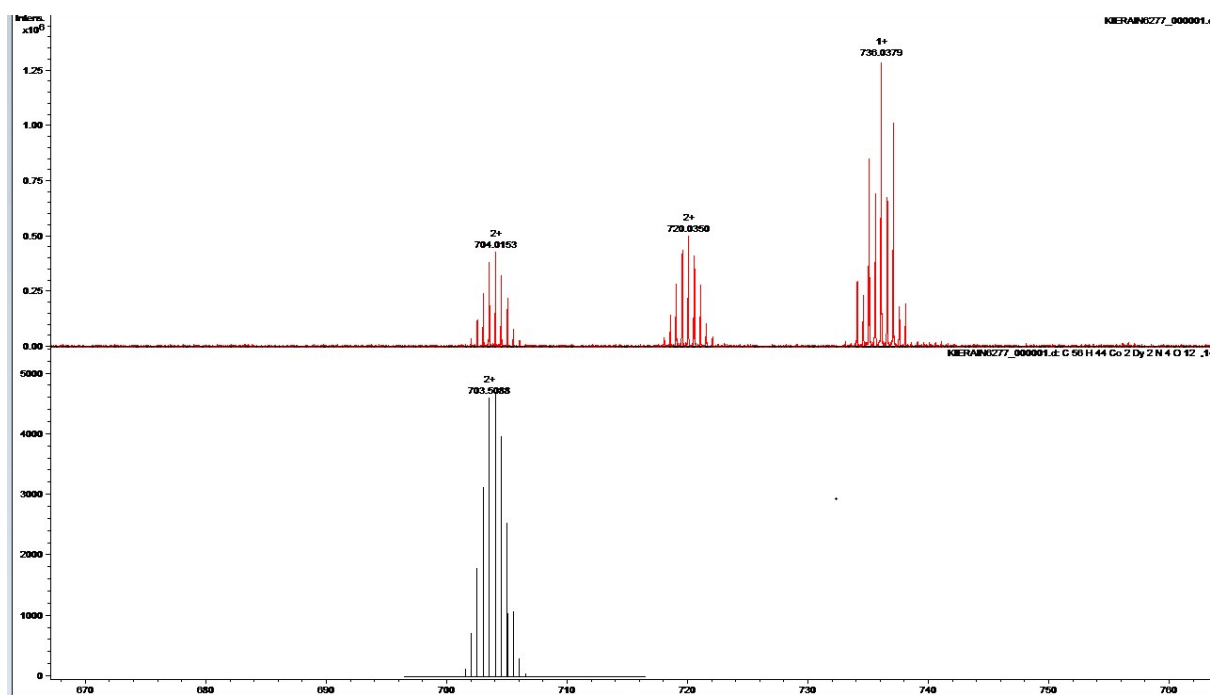


Figure S10. ESI-MS of Dy₂Co₂. [Co^{II}Dy^{III}(C₁₄H₁₁NO₃)₄]²⁺ Fragment – 704.0153, [Dy^{II}Co^{III}(C₁₄H₁₁NO₃)₄(MeOH)]²⁺ Fragment – 720.0350, [Co^{II}Dy^{II}(C₁₄H₁₁NO₃)₄(NO₃)]²⁺ Fragment – 736.0379

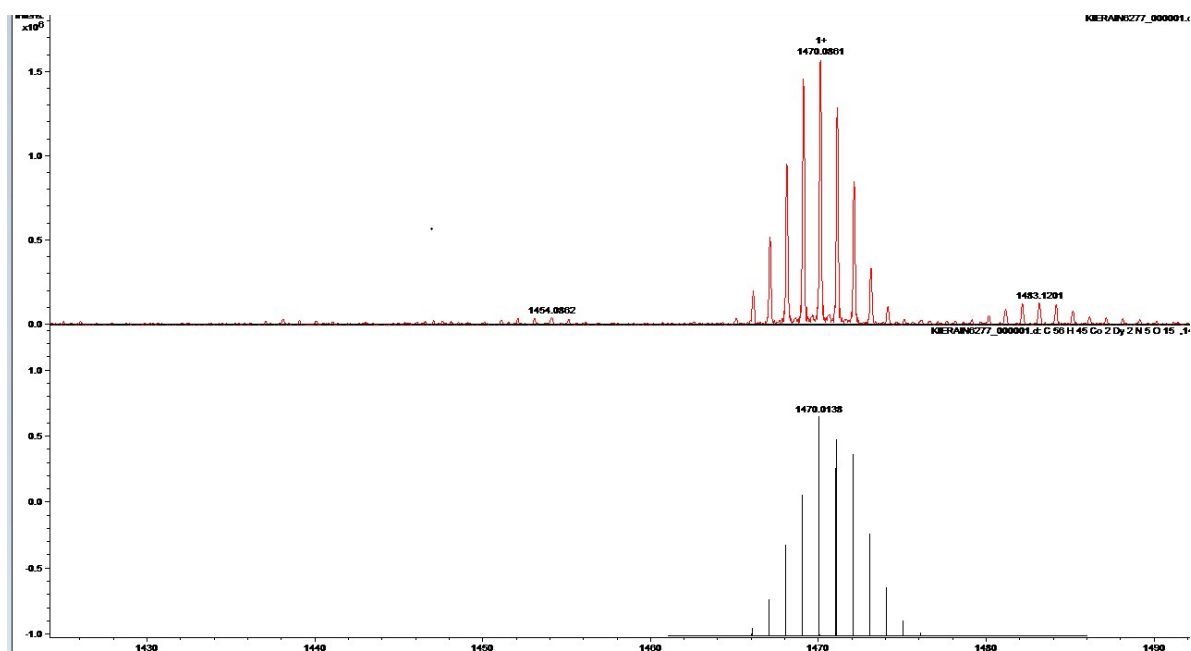


Figure S11. ESI-MS of Y₂Dy₂. [Ni^{II}Dy^{III}(C₁₄H₁₁NO₃)₄(NO₃)]¹⁺ Fragment -1470.0136

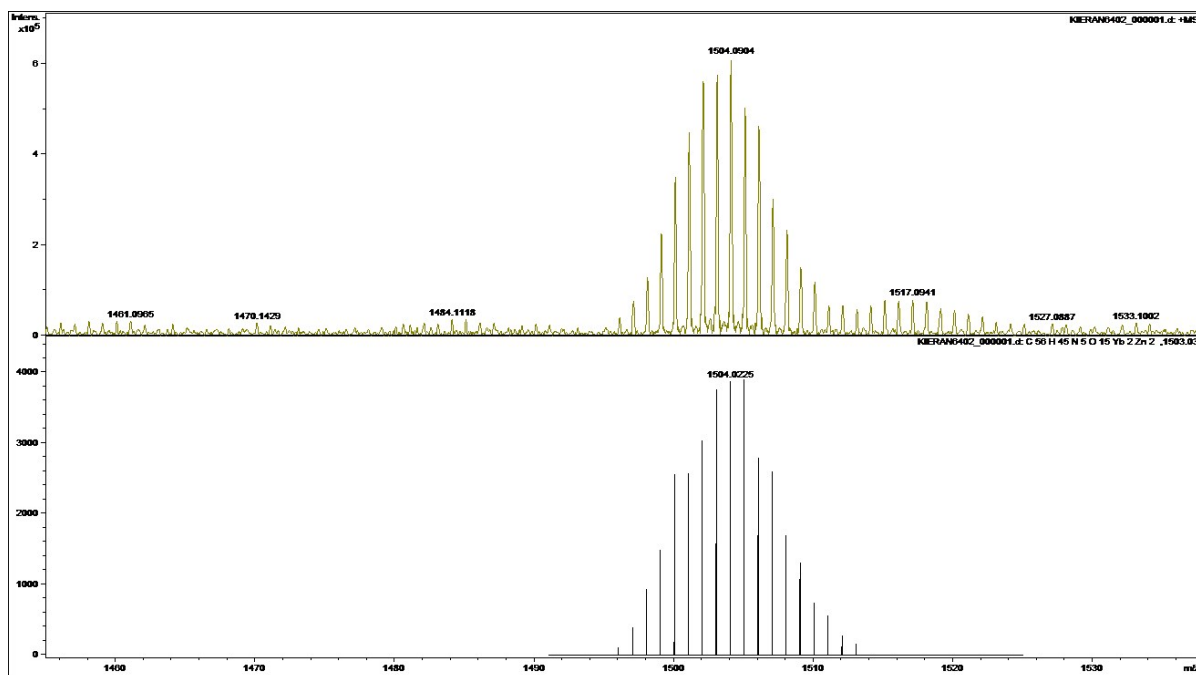


Figure S12. ESI-MS of 1-Yb [Yb₂Zn₂(C₁₄H₁₁NO₃)₄(NO₃)]¹⁺ Fragment

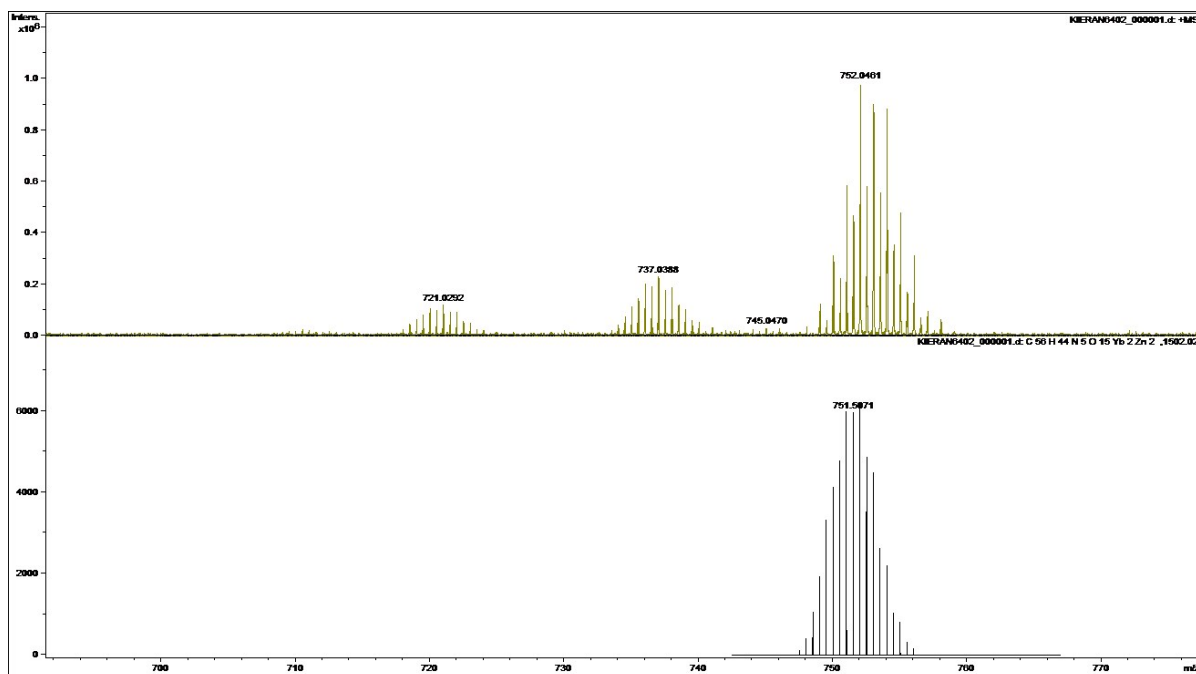


Figure S13. ESI-MS of 1-Yb [Yb₂Zn₂(C₁₄H₁₁NO₃)₄(NO₃)]²⁺ Fragment

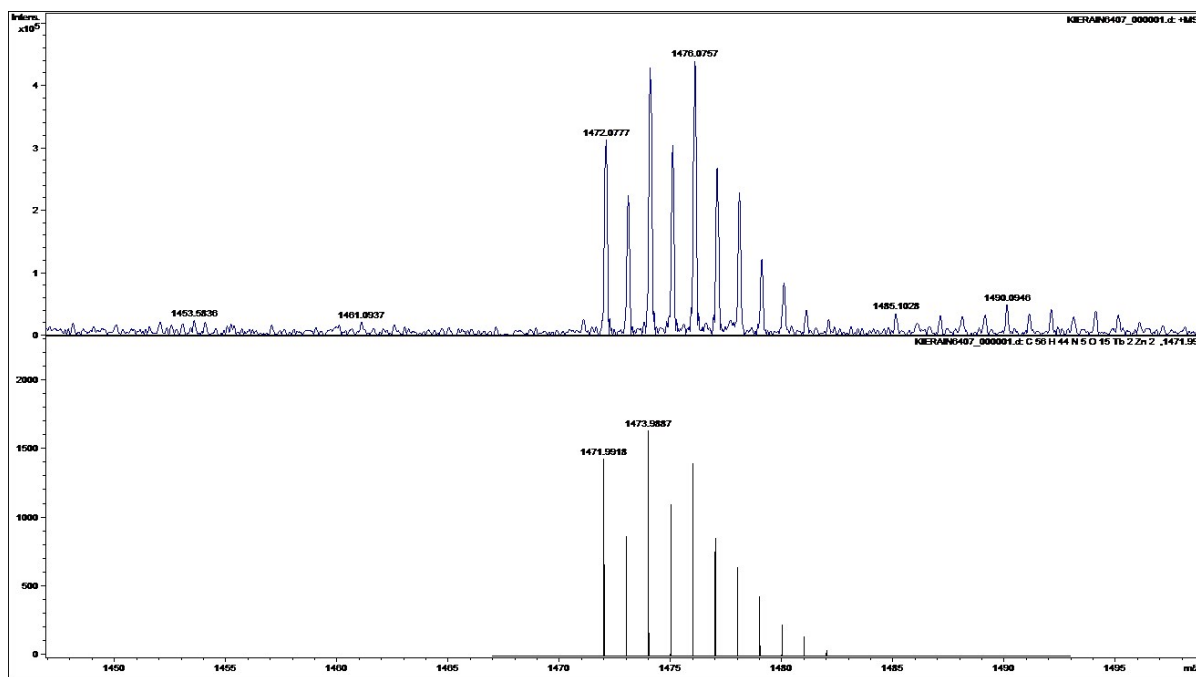


Figure S14. ESI-MS of 1-Tb [Tb₂Zn₂(C₁₄H₁₁NO₃)₄(NO₃)]¹⁺ Fragment

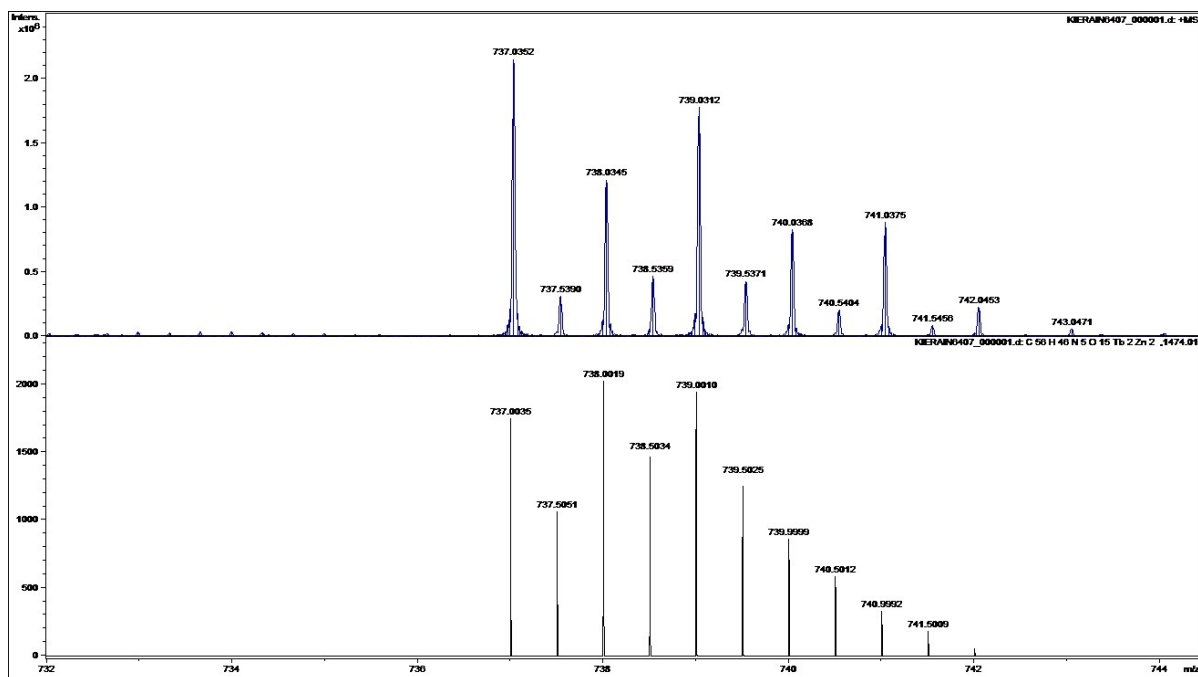


Figure S15. ESI-MS of 1-Tb [Tb₂Zn₂(C₁₄H₁₁NO₃)₄(NO₃)]²⁺ Fragment

1-Eu

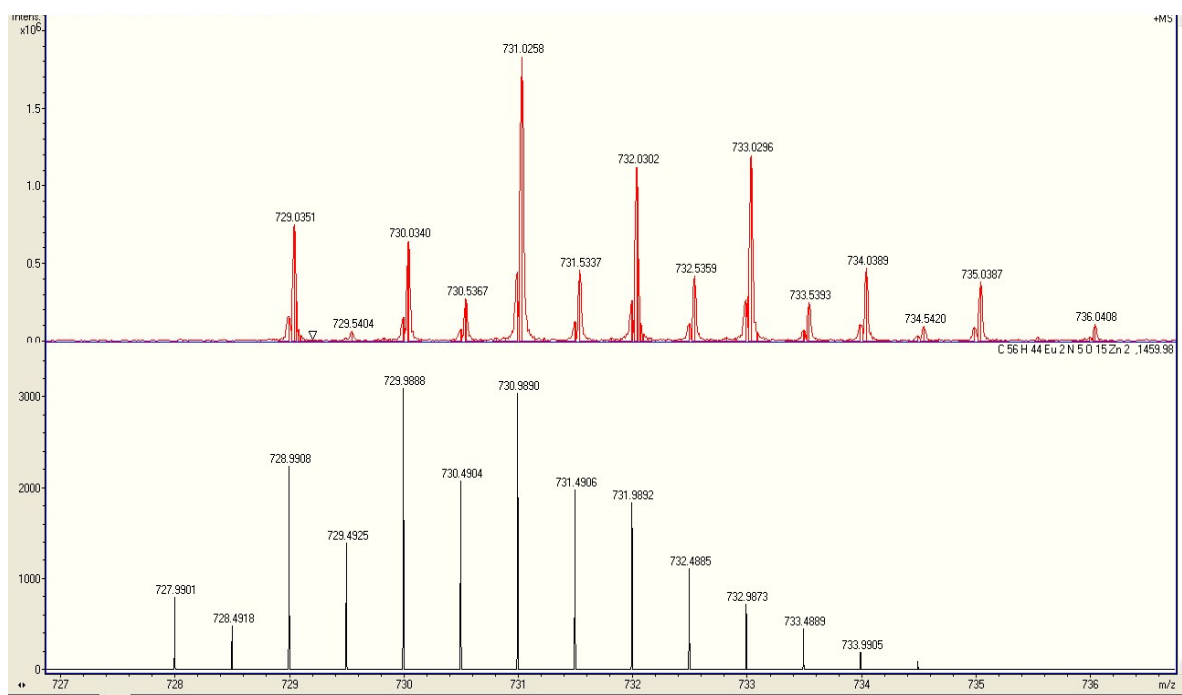


Figure S16. ESI-MS of 1-Eu $[\text{Eu}_2\text{Zn}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{2+}$ Fragment

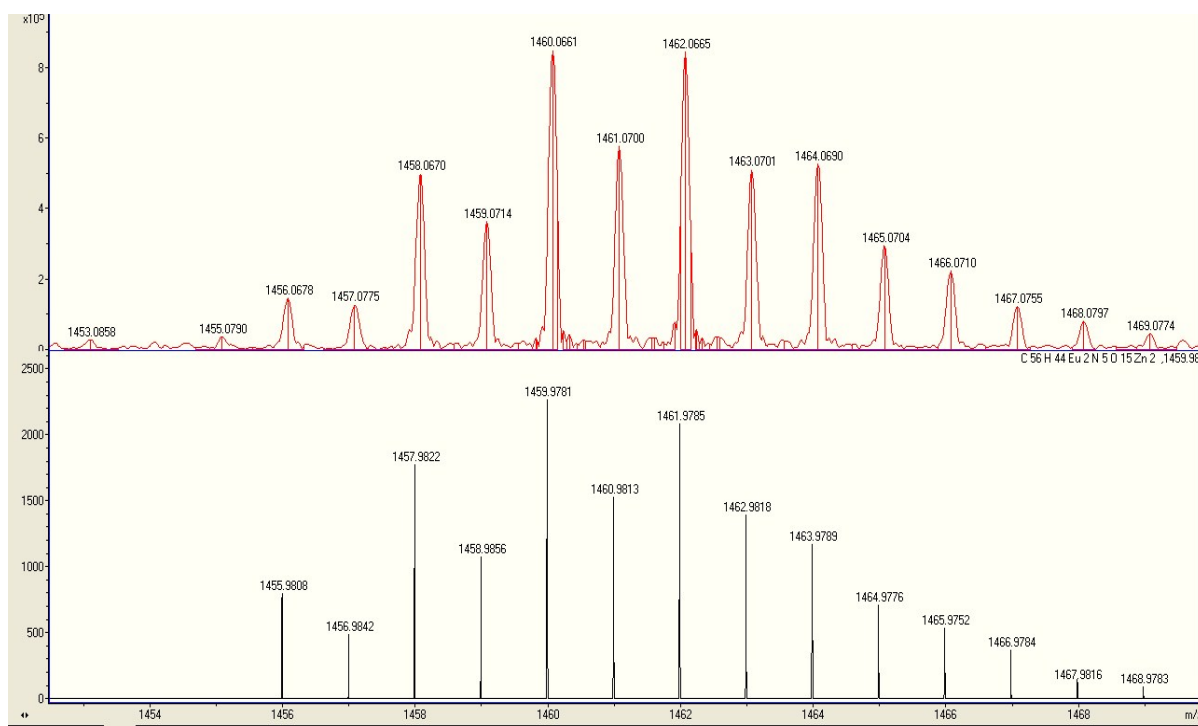


Figure S17. ESI-MS of 1-Eu $[\text{Eu}_2\text{Zn}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{1+}$ Fragment

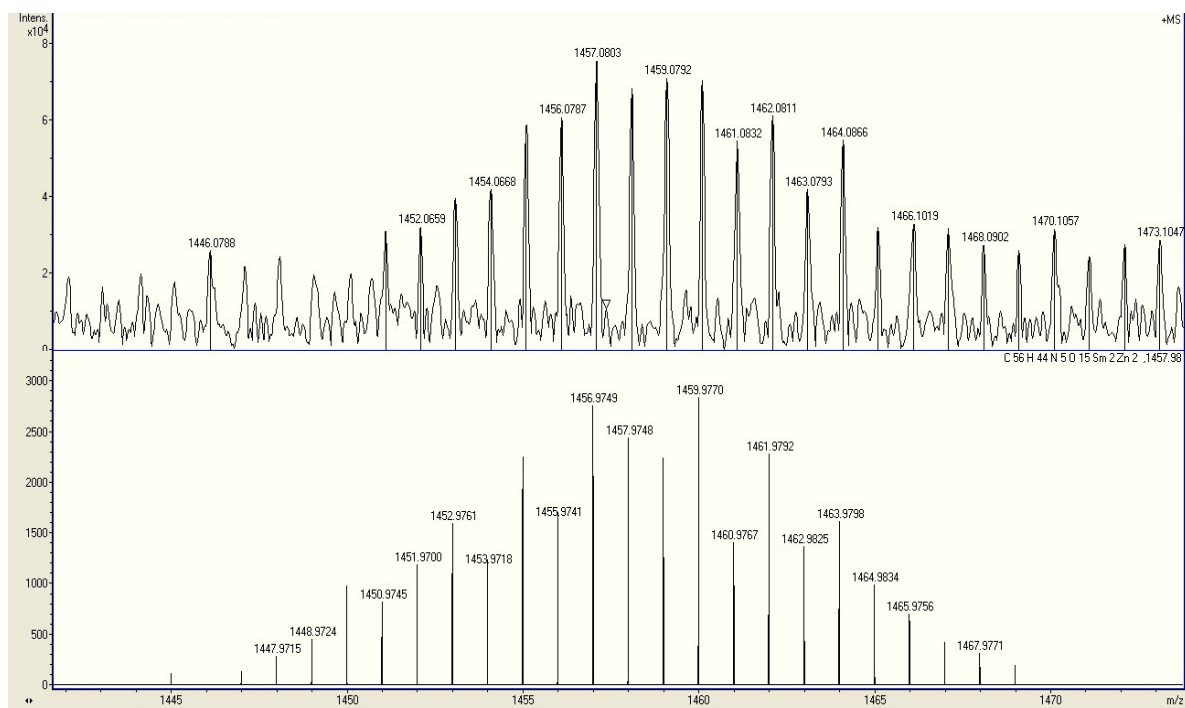


Figure S18. ESI-MS of 1-Sm $[\text{Sm}_2\text{Zn}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{1+}$ Fragment

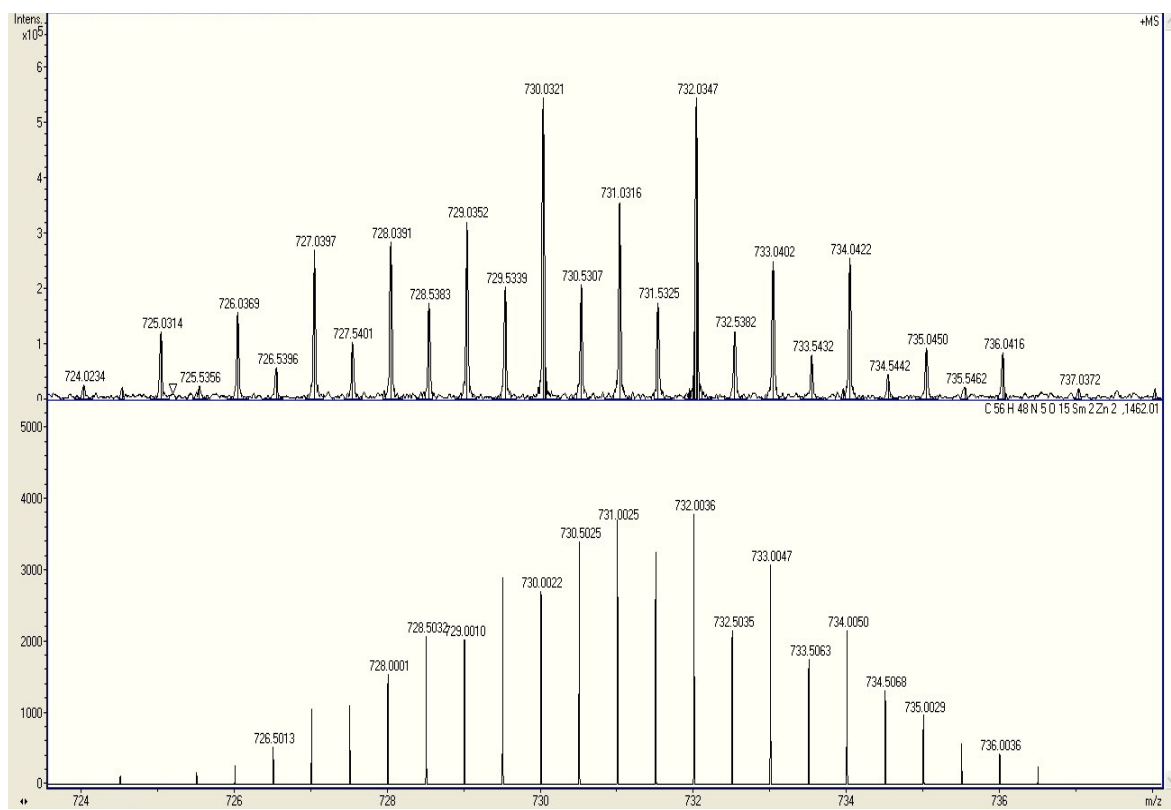
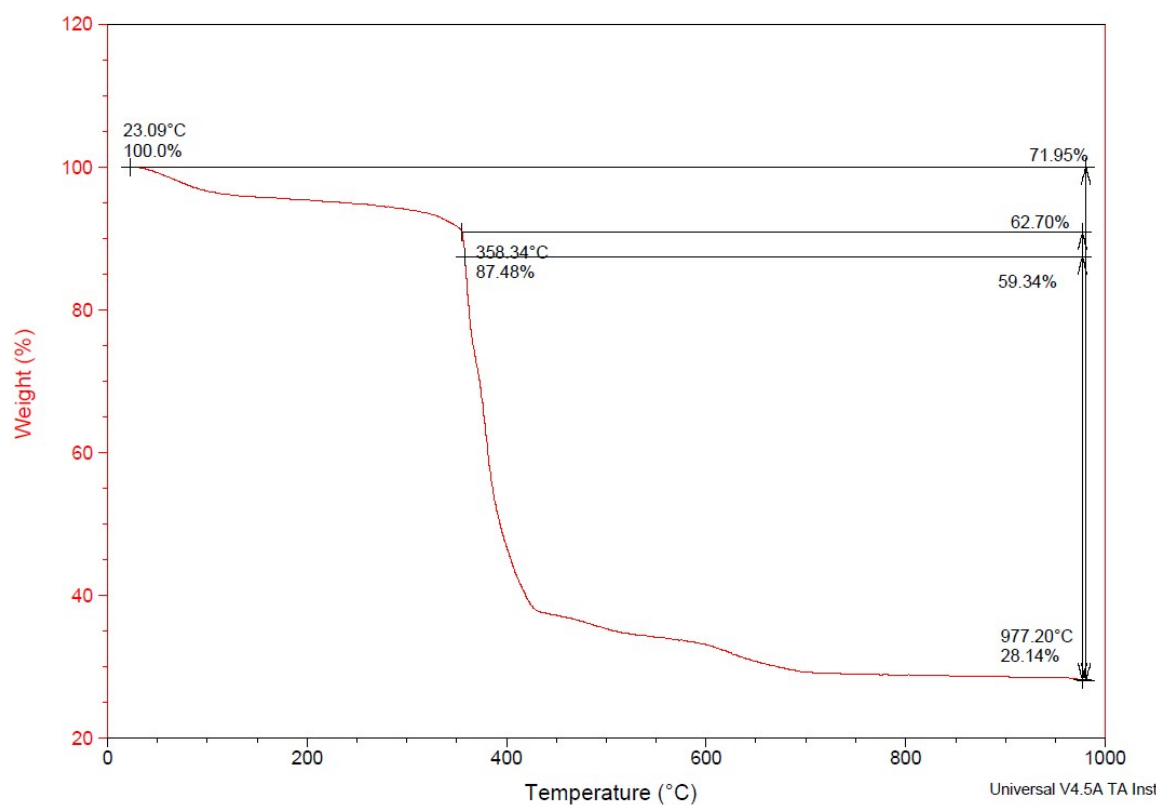


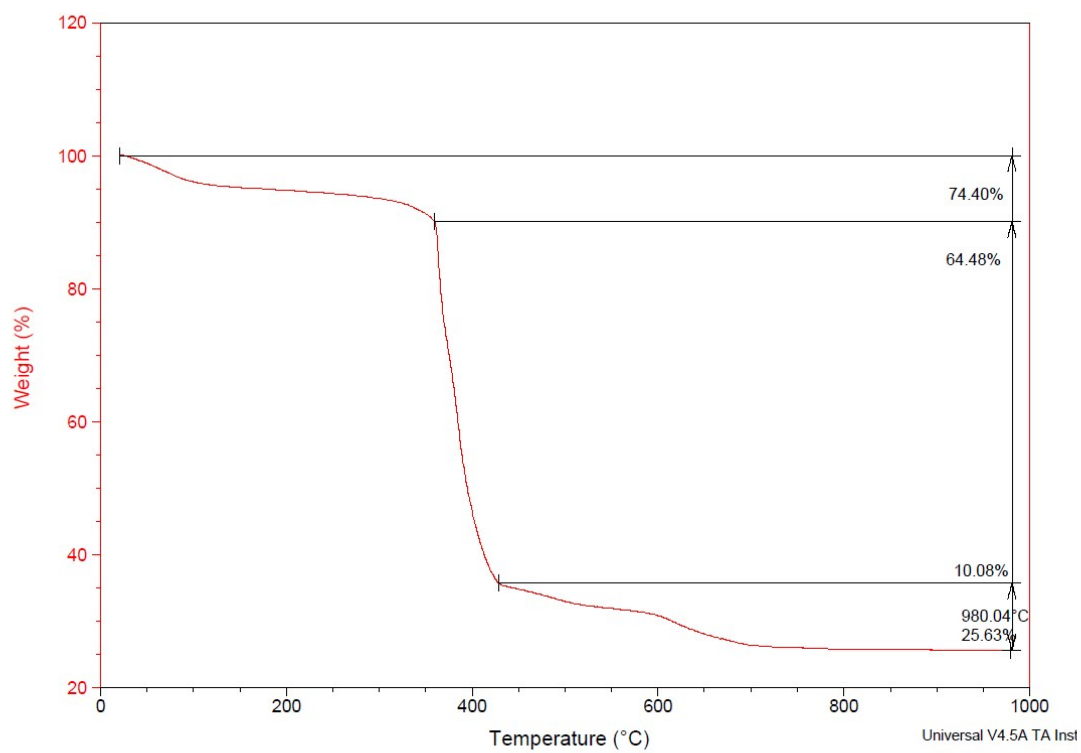
Figure S19. ESI-MS of 1-Sm $[\text{Sm}_2\text{Zn}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4(\text{NO}_3)]^{2+}$ Fragment

TGA of 1-Ln

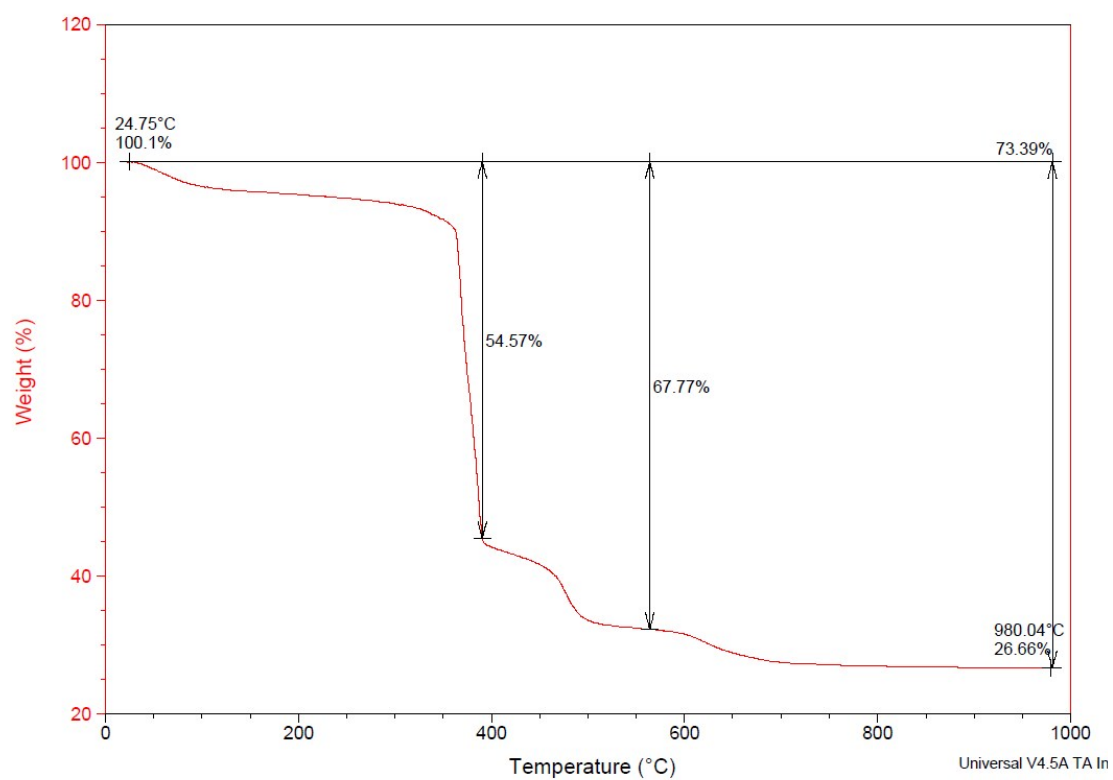
1-Y



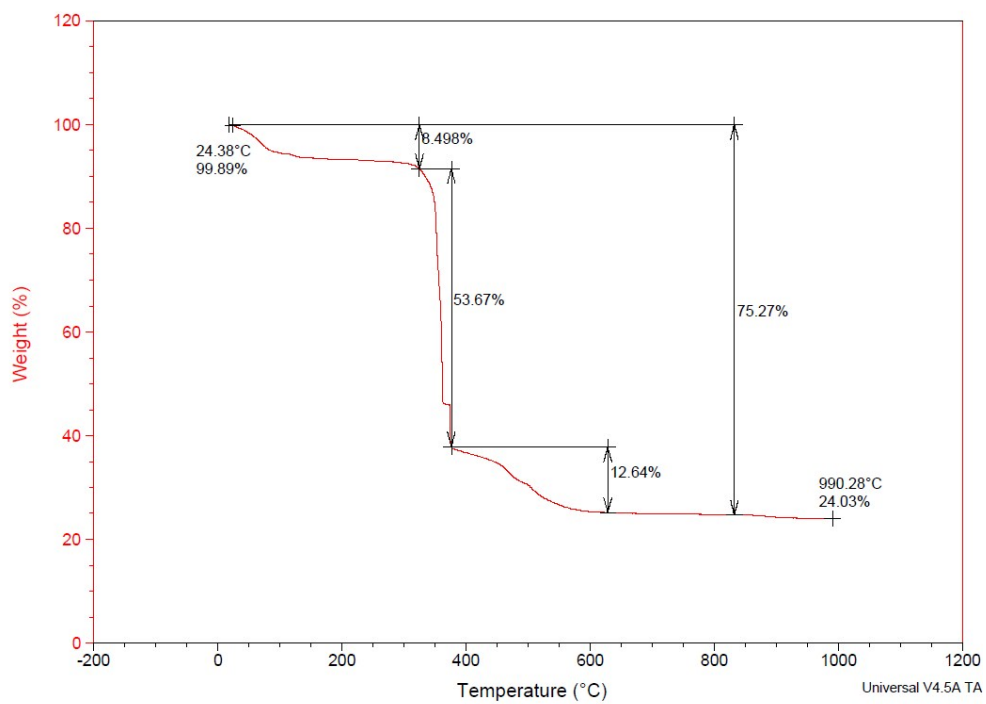
1-Dy



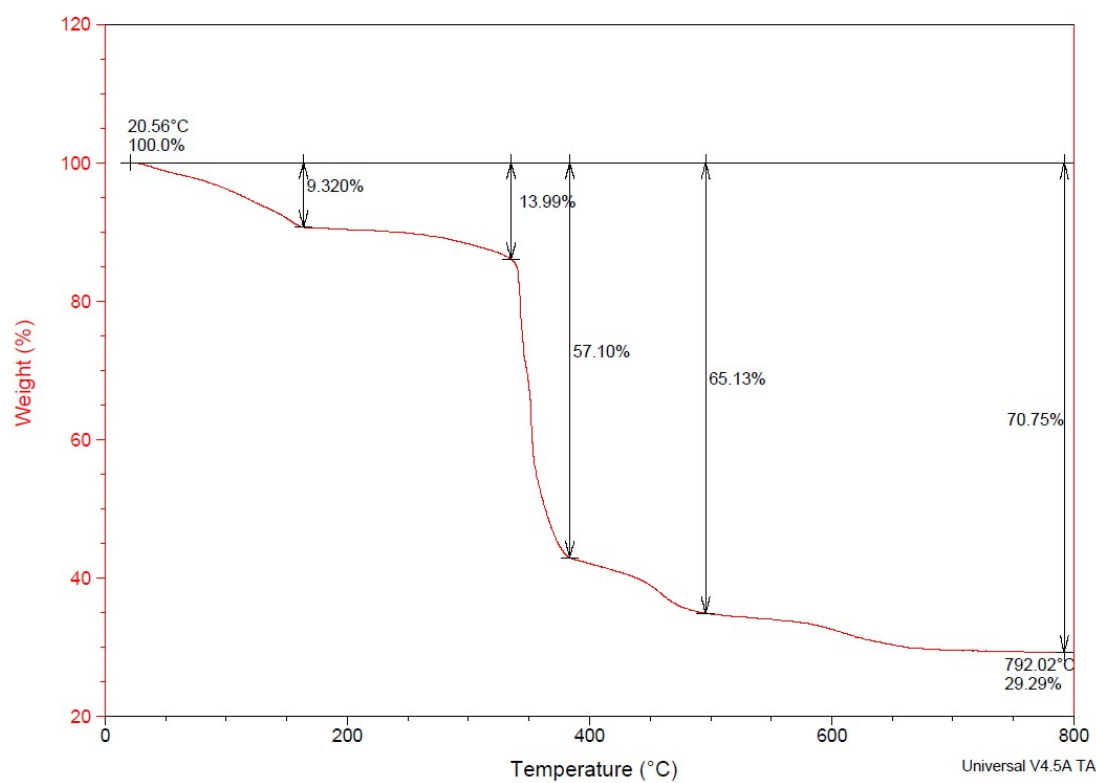
1-Gd



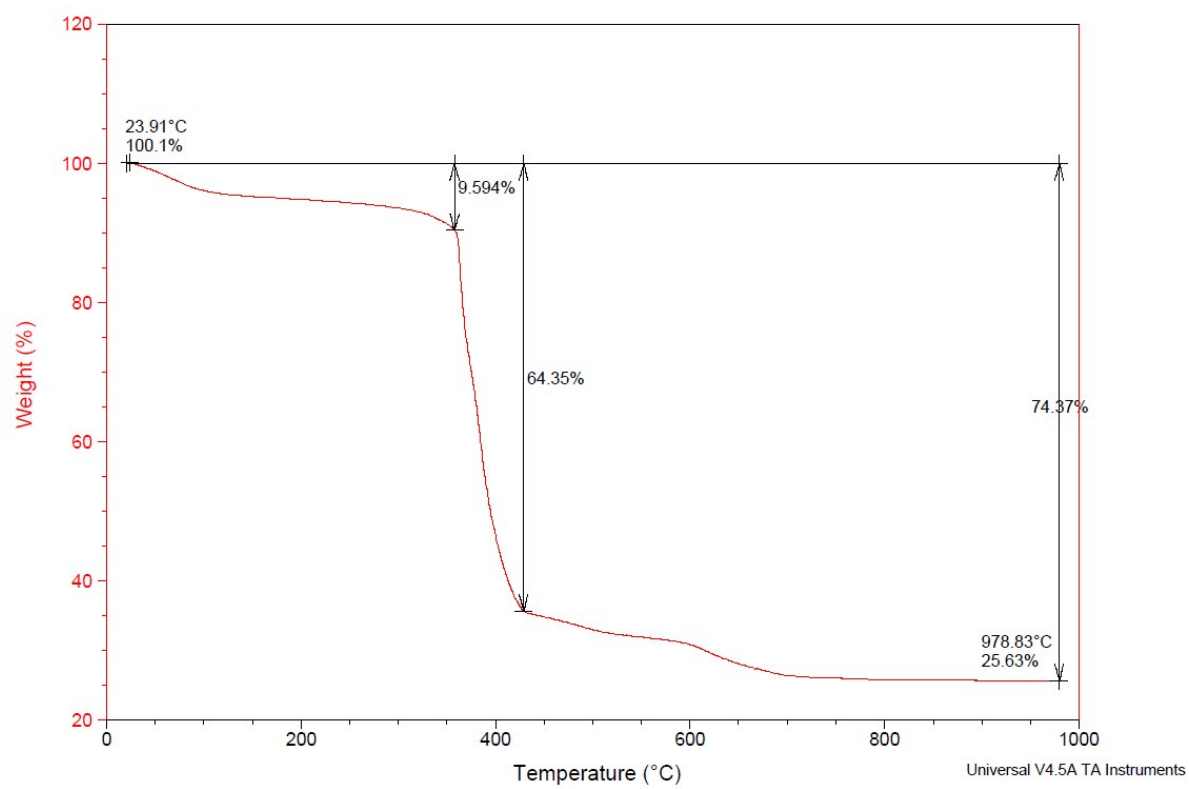
1-Tb



1-Yb



1-Eu



1Sm

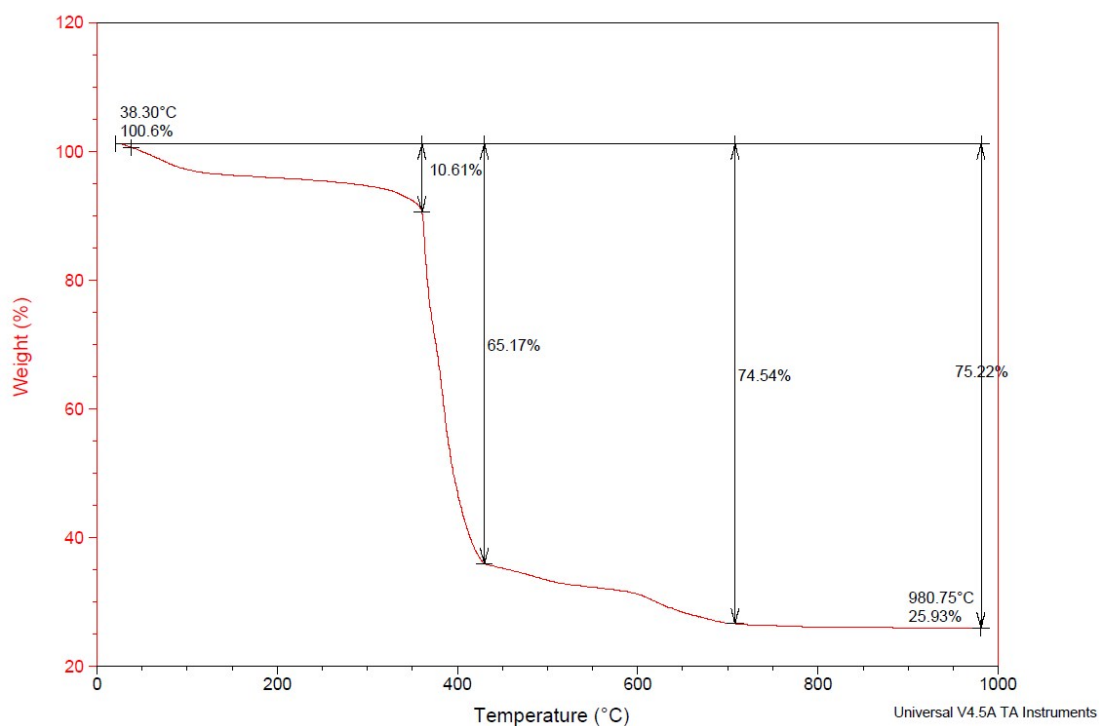


Table S3. Comparison of catalytic activity with multiple solvent systems

Entry ^[a]	Solvent	Loading/[mol%] ^[b]	Time/ h	Yield/ [%] ^[c]
1	Toluene	10	12	0
2	CHCl ₃	10	12	0
3	DME	10	12	0
4	DMF	10	12	16
5	MeCN	10	12	30
6	EtOH	10	12	95
7	EtOH/H ₂ O	10	12	Quantitative
8	MeCN/H ₂ O	10	12	42
9	MeOH/ H ₂ O	10	12	92
10	iPrOH/H ₂ O	10	12	70

[a] Reaction conditions: Indole, 1 mmol; benzaldehyde, 0.5 mmol; solvent 10mL; room temperature. [b] Catalyst loading calculated per equivalent of Ln^{III}. [c] Determined by ¹H NMR spectroscopy

Table S4. Comparison of catalytic activity of **1Dy** with a range of EtOH and H₂O ratios

Entry ^[a]	% EtOH	Loading/[mol%] ^[b]	Time/ h	Yield/ [%] ^[c]
1	100	2.5	12	89
2	90	2.5	12	92
3	80	2.5	12	95
4	70	2.5	12	97
5	60	2.5	12	Quantitative
6	50	2.5	12	Quantitative

[a] Reaction conditions: Indole, 1 mmol; benzaldehyde, 0.5 mmol; solvent 10mL; room temperature. [b] Catalyst loading calculated per equivalent of Ln^{III}. [c] Determined by ¹H NMR spectroscopy

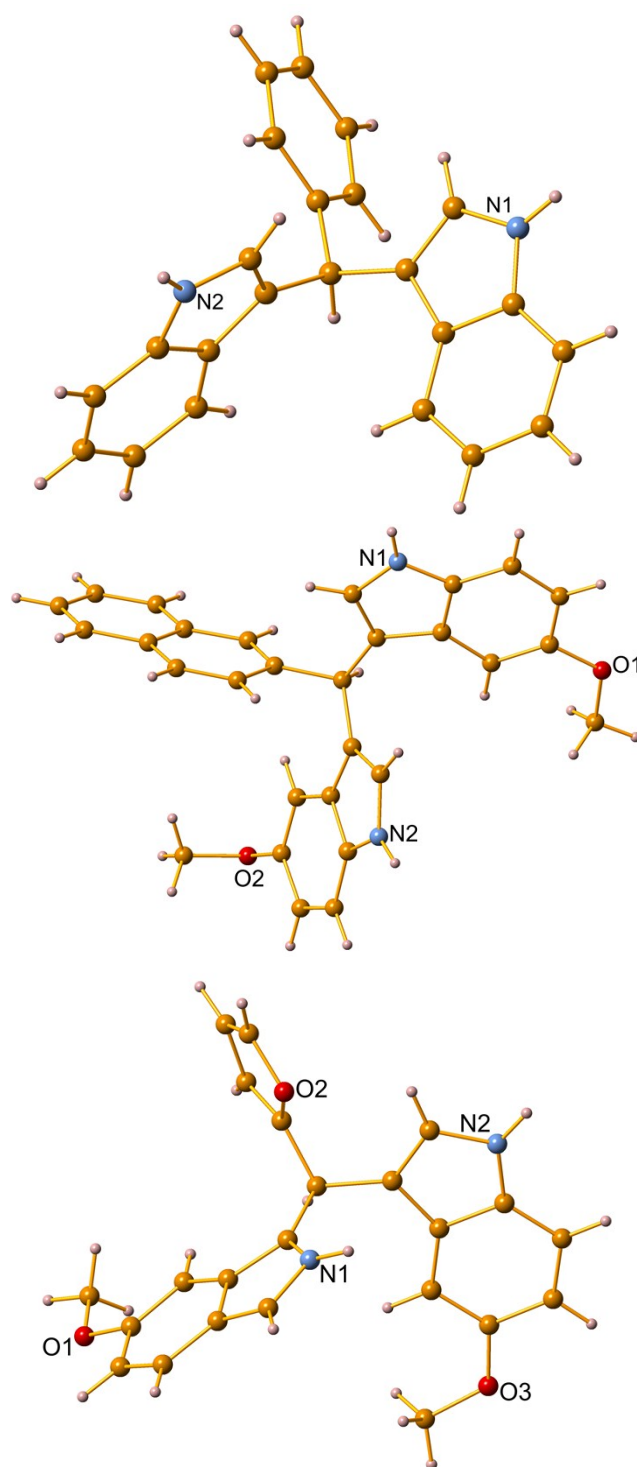


Figure S20. The crystal structures of **7a** (upper), **8c** (middle) and **8f** (lower)

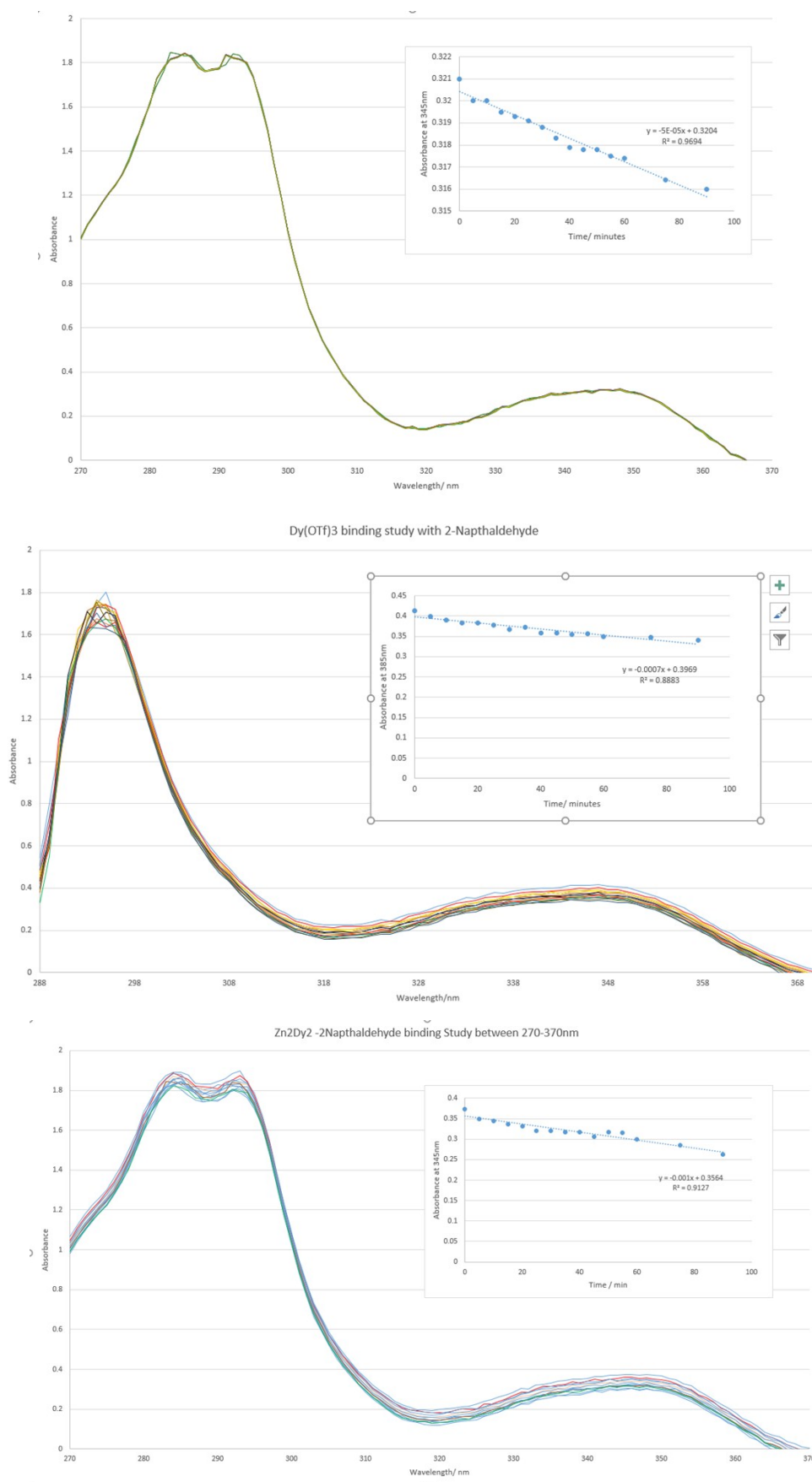


Figure S21 UV-Vis binding studies of Zn(OTf)₂, Dy(OTf)₃ and **1Dy** with 2-Naphthaldehyde

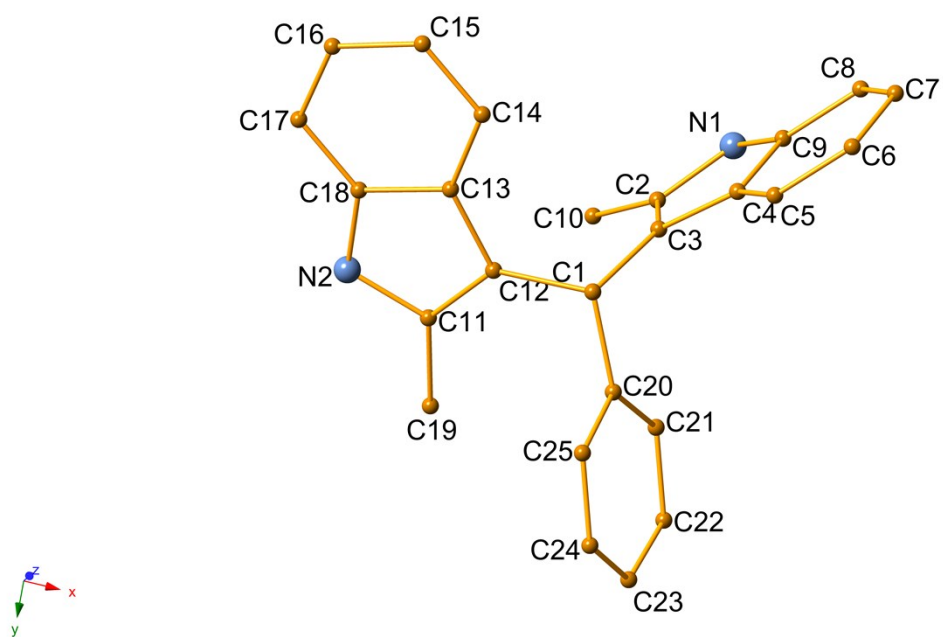
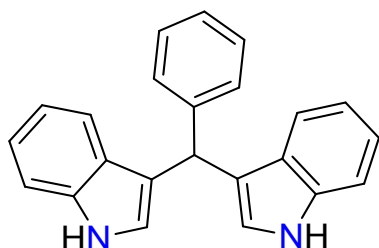


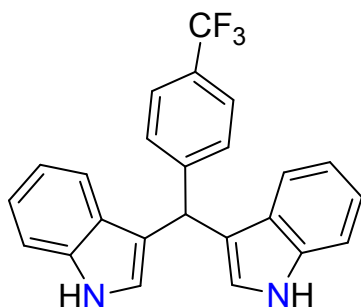
Figure S22. The crystal structure of compound **10**.

(7a) 3,3'-(phenylmethylene)bis(1H-indole)



To a mixed solution of EtOH/H₂O (2:1 in 10mL), benzaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to benzaldehyde). The resultant solution was stirred for 12H, upon which time product had precipitated. The cloudy solution was filtered and precipitate washed with hexanes (3x10mL) and water (3x10mL). ¹H NMR (500 MHz, CDCl₃) δ 7.74 (s, 2H), 7.47 – 7.17 (m, 10H), 7.05 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 6.61 (dd, *J* = 2.5, 1.1 Hz, 2H), 5.92 (s, 1H). ¹³C NMR (126 MHz, cdcl₃) δ 165.91, 144.07, 136.72, 128.75, 128.23, 127.13, 126.15, 123.63, 123.61, 121.93, 119.95, 119.72, 119.26, 117.73, 111.06, 77.30, 77.04, 76.79, 40.26, 40.24, -8.79.

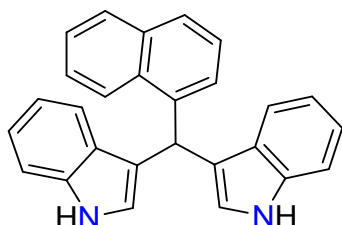
(7b) 3,3'-((4-(trifluoromethyl)phenyl)methylene)bis(1H-indole)



To a mixed solution of EtOH/H₂O (2:1 in 10mL), 4-(trifluoromethyl) benzaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to benzaldehyde). The resultant solution was stirred for 12H, upon which time product had precipitated. The cloudy solution was filtered and precipitate washed with hexanes (3x10mL) and water (3x10mL). ¹H NMR (500 MHz,) δ 8.28 (s, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 4H), 7.18 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 2H), 7.02 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 2H), 6.62 (dd, *J* = 2.5,

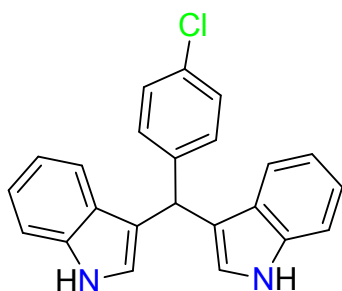
1.1 Hz, 2H), 5.95 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 136.71, 128.99, 126.85, 125.22, 125.19, 125.16, 123.59, 122.17, 119.70, 119.45, 118.83, 111.10, 77.23, 76.97, 76.72, 40.12. ESI-MS expected $\text{C}_{24}\text{H}_{17}\text{F}_3\text{N}_2$: 390.1; observed 389.1243.

(7d) 3,3'-(naphthalen-1-ylmethylene)bis(1H-indole)



To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 1-Napthaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO_4 and concentrated under reduced pressure. The resulting oil was washed with Hexanes (60mL) resulting in a red solid which was further washed with water (3x10mL). ^1H NMR (500 MHz,) δ 8.21 – 8.15 (m, 1H), 7.89 (d, J = 8.0 Hz, 3H), 7.75 (d, J = 8.1 Hz, 1H), 7.37 (pd, J = 20.9, 20.4, 10.5 Hz, 8H), 7.19 (t, J = 7.7 Hz, 2H), 7.01 (t, J = 7.9 Hz, 2H), 6.68 (s, 1H), 6.59 (s, 2H).

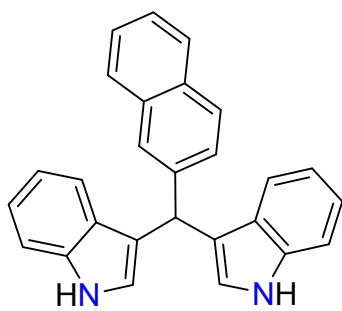
(7e) 3,3'-((4-chlorophenyl)methylene)bis(1H-indole)



To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 4-Chlorobenzaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water

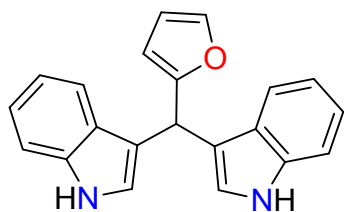
(20mL). The ethyl acetate layer was dried with MgSO_4 and concentrated under reduced pressure. The resulting oil was washed with Hexanes (60mL) resulting in a red solid which was further washed with water (3x10mL). ^1H NMR (500 MHz, CDCl_3) δ 7.90 (s, 2H), 7.37 (t, J = 8.5 Hz, 5H), 7.31 – 7.15 (m, 6H), 7.03 (t, J = 7.5 Hz, 2H), 6.63 (d, J = 2.4 Hz, 2H), 5.87 (s, 1H), 1.29. ^{13}C NMR (126 MHz, cdcl_3) δ 142.57, 136.72, 131.79, 130.05, 128.33, 126.91, 123.55, 122.06, 119.79, 119.35, 119.23, 111.08, 77.24, 76.99, 76.73, 39.65. ESI-MS expected $\text{C}_{23}\text{H}_{17}\text{ClN}_2$: 356.1; observed 355.0977.

(7c) 3,3'-(naphthalen-2-ylmethylene)bis(1H-indole)



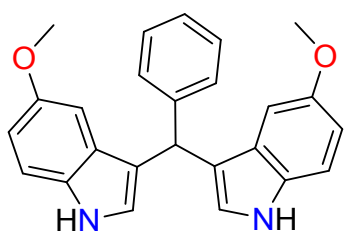
To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 2-napthaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to benzaldehyde). The resultant solution was stirred for 12H, upon which time product had precipitated. The cloudy solution was filtered and precipitate washed with hexanes (3x10mL) and water (3x10mL). ^1H NMR (500 MHz, CDCl_3) δ 7.89 (s, 2H), 7.75 (td, J = 29.9, 24.9, 5.8 Hz, 4H), 7.55 – 7.49 (m, 1H), 7.41 (d, J = 7.9 Hz, 4H), 7.35 (d, J = 8.2 Hz, 2H), 7.20 – 7.13 (m, 2H), 6.99 (d, J = 7.9 Hz, 2H), 6.67 (s, 2H), 6.06 (s, 1H). ^{13}C NMR (126 MHz, cdcl_3) δ 141.58, 136.73, 133.61, 132.37, 127.88, 127.72, 127.70, 127.53, 127.13, 126.74, 125.63, 125.23, 123.72, 121.96, 119.94, 119.60, 119.29, 110.99, 77.23, 76.98, 76.78, 76.73, 40.34, 1.00.

(7f) 3,3'-(furan-2-ylmethylene)bis(1H-indole)



To a mixed solution of EtOH/H₂O (2:1 in 10mL), furaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO₄ and concentrated under reduced pressure. The resulting oil was washed with Hexanes (60mL) resulting in a white solid which was further washed with water (3x10mL). ¹H NMR (500 MHz,) δ 7.64 – 7.54 (m, 5H), 7.43 (dd, J = 1.8, 0.9 Hz, 1H), 7.18 (ddd, J = 7.9, 6.6, 1.5 Hz, 3H), 6.75 – 6.70 (m, 2H), 6.39 (dd, J = 3.2, 1.8 Hz, 1H), 6.18 – 6.13 (m, 1H), 6.06 – 6.02 (m, 1H). ¹³C NMR (126 MHz, cdcl₃) δ 157.04, 153.87, 141.19, 131.74, 127.23, 123.81, 116.89, 112.06, 111.73, 110.12, 109.99, 106.64, 101.73, 77.24, 76.99, 76.74, 34.21. ESI-MS expected C₂₁H₁₆N₂O: 312.1; observed 311.1173.

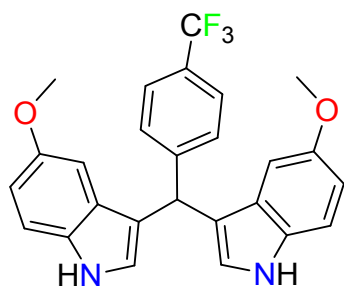
(8a) 3,3'-(phenylmethylene)bis(5-methoxy-1H-indole)



To a mixed solution of EtOH/H₂O (2:1 in 10mL), benzaldehyde (0.5mmol) and 5-methoxyIndole (1mmol) were added followed by catalyst (2.5% with respect to benzaldehyde). The resultant solution was stirred for 12H, upon which time product had precipitated. The cloudy solution was filtered and precipitate washed with hexanes (3x10mL) and water (3x10mL).

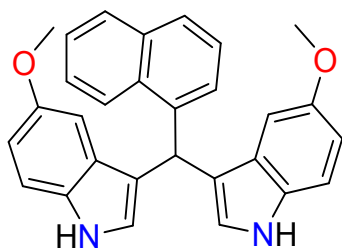
^1H NMR (500 MHz, CDCl_3) δ 7.80 (s, 2H), 7.35 (d, J = 7.7 Hz, 2H), 7.25 (dt, J = 21.8, 10.3 Hz, 5H), 6.86 – 6.78 (m, 4H), 6.67 (d, J = 2.3 Hz, 2H), 5.77 (s, 1H), 3.69 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 153.75, 143.91, 131.90, 128.71, 128.17, 127.55, 126.08, 124.37, 119.36, 111.92, 111.59, 102.08, 77.22, 76.97, 76.94, 76.72, 55.85, 40.32. ESI-MS expected $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_2$: 382.2; observed 381.1582.

(8b) 3,3'-((4-(trifluoromethyl)phenyl)methylene)bis(5-methoxy-1H-indole)



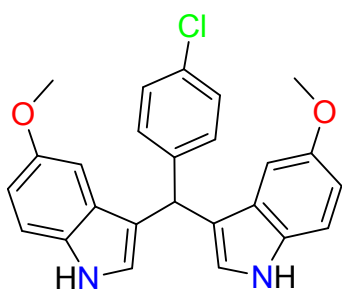
To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 4-(Trifluoromethyl)benzaldehyde (0.5mmol) and 5-methoxyIndole (1mmol) were added followed by catalyst (2.5% with respect to benzaldehyde). The resultant solution was stirred for 12H, upon which time product had precipitated. The cloudy solution was filtered and precipitate washed with hexanes (3x10mL) and water (3x10mL). ^1H NMR (500 MHz, CDCl_3) δ 7.83 (s, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.22 (s, 1H), 6.87 – 6.81 (m, 2H), 6.75 (s, 2H), 6.62 (s, 2H), 5.82 (s, 1H), 3.68 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 162.17, 153.90, 148.12, 131.91, 129.02, 128.60, 128.34, 127.31, 125.46, 125.22, 125.19, 125.15, 125.13, 124.46, 123.30, 118.37, 112.09, 111.89, 111.80, 109.99, 101.92, 77.25, 76.99, 76.74, 55.88, 40.19. ESI-MS expected $\text{C}_{26}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_2$: 450.2; observed 449.1446.

(8d) 3,3'-(naphthalen-1-ylmethylene)bis(5-methoxy-1H-indole)



To a mixed solution of EtOH/H₂O (2:1 in 10mL), 1-naphthadehyde (0.5mmol) and 5-methoxyIndole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO₄ and concentrated under reduced pressure. The resulting oil was washed with Hexanes (60mL) resulting in a pink solid which was further washed with water (3x10mL). ¹H NMR (500 MHz,) δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.47 – 7.22 (m, 4H), 6.87 – 6.78 (m, 4H), 6.58 (s, 2H), 6.52 (s, 1H), 3.66 (s, 6H). ¹³C NMR (126 MHz, cdCl₃) δ 153.83, 131.96, 128.60, 126.94, 126.14, 125.71, 125.44, 125.17, 125.06, 124.34, 119.01, 111.87, 111.63, 109.99, 102.04, 88.22, 77.22, 76.97, 76.72, 55.92, 36.03. ESI-MS expected C₂₉H₂₄O₂N₂: 432.2; observed 431.1744.

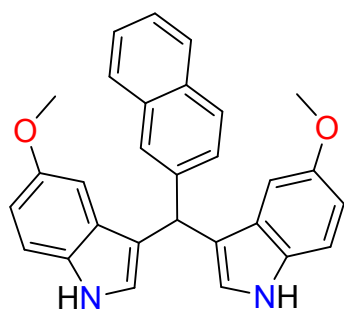
(8e) 3,3'-((4-chlorophenyl)methylene)bis(5-methoxy-1H-indole)



To a mixed solution of EtOH/H₂O (2:1 in 10mL), 4-chlorobenzaldehyde (0.5mmol) and 5-methoxyIndole (1mmol) were added followed by catalyst (2.5% with respect to benzaldehyde). The resultant solution was stirred for 12H, upon which time product had

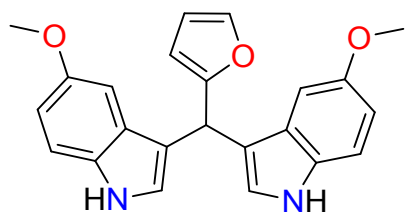
precipitated. The cloudy solution was filtered and precipitate washed with hexanes (3x10mL) and water (3x10mL). ^1H NMR (500 MHz,) δ 7.81 (s, 2H), 7.24 (p, J = 9.0 Hz, 5H), 6.87 – 6.81 (m, 2H), 6.78 (s, 2H), 6.60 (s, 2H), 5.74 (s, 1H), 3.70 (s, 6H). ^{13}C NMR (126 MHz, cdCl_3) δ 206.29, 153.82, 142.50, 131.92, 131.77, 130.05, 128.32, 127.36, 124.42, 118.76, 111.99, 111.74, 102.04, 89.91, 77.25, 77.00, 76.75, 55.90, 39.71. ESI-MS expected $\text{C}_{25}\text{H}_{21}\text{ClO}_2\text{N}_2$: 416.1; observed 415.118.

(8c) 3,3'-(naphthalen-2-ylmethylene)bis(5-methoxy-1H-indole)



To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 2-naphthadehyde (0.5mmol) and 5-methoxyIndole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO_4 and concentrated under reduced pressure. The resulting oil was washed with Hexanes (60mL) resulting in a pink solid which was further washed with water (3x10mL). ^1H NMR (500 MHz,) δ 7.77 (s, 3H), 7.72 (s, 2H), 7.68 (s, 1H), 7.49 (s, 1H), 7.38 (s, 2H), 6.80 (s, 4H), 6.64 (s, 2H), 6.37 (s, 1H), 5.91 (s, 1H), 3.64 – 3.60 (m, 6H). ^{13}C NMR (126 MHz, cdCl_3) δ 165.91, 144.07, 136.72, 128.75, 128.23, 127.13, 126.15, 123.63, 123.61, 121.93, 119.95, 119.72, 119.26, 117.73, 111.06, 77.30, 77.04, 76.79, 40.26, 40.24, -8.79. ESI-MS expected $\text{C}_{29}\text{H}_{24}\text{O}_2\text{N}_2$: 432.2; observed 431.1734.

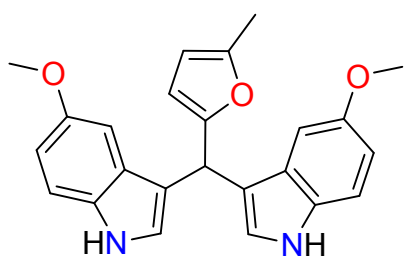
(8f) 3,3'-(furan-2-ylmethylene)bis(5-methoxy-1H-indole)



To a mixed solution of EtOH/H₂O (2:1 in 10mL), furfural (0.5mmol) and 5-methoxyindole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO₄ and concentrated under reduced pressure. The resulting oil was washed with Hexanes (60mL) resulting in a pink solid which was further washed with water (3x10mL)

¹H NMR (500 MHz, CDCl₃) δ 7.85 (s, 2H), 7.38 (s, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.92 (s, 2H), 6.85 (d, *J* = 7.8 Hz, 4H), 6.32 (s, 1H), 6.09 (s, 1H), 5.85 (s, 1H), 3.75 (s, 6H). ¹³C NMR (126 MHz, cdcl₃) δ 157.04, 153.87, 141.19, 131.74, 127.23, 123.81, 116.89, 112.06, 111.73, 110.12, 109.99, 106.64, 101.73, 77.24, 76.99, 76.74, 55.87, 34.21.

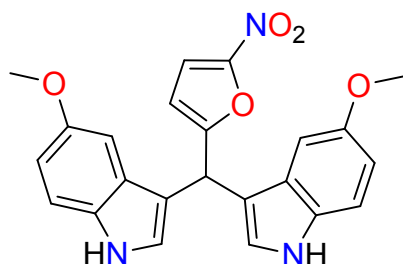
(8g) 3,3'-((5-methylfuran-2-yl)methylene)bis(5-methoxy-1H-indole)



To a mixed solution of EtOH/H₂O (2:1 in 10mL), 5-methyl-2-furaldehyde (0.5mmol) and 5-methoxyindole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO₄ and concentrated under reduced pressure. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (s, 2H), 7.25 – 7.19 (m, 2H), 6.95 (s,

2H), 6.84 (d, $J = 9.9$ Hz, 4H), 5.93 (s, 1H), 5.89 (s, 1H), 5.79 (s, 1H), 3.75 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, cdCl_3) δ 153.77, 153.72, 145.68, 131.76, 127.35, 123.76, 117.32, 114.23, 111.94, 111.60, 109.85, 101.93, 77.23, 76.98, 76.72, 55.86, 34.13, 11.42, 9.93.

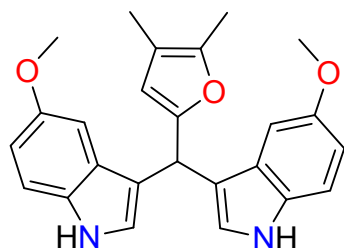
(8i) 3,3'-((5-nitrofuran-2-yl)methylene)bis(5-methoxy-1H-indole)



To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 2-nitro-2-furaldehyde (0.5mmol) and 5-methoxyindole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO_4 and concentrated under reduced pressure.

^1H NMR (500 MHz, CDCl_3) δ 8.03 (s, 2H), 7.32 – 7.22 (m, 4H), 6.96 (d, $J = 2.5$ Hz, 2H), 6.93 – 6.85 (m, 4H), 6.35 – 6.30 (m, 1H), 5.91 (d, $J = 1.4$ Hz, 1H), 3.77 (d, $J = 1.9$ Hz, 6H).

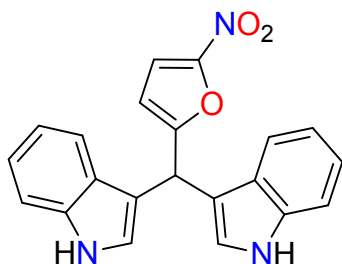
(8h) 3,3'-((5-methylfuran-2-yl)methylene)bis(1H-indole)



To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 5-methyl-furaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO_4 and concentrated under reduced

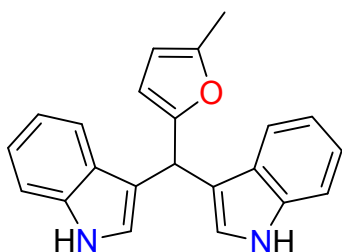
pressure. ^1H NMR (500 MHz,) δ 7.86 (s, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 2.7 Hz, 2H), 6.90 – 6.81 (m, 4H), 5.83 (s, 1H), 5.74 (s, 1H), 3.75 (s, 6H), 2.18 (d, J = 3.9 Hz, 6H). ^{13}C NMR (126 MHz, cdCl_3) δ 155.06, 153.79, 150.59, 132.28, 131.76, 127.31, 123.82, 117.17, 111.98, 111.66, 107.33, 105.96, 101.87, 77.25, 77.00, 76.74, 55.87, 34.24, 13.69.

(7i) 3,3'-((5-nitrofuran-2-yl)methylene)bis(1H-indole)



To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 2-nitro-2-furaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO_4 and concentrated under reduced pressure. ^1H NMR (500 MHz,) δ 8.08 (s, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.31 (m, 3H), 7.29 – 7.19 (m, 4H), 7.16 – 7.05 (m, 2H), 6.96 (dd, J = 2.5, 1.2 Hz, 2H), 6.34 – 6.29 (m, 1H), 6.01 (s, 1H). ^{13}C NMR (126 MHz, cdCl_3) δ 161.40, 136.58, 126.29, 123.35, 122.42, 119.79, 119.20, 114.73, 112.72, 111.35, 110.59, 77.23, 76.98, 76.72, 60.35, 34.77.

(7g) 3,3'-((5-methylfuran-2-yl)methylene)bis(1H-indole)

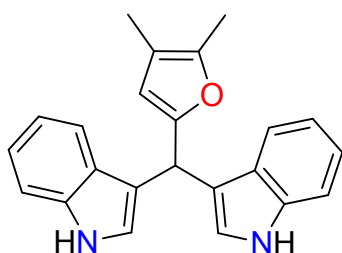


To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 2-nitro-2-furaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution

was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO_4 and concentrated under reduced pressure.

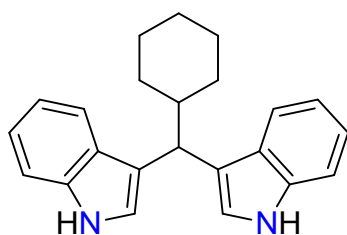
^1H NMR (500 MHz,) δ 7.90 (s, 2H), 7.58 (d, J = 7.9 Hz, 2H), 7.36 (d, J = 7.9 Hz, 4H), 7.04 (dd, J = 16.9, 8.9 Hz, 3H), 6.95 (s, 2H), 5.87 (d, J = 17.3 Hz, 1H), 4.69 (s, 1H), 1.83 (s, 3H). ESI-MS expected $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}$: 326.1; observed 325.1326

(7h) 3,3'-((4,5-dimethylfuran-2-yl)methylene)bis(1H-indole)



To a mixed solution of EtOH/ H_2O (2:1 in 10mL), 2-nitro-2-furaldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO_4 and concentrated under reduced pressure. ^1H NMR (500 MHz,) δ 7.72 (d, 1H), 7.63 – 7.54 (m, 2H), 7.39 (d, 1H), 7.37 – 7.16 (m, 7H), 7.14 – 7.04 (m, 2H), 6.60 (s, 1H), 5.89 (s, 1H), 2.20 (s, 3H), 1.92 (s, 3H). ESI-MS expected $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}$: 340.1; observed 360.1475.

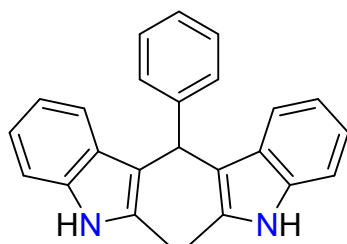
3,3'-((cyclohexylmethylene)bis(1H-indole)



To a mixed solution of EtOH/ H_2O (2:1 in 10mL), cha (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The clear solution was

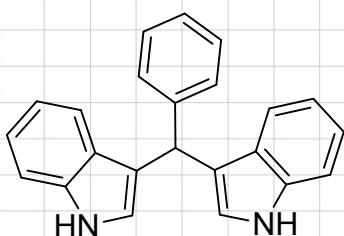
concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with MgSO_4 and concentrated under reduced pressure. The compound was isolated via column chromatography (40 ethyl acetate: 60 hexanes) and concentrated under reduced pressure to yield a colourless oil. 12%. ^1H NMR (500 MHz,) δ 7.89 (s, 2H), 7.67 (ddd, J = 7.9, 1.6, 0.8 Hz, 2H), 7.41 – 7.25 (m, 2H), 7.21 – 7.02 (m, 6H), 4.29 (d, J = 8.8 Hz, 1H), 2.27 (dt, J = 11.8, 8.7, 3.3 Hz, 1H), 1.85 (dd, J = 13.9, 4.0 Hz, 2H), 1.67 (ddt, J = 17.4, 12.3, 3.9 Hz, 3H), 1.20 – 1.01 (m, 3H), 0.94 – 0.84 (m, 3H). ESI-MS expected $\text{C}_{23}\text{H}_{24}\text{N}_2$: 328.2; observed 351.1837 ($\text{C}_{23}\text{H}_{24}\text{N}_2\text{Na}$).

3,3'-(phenylmethylene)bis(2-methyl-1H-indole)

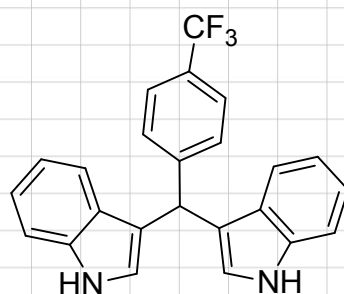


To a mixed solution of EtOH/ H_2O (2:1 in 10mL,) benzaldehyde (0.5mmol) and 5-methoxyIndole (1mmol) were added followed by catalyst (2.5% with respect to benzaldehyde). The resultant solution was stirred for 12H, upon which time product had precipitated. The cloudy solution was filtered and precipitate washed with hexanes (3x10mL) and water (3x10mL). ^1H NMR (500 MHz, CDCl_3) δ 7.72 (s, 2H), 7.32 – 7.18 (m, 6H), 7.08 – 6.96 (m, 4H), 6.86 (t, J = 7.9 Hz, 2H), 6.02 (s, 1H), 2.07 (d, J = 2.5 Hz, 6H), 1.27 (s, 1H). We were not able to record a ^{13}C -NMR and ESI-MS of this compound, due to poor solubility. Its synthesis was confirmed by single crystal X-ray crystallography (Figure S4).

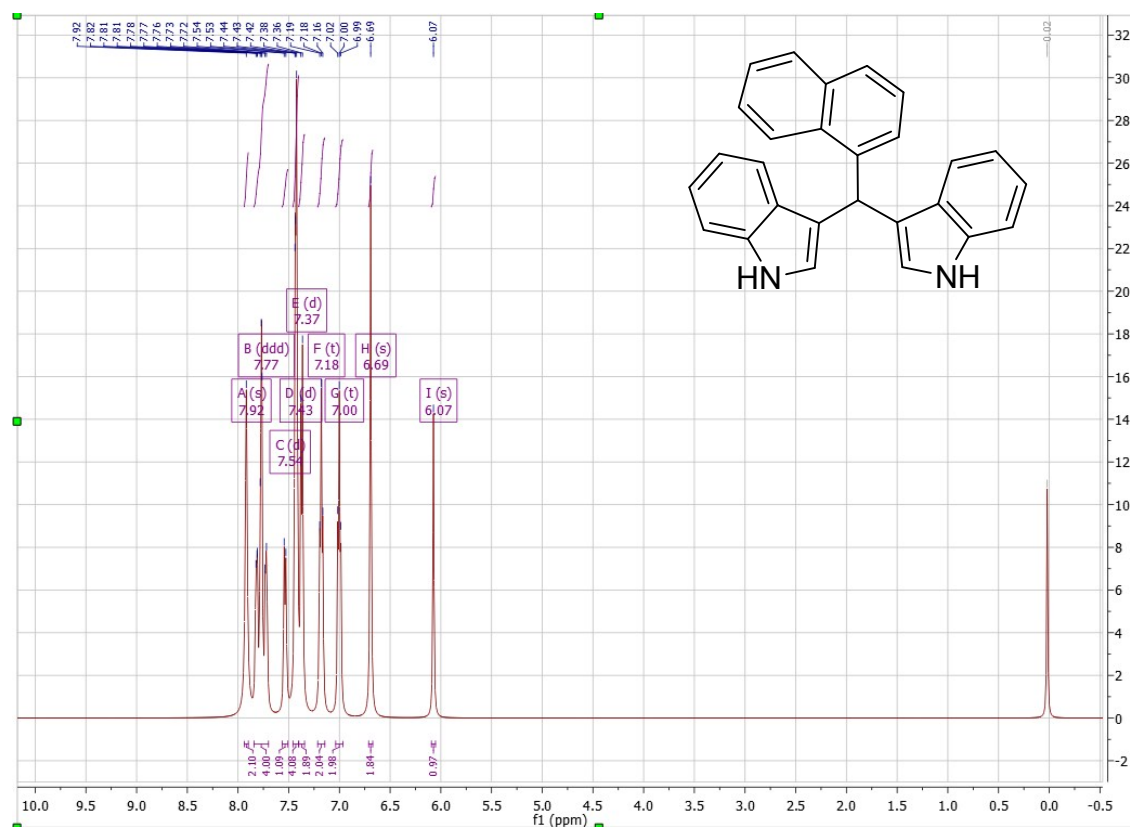
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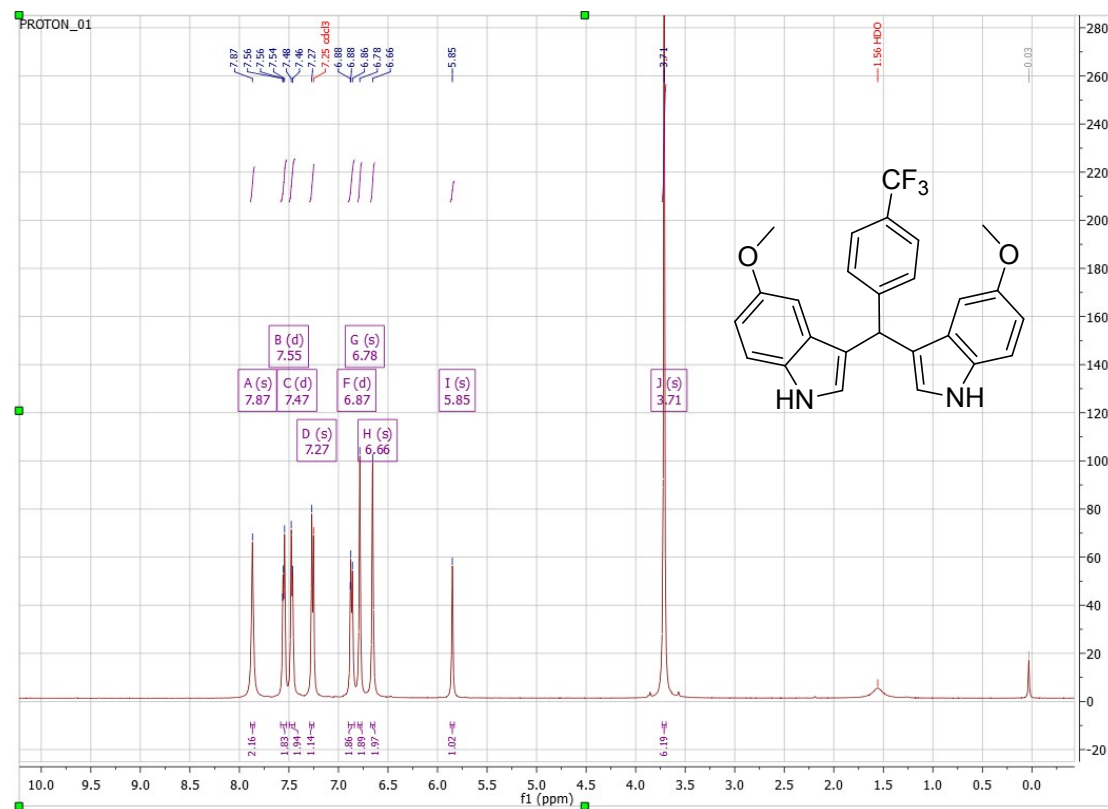
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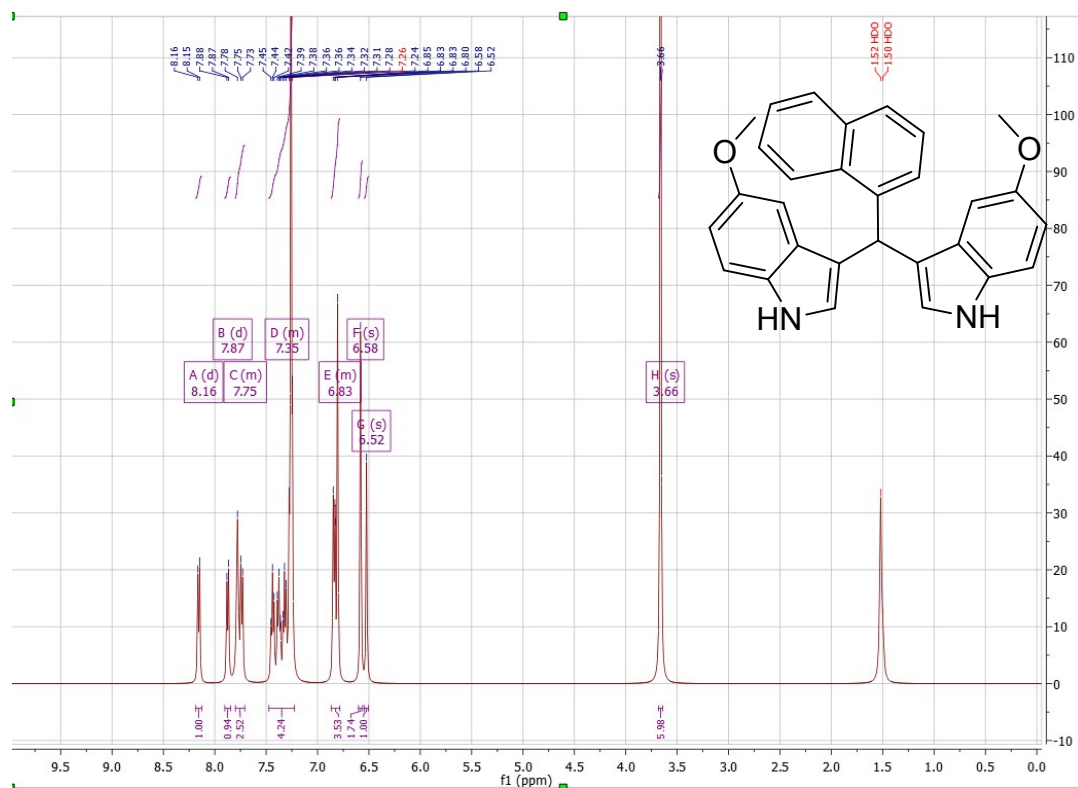
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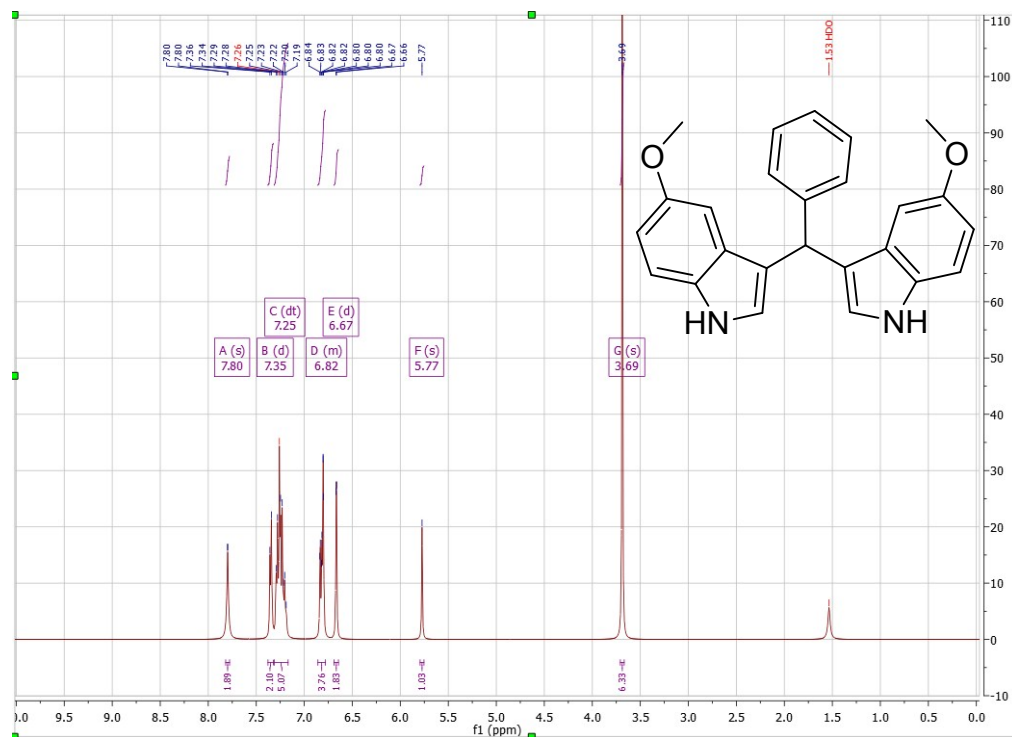
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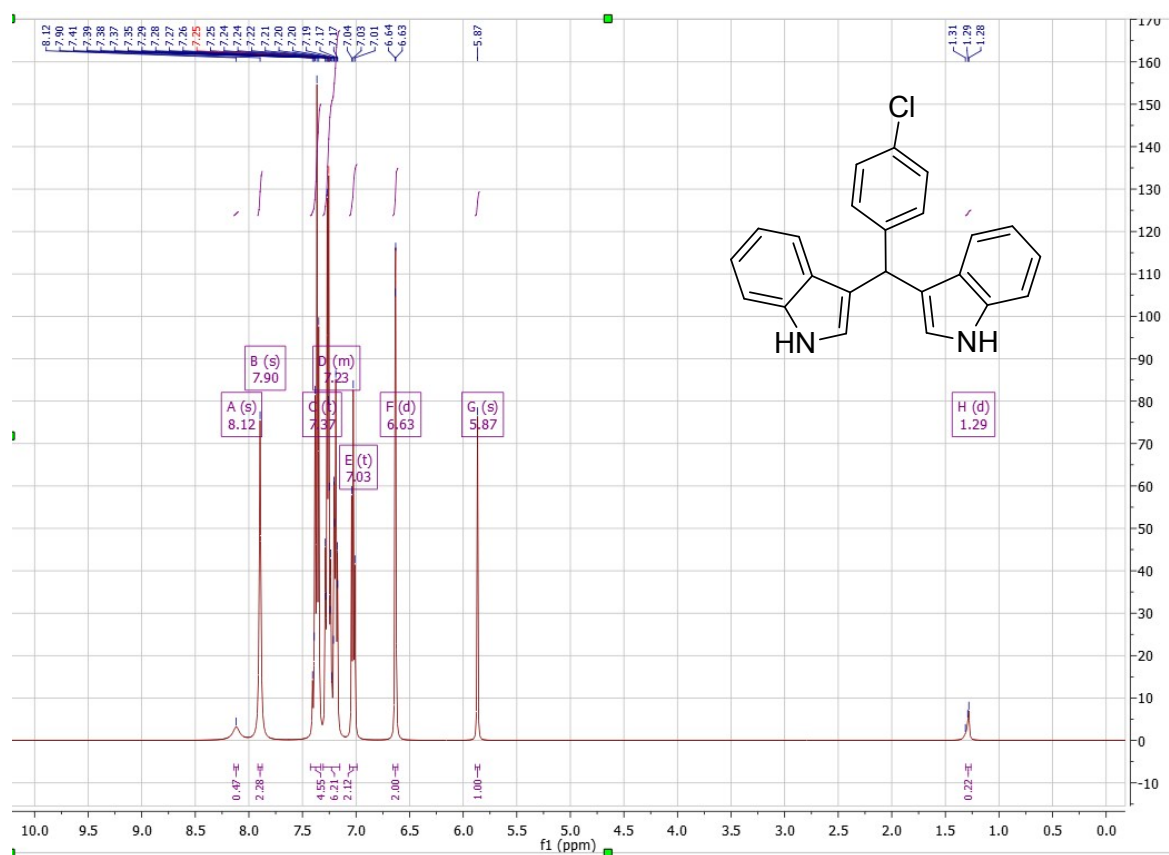
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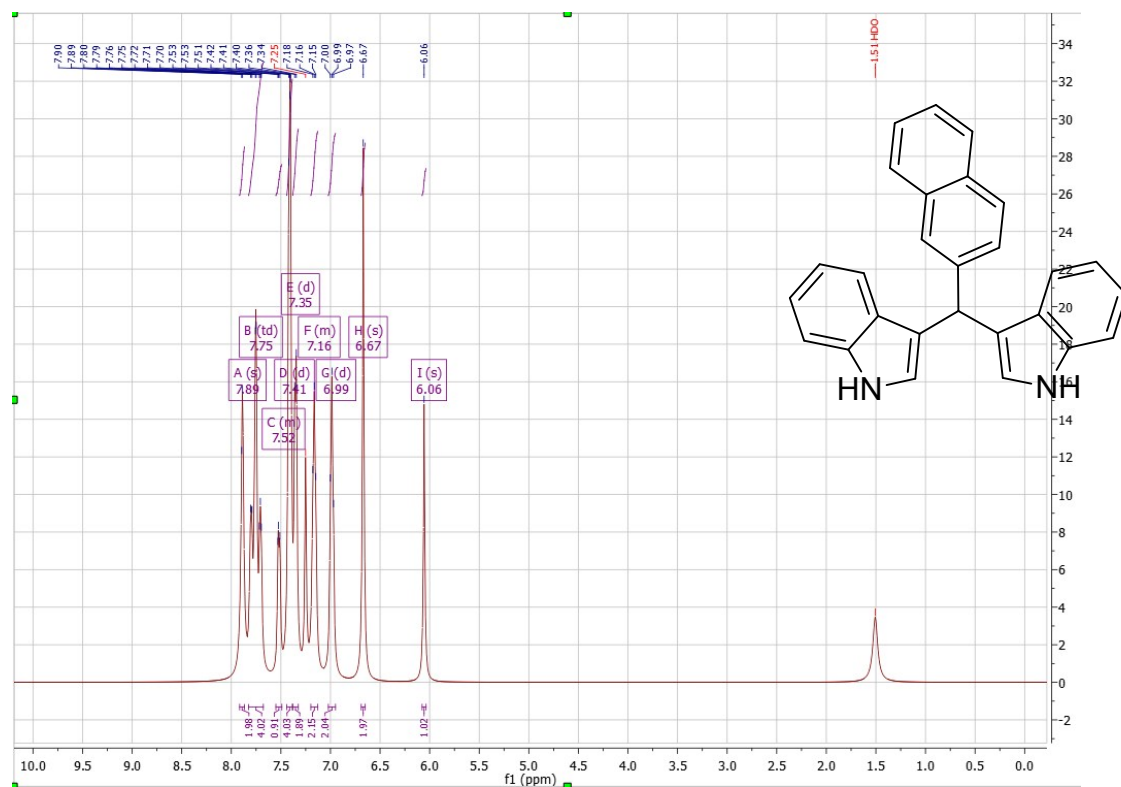
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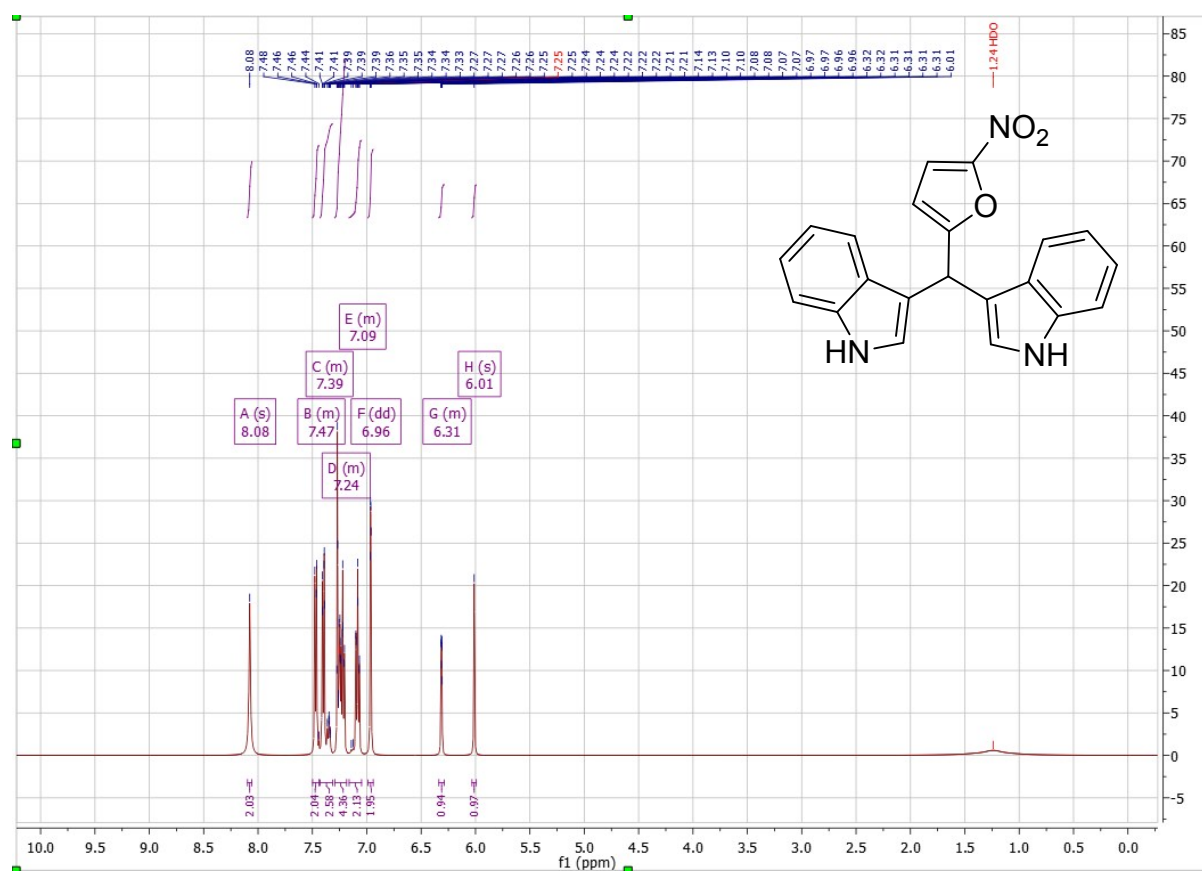
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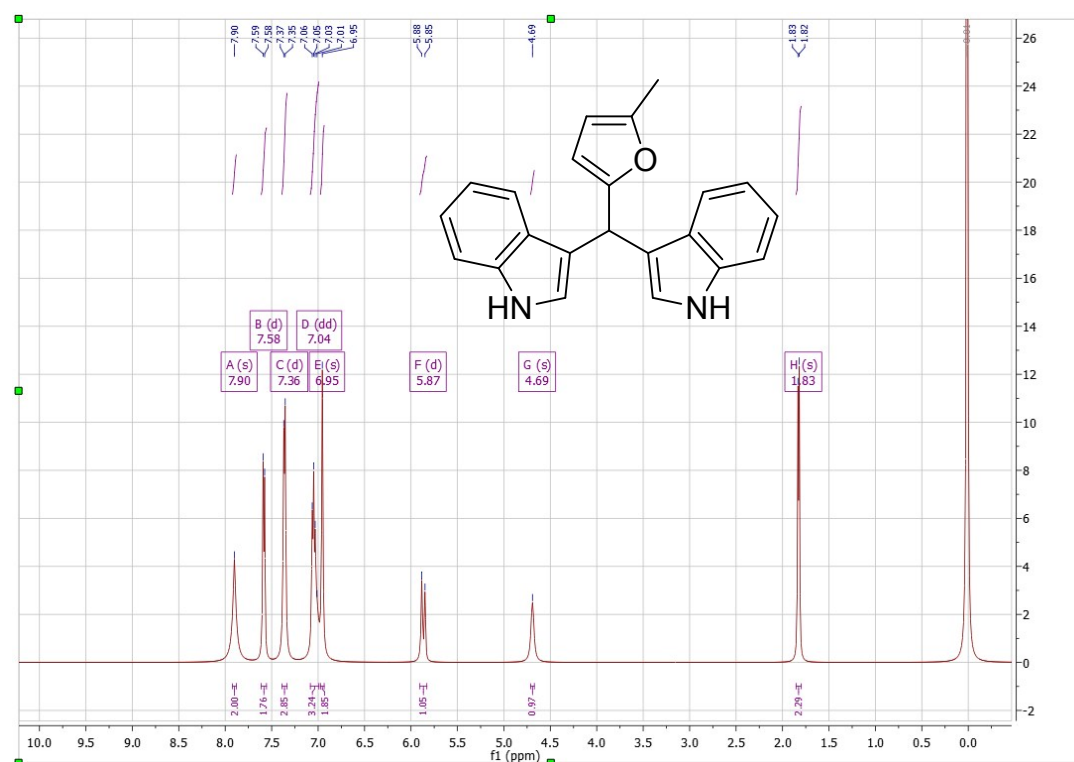
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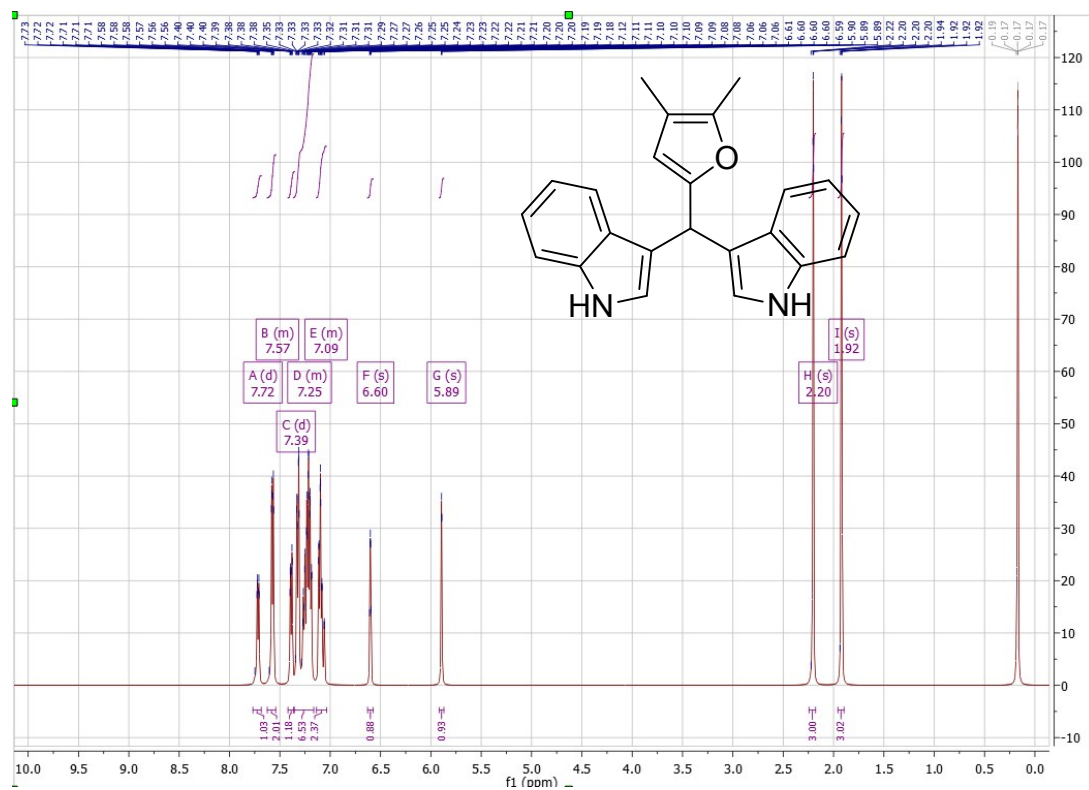
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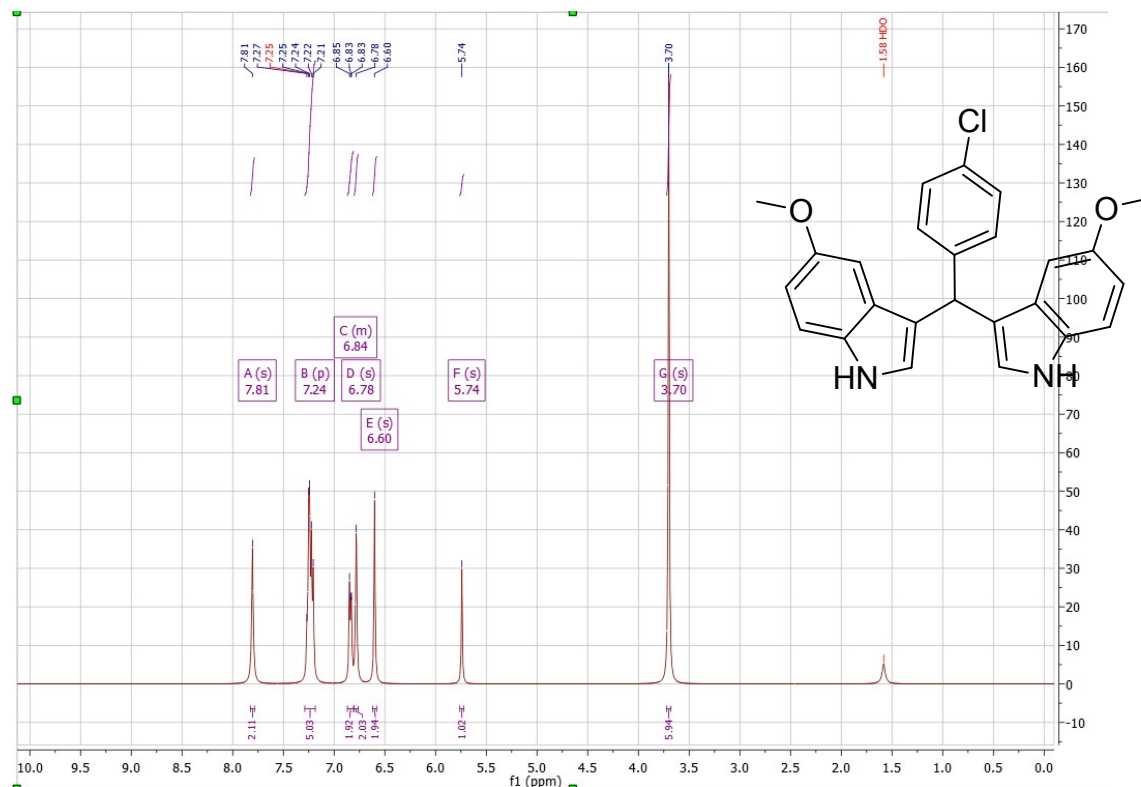
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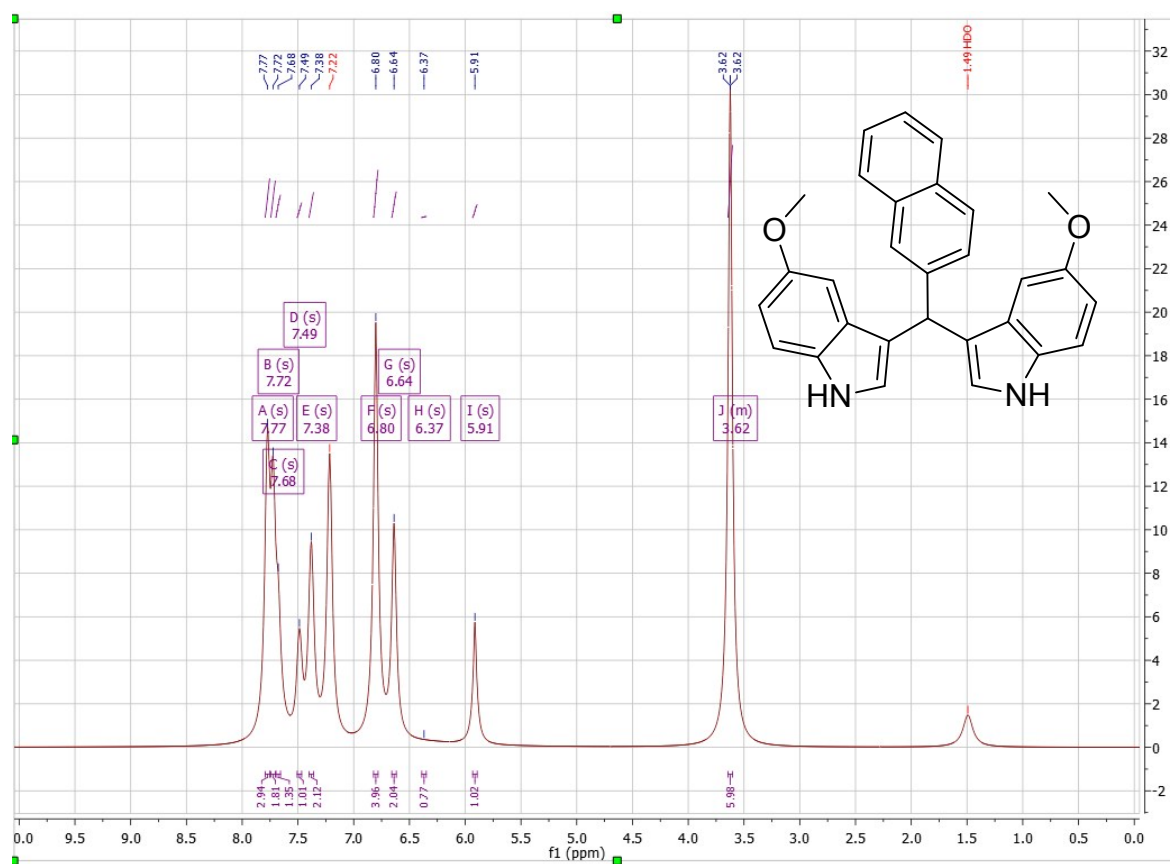
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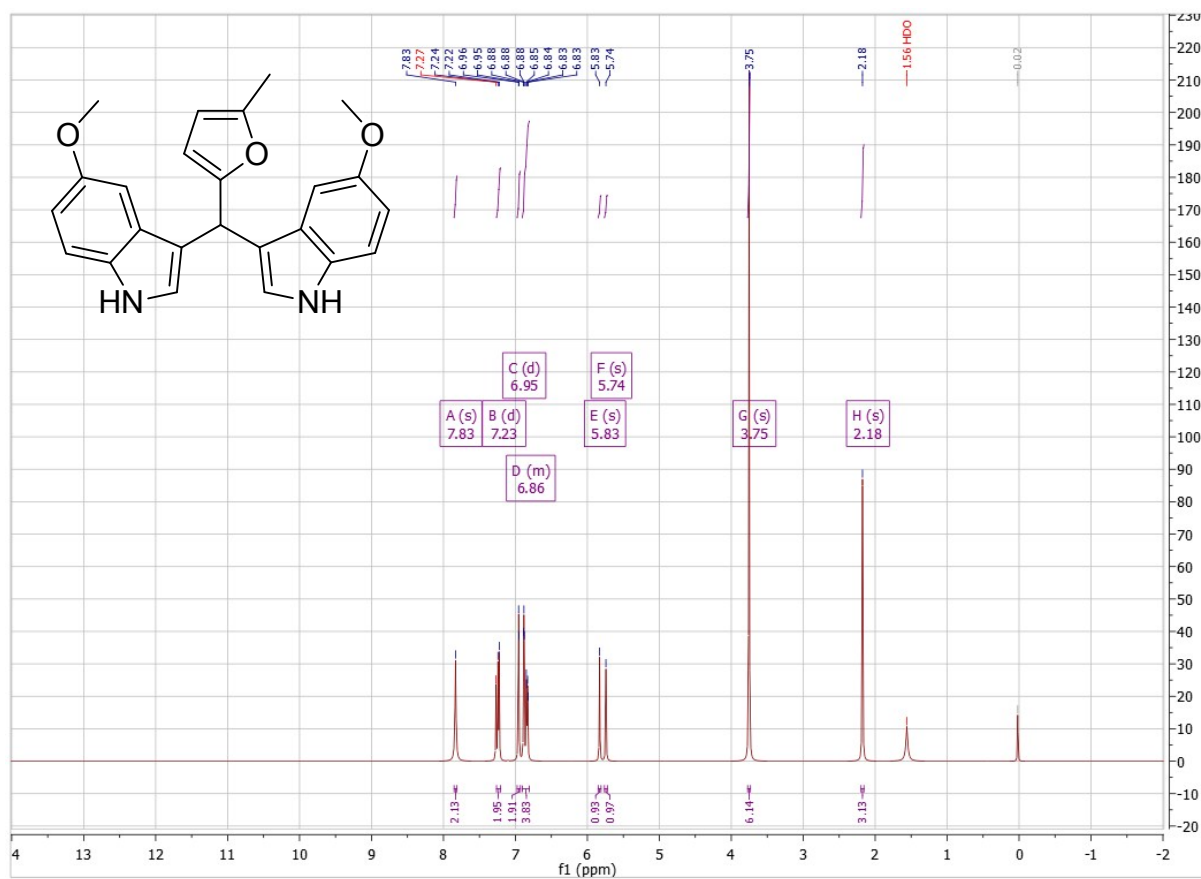
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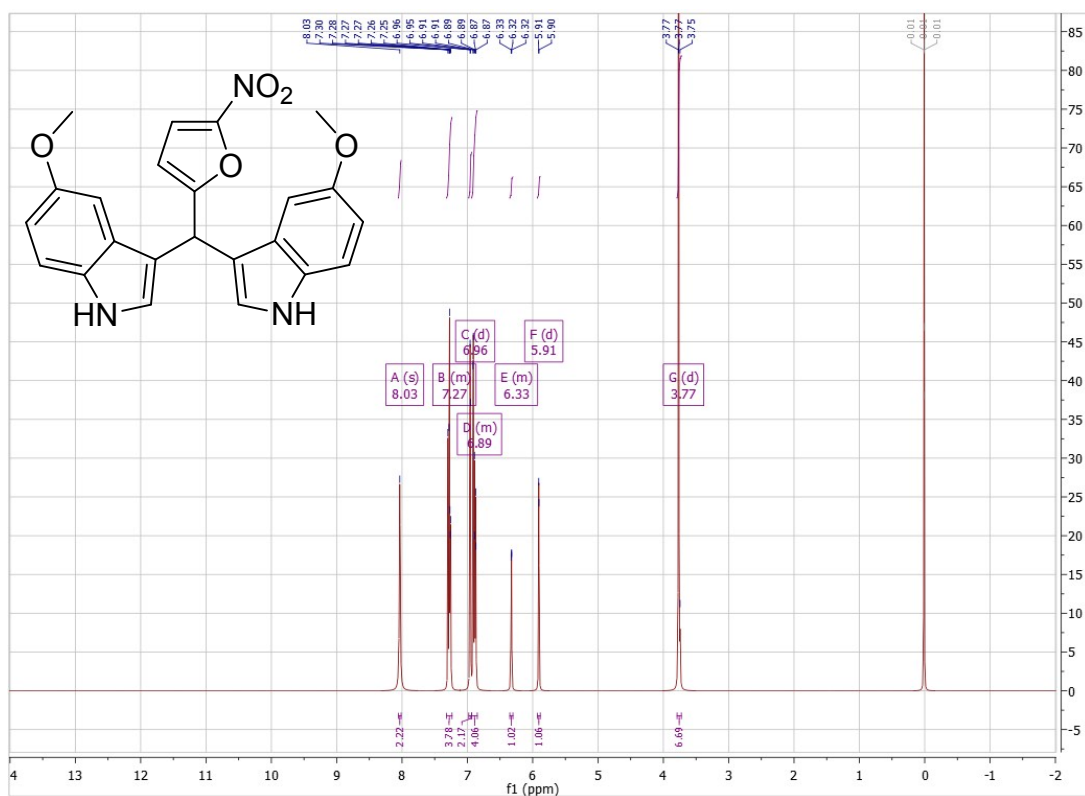
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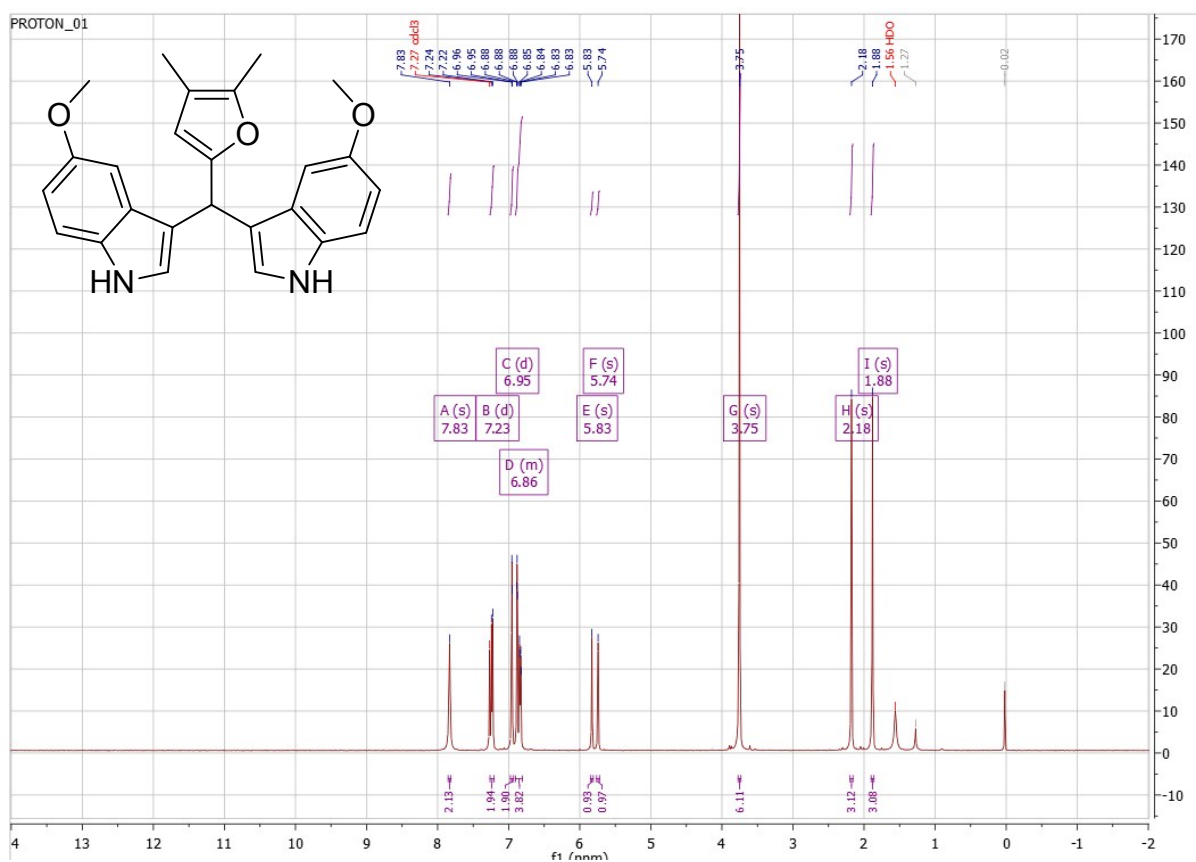
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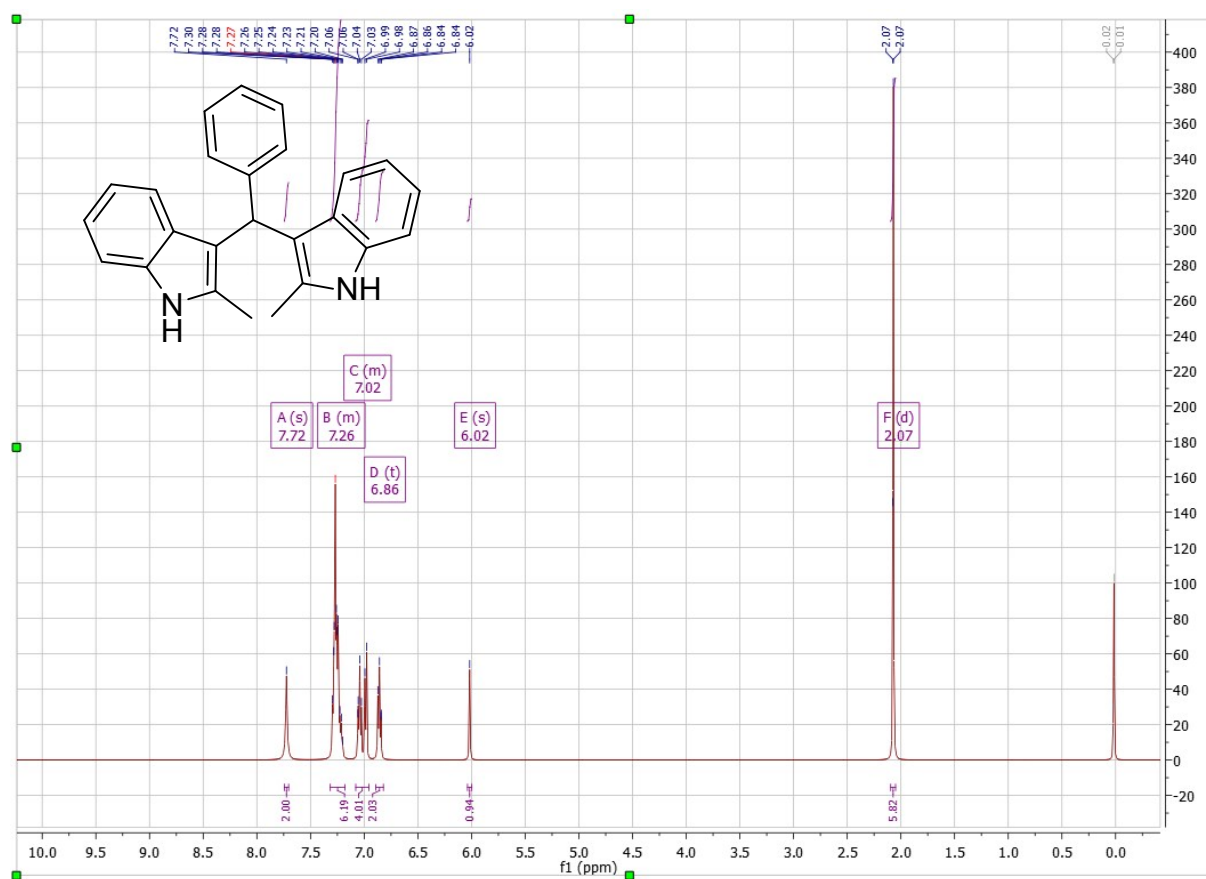


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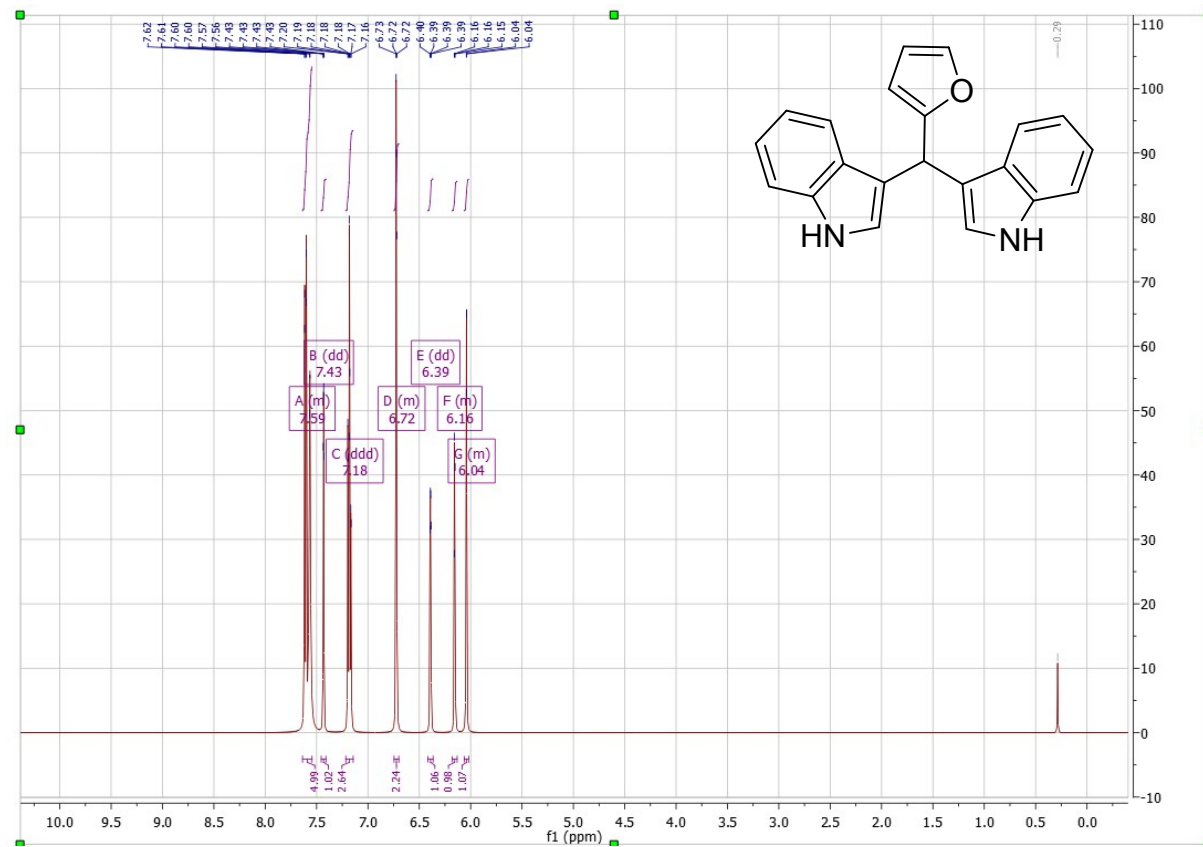
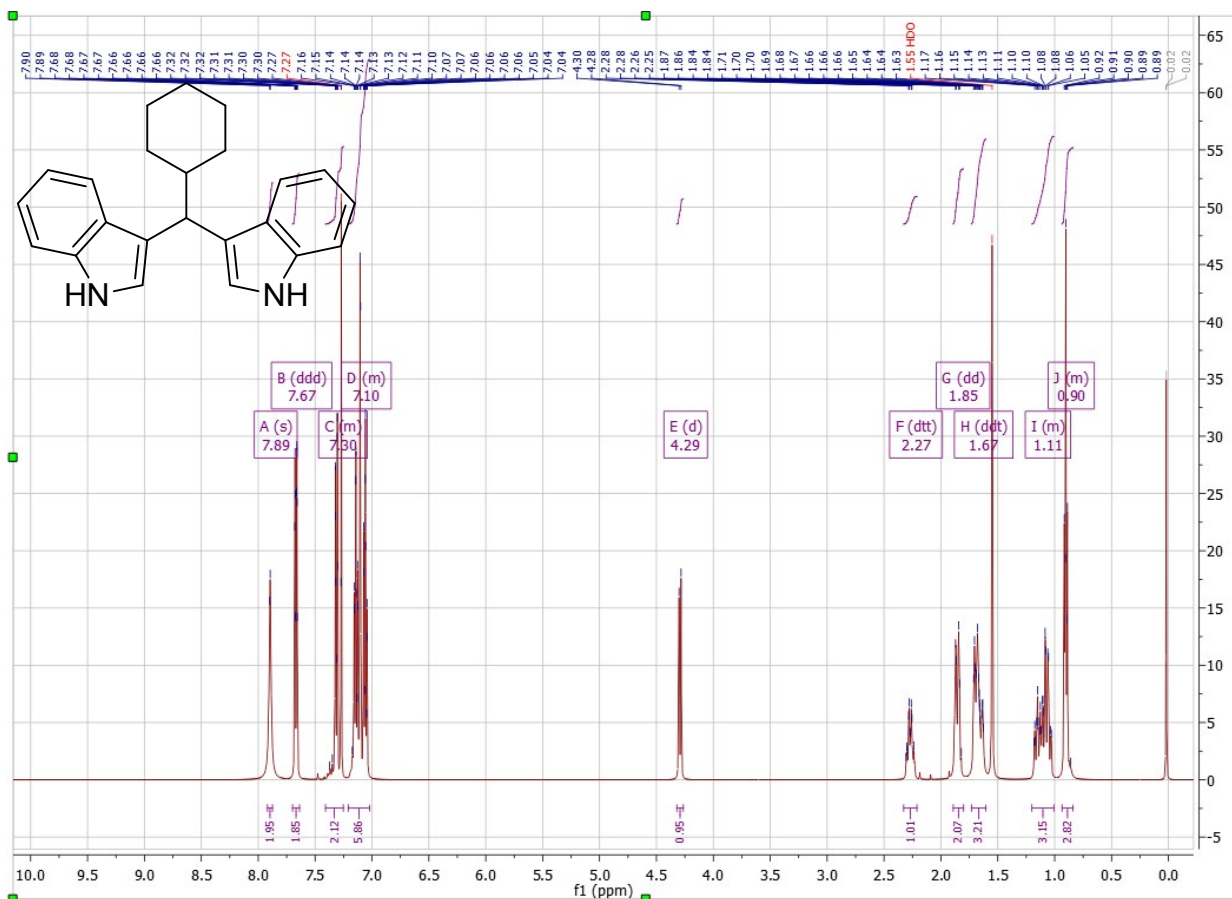


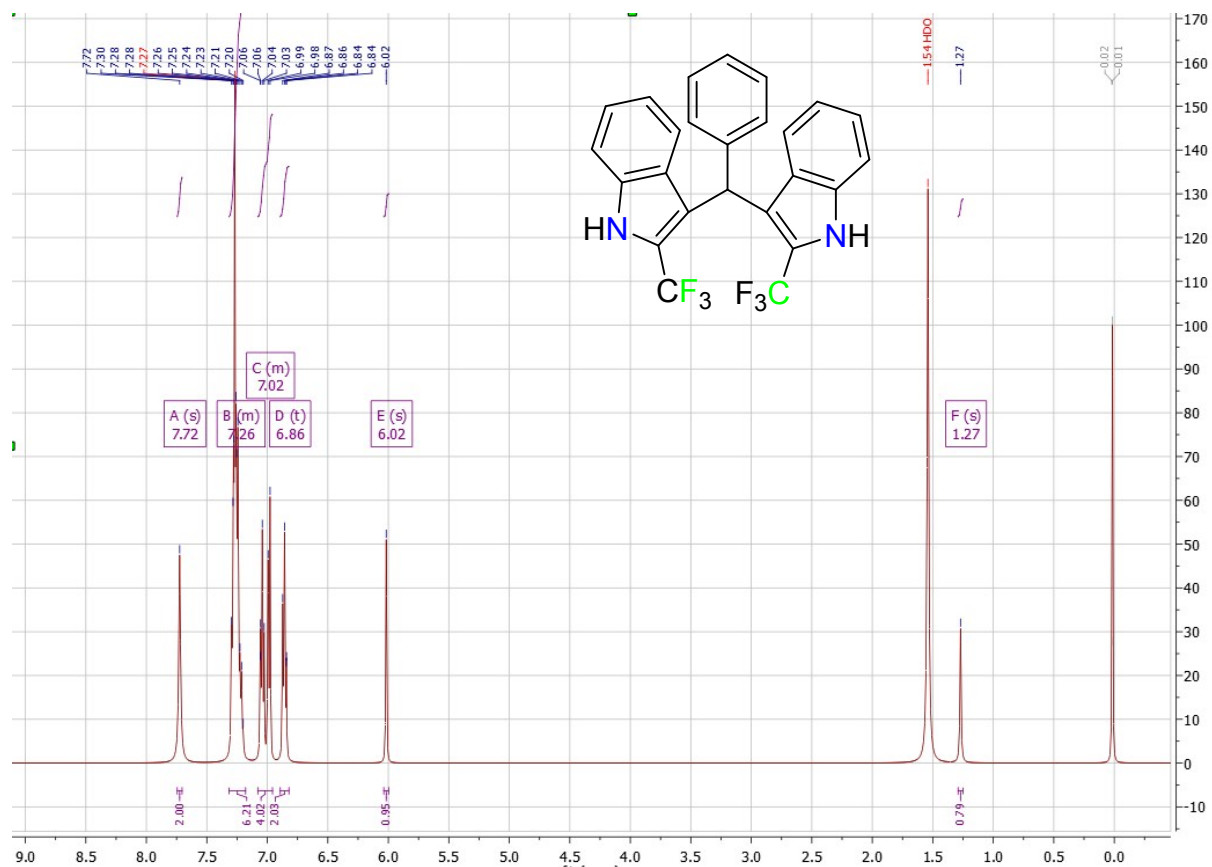
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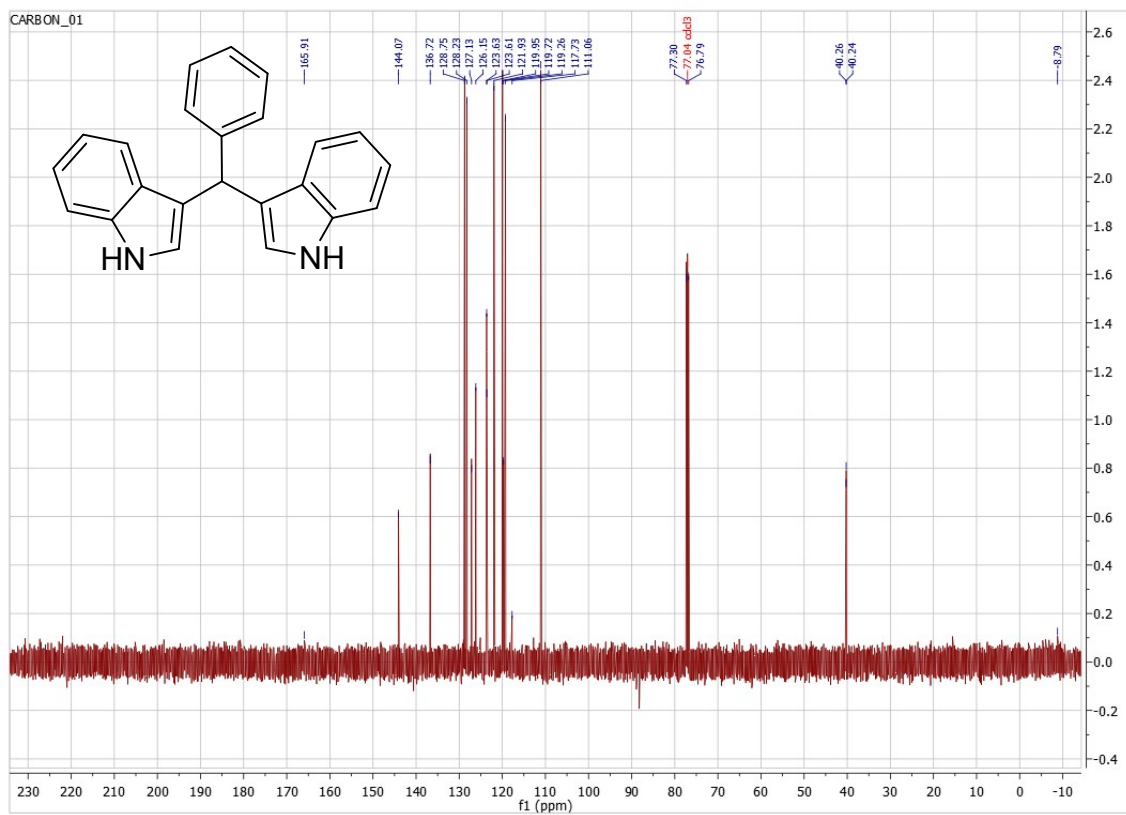
IB-CHA



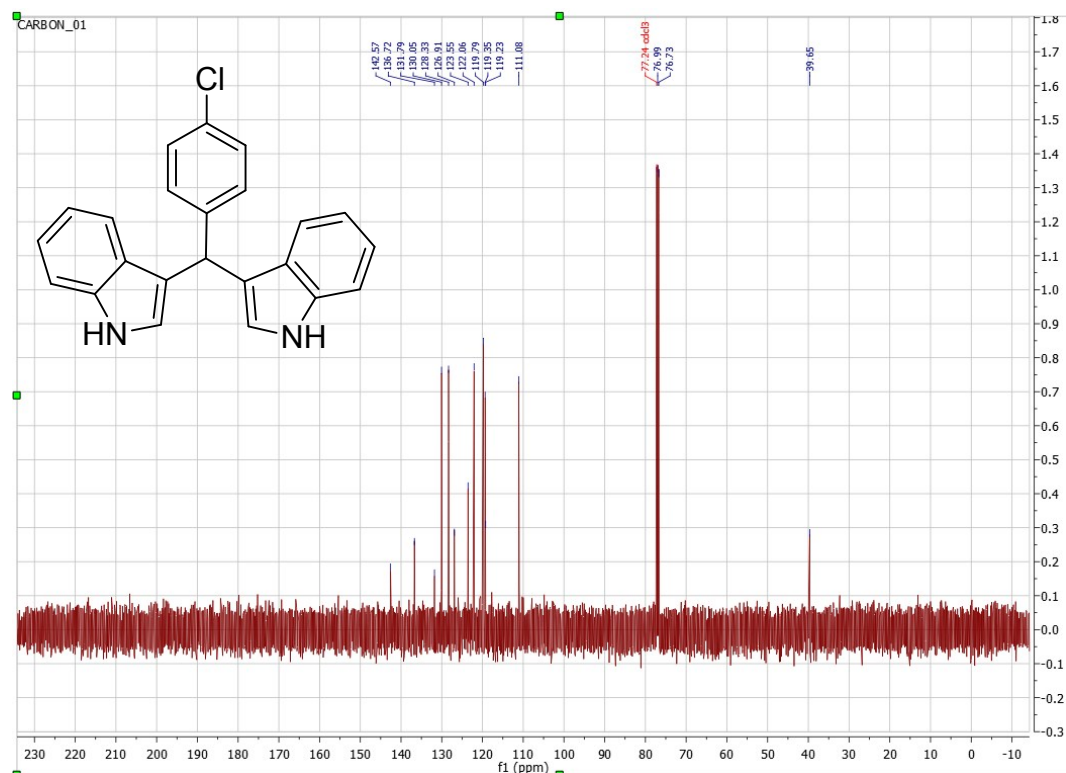


¹³C NMR

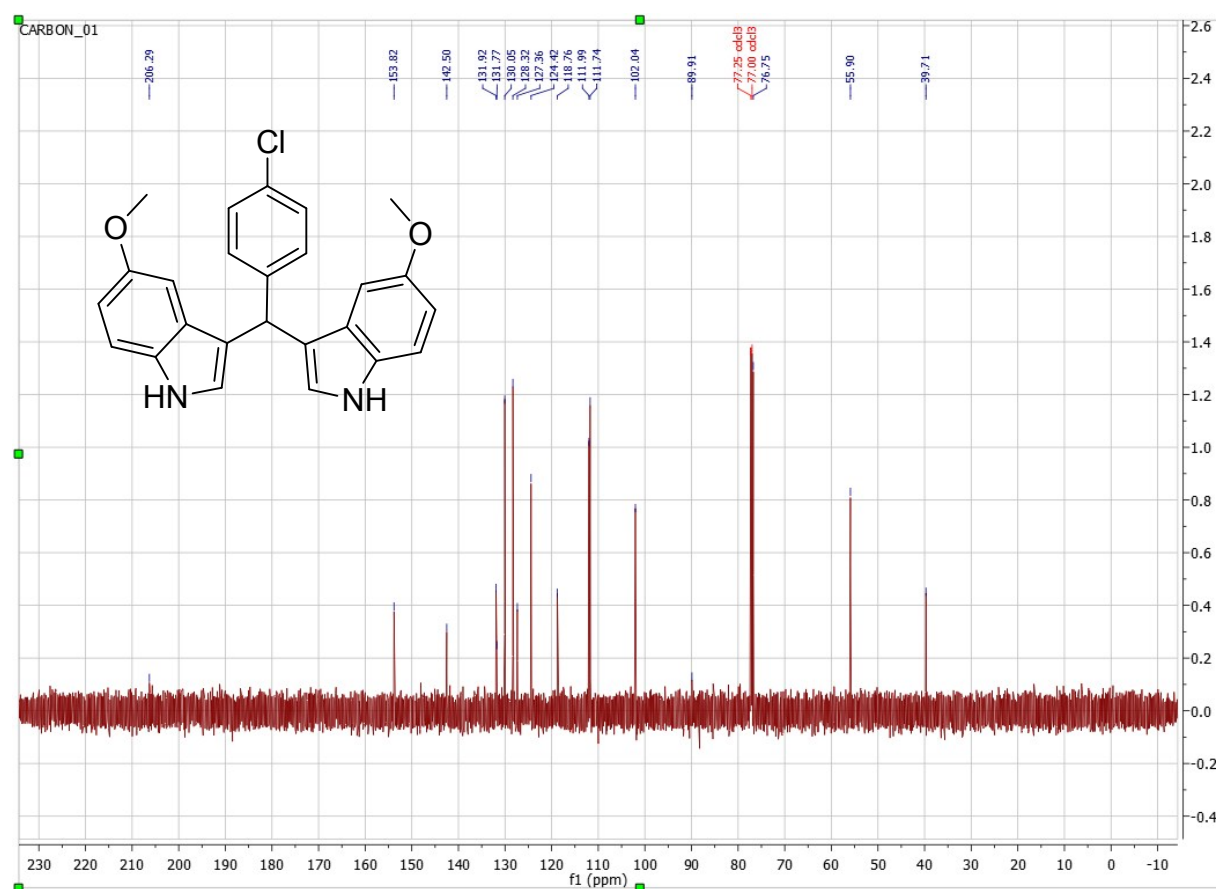
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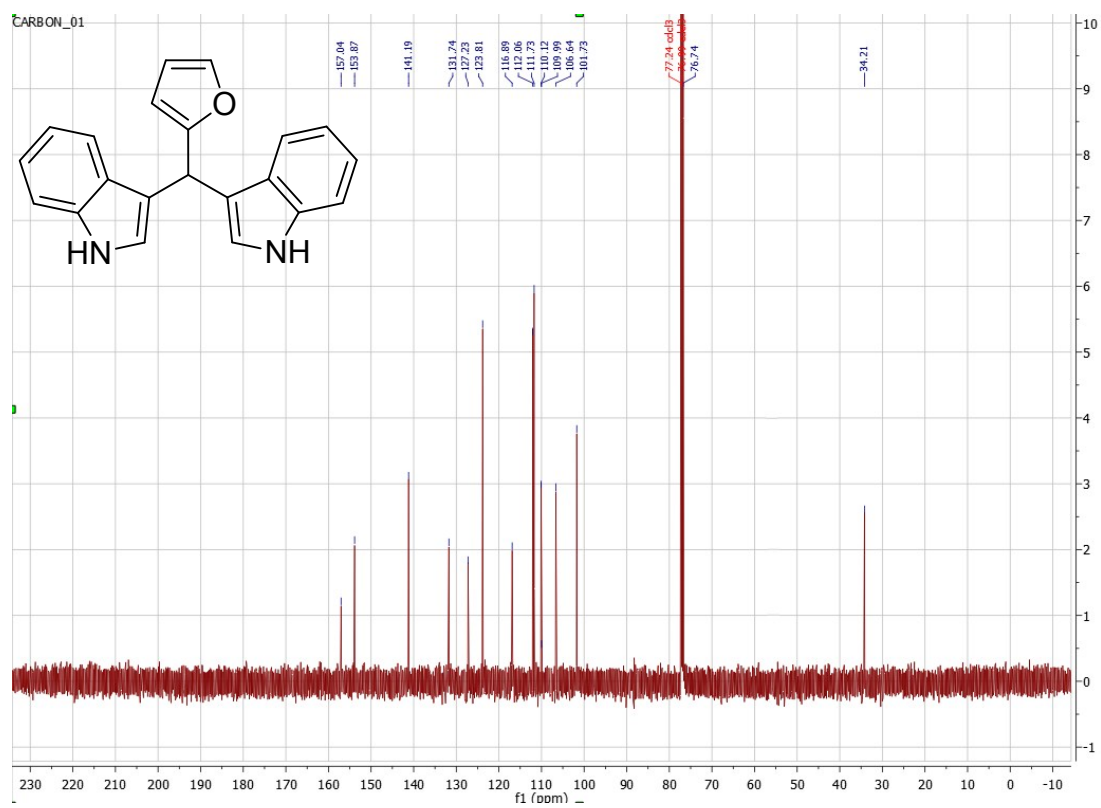
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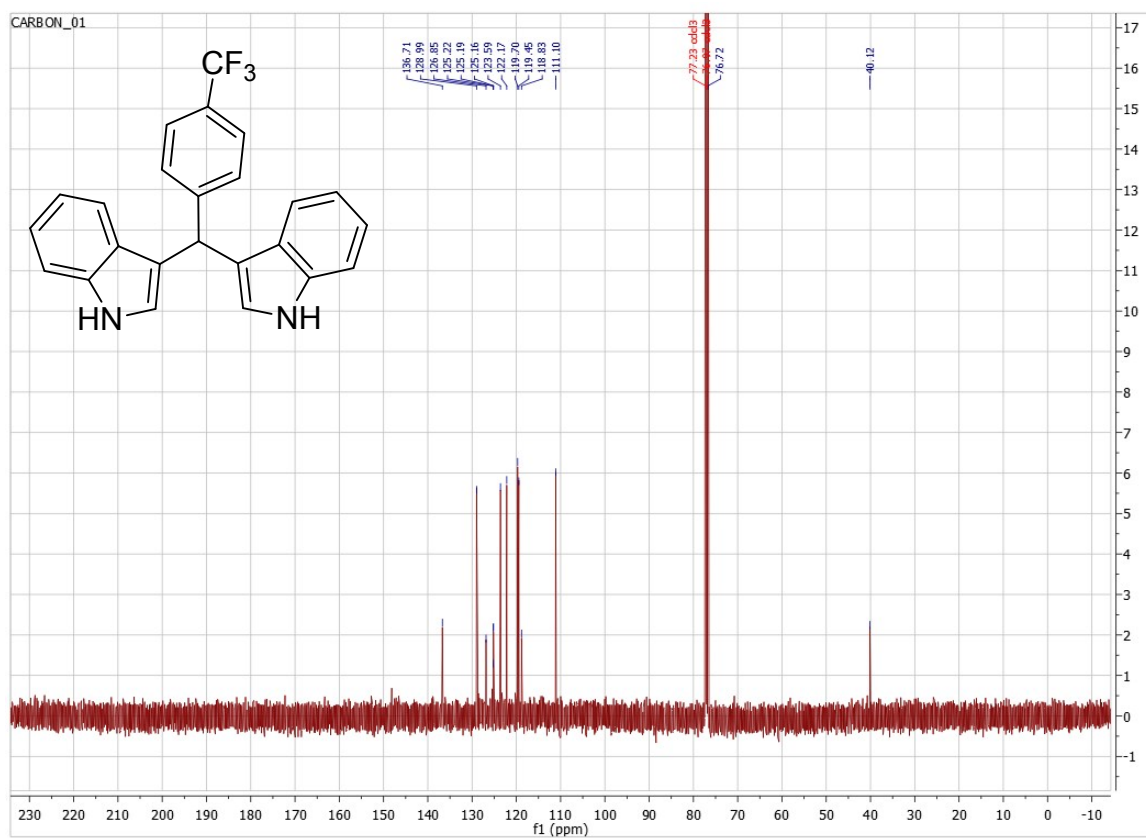
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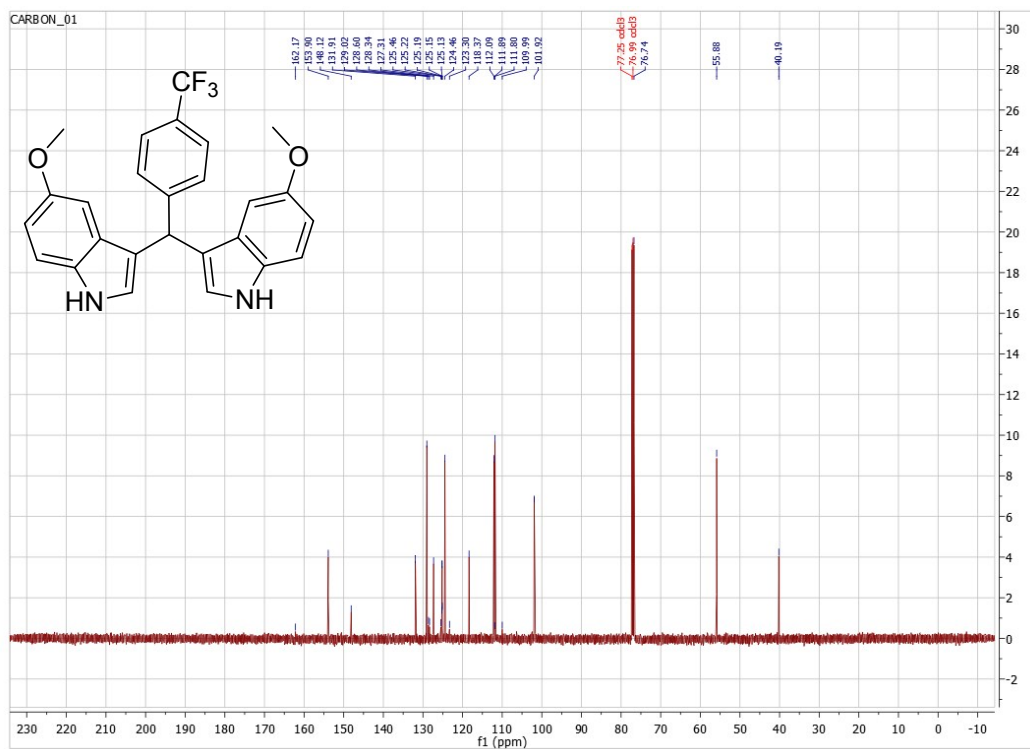
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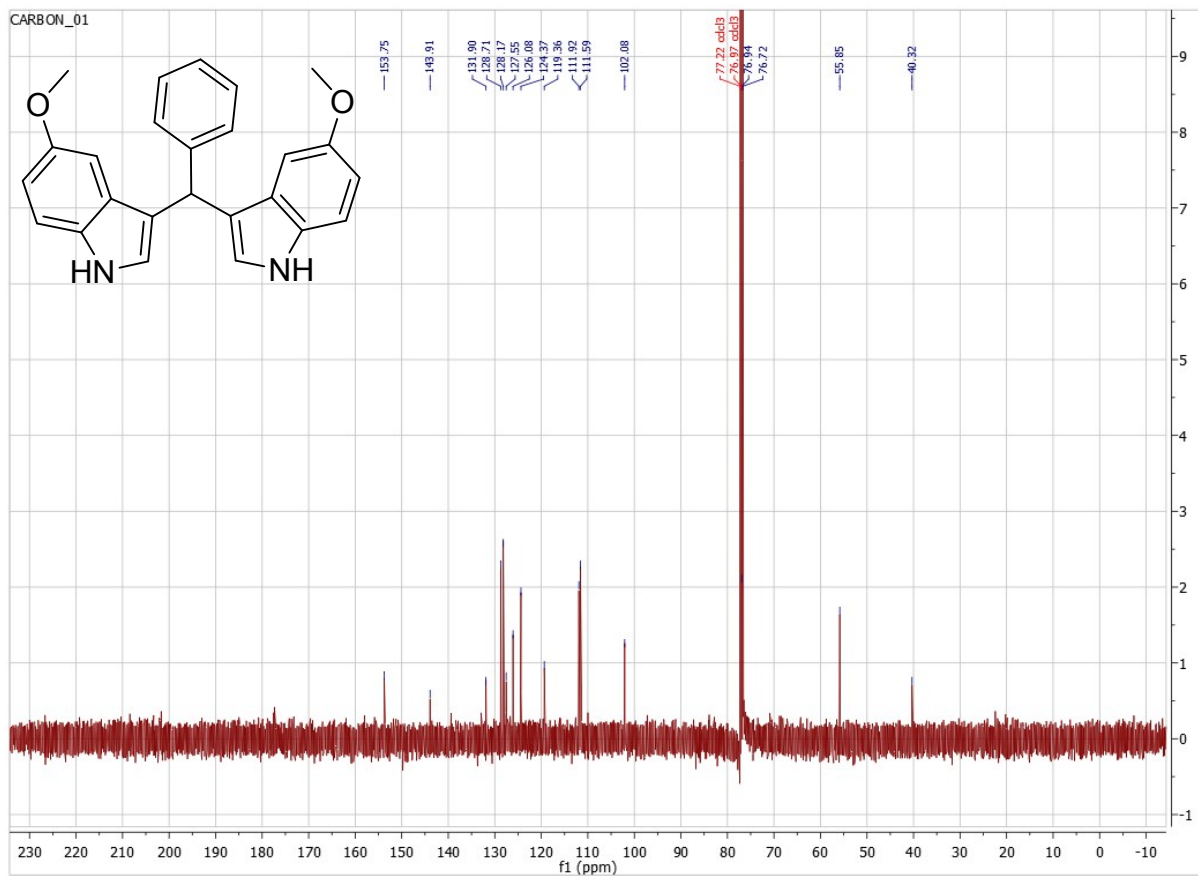
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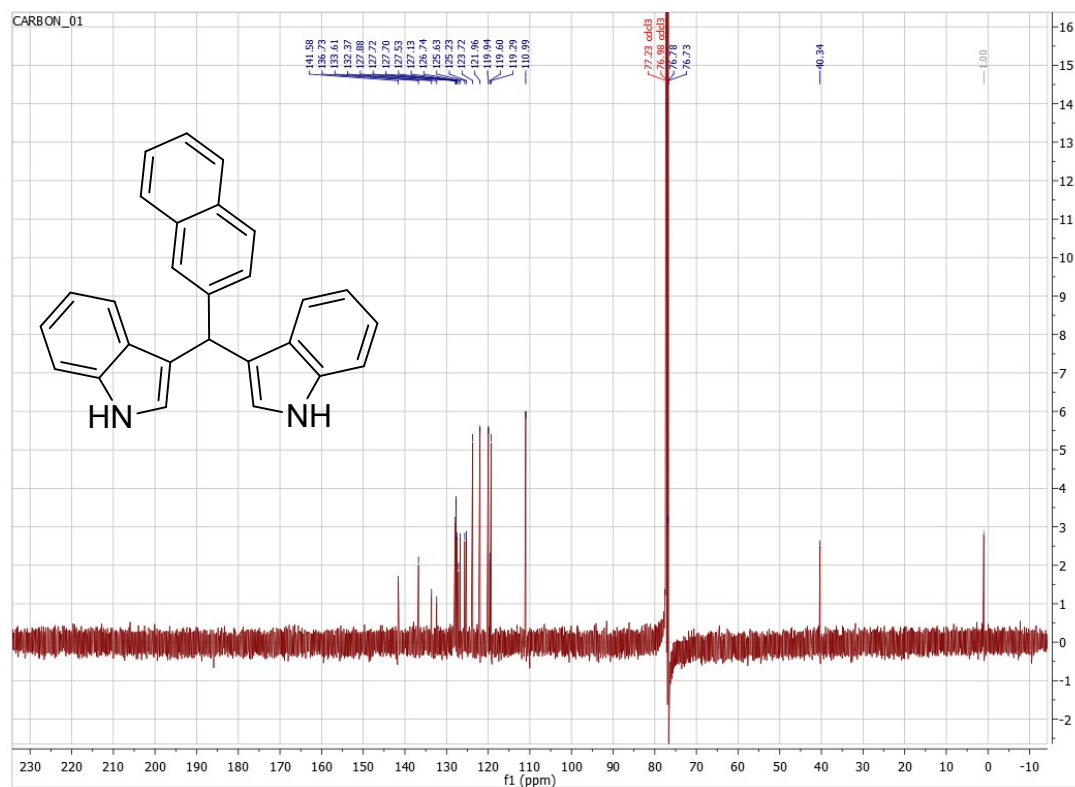
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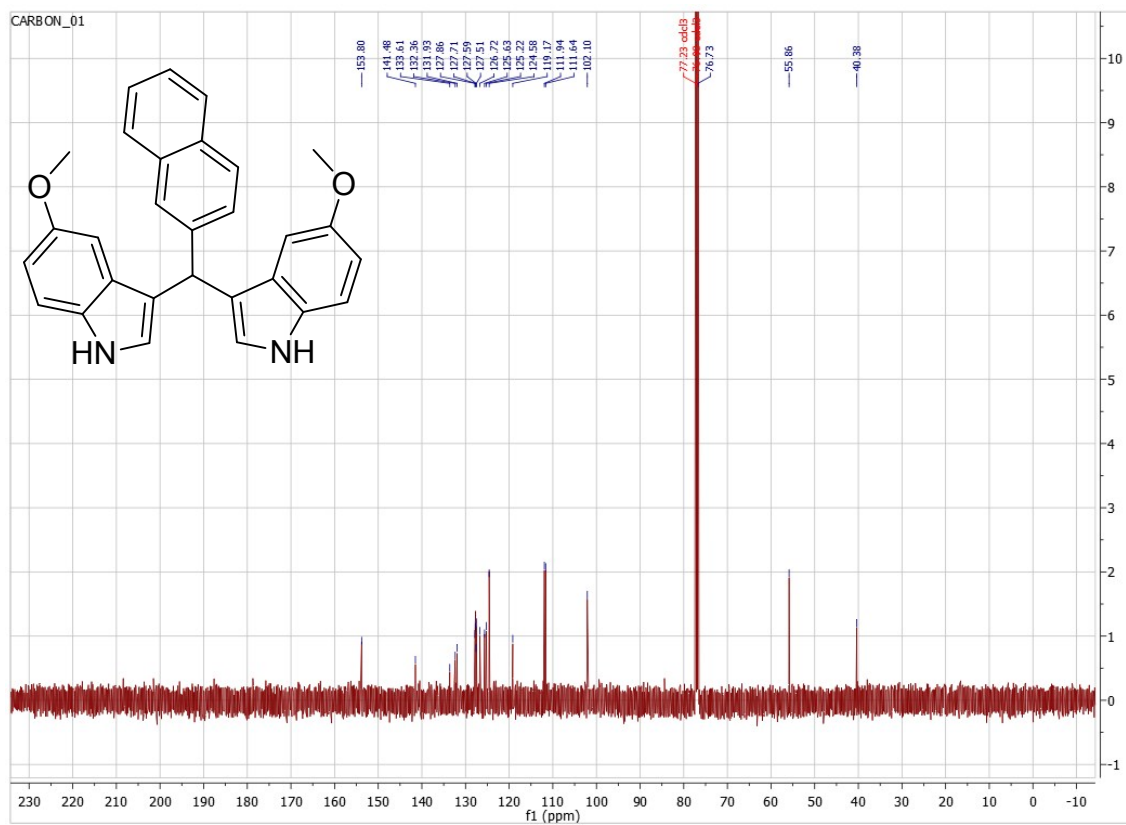
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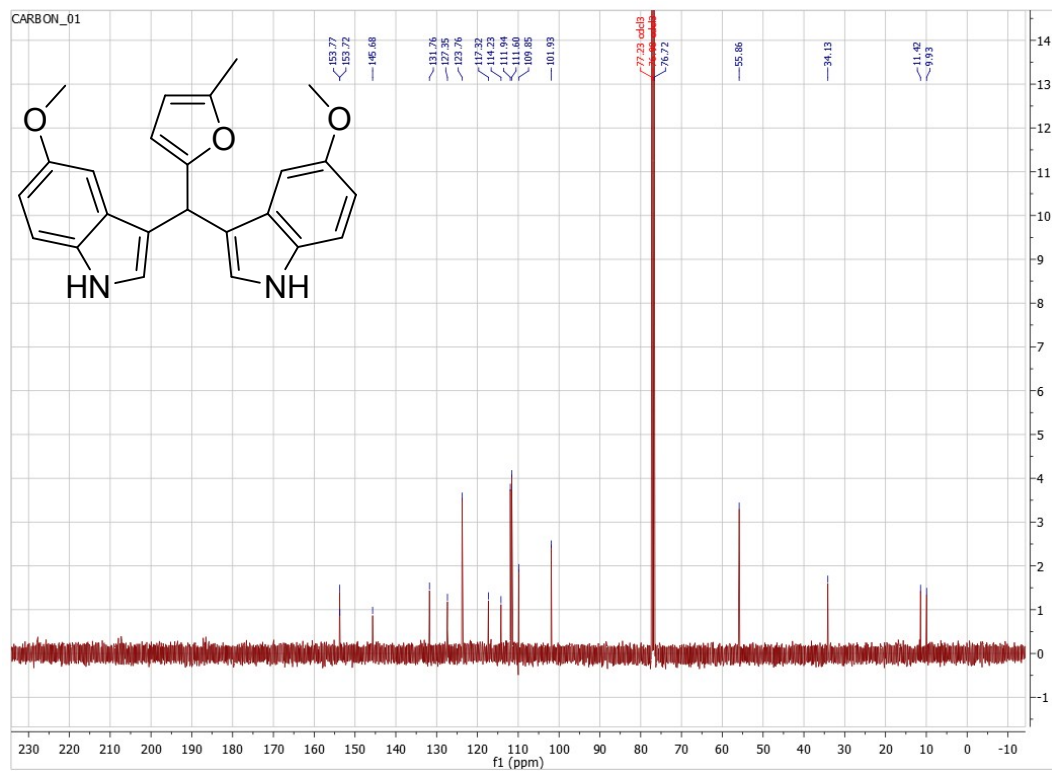
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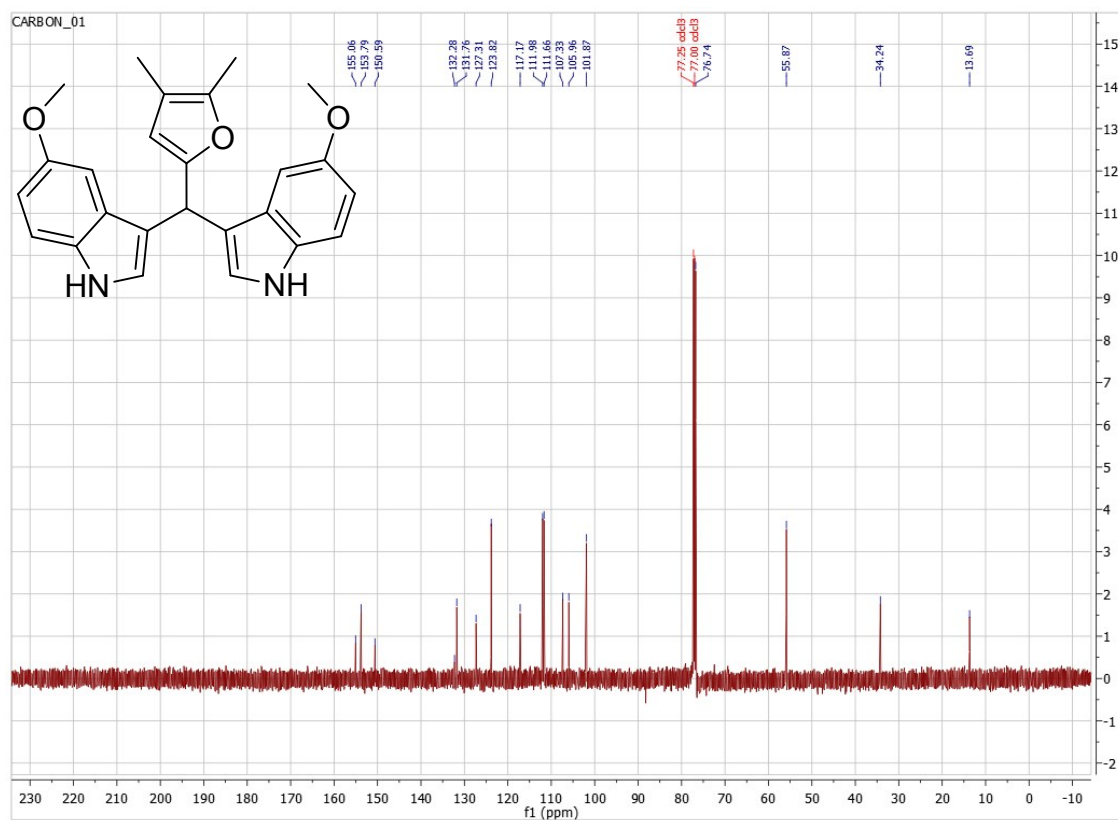
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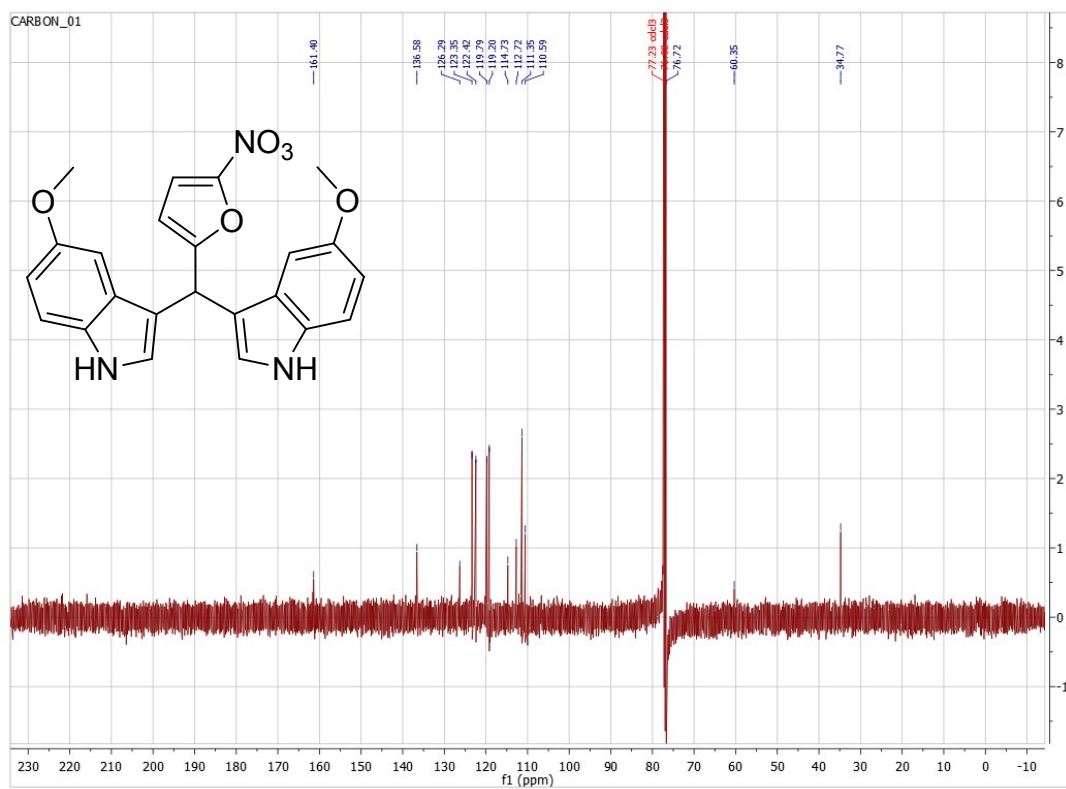
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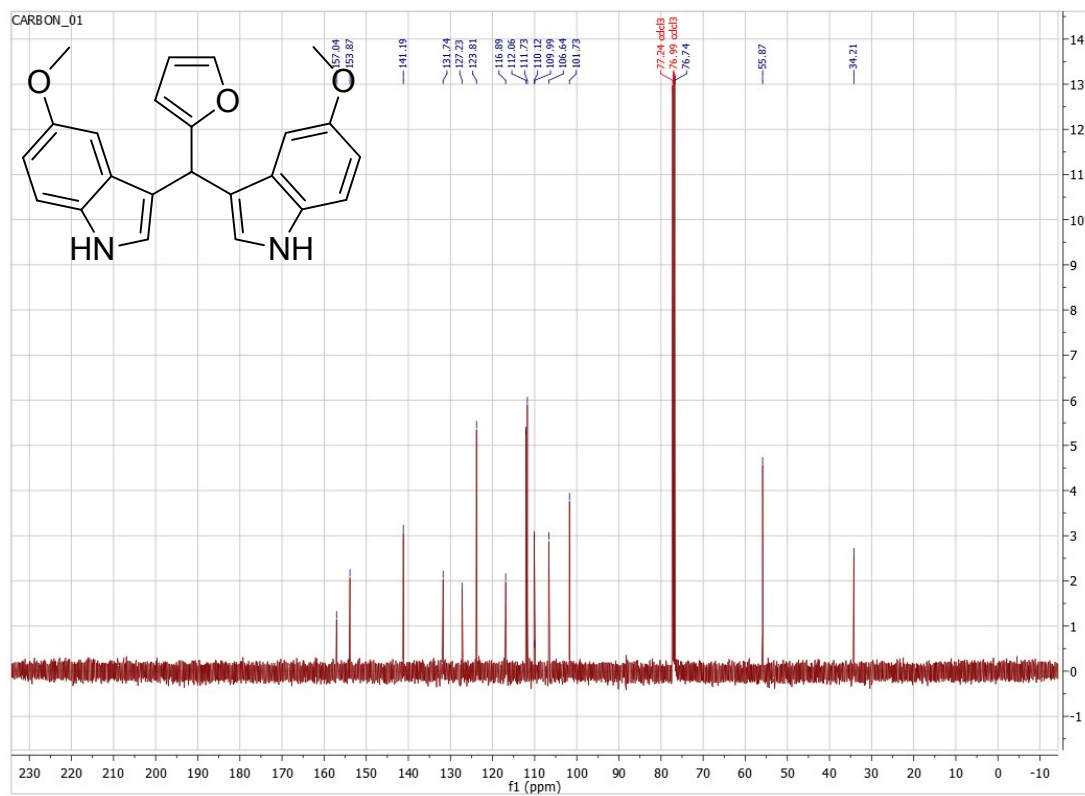
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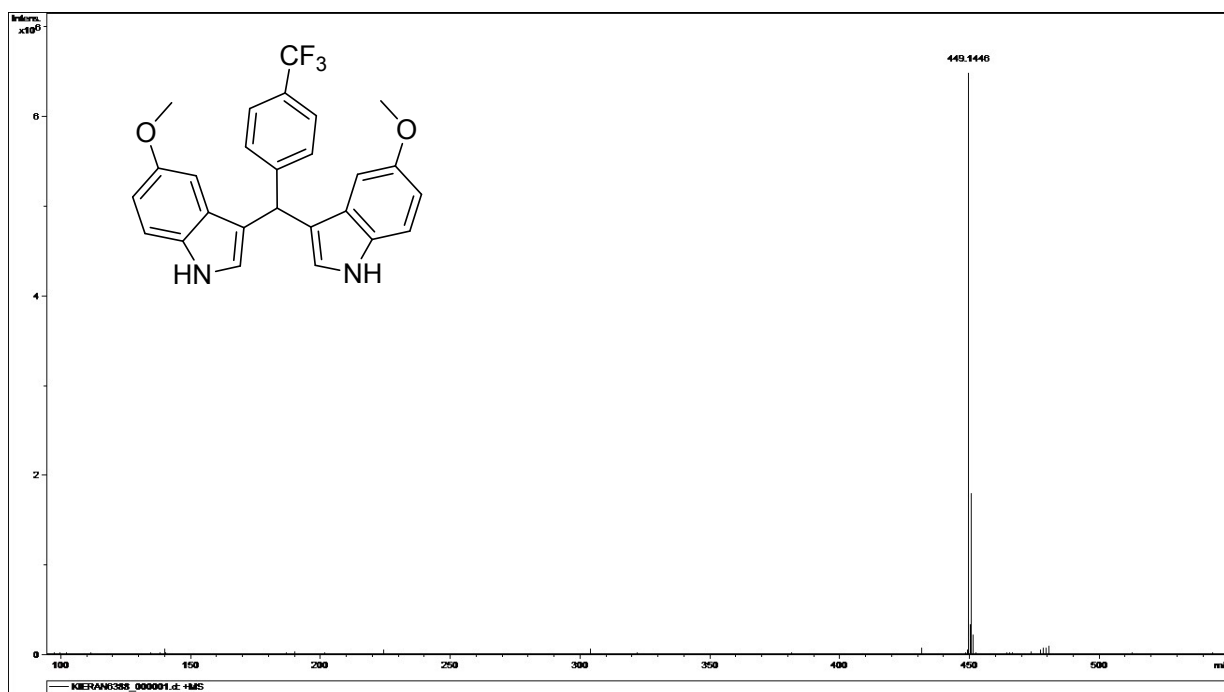


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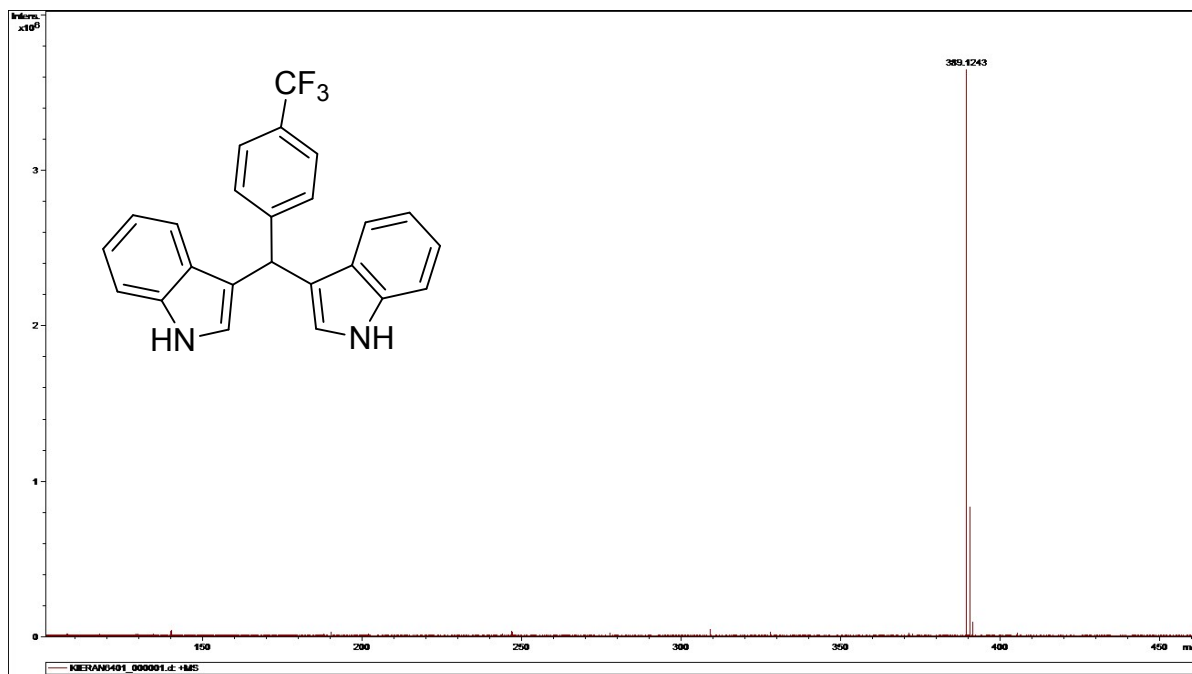


ESI-MS Organic Compounds

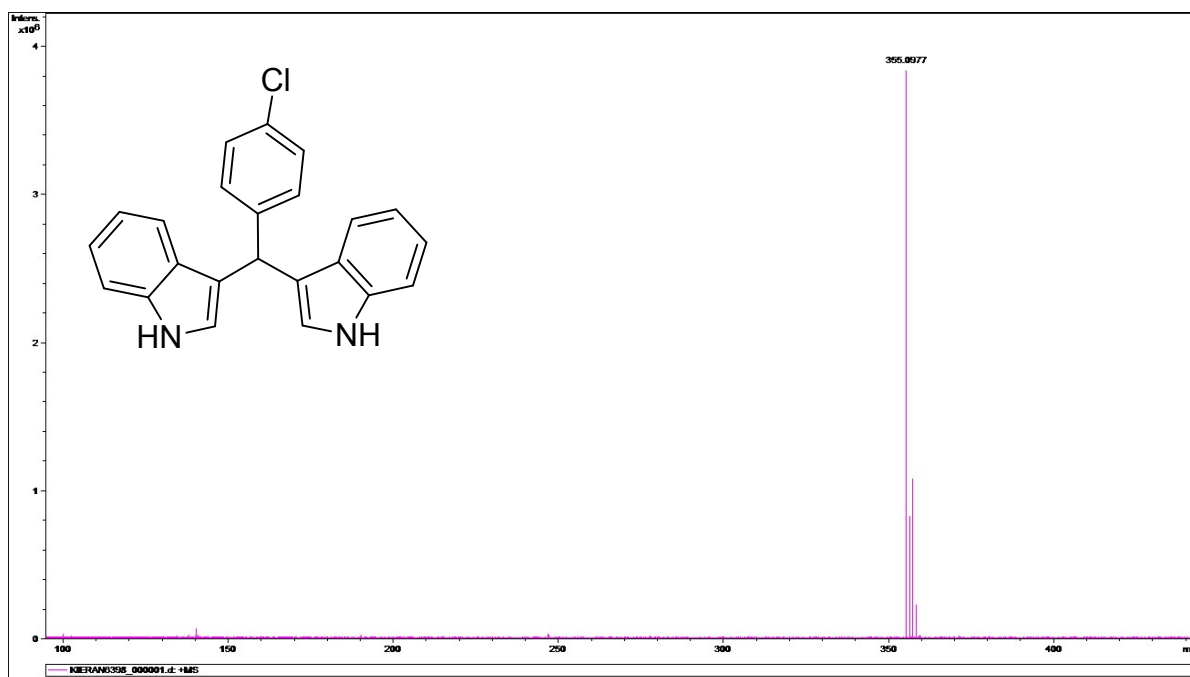
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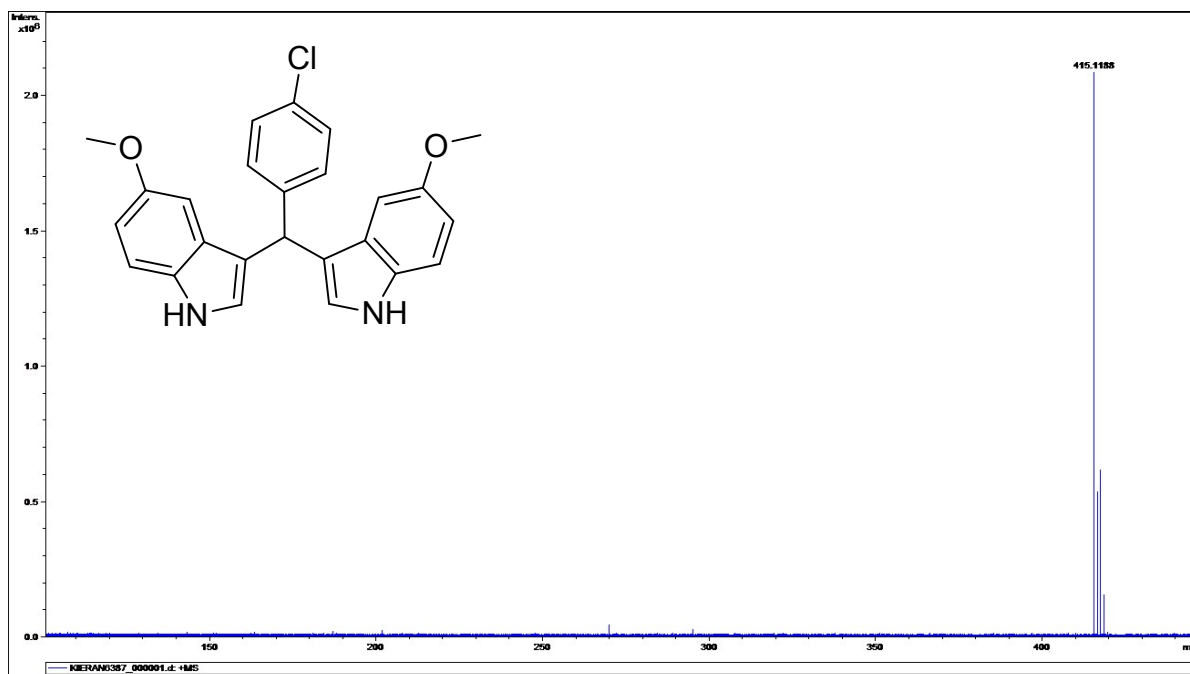
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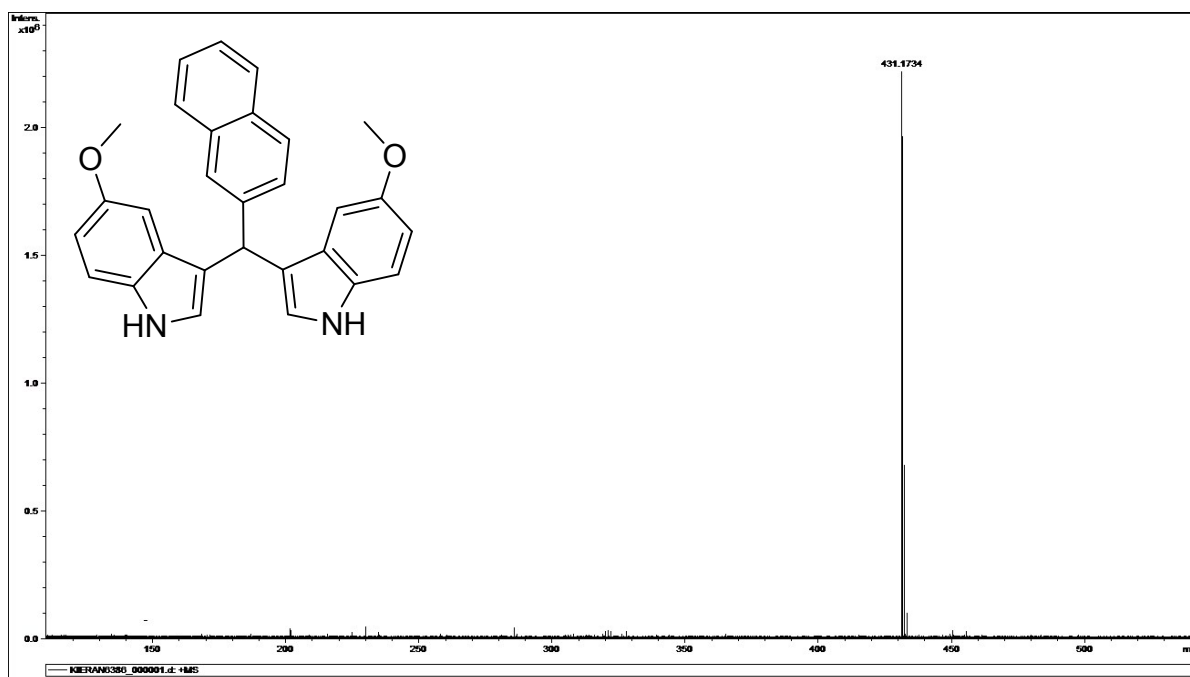
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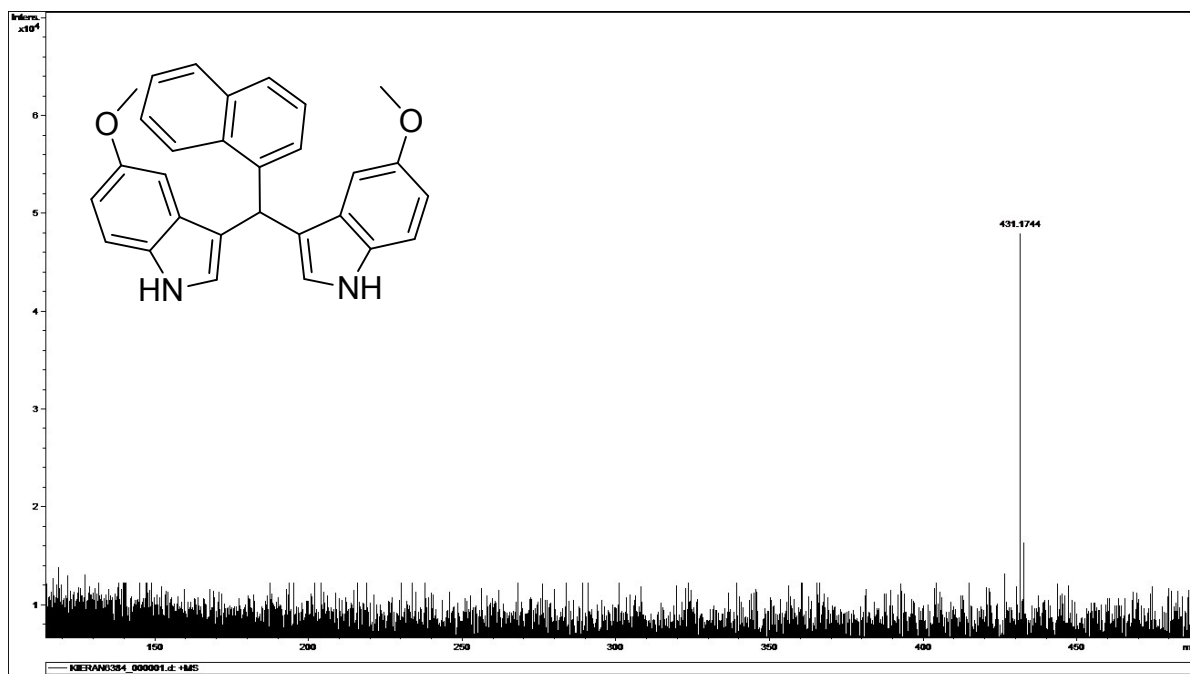
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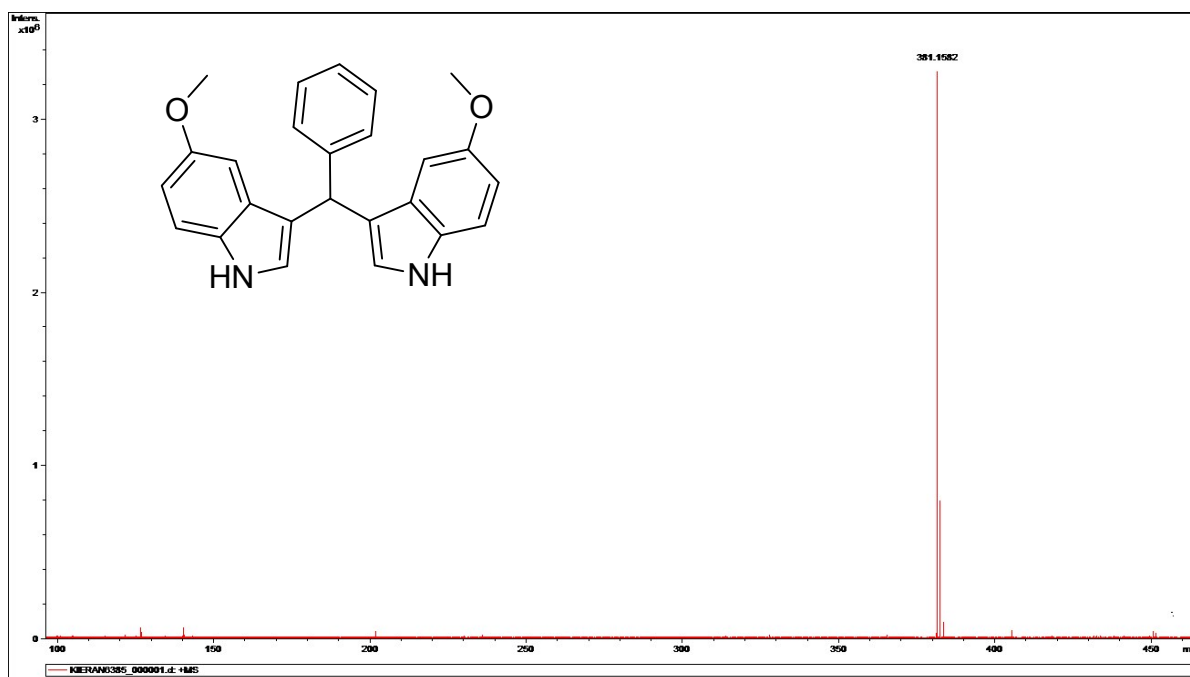
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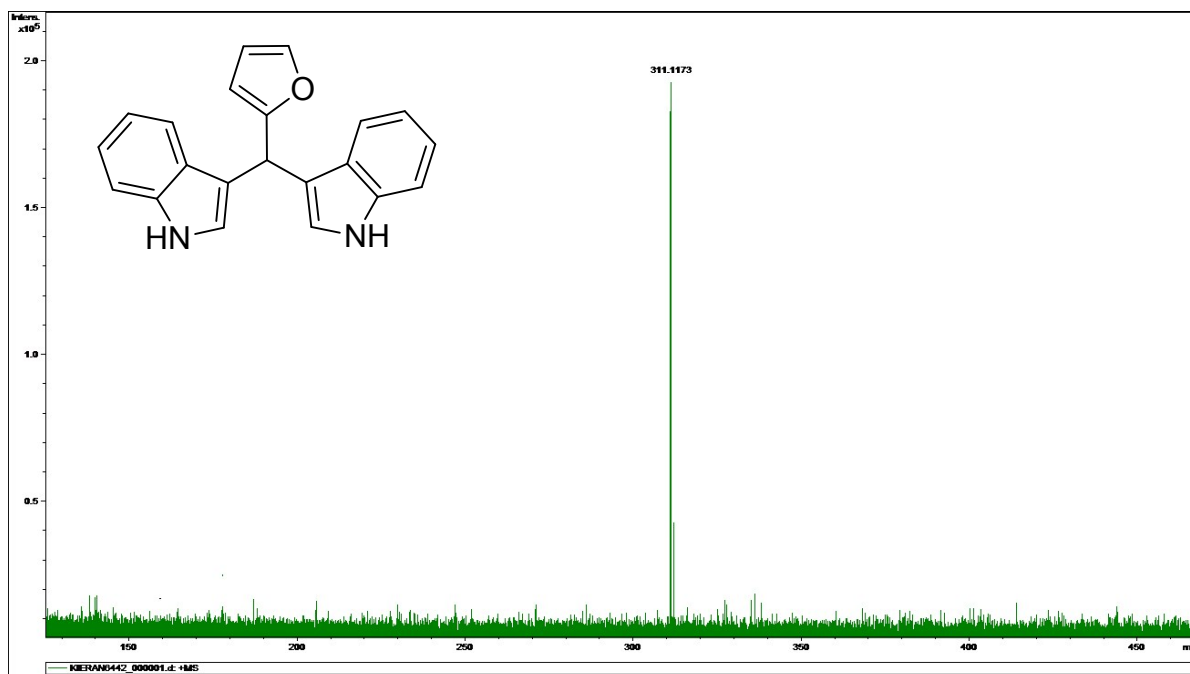
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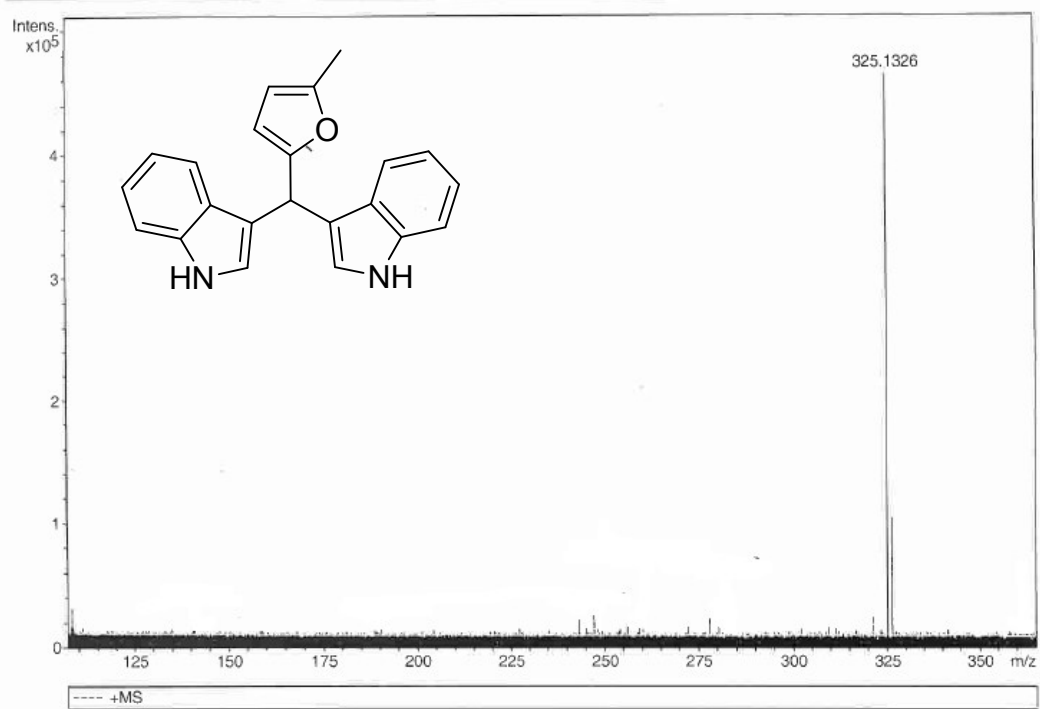
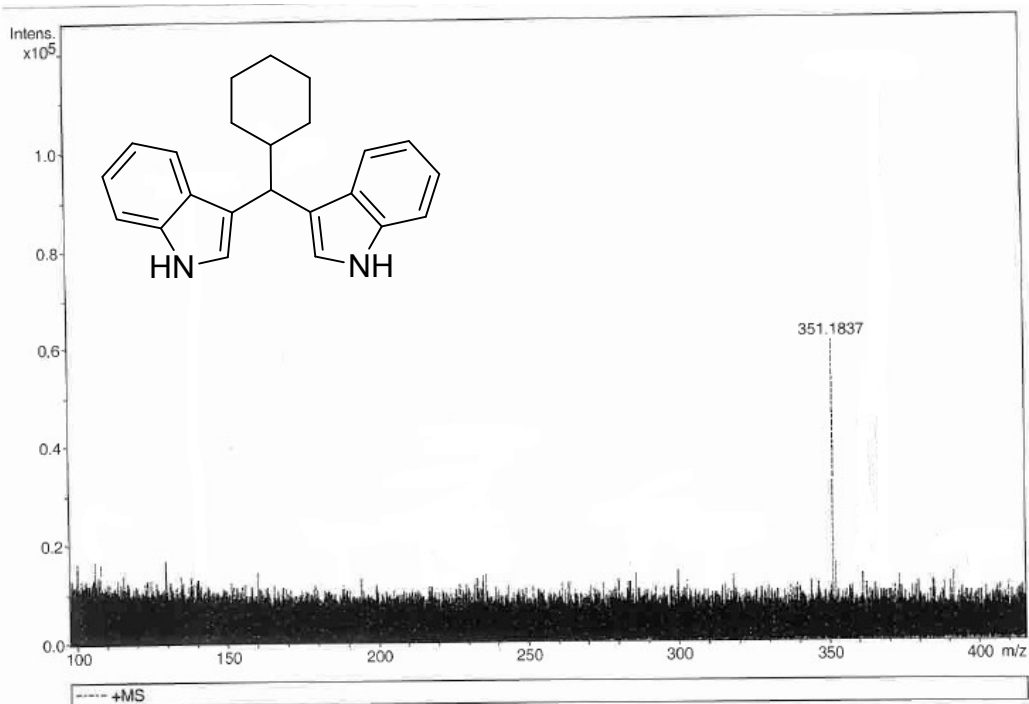


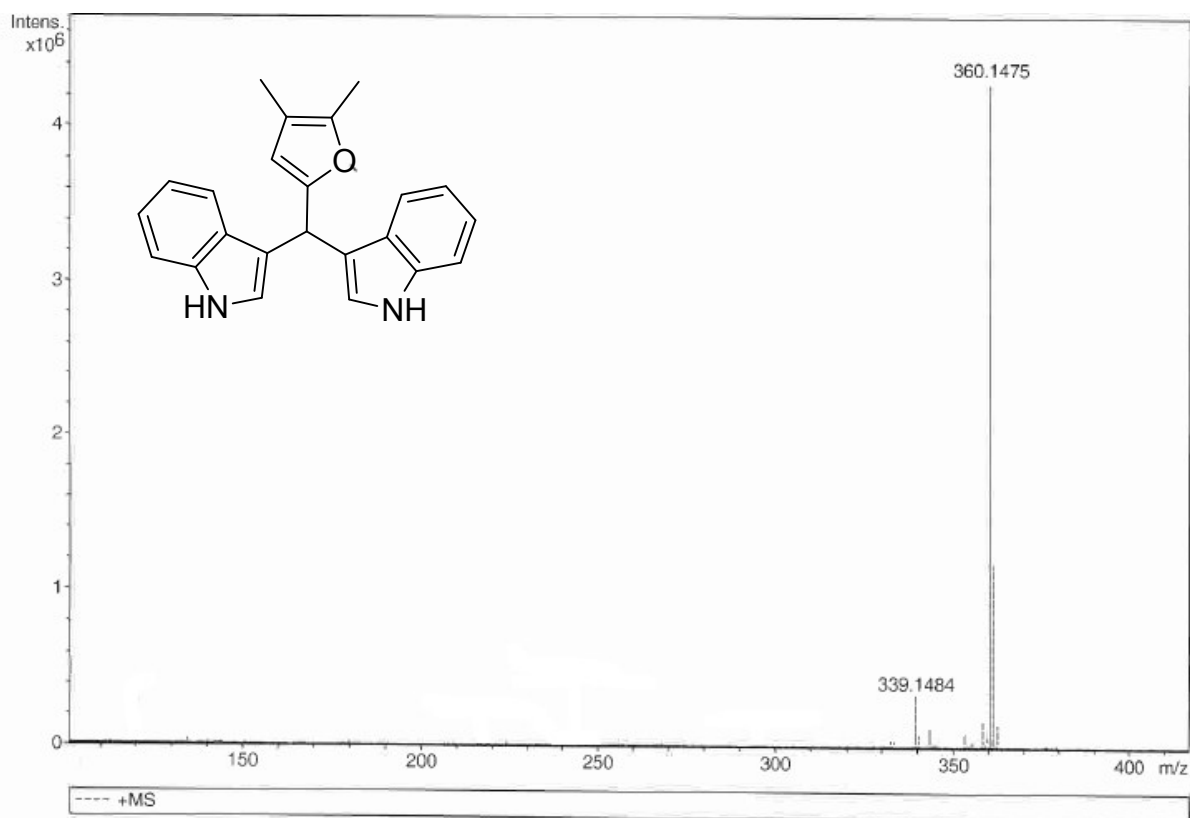
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7f







Sum	Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdB	N Rule	e ⁻
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