

Electronic Supporting Information

Synthesis of 2,3-dihydroquinazolinimines and 1,3-diimino isoindolines catalyzed by rare earth metal alkyl complexes through tandem addition/cyclization of nitriles with amines

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Molecular structures of complexes

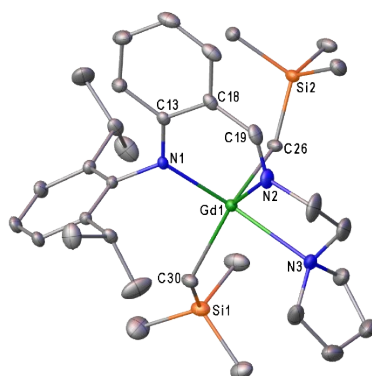


Fig. S1 Molecular structure of **1a**. All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Gd1–N1 2.311(3), Gd1–N2 2.443(5), Gd1–N3 2.552(4), Gd1–C26 2.464(5), Gd1–C30 2.410(5), N1–C13 1.357(5), N2–C19 1.279(7), C13–C18 1.434(6), C18–C19 1.418(8), C26–Gd1–C30 112.63(17).

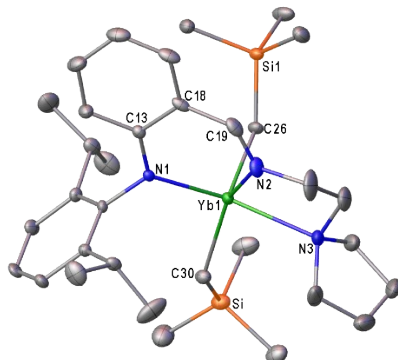


Fig. S2 Molecular structure of **1c**. All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb1–N1 2.256(5), Yb1–N2 2.331(8), Yb1–N3 2.463(7), Yb1–C26 2.326(7), Yb1–C30 2.372(7), N1–C13 1.354(8), N2–C19 1.278(12), C13–C18 1.427(10), C18–C19 1.437(12), C26–Yb1–C30 110.7(3).

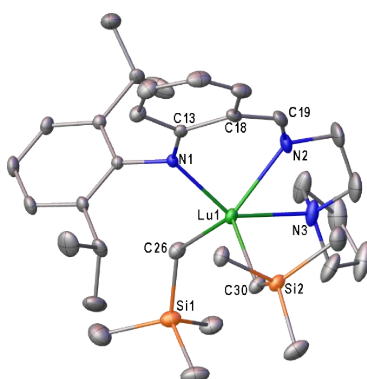


Fig. S3 Molecular structure of **1d**. All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Lu1–N1 2.245(5), Lu1–N2 2.337(7), Lu1–N3 2.462(6), Lu1–C26 2.380(6), Lu1–C30 2.318(7), N1–C13 1.369(7), N2–C19 1.283(10), C13–C18 1.434(8), C18–C19 1.421(11), C26–Lu1–C30 111.0(3).

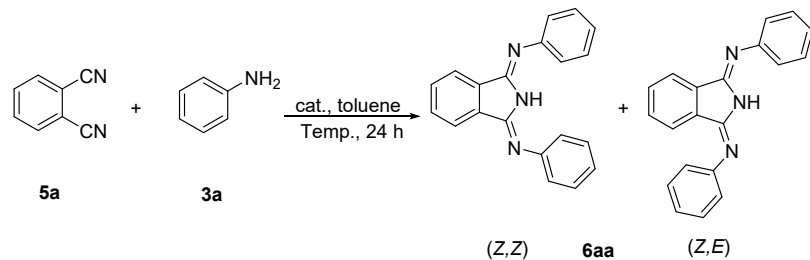
Table S1. Crystallographic data of complexes 1a-1d

	1a (Gd)	1b (Y)	1c (Yb)	1d (Lu)
CCDC	2416306	2416307	2416304	2416308
Empirical formula	C ₃₃ H ₅₆ N ₃ Si ₂ Gd	C ₃₃ H ₅₆ N ₃ Si ₂ Y	C ₃₃ H ₅₆ N ₃ Si ₂ Yb	C ₃₃ H ₅₆ N ₃ Si ₂ Lu
Formula weight	708.23	639.89	724.02	725.95
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	10.6951(5)	10.6821(7)	10.650(2)	10.6677(9)
<i>b</i> (Å)	16.8616(8)	16.8434(11)	16.761(4)	16.8105(14)
<i>c</i> (Å)	20.6165(10)	20.6095(13)	20.549(4)	20.5975(17)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	90	90	90	90
<i>V</i> (Å ³)	3717.9(3)	3708.1(4)	3668.1(14)	3693.7(5)
<i>Z</i>	4	4	4	4
<i>D</i> _{calcd} (mg m ⁻³)	1.265	1.146	1.311	1.305
μ (mm ⁻¹)	1.871	1.660	2.638	2.761
<i>F</i> (000)	1468	1368	1492	1496
θ range (°)	1.560 to 27.492	1.561 to 27.502	1.568 to 27.132	1.564 to 27.511
Reflections collected	43783	43185	40340	43445
Data/restraints/parameters	8520/0/362	8503/0/362	8063/1/362	8467/0/362
Goodness-of-fit on F ²	1.023	0.970	1.019	1.013
R(int)	0.0362	0.0656	0.0702	0.0566
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0276, 0.0555	0.0421, 0.0747	0.0391, 0.0666	0.0343, 0.0606
Largest diff peak/hole (e Å ⁻³)	0.593 and -0.386	0.237 and -0.211	0.641 and -0.841	1.201 and -0.529

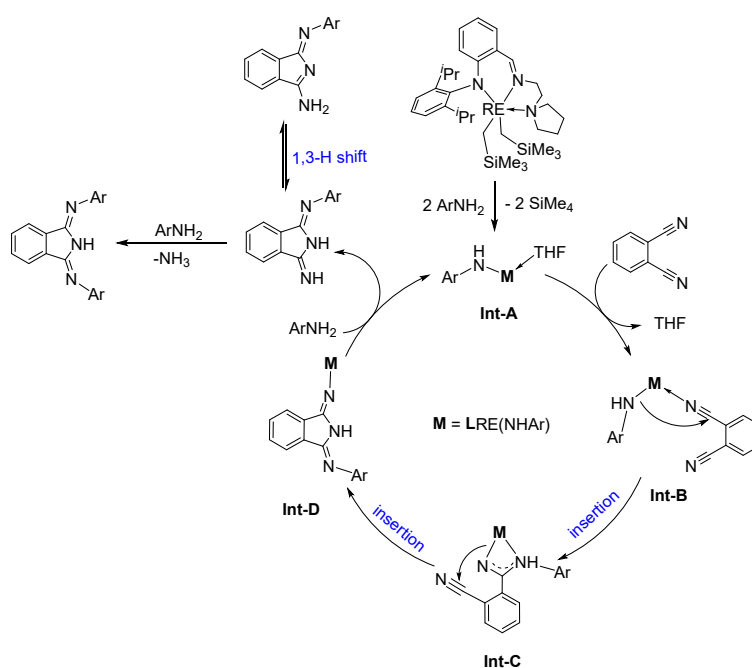
Table S2. Crystallographic data of complexes 7b, 8b, 4aaa and 4akb

	7b (Y)	8b (Y)	4aaa	4akb
CCDC	2416303	2416309	2416305	2416310
Empirical formula	C ₄₁ H ₅₄ N ₅ OY	C ₄₉ H ₇₀ N ₅ Y	C ₁₉ H ₁₆ N ₄	C ₂₁ H ₁₉ N ₃
Formula weight	721.80	818.01	300.36	313.39
Crystal system	Monoclinic	Monoclinic	triclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P$\bar{1}$</i>	<i>P2₁/c</i>
<i>a</i> (Å)	19.0772(15)	12.5530(13)	10.9173(14)	10.4897(15)
<i>b</i> (Å)	11.2927(9)	15.6876(16)	11.7318(13)	14.543(2)
<i>c</i> (Å)	18.0046(15)	27.880(3)	13.9226(18)	11.5681(14)
α (°)	90	90	74.158(3)	90
β (°)	100.2510(10)	98.070(2)	75.580(4)	105.772(4)
γ (°)	90	90	68.158(3)	90
<i>V</i> (Å ³)	3816.9(5)	5436.0(10)	1570.5(3)	1698.3(4)
<i>Z</i>	4	4	4	4
<i>D</i> _{calcd} (mg m ⁻³)	1.256	1.000	1.270	1.226
μ (mm ⁻¹)	1.565	1.104	0.078	0.074
<i>F</i> (000)	1528	1752	632.0	664.0
θ range (°)	2.105 to 27.509	1.965 to 27.562	6.168 to 54.994	5.43 to 49.998
Reflections collected	32728	46611	43568	58041
Data/restraints/parameters	8725/785/590	12449/168/516	7192/0/415	2984/0/219
Goodness-of-fit on F ²	1.008	1.017	1.025	1.062
R(int)	0.0475	0.0735	0.1549	0.1617
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0458, 0.1022	0.0664, 0.1495	0.0878, 0.2209	0.1157, 0.2017
Largest diff peak/hole (e Å ⁻³)	0.375 and -0.362	0.594 and -0.506	0.59 and -0.26	0.35 and -0.42

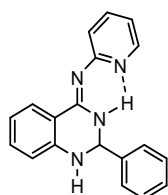
Table S3 Optimization of the reaction conditions

				
Entry	Cat. (mol%)	Temp.(°C)	PhNH ₂ (equiv)	Yield (%) ^b
1	\	130	2	NR
2	1b (5)	130	2	64
3	1b (5)	120	2	57
4	1b (5)	110	2	50
5	1b (5)	130	3	87
6	1b (5)	130	4	98
7	1b (4)	130	4	93
8	1b (4)	130	4	95 ^c
9	1a (5)	130	4	96
10	1c (5)	130	4	95
11	1d (5)	130	4	93
12	Y[C] ₃ (5)	130	4	47

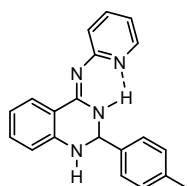
^aReaction conditions: Into a Schlenk glass reactor were successively placed **5a** (1.0 mmol), **3a** and catalyst in toluene (1.5 mL). ^bIsolated yields were based on phthalonitrile. ^cY[C]₃ refers to Y(CH₂SiMe₃)₃(THF)₂.

**Scheme S1** A proposed mechanism for the synthesis of 1, 3-diimino isoindolines

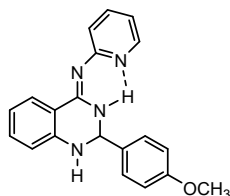
Data of 2,3-dihydroquinolinimines



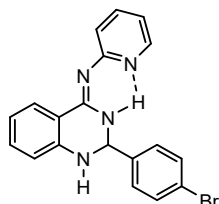
(*Z*)-*N*-(2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 133–135 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 11.55 (br, 1H, *NH*), 8.31 (d, *J* = 8.0 Hz, 1H, *ArH*), 8.11–8.09 (m, 1H, *ArH*), 7.65–7.57 (m, 3H, *ArH*), 7.46–7.45 (m, 3H, *ArH*), 7.29–7.24 (m, 2H, *ArH*), 6.92 (t, *J* = 7.5 Hz, 1H, *ArH*), 6.81 (t, *J* = 7.5 Hz, 1H, *ArH*), 6.65 (d, *J* = 8.0 Hz, 1H, *ArH*), 5.81 (s, 1H, *CH*), 4.43 (br, 1H, *NH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 163.0 (C=N), 153.9, 146.3, 145.6, 139.6, 137.2, 132.3, 129.5, 128.9, 127.6, 127.4, 122.3, 119.6, 118.4, 117.0, 115.0 (*ArC*), 67.5 (*CH*). HRMS (ESI): calcd for C₁₉H₁₆N₄ [M+H]⁺: 301.1448, found: 301.1461.



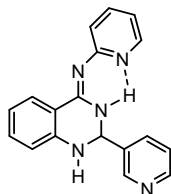
(*Z*)-*N*-(2-(*p*-tolyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 151–153 °C. ¹H NMR (500 MHz, CDCl₃, ppm): δ 11.51 (br, 1H, *NH*), 8.34 (d, *J* = 7.5 Hz, 1H, *ArH*), 8.15–8.14 (m, 1H, *ArH*), 7.62 (t, *J* = 7.5 Hz, 1H, *ArH*), 7.56 (d, *J* = 7.5 Hz, 2H, *ArH*), 7.32–7.28 (m, 4H, *ArH*), 6.95 (t, *J* = 7.5 Hz, 1H, *ArH*), 6.84 (t, *J* = 6.0 Hz, 1H, *ArH*), 6.68 (d, *J* = 8.0 Hz, 1H, *ArH*), 5.83 (s, 1H, *CH*), 4.37 (br, 1H, *NH*), 2.44 (s, 3H, *CH*₃). ¹³C{¹H} NMR (125 MHz, CDCl₃, ppm): δ 163.1 (C=N), 153.9, 146.4, 145.7, 139.5, 137.2, 136.6, 132.2, 129.6, 127.6, 127.3, 122.3, 119.6, 118.4, 116.9, 114.9 (*ArC*), 67.3 (*CH*), 21.3 (*CH*₃). HRMS (ESI): calcd for C₂₀H₁₈N₄ [M+H]⁺: 315.1604, found: 315.1618.



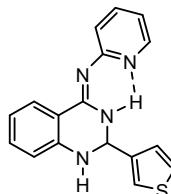
(*Z*)-2-(4-methoxyphenyl)-*N*-(pyridin-2-yl)-2,3-dihydroquinazolin-4(1*H*)-imine. Yellow solid. M.p.: 187–189 °C. ¹H NMR (500 MHz, CDCl₃, ppm): δ 11.42 (br, 1H, *NH*), 8.30 (d, *J* = 7.5 Hz, 1H, *ArH*), 8.19–8.12 (m, 1H, *ArH*), 7.58 (d, *J* = 8.0 Hz, 3H, *ArH*), 7.29 (d, *J* = 7.5 Hz, 1H, *ArH*), 7.23 (d, *J* = 8.0 Hz, 1H, *ArH*), 6.98 (d, *J* = 8.4 Hz, 2H, *ArH*), 6.92 (t, *J* = 7.5 Hz, 1H, *ArH*), 6.80 (t, *J* = 6.0 Hz, 1H, *ArH*), 6.65 (d, *J* = 8.0 Hz, 1H, *ArH*), 5.79 (s, 1H, *CH*), 4.32 (br, 1H, *NH*), 3.86 (s, 3H, *OCH*₃). ¹³C{¹H} NMR (125 MHz, CDCl₃, ppm): δ 163.1 (C=N), 160.5, 154.0, 146.5, 145.7, 137.2, 132.2, 131.7, 128.8, 127.7, 122.3, 119.7, 118.5, 116.9, 114.9, 114.2 (*ArC*), 67.2 (*CH*), 55.4 (*OCH*₃). HRMS (ESI): calcd for C₂₀H₁₈N₄O [M+H]⁺: 331.1553, found: 331.1568.



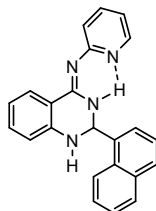
(*Z*)-2-(4-bromophenyl)-*N*-(pyridin-2-yl)-2,3-dihydroquinazolin-4(1*H*)-imine. White solid. M.p.: 158–160 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 11.55 (br, 1H, *NH*), 8.29 (d, *J* = 8.0 Hz, 1H, *ArH*), 8.14–8.12 (m, 1H, *ArH*), 7.62–7.57 (m, 3H, *ArH*), 7.51 (d, *J* = 8.4 Hz, 2H, *ArH*), 7.29 (d, *J* = 7.2 Hz, 1H, *ArH*), 7.24 (d, *J* = 8.0 Hz, 1H, *ArH*), 6.93 (t, *J* = 7.6 Hz, 1H, *ArH*), 6.83 (t, *J* = 7.5 Hz, 1H, *ArH*), 6.67 (d, *J* = 8.0 Hz, 1H, *ArH*), 5.80 (s, 1H, *CH*), 4.37 (br, 1H, *NH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 163.0 (C=N), 153.6, 146.0, 145.6, 138.8, 137.3, 132.4, 132.1, 129.2, 127.6, 123.6, 122.4, 119.9, 118.4, 117.2, 115.0 (*ArC*), 67.0 (*CH*). HRMS (ESI): calcd for C₁₉H₁₅N₄Br [M+H]⁺: 379.0553, found: 379.0566.



(*Z*)-*N*-(2-(pyridin-3-yl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 106–108 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 11.61 (br, 1H, *NH*), 8.71 (s, 1H, *ArH*), 8.62 (d, *J* = 4.0 Hz, 1H, *ArH*), 8.27 (d, *J* = 7.6 Hz, 1H, *ArH*), 8.08 (d, *J* = 3.6 Hz, 1H, *ArH*), 7.98 (d, *J* = 7.6 Hz, 1H, *ArH*), 7.60–7.56 (m, 1H, *ArH*), 7.34–7.31 (m, 1H, *ArH*), 7.28–7.22 (m, 2H, *ArH*), 6.90 (t, *J* = 7.6 Hz, 1H, *ArH*), 6.81 (t, *J* = 6.0 Hz, 1H, *ArH*), 6.68 (d, *J* = 7.6 Hz, 1H, *ArH*), 5.81 (s, 1H, *CH*), 4.80 (br, 1H, *NH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 162.7 (C=N), 153.5, 150.7, 148.8, 145.9, 145.5, 137.3, 135.5, 135.1, 132.1, 127.5, 123.8, 122.3, 119.8, 118.1, 117.2, 115.1 (*ArC*), 65.1 (*CH*). HRMS (ESI): calcd for C₁₈H₁₅N₅ [M+H]⁺: 302.1400, found: 302.1413.

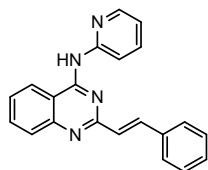


(*Z*)-*N*-(2-(thiophen-3-yl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 85–87 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 11.60 (br, 1H, *NH*), 8.30 (d, *J* = 7.6 Hz, 1H, *ArH*), 8.17–8.16 (m, 1H, *ArH*), 7.62–7.58 (m, 1H, *ArH*), 7.51–7.50 (m, 1H, *ArH*), 7.41–7.28 (m, 3H, *ArH*), 7.24 (d, *J* = 8.0 Hz, 1H, *ArH*), 6.93 (t, *J* = 7.2 Hz, 1H, *ArH*), 6.83 (t, *J* = 6.4 Hz, 1H, *ArH*), 6.68 (d, *J* = 8.0 Hz, 1H, *ArH*), 5.96 (s, 1H, *CH*), 4.41 (br, 1H, *NH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 163.0 (C=N), 153.7, 146.1, 145.6, 141.3, 137.2, 132.2, 127.6, 127.0, 126.0, 124.0, 122.3, 119.7, 118.5, 117.0, 115.1 (*ArC*), 62.8 (*CH*). HRMS (ESI): calcd for C₁₇H₁₄N₄S [M+H]⁺: 307.1012, found: 307.1025.

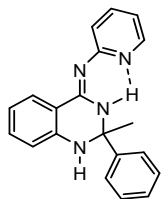


(*Z*)-*N*-(2-(naphthalen-1-yl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 144–146 °C. ¹H NMR (500 MHz, CDCl₃, ppm): δ 11.52 (br, 1H, *NH*), 8.55 (d, *J* = 7.5 Hz, 1H, *ArH*), 8.17 (d, *J* = 8.0 Hz, 1H, *ArH*), 8.05 (t, *J* = 8.0 Hz, 2H, *ArH*), 7.99 (s, 1H, *ArH*), 7.84 (d, *J* = 7.0 Hz, 1H, *ArH*), 7.68–7.60 (m, 4H, *ArH*), 7.31 (t, *J* = 7.5 Hz, 1H, *ArH*), 7.14 (d, *J* = 8.0 Hz,

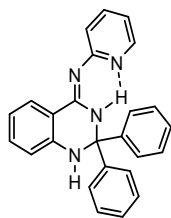
1H, ArH), 6.83–6.80 (m, 3H, ArH), 6.66 (s, 1H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): δ 162.6 (C=N), 153.3, 147.6, 145.6, 141.3, 137.6, 135.3, 133.7, 132.4, 129.4, 128.7, 126.9, 126.4, 126.0, 125.4, 125.3, 124.0, 121.8, 117.5, 116.8, 116.2, 115.0 (ArC), 63.9 (CH). HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{18}\text{N}_4$ $[\text{M}+\text{H}]^+$: 351.1604, found: 351.1620.



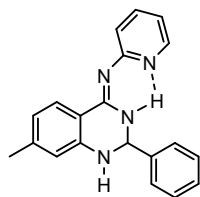
(*E*)-*N*-(pyridin-2-yl)-2-styrylquinazolin-4-amine.¹ Yellow solid. M.p.: 113–115 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.89 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 4.0 Hz, 1H), 8.29 (br, 1H, NH), 8.04 (d, J = 15.6 Hz, 1H, CH=CH), 7.97–7.86 (m, 3H), 7.82 (t, J = 7.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 7.2 Hz, 1H), 7.32 (d, J = 15.6 Hz, 1H, CH=CH), 7.12–7.09 (m, 1H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm): δ 160.3, 156.1, 152.1, 150.9, 148.0, 138.1, 137.9, 136.3, 133.3, 128.9, 128.9, 128.8, 128.7, 127.6, 126.5, 120.6, 119.1, 114.7, 113.9 (ArC).



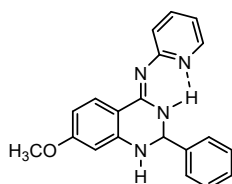
(*Z*)-*N*-(2-methyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 118–120 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 12.22 (br, 1H, NH), 8.32 (d, J = 3.6 Hz, 1H, ArH), 8.24 (d, J = 7.6 Hz, 1H, ArH), 7.67–7.63 (m, 1H, ArH), 7.49 (d, J = 7.2 Hz, 2H, ArH), 7.31–7.21 (m, 5H, ArH), 6.90 (t, J = 6.0 Hz, 1H, ArH), 6.83 (t, J = 7.6 Hz, 1H, ArH), 6.68 (d, J = 8.0 Hz, 1H, ArH), 4.83 (br, 1H, NH), 1.89 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm): δ 163.2 (C=N), 153.7, 145.7, 145.6, 144.5, 137.2, 132.3, 128.4, 127.6, 127.3, 125.2, 122.4, 119.2, 118.1, 116.9, 115.3 (ArC), 69.3 (CH), 30.6 (CH_3). HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{18}\text{N}_4$ $[\text{M}+\text{H}]^+$: 315.1604, found: 315.1619.



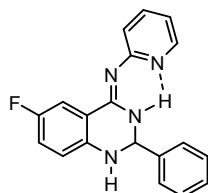
(*Z*)-*N*-(2,2-diphenyl-2,3-dihydroquinazolin-4(1H)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 203–205 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 12.53 (br, 1H, NH), 8.20–8.18 (m, 2H, ArH), 7.64–7.60 (m, 1H, ArH), 7.47–7.45 (m, 4H, ArH), 7.35–7.22 (m, 8H, ArH), 6.87–6.80 (m, 2H, ArH), 6.70 (d, J = 8.0 Hz, 1H, ArH), 4.99 (br, 1H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm): δ 163.2 (C=N), 153.6, 145.7, 144.4, 137.3, 132.5, 128.4, 128.2, 128.0, 127.4, 127.3, 126.9, 122.5, 119.4, 118.2, 117.0, 115.4 (ArC), 74.5 (CH). HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{N}_4$ $[\text{M}+\text{H}]^+$: 377.1761, found: 377.1777.



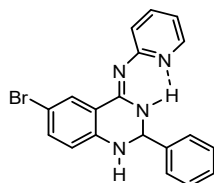
(*Z*)-*N*-(7-methyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 174–176 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 11.50 (br, 1H, NH), 8.18 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.10 (d, *J* = 3.6 Hz, 1H, Ar*H*), 7.65–7.56 (m, 3H, Ar*H*), 7.46–7.44 (m, 3H, Ar*H*), 7.22 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.79 (t, *J* = 6.0 Hz, 1H, Ar*H*), 6.75 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.47 (s, 1H, Ar*H*), 5.81 (s, 1H, CH), 4.31 (br, 1H, NH), 2.31 (s, 3H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 163.1 (C=N), 154.1, 146.3, 145.6, 142.9, 139.7, 137.1, 129.5, 128.9, 127.6, 127.4, 122.2, 120.9, 116.7, 115.8, 115.3 (ArC), 67.5 (CH), 21.6 (CH₃). HRMS (ESI): calcd for C₂₀H₁₈N₄ [M+H]⁺: 315.1604, found: 315.1615.



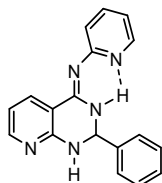
(*Z*)-*N*-(7-methoxy-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine. White solid. M.p.: 166–168 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 11.49 (br, 1H, NH), 8.23 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.09 (d, *J* = 4.0 Hz, 1H, Ar*H*), 7.65–7.63 (m, 2H, Ar*H*), 7.59–7.55 (m, 1H, Ar*H*), 7.46–7.44 (m, 3H, Ar*H*), 7.20 (d, *J* = 4.0 Hz, 1H, Ar*H*), 6.78 (t, *J* = 6.4 Hz, 1H, Ar*H*), 6.50–6.48 (m, 1H, Ar*H*), 6.15 (d, *J* = 2.0 Hz, 1H, Ar*H*), 5.83 (s, 1H, CH), 4.38 (br, 1H, NH), 3.80 (s, 3H, OCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 163.2 (C=N), 154.0, 147.8, 145.6, 139.6, 137.1, 129.5, 128.9, 127.3, 122.0, 116.6, 111.4, 106.6, 99.0 (ArC), 67.5 (CH), 55.2 (OCH₃). HRMS (ESI): calcd for C₂₀H₁₈N₄O [M+H]⁺: 331.1553, found: 331.1569.



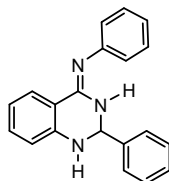
(*Z*)-*N*-(6-fluoro-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 155–157 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 11.53 (br, 1H, NH), 8.13–8.12 (m, 1H, Ar*H*), 8.02 (dd, *J* = 3.2, 9.6 Hz, 1H, Ar*H*), 7.66–7.59 (m, 3H, Ar*H*), 7.47–7.45 (m, 3H, Ar*H*), 7.24 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.02 (dt, *J* = 2.8, 8.4 Hz, 1H, Ar*H*), 6.84 (t, *J* = 6.0 Hz, 1H, Ar*H*), 6.65–6.61 (m, 1H, Ar*H*), 5.81 (s, 1H, CH), 4.28 (br, 1H, NH). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 162.7 (C=N), 156.8 (d, ¹*J*_{C-F} = 236.0 Hz), 152.9, 145.7, 142.5, 139.3, 137.3, 129.6, 128.9, 127.3, 122.4, 119.8 (d, ³*J*_{C-F} = 7.0 Hz), 119.4 (d, ²*J*_{C-F} = 24.0 Hz), 117.3, 116.4 (d, ³*J*_{C-F} = 7.0 Hz), 113.5 (d, ²*J*_{C-F} = 24.0 Hz) (ArC), 67.7 (CH). ¹⁹F NMR (376 MHz, CDCl₃, ppm): δ –123.8. HRMS (ESI): calcd for C₁₉H₁₅N₄F [M+H]⁺: 319.1354, found: 319.1369.



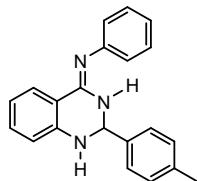
(*Z*)-*N*-(6-bromo-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine. Yellow solid. M.p.: 223–225 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 11.53 (br, 1H, *NH*), 8.43 (d, *J* = 2.0 Hz, 1H, *ArH*), 8.12 (d, *J* = 4.0 Hz, 1H, *ArH*), 7.63–7.59 (m, 3H, *ArH*), 7.46–7.45 (m, 3H, *ArH*), 7.35 (dd, *J* = 2.0, 8.4 Hz, 1H, *ArH*), 7.24 (s, 1H, *ArH*), 6.84 (t, *J* = 6.4 Hz, 1H, *ArH*), 6.55 (d, *J* = 8.4 Hz, 1H, *ArH*), 5.82 (s, 1H, *CH*), 4.39 (br, 1H, *NH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 162.7 (C=N), 152.5, 145.7, 145.1, 139.3, 137.4, 134.8, 130.2, 129.7, 129.0, 127.4, 122.5, 120.1, 117.4, 116.7, 111.8 (ArC), 67.4 (CH). HRMS (ESI): calcd for C₁₉H₁₅N₄Br [M+H]⁺: 379.0553, found: 379.0568.



(*Z*)-*N*-(2-phenyl-2,3-dihydropyrido[2,3-*d*]pyrimidin-4(1*H*)-ylidene)pyridin-2-amine. White solid. M.p.: 253–255 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 11.55 (br, 1H, *NH*), 8.52 (dd, *J* = 1.6, 8.0 Hz, 1H, *ArH*), 8.14–8.08 (m, 2H, *ArH*), 7.64–7.59 (m, 3H, *ArH*), 7.48–7.45 (m, 3H, *ArH*), 7.22 (d, *J* = 8.0 Hz, 1H, *ArH*), 6.86–6.80 (m, 2H, *ArH*), 6.01 (s, 1H, *CH*), 5.53 (br, 1H, *NH*). ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 11.36 (s, 1H, *NH*), 8.31–8.29 (m, 2H, *ArH*), 8.15 (s, 1H, *ArH*), 8.03 (s, 1H, *CH*), 7.76–7.67 (m, 1H, *ArH*), 7.47–7.45 (m, 2H, *ArH*), 7.37–7.30 (m, 3H, *ArH*), 7.13–7.11 (m, 1H, *ArH*), 6.99–6.91 (m, 1H, *ArH*), 6.80–6.68 (m, 1H, *ArH*), 6.06 (s, 1H, *NH*). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆, ppm): δ 162.3 (C=N), 156.6, 152.0, 146.1, 142.3, 137.8, 134.8, 128.6, 128.4, 126.2, 121.7, 117.4, 114.0, 111.2 (ArC), 64.4 (CH). HRMS (ESI): calcd for C₁₈H₁₅N₅ [M+H]⁺: 302.1400, found: 302.1411.

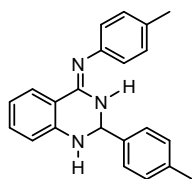


(*Z*)-*N*-(2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)aniline. Yellow solid. M.p.: 150–152 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.24 (s, 1H, *ArH*), 7.51 (s, 2H, *ArH*), 7.40–7.38 (m, 3H, *ArH*), 7.29 (t, *J* = 7.8 Hz, 3H, *ArH*), 7.00–7.94 (m, 4H, *ArH*), 6.69 (d, *J* = 8.0 Hz, 1H, *ArH*), 5.58 (s, 1H, *CH*), 5.10 (br, 1H, *NH*), 4.34 (br, 1H, *NH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 152.3 (C=N), 146.9, 139.0, 133.2, 129.5, 129.4, 128.9, 127.6, 127.3, 123.8, 122.5, 119.2, 115.6, 114.3 (ArC), 67.6 (CH). HRMS (ESI): calcd for C₂₀H₁₇N₃ [M+H]⁺: 300.1495, found: 300.1502.

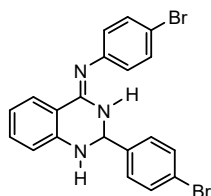


(*Z*)-*N*-(2-(*p*-tolyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)aniline. Yellow solid. M.p.: 229–231 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.23 (d, *J* = 8.0 Hz, 1H, *ArH*), 7.39 (d, *J* = 7.6 Hz, 2H, *ArH*), 7.30–7.28 (m, 3H, *ArH*), 7.19 (d, *J* = 8.0 Hz, 2H, *ArH*), 6.99–6.91 (m, 4H, *ArH*), 6.68 (d, *J* = 8.0 Hz, 1H, *ArH*), 5.54 (s, 1H, *CH*), 5.06 (br, 1H, *NH*), 4.30 (br, 1H, *NH*), 2.36 (s, 3H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 149.9 (C=N), 149.3, 146.0, 139.9, 136.0, 132.0, 129.6, 129.5,

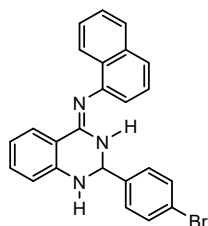
127.5, 127.4, 122.7, 121.9, 119.8, 117.3, 115.1 (ArC), 68.2 (CH), 21.2 (CH₃). HRMS (ESI): calcd for C₂₁H₁₉N₃ [M+H]⁺: 314.1652, found: 314.1664.



(Z)-4-methyl-N-(2-(p-tolyl)-2,3-dihydroquinazolin-4(1H)-ylidene)aniline. Yellow solid. M.p.: 155–157 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.23 (d, *J* = 6.8 Hz, 1H, Ar*H*), 7.39 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.29 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.19 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.08 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.94–6.85 (m, 3H, Ar*H*), 6.67 (d, *J* = 8.0 Hz, 1H, Ar*H*), 5.53 (s, 1H, CH), 5.10 (br, 1H, NH), 4.30 (br, 1H, NH), 2.36 (s, 3H, CH₃), 2.27 (s, 3H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 150.1 (C=N), 146.5, 146.0, 139.8, 136.1, 131.9, 130.0, 129.5, 127.4, 127.2, 121.6, 119.7, 117.4, 115.0 (ArC), 68.2 (CH), 21.2 (CH₃), 20.8 (CH₃). HRMS (ESI): calcd for C₂₂H₂₁N₃ [M+H]⁺: 328.1808, found: 328.1821.

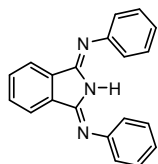


(Z)-4-bromo-N-(2-(4-bromophenyl)-2,3-dihydroquinazolin-4(1H)-ylidene)aniline. Yellow solid. M.p.: 200–202 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.00–7.95 (m, 1H, Ar*H*), 7.53 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.41–7.37 (m, 4H, Ar*H*), 7.32–7.28 (m, 1H, Ar*H*), 7.00 (s, 2H, Ar*H*), 6.91 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.70 (d, *J* = 8.0 Hz, 1H, Ar*H*), 5.61 (s, 1H, CH), 4.34 (br, 1H, NH). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 150.9 (C=N), 146.3, 138.5, 132.6, 132.3, 131.9, 129.9, 129.0, 126.3, 123.4, 123.3, 119.5, 115.7, 115.5, 115.3 (ArC), 68.0 (CH). HRMS (ESI): calcd for C₂₀H₁₅N₃Br₂ [M+H]⁺: 455.9705, found: 455.9711.

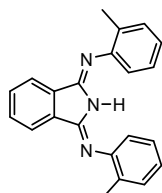


(Z)-N-(2-(4-bromophenyl)-2,3-dihydroquinazolin-4(1H)-ylidene)naphthalen-1-amine. Yellow solid. M.p.: 185–187 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.43 (d, *J* = 7.6 Hz, 1H, Ar*H*), 8.08 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.80 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.51 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.49–7.44 (m, 4H, Ar*H*), 7.40–7.35 (m, 2H, Ar*H*), 7.33–7.29 (m, 2H, Ar*H*), 7.01 (t, *J* = 7.8 Hz, 2H, Ar*H*), 6.73 (d, *J* = 8.0 Hz, 1H, Ar*H*), 5.52 (s, 1H, CH), 5.00 (br, 1H, NH), 4.35 (br, 1H, NH). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 149.7 (C=N), 145.7, 145.3, 137.9, 134.6, 132.3, 132.0, 129.1, 127.9, 127.6, 127.5, 126.2, 126.1, 125.2, 123.9, 123.8, 122.9, 120.0, 117.1, 116.3, 115.2 (ArC), 67.7 (CH). HRMS (ESI): calcd for C₂₄H₁₈N₃Br [M+H]⁺: 428.0757, found: 428.0773.

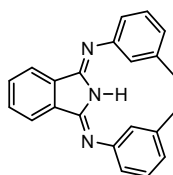
Data of 1,3-diimino isoindolines



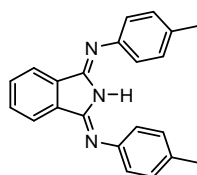
(1Z, 3Z)-*N*¹,*N*³-diphenylisoindoline-1,3-diimine.² Yellow solid. M.p.: 119–121 °C. *Z,Z*: *Z,E* = 2:1. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.06–8.04 (m, 2H, *ArH*), 7.69–7.67 (m, 2H, *ArH*), 7.41–7.31 (m, 6H, *ArH*), 7.02 (d, *J* = 7.6 Hz, 4H, *ArH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 150.1, 147.9, 134.6, 131.8, 129.4, 124.3, 122.3, 121.1 (*ArC*).



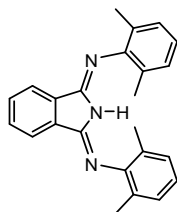
(1Z,3Z)-*N*¹,*N*³-di-*o*-tolylisoindoline-1,3-diimine.² Yellow solid. M.p.: 140–142 °C. (*Z,Z*): (*Z,E*) = 1:1. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.11–8.09 (m, 2H, *ArH*), 7.73–7.71 (m, 2H, *ArH*), 7.21 (d, *J* = 8.0 Hz, 4H, *ArH*), 7.01 (d, *J* = 7.6 Hz, 2H, *ArH*), 6.85 (d, *J* = 7.6 Hz, 2H, *ArH*), 2.22 (s, 6H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 149.4, 146.6, 134.7, 131.8, 130.9, 129.9, 126.7, 124.3, 122.4, 119.6 (*ArC*), 17.8 (CH₃).



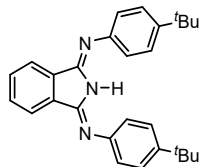
(1Z,3Z)-*N*¹,*N*³-di-*m*-tolylisoindoline-1,3-diimine. Yellow solid. M.p.: 118–120 °C. (*Z,Z*): (*Z,E*) = 2:1. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.05–8.03 (m, 2H, *ArH*), 7.70–7.68 (m, 2H, *ArH*), 7.22 (t, *J* = 7.6 Hz, 2H, *ArH*), 6.91 (d, *J* = 7.6 Hz, 3H, *ArH*), 6.85 (d, *J* = 7.6 Hz, 3H, *ArH*), 2.33 (s, 6H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 150.2, 148.1, 139.4, 134.7, 131.8, 129.3, 125.2, 122.3, 122.0, 118.3 (*ArC*), 21.4 (CH₃). HRMS (ESI): calcd for C₂₂H₁₉N₃ [M+H]⁺: 326.1652, found: 326.1660.



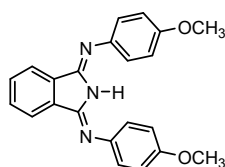
(1Z,3Z)-*N*¹,*N*³-di-*p*-tolylisoindoline-1,3-diimine.³ Yellow solid. M.p.: 145–147 °C. (*Z,Z*): (*Z,E*) = 2:1. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.04–8.02 (m, 2H, *ArH*), 7.67–7.65 (m, 2H, *ArH*), 7.15 (d, *J* = 8.4 Hz, 4H, *ArH*), 6.93 (d, *J* = 8.0 Hz, 4H, *ArH*), 2.32 (s, 6H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 150.0, 145.3, 134.7, 133.9, 131.7, 130.1, 122.2, 121.1 (*ArC*), 20.8 (CH₃).



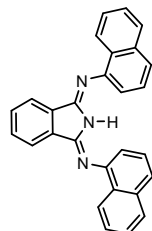
(1*Z*,3*Z*)-*N*¹,*N*³-bis(2,6-dimethylphenyl)isoindoline-1,3-diimine. Light yellow solid. M.p.: 169–171 °C. (*Z,Z*): (*Z,E*) = 1:1. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.13–8.11 (m, 2H, *ArH*), 7.74–7.72 (m, 2H, *ArH*), 6.99 (d, *J* = 8.0 Hz, 4H, *ArH*), 6.87 (t, *J* = 7.6 Hz, 2H, *ArH*), 2.07 (s, 12H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 149.2, 145.5, 134.5, 131.8, 128.1, 127.8, 123.6, 122.5 (*ArC*), 17.9 (CH₃). HRMS (ESI): calcd for C₂₄H₂₃N₃ [M+H]⁺: 354.1965, found: 354.1974.



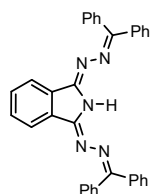
(1*Z*,3*Z*)-*N*¹,*N*³-bis(4-(*tert*-butyl)phenyl)isoindoline-1,3-diimine. Yellow solid. M.p.: 207–209 °C. (*Z,Z*): (*Z,E*) = 2:1. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.06–8.04 (m, 2H, *ArH*), 7.68–7.66 (m, 2H, *ArH*), 7.36 (d, *J* = 8.4 Hz, 4H, *ArH*), 6.96 (d, *J* = 8.4 Hz, 4H, *ArH*), 1.29 (s, 18H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 150.3, 147.3, 145.6, 134.8, 131.7, 126.3, 122.3, 121.0 (*ArC*), 34.3 (C(CH₃)₃), 31.3 (CH₃). HRMS (ESI): calcd for C₂₈H₃₁N₃ [M+H]⁺: 410.2591, found: 410.2596.



(1*Z*,3*Z*)-*N*¹,*N*³-bis(4-methoxyphenyl)isoindoline-1,3-diimine.⁴ Yellow solid. M.p.: 124–126 °C. (*Z,Z*): (*Z,E*) = 2:1. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.03–8.01 (m, 2H, *ArH*), 7.68–7.65 (m, 2H, *ArH*), 6.97 (d, *J* = 8.8 Hz, 4H, *ArH*), 6.88 (d, *J* = 8.8 Hz, 4H, *ArH*), 3.79 (s, 6H, OCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 156.5, 150.1, 141.1, 134.7, 131.7, 122.4, 122.2, 114.8 (*ArC*), 55.4 (OCH₃).

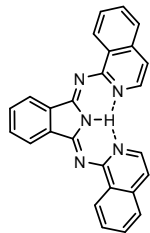


(1*Z*,3*Z*)-*N*¹,*N*³-di(naphthalen-1-yl)isoindoline-1,3-diimine.⁵ Yellow solid. M.p.: 148–150 °C. (*Z,Z*): (*Z,E*) = 2:1. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.27–8.25 (m, 2H, *ArH*), 8.08 (d, *J* = 8.0 Hz, 2H, *ArH*), 7.93–7.90 (m, 2H, *ArH*), 7.81–7.79 (m, 2H, *ArH*), 7.57–7.54 (m, 4H, *ArH*), 7.31 (d, *J* = 7.6 Hz, 2H, *ArH*), 7.26 (d, *J* = 8.0 Hz, 2H, *ArH*), 6.92 (d, *J* = 7.2 Hz, 2H, *ArH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 150.6, 144.4, 134.8, 134.3, 132.0, 129.0, 128.2, 127.8, 126.4, 125.7, 124.5, 123.7, 122.6, 115.2 (*ArC*).

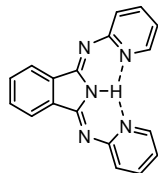


(1*Z*,3*Z*)-1,3-bis((diphenylmethylene)hydrazono)isoindoline. Yellow solid. M.p.: 177–179 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.38 (br, 1H, NH), 7.76–7.72 (m, 6H, *ArH*), 7.50–7.37 (m, 18H,

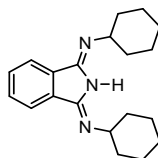
ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm): δ 165.0, 152.8, 138.6, 135.2, 133.5, 130.9, 130.4, 130.0, 129.2, 128.9, 128.1, 127.5, 122.4 (ArC). HRMS (ESI): calcd for $\text{C}_{34}\text{H}_{25}\text{N}_5$ $[\text{M}+\text{H}]^+$: 504.2183, found: 504.2190.



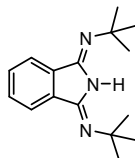
(1Z,3Z)- N^1,N^3 -di(isoquinolin-1-yl)isoindoline-1,3-diimine.⁶ Yellow solid. M.p.: 225–227 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 14.32 (br, 1H, NH), 9.03 (d, J = 8.4 Hz, 2H, ArH), 8.56 (d, J = 6.0 Hz, 2H, ArH), 8.27 (dd, J = 3.2, 5.6 Hz, 2H, ArH), 7.83 (d, J = 8.0 Hz, 2H, ArH), 7.75–7.65 (m, 6H, ArH), 7.52 (d, J = 5.6 Hz, 2H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm): δ 158.4, 154.4, 140.9, 137.7, 136.1, 131.7, 130.4, 127.1, 126.9, 126.5, 126.2, 122.7, 118.2 (ArC).



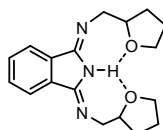
(1Z,3Z)- N^1,N^3 -di(pyridin-2-yl)isoindoline-1,3-diimine.⁷ Yellow solid. M.p.: 185–187 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 14.0 (br, 1H, NH), 8.63–8.61 (m, 2H, ArH), 8.10–8.05 (m, 2H, ArH), 7.76 (dt, J = 2.0, 7.6 Hz, 2H, ArH), 7.68–7.63 (m, 2H, ArH), 7.46 (d, J = 8.0 Hz, 2H, ArH), 7.14–7.11 (m, 2H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C, ppm): δ 160.4, 153.7, 147.7, 138.0, 135.7, 131.6, 123.2, 122.5, 120.1 (ArC).



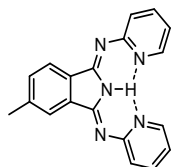
(1Z,3Z)- N^1,N^3 -dicyclohexylisoindoline-1,3-diimine.⁸ Colorless solid. M.p.: 102–104 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, ppm): δ 8.03 (s, 2H, ArH), 7.57–7.55 (m, 2H, ArH), 4.14–4.10 (m, 2H, NCH), 1.89 (d, J = 10.0 Hz, 4H, CyH), 1.77 (d, J = 12.0 Hz, 4H, CyH), 1.63 (d, J = 12.0 Hz, 2H, CyH), 1.51–1.30 (m, 8H, CyH), 1.19 (t, J = 12.0 Hz, 2H, CyH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO}-d_6$, ppm): δ 167.5, 136.5, 130.8, 121.7 (ArC), 54.1, 48.5, 32.5, 25.2, 24.5 (CyC).



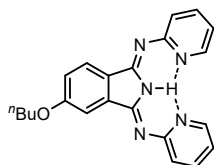
(1Z,3Z)- N^1,N^3 -di-tert-butylisoindoline-1,3-diimine.⁵ Colorless solid. M.p.: 90–92 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, ppm): δ 7.77 (s, 2H, ArH), 7.45–7.43 (m, 2H, ArH), 1.49 (s, 18H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO}-d_6$, ppm): δ 164.2, 137.5, 129.6, 120.6 (ArC), 53.7 ($\text{C}(\text{CH}_3)_3$), 29.9 (CH_3).



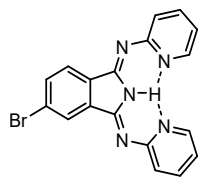
(1*Z*,3*Z*)-*N*¹,*N*³-bis((tetrahydrofuran-2-yl)methyl)isoindoline-1,3-diimine. Colorless solid. M.p.: 110–112 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.63 (s, 2H, Ar*H*), 7.34 (s, 2H, Ar*H*), 4.22–4.19 (m, 2H, OCH), 3.90–3.85 (m, 4H, OCH₂), 3.75–3.71 (m, 4H, NCH₂), 2.00–1.98 (m, 2H, CH₂), 1.88–1.85 (m, 4H, CH₂), 1.68–1.66 (m, 2H, CH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 167.8, 137.4, 129.8, 120.2 (ArC), 78.5 (OCH), 68.0 (OCH₂), 51.0 (NCH₂), 29.1 (CH₂), 25.6 (CH₂). HRMS (ESI): calcd for C₁₈H₂₃N₃O₂ [M+H]⁺: 314.1863, found: 314.1876.



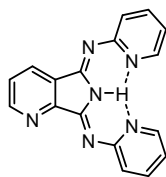
(1*Z*,3*Z*)-5-methyl-*N*¹,*N*³-di(pyridin-2-yl)isoindoline-1,3-diimine.⁹ Yellow solid. M.p.: 184–186 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 13.91 (br, 1H, NH), 8.57 (m, 2H, Ar*H*), 7.92 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.85 (s, 1H, Ar*H*), 7.72 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.44–7.39 (m, 3H, Ar*H*), 7.09–7.06 (m, 2H, Ar*H*), 2.49 (s, 3H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 160.4, 160.3, 153.9, 153.8, 147.7, 142.3, 137.9, 135.9, 133.0, 132.5, 123.1, 123.0, 122.9, 122.3, 120.0, 119.9 (ArC), 21.8 (CH₃).



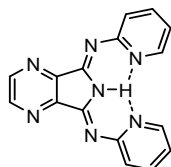
(1*Z*,3*Z*)-5-butoxy-*N*¹,*N*³-di(pyridin-2-yl)isoindoline-1,3-diimine. Yellow solid. M.p.: 160–162 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 13.85 (br, 1H, NH), 8.58 (t, *J* = 5.2 Hz, 2H, Ar*H*), 7.93 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.76–7.70 (m, 2H, Ar*H*), 7.52–7.51 (m, 1H, Ar*H*), 7.42 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.14–7.06 (m, 3H, Ar*H*), 4.11 (t, *J* = 6.4 Hz, 2H, OCH₂), 1.85–1.78 (m, 2H, CH₂), 1.57–1.48 (m, 2H, CH₂), 0.99 (t, *J* = 7.6 Hz, 3H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 162.6, 160.6, 160.4, 153.8, 153.7, 147.8, 147.7, 138.0, 137.9, 127.7, 123.8, 123.0, 122.9, 120.1, 119.9, 119.7, 106.4 (ArC), 68.3 (OCH₂), 31.2 (CH₂), 19.2 (CH₂), 13.8 (CH₃). HRMS (ESI): calcd for C₂₂H₂₁N₅O [M+H]⁺: 372.1819, found: 372.1833.



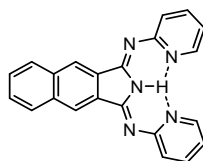
(1*Z*,3*Z*)-5-bromo-*N*¹,*N*³-di(pyridin-2-yl)isoindoline-1,3-diimine. Yellow solid. M.p.: 210–212 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 13.95 (br, 1H, NH), 8.58 (d, *J* = 3.6 Hz, 2H, Ar*H*), 8.18 (s, 1H, Ar*H*), 7.89 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.76–7.71 (m, 3H, Ar*H*), 7.41 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.12–7.09 (m, 2H, Ar*H*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 160.2, 160.1, 152.8, 152.3, 147.8, 138.1, 137.6, 134.6, 134.5, 126.0, 125.8, 123.9, 123.4, 123.3, 120.5, 120.4 (ArC). HRMS (ESI): calcd for C₁₈H₁₂N₅Br [M+H]⁺: 378.0349, found: 378.0357.



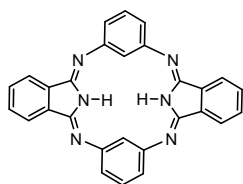
(5*Z*,7*Z*)-*N*⁵,*N*⁷-di(pyridin-2-yl)-5*H*-pyrrolo[3,4-*b*]pyridine-5,7(6*H*)-diimine.⁹ Yellow solid. M.p.: 180–182 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 14.20 (s, 1H, *NH*), 8.87 (d, *J* = 4.8 Hz, 1H, *ArH*), 8.58–8.57 (m, 2H, *ArH*), 8.31 (d, *J* = 7.6 Hz, 1H, *ArH*), 7.76–7.70 (m, 2H, *ArH*), 7.64 (d, *J* = 8.0 Hz, 1H, *ArH*), 7.50–7.47 (m, 1H, *ArH*), 7.40 (d, *J* = 8.0 Hz, 1H, *ArH*), 7.12–7.08 (m, 2H, *ArH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 160.0, 159.9, 154.5, 153.2, 151.2, 150.8, 147.7, 147.6, 138.0, 130.6, 130.3, 125.3, 124.4, 123.3, 120.7, 120.5 (*ArC*).



(5*Z*,7*Z*)-*N*⁵,*N*⁷-di(pyridin-2-yl)-5*H*-pyrrolo[3,4-*b*]pyrazine-5,7(6*H*)-diimine. Yellow solid. M.p.: 270–272 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 14.42 (s, 1H, *NH*), 8.83 (s, 2H, *ArH*), 8.61–8.60 (m, 2H, *ArH*), 7.77 (dt, *J* = 2.0, 8.0 Hz, 2H, *ArH*), 7.63 (d, *J* = 8.0 Hz, 2H, *ArH*), 7.16–7.13 (m, 2H, *ArH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 159.6, 149.2, 148.5, 147.7, 147.2, 138.2, 124.6, 121.1 (*ArC*). HRMS (ESI): calcd for C₁₆H₁₁N₇ [*M*+*H*]⁺: 302.1149, found: 302.1154.



(1*Z*,3*Z*)-*N*¹,*N*³-di(pyridin-2-yl)-1*H*-benzo[*f*]isoindole-1,3(2*H*)-diimine.⁶ Yellow solid. M.p.: 212–214 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 14.31 (br, 1H, *NH*), 8.62 (d, *J* = 4.0 Hz, 2H, *ArH*), 8.56 (s, 2H, *ArH*), 8.04–8.02 (m, 2H, *ArH*), 7.79–7.75 (m, 2H, *ArH*), 7.61–7.58 (m, 2H, *ArH*), 7.48 (d, *J* = 8.0 Hz, 2H, *ArH*), 7.13–7.10 (m, 2H, *ArH*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 160.5, 153.6, 147.7, 138.0, 135.0, 131.9, 129.7, 127.8, 123.0, 123.0, 120.0 (*ArC*)



Yellow solid.² M.p.: 116–118 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 10.39 (br, 2H, *NH*), 7.97–7.95 (m, 4H, *ArH*), 7.75–7.73 (m, 4H, *ArH*), 7.34 (t, *J* = 8.0 Hz, 2H, *ArH*), 6.95 (s, 2H, *NH*), 6.77–6.75 (m, 4H, *ArH*). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆, ppm): δ 151.2, 149.6, 134.7, 131.9, 130.0, 122.1, 118.2, 113.5 (*ArC*).

Copies of the proligand

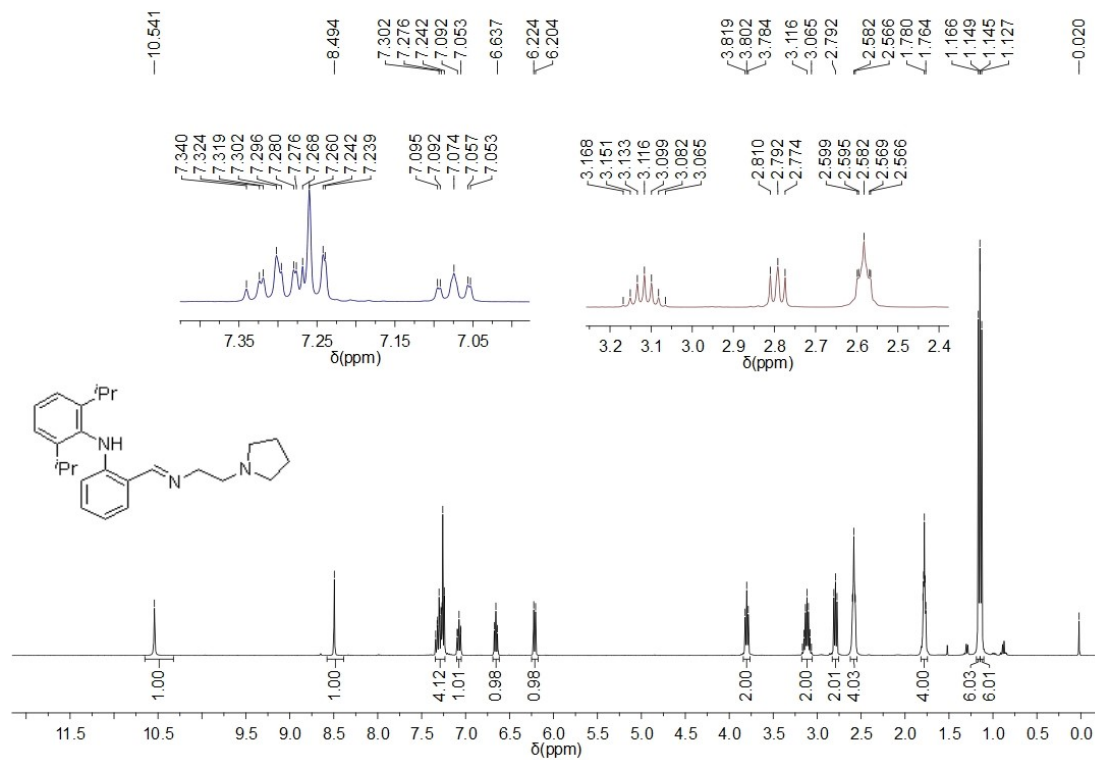


Fig. S4. ¹H NMR spectrum of **HL** (400 MHz, CDCl₃, 20 °C)

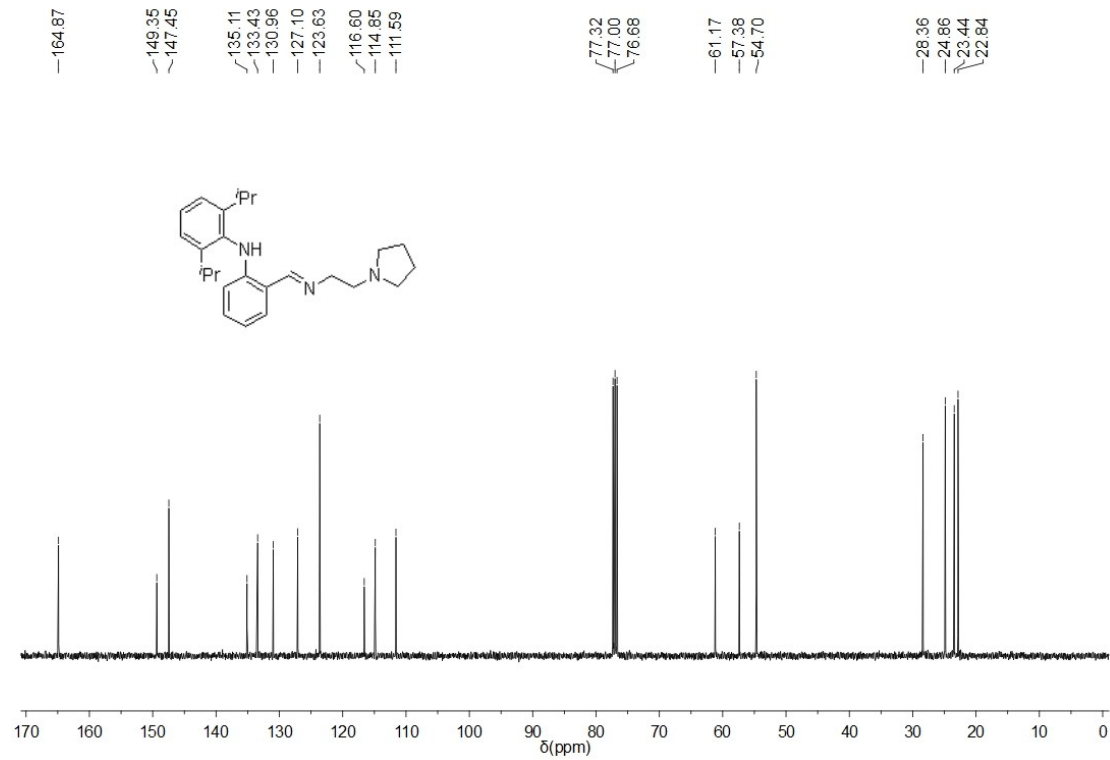


Fig. S5. ¹³C NMR spectrum of **HL** (100 MHz, CDCl₃, 20 °C)

Copies of rare earth metal complexes

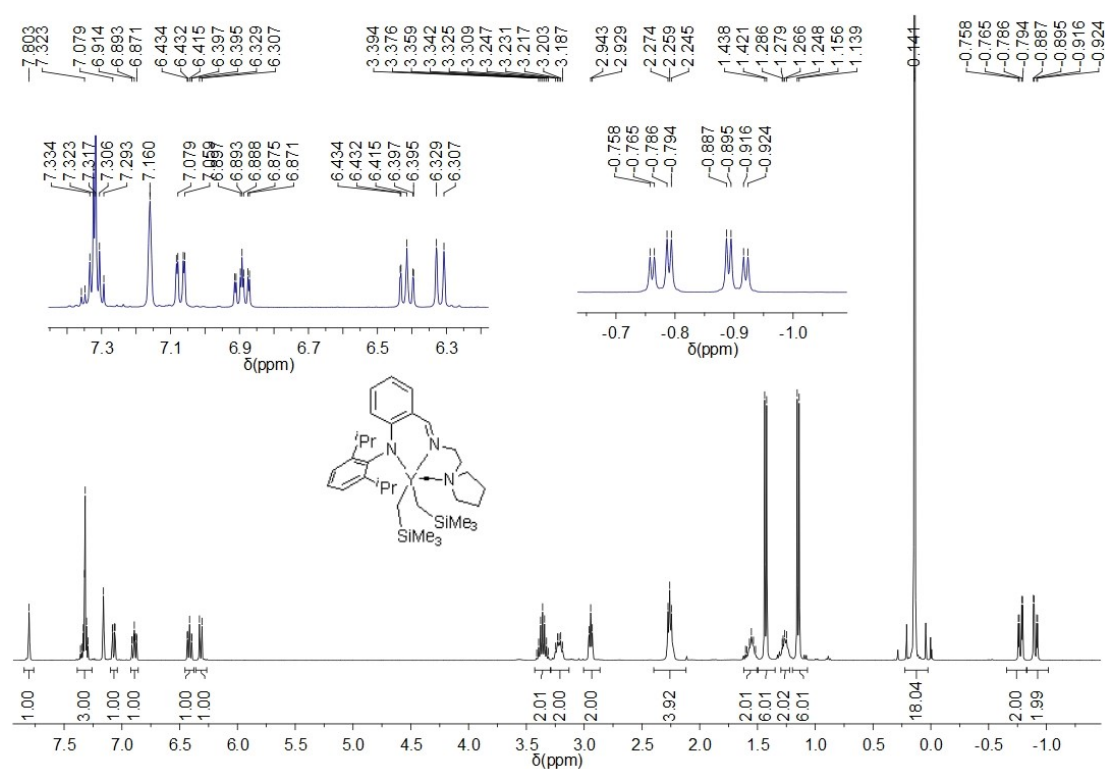


Fig. S6. ¹H NMR spectrum of **1b** (400 MHz, C₆D₆, 20 °C)

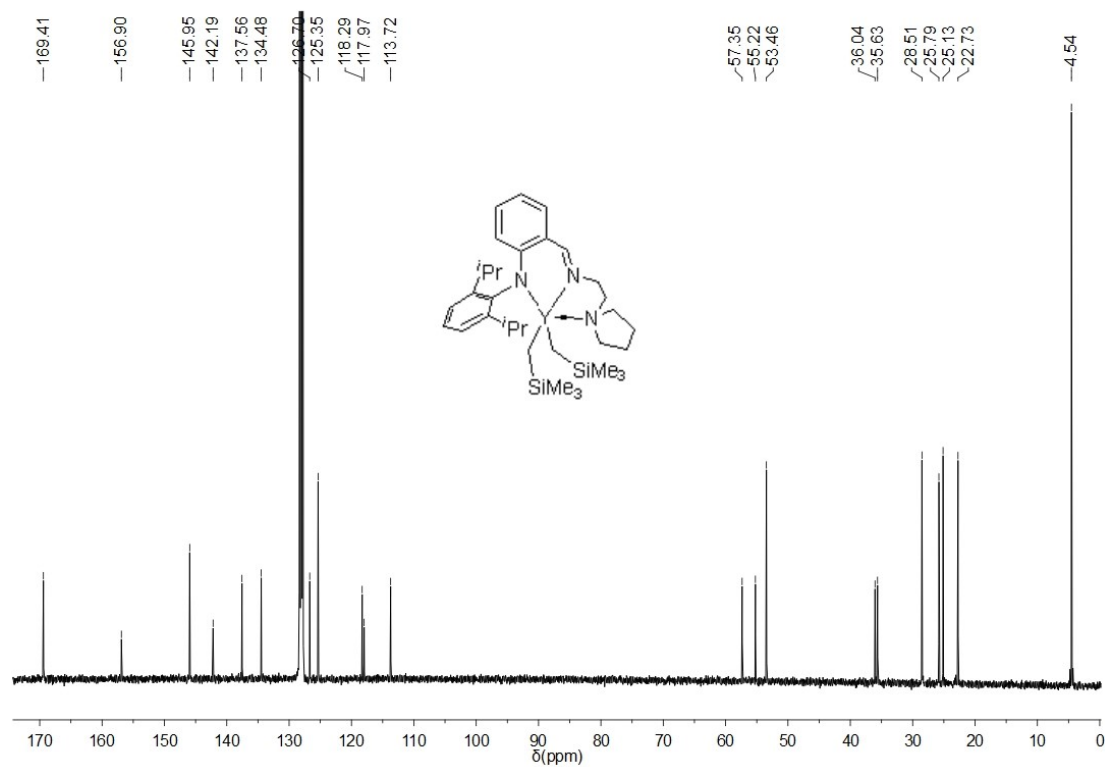


Fig. S7. ¹³C NMR spectrum of **1b** (100 MHz, C₆D₆, 20 °C)

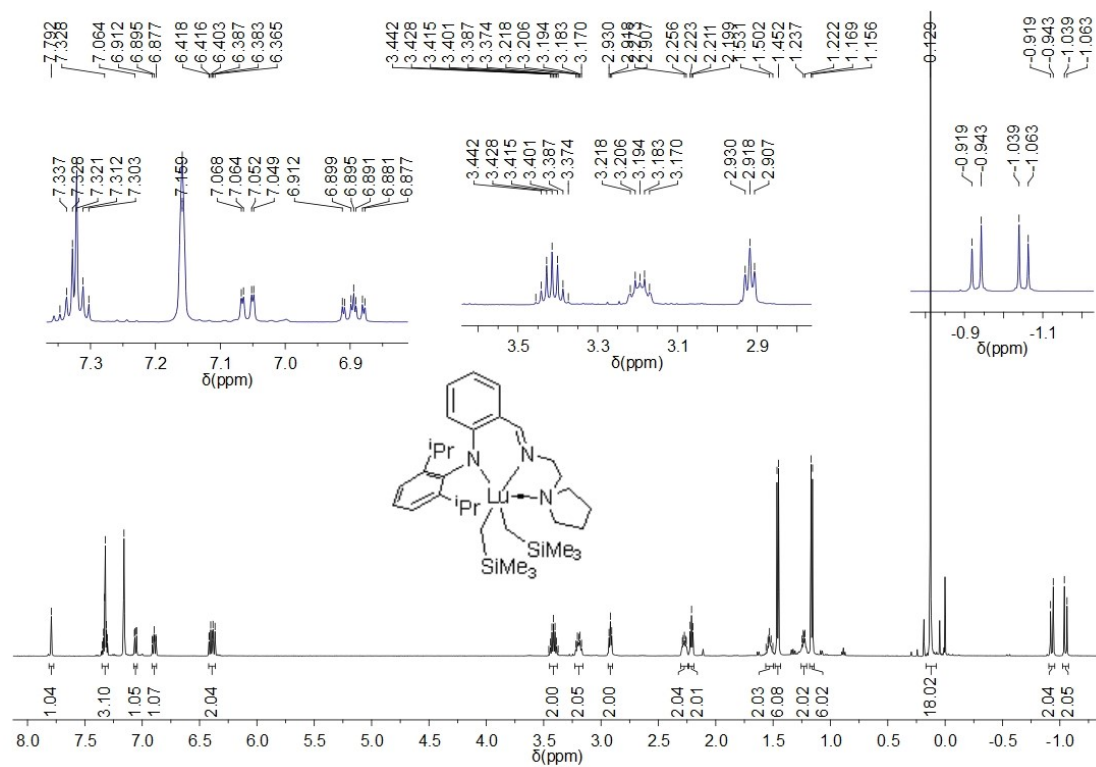


Fig. S8. ¹H NMR spectrum of **1d** (500 MHz, C₆D₆, 20 °C)

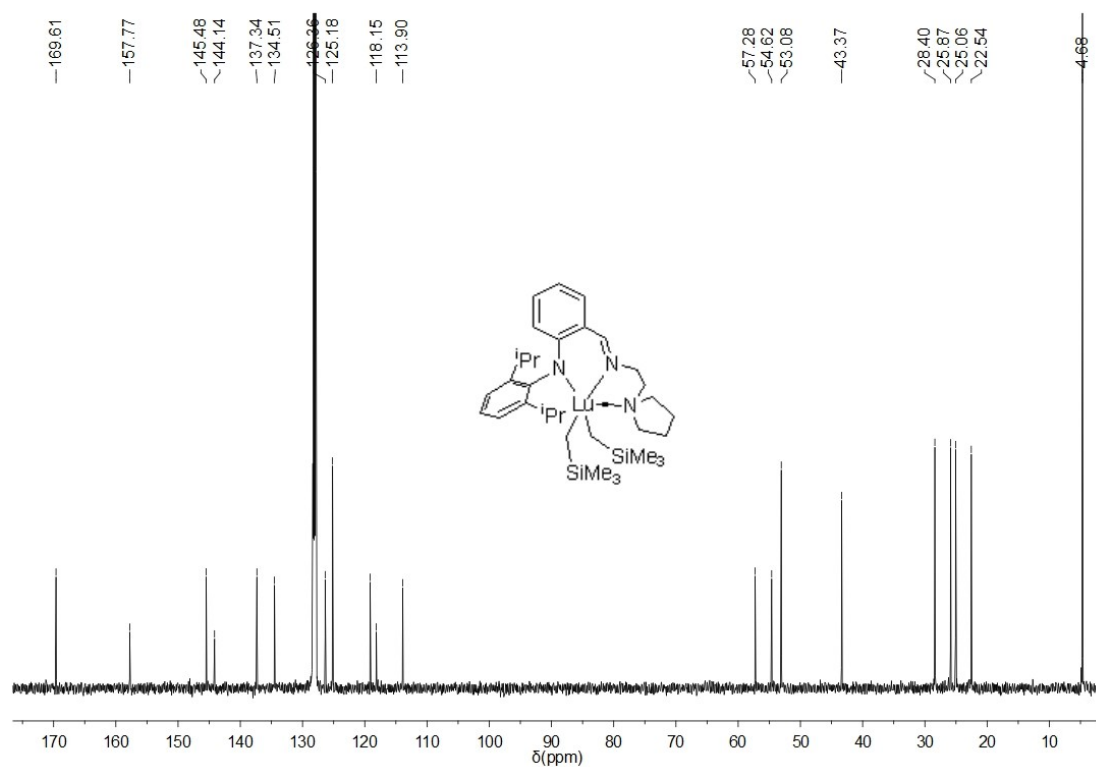


Fig. S9. ¹³C NMR spectrum of **1d** (125 MHz, C₆D₆, 20 °C)

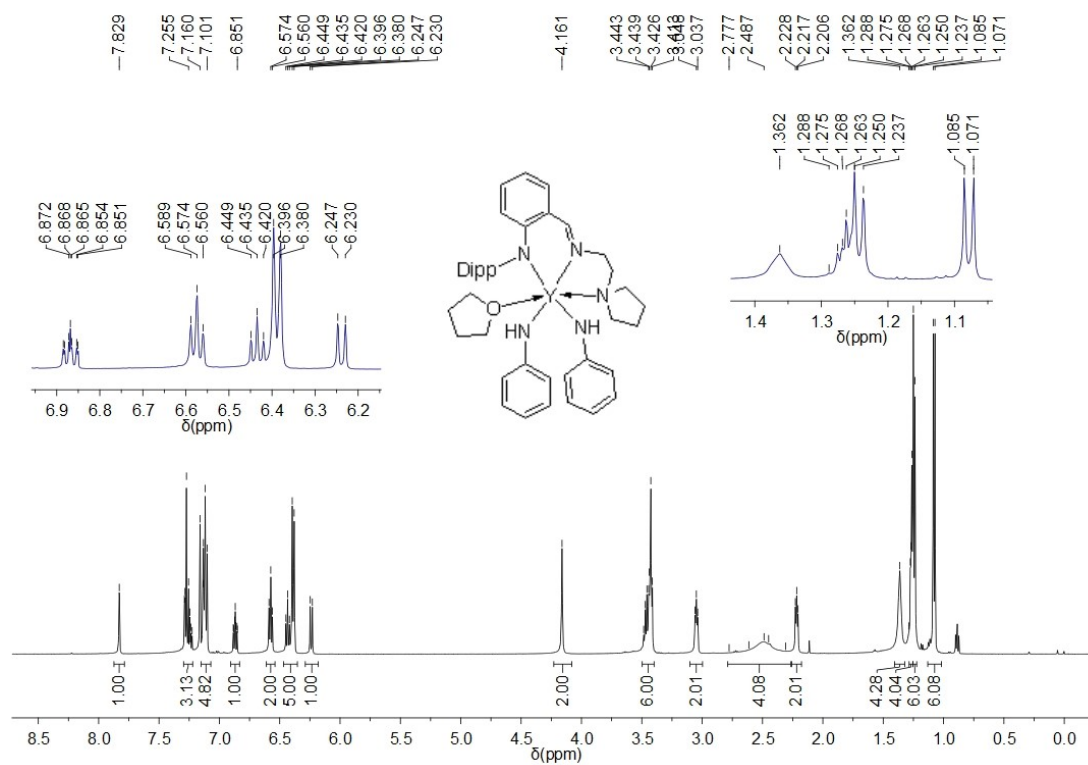


Fig. S10. ¹H NMR spectrum of **7b** (500 MHz, C₆D₆, 20 °C)

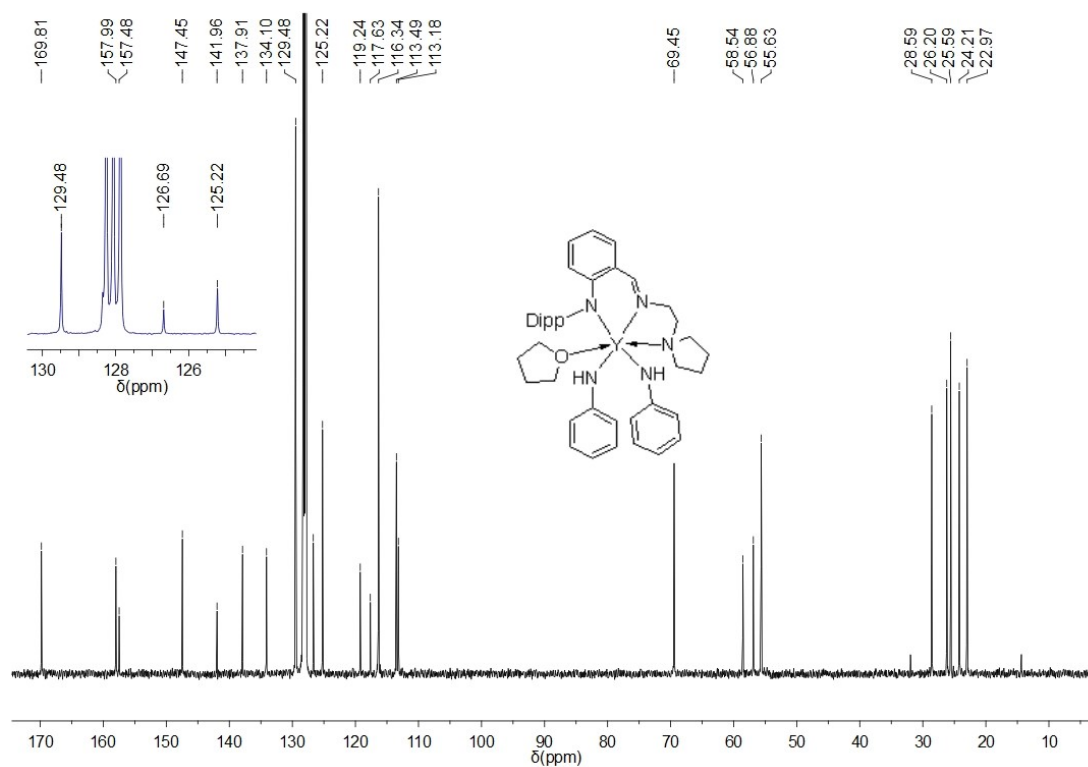


Fig. S11. ¹³C NMR spectrum of **7b** (125 MHz, C₆D₆, 20 °C)

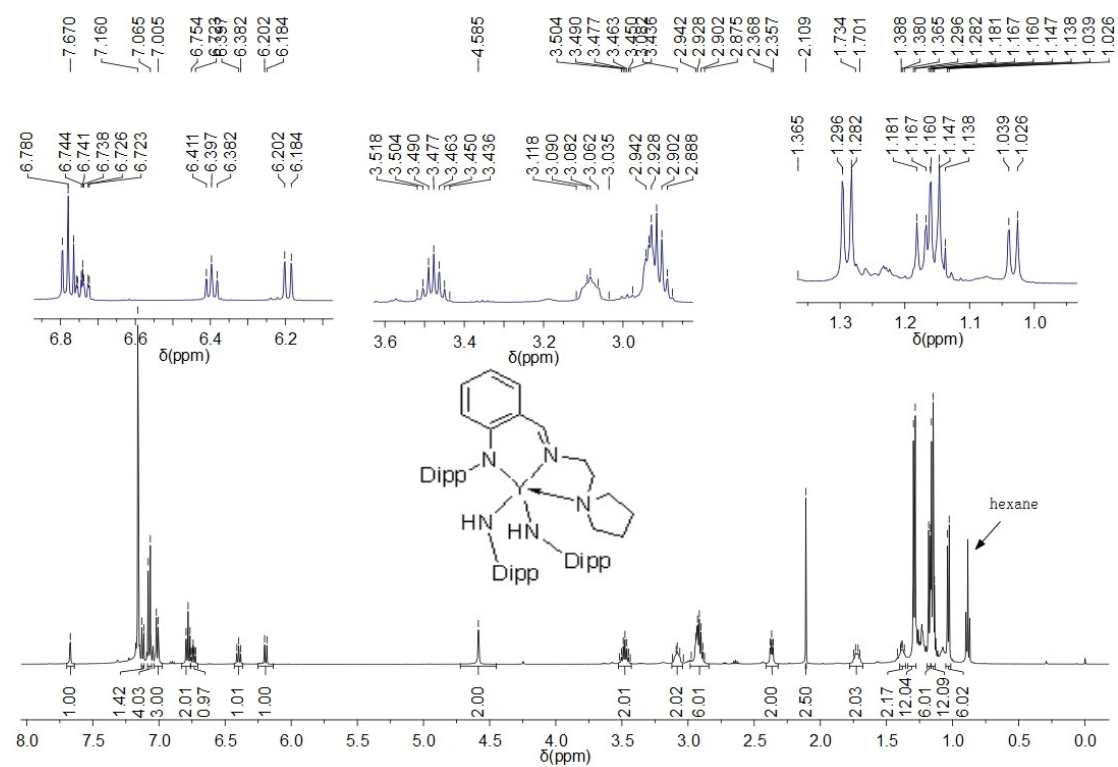


Fig. S12. ¹H NMR spectrum of **8b** (500 MHz, C₆D₆, 20 °C)

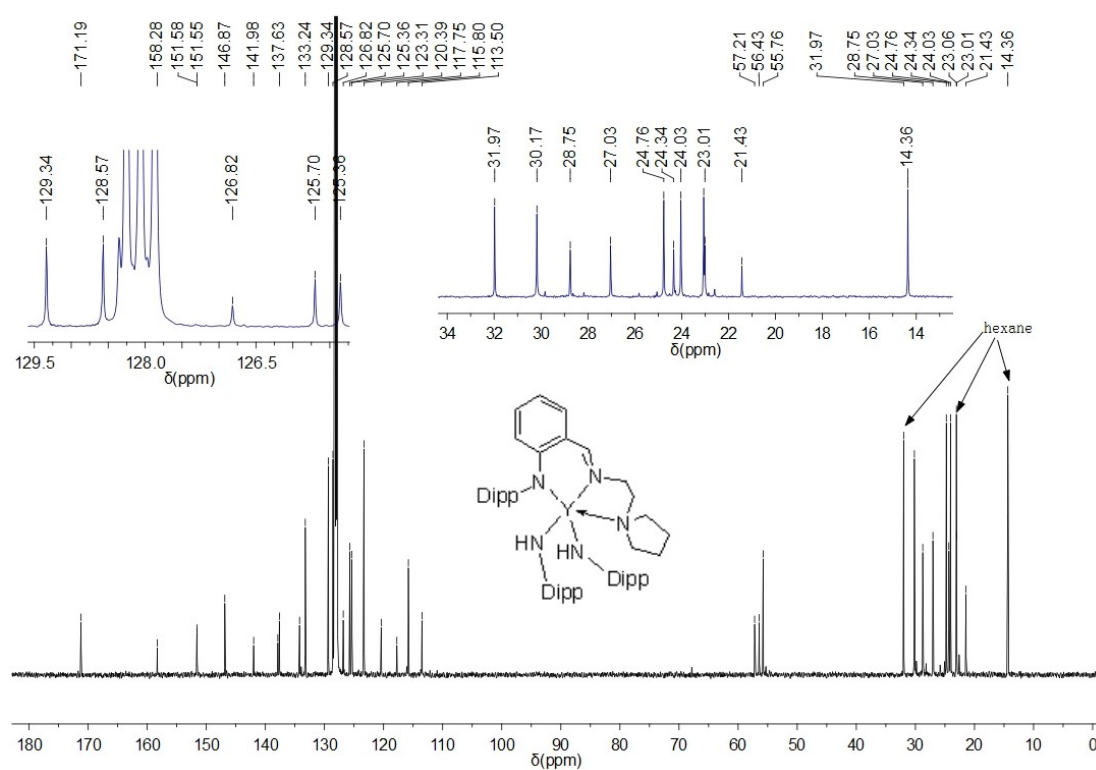


Fig. S13. ¹³C NMR spectrum of **8b** (125 MHz, C₆D₆, 20 °C)

Copies of 2,3-dihydroquinazolines

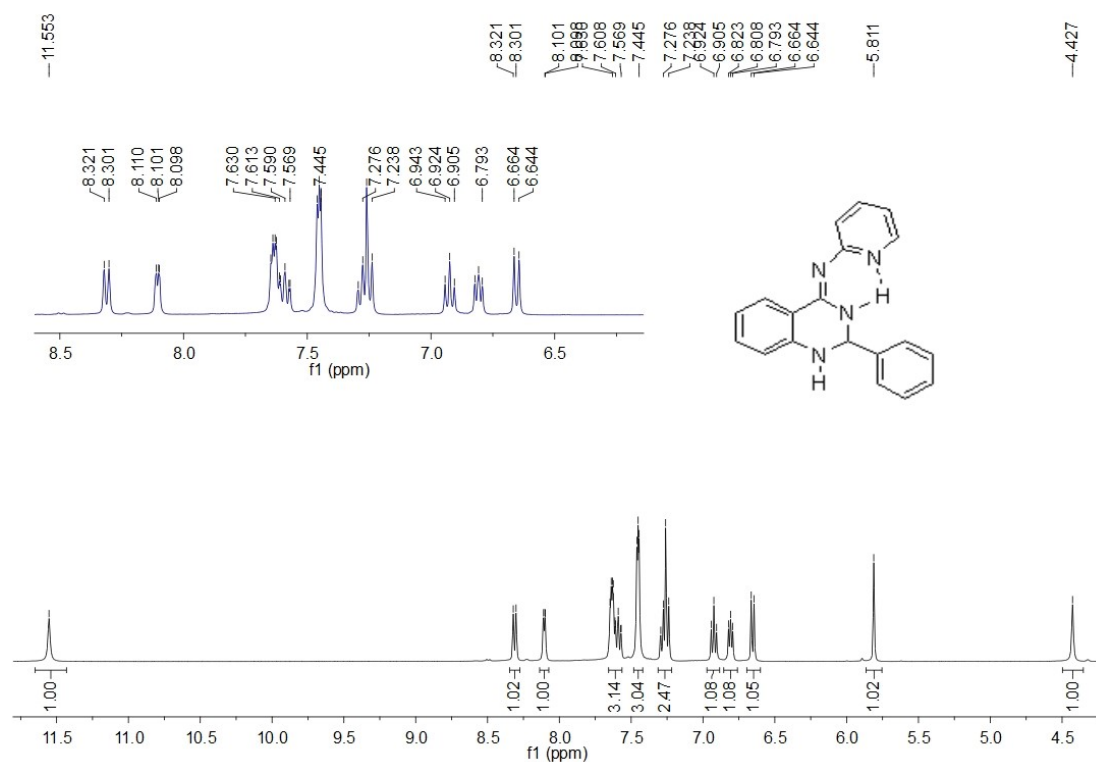


Fig. S14. ¹H NMR spectrum of **4aaa** (400 MHz, CDCl₃, 20 °C)

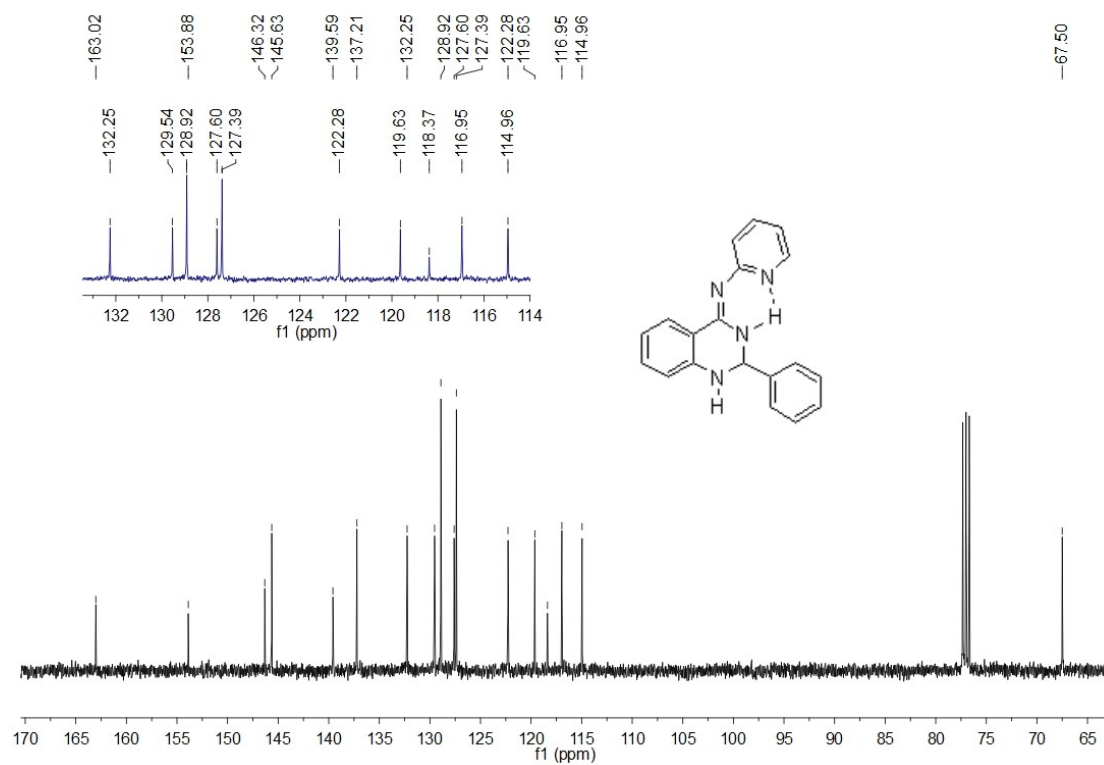


Fig. S15. ¹³C NMR spectrum of **4aaa** (100 MHz, CDCl₃, 20 °C)

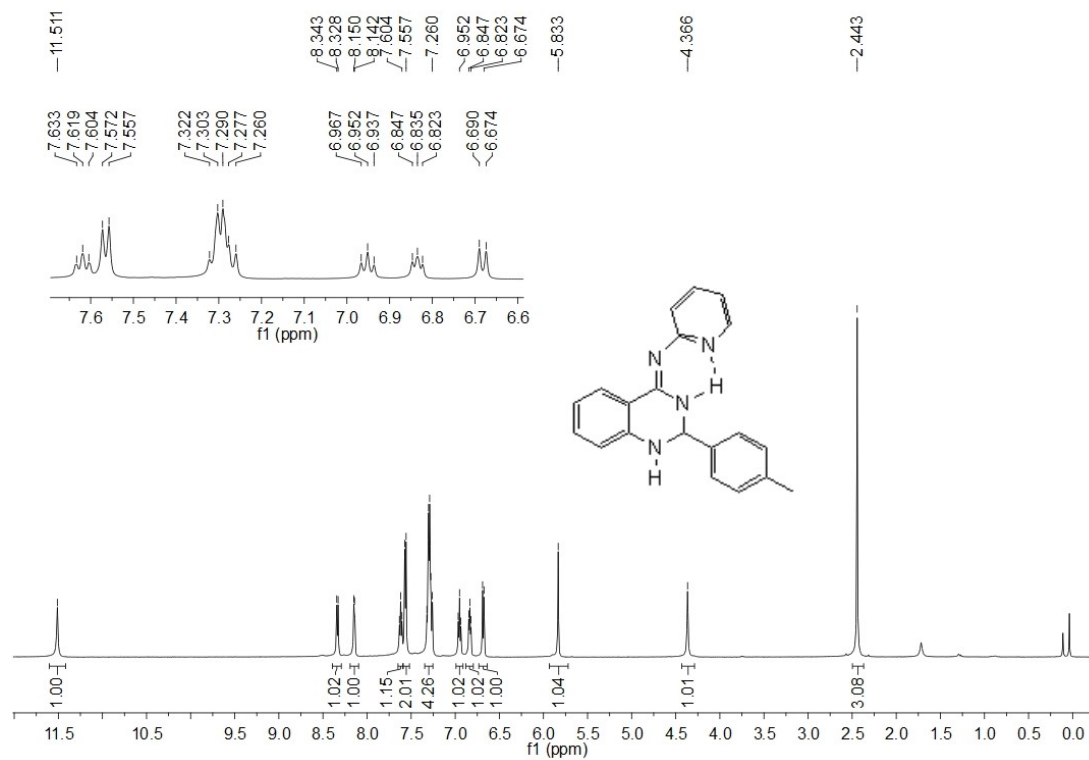


Fig. S16. ¹H NMR spectrum of **4aab** (500 MHz, CDCl₃, 20 °C)

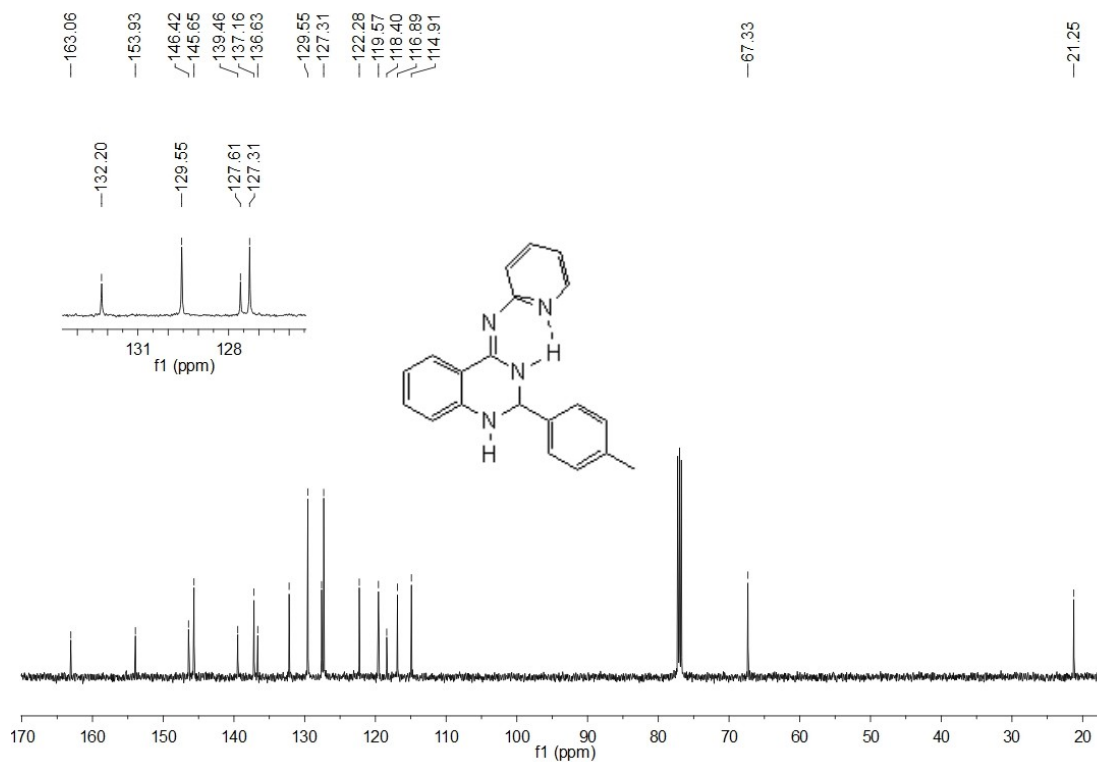


Fig. S17. ¹³C NMR spectrum of **4aab** (125 MHz, CDCl₃, 20 °C)

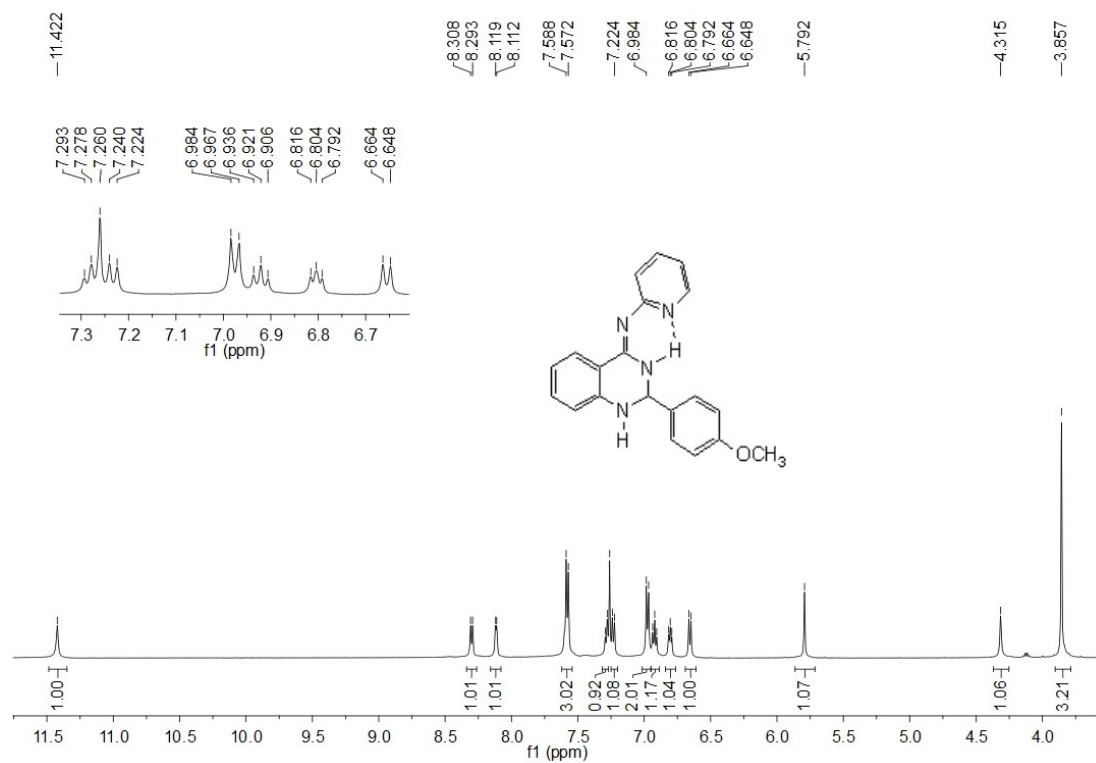


Fig. S18. ¹H NMR spectrum of **4aac** (500 MHz, CDCl₃, 20 °C)

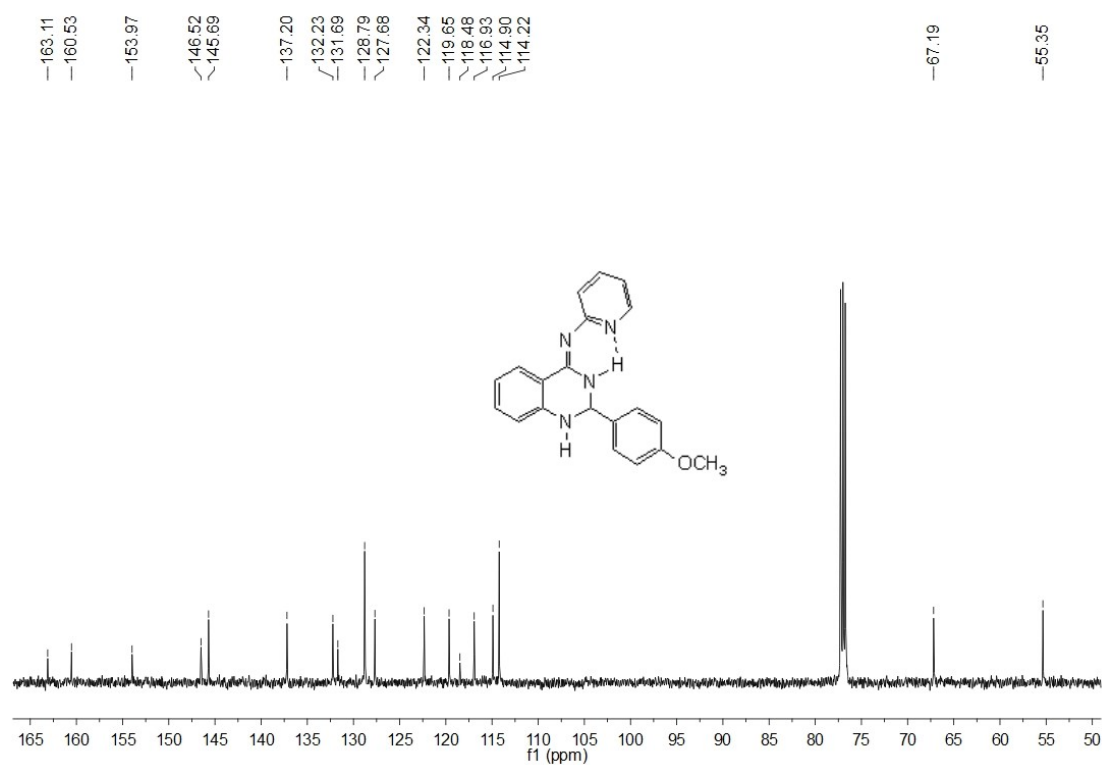


Fig. S19. ¹³C NMR spectrum of **4aac** (125 MHz, CDCl₃, 20 °C)

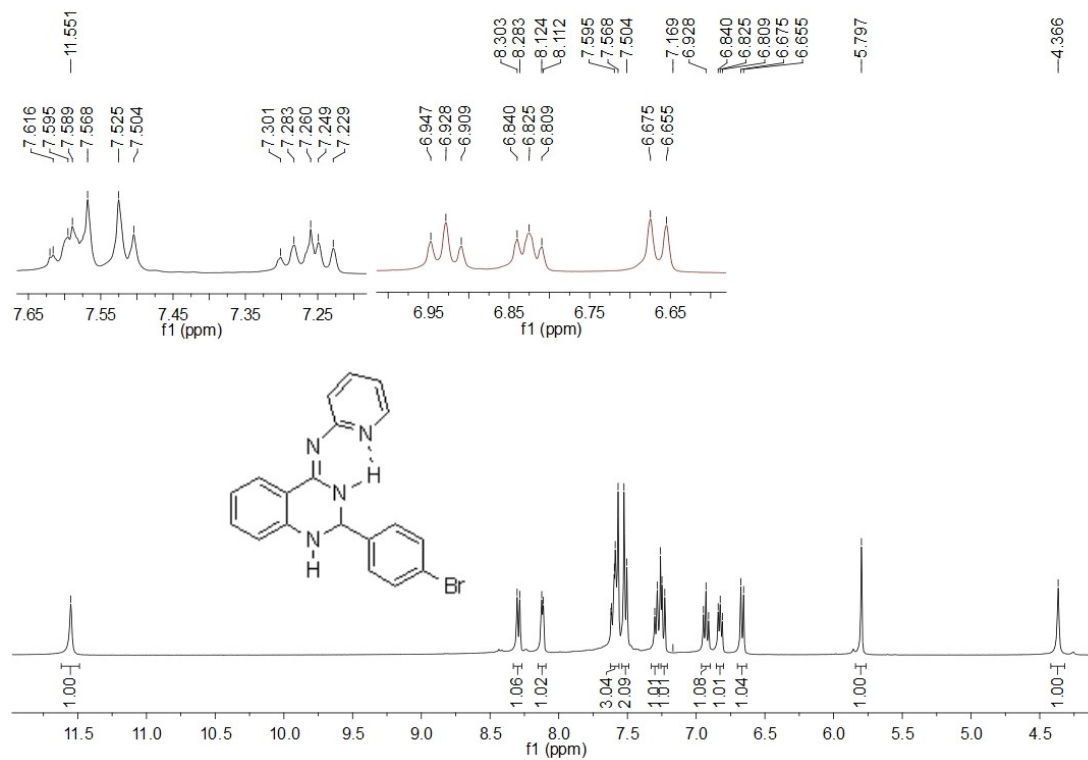


Fig. S20. ¹H NMR spectrum of **4aad** (400 MHz, CDCl₃, 20 °C)

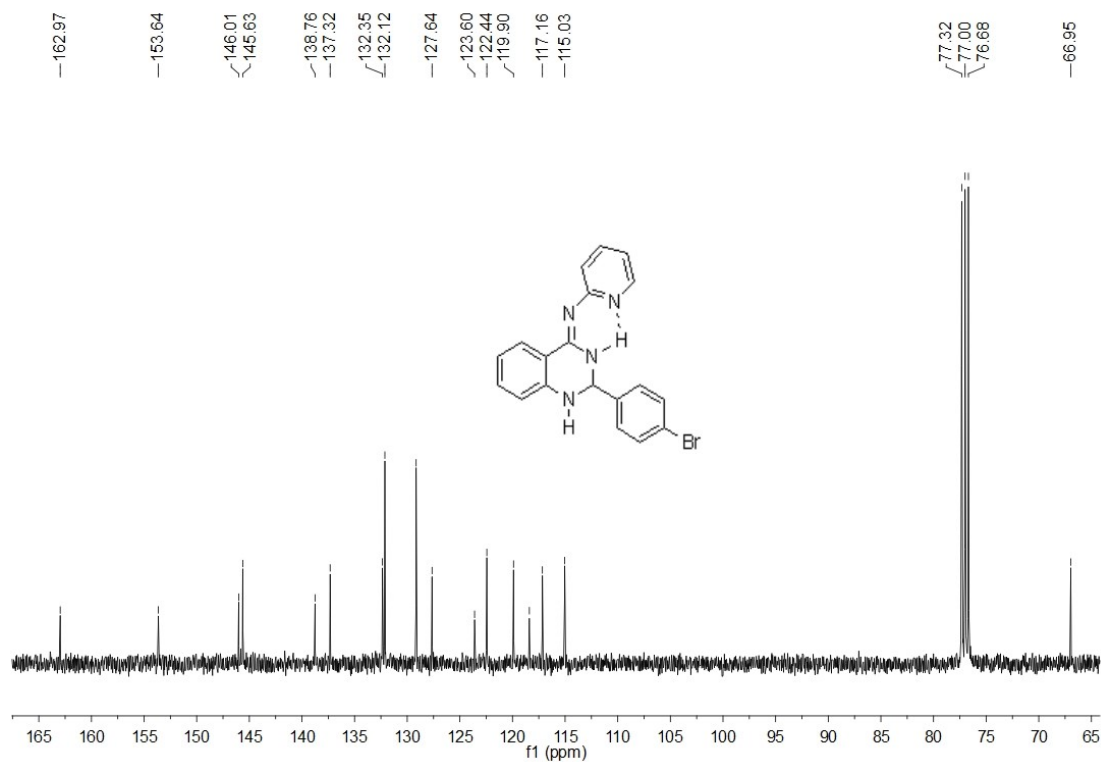


Fig. S21. ¹³C NMR spectrum of **4aad** (100 MHz, CDCl₃, 20 °C)

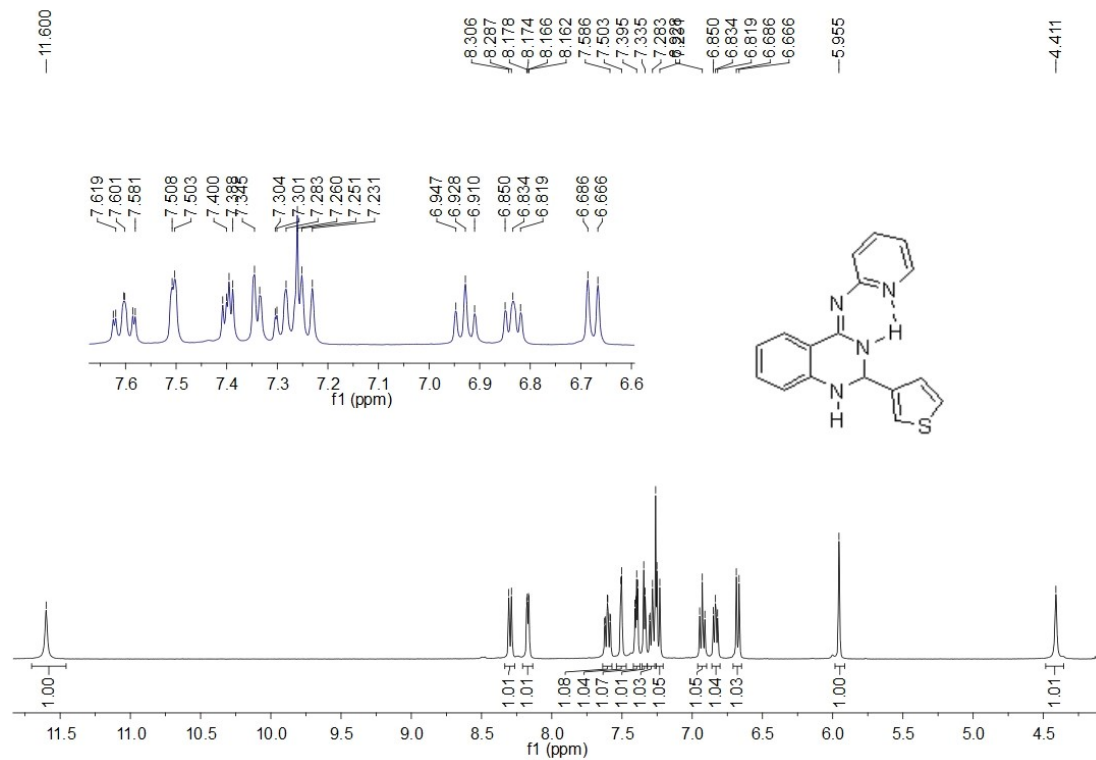


Fig. S24. ¹H NMR spectrum of **4aaf** (400 MHz, CDCl₃, 20 °C)

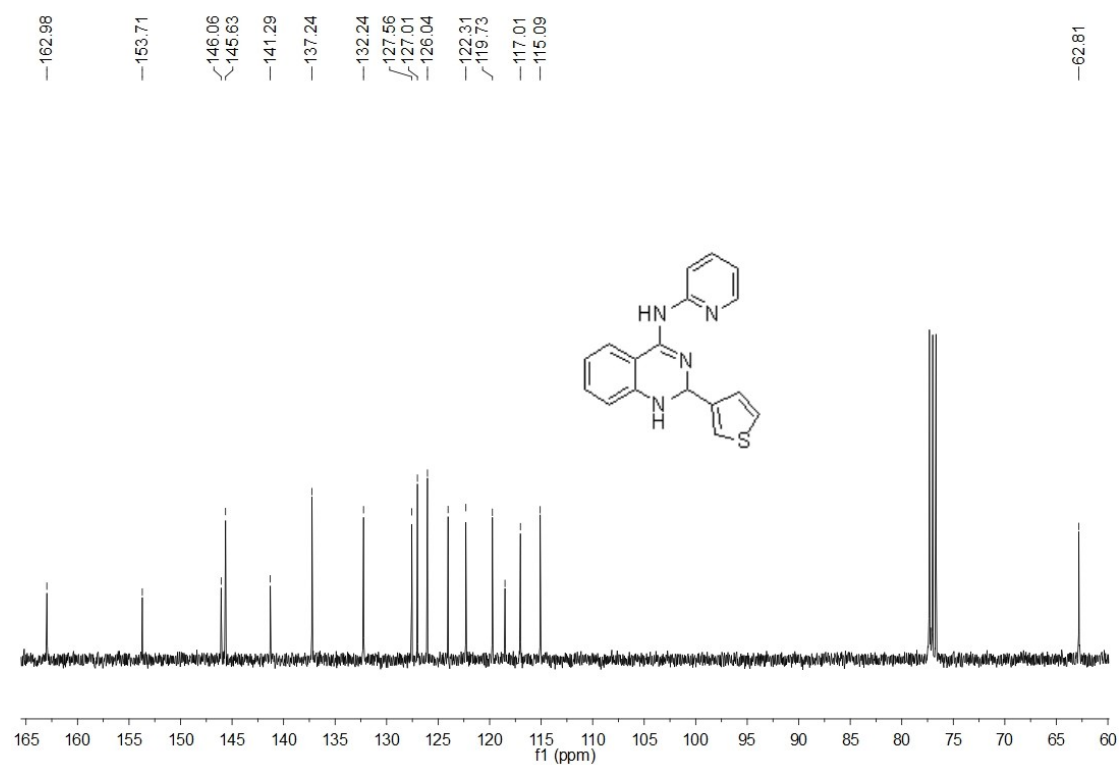


Fig. S25. ¹³C NMR spectrum of **4aaf** (100 MHz, CDCl₃, 20 °C)

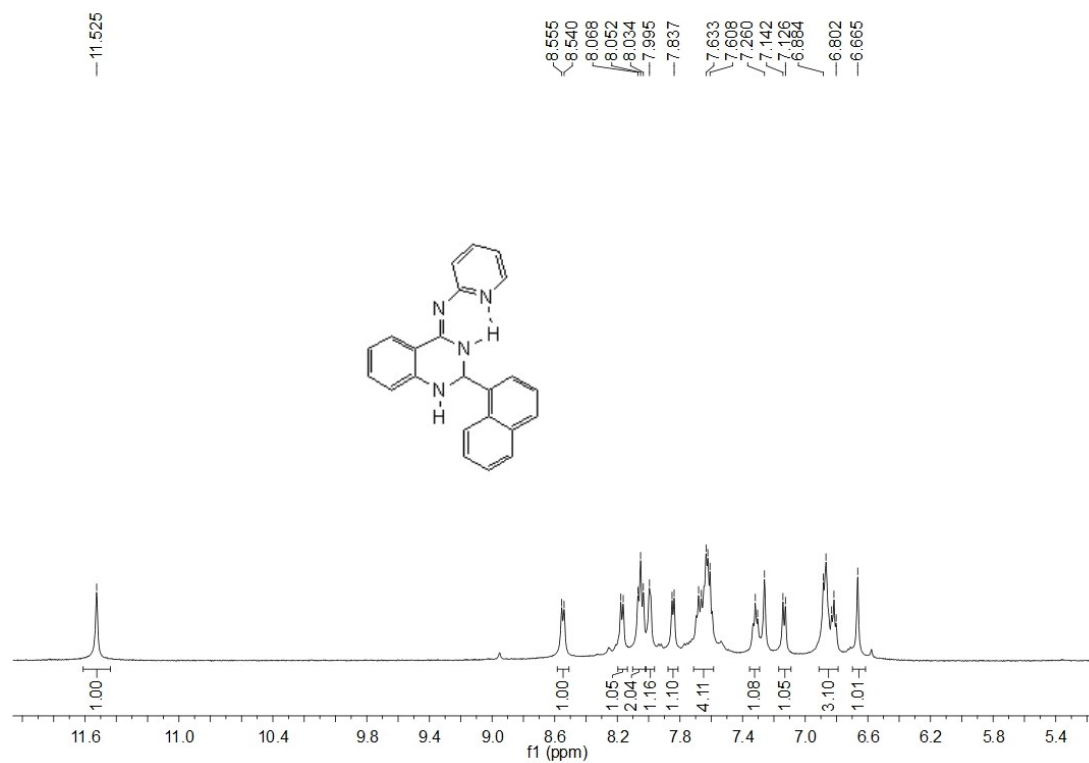


Fig. S26. ¹H NMR spectrum of **4aag** (500 MHz, CDCl₃, 20 °C)

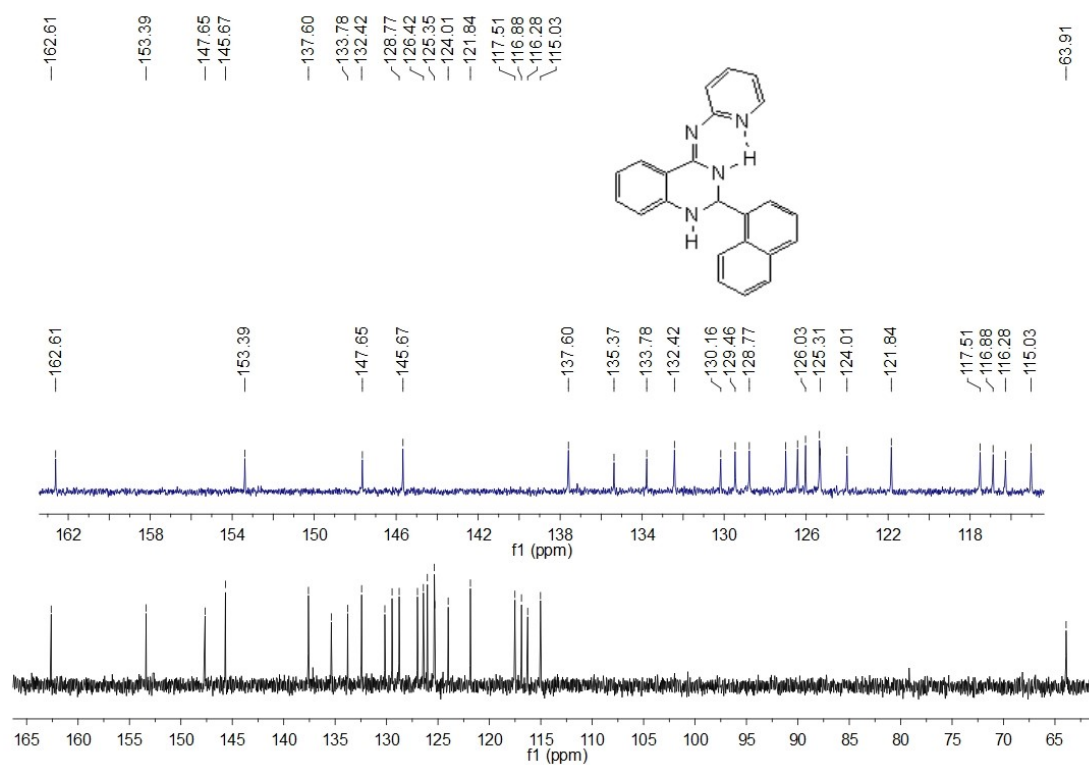


Fig. S27. ¹³C NMR spectrum of **4aag** (125 MHz, CDCl₃, 20 °C)

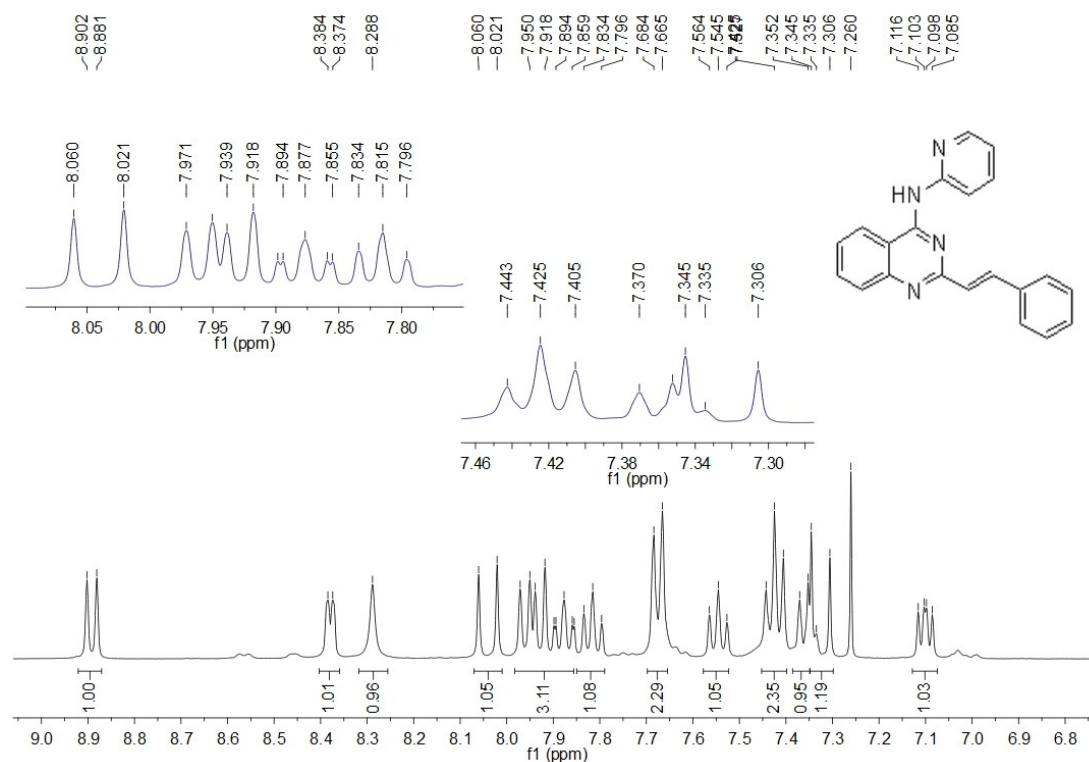


Fig. S28. ¹H NMR spectrum of **4aah'** (400 MHz, CDCl₃, 20 °C)

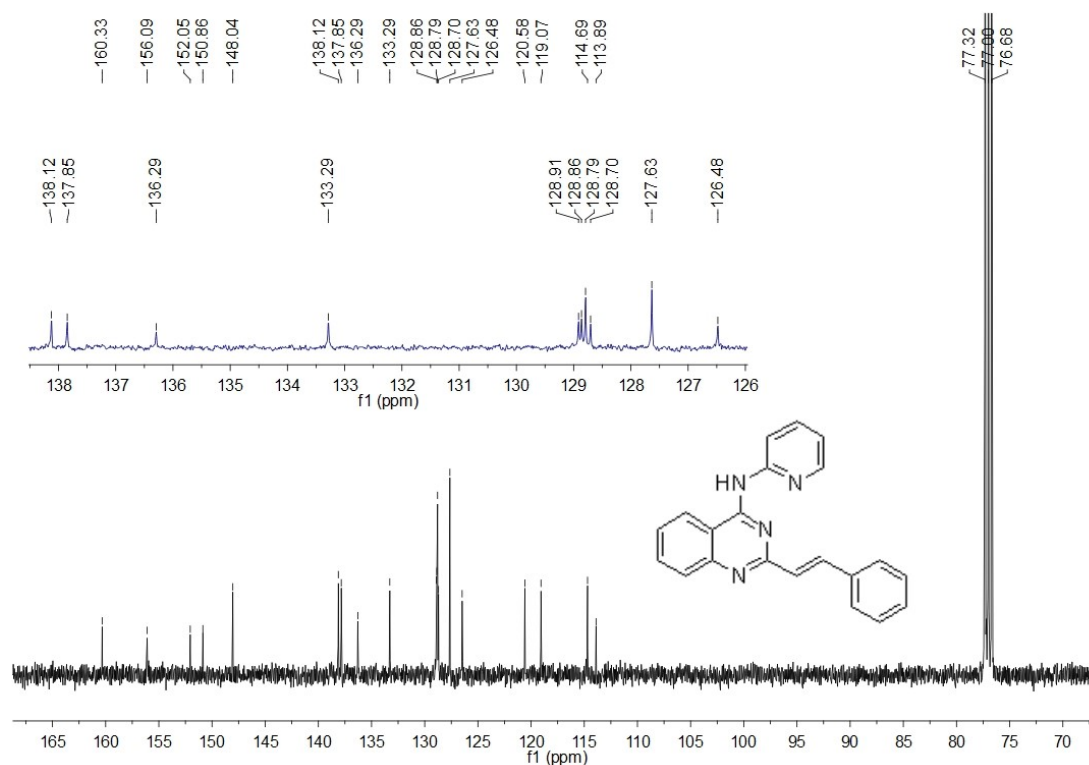


Fig. S29. ¹³C NMR spectrum of **4aah'** (100 MHz, CDCl₃, 20 °C)

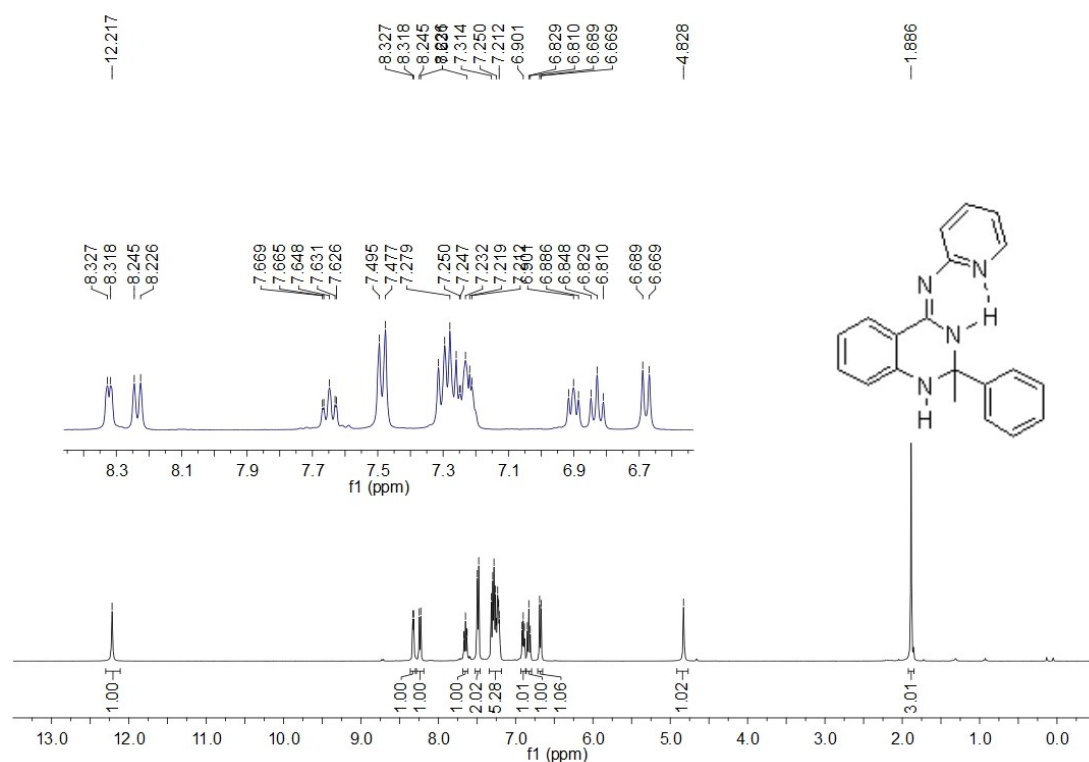


Fig. S30. ¹H NMR spectrum of **4aai** (400 MHz, CDCl₃, 20 °C)

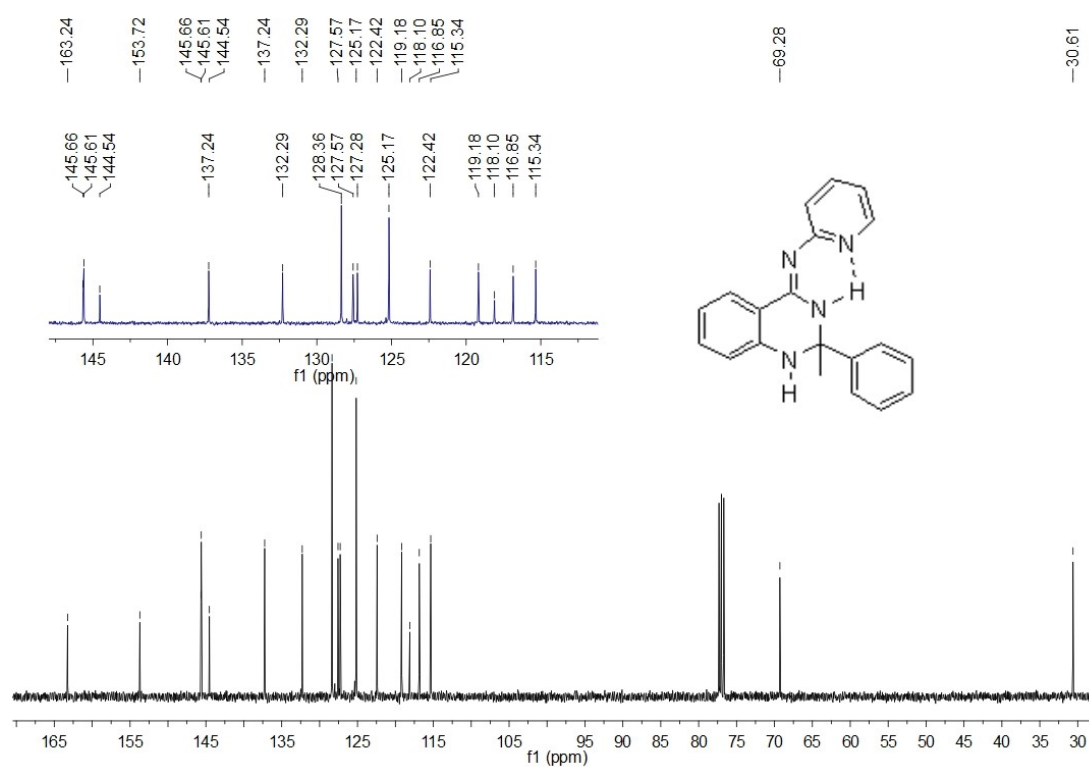


Fig. S31. ¹³C NMR spectrum of **4aai** (100 MHz, CDCl₃, 20 °C)

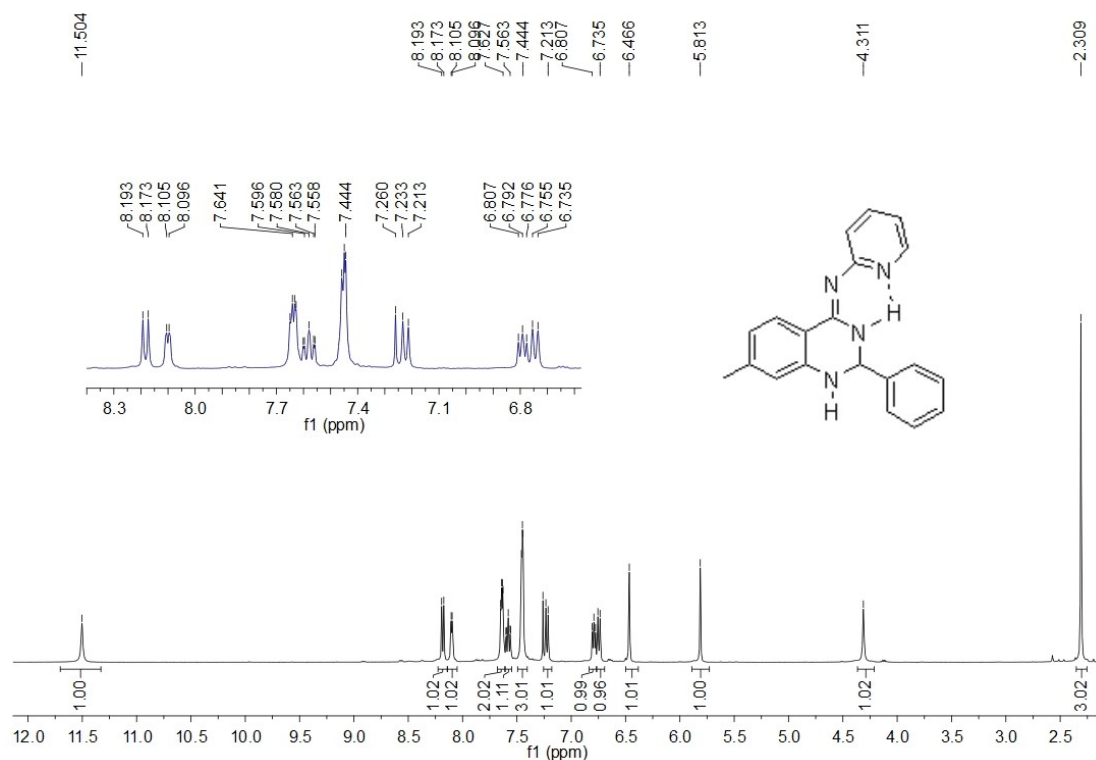


Fig. S34. ¹H NMR spectrum of **4baa** (400 MHz, CDCl₃, 20 °C)

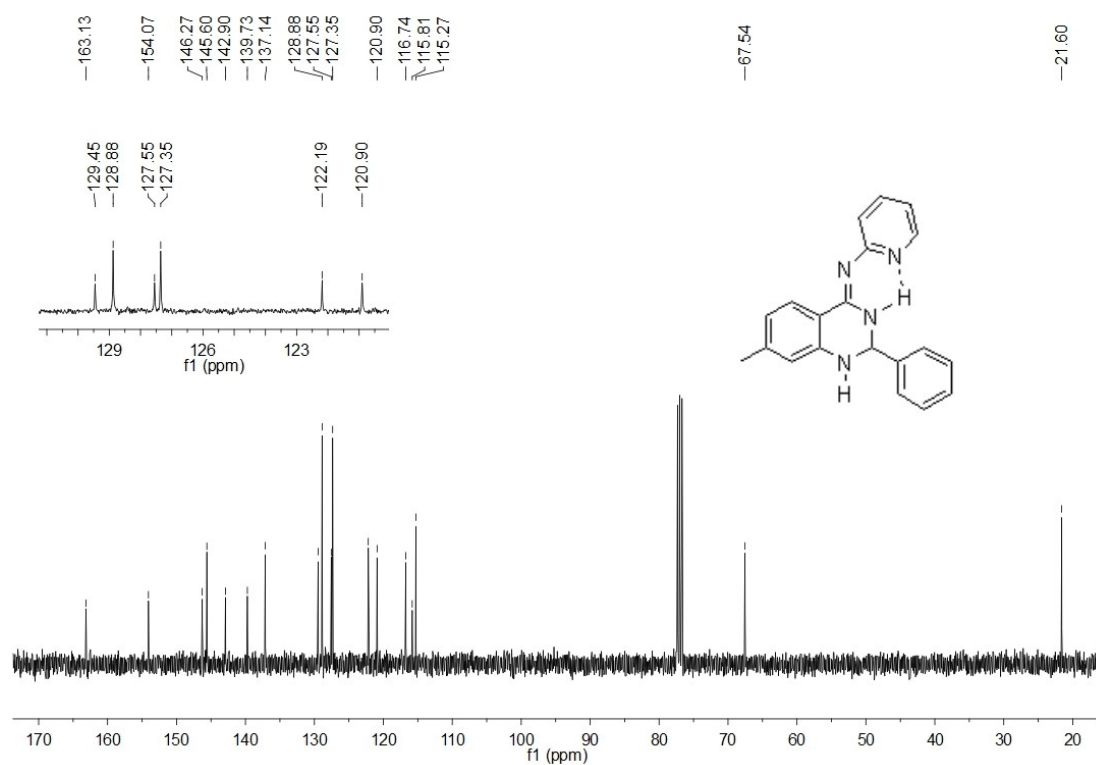


Fig. S35. ¹³C NMR spectrum of **4baa** (100 MHz, CDCl₃, 20 °C)

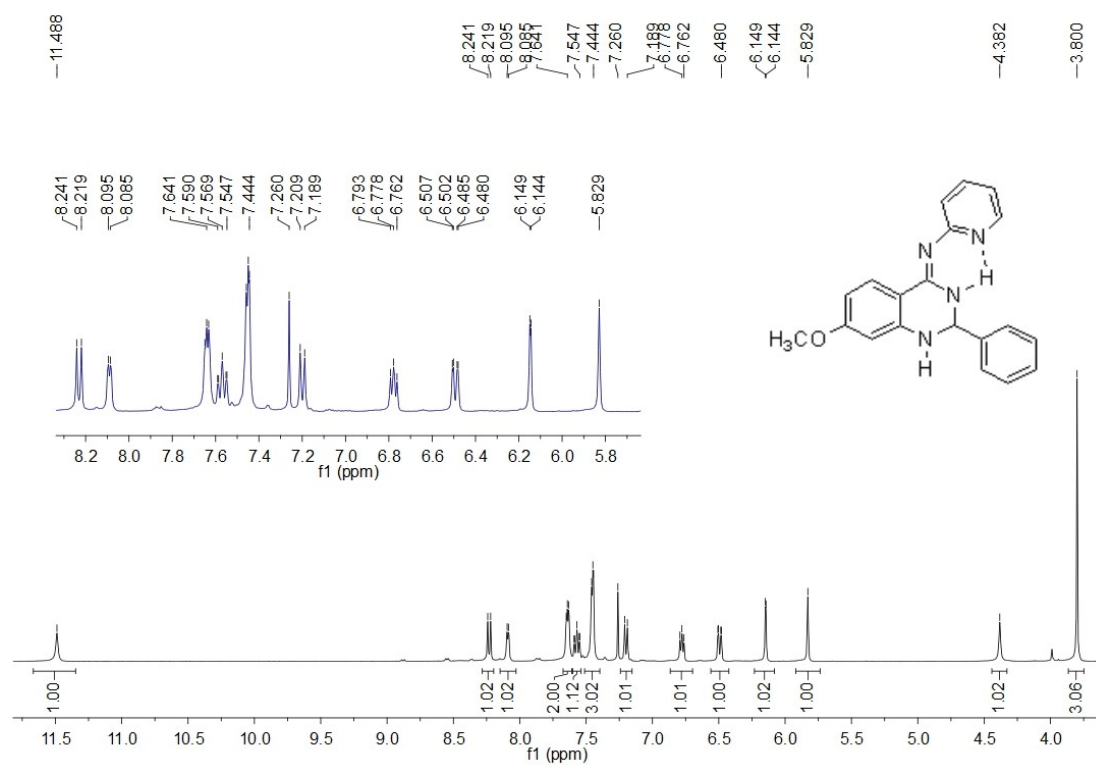


Fig. S36. ¹H NMR spectrum of **4caa** (400 MHz, CDCl₃, 20 °C)

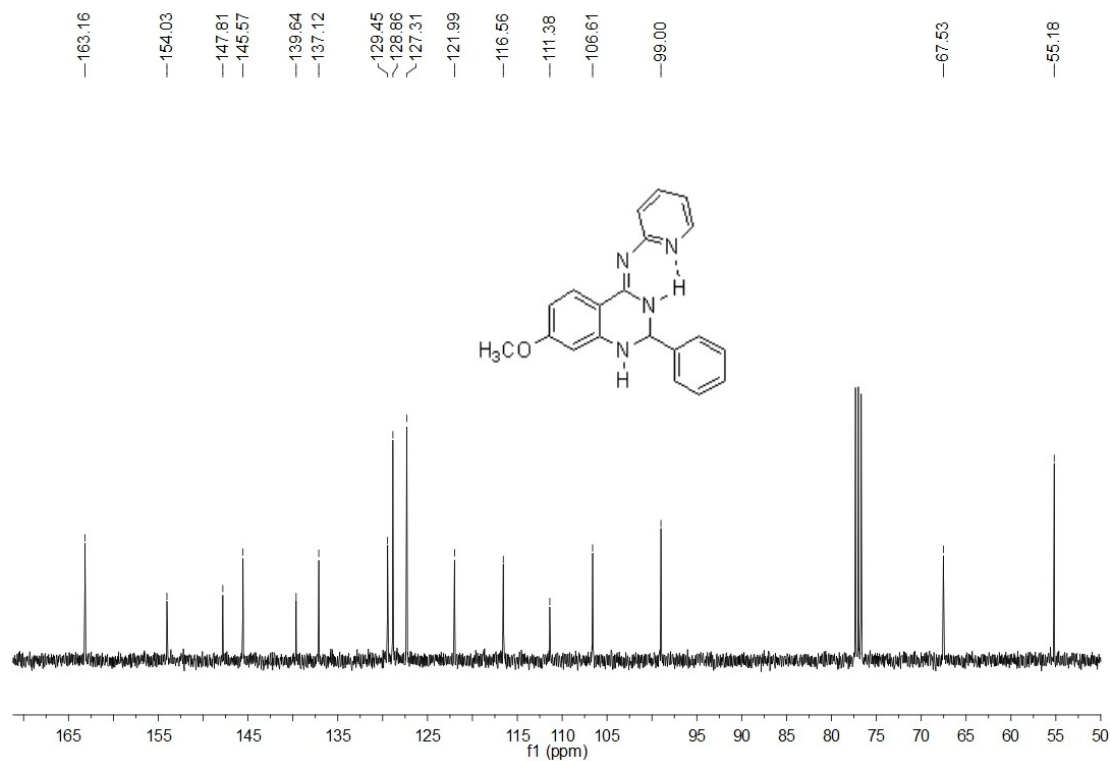


Fig. S37. ¹³C NMR spectrum of **4caa** (100 MHz, CDCl₃, 20 °C)

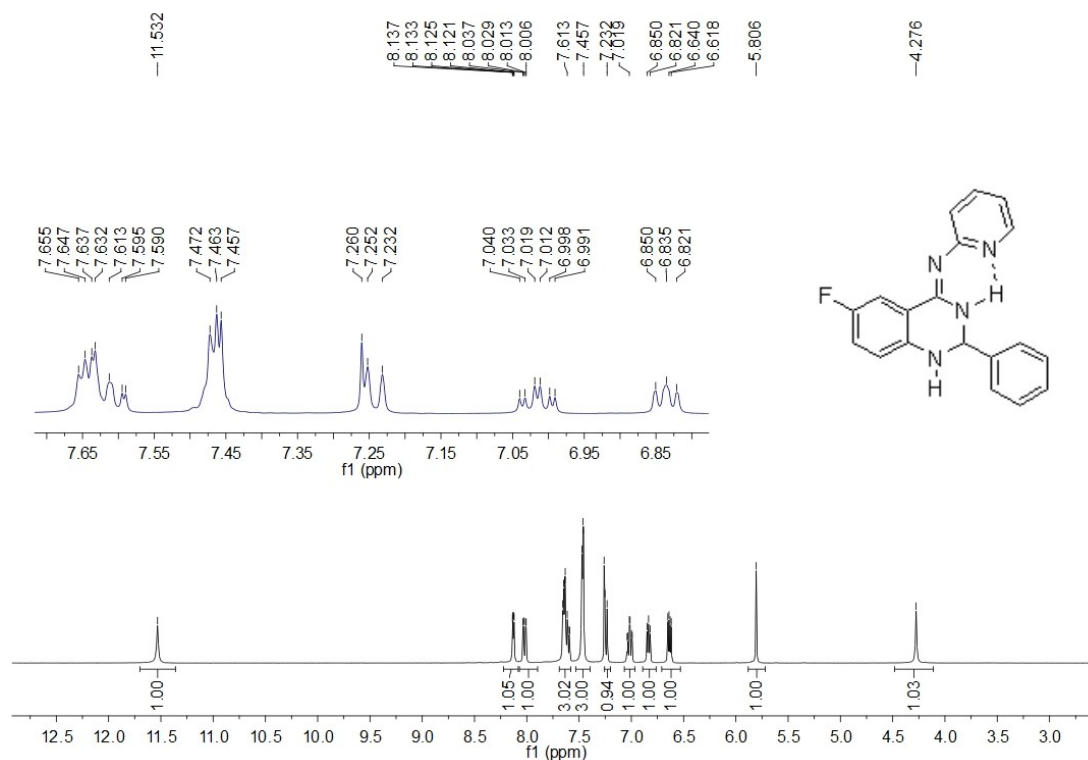


Fig. S38. ¹H NMR spectrum of **4daa** (400 MHz, CDCl₃, 20 °C)

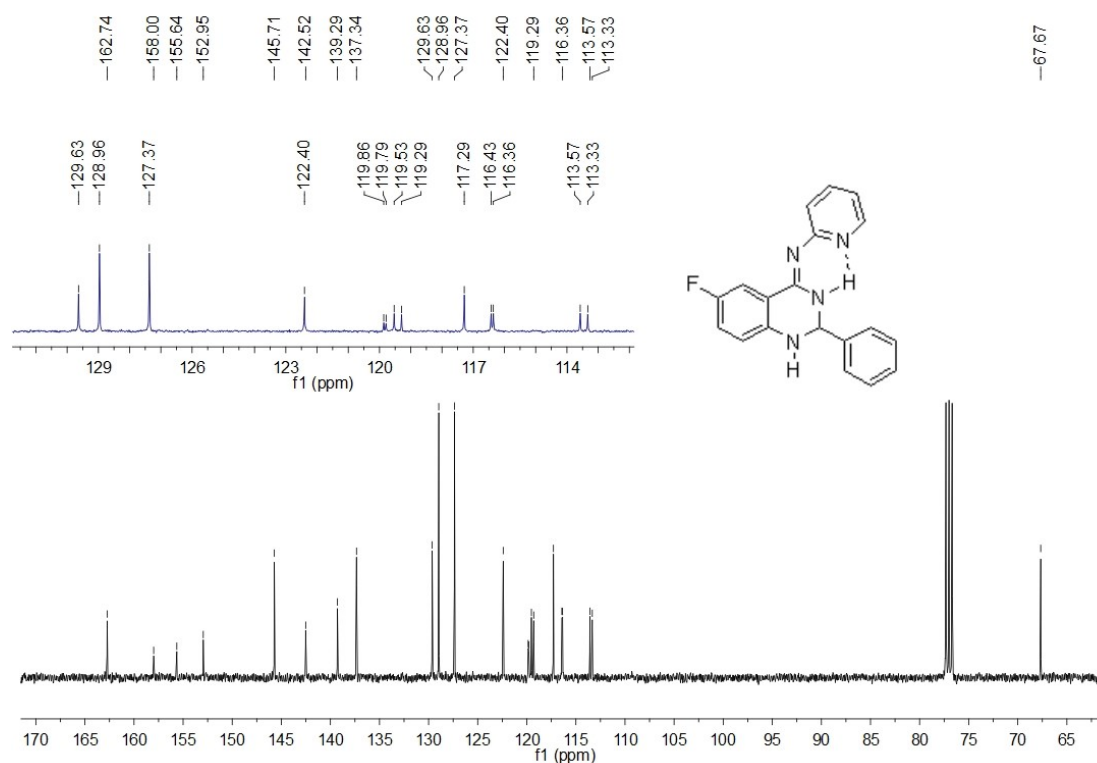


Fig. S39. ¹³C NMR spectrum of **4daa** (100 MHz, CDCl₃, 20 °C)

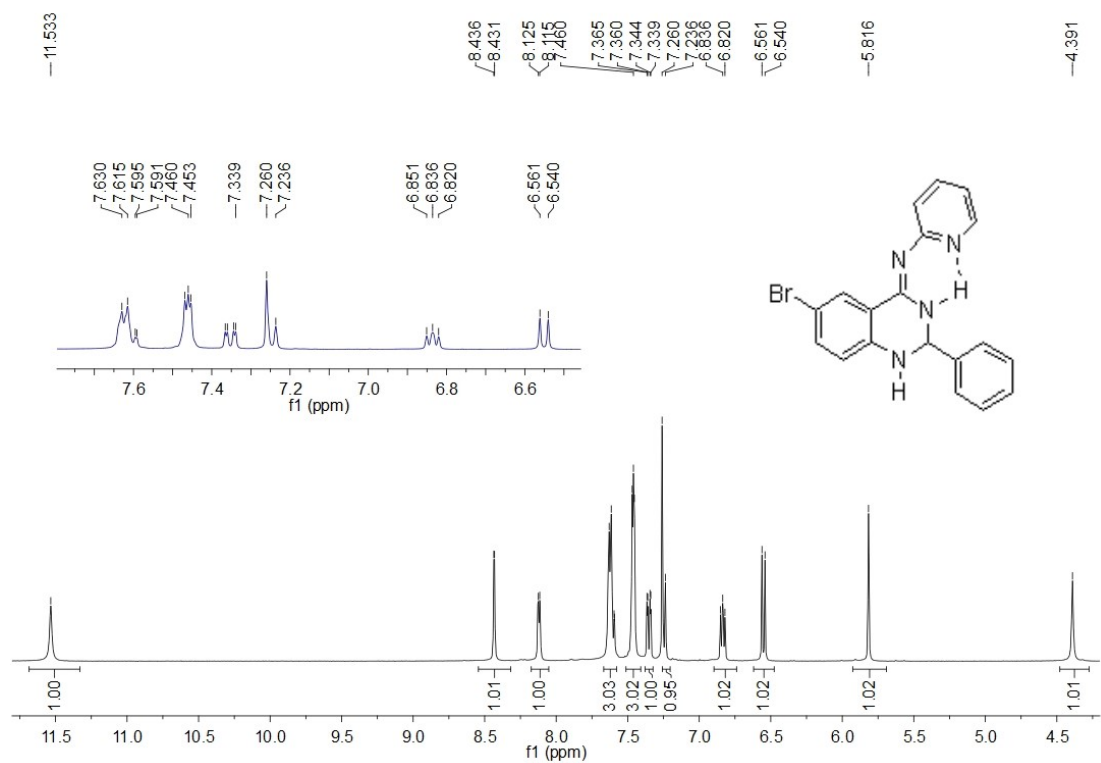


Fig. S40. ¹H NMR spectrum of **4eaa** (400 MHz, CDCl₃, 20 °C)

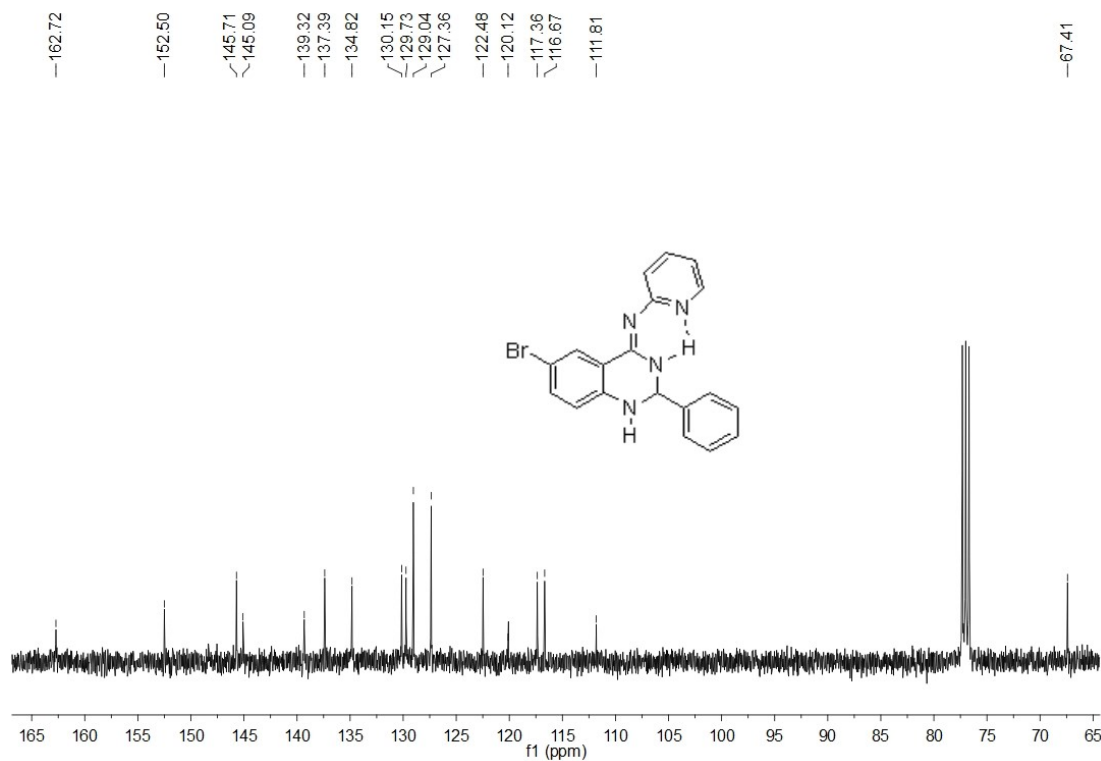


Fig. S41. ¹³C NMR spectrum of **4eaa** (100 MHz, CDCl₃, 20 °C)

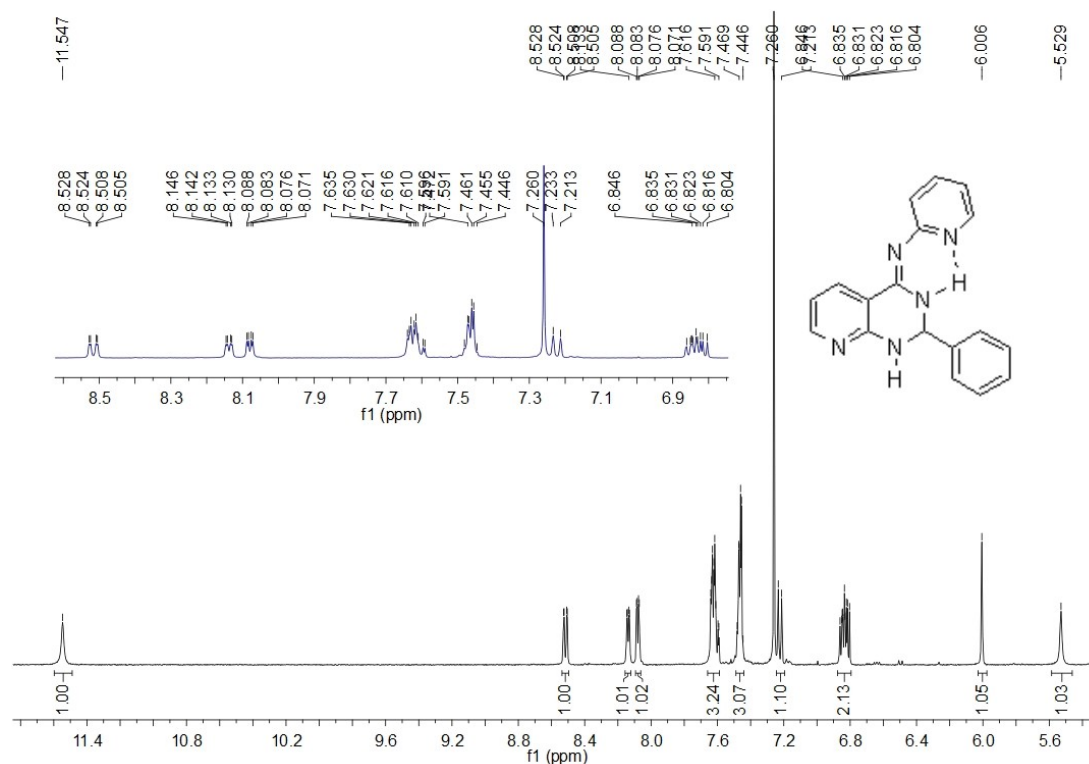


Fig. S42. ¹H NMR spectrum of **4faa** (400 MHz, CDCl₃, 20 °C)

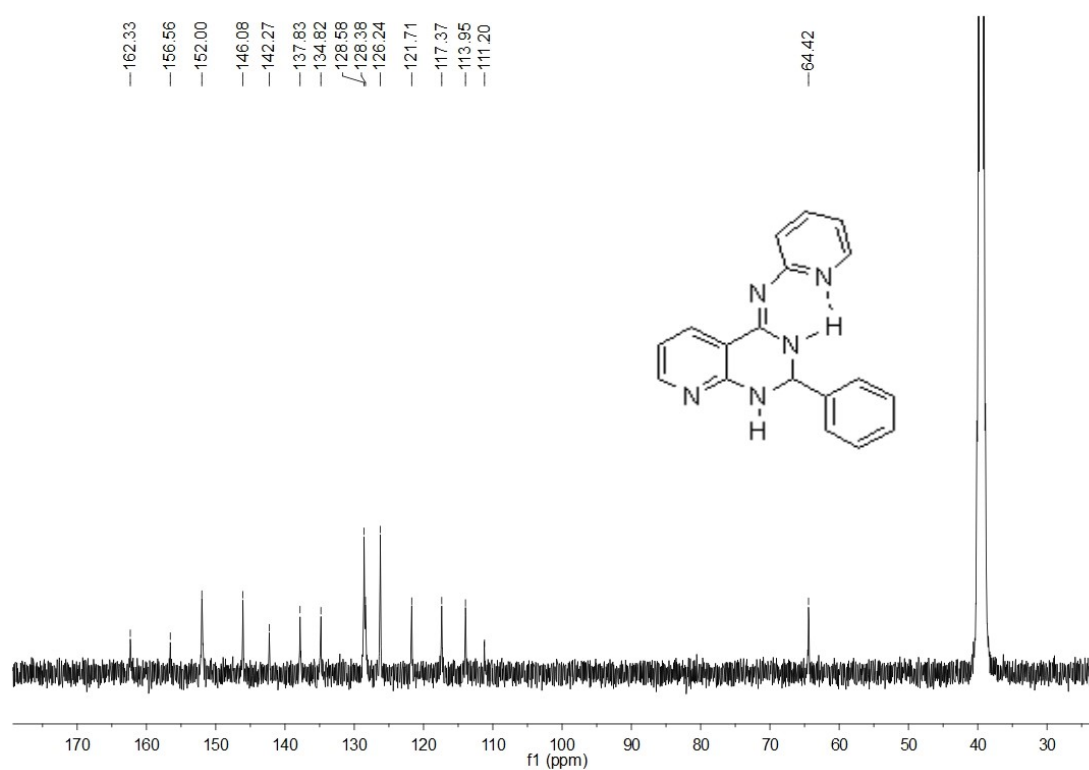


Fig. S43. ¹³C NMR spectrum of **4faa** (100 MHz, CDCl₃, 20 °C)

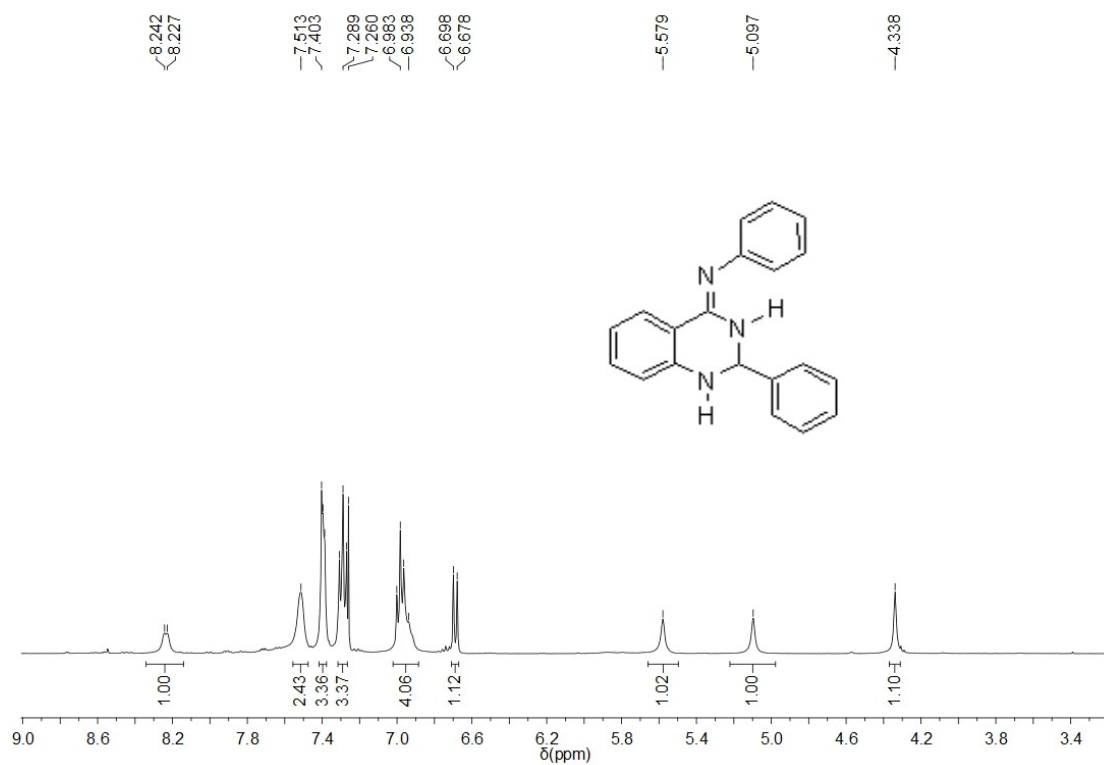


Fig. S44. ¹H NMR spectrum of **4aba** (400 MHz, CDCl₃, 20 °C)

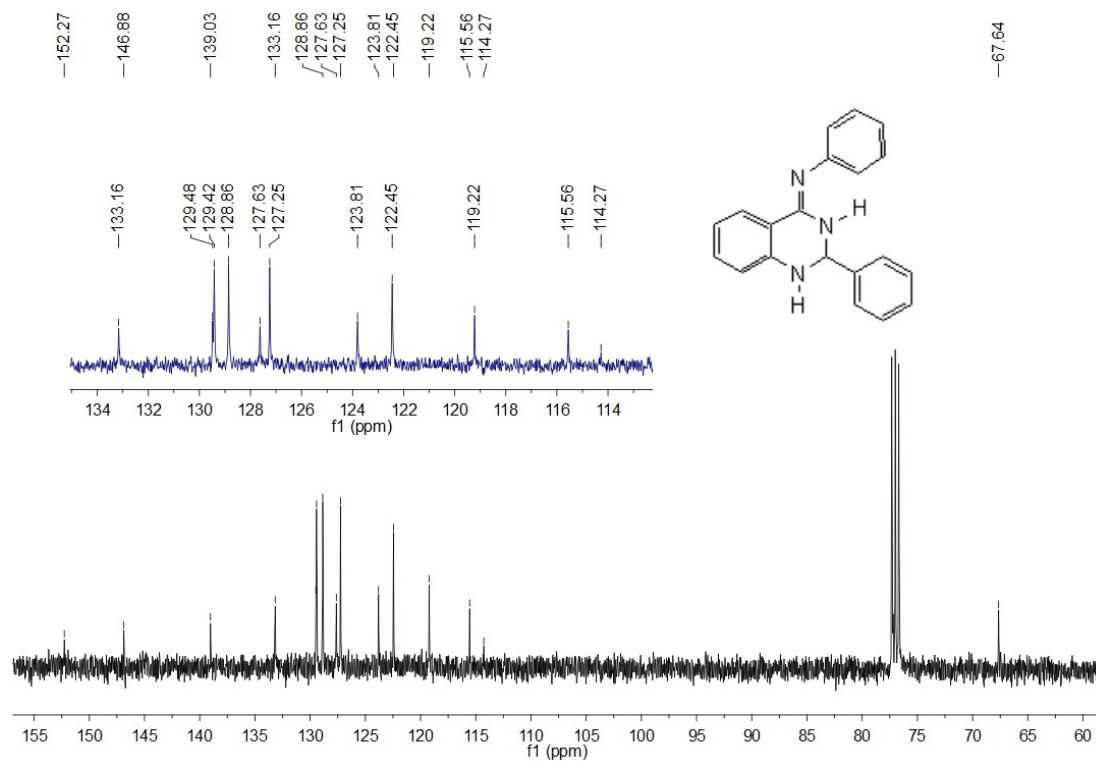


Fig. S45. ¹³C NMR spectrum of **4aba** (100 MHz, CDCl₃, 20 °C)

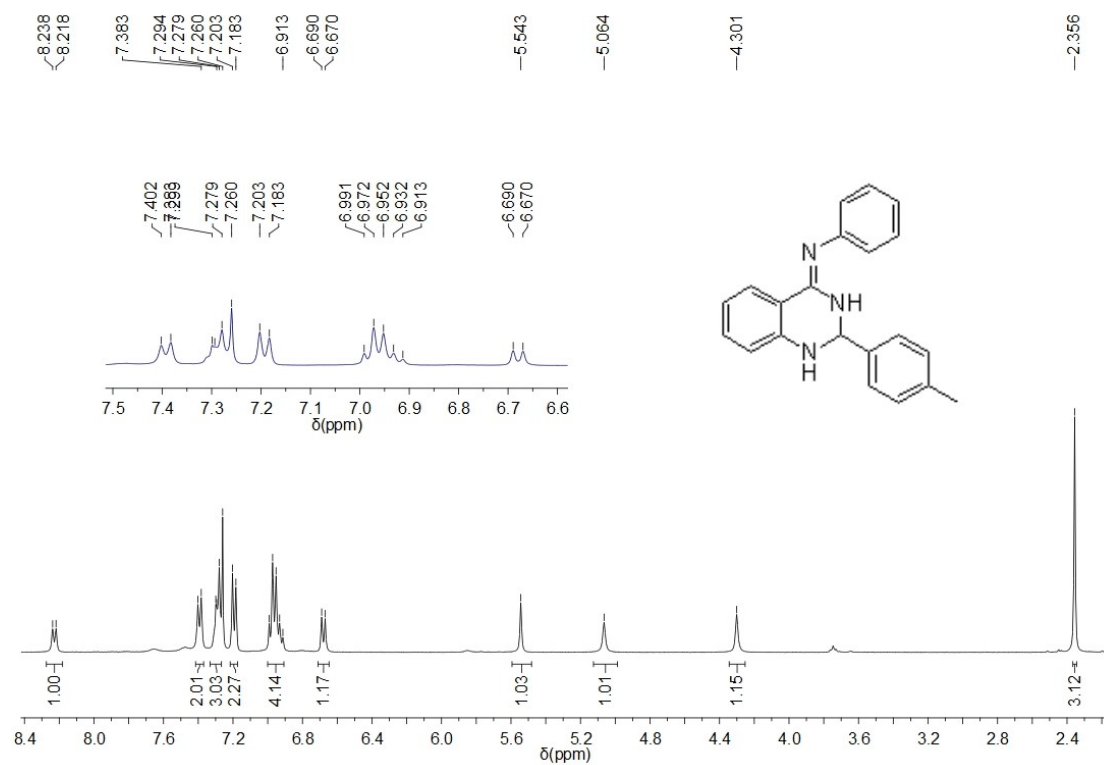


Fig. S46. ¹H NMR spectrum of **4akb** (400 MHz, CDCl₃, 20 °C)

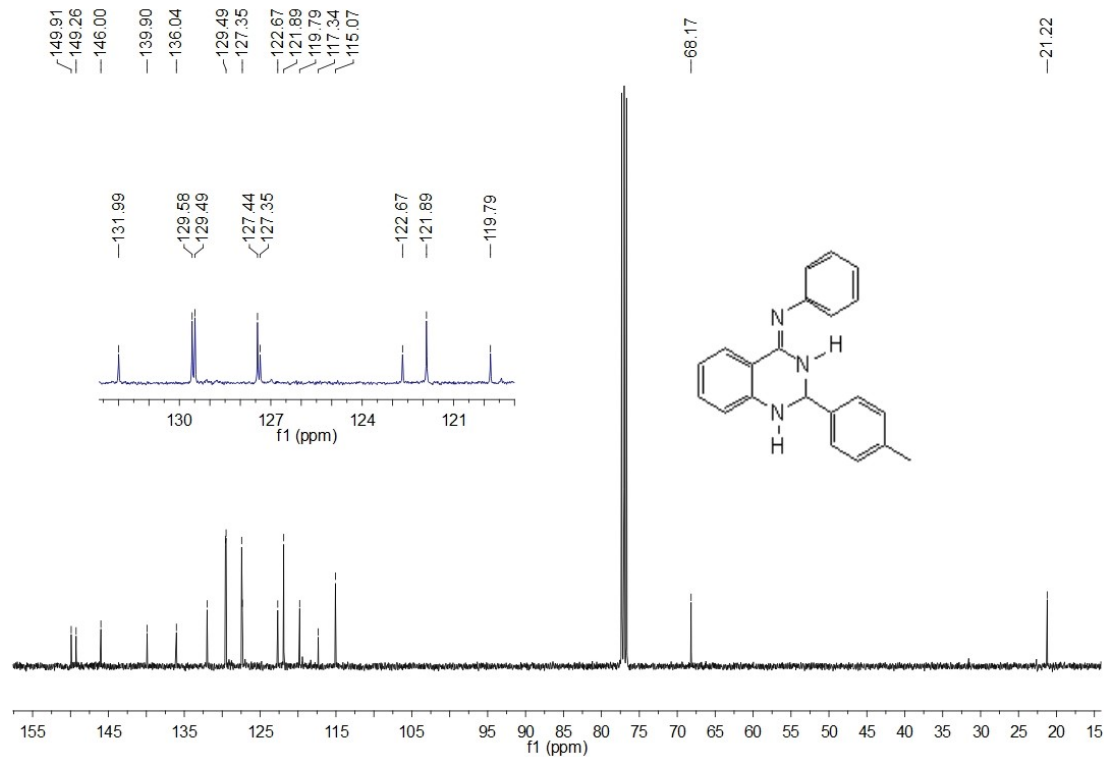


Fig. S47. ¹³C NMR spectrum of **4akb** (100 MHz, CDCl₃, 20 °C)

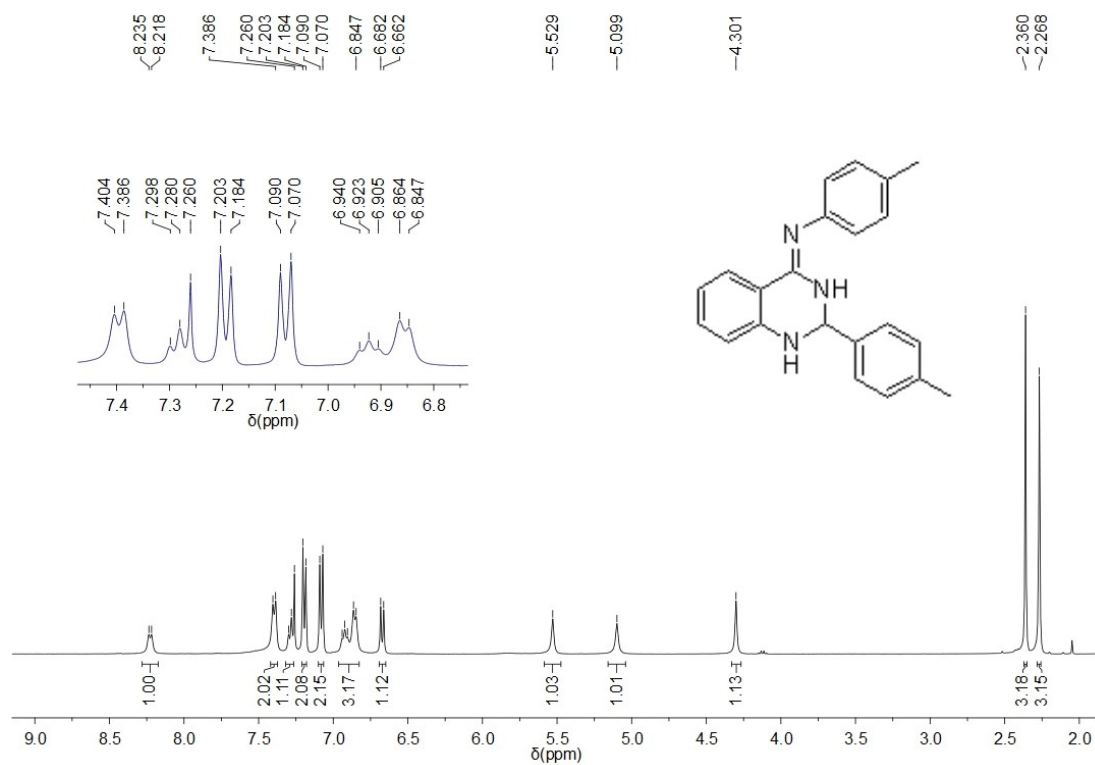


Fig. S48. ¹H NMR spectrum of **4abb** (400 MHz, CDCl₃, 20 °C)

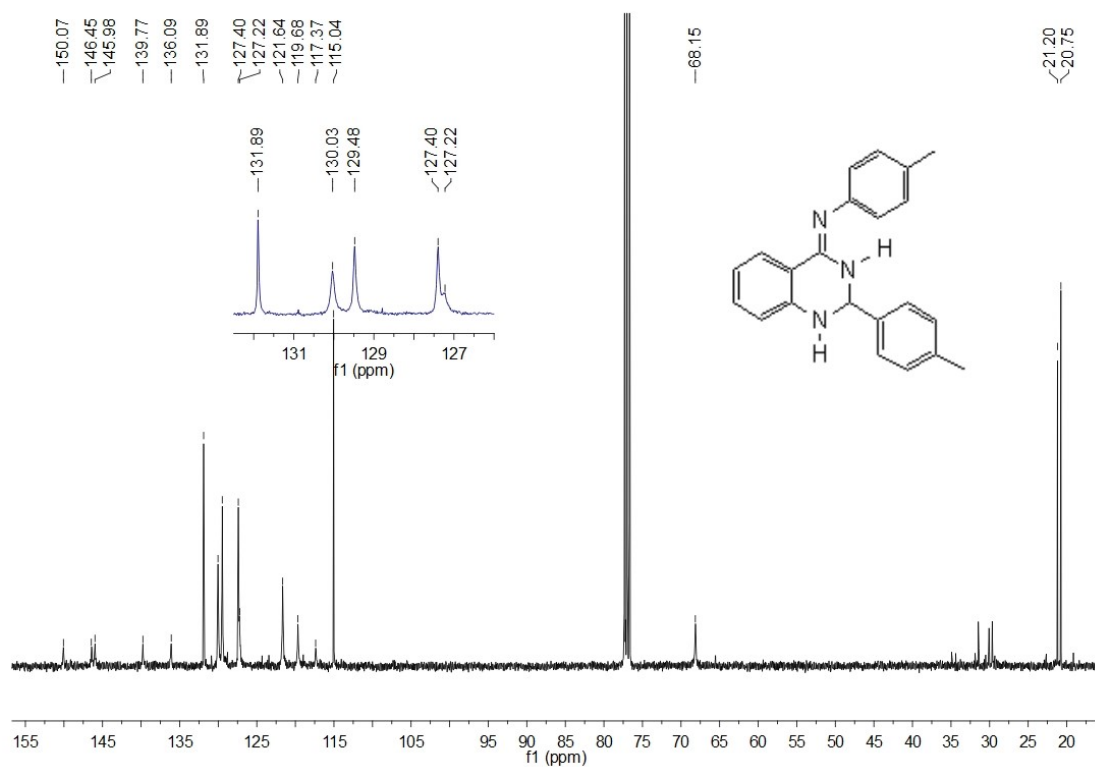


Fig. S49. ¹³C NMR spectrum of **4abb** (100 MHz, CDCl₃, 20 °C)

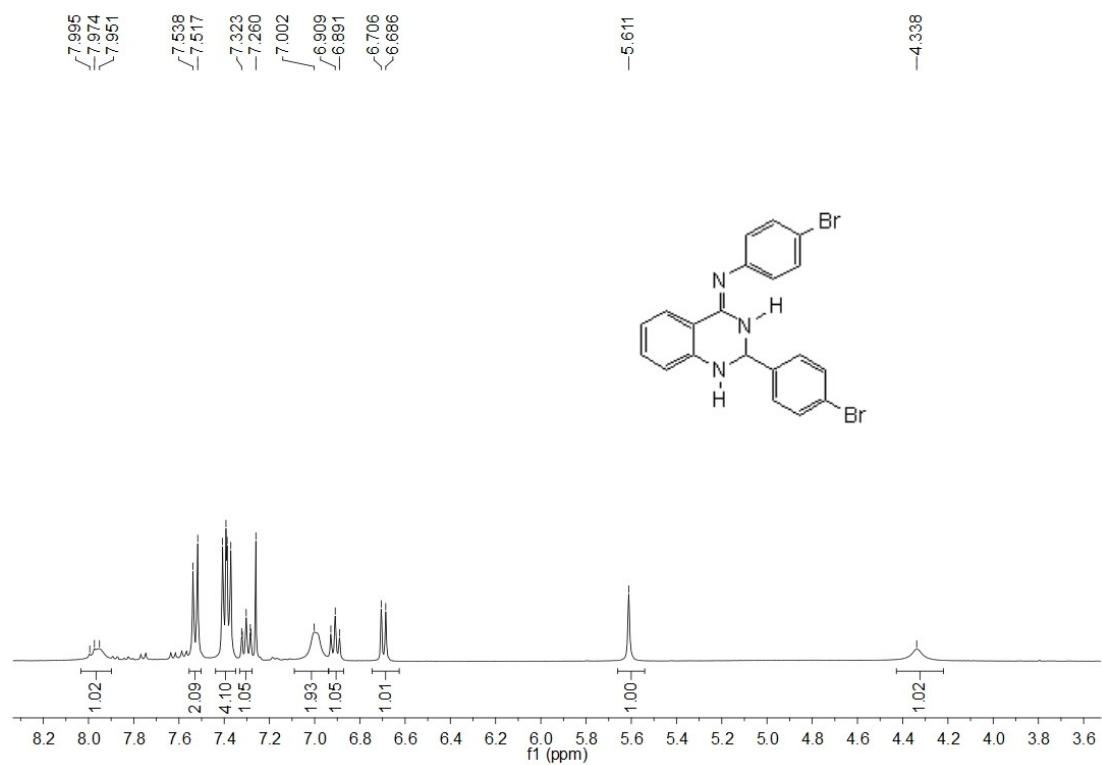


Fig. S50. ¹H NMR spectrum of **4add** (400 MHz, CDCl₃, 20 °C)

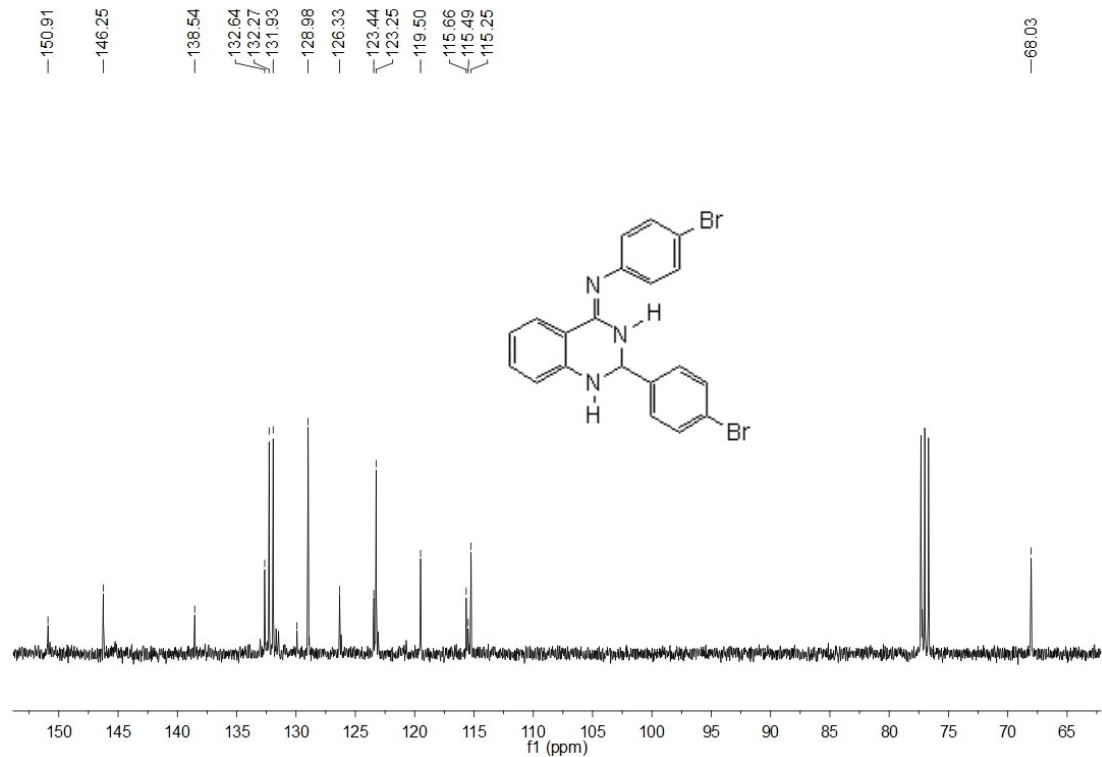


Fig. S51. ¹³C NMR spectrum of **4add** (100 MHz, CDCl₃, 20 °C)

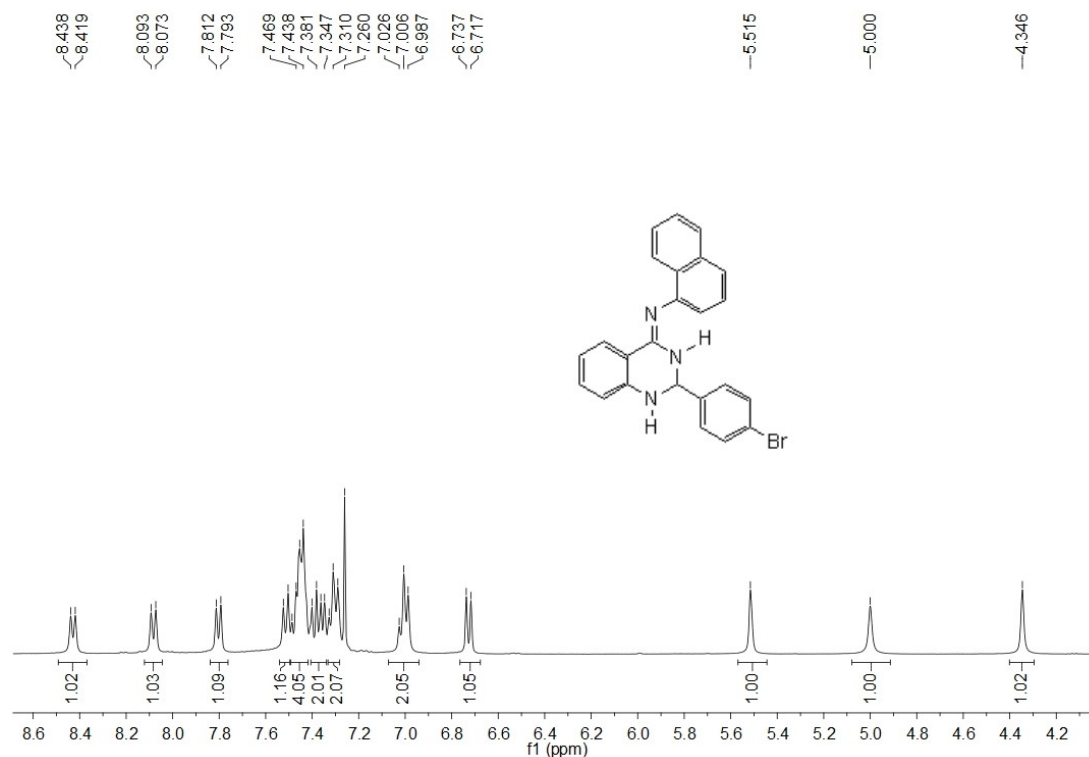


Fig. S52. ¹H NMR spectrum of **4agd** (400 MHz, CDCl₃, 20 °C)

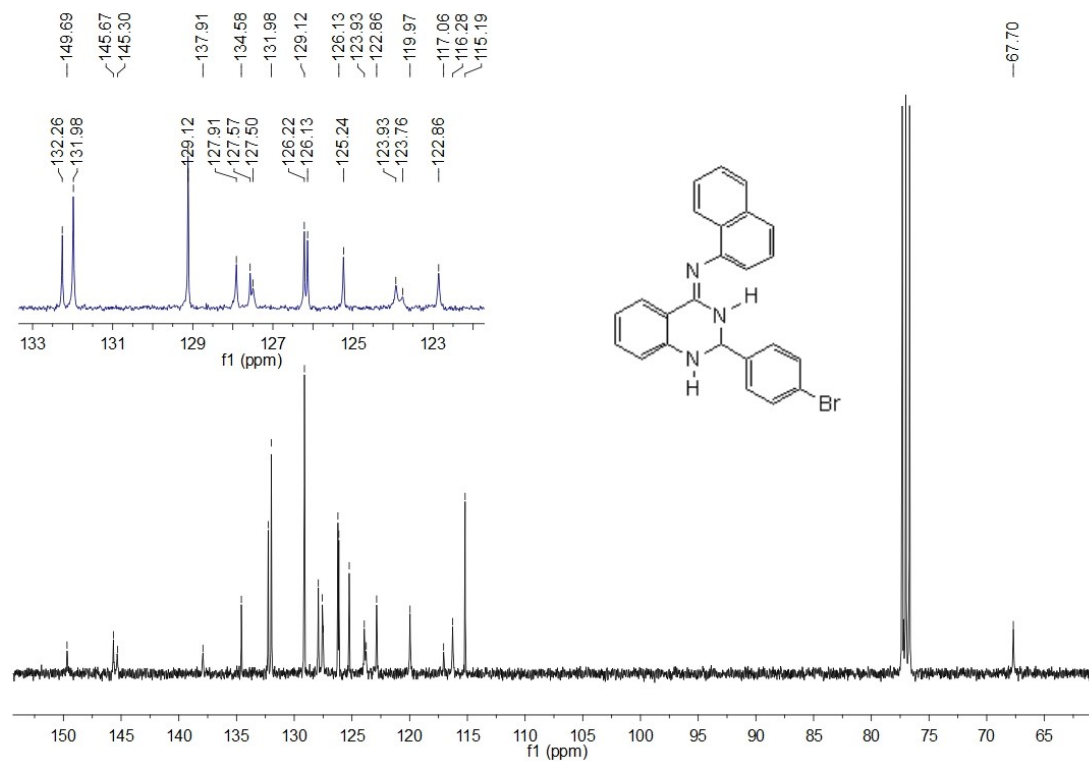


Fig. S53. ¹³C NMR spectrum of **4agd** (100 MHz, CDCl₃, 20 °C)

Copies of 1,3-diimino isoindolines

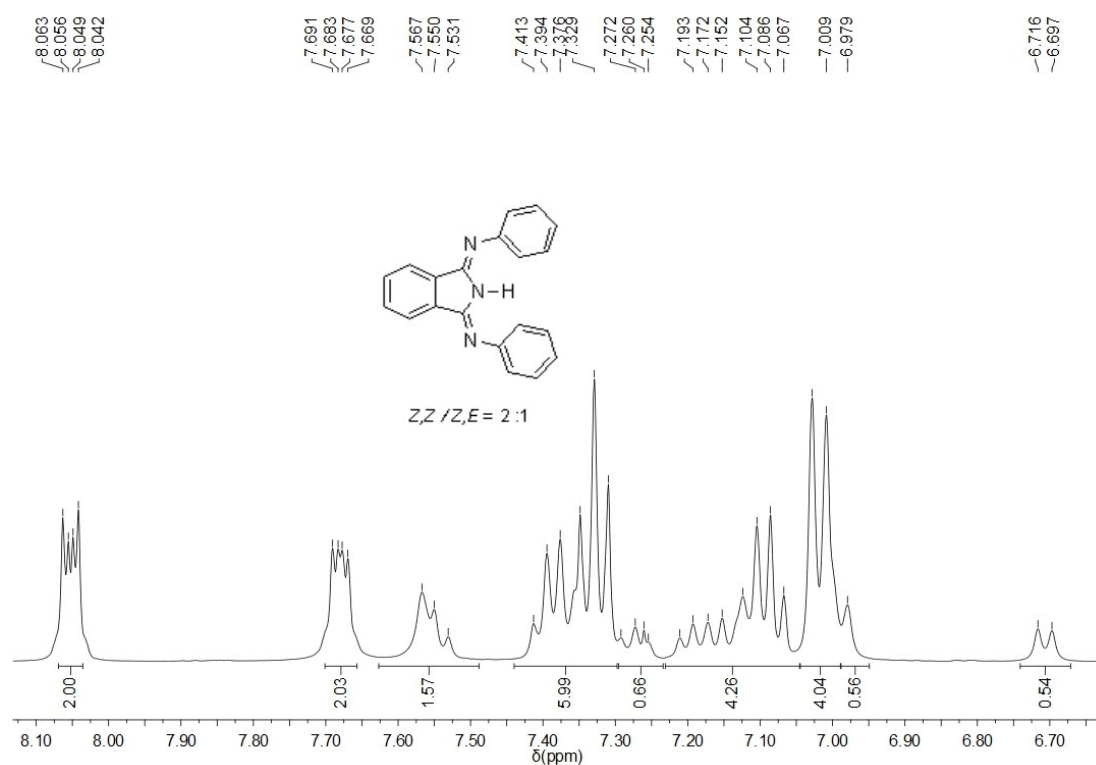


Fig. S54. ^1H NMR spectrum of **6aa** (400 MHz, CDCl_3 , 20 °C)

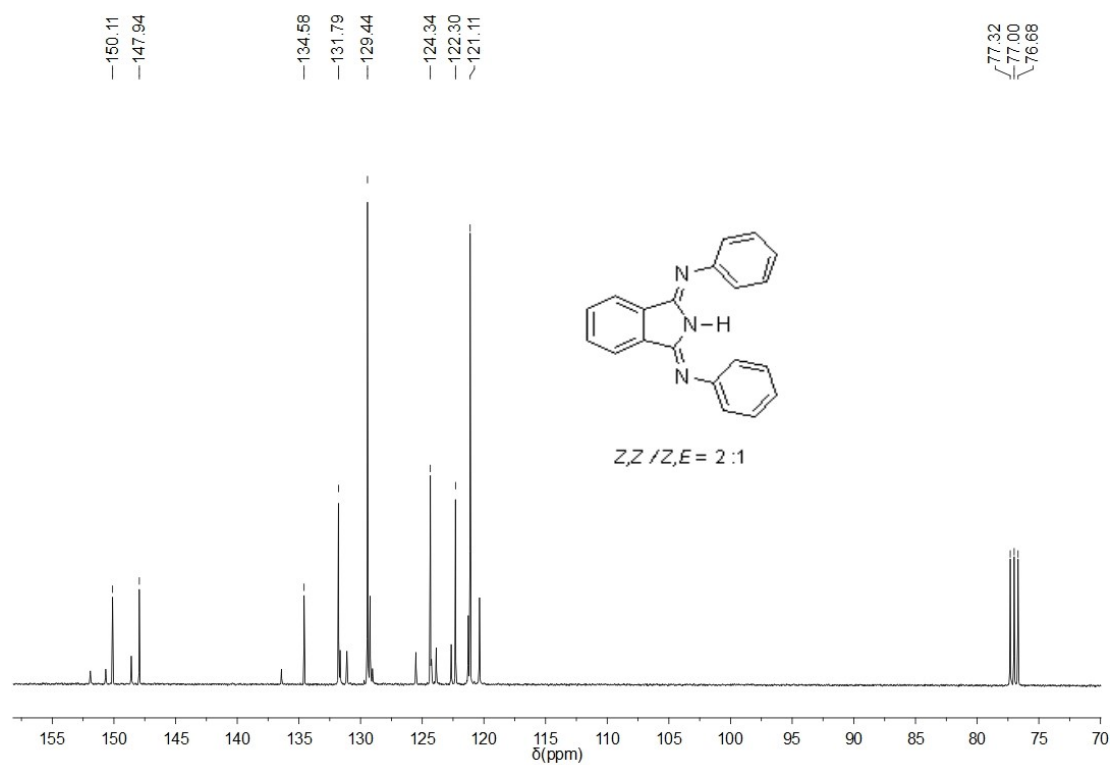


Fig. S55. ^{13}C NMR spectrum of **6aa** (100 MHz, CDCl_3 , 20 °C)

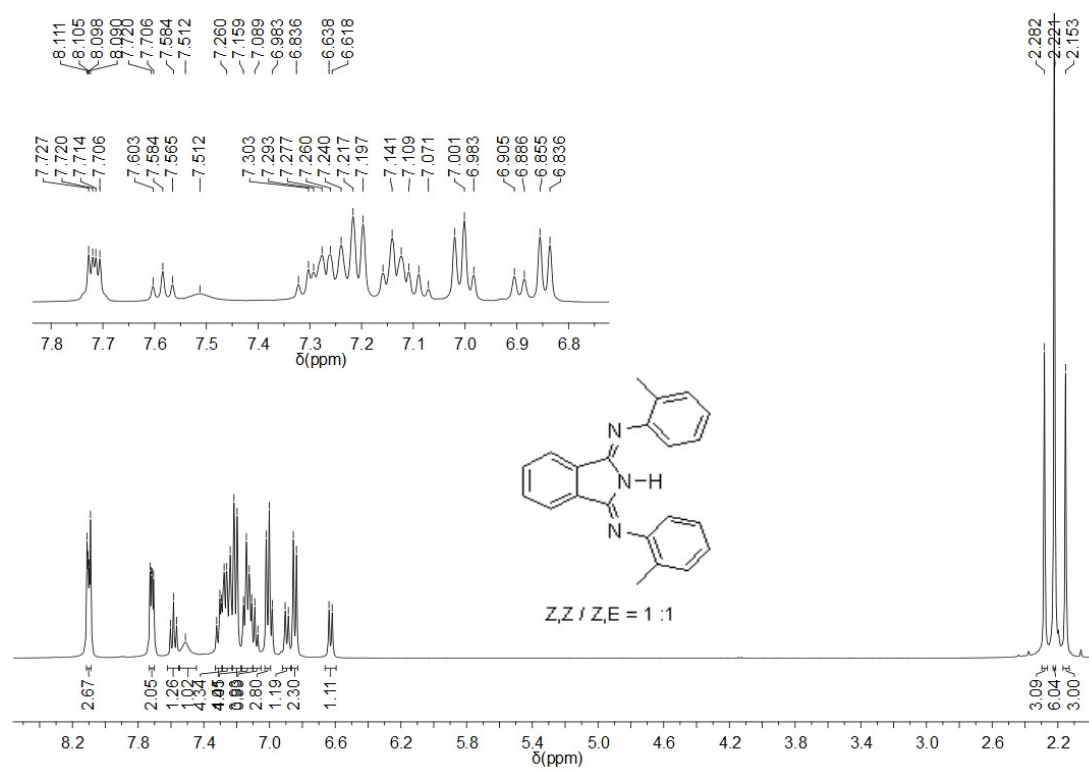


Fig. S56. ¹H NMR spectrum of **6ab** (400 MHz, CDCl₃, 20 °C)

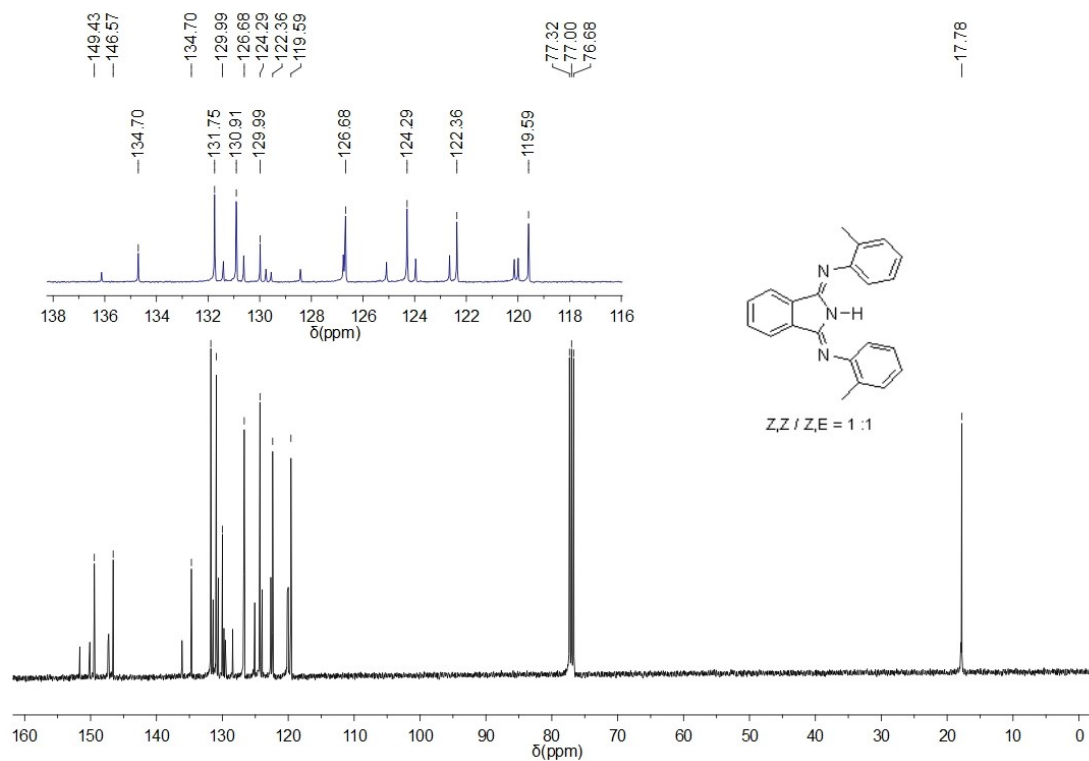


Fig. S57. ¹³C NMR spectrum of **6ab** (100 MHz, CDCl₃, 20 °C)

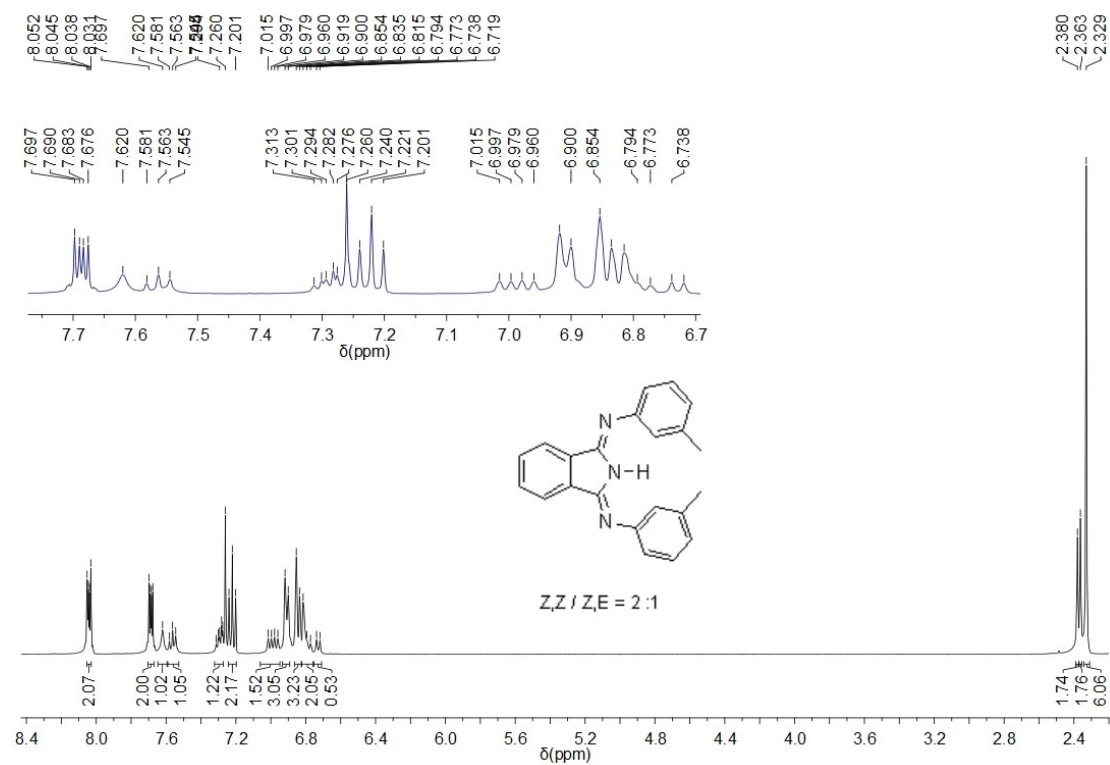


Fig. S58. ¹H NMR spectrum of **6ac** (400 MHz, CDCl₃, 20 °C)

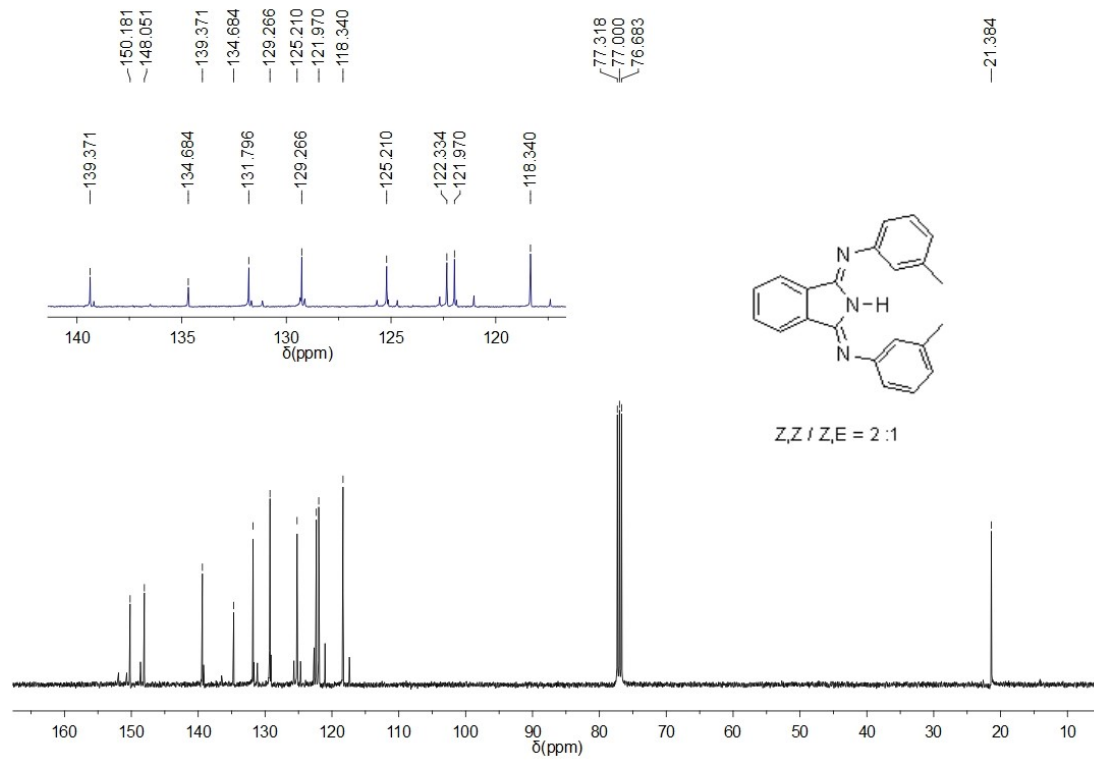


Fig. S59. ¹³C NMR spectrum of **6ac** (100 MHz, CDCl₃, 20 °C)

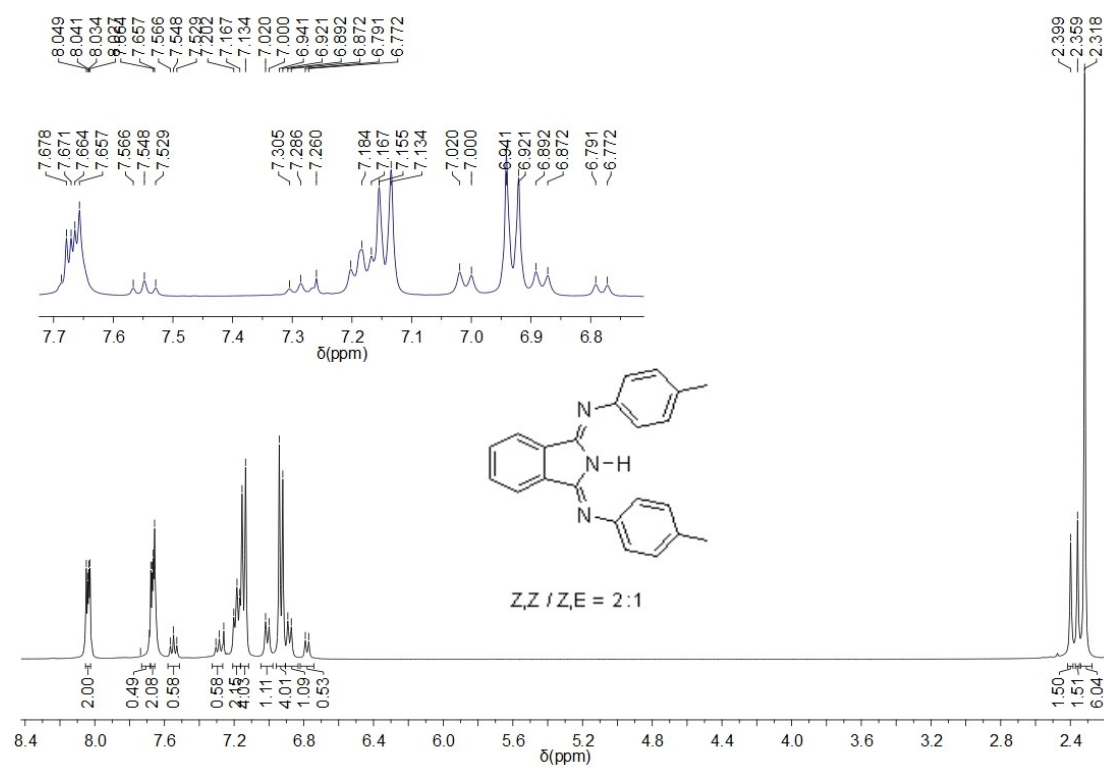


Fig. S60. ^1H NMR spectrum of **6ad** (400 MHz, CDCl_3 , 20 °C)

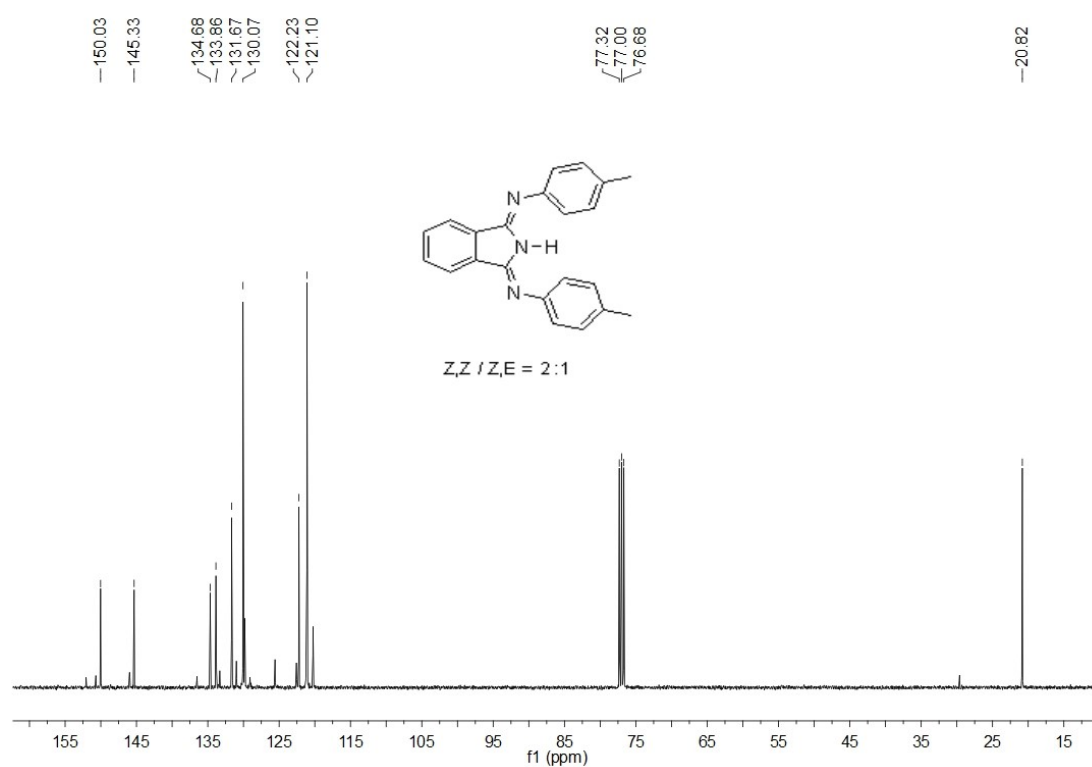


Fig. S61. ^{13}C NMR spectrum of **6ad** (100 MHz, CDCl_3 , 20 °C)

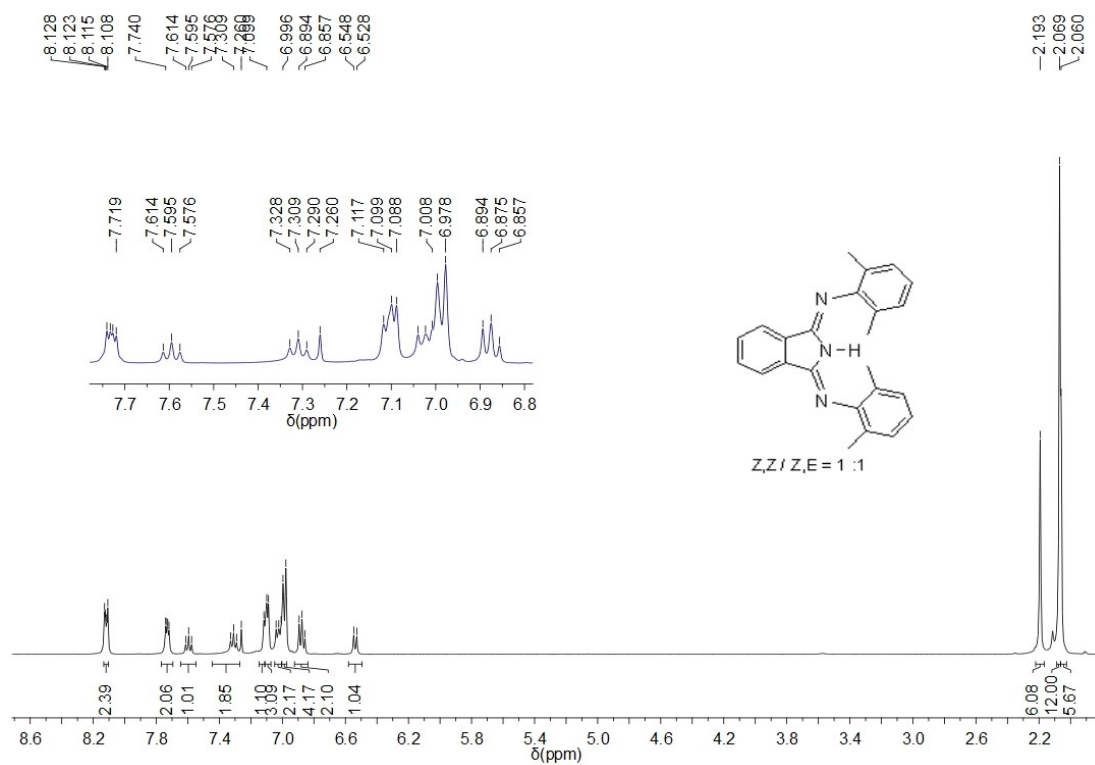


Fig. S62. ¹H NMR spectrum of **6ae** (400 MHz, CDCl₃, 20 °C)

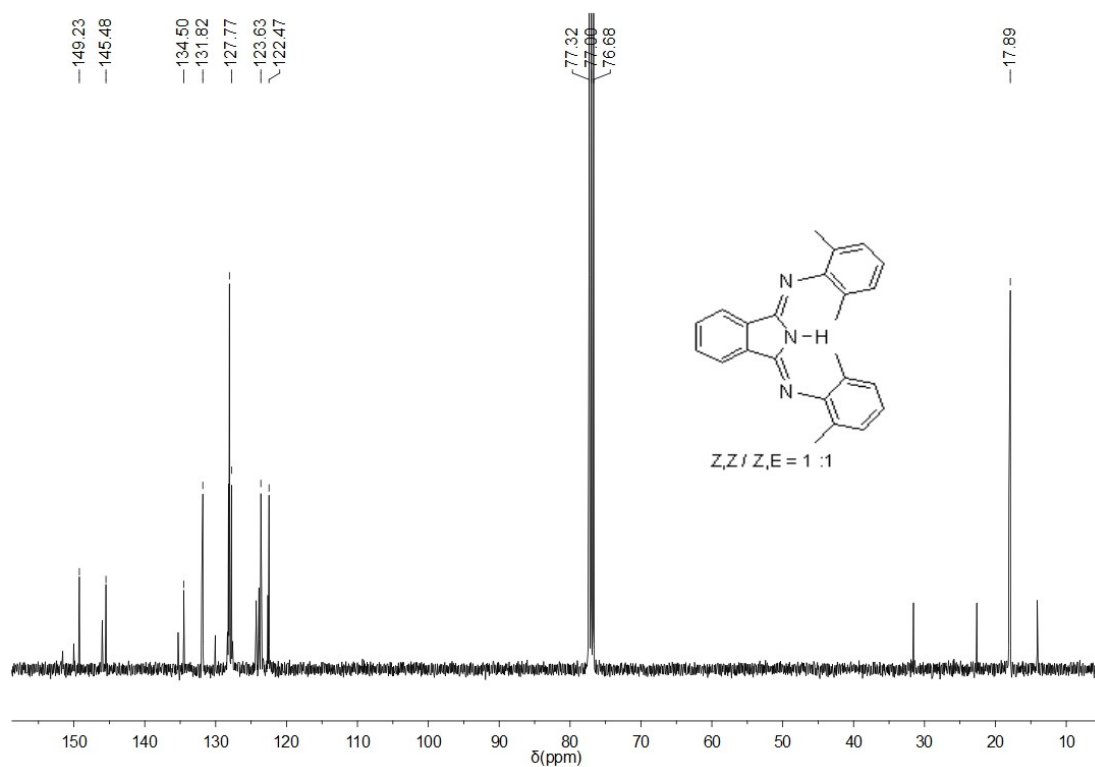


Fig. S63. ¹³C NMR spectrum of **6ae** (100 MHz, CDCl₃, 20 °C)

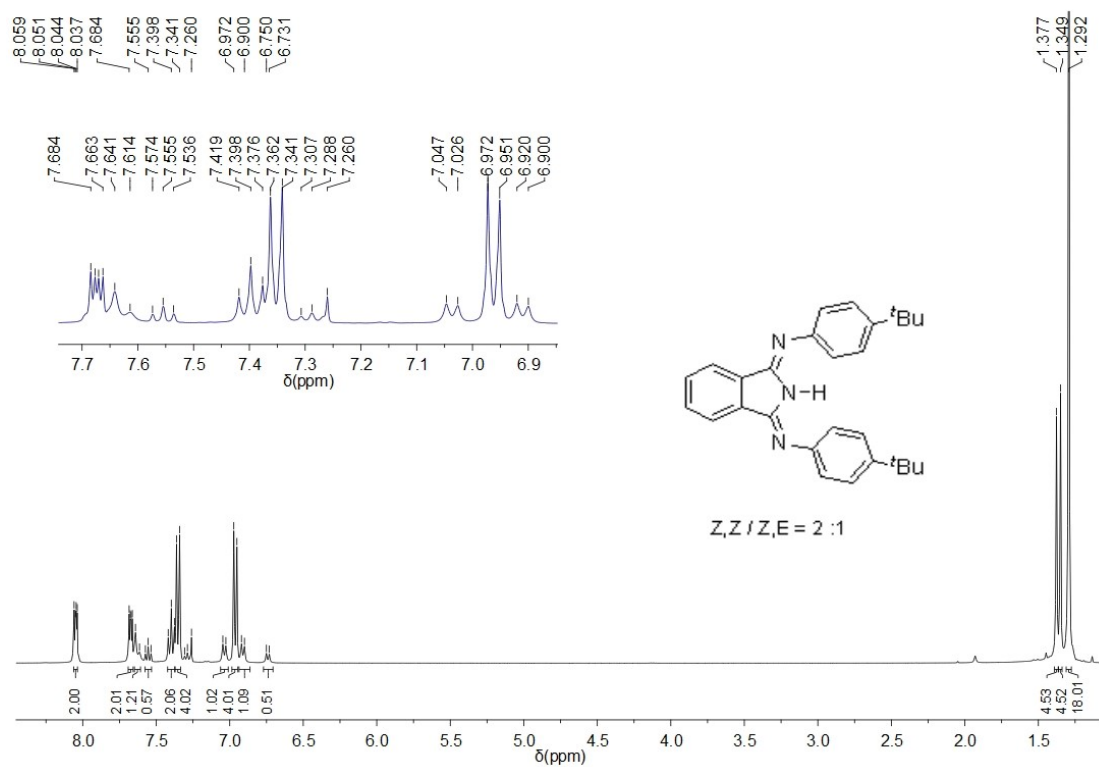


Fig. S64. ¹H NMR spectrum of **6af** (400 MHz, CDCl₃, 20 °C)

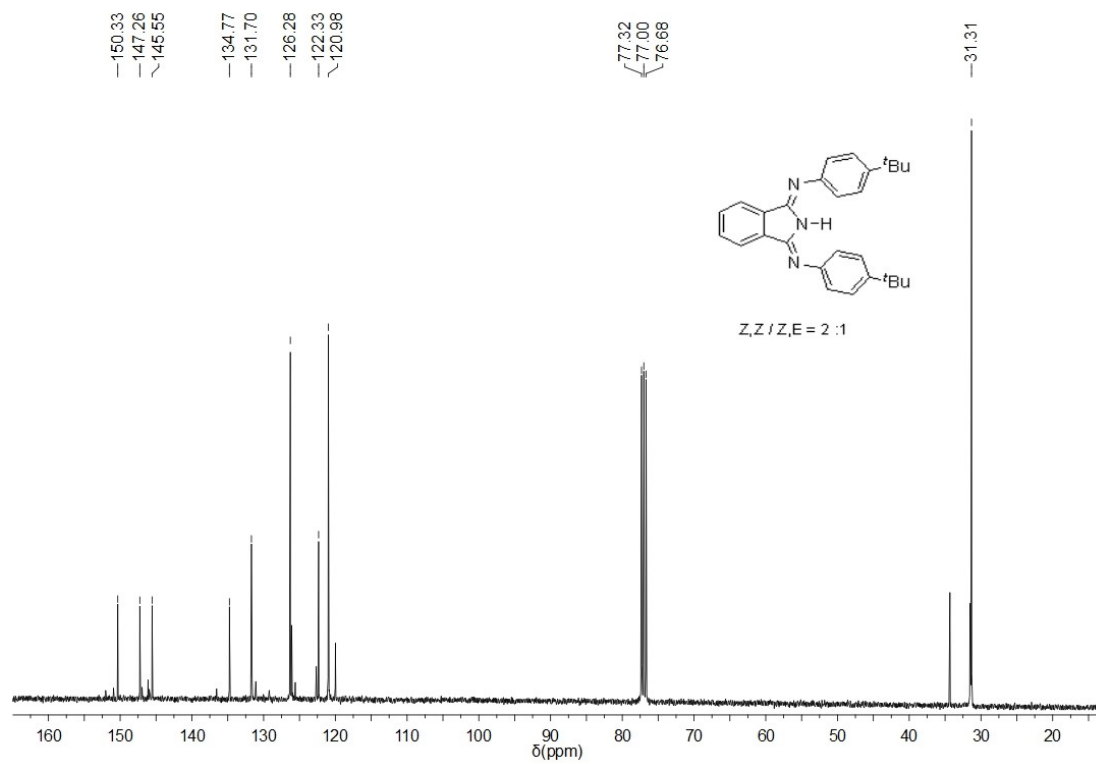


Fig. S65. ¹³C NMR spectrum of **6af** (100 MHz, CDCl₃, 20 °C)

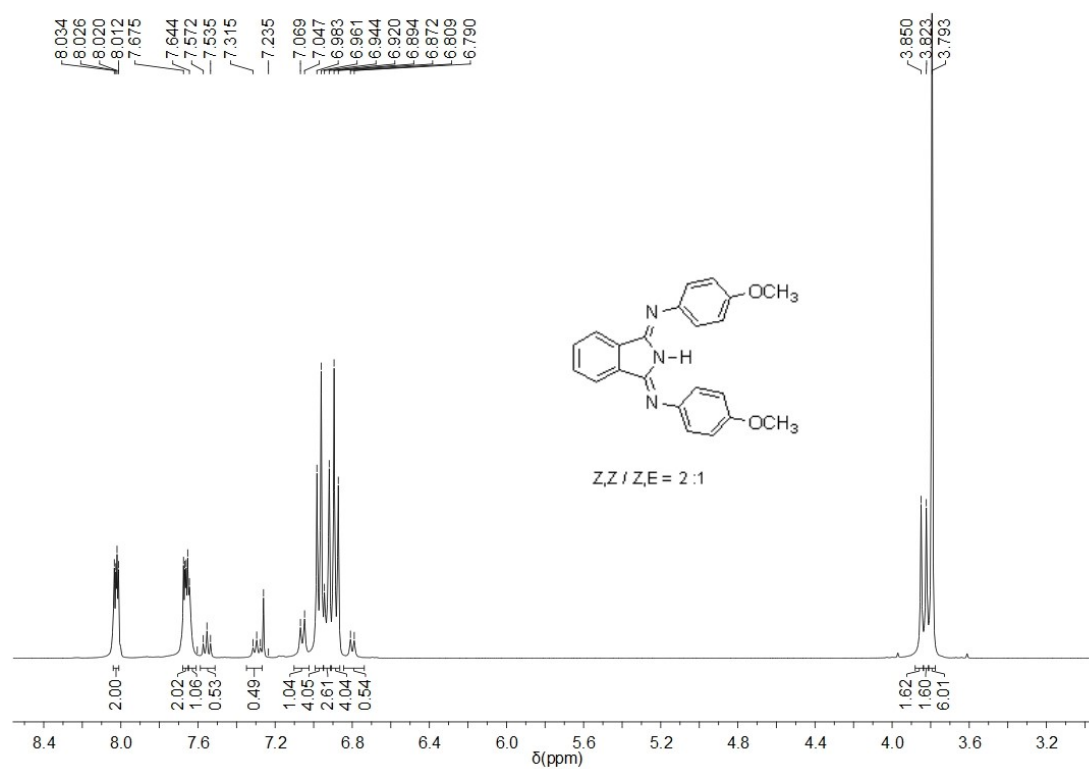


Fig. S66. ^1H NMR spectrum of **6ag** (400 MHz, CDCl_3 , 20 °C)

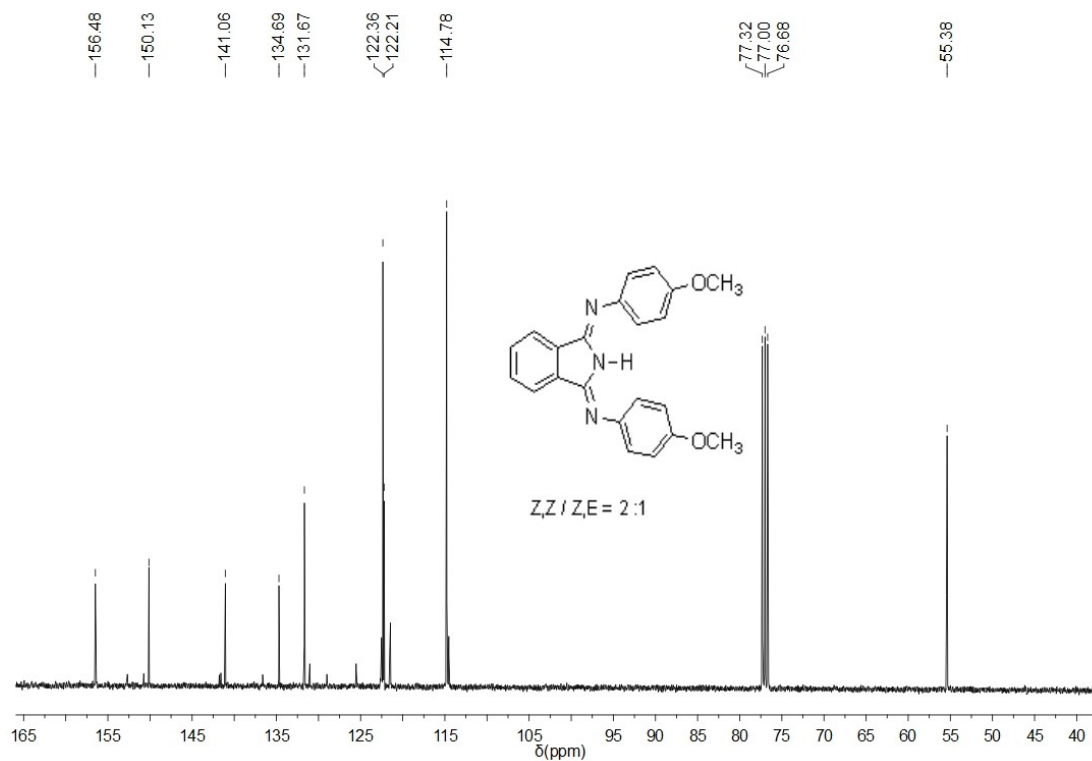


Fig. S67. ^{13}C NMR spectrum of **6ag** (100 MHz, CDCl_3 , 20 °C)

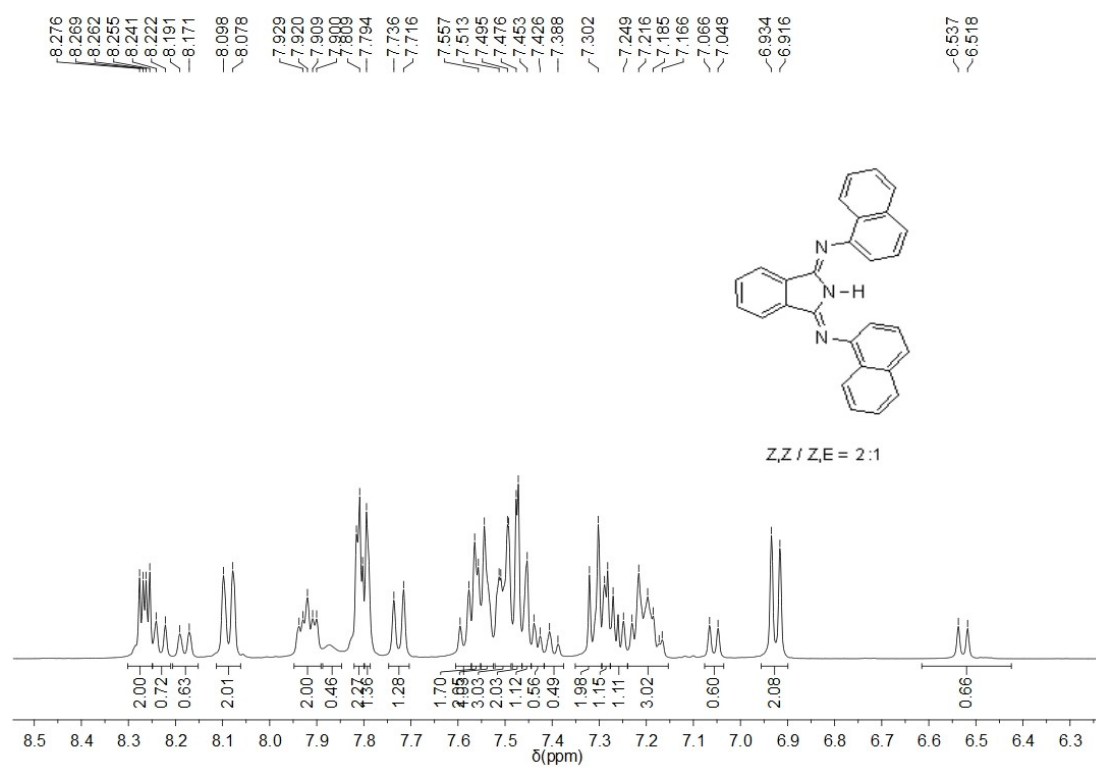


Fig. S68. ^1H NMR spectrum of **6ah** (400 MHz, CDCl_3 , 20 °C)

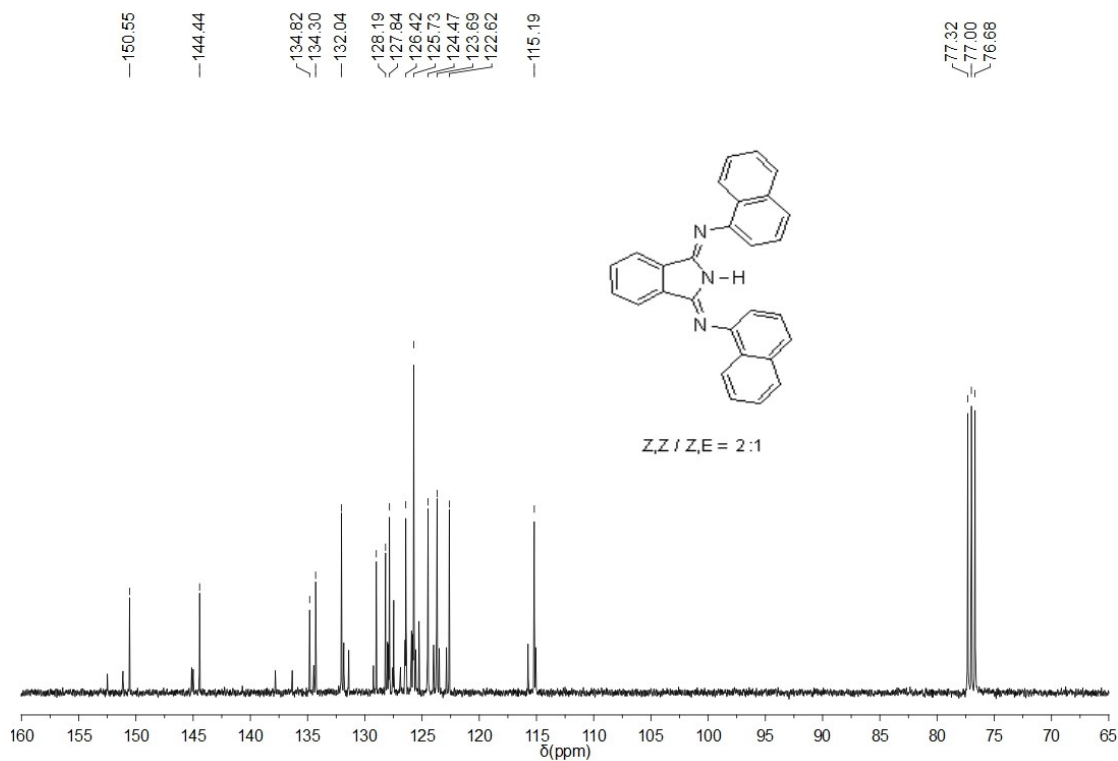


Fig. S69. ^{13}C NMR spectrum of **6ah** (100 MHz, CDCl_3 , 20 °C)

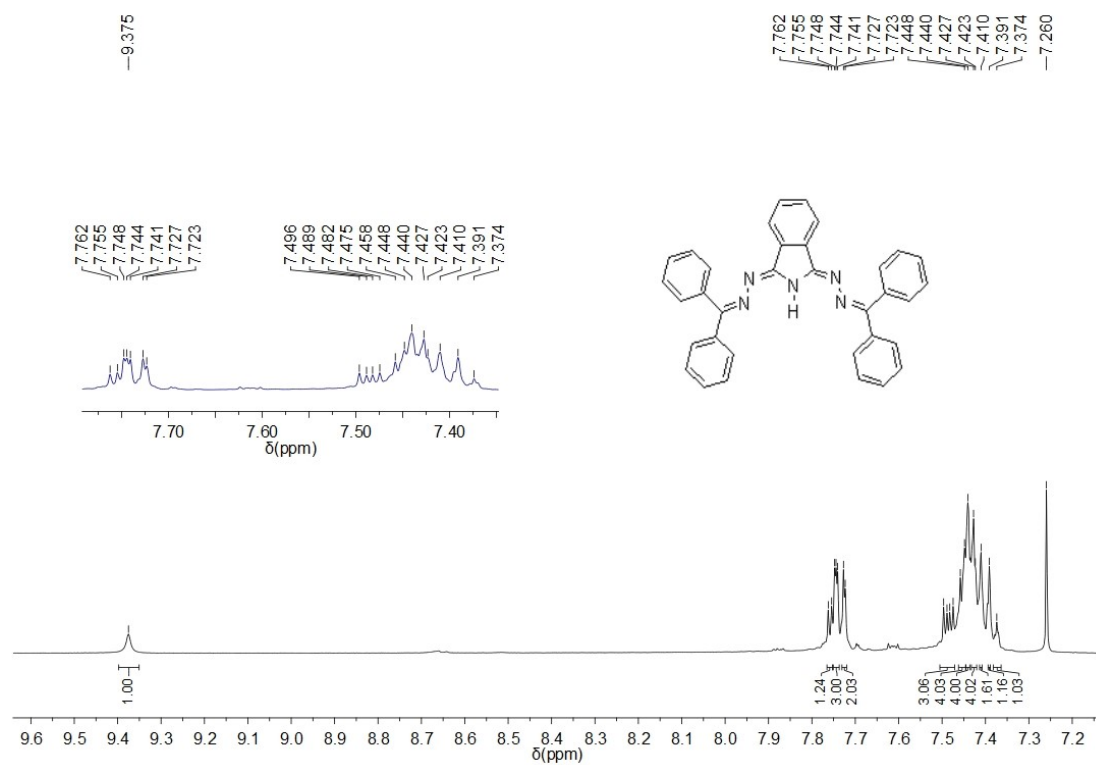


Fig. S70. ¹H NMR spectrum of **6ai** (400 MHz, CDCl₃, 20 °C)

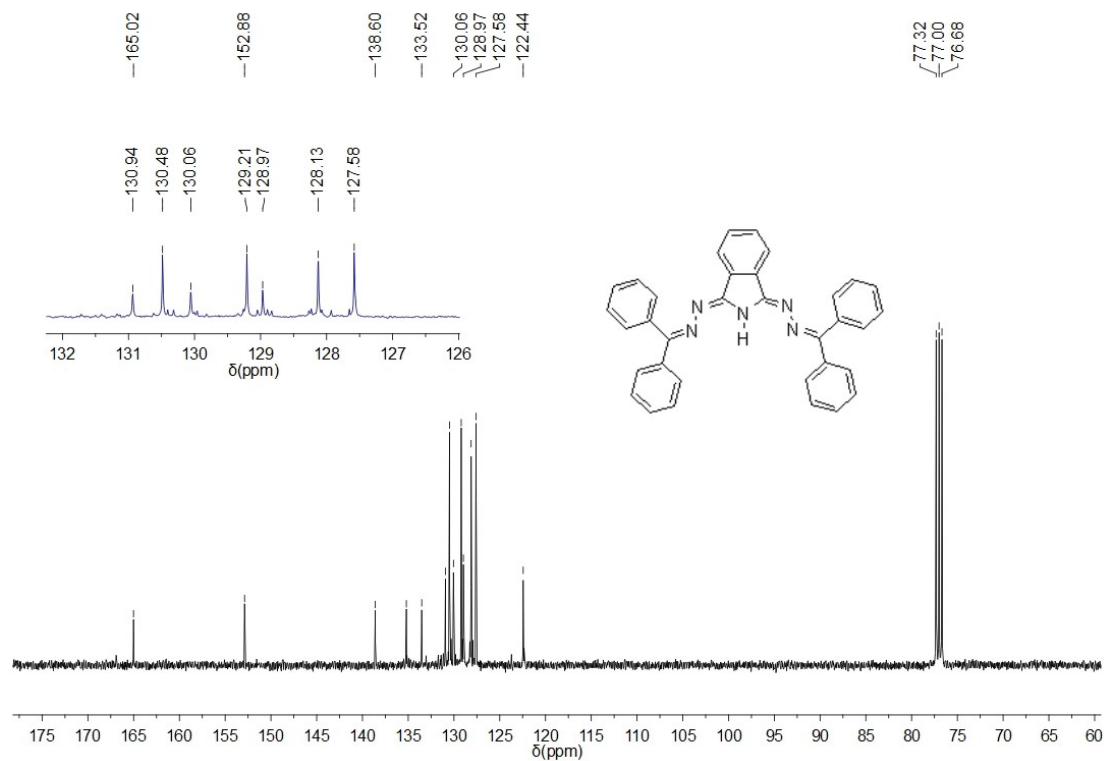


Fig. S71. ¹³C NMR spectrum of **6ai** (100 MHz, CDCl₃, 20 °C)

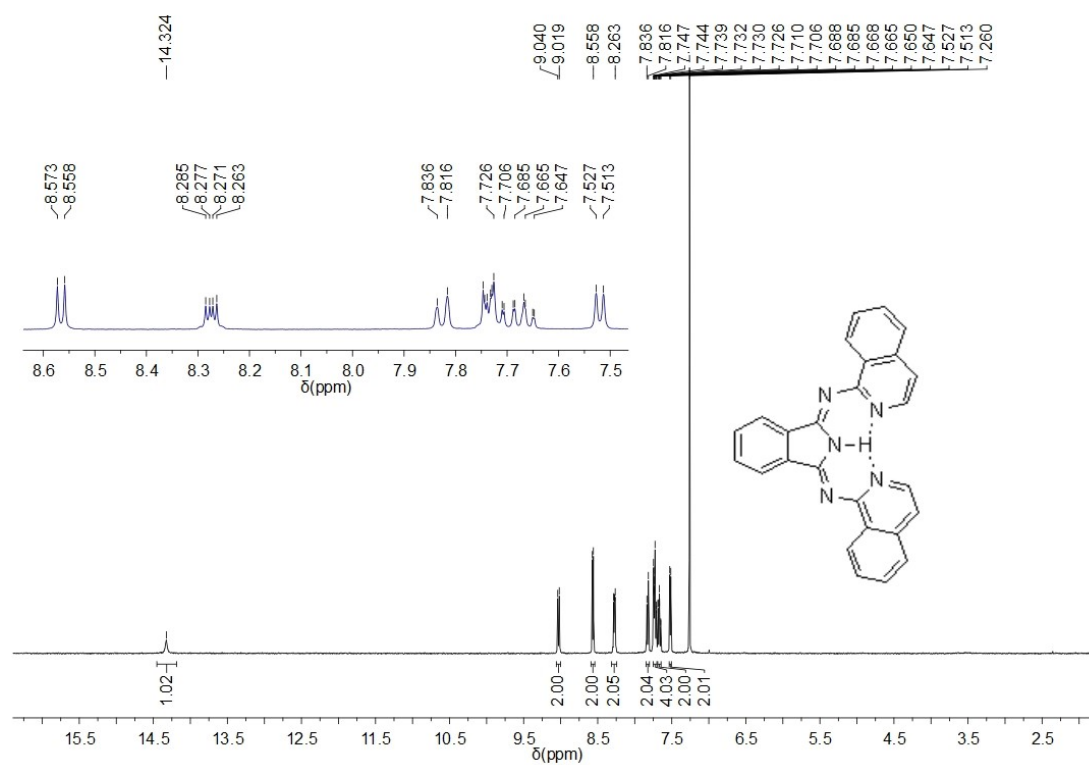


Fig. S72. ¹H NMR spectrum of **6aj** (400 MHz, CDCl₃, 20 °C)

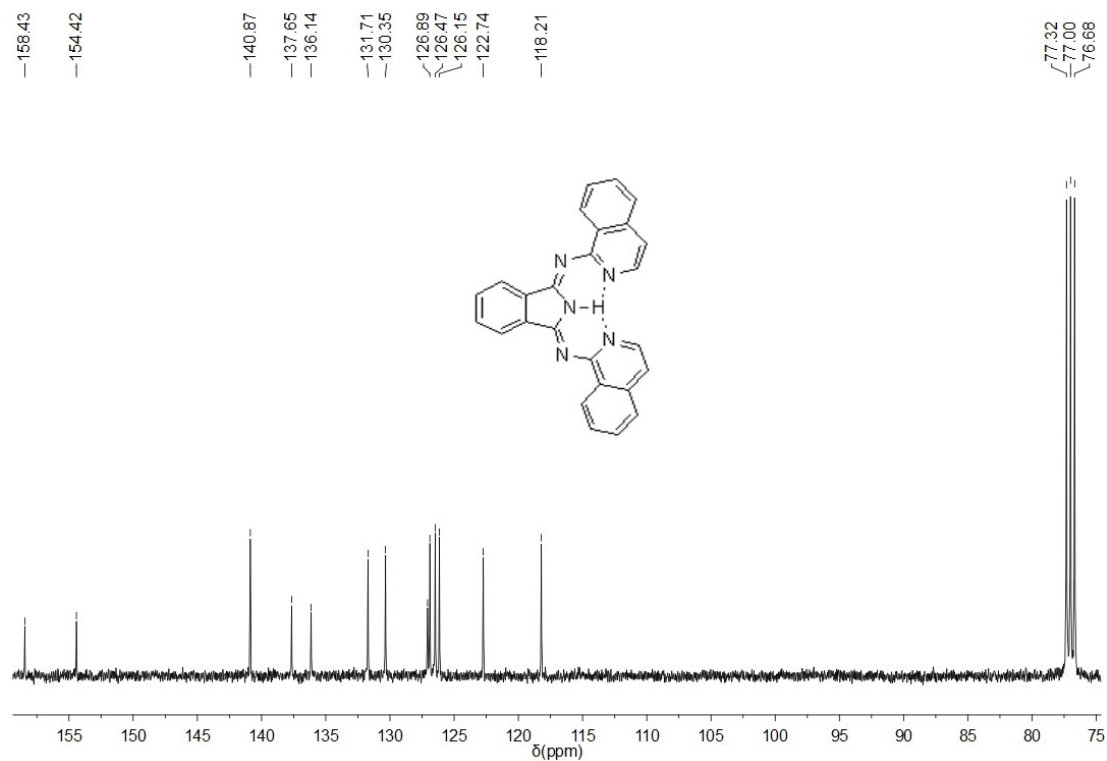


Fig. S73. ¹³C NMR spectrum of **6aj** (100 MHz, CDCl₃, 20 °C)

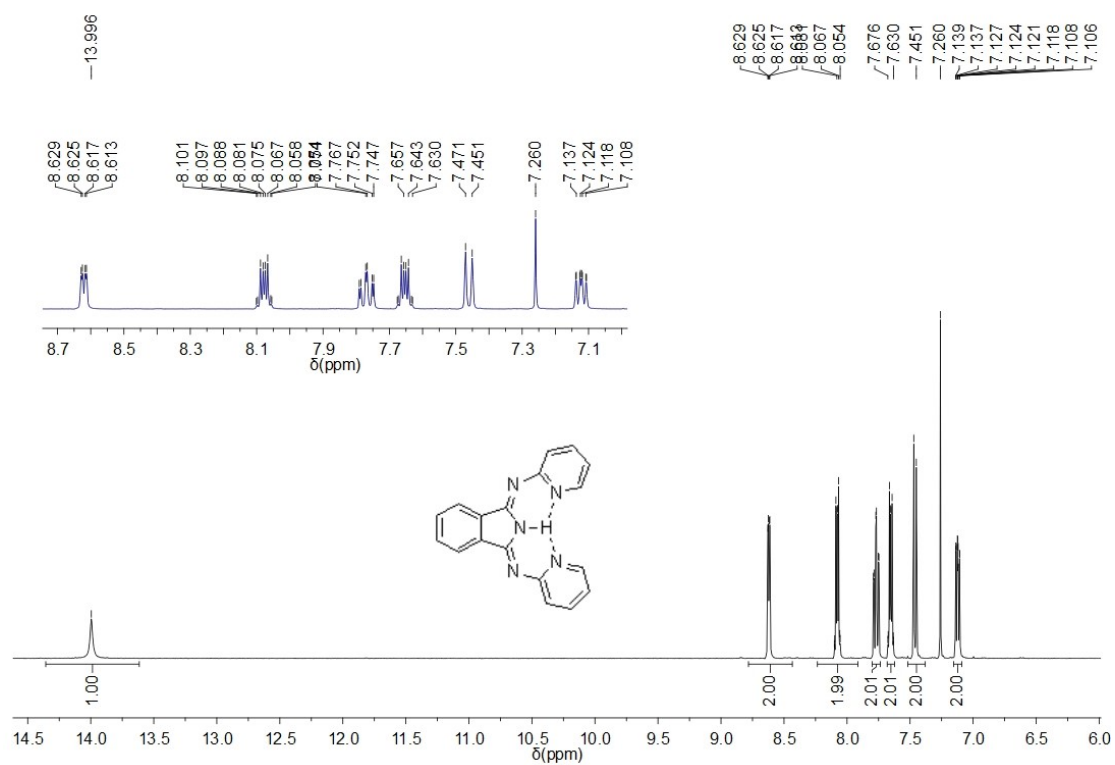


Fig. S74. ¹H NMR spectrum of **6ak** (400 MHz, CDCl₃, 20 °C)

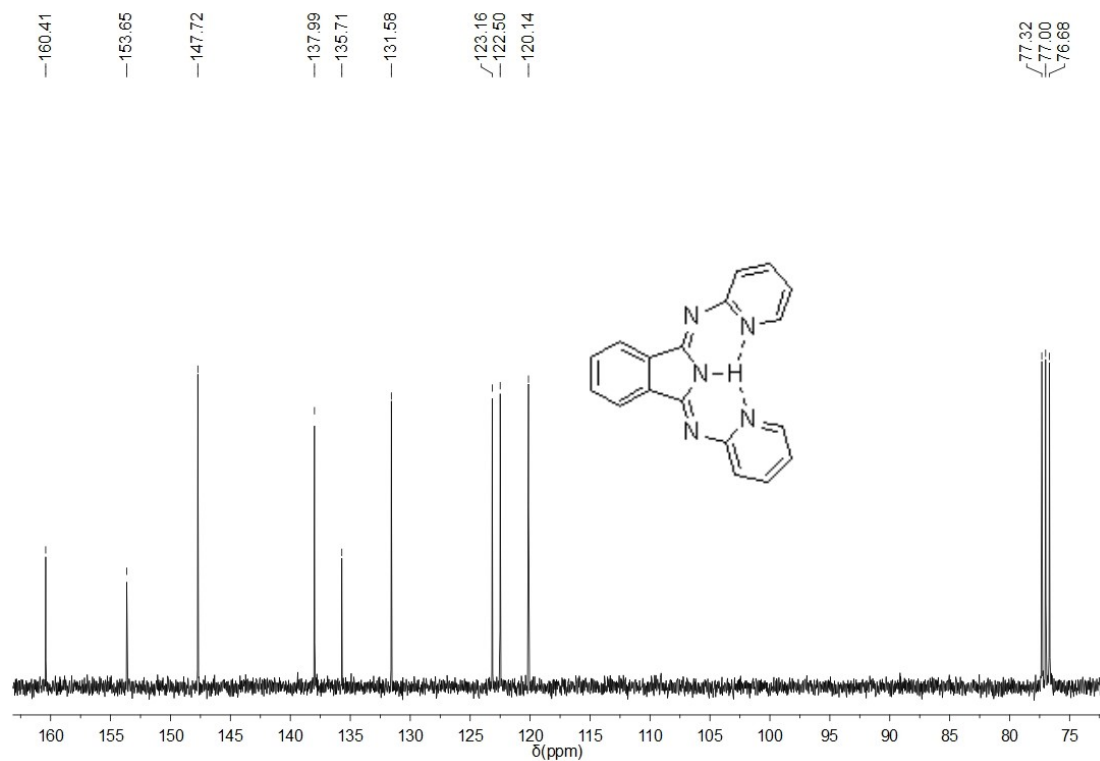


Fig. S75. ¹³C NMR spectrum of **6ak** (100 MHz, CDCl₃, 20 °C)

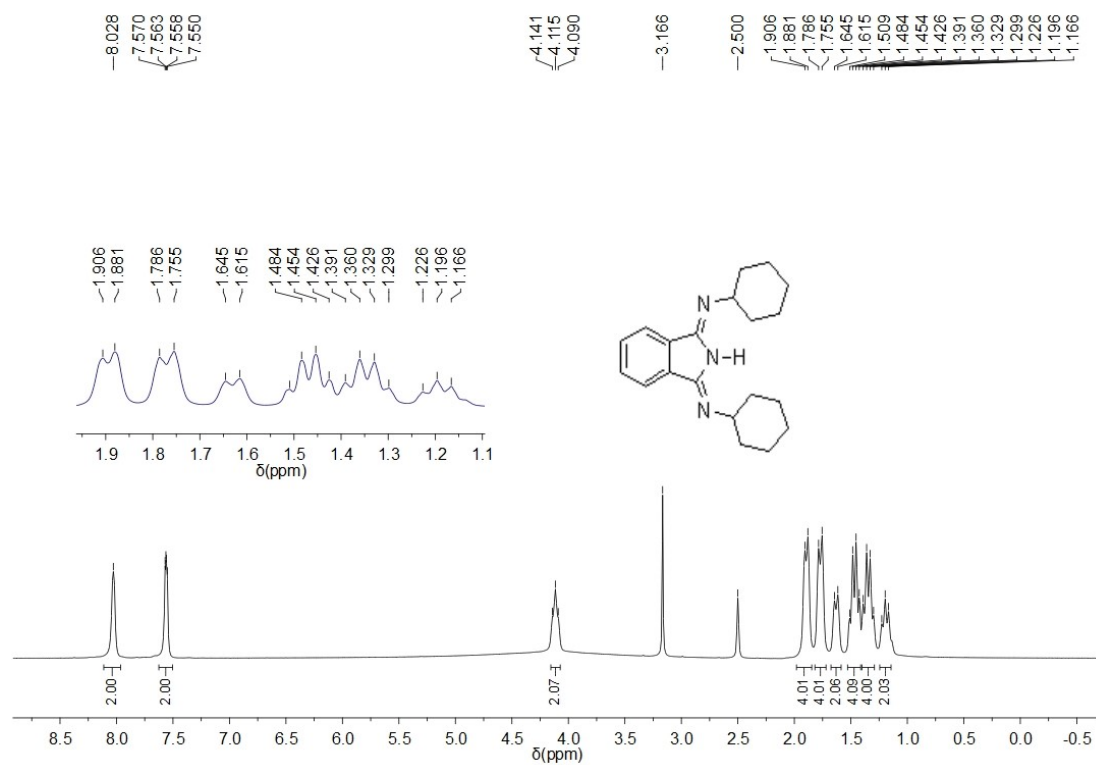


Fig. S76. ¹H NMR spectrum of **6al** (400 MHz, DMSO-*d*₆, 20 °C)

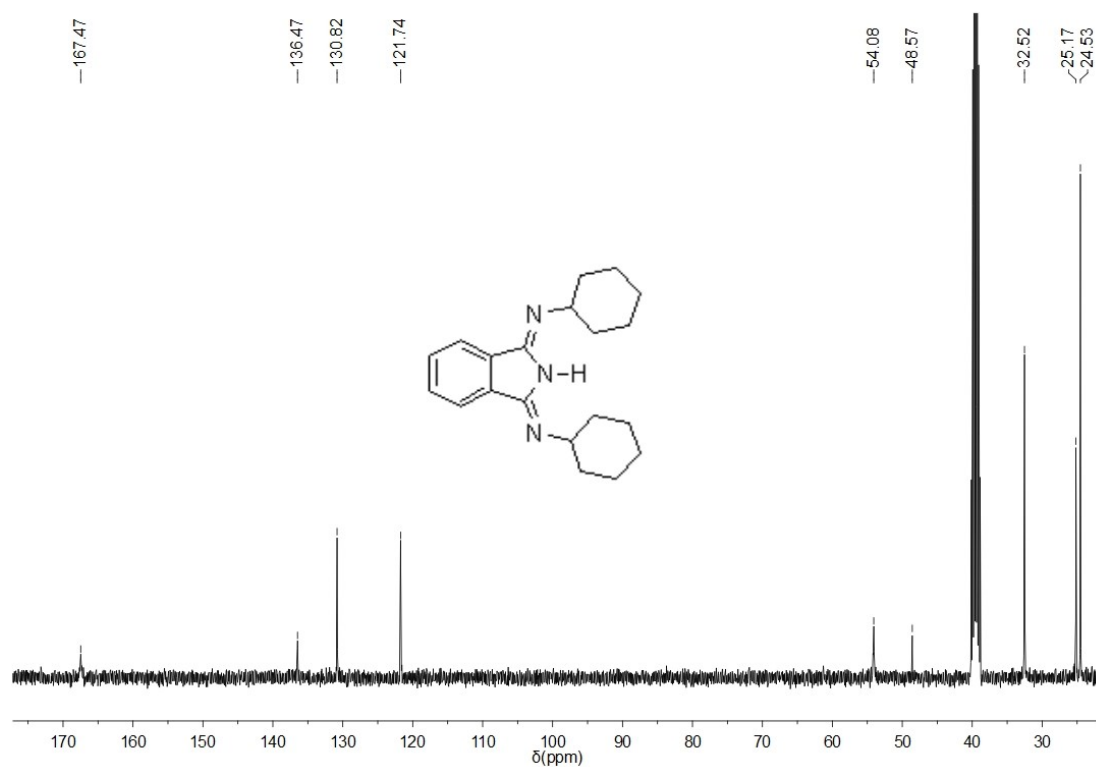


Fig. S77. ¹³C NMR spectrum of **6al** (100 MHz, DMSO-*d*₆, 20 °C)

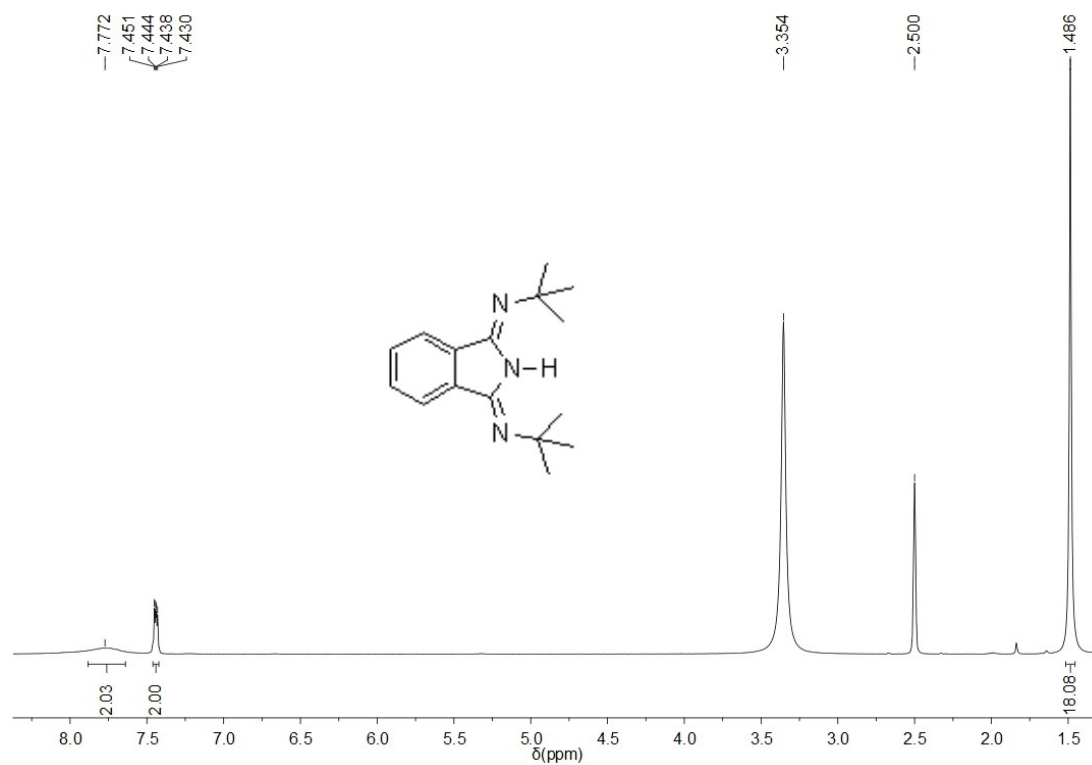


Fig. S78. ¹H NMR spectrum of **6am** (400 MHz, DMSO-*d*₆, 20 °C)

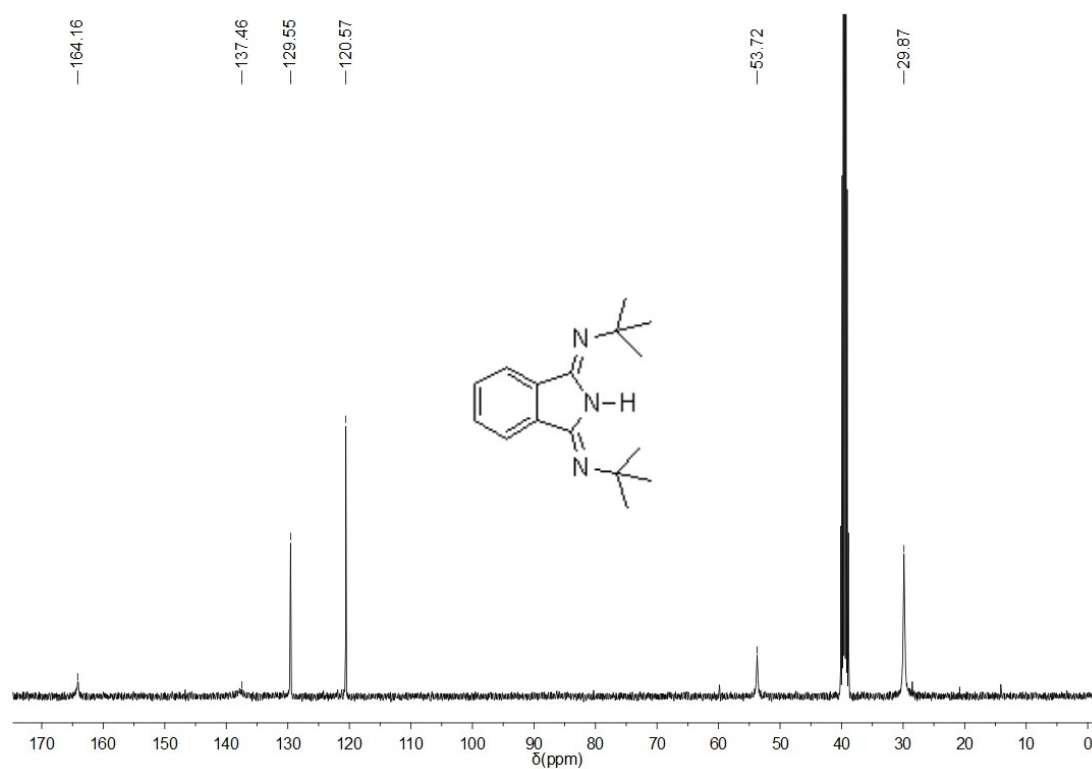


Fig. S79. ¹³C NMR spectrum of **6am** (100 MHz, DMSO-*d*₆, 20 °C)

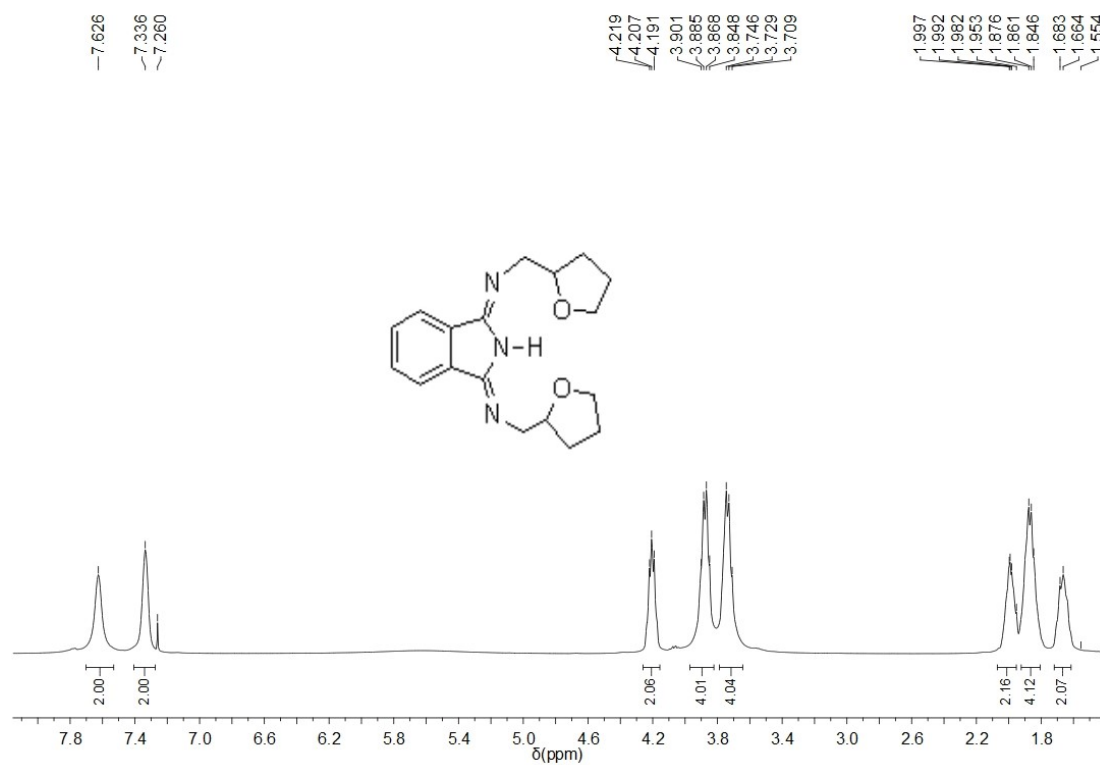


Fig. S80. ¹H NMR spectrum of **6an** (400 MHz, CDCl₃, 20 °C)

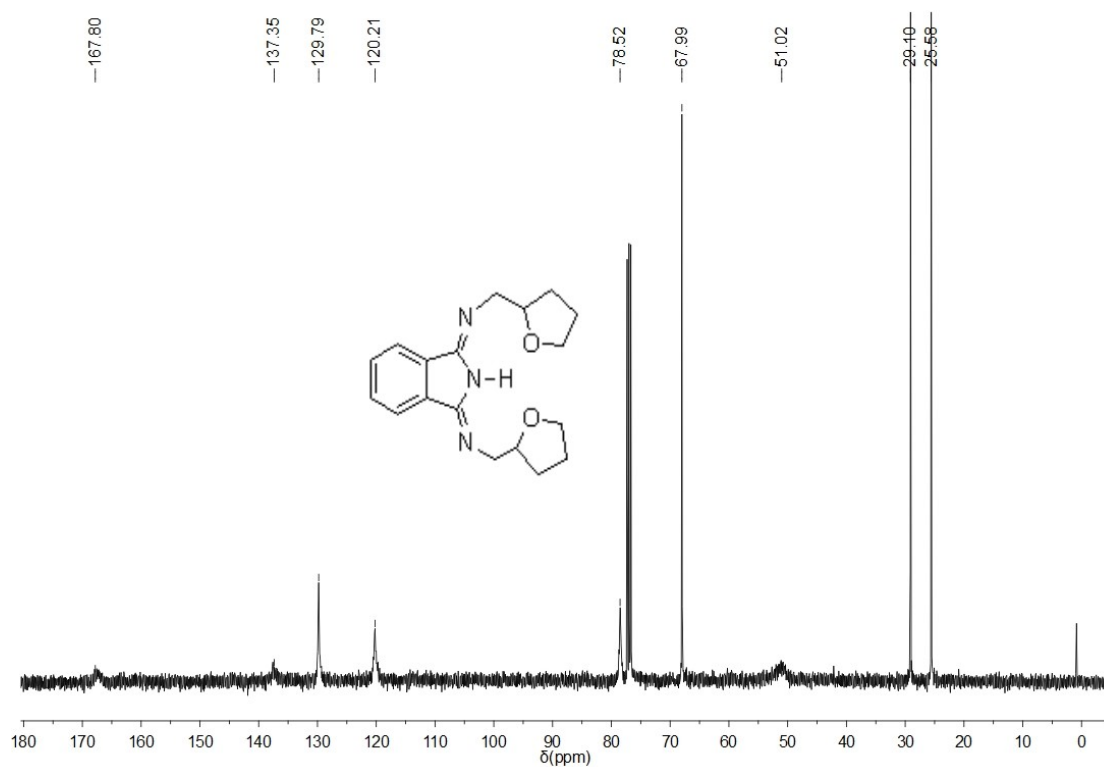


Fig. S81. ¹³C NMR spectrum of **6an** (100 MHz, CDCl₃, 20 °C)

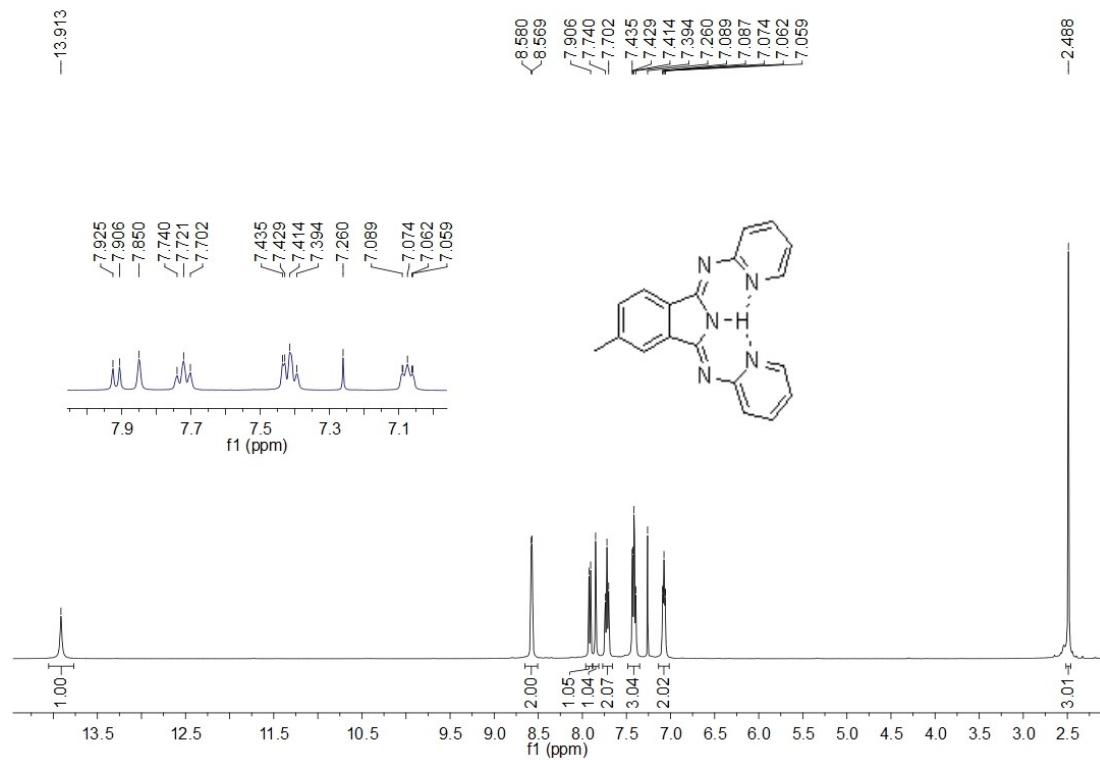


Fig. S82. ¹H NMR spectrum of **6bk** (400 MHz, CDCl₃, 20 °C)

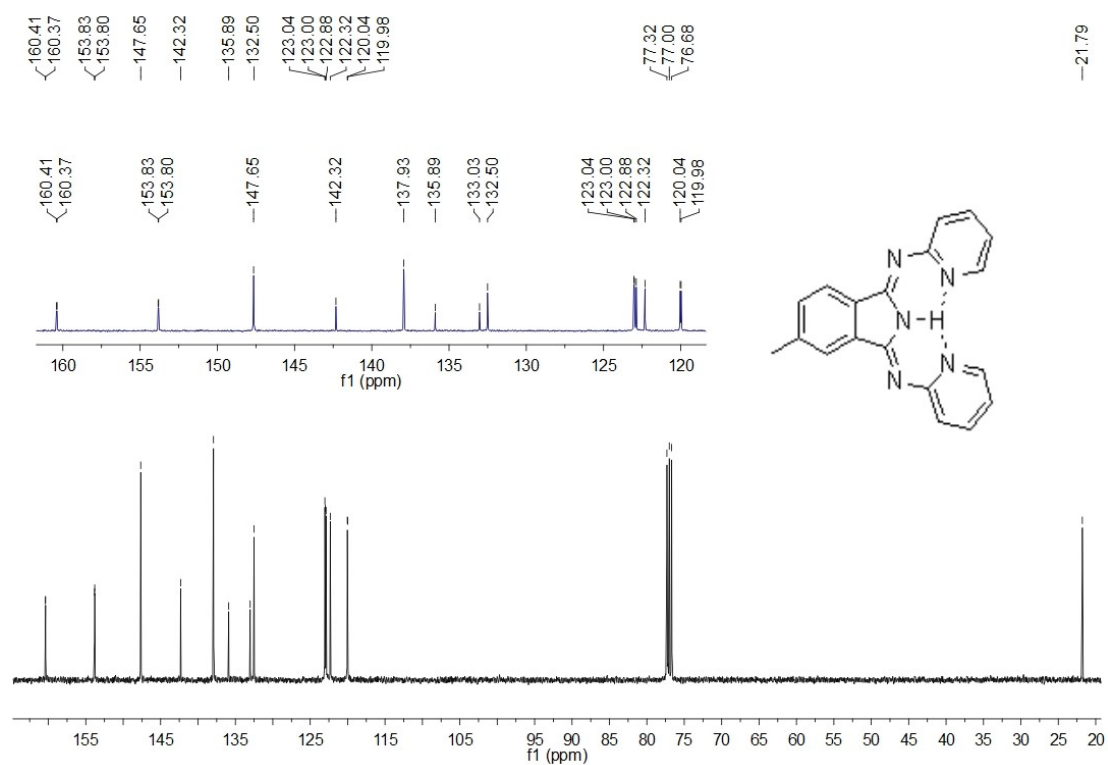


Fig. S83. ¹³C NMR spectrum of **6bk** (100 MHz, CDCl₃, 20 °C)

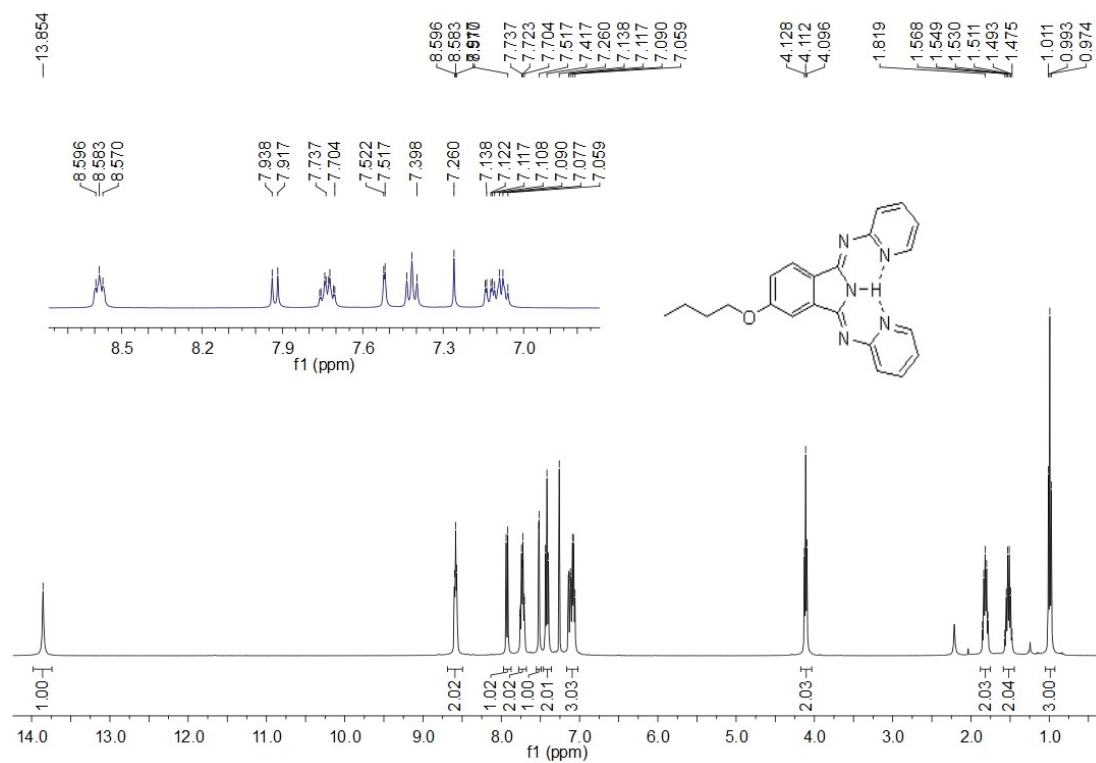


Fig. S84. ¹H NMR spectrum of **6fk** (400 MHz, CDCl₃, 20 °C)

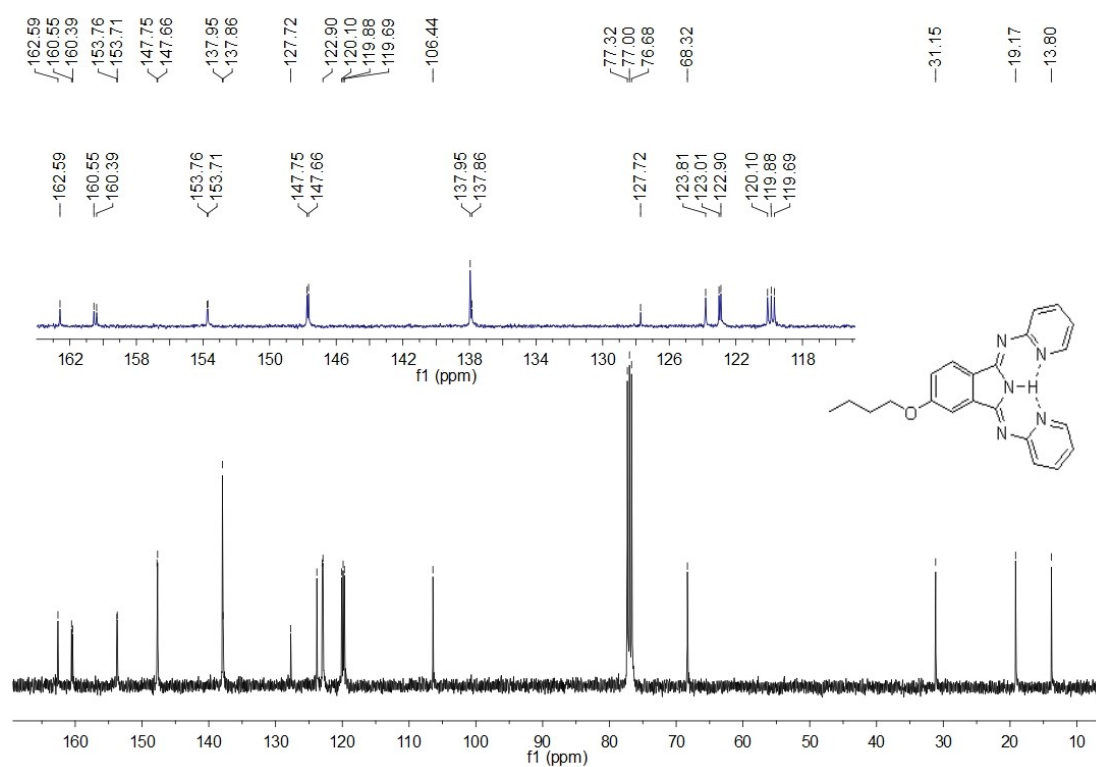


Fig. S85. ¹³C NMR spectrum of **6fk** (100 MHz, CDCl₃, 20 °C)

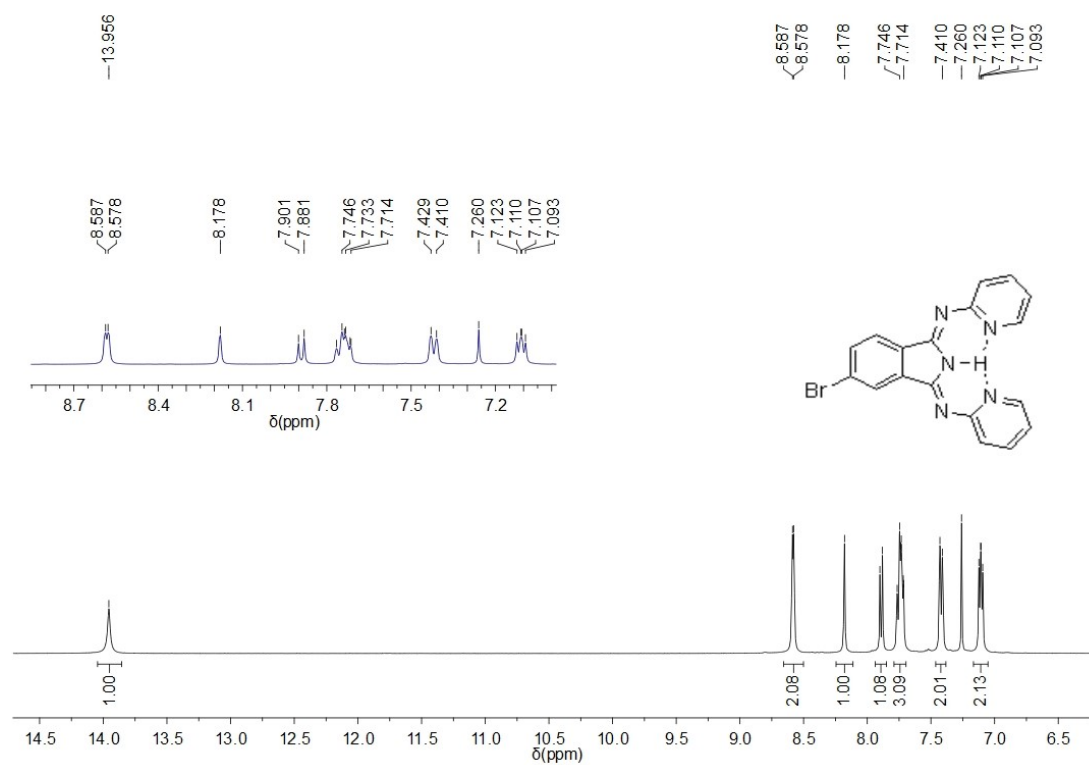


Fig. S86. ¹H NMR spectrum of **6pk** (400 MHz, CDCl₃, 20 °C)

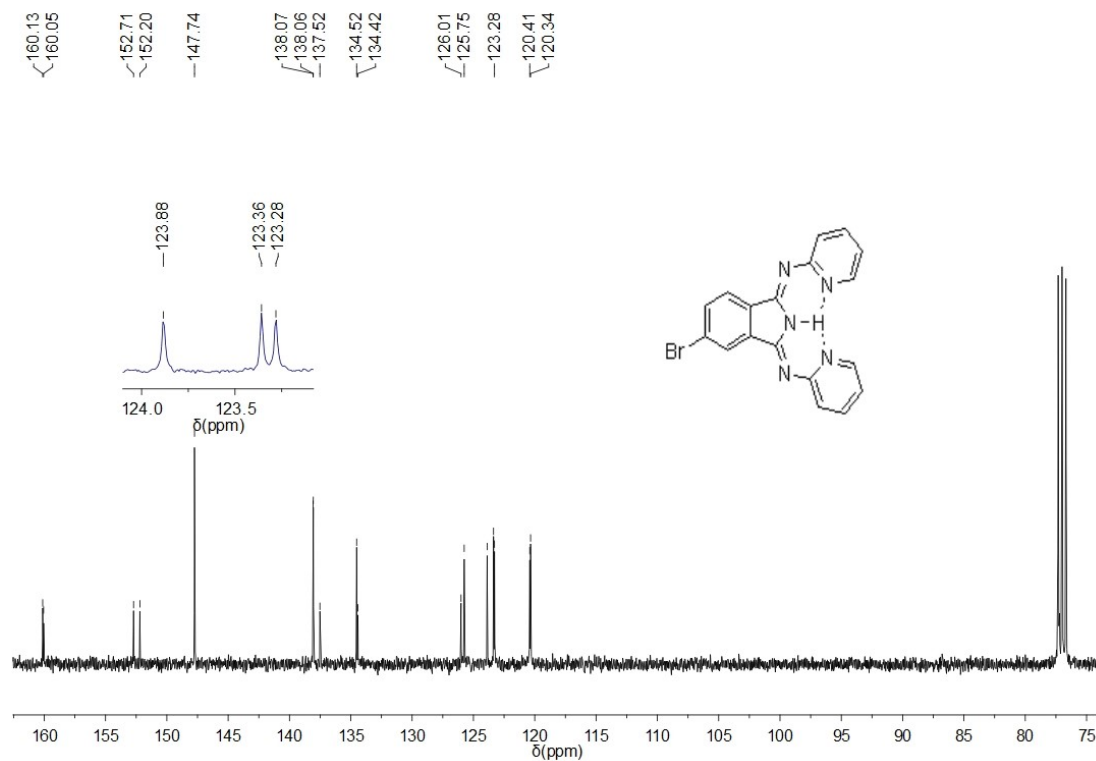


Fig. S87. ¹³C NMR spectrum of **6pk** (100 MHz, CDCl₃, 20 °C)

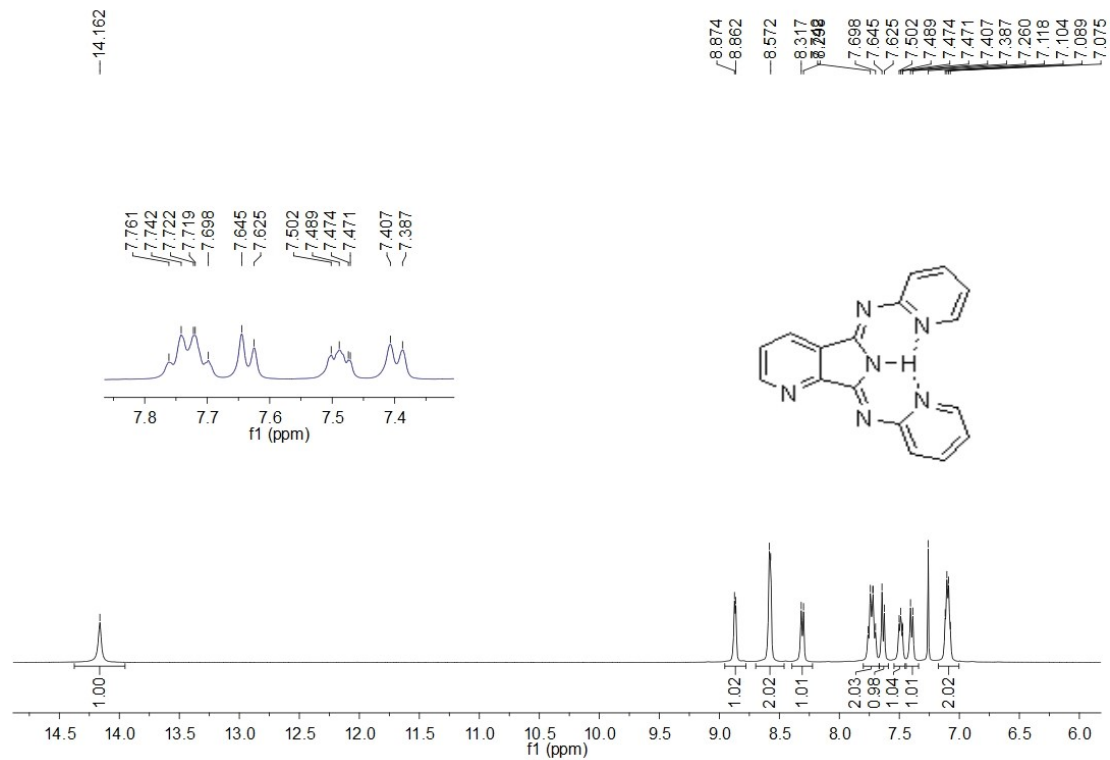


Fig. S88. ¹H NMR spectrum of **6qk** (400 MHz, CDCl₃, 20 °C)

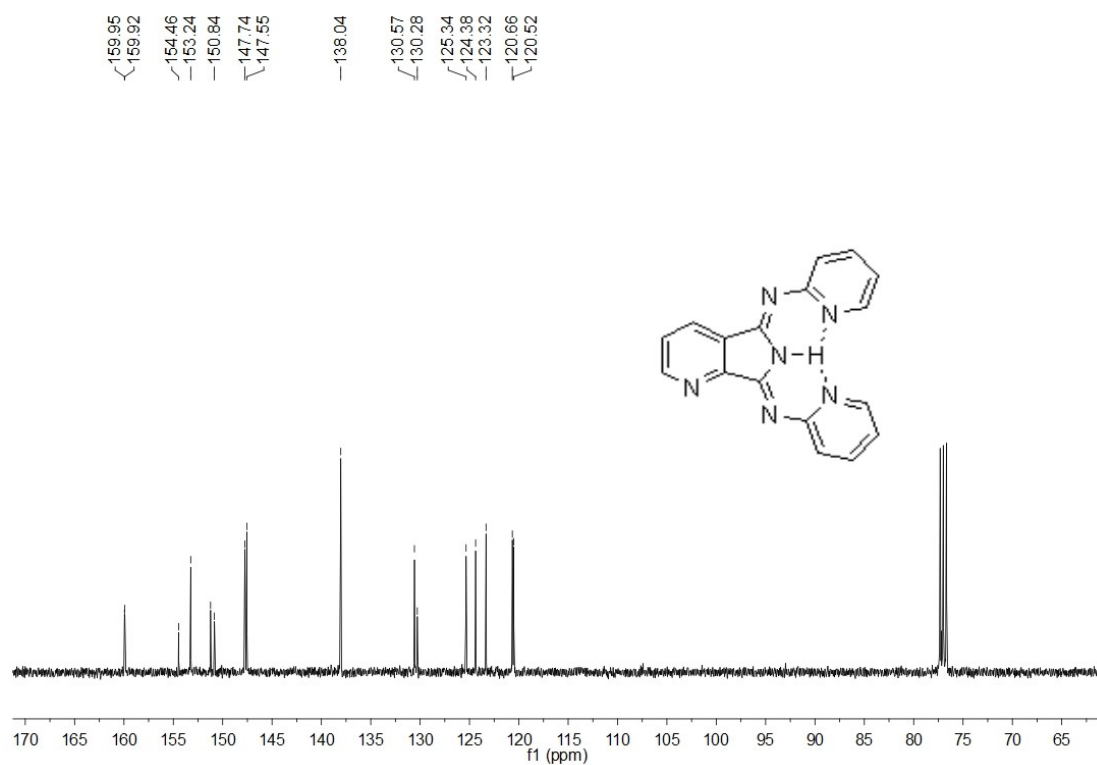


Fig. S89. ¹³C NMR spectrum of **6qk** (100 MHz, CDCl₃, 20 °C)

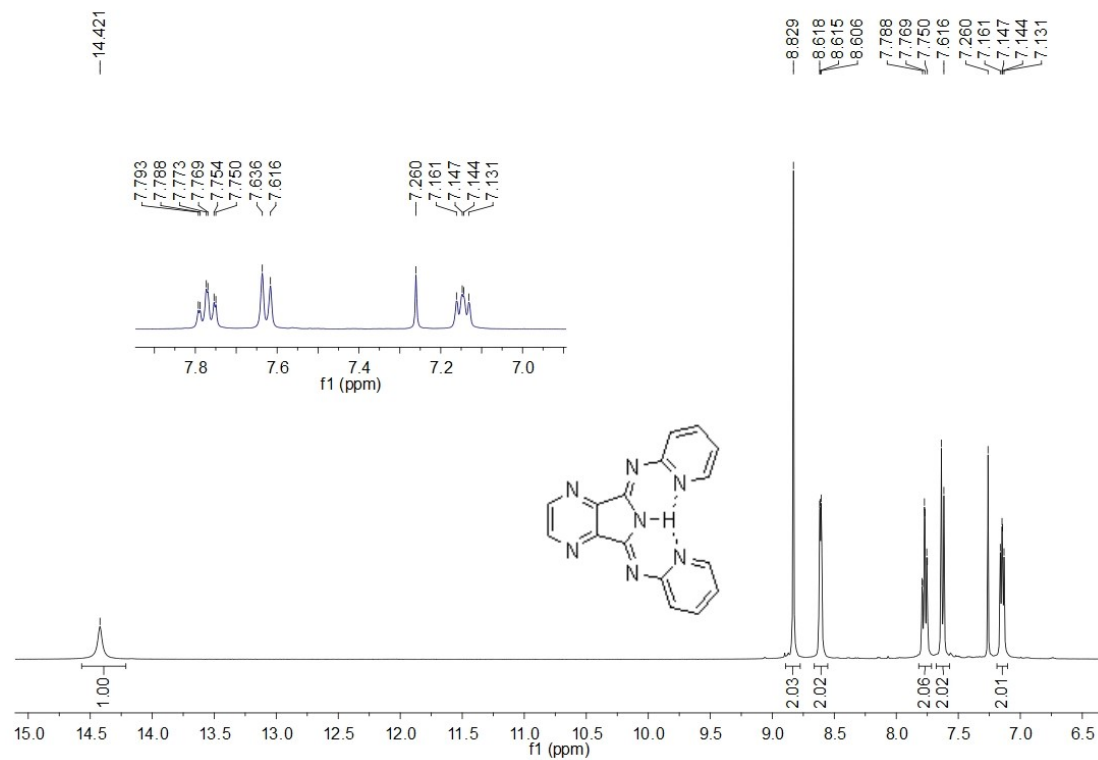


Fig. S90. ¹H NMR spectrum of **6rk** (400 MHz, CDCl₃, 20 °C)

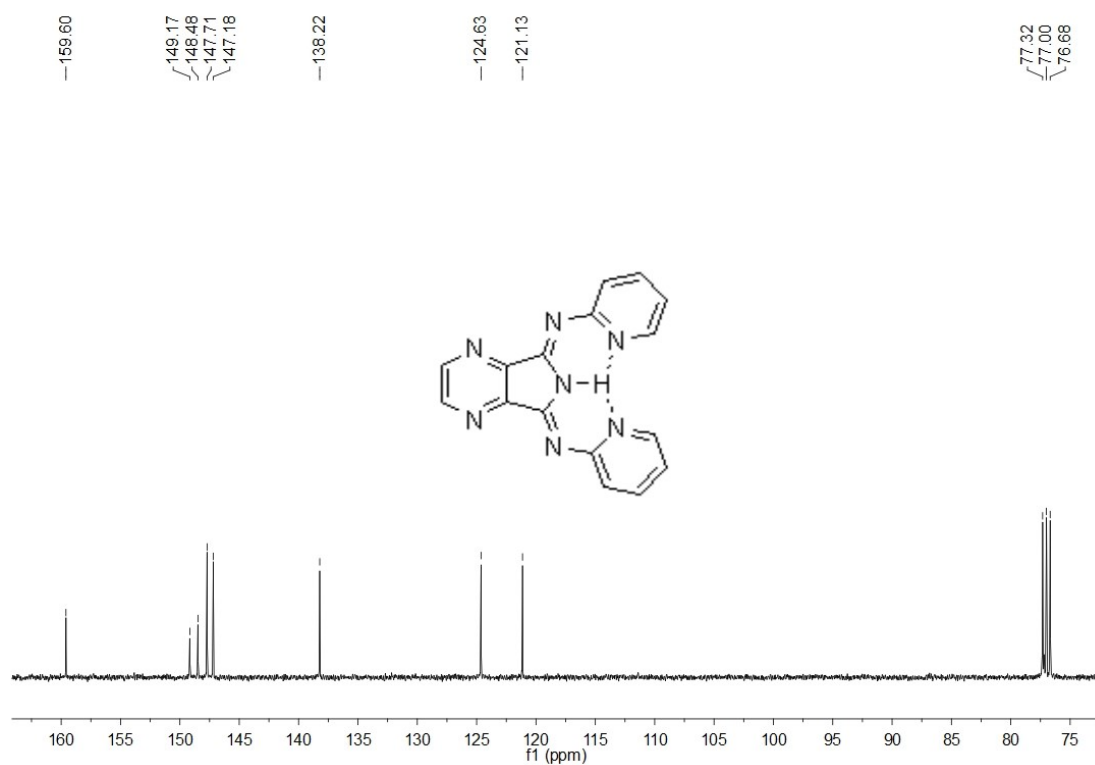


Fig. S91. ¹³C NMR spectrum of **6rk** (100 MHz, CDCl₃, 20 °C)

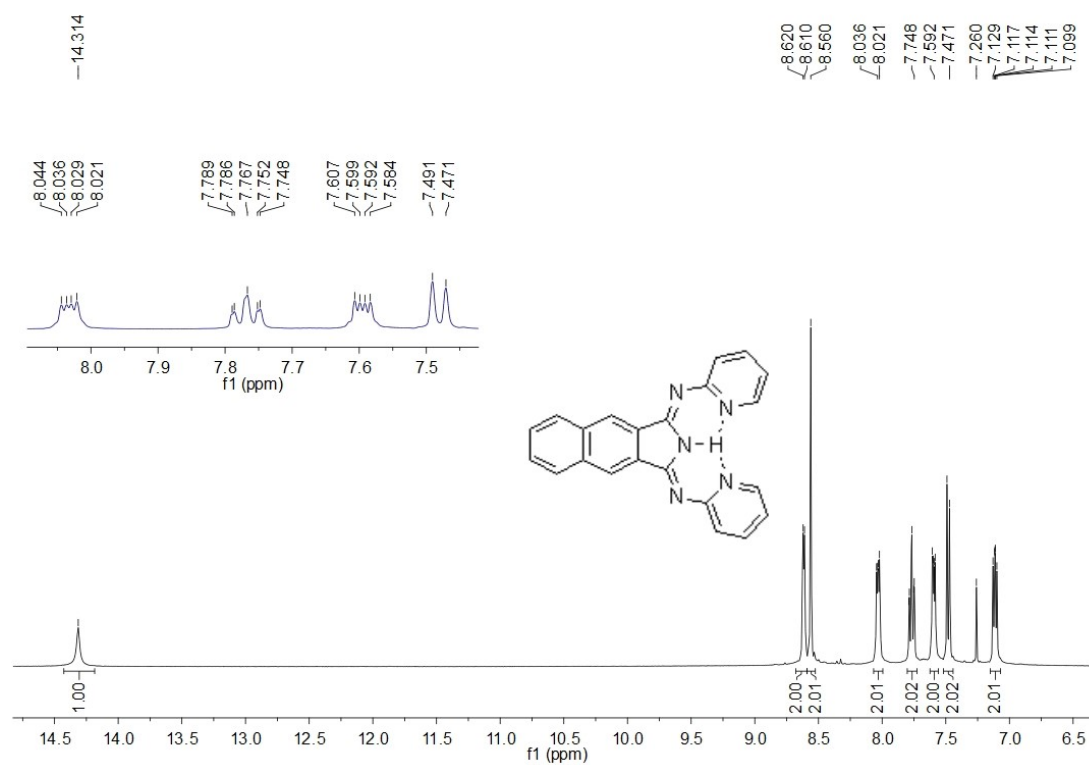


Fig. S92. ¹H NMR spectrum of **6sk** (400 MHz, CDCl₃, 20 °C)

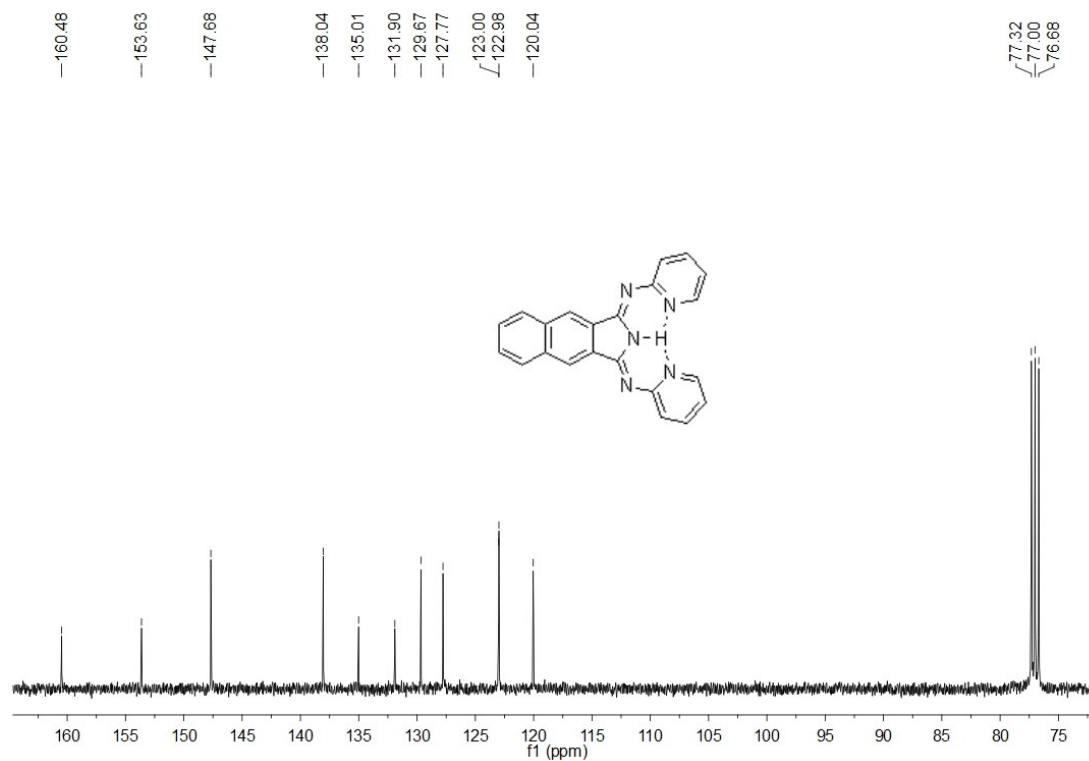


Fig. S93. ¹³C NMR spectrum of **6sk** (100 MHz, CDCl₃, 20 °C)

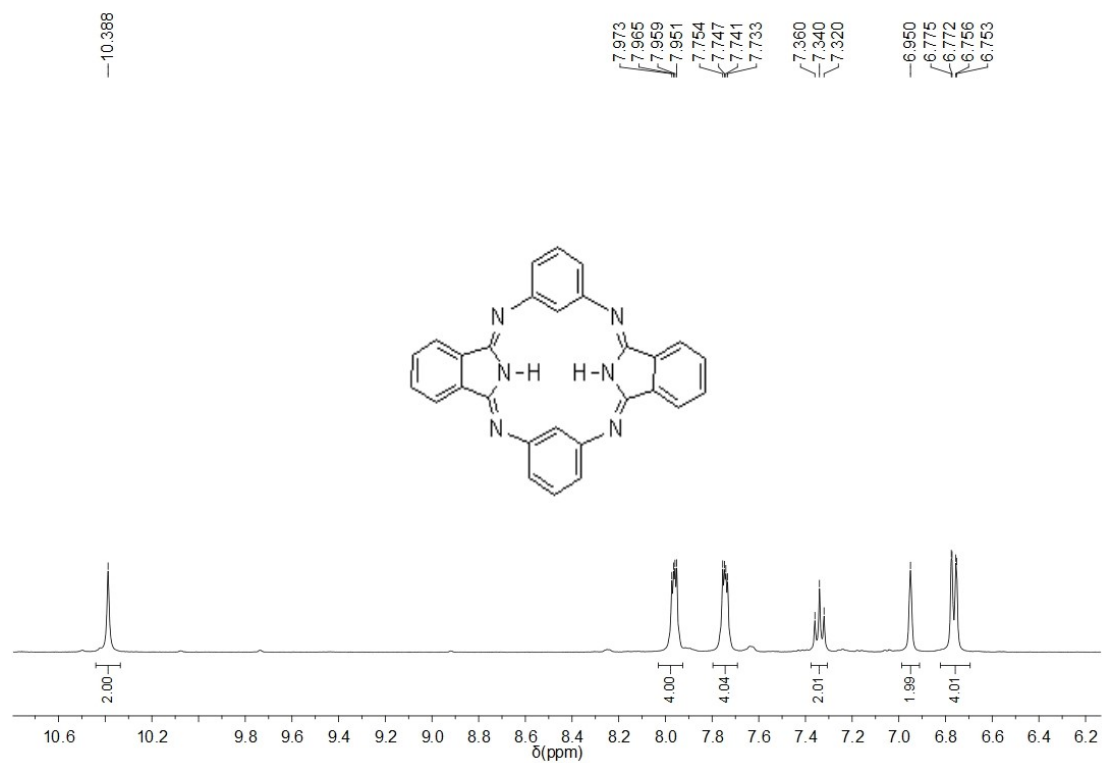


Fig. S94. ^1H NMR spectrum of **6ao** (400 MHz, $\text{DMSO}-d_6$, 20 °C)

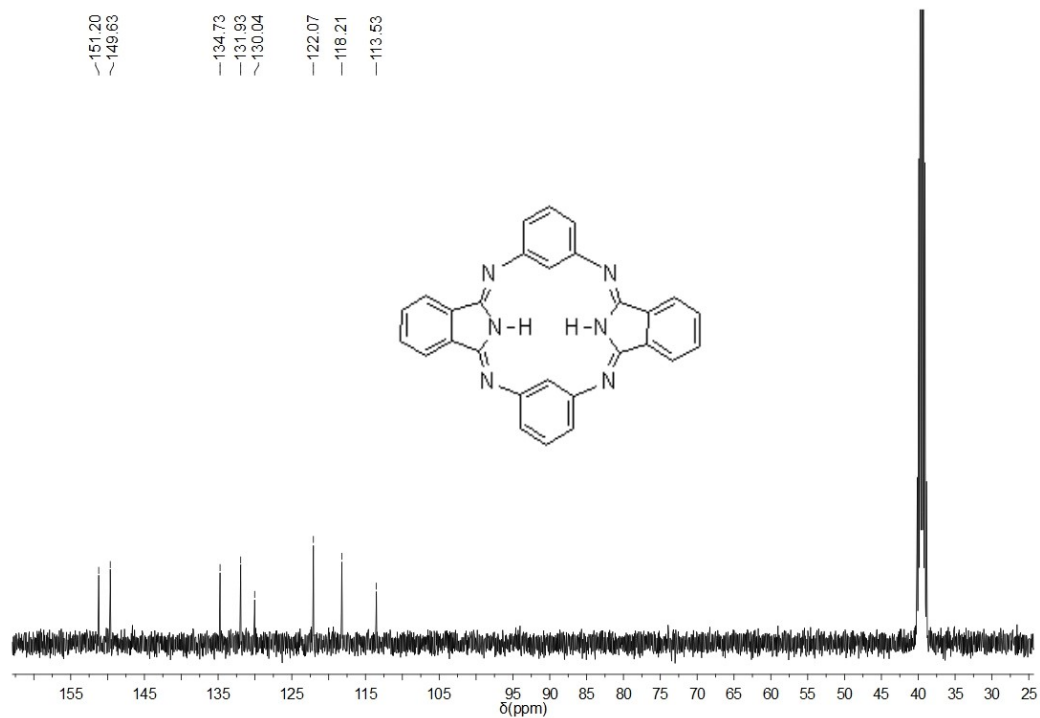


Fig. S95. ^{13}C NMR spectrum of **6ao** (100 MHz, $\text{DMSO}-d_6$, 20 °C)

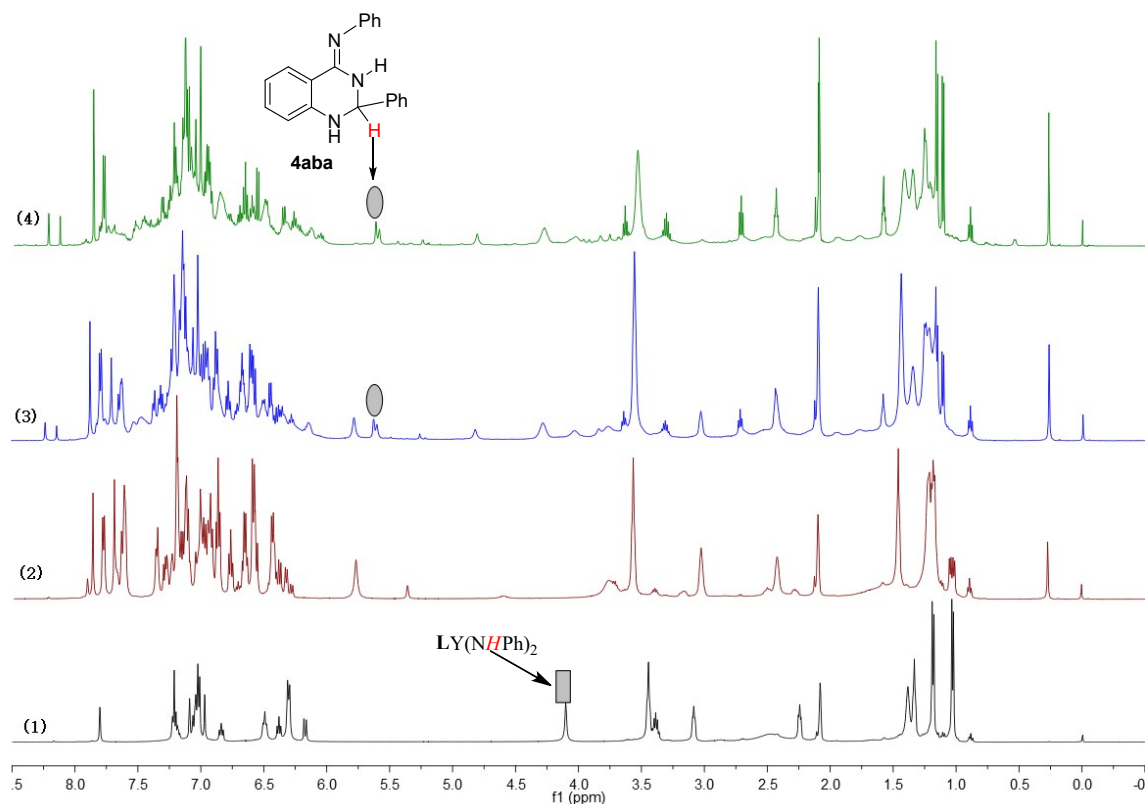


Fig. S96. The ^1H NMR (500 MHz, toluene- d_8) monitoring reaction of complex $\text{LY}(\text{NHPh})_2$ (**7b**) with 2-(benzylideneamino)benzonitrile (**2aa**). (1) **7b** (0.03 mmol) at room temperature; (2) **7b** (0.03 mmol) and **2aa** (0.03 mmol) at 110 °C for 30 min; (3) the mixture at 110 °C for 3 h; (4) the mixture at 110 °C for 24 h. The rectangle and the oval represent the protons of $\text{LY}(\text{NHPh})_2$ and the methyne of **4aba**, respectively.

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