Supplementary Information for

Evaluation of oxygen-containing pentadentate ligands with pyridine/quinoline/isoquinoline binding sites *via* structural and electrochemical properties of mononuclear copper(II) complexes†

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INDEX

Preparation of copper(II) complexes

PPI-Cu ([Cu(PPI)(ClO_4)]ClO_4)

To a solution of **PQP** (9.3 mg, 24 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (10.7 mg, 29 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to give **PPI-Cu** as a blue powder (5.7 mg, 8.8 μmol, 37%).

HRMS (ESI) *m*/*z*: [**PPI** + Cu + ClO_4]$^+$ calcd. for $C_{24}H_{24}ClCuN_4O_5$ 546.07315; found 546.07146.

mp 211-214 °C.

PQP-Cu ([Cu(PQP)(ClO_4)]ClO_4)

To a solution of **PQP** (20.2 mg, 52 μmol) in methanol (0.6 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (18.5 mg, 51 μmol) and $NaClO_4 \cdot H_2O$ (70.2 mg, 500 mmol) in methanol (0.4 mL), and the solution kept at 4 °C under ether diffusion conditions. The green powder was recrystallized with acetonitrile (0.5 mL) at 4 °C under ether diffusion conditions to afford **PQP-Cu** as green crystals suitable for X-ray crystallography (11.0 mg, 17 μmol, 33%).

Anal Calcd. for $C_{24}H_{24}Cl_2CuN_4O_9$ (**PQP-Cu**): C, 44.56; H, 3.74; N, 8.66. Found: C, 44.75; H, 3.78; N, 8.87.

PQQ-Cu ([Cu(PQQ)](ClO_4)$_2$)

To a solution of **PQQ** (11.1 mg, 26 μmol) in ethanol (0.5 mL) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (11.7 mg, 27 μmol) in ethanol (0.5 mL). The solution was kept at 4 °C under ether diffusion conditions to afford **PQQ-Cu** as green crystals suitable for X-ray crystallography (11.7 mg, 17 μmol, 65%).

HRMS (ESI) *m*/*z*: [**PQQ** + Cu + ClO_4]$^+$ calcd. for $C_{28}H_{26}ClCuN_4O_5$ 596.08877; found 596.08659.

mp 174-176 °C.

PQI-Cu ([Cu(PQI)(ClO_4)]ClO_4)

To a solution of **PQI** (11.6 mg, 27 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (10.2 mg, 27 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **PQI-Cu** as a green powder (11.8 mg, 17 μmol, 65%).

HRMS (ESI) *m*/*z*: [**PQI** + Cu + ClO_4]$^+$ calcd. for $C_{28}H_{26}ClCuN_4O_5$ 596.08877; found 596.08606.

mp 201-205 °C.

PIP-Cu·CH_3CN ([Cu(PIP)(ClO_4)]ClO_4·CH_3CN)

To a solution of **PIP** (10.7 mg, 28 μmol) in ethanol (0.5 mL) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (11.9 mg, 32 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol. The green powder was recrystallized with acetonitrile (1.0 mL) in the presence of $NaClO_4 \cdot H_2O$ (11 mg, 90 μmol) at 4 °C under ether diffusion conditions to afford **PIP-Cu**·CH_3CN as green crystals suitable for X-ray crystallography (12.0 mg, 19 μmol, 68%).

Anal Calcd. for $C_{26}H_{27}Cl_2CuN_5O_9$ (**PIP-Cu**·CH_3CN): C, 45.39; H, 3.96; N, 10.18. Found: C, 45.06; H, 3.93; N, 10.12.

mp 212-214 °C.

PIQ-Cu ([Cu(PIQ)](ClO_4)$_2$)

To a solution of **PIQ** (19.8 mg, 23 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (8.3 mg, 22 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **PIQ-Cu** as a blue powder (11.1 mg, 16 μmol, 72%).

HRMS (ESI) *m*/*z*: [**PIQ** + Cu + ClO_4]$^+$ calcd. for $C_{28}H_{26}ClCuN_4O_5$ 596.08877; found 596.08768.

mp 195-197 °C.

PII-Cu ([Cu(PII)(ClO_4)]ClO_4)

To a solution of **PII** (10.6 mg, 24 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (11.9 mg, 32 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **PII-Cu** as a blue powder (10.6 mg, 15 μmol, 63%).

HRMS (ESI) *m*/*z*: [**PII** + Cu + ClO_4]$^+$ calcd. for $C_{28}H_{26}ClCuN_4O_5$ 596.08877; found 596.0874.

mp 195-197 °C.

QQP-Cu ([Cu(QQP)(ClO_4)]ClO_4)

To a solution of **QQP** (10.5 mg, 24 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (9.4 mg, 25 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **QQP-Cu** as a green powder (9.1 mg, 13 μmol, 54%).

HRMS (ESI) *m*/*z*: [**QQP** + Cu]$^+$ calcd. for $C_{28}H_{26}CuN_4O_1$ 497.14026; found 497.14917.

mp 181-184 °C.

QQQ-Cu ([Cu(QQQ)](ClO_4)$_2$)

To a solution of **QQQ** (13.1 mg, 27 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (11.2 mg, 30 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **QQQ-Cu** as a green powder (1.5 mg, 2.0 μmol, 7%).

HRMS (ESI) *m*/*z*: [**QQQ** + Cu + ClO_4]$^+$ calcd. for $C_{32}H_{28}ClCuN_4O_5$ 646.10442; found 646.10210.

mp 201-204 °C.

QQI-Cu ([Cu(QQI)(ClO_4)]ClO_4)

To a solution of **QQI** (5.6 mg, 12 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (5.2 mg, 14 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate

was collected by filtration and washed with ethanol to afford **QQI-Cu** as a green powder (3.0 mg, 4.0 μmol, 35%).

HRMS (ESI) *m*/*z*: [**QQI** + Cu + ClO_4]$^+$ calcd. for $C_{32}H_{28}ClCuN_4O_5$ 646.10442; found 646.10282.

mp 180-183 °C.

QIP-Cu

To a solution of **QIP** (13.0 mg, 30 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (14.1 mg, 38 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **QIP-Cu** as a green powder (10.1 mg, 14 μmol, 48%).

HRMS (ESI) *m*/*z*: [**QIP** + Cu + ClO_4]$^+$ calcd. for $C_{28}H_{26}ClCuN_4O_5$ 596.08877; found 596.0862.

mp 247-250 °C.

QIQ-Cu

To a solution of **QIQ** (13.1 mg, 27 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (10.1 mg, 27 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **QIQ-Cu** as a green powder (10.0 mg, 13 μmol,50%).

Anal Calcd. for $C_{32}H_{28}Cl_2CuN_4O_9$ (**QIQ-Cu**): C, 51.45; H, 3.78; N, 7.50. Found: C, 52.00; H, 3.74; N, 7.41.

QII-Cu

To a solution of **QII** (12.5 mg, 26 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2 \cdot 6H_2O$ (9.6 mg, 26 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **QII-Cu** as a yellow green powder (6.6 mg, 8.8 μmol, 34%).

Anal Calcd. for $C_{32}H_{28}Cl_2CuN_4O_9$ (**QII-Cu**): C, 51.45; H, 3.78; N, 7.50. Found: C, 51.72; H, 3.76; N, 7.30.

IIP-Cu

To a solution of **IIP** (11.4 mg, 26 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2{\cdot}6H_2O$ (9.8 mg, 26 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **IIP-Cu** as a blue powder (11.9 mg, 17 μmol, 65%).

Anal Calcd. for $C_{28}H_{27}Cl_2CuN_4O_{9.5}$ (**IIP-Cu**·$0.5H_2O$): C, 47.64; H, 3.85; N, 7.94. Found: C, 47.87; H, 3.60; N, 7.93.

mp 229-232 °C.

IIQ-Cu

To a solution of **IIQ** (12.5 mg, 26 μmol) in ethanol (0.5 mL) were added $Cu(ClO_4)_2{\cdot}6H_2O$ (9.5 mg, 26 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol to afford **QQI-Cu** as a blue powder (14.9 mg, 20 μmol, 78%).

Anal Calcd. for $C_{32}H_{30}Cl_2CuN_4O_{10}$ (**IIQ-Cu**·H_2O): C, 50.24; H, 3.95; N, 7.32. Found: C, 49.95; H, 3.71; N, 7.23.

mp 228-232 °C.

III-Cu·CH_3CN ($[Cu(III)(ClO_4)]ClO_4{\cdot}CH_3CN$)

To a solution of **III** (12.0 mg, 25 μmol) in ethanol (0.5 mL) was added $Cu(ClO_4)_2{\cdot}6H_2O$ (10.9 mg, 29 μmol) in ethanol (0.5 mL). After stirring for 5 min, resulting precipitate was collected by filtration and washed with ethanol. The green powder was recrystallized with acetonitrile (0.7 mL) in the presence of $NaClO_4{\cdot}H_2O$ (22 mg, 180 μmol) at 4 °C under ether diffusion conditions to afford **PIP-Cu**·CH_3CN as green crystals suitable for X-ray crystallography (9.0 mg, 12 μmol, 48%).

Anal Calcd. for $C_{32}H_{29}Cl_2CuN_4O_{9.5}$ (**III-Cu**·0.5H_2O): C, 50.84; H, 3.87; N, 7.41. Found: C, 50.94; H, 3.72; N, 7.34.

mp 229-231 °C.

X-ray crystallography

Table S1. Crystallographic data for [Cu(**PQP**)(ClO_4)]ClO_4 (**PQP-Cu**) and [Cu(**PQQ**)](ClO_4)$_2$ (**PQQ-Cu**)

	PQP-Cu	**PQQ-Cu**
Formula	$C_{24}H_{24}Cl_2CuN_4O_9$	$C_{28}H_{26}Cl_2CuN_4O_9$
FW	646.93	696.99
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/c$
a, Å	8.9204(11)	19.122(5)
b, Å	10.8760(14)	8.046(2)
c, Å	14.6803(19)	19.183(5)
α, deg	74.810(5)	90
β, deg	77.611(6)	103.718(3)
γ, deg	70.889(5)	90
V, Å^3	1285.7(3)	2867.1(13)
Z	2	4
D_{calc}, g cm^{-3}	1.671	1.615
μ, mm^{-1}	1.193	1.0104
$2\theta_{max}$, deg	55	54.9
temp, K	173	173
no. reflns collected	9838	21517
no. reflns used	5564	6536
no. of params	361	406
R_{int}	0.0179	0.0270
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0343	0.0570
*wR*2 (all data)[b]	0.0995	0.1566
GOF	1.014	1.065

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S2. Crystallographic data for [Cu(**PIP**)(ClO_4)]ClO_4·CH_3CN (**PIP-Cu**·CH_3CN) and [Cu(**III**)(ClO_4)]ClO_4·CH_3CN (**III-Cu**·CH_3CN)

	PIP-Cu·CH_3CN	**III-Cu**·CH_3CN
Formula	$C_{26}H_{27}Cl_2CuN_5O_9$	$C_{34}H_{31}Cl_2CuN_5O_9$
FW	687.98	788.10
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/c$
a, Å	9.9443(1)	11.4717(13)
b, Å	11.5048(3)	13.2852(15)
c, Å	13.8412(1)	22.475(3)
α, deg	77.424(14)	90
β, deg	65.657(12)	103.2305(10)
γ, deg	80.071(14)	90
V, Å^3	1402.03(15)	3334.4(7)
Z	2	4
D_{calc}, g cm^{-3}	1.630	1.570
μ, mm^{-1}	1.0328	0.8799
$2\theta_{max}$, deg	54.9	55
temp, K	153	153
no. reflns collected	10945	33274
no. reflns used	6077	7630
no. of params	389	461
R_{int}	0.0226	0.0557
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0502	0.0572
*wR*2 (all data)[b]	0.1331	0.1697
GOF	1.124	1.081

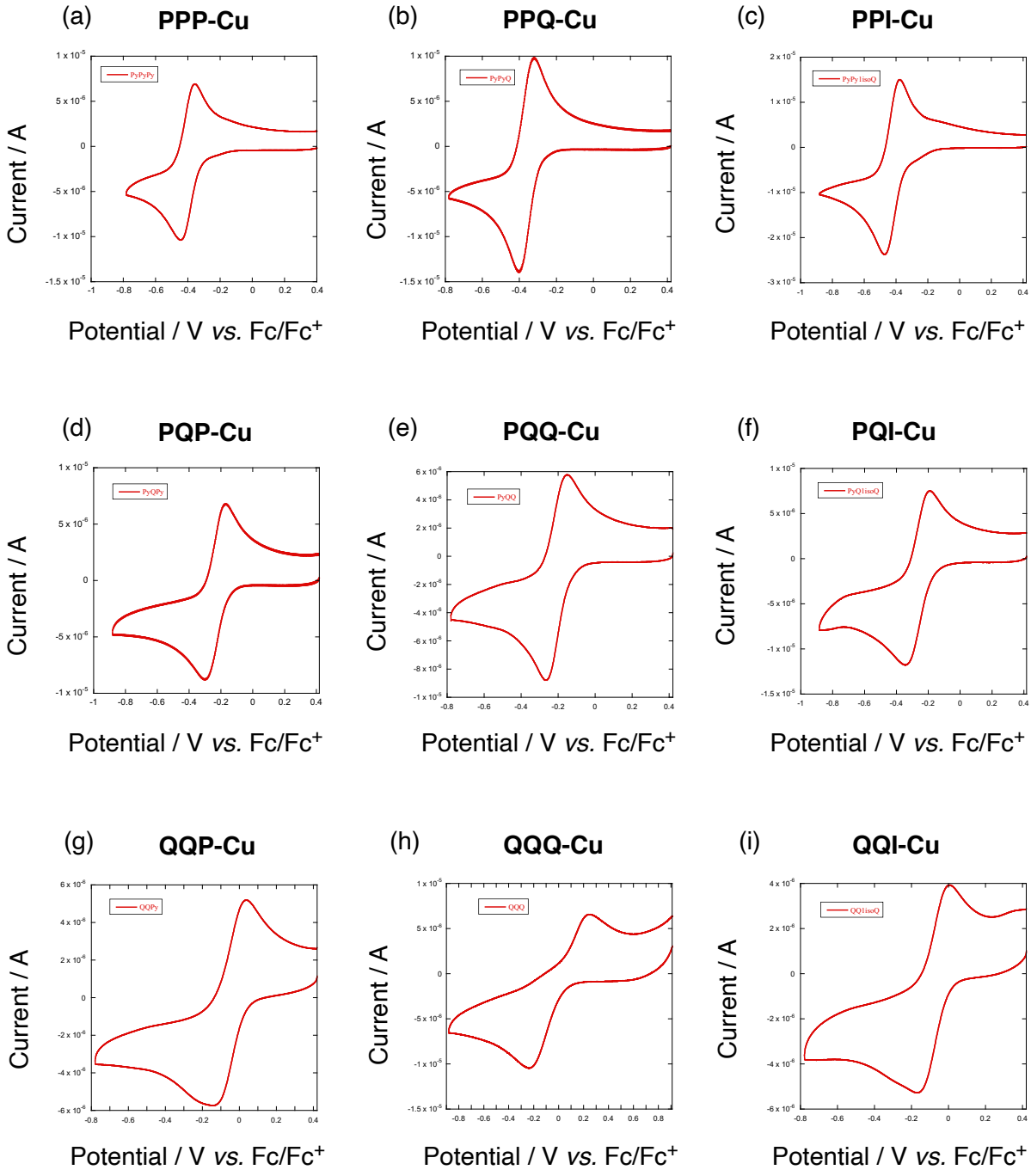
[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S3. Selected Bond Angles (°) for **PPP-Cu**, **PPQ-Cu**, **PQP-Cu**, **PQQ-Cu**, **PIP-Cu** and **III-Cu**

	PPP-Cu[a]	**PPQ-Cu**[a]	**PQP-Cu**	**PQQ-Cu**	**PIP-Cu**	**III-Cu**
O1-Cu-N1	81.0	83.7	82.2	84.1	84.4	83.6
O1-Cu-N2	91.1	97.5	100.3	100.9	94.7	98.4
O1-Cu-N3	97.6	98.1	96.9	95.6	96.5	99.1
O1-Cu-N4	75.0	77.3	77.0	78.9	77.6	76.0
N1-Cu-N2	84.3	84.2	83.3	83.7	83.4	84.2
N1-Cu-N3	82.7	83.5	81.5	82.3	83.7	82.4
N1-Cu-N4	155.8	160.9	158.7	161.6	161.9	159.4
N2-Cu-N3	163.0	158.8	155.2	157.1	162.0	156.7
N2-Cu-N4	94.0	98.0	95.9	92.6	99.9	95.5
N3-Cu-N4	102.4	99.3	105.4	106.2	96.3	103.7
O1-Cu-O2	169.8	–	164.6	–	172.0	170.0
O2-Cu-N1	109.1	–	112.5	–	88.1	87.5
O2-Cu-N2	87.8	–	86.4	–	81.5	76.0
O2-Cu-N3	86.3	–	81.5	–	85.6	84.4
O2-Cu-N4	95.0	–	88.6	–	110.0	112.5

[a] Ref. S1.

Cyclic voltammetry



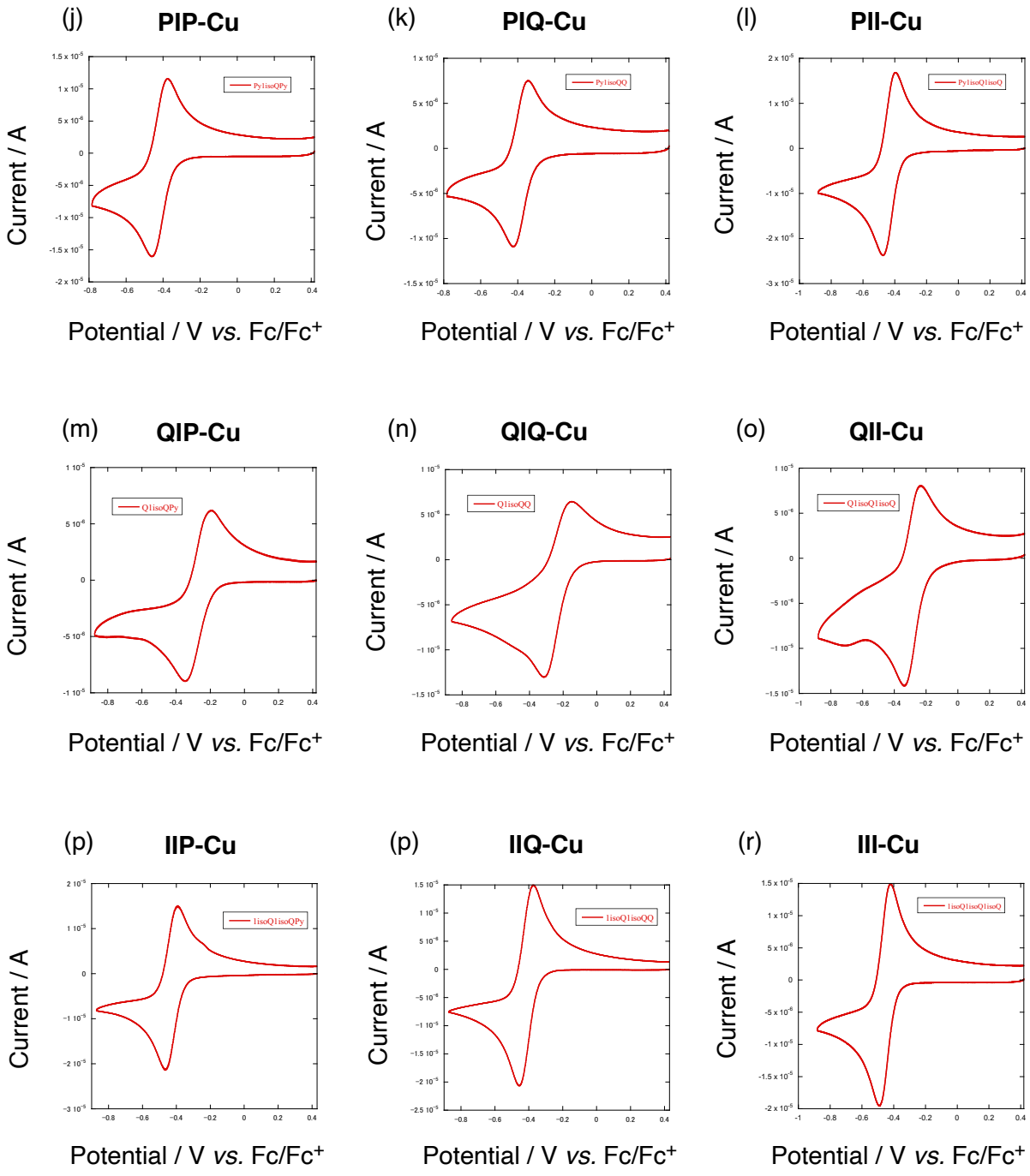
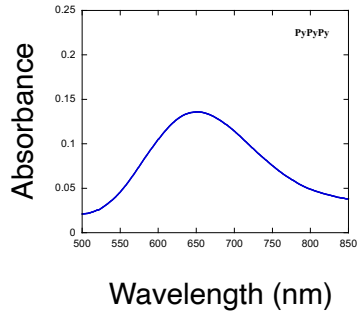


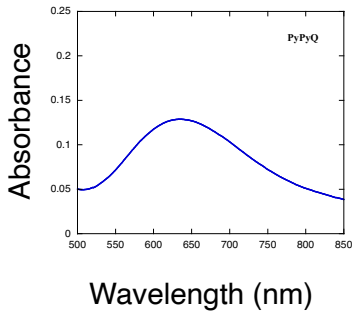
Fig. S1. Cyclic voltammogram of copper(II) complexes in acetonitrile (1 mM, scan rate 100 mV/s). (a) **PPP-Cu**, (b) **PPQ-Cu**, (c) **PPI-Cu**, (d) **PQP-Cu**, (e) **PQQ-Cu**, (f) **PQI-Cu**, (g) **QQP-Cu**, (h) **QQQ-Cu**, (i) **QQI-Cu**, (j) **PIP-Cu**, (k) **PIQ-Cu**, (l) **PII-Cu**, (m) **QIP-Cu**, (n) **QIQ-Cu**, (o) **QII-Cu**, (p) **IIP-Cu**, (q) **IIQ-Cu** and (r) **III-Cu**.

Absorption spectrum

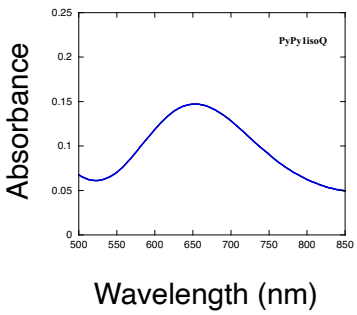
(a) **PPP-Cu**



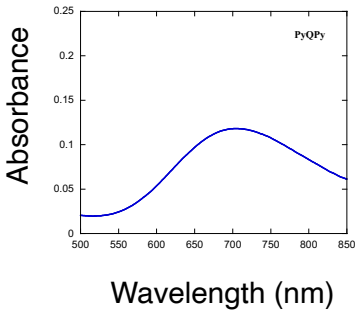
(b) **PPQ-Cu**



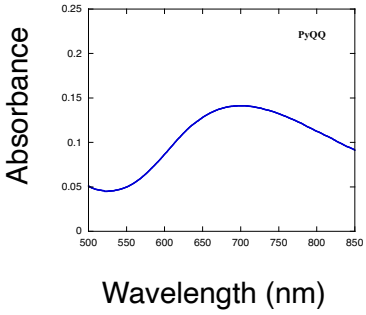
(c) **PPI-Cu**



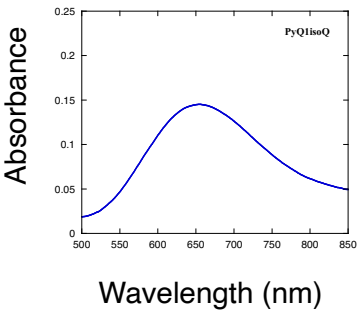
(d) **PQP-Cu**



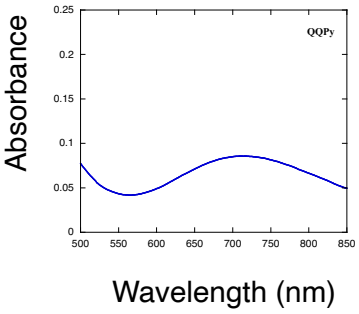
(e) **PQQ-Cu**



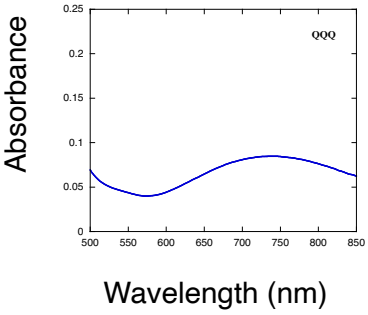
(f) **PQI-Cu**



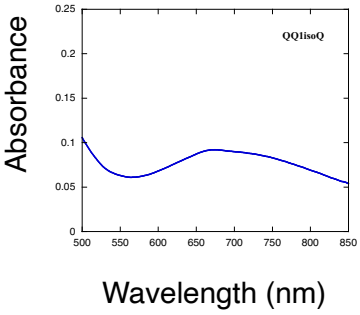
(g) **QQP-Cu**



(h) **QQQ-Cu**



(i) **QQI-Cu**



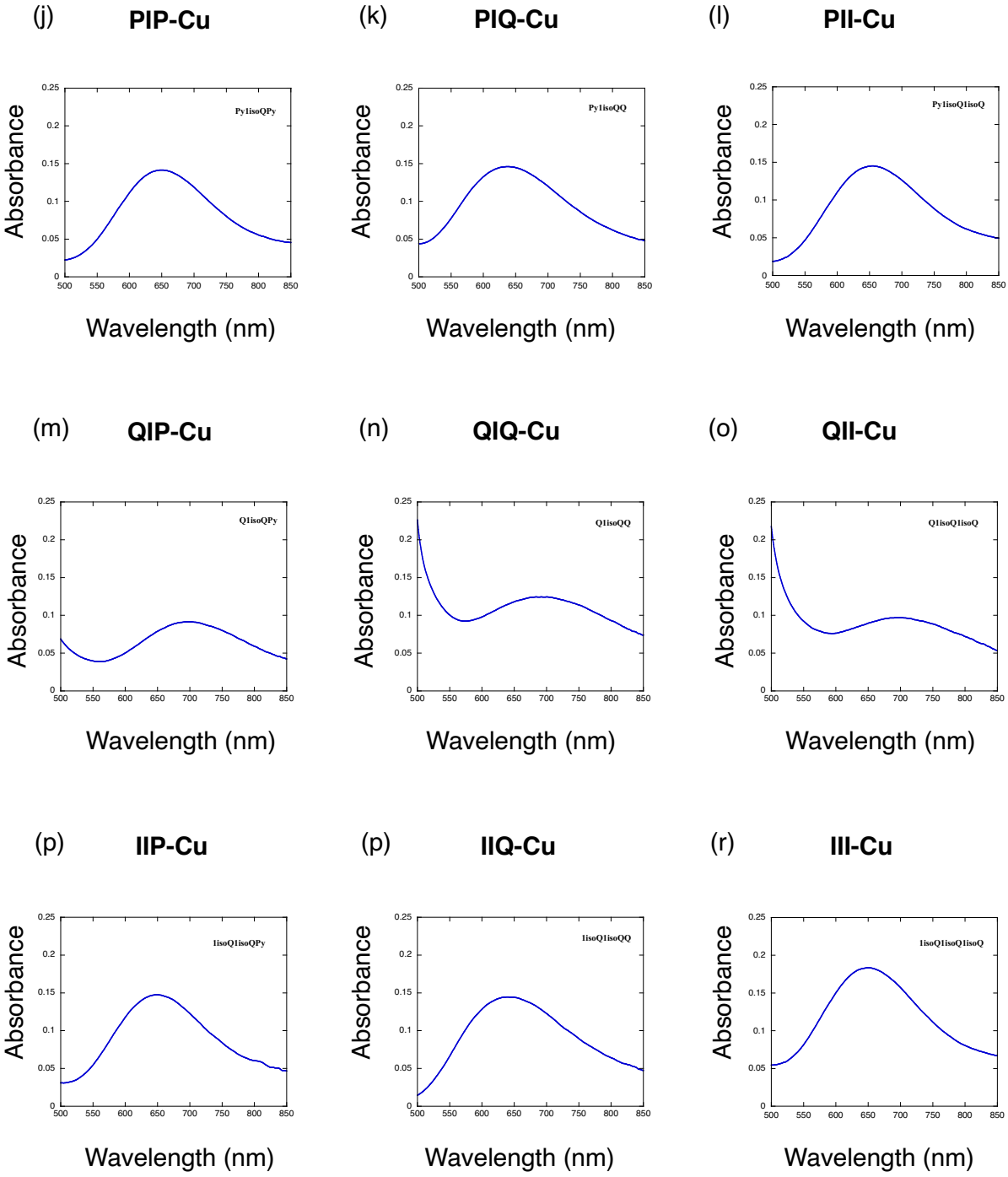
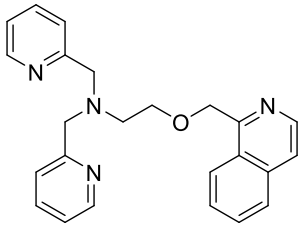
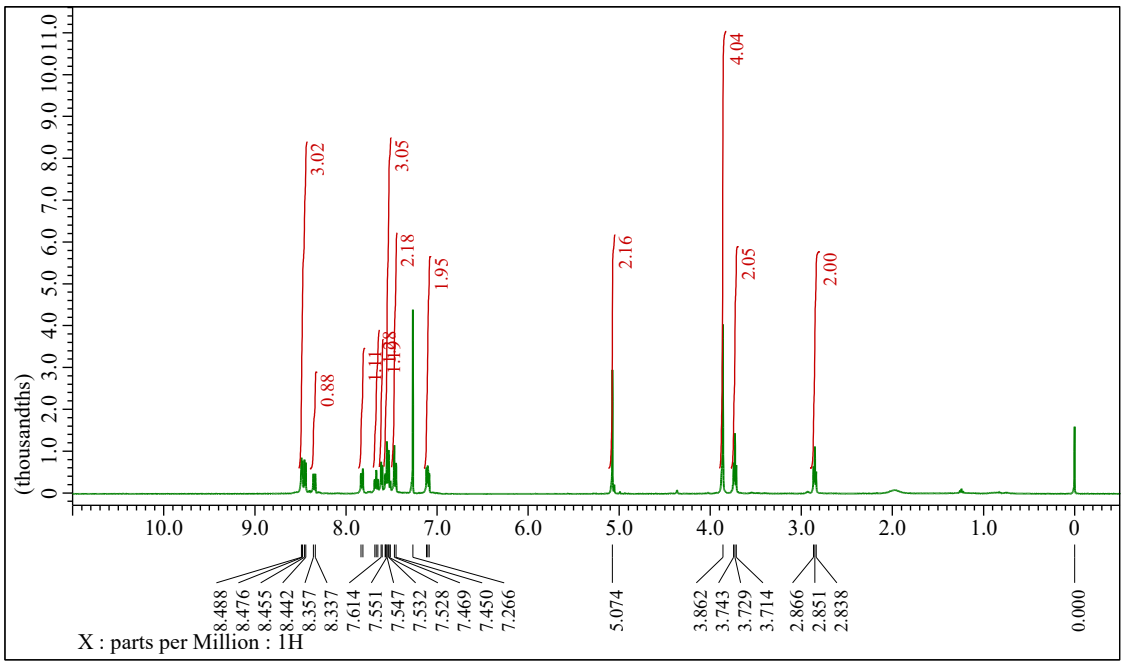


Fig. S2. Absorption spectrum of copper(II) complexes in methanol (1 mM). (a) **PPP-Cu**, (b) **PPQ-Cu**, (c) **PPI-Cu**, (d) **PQP-Cu**, (e) **PQQ-Cu**, (f) **PQI-Cu**, (g) **QQP-Cu**, (h) **QQQ-Cu**, (i) **QQI-Cu**, (j) **PIP-Cu**, (k) **PIQ-Cu**, (l) **PII-Cu**, (m) **QIP-Cu**, (n) **QIQ-Cu**, (o) **QII-Cu**, (p) **IIP-Cu**, (q) **IIQ-Cu** and (r) **III-Cu**.

$^{1}H/^{13}C$ NMR spectrum



PPI



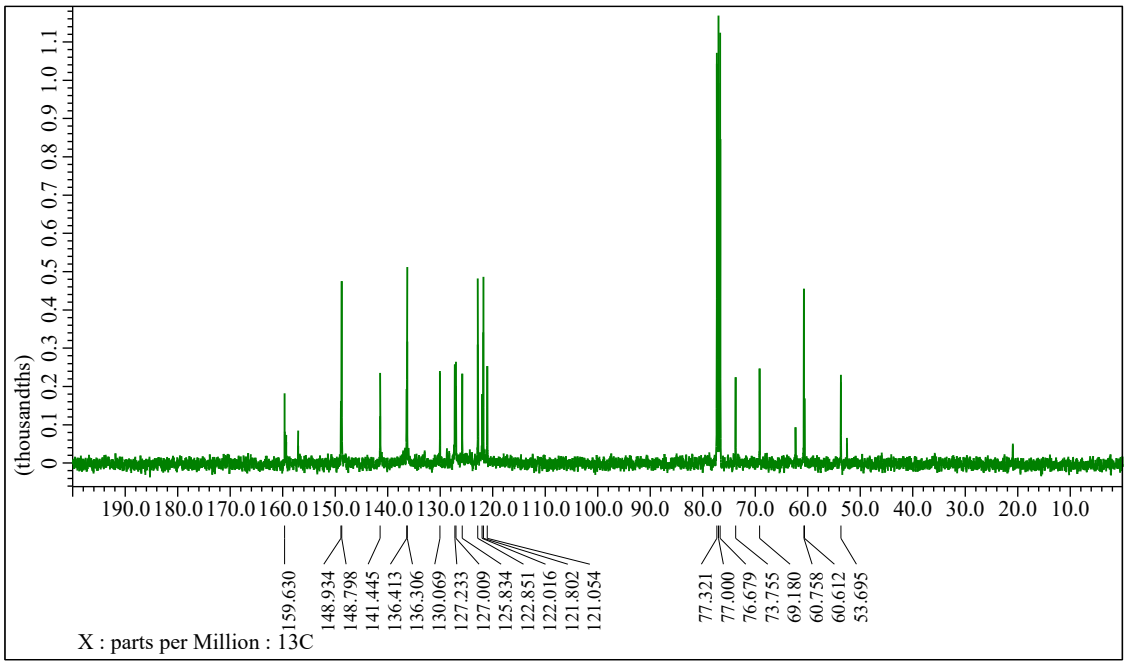


Fig. S3. $^{1}H/^{13}C$ NMR spectrum of **PPI** in $CDCl_3$.

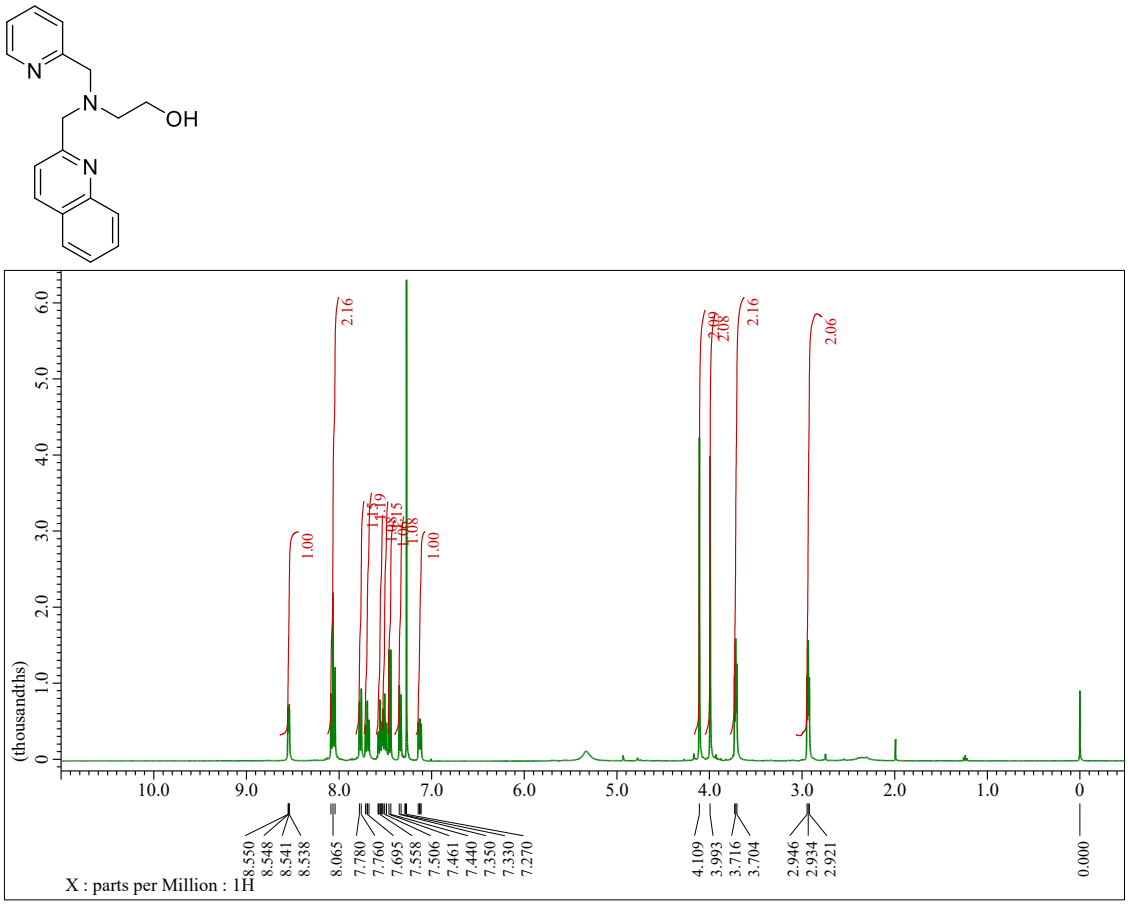


Fig. S4. ^{1}H NMR spectrum of 2-((2-pyridylmethyl)(2-quinolylmethyl)-amino)ethanol in $CDCl_3$.

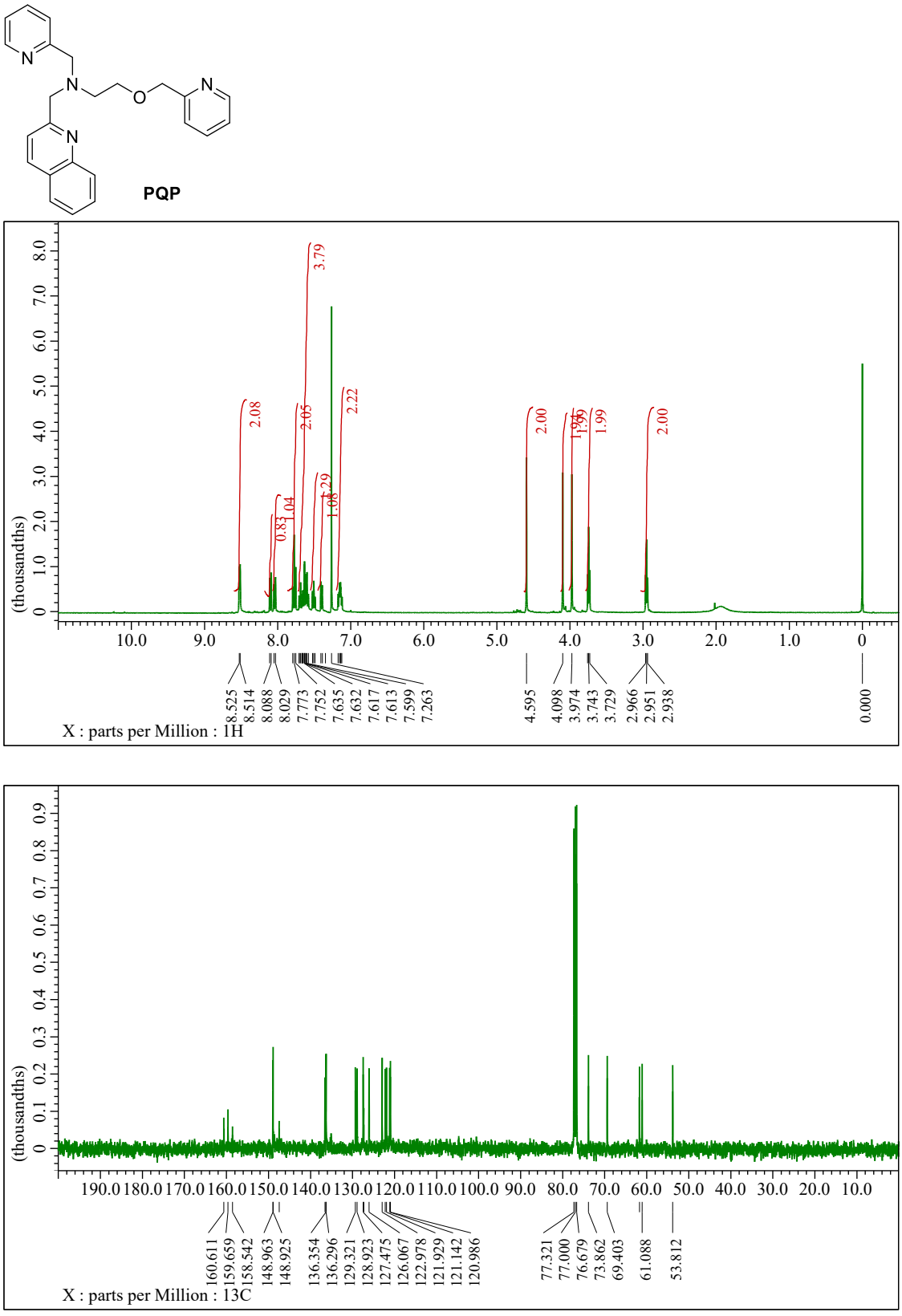


Fig. S5. $^{1}H/^{13}C$ NMR spectrum of **PQP** in $CDCl_3$.

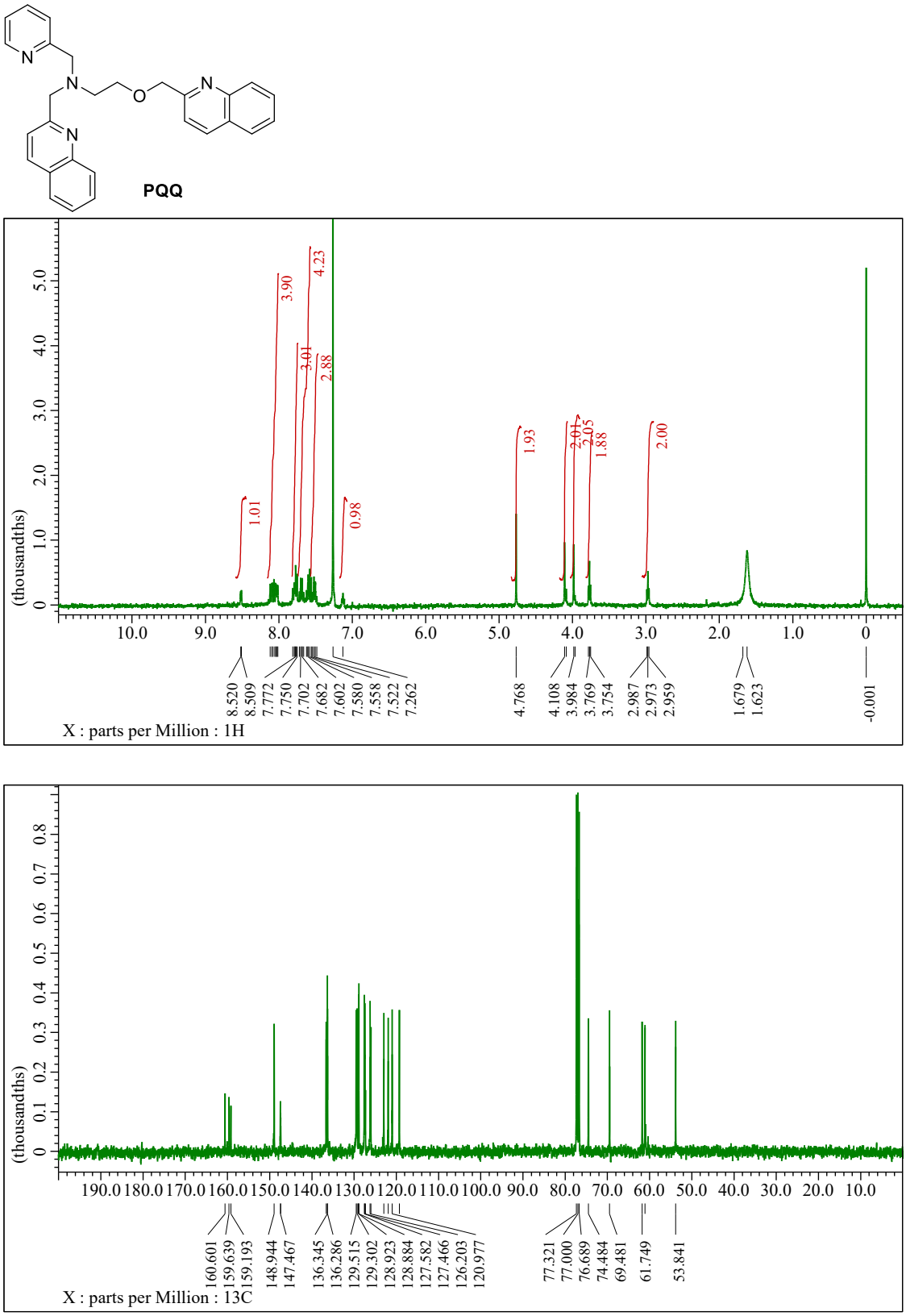


Fig. S6. $^{1}H/^{13}C$ NMR spectrum of **PQQ** in $CDCl_3$.

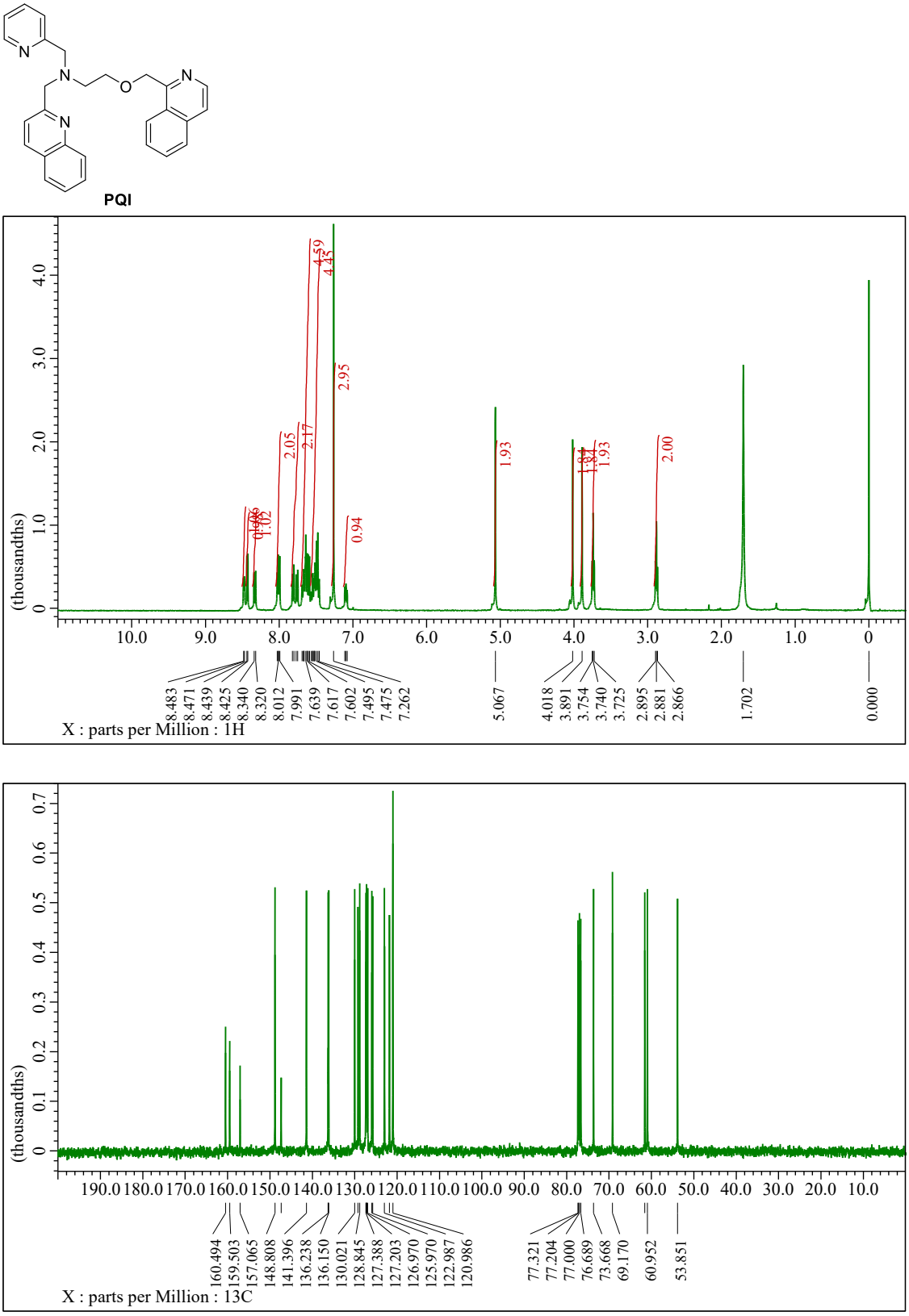


Fig. S7. $^{1}H/^{13}C$ NMR spectrum of **PQI** in $CDCl_3$.

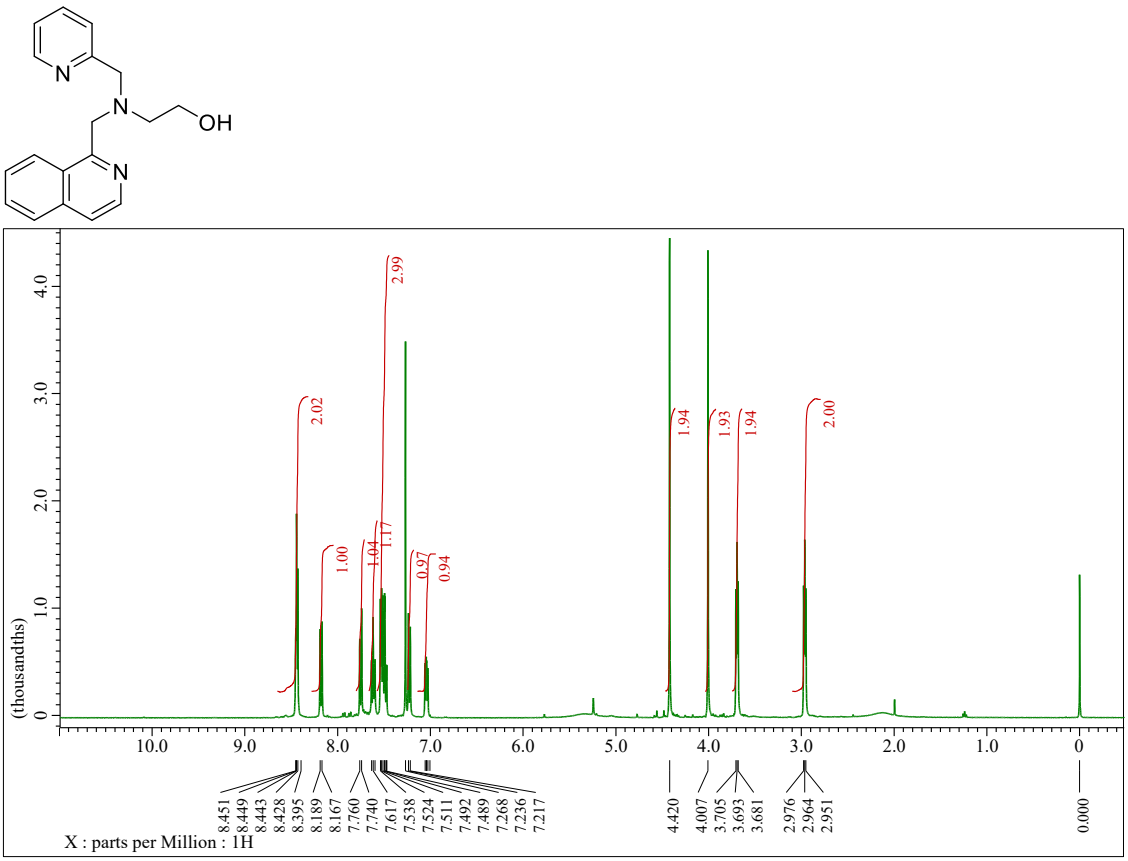


Fig. S8. ^{1}H NMR spectrum of 2-((2-pyridylmethyl)(1-isoquinolylmethyl)-amino)ethanol in $CDCl_3$.

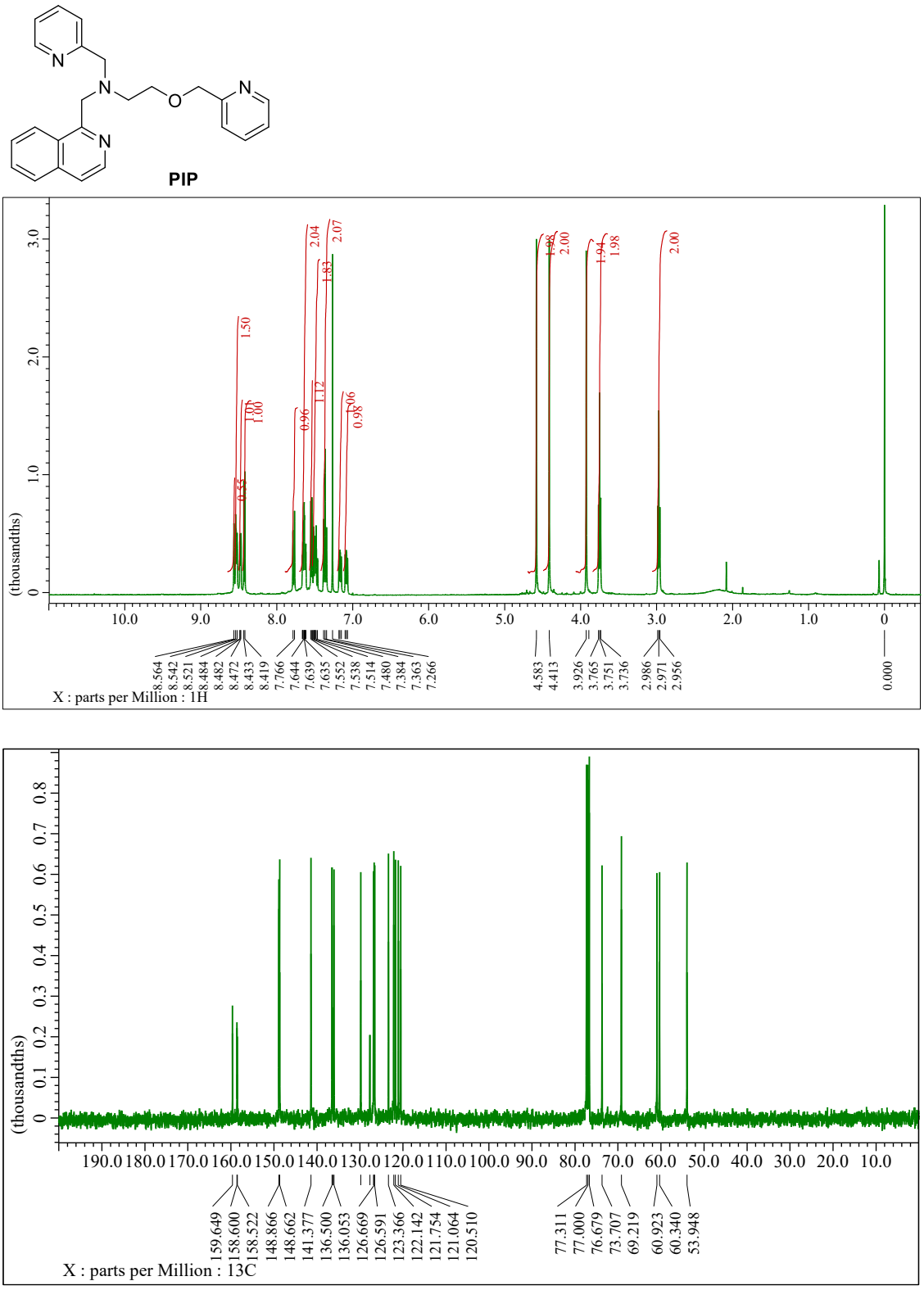


Fig. S9. $^{1}H/^{13}C$ NMR spectrum of **PIP** in $CDCl_3$.

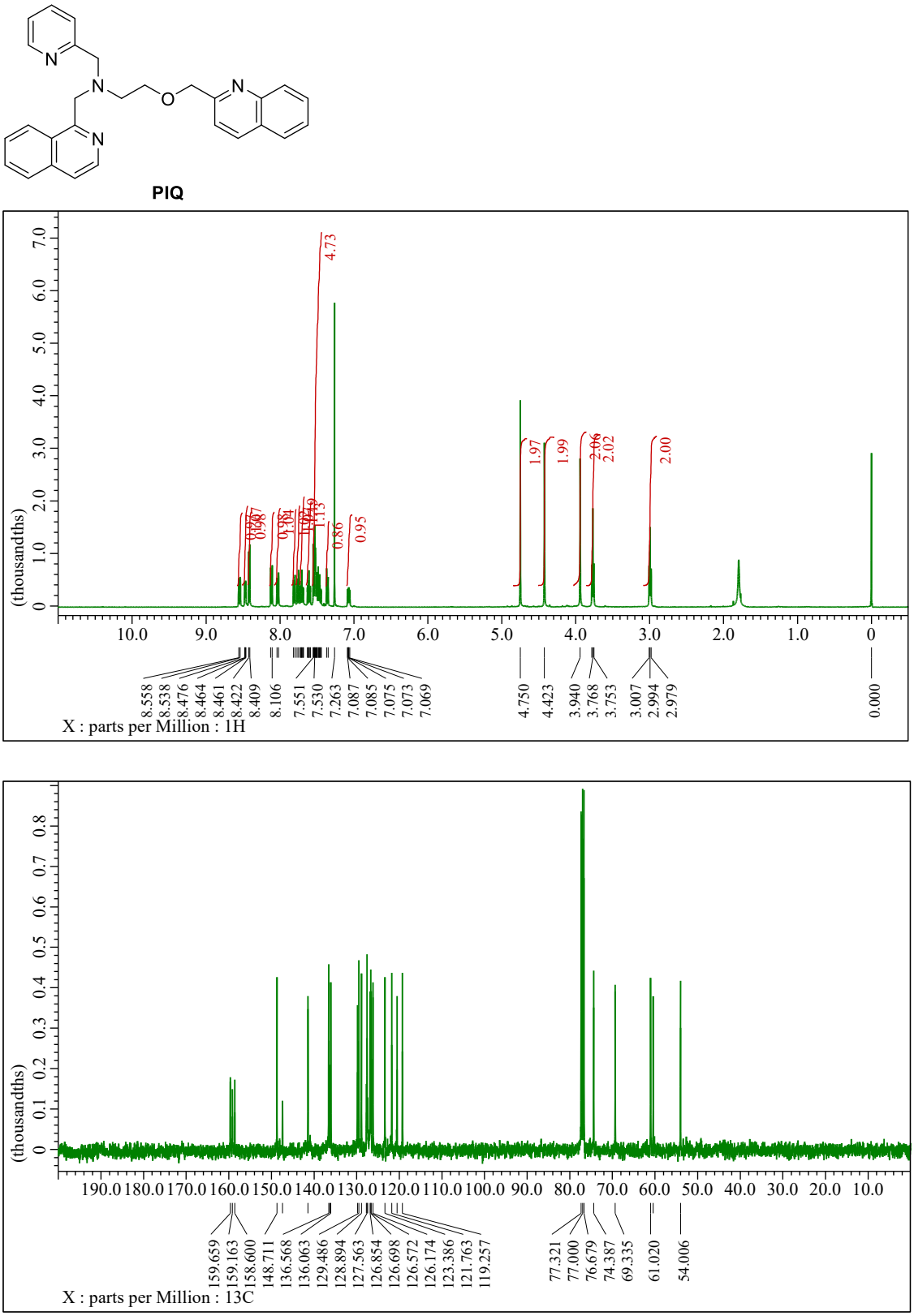


Fig. S10. $^{1}H/^{13}C$ NMR spectrum of **PIQ** in $CDCl_3$.

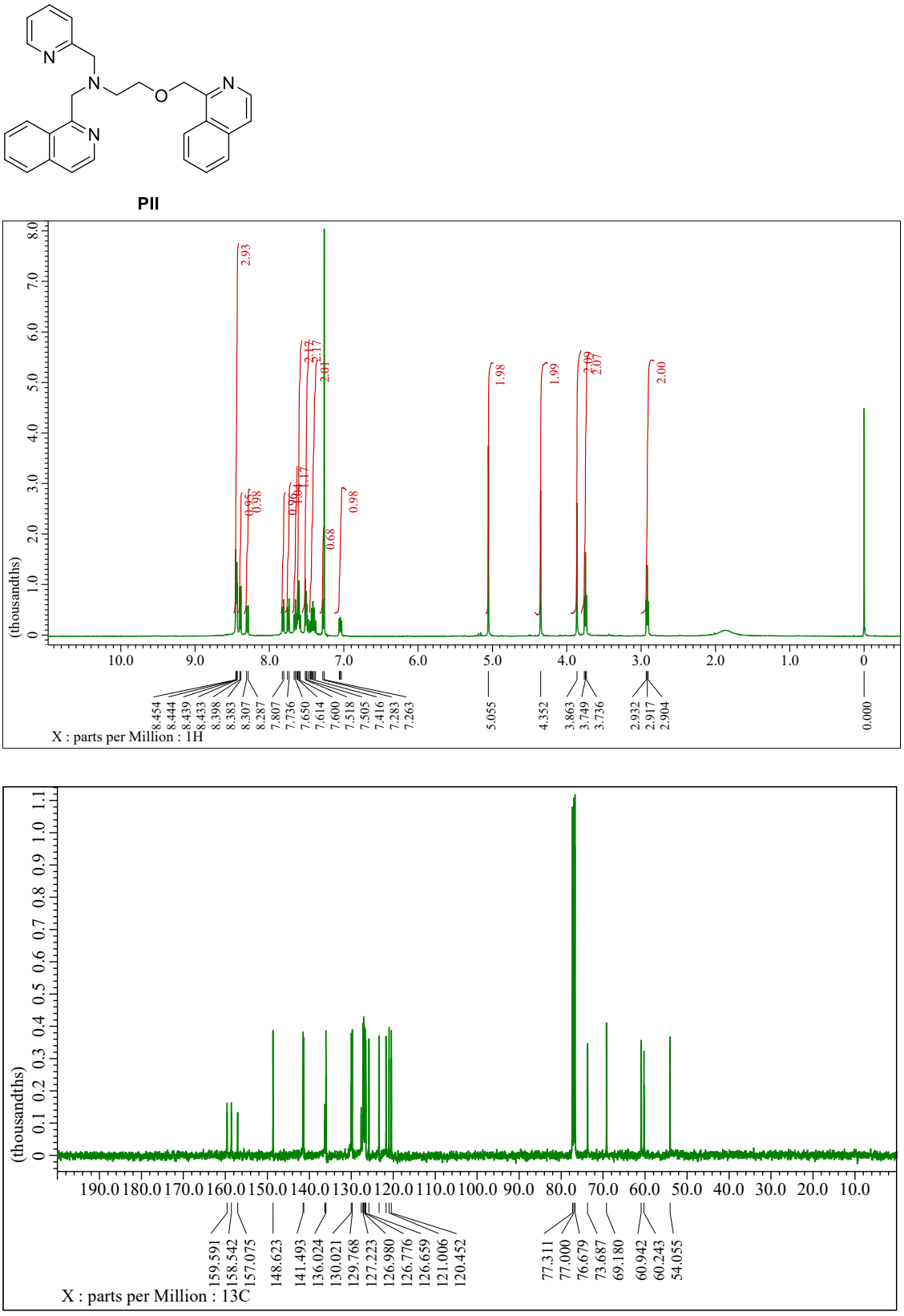


Fig. S11. $^{1}H/^{13}C$ NMR spectrum of **PII** in $CDCl_3$.

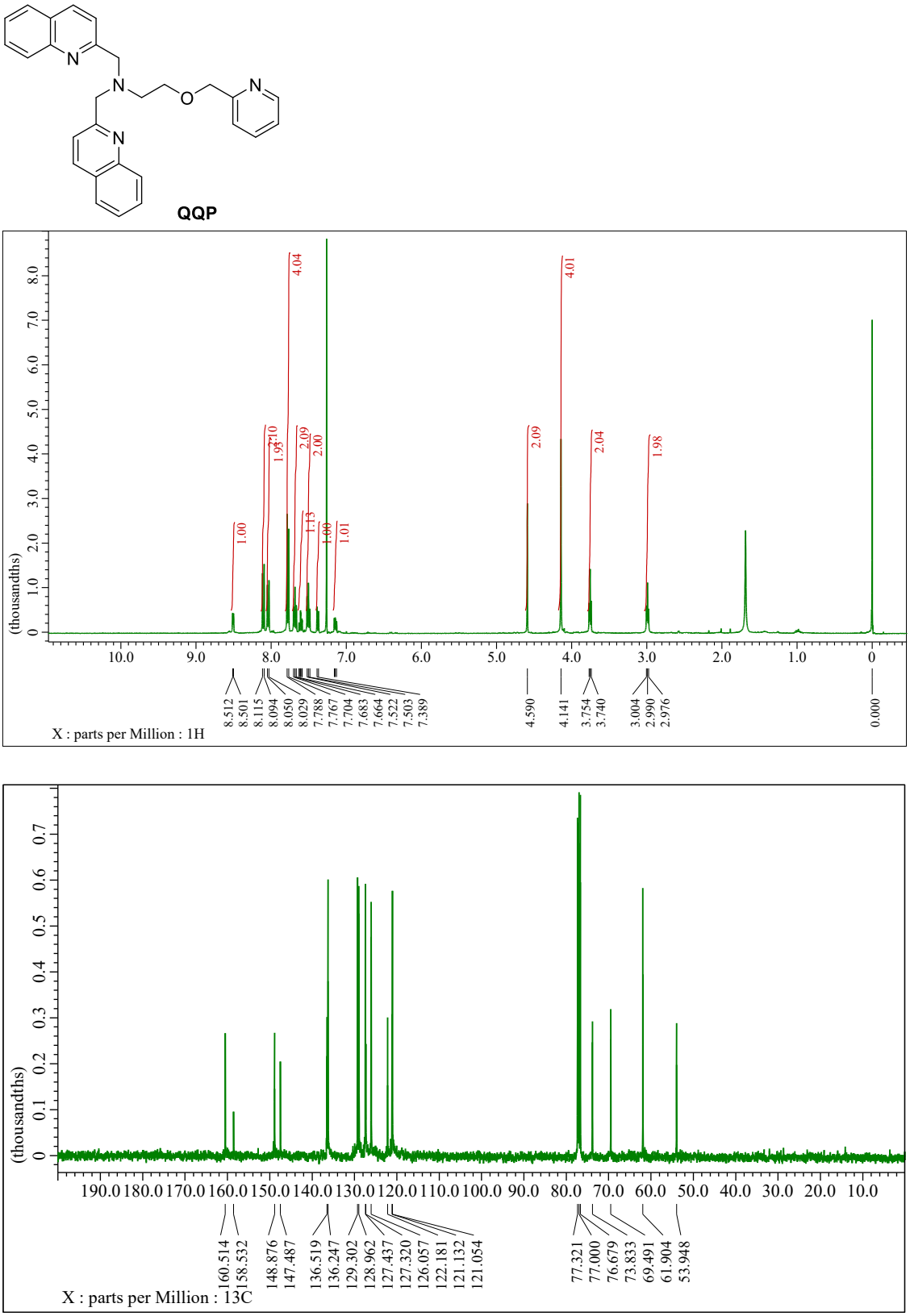


Fig. S12. $^{1}H/^{13}C$ NMR spectrum of **QQP** in $CDCl_3$.

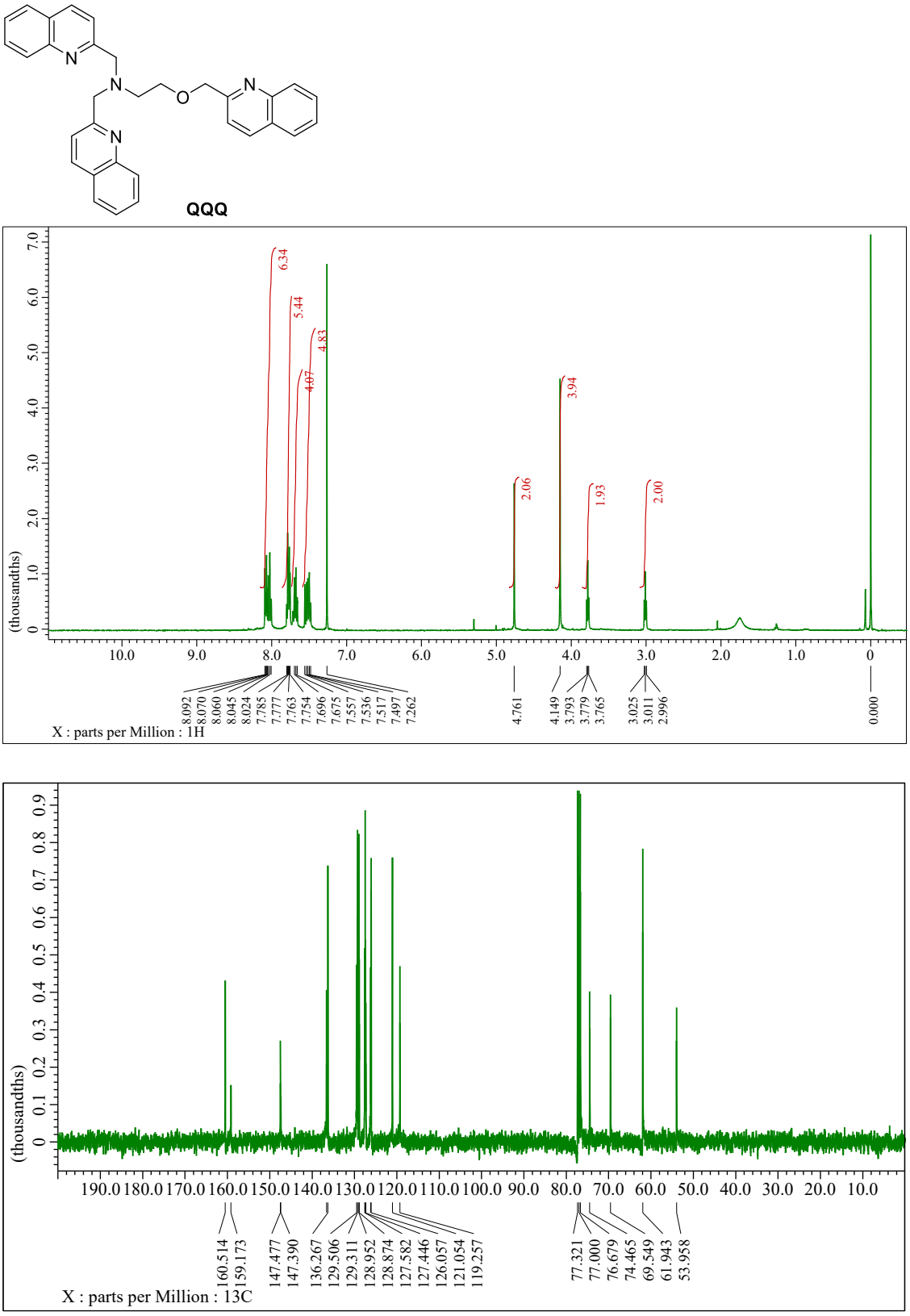


Fig. S13. $^{1}H/^{13}C$ NMR spectrum of **QQQ** in $CDCl_3$.

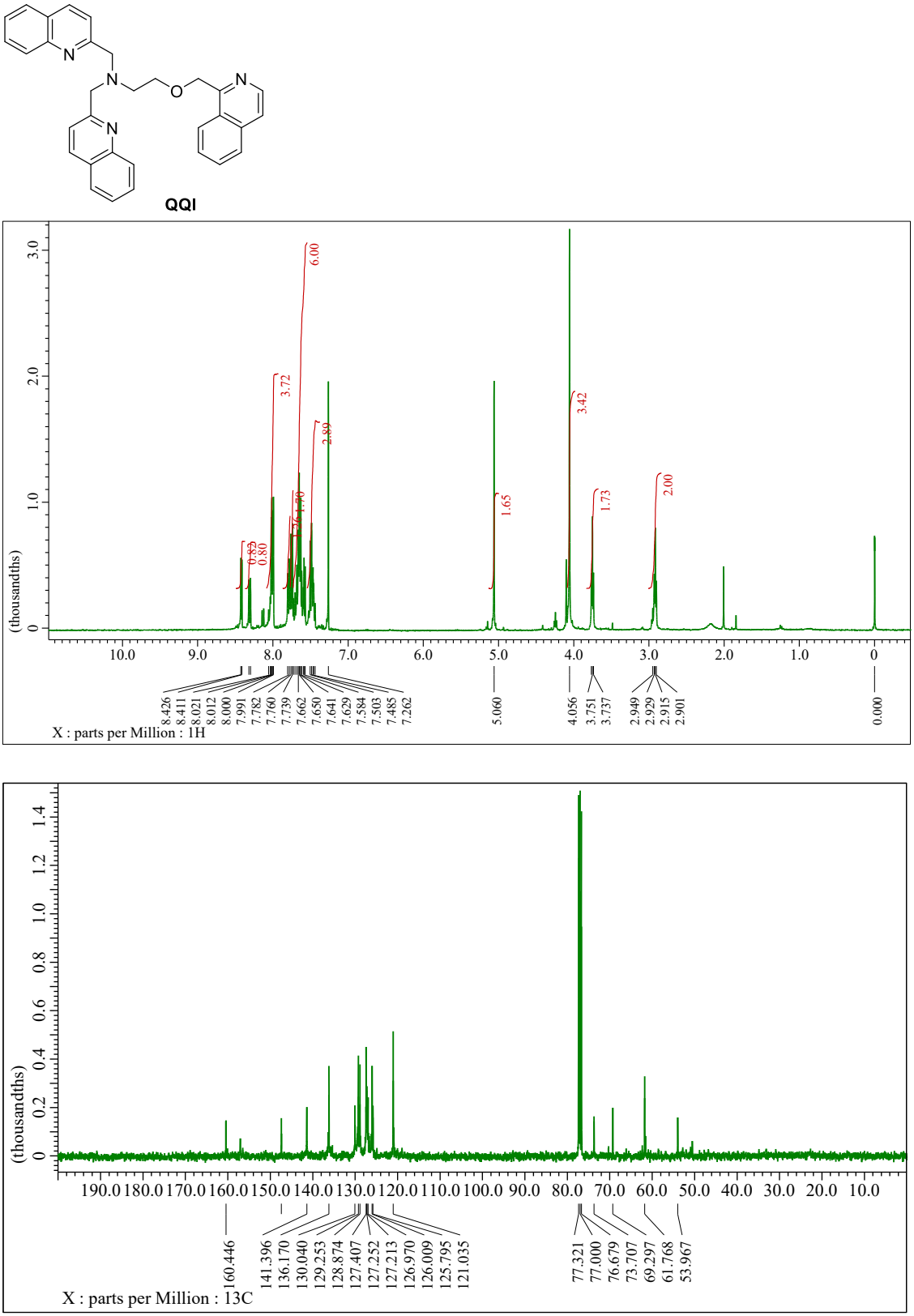


Fig. S14. $^{1}H/^{13}C$ NMR spectrum of **QQI** in $CDCl_3$.

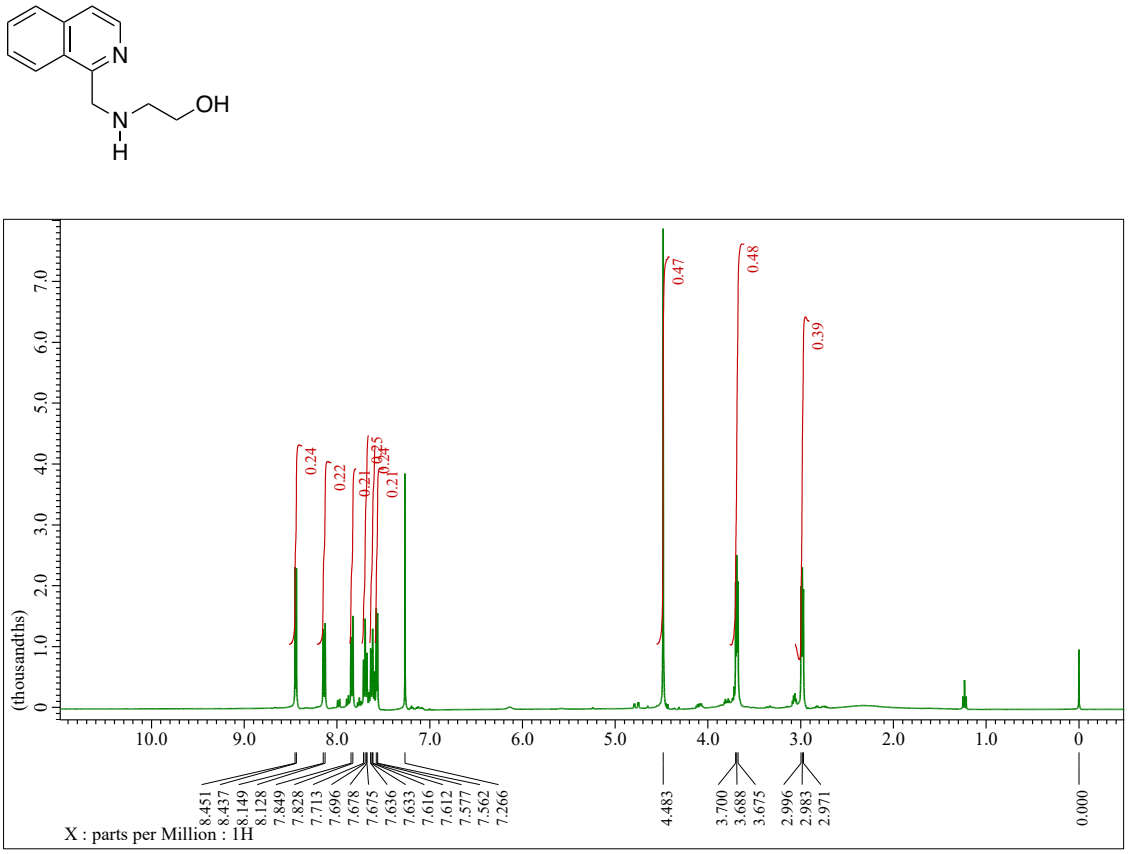


Fig. S15. ^{1}H NMR spectrum of 2-((1-isoquinolylmethyl)amino)ethanol in $CDCl_3$.

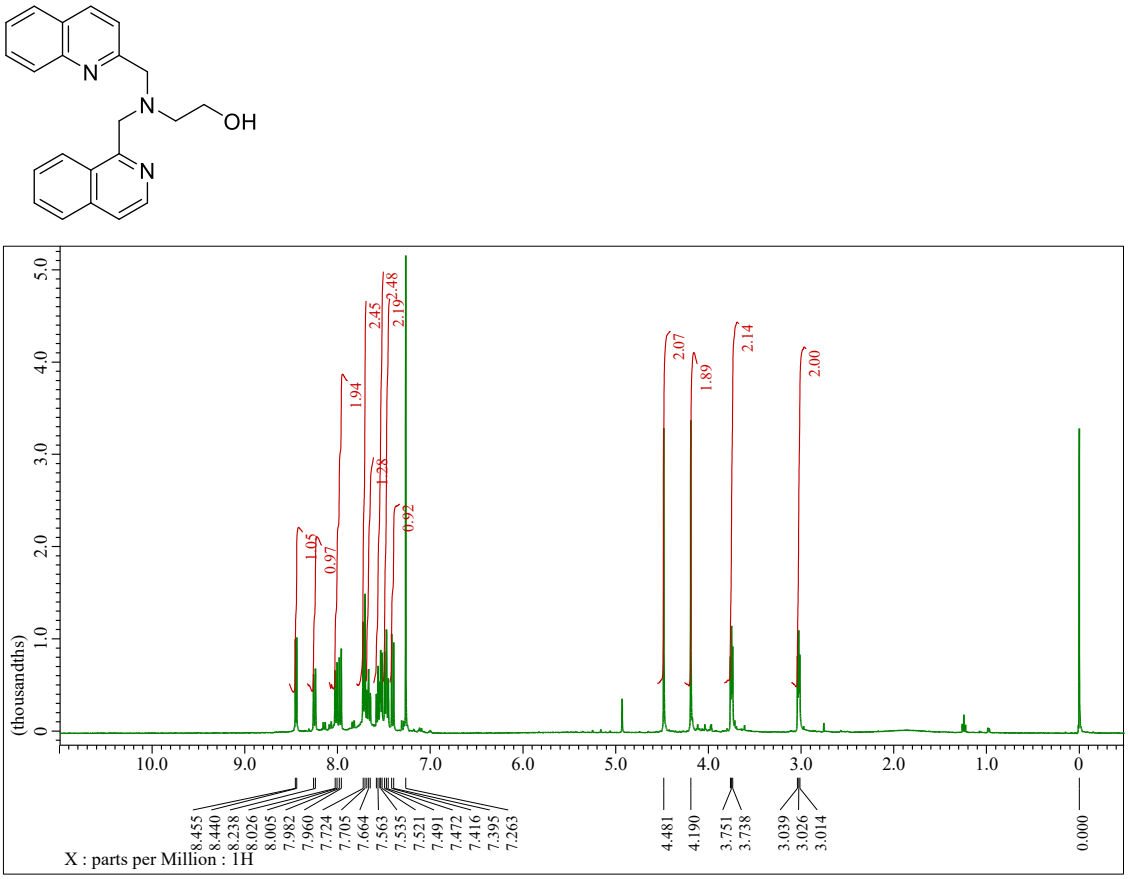


Fig. S16. ^{1}H NMR spectrum of 2-((2-quinolylmethyl)(1-isoquinolylmethyl)-amino)ethanol in $CDCl_3$.

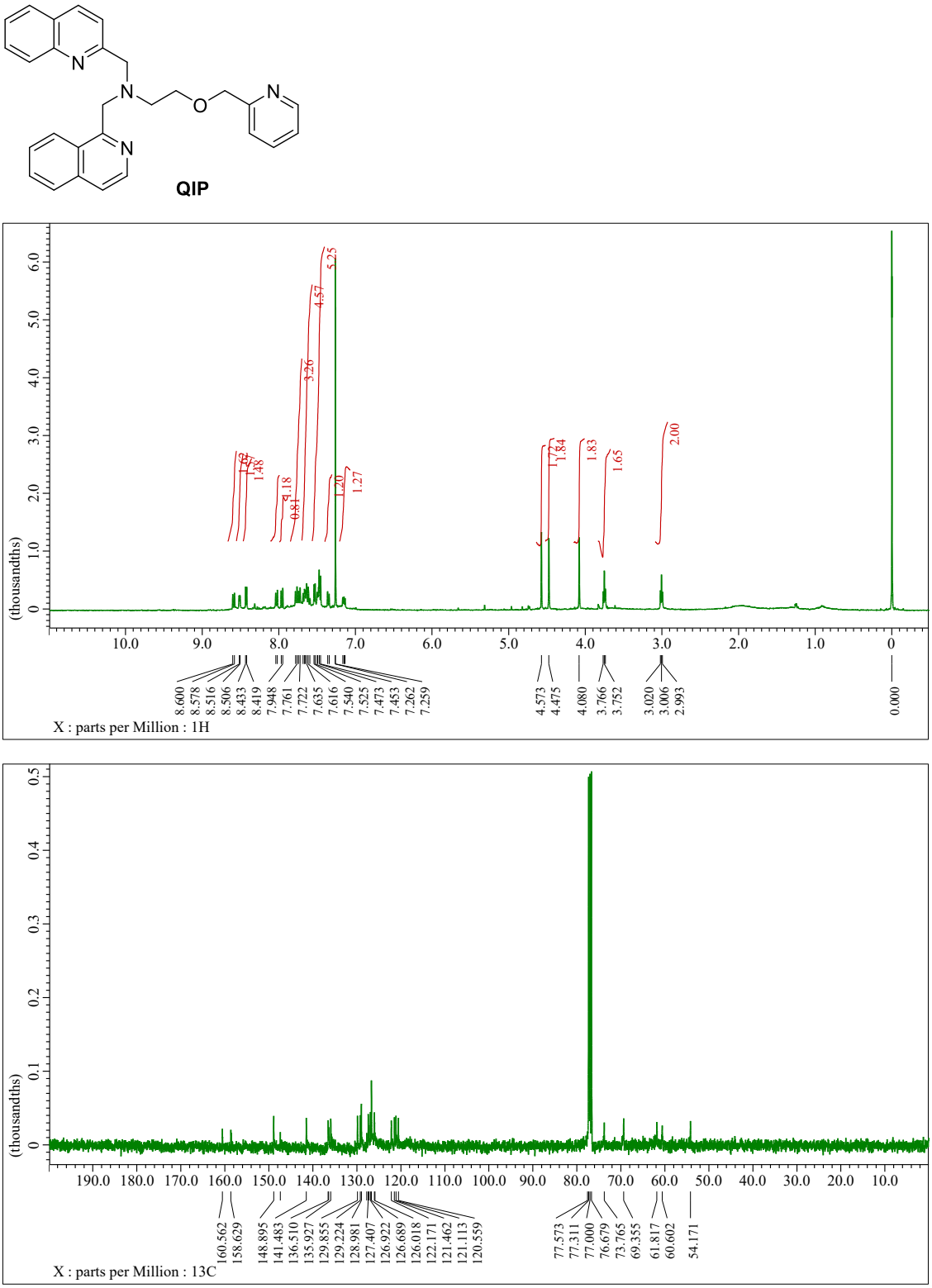


Fig. S17. $^{1}H/^{13}C$ NMR spectrum of **QIP** in $CDCl_3$.

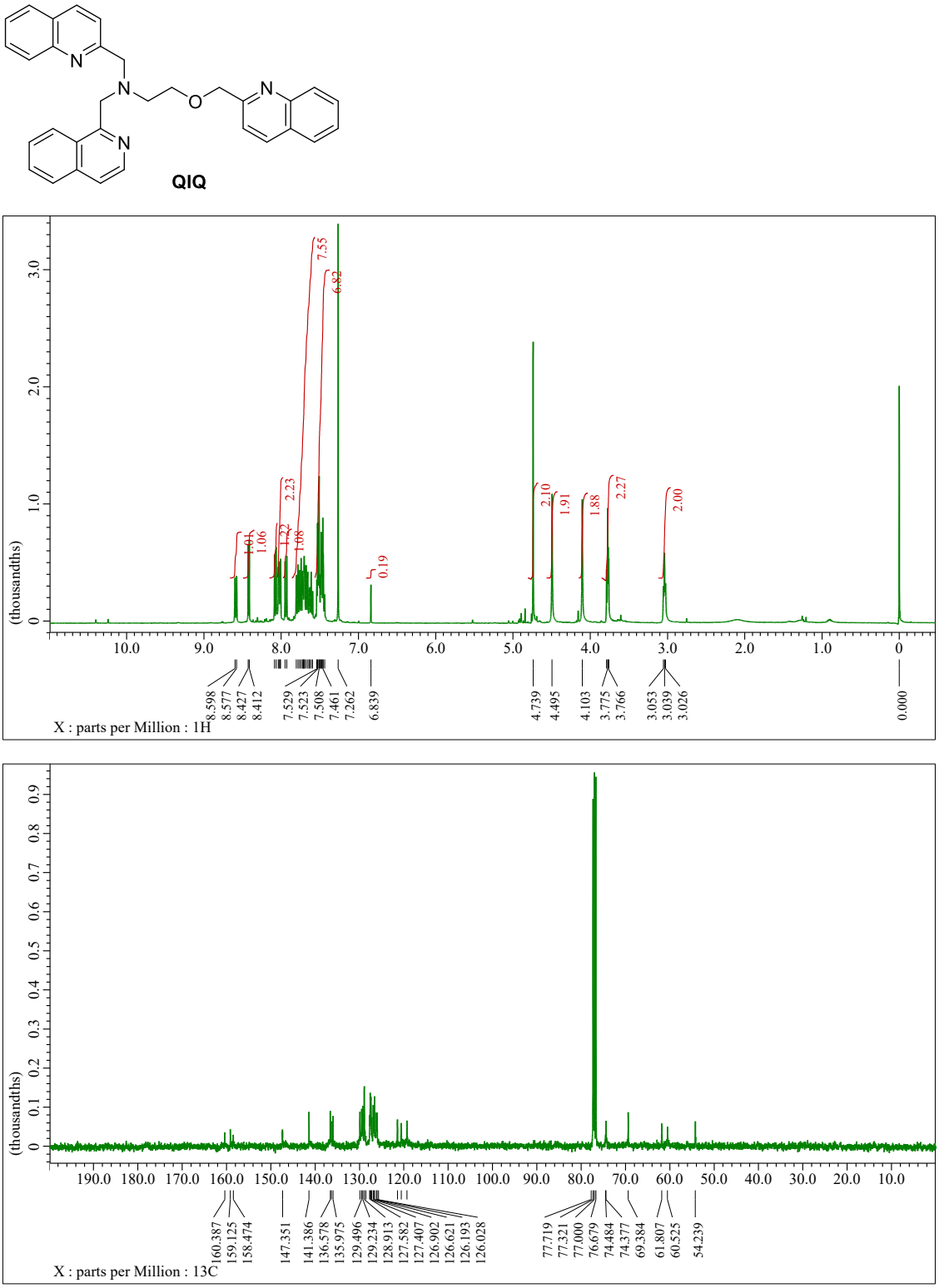


Fig. S18. $^{1}H/^{13}C$ NMR spectrum of **QIQ** in $CDCl_3$.

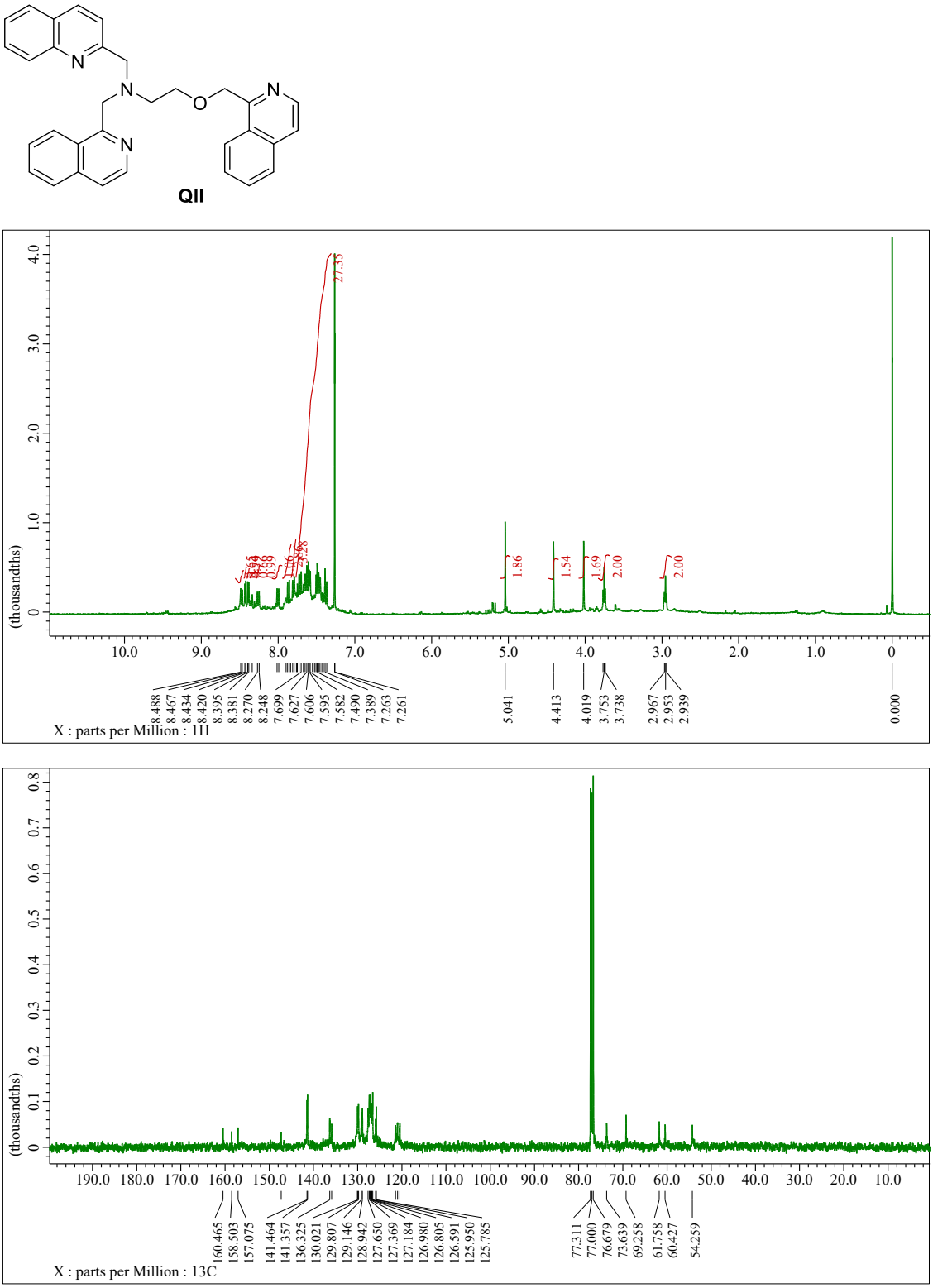


Fig. S19. $^{1}H/^{13}C$ NMR spectrum of **QII** in $CDCl_3$.

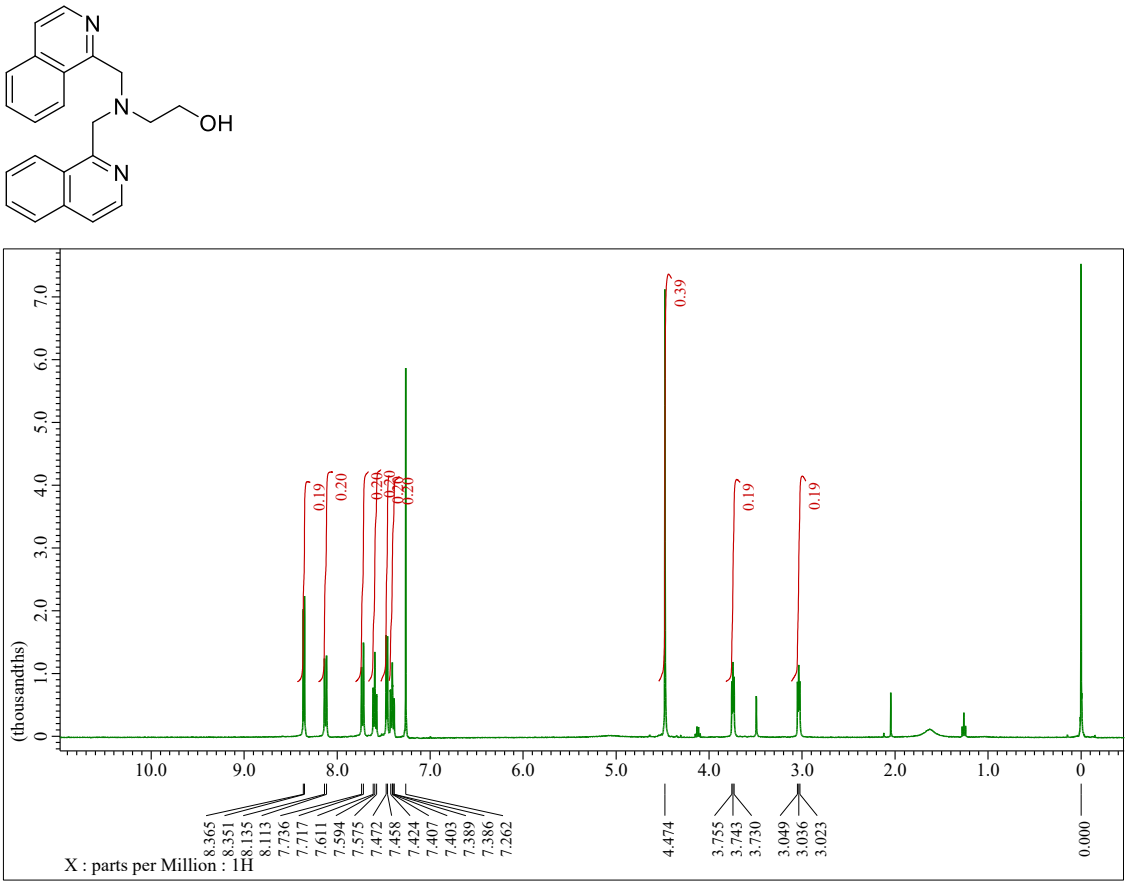


Fig. S20. ^{1}H NMR spectrum of 2-(bis(1-isoquinolylmethyl)amino)ethanol in $CDCl_3$.

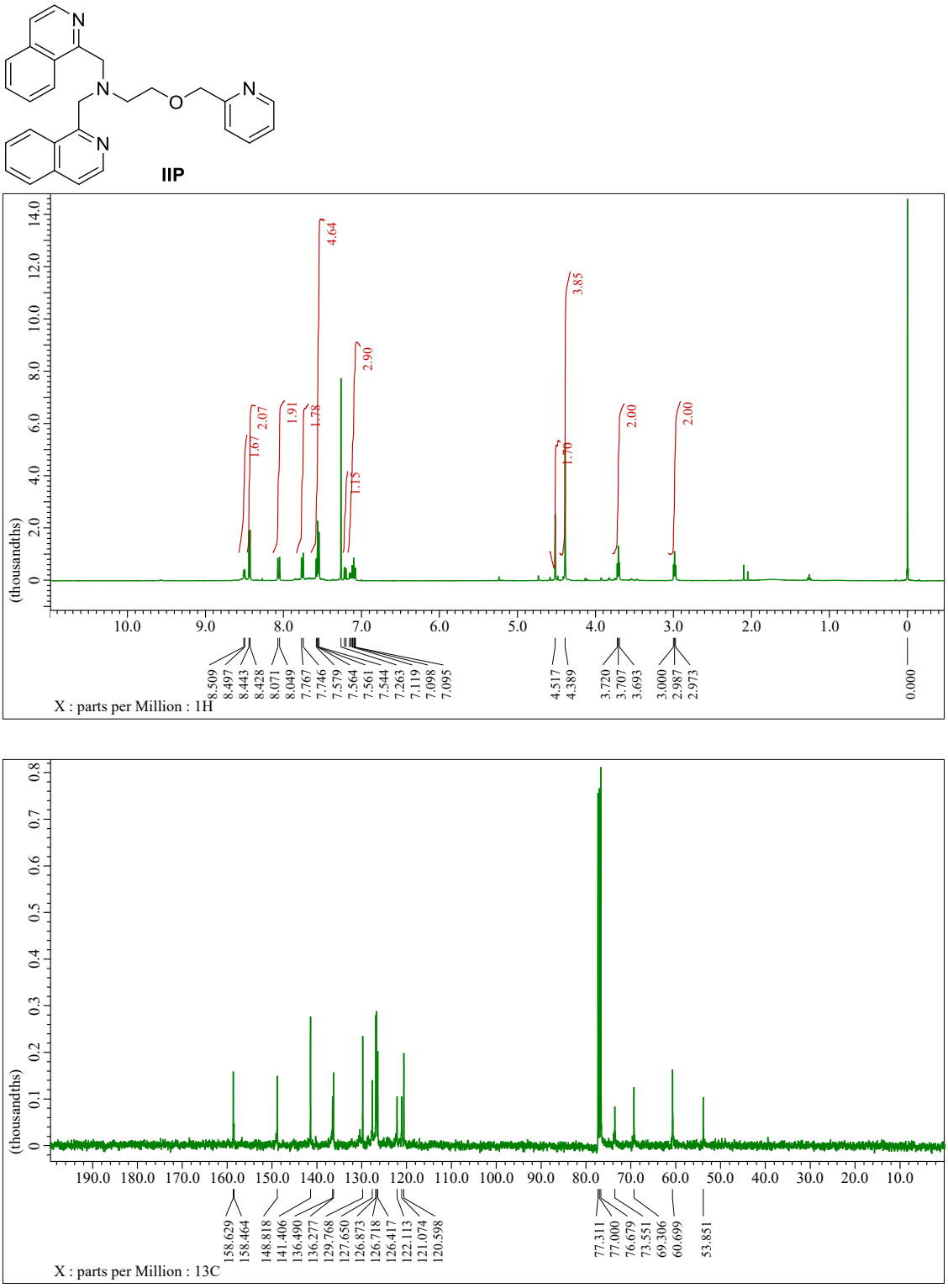
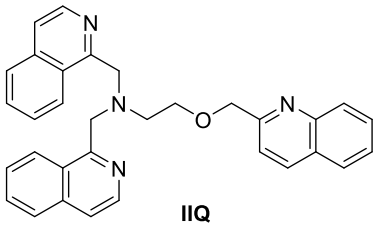
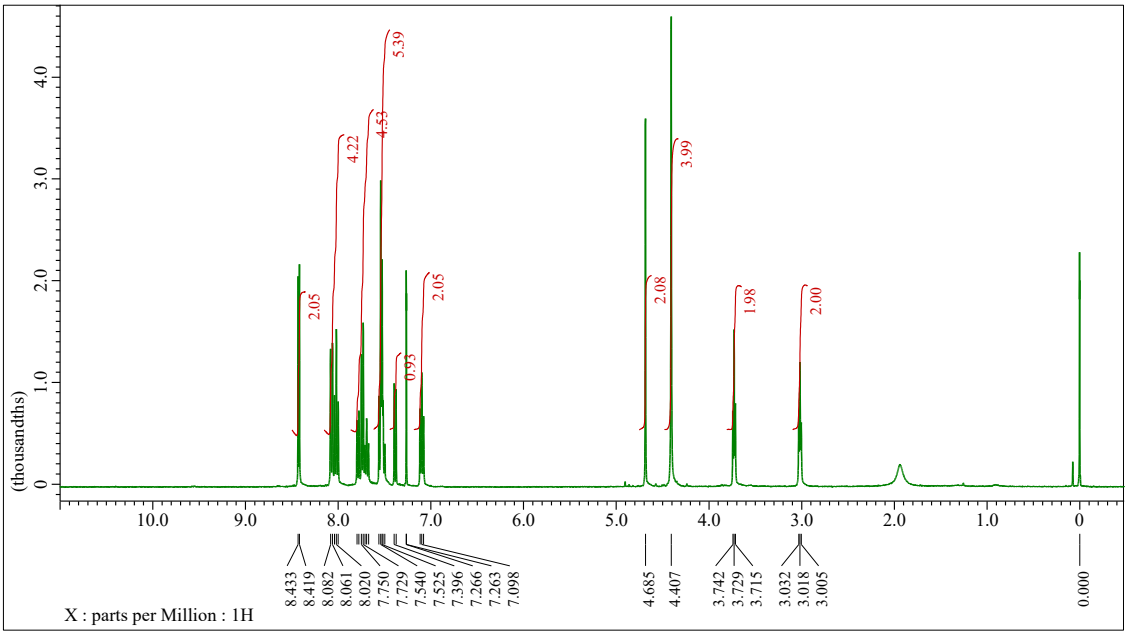


Fig. S21. $^{1}H/^{13}C$ NMR spectrum of **IIP** in $CDCl_3$.



IIQ



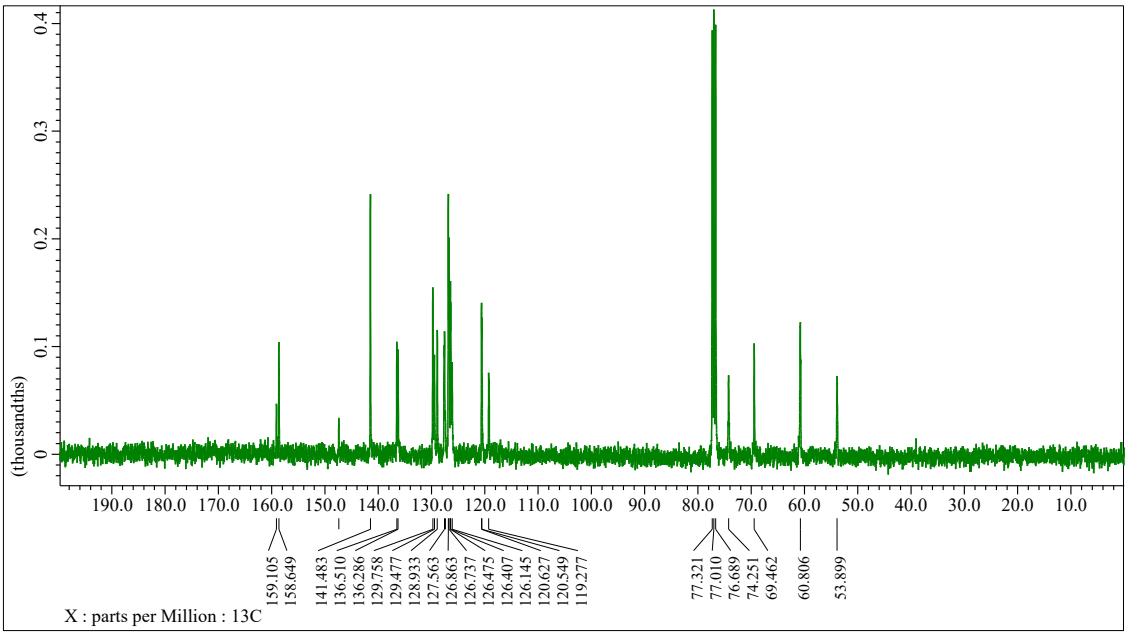
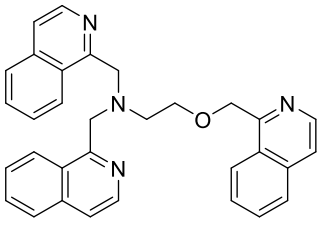
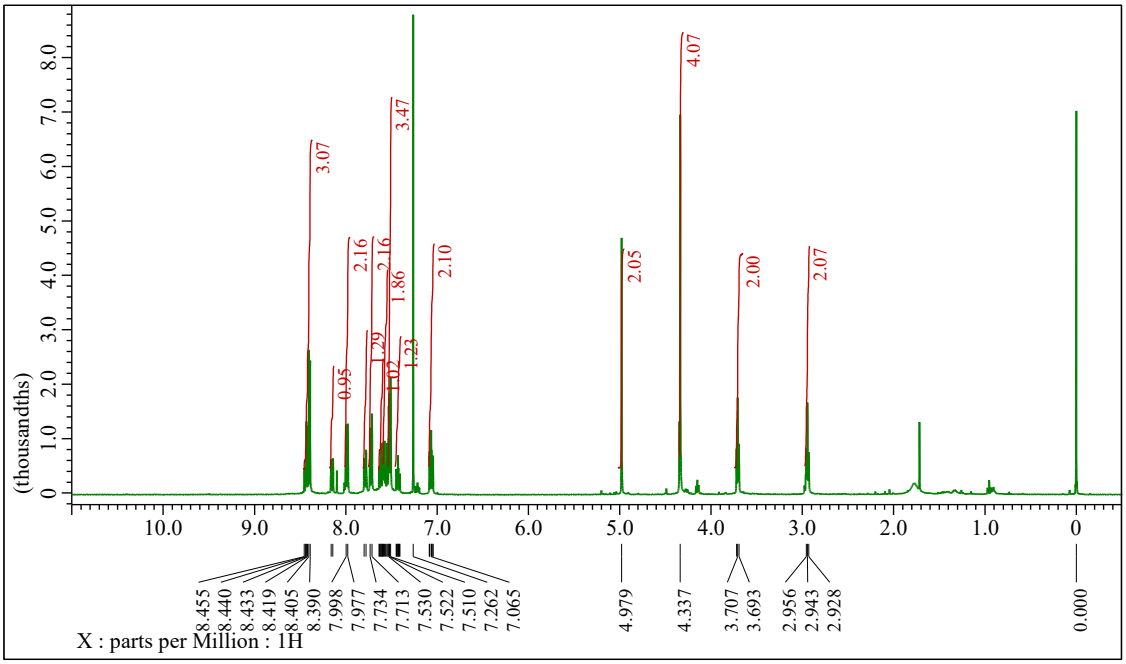


Fig. S22. $^{1}H/^{13}C$ NMR spectrum of **IIQ** in $CDCl_3$.



III



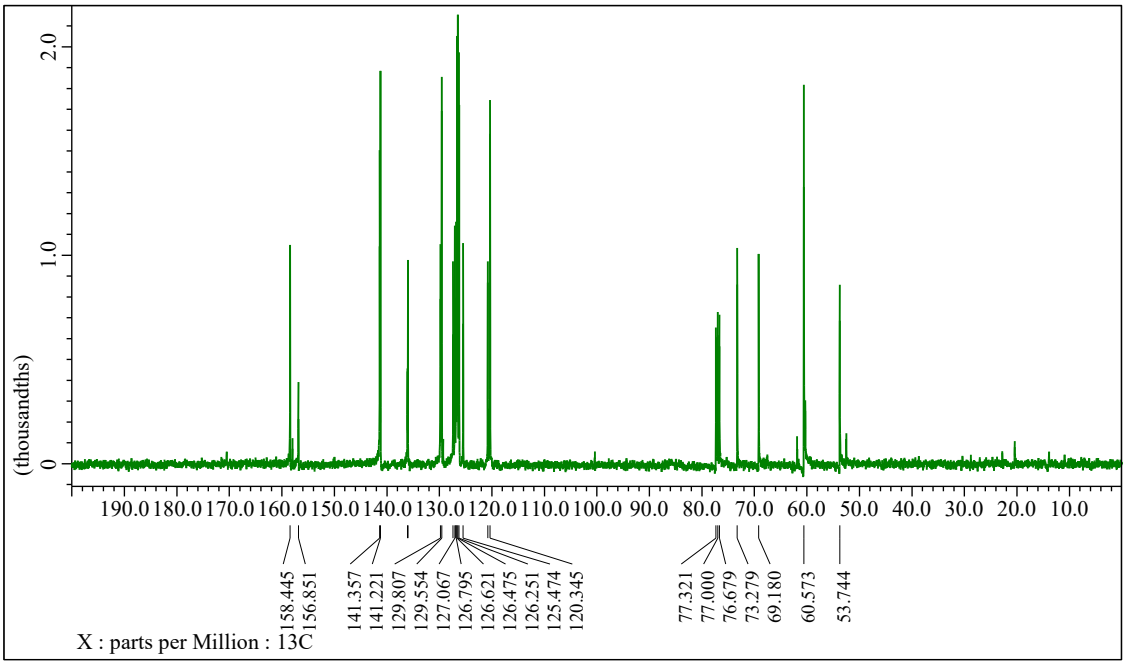


Fig. S23. $^{1}H/^{13}C$ NMR spectrum of **III** in $CDCl_3$.

References

S1. Y. Mikata, T. Fujimoto, N. Imai and S. Kondo, *Eur. J. Inorg. Chem.* 4310-4317 (2012).