

Brønsted acid on USY zeolite boost the direct alkenylation of 2-methylquinoline with aldehydes

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1 Density functional theory (DFT) calculation

Density functional theory (DFT) calculations were conducted using wb97XD [Phys. Chem. Chem. Phys., 2008, 10, 6615-6620] hybrid exchange-correlation functional with def2-SVP basis set [Phys. Chem. Chem. Phys., 2005, 7, 3297-3305.]. Geometry optimization was performed with the Gaussian 16 program [M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016].

2 Detailed synthesis procedure of zeolite

The USYzeolite were synthesized according to previously published works.¹

A typical synthesis of mesoporous zeolite Beta was performed as follows. First, 0.34 kg of NaOH was dissolved in 19 L of H₂O with stirring followed by addition of 0.73 kg of NaAlO₂ and 6 L of 25 wt.% tetraethylammonium hydroxide (TPAOH). After stirring at room temperature for 1 h, 8.5 kg of silica gel was added to the solution and stirred for 1 h. A cationic copolymer (4.5 L) containing quaternary ammonium groups (RCC) was added dropwise, and the mixture was stirred for 2 h to obtain a gel. The composition of this final gel was Al₂O₃/ 32 SiO₂/2 Na₂O/0.01 RCC/2.6 TPAOH/296 H₂O. This gel was transferred into a 50 L autoclave for dynamic crystallization at 140 °C for 6 days. The solid product was collected by filtration, dried, and calcined at 550

°C for 6 h to remove the organic template.²

The zeolite ZSM-5 was synthesized in the presence of tetraethylammonium hydroxide (TPAOH) from an aluminosilicate gel with a molar composition of Al_2O_3 : 89 SiO_2 : 24 Na_2O : 3 TPAOH: 0.07 TPOAB: 3200 H_2O . In a 5 L stainless steel autoclave, 0.88 L of water glass, 0.14 L of TPAOH (25.0 wt.%), and 0.56 L of H_2O were sequentially added under stirring. After the mixture was stirred for 1 h, 0.44 L of TPOAB was slowly added, and the gel was further stirred for 2 h. Subsequently, 1.90 L of acidic aluminum sulfate solution (0.03 mol/L) was slowly added. The gel was further stirred for 2 h and crystallized at 175 °C for 44 h. The obtained mixture was filtrated and washed, and the obtained solid product was dried at 120 °C overnight and calcined in air atmosphere at 550 °C for 5 h.³

3 Recycle performance and scale-up experiments of the catalyst

The recycle experiment for the USY catalyst was performed in a 10 mL reaction tube. When the reaction was finished, the catalyst was separated from the reaction mixture by filtration and thoroughly washed with ethyl acetate. After that, the sample was dried at 100 °C for 12 h and calcined at 550 °C for 4 h in air before use in the next cycle. After 5 runs for the catalyst, the catalyst was denoted as S-USY, which was characterized by XRD patterns, N_2 adsorption-desorption isotherm, NH_3 -TPD curves.

To expand the practicality of USY molecular sieve in catalyzing the alkylation reaction of 2-methylquinoline and benzaldehyde, a tenfold amplification experiment was conducted. The specific experimental process is as follows: 2-methylquinoline (3 mmol), benzaldehyde (2 mmol), 300 mg of catalyst and 10 mL of toluene are heated and stirred at 150 °C for 24 hours to obtain the target product 3a with a yield of 96%.

4. Figures

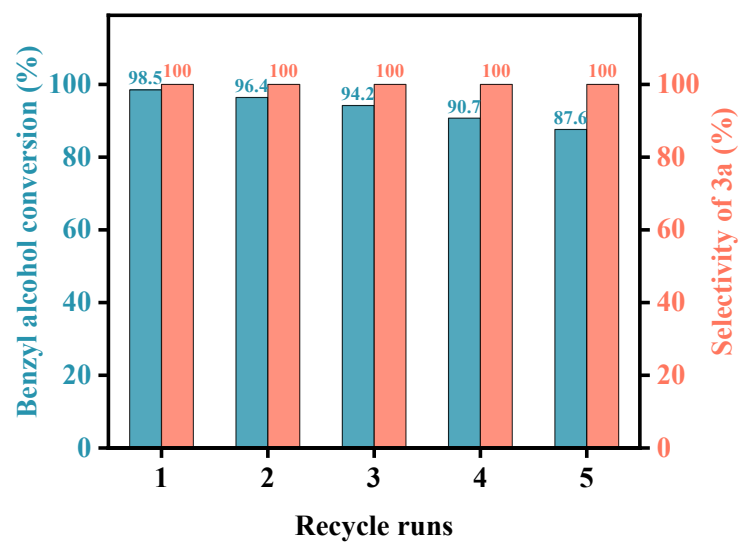


Fig. S1. Recyclability of USY catalyst for direct alkenylation of 2-methylquinoline with benzaldehyde. (Reaction conditions: 0.3 mmol **1a**, 0.2 mmol **2a**, catalyst 30 mg and toluene 1 mL, at 150 °C for 24 h.)

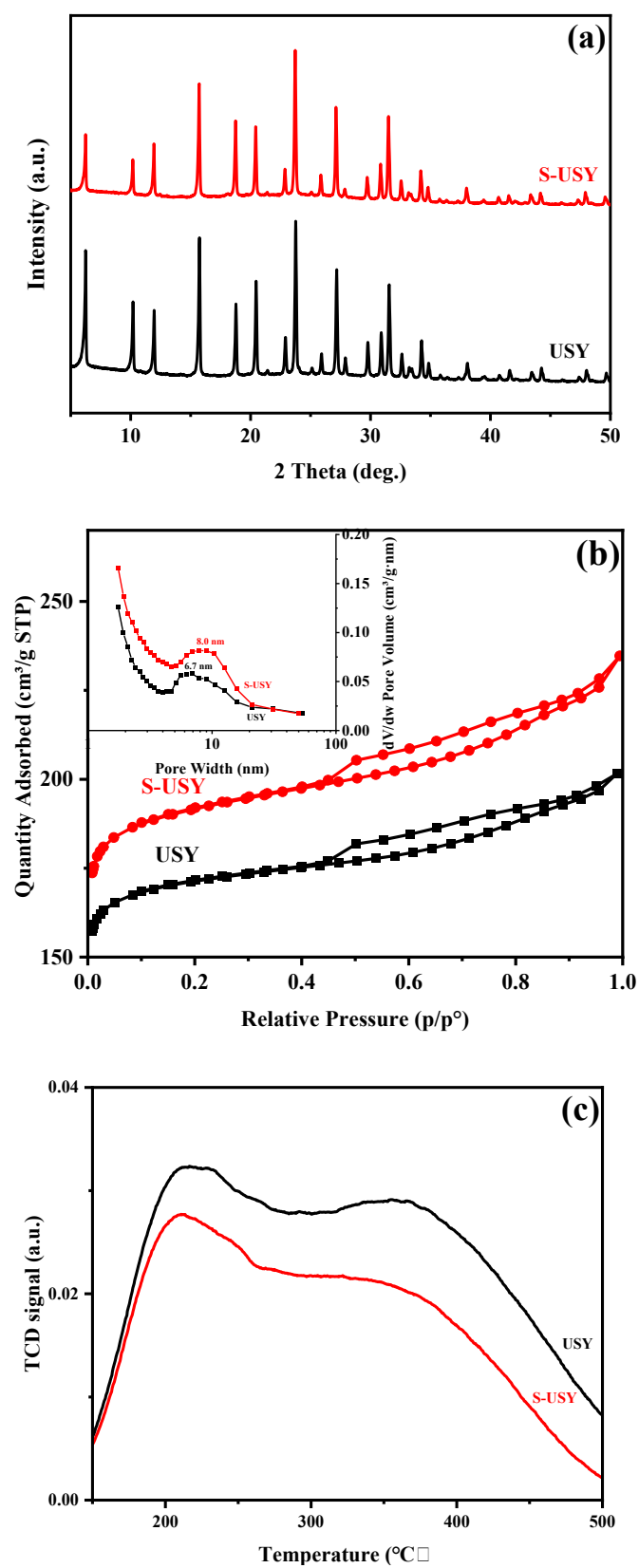


Fig. S2. (a) XRD patterns, (b) N₂ adsorption-desorption isotherms, (c) NH₃-TPD curves of USY and S-USY.

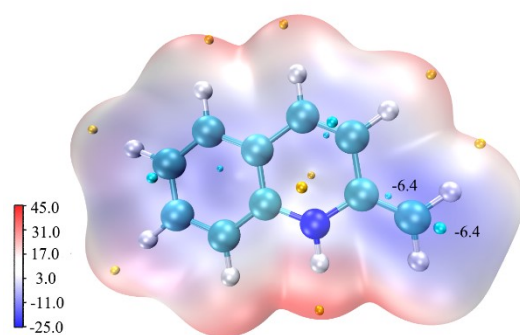
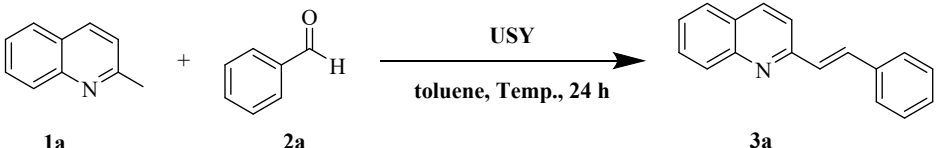
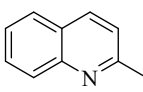
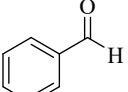
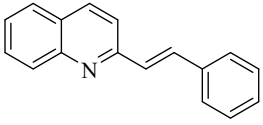


Fig. S3. The ESP of 2-methylene-1,2-dihydroquinoline.

5. Tables

Table S1 Temperature screening under the same reaction conditions. ^a

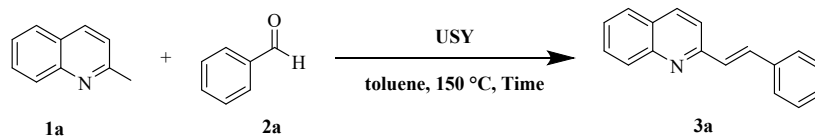
  1a +  2a $\xrightarrow[\text{toluene, Temp., 24 h}]{\text{USY}}$  3a			
Entry	Temp. (°C) ^b	Conv. (%) ^c	Sel. (%) ^c
1	150	98.5	100
2	140	88.7	100
3	130	52.2	100
4	120	33.3	100
5	110	32.4	100
6	100	25.4	100

^aReaction Conditions, 2-methylquinoline (**1a**, 0.3 mmol), benzaldehyde (**2a**, 0.2 mmol), catalyst 30 mg and toluene 1 mL at different temperature for 24 h.

^bTemperature.

^c Conversion and Selectivity, the data was analyzed by GC.

Table S2 Time screening in same reaction conditions. ^a



Entry	Time(h) ^b	Conv. (%) ^c	Sel. (%) ^c
1	24	98.5	100
2	20	87.5	100
3	16	74.3	100

^aReaction Conditions: 0.3 mmol **1a**, 0.2 mmol **2a**, catalyst 30 mg and toluene 1 mL at 150 °C for different hours.

^bTime.

^c Conversion and Selectivity, the data was analyzed by GC.

Table S3 Solvent screening in same reaction conditions. ^a

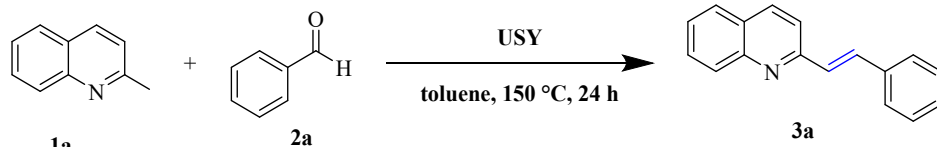
Entry	Solvent ^b	Conv. (%) ^c	Sel. (%) ^c
1	1,4-Dioxane	31.2	100
2	DMF	82.6	100
3	ACN	41.9	100
4	DMSO	71.9	100
5	H ₂ O	-	-
6	DCE	68.7	100
7	THF	17.2	45.4
8	TL	98.5	100

^aReaction Conditions: 0.3 mmol **1a**, 0.2 mmol **2a**, catalyst 30 mg and different solvents 1 mL at 150 °C for 24 h.

^bSolvent: DMF represent dimethylformamide, ACN represent acetonitrile, DMSO represent dimethyl sulfoxide, DCE represent dichloroethane, THF represent tetrahydrofuran, TL represent toluene.

^cConversion and Selectivity, the data was analyzed by GC.

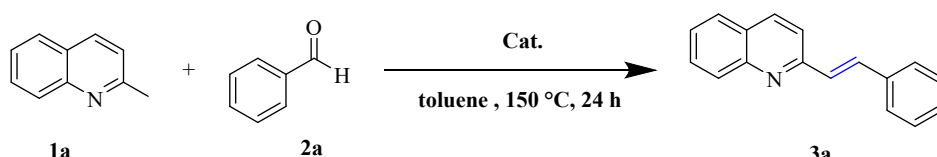
Table S4 Amplification experiment of USY zeolite catalyzed alkenylation of 2-methylquinoline and benzaldehyde. ^a

		
Entry	Conv. (%) ^c	Sel. (%) ^c
1	96.0	100

^aReaction Conditions: 2-methylquinoline (**1a**, 3 mmol), benzaldehyde (**2a**, 2 mmol), catalyst 300 mg, solvent (10 mL), 150 °C (external temperature), 24 h.

^b Conversion and Selectivity, the data was analyzed by GC.

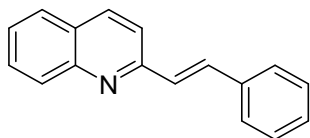
Table S5 The influence of the reaction without catalyst and γ -alumina. ^a

 1a 2a 3a			
Entry	Catalyst	Conv. (%) ^b	Sel. (%) ^b
1	-	51.9	100
2	γ -Al ₂ O ₃	30.0	100
3	SiO ₂ -Al ₂ O ₃ .	90.1	100

^aReaction Conditions: 2-methylquinoline (**1a**, 0.3 mmol), benzaldehyde (**2a**, 0.2 mmol), catalyst 30 mg, solvent (1.0 mL), 150 °C (external temperature), 24 h.

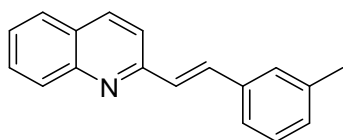
^bConversion and Selectivity, the data was analyzed by GC.

6 Characterization of the products



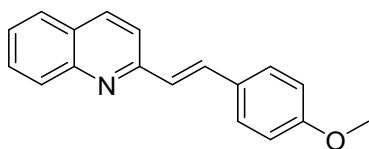
(E)-2-styrylquinoline(**3a**)⁴: Pale yellow solid

¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.1 Hz, 1H), 7.73 – 7.63 (m, 5H), 7.49 (t, J = 7.5 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.33 (t, J = 7.3 Hz, 1H).



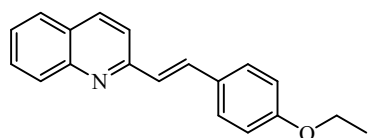
(E)-2-(3-methylstyryl)quinoline (**3b**)⁴: Pale yellow solid

¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, J = 13.9, 8.6 Hz, 2H), 7.78 (dd, J = 8.1, 1.4 Hz, 1H), 7.73 – 7.63 (m, 3H), 7.52 – 7.38 (m, 4H), 7.30 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 2.40 (s, 3H).



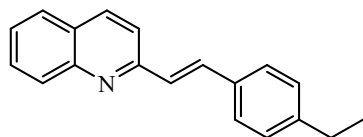
2-[(1E)-2-(4-Methoxyphenyl)ethenyl]quinoline(**3c**)⁴ : Pale yellow solid

¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 (t, J = 7.8 Hz, 2H), 7.77 (d, J = 8.1 Hz, 1H), 7.74 – 7.55 (m, 5H), 7.48 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 16.3 Hz, 1H), 6.94 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H).



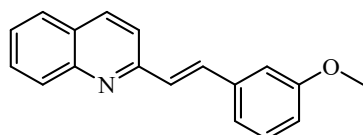
(E)-2-(4-ethoxystyryl)quinoline(**3d**)⁵ : Pale yellow solid

^1H NMR (400 MHz, Chloroform-*d*) δ 8.04 (t, J = 8.5 Hz, 2H), 7.72 (d, J = 8.1 Hz, 1H), 7.67 – 7.50 (m, 5H), 7.46 – 7.41 (m, 1H), 7.22 (d, J = 2.1 Hz, 1H), 6.87 (d, J = 8.7 Hz, 2H), 4.02 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.0 Hz, 3H).



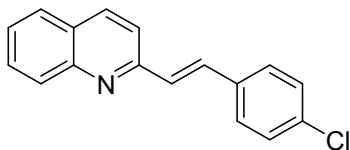
(E)-2-(4-Ethylstyryl)quinoline(**3e**)⁶ : Pale yellow solid

^1H NMR (400 MHz, Chloroform-*d*) δ 8.10 (t, J = 7.9 Hz, 2H), 7.77 (d, J = 6.7 Hz, 1H), 7.73 – 7.64 (m, 3H), 7.58 (d, J = 8.2 Hz, 2H), 7.49 (t, J = 8.1 Hz, 1H), 7.39 (d, J = 16.3 Hz, 1H), 7.24 (d, J = 8.2 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H).



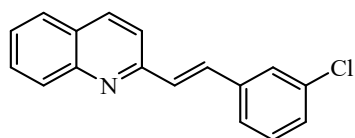
2-[(1E)-2-(3-Methoxyphenyl)ethenyl]quinoline(**3f**)⁴ : Pale yellow solid

^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, J = 15.0, 8.6 Hz, 2H), 7.80 (d, J = 8.2 Hz, 1H), 7.75 – 7.64 (m, 3H), 7.54 – 7.43 (m, 2H), 7.32 (t, J = 7.9 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.90 (dd, J = 8.1, 2.6 Hz, 1H), 3.87 (s, 3H).



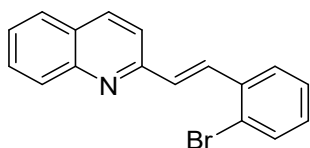
(E)-2-(4-chlorostyryl)quinoline(**3h**)⁴: Pale yellow solid

^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.06 (m, 2H), 7.78 (dd, J = 8.1, 1.4 Hz, 1H), 7.71 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.57 – 7.48 (m, 3H), 7.41 – 7.33 (m, 3H).



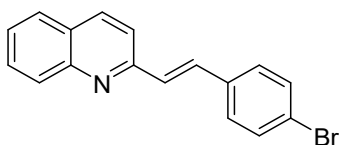
(E)-2-(3-chlorostyryl)quinoline (**3i**)⁷: Pale yellow solid

¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, J = 8.6 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.62 (t, J = 7.0 Hz, 3H), 7.53 – 7.48 (m, 2H), 7.40 (d, J = 16.3 Hz, 1H), 7.35 – 7.27 (m, 2H).



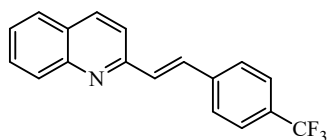
(E)-2-(2-bromostyryl)quinoline(**3j**)⁷ : White solid

¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, J = 8.6 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 16.3 Hz, 1H), 7.83 – 7.76 (m, 3H), 7.74 – 7.69 (m, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.20 – 7.15 (m, 1H).



(E)-2(4-bromostyryl)quinoline(**3k**)⁴: Pale yellow solid

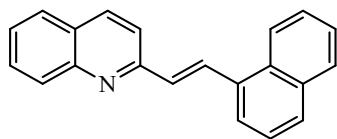
¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, J = 14.9, 8.5 Hz, 2H), 7.78 (d, J = 8.1 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.65 – 7.59 (m, 2H), 7.51 (t, J = 5.6 Hz, 5H), 7.39 (d, J = 16.2 Hz, 1H).



2-[(1E)-2-[4-(Trifluoromethyl)phenyl]ethenyl]quinoline(**3l**)⁸: White solid

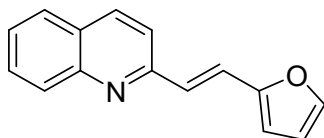
¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, J = 24.0, 8.5 Hz, 2H), 7.81 (d, J = 9.6

Hz, 1H), 7.76 – 7.62 (m, 7H), 7.56 – 7.45 (m, 2H).



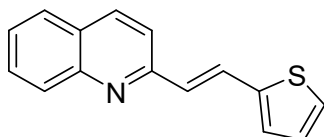
(E)-2-(2-(naphthalen-1-yl)vinyl)quinolines(**3m**)⁴: White solid

¹H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, J = 16.0 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.19 (t, J = 9.8 Hz, 2H), 7.91 (dd, J = 12.7, 9.3 Hz, 3H), 7.79 (td, J = 14.3, 8.2 Hz, 3H), 7.54 (dt, J = 14.8, 7.3 Hz, 5H).



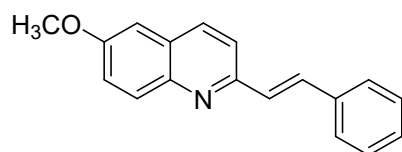
2-[(1E)-2-(2-furanyl)ethenyl]quinoline(**3n**)⁴: red solid

¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 (t, J = 9.3 Hz, 2H), 7.72 (d, J = 9.4 Hz, 1H), 7.65 (t, J = 8.4 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.47 – 7.40 (m, 2H), 7.22 (d, J = 2.4 Hz, 1H), 6.52 – 6.39 (m, 2H).



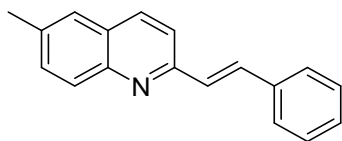
2-[(1E)-2-(2-thienyl)ethenyl]quinoline(**3o**)⁴ : Yellow solid

¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (dd, J = 8.5, 4.4 Hz, 2H), 7.91 (d, J = 16.0 Hz, 1H), 7.84 – 7.74 (m, 2H), 7.63 (d, J = 8.6 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.38 – 7.28 (m, 3H), 7.14 – 7.10 (m, 1H).



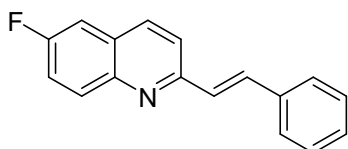
(E)-6-methoxy-2-styrylquinoline(**3p**)⁴: Pale yellow solid

^1H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.99 (m, 2H), 7.66 – 7.60 (m, 4H), 7.43 – 7.31 (m, 5H), 7.06 (d, J = 2.8 Hz, 1H), 3.94 (s, 3H).



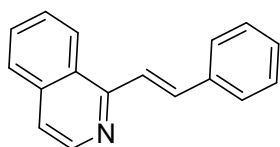
(E)-6-methyl-2-styrylquinoline(**3q**)⁷: White solid

^1H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 9.1 Hz, 1H), 7.68 – 7.63 (m, 4H), 7.54 (d, J = 6.9 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.32 (t, J = 7.3 Hz, 1H), 2.53 (s, 3H).



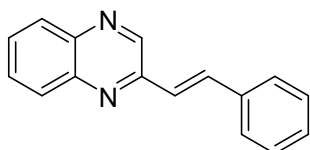
(E)-6-fluoro-2-styrylquinoline(**3r**)⁷: White solid

^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.06 (m, 2H), 7.73 – 7.62 (m, 4H), 7.48 (td, J = 8.8, 2.9 Hz, 1H), 7.44 – 7.31 (m, 5H).



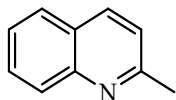
1-[(1E)-2-Phenylethenyl]isoquinoline(**3s**)⁴: light yellow solid.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, J = 5.6 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.01 (s, 2H), 7.84 (d, J = 8.1 Hz, 1H), 7.68 (dd, J = 26.5, 7.0 Hz, 4H), 7.58 (d, J = 5.7 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H).



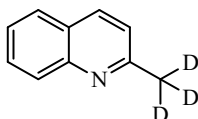
2-[(1E)-2-Phenylethenyl]quinoxaline(**3t**)⁷: Red solid

^1H NMR (400 MHz, Chloroform-*d*) δ 9.06 (s, 1H), 8.08 (d, J = 7.9 Hz, 2H), 7.89 (d, J = 16.4 Hz, 1H), 7.80 – 7.69 (m, 2H), 7.67 (d, J = 6.6 Hz, 2H), 7.46 – 7.34 (m, 4H).



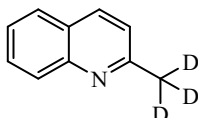
2-methylquinoline(**1a**): Yellow liquid

^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, J = 8.4 Hz, 1H), 7.89 (t, J = 7.0 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.38 (d, J = 7.9 Hz, 1H), 7.16 – 7.11 (m, 1H), 2.66 (s, 3H).



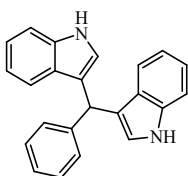
*d*₃-2-methylquinoline(***d*₃-1a**): Yellow liquid

^1H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H). 2.66 (s, 0.28H)



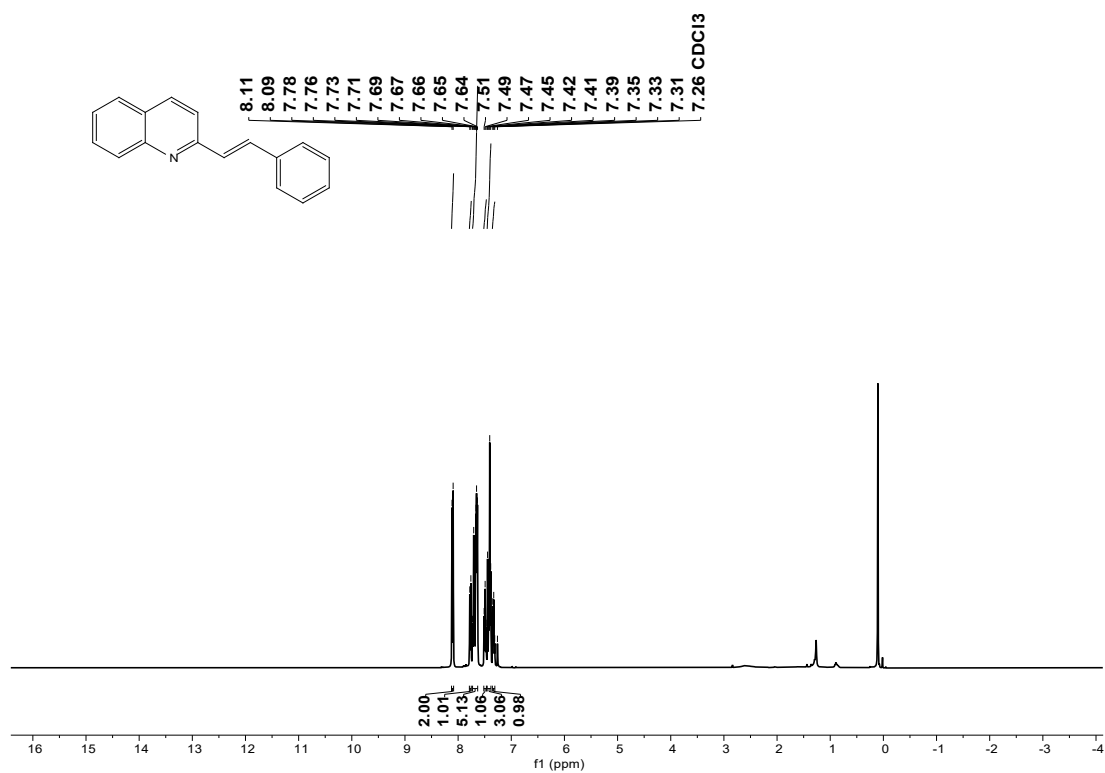
*d*₃-2-methylquinoline(***d*₃'-1a**): Yellow liquid

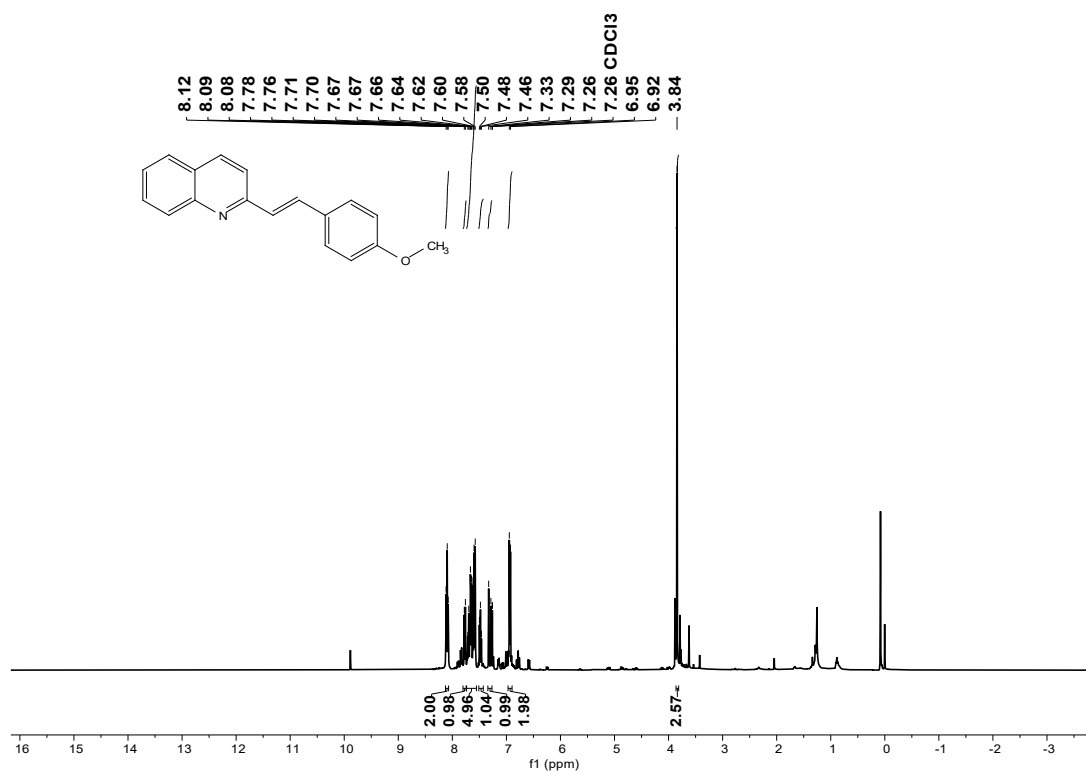
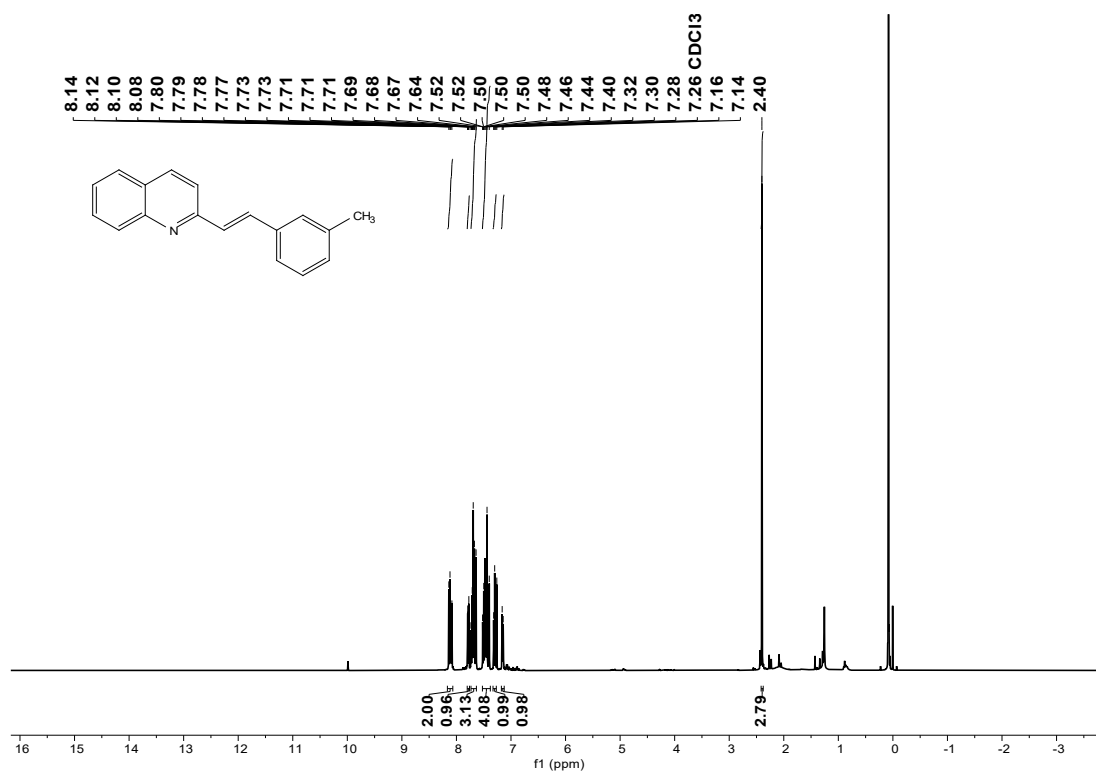
^1H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, J = 3.2 Hz, 1H), 7.93 (d, J = 3.2 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.38 (t, J = 8.1 Hz, 1H), 7.17 (d, J = 8.5 Hz, 1H), 2.65 (s, 1H).

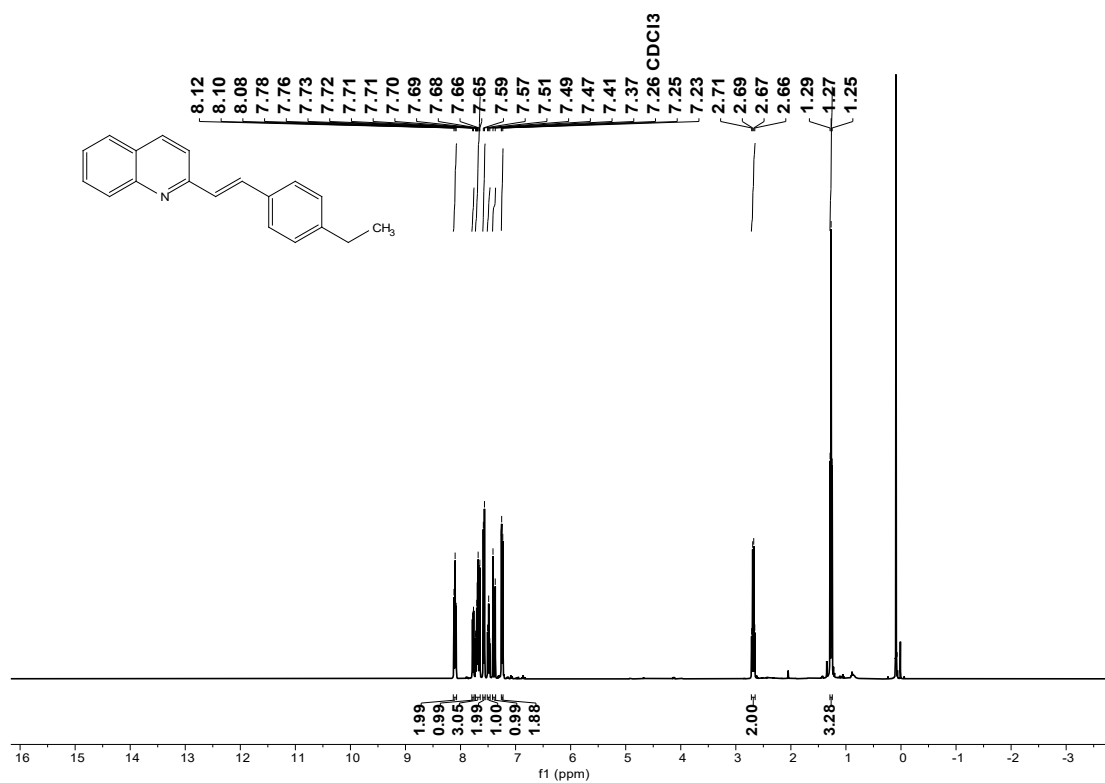
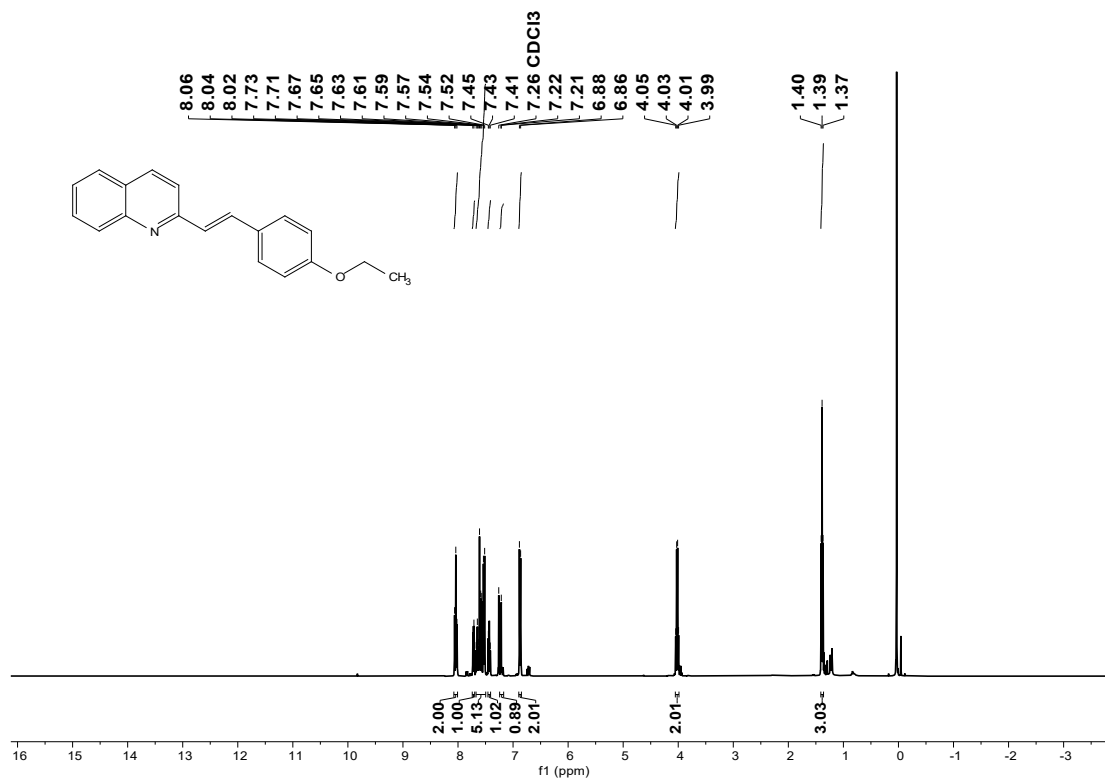


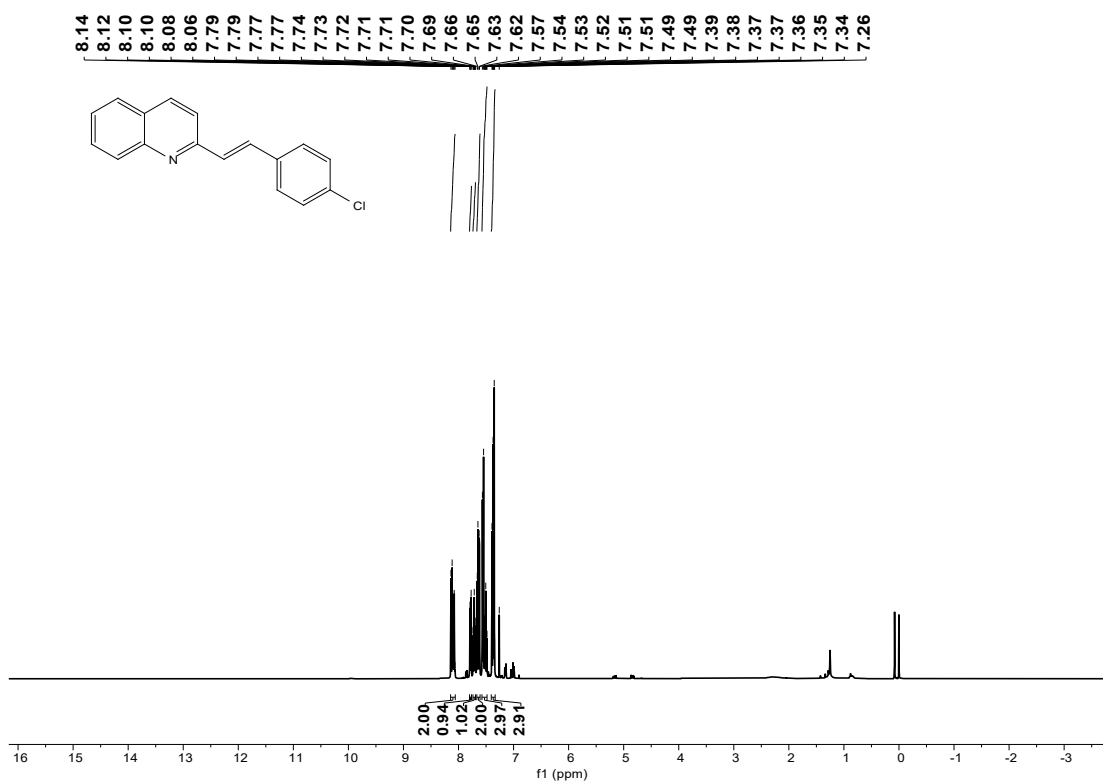
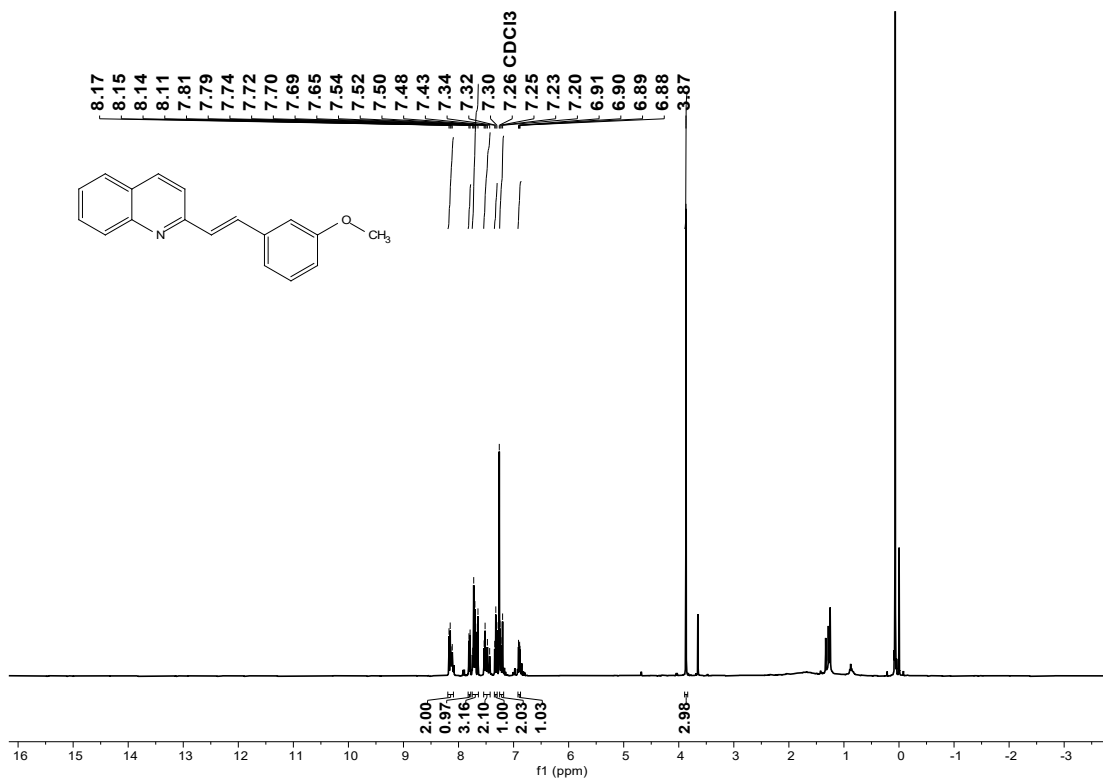
3,3'-(Phenylmethylene)bis[1*H*-indole](**6a**)⁹: Red solid

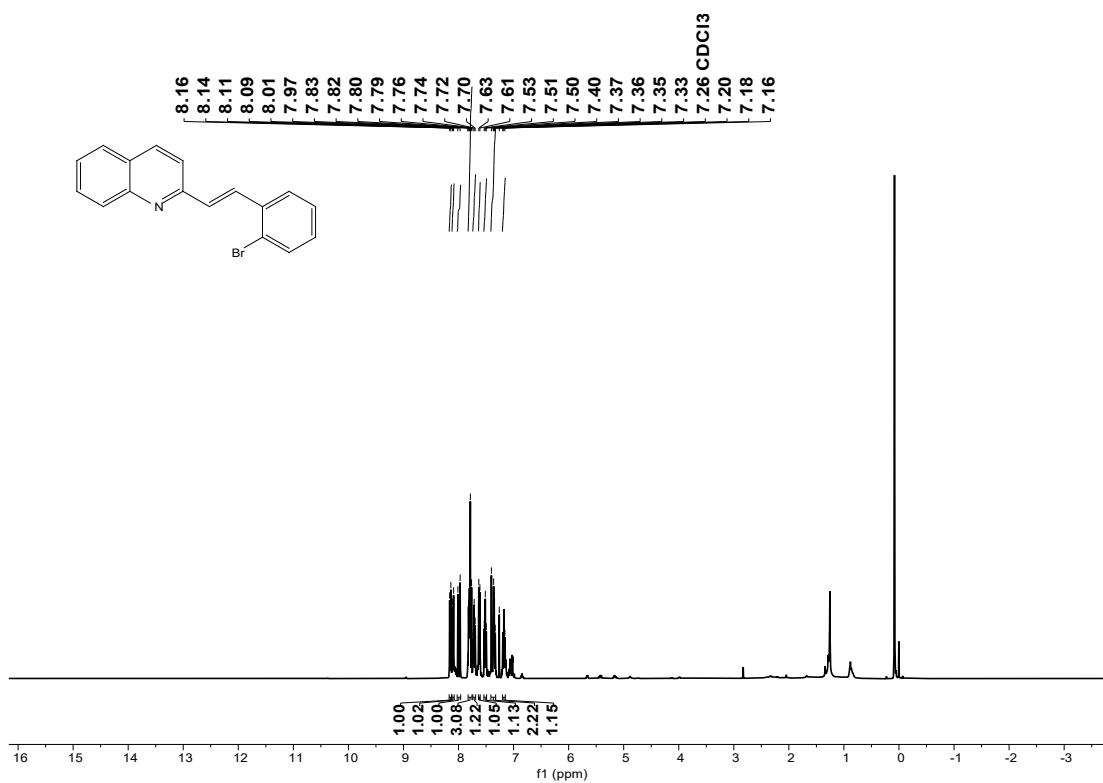
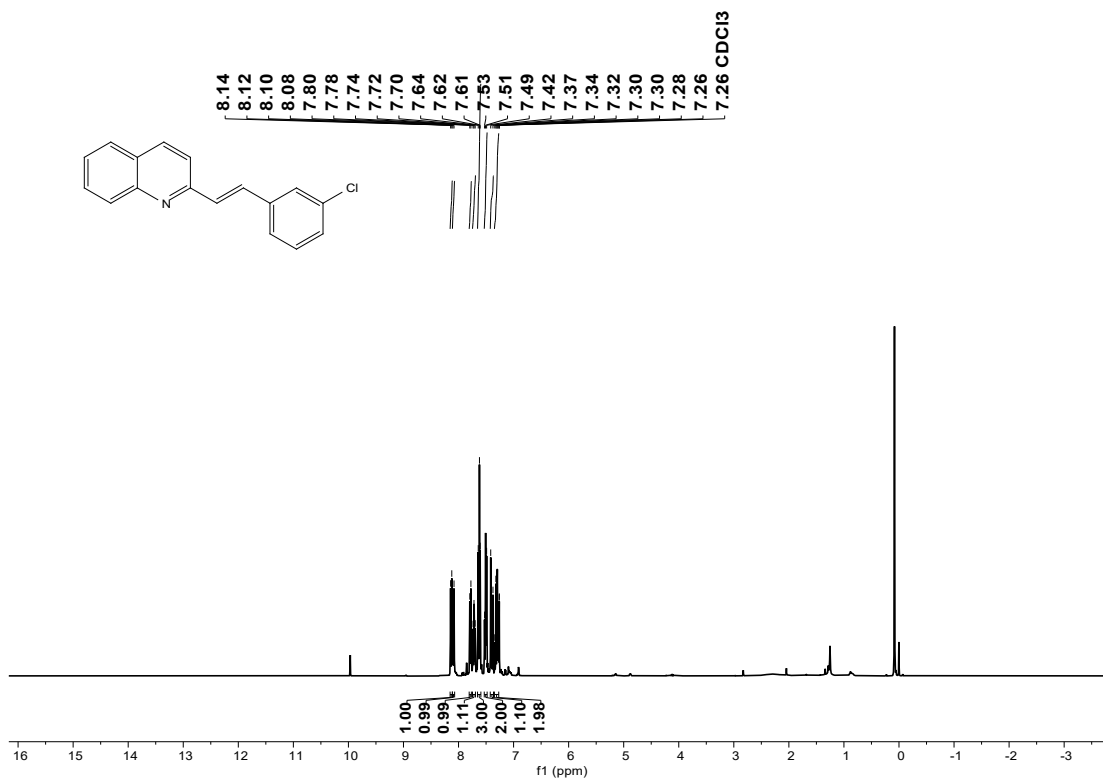
¹H NMR (400 MHz, Chloroform-*d*) δ 7.58 (s, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.13 (m, 4H), 7.12 – 7.09 (m, 1H), 7.08 – 7.03 (m, 2H), 6.89 (ddd, $J = 8.0, 7.0, 1.1$ Hz, 2H), 6.41 (dd, $J = 2.4, 1.1$ Hz, 2H), 5.76 (s, 1H).

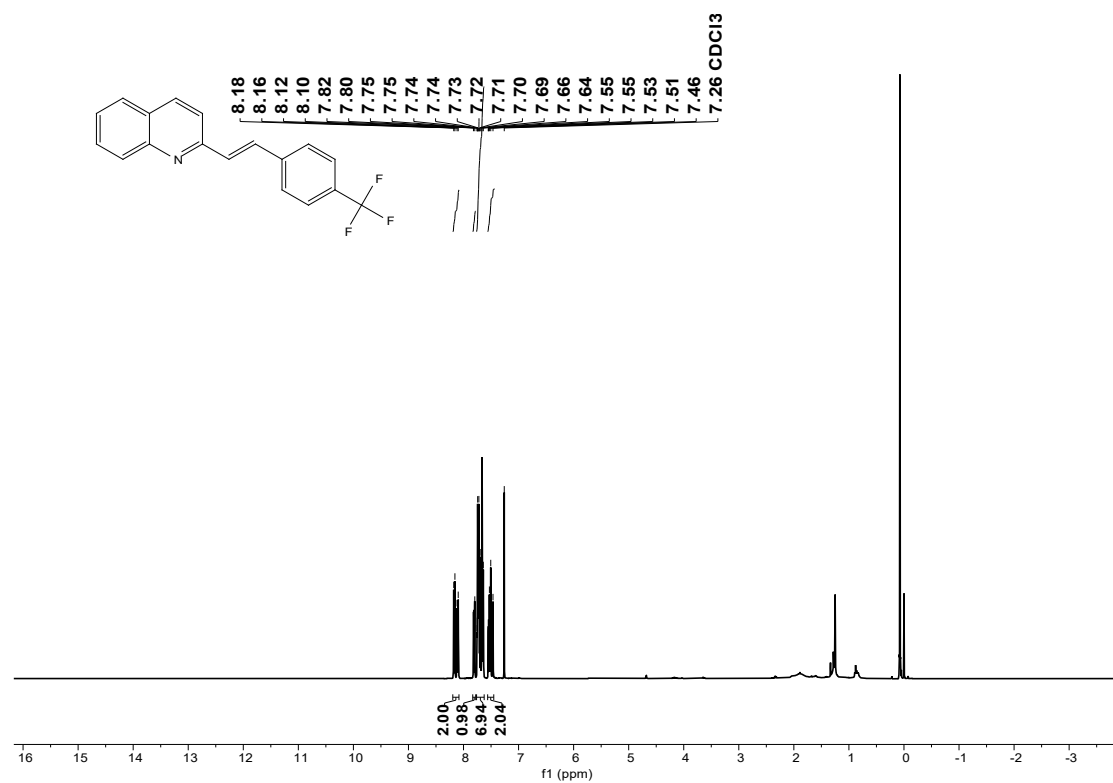
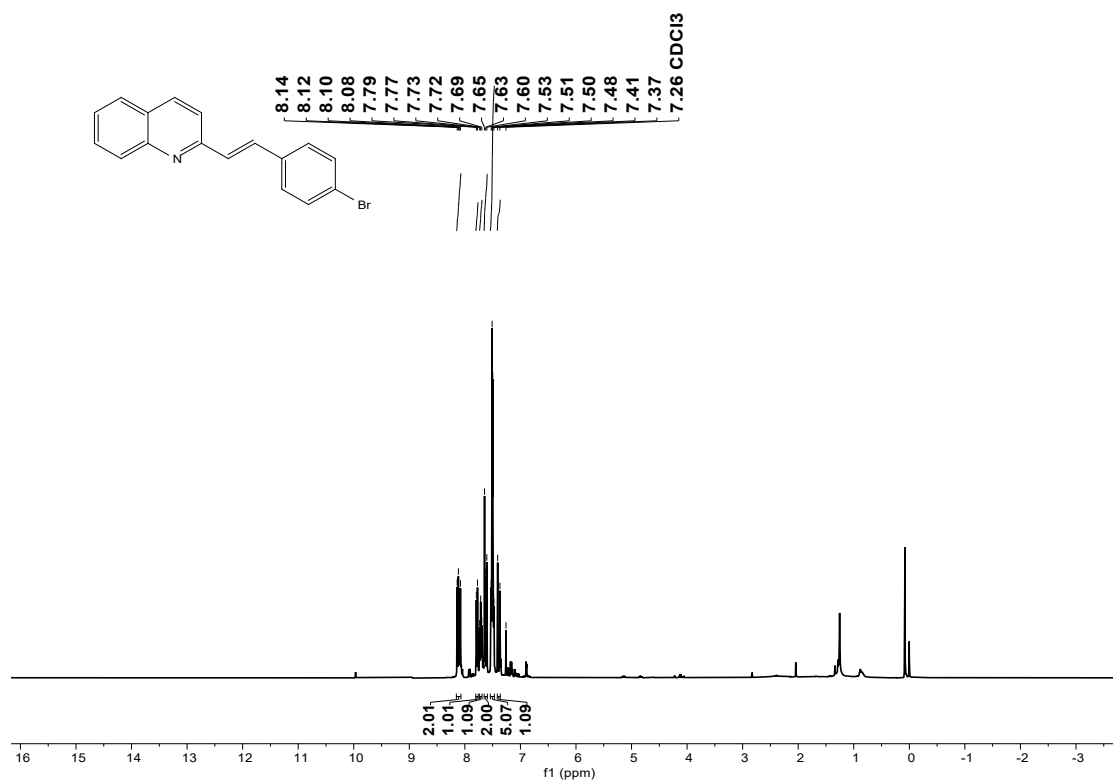


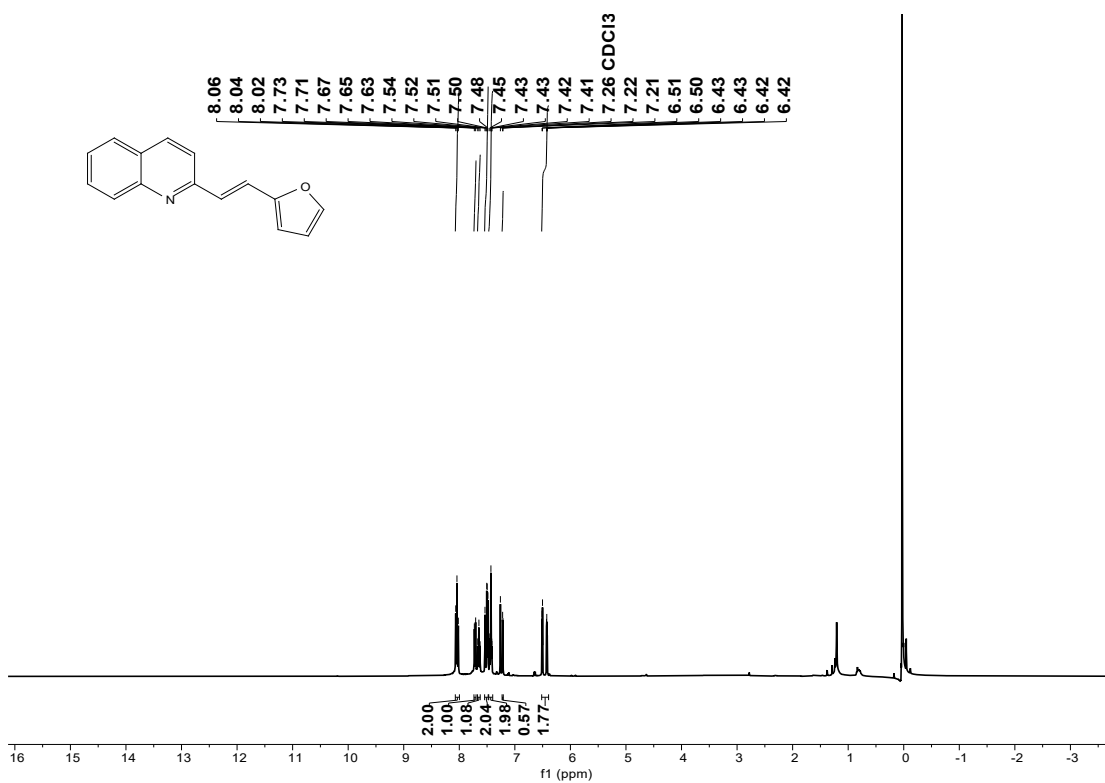
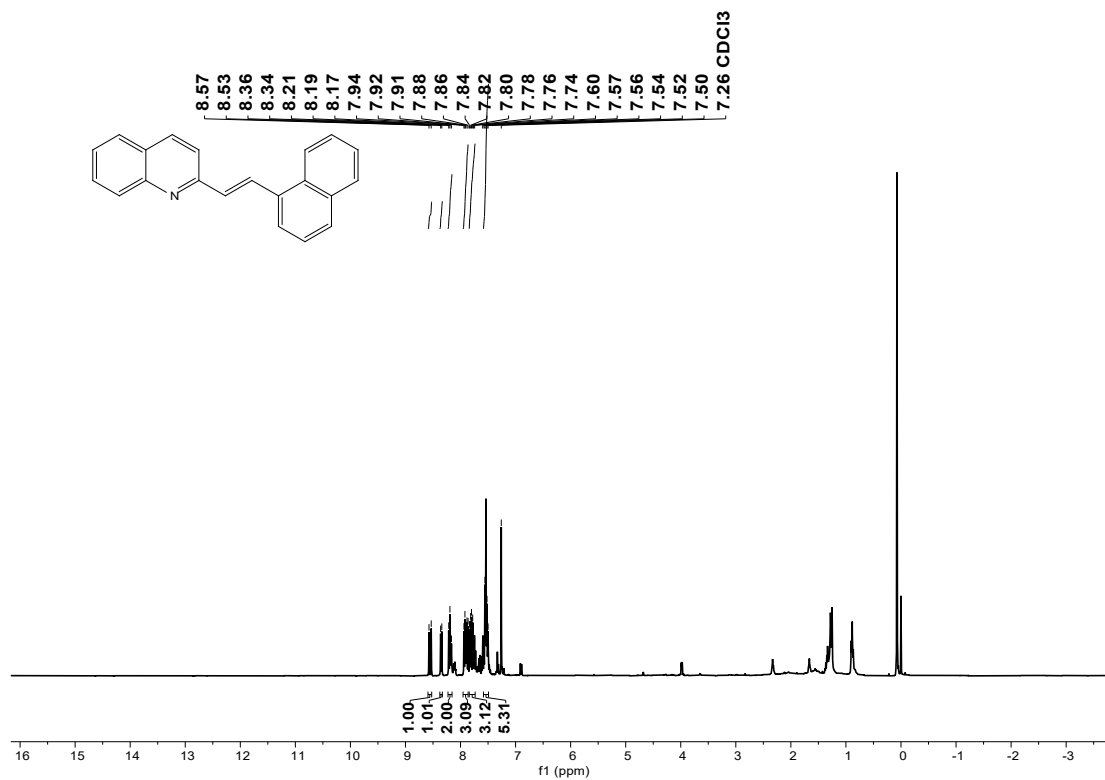


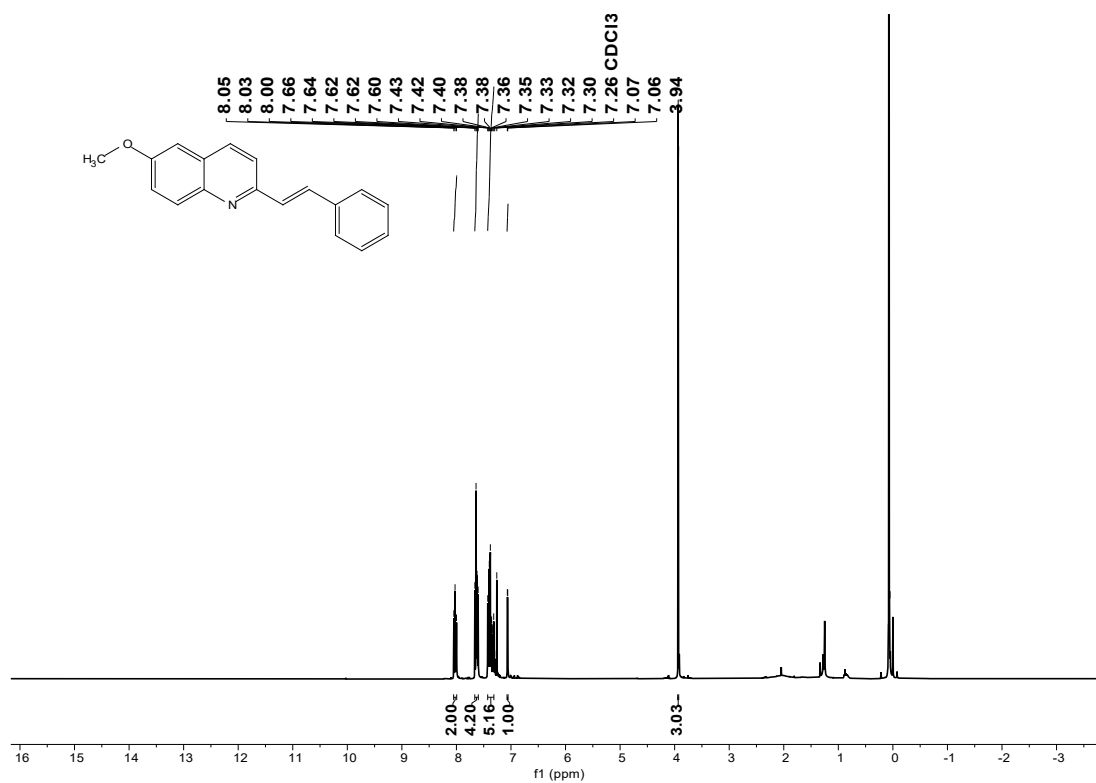
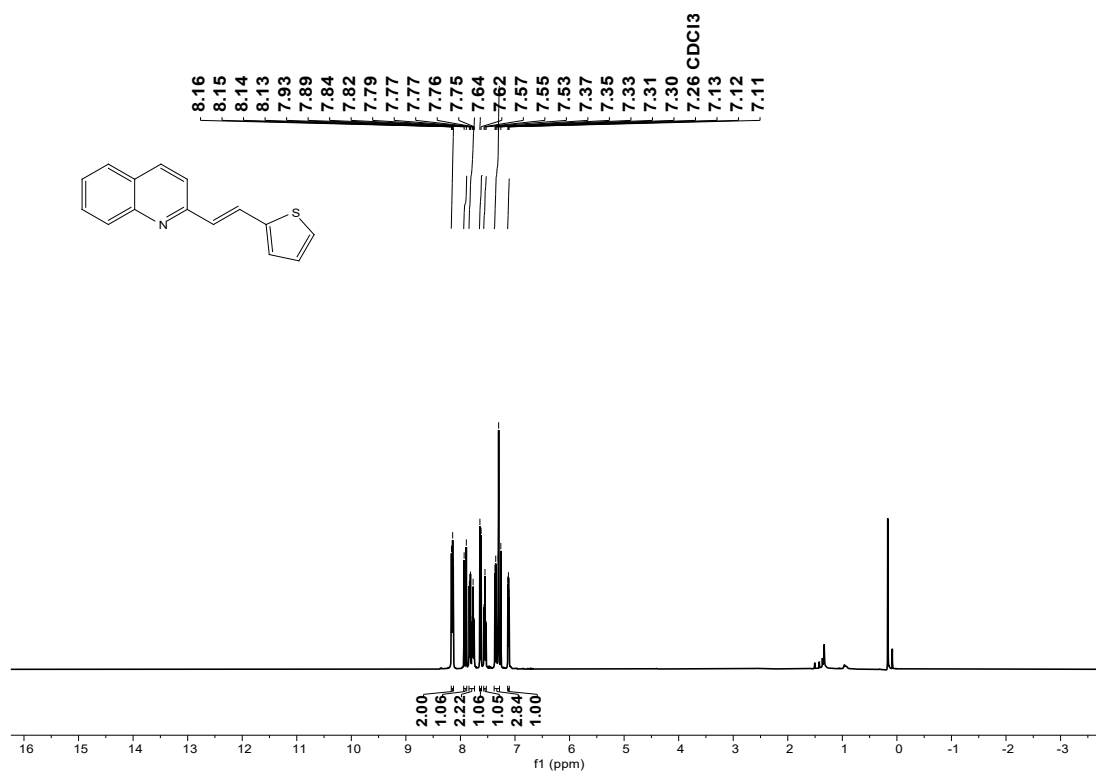


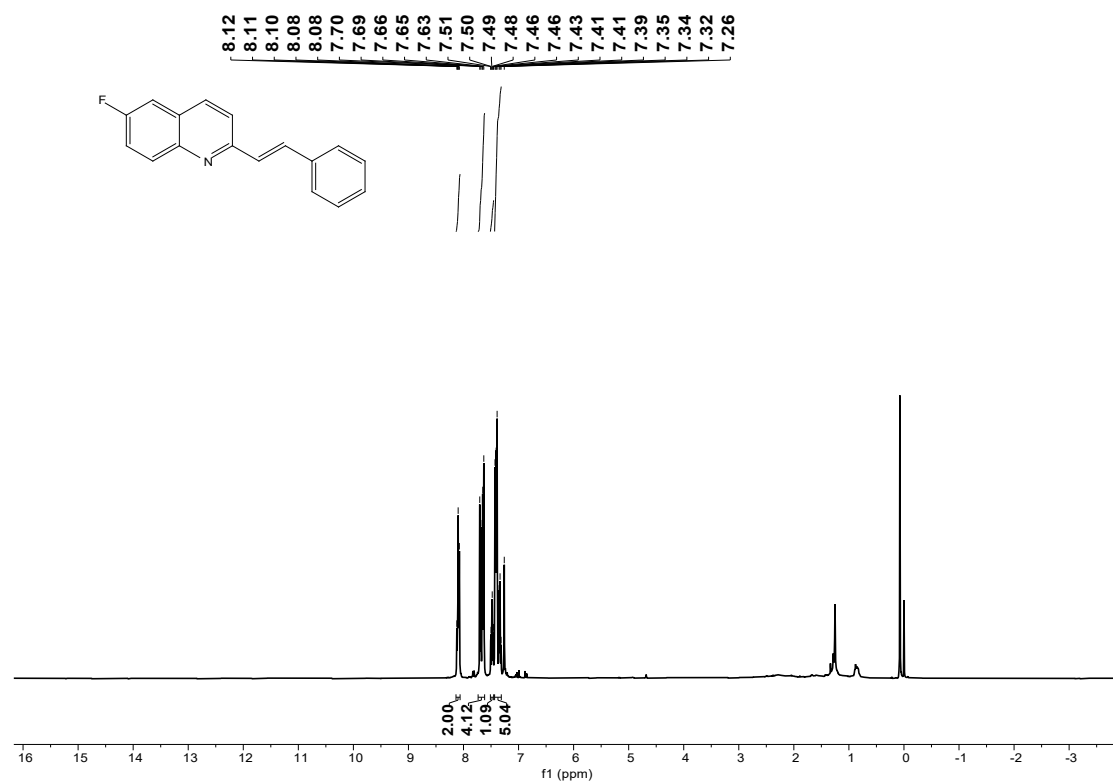
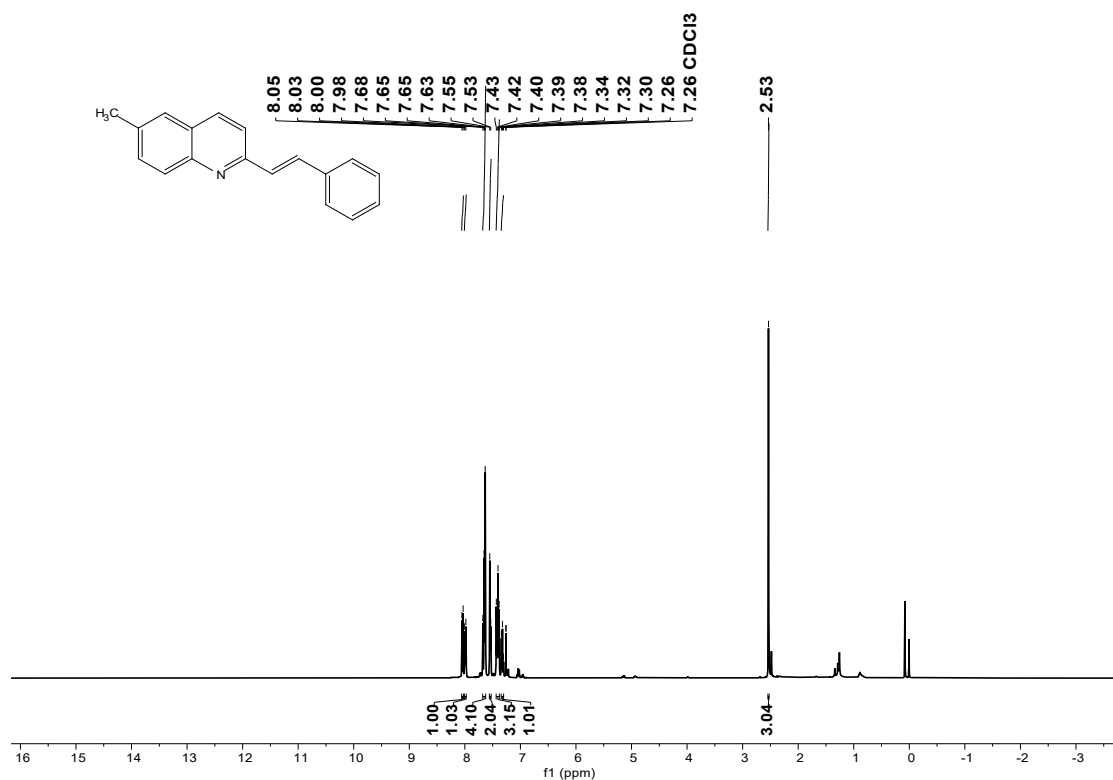


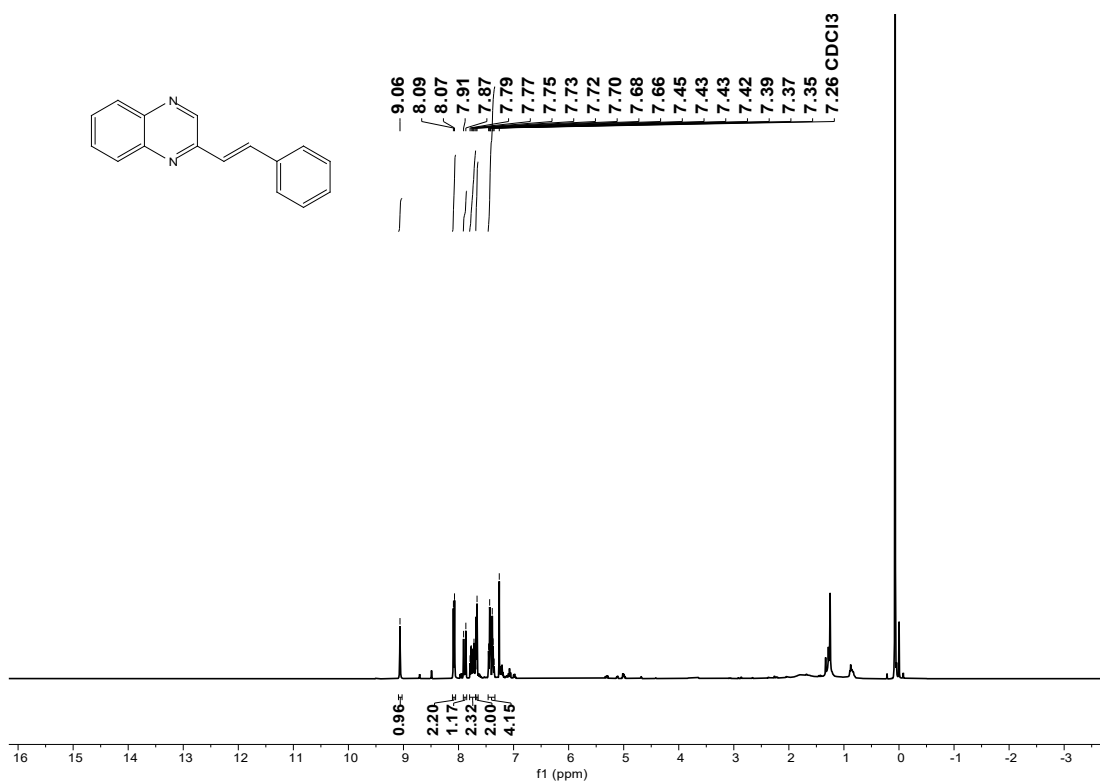
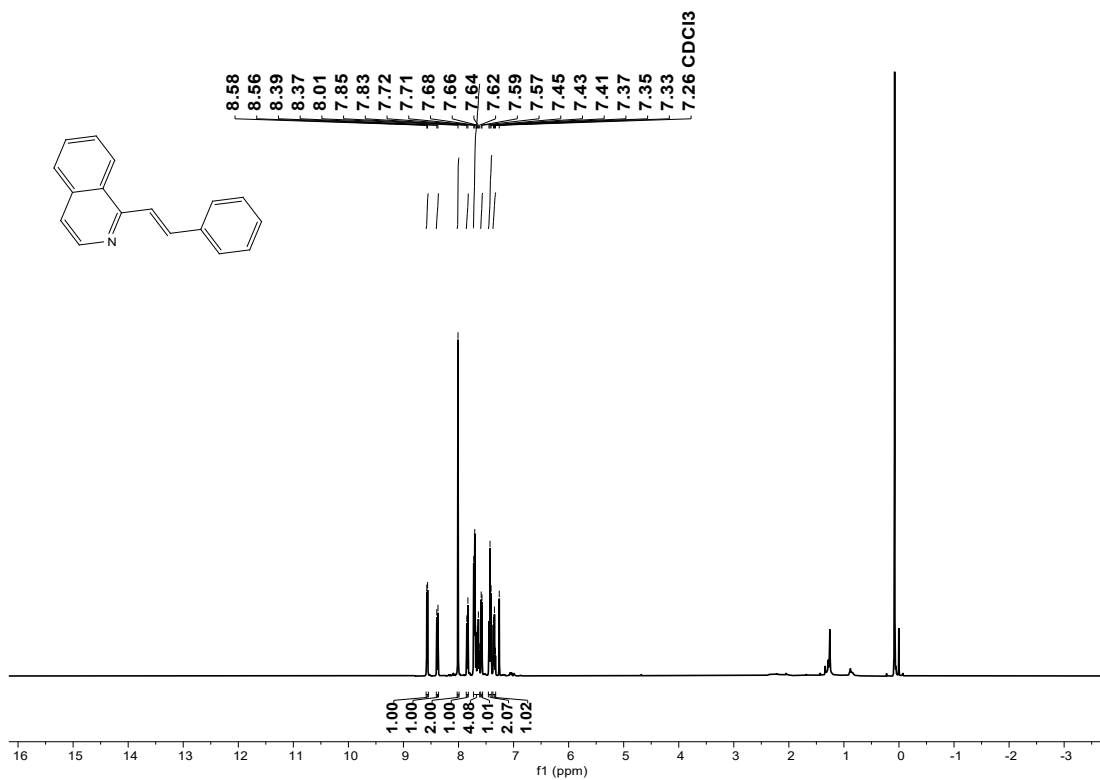


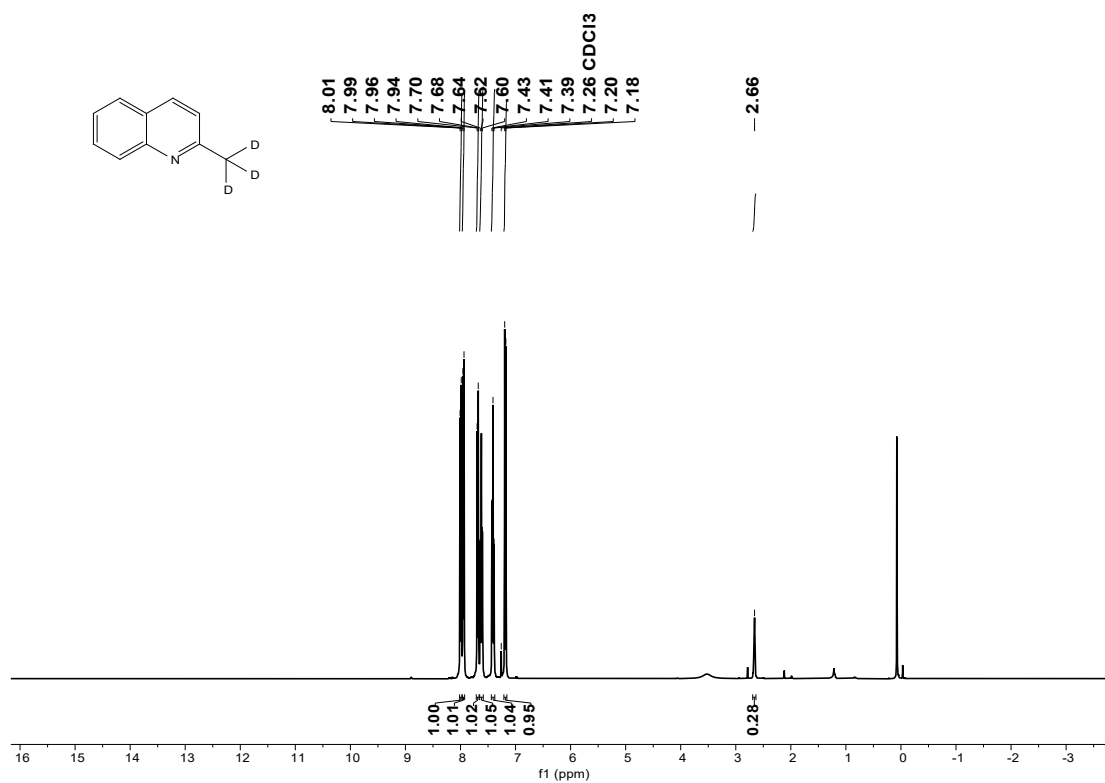
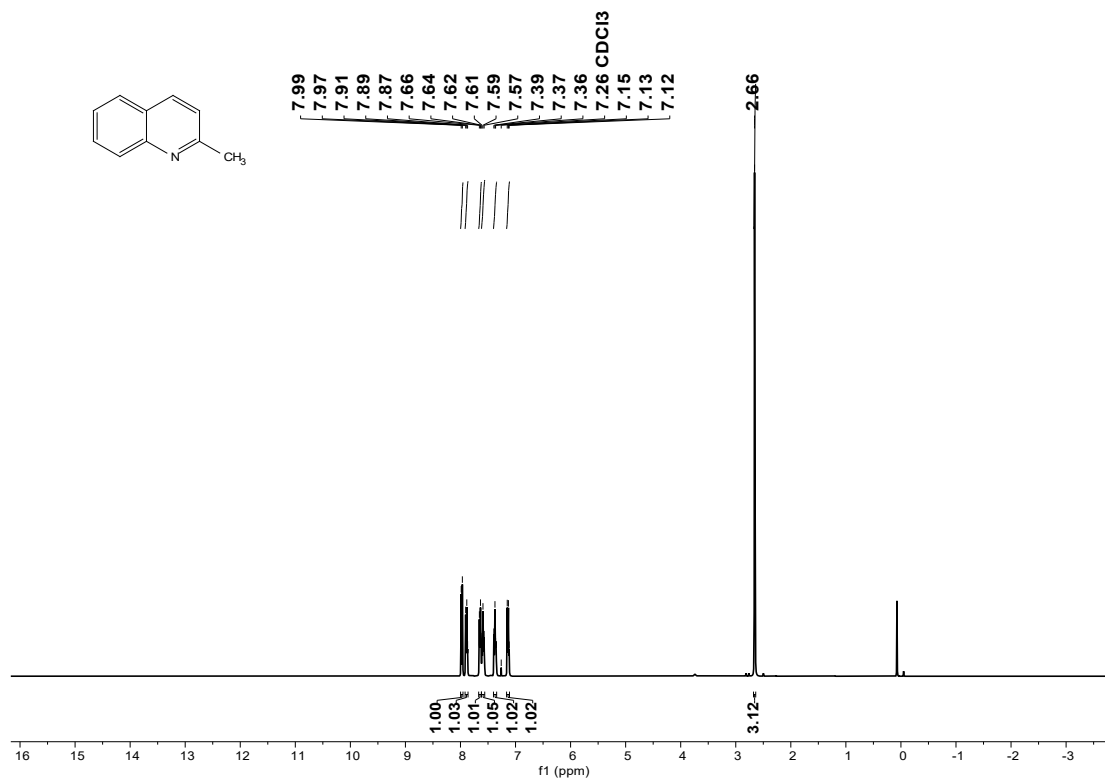


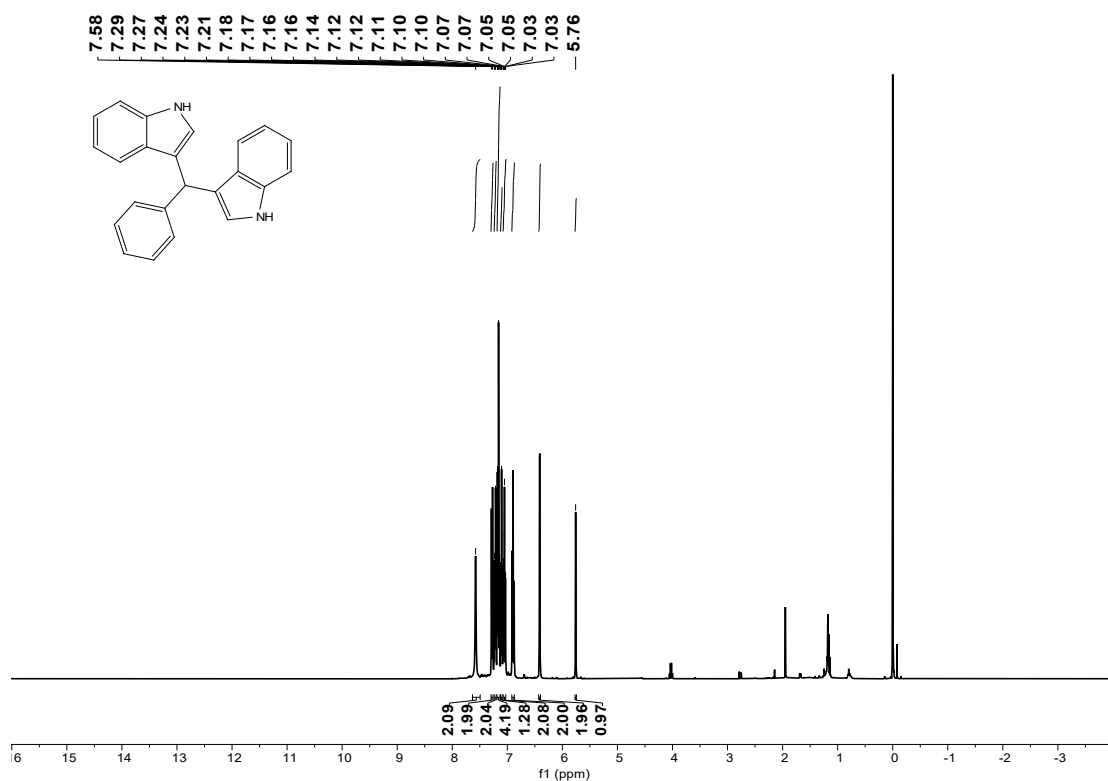
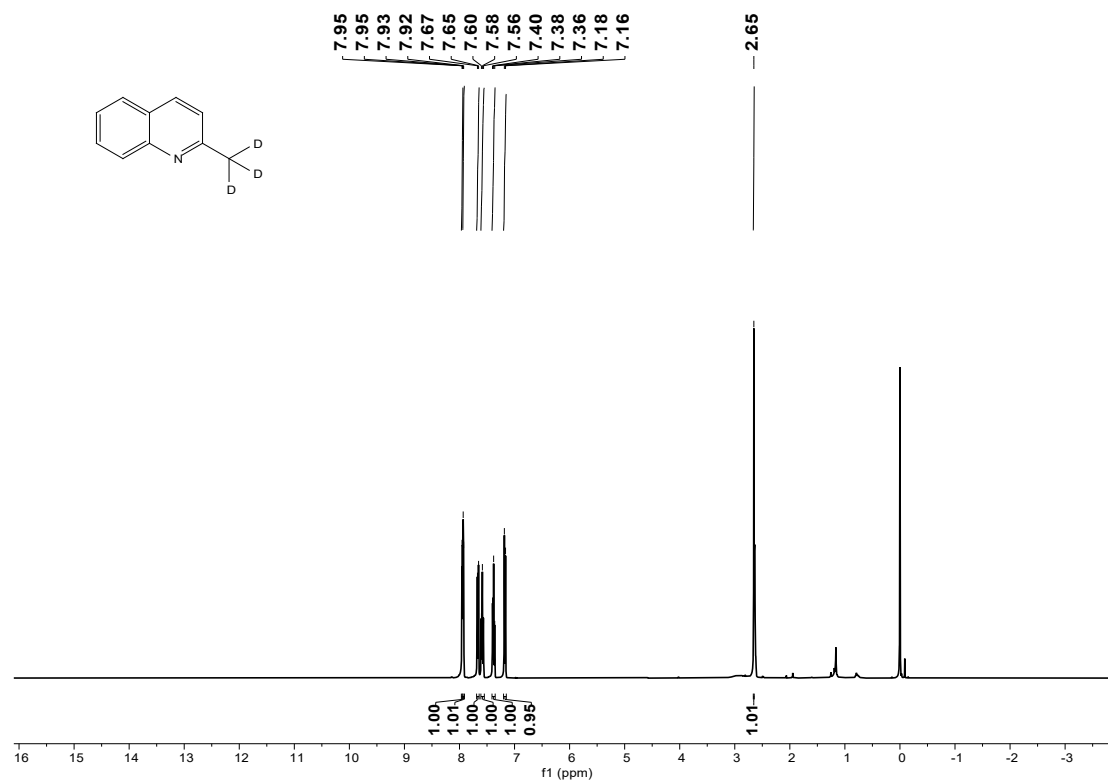












7 Reference

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