SUPPORTING INFORMATION

Silver(I)-catalyzed C-X, C-C, C-N and C-O cross couplings using aminoquinoline directing group via elusive aryl-Ag(III) species

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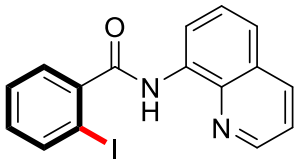
General considerations

All reagents and solvents were purchased from Sigma Aldrich, Fisher Scientific or Fluorochem and used without further purification. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker 400 AVANCE spectrometer in the corresponding deuterated solvent ($CDCl_3$ and D_6-DMSO) and calibrated relative to the residual protons of the solvent. Quantification of reaction yields through integration of peaks was performed using an internal reference (1,3,5-trimethoxybenzene). High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF-Q IITM instrument using ESI source at Serveis Tècnics, University of Girona. IR Spectra (FTIR) were recorded on a FT-IR Alpha spectrometer from Bruker with a PLATINUM-ATR attachment using OPUS software to process the data. All reactions were carried out in a N_2 drybox with O_2 and H_2O concentrations <1 ppm.

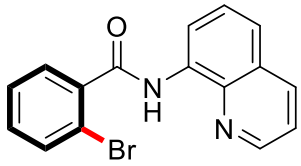
1. Synthesis and characterization data for substrates

2-iodo-*N*-(quinolin-8-yl)benzamide (L_1-I)



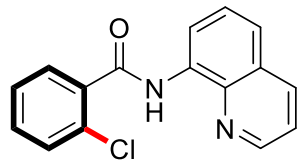
This substrate has been synthesized according to the procedure described in the literature from 8-aminoquinoline and the benzoyl chloride:[1] To a solution of 8-aminoquinoline (0.50 g, 3.47 mmol), 2-iodobenzoyl chloride (0.92 g, 3.47 mmol) in pyridine (10 mL), was heated to 130 ºC and stirred for 1 hour. After the reaction time, the mixture was left to cool to 70 ºC and poured into 50 mL of ice-cold water. The resulting crude mixture was extracted with dichloromethane (3 x 20 mL) and the organic layers were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. Purification by column chromatography in dichloromethane afforded a crystalline solid (1.03 g, 80 % of a pale yellow solid). **^{1}H-NMR** ($CDCl_3$, 400MHz, 298 K) δ (ppm): 10.15 (s, 1H), 8.95 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.78 (dd, *J* = 4.2 Hz, 1.6 Hz, 1H), 8.18 (dd, *J* = 8.3 Hz, 1.6 Hz, 1H), 7.97 (dd, *J* = 8.0 Hz, 0.8, 1H), 7.64-7.56 (m, 3H), 7.49-7.44 (m, 2H), 7.18 (ddd, *J* = 8.0 Hz, 7.2 Hz, 1.6 Hz, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298K) δ (ppm): 167.5, 148.4, 142.3, 140.3, 138.6, 136.4, 134.3, 131.4, 128.5, 128.3, 128.0, 127.4, 122.2, 121.7, 116.9, 92.8. **HRMS** (ESI, m/z): Calculated for $C_{16}H_{11}IN_2O$ $[M+H]^+$ 374.9989, Found 374.9984. **R_f**: 0.64 (dichloromethane). This compound is known and the data described are in agreement with the previous reports.[2]

2-bromo-*N*-(quinolin-8-yl)benzamide (L_1-Br)



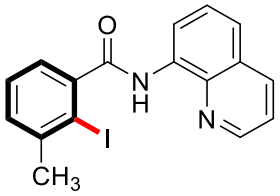
This substrate was prepared according to the general procedure described above for the synthesis of substrate L_1-I. 8-Aminoquinoline (0.50 g, 3.47 mmol), 2-bromobenzoyl chloride (0.76 g, 3.47 mmol) were used (0.88 g, 78 % of a white solid). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298K) δ (ppm): 10.29 (s, 1H), 8.95 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.79 (dd, *J* = 4.4 Hz, 2.0 Hz, 1H), 8.19 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.73-7.69 (m, 2H), 7.63-7.57 (m, 2H), 7.48-7.43 (m, 2H), 7.35 (ddd, *J* = 7.9 Hz, 7.2 Hz, 1.6 Hz, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 166.0, 148.4, 138.7, 138.4, 136.4, 134.3, 133.7, 131.5, 129.6, 128.0, 127.7, 127.4, 122.2, 121.7, 119.7, 116.8. **HRMS** (ESI, m/z): Calculated for $C_{16}H_{11}BrN_2O$ $[M+H]^+$ 327.0128, Found 327.0132. **R_f**: 0.55 (dichloromethane). This compound is known and the data described are in agreement with the previous reports.[3]

2-chloro-*N*-(quinolin-8-yl)benzamide (L_1-Cl)



This substrate was prepared according to the general procedure described above for the synthesis of substrate L_1-I. 8-Aminoquinoline (0.50 g, 3.47 mmol), 2-chlorobenzoyl chloride (0.61 g, 3.47 mmol) were used (0.73 g, 75 % of white solid). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 10.49 (s, 1H), 8.96 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.80 (dd, *J* = 4 Hz, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.82 (dd, *J* = 6.8 Hz, 2.4 Hz, 1H), 7.63-7.56, (m, 2H), 7.52-7.39 (m, 4H). **^{13}C-NMR** ($CDCl_3$, 1 00 MHz, 298 K) δ (ppm): 164.9, 148.4, 138.7, 136.4, 135.9, 134.5, 131.5, 131.5, 130.6, 130.1, 128.0, 127.4, 127.2, 122.2, 121.7, 116.9. **HRMS** (ESI, m/z): Calculated for $C_{16}H_{11}ClN_2O$ $[M+H]^+$ 283.0633, Found 283.0643. **R_f**: 0.56 (dichloromethane). This compound is known and the data described are in agreement with the previous reports.[4]

2-iodo-3-methyl-*N*-(quinolin-8-yl)benzamide (L_2-I)



This substrate has been synthesized according to the procedure described in the literature from 8-aminoquinoline and the benzoic acid.[5] Oxoalyl chloride (0.4 mL, 1.2 equiv., 4.57 mmol) was added dropwise to a solution of 2-iodo-3-methylbenzoic acid (1 g, 3.81 mmol), DMF (3 drops) in anhydrous CH_2Cl_2 (15 mL) at 0ºC under N_2 atmosphere. The mixture was allowed to warm to room temperature and stirred during 5 h and then the solvent was removed. To a solution of 8-aminoquinoline (0.71 g, 1.3 equiv., 4.93 mmol), Et_3N (1.0 mL, 2.0 equiv., 7.62 mmol) and anhydrous CH_2Cl_2 (20 mL) were added. Acid chloride in anhydrous CH_2Cl_2 (5 mL) was added dropwise at 0ºC, and the solution was stirred overnight at room temperature. The resulting crude mixture was quenched with $NaHCO_3$ (15 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL) and the combined organic layers were washed with aqueous HCl (15 mL, 1M), and brine (5 mL), dried over magnesium sulfate, filtered and evaporated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (eluent: dichloromethane) to afford the desired compound (0.46 g, 31 % of a white solid). **^{1}H-NMR** ($CDCl_3$, 400MHz, 298 K) δ (ppm): 10.07 (s, 1H), 8.95 (dd, *J* = 7.3 Hz, *J* = 2.0 Hz, 1H), 8.77 (dd, J = 4.2 Hz, 1.7 Hz, 1H), 8.19 (dd, J = 8.3 Hz, 1.7 Hz, 1H), 7.64-7.55 (m, 2H), 7.46 (dd, *J* = 8.2 Hz, 4.3 Hz, 1H), 7.35 (s, 3H), 2.55 (s, 3H). **^{13}C-NMR** (CDCl3, 100 MHz, 298K) δ (ppm): 168.7, 148.5, 144.2, 143.3, 138.7, 136.5, 134.5, 130.9, 128.4, 128.2, 127.6, 125.4, 122.3, 121.9, 117.1, 99.7, 29.4. **IR (ATR)**: ῡ = 3339, 1669, 1567, 1519, 1483, 1421, 1385, 1325, 1278, 1150, 1009, 931, 821, 783, 763, 735, 715, 671, 610, 497, 443. **HRMS** (ESI, m/z): Calculated for $C_{17}H_{13}IN_2O$ $[M+Na]^+$ 410.9965, Found 410.9956. **R_f**: 0.68 (dichloromethane).

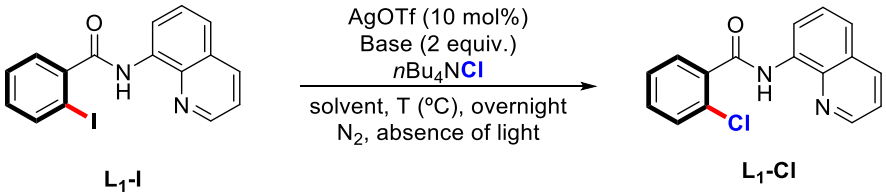
3. Silver-catalyzed cross-coupling reactions

3.1 Optimization of halide exchange reactions

General procedure for the optimization experiments

37.4 mg of **L1-I** (0.1 mmol), *n*Bu$_4$NCl, base (2 equiv., 0.2 mmol), AgOTf (2.6 mg, 10 mol%, 0.01 mmol) with 2.5 mL of solvent were added to a glass vial under an inert-atmosphere, and the vial sealed and covered with aluminum foil. The reaction mixture was stirred overnight at specified temperature. The crude mixture was extracted with ethyl acetate (3 x 10 mL) and the combined organic layers were dried over magnesium sulfate. The solvent was removed under reduced pressure. The crude reaction was analyzed by ^{1}H-NMR spectroscopy ($CDCl_3$) using 1,3,5-trimethoxybenzene as internal standard.

Table S1. Optimization of halide exchange catalysis



Entry	Base	Equiv. of *n*Bu4NCl	T (°C)	Solvent	AgOTf (mol %)	Yield (%) of L1-Cl[a]
1	-	10	100	CH_3CN	10	0
2	NaOAc	10	100	CH_3CN	10	12
3	K_3PO_4	10	100	CH_3CN	10	11
4	K_2CO_3	10	100	CH_3CN	10	0
5	Na_2CO_3	10	100	CH_3CN	10	95
6	Na_2CO_3	5	100	CH_3CN	10	48
7	Na_2CO_3	1	100	CH_3CN	10	0
8	Na_2CO_3	10	70	CH_3CN	10	33
9	Na_2CO_3	10	50	CH_3CN	10	25
10	Na_2CO_3	10	r.t.	CH_3CN	10	0
11	Na_2CO_3	10	100	DMSO	10	82
12	Na_2CO_3	10	100	DMSO	-	20
13	Na_2CO_3	10	100	CH_3CN	-	0

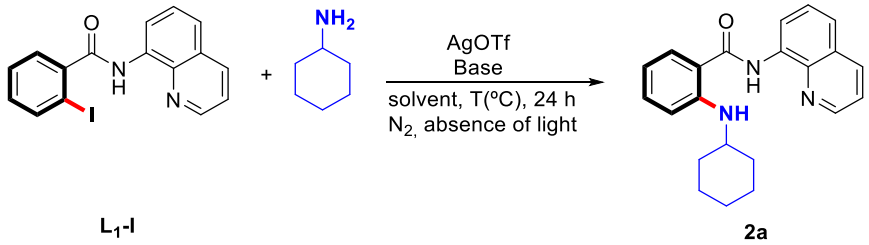
[a]Yield calculated from ^{1}H-NMR of crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

3.2 Optimization of C-N bond formation reactions

General procedure for the optimization experiments:

37.4 mg of **L1-I** (0.1 mmol), cyclohexanamine, base and catalytic amounts of AgOTf with 1 mL of solvent were added to a glass vial under an inert-atmosphere, and the vial was sealed and covered with aluminum foil. The reaction mixture was stirred at 100 °C for 24 hours. The resulting crude mixture was extracted with ethyl acetate (3 x 10 mL) and the organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure. The crude reaction was analyzed by ^{1}H-NMR spectroscopy ($CDCl_3$) using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Optimization of C-N bond formation catalysis using cyclohexanamine as nucleophile



L_1-I 2a

Entry	Equiv. of cyclohexanamine	Base	Equiv. of base	Solvent	AgOTf (mol%)	Yield (%) of 2a[a]
1	4	CsF	2	THF	10	17 % of **2a**
2	4	KOAc	2	THF	10	9 % of **2a**
3	4	CsOPiv	2	THF	10	17 % of **2a**
4	4	Na_2CO_3	2	THF	10	tr of **2a**
5	4	^{t}BuOK	2	THF	10	0 % of **2a**
6	4	CsF	2	Toluene	10	13 % of **2a**
7	4	CsF	2	CH_3CN	10	tr of **2a**
8	4	CsF	2	DMSO	10	21 % of **2a**
9	4	CsF	4	DMSO	10	23 % of **2a**
10	4	CsF	6	DMSO	10	20 % of **2a**
11	**12**	**CsF**	**4**	**DMSO**	**20**	**53 % of 2a**
12	12	CsF	4	DMSO	-	0 % of **2a**

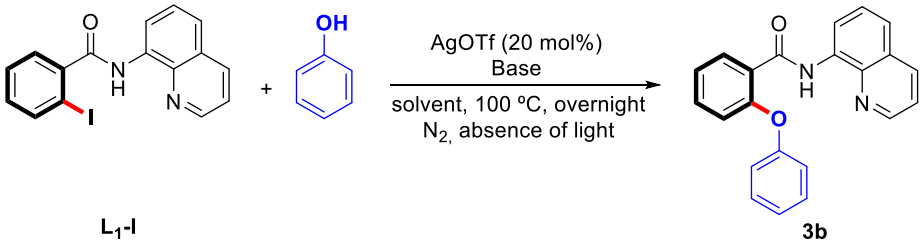
[a]Yield calculated from ^{1}H-NMR of crude using 1,3,5-trimethoxybenzene as internal standard.

3.3 Optimization of C-O bond formation reactions

General procedure for the optimization experiments:

37.4 mg of **L_1-I** (0.1 mmol), phenol, base and AgOTf (5.1 mg, 20 mol%, 0.02 mmol) with 1 mL of solvent were added to a glass vial under an inert atmosphere, and the vial was sealed and covered with aluminum foil. The reaction mixture was stirred at 100 °C overnight. The crude reaction mixture was extracted with ethyl acetate (3 x 10 mL) and the organic layers were combined and dried over magnesium sulfate and the solvent was then removed under reduced pressure. The crude reaction mixture was analyzed by ^{1}H-NMR spectroscopy ($CDCl_3$) using 1,3,5-trimethoxybenzene as internal standard.

Table S3. Optimization of C-O bond formation catalysis using phenol as nucleophile



L_1-I 3b

Entry	Equiv. of phenol	Base	Equiv. of base	Solvent	AgOTf (mol%)	Yield (%) of 3b[a]
1	10	^{t}BuOK	2	DMSO	20	55 % of **3b**
2	10	CsF	2	DMSO	20	30 % of **3b**
3	10	Na_2CO_3	2	DMSO	20	21 % of **3b**
4	10	^{t}BuOK	4	DMSO	20	75 % of **3b**
5	10	^{t}BuOK	4	CH_3CN	20	59 % of **3b**

[a] Yield calculated from ^{1}H-NMR of crude using 1,3,5-trimethoxybenzene as internal standard.

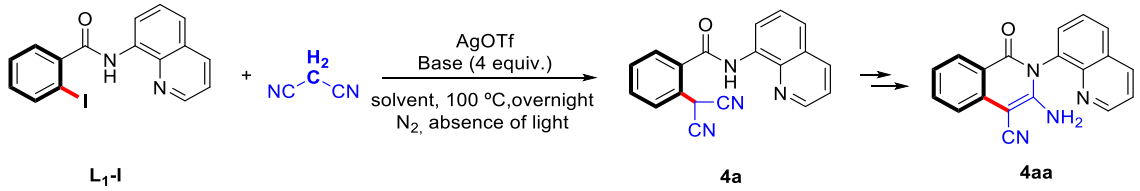
3.4 Optimization of C-C bond formation reactions

3.4.1 Activated methylene

General procedure for the optimization experiments:

37.4 mg of **L_1-I** (0.1 mmol), malononitrile, base (4 equiv., 0.4 mmol) and catalytic amounts of AgOTf with 2.5 mL of solvent were added to a glass vial under an inert-atmosphere, and the vial sealed and covered with aluminum foil. The reaction mixture was stirred at 100 °C overnight. The resulting crude mixture was extracted with ethyl acetate (3 x 10 mL) and the organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure. The crude reaction mixture was analyzed by ^{1}H-NMR spectroscopy ($CDCl_3$) using 1,3,5-trimethoxybenzene as internal standard.

Table S4. Optimization of C-C bond formation catalysis using malononitrile as nucleophile



L_1-I 4a 4aa

Entry	Base	Equiv. of malononitrile	T (°C)	Solvent	AgOTf (mol%)	Yield (%) of 4a/4aa[a]
1	Na_2CO_3	2	100	CH_3CN	10	0 % of **4aa**
2	^{t}BuOK	2	100	CH_3CN	10	45 % of **4aa**
3	^{t}BuOK	2	100	CH_3OH	10	18 % of **4aa**
4	^{t}BuOK	2	100	Toluene	10	0 % of **4aa**
5	^{t}BuOK	2	100	DMSO	10	65 % of **4aa**
6	^{t}BuOK	2	100	DMSO	20	74 % of **4aa**
7	^{t}BuOK	2	100	CH_3CN	20	90 % of **4aa**
8	^{t}BuOK	2	100	DMSO	-	0 % of **4a/4aa**

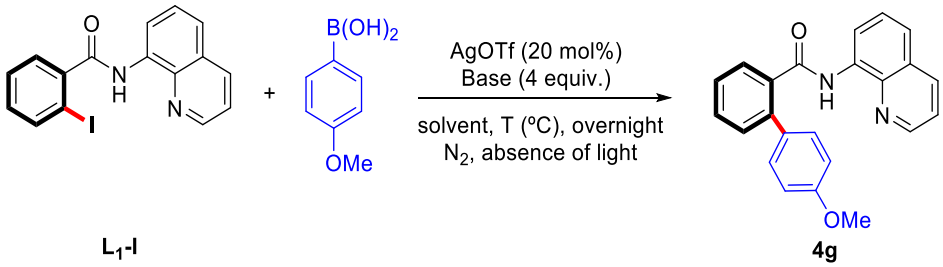
[a] Yield calculated from ^{1}H-NMR of crude using 1,3,5-trimethoxybenzene as internal standard.

3.4.2 Arylboronic acids

General procedure for the optimization experiments:

37.4 mg of **L_1-I** (0.1 mmol), (4-methoxyphenyl)boronic acid, base (4 equiv., 0.4 mmol), AgOTf (5.1 mg, 20 mol%, 0.02 mmol) with 1 mL of solvent were added to a glass vial under an inert-atmosphere, and the vial was sealed and covered with aluminum foil. The reaction mixture was stirred overnight at the specified temperature. The resulting crude mixture was extracted with ethyl acetate (3 x 10 mL) and the organic layers were combined and dried over magnesium sulfate. The solvent was then removed under reduced pressure and the resulting crude was analyzed by ^{1}H-NMR spectroscopy ($CDCl_3$) using 1,3,5-trimethoxybenzene as internal standard.

Table S5. Optimization of C-C bond formation catalysis using 4-methoxyphenylboronic acid as nucleophile



L_1-I 4g

Entry	Base	Equiv. of (4-methoxyphenyl) boronic acid	T (ºC)	Solvent	AgOTf (mol%)	Yield[a] (%)
1	^{t}BuOK	4	100	DMSO	20	10 % of **4g**
3	^{t}BuOK	10	100	DMSO	20	15 % of **4g**
4	^{t}BuOK	10	120	DMSO	20	20 % of **4g**
5	^{t}BuOK	10	120	CH_3CN	20	7 % of **4g**
6[b]	^{t}BuOK	10	120	CH_3CN/MeOH	20	0 % of **4g**
7	Na_2CO_3	10	120	DMSO	20	11 % of **4g**
8	CsF	10	120	DMSO	20	11 % of **4g**
9	^{t}BuOK	10	120	DMSO	-	0 % of **4g**

[a] Yield calculated from ^{1}H-NMR of crude using 1,3,5-trimethoxybenzene as internal standard. [b] The reaction was performed using a mixture of CH_3CN/MeOH (1:1).

4. Mechanistic study

4.1 DFT calculations

We carried out all calculations with Gaussian 09 program.[6] Geometry optimizations were obtained using the Becke three-parameter functional with the Becke 88 exchange functional and the Lee, Yang, and Parr correlation functional (B3LYP)[7-8,9-10] along with a modified combination of basis sets and functions. This basis set was composed in the following manner: 6-311+G* [11-16] for **C, H, N, O, Cl**; SSD basis set[17-18] with its corresponding Effective Core Potential (ECP) for **Ag** and **I** with the addition of 4 extra functions for **I** (*s, p, d* functions from aug-cc-pVDZ[19] to add diffusion and a *d* function from 6-311+G* to add polarization) and 4 extra functions for **Ag** (*s, p, d* functions from aug-cc-pVDZ to add diffusion and a *d* function from cc-pVDZ-PP to add polarization).
Empirical dispersion was added using the D3 version of Grimme's model with Becke-Johnson damping function (**GD3BJ**)[20] along with solvation effects in d**imethyl sulfoxide** simulated by the SMD method developed by Truhlar *et al.*[21] Subsequent frequency calculations at the same level of theory were performed to evaluate enthalpy and entropy corrections at 298.15 K (G_{corr}) and ensured that all local minima had only real frequencies while a single imaginary frequency confirmed the presence of transition states. All the transition states were connected to the corresponding reactants and products by IRC calculations. Also, Single Point Energy (SPE) calculations under the same conditions but with a more flexible basis set were performed. In this case, for **C, H, N, O, Cl,** we used May-cc-pPVTZ[22]; for **Ag** and **I**, we used a modified version of aug-cc-pVTZ (we just removed the 2 largest angular momenta from the basis set to make it more comparable to May-cc-pVTZ) with its respective ECP (**aug-cc-pVTZPP**). Finally, standard state gas-phase concentration correction from 1 atm to 1 Molar was applied to all Final Gibbs energy values.[23]

XYZ coordinates of DFT geometry-optimized structures

Table S6. Geometry-optimized XYZ coordinates for **(L_1-I)Ag^ICl**.

C	-4.277310000	-0.377013000	1.491514000
C	-3.790778000	0.004501000	0.241146000
C	-2.536340000	0.606298000	0.148679000
C	-1.753585000	0.846446000	1.280524000
C	-2.271076000	0.470626000	2.528014000
C	-3.516163000	-0.142596000	2.637570000
H	-5.248761000	-0.853604000	1.562587000
H	-4.381774000	-0.172038000	-0.648888000
H	-1.674961000	0.656728000	3.415120000
H	-3.889713000	-0.438007000	3.611792000
C	-0.393065000	1.517107000	1.242223000
O	-0.332151000	2.694103000	1.645885000
N	0.585436000	0.714335000	0.790088000
C	1.900408000	1.131476000	0.633096000
C	2.863187000	0.139989000	0.183815000
C	2.388131000	2.424556000	0.851578000
C	4.235488000	0.500772000	-0.004918000
C	3.744467000	2.761080000	0.653239000
H	1.698413000	3.183150000	1.184869000
C	3.305104000	-2.049289000	-0.457154000
C	5.132207000	-0.508036000	-0.437066000
C	4.665285000	1.829275000	0.236234000
H	4.054849000	3.784180000	0.840539000
C	4.675444000	-1.784035000	-0.662777000
H	2.907798000	-3.045019000	-0.630995000
H	6.176488000	-0.250991000	-0.583085000
H	5.709114000	2.083279000	0.087111000
H	5.336055000	-2.576834000	-0.992808000
N	2.444711000	-1.132950000	-0.054361000
I	-1.840056000	1.164670000	-1.816521000
Ag	0.067838000	-1.445813000	0.212654000
Cl	-1.243246000	-3.470269000	-0.192755000

Table S7. Geometry-optimized XYZ coordinates for **TS1.**

C	-4,224980000	-0,546250000	-1,413626000
C	-3,301421000	0,237424000	-0,715653000
C	-2,076612000	-0,330304000	-0,388598000
C	-1,737991000	-1,650578000	-0,708305000
C	-2,701160000	-2,420210000	-1,369168000
C	-3,935279000	-1,877766000	-1,723241000
H	-5,180256000	-0,112356000	-1,689470000
H	-3,539000000	1,252707000	-0,430093000
H	-2,442161000	-3,442718000	-1,624418000
H	-4,665559000	-2,485383000	-2,245556000
C	-0,362811000	-2,208279000	-0,449184000
O	-0,194677000	-3,427934000	-0,288535000
N	0,576348000	-1,231047000	-0,459080000
C	1,926386000	-1,404492000	-0,224590000
C	2,729952000	-0,197989000	-0,201413000
C	2,586761000	-2,618296000	-0,019230000
C	4,139907000	-0,277583000	0,010226000
C	3,981331000	-2,675485000	0,191446000
H	2,006985000	-3,528180000	-0,029818000
C	2,834077000	2,122300000	-0,356563000
C	4,875826000	0,933577000	0,025132000
C	4,756630000	-1,539016000	0,207451000
H	4,442006000	-3,646151000	0,343986000
C	4,230423000	2,132826000	-0,157943000
H	2,290520000	3,050186000	-0,503670000
H	5,948257000	0,892019000	0,185469000
H	5,827681000	-1,582254000	0,371453000
H	4,765125000	3,074787000	-0,150889000
N	2,119136000	1,012707000	-0,375817000
I	-1,553625000	0,337010000	2,104007000
Ag	-0,209408000	0,847142000	-0,601629000
Cl	-0,994500000	3,042514000	-1,502982000

Table S8. Geometry-optimized XYZ coordinates for **(L_1-Ag^{III}-Cl)I**.

C	4,758722000	0,465102000	-0,579967000
C	3,559007000	-0,138966000	-0,987400000
C	2,372269000	0,474031000	-0,628023000
C	2,332934000	1,654174000	0,118386000
C	3,536398000	2,240215000	0,515731000
C	4,747601000	1,645498000	0,165291000
H	5,700607000	0,000089000	-0,851275000
H	3,572937000	-1,055346000	-1,561881000
H	3,500156000	3,154844000	1,098907000
H	5,682986000	2,098299000	0,474098000
C	1,009093000	2,245844000	0,483442000
O	0,882279000	3,270253000	1,150416000
N	-0,023425000	1,495128000	-0,020423000
C	-1,393453000	1,707680000	0,146416000
C	-2,255941000	0,744911000	-0,475053000
C	-1,982990000	2,751064000	0,852622000
C	-3,669577000	0,856719000	-0,370927000
C	-3,389057000	2,852982000	0,950178000
H	-1,355551000	3,486672000	1,330270000
C	-2,443532000	-1,207267000	-1,750774000
C	-4,455555000	-0,136216000	-1,006546000
C	-4,227030000	1,936658000	0,358120000
H	-3,805136000	3,681892000	1,512246000
C	-3,850305000	-1,162427000	-1,692930000
H	-1,924274000	-2,000307000	-2,276671000
H	-5,536140000	-0,071005000	-0,938553000
H	-5,304918000	2,018165000	0,437833000
H	-4,426615000	-1,934934000	-2,185858000
N	-1,687092000	-0,295048000	-1,167823000
I	-0,000137000	-1,915551000	2,185150000
Ag	0,479580000	-0,189492000	-1,065807000
Cl	1,081579000	-2,064156000	-2,366832000

Table S9. Geometry-optimized XYZ coordinates for **TS2.**

C	-3,905757000	2,173923000	-0,486452000
C	-3,151784000	1,205220000	0,180920000
C	-1,782036000	1,404631000	0,278001000
C	-1,130112000	2,535603000	-0,224140000
C	-1,922765000	3,503570000	-0,851103000
C	-3,298546000	3,330277000	-0,985841000
H	-4,975388000	2,025441000	-0,589728000
H	-3,621085000	0,333232000	0,613822000
H	-1,421849000	4,377376000	-1,255579000
H	-3,895517000	4,086481000	-1,482679000
C	0,368190000	2,669368000	-0,211238000
O	0,911164000	3,781823000	-0,276354000
N	0,973422000	1,453876000	-0,171485000
C	2,337257000	1,222821000	-0,174879000
C	2,748030000	-0,162853000	-0,078401000
C	3,344540000	2,183538000	-0,286186000
C	4,132409000	-0,508024000	-0,103082000
C	4,709186000	1,822217000	-0,312384000
H	3,062865000	3,222351000	-0,359964000
C	2,140072000	-2,402147000	0,128277000
C	4,472840000	-1,879917000	0,001246000
C	5,112126000	0,509686000	-0,223773000
H	5,449975000	2,609897000	-0,403694000
C	3,484589000	-2,827772000	0,118984000
H	1,329748000	-3,119779000	0,209727000
H	5,520783000	-2,161014000	-0,012915000
H	6,160552000	0,233395000	-0,239474000
H	3,714602000	-3,883045000	0,200929000
N	1,790661000	-1,132634000	0,036152000
I	-2,001148000	-2,485147000	-0,369370000
Ag	-0,362461000	-0,272189000	0,071937000
Cl	-1,224441000	0,917485000	2,473740000

Table S10. Geometry-optimized XYZ coordinates for **(L_1-Cl)Ag^II.**

C	3,853414000	2,050722000	-0,659899000
C	3,250403000	2,049524000	0,596647000
C	1,864885000	2,156405000	0,683564000
C	1,057160000	2,267535000	-0,448731000
C	1,686664000	2,275742000	-1,699521000
C	3,070647000	2,164803000	-1,809895000
H	4,930994000	1,958871000	-0,734361000
H	3,847171000	1,956024000	1,495661000
H	1,073170000	2,357208000	-2,590418000
H	3,536196000	2,161376000	-2,789083000
C	-0,453966000	2,395213000	-0,379802000
O	-0,936405000	3,539563000	-0,472730000
N	-1,070092000	1,209335000	-0,252521000
C	-2,447835000	1,062925000	-0,174388000
C	-2,962536000	-0,292973000	-0,086106000
C	-3,390463000	2,096156000	-0,164384000
C	-4,372242000	-0,524111000	-0,002166000
C	-4,777108000	1,846636000	-0,076001000
H	-3,037088000	3,113063000	-0,228075000
C	-2,538657000	-2,576922000	-0,006322000
C	-4,819905000	-1,866426000	0,076216000
C	-5,275857000	0,567772000	0,002123000
H	-5,455562000	2,693771000	-0,071794000
C	-3,910363000	-2,896279000	0,072766000
H	-1,791258000	-3,364530000	-0,005962000
H	-5,886245000	-2,058657000	0,138769000
H	-6,340637000	0,371989000	0,067104000
H	-4,221060000	-3,932497000	0,131297000
N	-2,088853000	-1,337807000	-0,082248000
Cl	1,126684000	2,126225000	2,294252000
Ag	0,213230000	-0,697345000	-0,118035000
I	2,542779000	-2,126505000	0,032318000

4.2 Ion spectroscopy experiments

General procedure for the ion spectroscopy experiments

L_2-I (0.0388 g, 0.1 mmol), $AgClO_4$ (0.041 g, 0.2 mmol) and Na_2CO_3 (0.021 g, 0.2 mmol) were dissolved in 1 mL of acetonitrile under nitrogen and covered with aluminum foil. The reaction mixture was stirred at 50 °C for 45 minutes. For the ion spectroscopy measurements an aliquot of the reaction mixture was diluted 100 times in acetonitrile (acetonitrile-d_3). The diluted solutions were kept at −30 °C during measurements.

The ions were transferred to the gas phase by electrospray ionization (ESI). The diluted solution was pushed from a glass vial by 1 psi pressure of nitrogen to the ESI ion source through 100 μm (i. d.) fused-silica capillary at a rate approximately 0.1 ml hr^{-1}. The spraying voltage of 2.5 kV was connected to the solution in the vial by a 0.3 mm stainless steel wire. The sheath gas pressure was 10 psi and the heated capillary was kept at 170 °C. Two different ionization conditions were used: soft (20 V capillary voltage, 140 V tube lens voltage) and hard (100 V capillary voltage, 250 V tube lens voltage). The hard conditions were optimized to maximize the IR attenuation at 1740 cm^{-1} peak.

IR spectra were measured with the ISORI instrument.[24-25] The ions generated ions in the ESI ion source were mass selected and trapped and thermalized by helium (or helium with 10 % D_2) buffer gas in the wire-quadrupole ion trap at 3 K and 20 K, respectively. In the process, some ions attach He atom (D_2 molecule) to form weakly-bound clusters. The trapped ions were irradiated for 900 ms by the pulsed IR laser (OPO/OPA system from LaserVision) and then extracted by lowering the exit electrode potential, mass analyzed by a quadrupole and counted by a Daly-type detector. Photodissociation spectra were constructed as a frequency-dependent reduced signal ($1 - N_i/N_{i0}$), where N_i and N_{i0} are the numbers of the He- (D_2-) tagged ions extracted from the trap in the cycles with (N_i) and without (N_{i0}) laser irradiation. The pulse sequence of one cycle is shown in Figure S2.

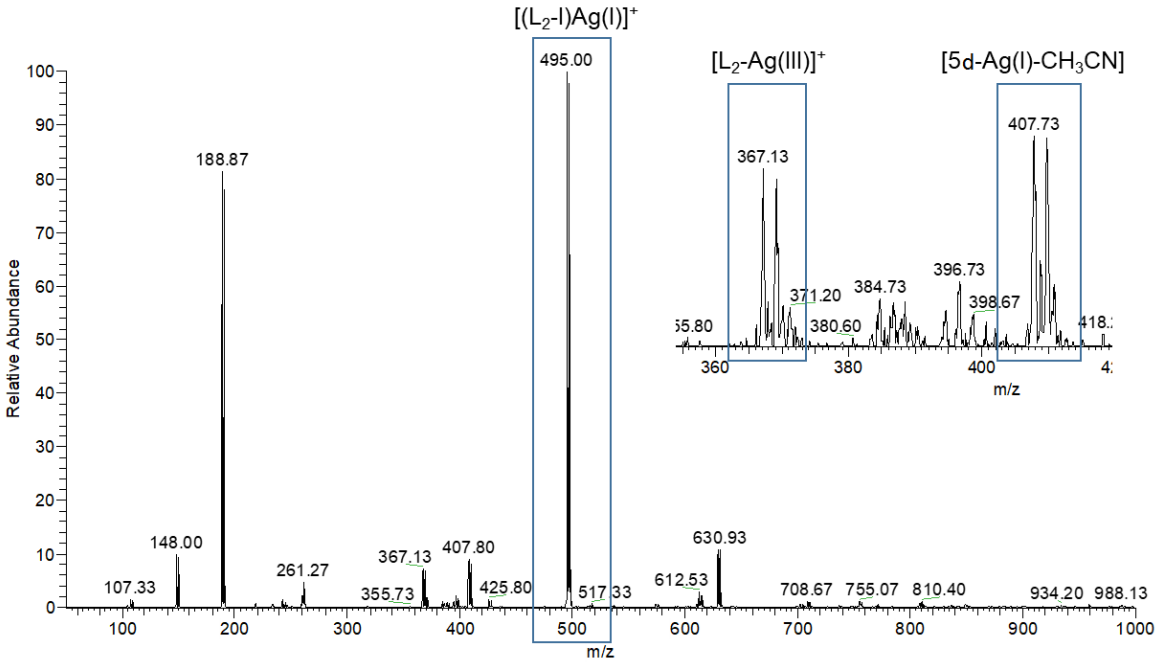


Figure S1. ESI analysis of the crude mixture obtained for the ion spectroscopy experiments

Computational details

The density functional theory (DFT) calculations were performed with the Gaussian 16 rev. A.03 package.[6] We have used the B3LYP[8, 10, 26-27] functional with D3BJ[28-29] corrections for the dispersion interactions. The basis set was 6-311+g(2d,p) for C, H, N and O atoms and SDD for the Ag and I atoms. The vibrational analysis provided the harmonic frequencies and confirmed the structures as minima on the potential energy surface. We also performed anharmonic VPT2 analysis[30-31] to calculate anharmonic IR spectra with the default setting in the Gaussian 16 package. Optimized geometries can be found in the end of this Supporting Information.

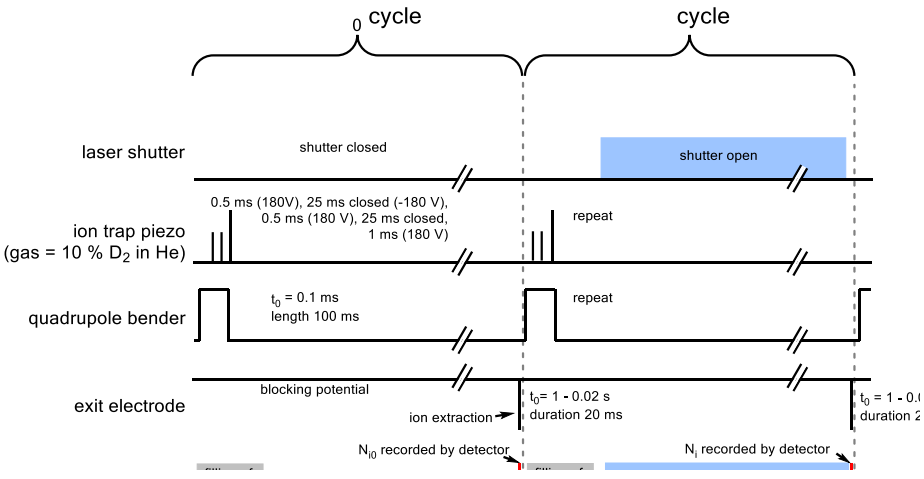


Figure S2. Timing sequence used during the acquisition of the IRPD spectra with the ISORI instrument.

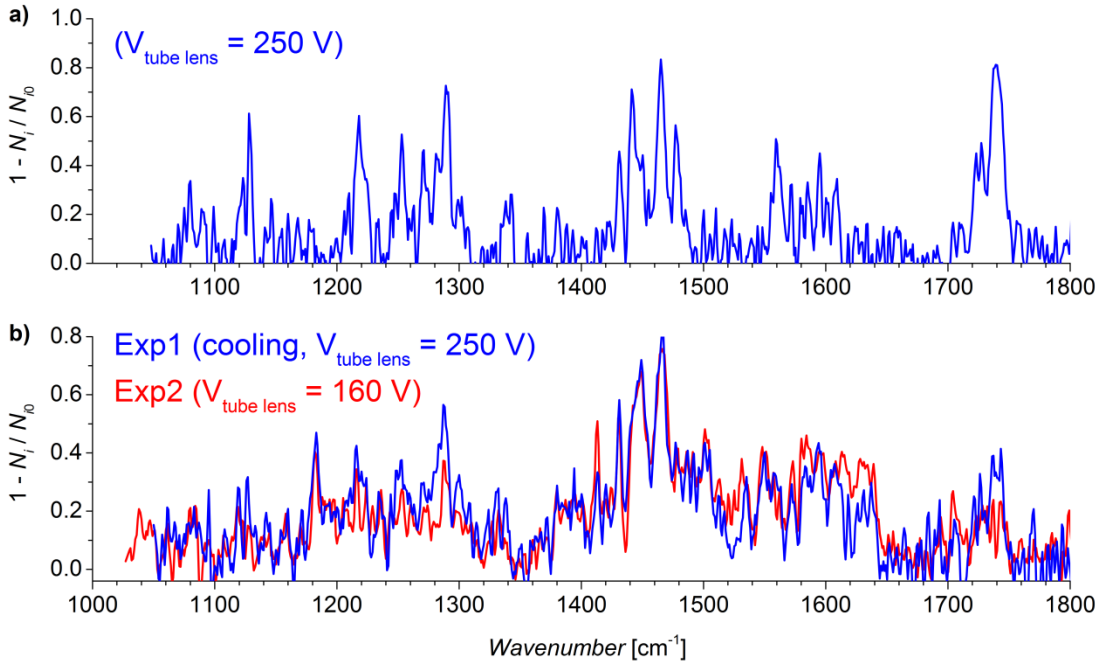


Figure S3. a) D_2-IRPD spectrum of *m/z* 408 ions. b) He-IRPD spectra of *m/z* 408 ions. The blue spectrum was obtained at higher potential in the ion-transfer range (harder ionization conditions), the reaction mixture was cooled to -30 °C. The red spectrum was obtained at softer ionization conditions.

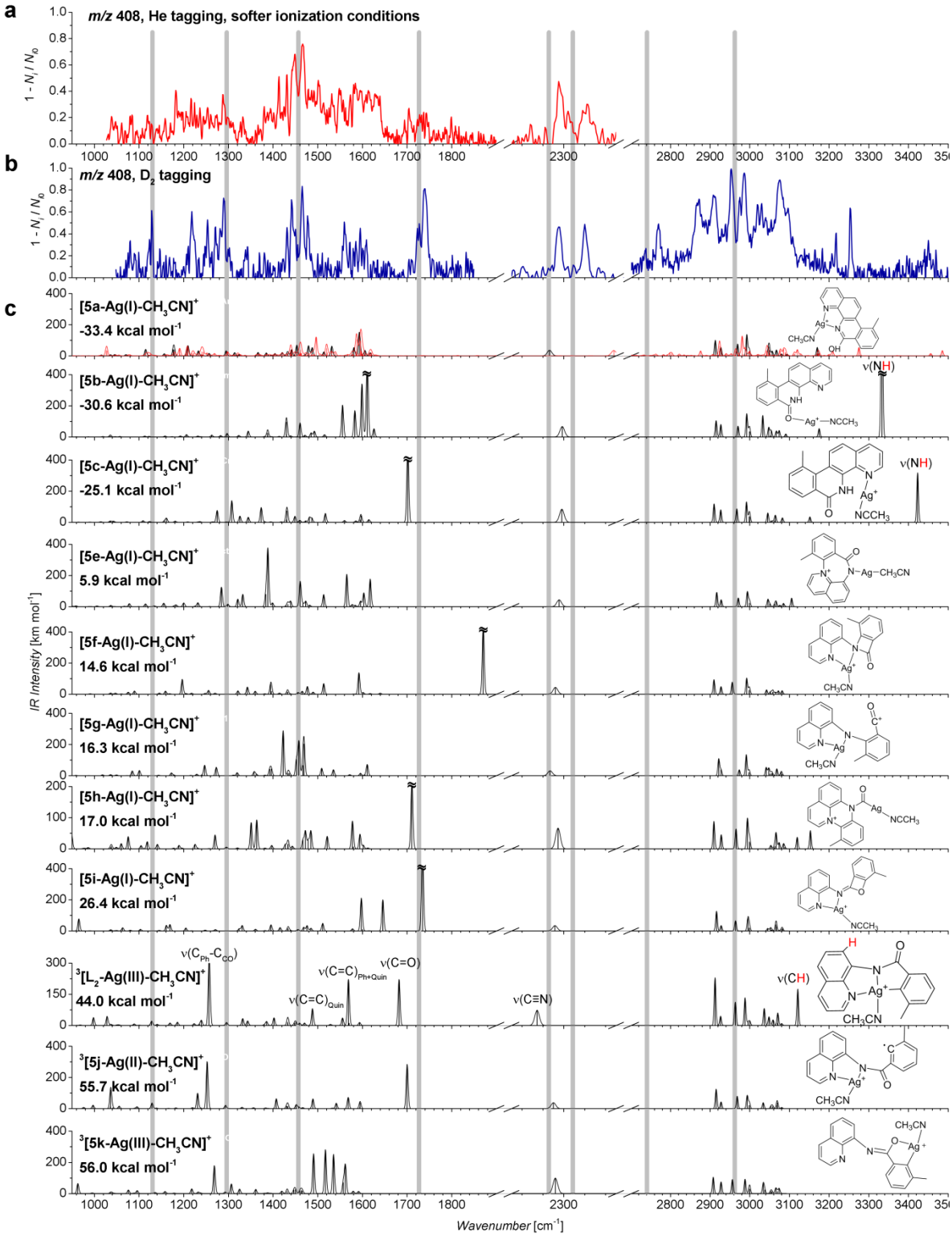


Figure S4. a) Helium tagging IRPD spectra of *m/z* 408 ions acquired with softer ionization conditions (see Experimental Details). b) D_2 tagging IRPD spectra of ions with *m/z* 408. b) IR spectra of different isomers with *m/z* 408 calculated at B3LYP-D3BJ/6-311+G(2d,p) :SDD(Ag) level (black lines). Frequency scaling factors are 0.98 < 2000 cm^{-1}, 0.96 >2000 cm^{-1}. Energies given are enthalpies at 0 K. The anharmonic IR spectra (B3LYP-D3BJ/6-311+g(2d,p):SDD-Ag) are in red and were not scaled. All predicted IR intensities above 2700 cm^{-1} were multiplied by 10.

Optimized Structures

The format of individual records is following:

number_of_atoms
NAME charge multiplicity electronic_energy(Hartree) zero_point_energy(Hartree) number_of_imaginary_frequencies method/basis_set
atom1 x y z
...

35
[(L2-I)-Ag(I)]+ 1 1 -998.9671407 0.2612317 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C 5.2719167284 -0.6091187547 -0.1625636878
C 4.4178182521 0.4982558791 0.0249667474
C 3.0193496905 0.3216186914 -0.200688361
N 2.5270825067 -0.9135703671 -0.5355452781
C 3.365339591 -1.9266793818 -0.7045060899
C 4.7523957971 -1.816884796 -0.5441515333
C 2.1699322395 1.4556899582 -0.0671266522
C 2.6941934228 2.6595680799 0.3345258446
C 4.0673986091 2.8173703944 0.5950542667
C 4.9163999175 1.758137466 0.4279989987
N 0.7732162942 1.3834141807 -0.382161541
C -0.2121141281 1.374578235 0.5904856173
O 0.0173163172 1.1480131286 1.7568845652
Ag 0.3997490868 -1.3264408417 -0.2758742302
I -2.2002980462 -1.3664602448 0.5528053974
C -2.6076500971 0.6899311121 0.0002549479
C -1.5936761383 1.642316208 0.0558475836
C -1.8864115001 2.943973948 -0.3519156712
C -3.1652319854 3.2745980219 -0.7739597987
C -4.1536110998 2.3045679957 -0.8035995256
C -3.9030709867 0.9808369584 -0.4242607304
C -5.0091858945 -0.0343349023 -0.4901482395
H -5.1523178733 2.5642524705 -1.13149748
H -3.3914991274 4.2890325455 -1.074994373
H -1.1119117582 3.6998895416 -0.3078898404
H 5.9796698555 1.8656955322 0.6024941878
H 4.4431596436 3.780699462 0.9127334622
H 2.026880358 3.5046487813 0.445587034
H 6.3360749373 -0.4868444386 -0.0009454562
H 5.3786005171 -2.6833096974 -0.7045441002
H 2.9266964747 -2.8794339331 -0.9728430651
H 0.4944453887 1.6700825654 -1.3112022089
H -5.2088514 -0.4716634839 0.4909112457
H -5.9294050989 0.4291534788 -0.8406472642
H -4.7616914938 -0.8508757933 -1.1720217718

39
[5a-Ag(I)-CH3CN]+ 1 1 -1119.8036943 0.2982073 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C -8.3555284473 -1.7762991323 0.9668452506
C -7.6205332909 -2.5502942501 1.8964378016
C -6.3011014593 -2.1542555373 2.2220477679
C -5.7456139501 -0.9703490916 1.6244107982
C -6.5197484181 -0.1742272841 0.7611410377
C -7.8259126177 -0.6448588976 0.4277141937
C -8.1355186135 -3.7147730661 2.4998259947
C -7.3586165439 -4.4263605581 3.3776055201
N -5.5482863771 -2.88263378 3.0907634533
Ag -3.4376944825 -2.0967050231 3.4307363319
N -4.4353121124 -0.6755864943 1.9225737388
C -5.929753993 1.0465369884 0.2236590212
C -4.5470498804 1.2632557403 0.4897170558
C -3.8689030998 0.3507028082 1.3588635843
C -6.6128268777 2.0498127108 -0.5274991466
C -5.8788844512 3.1162700128 -1.0272661922
C -4.5083957557 3.2715018184 -0.814552547
C -3.8436250861 2.3574987529 -0.0374035376
O -2.5766159733 0.605779901 1.6098421477
C -6.0603927391 -3.969154452 3.644615807
C -8.0991100352 2.0917975174 -0.7890143916
N -1.630932221 -2.4329477991 4.4797724205
C -0.6666357967 -2.6326923598 5.0658462269
C 0.5534180774 -2.8870431942 5.8084836754
H -9.3481098138 -2.1014299265 0.6814984732
H -2.2301193697 -0.0803402873 2.2005696567
H -8.4129996711 -0.1124107937 -0.2946351031
H -9.142892187 -4.0339220367 2.2610355955
H -7.7218023436 -5.323200424 3.8602951672
H -6.4034910199 3.8724335094 -1.5983779763
H -3.9872871575 4.1210277873 -1.236079821
H -2.7928899233 2.4689577019 0.1848749979
H -5.4219246756 -4.5101116692 4.3322628298
H -8.6816661216 1.8962428554 0.1115319272
H -8.373206149 3.0826900451 -1.1478113046
H -8.4076691138 1.3793743487 -1.5579723911
H 0.9634384174 -1.9456000554 6.177204714
H 0.3397874614 -3.5420948822 6.6544458663
H 1.2855579165 -3.3676816178 5.1577686532

39
[5b-Ag(I)-CH3CN]+ 1 1 -1119.7996926 0.2987492 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C -8.3567411647 -1.9028242144 0.7897545212
C -7.6172092991 -2.6198874018 1.7619167832
C -6.3724328691 -2.0972862693 2.1760904983
C -5.9219709386 -0.8674147167 1.6168755042
C -6.6605144441 -0.1356969769 0.6915216501
C -7.8980778789 -0.7223795702 0.2799766133
C -8.0273386767 -3.839197024 2.3414995754
C -7.2144333282 -4.4506656329 3.2613705687
N -5.5691984123 -2.7096895898 3.0813834089
Ag -1.5952819712 0.0468597359 3.3347486892
N -4.6805717806 -0.442611056 2.0402907715
C -6.0965090041 1.1286088207 0.2067426626
C -4.7779538877 1.4720514946 0.6326759199
C -4.0561466706 0.649285466 1.5858880974
C -6.7594953093 2.0538660842 -0.6499628149
C -6.0725864871 3.1871702304 -1.0699549848
C -4.7670753024 3.4775301871 -0.6819104499
C -4.1252111053 2.6260168448 0.1835675675
O -2.8941721281 0.9606728372 1.9814926311
C -5.9866564314 -3.8454812017 3.6007275781
C -8.1859546731 1.9343490606 -1.1282158348
N -0.2026806891 -0.7525647588 4.6545982453
C 0.5889597286 -1.1634043831 5.37225142
C 1.5923733744 -1.6824137929 6.2804866635
H -9.2995150018 -2.3069454243 0.4424486411
H -4.2367179743 -1.0607869786 2.7177685663
H -8.4935104787 -0.2404715928 -0.4699733143
H -8.9754762115 -4.2773251772 2.0536322225
H -7.4963444817 -5.3856619149 3.7267089686
H -6.5871672808 3.8803465472 -1.7240348541
H -4.278041521 4.3726050363 -1.0431910102
H -3.124857501 2.8261227526 0.53817045
H -5.33151872 -4.3191516996 4.3242275766
H -8.8812956377 1.7551841677 -0.3074960326
H -8.4841539627 2.8632458897 -1.6116590651
H -8.3109477132 1.1367133489 -1.8639575548
H 2.4209754018 -0.976009744 6.3518380473
H 1.1535880329 -1.8249150452 7.2692588135
H 1.9642675195 -2.6383764087 5.9085105625

39
[5c-Ag(I)-CH3CN]+ 1 1 -1119.7906839 0.2984307 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C -8.4603863971 -1.726158735 0.934164467
C -7.7428163425 -2.7194740375 1.6363633365
C -6.3532826947 -2.5277520749 1.8609319934
C -5.7117895813 -1.3920213799 1.2892901055
C -6.4541153588 -0.3398069724 0.7467958405
C -7.8429800809 -0.5737583663 0.5417871494
C -8.3358678863 -3.9033723781 2.1138644684
C -7.5804843345 -4.8186625974 2.8035972901
N -5.6384850684 -3.4171778616 2.6274858492
Ag -3.8615509463 -2.8130277919 3.7103083002
N -4.3317285483 -1.3468483408 1.2828272159
C -5.7511416213 0.8923513643 0.3592489295
C -4.3320101486 0.8631838694 0.3196319835
C -3.5694691518 -0.320838543 0.7399935361
C -6.390790224 2.1244773118 0.0548490758
C -5.6049511209 3.1958196385 -0.3625630082
C -4.2211633653 3.1216457063 -0.4729675931
C -3.5814544109 1.9561860802 -0.108396562
O -2.3602982709 -0.450340019 0.6665187838
C -6.2397356143 -4.5204891481 3.0659670906
C -7.8667438177 2.404270519 0.2104546585
N -2.1164150118 -2.2763766979 4.7290741636
C -1.1158768079 -1.9120545547 5.149481559
C 0.1518768551 -1.4502112494 5.6777873593
H -9.5080030109 -1.8876639761 0.7160435357
H -3.8270404734 -2.2218044821 1.3349766011
H -8.4242066283 0.1552722203 0.008556171
H -9.3894473488 -4.0773248319 1.9312218727
H -8.0028987201 -5.7416706736 3.1751733039
H -6.0996090886 4.1311558186 -0.5950271086
H -3.6556907505 3.9800304227 -0.8115949055
H -2.5049506876 1.8597420691 -0.1344457101
H -5.6417059748 -5.1936340794 3.6665109862
H -8.2764166785 1.9727995708 1.1237433357
H -8.0261792549 3.4807901896 0.2550410453
H -8.4535746063 2.0333836813 -0.6340764964
H 0.6937558399 -0.9109090459 4.8990089418
H -0.0234689092 -0.7846177207 6.5243641087
H 0.7457573358 -2.304531025 6.0063456211

39
[5d-Ag(I)-CH3CN]+ 1 1 -1119.7485974 0.2963955 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C -8.2740295104 -1.8552415821 0.7257583657
C -7.6031827914 -2.5065502115 1.8331484426
C -6.2668763811 -2.1992720065 2.1292137518
C -5.5731127772 -1.1482527336 1.3688303153
C -6.247602201 -0.5089546188 0.17416347
C -7.6684878798 -0.9370730077 -0.0285947406
C -8.234868371 -3.4773962053 2.6231583068
C -7.5319979147 -4.0865337836 3.6410356507
N -5.5865055327 -2.8040451372 3.1176087676
Ag -3.2560658472 -1.9434807017 3.2909747103
N -4.3847815686 -0.8133928691 1.7349480646
C -5.8641338714 0.9771378577 0.0609733925
C -4.5362630559 1.2658488931 0.4272106196
C -3.6973045186 0.2448508048 1.0821183828
C -6.6647249954 2.0110484519 -0.4517039062
C -6.0827501317 3.2772929541 -0.5940398802
C -4.7620416842 3.5445922958 -0.2664924225
C -3.9813361462 2.532222761 0.2559505438
O -2.4922080852 0.296576892 1.1781181694
C -6.1986270138 -3.7210444326 3.8527140639
C -8.1186899982 1.893131825 -0.8453937221
N -1.5916774526 -2.4711650006 4.4941793749
C -0.6389054039 -2.6989629906 5.0876124345
C 0.571397613 -2.9826661617 5.8355579097
H -9.2847882912 -2.1688806619 0.4944513591
H -5.7218678831 -0.97304513 -0.6828185281
H -8.1763711726 -0.5480850138 -0.894384995
H -9.2661792528 -3.742251111 2.4248058296
H -7.9906537588 -4.840458455 4.2668273573
H -6.7014209297 4.0804998941 -0.9752397845
H -4.3569629819 4.5382573778 -0.4061213454
H -2.9525847529 2.6940284859 0.5469844849
H -5.6131060017 -4.1887963955 4.6350330322
H -8.7216318687 1.4230244981 -0.0691082396
H -8.5289436269 2.8866864619 -1.0195140175
H -8.2518565034 1.328488756 -1.771291363
H 1.400262775 -2.4055637694 5.4228832535
H 0.4297461458 -2.7102563477 6.882411986
H 0.8053457081 -4.0461390003 5.7690531935

39
[5e-Ag(I)-CH3CN]+ 1 1 -1119.7396162 0.296797 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C -3.536850002 -22.8586621251 2.2290647698
C -3.1740709453 -24.179763878 1.8882149628
C -3.5393858407 -24.7194158682 0.6796989221
C -4.1036544264 -23.8802674506 -0.2747742551
N -4.3938597784 -22.6029908165 -0.0072920247
C -4.3011061885 -22.1024172937 1.2873512358
C -3.2450640919 -22.3098993693 3.4909866154
C -3.7558221742 -21.07296149 3.8113091699
C -4.6433536675 -20.4270767683 2.9508061916
C -5.0158541949 -20.9431681498 1.7040473329
N -6.1456484038 -20.4359634816 1.1065008097
C -6.5758217347 -20.5796040025 -0.1734569076
C -5.5998301699 -20.8534508206 -1.2669770149
O -7.7430674139 -20.3052741123 -0.4576410981
C -4.5042108669 -21.702632452 -1.1482232228
C -3.4813440858 -21.7340710369 -2.1091860767
C -3.6586427464 -20.9535602622 -3.2518221372
C -4.7920724582 -20.1747153315 -3.4326471676
C -5.7522103371 -20.1117961318 -2.4364944555
Ag -7.8277584731 -19.5534821836 2.1276773216
N -9.3944938193 -18.6711244961 3.21293495
C -10.3009712036 -18.1907631233 3.7214742295
C -11.4501417142 -17.582188173 4.3641333949
C -2.1914933056 -22.5024900858 -1.9492691301
H -2.6300108611 -24.7727372247 2.613342377
H -3.3304092646 -25.7474550333 0.4224926133
H -4.2647162682 -24.1913422716 -1.2953252284
H -2.6558239876 -22.8808616905 4.1955294921
H -3.5268648568 -20.6211344537 4.7677827691
H -5.1386211657 -19.5201552216 3.2758483189
H -2.8813326088 -20.9563190337 -4.0059378159
H -4.9100191441 -19.5926007115 -4.3374418249
H -6.6270477251 -19.4837841736 -2.5292732714
H -11.7010944267 -18.1352866324 5.2703611697
H -12.3026138268 -17.6007911175 3.6834799446
H -11.2208114498 -16.5480432006 4.6251821393
H -1.3968059615 -21.981953962 -2.4824978765
H -1.8850830484 -22.5878725972 -0.9065519408
H -2.247655269 -23.5105894132 -2.3670171631

39
[5f-Ag(I)-CH3CN]+ 1 1 -1119.7232244 0.2943157 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C 7.0221158463 -2.3393274883 1.2057078229
C 6.9162663708 -3.6687249514 0.7424172706
C 5.7128459692 -4.140160678 0.2907689241
C 4.6122687346 -3.2699845984 0.2724903323
N 4.6680107649 -2.0214311453 0.7062782124
C 5.8451342191 -1.5359546922 1.2038163156
C 8.2441229113 -1.7938747448 1.6606396609
C 8.2968205213 -0.4991819337 2.1031133575
C 7.130004045 0.2864203884 2.1403587658
C 5.9193991349 -0.2093015507 1.7136620389
N 4.7235388955 0.5647605558 1.8002059953
C 3.9949859068 0.6209288272 3.1796383263
C 4.0667679326 2.102451901 3.1066086332
O 3.6265529531 -0.2747111183 3.8529664519
C 4.7809870414 2.0139002772 1.9168542358
C 5.2413177177 3.0952419789 1.1995445639
C 4.8981011756 4.3248530323 1.795917284
C 4.1694267513 4.4360475616 2.9846167504
C 3.7225454243 3.3095075424 3.6828363444
Ag 2.9824299184 -0.6251236656 0.4473228175
N 1.1114194081 0.1816555755 -0.1035345641
C 0.0874806256 0.6249400215 -0.3622526126
C -1.2111398058 1.1814875509 -0.690873683
H 7.7952908356 -4.3018857669 0.7491314629
H 5.5967188467 -5.1540085218 -0.0663691898
H 3.6604229299 -3.6068214685 -0.1178862678
H 9.13052452 -2.4155460904 1.6536109335
H 9.2310821592 -0.0767487019 2.4489917724
H 7.1792618789 1.2962404026 2.5281013999
C 6.0253477261 2.981525987 -0.0741641244
H 5.2133726478 5.2362443443 1.3006189119
H 3.9524481404 5.4231668248 3.3711823686
H 3.1667180233 3.392025734 4.6066852454
H -1.1484899399 2.2701463697 -0.7236391921
H -1.9385528698 0.8854596211 0.06656198
H -1.5345797826 0.8098436852 -1.6643360987
H 7.0589777772 2.6847065954 0.1237179303
H 6.0464738759 3.9305117549 -0.6089849093
H 5.595181569 2.2241206635 -0.7331252566

39
[5g-Ag(I)-CH3CN]+ 1 1 -1119.7199149 0.2937373 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C -0.7607062109 -0.1451520419 0.1052052224
C -0.4154400592 0.2040256333 1.4288791684
C 0.596694927 -0.5631844426 2.0732251759
N 1.1904341245 -1.6134380466 1.4375031259
C 0.8334162593 -1.9174568406 0.2005638179
C -0.1368116186 -1.1972916283 -0.5121756091
C 1.0034693842 -0.2277146926 3.4058078526
C 0.3374408325 0.8066043489 4.0465430137
C -0.6649242942 1.5524181729 3.4066597593
C -1.0344300357 1.2726059809 2.1161979043
N 1.9464738252 -1.0139190756 4.0461947846
C 2.5171894927 -2.5555138206 6.1166679846
O 1.9240648846 -3.5205204988 6.270750157
C 3.2289238959 -1.4156158391 5.99467636
C 2.8238340442 -0.5234314245 4.9163574362
C 3.4971725519 0.7530311926 4.8768210775
C 4.4539767498 1.0172504692 5.8246770879
C 4.8309882708 0.1236792857 6.8668504762
C 4.2462799563 -1.094684439 6.9542250241
C 3.2960505535 1.7145030127 3.738270391
H 4.9913304095 1.9558816647 5.7502331292
H 5.6013804511 0.4148215722 7.5674975507
H 4.5144943475 -1.8105383953 7.719171141
H -1.8028780274 1.8482794685 1.6165562043
H -1.151495232 2.3530300533 3.9492415934
H 0.5906472621 1.0294974163 5.0753648642
H -1.5236406963 0.4272111801 -0.4088264397
H -0.3805626262 -1.486879137 -1.5251033779
H 1.3282270469 -2.7660788055 -0.2548830314
H 3.2011811112 1.1841919845 2.7891592337
H 2.3928465881 2.3150562624 3.8544024861
H 4.1479956567 2.3902693791 3.6700449506
Ag 2.5731727685 -2.8459640436 2.6769308538
N 3.8486378094 -4.5083019607 3.0017884709
C 4.511840698 -5.4302761058 3.1539183374
C 5.3496097286 -6.6003777495 3.3401207122
H 5.413476414 -7.1591296583 2.4051707852
H 6.3515106545 -6.292656877 3.642983174
H 4.9209494921 -7.241205733 4.1120697481

39
[5h-Ag(I)-CH3CN]+ 1 1 -1119.7214904 0.2964476 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C 1.4003308358 -3.193413169 -7.0834227409
C 0.811505808 -3.9640209555 -6.107813828
C 1.1744557952 -3.7884117555 -4.7786215164
N 2.089481477 -2.875794162 -4.4149028632
C 2.5530942646 -1.9541568842 -5.3443678194
C 2.2691285304 -2.14491801 -6.7241556877
C 3.2379837893 -0.8109609421 -4.8942622143
C 3.7648414074 0.0561885688 -5.8368453594
C 3.5595042721 -0.1706141244 -7.2083668838
C 2.8103055664 -1.2309457126 -7.653635613
C 2.6634144854 -2.854630366 -3.0915196672
C 3.1948748989 -1.6254197602 -2.6616730648
N 3.222971621 -0.5277567837 -3.5224429089
C 2.7874312538 -4.0161373786 -2.3043395756
C 3.3021194073 -3.857463758 -1.0187387364
C 3.7494182779 -2.6293886732 -0.5515521547
C 3.7372992937 -1.5226057497 -1.3820380343
Ag 1.8469909116 1.0011551458 -1.1512050993
C 2.5076626021 -5.4267379405 -2.7681667757
C 2.6923600006 0.8032414154 -3.0684864566
O 2.7273885205 1.6967022544 -3.8681623284
N 0.9326894109 1.4290598911 0.7232900267
C 0.4436659472 1.7549438386 1.7061626652
C -0.1758615993 2.1719765162 2.9498915961
H 1.1677984491 -3.353606708 -8.1288583455
H 0.0823500273 -4.7240505018 -6.3488862169
H 0.7497886671 -4.3827423296 -3.9909929999
H 4.3116882922 0.9239226785 -5.5069318018
H 3.9815008243 0.5272627528 -7.9196231519
H 2.6075362746 -1.3713196757 -8.7070737612
H 3.4038993628 -4.7350332732 -0.3933348093
H 4.1739001277 -2.5534108588 0.4412145093
H 4.2010384245 -0.5945920545 -1.0822457846
H 2.7320793797 -5.5712551028 -3.825663258
H 3.137106536 -6.113412616 -2.2041501572
H 1.4725026649 -5.734081819 -2.5971150199
H 0.5735795717 2.627923264 3.5984975806
H -0.9610955231 2.9002256861 2.7416443603
H -0.6108294675 1.3078787689 3.4539933653

39
[5i-Ag(I)-CH3CN]+ 1 1 -1119.7045681 0.2944075 0
RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C 0.476660107 -1.7348317546 0.4721782187
C 1.8234858523 -1.9010539239 0.0285104355
N 2.5507342166 -0.8112649999 -0.3543351476
C 3.7889148234 -0.9801636286 -0.7844818564
C 4.406694751 -2.2379628244 -0.8774755234
C 3.7077452404 -3.3456345633 -0.4784276019
C 2.3855001344 -3.2083191619 -0.0015945749
C 1.6204068769 -4.3108720574 0.4421643524
C 0.347212627 -4.1186051014 0.910434061
C -0.2227957039 -2.8332189232 0.9266947555
N -0.0409938548 -0.4302956292 0.4711558665
C -1.2644445164 -0.1841792962 0.3116057805
C -2.5951200614 -0.760018197 0.0166687513
C -3.4288764264 -1.8231755481 -0.2620448302
C -4.7625933171 -1.4618808778 -0.4965550621
C -5.1893512179 -0.1331796899 -0.4454637959
C -4.34053703 0.9633340172 -0.1664620089
C -3.0575999434 0.5433406565 0.049615853
C -4.8034439798 2.3886518844 -0.1203891366
O -1.7820447192 1.130116365 0.3430214612
Ag 1.6261781458 1.2171306186 0.0178780769
H -6.2361598376 0.0768813442 -0.6321473393
H -5.488386591 -2.2319075971 -0.7216786762
H -3.1054366843 -2.8536888422 -0.3045431998
H 2.0598954911 -5.300037836 0.4169603394
H -0.2318674914 -4.9568993878 1.2752618474
H -1.2187195093 -2.7002045496 1.3264835567
H 4.1551091176 -4.3314517354 -0.519613178
H 5.4200617382 -2.3088426902 -1.2479167033
H 4.3305649194 -0.0862231543 -1.0677698409
H -4.6190385112 2.8289910584 0.8619419612
H -4.2733799045 2.9969221929 -0.8566762675
H -5.8705397701 2.4562913885 -0.3286264152
N 1.7105227543 3.3338155415 0.0941306035
C 1.7141045435 4.4767991248 0.1680637553
C 1.7197366799 5.9246560711 0.2620700233
H 2.6429494386 6.2590602519 0.7375531903
H 0.8679543168 6.2584752571 0.8563462699
H 1.6533745846 6.3580772206 -0.7369213607

39
[L2–Ag(III)–(CH3CN)]+ 1 1 -1119.691478 0.2954502
0 RB3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C 0.086415709 0.2157204768 0.0410873432
C 0.0344258669 -0.0933692674 1.3890870236
C 1.1539621934 -0.3877619335 2.1517707924
C 2.376512732 -0.3521976162 1.4542605907
C 2.4616557468 -0.0459534135 0.103674691
C 1.3118901068 0.2410340819 -0.6137884208
Ag -1.9626016207 -0.0420772685 2.0595913324
N -1.8123176463 -0.5345650172 4.1034937054
C 1.1731648724 -0.731423492 3.6162137358
C -1.1677901108 0.5174978413 -0.6932002122
O -1.2312866568 0.7988921576 -1.8709931245
N -2.2730219756 0.4388365809 0.1367153424
C -3.6082460106 0.6615685171 -0.2226328634
C -4.570675736 0.5196556365 0.8147008716
C -5.9547596949 0.7225710208 0.5620604556
C -6.3697337828 1.0699813099 -0.741951181
C -5.4301610809 1.2029254448 -1.7306475699
C -4.0569642967 1.0037530614 -1.4892002998
N -4.1327273792 0.1815709348 2.0685088095
C -4.9938182723 0.0398215564 3.0599546969
C -6.3719034099 0.2232638568 2.8880976993
C -6.8449031149 0.5626472915 1.6443563821
H 3.2799695326 -0.5757403673 2.0096043788
H 3.4281560507 -0.032899241 -0.3831921503
H 1.3233446493 0.4861374016 -1.669456359
H -7.4219248113 1.2259476429 -0.9413313746
H -5.7370171903 1.4689762027 -2.7341488652
H -3.3446977247 1.1162356937 -2.2888619475
H -7.9053504884 0.7113466946 1.4798004566
H -7.0368010416 0.0957655994 3.7309932662
H -4.5856410765 -0.2280393834 4.0260475097
H 0.7712006579 0.083367272 4.219834408
H 0.592741221 -1.6322988394 3.819558691
H 2.1956431092 -0.9138696862 3.9423537866
C -1.8447006704 -0.7912073737 5.2179756695
C -1.8454817017 -1.120261998 6.6287485711
H -0.8203193885 -1.303374164 6.956524141
H -2.2639297114 -0.2907147029 7.2010458217
H -2.4435192326 -2.0171375003 6.7982684898

39
(triplet)[L2–Ag(III)–(CH3CN)]+ 1 3 -1119.6749117
0.2927754 0 B3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C 0.0337938781 0.2104596794 0.0869548068
C 0.019677996 -0.1056674727 1.4483004457
C 1.1892686699 -0.3896733981 2.1441659687
C 2.3886151586 -0.3466475236 1.4249697127
C 2.4225667307 -0.0332554422 0.0665033342
C 1.2503185054 0.2458758138 -0.6072823571
Ag -1.9716332039 -0.0886825414 2.2633852015
N -2.0481864995 -0.5946362446 4.4663338748
C 1.2037097578 -0.733421549 3.6111758858
C -1.2026183546 0.5143948948 -0.6645415372
O -1.2328930825 0.7926261642 -1.8436589284
N -2.3709305514 0.4450148455 0.1537797616
C -3.6200079622 0.6668414026 -0.2401147516
C -4.664629677 0.5371223377 0.781675014
C -6.0173582483 0.7590224737 0.4336813344
C -6.3503982471 1.1055324324 -0.9030805269
C -5.3638874092 1.2274463871 -1.8655030448
C -4.0271029393 1.0170355174 -1.5596518526
N -4.3088728036 0.2065691535 2.0399151709
C -5.2419954727 0.0860520944 2.9725425741
C -6.6037147176 0.2869875725 2.7184156789
C -6.9906972547 0.6246771955 1.4435121415
H 3.3160737516 -0.5640005323 1.9430955401
H 3.37030456 -0.0100139406 -0.4557003536
H 1.2410700011 0.4927321691 -1.661287926
H -7.3899631459 1.2729020758 -1.1569682104
H -5.6340887745 1.4921286035 -2.8795425617
H -3.265449625 1.1141273623 -2.3154245563
H -8.0340162657 0.7893082754 1.2030346897
H -7.3245462562 0.175705904 3.5168016384
H -4.894848913 -0.1813080709 3.9637553138
H 0.7881282977 0.0817793151 4.2071159757
H 0.6101966271 -1.6286151965 3.8080903134
H 2.2204103624 -0.9196670025 3.9561415772
C -1.7950628411 -0.8736681468 5.5496106691
C -1.4528808479 -1.2276382982 6.9144196356
H -0.3722727873 -1.3587698182 6.9947216579
H -1.7689737971 -0.4349145176 7.5939036123
H -1.9483179979 -2.1591379698 7.1916823699

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(triplet)[5j-Ag(II)-CH3CN]+ 1 3 -1119.6547779
0.2913757 0 B3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
C -8.4448807333 -2.9503387573 0.351204948
C -7.8775768194 -3.1231371899 1.6433423424
C -6.5942174232 -2.5982253873 1.9207565085
C -5.8772752601 -1.8608376799 0.8791388561
C -6.4947021865 -1.7462129919 -0.3974396997
C -7.7508153651 -2.2798251982 -0.6414995352
C -8.5411775036 -3.8138103371 2.677285389
C -7.9276349147 -3.9570870213 3.8981479452
N -6.0057419588 -2.7555275356 3.1220584552
Ag -3.8407539706 -1.8598773871 3.2294694584
N -4.6995605919 -1.3510496212 1.1788777833
C -5.5043630165 1.3231067338 0.6245336393
C -4.3788913975 0.7949750678 0.0328573065
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C -6.6501814479 -3.4123658776 4.0778206413
C -7.2288419031 3.0955447922 1.1810930709
N -2.1122707928 -1.6947815394 4.4484961511
C -1.129874243 -1.6064084031 5.0310451721
C 0.1160780147 -1.4937269282 5.7655991157
H -9.4263942524 -3.3619438493 0.1518164316
H -5.9641314033 -1.2329383134 -1.187446067
H -8.1912663173 -2.1707748003 -1.6239924369
H -9.5263901846 -4.2264672771 2.4970130877
H -8.4068109118 -4.4822463031 4.7130436734
H -5.5584473002 4.4360161987 -0.5398092009
H -3.5209510246 3.6106758952 -1.6492364674
H -2.7502577839 1.2643510933 -1.2870238125
H -6.1366636911 -3.5159224978 5.0257199226
H -7.0076088998 3.3457114626 2.2218008948
H -7.6174182528 3.9912729266 0.6968661991
H -8.0118814402 2.3365131449 1.1840981678
H 0.94179145 -1.3502157122 5.0670414669
H 0.0668643274 -0.6408640171 6.4441763225
H 0.2873569643 -2.4032920923 6.3431261807

39
(triplet)[5k-Ag(III)-CH3CN]+ 1 3 -1119.6544577
0.2914456 0 B3LYP-D3BJ/6-311+g(2d,p):SDD-Ag
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C -5.2319482747 -4.0866400735 1.4045547182
C -4.6454331777 -2.8056512513 1.5506097089
C -4.9531465426 -2.0113065172 2.7418824139
C -5.8462548449 -2.5644850286 3.7054923116
C -6.3989210448 -3.8218901463 3.53367122
C -4.9146894226 -4.8107932532 0.2378951782
C -4.0720245747 -4.2516448757 -0.6935680877
N -3.8278761091 -2.2706263451 0.6367279269
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C -3.2349994438 1.5950940235 0.4591148723
C -4.1451760271 0.7930251492 1.1508031932
C -3.598601881 -0.1173236244 2.1728973209
C -3.5895564071 2.4610508264 -0.5551840073
C -4.9593833872 2.5278599717 -0.8574801497
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C -2.5888945637 3.3155915874 -1.2901651052
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C 1.9694289701 1.5882332178 1.8983089382
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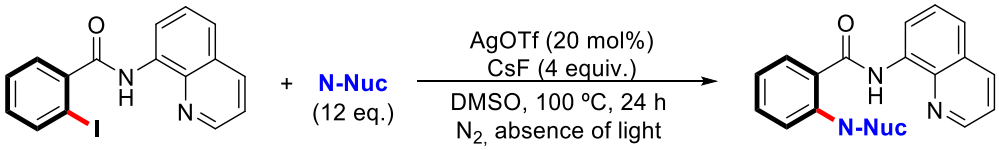
H -3.808651631 -4.7790346378 -1.6007092195
H -5.2841963098 3.1994413571 -1.6444342137
H -6.9443342511 1.8415717072 -0.4360133326
H -6.2222527016 0.2939379397 1.3680926929
H -2.8906647903 -2.5029978187 -1.1731360559
H -1.6656879958 2.7678079589 -1.491450009
H -2.991051808 3.6543980877 -2.2446778773
H -2.3305405662 4.2015811742 -0.7043471389
H 3.5963475037 2.6578178254 2.6504288249
H 3.5612584975 0.9300339289 3.0755367212
H 3.9967799482 1.4315756368 1.424134534

5. Characterization data

5.1 ^{1}H and ^{13}C $\{^{1}H\}$ NMR and mass spectrometry data

5.1.1 C-N bond formation reactions

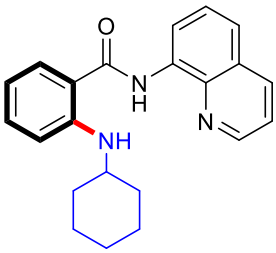
All the C-N bond formation products were synthesized using the optimized reaction conditions from section 3.2.



L_1-I **(a-e)** **2a-2e**

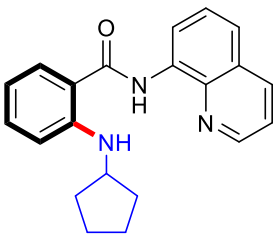
L_1-I, (0.1 mmol/0.25 mmol), AgOTf (20 mol%), CsF (4 equiv.), amine (**a-e**) (12 equiv.) and 1 -2.5 mL of dimethylsulfoxide were added to a glass vial under inert atmosphere and the vial was sealed. The resulting mixture was stirred at 100 °C for 24 h. The resulting crude mixture was extracted with ethyl acetate (3 x 10 mL) and the organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the product was purified using column chromatography.

2-(cyclohexylamino)-*N*-(quinolin-8-yl)benzamide (2a)



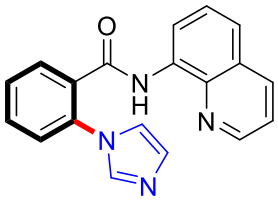
Prepared in accordance to the general synthesis described for above: **L_1-I** (37.4 mg, 0.1 mmol in 1 mL of DMSO) as converted to **2a**; 17.7 mg as a pale yellow solid (51 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 10.61 (s, 1H), 8.84-8.82 (m, 2H), 8.17 (dd, *J* = 8.1 Hz, 1.8 Hz, 1H), 7.85 (bs, 1H), 7.80 (dd, *J* = 8.0 Hz, 1.4 Hz, 1H), 7.60-7.50 (m, 2H), 7.46 (dd, *J* = 4.9 Hz, 1H), 7.34 (ddd, *J* = 6.7 Hz, 1.9 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.68 (ddd, *J* = 8.0 Hz, 7.2 Hz, 1.1 Hz, 1H), 3.41 (s, 1H), 2.09-2.06 (m,2H), 1.82-1.78 (m, 2H), 1.66-1.56 (m, 2H), 1.46-1.30 (m, 4H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 168.5, 149.7, 148.3, 139.0, 136.5, 135.1, 133.3, 128.4, 128.2, 127.6, 121.8, 121.4, 116.4, 115.0, 114.4, 112.4, 50.9, 33.1, 26.1, 25.0. **IR (ATR):** $\bar{\upsilon}$ = 3335, 2922, 2848, 1646, 1574, 1510, 1483, 1453, 1421, 1386, 1324, 1249, 1165, 894, 822, 791, 752, 694, 922, 522, 461, 439. **HRMS** (ESI, m/z): Calculated for $C_{22}H_{23}N_3O$ $[M+H]^+$ 346.1914, Found 346.1921. **R_f**: 0.77 (dichloromethane).

2-(cyclopentylamino)-N(quinolin-8-yl)benzamide (2b)



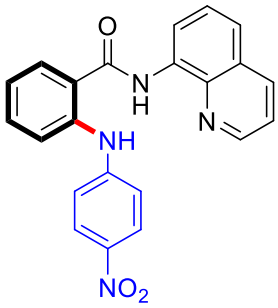
Prepared in accordance to the general synthesis described above: **L_1-I** (37.4 mg, 0.1 mmol in 1 mL of DMSO) was converted to **2b**; 10.2 mg as a pale yellow solid (31 %). ^{1}H-NMR (CDCl3, 400 MHz, 298 K) δ (ppm): 10.61 (bs, 1H), 8.84-8.81 (m, 1H), 8.17 (dd, J = 8.3 Hz, 1.8 Hz), 7.85 (d, *J*=4.6 Hz, 1H), 7.79 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H), 7.60-7.50 (m, 2H), 7.47 (dd, *J* = 8.3 Hz, 3.9 Hz, 1H), 7.36 (ddd, *J* = 8.3 Hz, 7.0 Hz, 1.6 Hz, 1H), 6.79 (dd, *J* = 8.3 Hz, 1.1 Hz, 1H), 6.70 (ddd, *J* = 7.9 Hz, 7.2 Hz, 1.1 Hz, 1H), 3.89 (m, 1H), 2.09-2.04 (m, 2H), 1.81-1.76 (m, 2H), 1.65-1.61 (m, 4H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 168.5, 150.2, 148.3, 139.1, 136.5, 135.1, 133.3, 128.3, 128.2, 127.6, 121.8, 121.4, 116.4, 115.2, 114.6, 112.8, 54.0, 33.7, 24.3. **IR (ATR):** $\bar{\upsilon}$ = 3352, 2953, 1642, 1579, 1413, 1483, 1420, 1381, 1323, 1239, 1164, 894, 826, 791, 763, 735, 669, 601, 525. **HRMS** (ESI, m/z): Calculated for $C_{21}H_{20}N_3O$ $[M+Na]^+$ 354.1577, Found 354.1581. **R_f**: 0.47 (dichloromethane).

2-(1*H*-imidazol-1-yl)-*N*-(quinolin-8-yl)benzamide (2c)



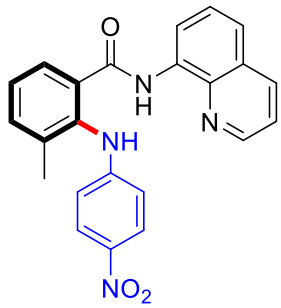
Prepared in accordance to the general synthesis described above: **L_1-I** (93.5 mg, 0.25 mmol in 2.5 mL of DMSO) was converted to **2c**; 42.3 mg as white solid (54 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 9.97 (s, 1H), 8.77 (m, 1H), 8.68 (dd, *J* = 4.2 Hz, 1.7 Hz, 1H), 8.13 (dd, *J* = 6.6 Hz, 1.6 Hz, 1H), 7.92 (dd, *J* = 7.5 Hz, 1.6 Hz, 1H), 7.82 (s, 1H), 7.65-7.56 (m, 2H), 7.54-7.51 (m, 2H), 7.44-7.40 (m, 2H), 7.24 (s, 1H), 7.05 (s, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 164.6, 148.3, 138.4, 137.5, 136.4, 134.9, 134.1, 133.0, 131.8, 130.2, 129.9, 129.0, 128.0, 127.2, 126.7, 122.4, 121.9, 120.7, 116.8. **IR (ATR):** $\bar{\upsilon}$ = 2919, 1669, 1545, 1504, 1423, 1371, 1321, 1237, 1058, 911, 824, 794, 782, 753, 730, 657, 597, 537, 491, 446. **HRMS** (ESI, m/z): Calculated for $C_{19}H_{14}N_4O$ $[M+H]^+$ 315.1240, Found 315.1239. **R_f**: 0.65 (dichloromethane).

2-((4-chlorophenyl)amino)-*N*-(quinolin-8-yl)benzamide (2d)



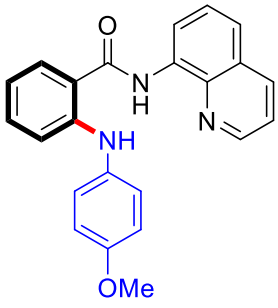
Prepared in accordance to the general synthesis described above: **L_1-I** (93.5 mg, 0.25 mmol in 2.5 mL of DMSO) was converted to **2d;** 59.0 mg as a yellow solid (61 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 10.75 (s, 1H), 9.96 (s, 1H), 8.85-8.83 (m, 2H), 8.21 (dd, *J* = 8.4 Hz, 1.9 Hz, 1H), 8.16 (d, *J* = 9.1 Hz, 2H), 7.94 (dd, *J* = 8.4 Hz, 1.9 Hz, 1H), 7.63-7.60 (m, 3H), 7.53-7.49 (m, 2H), 7.24-7.15 (m, 3H), 7.19-7.15 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 167.3, 148.6, 148.5, 142.4, 141.0, 138.9, 136.7, 134.3, 132.7, 128.5, 128.2, 127.5, 126.1, 122.6, 122.4, 122.0, 121.9, 118.9, 116.8, 116.6. **HRMS** (ESI, m/z): Calculated for $C_{22}H_{16}N_4O_3$ $[M+H]^+$ 385.1295, Found 385.1288. **R_f** = 0.80 (dichloromethane). This compound is known and the data described are in agreement with the previous reports.[32]

3-methyl-2-((4-nitrophenyl)amino)-N-(quinolin-8-yl)benzamide (2e)



Prepared in accordance to the general synthesis described above: **L_2-I** (38.9 mg, 0.1 mmol in 1 mL of DMSO) was converted to **2e;** 23.3 mg as yellow solid (59 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 10.68 (s, 1H), 8.80 (dd, J = 5.8 Hz, 3.1 Hz, 1H), 8.75 (dd, J = 4.3 Hz, 1.7 Hz, 1H), 8.37 (s, 1H), 8.16 (dd, J = 8.3 Hz, 1.7 Hz, 1H), 8.06-8.03 (m, 2H), 7.81 (dd, J = 7.8 Hz, 1.7 Hz, 1H), 7.55-7.53 (m, 2H), 7.48-7.43 (m, 2H), 7.34 (t, J = 7.6 Hz, 1H), 6.65-6.61 (m, 2H), 2.22 (s, 3H).). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 166.7, 151.0, 148.5, 140.0, 138.7, 138.0, 136.6, 135.9, 134.8, 134.4, 131.0, 128.1, 127.4, 126.5, 126.0, 125.9, 122.4, 121.9, 116.9, 114.5, 19.1. **IR (ATR):** $\bar{\upsilon}$ = 3323, 1654, 1596, 1518, 1483, 1321, 1178, 1109, 825, 790, 751. **HRMS** (ESI, m/z): Calculated for $C_{23}H_{19}N_4O_3$ $[M+Na]^+$, 421. 1271, Found 421.1261. **R_f** = 0.65 (AcOEt/Hexane(6:4)).

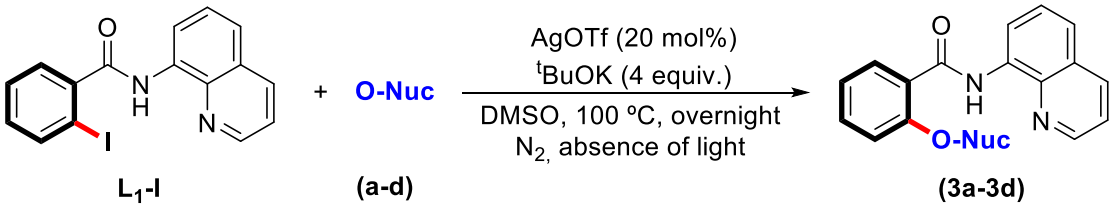
2-((4-methoxyphenyl)amino)-N-(quinolin-8-yl)benzamide (2f)



Prepared in accordance to the general synthesis described above: **L_1-I** (93.5 mg, 0.25 mmol in 2.5 mL of DMSO) was converted to **2f**; 28.1 mg as yellow solid (30 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 10.73 (s, 1H), 9.46 (s, 1H), 8.88-8.84 (m, 2H), 8.18 (dd, *J* = 8.3 Hz, 1.7 Hz, 1H), 7.85 (dd, *J* = 7.9 Hz, 1.3 Hz, 1H), 7.61-7.52 (m, 2H), 7.48 (dd, *J* = 7.9 Hz, 4.2 Hz, 1H), 7.29 (ddd, *J* = 8.4 Hz, 7.1 Hz, 1.3 Hz, 1H), 7.23-7.19 (m, 2H), 7.14 (dd, *J* = 8.4 Hz, 1.3 Hz, 1H), 6.93-6.89 (m, 2H), 6.84 (ddd, *J* = 8.1 Hz, 7.1 Hz, 1.3 Hz, 1H), 3.82 (s, 3H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 168.2, 156.3, 148.4, 139.0, 136.5, 134.8, 134.2, 132.9, 128.2, 128.1, 127.5, 125.1, 121.8, 121.7, 117.0, 116.9, 116.4, 114.8, 114.6, 55.6. **HRMS** (ESI, m/z): Calculated for $C_{23}H_{19}N_3O_2$ $[M+H]^+$ 370.1550, Found 370.1546. **R_f**: 0.79 (dichloromethane). This compound is known and the data described are in agreement with the previous reports.[32]

5.1.2 C-O bond formation reactions

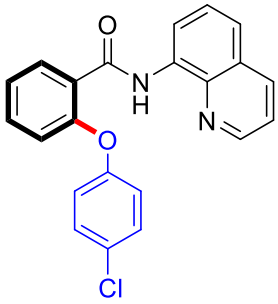
All the C-O bond formation products were synthesized using the optimized reaction conditions from section 3.3



L_1-I (3a-3d)

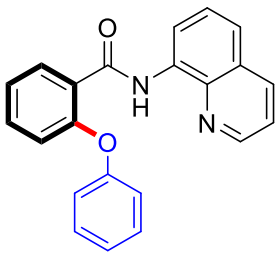
L_1-I, (0.1 mmol), AgOTf (5.2 mg, 20 mol%, 0.02 mmol), ^{t}BuOK (45.0 mg, 4 equiv., 0.4 mmol), phenol (a-d) (10 equiv., 1.0 mmol) and 1 mL of dimethylsulfoxide were added to a glass vial under inert atmosphere and the vial was sealed. The resulting mixture was stirred at 100 °C overnight. The resulting crude mixture was extracted with ethyl acetate (3 x 10 mL) and the organic layers were combined, cleaned with NaOH (2M) and dried over magnesium sulfate. The solvent was removed under reduced pressure and the product was purified using column chromatography.

2-(4-chlorophenoxy)-*N*-(quinolin-8-yl)benzamide (3a)



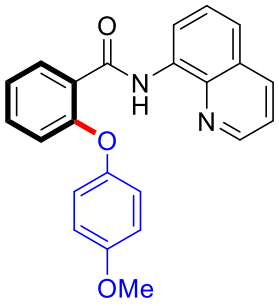
Prepared in accordance to the general synthesis described above: L_1-I (37.4 mg, 0.1 mmol) was converted to **3a**; 27.2 mg as white solid (73 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 12.09 (s, 1H), 8.98 (dd, *J* = 8.3 Hz, 1.3 Hz, 1H), 8.59 (dd, *J* = 4.2 Hz, 1.6 Hz, 1H), 8.39 (dd, *J* = 7.8 Hz, 1.7 Hz, 1H), 8.13 (dd, *J* = 8.3 Hz, 1.6 Hz, 1H), 7.57 (t, *J* = 8.3 Hz, 1H), 7.52-7.46 (m, 2H), 7.40 (dd, *J* = 8.4 Hz, 4.1 Hz, 1H), 7.38-7.35 (m, 2H), 7.31 (ddd, *J* = 8.4 Hz, 7.8 Hz, 1.1 Hz, 1H), 7.21-7.17 (m, 2H), 7.02 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm):163.0, 155.0, 154.8, 148.2, 139.2, 136.3,1 35.4, 133.2, 132.7, 130.1, 129.5, 128.1, 127.6, 125.3, 124.3, 121.8, 121.7, 120.9, 118.7, 117.3. **IR (ATR)**: $\bar{\upsilon}$ = 3296, 2919, 2850, 1663, 1524, 1474, 1385, 1325, 1280, 1224, 1097, 905, 868, 823, 792, 750, 701, 685, 662, 594, 520, 489, 442. **HRMS** (ESI, m/z): Calculated for $C_{22}H_{15}ClN_2O_2$ $[M+Na]^+$ 397.0714, Found 397.0707. **R_f**: 0.69 (AcOEt/Hexane (3:7)).

2-phenoxy-*N*-(quinoline-8-yl)benzamide (3b)



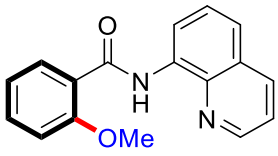
Prepared in accordance to the general synthesis described above: L_1-I (37.4 mg, 0.1 mmol) was converted to **3b**; 20.4 mg as a pale yellow solid (60 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 12.23 (s, 1H), 9.00 (dd, *J* = 7.9 Hz, 1.3 Hz, 1H), 8.57 (dd, *J* = 4.0 Hz, 1.8 Hz, 1H), 8.40 (dd, *J* = 7.7 Hz, 1.9 Hz, 1H), 8.11 (dd, *J* = 8.3 Hz, 1.8 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.51-7.40 (m, 4H), 7.37 (dd, *J* = 8.1 Hz, 4.1 Hz, 1H), 7.30-7.26 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 163.3, 156.1, 155.6, 148.2, 139.3, 136.2, 135.6, 133.1, 132.5, 130.0, 128.1, 127.6, 125.1, 124.4, 123.8, 121.7,121.6, 119.8, 118.6, 117.3. **IR (ATR):** $\bar{\upsilon}$ = 3286, 3042, 2962, 2923, 1652, 1597, 1527, 1474, 1328, 1259, 1226, 1095, 1016, 906, 867, 789, 748, 683, 594, 520, 467. **HRMS** (ESI, m/z): Calculated for $C_{22}H_{16}N_2O_2$ $[M+Na]^+$ 363.1104, Found 363.1102. **R_f**: 0.50 (dichloromethane).

2-(4-methoxyphenoxy)-*N*-(quinolin-8-yl)benzamide (3c)



Prepared in accordance to the general synthesis described above: **L_1-I** (37.4 mg, 0.1 mmol) was converted to **3c;** 8.3 mg as a yellow solid (22 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 12.31 (s, 1H), 9.01 (dd, *J* = 7.6 Hz, 1.1 Hz, 1H), 8.56 (dd, *J* = 4.3 Hz, 1.8 Hz, 1H), 8.38 (dd, *J* = 7.9 Hz, 1.8 Hz, 1H), 8.11 (dd, *J* = 8.2 Hz, 1.8 Hz, 1H), 7.57-7.55 (m, 1H), 7.51-7.49 (m, 1H), 7.42 (ddd, *J* = 8.2 Hz, 7.3 Hz, 1.8 Hz, 1H), 7.37 (dd, *J* = 8.2 Hz, 4.3 Hz, 1H), 7.25-7.20 (m, 3H), 6.98-6.95 (m, 3H), 3.84 (s, 3H).**^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 163.4, 156.6, 149.1, 148.2, 139.3, 136.2, 135.7, 133.0, 132.5, 129.0, 128.1, 127.6, 124.3, 123.1, 121.6, 121.6, 121.4, 117.3, 117.2, 115.1, 55.8. **IR (ATR):** $\bar{\upsilon}$ = 3259, 3044, 3002, 2954, 1654, 1597, 1530, 1503, 1389, 1328, 1285, 1219, 1153, 1102, 1029, 908, 846, 825, 792, 746, 684, 595, 518, 484. **HRMS** (ESI, m/z): Calculated for $C_{23}H_{18}N_2O_3$ $[M+Na]^+$ 393.1210, Found 393.1203. **R_f:** 0.75 (dichloromethane).

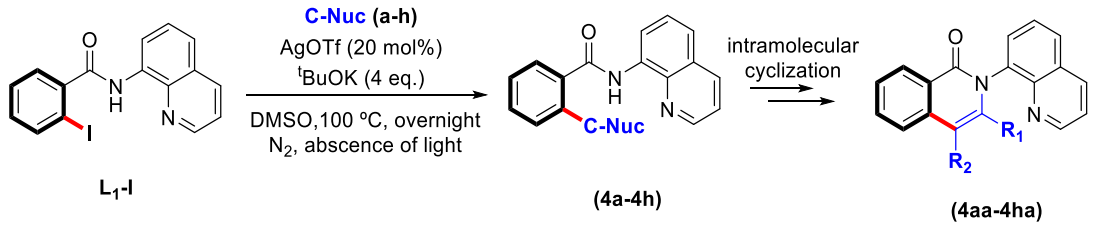
2-methoxy-N-(quinolin-8-yl)benzamide (3e)



Prepared in accordance to the general synthesis described above: **L_1-I** (37.4 mg, 0.1 mmol in 1 mL of CH_3OH) was converted to **3e** 3.50 mg as a pale yellow solid (13 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 12.35 (s, 1H), 9.04 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 8.89 (dd, J = 4.2 Hz, 1.6 Hz, 1H), 8.36 (dd, J = 7.8 Hz, 1.8 Hz, 1H), 8.18 (dd, J = 8.2 Hz, 1.6 Hz, 1H), 7.59 (t, J = 8.2 Hz, 1H), 7.54- 7.50 (m, 2H), 7.47 (dd, J = 8.2 Hz, 3.7 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 4.22 (s, 3H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 163.7, 157.8, 148.3, 139.3, 136.3, 135.8, 133.1, 132.4, 128.1, 127.6, 122.4, 121.5, 121.4, 121.3, 117.4, 111.6, 56.2. **HRMS** (ESI, m/z): Calculated for $C_{17}H_{14}N_2O_2$ $[M + Na]^+$ 301.0947, Found 301.0948. **R_f** : 0.47 (dichloromethane). This compound is known and the data described are in agreement with the previous reports.[33]

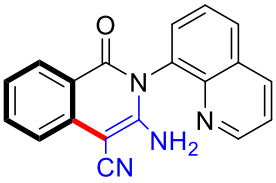
5.1.3 C-C bond formation reactions

The C-C coupling products using activated methylene substrates were synthesized using the optimized reaction conditions from section 3.4.1:



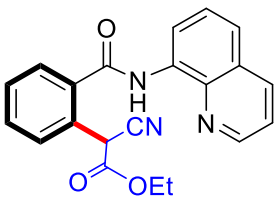
L_1-I, (0.10 mmol), AgOTf (5.2 mg, 20 mol%, 0.02 mmol), ^{t}BuOK (45.0 mg, 4 equiv., 0.40 mmol), activated methylene (2 equiv. of **a** and 4 equiv. of **b-f**) and 2.5 mL of dimethylsulfoxide were added to a glass vial under inert atmosphere and the vial was sealed. The resulting mixture was stirred at 100 °C overnight. The resulting crude mixture was extracted with ethyl acetate (3 x 10 mL) and the organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the product was purified using column chromatography.

3-amino-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinoline-4-carbonitrile (4aa)



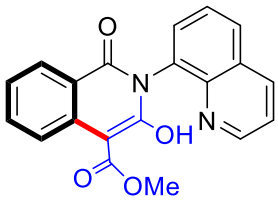
Prepared in accordance to the general synthesis described above: **L_1-I** (37.4 mg, 0.10 mmol) was converted to **4aa**; 22.1 mg of a pale orange solid (71 %). This compound was isolated by precipitation using dichloromethane as solvent. **^{1}H-NMR** (DMSO d_6, 400 MHz, 298 K) δ (ppm): 8.82 (dd, *J* = 4.2 Hz, 1.7 HZ, 1H), 8.51 (dd, *J* = 8.3 Hz, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.3 Hz, 1.4 Hz, 1H), 7.92 (dd, *J* = 8.01 Hz, 1.0 Hz, 1H), 7.84 (dd, *J* = 7.1 Hz, J = 1.4 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.67 (ddd, *J* = 8.5 Hz, 7.3 Hz, 1.5 Hz, 1H), 7.60 (dd, *J* = 8.3 Hz, 4.2 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.14 (ddd, *J* = 8.1 Hz, 7.1 Hz, 1.0 Hz, 1H), 6.74 (bs, 2H). **^{13}C-NMR** (DMSO d_6, 100 MHz, 298 K) δ (ppm): 161.6, 155.3, 151.0, 143.8, 137.5, 136.6, 134.1, 132.9, 131.2, 130.1, 129.4, 128.0, 126.9, 122.1, 122.0, 120.5, 118.5, 118.1, 63.9. **IR (ATR):** $\tilde{\upsilon}$ = 3414, 3058, 2195, 1672, 1624, 1544, 1493, 1429, 1386, 1323, 1161, 992, 889, 843, 824, 786, 771, 754, 690, 634, 511, 467. **HRMS** (ESI, m/z): Calculated for $C_{19}H_{12}N_4O$ $[M+H]^+$ 313.1084, Found 313.1089.

Ethyl (S)-2-cyano-2-(2-(quinolin-8-ylcarbamoyl)phenyl)acetate (4b)



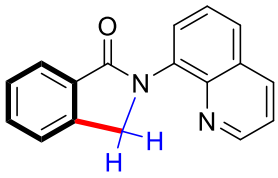
Prepared in accordance to the general synthesis described above: **L_1-I** (37.4 mg, 0.10 mmol) was converted to **4b**; 15.1 mg as lightless orange liquid (42 %). **^{1}H-NMR** (CD_3Cl, 400 MHz, 298 K) δ (ppm): 10.52 (s, 1H), 8.88-8.83 (m, 1H), 8.81 (dd, *J* = 4.2 Hz, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3 Hz, 1.6 Hz, 1H), 7.92 (dd, *J* = 7.3 Hz, 1.6 Hz, 1H), 7.77 (dd, *J* = 7.5 Hz, 1.6 Hz, 1H), 7.65- 7.57 (m, 4H), 7.48 (dd, *J* = 8.2 Hz, 4.3 Hz, 1H), 6.16 (s, 1H), 4.22 (qd, *J* = 7.2 Hz, 2.6 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 166.5, 165.2, 148.6, 138.7, 136.6, 134.9, 134.4, 131.8, 130.4, 130.2, 129.7, 128.1, 127.9, 127.5, 122.5, 122.0, 116.9, 116.2, 63.3, 40.3, 13.9. **HRMS** (ESI, m/z): Calculated for $C_{21}H_{17}N_3O_3$ $[M+H]^+$ 360.1343, Found 360.1358. **R_f**: 0.56 (dichloromethane). This compound is known and the data described is in agreement with the previous reports.[34]

Methyl 3-hydroxy-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinoline-4-carboxylate (4ca)



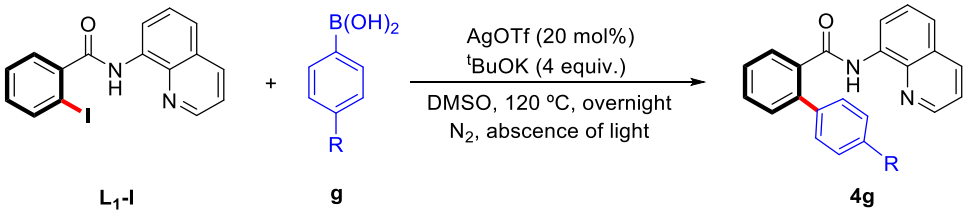
Prepared in accordance to the general synthesis described above: **L1-I** (37.4 mg, 0.1 mmol) was converted to **4ca.** This product could not be isolated and the yield was calculated from crude mixture using trimethoxybenzene as internal standard (62 %). **^{1}H-NMR** (DMSO d_6, 400 MHz, 298 K) δ (ppm): 8.74 (dd, *J* = 4.1 Hz, 1.6 Hz, 1H), 8.40 (m, 2H), 7.95 (dd, *J* = 8.1 Hz, 1.1 Hz, 1H), 7.87 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H), 7.65 (m, 1H), 7.49 (m, 2H), 7.33 (ddd, *J* = 8.6 Hz, 6.9 Hz, 1.6 Hz, 1H), 6.78 (m, 1H), 3.71 (s, 3H). **HRMS** (ESI, m/z): Calculated for $C_{20}H_{14}N_2O_4$ $[M+H]^+$ 347.1026, Found 347.1024.

2-(quinolin-8-yl)isoindolin-1-one (4fa)



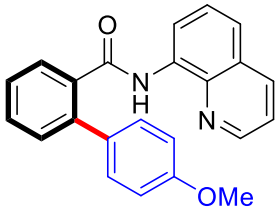
Prepared in accordance to the general synthesis described above: **L_1-I** (37.4 mg, 0.10 mmol) was converted to **4f**; 12.3 mg as pale orange solid (47 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 8.88 (dd, *J* = 4.2 Hz, 1.7 Hz, 1H), 8.21 (dd, *J* = 8.3 Hz, 1.7 Hz, 1H), 8.01 (dt, *J* = 7.6 Hz, 1.1 Hz, 1 H), 7.94 (dd, *J* = 7.4 Hz, 1.4 Hz, 1H), 7.83 (dd, *J* = 8.3 Hz, 1.4 Hz, 1H), 7.66-7.59 (m, 2H), 7.54-7.50 (m, 2H), 7.43 (dd, *J* = 8.3 Hz, 4.2 Hz, 1H), 5.30 (s, 2H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 169.0, 150.1, 144.4, 142.6, 136.5, 135.7, 132.7, 131.8, 129.6, 128.8, 128.0, 127.7, 126.6, 124.5, 122.9, 121.6, 54.0. **IR (ATR):** $\bar{\upsilon}$ = 2921, 2853, 1682, 1502, 1471, 1427, 1400, 1297, 1197, 1131, 912, 890, 829, 795, 760, 731, 682, 614, 560, 484, 462, 414. **HRMS** (ESI, m/z): Calculated for $C_{17}H_{12}N_2O$ $[M+H]^+$ 261.1022, Found 261.1033. **R_f** : 0.37 (AcOEt/Hexane: 7/3). Column: AcOEt/Hexane (7:3) to AcOEt.

The product using arylboronic acid as a nucleophile was synthesized using the optimized reaction conditions from section 3.4.2:



L_1-I, (0.1 mmol), AgOTf (5.2 mg, 20 mol%, 0.02 mmol), ^{t}BuOK (45.0 mg, 4 equiv., 0.40 mmol), boronic acid (**g**) (10 equiv., 1 mmol) and 1 mL of dimethylsulfoxide were added to a glass vial under inert atmosphere and the vial was sealed. The resulting mixture was stirred at 120 °C overnight. The resulting crude mixture was extracted with ethyl acetate (3 x 10 mL) and the organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the product was purified using column chromatography.

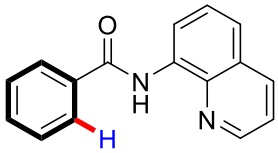
4-methoxy-*N*-(quinolin-8-yl)-[1,1-biphenyl]-2-carboxamide (4g)



Prepared in accordance to the general synthesis described above: **L_1-I** (37.4 mg, 0.1 mmol) was converted to **4g**; 5.3 mg as a pale orange solid (15 %). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 9.81 (s, 1H), 8.82 (dd, *J* = 7.6 Hz, 1.3 Hz, 1H), 8.53 (dd, *J* = 4.2 Hz, 1.7 Hz, 1H), 8.08 (dd, *J* = 8.3 Hz, 1.7 Hz, 1H), 7.90 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H), 7.57-7.51 (m, 2H), 7.48-7.43 (m, 5H), 7.35 (dd, *J* = 8.2 Hz, 4.2 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.65 (s, 3H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 168.2, 160.0, 147.9, 140.1, 138.6, 136.1, 136.0, 134.8, 132.6, 130.8, 130.6, 130.3, 129.4, 127.9, 127.5, 127.4, 121.6, 121.5, 116.5, 114.1, 55.3. **HRMS** (ESI, m/z): Calculated for $C_{23}H_{18}N_2O_2$ $[M+Na]^+$ 377.1260, Found 377.1249. **R_f**: 0.77 (dichloromethane). This compound is known and the data described are in agreement with the previous reports.[35]

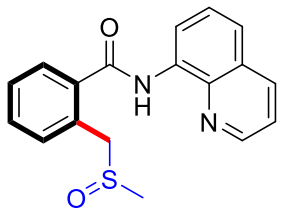
5.1.4. Byproducts

N-(quinolin-8-yl)benzamide (L_1-H)



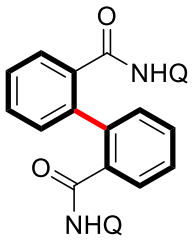
^{1}H-NMR (CDCl3, 400 MHz, 298 K) δ (ppm): 10.74 (s, 1H), 8.95 (dd, *J* = 7.6 Hz, 1.4 Hz, 1H), 8.83 (dd, *J* = 4.2 Hz, 1.7 Hz, 1H), 8.15 (dd, *J* = 8.4 Hz, 1.7 Hz, 1H), 8.10-8.08 (m, 2H), 7.60-7.51 (m, 5H), 7.45 (dd, *J* = 8.4 Hz, 4.2 Hz, 1H).**^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 165.5, 148.4, 138.8, 136.5, 135.2, 134.7, 131.9, 128.9, 128.1, 127.5, 127.4, 121.8, 116.6. **HRMS** (ESI, m/z): Calculated for $C_{16}H_{12}N_2O$ $[M+Na]^+$ 271.0842, Found 271.0836. This compound is known and the data described are in agreement with the previous reports.[33]

2-((methylsulfinyl)methyl)-N-(quinolin-8-yl)benzamide (L_1-DMSO)



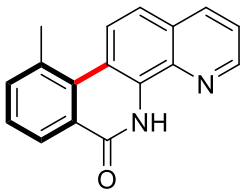
^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 10.44 (s, 1H), 8.85 (dd, *J* = 6.2 Hz, 2.7 Hz, 1H), 8.81 (dd, *J* = 4.2 Hz, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3 Hz, 1.7 Hz, 1H), 7.87 (m, 1H), 7.62-7.50 (m, 5H), 7.48 (dd, *J* = 8.2 Hz, 4.2 Hz, 1H), 4.61 (d, *J* = 12.9 Hz, 1H), 4.25 (d, *J* = 12.9 Hz, 1H), 2.60 (s, 3H). **^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 167.1, 148.6, 138.8, 136.5, 136.2, 134.6, 133.0, 131.3, 130.7, 128.9, 128.2, 127.9, 127.5, 122.4, 122.0, 116.9, 58.2, 38.3. **HRMS** (ESI, m/z): Calculated for $C_{18}H_{16}N_2O_2S$ $[M+Na]^+$ 347.0825, Found 347.0831. **IR (ATR):** $\bar{\upsilon}$ = 3374, 3284, 2962, 1671, 1651, 1595, 1523, 1477, 1328, 1259, 1090, 1020, 789, 751, 684, 594. **R_f**: 0.13 (ethylacetate).

N^2,N^2-di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (L_1-L_1 homocoupling)



^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 10.36 (s, 2H), 8.69 (dd, J = 7.2 Hz, 1.9 Hz, 2H), 8.46 (dd, J = 4.2, 1.8 Hz, 2H), 7.95 (dd, J = 8.2 Hz, 1.8 Hz, 2H), 7.86 (dt, J = 7.2 Hz, 1.2 Hz, 2H), 7.46-7.43 (m, 4H), 7.42-7.37 (m, 2H), 7.31-7.23 (m, 6H).**^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 167.6, 147.8, 139.8, 138.5, 136.5, 135.9, 134.8, 131.0, 130.6, 128.1, 128.0, 127.6, 127.2, 121.5, 121.4, 116.7. **HRMS** (ESI, m/z): Calculated for $C_{32}H_{22}N_4O_2$ $[M+Na]^+$ 517.1635, Found 517.1623. This compound is known and the data described are in agreement with the previous reports.[3]

10-methylbenzo[c][1,10]phenanthrolin-6(5H)-one (5a)



L_2-I, (0.077 g, 0.2 mmol), $AgClO_4$ (0.082 g, 0.4 mmol), $NaCO_3$ (0.042 g, 0.4 mmol), 2 mL of CH_3CN were added to a glass vial under inert atmosphere and the vial was sealed and covered with aluminum foil. The resulting mixture was stirred at 100 °C for 24 h. The resulting crude mixture was extracted with dichloromethane (3 x 10 mL) and the organic layers were combined and dried over magnesium sulfate. The solvent was then removed under reduced pressure and the product was purified using column chromatography (CH_2Cl_2/AcOEt (7:3)). **^{1}H-NMR** ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 10.40 (s, 1H), 8.96 (dd, J = 4.3 Hz, 1.7 Hz, 1 H), 8.48 (d, J = 8.8 Hz, 1H), 8.46 (m, 1H), 8.27 (dd, J = 8.3 Hz, 1.7 Hz, 1H), 7.65 (dd, J = 8.3 Hz, 4.3 Hz, 1H), 7.59 (m, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.29 (m, 1H), 2.76 (s, 3H).**^{13}C-NMR** ($CDCl_3$, 100 MHz, 298 K) δ (ppm): 178.3, 148.7, 139.1, 138.2, 137.7, 136.5, 134.0, 130.2, 125.4, 124.8, 124.2, 124.1, 123.2, 122.3, 119.8, 118.9, 17.0. **HRMS** (ESI, m/z): Calculated for $C_{17}H_{12}N_2O$ $[M+H]^+$ 261.1022, Found 261.1028. **IR (ATR):** $\bar{\upsilon}$ = 3371.7, 2959.8, 2923.4, 2854.2, 1730.3, 1668.9, 1586.9, 1535.6, 1453.3, 1259.5, 1095.1, 1076.2, 1015.1, 791.7, 750.4, 616.6, 452.1. **R_f**: 0.72 (CH_2Cl_2/AcOEt (7:3)).

5.2 Original ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of substrates

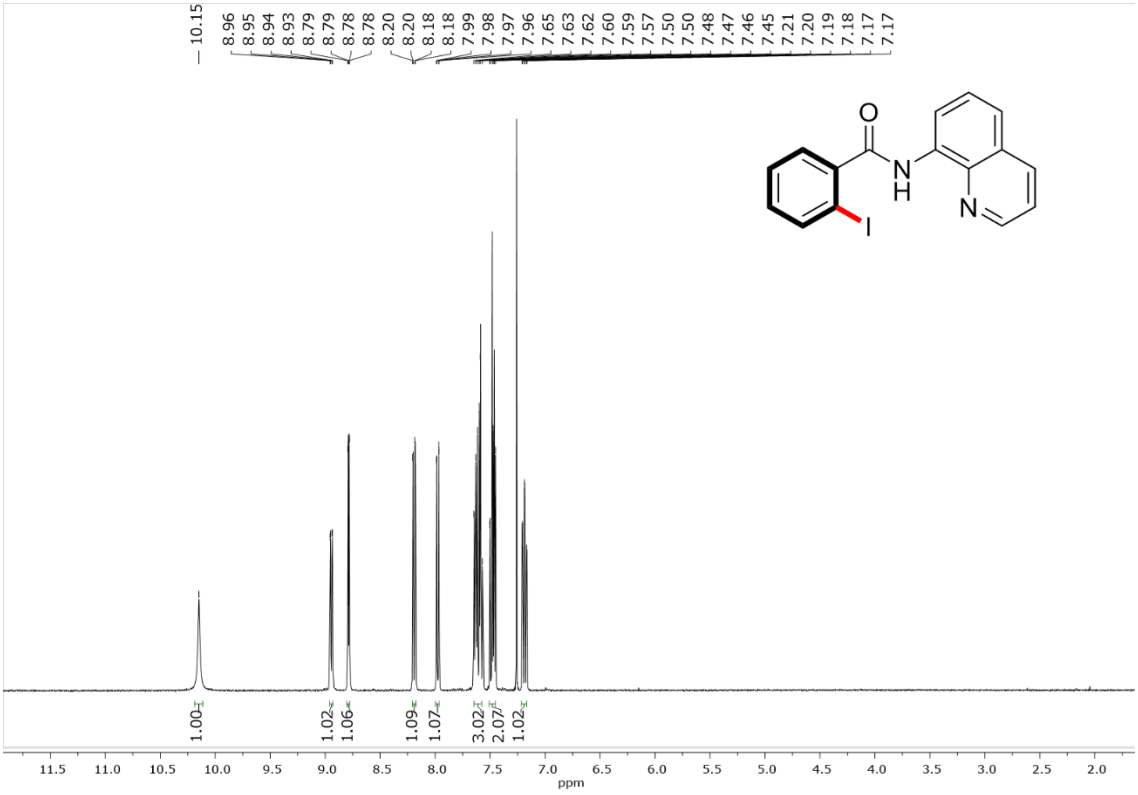


Figure S5. 400 MHz ^{1}H-NMR spectrum of **L_1-I** in $CDCl_3$, 298 K.

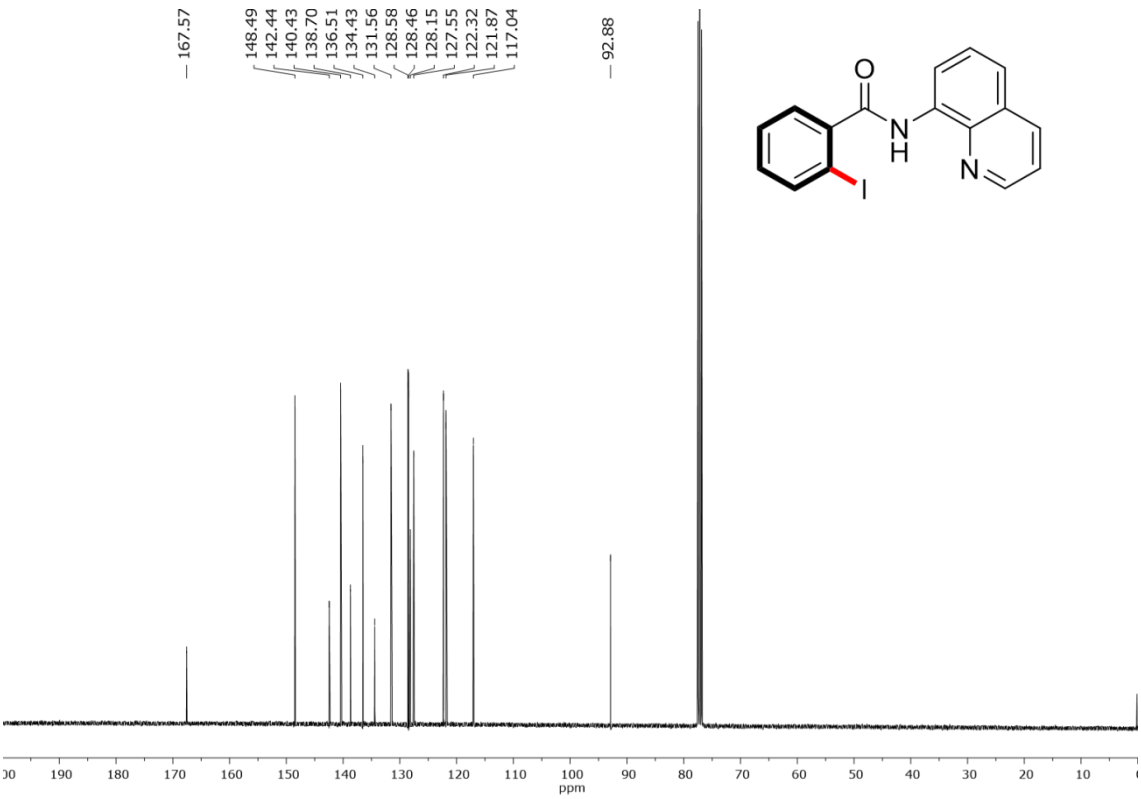


Figure S6. 100 MHz ^{13}C-NMR spectrum of **L_1-I** in $CDCl_3$, 298 K.

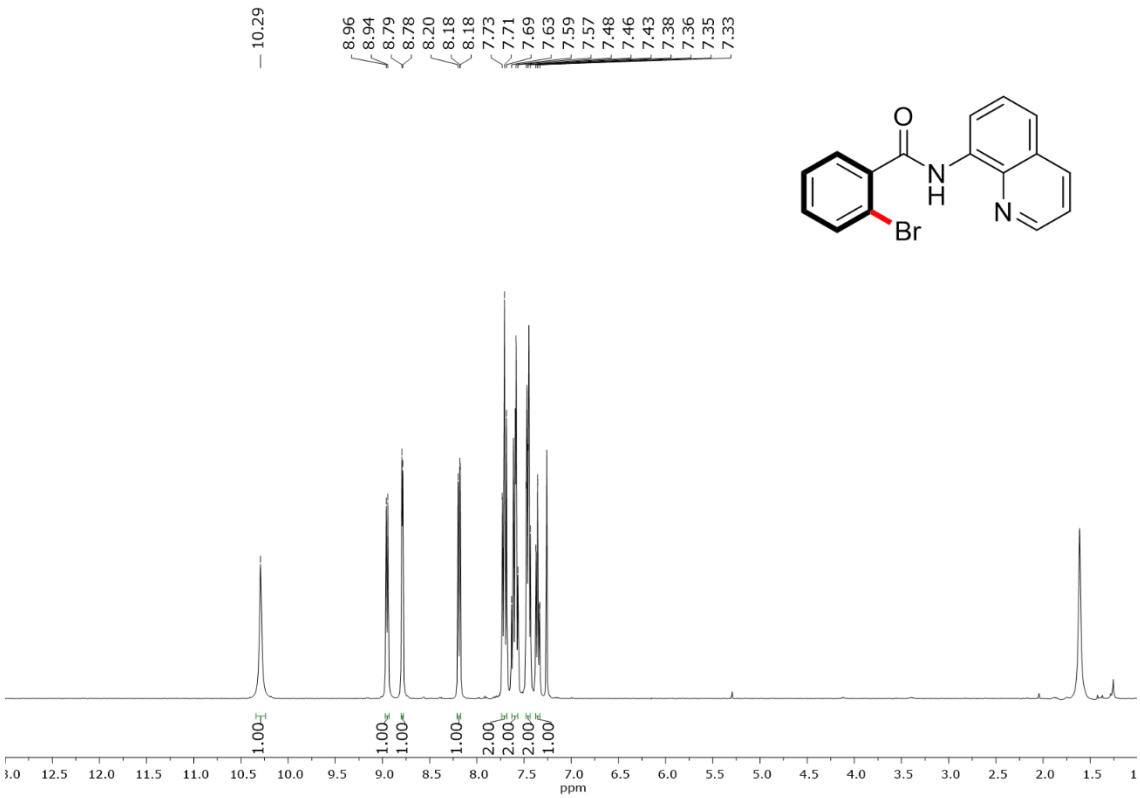


Figure S7. 400 MHz ^{1}H-NMR spectrum of **L_1-Br** in $CDCl_3$, 298 K.

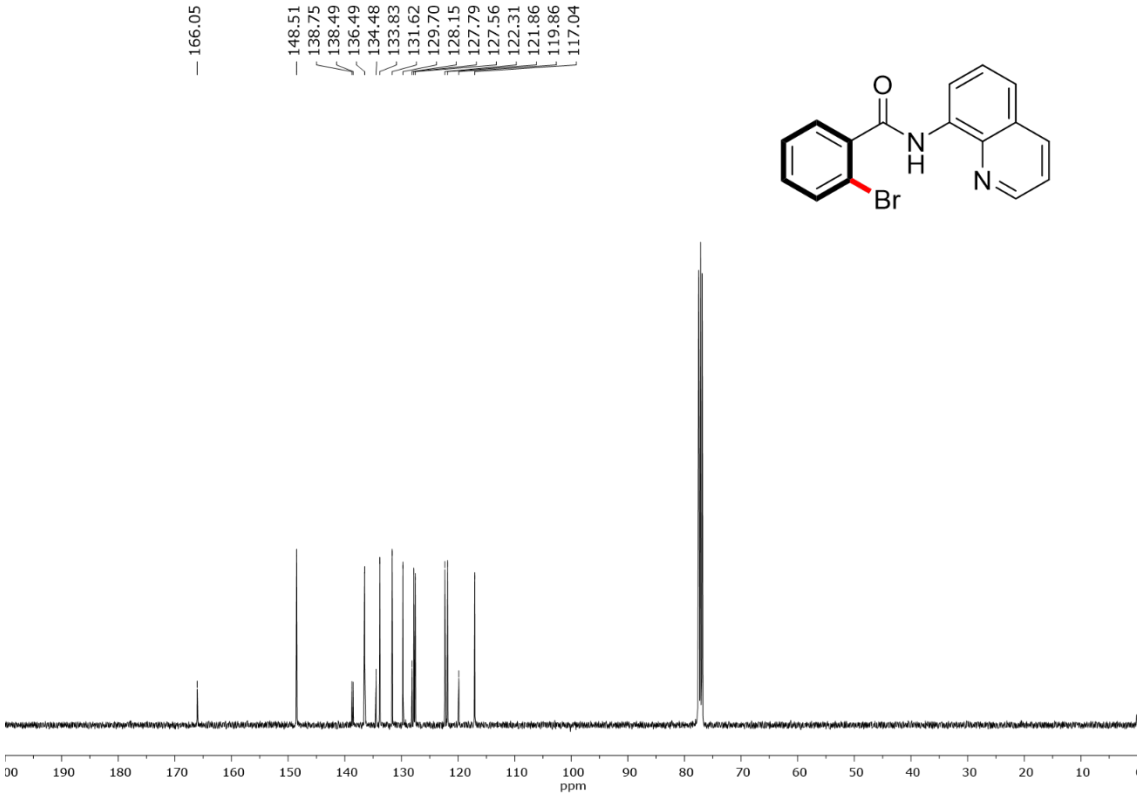


Figure S8. 100 MHz ^{13}C-NMR spectrum of **L_1-Br** in $CDCl_3$, 298 K.

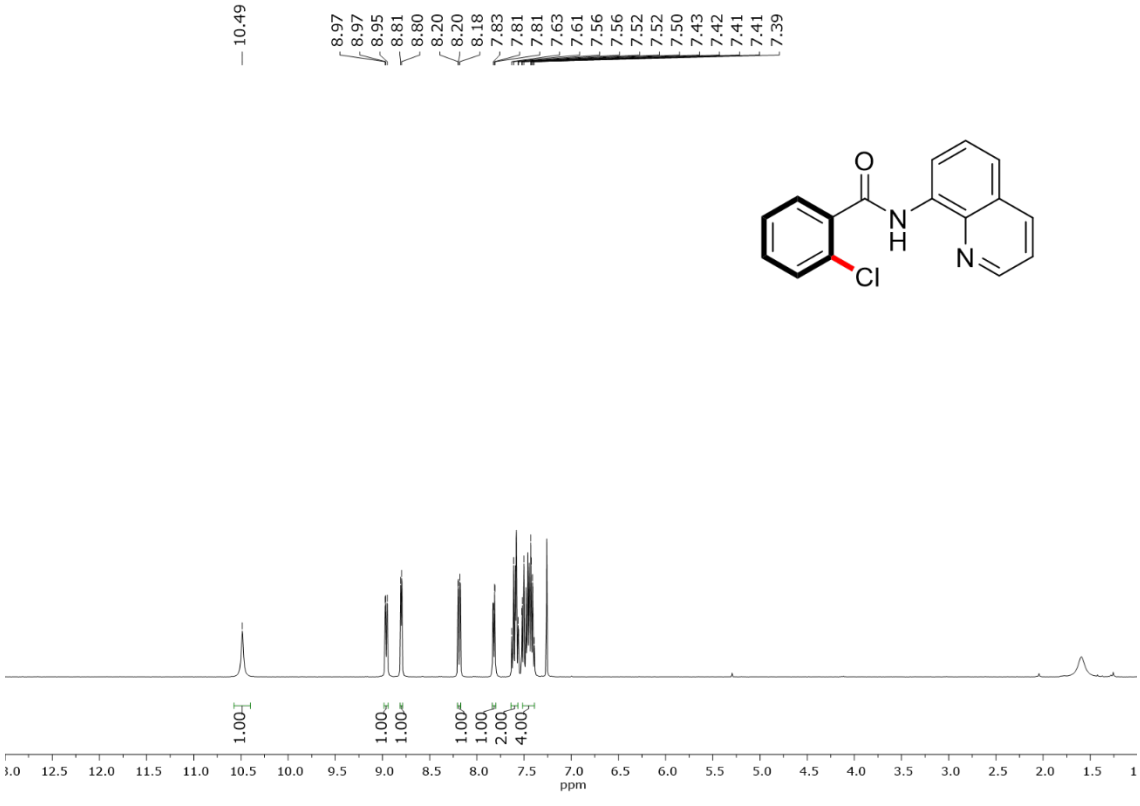


Figure S9. 400 MHz ^{1}H-NMR spectrum of **L_1-Cl** in $CDCl_3$, 298 K.

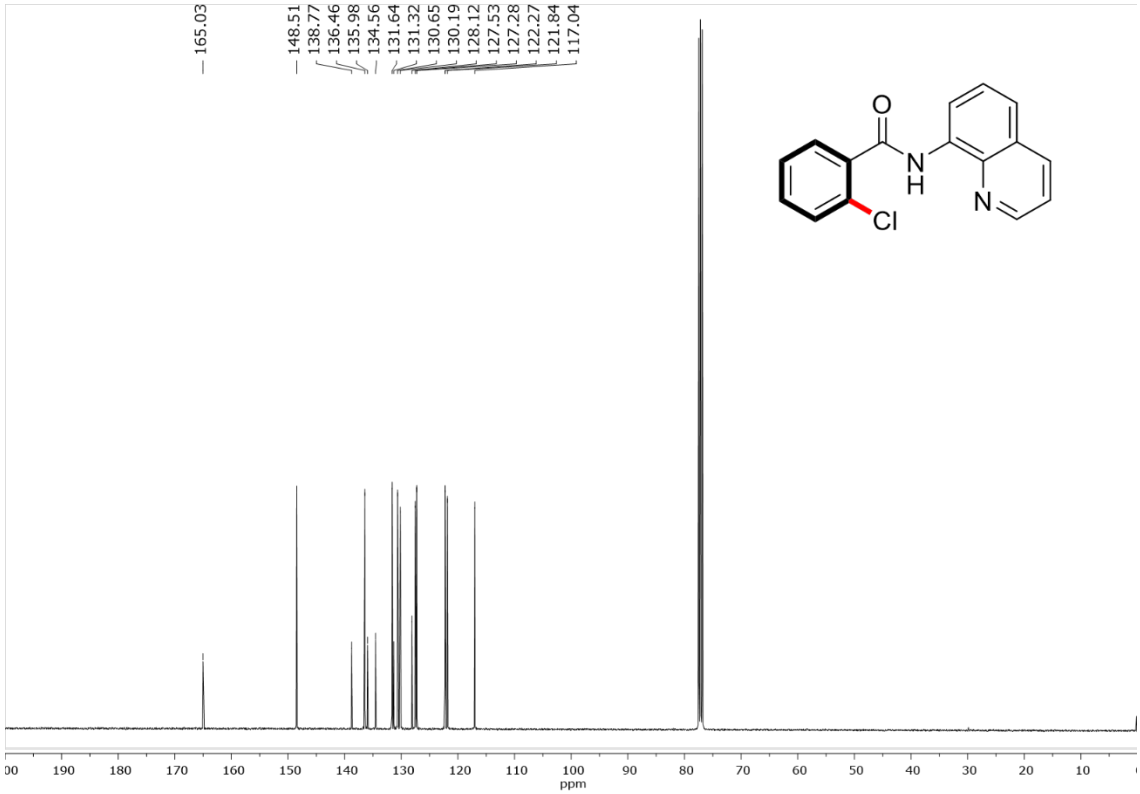


Figure S10. 100 MHz ^{13}C-NMR spectrum of **L_1-Cl** in $CDCl_3$, 298 K.

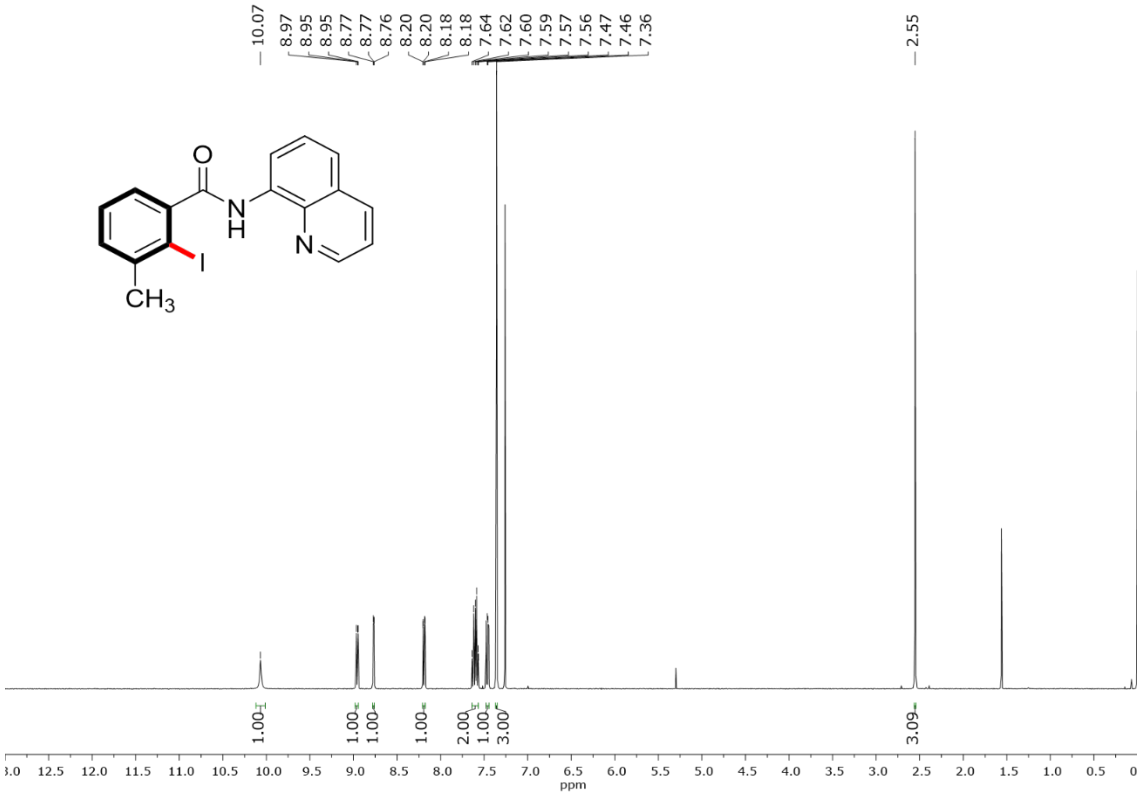


Figure S11. 400 MHz ^{1}H-NMR spectrum of **L_2-I** in $CDCl_3$, 298 K.

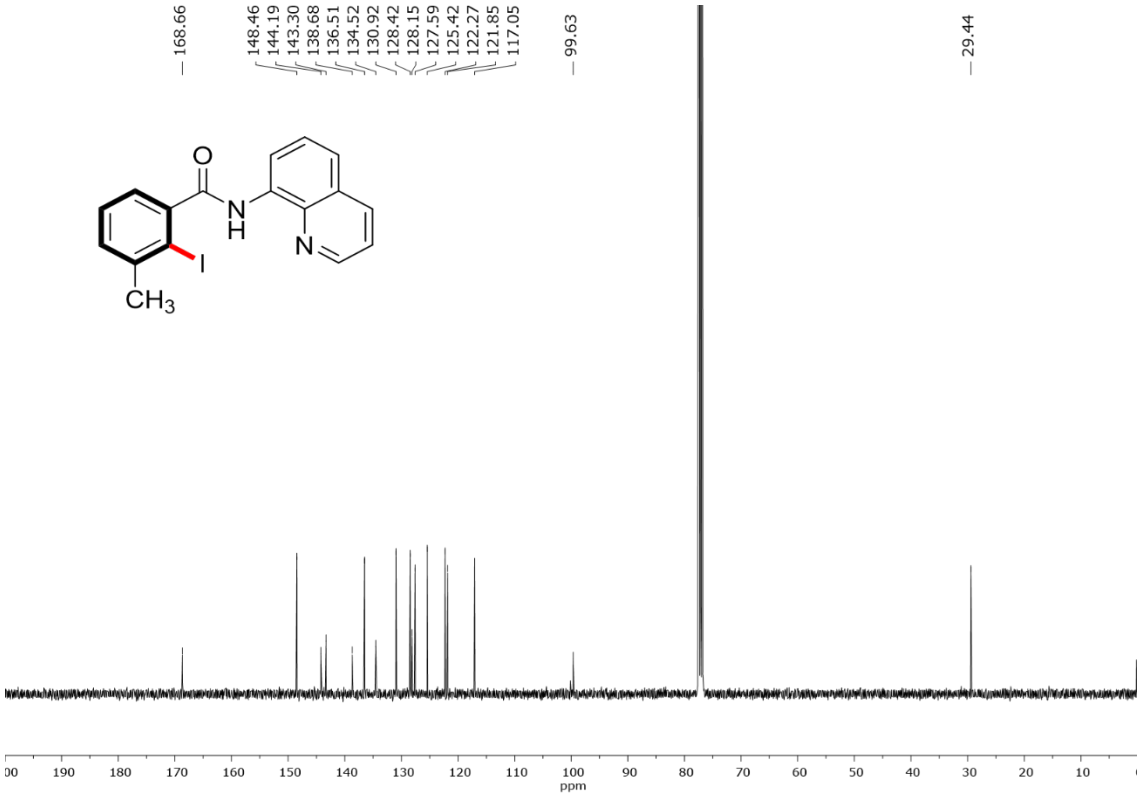


Figure S12. 100 MHz ^{13}C-NMR spectrum of **L_2-I** in $CDCl_3$, 298 K.

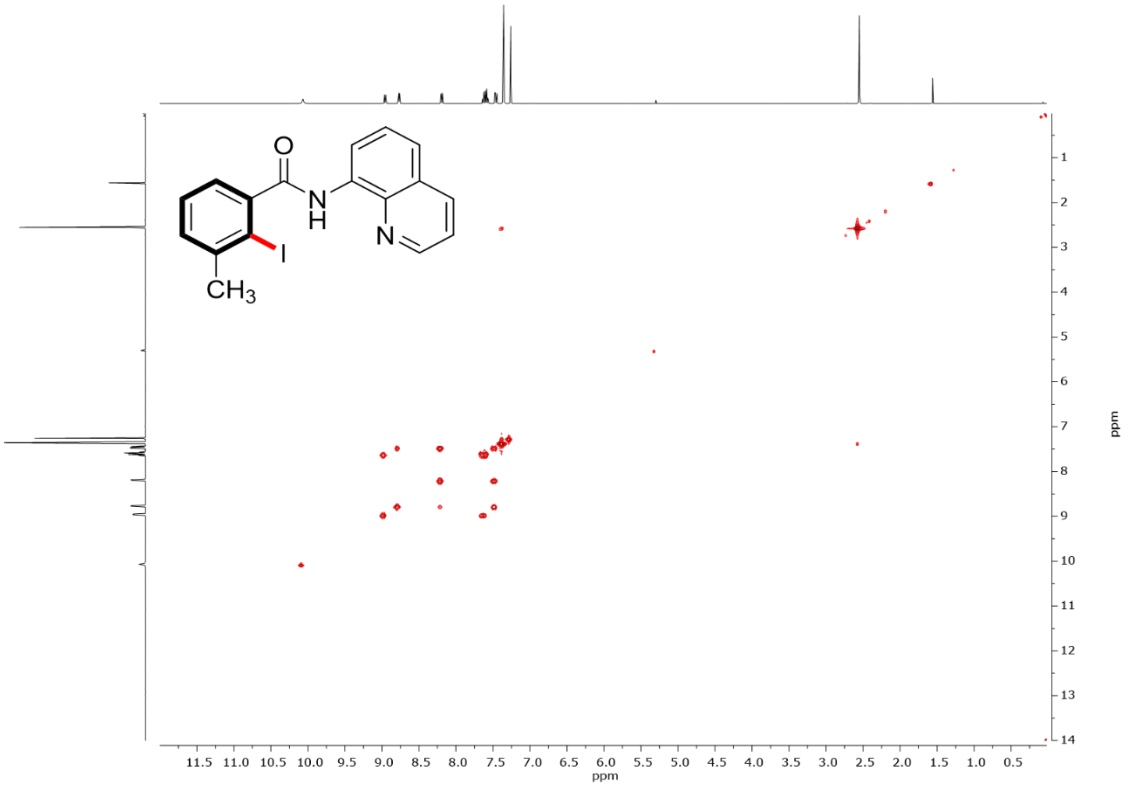


Figure S13. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **L_2-I** in $CDCl_3$, 298 K.

5.3. Original ^{1}H and ^{13}C {^{1}H} NMR spectra of products

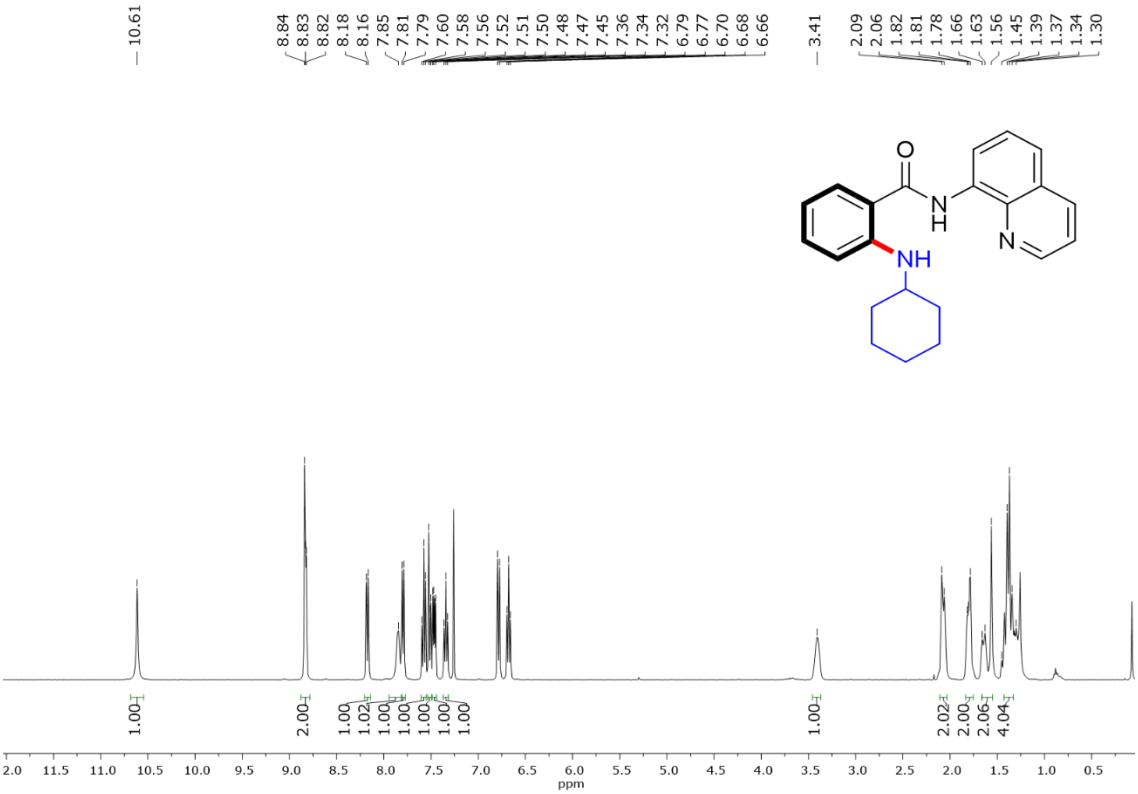


Figure S14. 400 MHz ^{1}H-NMR spectrum of **2a** in $CDCl_3$, 298 K.

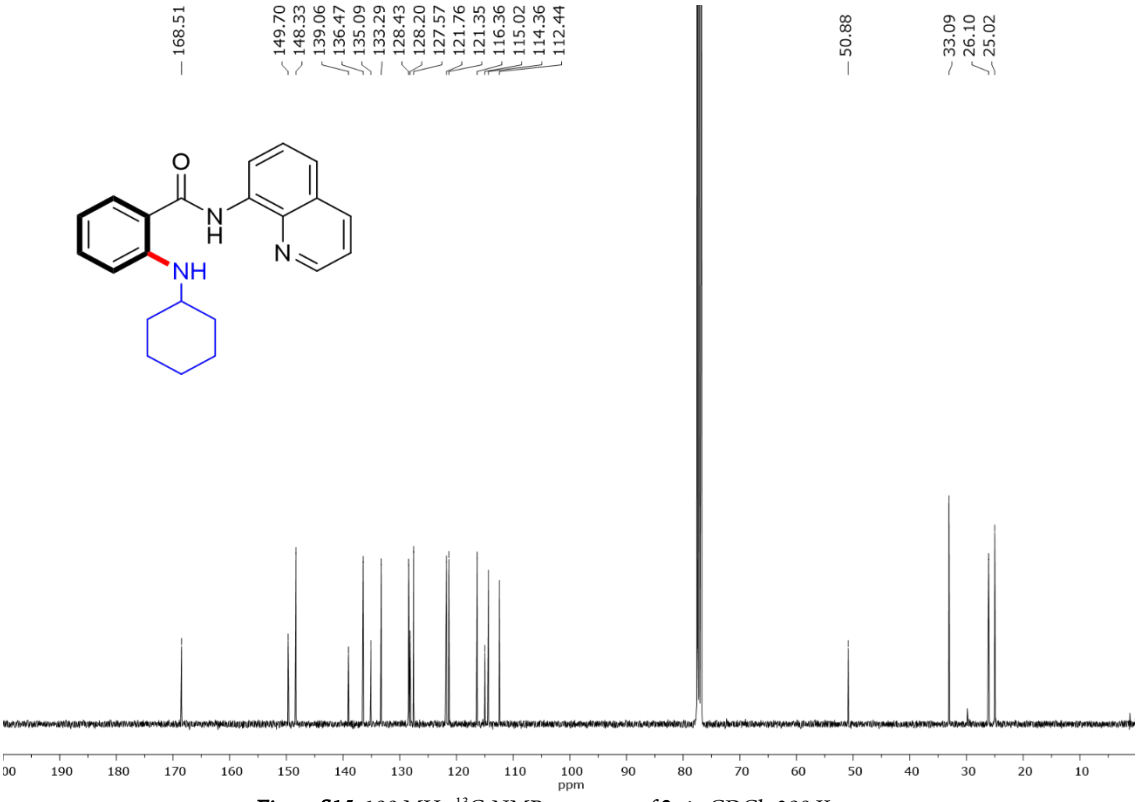


Figure S15. 100 MHz ^{13}C-NMR spectrum of **2a** in $CDCl_3$, 298 K.

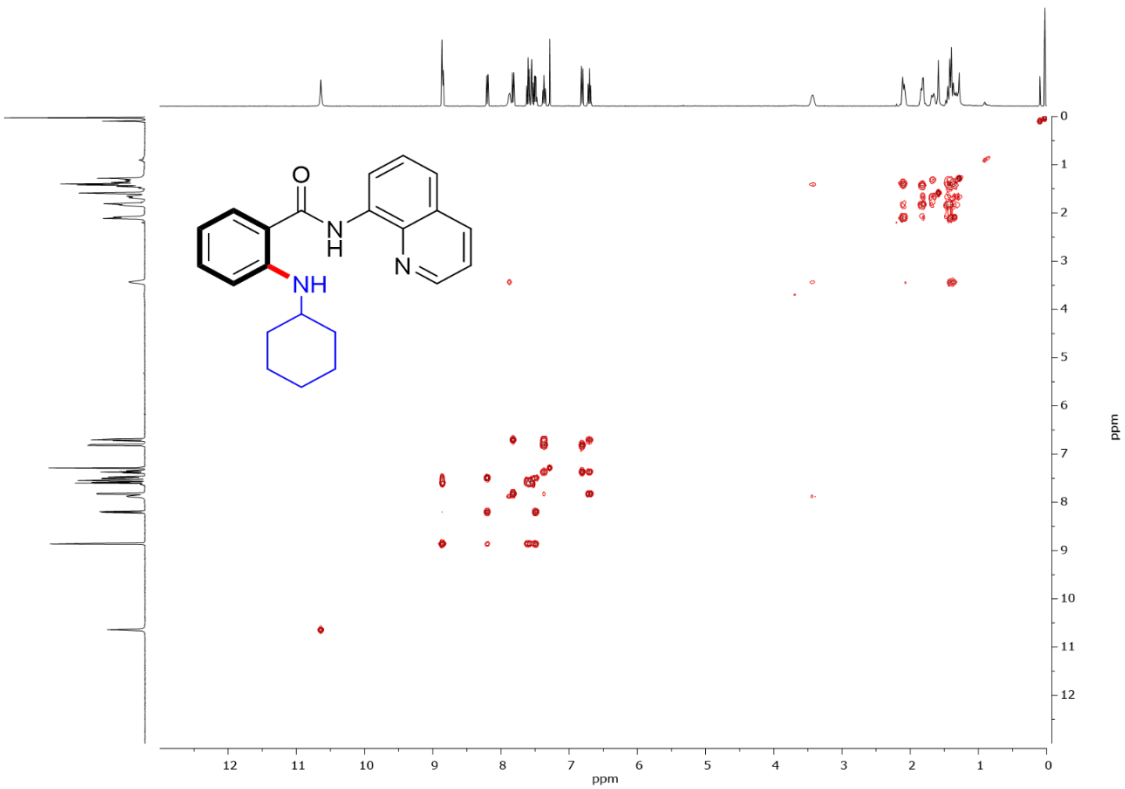


Figure S16. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **2a** in $CDCl_3$, 298 K.

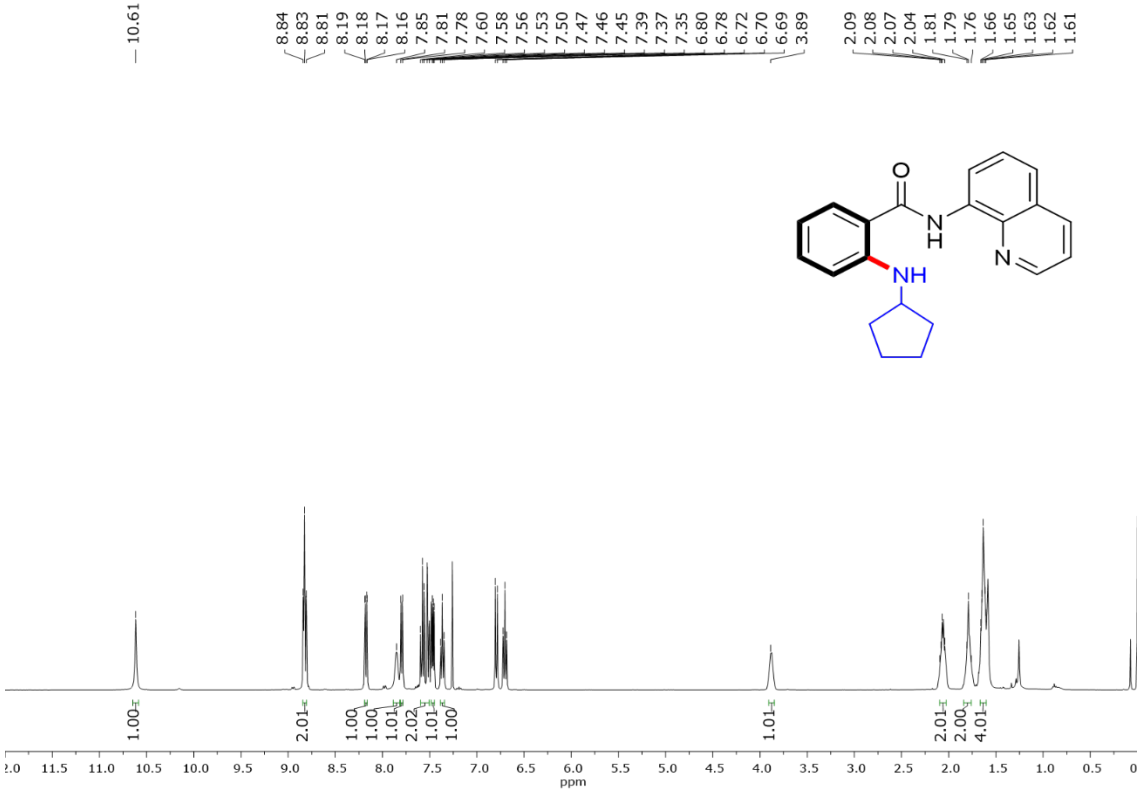


Figure S17. 400 MHz ^{1}H-NMR spectrum of **2b** in $CDCl_3$, 298 K.

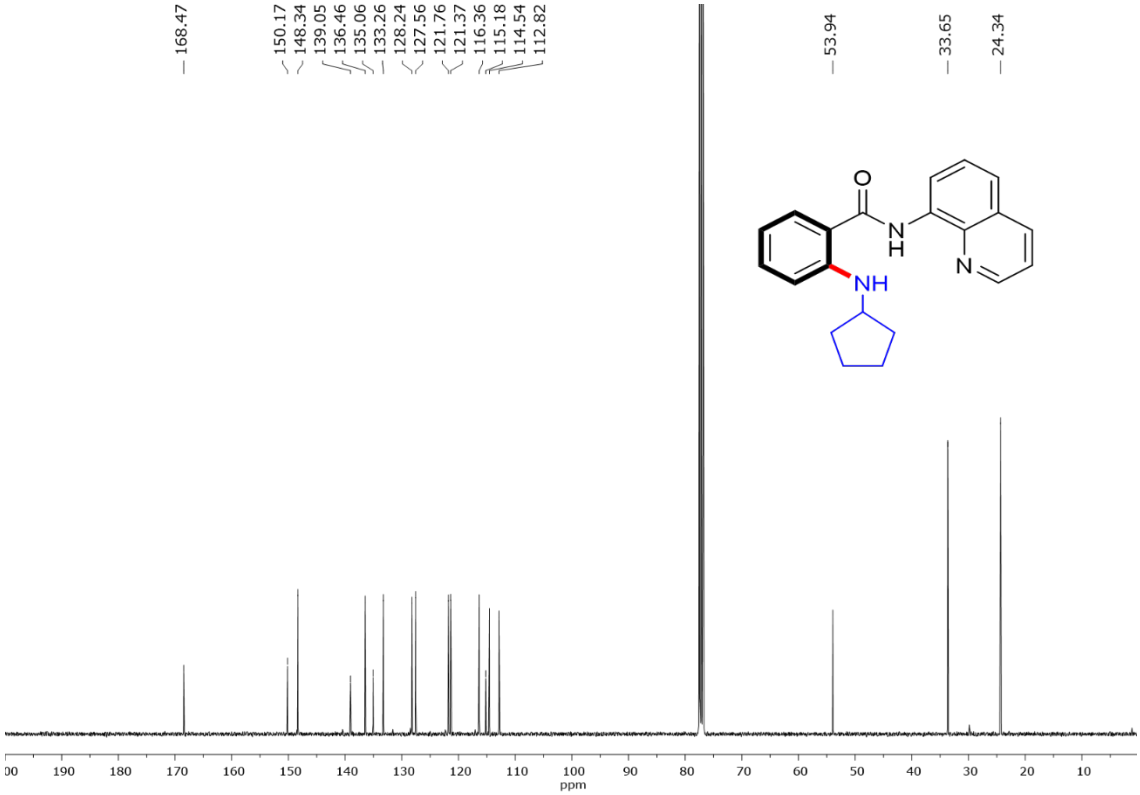


Figure S18. 100 MHz ^{13}C-NMR spectrum of **2b** in $CDCl_3$, 298 K.

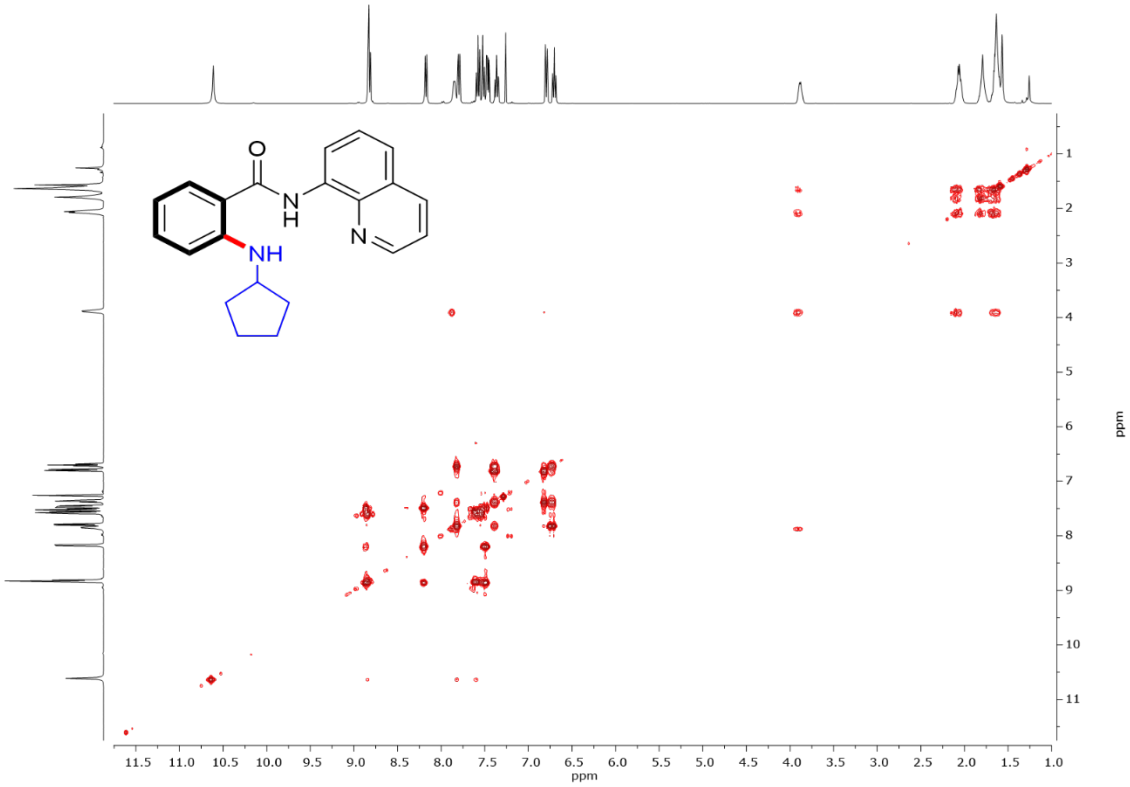


Figure S19. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **2b** in $CDCl_3$, 298 K.

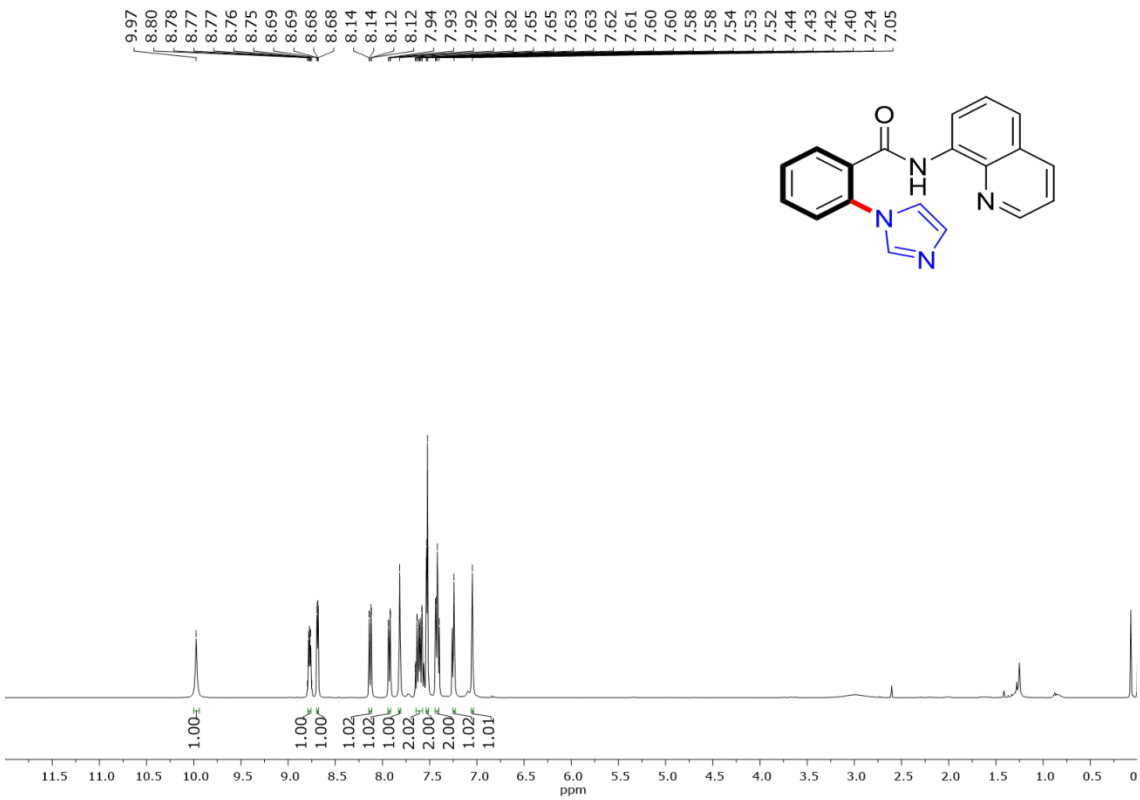


Figure S20. 400 MHz ^{1}H-NMR spectrum of **2c** in $CDCl_3$, 298 K.

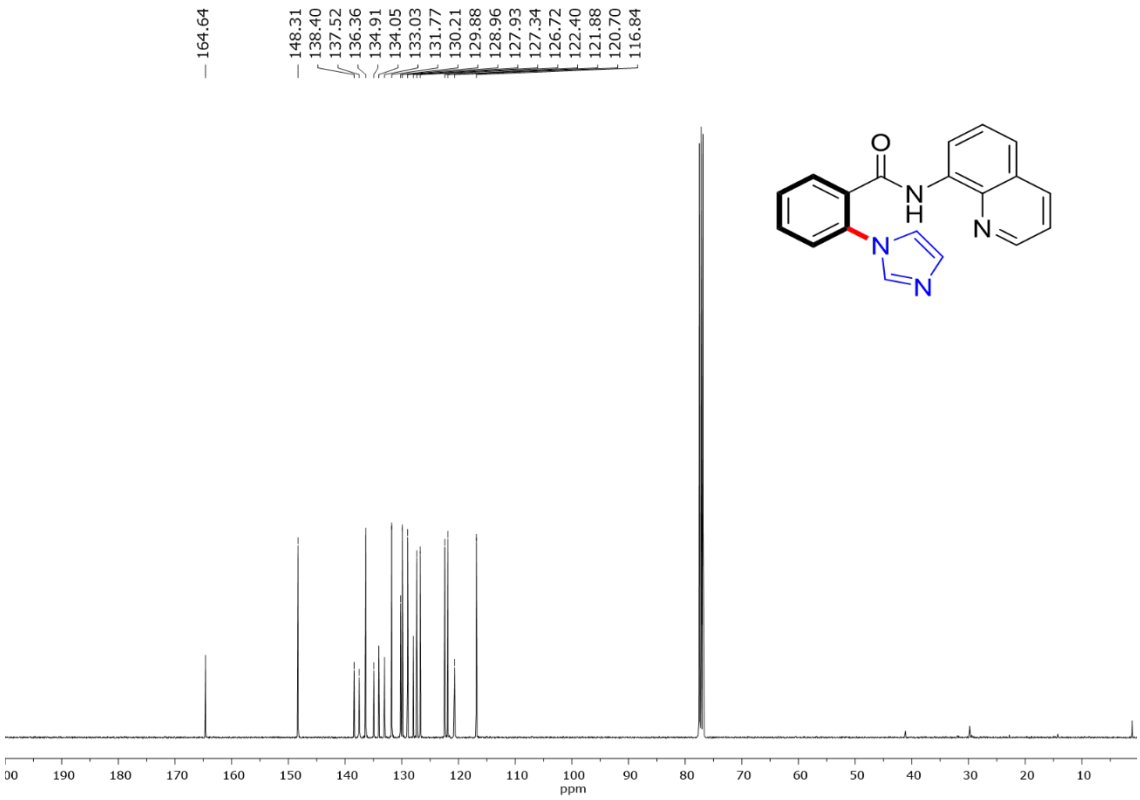


Figure S21. 100 MHz ^{13}C-NMR spectrum of **2c** in $CDCl_3$, 298 K.

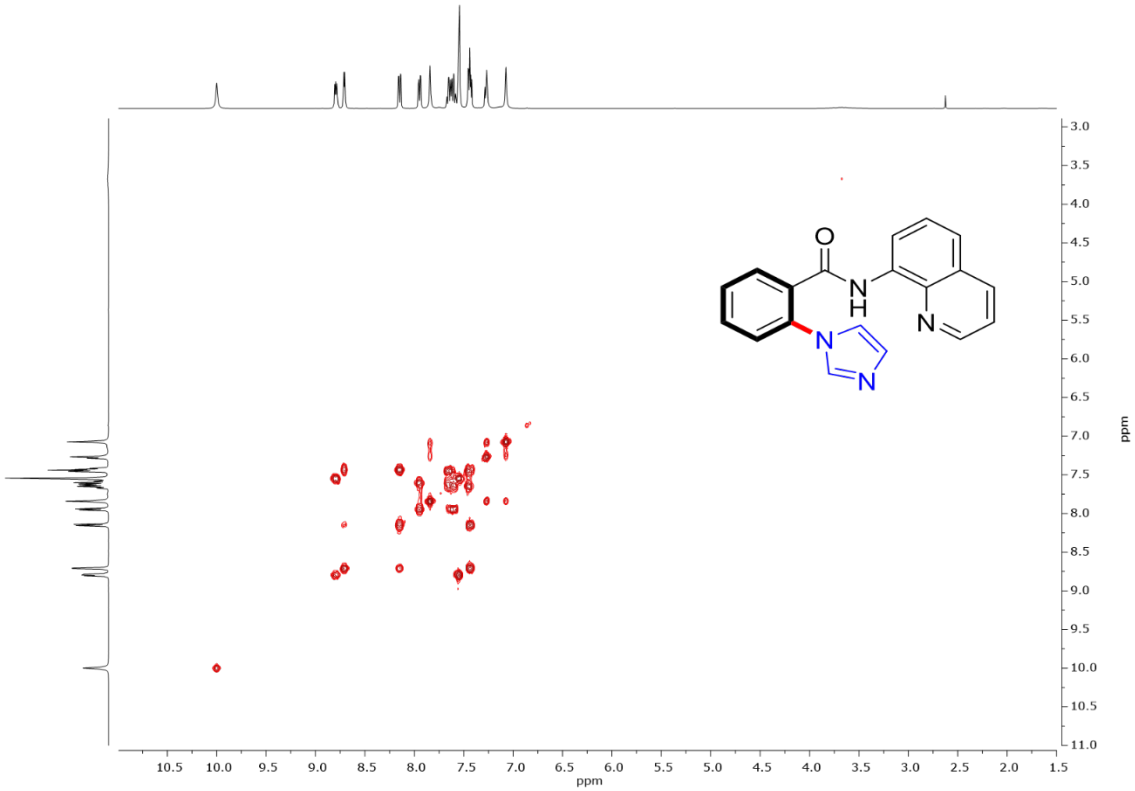


Figure S22. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **2c** in $CDCl_3$, 298 K.

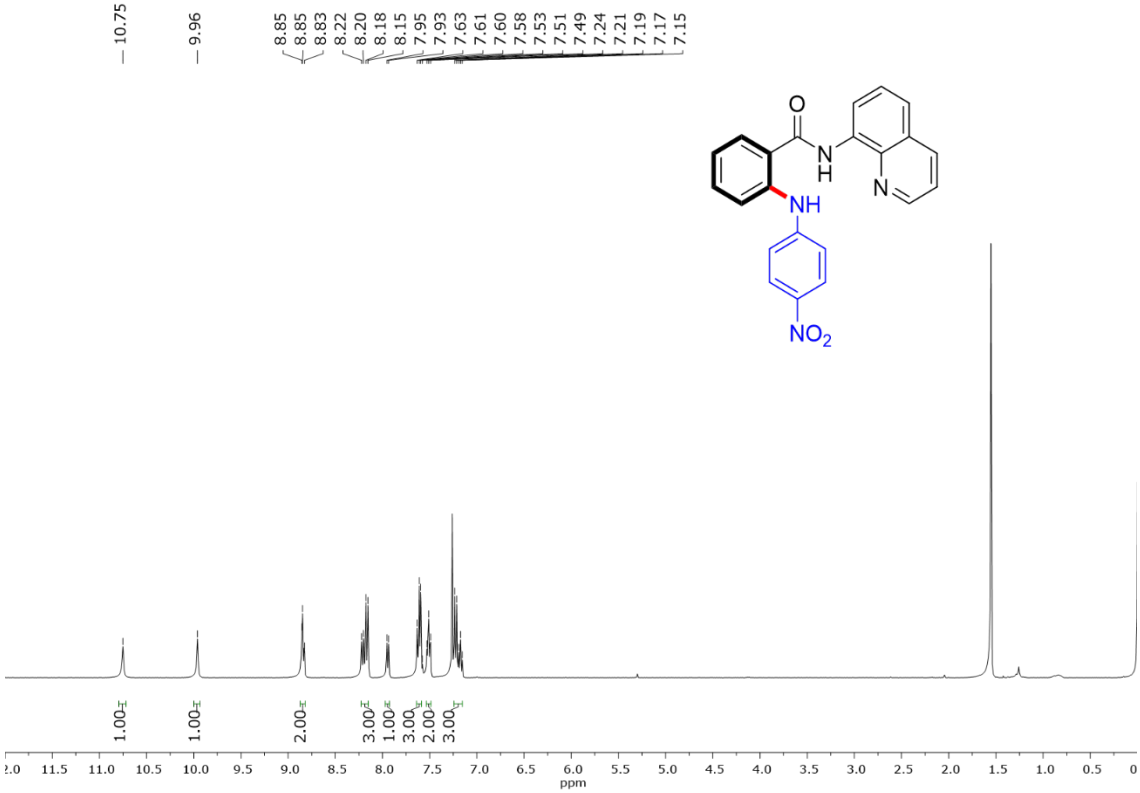


Figure S23. 400 MHz ^{1}H-NMR spectrum of **2d** in $CDCl_3$, 298 K.

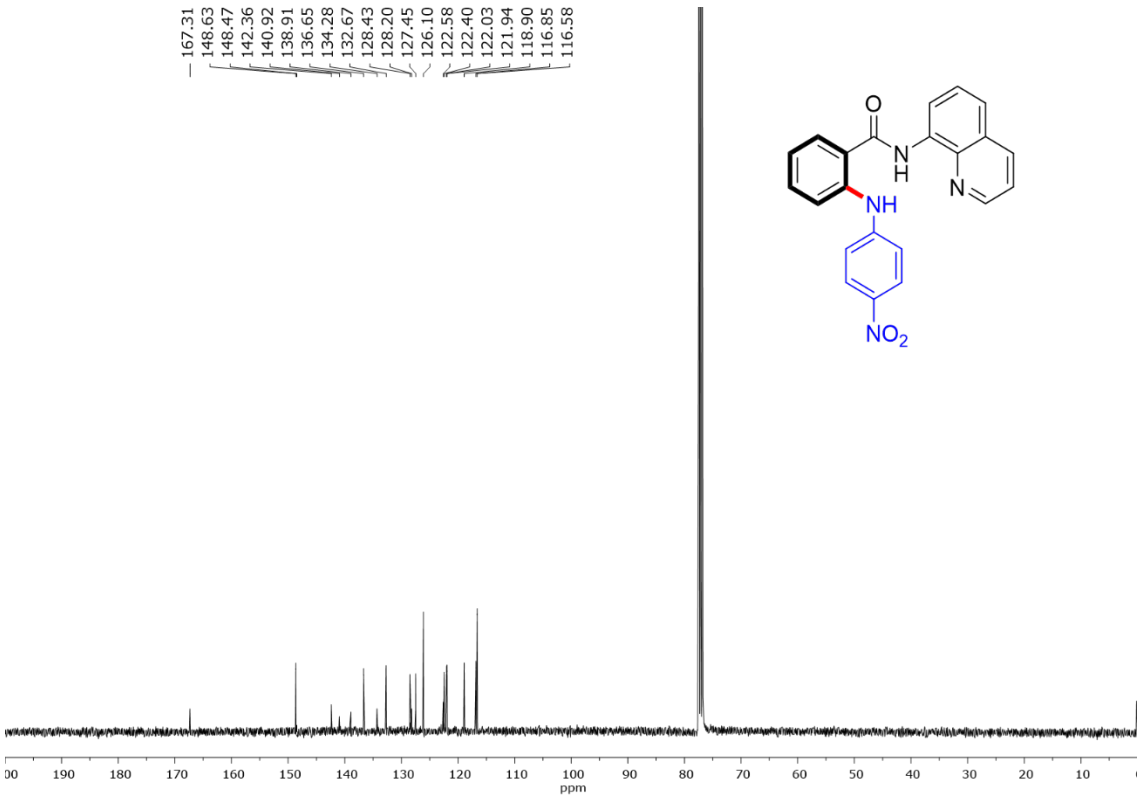


Figure S24. 100 MHz ^{13}C-NMR spectrum of **2d** in $CDCl_3$, 298 K.

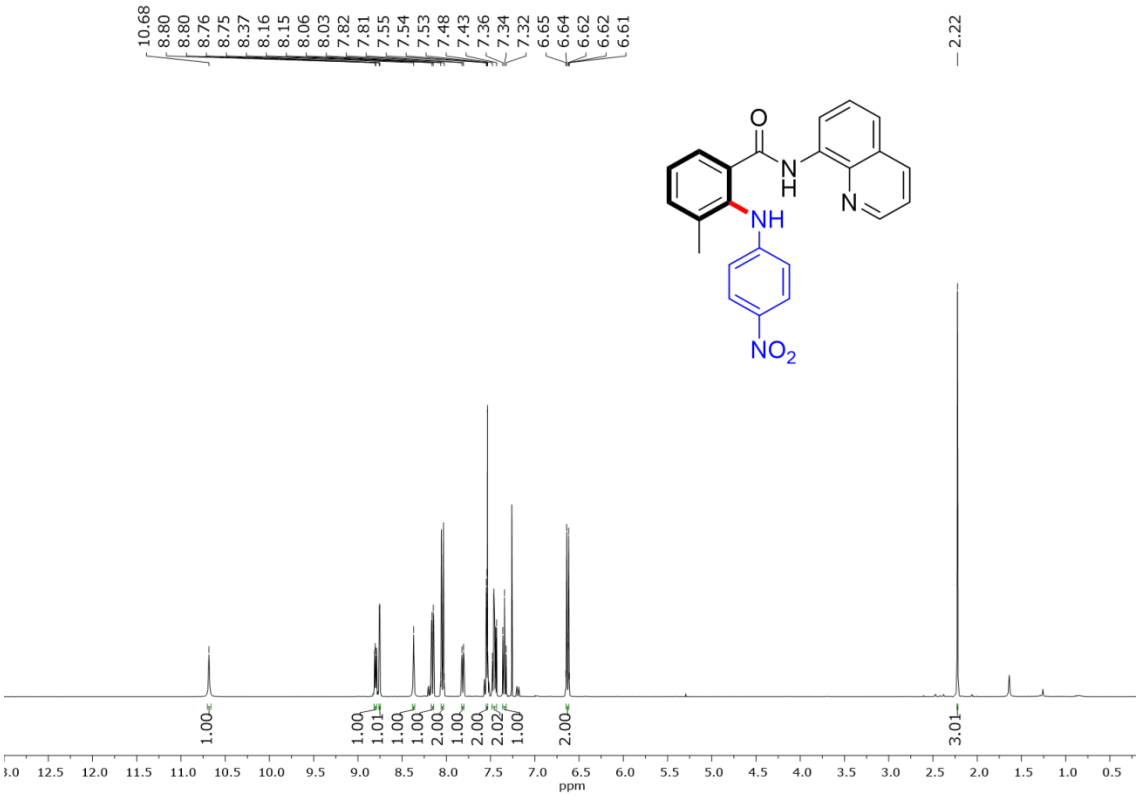


Figure S25. 400 MHz ^{1}H-NMR spectrum of **2e** in $CDCl_3$, 298 K.

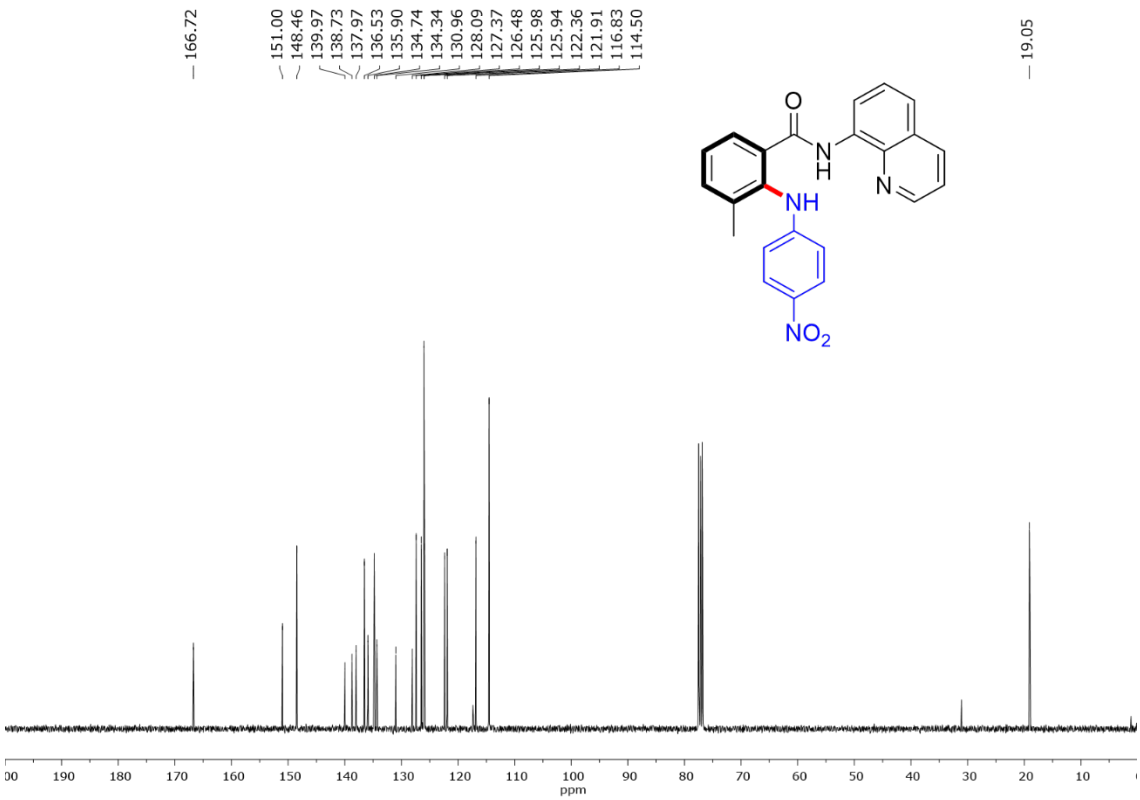


Figure S26. 100 MHz ^{13}C-NMR spectrum of **2e** in $CDCl_3$, 298 K.

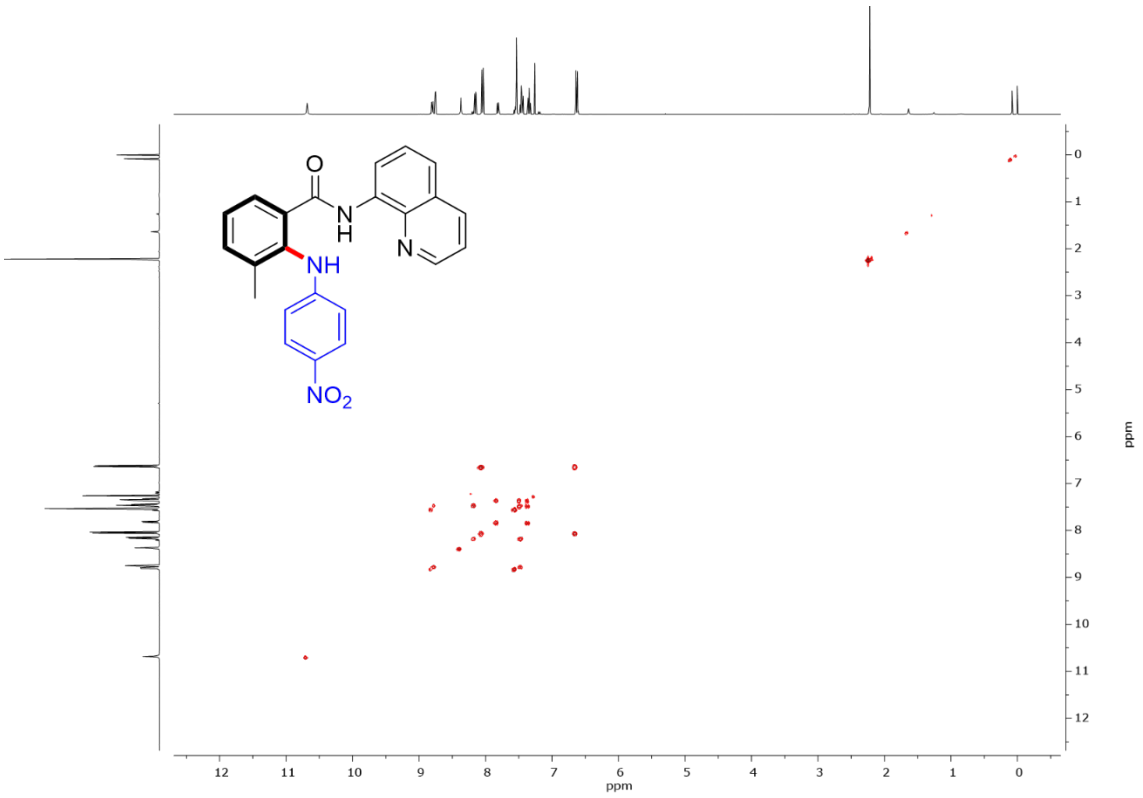


Figure S27. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **2e** in $CDCl_3$, 298 K.

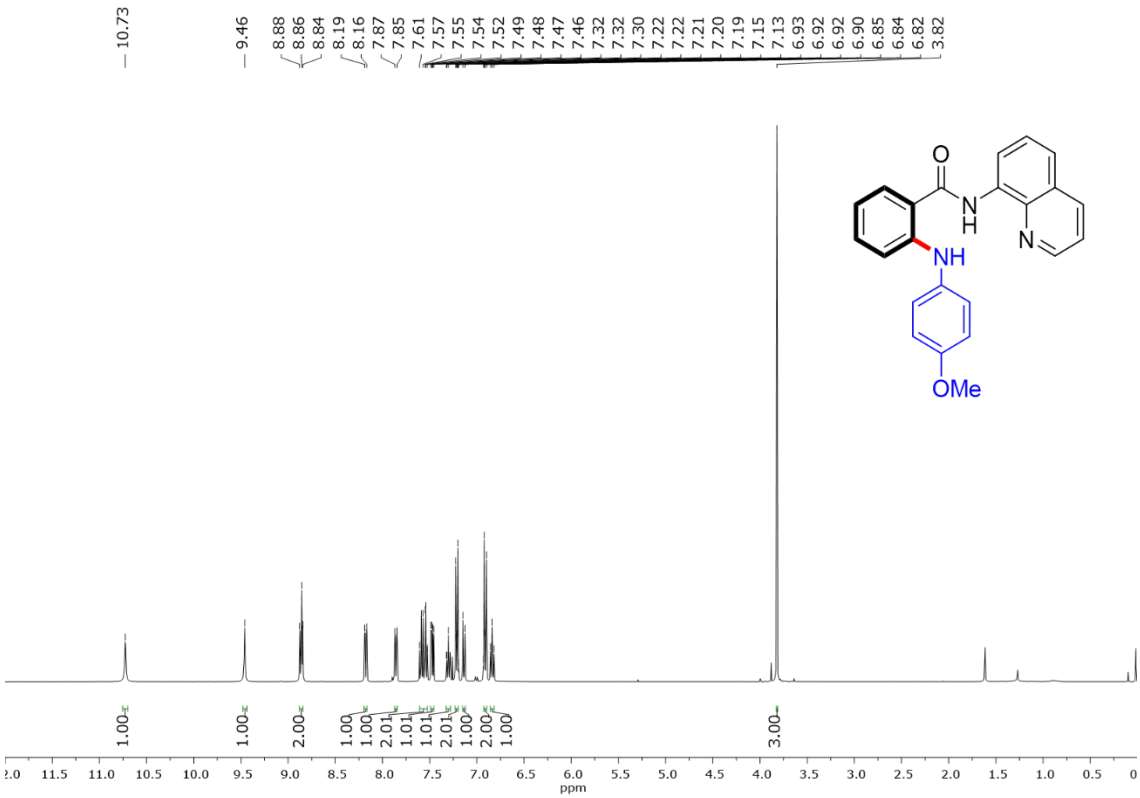


Figure S28. 400 MHz ^{1}H-NMR spectrum of **2f** in $CDCl_3$, 298 K.

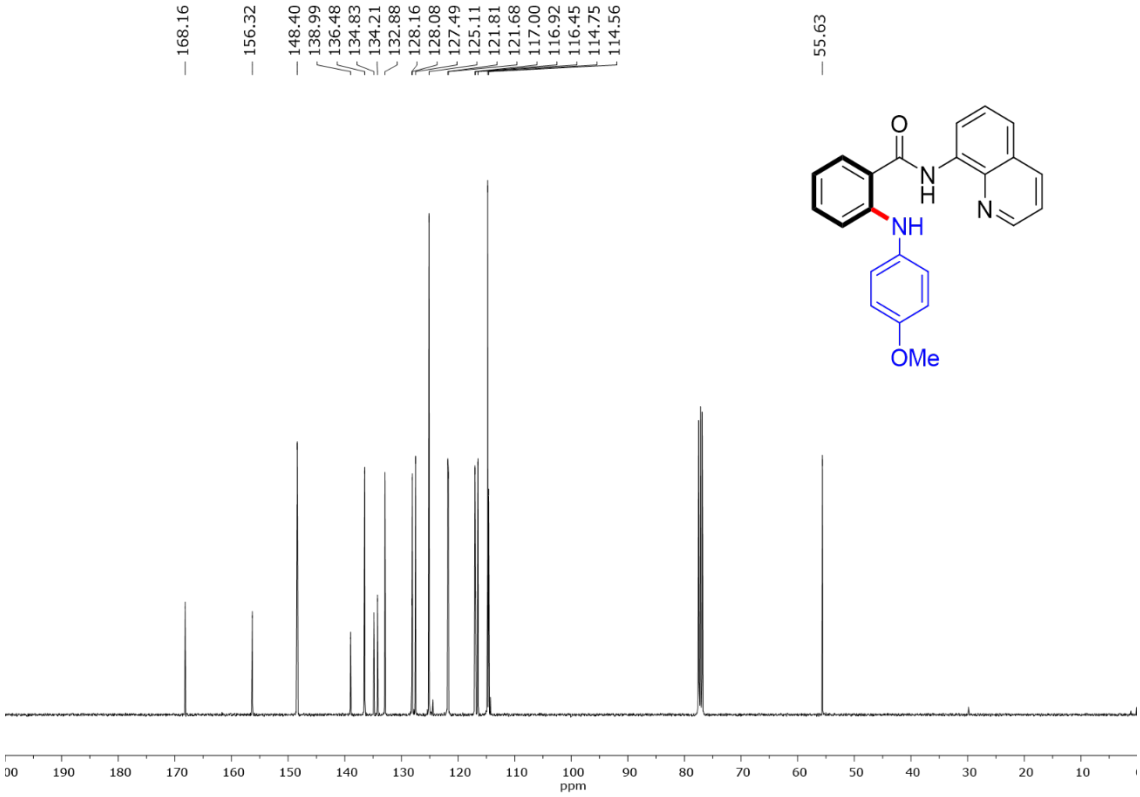


Figure S29. 100 MHz ^{13}C-NMR spectrum of **2f** in $CDCl_3$, 298 K.

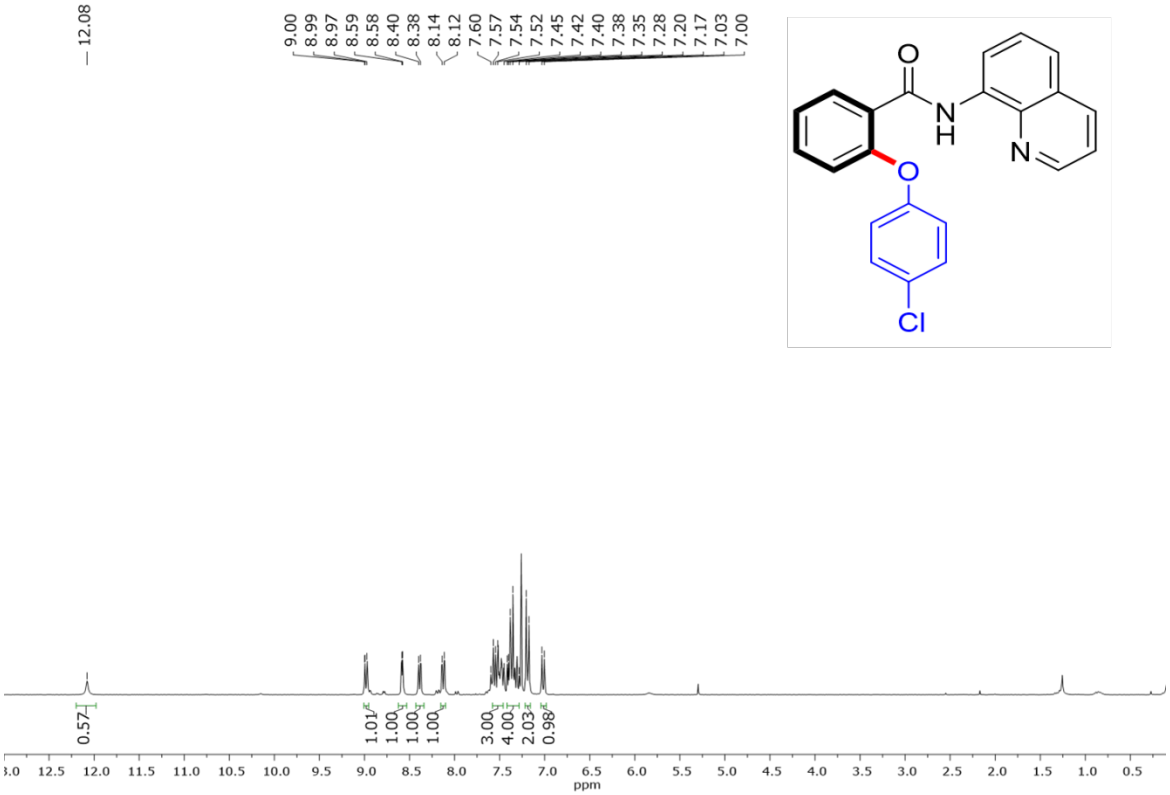


Figure S30. 400 MHz ^{1}H-NMR spectrum of **3a** in $CDCl_3$, 298 K.

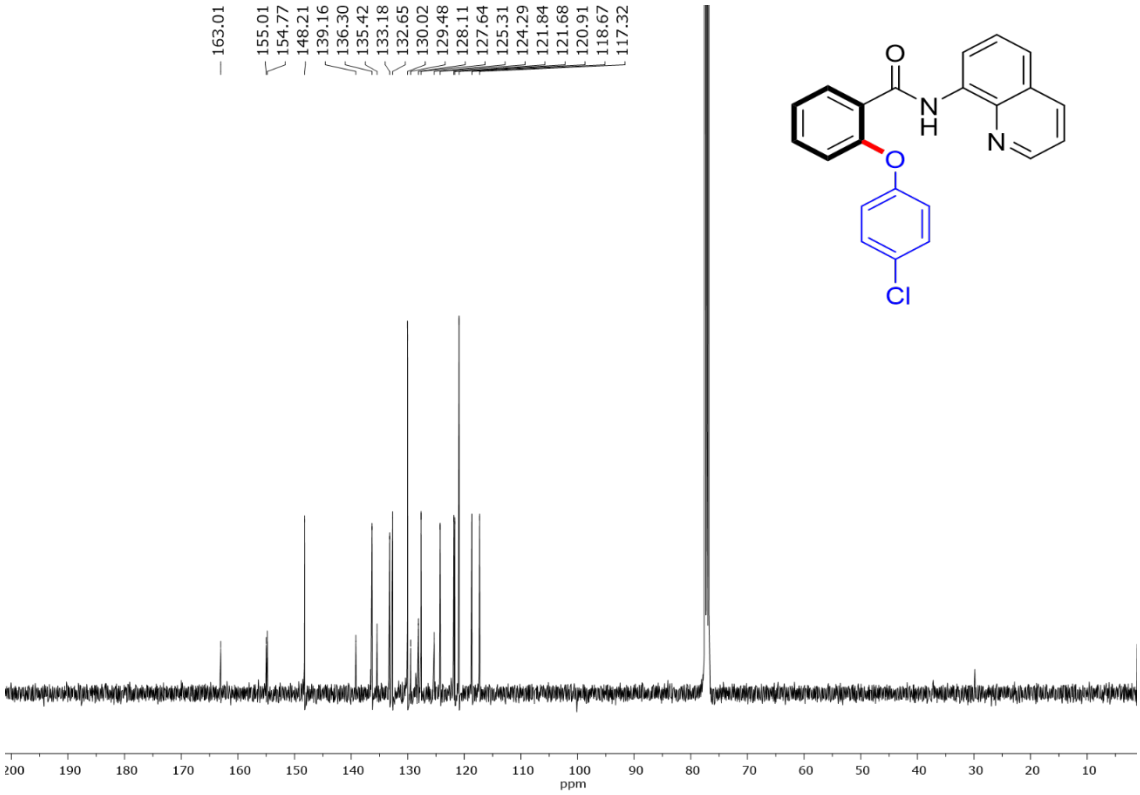


Figure S31. 100 MHz ^{13}C-NMR spectrum of **3a** in $CDCl_3$, 298 K.

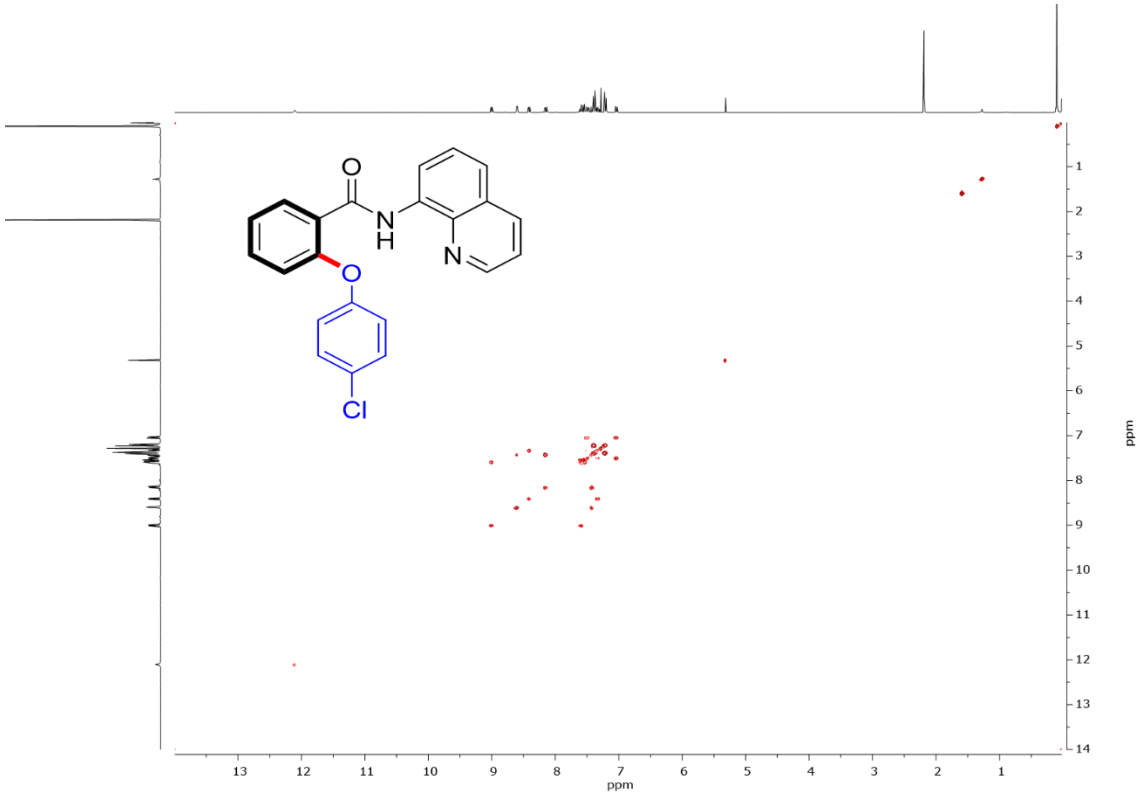


Figure S32. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **3a** in $CDCl_3$, 298 K.

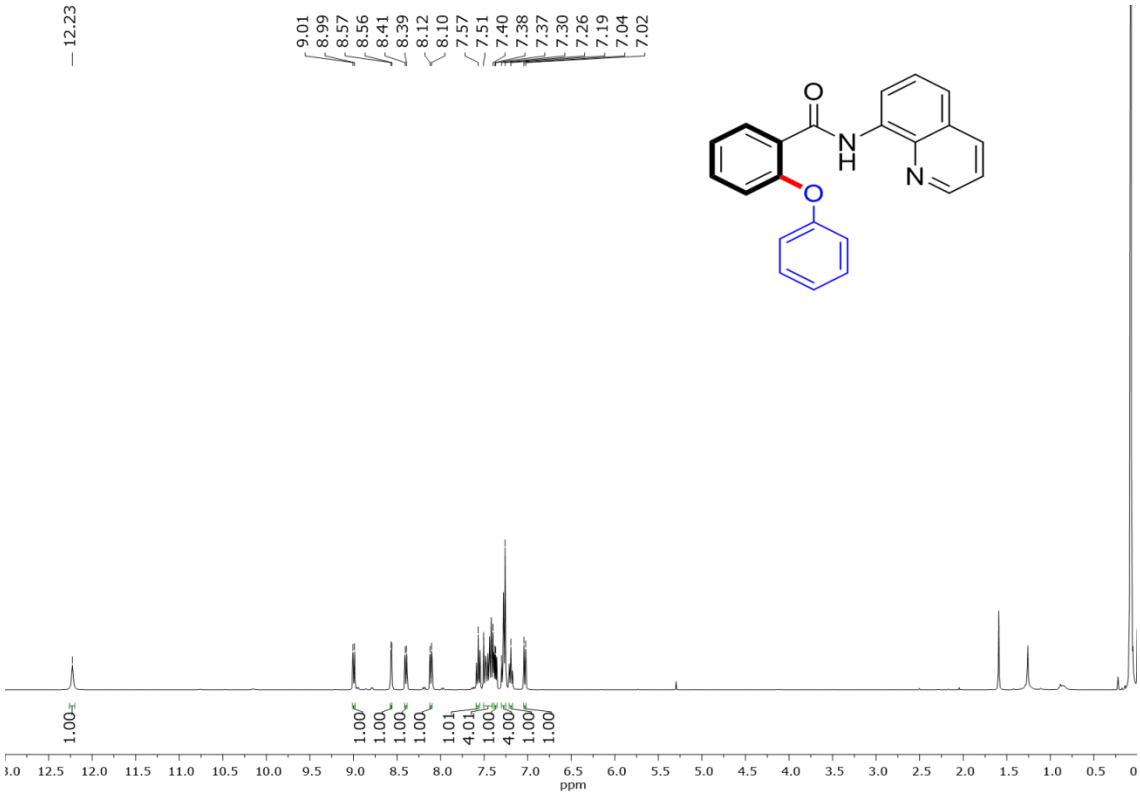


Figure S33. 400 MHz ^{1}H-NMR spectrum of **3b** in $CDCl_3$, 298 K.

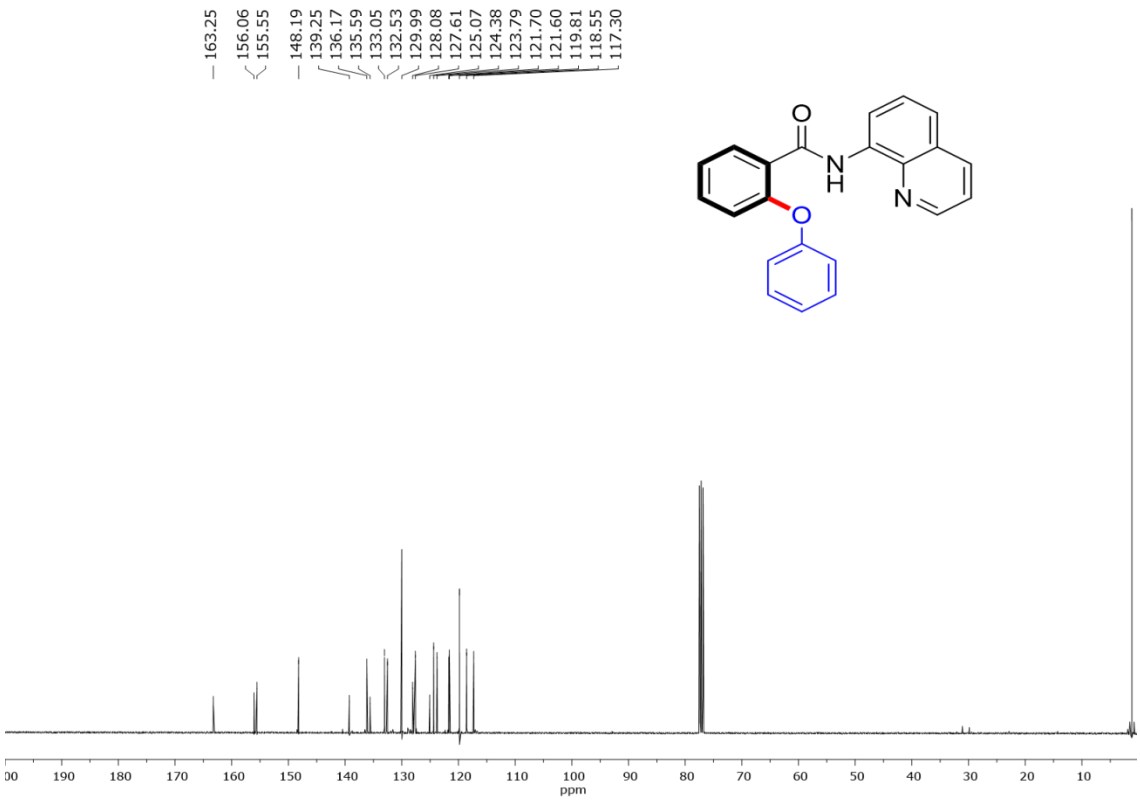


Figure S34. 100 MHz ^{13}C-NMR spectrum of **3b** in $CDCl_3$, 298 K.

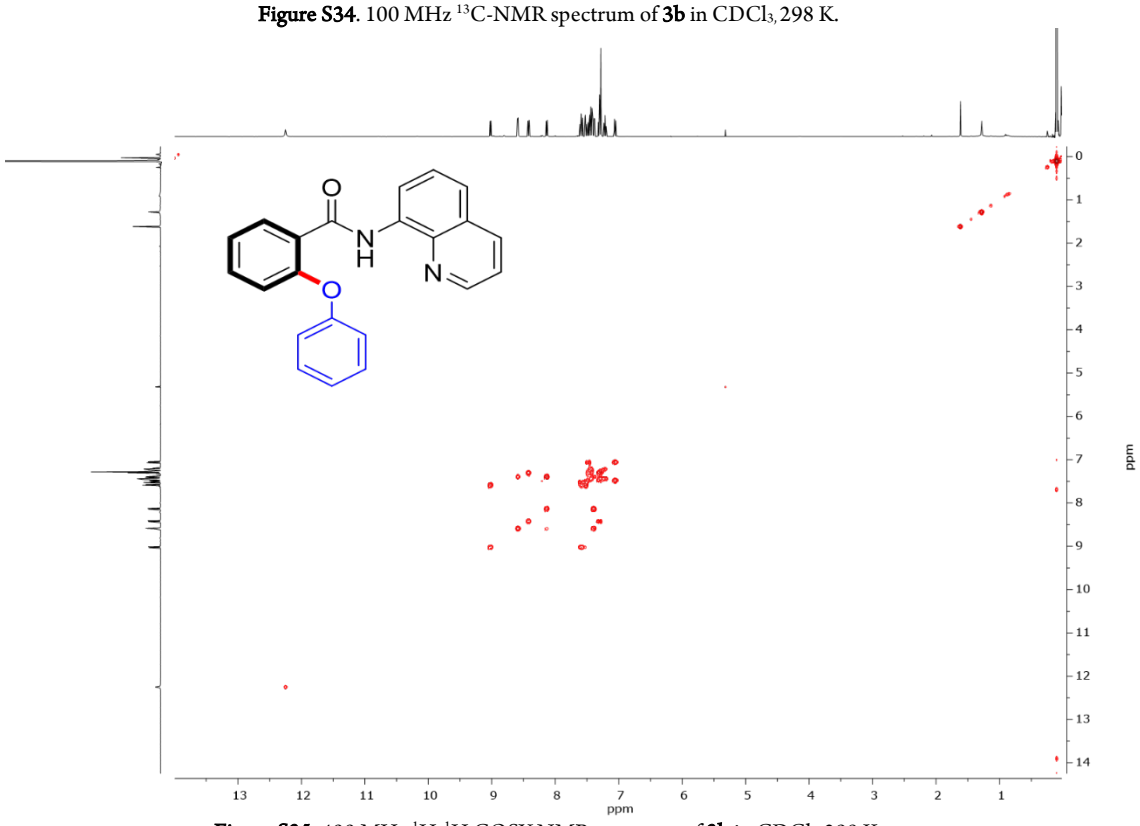


Figure S35. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **3b** in $CDCl_3$, 298 K.

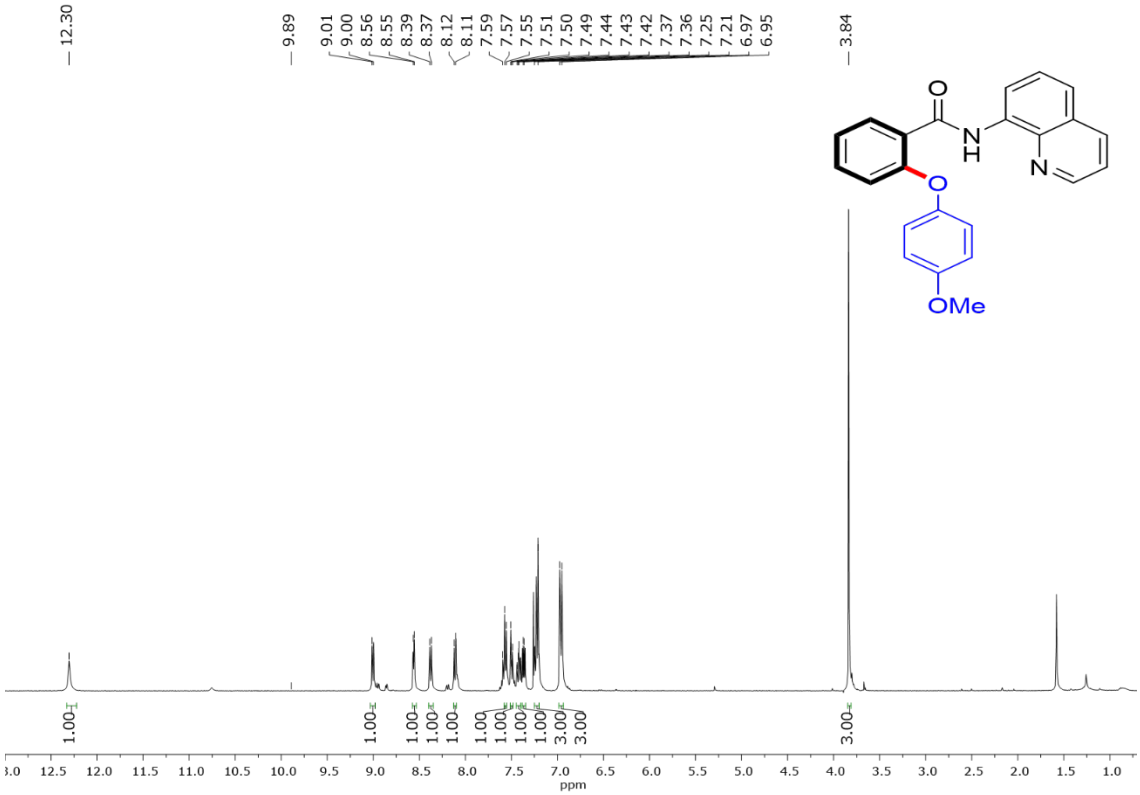


Figure S36. 400 MHz ^{1}H-NMR spectrum of **3c** in $CDCl_3$, 298 K.

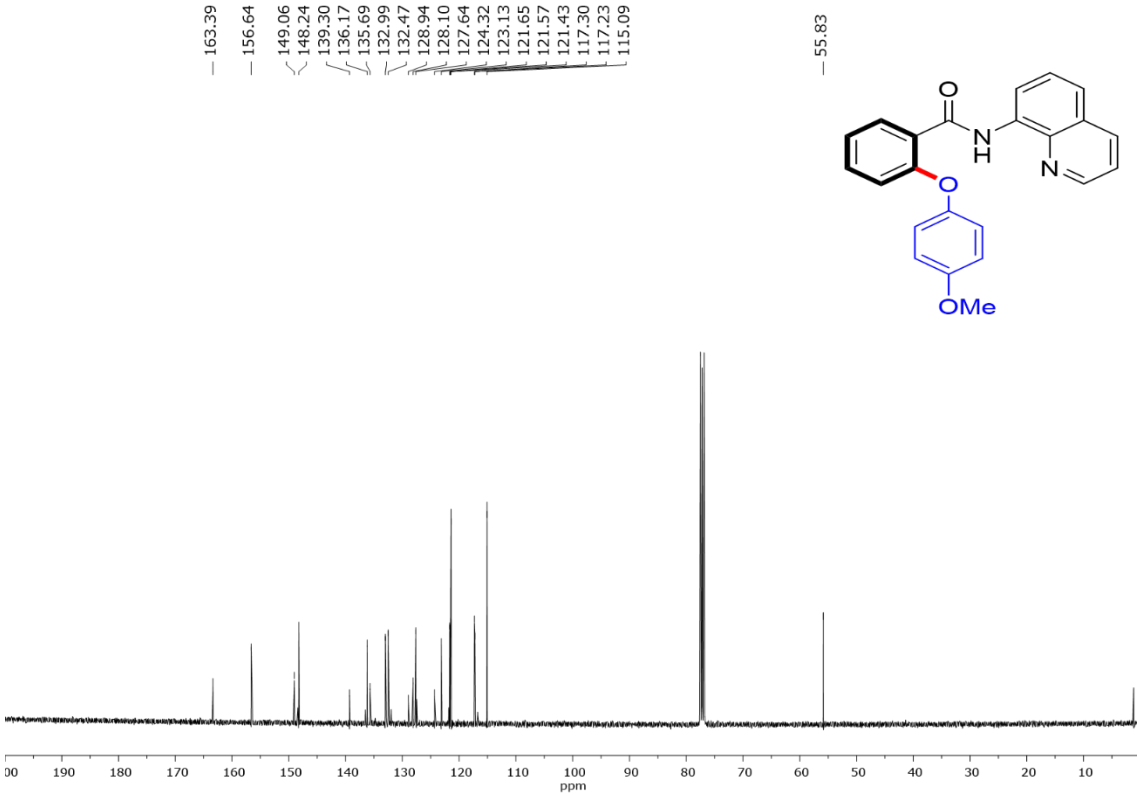


Figure S37. 100 MHz ^{13}C-NMR spectrum of **3c** in $CDCl_3$, 298 K.

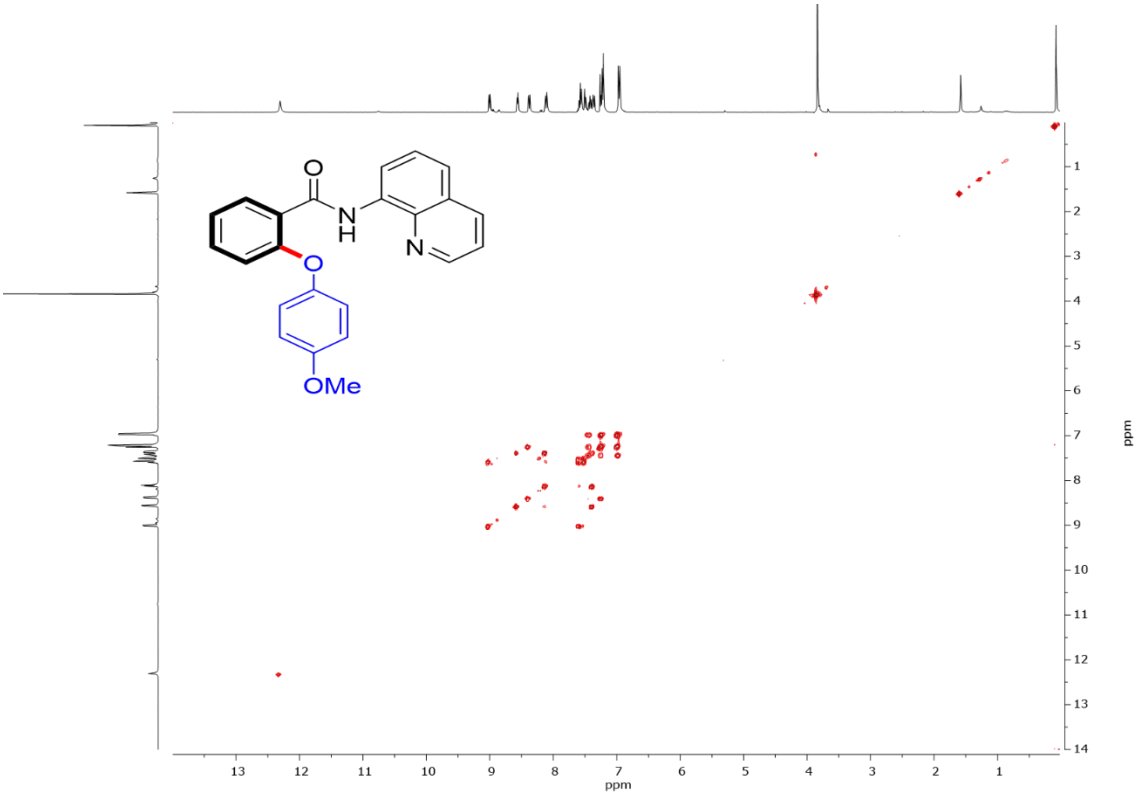


Figure S38. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **3c** in $CDCl_3$, 298 K.

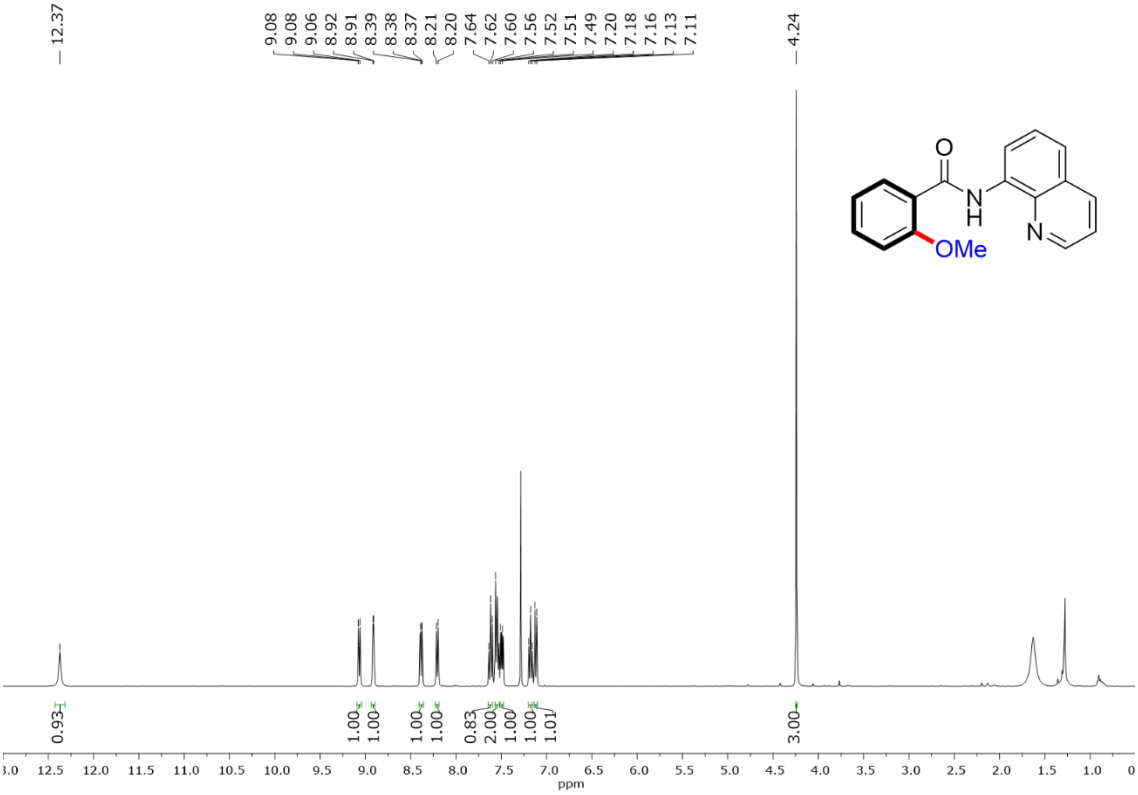


Figure S39. 400 MHz ^{1}H-NMR spectrum of **3e** in $CDCl_3$, 298 K.

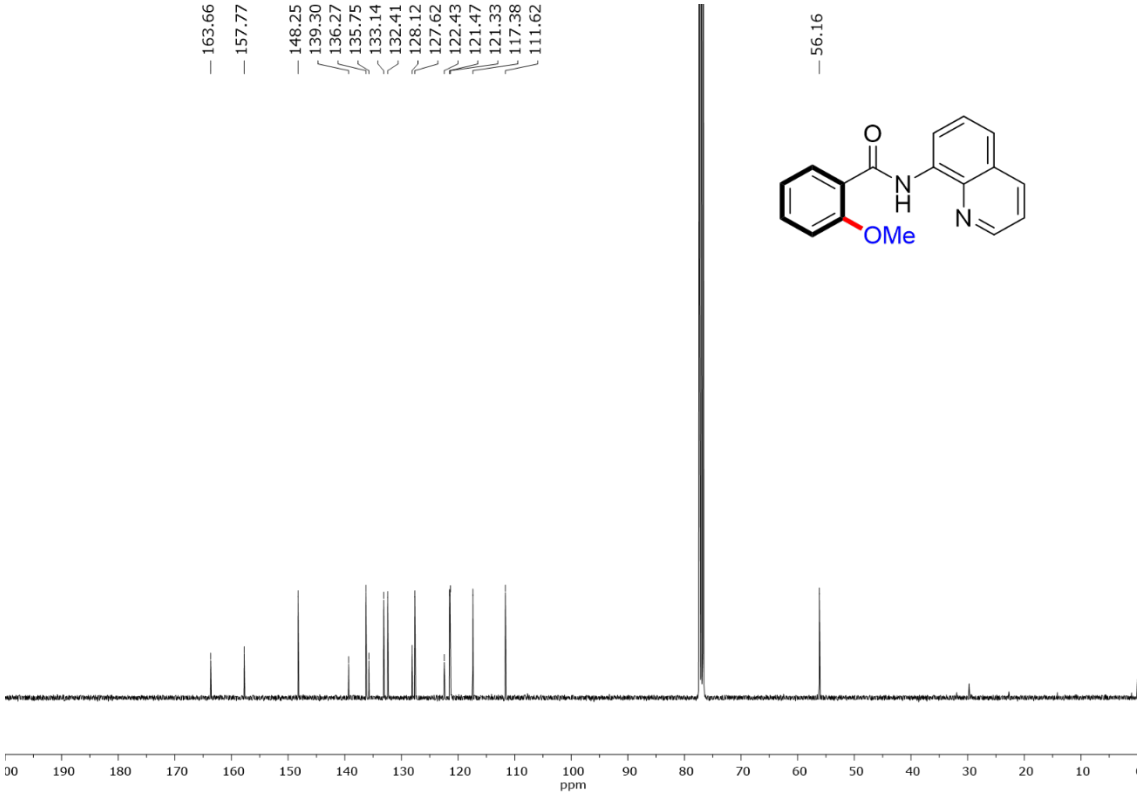


Figure S40. 100 MHz ^{13}C-NMR spectrum of **3e** in $CDCl_3$, 298 K.

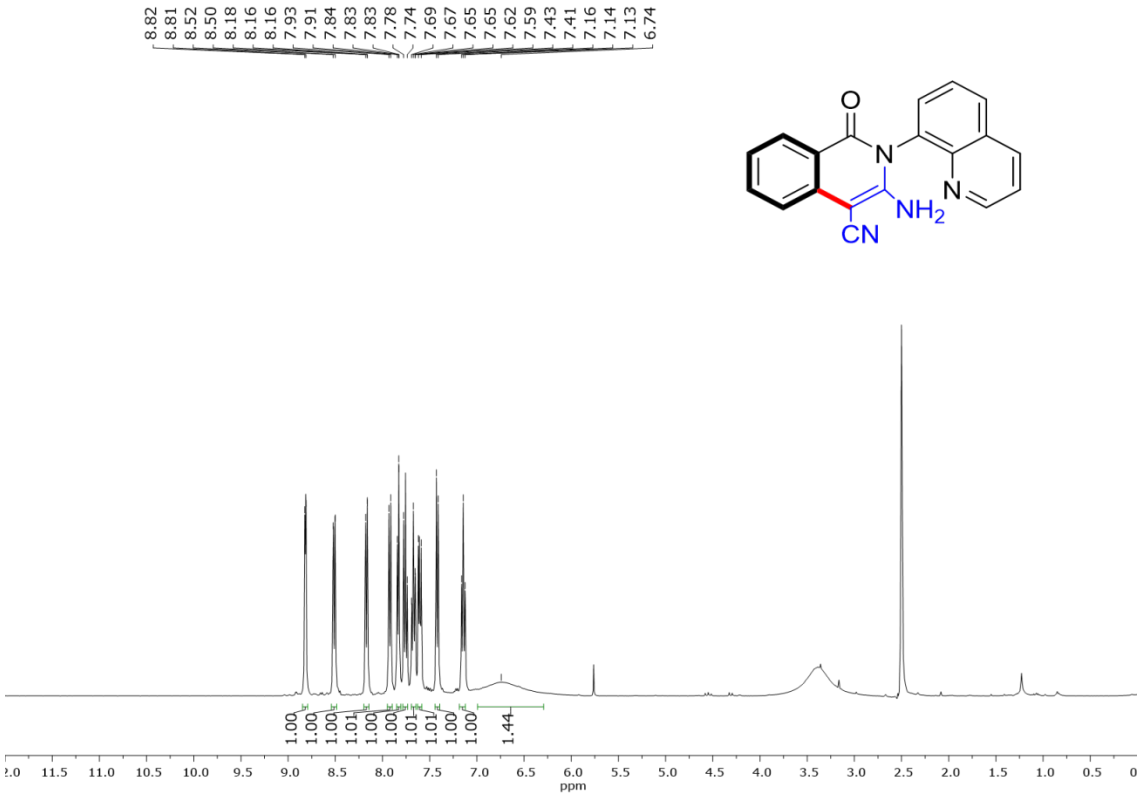


Figure S41. 400 MHz ^{1}H-NMR spectrum of **4aa** in DMSO d_6, 298 K.

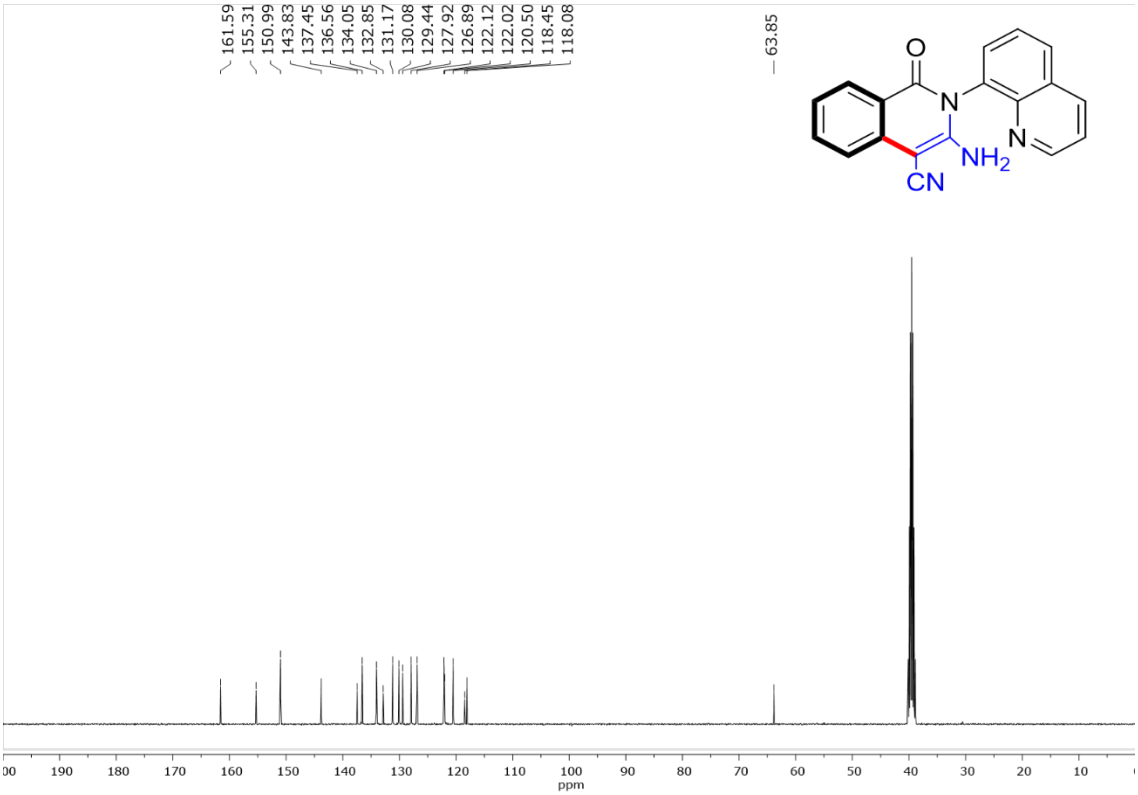


Figure S42. 100 MHz ^{13}C-NMR spectrum of **4aa** in DMSO d_6, 298 K.

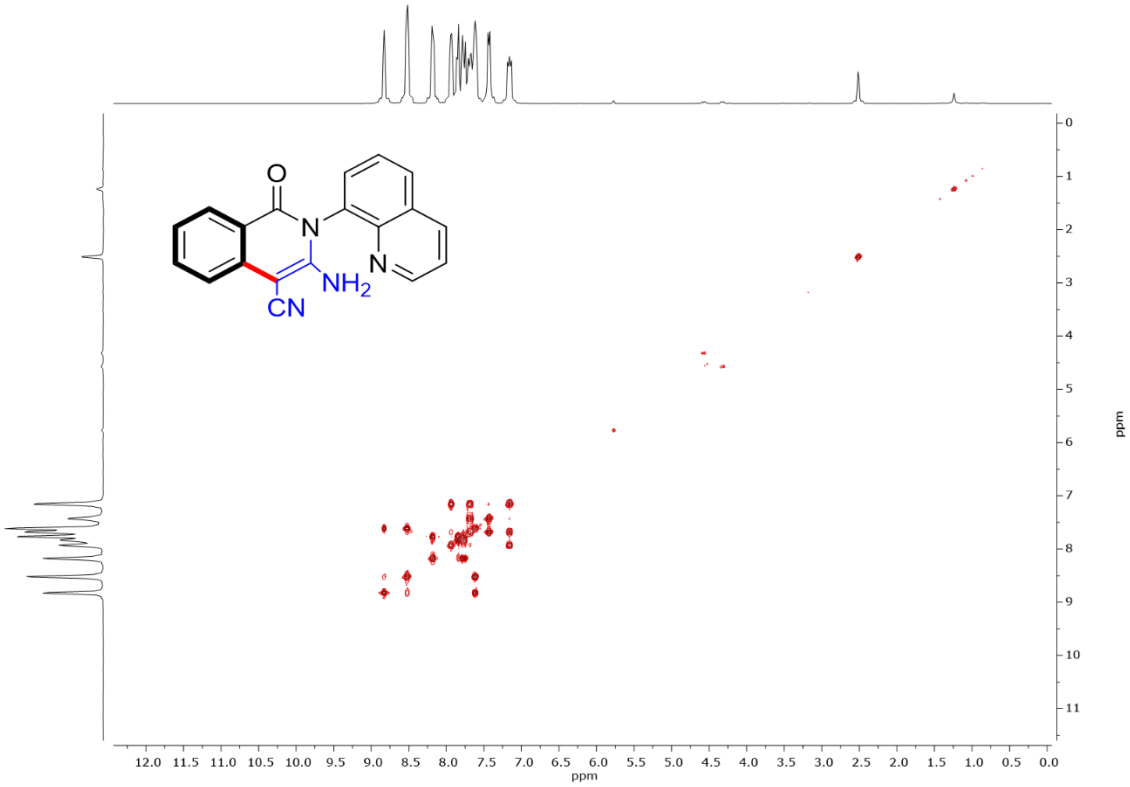


Figure S43. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **4aa** in DMSO d_6, 298 K.

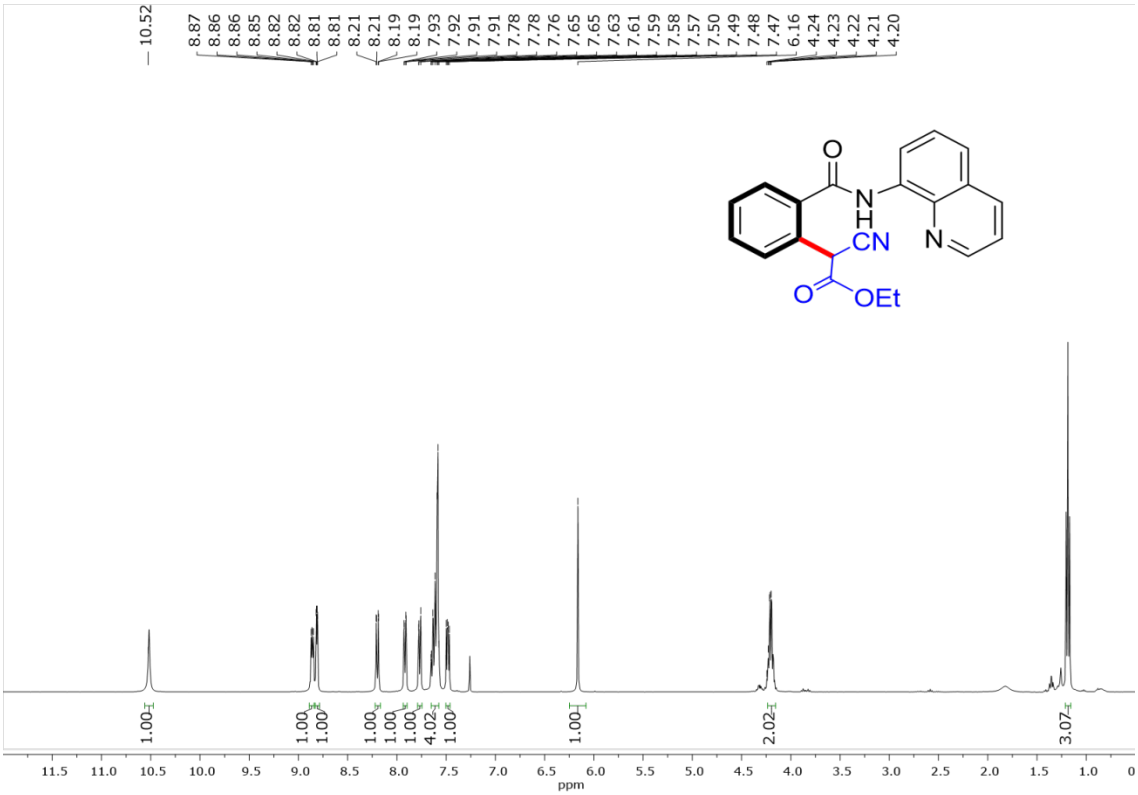


Figure S44. 400 MHz ^{1}H-NMR spectrum of **4b** in $CDCl_3$, 298 K.

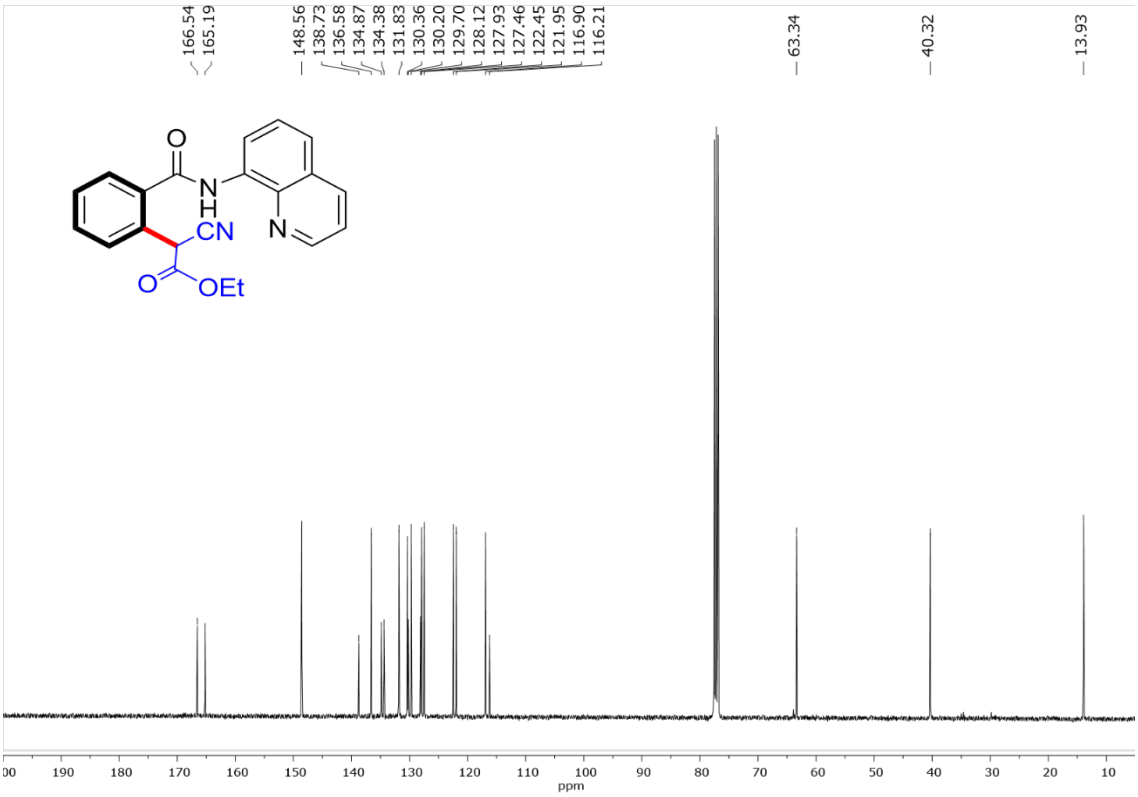


Figure S45. 100 MHz ^{13}C-NMR spectrum of **4b** in $CDCl_3$, 298 K.

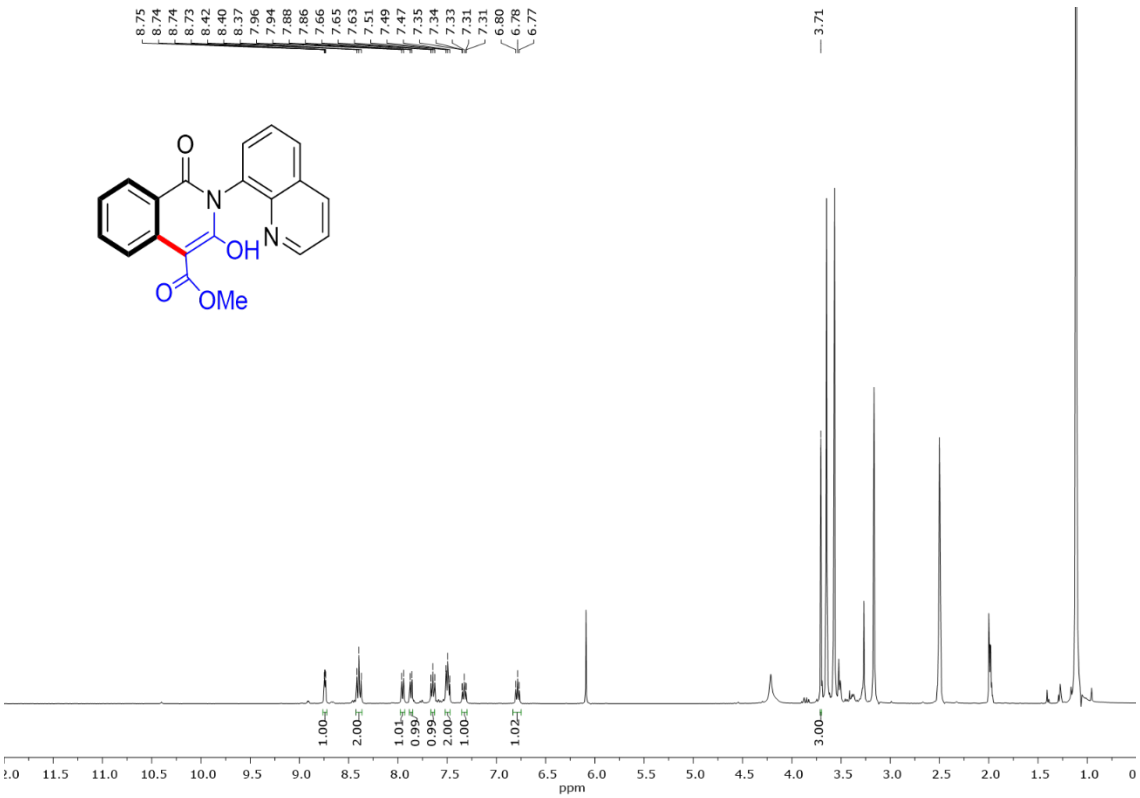


Figure S46. 400 MHz ^{1}H-NMR spectrum of **4ca** in DMSO d_6, 298 K.

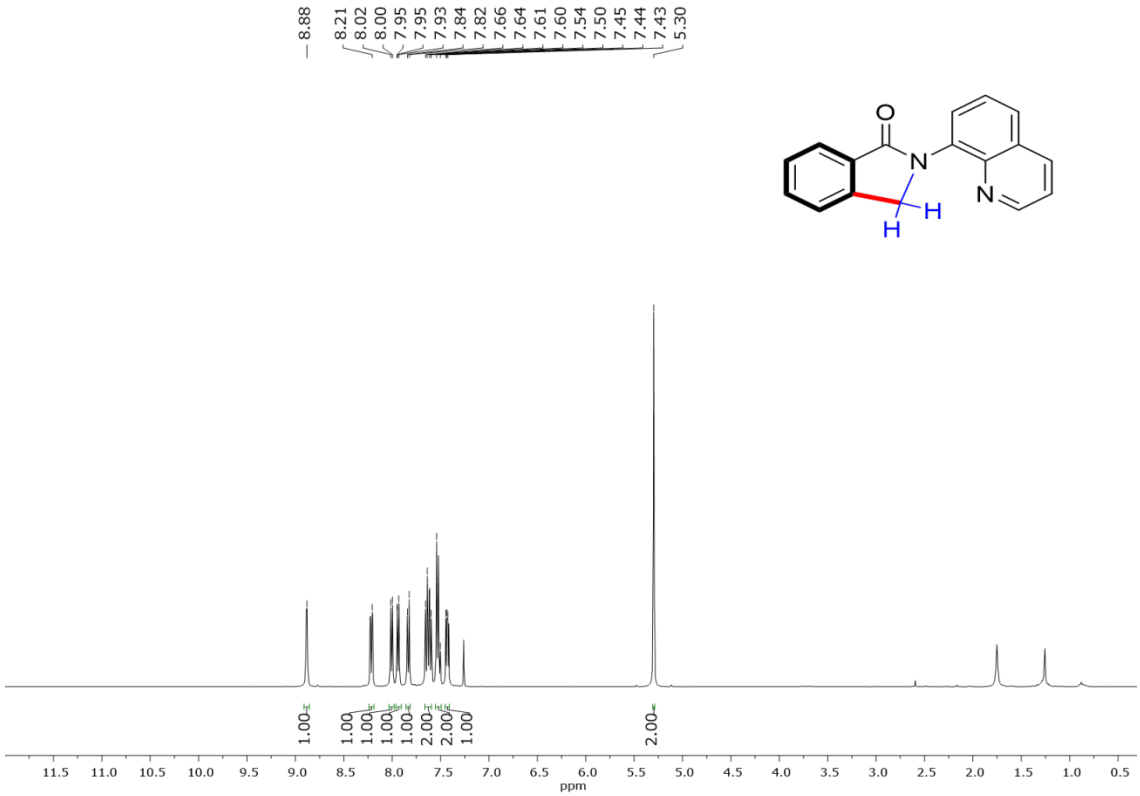


Figure S47. 400 MHz ^{1}H-NMR spectrum of **4fa** in $CDCl_3$, 298 K.

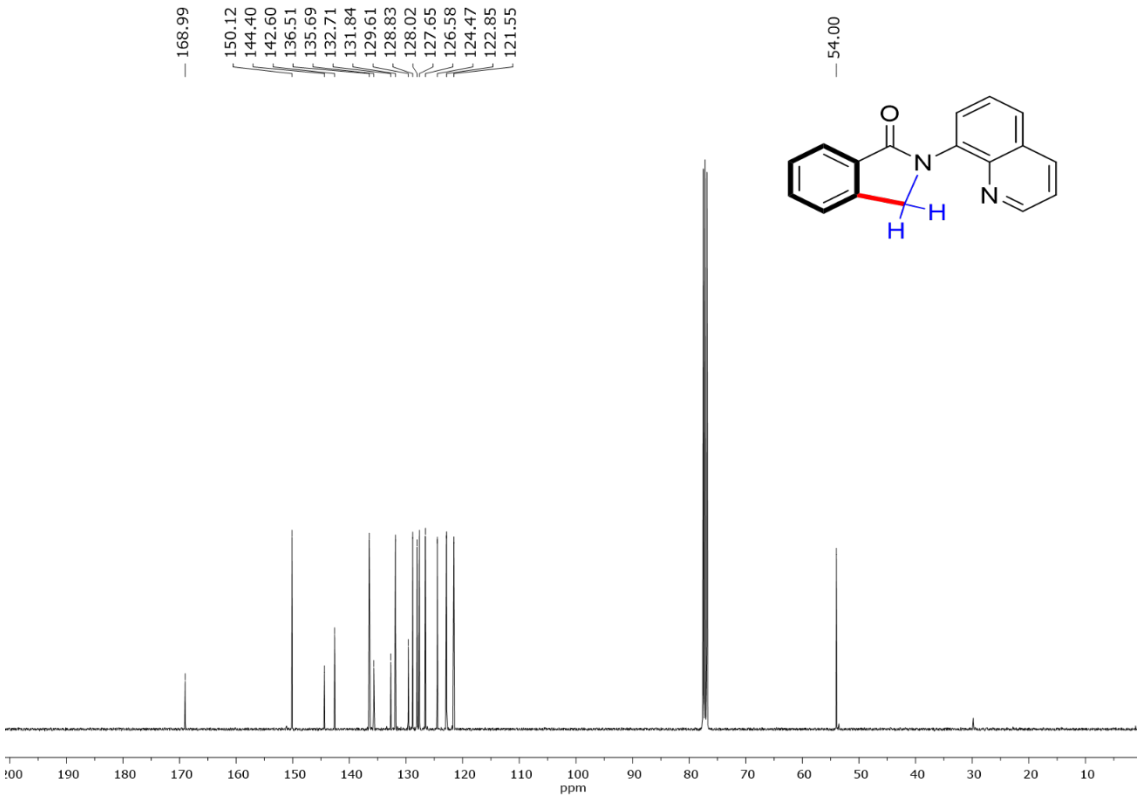


Figure S48. 100 MHz ^{13}C-NMR spectrum of **4fa** in $CDCl_3$, 298 K.

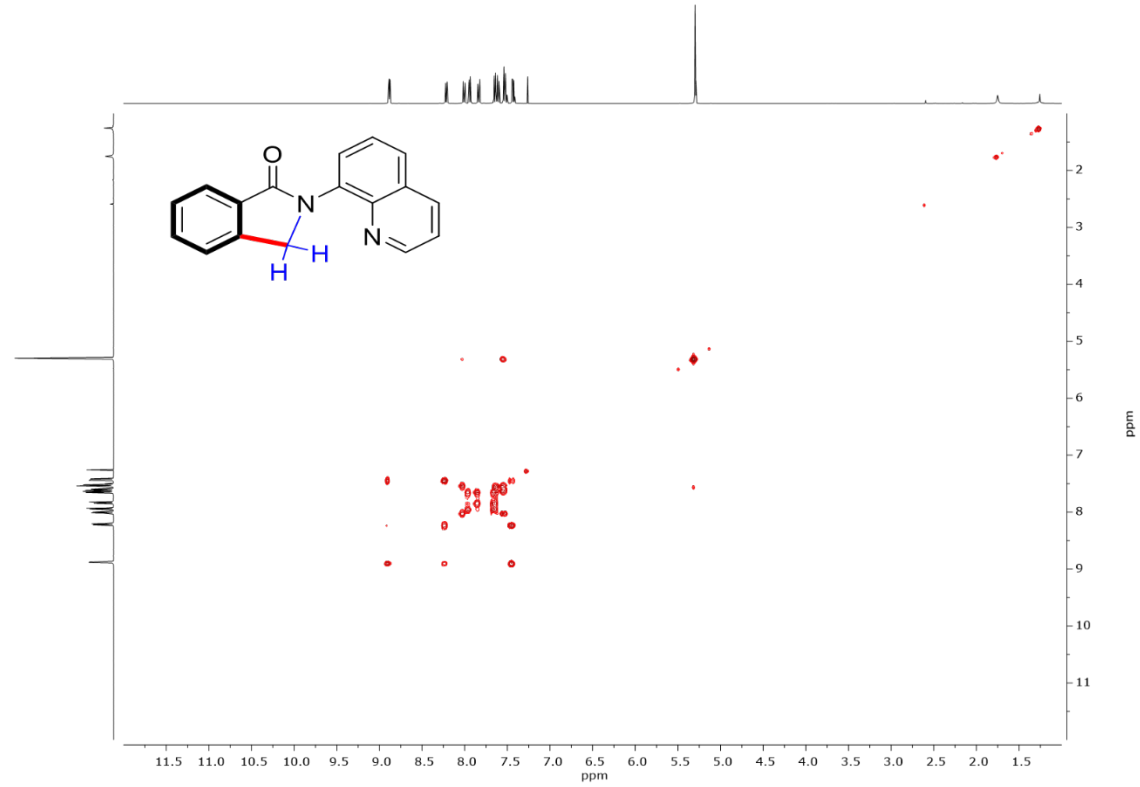


Figure S49. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **4fa** in $CDCl_3$, 298 K.

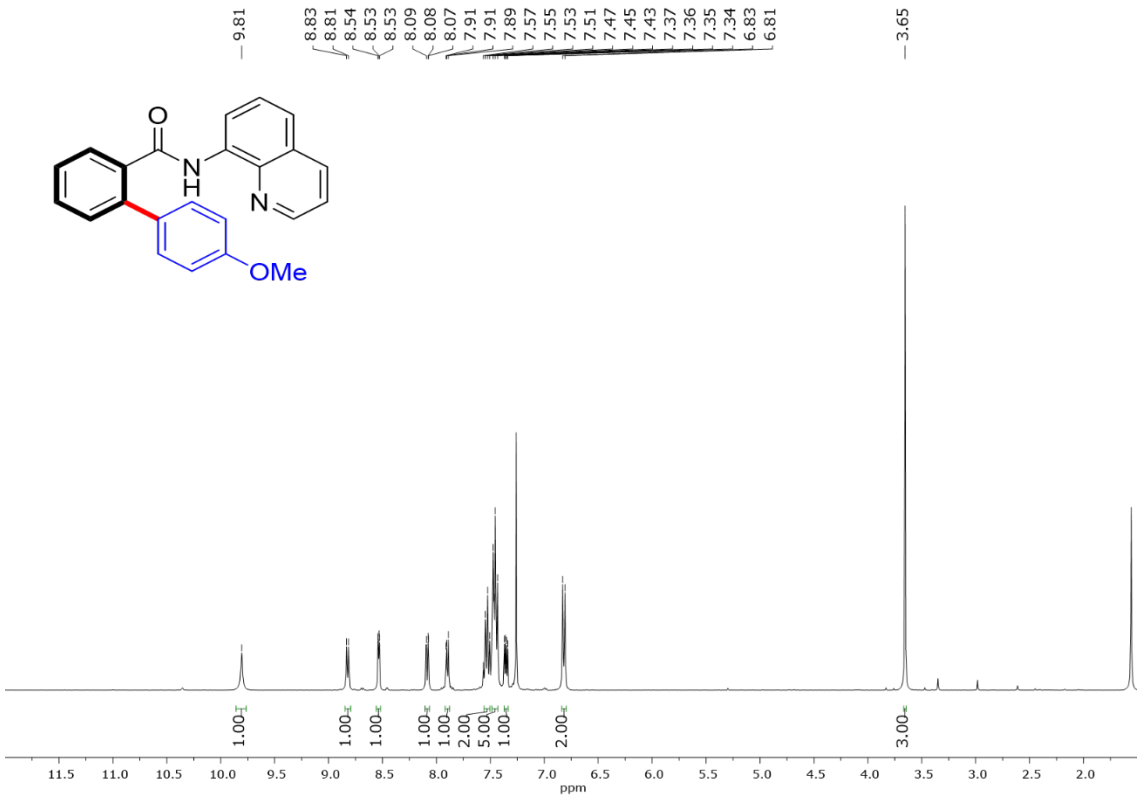


Figure S50. 400 MHz ^{1}H-NMR spectrum of **4g** in $CDCl_3$, 298 K.

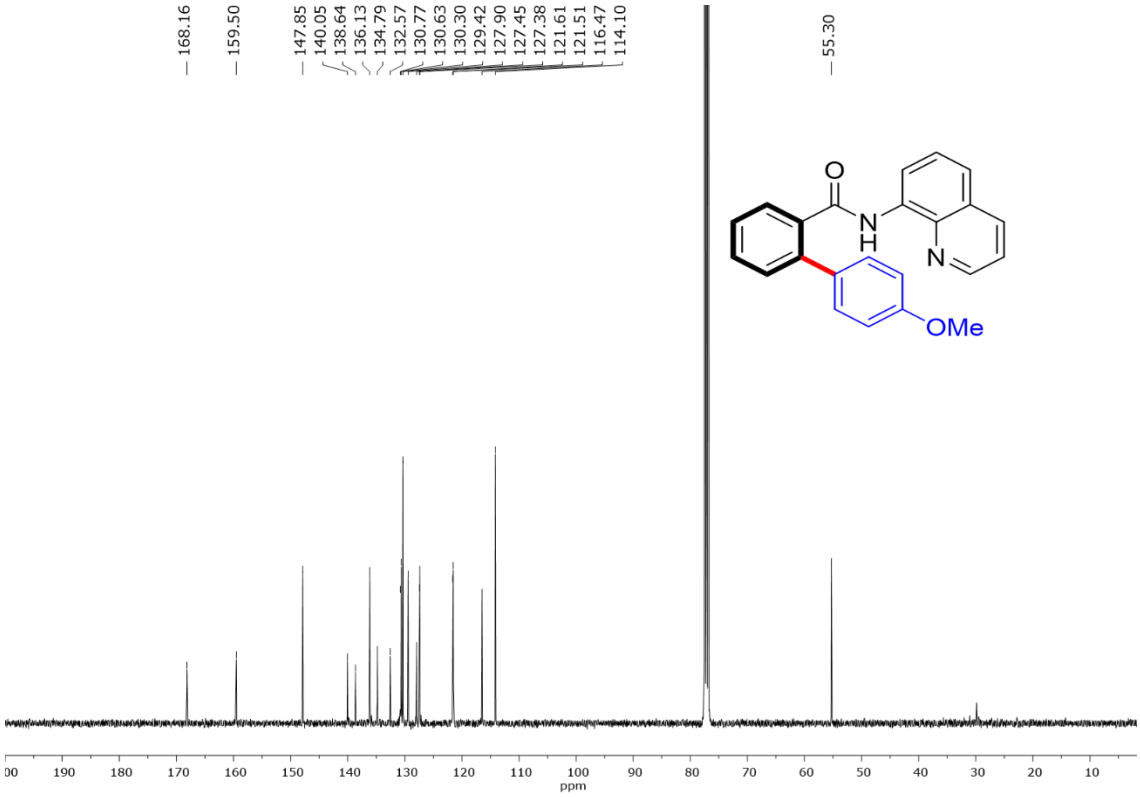


Figure S51. 100 MHz ^{13}C-NMR spectrum of **4g** in $CDCl_3$, 298 K.

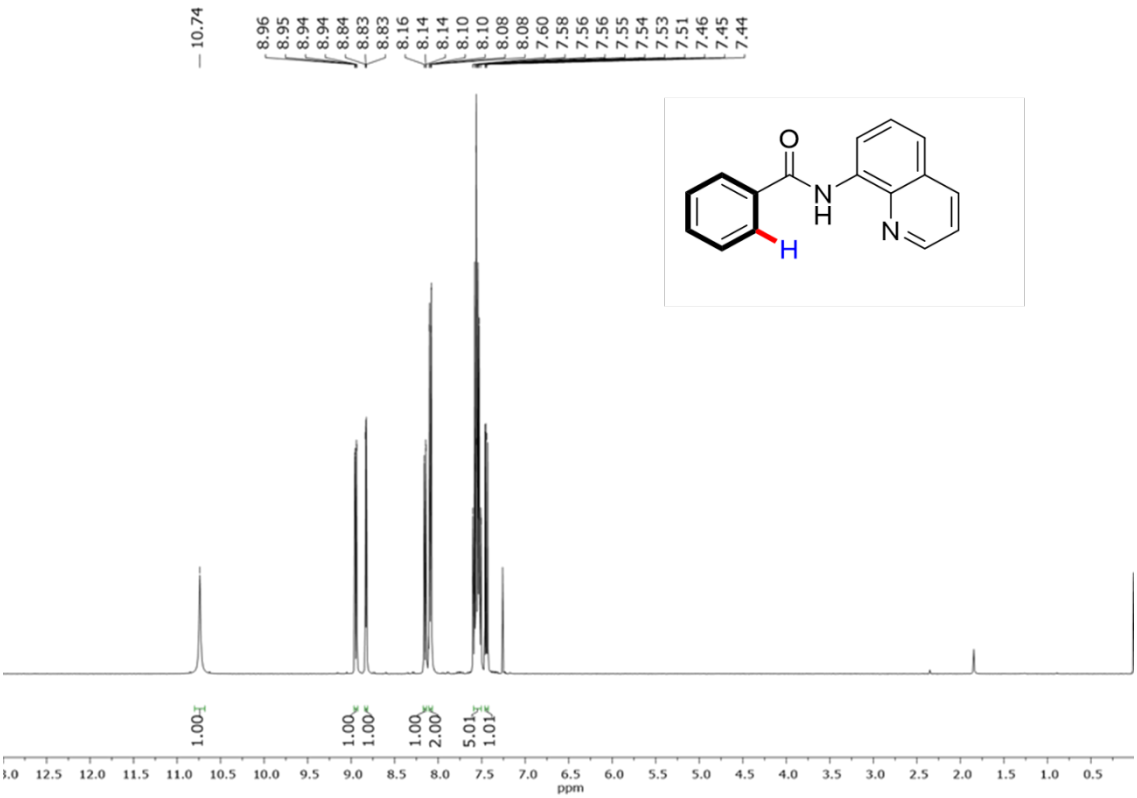


Figure S52. 400 MHz ^{1}H-NMR spectrum of **L_1-H** in $CDCl_3$, 298 K.

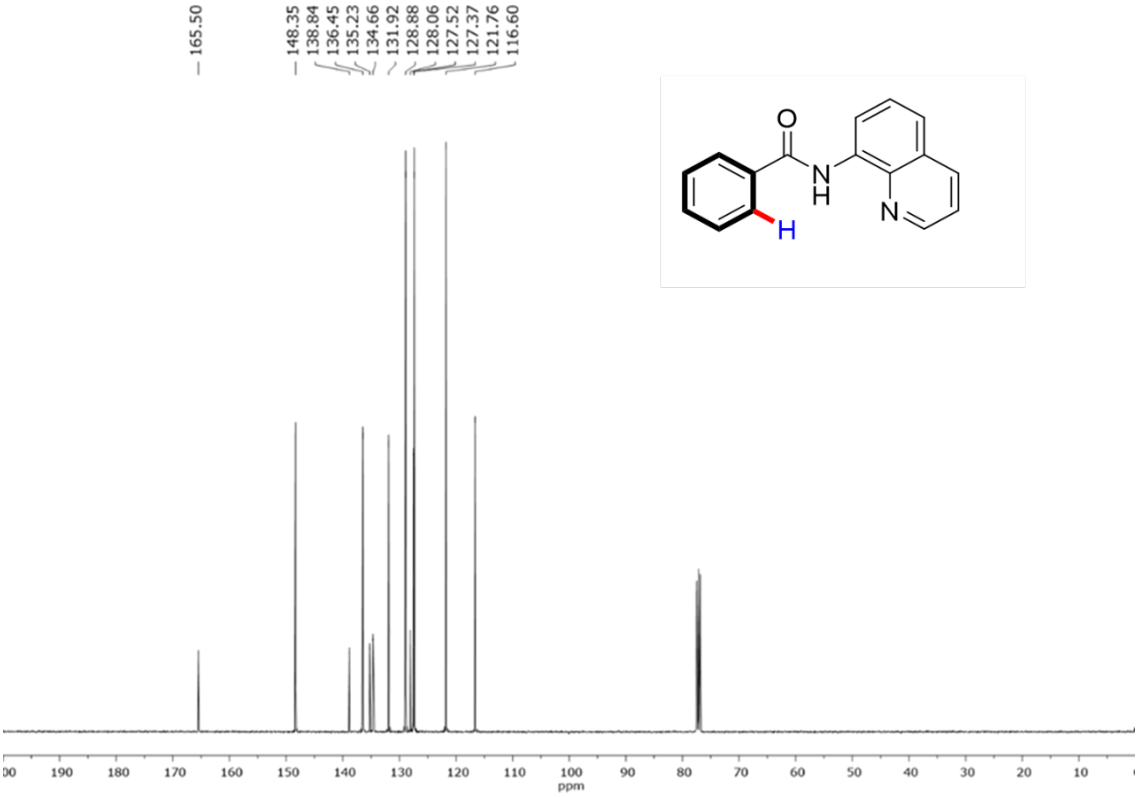


Figure S53. 100 MHz ^{13}C-NMR spectrum of **L_1-H** in $CDCl_3$, 298 K.

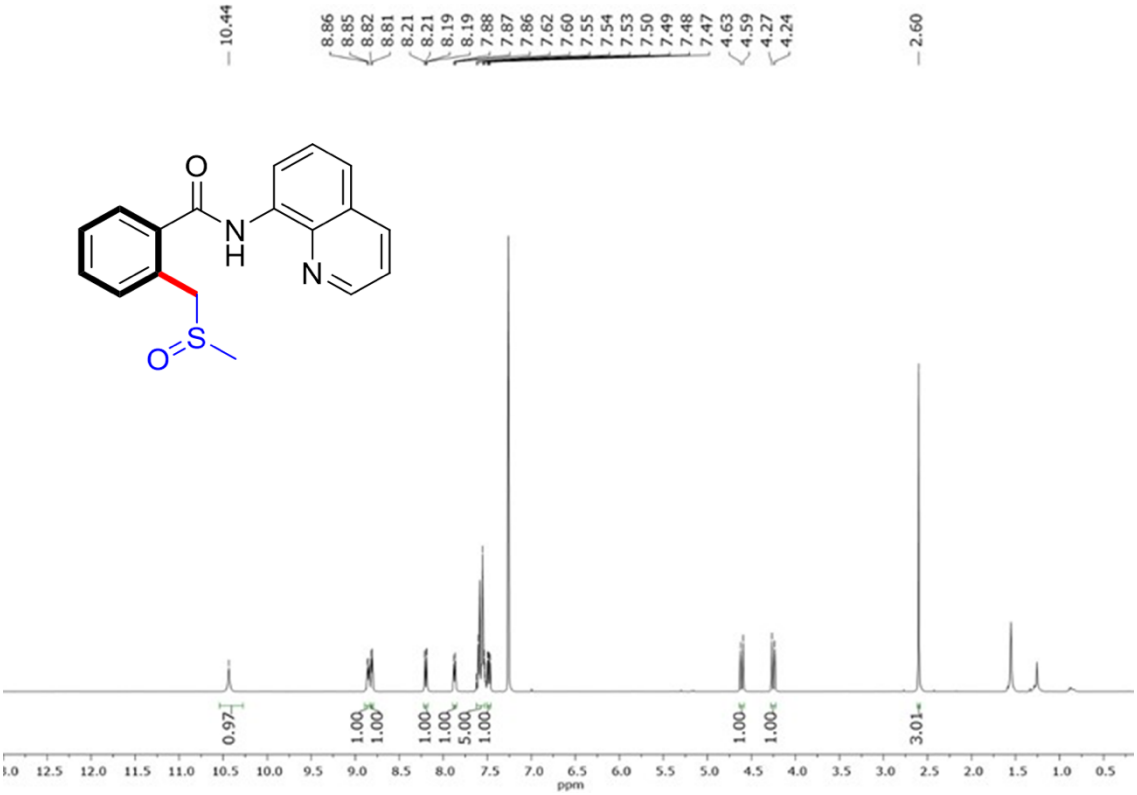


Figure S54. 400 MHz ^{1}H-NMR spectrum of **L_1-DMSO** in $CDCl_3$, 298 K.

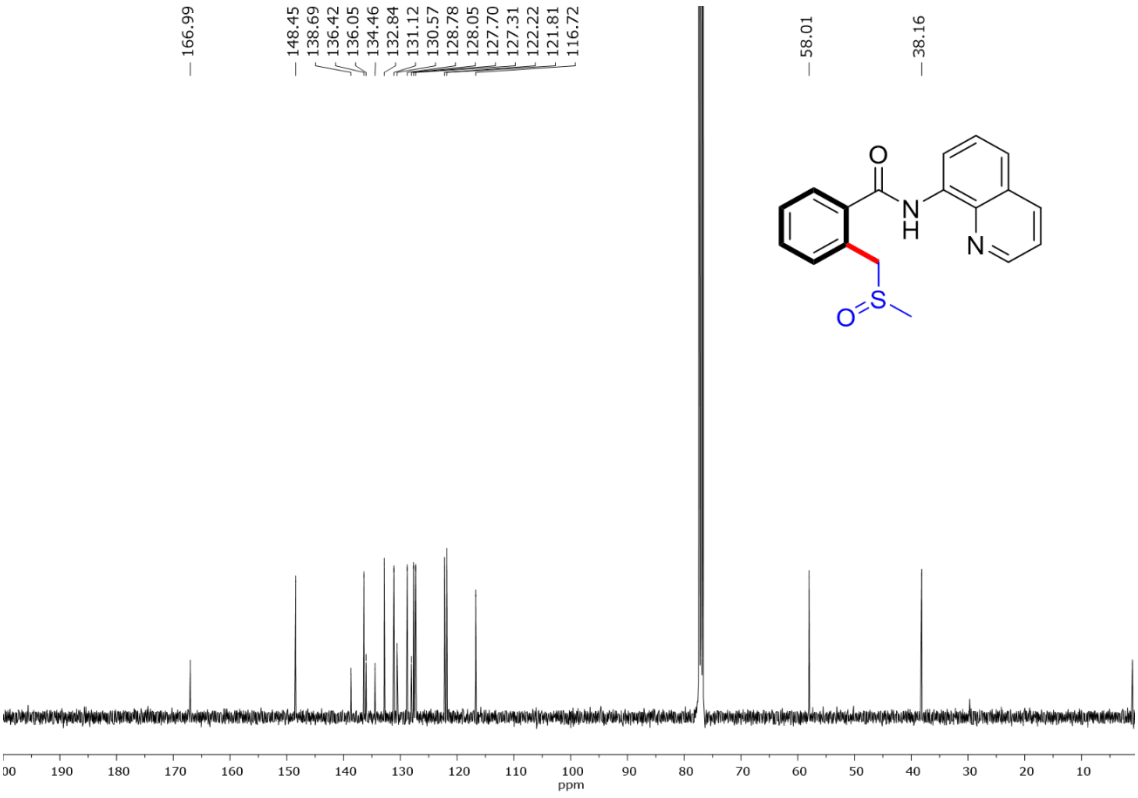


Figure S55. 100 MHz ^{13}C-NMR spectrum of **L_1-DMSO** in $CDCl_3$, 298 K.

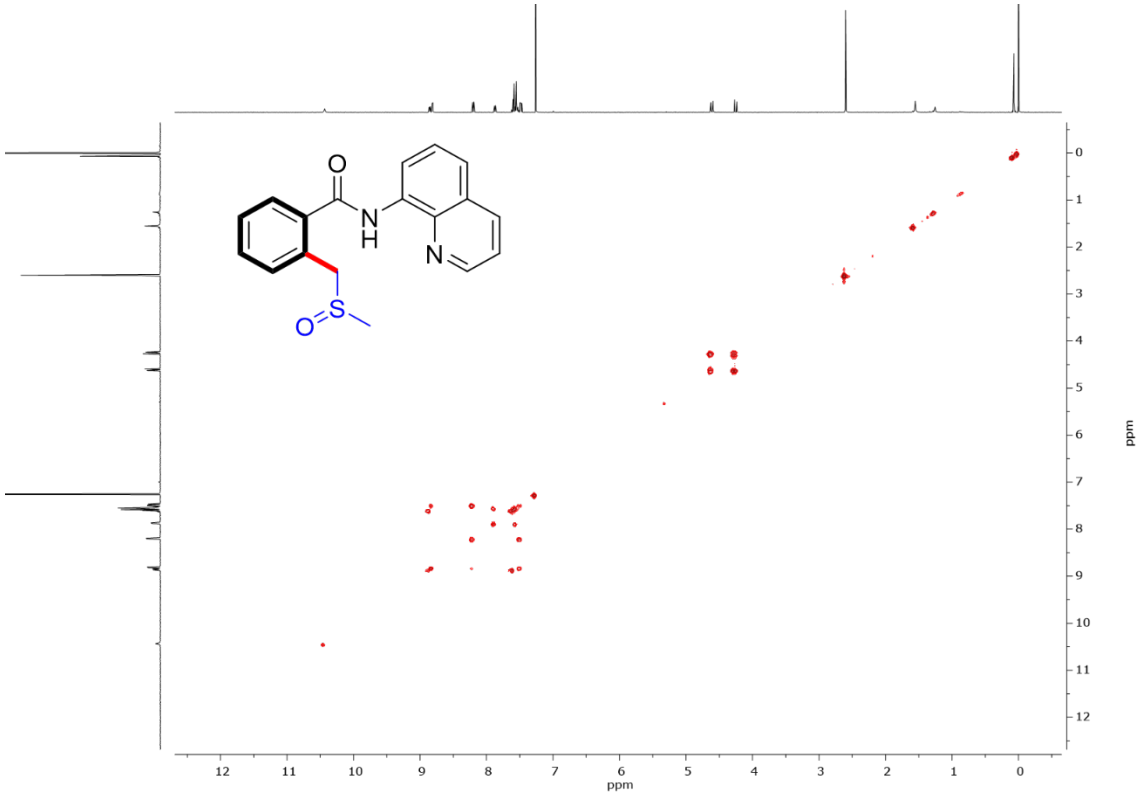


Figure S56. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **L_1-DMSO** in $CDCl_3$, 298 K.

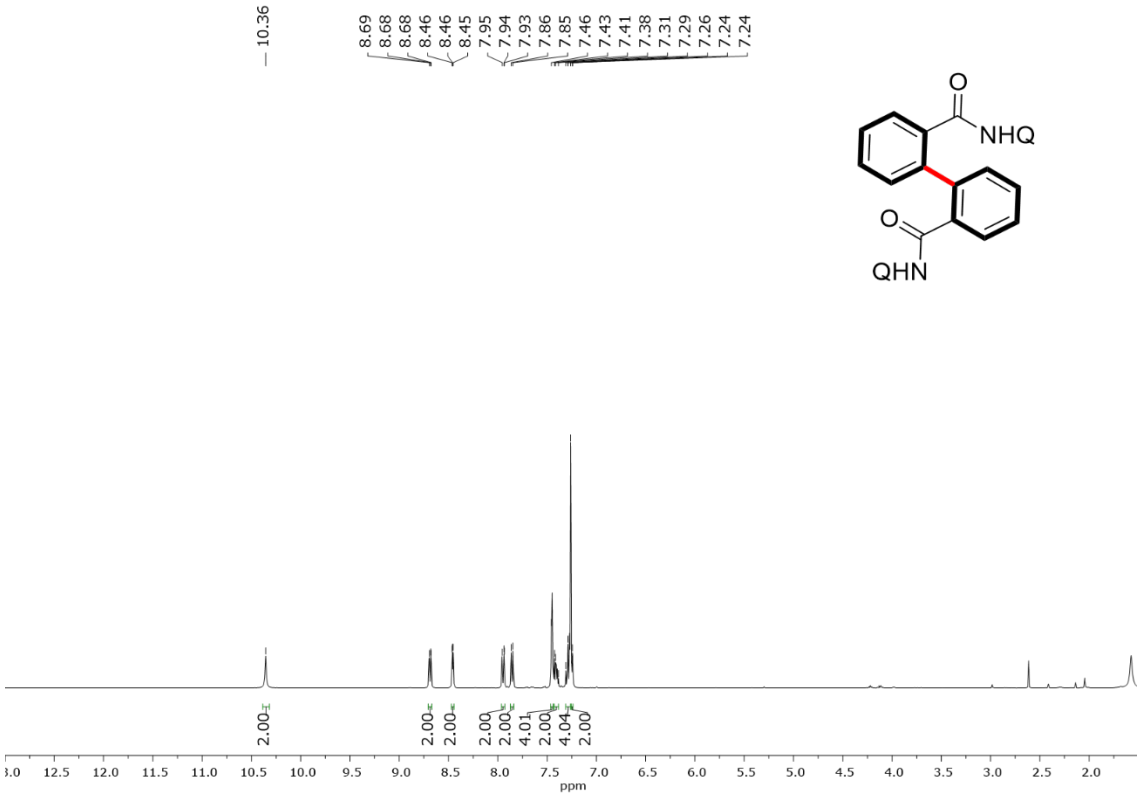


Figure S57. 400 MHz ^{1}H-NMR spectrum of **L_1-L_1 Homocoupling** in $CDCl_3$, 298 K.

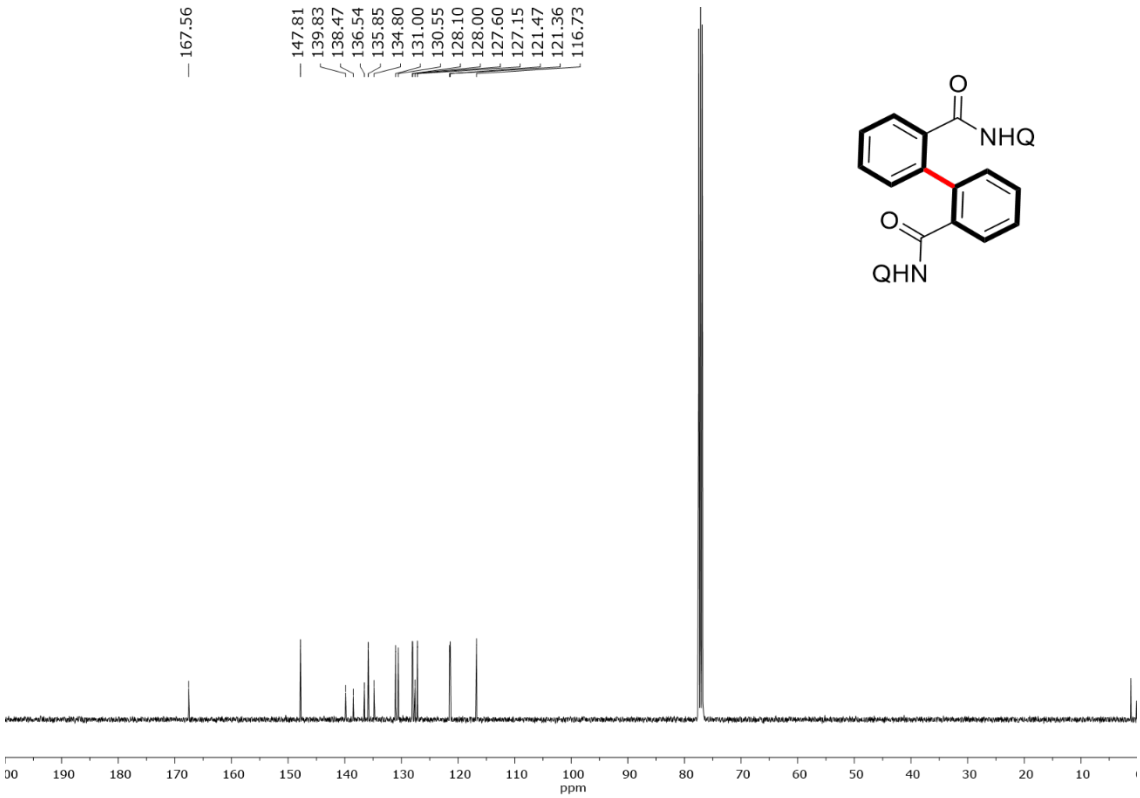


Figure S58. 100 MHz ^{13}C-NMR spectrum of **L_1-L_1 Homocoupling** in $CDCl_3$, 298 K.

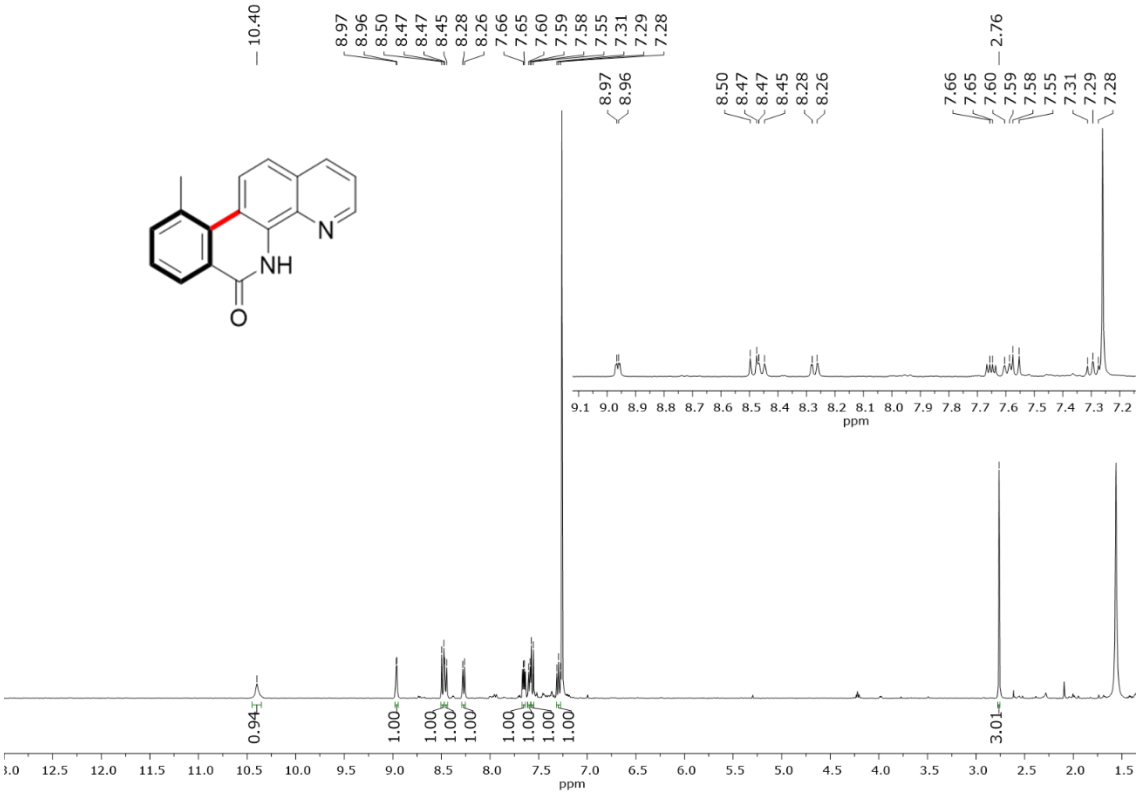


Figure S59. 400 MHz ^{1}H-NMR spectrum of **5a** in $CDCl_3$, 298 K.

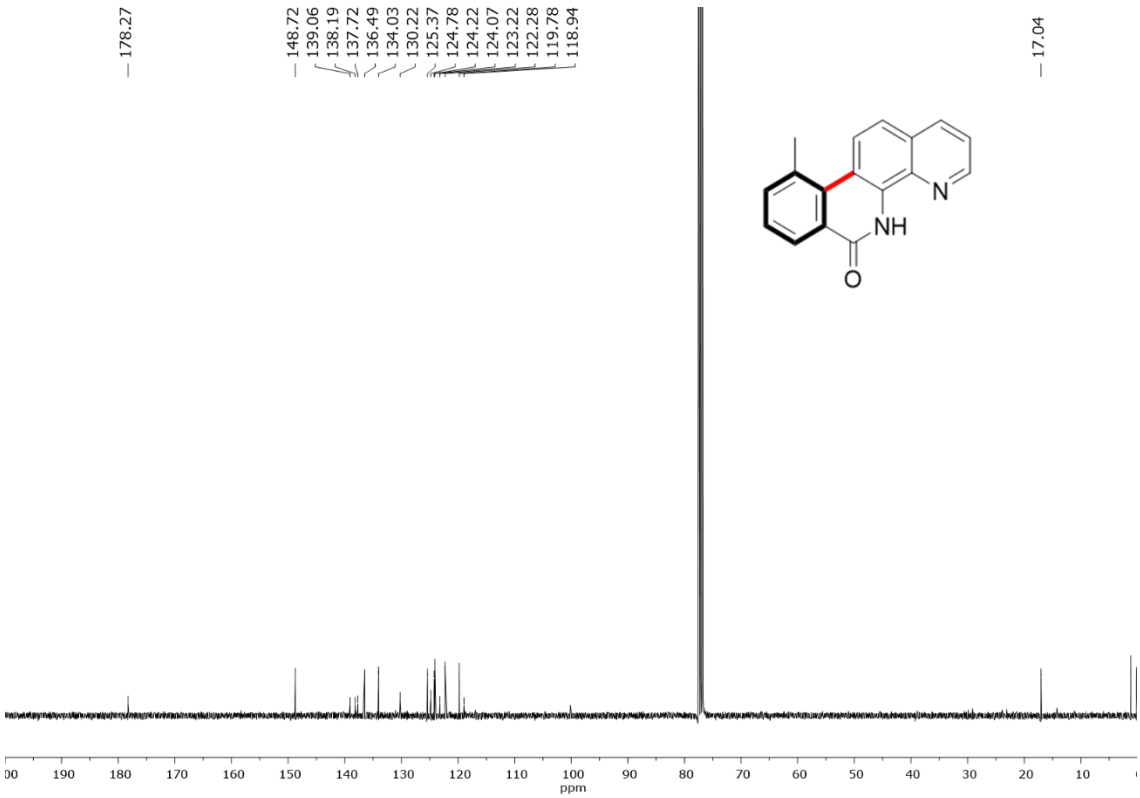


Figure S60. 100 MHz ^{13}C-NMR spectrum of **5a** in $CDCl_3$, 298 K.

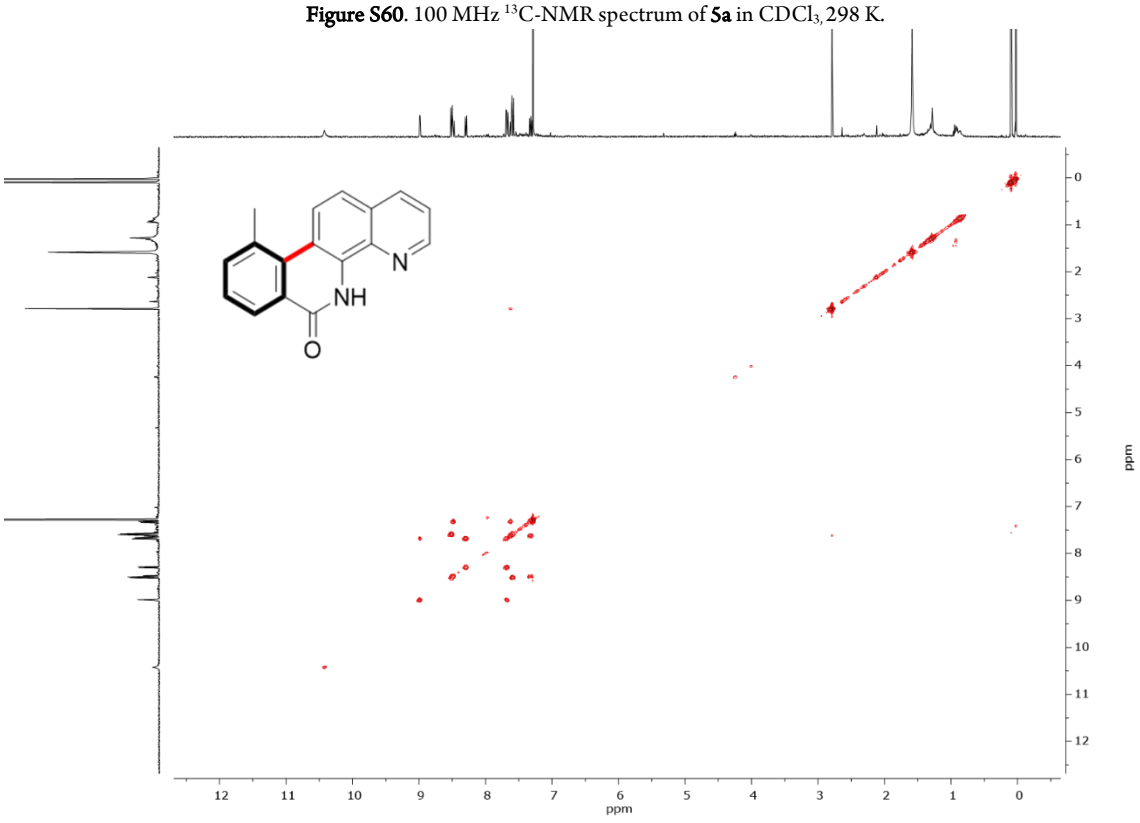


Figure S61. 400 MHz ^{1}H-^{1}H COSY NMR spectrum of **5a** in $CDCl_3$, 298 K.

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