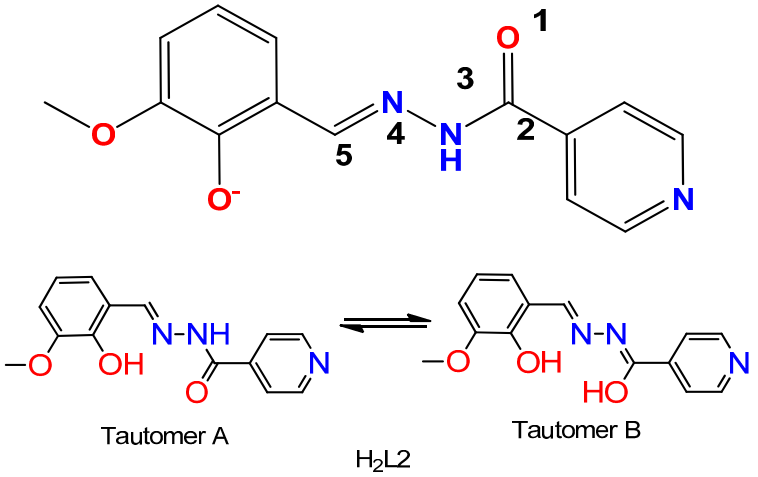
Supplementary Materials

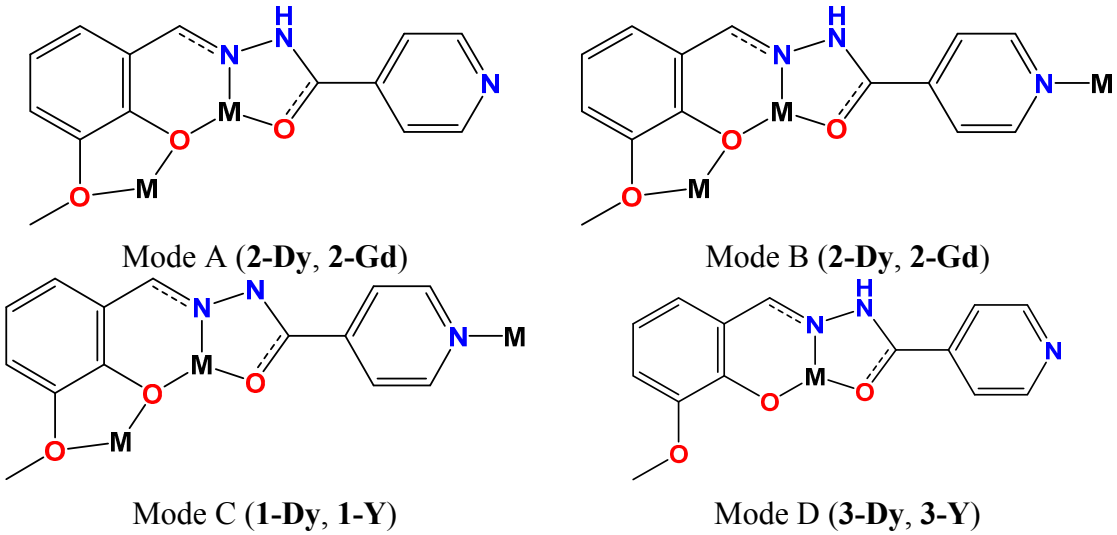
Table S1. Relevant bond distances that confirm the presence of the ligand molecule as Tautomer A or B.



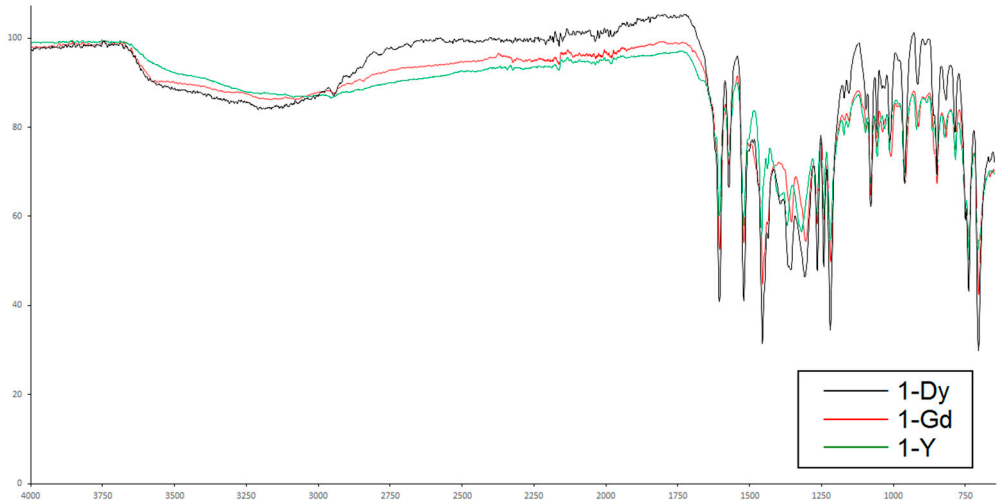
Tautomer A Tautomer B

H_2L2

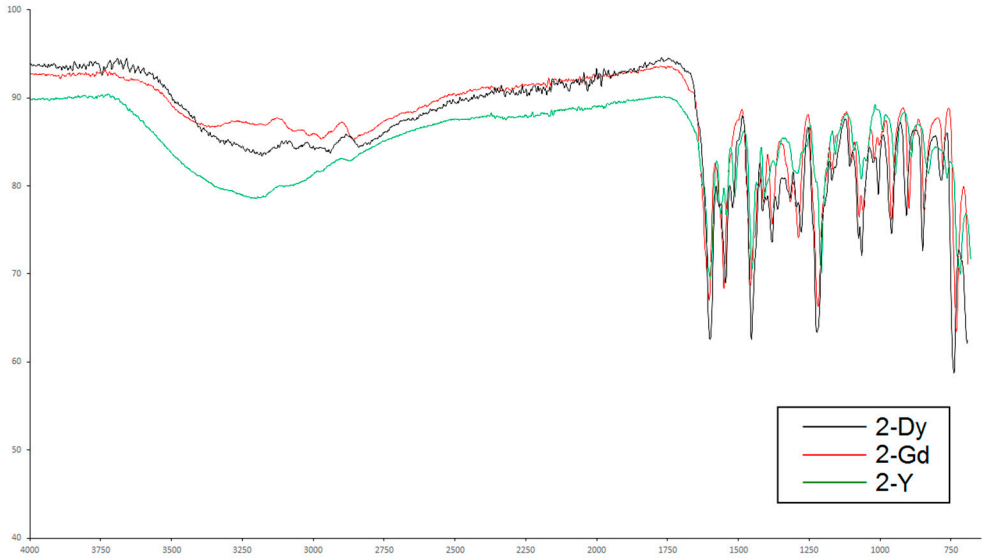
Compound	O1–C2 (Å)	C2–N3 (Å)	N3–N4 (Å)	N4–C5 (Å)	Tautomer
CANCOK (L)	1.213	1.357	1.370	1.279	A
CANCOK01 (L)	1.212	1.355	1.372	1.279	A
CANCOK02 (L)	1.216	1.352	1.373	1.275	A
CUVXUN	1.327	1.317	1.403	1.303	B
CUVYEY	1.298	1.301	1.402	1.288	B
CUVYOI	1.319	1.277	1.397	1.280	B
ERIKAS (1st L)	1.299	1.306	1.404	1.295	B
ERIKAS (2nd L)	1.301	1.304	1.406	1.294	B
KANYIJ	1.326	1.280	1.396	1.295	B
KANYIJ01	1.331	1.298	1.398	1.295	B
ODAROB ($L{\cdot}Cl^{-}$ 0.5 H_2O)	1.223	1.346	1.369	1.280	A
RIHQEG	1.220	1.364	1.371	1.281	A
VAKBIU	1.304	1.295	1.414	1.285	B
VAKBOA	1.217	1.360	1.368	1.276	A
VAKBUG	1.313	1.297	1.404	1.292	B
WISKEQ	1.233	1.337	1.390	1.283	A
XOLSAT (**1-Dy**)	1.292	1.298	1.405	1.280	B
XOLSIB	1.300	1.294	1.414	1.284	B
2-Dy (1st L)	1.232	1.326	1.383	1.294	A
2-Dy (2nd L)	1.237	1.334	1.384	1.312	A
2-Dy (3rd L)	1.258	1.323	1.407	1.300	A
3-Dy	1.249	1.328	1.403	1.289	A
3-Dy	1.247	1.324	1.399	1.289	A
2-Gd (1st L)	1.293	1.285	1.406	1.271	A
2-Gd (2nd L)	1.241	1.308	1.423	1.285	A
2-Gd (3rd L)	1.277	1.299	1.388	1.234	A
1-Y	1.290	1.308	1.416	1.294	B
3-Y (1st L)	1.251	1.337	1.410	1.294	A
3-Y (2nd L)	1.250	1.339	1.400	1.293	A



Scheme S1. The coordination modes of the H_2L2 ligand.



(A)



(B)

Figure S1. (**A**) IR comparison of **1-Dy**, **1-Gd**, **1-Y**; (**B**) IR comparison of **2-Dy**, **2-Gd**, **2-Y**.

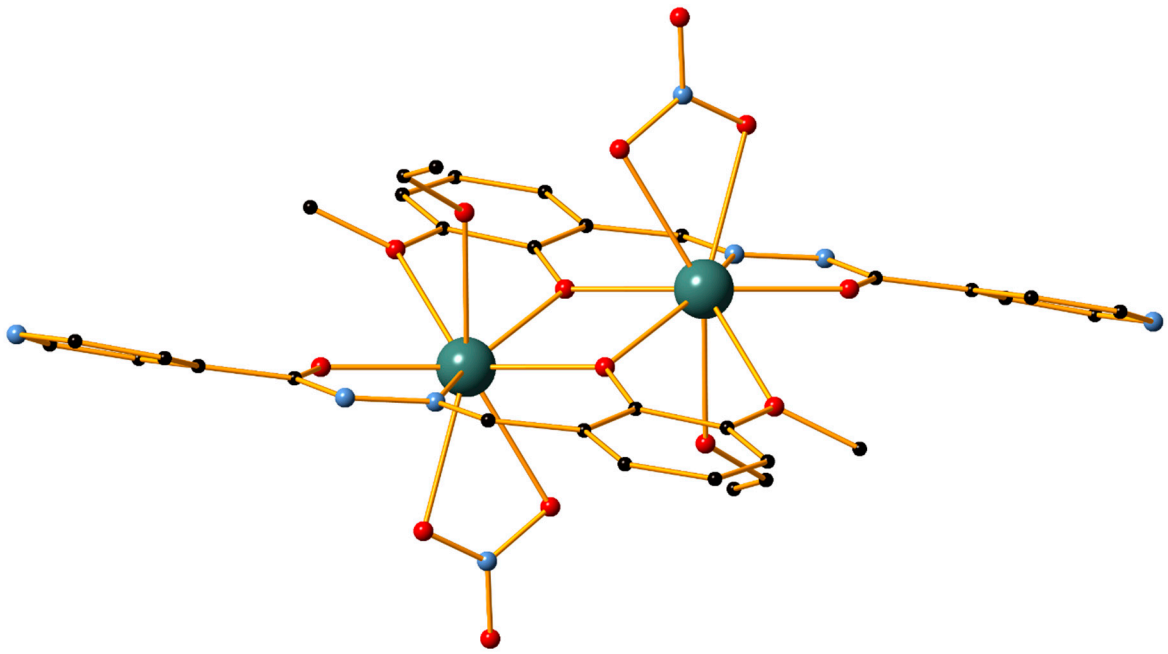


Figure S2. The structure of **1-Y**. H atoms and solvent molecules are omitted for clarity. Colour code Y (dark green), C (black), N (light blue), O (red).

Table S2. Selected bond lengths (Å) for **2-Dy**.

Dy1–O2	2.393(5)	Dy2–O2	2.370(4)
Dy1–O5	2.332(5)	Dy2–O5	2.318(5)
Dy1–O8	2.277(4)	Dy2–O8	2.350(5)
Dy1–O7	2.283(5)	Dy2–O9	2.551(5)
Dy1–O3	2.524(5)	Dy2–O4	2.454(5)
Dy1–O6	2.570(5)	Dy2–O1	2.353(5)
Dy1–Cl2	2.359(5)	Dy2–Cl1	2.376(6)
Dy1–N7	2.495(7)	Dy2–N1	2.564(6)
Dy1–N3 [1]	2.692(6)	Dy2–N4	2.555(6)

[1] 1/2 − X, 1/2 + Y, 1/2 − Z.

Table S3. Selected bond lengths (Å) for **3-Dy**.

Dy1–O13	2.449(3)	Dy2–O16	2.389(3)
Dy1–O7	2.402(3)	Dy2–O20	2.523(3)
Dy1–O1	2.402(3)	Dy2–O4	2.368(3)
Dy1–O9	2.497(3)	Dy2–O21	2.485(3)
Dy1–O10	2.567(3)	Dy2–O17	2.452(3)
Dy1–O2	2.175(3)	Dy2–O15	2.375(3)
Dy1–O8	2.375(3)	Dy2–O5	2.179(3)
Dy1–N1	2.486(3)	Dy2–O19	2.534(3)
Dy1–O12	2.514(3)	Dy2–N4	2.528(3)

Table S4. Selected bond lengths (Å) for **3-Y**.

Y1–O1	2.398(2)
Y1–O5	2.212(2)
Y1–O4	2.401(2)
Y1–O7	2.358(2)
Y1–O2	2.211(2)
Y1–O8	2.368(2)
Y1–N1	2.509(3)
Y1–N4	2.482(3)

Table S5. Hydrogen bonds for compound **3-Dy**.

D–H· · ·A	**D–H [Å]**	**H· · ·A [Å]**	**D· · ·A [Å] [Å]**	**D–H· · ·A [°]**
N2–H2···O21 [1]	0.88	2.23	2.998(5)	146
N5–H5A···O11 [2]	0.88	2.12	2.899(5)	147
O7–H7···N6	0.85(5)	1.85(5)	2.685(6)	171(4)
O16–H16···N3	0.84(5)	1.92(6)	2.742(5)	165(4)
O8–H8···O18 [3]	0.84(3)	1.90(4)	2.740(5)	173(3)
O15–H15···O14 [4]	0.85(3)	1.91(3)	2.751(5)	173(4)

[1] 1 + X, Y, Z; [2] 1−X, 1−Y, −Z; [3] X, −1 + Y, Z; [4] X, 1 + Y, Z.

Table S6. Hydrogen bonds for compound **3-Y**.

D–H· · ·A	**D–H [Å]**	**H· · ·A [Å]**	**D· · ·A [Å] [Å]**	**D–H· · ·A [°]**
N2–H2···Cl1	0.86	2.32	3.138(3)	160
N5–H5···Cl1 [1]	0.86	2.32	3.157(3)	164
O7–H7···N3 [2]	0.86(2)	1.85(3)	2.697(4)	170(3)
O8–H8···N6 [3]	0.861(14)	1.859(14)	2.719(4)	177(2)

[1] X, 3/2 − Y, −1/2 + Z; [2] 1 − X, 1 − Y, 2 − Z; [3] −X, 1 − Y, 1 − Z.

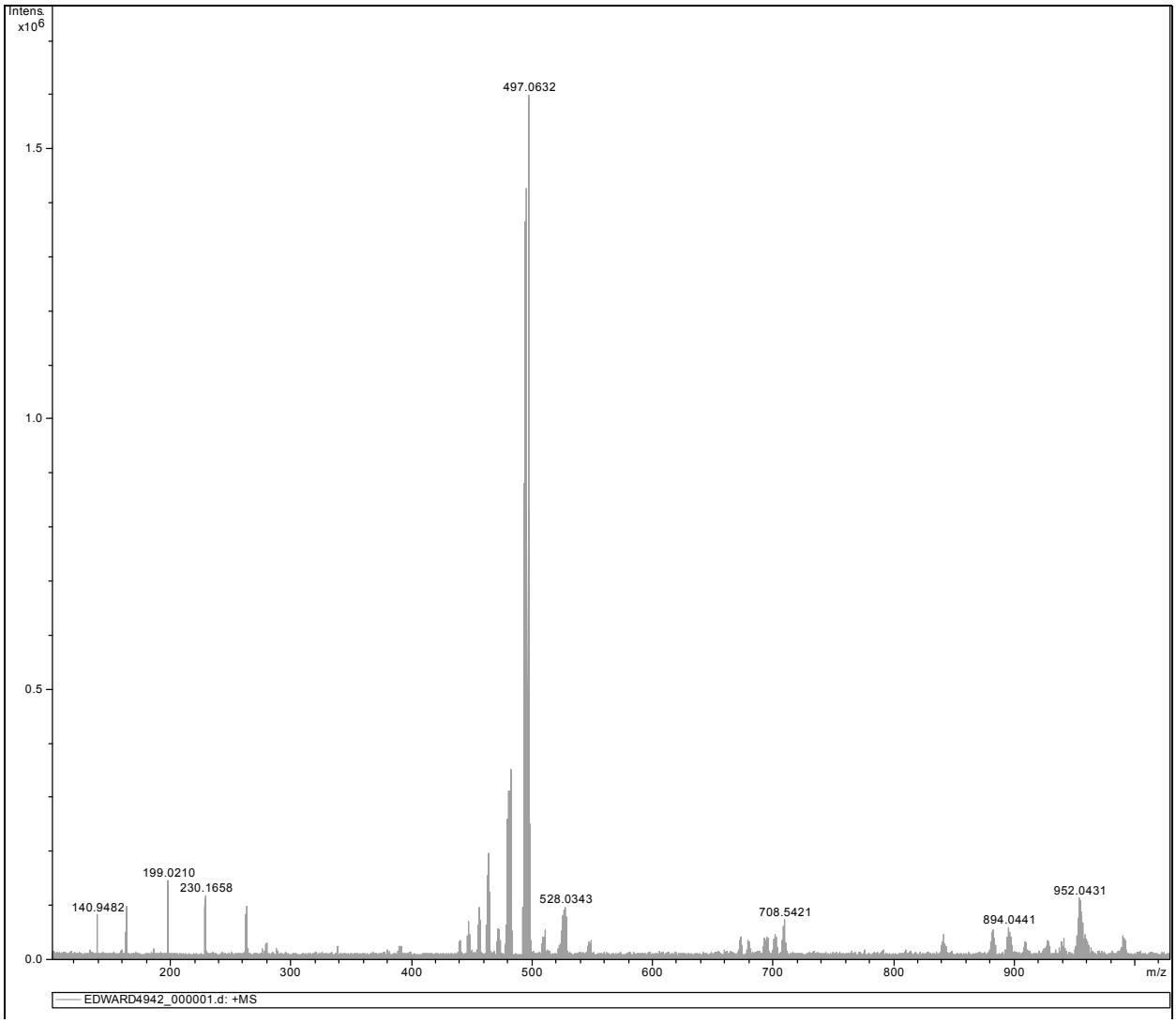


Figure S3. ESI-MS of **1-Dy**.

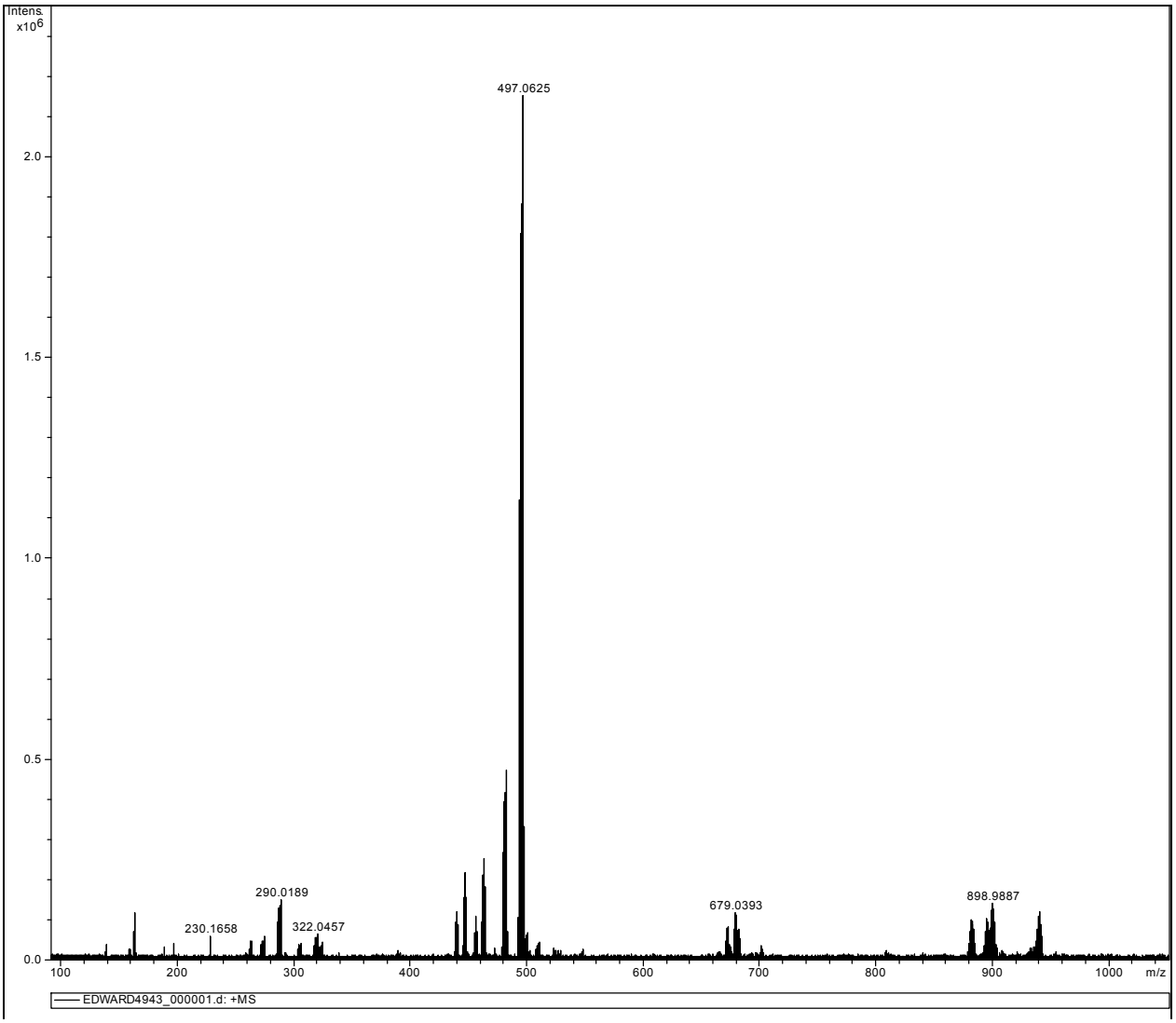


Figure S4. ESI-MS of **2-Dy**.

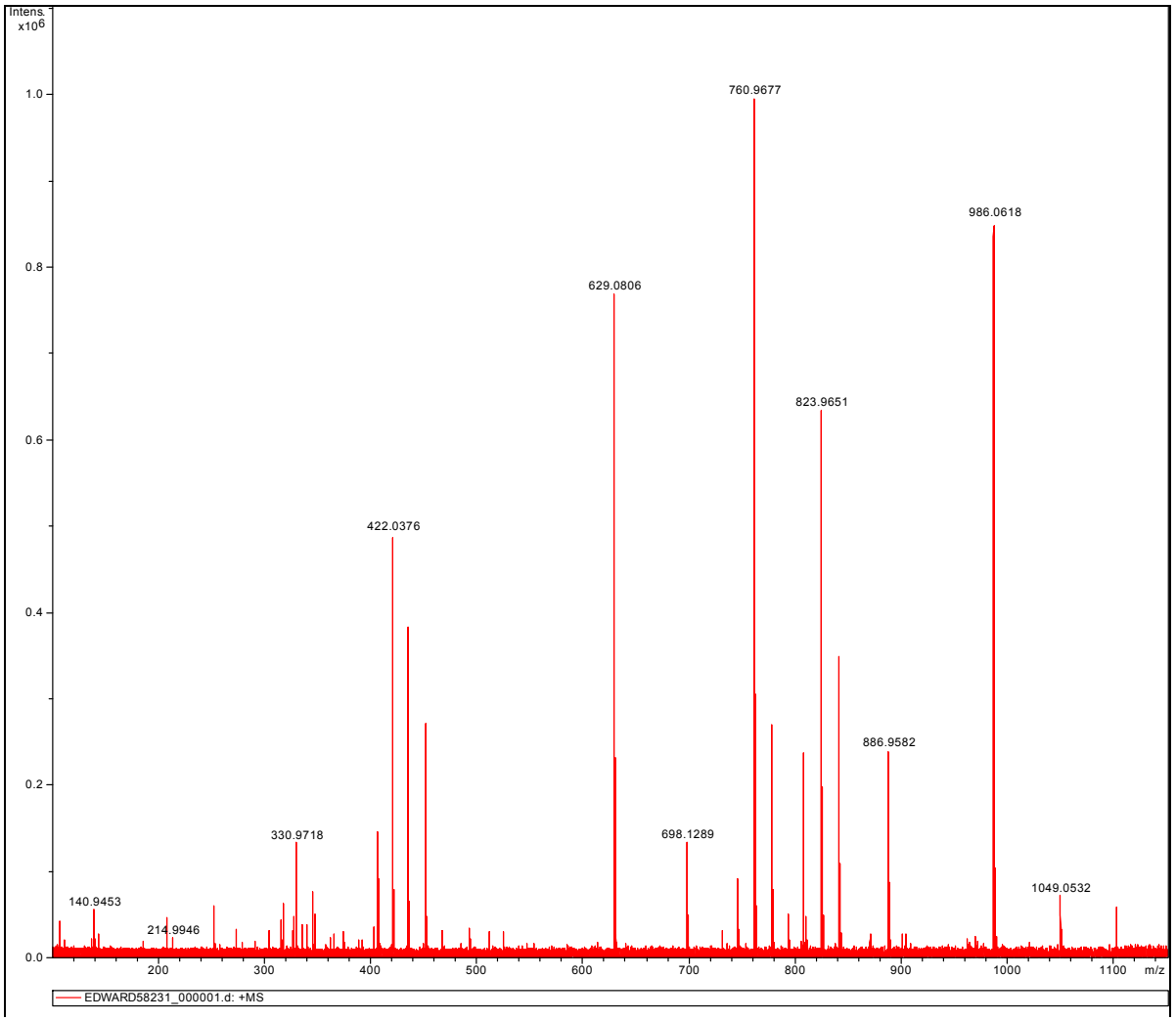


Figure S5. ESI-MS of **1-Y**.

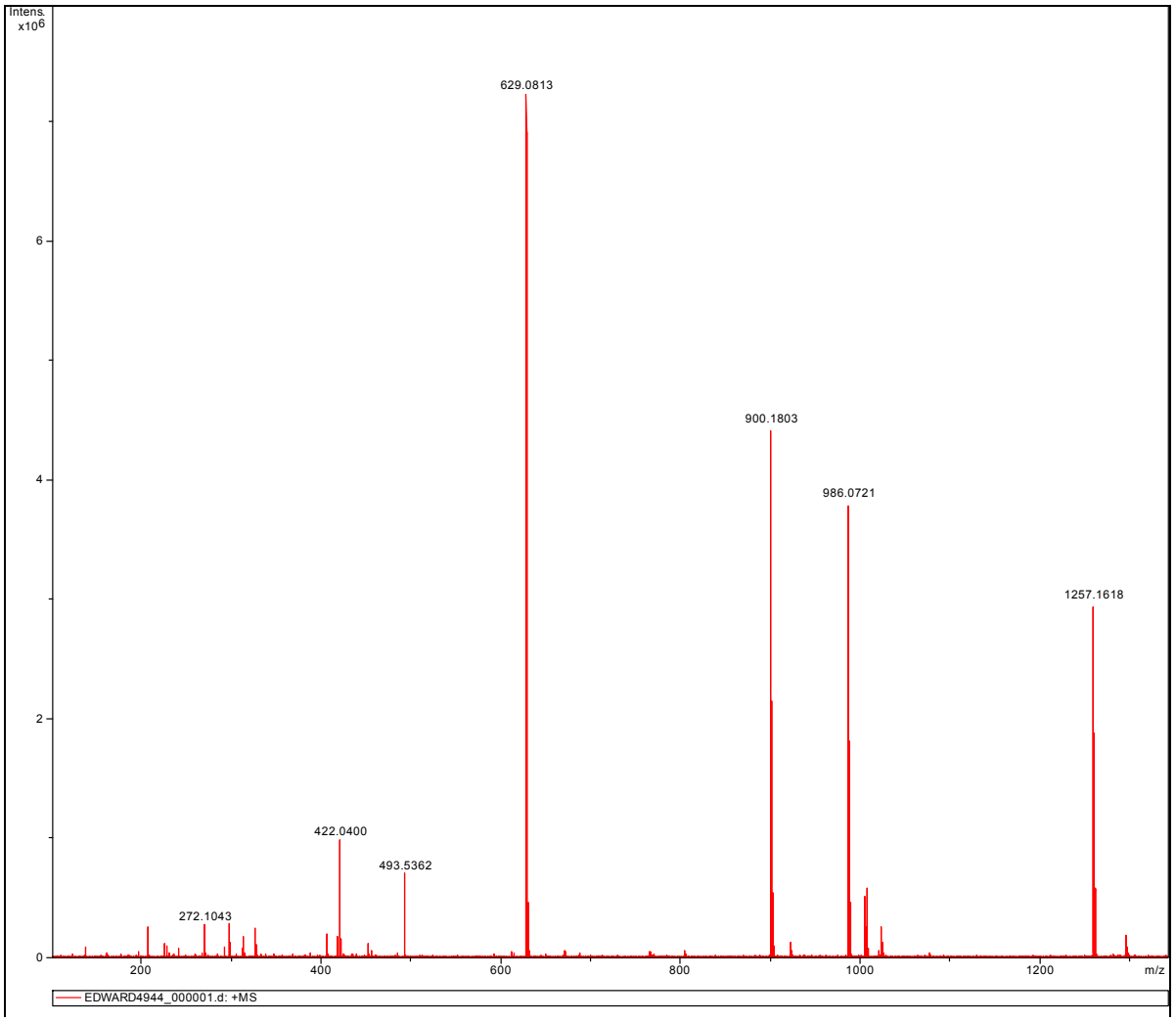


Figure S6. ESI-MS of **2-Y**.

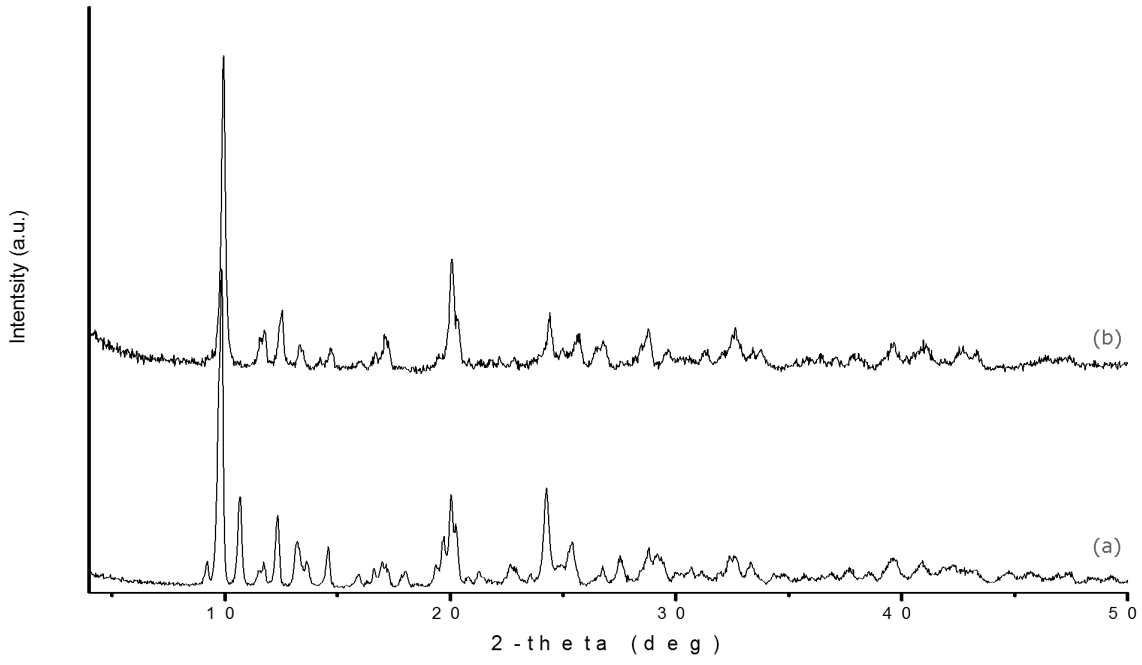
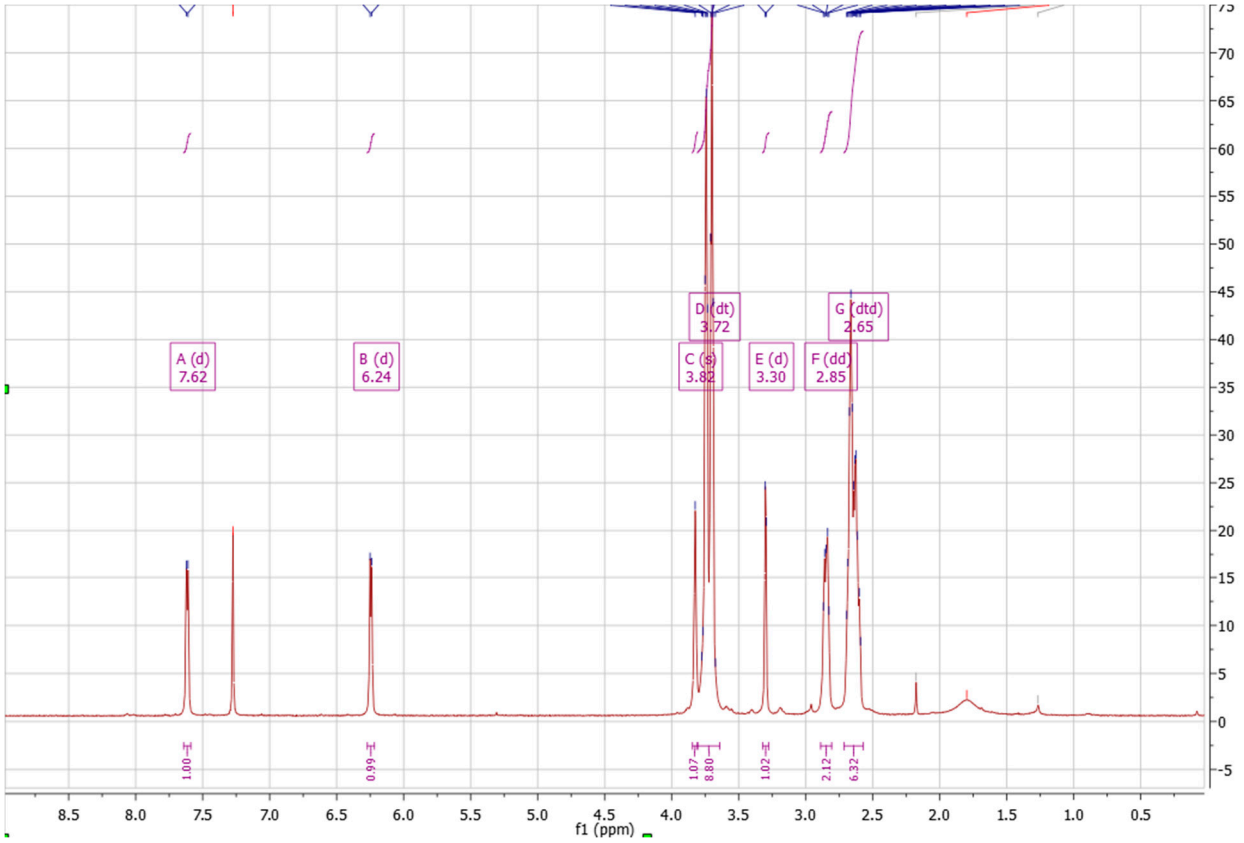


Figure S7. XRPD patterns of **1-Y** (**a**) and **1-Dy** (**b**).

Catalytic Protocols

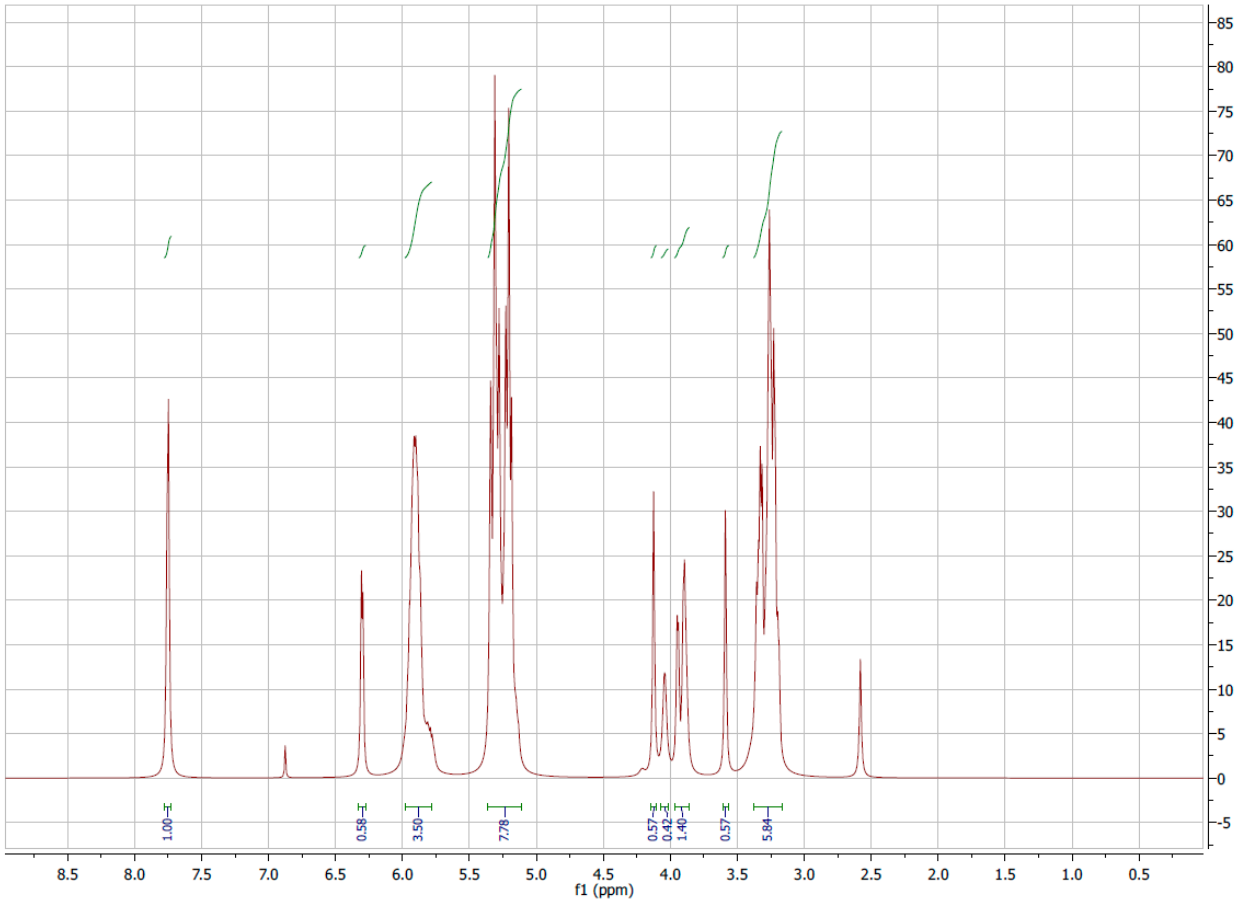
trans-4,5-Dimorpholin-4-yl-cyclopent-2-enone (4a)

In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vial equipped with a magnetic stirbar. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 µL), morpholine (1 mmol, 91 µL) and the appropriate amount of catalyst (10%–0.5% total of Ln) were added. The resultant mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure and the residue purified by column chromatography (30% ethyl acetate in 70% Hexanes). The product was obtained as yellow oil which solidified on standing. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 6.3 Hz, 1H), 6.24 (d, *J* = 6.4 Hz, 1H), 3.82 (s, 1H), 3.72 (dt, *J* = 21.2, 4.5 Hz, 9H), 3.30 (d, *J* = 3.1 Hz, 1H), 2.85 (dd, *J* = 10.8, 5.2 Hz, 2H), 2.65 (dtd, *J* = 20.7, 11.4, 10.7, 5.3 Hz, 6H).



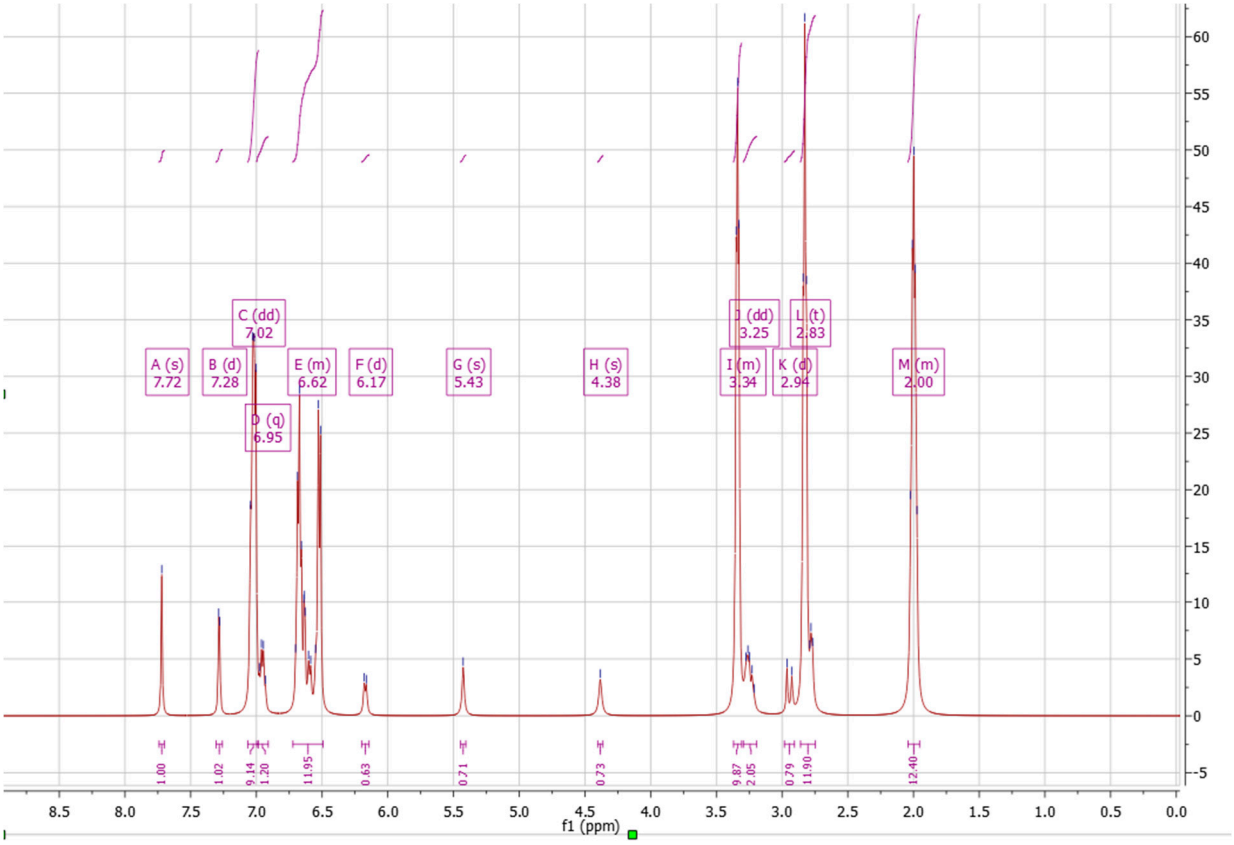
***trans*-4,5-Bis-diallylaminocyclopent-2-enone (4b)**

In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vial equipped with a magnetic stirbar. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 µL), diallylamine (1 mmol, 121 µL) and the appropriate amount of catalyst (2.5% total of Y in **1-Y**) were added. The resultant mixture was stirred at room temperature for 16 h. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure and the residue purified by column chromatography (5% ethyl acetate in 95% Hexanes). The product was obtained as a yellow oil which solidified on standing. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (1H, dd, J = 6.0, 2.0 Hz), 6.16 (1H, dd, J = 6.0, 2.0 Hz), 5.91–5.77 (4H, m), 5.26–5.10 (8H, m), 4.11 (1H, ddd, J = 3.0, 2.0, 2.0 Hz), 3.59 (1H, d, J = 3.0Hz), 3.38–3.31 (2H, m), 3.23–3.10 (6H, m).



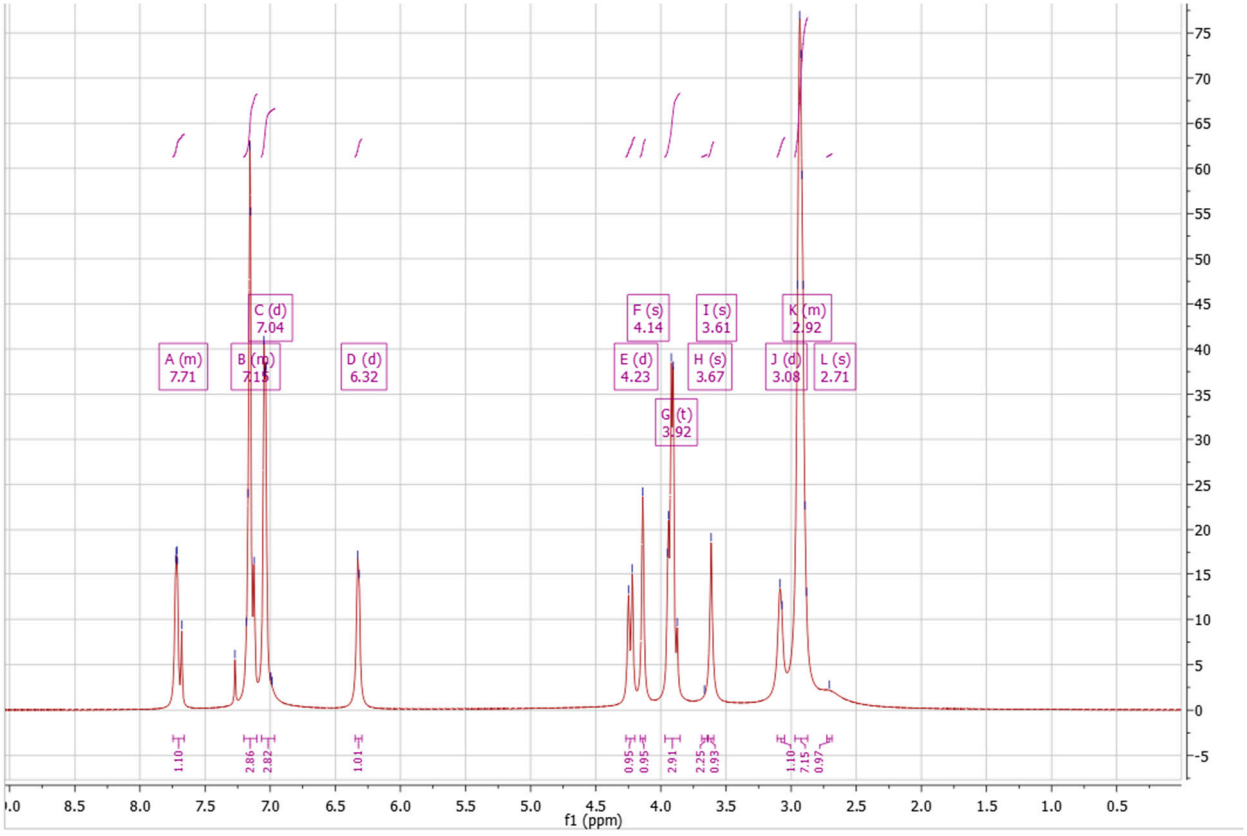
***trans*-4,5-Bis-(3,4-dihydro-*1H*-isoquinolin-2-yl)-cyclopent-2-enone (4d)**

In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vial equipped with a magnetic stirbar. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 µL), 1,2,3,4- Tetrahydroisoquinoline (1 mmol, 125 µL) and the appropriate amount of catalyst (2.5% total of Y in **1-Y**) were added. The resultant mixture was stirred at room temperature for 4h. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure and the residue purified by column chromatography (30% ethyl acetate in 70% Hexanes). The product was obtained as yellow oil which solidified on standing. ^{1}H NMR (500 MHz,) δ 7.75–7.66 (m, 1H), 7.20–7.10 (m, 3H), 7.04 (d, J = 7.2 Hz, 3H), 6.32 (d, J = 6.3 Hz, 1H), 4.23 (d, J = 14.7 Hz, 1H), 4.14 (s, 1H), 3.92 (t, J = 11.1 Hz, 3H), 3.67 (s, 2H), 3.61 (s, 1H), 3.08 (d, J = 8.2 Hz, 1H), 2.97–2.87 (m, 7H), 2.71 (s, 1H).



***trans*-4,5-Bis-(3,4-dihydro-2*H*-quinolin-1-yl)-cyclopent-2-enone (4e)**

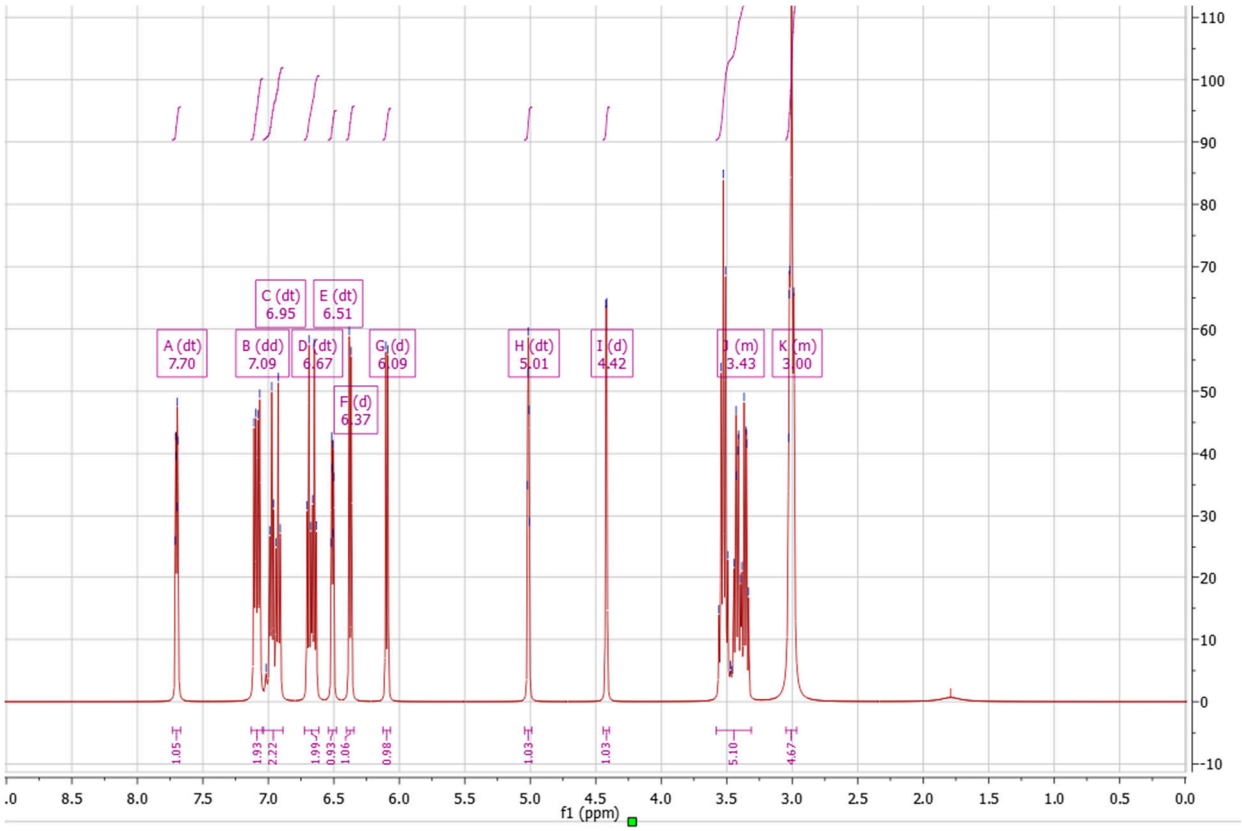
In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vial equipped with a magnetic stirbar. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 µL), 1,2,3,4-Tetrahydroquinoline (1 mmol, 125.5 µL) and the appropriate amount of catalyst (2.5% total of Y in **1-Y**) were added. The resultant mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure and the residue purified by column chromatography (20% ethyl acetate in 80% Hexanes). The product was obtained as yellow oil which solidified on standing. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.02 (dd, *J* = 12.9, 7.2 Hz, 1H), 6.95 (q, *J* = 7.9 Hz, 1H), 6.72–6.49 (m, 2H), 6.17 (d, *J* = 8.3 Hz, 1H), 5.43 (s, 1H), 4.38 (s, 1H), 3.37–3.31 (m, 2H), 3.31–3.18 (m, 1H), 2.94 (d, *J* = 18.4 Hz, 1H), 2.83 (t, *J* = 6.2 Hz, 2H), 2.04–1.95 (m, 2H).



***trans*-4,5-Bis-(2,3-dihydroindol-1-yl)-cyclopent-2-enone (4c)**

In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vial equipped with a magnetic stirbar. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 µL), Indoline (1 mmol, 112 µL) and the appropriate amount of catalyst (2.5% total of Y in **1-Y**) were added. The resultant mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure and the residue purified by column chromatography (20% ethyl acetate in 80% Hexanes). The product was obtained as yellow oil which solidified on standing.

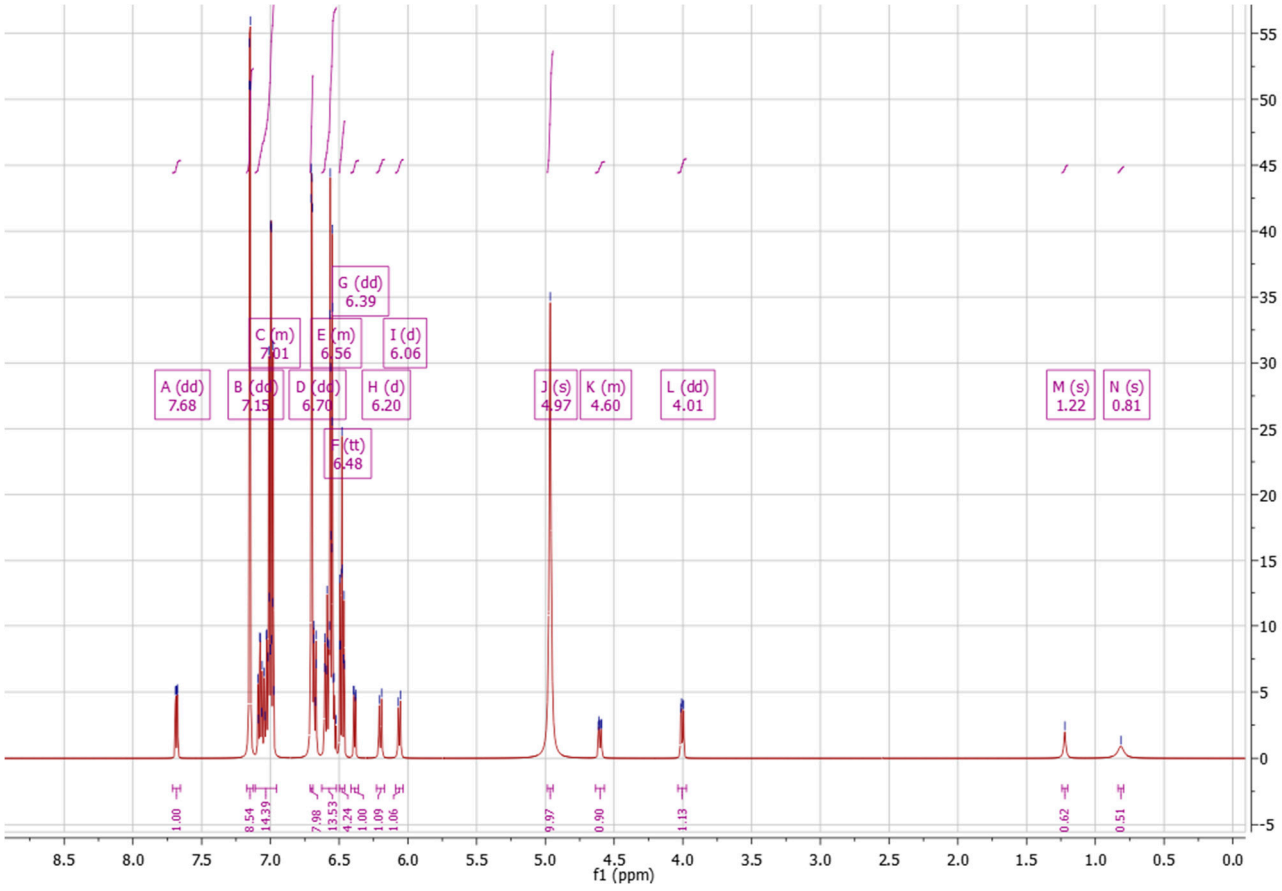
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (dt, *J* = 6.5, 1.6 Hz, 1H), 7.09 (dd, *J* = 14.8, 7.2 Hz, 2H), 6.95 (dt, *J* = 24.6, 7.8 Hz, 2H), 6.67 (dt, *J* = 20.7, 7.3 Hz, 2H), 6.51 (dt, *J* = 6.3, 1.6 Hz, 1H), 6.37 (d, *J* = 7.9 Hz, 1H), 6.09 (d, *J* = 7.8 Hz, 1H), 5.01 (dt, *J* = 3.5, 1.8 Hz, 1H), 4.42 (d, *J* = 3.7 Hz, 1H), 3.58–3.31 (m, 5H), 3.06–2.95 (m, 4H).



(*1E*,*2Z*,*4E*)-5-(phenylamino)-1-(phenyliminio)penta-2,4-dien-2-olate (5a)

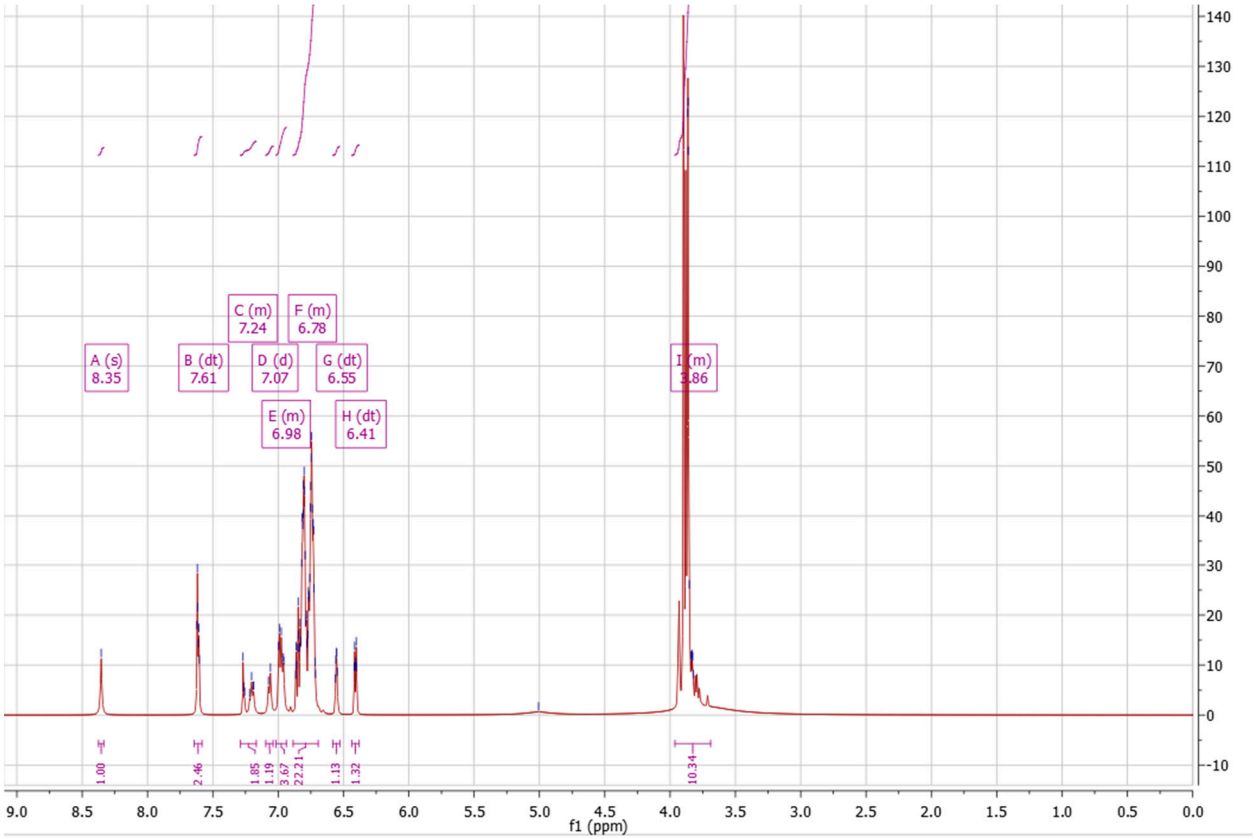
In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vial equipped with a magnetic stirbar. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 µL), Aniline (1 mmol, 91 µL) and the appropriate amount of catalyst (10%–2.5% total of **1-Y**) were added. The resultant mixture was stirred at room temperature for 8 h. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure. The residue was purified by column chromatography (10% ethyl acetate in 90% Hexanes). The product was obtained as red oil which solidified on standing.

^{1}H NMR (500 MHz,) δ 7.68 (dd, *J* = 6.0, 1.9 Hz, 1H), 7.15 (dd, *J* = 3.5, 0.9 Hz, 9H), 7.11–6.96 (m, 14H), 6.70 (dd, *J* = 3.4, 1.8 Hz, 8H), 6.63–6.52 (m, 14H), 6.48 (tt, *J* = 7.3, 1.2 Hz, 4H), 6.39 (dd, *J* = 6.1, 1.5 Hz, 1H), 6.20 (d, *J* = 8.6 Hz, 1H), 6.06 (d, *J* = 7.5 Hz, 1H), 4.97 (s, 10H), 4.63–4.57 (m, 1H), 4.01 (dd, *J* = 7.5, 3.4 Hz, 1H), 1.22 (s, 1H), 0.81 (s, 1H).



(*1E*,*2Z*,*4E*)-5-((2-methoxyphenyl)amino)-1-((2-methoxyphenyl)iminio)penta-2,4-dien-2-olate (5b)

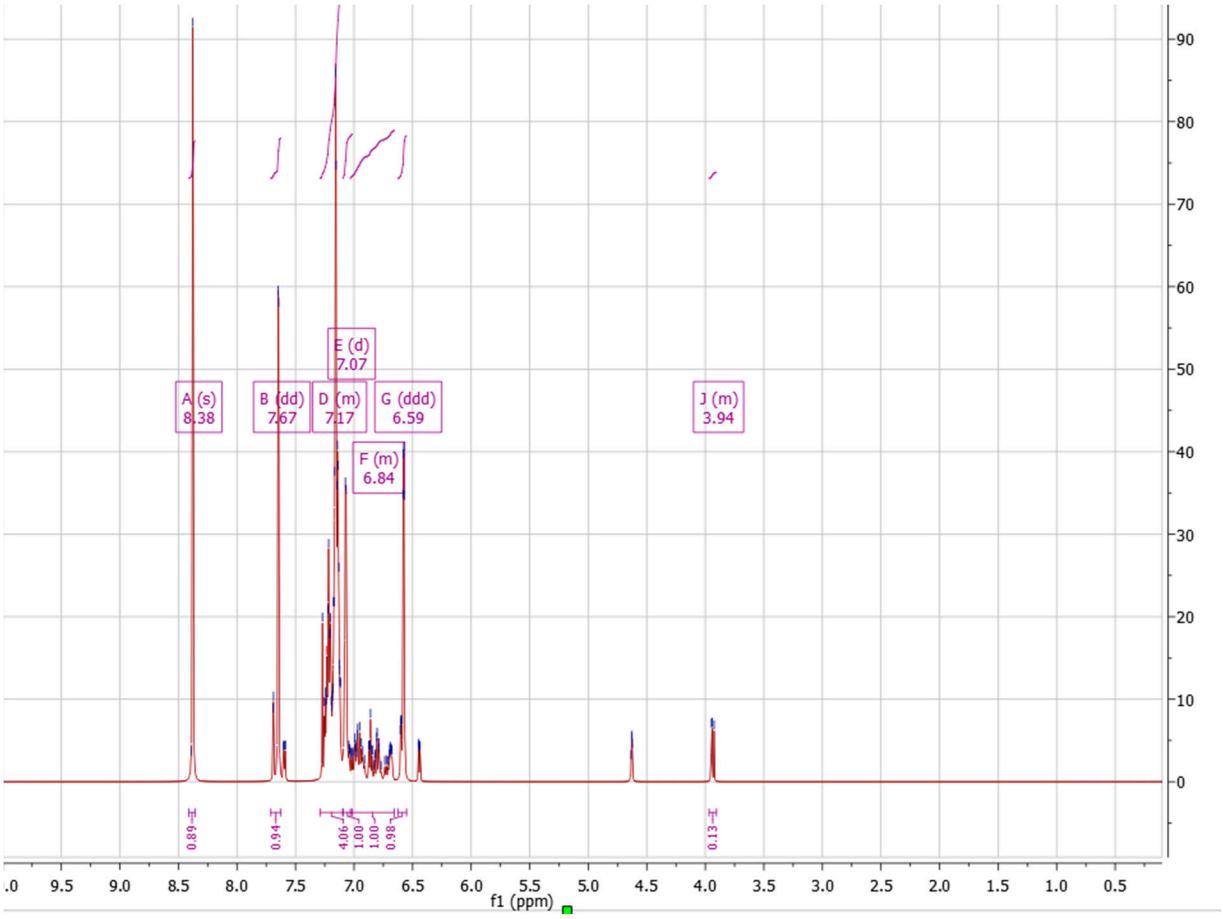
In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vial equipped with a magnetic stirbar. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 µL), *O*-anisidine (1 mmol, 112 µL) and the appropriate amount of catalyst (2.5% total of **1-Y**) were added. The resultant mixture was stirred at room temperature for 8 h. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure. The residue was purified by column chromatography (10% ethyl acetate in 90% Hexanes). The product was obtained as red oil. ^{1}H NMR (500 MHz,) δ 8.35 (s, 1H), 7.61 (dt, J = 6.1, 1.7 Hz, 2H), 7.29–7.17 (m, 2H), 7.07 (d, J = 7.8 Hz, 1H), 7.02–6.94 (m, 4H), 6.89–6.69 (m, 22H), 6.55 (dt, J = 3.5, 1.7 Hz, 1H), 6.41 (dt, J = 6.1, 1.4 Hz, 1H), 3.96–3.69 (m, 10H).



(*1E*,*2Z*,*4E*)-5-((2-fluorophenyl)amino)-1-((2-fluorophenyl)iminio)penta-2,4-dien-2-olate (5c)

In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vial equipped with a magnetic stirbar. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 µL), 2-Fluoroanaline (1 mmol, 97 µL) and the appropriate amount of catalyst (2.5% total of **1-Y**) were added. The resultant mixture was stirred at room temperature for 8 h. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure. The residue was purified by column chromatography (5% ethyl acetate in 95% Hexanes). The product was obtained as yellow oil.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.35 (s, 1H), 7.61 (dt, J = 6.1, 1.7 Hz, 2H), 7.29–7.17 (m, 2H), 7.07 (d, J = 7.8 Hz, 1H), 7.02–6.94 (m, 4H), 6.89–6.69 (m, 22H), 6.55 (dt, J = 3.5, 1.7 Hz, 1H), 6.41 (dt, J = 6.1, 1.4 Hz, 1H), 3.96–3.69 (m, 27H).



(*1E*,*2Z*,*4E*)-5-((2-(trifluoromethyl)phenyl)amino)-1-((2-(trifluoromethyl)phenyl)iminio)penta-2,4-dien-2-olate (5d)

In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vial equipped with a magnetic stirbar. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 µL), 2(trifluoromethyl)- analine (1 mmol, 124.4 µL) and the appropriate amount of catalyst (2.5% total of **1-Y**) were added. The resultant mixture was stirred at room temperature for 8 h. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure. The residue was purified by column chromatography (20% ethyl acetate in 80% Hexanes). The product was obtained as red oil which solidified on standing. ^{1}H NMR (500 MHz) δ 8.19 (s, 1H), 8.01–7.95 (m, 1H), 7.75–7.44 (m, 15H), 7.36–7.29 (m, 4H), 7.25 (d, J = 5.1 Hz, 1H), 7.12 (s, 1H), 7.06 (d, J = 7.5 Hz, 1H), 6.94–6.84 (m, 7H), 6.73 (d, J = 8.7 Hz, 1H), 6.64–6.57 (m, 4H).