Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Photocatalytic C(sp^3)–H bonds functionalization by Cu(I) halide cluster-mediated O_2 activation

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1. Experimental Section.

1.1 Materials and instruments

All chemicals and solvents were of reagent grade quality obtained from commercial sources and used without further purification. ESI mass spectra were carried out on Thermo Fisher Q Exactive mass spectrometer using acetonitrile as mobile phase. The solution fluorescent spectra were measured on Horiba FL-3 spectrophotometer. UV-vis spectra were measured on Shimadzu UV3600 spectrometer. GC-MS analyses were performed on Agilent 5977C GC/MSD. NMR spectra were measured on Bruker 400 M spectrometer with chemical shifts reported as ppm (in DMSO-d_6 or $CDCl_3$, TMS as internal standard). EPR spectra were measured on Bruker EMX PLUS spectrometer. Raman spectra were measured on Horiba LabRAM Aramis spectrometer.

1.2 Fluorescence measurements

For fluorescence measurements, a 10.0 μM stock CH_3CN solution of $\mathbf{1_X}$ (X = Cl, Br, I) was added to a sample tube and capped with a septum. The sample tube was then degassed by bubbling argon for 15 min, and the emission spectra were continuously monitored when the solution exposed to O_2. Fluorescence was excited at 378 nm.

1.3 Raman measurements

For Raman measurements, a 1.0 mM stock 2-MeTHF solution of $\mathbf{1_{Cl}}$ was added to a sample tube and capped with a septum. The sample tube was placed in a cold bath (acetone/liq N_2, 179 K) and oxygenated by bubbling dioxygen. After being illuminated by 395nm LED for 5 min, the Raman data was obtained upon the excitation at 532 nm.

1.4 TMB oxidation measurements

Typically, 5.0 mg (0.02 mmol) of 3,3',5,5'-Tetramethylbenzidine (TMB) was dissolved with 3.0 mL CH_3CN/H_2O (2:1) solution. $\mathbf{1_X}$ (X = Cl, Br, I) was then added into the mixture solution to reach the specified concentration (0.4 mM) in O_2 atmosphere under 395 nm light irradiation. The samples were then taken at different time intervals for UV−vis measurements. In order to verify the specific reactive oxygen

species (ROS), various scavengers, including tert-butanol (0.02 mmol), 1,4-diazabicyclo [2,2,2] octane (DABCO, 2.0 mg, 0.02 mmol) and superoxide dismutase (SOD, 4.0 kU), respectively, were added into the TMB solution before the light irradiation.[1]

1.5 EPR detection

Hydrogen atom transfer (HAT) by Cu(II)-$O_2^{\bullet-}$ was probed using 2,2,6,6-tetramethylpiperidin-1-ol (TEMPO−H, 10.0 mM) with $\mathbf{1_{Cl}}$ (1.0 mM) in CH_3CN under O_2 (acetone/liq N_2, 179 K). After being illuminated by 395 nm LED for 1 min, the sample tube was frozen in liquid N_2 for EPR detection.

The ROS generated by $\mathbf{1_X}$ have been detected by EPR in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethyl-piperidine (TEMP), respectively.[1] Typically, 30.0 μL DMPO or TEMP in 1.0 mL CH_3CN was mixed with 1.0 μmol $\mathbf{1_{Cl}}$. The formed mixture was added into an EPR tube. EPR measurements were carried out after the EPR tube being illuminated by 395 nm LED for one minute in the presence of O_2.

1.6 Photocatalytic oxidation of *α*-terpinene

The reactive oxygen species generated by $\mathbf{1_X}$ was determined by photocatalytic oxidation of *α*-terpinene.[2] Typically, *α*-terpinene (0.1 mmol) and $\mathbf{1_{Cl}}$ (4.0 μmol) were added into a 15 mL flask containing 2.0 mL CH_3CN solution. The reaction was carried out at ambient temperature under a 395 nm LED irradiation in O_2 atmosphere for 3 h. Yields of products were determined by GC-MS analysis and analyzed by NMR spectroscopy.

1.7 Syntheses of tetrahydroisoquinolines 2a-h

The substrate tetrahydroisoquinolines **2a-h** were prepared in the same way using optimized literature procedure.[3] For example, **2a** was prepared according to this procedure: first, copper(I) iodide (0.2 g, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were put into a Schlenk-tube. The Schlenk-tube was then evacuated and back filled with nitrogen. After that, 2-Propanol (10 mL), ethylene glycol (1.11 mL,

20.0 mmol), 1,2,3,4-tetrahydroisoquinoline (2.0 mL, 15.0 mmol) and iodobenzene (1.12 mL, 10.0 mmol) were added successively at room temperature. The reaction mixture was heated at 90 °C and kept for 24 h. Diethyl ether (20 mL) and water (20 mL) were added after the reaction mixture cooling to room temperature. The organic layer was extracted with diethyl ether (2 × 20 mL) and washed with brine before dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel using hexane/ethyl acetate as eluent.

1.8 General procedure for photocatalytic C(sp^3)−H monooxygenations

Typically, 0.1 mmol tetrahydroisoquinolines **2a-h** or other hydrocarbons and 4.0 mol% $\mathbf{1_{Cl}}$ were added into a 15 mL flask containing 2.0 mL CH_3CN solution. The reactions were carried out at ambient temperature under a 395 nm LED irradiation in O_2 atmosphere. Then, the conversion and selectivity were quantified by GC-MS analysis and the products were confirmed by ^{1}H NMR analysis.

1.9 General procedure for photocatalytic cross-coupling reactions

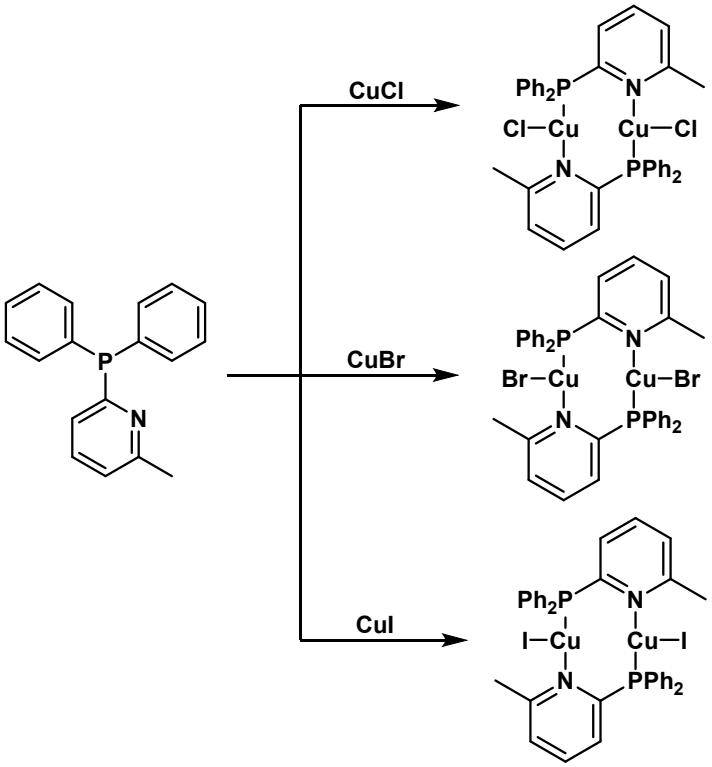
Typically, tetrahydroisoquinolines **2a-h** (0.1 mmol) and nucleophile ($MeNO_2$ or dimethyl malonate, 1.0 mmol) were added into a 15 mL flask containing 2.0 mL CH_3CN/H_2O (2:1) mixture solution. And then $\mathbf{1_{Cl}}$ (4.0 mol%) was added. The reactions were carried out at ambient temperature under a 395 nm LED irradiation in the presence of O_2. Then, the conversion and selectivity were quantified by GC-MS analysis and the products were confirmed by ^{1}H NMR analysis.

1.10 Reaction condition of TEMPO• trapping experiment

Typically, tetraline (0.1 mmol) and TEMPO• (0.3 mmol) were added into a 15 mL flask containing 2.0 mL CH_3CN, and then $\mathbf{1_{Cl}}$ (4.0 mol%) was added. The reaction was irradiated with a 395 nm LED in O_2 atmosphere for 3 h. After reaction, the mixture was filtered and submitted to mass spectrometry and the TEMPO• trapped product was found.[4] ESI-MS *m/z* calcd. for $[M+H]^+$ 288.2322, found 288.2312.

2. Preparation and Characterizations.

2.1 Syntheses of cooper catalysts

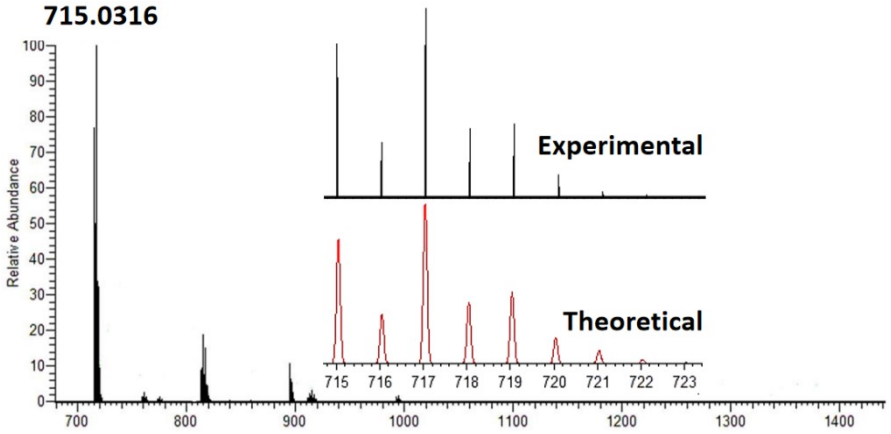


Scheme S1. The synthetic route of the copper(I) clusters $\mathbf{1_X}$ (X = Cl, Br, I).

The Cu(I) clusters $\mathbf{1_X}$ (X = Cl, Br, I) were prepared using the optimized literature procedure.[5] Adding the respective copper(I) halide (0.36 mmol: CuCl 36.0 mg, CuBr 52.0 mg, CuI 69.0 mg) into 10.0 mL dichloromethane solution containing 2-diphenylphosphanyl-6-methylpyridine (0.36 mmol, 0.1 g). The mixture was kept stirring under room temperature until a large amount of yellowish white solid was separated. The solid was collected by filtration, washed with ethyl ether and dried in vacuum. Yield (%): 82%. ^{1}H NMR (400 MHz, CD_3CN) for $\mathbf{1_{Cl}}$: δ (ppm) 7.57-7.42 (m，14H), 7.38-7.36 (m, 8H), 7.18 (d, J = 6.8 Hz, 2H), 7.10 (s, 2H), 2.32 (s, 6H); ^{1}H NMR (400 MHz, CD_3CN) for $\mathbf{1_{Br}}$: δ (ppm) 7.60-7.52 (m, 10H), 7.46-7.42 (m, 4H), 7.38-7.34 (m, 8H), 7.21-7.19 (m, 4H), 2.40 (s, 6H); ^{1}H NMR (400 MHz, CD_3CN) for $\mathbf{1_I}$: δ (ppm) 7.67-7.64 (td, J = 7.8 Hz, 2.9 Hz, 2H), 7.57-7.52 (m, 8H), 7.49-7.45 (m, 4H), 7.42-7.38 (m, 8H), 7.28-7.23 (m, 4H), 2.60 (s, 6H).

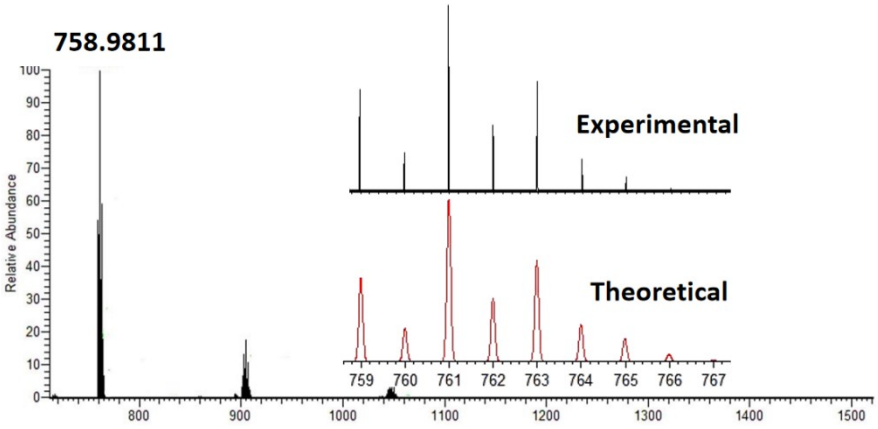
2.2 ESI-MS Spectra.

Figure S1. ESI-MS spectrum of $\mathbf{1_{Cl}}$ (0.1 mM) in CH_3CN solution. The insert shows the measured and simulated isotopic patterns at *m/z* = 715.0316.



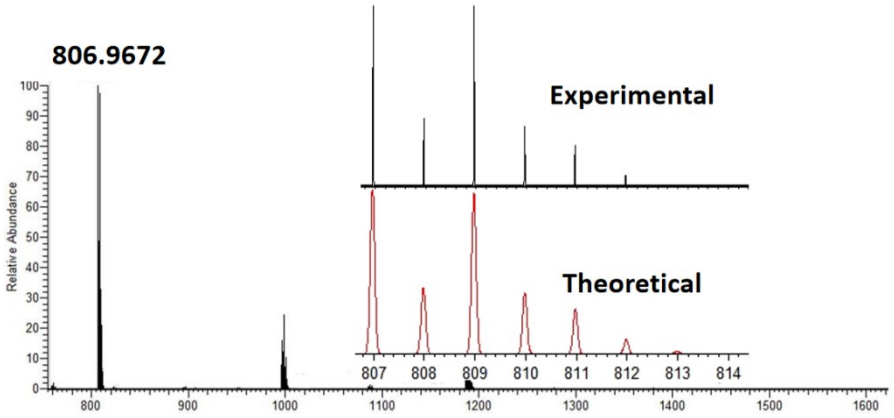
Peak	Value of *m/z*	Species assigned
1	715.0316	$[Cu^{I}_2Cl(N\text{^}P)_2]^+$

Figure S2. ESI-MS spectrum of $\mathbf{1_{Br}}$ (0.1 mM) in CH_3CN solution. The insert shows the measured and simulated isotopic patterns at *m/z* = 758.9811.



Peak	Value of *m/z*	Species assigned
1	758.9811	$[Cu^{I}_2Br(N\text{^}P)_2]^+$

Figure S3. ESI-MS spectrum of $\mathbf{1_I}$ (0.1 mM) in CH_3CN solution. The insert shows the measured and simulated isotopic patterns at *m/z* = 806.9672.



Peak	Value of *m/z*	Species assigned
1	806.9672	$[Cu^{I}_{2}I(N\text{^}P)_2]^+$

3. Spectroscopy Representation.

Figure S4. Continuous monitoring the emission spectra of $\mathbf{1_{Br}}$ (10.0 μM) in CH_3CN solution when exposed to O_2. Time interval between each spectrum was 10 s, and fluorescence was excited at 378 nm.

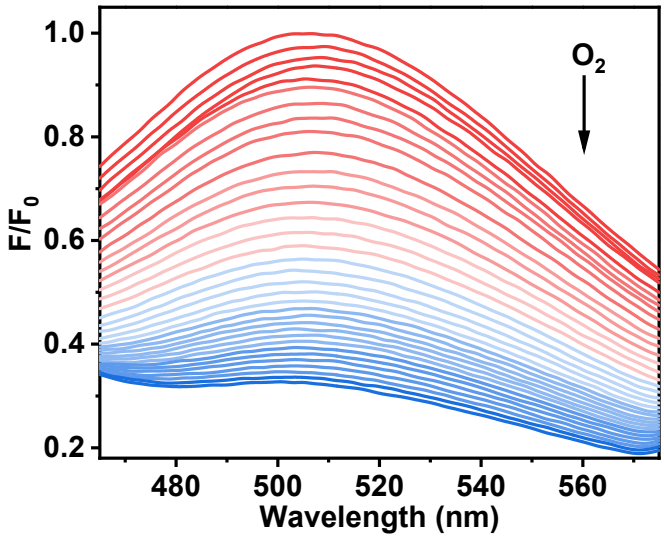


Figure S5. Continuous monitoring the emission spectra of $\mathbf{1_I}$ (10.0 μM) in CH_3CN solution when exposed to O_2. Time interval between each spectrum was 10 s, and fluorescence was excited at 378 nm.

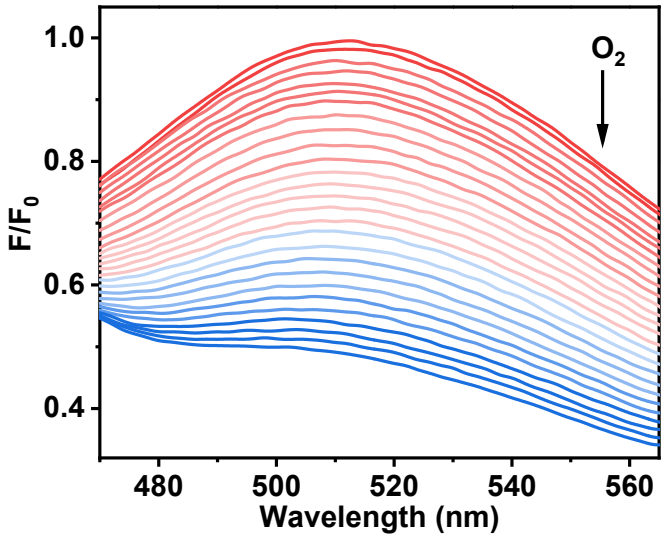


Figure S6. The UV−vis spectra of $\mathbf{1}_{Cl}$ (10.0 μM) in CH_3CN solution (black line) and when $\mathbf{1}_{Cl}$ (10.0 μM) was exposed to O_2 in absence of light for 10 minutes (red line) and when $\mathbf{1}_{Cl}$ (10.0 μM) was exposed to O_2 upon the irradiation of 395 nm LED for 10 minutes (blue line).

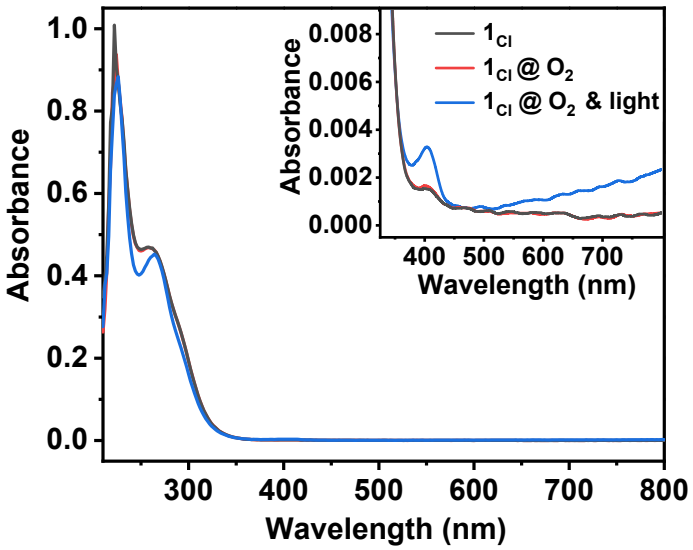


Figure S7. (a) UV−vis spectra of a CH_3CN solution containing $\mathbf{1_{Cl}}$ (0.1 mM, blue) and $\mathbf{1_{Cl}}$ (0.1 mM, blue) with TEMPO−H (1.0 mM, red), (b) UV−vis spectra of the above solution upon the irradiation of 395 nm LED in the presence of O_2.

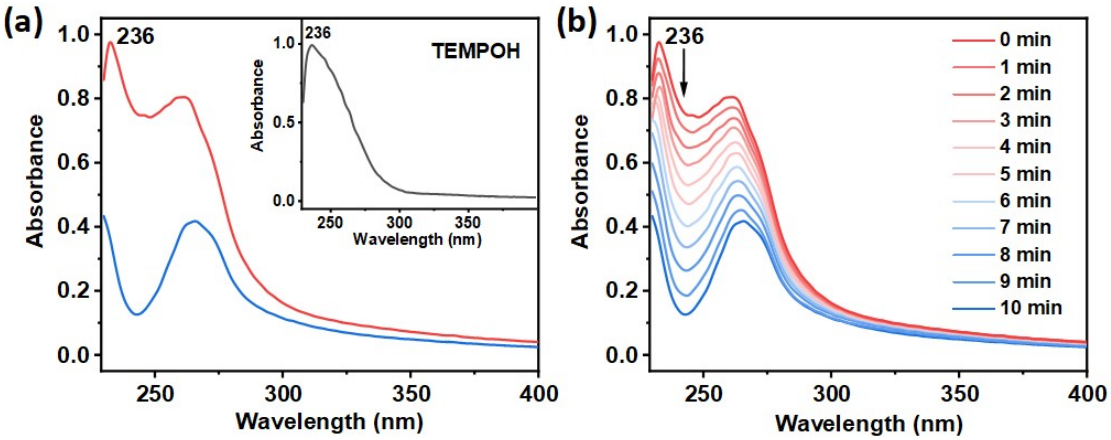
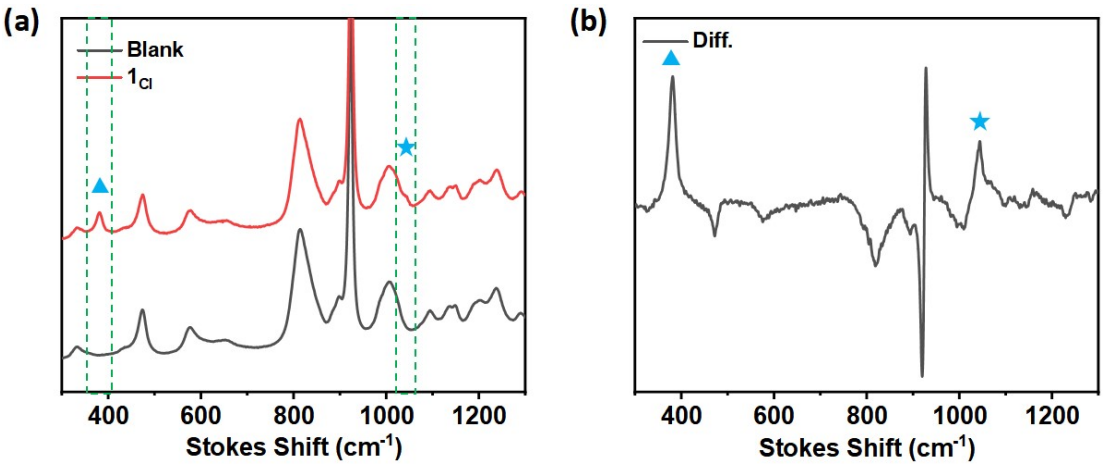


Figure S8. (a) Raman spectra (179 K, excitation at 532 nm) of $\mathbf{1_{Cl}}$ (1.0 mM) in 2-MeTHF solutions after 395 nm light illumination for 5 min under O_2 atmosphere, along with a difference spectrum. (b) Corresponding difference Raman spectra.



4. Data Relative to Photocatalytic Reactions.

Figure S9. Time-dependent UV−vis absorption at 340 nm in 2:1 CH_3CN/H_2O solution, recording TMB oxidation in the presence of different $\mathbf{1_X}$ (X = Cl, Br, I) (0.4 mM) under O_2 atmosphere upon 395 nm irradiation.

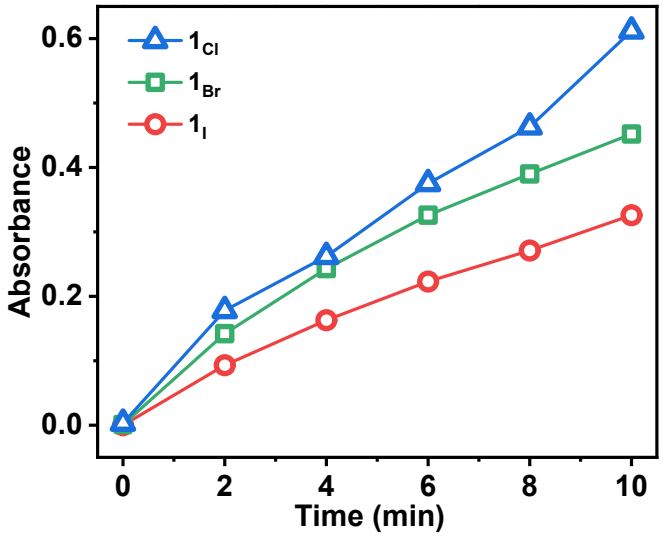


Figure S10. Time-dependent UV−vis absorption spectra recording TMB oxidation with $\mathbf{1_{Cl}}$ (0.4 mM) in CH_3CN/H_2O (2:1) solution under O_2 atmosphere upon 395 nm light irradiation.

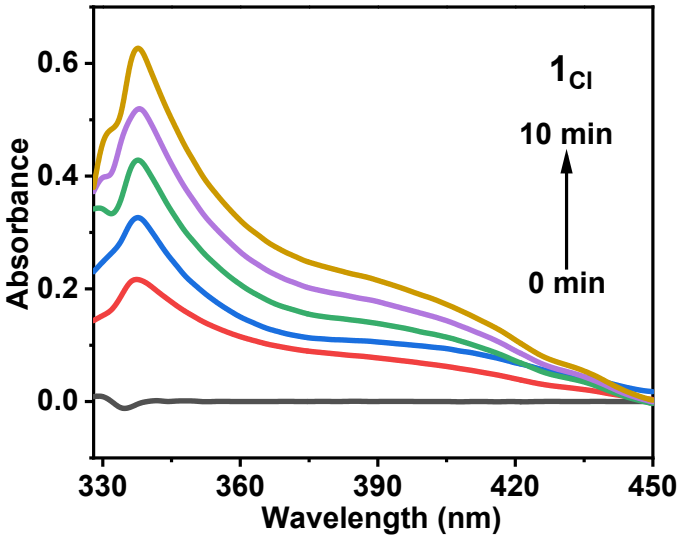


Figure S11. Time-dependent UV−vis absorption spectra recording TMB oxidation with $\mathbf{1_{Br}}$ (0.4 mM) in CH_3CN/H_2O (2:1) solution under O_2 atmosphere upon 395 nm light irradiation.

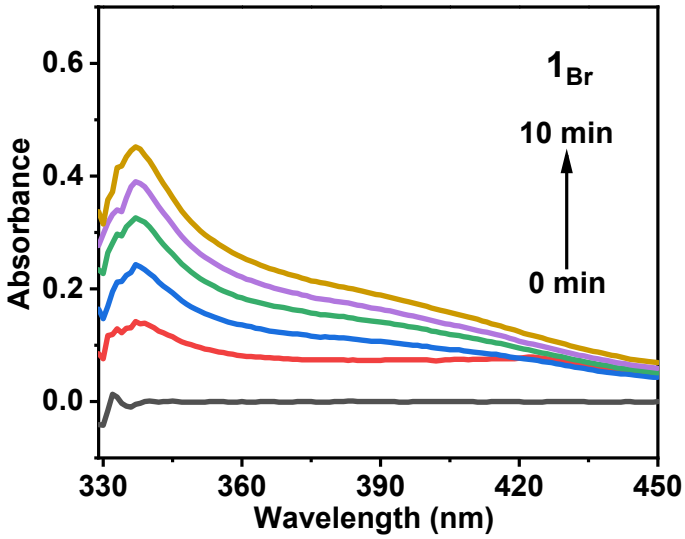


Figure S12. Time-dependent UV−vis absorption spectra recording TMB oxidation with $\mathbf{1_I}$ (0.4 mM) in CH_3CN/H_2O (2:1) solution under O_2 atmosphere upon 395 nm light irradiation.

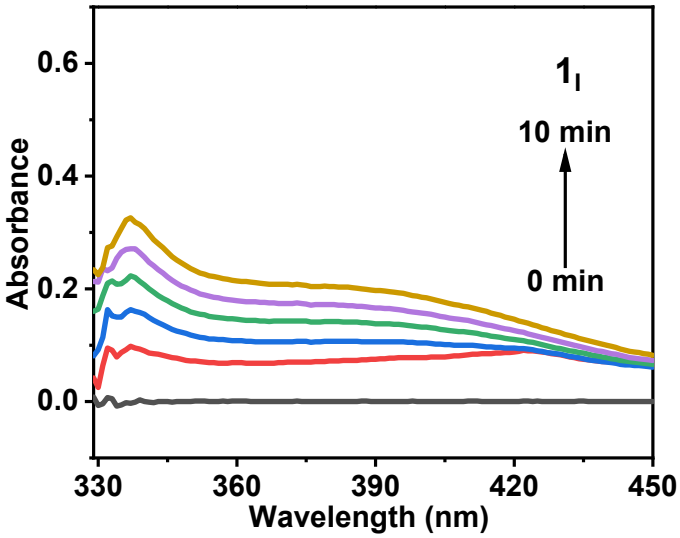


Figure S13. Time-dependent UV−vis absorption spectra recording TMB oxidation with $\mathbf{1}_{Cl}$ (0.4 mM) and tert-butanol (scavenger molecule of •OH) in CH_3CN/H_2O (2:1) solution under O_2 atmosphere upon 395 nm light irradiation.

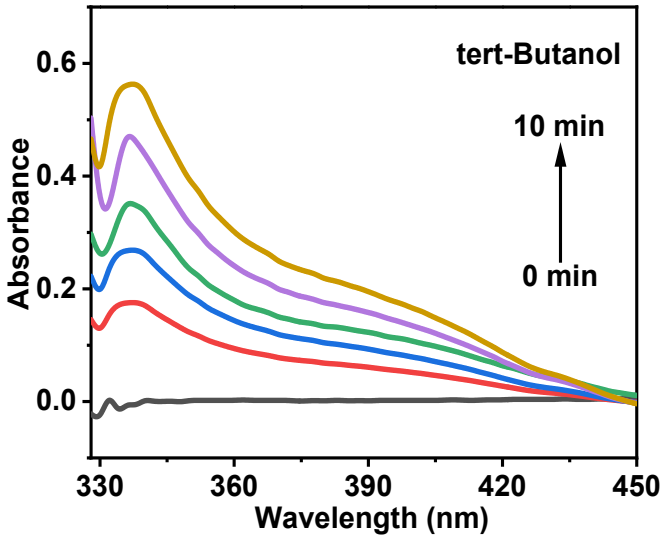


Figure S14. Time-dependent UV−vis absorption spectra recording TMB oxidation with $\mathbf{1_{Cl}}$ (0.4 mM) and superoxide dismutase (SOD, scavenger molecule of R-$O_2^{\bullet-}$) in CH_3CN/H_2O (2:1) solution under O_2 atmosphere upon 395 nm light irradiation.

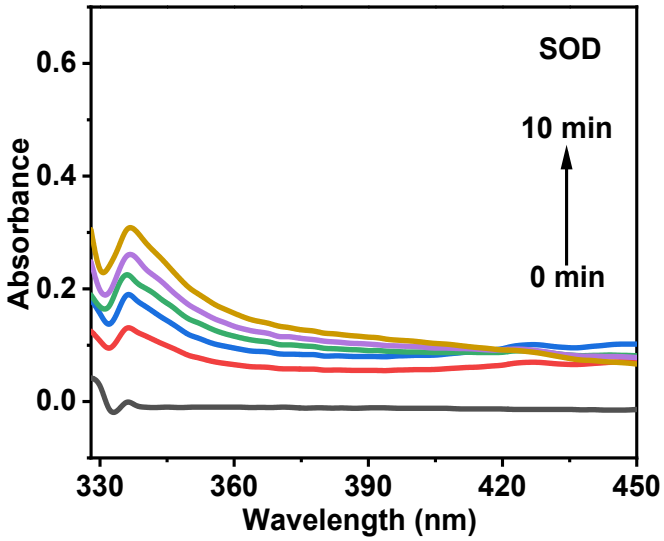


Figure S15. Time-dependent UV−vis absorption spectra recording TMB oxidation with $\mathbf{1}_{\mathbf{Cl}}$ (0.4 mM) and 1,4-diazabicyclo [2,2,2] octane (DABCO, scavenger molecule of $^1O_2$) in CH_3CN/H_2O (2:1) solution under O_2 atmosphere upon 395 nm light irradiation.

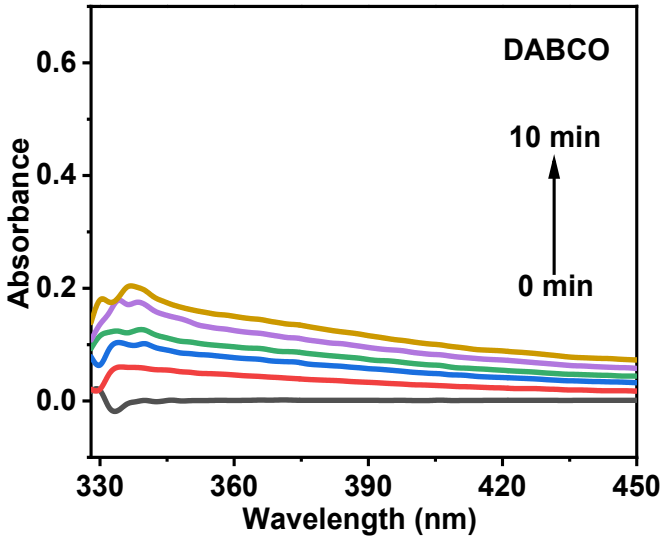


Figure S16. EPR spectra of $\mathbf{1}_{Cl}$ (1.0 μmol) in CH_3CN after adding DMPO (red) or TEMP (blue), and illuminated by 395 nm LED for 1 min in the presence of O_2.

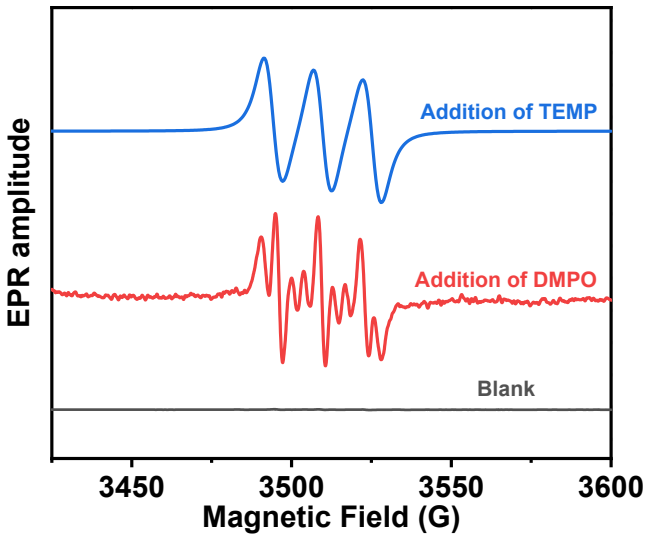


Figure S17. ESI-MS spectrum of TEMPO• trapping experiment in CH_3CN solution. The insert shows the measured and simulated isotopic patterns at *m/z* = 288.2312. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57-7.54 (m, 1H), 7.18-6.99 (m, 3H), 4.81-4.79 (m, 1H), 2.80-2.61 (m, 2H), 2.00-1.88 (m, 3H), 1.74-1.60 (m, 1H), 1.49-1.07 (m, 15H), 0.65 (s, 3H).

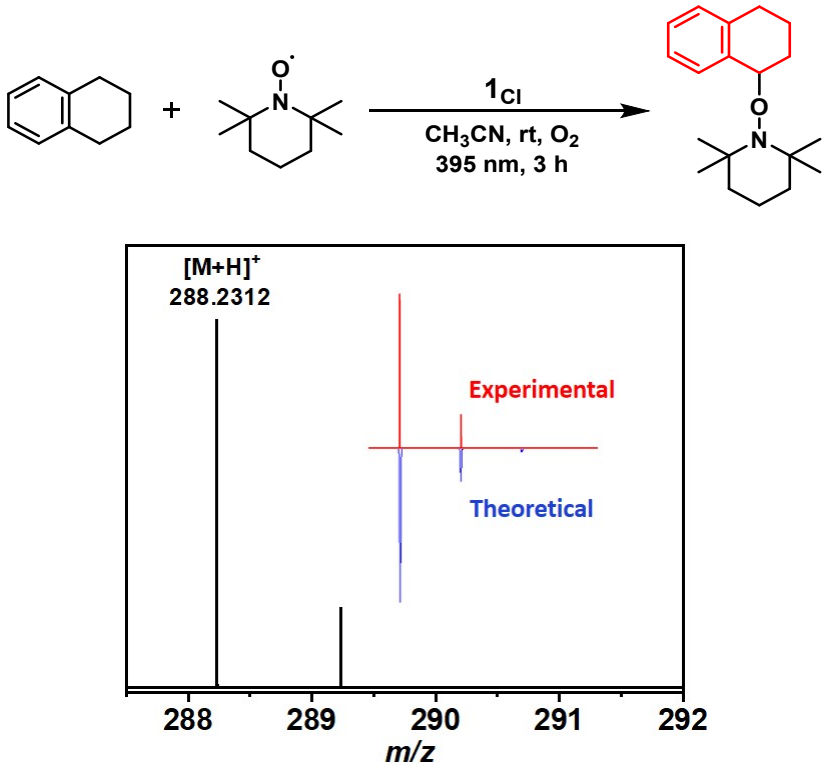


Figure S18. Family of luminescence spectra of $\mathbf{1}_{Cl}$ (10.0 μM) in methanol solution upon the addition of **2a**. Fluorescence was excited at 378 nm.

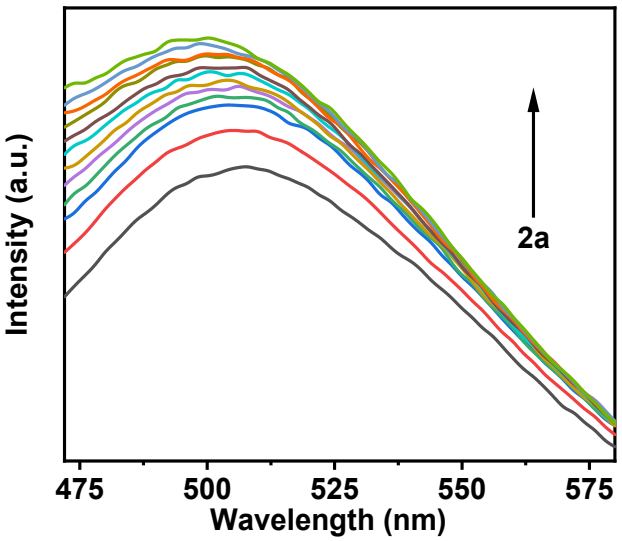
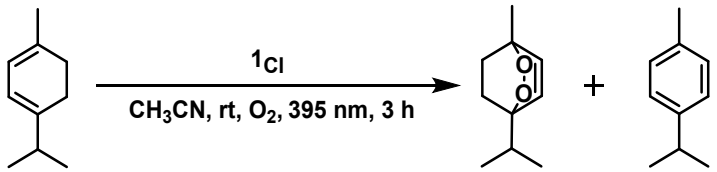


Table S1. Photocatalytic oxidation of α-terpinene in CH_3CN solution under different atmosphere upon 395 nm light irradiation.

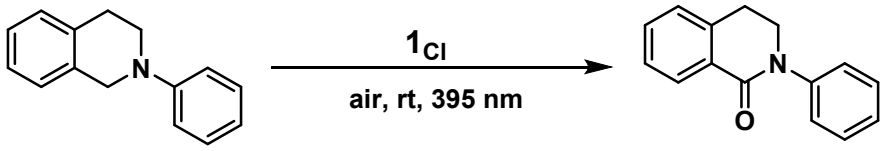


A **B**

Entry	Catalyst	Atm.	Conversion (%)	
			A	B
1	$\mathbf{1_{Cl}}$	Ar	---	---
2	---	O_2	---	28.3
3	$\mathbf{1_{Cl}}$	O_2	41.5	58.5

Reaction conditions: α-terpinene (0.1 mmol), catalyst $\mathbf{1_{Cl}}$ (4.0 μmol) in CH_3CN (2.0 mL) under O_2 atmosphere at 298 K with 395 nm light irradiation for 3 h. The selectivity was determined by GC-MS analysis.

Table S2. The photocatalytic C(sp^3)−H monooxygenation of **2a** upon the addition of scavengers.[a]

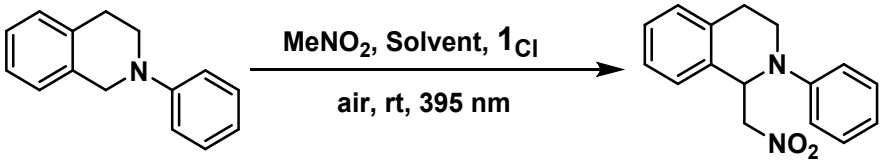


2a **3a**

Entry	Difference from the standard conditions	Yield (%)
1	None	99.0
2	In the presence of SOD	11.1
3	In the presence of $AgNO_3$	36.4
4	In the presence of DABCO	78.9
5	In the presence of t-BuOH	94.6

[a]Standard reaction conditions: **2a** (0.1 mmol), catalyst $\mathbf{1_{Cl}}$ (4.0 μmol), CH_3CN (2.0 mL), under O_2 atmosphere at 298 K with 395 nm light irradiation for 3 h. The yields were determined by GC-MS analysis of products.

Table S3. The yield of cross-dehydrogenative coupling reaction in different solvents.[a]

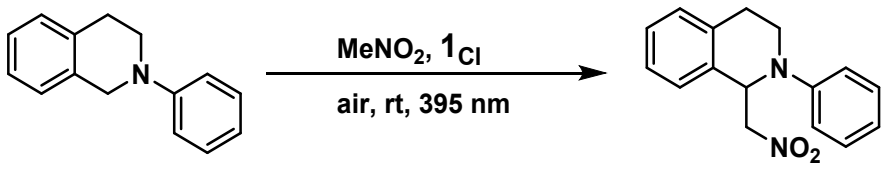


2a **5a**

Entry	Nucleophile	Catalyst	Solvent	Yield(%)
1	$MeNO_2$	$\mathbf{1_{Cl}}$	CH_3CN	57.5
2	$MeNO_2$	$\mathbf{1_{Cl}}$	CH_3CN/H_2O (1:1)	78.3
3	$MeNO_2$	$\mathbf{1_{Cl}}$	CH_3CN/H_2O (2:1)	79.1
4[b]	$MeNO_2$	$\mathbf{1_{Cl}}$	CH_3CN/H_2O (2:1)	79.8
5[c]	DMM	$\mathbf{1_{Cl}}$	CH_3CN	54.3
6	DMM	$\mathbf{1_{Cl}}$	CH_3CN/H_2O (1:1)	86.4
7	DMM	$\mathbf{1_{Cl}}$	CH_3CN/H_2O (2:1)	89.2

[a]Standard reaction conditions: **2a** (0.1 mmol), catalyst $\mathbf{1_{Cl}}$ (4.0 μmol), nucleophile reagent (1.0 mmol), solvent (2.0 mL), in the presence of O_2 at 298 K with 395 nm light irradiation for 12 h. [b]$MeNO_2$ (2.0 mmol). [c]Dimethyl malonate is denoted as DMM. The yields were determined by GC-MS analysis of products.

Table S4. The photocatalytic cross-coupling reaction of **2a** upon the addition of scavengers.[a]



2a **5a**

Entry	Variation from the standard conditions	Yield (%)
1	None	79.1
2	In the presence of SOD	40.5
3	In the presence of $AgNO_3$	46.4
4	In the presence of DABCO	66.9
5	In the presence of t-BuOH	72.2

[a]Standard reaction conditions: **2a** (0.1 mmol), catalyst $\mathbf{1_{Cl}}$ (4.0 μmol), $MeNO_2$ (1.0 mmol), 2:1 CH_3CN/H_2O (2.0 mL), in the presence of O_2 at 298 K with 395 nm light irradiation for 12 h. The yields were determined by GC-MS analysis of products.

5. Kinetics of Photocatalytic Reactions.

Figure S19. GC-MS data of photocatalytic oxidation of α-terpinene (0.1 mmol) in CH_3CN solution under different condition: with catalyst $\mathbf{1_{Cl}}$ (4.0 μmol) under Ar (black), without catalyst $\mathbf{1_{Cl}}$ (4.0 μmol) under O_2 (red), with catalyst $\mathbf{1_{Cl}}$ (4.0 μmol) under O_2 (blue).

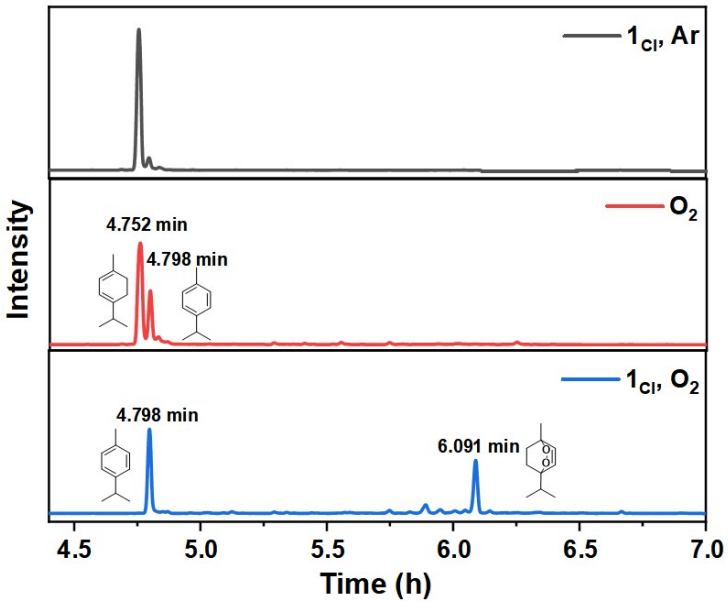


Figure S20. GC-MS data of photocatalytic C(sp^3)−H monooxygenation in CH_3CN solution with substrate **2a** (50.0 mM) and catalyst $\mathbf{1}_{Cl}$ (3.0 mM) in different time.

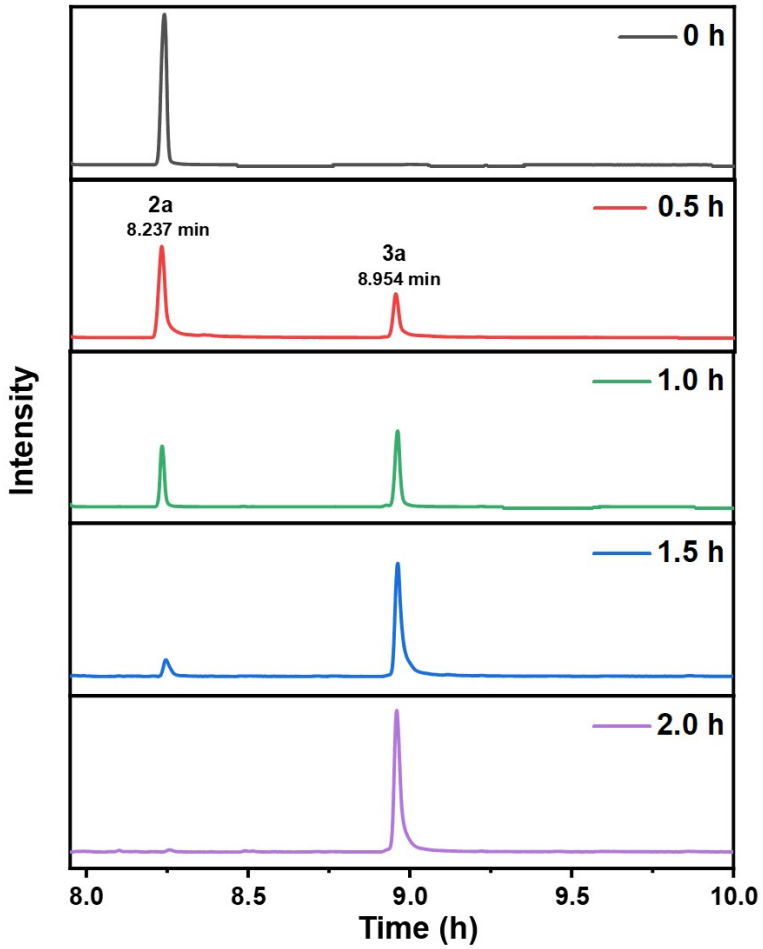


Figure S21. GC-MS data of photocatalytic cross-coupling reaction in CH_3CN/H_2O (2:1) solution with fixed substrates **2a** (50.0 mM) and $MeNO_2$ (0.5 M), catalyst $\mathbf{1}_{Cl}$ (3.0 mM) in different time.

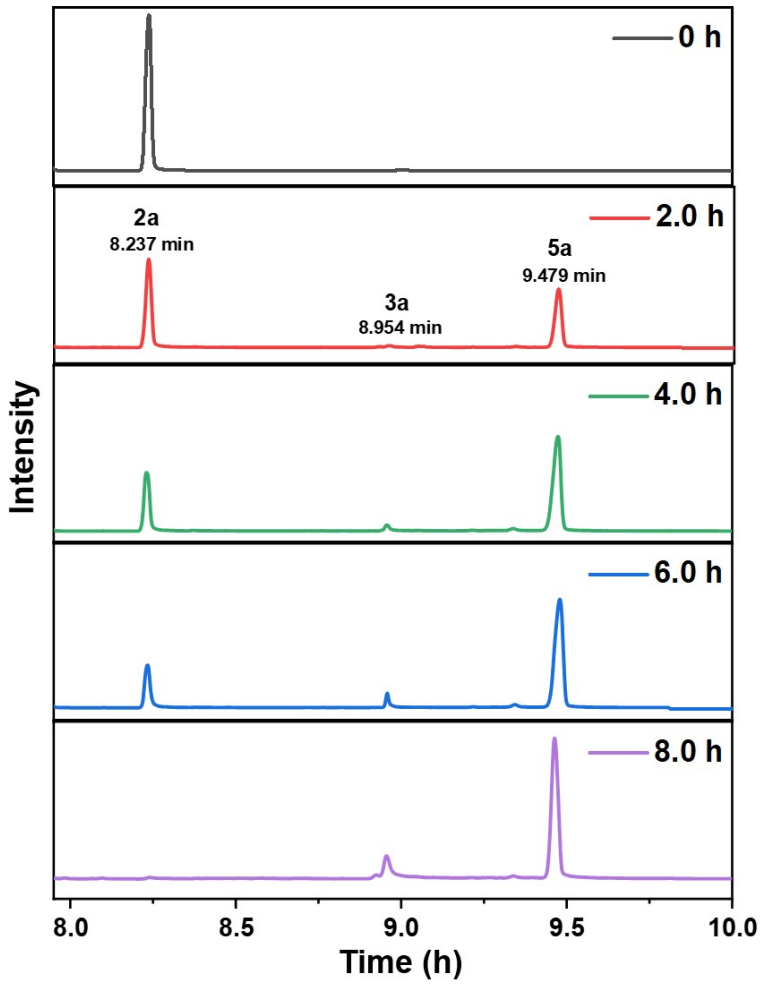


Figure S22. The initial rate of **3a** as a function of O_2 content with **2a** (50.0 mM) and $\mathbf{1}_{Cl}$ (2.0 mM) remaining fixed in CH_3CN upon the irradiation with a 395 nm LED.

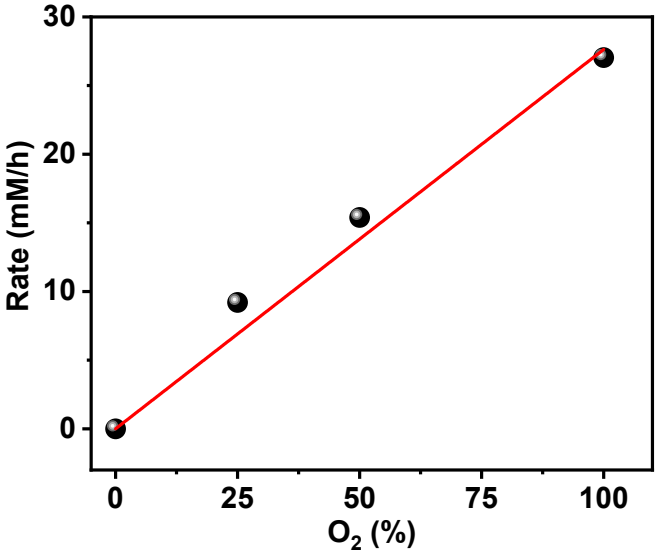


Figure S23. Yield of **5a** as a function of $\mathbf{1}_{Cl}$ concentration with **2a** (50.0 mM) remaining fixed in CH_3CN/H_2O (2:1) solution upon irradiation with a 395 nm LED in the presence of O_2. The inset: initial rate *vs*. $\mathbf{1}_{Cl}$ concentration.

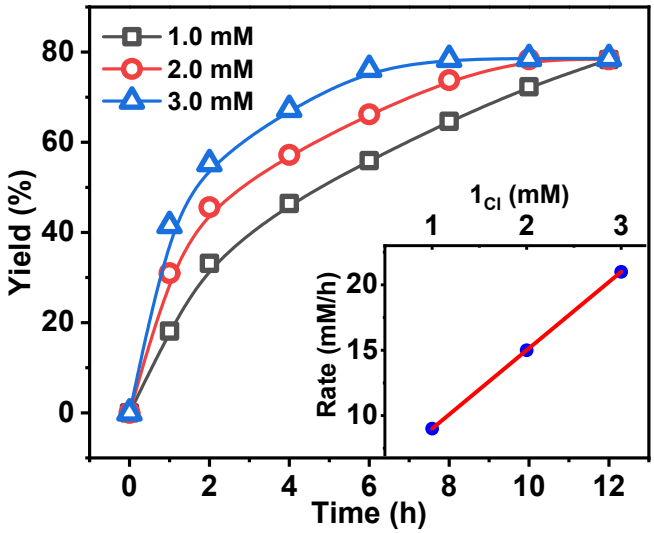


Figure S24. Production of **5a** as a function of **2a** concentration with $\mathbf{1}_{Cl}$ (3.0 mM) remaining fixed in CH_3CN/H_2O (2:1) solution upon irradiation with a 395 nm LED in the presence of O_2. The inset: initial rate *vs*. **2a** concentration.

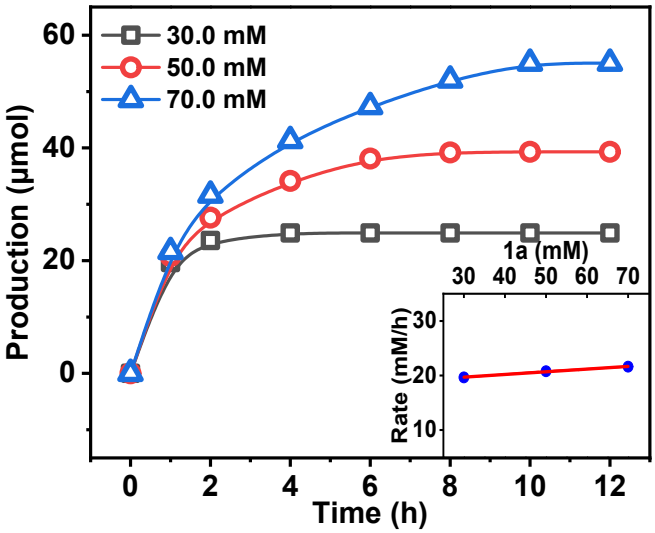


Figure S25. Yield of **5a** with fixed **2a** (50.0 mM) and 2.0 mM of different catalyst in CH_3CN/H_2O (2:1) solution: $\mathbf{1_{Cl}}$ (blue), $\mathbf{1_{Br}}$ (red), and $\mathbf{1_{I}}$ (black), respectively, upon irradiation with a 395 nm LED in the presence of O_2.

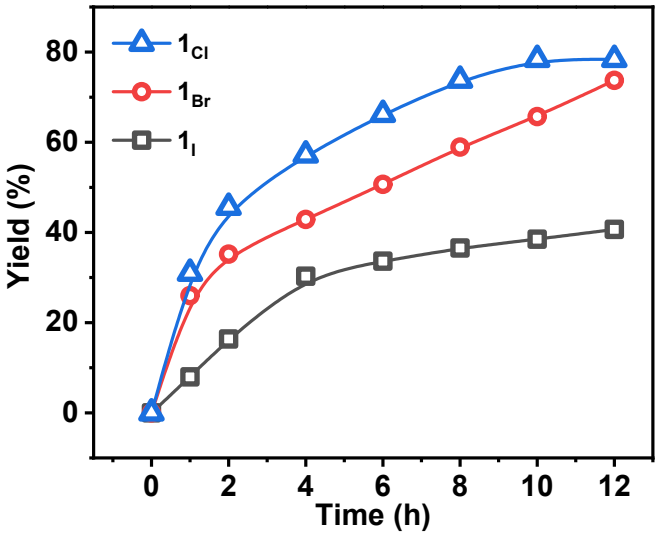
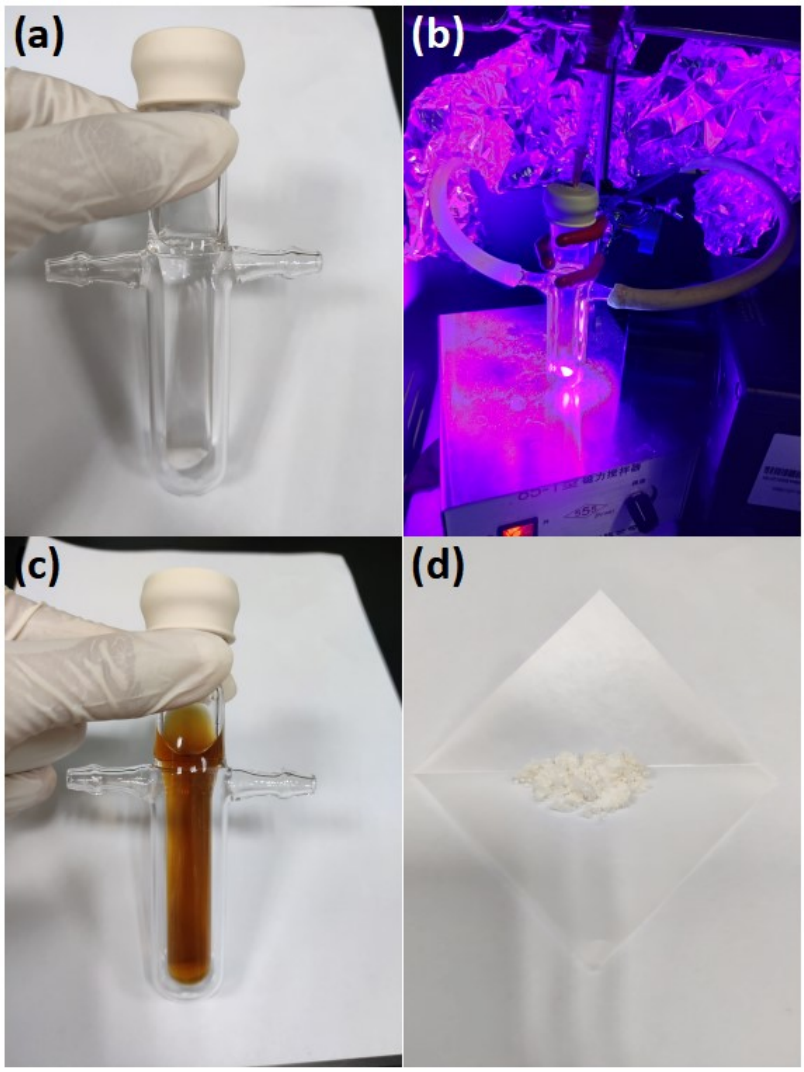


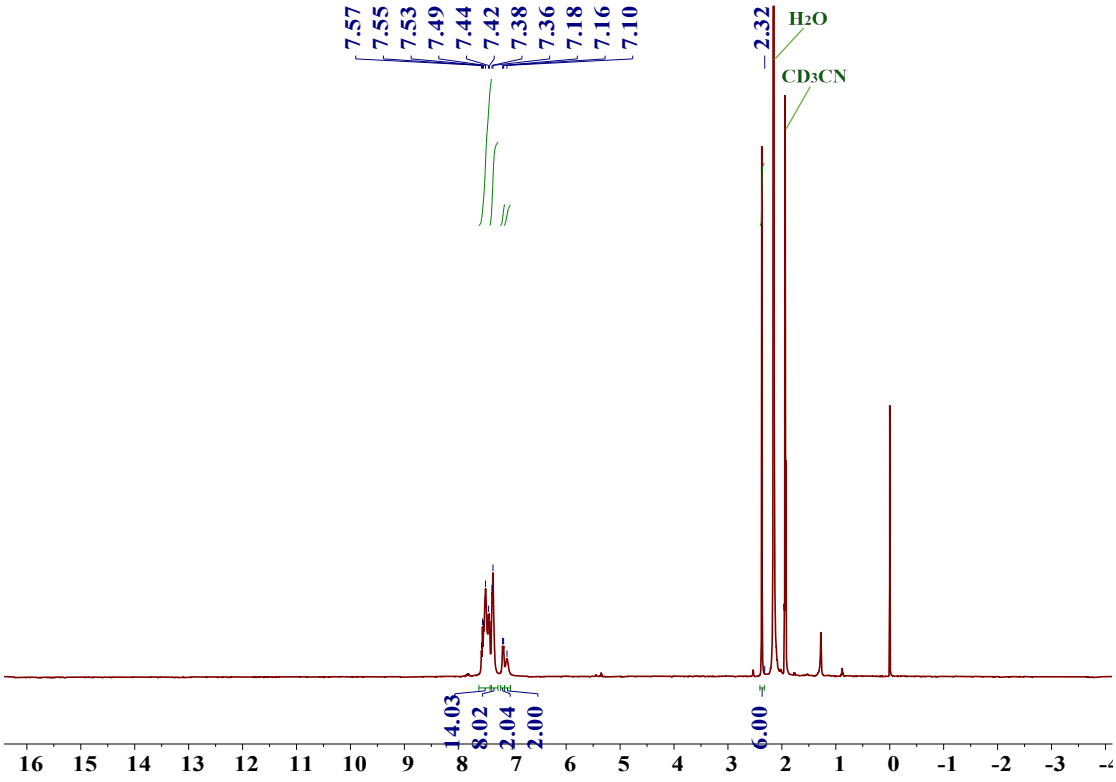
Figure S26. The detailed picture of 0.5 mmol scale-up reaction of **2a** on the basis of the original catalytic experiment under irradiation of 395 nm LED. (a) Before reaction; (b) in the process of reaction; (c) after reaction; and (d) the product **3a** purified by silica gel column chromatography.



6. NMR Spectra for Photocatalytic Reactions.

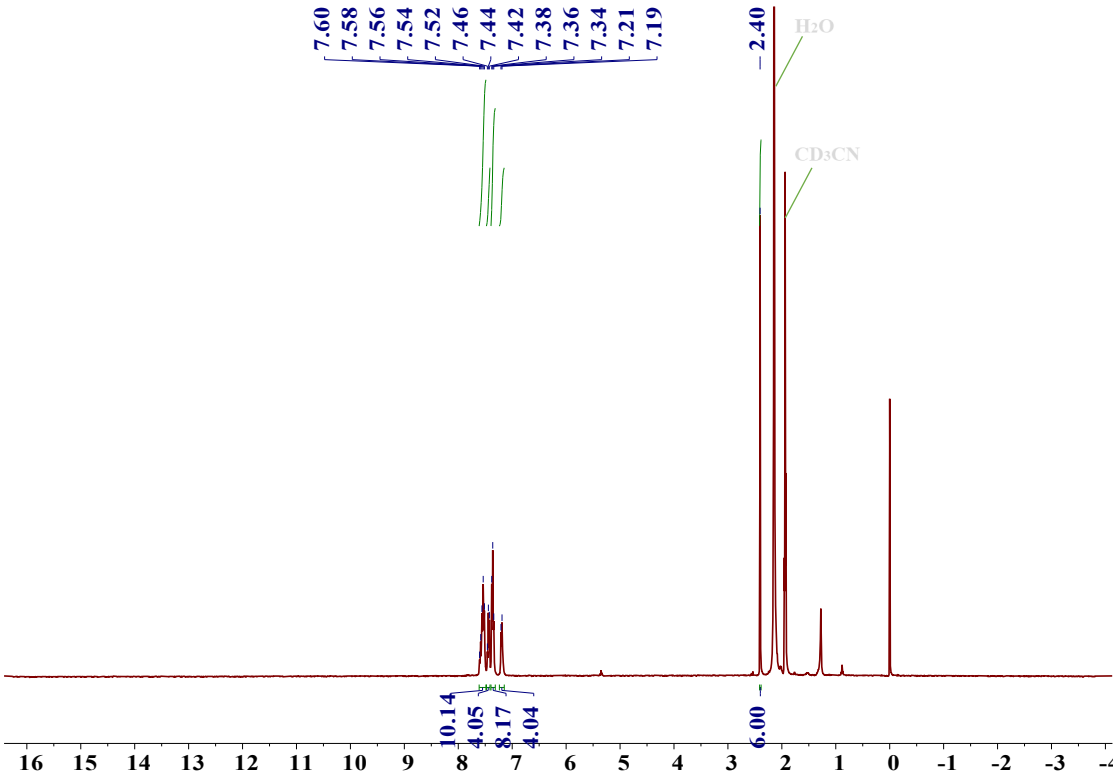
^{1}H NMR spectrum of $\mathbf{1_{Cl}}$.

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 7.57-7.42 (m，14H), 7.38-7.36 (m, 8H), 7.18 (d, J = 6.8 Hz, 2H), 7.10 (s, 2H), 2.32 (s, 6H).



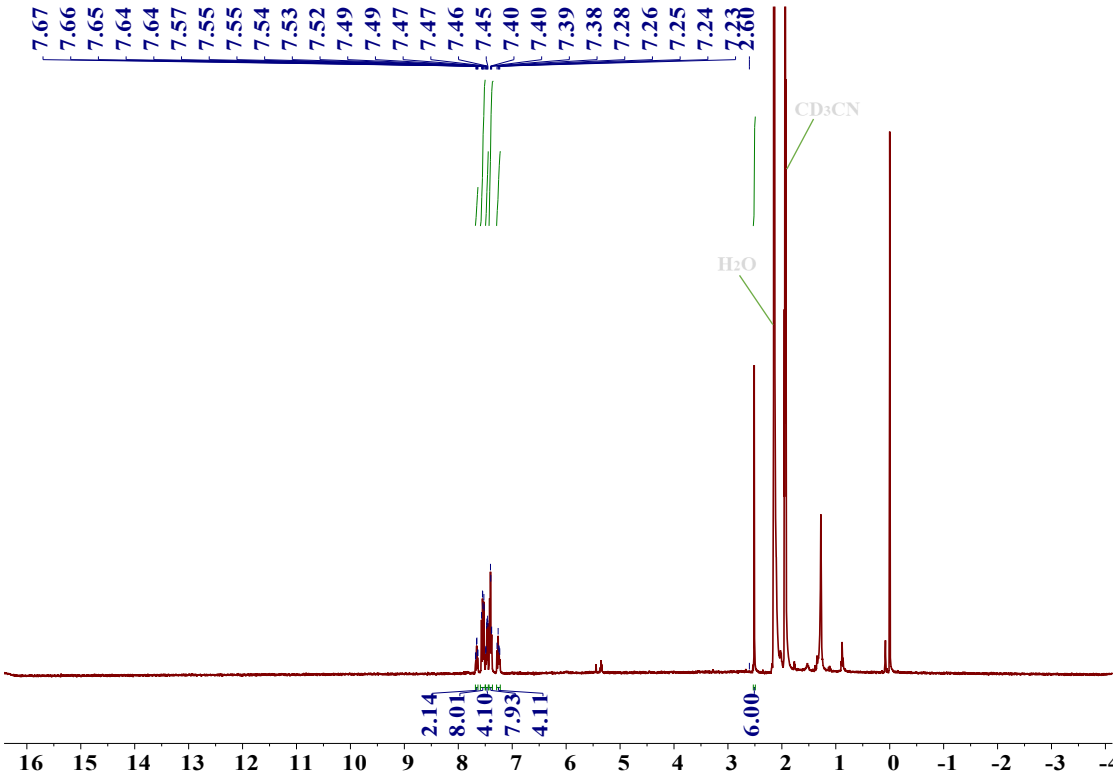
^{1}H NMR spectrum of 1_{Br}.

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 7.60-7.52 (m, 10H), 7.46-7.42 (m, 4H), 7.38-7.34 (m, 8H), 7.21-7.19 (m, 4H), 2.40 (s, 6H).



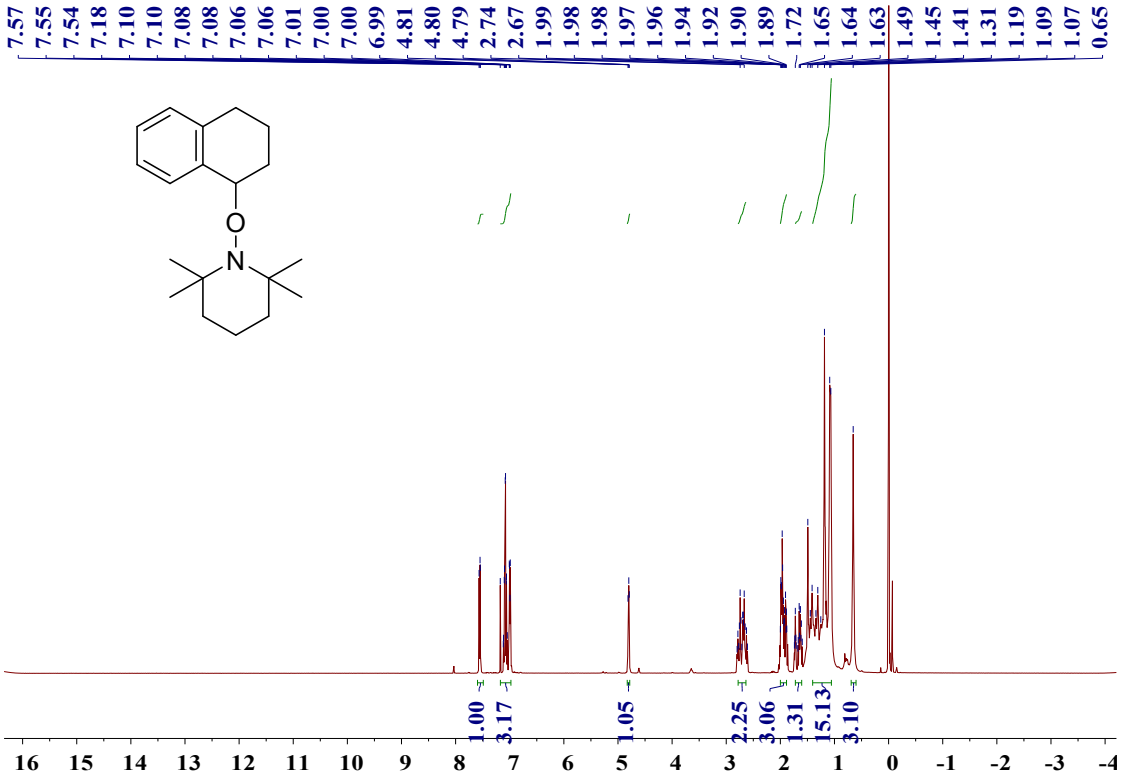
^{1}H NMR spectrum of $\mathbf{1_I}$.

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 7.67-7.64 (td, J = 7.8 Hz, 2.9 Hz, 2H), 7.57-7.52 (m, 8H), 7.49-7.45 (m, 4H), 7.42-7.38 (m, 8H), 7.28-7.23 (m, 4H), 2.60 (s, 6H).

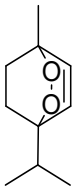


^{1}H NMR spectrum of 2,2,6,6-tetramethyl-1-((1,2,3,4-tetrahydronaphthalen-1-yl)oxy)piperidine.

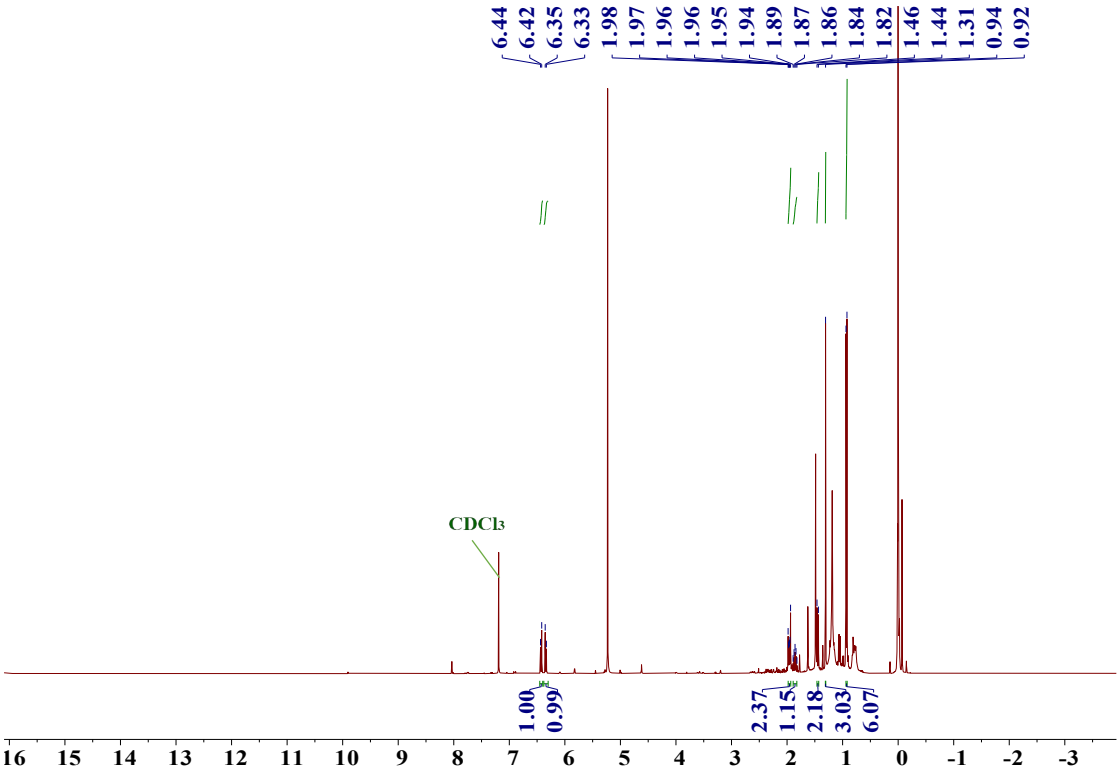
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57-7.54 (m, 1H), 7.18-6.99 (m, 3H), 4.81-4.79 (m, 1H), 2.80-2.61 (m, 2H), 2.00-1.88 (m, 3H), 1.74-1.60 (m, 1H), 1.49-1.07 (m, 15H), 0.65 (s, 3H).



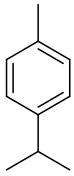
^{1}H NMR spectrum of ascaridole.



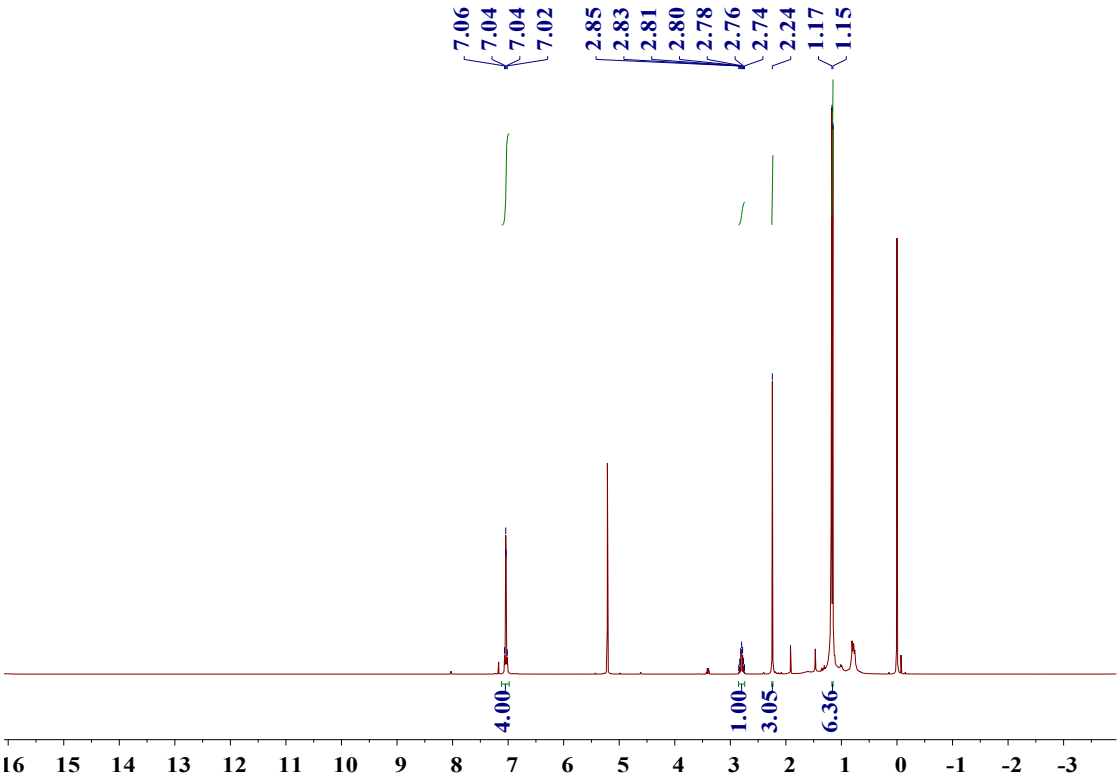
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.44 (d, J = 8.6 Hz, 1H), 6.35 (d, J = 8.6 Hz, 1H), 1.98-1.94 (m, 2H), 1.89-1.82 (m, 1H), 1.46-1.44 (m, 2H), 1.31 (s, 3H), 0.94 (d, J = 6.9 Hz, 6H).



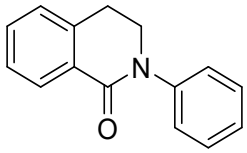
^{1}H NMR spectrum of *p*-cymene.



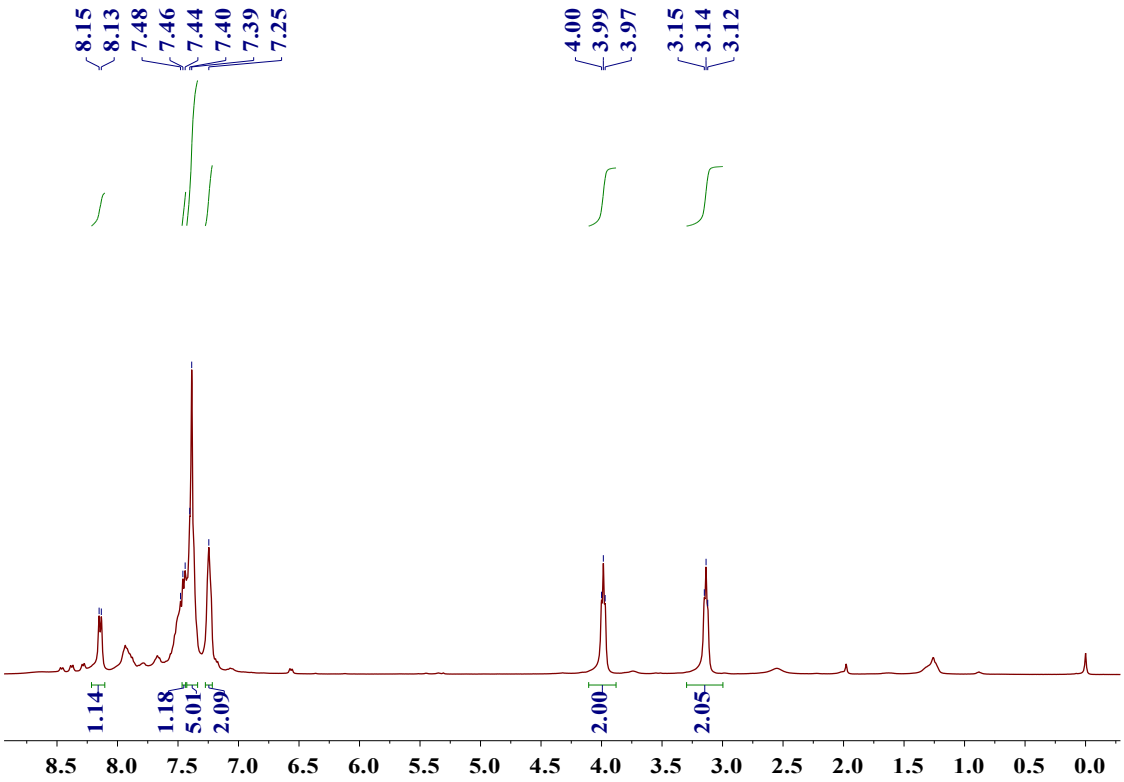
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.06-7.02 (m, 4H), 2.85-2.74 (m, 1H), 2.24 (s, 3H), 1.17 (d, J = 6.9 Hz, 6H).



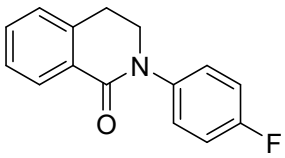
^{1}H NMR spectrum of 3a.



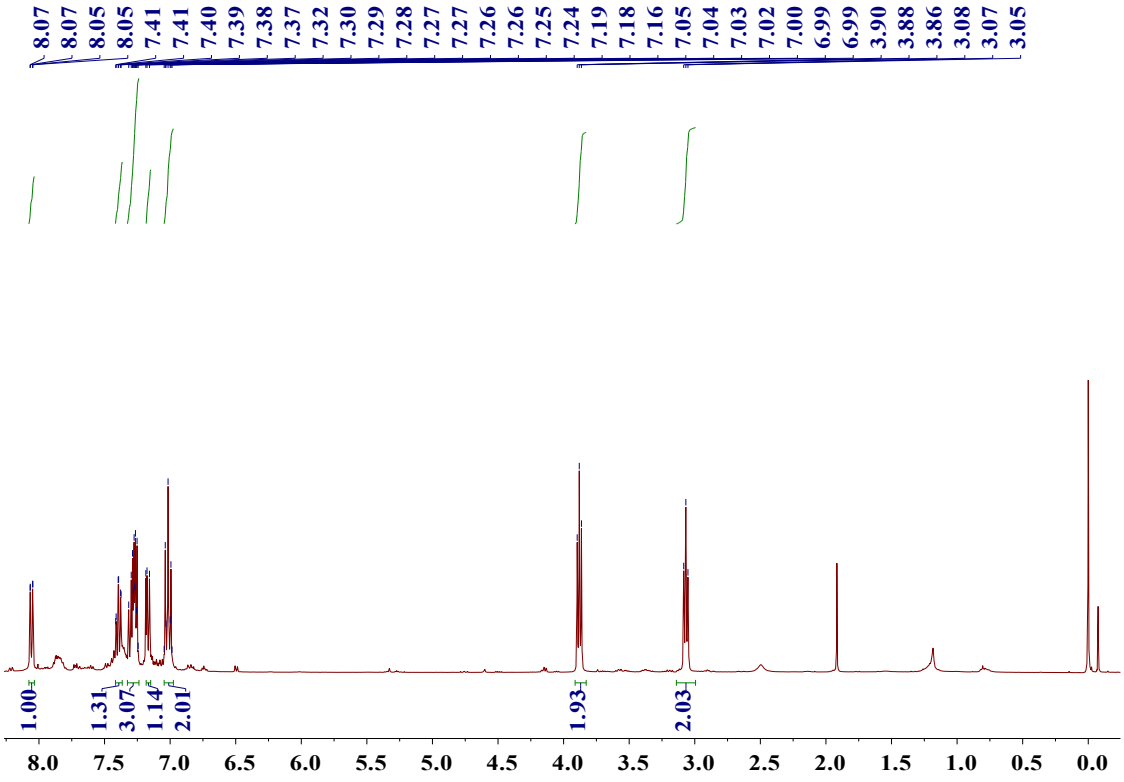
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (d, J = 7.5 Hz, 1H), 7.48-7.44 (m, 1H), 7.44-7.39 (m, 5H), 7.25 (m, 2H), 4.00 (t, J = 6.1 Hz, 2H), 3.15 (t, J = 6.0 Hz, 2H).



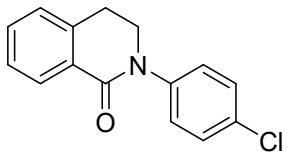
^{1}H NMR spectrum of 3b.



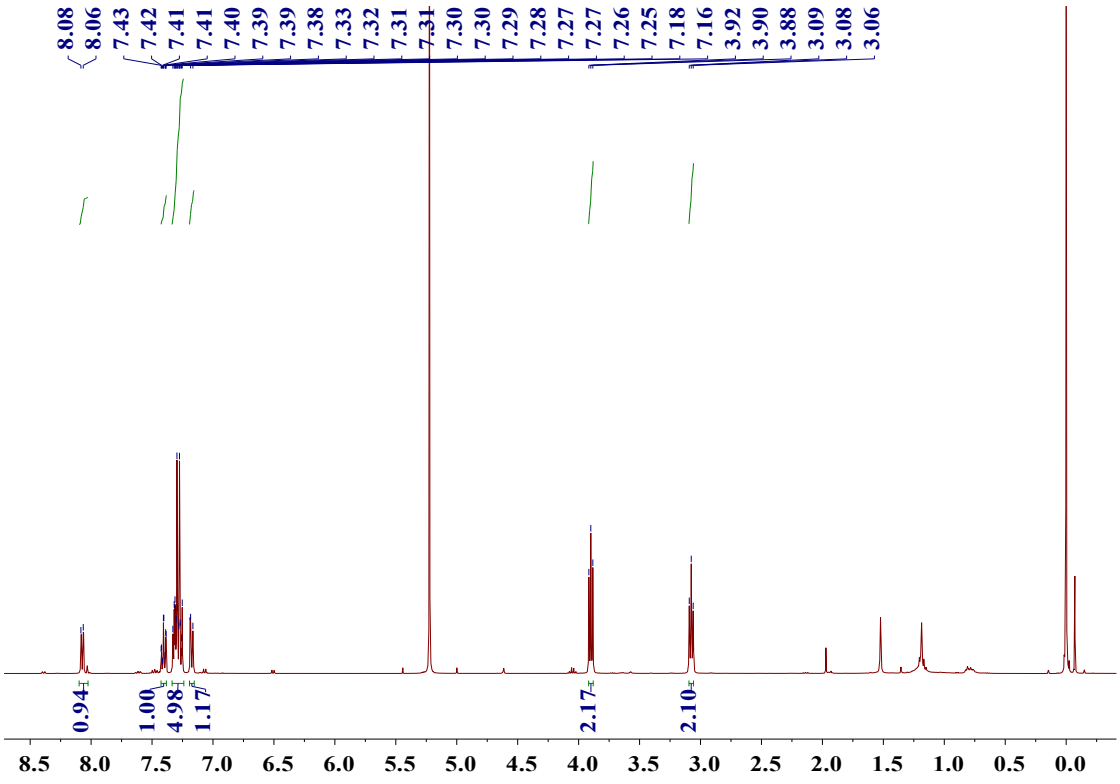
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.07 (dd, J = 7.7, 0.9 Hz, 1H), 7.41-7.37 (m, 1H), 7.32-7.24 (m, 3H), 7.19 (d, J = 8.9 Hz, 1H), 7.05-6.99 (m, 2H), 3.90 (t, J = 6.5 Hz, 2H), 3.08 (t, J = 6.5 Hz, 2H).



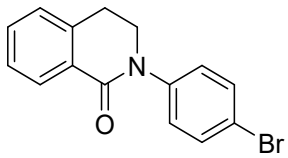
^{1}H NMR spectrum of 3c.



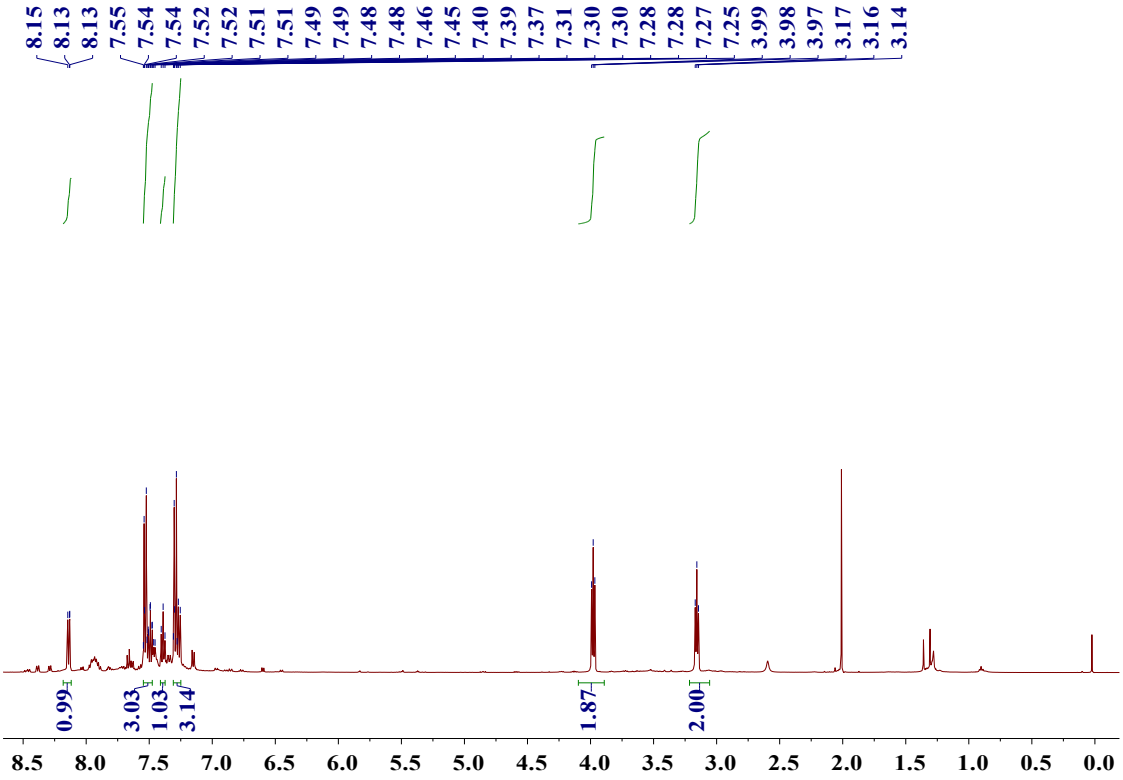
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08 (d, J = 7.6 Hz, 1H), 7.43-7.38 (m, 1H), 7.33-7.25 (m, 5H), 7.18 (d, J = 7.5 Hz, 1H), 3.90 (t, J = 6.5 Hz, 2H), 3.08 (t, J = 6.4 Hz, 2H).



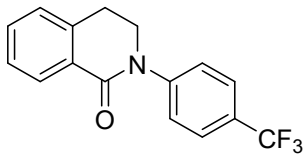
^{1}H NMR spectrum of 3d.



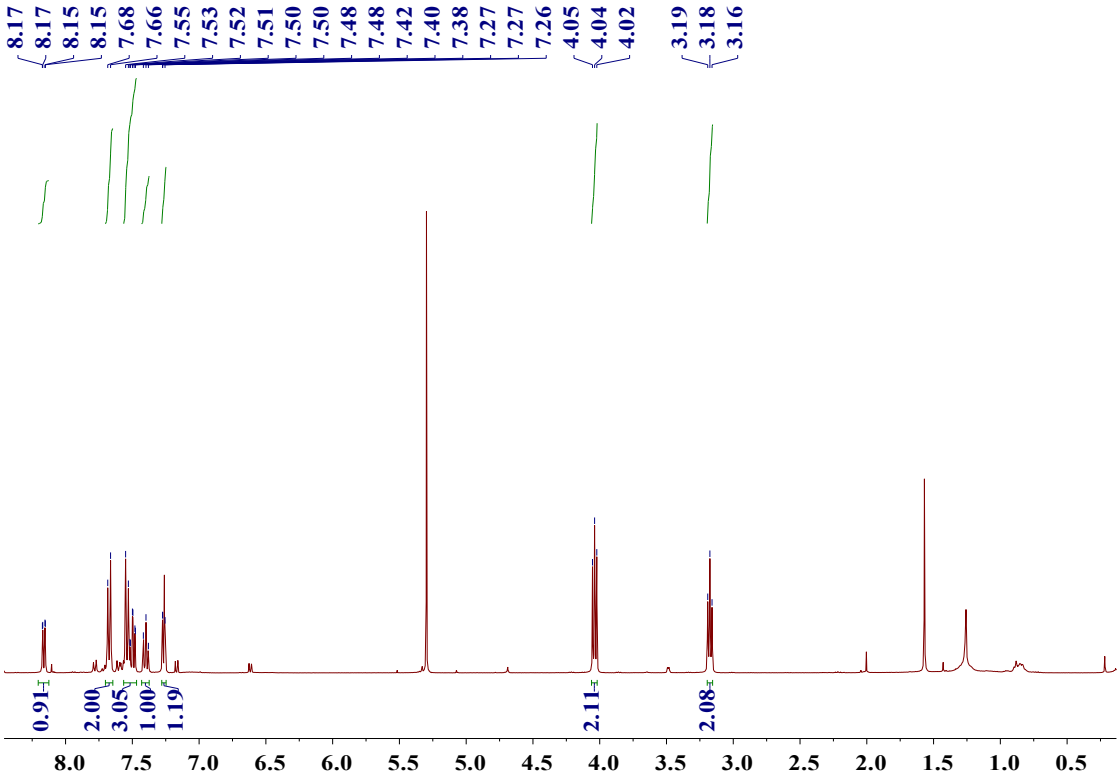
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (d, J = 7.6 Hz, 1H), 7.55-7.48 (m, 3H), 7.40-7.37 (m, 1H), 7.31 (dd, J = 14.5, 8.1 Hz, 3H), 3.99 (t, J = 6.4 Hz, 2H), 3.17 (t, J = 6.4 Hz, 2H).



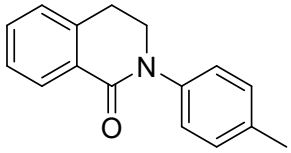
^{1}H NMR spectrum of 3e.



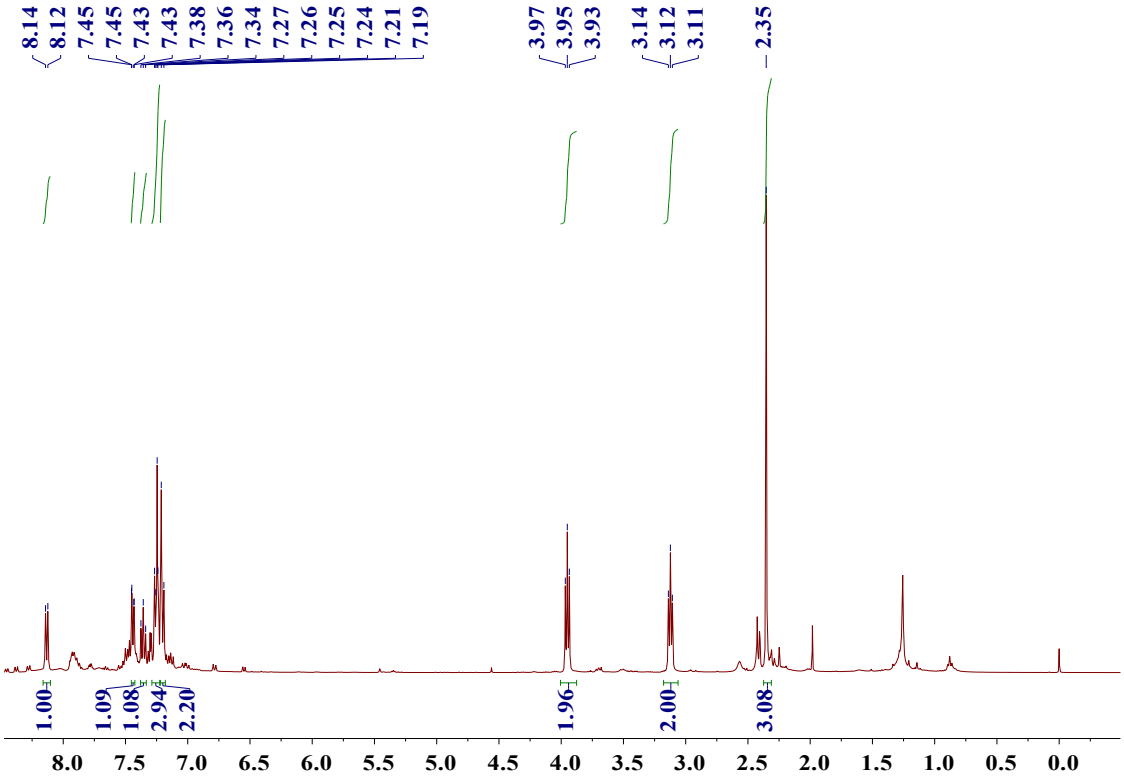
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.17 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.50 (td, J = 7.4, 1.0 Hz, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 4.04 (t, J = 6.4 Hz, 2H), 3.18 (t, J = 6.4 Hz, 2H).



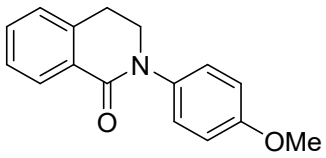
^{1}H NMR spectrum of 3f.



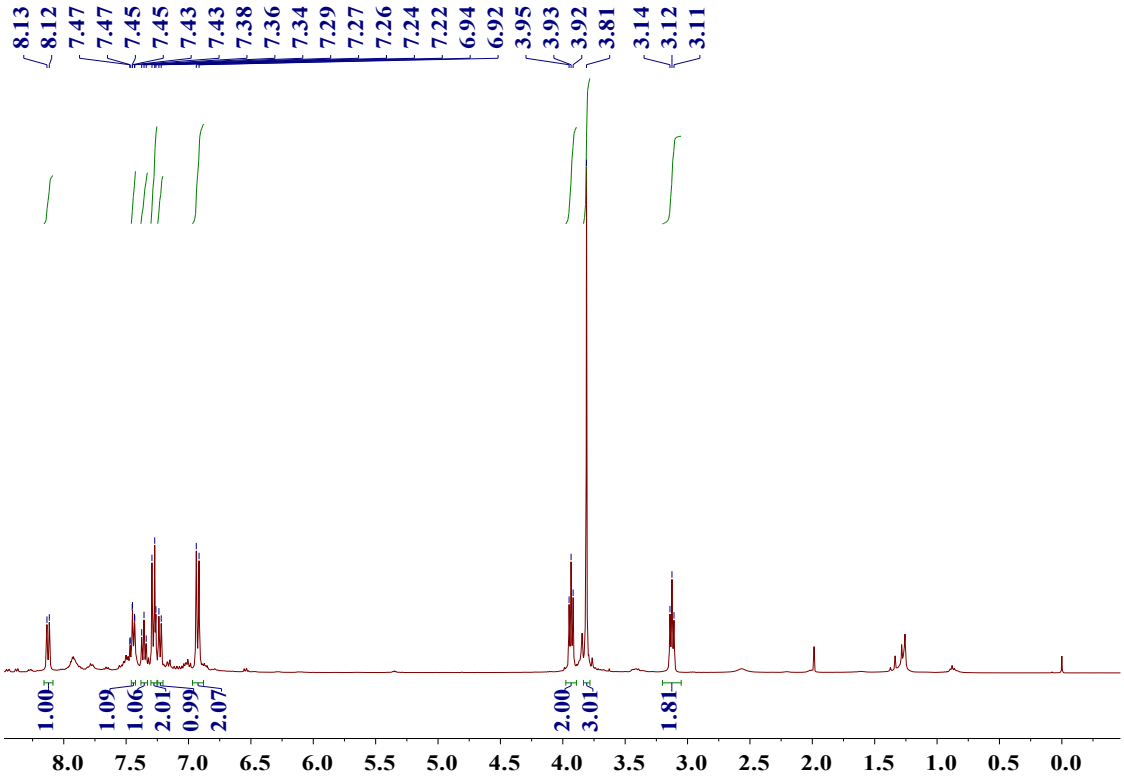
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.14 (dd, J = 7.8, 1.4 Hz, 1H), 7.45 (dd, J = 7.5 Hz, 1.1 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.27-7.24 (m, 3H), 7.21-7.19 (m, 2H), 3.97 (t, J = 6.4 Hz, 2H), 3.14 (t, J = 6.4 Hz, 2H), 2.35 (s, 3H).



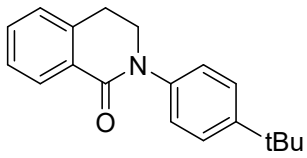
^{1}H NMR spectrum of 3g.



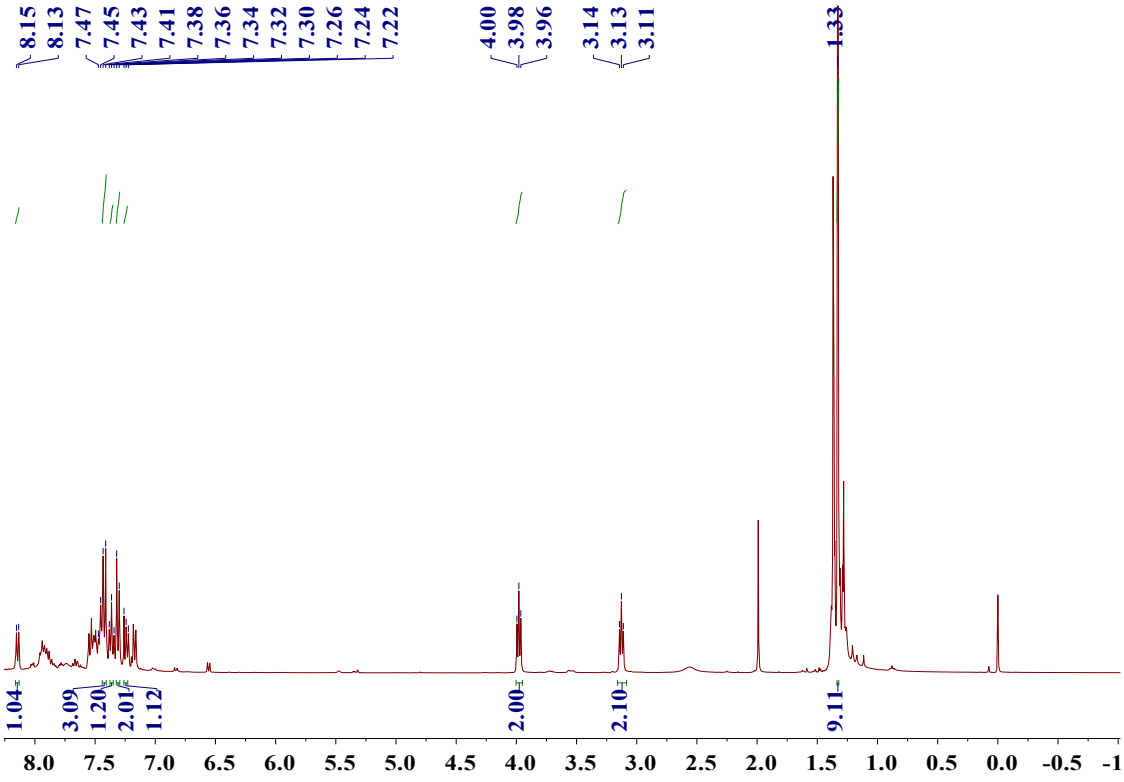
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.13 (d, J = 7.5 Hz, 1H), 7.47-7.43 (m, 1H), 7.38-7.34 (t, J = 7.5 Hz, 1H), 7.29-7.26 (m, 2H), 7.24 (d, J = 7.3 Hz, 1H), 6.93-6.91 (m, 2H), 3.95 (t, J = 6.4 Hz, 2H), 3.81 (s, 3H), 3.14 (t, J = 6.4 Hz, 2H).



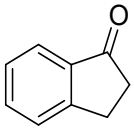
^{1}H NMR spectrum of 3h.



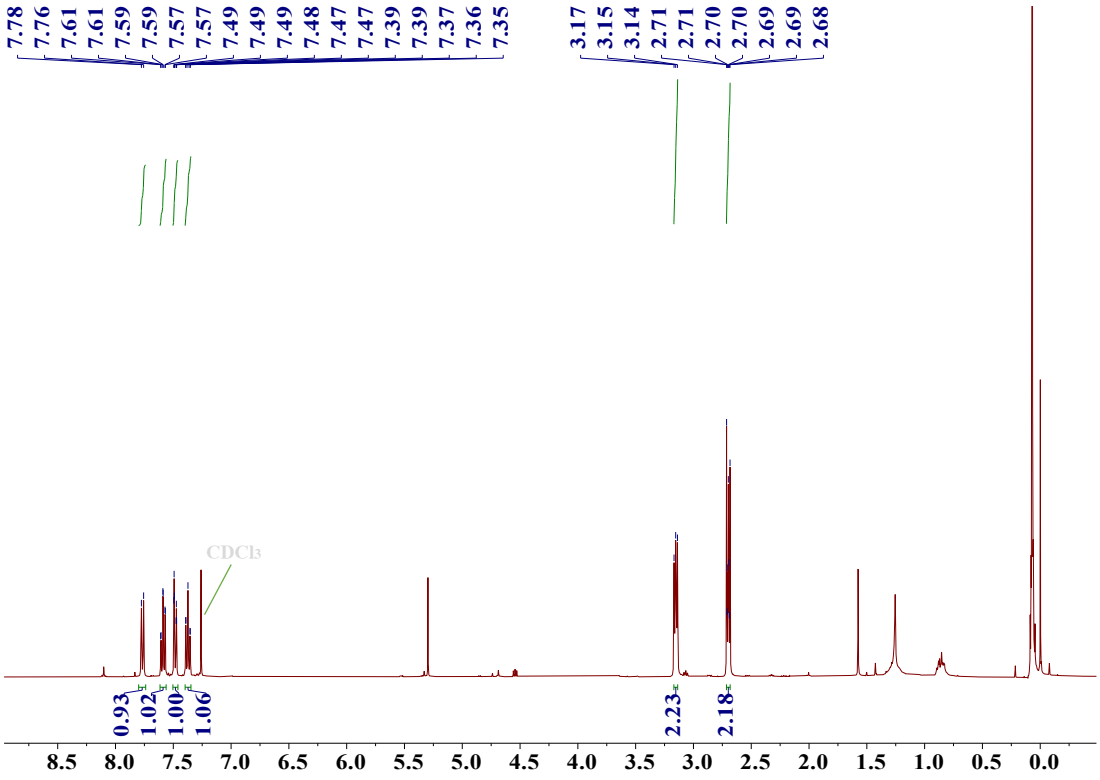
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (d, J = 7.6 Hz, 1H), 7.47-7.41 (m, 3H), 7.38-7.34 (m, 1H), 7.32 (d, J = 8.6 Hz, 2H), 7.26-7.22 (m, 1H), 4.00 (t, J = 6.5 Hz, 2H), 3.14 (t, J = 6.4 Hz, 2H), 1.33 (s, 9H).



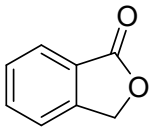
^{1}H NMR spectrum of 4a.



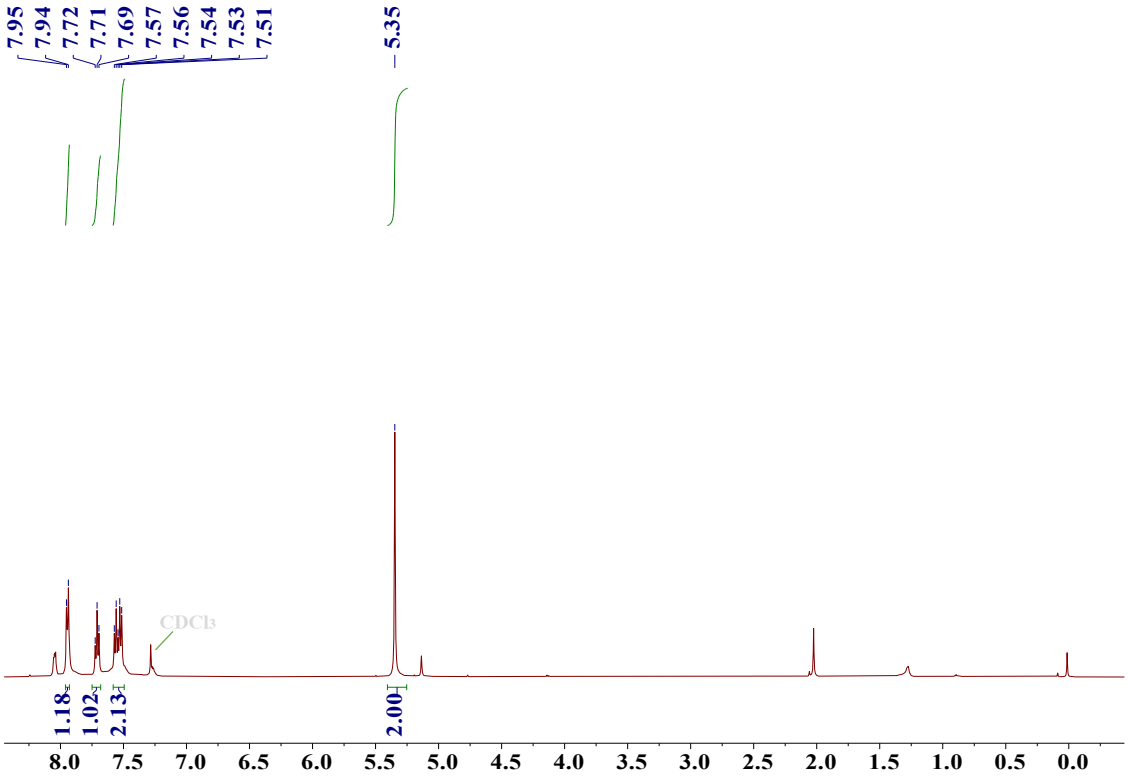
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78-7.76 (m, 1H), 7.61 (td, J = 7.6, 1.2 Hz, 1H), 7.49-7.47 (m, 1H), 7.39-7.35 (m, 1H), 3.17-3.14 (m, 2H), 2.71-2.68 (m, 2H).



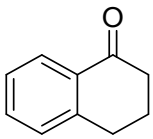
^{1}H NMR spectrum of 4b.



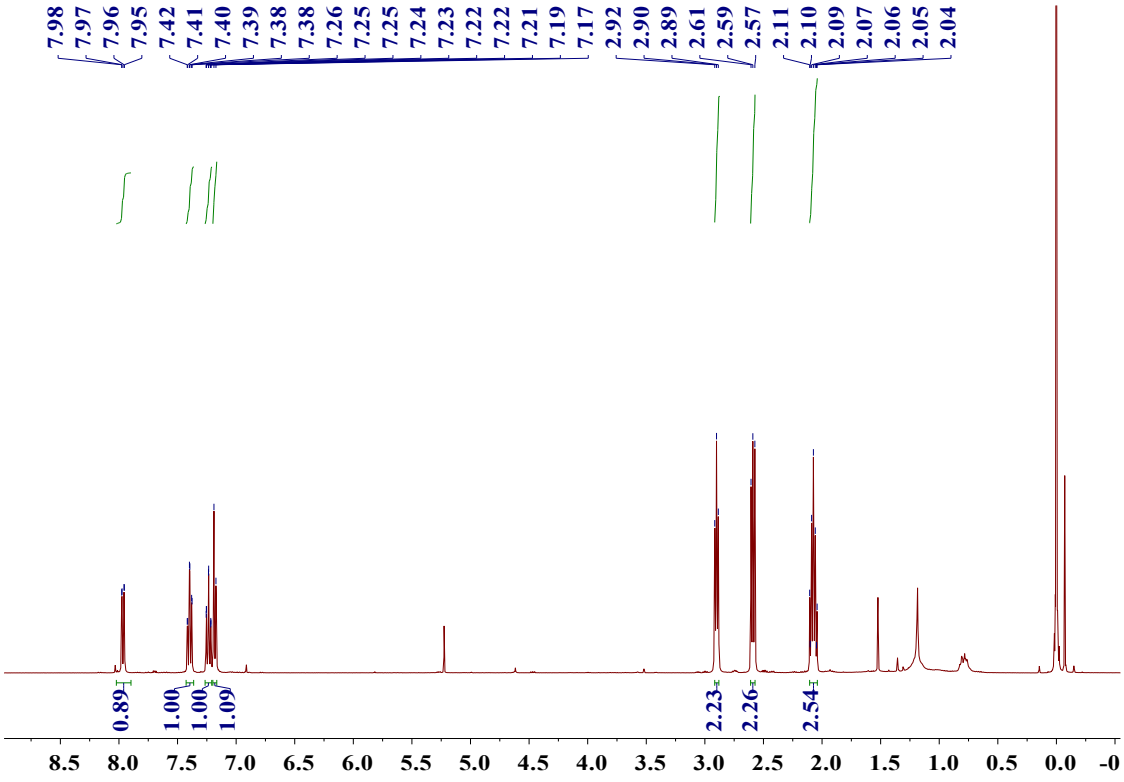
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95 (d, J = 7.7 Hz, 1H), 7.72 (t, J = 6.1Hz, 1H), 7.57-7.51 (m, 2H), 5.35 (s, 2H).



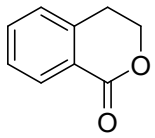
^{1}H NMR spectrum of 4c.



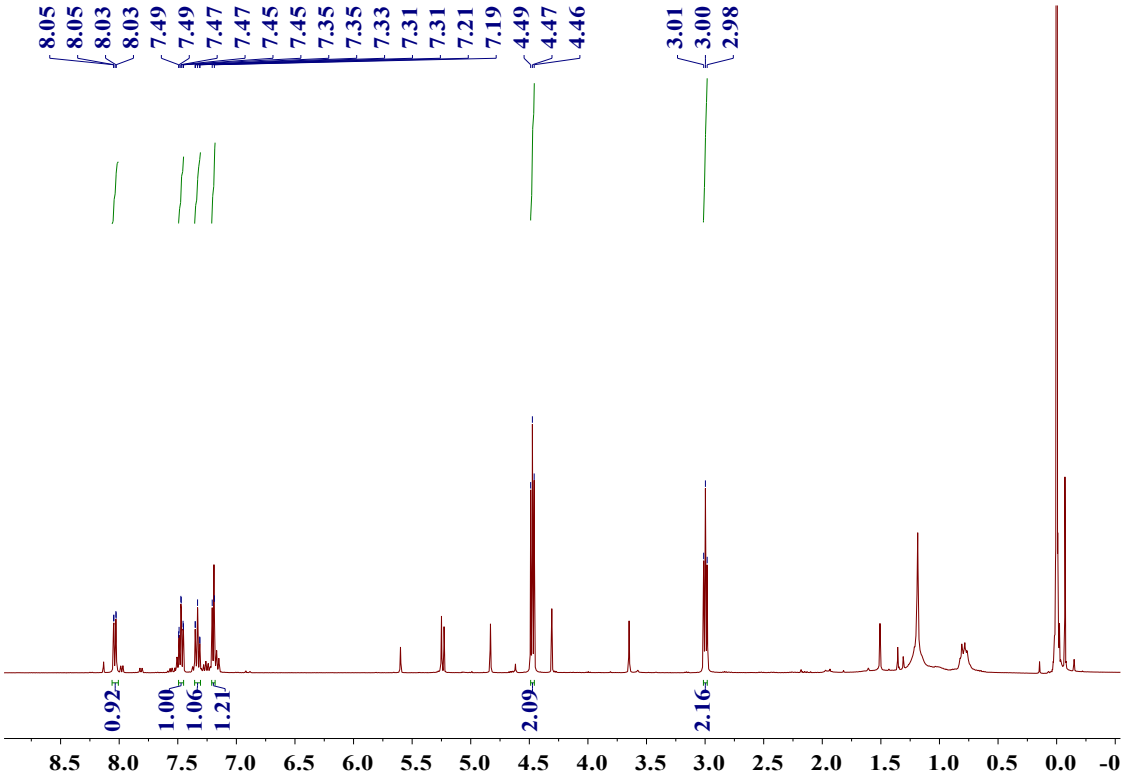
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98 (dd, J = 7.8, 0.8 Hz, 1H), 7.42 (td, J = 7.5, 1.3 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 8.3 Hz, 1H), 2.92 (t, J = 6.1 Hz, 2H), 2.61-2.57 (m, 2H), 2.11-2.04 (m, 2H).



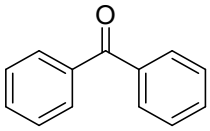
^{1}H NMR spectrum of 4d.



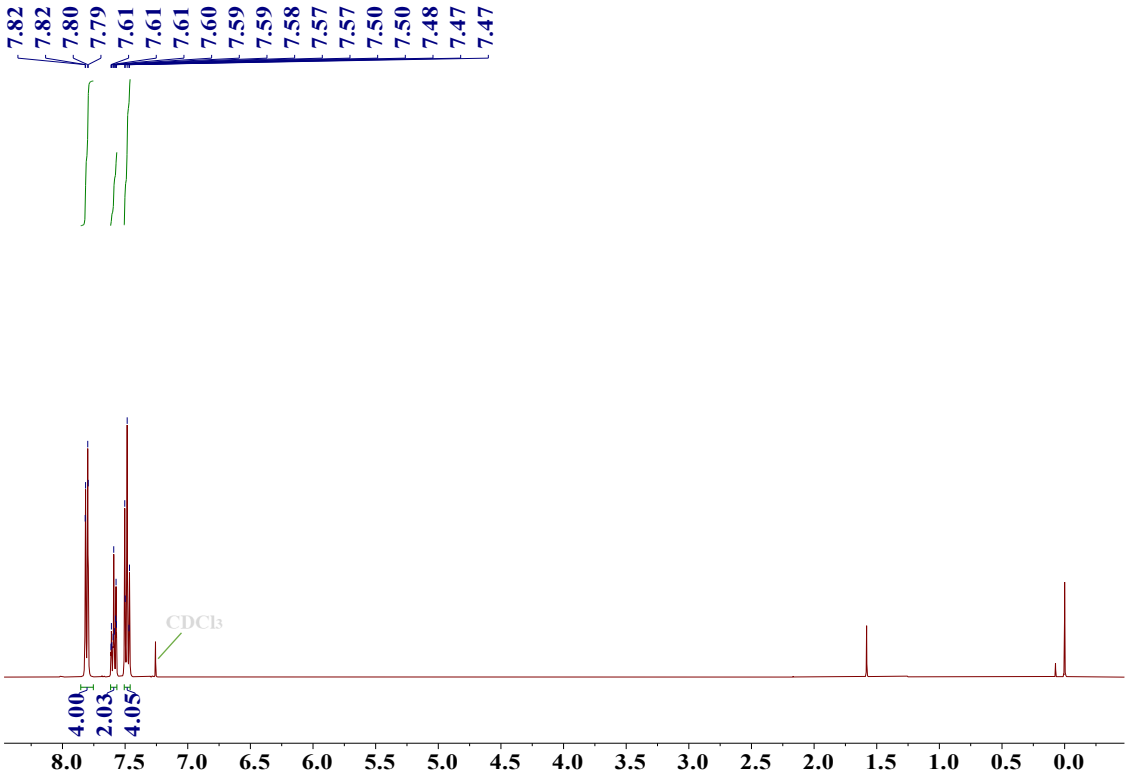
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.05 (dd, J = 7.8, 1.7 Hz, 1H), 7.49 (td, J = 7.5, 1.7 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 4.49 (t, J = 6.0 Hz, 2H), 3.01 (t, J = 6.0 Hz, 2H).



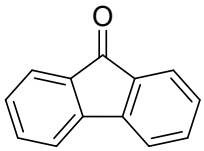
^{1}H NMR spectrum of 4e.



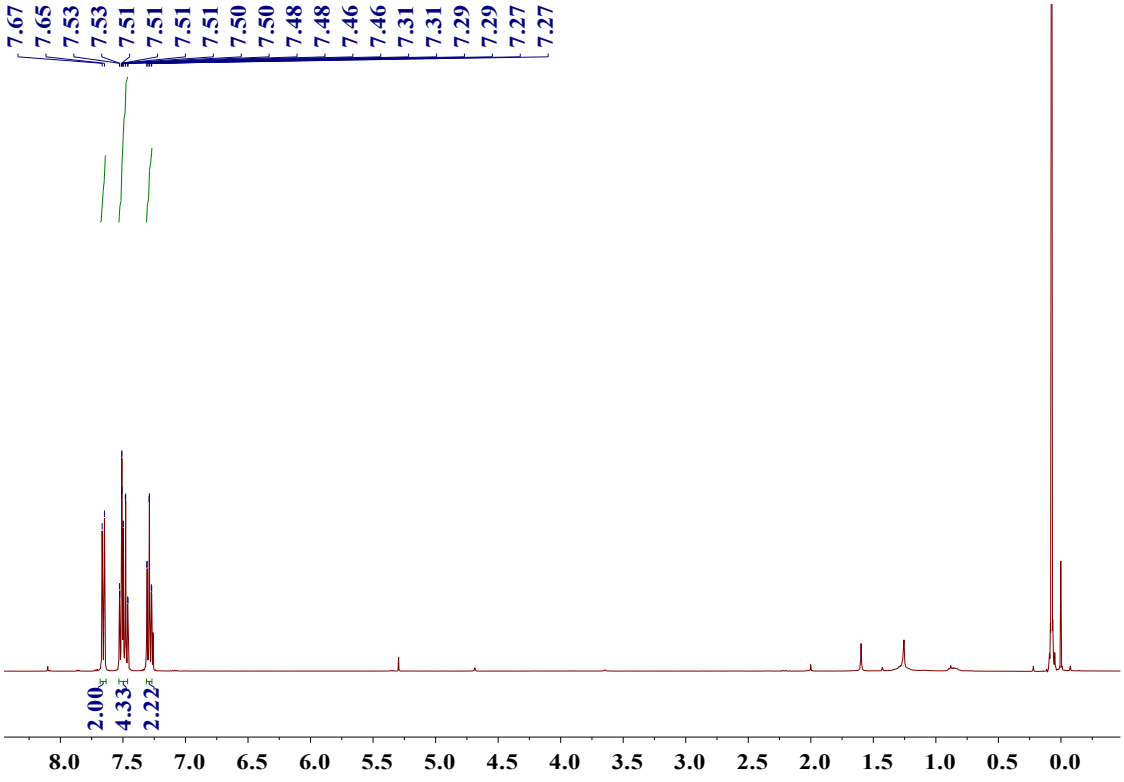
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.82 (dd, J = 5.1, 3.3 Hz, 4H), 7.61-7.57 (m, 2H), 7.50-7.47 (m, 4H).



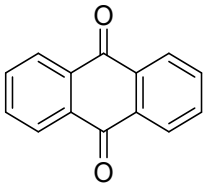
^{1}H NMR spectrum of 4f.



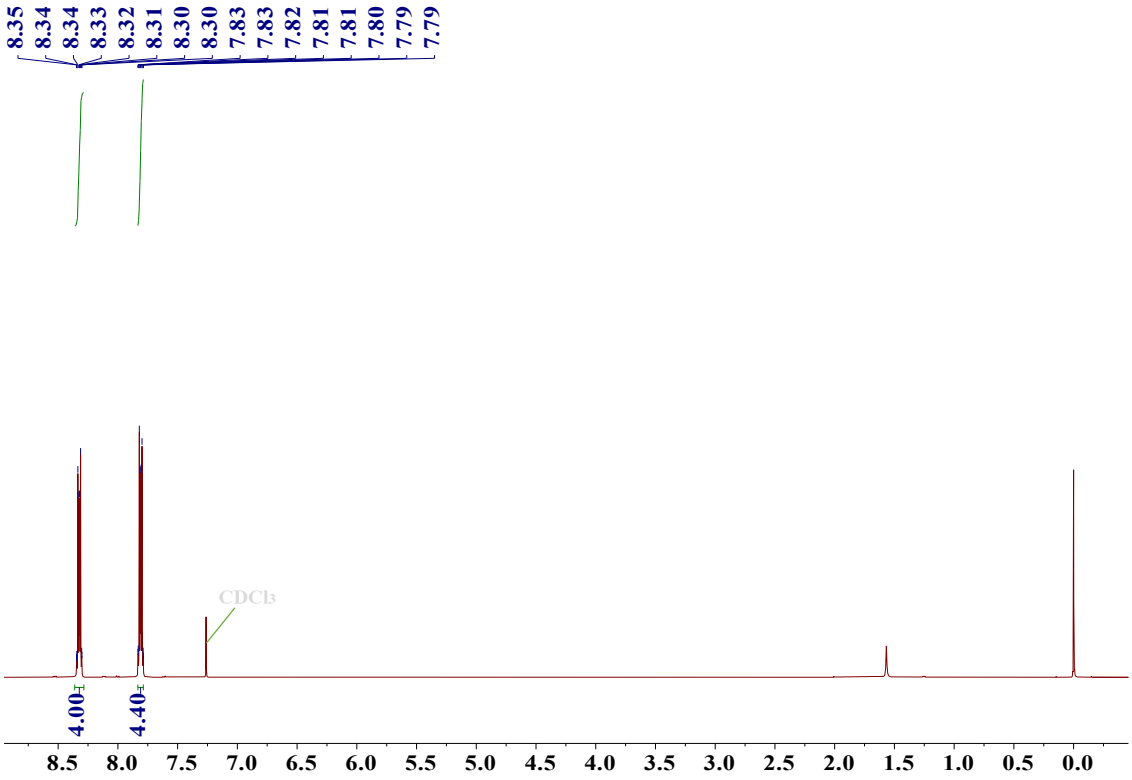
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (d, J = 7.2 Hz, 2H), 7.53-7.46 (m, 4H), 7.31 (dt, J = 7.6, 1.6 Hz, 2H).



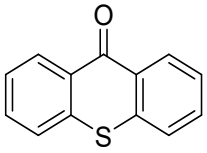
^{1}H NMR spectrum of 4g.



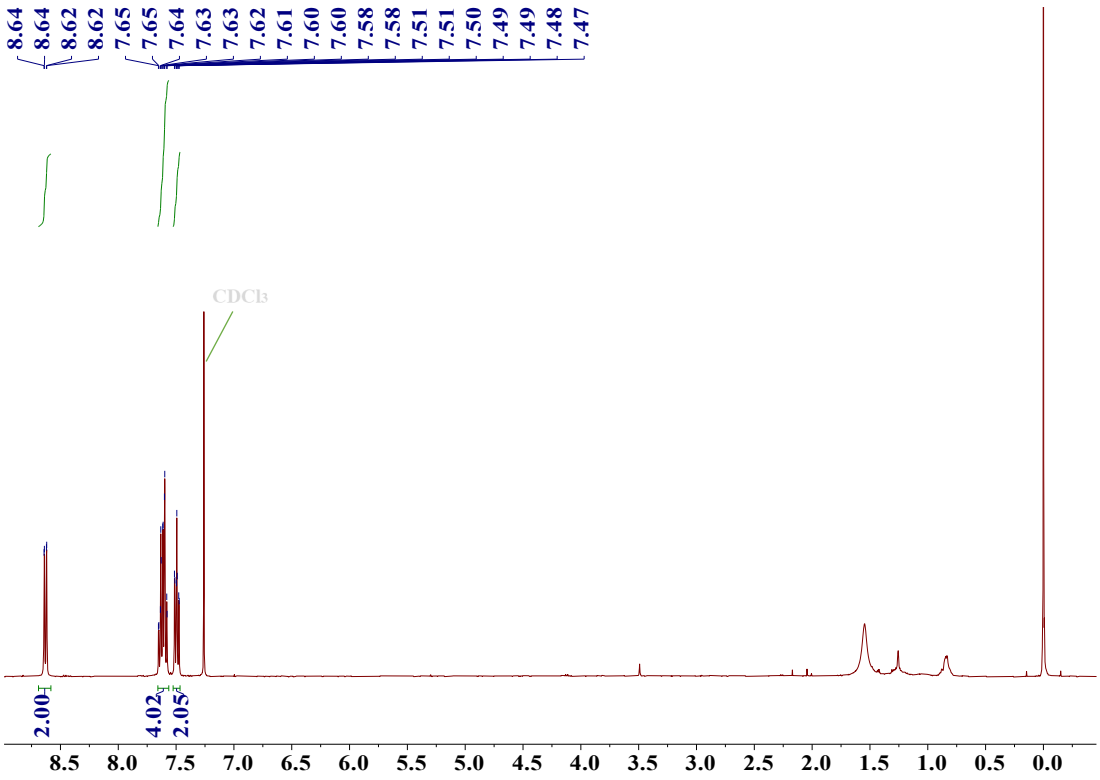
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.35-8.30 (m, 4H), 7.83-7.79 (m, 4H).



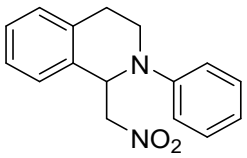
^{1}H NMR spectrum of 4h.



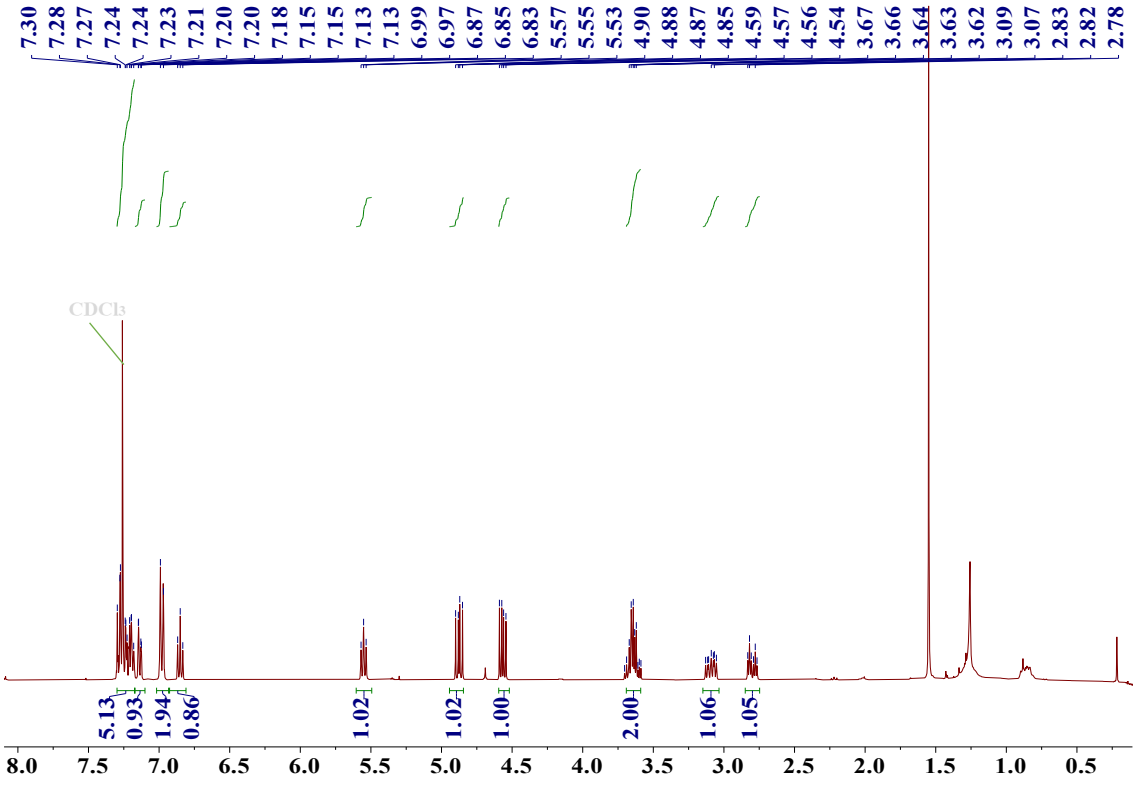
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.64 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 7.65-7.58 (m, 4H), 7.51-7.47 (m, 2H).



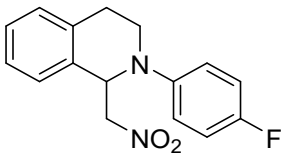
^{1}H NMR spectrum of 5a.



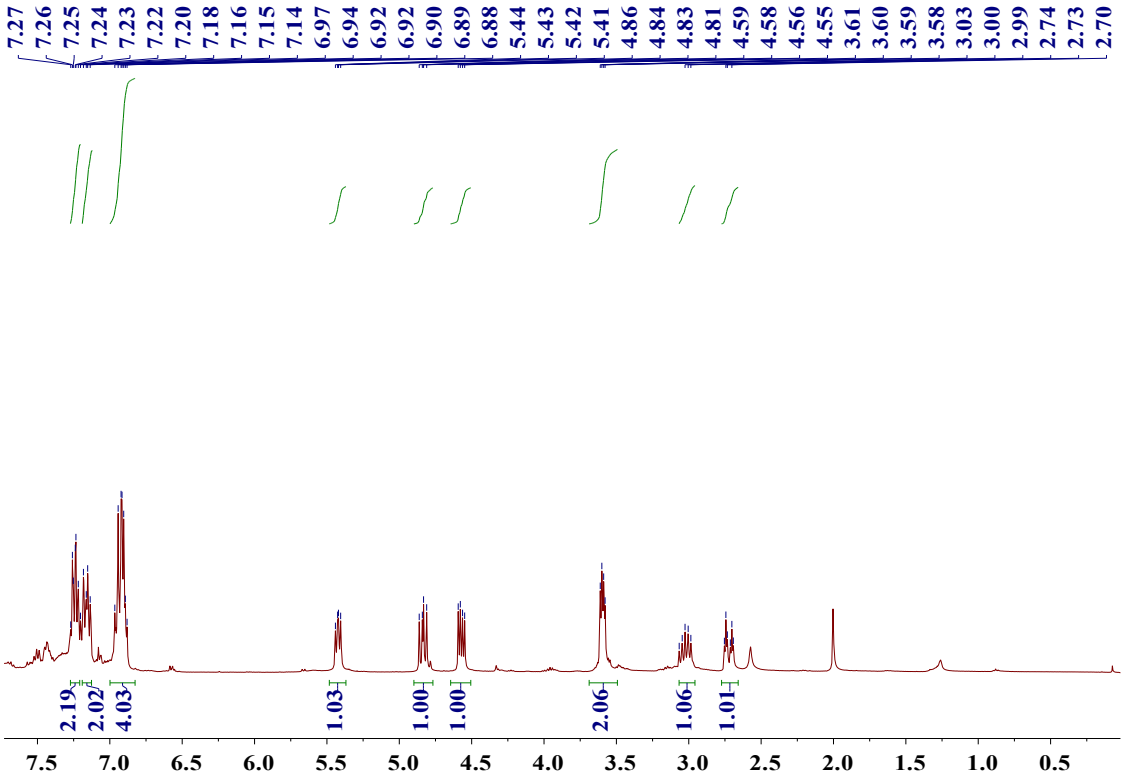
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30-7.18 (m, 5H), 7.15-7.13 (m, 1H), 6.99-6.97 (m, 2H), 6.87-6.83 (m, 1H), 5.57-5.53 (m, 1H) 4.90 (dd, J = 11.9 Hz, 7.8 Hz, 1H), 4.59 (dd, J = 11.9 Hz, 6.6 Hz, 1H), 3.67-3.62 (m, 2H), 3.13-3.09 (m, 1H), 2.82 (ddd, J = 16.4 Hz, 5.0 Hz, 5.0 Hz, 1H).



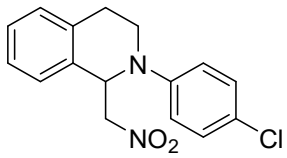
^{1}H NMR spectrum of 5b.



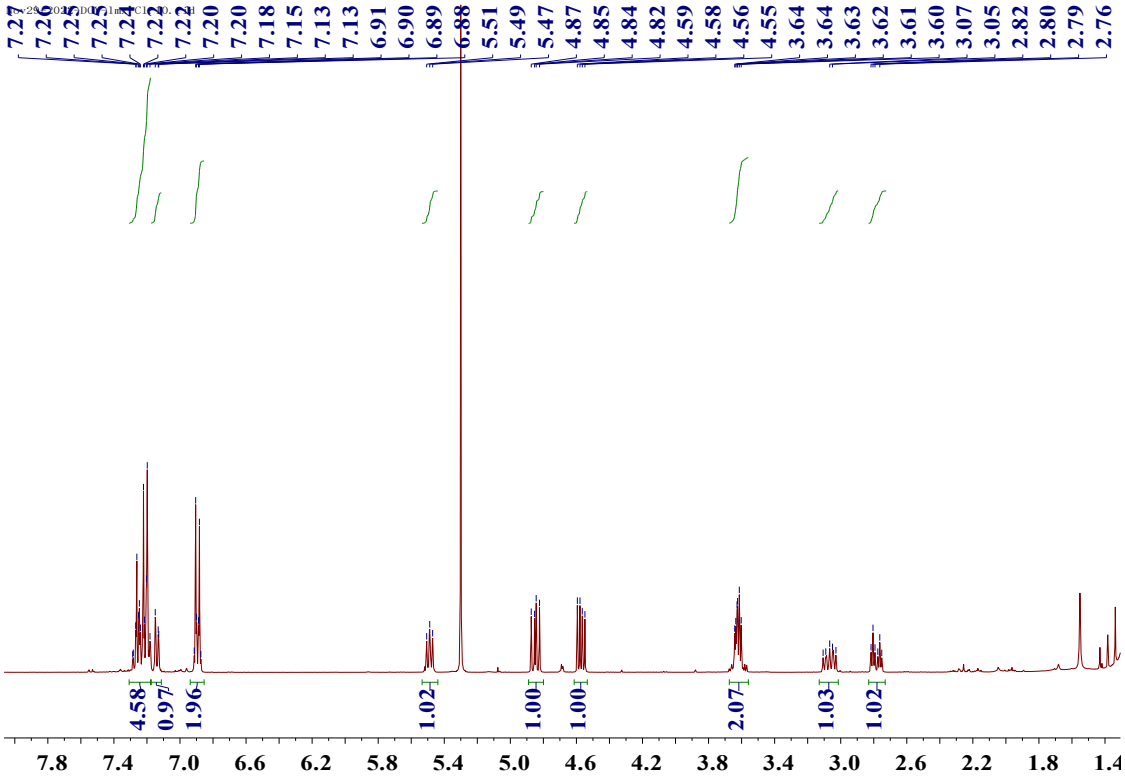
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.27-7.14 (m, 4H), 6.97-6.88 (m, 4H), 5.44 (dd, J = 8.3, 6.1 Hz, 1H), 4.86 (dd, J = 12.0, 8.7 Hz, 1H), 4.59 (dd, J = 12.0, 5.9 Hz, 1H), 3.61-3.58 (m, 2H), 3.03-2.99 (m, 1H), 2.74 (ddd, J = 16.5, 4.1 Hz, 4.1 Hz, 1H).



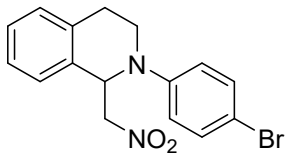
^{1}H NMR spectrum of 5c.



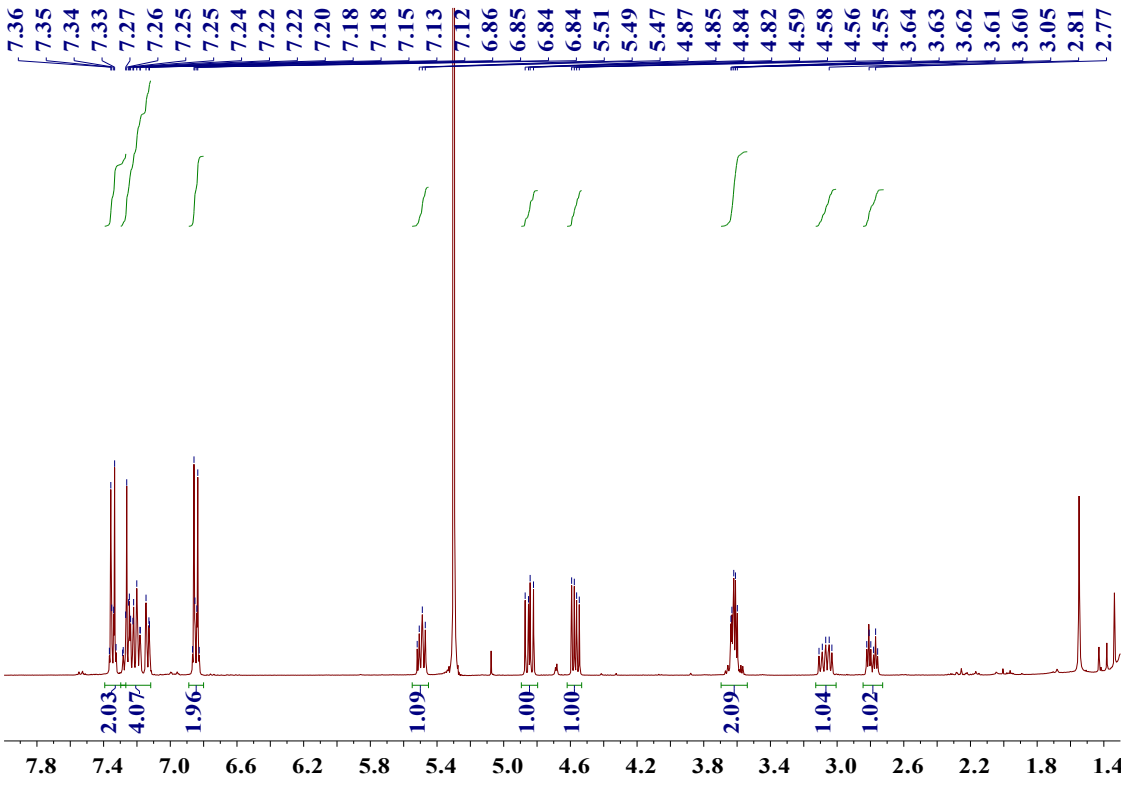
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.27-7.18 (m, 5H), 7.15-7.13 (m, 1H), 6.91 (d, J = 9.1 Hz, 2H), 5.49 (t, J = 7.2 Hz, 1H), 4.85 (dd, J = 12.0, 8.1 Hz, 1H), 4.58 (dd, J = 12.0, 6.3 Hz, 1H), 3.64-3.60 (m, 2H), 3.11-3.03 (m, 1H), 2.78 (ddd, J = 16.3 Hz, 4.8 Hz, 4.8 Hz, 1H).



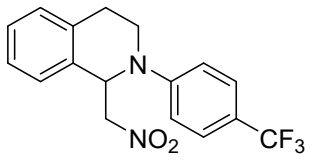
^{1}H NMR spectrum of 5d.



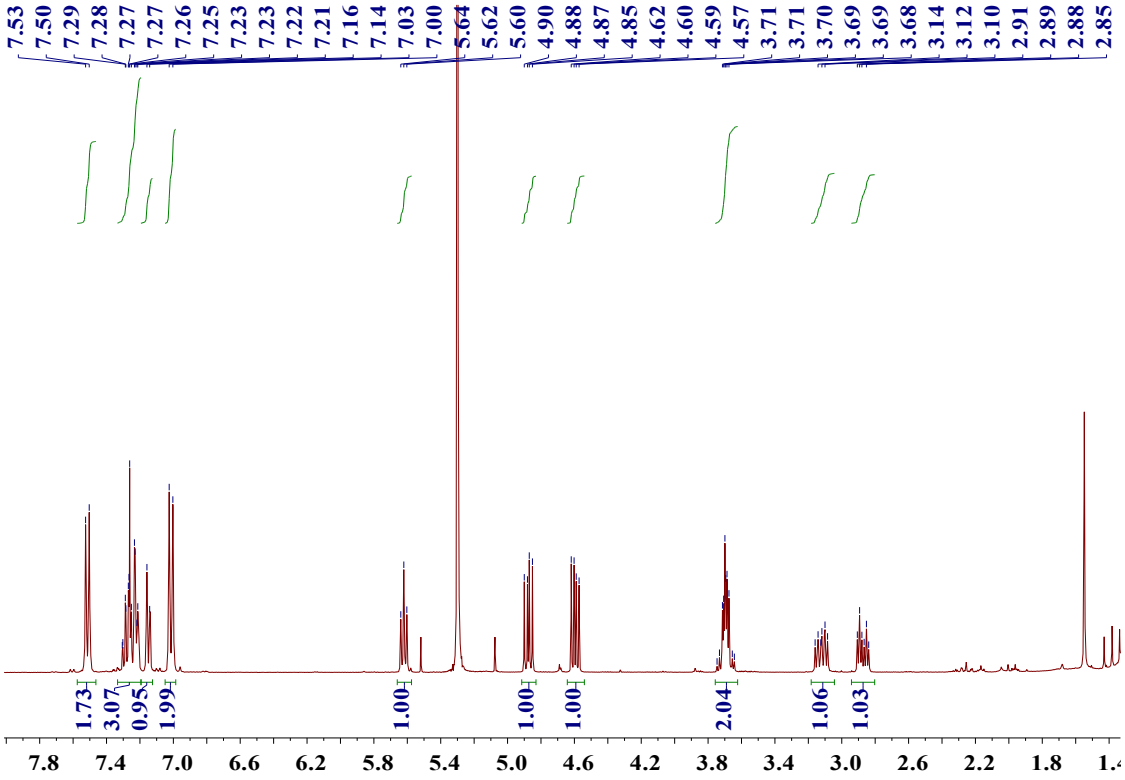
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37-7.33 (m, 2H), 7.29-7.18 (m, 3H), 7.15-7.12 (m, 1H), 6.87-6.83 (m, 2H), 5.52-5.47 (m, 1H), 4.85 (dd, J = 12.0 Hz, 8.0 Hz, 1H), 4.58 (dd, J = 12.0 Hz, 6.5 Hz, 1H), 3.64-3.60 (m, 2H), 3.11-3.03 (m, 1H), 2.80 (ddd, J = 16.5 Hz, 4.9 Hz, 4.9 Hz, 1H).



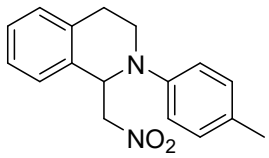
^{1}H NMR spectrum of 5e.



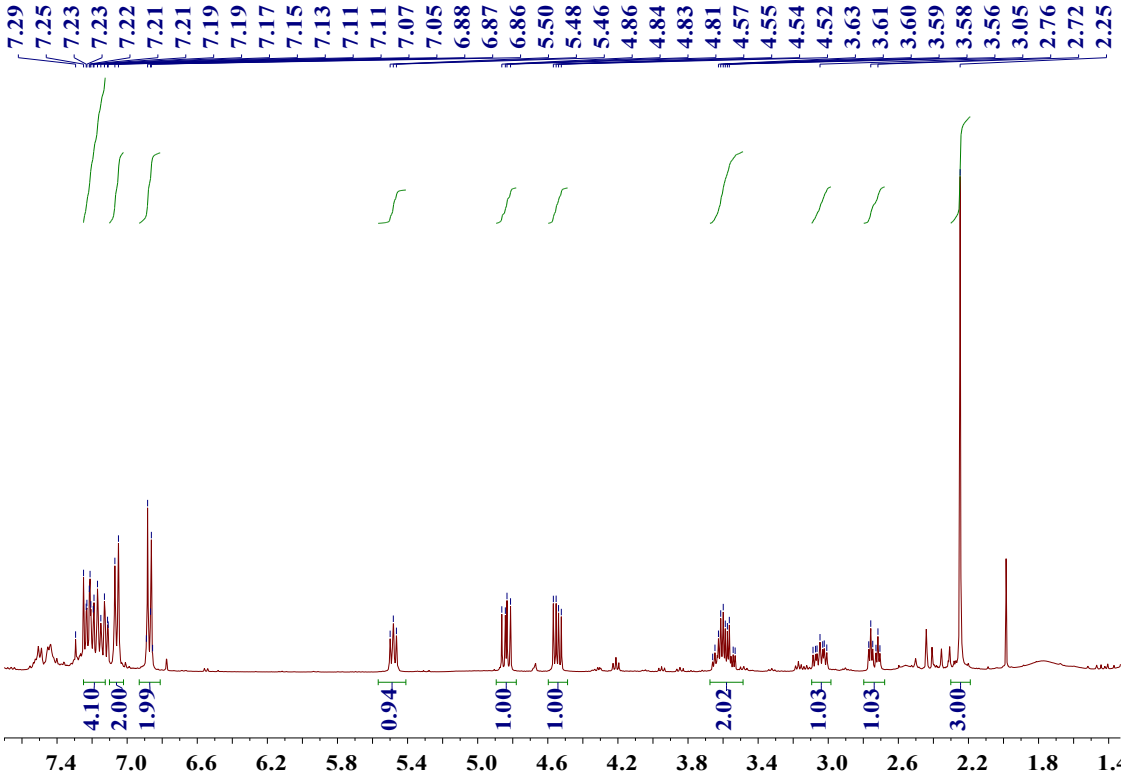
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50 (d, J = 8.5 Hz, 2H), 7.31-7.21 (m, 3H), 7.16-7.14 (m, 1H), 7.03 (d, J = 8.8 Hz, 2H), 5.62 (t, J = 7.2 Hz, 1H), 4.87 (dd, J = 11.9, 7.6 Hz, 1H), 4.60 (dd, J = 11.9, 6.8 Hz, 1H), 3.75-3.64 (m, 2H), 3.16-3.08 (m, 1H), 2.87 (dt, J = 16.3, 5.5 Hz, 5.5 Hz, 1H).



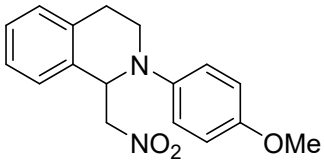
^{1}H NMR spectrum of 5f.



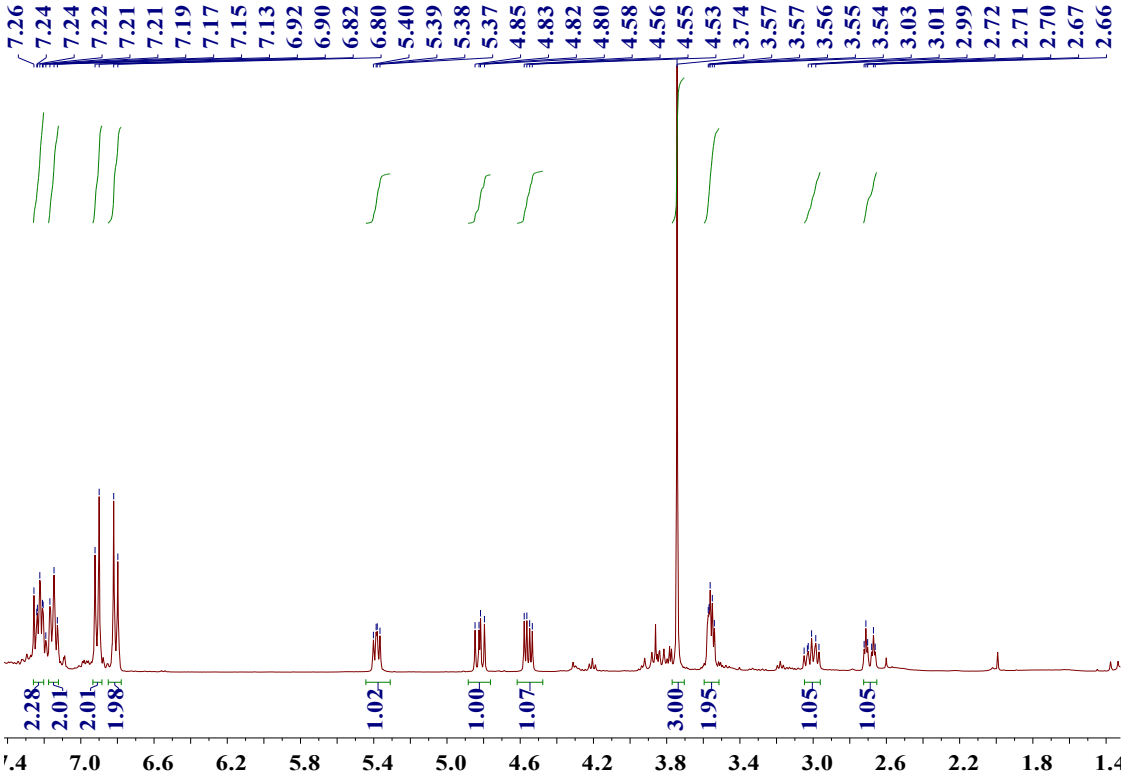
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.29-7.05 (m, 6H), 6.89 (d, J = 8.3 Hz, 2H), 5.50-5.46 (m, 1H), 4.86 (dd, J = 11.8 Hz, 8.1 Hz, 1H), 4.57 (dd, J = 11.8 Hz, 6.4 Hz, 1H), 3.66-3.53 (m, 2H), 3.09-3.01 (m, 1H), 2.77 (ddd, J = 16.4 Hz, 4.5 Hz, 4.5 Hz, 1H), 2.25 (s, 3H).



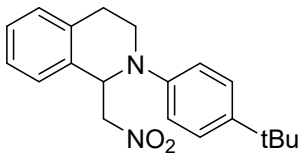
^{1}H NMR spectrum of 5g.



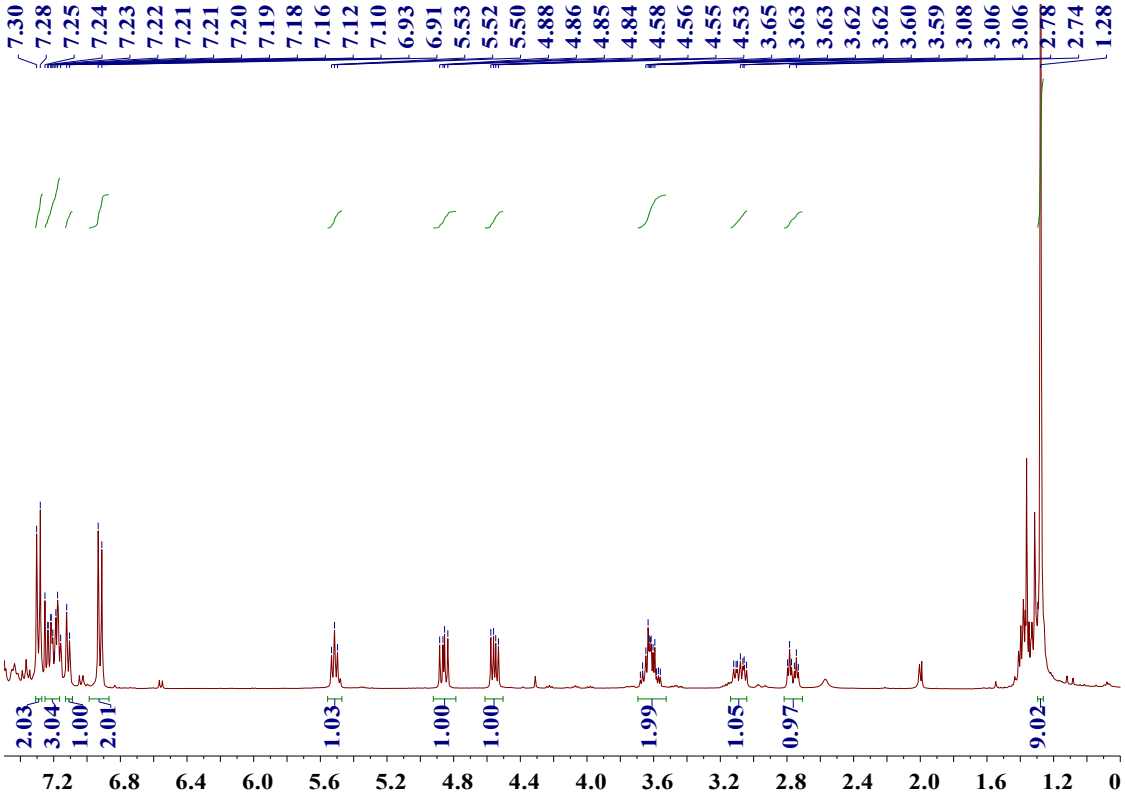
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26-7.13 (m, 4H), 6.92 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.9 Hz, 2H), 5.40-5.37 (m, 1H), 4.85 (dd, J = 11.9 Hz, 8.8 Hz, 1H), 4.58 (dd, J = 11.9 Hz, 5.8 Hz, 1H), 3.74 (s, 3H), 3.57-3.54 (m, 2H), 3.05-2.97 (m, 1H), 2.72-2.66 (m, 1H).



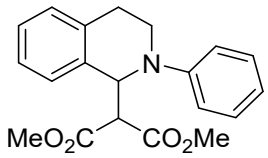
^{1}H NMR spectrum of 5h.



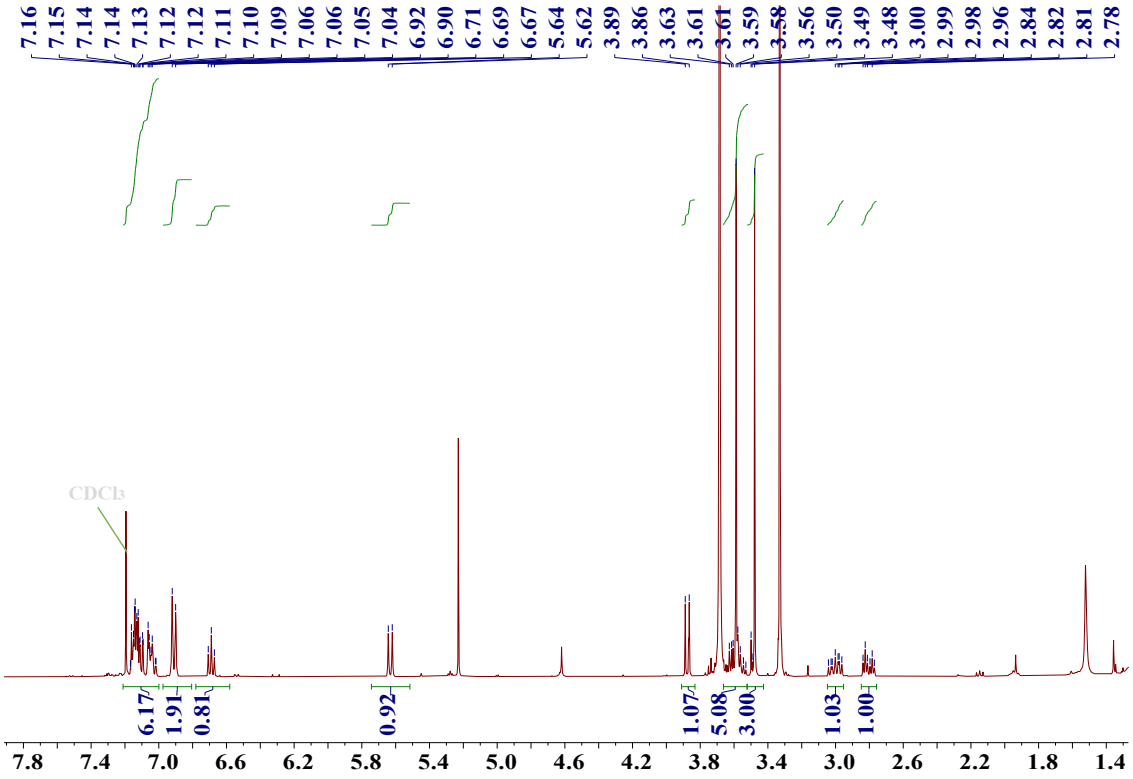
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30-7.28 (m, 2H), 7.25-7.16 (m, 3H), 7.12-7.10 (m, 1H), 6.93-6.91 (m, 2H), 5.53-5.50 (m, 1H), 4.88 (dd, J = 11.7 Hz, 7.9 Hz, 1H), 4.58 (dd, J = 11.7 Hz, 6.6 Hz, 1H), 3.67-3.58 (m, 2H), 3.12-3.04 (m, 1H), 2.78 (ddd, J = 16.4 Hz, 4.8 Hz, 4.8 Hz, 1H), 1.28 (s, 9H).



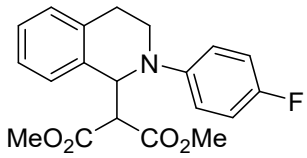
^{1}H NMR spectrum of 6a.



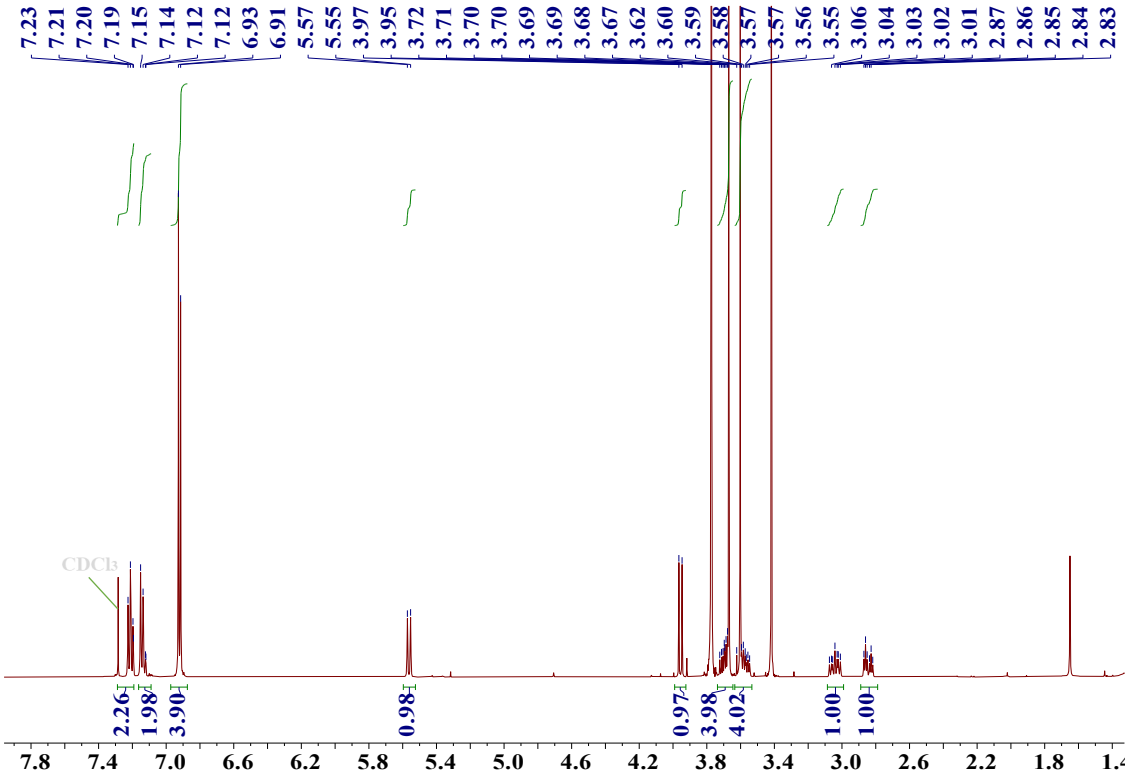
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19-7.02 (m, 6H), 6.92-6.90 (m, 2H), 6.71-6.67 (m, 1H), 5.64 (d, J = 9.4 Hz, 1H), 3.89 (d, J = 9.4 Hz, 1H), 3.63-3.53 (m, 2H), 3.59 (s, 3H), 3.48 (s, 3H), 3.04-2.96 (m, 1H), 2.84 (ddd, J = 16.5 Hz, 5.1 Hz, 5.1 Hz, 1H).



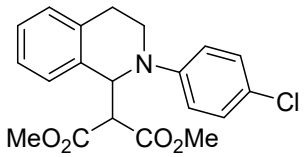
^{1}H NMR spectrum of 6b.



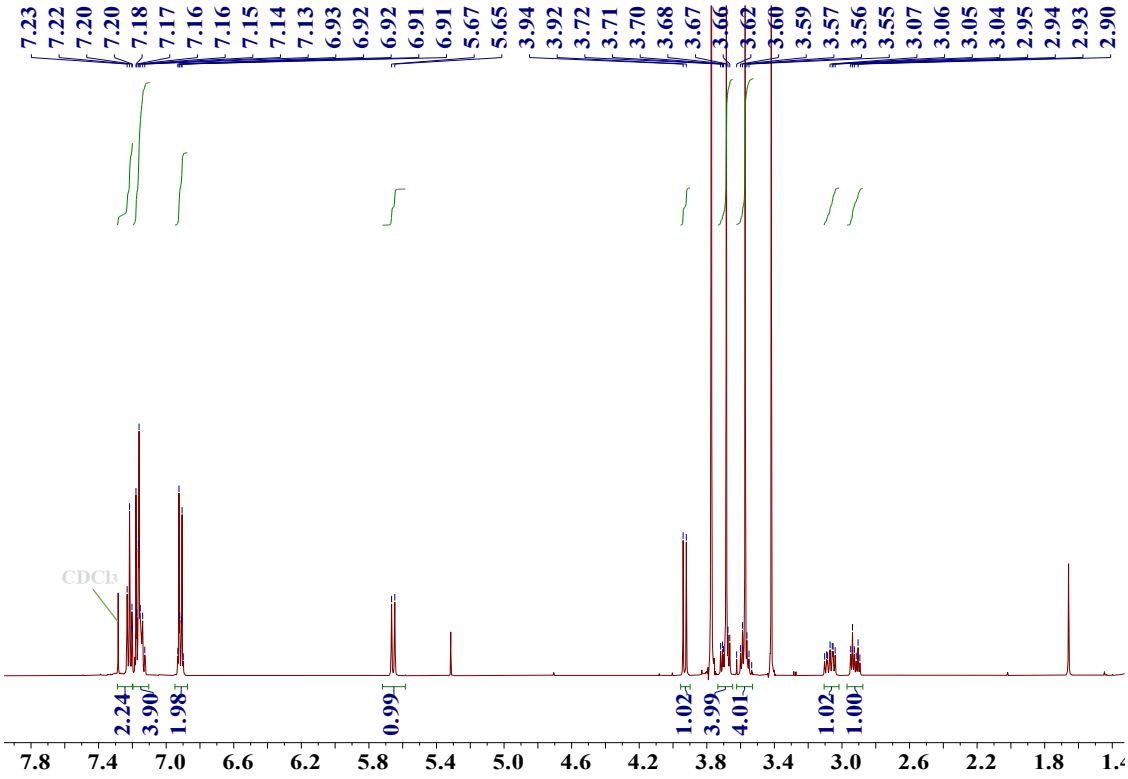
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.23-7.19 (m, 2H), 7.15-7.12 (m, 2H), 6.93 (d, J = 9.5 Hz, 4H), 5.57 (d, J = 9.5 Hz, 1H), 3.97 (d, J = 9.5 Hz, 1H), 3.72-3.68 (m, 1H), 3.67 (s, 1H), 3.62-3.55 (m, 1H), 3.60 (s, 1H), 3.07-3.01 (m, 1H), 2.87 (ddd, J = 15.0 Hz, 5.1 Hz, 5.1 Hz).



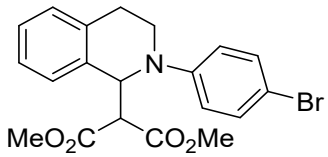
^{1}H NMR spectrum of 6c.



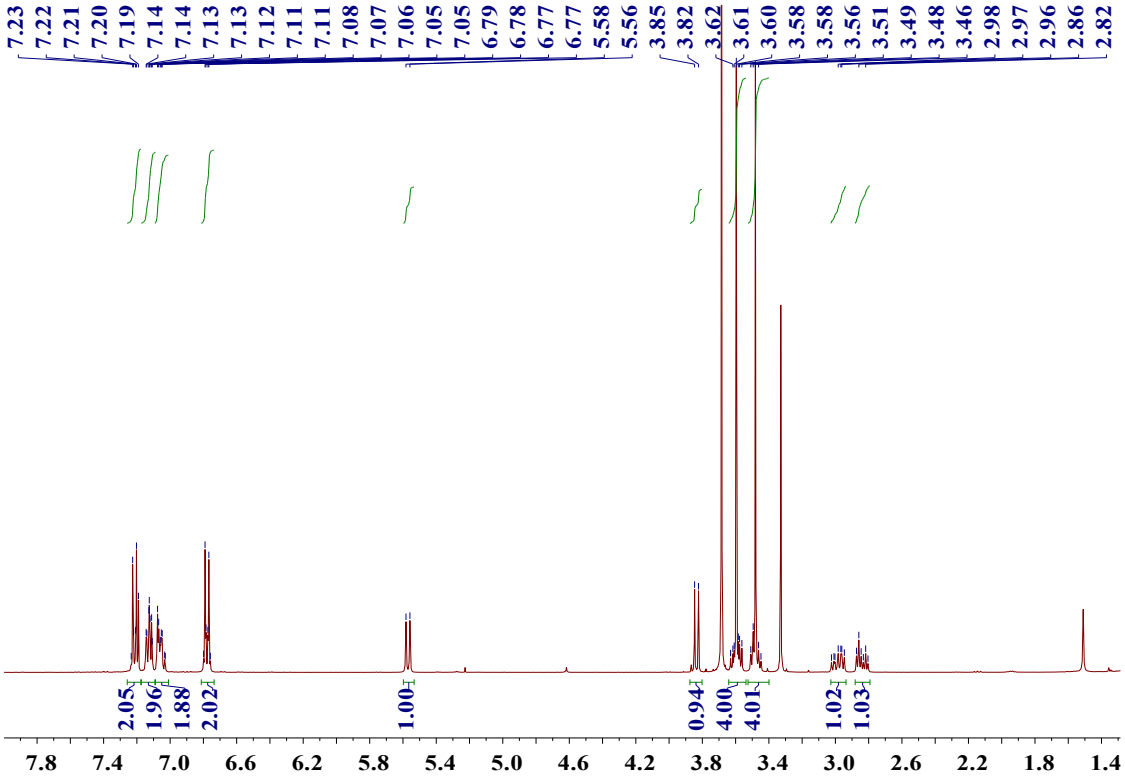
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.23-7.13 (m, 6 H), 6.93-6.90 (m, 2 H), 5.67 (d, J = 9.5 Hz, 1 H), 3.94 (d, J = 9.5 Hz, 1 H), 3.72-3.66 (m, 4 H), 3.62-3.53 (m, 4 H), 3.10 (m, 1 H), 2.95 (ddd, J = 16.4 Hz, 5.4 Hz, 5.4 Hz, 1 H).



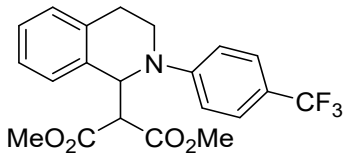
^{1}H NMR spectrum of 6d.



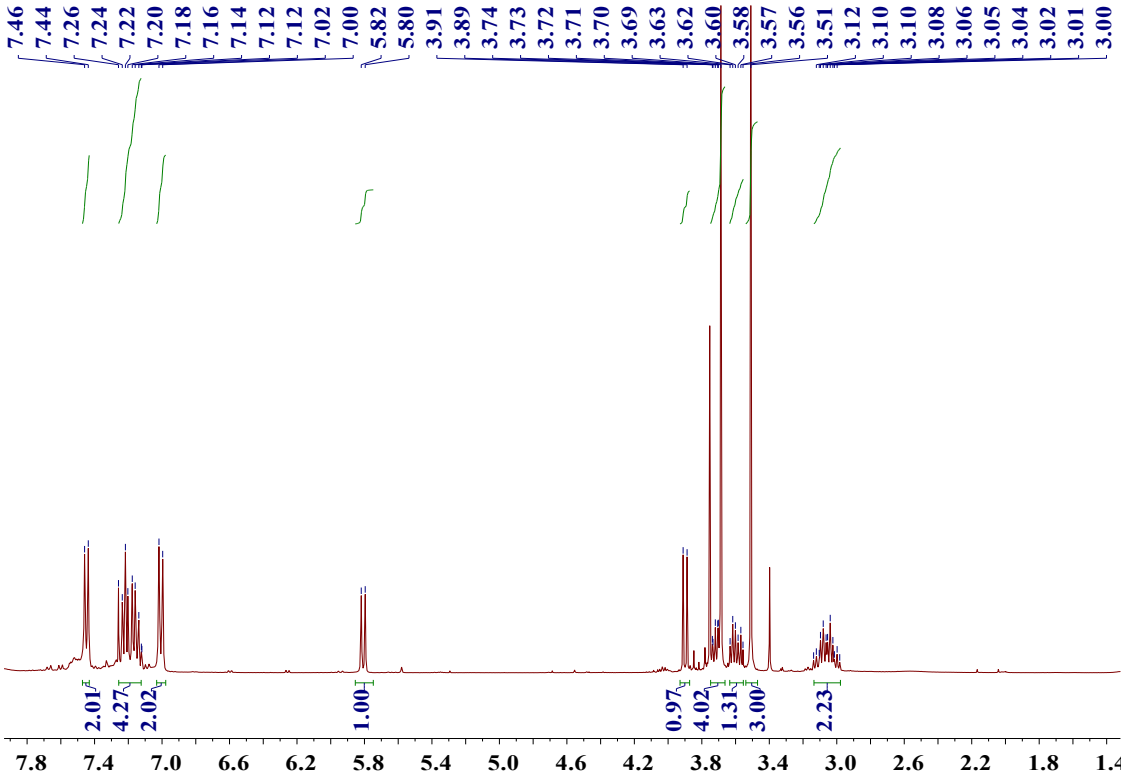
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.23-7.19 (m, 2H), 7.14-7.11 (m, 2H), 7.08-7.03 (m, 2H), 6.80 (m 2H), 5.58 (d, J = 9.4 Hz, 1H), 3.85 (d, J = 9.4 Hz, 1H), 3.60 (s, 3H), 3.63-3.56 (m, 1H), 3.48 (s, 3H), 3.51-3.45 (m, 1H), 3.02-2.95 (m, 1H), 2.87-2.80 (ddd, J = 16.4 Hz, 5.5 Hz, 5.5 Hz, 1H).



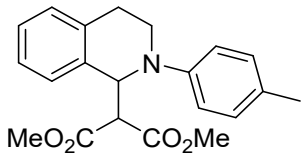
^{1}H NMR spectrum of 6e.



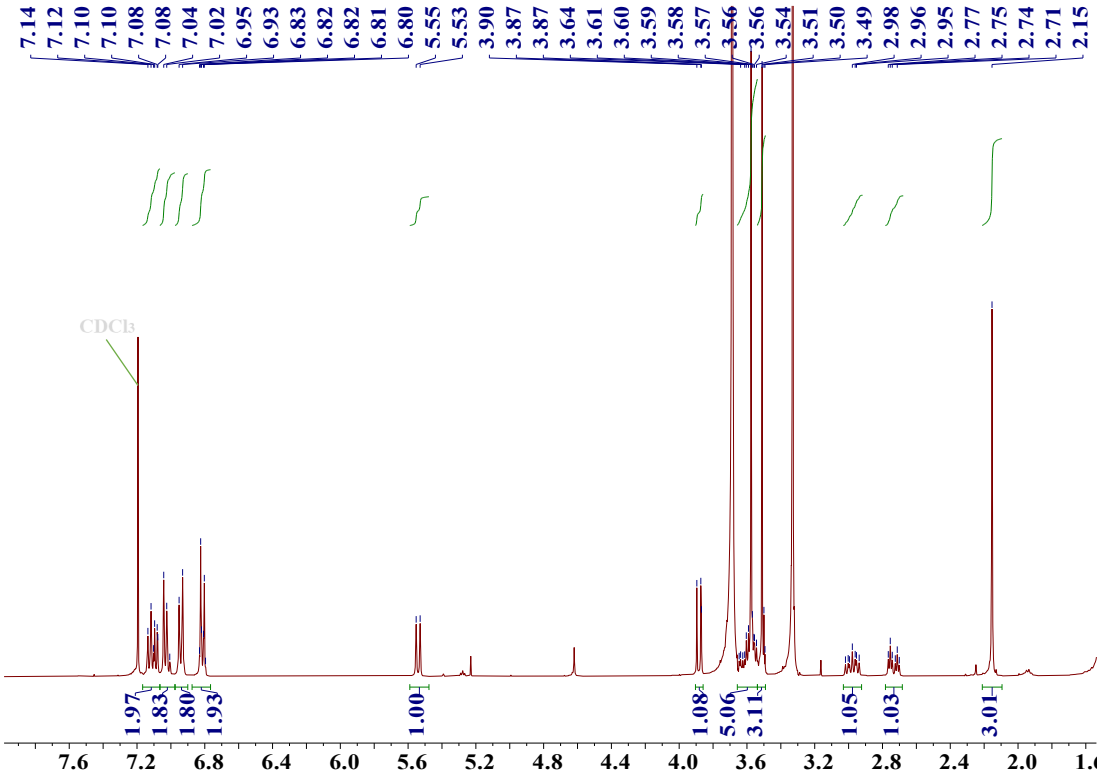
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (d, J = 9.2 Hz, 2H), 7.26-7.12 (m, 4H), 7.02 (d, J = 9.2 Hz, 2H), 5.82 (d, J = 9.1 Hz, 2H), 3.91 (d, J = 9.1 Hz, 2H), 3.74-3.70 (m, 1H), 3.69 (s, 3H), 3.63-3.56 (m, 1H), 3.51 (s, 3H), 3.14-2.98 (m, 2H).



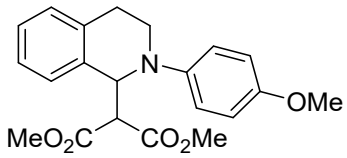
^{1}H NMR spectrum of 6f.



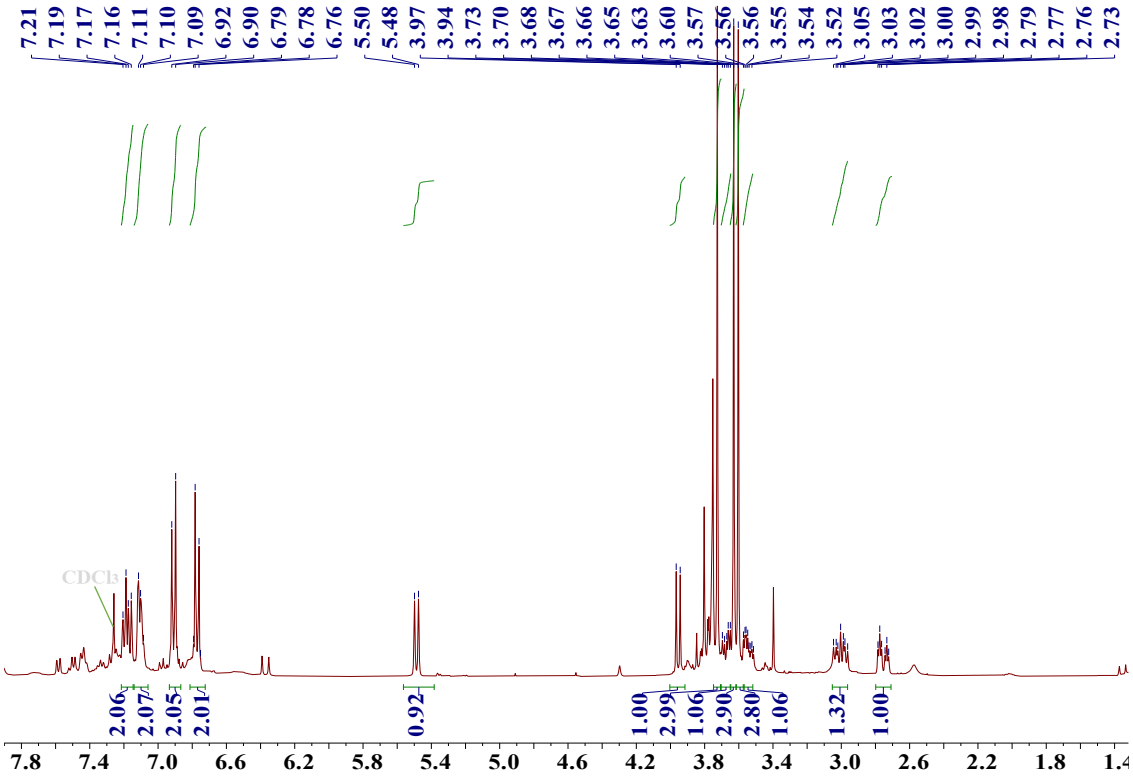
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.14-7.08 (m, 2H), 7.04-7.01 (m, 2H), 6.95-6.93 (m, 2H), 6.83-6.80 (m, 2H), 5.55 (d, J = 9.4 Hz, 1H), 3.90 (d, J = 9.4 Hz, 1H), 3.65-3.54 (m, 2H), 3.58 (s, 3H), 3.51 (s, 3H), 3.02-2.94 (m, 1H), 2.77 (ddd, J = 16.3 Hz, 4.6 Hz, 4.6 Hz, 1H), 2.15 (s, 3H).



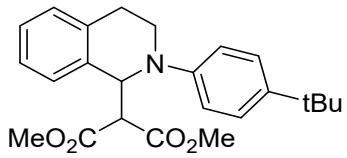
^{1}H NMR spectrum of 6g.



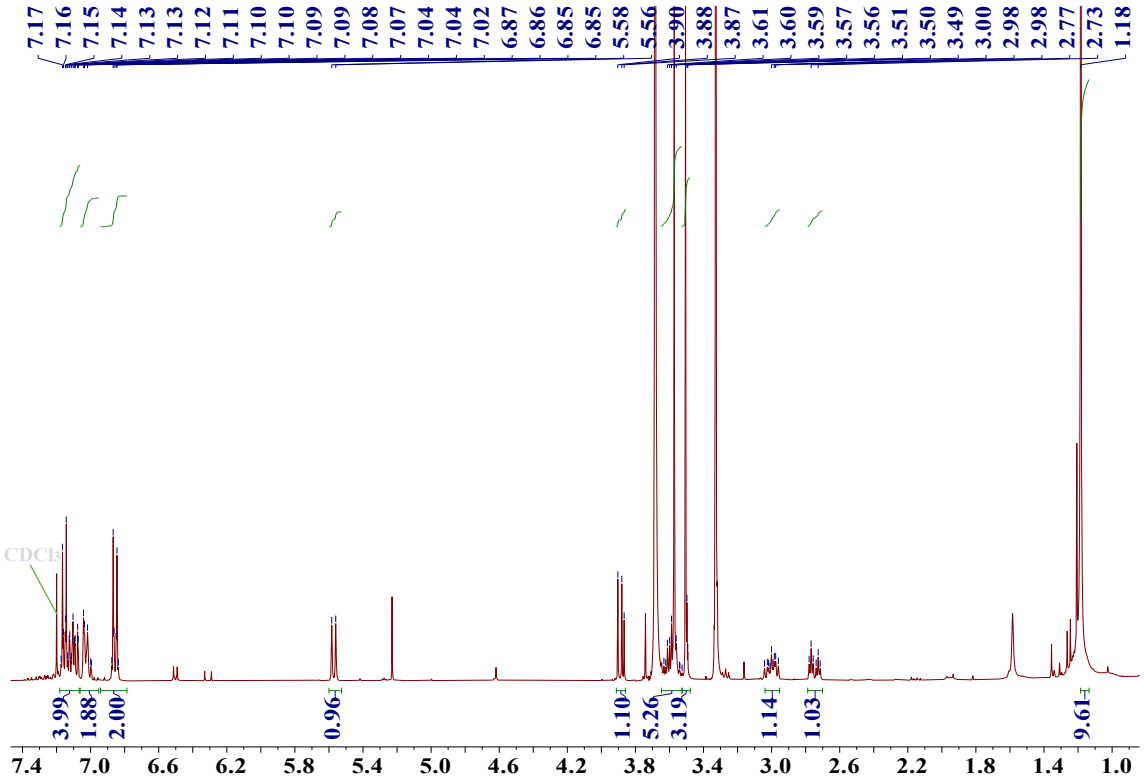
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.21-7.16 (m, 2H), 7.11-7.09 (m, 2H), 6.92-6.90 (m, 2H), 6.79-6.75 (m, 2H), 5.50 (d, J = 9.4 Hz, 1H), 3.97 (d, J = 9.4 Hz, 1H), 3.73 (s, 3H), 3.70-3.65 (m, 1H), 3.63 (s, 3H), 3.60 (s, 3H), 3.57-3.51 (m, 1H), 3.05-2.96 (m, 1H), 2.79 (ddd, J = 16.7 Hz, 4.0 Hz, 4.0 Hz, 1H).



^{1}H NMR spectrum of 6h.



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.17-7.07 (m, 4H), 7.04-7.00 (m, 2H), 6.88-6.84 (m, 2H), 5.58 (d, J = 9.4 Hz, 1H), 3.90 (d, J = 9.4 Hz, 1H), 3.63-3.54 (m, 2H), 3.57 (s, 3H), 3.51 (s, 1H), 3.04-2.96 (m,1H), 2.78-2.71 (ddd, J = 16.7 Hz, 4.0 Hz, 4.0 Hz, 1H), 1.18 (s, 9H).



7. References.

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