Analysis of Organophotocatalyst-Substrate Interactions for Understanding Triplet–Triplet Back Energy Transfer

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Supporting Information

General Considerations

General Reagent Information

2,2,2-Trifluoroethanol, 1,4-dioxane was purchased from Sigma-Aldrich in sure-seal bottles. All commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, Combi blocks or TCI companies and used without further purification. Flash column chromatography was performed using ZEOCHEM ZEOprep silica gel 60 (60-200 mesh).

General Analytical Information

The synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, and 564 MHz for ^{19}F NMR). Copies of ^{1}H and ^{13}C spectra can be found at the end of the Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^{1}H decoupling. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Nicolet 6700 Thermo Scientific FT-IR spectrometer. Reactions were monitored by thin layer chromatography and gas chromatography (GC). Mass spectral data of all unknown compounds were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high-resolution mass spectrometer. Melting points of unknown compounds were recorded on a Stuart SMP30 apparatus. Single crystal X-ray diffraction data were collected in Bruker-AXS SMART BREEZE X-ray diffractometers. The structures were solved with direct methods using the SHELXL programs.

Reaction Screening

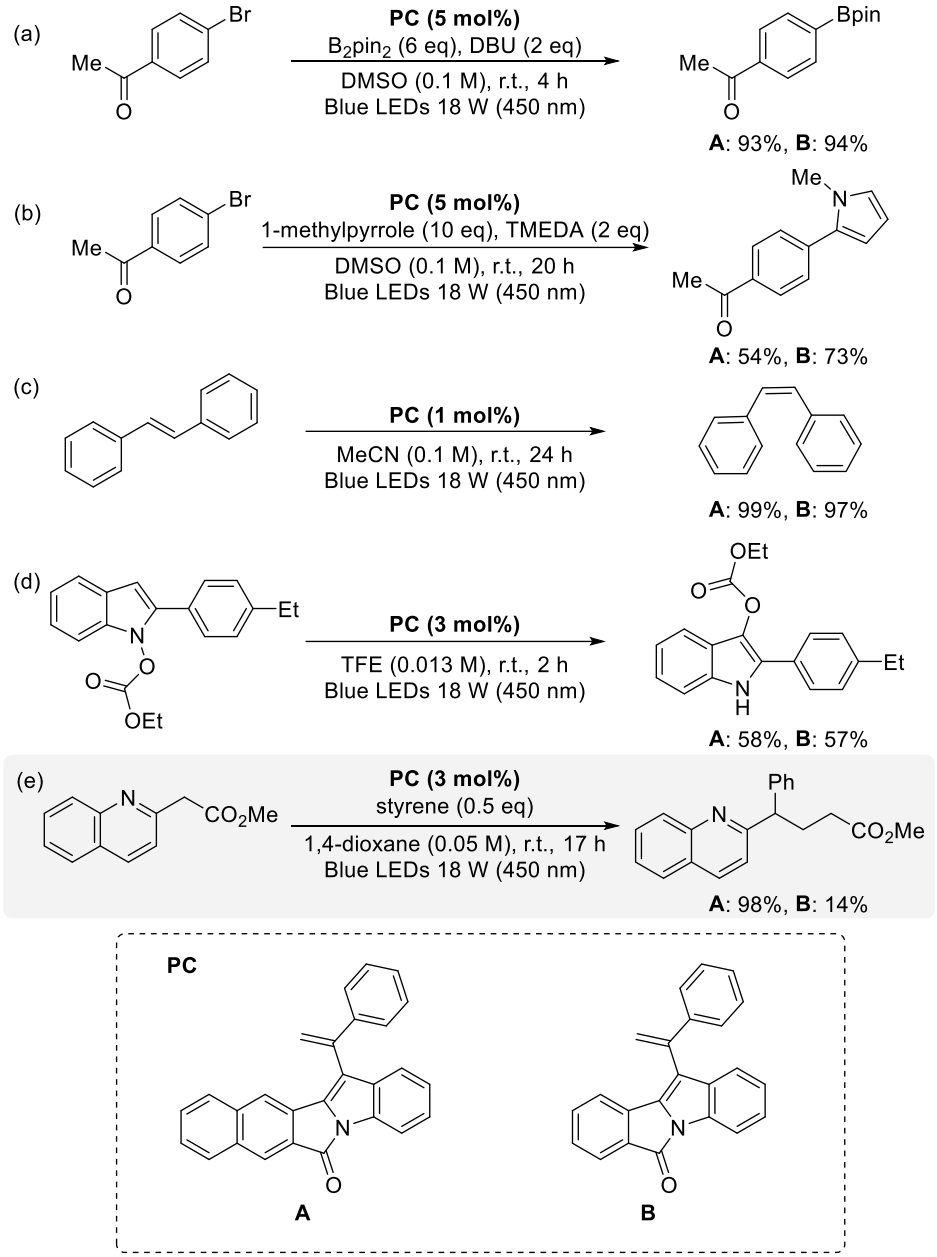


Figure S1. All the reactions were carried out on a 0.1 mmol scale under an argon atmosphere. Yields were determined by ^{1}H NMR spectrometry using dibromomethane, 1,3,5-trimethoxy benzene, bromoform as internal standards.

Experimental Details

Steady-state UV-vis Absorption Measurements. UV−vis absorption spectra were collected on an Agilent, Cary 300 spectrophotometer at 298 K. Sample solutions were prepared prior to measurements at a concentration of 10 μM for **A** or **B,** and 5.0 mM for **5** in 1,4-dioxane, unless otherwise stated. The solution was transferred to a quartz cell (Hellma, beam path length = 1 cm) for the measurements.

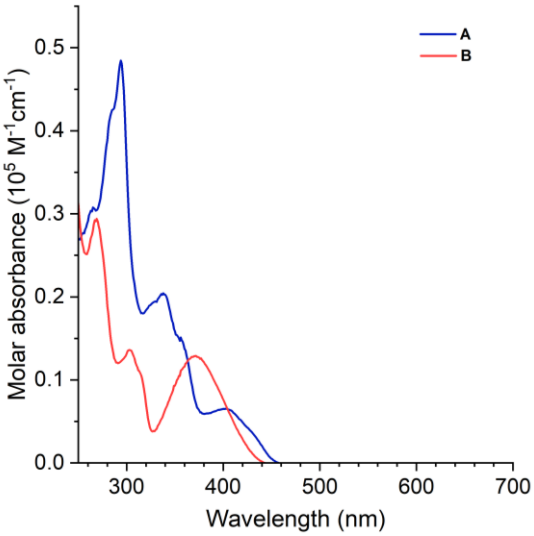


Figure S2. UV-vis absorption spectra of **A** and **B** recorded in 1,4-dioxane (10 μM) at 298 K.

Steady-State Photoluminescence Measurements. Photoluminescence spectra were obtained at 298 K using a Photon Technology International, Quanta Master 400 scanning spectrofluorometer. The solutions used for the steady-state UV−vis absorption studies were used for the photoluminescence measurements. A quartz cell (Hellma, beam path length = 1.0 cm) was used. The excitation wavelengths were 341 nm for **A** and 376 nm for **B**. The spectra were recorded in the emission range 400−700 nm.

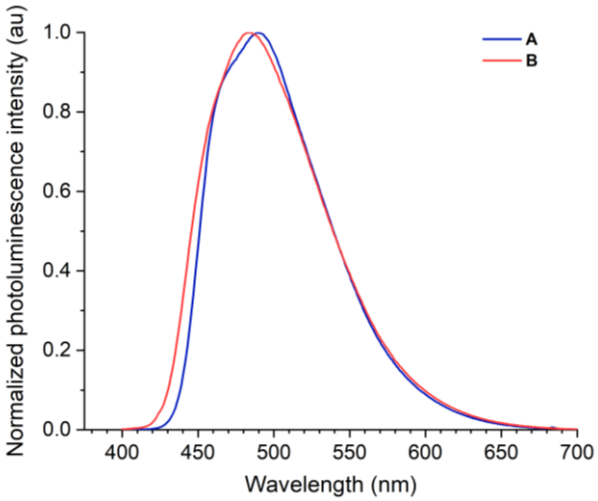


Figure S3. Photoluminescence spectra of **A** and **B** recorded in 1,4-dioxane (10 μM) at 298 K. Excitation wavelengths = 341 nm (**A**) and 376 nm (**B**).

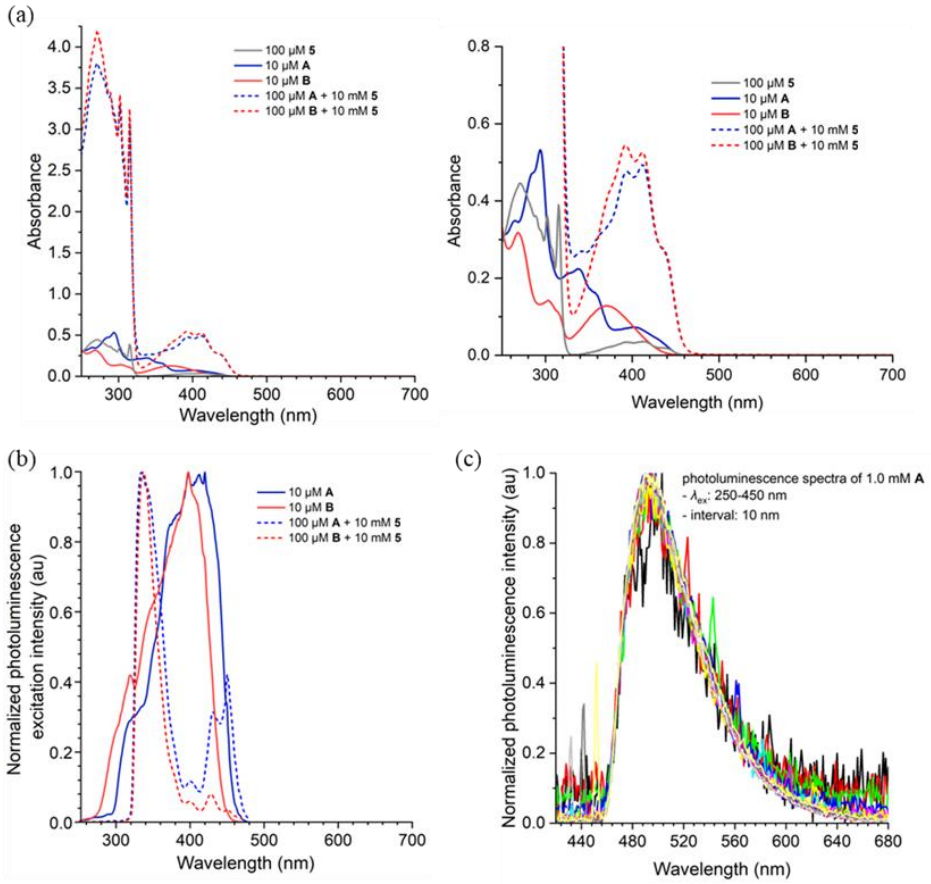
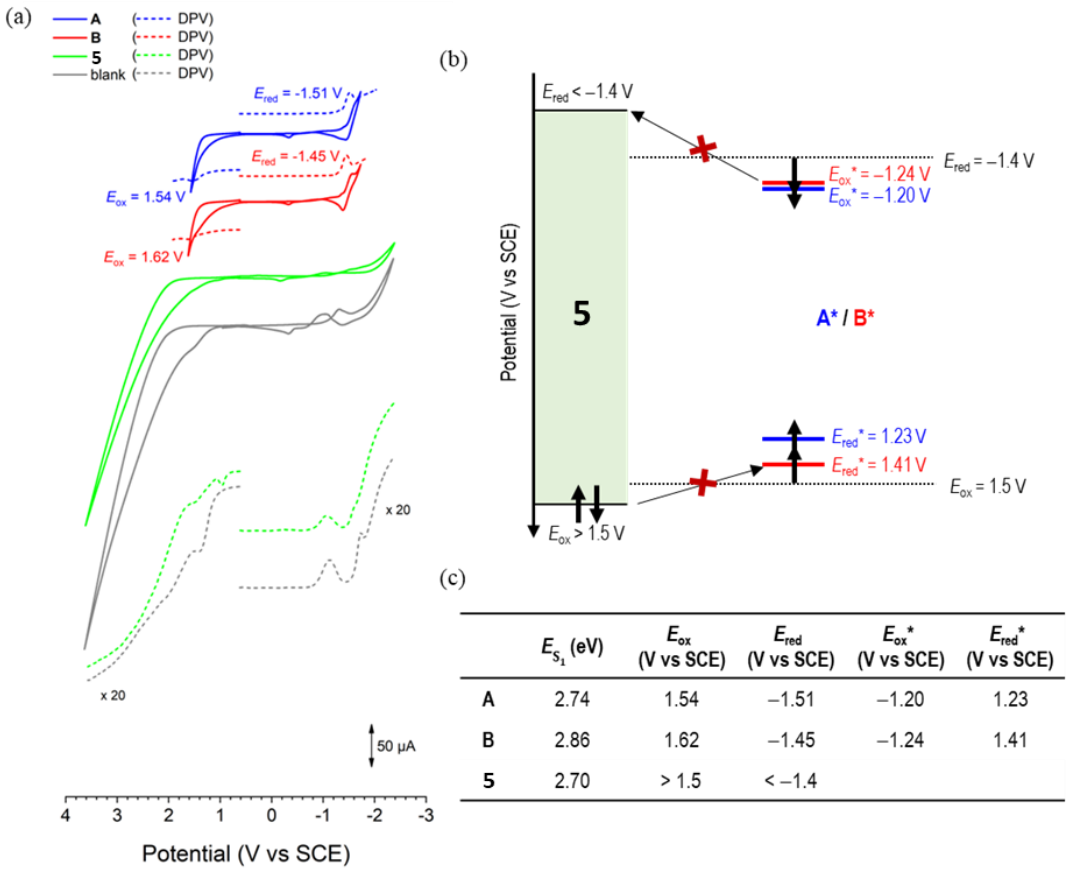


Figure S4. (a) The solid lines are the UV–vis absorption spectra of 10 μM **A**, 10 μM **B**, and 100 μM **5** recorded in 1,4-dioxane at 298 K. The dotted lines are the UV–vis absorption spectra of 100 μM **A** and **B** upon the addition 10 mM **5**. A magnified view is shown on the right. (b) The solid lines are the photoluminescence excitation spectra of **A** and **B** recorded in 1,4-

dioxane (10 μM) at 298 K. The dotted lines are the photoluminescence excitation spectra of 100 μM **A** and **B** after the addition 10 mM **5**. (c) Variable-excitation-wavelength photoluminescence spectra of 1.0 mM **A** with added 100 mM **5** in 1,4-dioxane (λ_{ex} = 280–450 nm, interval: 10 nm).

Determination of Photoluminescence Lifetime. Photoluminescence decay traces were acquired on the basis of time-correlated single-photon counting (TCSPC) techniques, using a PicoQuant, FluoTime 200 instrument after pulsed laser excitation at 377 (pulse duration = 25 ps). Transient photon signals were collected at λ_{obs} = 489 nm for **A** and 485 nm for **B** through an automated motorized monochromator. The photon acquisition was terminated when the accumulated photon count reached 10^5. Photoluminescence decay traces were analyzed using a monoexponential decay models embedded in the OriginLab, OriginPro 2018 software.

Electrochemical Characterization. The electrochemical properties of **A**, **B,** and **5** were characterized by standard cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. CV and DPV experiments were carried out using a CH Instruments, CHI630 B potentiostat using a three-electrode-cell assembly. A Pt disk and a Pt wire were used as the working and the counter electrodes, respectively. An $Ag/AgNO_3$ couple was used as a pseudo reference electrode. Measurements were carried out in Ar-saturated tetrahydrofuran (THF) using 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at scan rates of 0.1 V s^{-1} (CV) or 4.0 mV s^{-1} (DPV). A ferrocenium/ferrocene couple was employed as the external reference. A blank scan was performed in the same range in order to assess the validity of the reduction potential. The excited-state oxidation (E^*_{ox}) and reduction (E^*_{red}) potentials of **A*** and **B*** were calculated from the ground-state redox potentials and the singlet-state energy which was determined by optical bandgap from the onset of UV-vis absorption spectrum (2.74 and 2.86 eV). The ground-state redox potentials were determined for 2.0 mM **A**, **B,** and **5** by CV and DPV. Figure S5 displays the cyclic and differential pulse voltammograms of **A**, **B,** and **5**. The inset figure shows the thermodynamic disallowance for the oxidative and reductive quenching of **A*** or **B*** by **5**, and the table lists the singlet-state energy (for **A, B** and **5**), the ground-state (for **A**, **B,** and **5**), and the excited-state (for **A** and **B**) potentials.



(c)

	E_{S_1} (eV)	E_{ox} (V vs SCE)	E_{red} (V vs SCE)	E_{ox}* (V vs SCE)	E_{red}* (V vs SCE)
A	2.74	1.54	–1.51	–1.20	1.23
B	2.86	1.62	–1.45	–1.24	1.41
5	2.70	> 1.5	< –1.4		

Figure S5. (a) cyclic (solid lines) and differential pulse voltammograms (dotted lines) of 2.0 mM **A** (blue), **B** (red), and **5** (green) obtained in Ar-saturated THF. The grey line is an electrochemical response of a blank THF solution. (b) Comparison of electrochemical potentials of **A**, **B**, and **5**. (c) Summary of the ground- and excited-state redox potentials. It is inferred from Figure S5b that the excited-state organoPCs cannot be quenched by **5** through electron transfer. Therefore, the fluorescence quenching of organoPCs by **5** should be ascribed to EnT.

Photoluminescence Quenching Experiments. Photoluminescence quenching experiments were performed for 1,4-dioxane solution containing 1.0 mM **A** or **B** with added **5** (0–100 mM). A photoexcitation at a wavelength of 300 nm was used, as it could not photoexcite **5** (Figure S6). The photoluminescence changes were quantified by integrating fluorescence spectra over the entire emission region, which were subsequently analyzed using the Benesi–Hildebrand and the Stern–Volmer equations and described in the main text. The photoluminescence quenching of organoPCs was further monitored by the transient photoluminescence experiments for 1.0 mM **A** or **B** (1,4-dioxane) performed in the absence and presence of **5**. The

quenching rate was quantitated as $1/\tau - 1/\tau_0$, where τ and τ_0 are the photoluminescence lifetime of **A** or **B** in the presence and absence of the **5**, respectively.

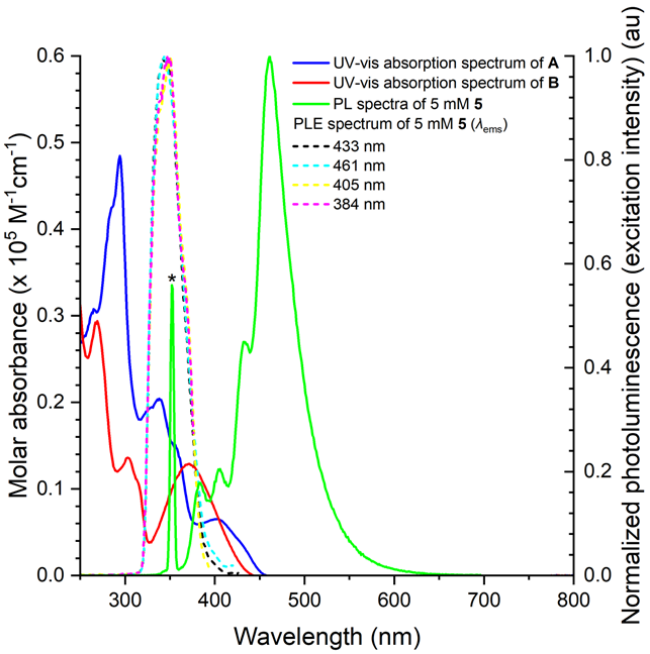


Figure S6. Comparison of the UV-vis absorption spectra of **A** and **B** (10 μM in 1,4-dioxane), the normalized photoluminescence (PL), and photoluminescence excitation (PLE) spectra of **5** (5 mM in 1,4-dioxane) to optimize of the PL titration experimental conditions. The peak marked with an asterisk (*) is the excitation beam.

Photoluminescence quenching experiments were further performed for 1,4-dioxane solution containing increased concentrations (100–500 μM) of **A** or **B** in the absence of **5**. Photoexcitation wavelengths were 341 nm for **A** and 376 nm for **B**. As shown in Figure S7, the photoluminescence intensity decreased with the concentration of organoPC. The fluorescence decreases were quantified by integrating fluorescence spectra over the entire emission region, which were subsequently analyzed using the Stern–Volmer equation $I/I' = 1 + k_{sq} \cdot \tau_0 \cdot$[**organoPC**] where I and I' are integrated fluorescence intensities obtained at concentrations of 100 μM and 200–500 μM, respectively, k_{sq} is the bimolecular rate constant for fluorescence self-quenching, τ_0 is the fluorescence lifetime of the organoPC, and [**organoPC**] is the molar concentration of organoPC.

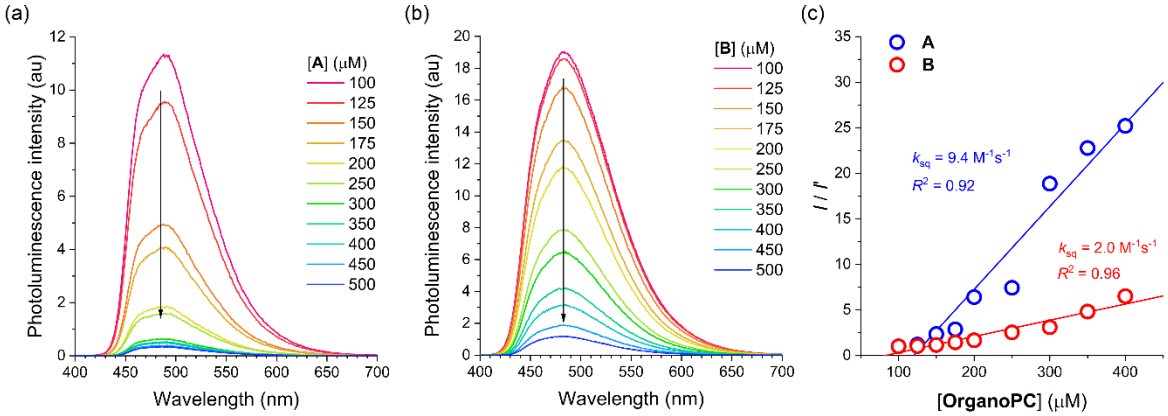
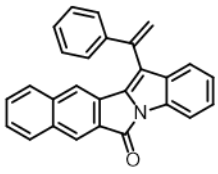
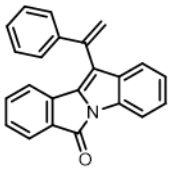
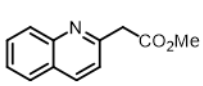
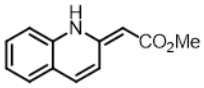


Figure S7. Photoluminescence spectra of increased concentrations (100–500 μM) of **A** (a) and **B** (b) acquired in deaerated 1,4-dioxane. (c) Stern–Volmer plots for the photoluminescence quenching isotherms for **A** (blue) and **B** (red). See the above text for the details about the Stern–Volmer analyses.

Computational details

Geometry optimization was performed using the Becke's three-parameter exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP)[S1] and the 6–311+G(d,p)[S2] basis set. Frequency calculations were subsequently performed to assess the stability of the convergence. Time-dependent density functional theory (TD–DFT) calculations were carried out for the optimized geometries using the same functional and basis sets. Twenty states were considered for the TD–DFT calculations. Geometry optimization and single-point calculations were performed using the Gaussian 09 program.[S3] The TD–DFT calculation results for initial triplet states are summarized in Table S1 and Figure S8.

Table S1. Calculated electronic transition energies (eV) of organoPCs and **5**.

	 A	 B	 5	 quinoid form of 5
T_1	0.83	0.76	1.60	1.44
T_2			3.65	2.83
T_3			3.69	
T_4			3.82	

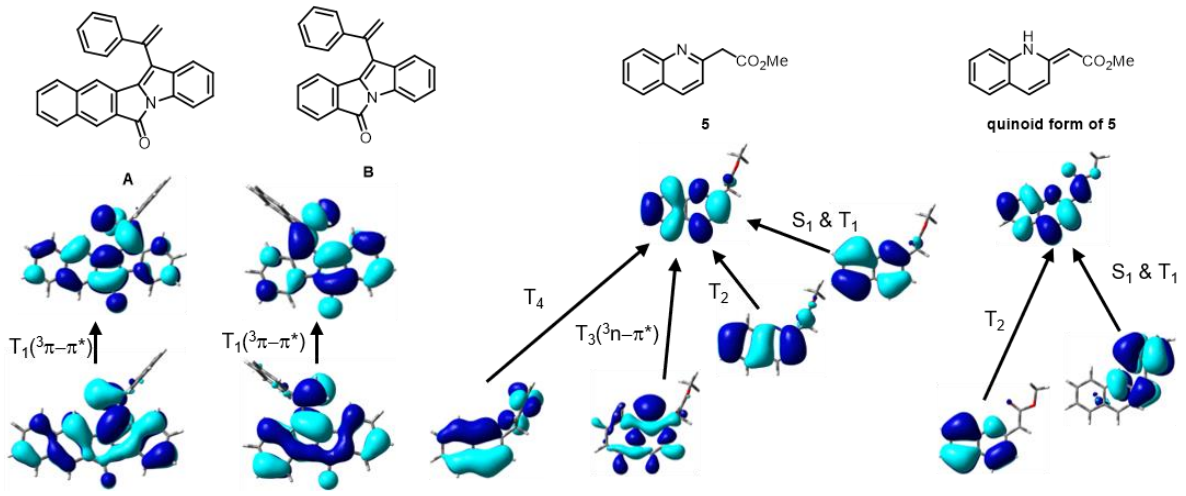
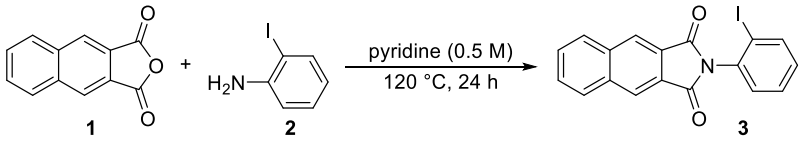


Figure S8. Isosurface plots of the molecular orbitals that participate in the electronic transition for organoPCs, **5** and the quinoid form of **5**.

Experimental Procedure

Procedure for the synthesis of 13-(1-phenylvinyl)-6H-benzo[5,6]isoindolo[2,1-a]indol-6-one (A)[S4]

Synthesis of 2-(2-iodophenyl)-1H-benzo[f]isoindole-1,3(2H)-dione (3)

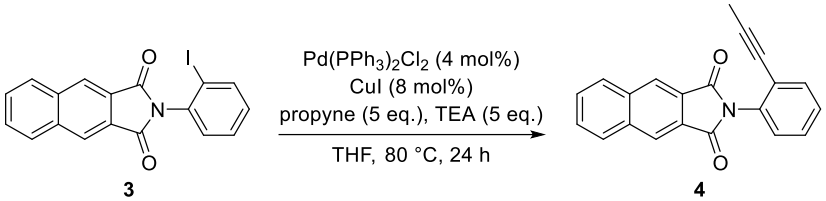


1 2 3

An oven-dried round-bottom flask equipped with a magnetic stir bar was charged with a 2,3-naphthalic anhydride **1** (1.0 eq.), 2-iodoaniline **2** (1.0 eq.), and pyridine (0.5 M). Then, the mixture was stirred at 120 ˚C for 24 h. After the reaction had completed, the reaction was quenched with NH_4Cl and extracted with DCM. The organic layer was washed with NH_4Cl and brine, dried over $MgSO_4$ and the mixture was concentrated in vacuo to give a crude residue. Hexanes were added to the crude, and then it was filtered with cold hexanes to give the product, **3** (white solid, 80%).

3: white solid; melting point 216~218 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.50 (s, 2H), 8.12 (dd, *J* = 6.1, 3.3 Hz, 2H), 8.01 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.75 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.53 (ddd, *J* = 7.8, 7.6, 1.3 Hz, 1H), 7.37 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.22 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 166.55, 140.12, 135.93, 135.68, 131.23, 130.63, 130.37, 129.68, 129.61, 127.80, 125.87, 99.04; **HRMS** (ESI) *m/z*: $[M]^+$ calc. for $C_{18}H_{10}INO_2$, 398.9756; found, 398.9758; **IR (neat)**: ν_{max} = 3059, 2353, 1717, 1372 cm^{-1}; ***R*$_f$** 0.32 (Hex/EtOAc, 4/1).

Synthesis of 2-(2-(prop-1-yn-1-yl)phenyl)-1H-benzo[f]isoindole-1,3(2H)-dione (4)



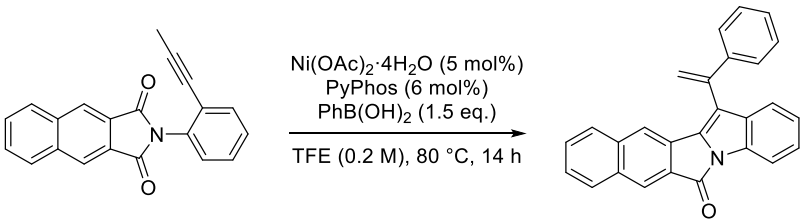
3 4

A pressure vessel equipped with a magnetic stir bar was charged **3** (1.0 eq.), $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (8 mol%), TEA (5.0 eq.), and THF (1.0 M) under argon. Then, argon was bubbled

through the reaction mixture for 10 min, this was followed by the addition of propyne (1.0 M in DMF, 5.0 eq.). Then, the mixture was stirred at 80 ˚C for 24 h. After the reaction had completed, the mixture was concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give the product, **4** (white solid, 78%).

4: white solid; melting point 212~214 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.48 (s, 2H), 8.11 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.74 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.59 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.44 (ddd, *J* = 7.7, 7.4, 1.6 Hz, 1H), 7.41 (ddd, *J* = 7.7, 7.5, 1.5 Hz, 1H), 7.34 (dd, *J* = 7.4, 1.5 Hz, 1H), 1.83 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.00, 135.87, 133.68, 133.35, 130.56, 129.51, 129.29, 129.05, 128.64, 128.04, 125.48, 124.12, 91.68, 76.00, 4.63; **HRMS** (ESI) *m/z*: $[M]^+$ calc. for $C_{21}H_{13}NO_2$, 311.0946; found, 311.0944; **IR (neat)**: ν_{max} = 3028, 2251, 1718, 1372 cm^{-1}; ***R*$_f$** 0.32 (Hex/EtOAc, 4/1).

Synthesis of A

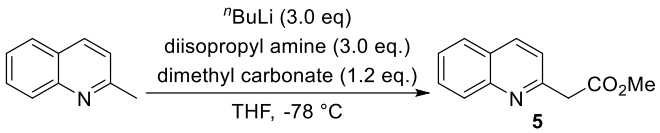


4 **A**

An oven-dried 100 mL round-bottom flask equipped with a magnetic stir bar was charged with **4** (1.0 eq.), Pyphos(6 mol%), $Ni(OAc)_2{\cdot}4H_2O$ (5 mol%), and phenyl boronic acid (1.5 eq.), and TFE (0.2 M) in a glove box. Then, the mixture was stirred at 80 ℃ for 14 h. Upon completion of the reaction, the reaction mixture was cooled to room temperature and filtered. The filter cake was washed with cold methanol with three times, then purified by silica gel column chromatography to give the product, **A** (yellow solid, 80%).

A: yellow solid; melting point 203~206 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.51 – 7.43 (m, 3H), 7.43 – 7.38 (m, 3H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.34 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.17 (dd, *J* = 7.9, 7.3 Hz, 1H), 6.94 (s, 1H), 6.01 (d, *J* = 1.3 Hz, 1H), 5.84 (d, *J* = 1.3 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.73, 140.94, 140.49, 136.26, 135.82, 134.78, 133.45, 132.83, 131.84, 130.17, 129.20, 129.16, 129.03, 128.92, 128.59, 127.91, 127.35, 126.49, 126.41, 124.39, 122.43, 121.99, 118.92, 117.79, 113.90; **UV-vis (1,4-dioxane)**: λ_{max} (ε) = 403 nm (6540); **HRMS** (ESI) *m/z*: $[M]^+$ calc. for $C_{27}H_{17}NO$, 371.1310; found, 371.1312; **IR (neat)**: ν_{max} = 3054, 1731, 1636, 1606 cm^{-1}; ***R*$_f$** 0.59 (Hex/EtOAc, 4/1).

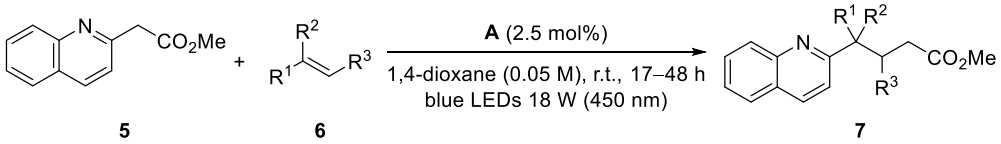
Procedure for the synthesis of methyl 2-(quinolin-2-yl)acetate (5)



5

Following the reported procedure,[S5] an oven-dried 100 mL round-bottom flask equipped with a magnetic stir bar was charged with to a diisopropyl amine (2.0 eq.) and dry THF (1.0 M) under argon atmosphere at 0 ºC. Then, ^{n}BuLi (2.0 M in hexanes, 2.0 eq.) was added to the solution and the solution was stirred at this temperature for 15 min. A solution of 2-methylquinoline (1.0 eq.) in dry THF (0.5 M) was added dropwise to the LDA solution at -78 ºC. The reaction mixture was stirred at this temperature for 2 h. After this time, dimethyl carbonate (1.2 eq.) was added to the reaction mixture quickly. After stirring at -78 ºC for 15 min, the reaction mixture was quenched by water and warmed to room temperature. The mixture was diluted by water (50 mL) and extracted with EtOAc (100 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by flash column chromatography to give the product, **5**. The analytical data of the synthesized compound (**5**) matched with reported literature data.[S5]

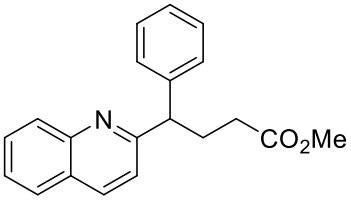
General procedure for [2+2] cycloaddition reaction[S6]



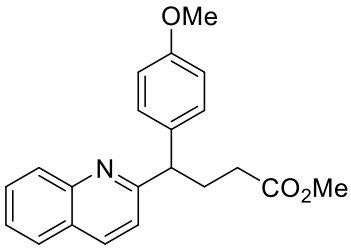
5 6 7

An oven-dried reusable test tube equipped with a magnetic stir bar was charged with a **5** (1.0 eq.) then was brought into a glove box. An alkene derivative **6** (5.0 eq.), **A** (2.5 mol%) and 1,4-dioxane (0.05 M) were added to the reaction mixture in the glove box and the tube was sealed with a silicon septum screw cap. The tube placed under the light from blue LEDs (18 W, 450 nm) at room temperature. The reaction progress was monitored by thin layer chromatography or gas chromatography (GC). Upon completion of the reaction, the mixture was concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give the corresponding 2+2 cycloaddition product, **7**.

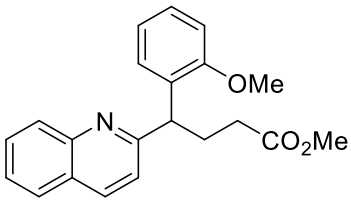
Analytic Data for Synthesized Compounds



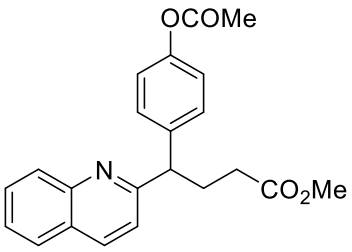
methyl 4-phenyl-4-(quinolin-2-yl)butanoate, **7a**: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.70 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.48 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.30 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 4.32 (t, *J* = 7.8 Hz, 1H), 3.64 (s, 3H), 2.83 – 2.75 (m, 1H), 2.61 – 2.52 (m, 1H), 2.47 – 2.35 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.05, 163.05, 147.88, 142.94, 136.39, 129.52, 129.40, 128.74, 128.34, 127.56, 127.00, 126.85, 126.11, 121.47, 53.43, 51.59, 32.54, 29.86; **IR (neat)**: ν_{max} = 3026, 2948, 1731, 1597, 1427, 1238, 1151 cm^{-1}; ***R*$_f$** 0.40 (Hex/EtOAc, 4/1).



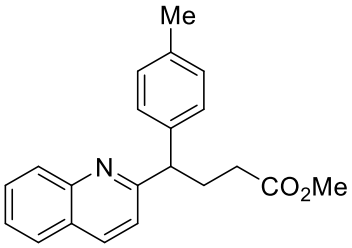
methyl 4-(4-methoxyphenyl)-4-(quinolin-2-yl)butanoate, **7b**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.68 (dd, *J* = 8.6, 6.9 Hz, 1H), 7.46 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.26 (t, *J* = 7.7 Hz, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 2.79 – 2.67 (m, 1H), 2.57 – 2.48 (m, 1H), 2.45 – 2.34 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.02, 163.38, 158.46, 147.81, 136.30, 134.97, 129.42, 129.31, 129.22, 127.51, 126.92, 126.00, 121.35, 114.08, 55.25, 52.54, 51.50, 32.49, 29.94; **IR (neat)**: ν_{max} = 2950, 2836, 1731, 1600, 1508, 1436, 1245, 1176, 1034 cm^{-1}; ***R*$_f$** 0.30 (Hex/EtOAc, 4/1).



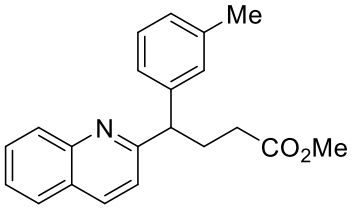
methyl 4-(2-methoxyphenyl)-4-(quinolin-2-yl)butanoate, **7c**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.68 (dd, *J* = 8.4, 6.9 Hz, 1H), 7.47 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.19 (ddd, *J* = 8.2, 7.4 Hz, 1H), 6.90 (dd, *J* = 7.6, 7.4 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 4.82 (t, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 3.63 (s, 3H), 2.83 – 2.72 (m, 1H), 2.52 – 2.44 (m, 1H), 2.45 – 2.39 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.34, 163.45, 157.17, 147.93, 136.00, 131.49, 129.58, 129.18, 128.88, 127.78, 127.53, 127.00, 125.91, 122.04, 120.93, 110.73, 55.62, 51.55, 45.06, 32.70, 29.14; **IR (neat)**: ν_{max} = 2948, 2837, 1731, 1598, 1436, 1239, 1150, 1027 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{21}H_{21}NO_3$ [M+] 335.1521, found 335.1523; ***R*$_f$** 0.36 (Hex/EtOAc, 4/1).



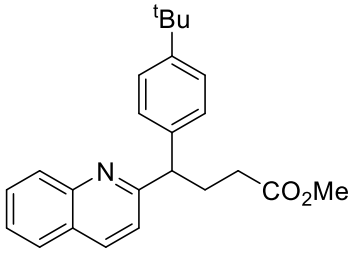
methyl 4-(4-acetoxyphenyl)-4-(quinolin-2-yl)butanoate **7d**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.69 (dd, *J* = 8.4, 6.9 Hz, 1H), 7.49 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 4.29 (t, *J* = 7.7 Hz, 1H), 3.63 (s, 3H), 2.78 – 2.69 (m, 1H), 2.57 – 2.46 (m, 1H), 2.42 – 2.32 (m, 2H), 2.26 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.06, 169.61, 162.75, 149.59, 147.95, 140.53, 136.58, 129.55, 129.53, 129.33, 127.65, 127.10, 126.25, 121.78, 121.54, 52.85, 51.69, 32.53, 30.05, 21.30; **IR (neat)**: ν_{max} = 2950, 1754, 1731, 1502, 1194, 1166 cm^{-1}; **HRMS m/z (EI) calc. for $C_{22}H_{21}NO_4$ [M+] 363.1471, found 363.1473; R_f 0.17 (Hex/EtOAc, 4/1).**



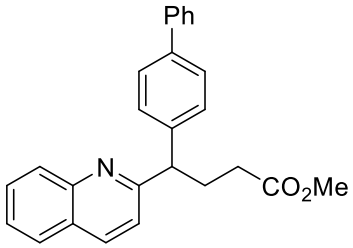
methyl 4-(quinolin-2-yl)-4-(p-tolyl)butanoate, **7e**: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.70 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.48 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.30 (t, *J* = 7.7 Hz, 1H), 3.65 (s, 3H), 2.83 – 2.75 (m, 1H), 2.63 – 2.51 (m, 1H), 2.45 – 2.40 (m, 2H), 2.32 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.03, 163.27, 147.83, 139.89, 136.31, 136.31, 129.46, 129.40, 129.31, 128.16, 127.51, 126.94, 126.01, 121.38, 53.00, 51.51, 32.52, 29.81, 21.07; **IR (neat)**: ν_{max} = 3019, 2949, 1735, 1600, 1503, 1435, 1239, 1153 cm^{-1}; R_f 0.44 (Hex/EtOAc, 4/1).



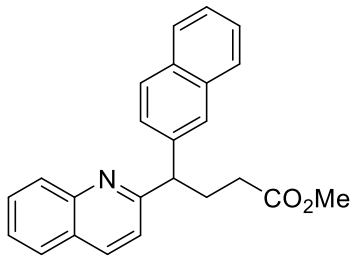
methyl 4-(quinolin-2-yl)-4-(m-tolyl)butanoate, **7f**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.69 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.49 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.19 – 7.14 (m, 3H), 7.03 – 6.99 (m, 1H), 4.25 (t, *J* = 7.7 Hz, 1H), 3.63 (s, 3H), 2.76 – 2.69 (m, 1H), 2.55 – 2.47 (m, 1H), 2.42 – 2.33 (m, 2H), 2.30 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.24, 163.30, 147.95, 142.93, 138.42, 136.48, 129.63, 129.46, 129.19, 128.70, 127.71, 127.65, 127.11, 126.18, 125.40, 121.53, 53.50, 51.70, 32.68, 29.87, 21.67; **IR (neat)**: ν_{max} = 3018, 2949, 1736, 1600, 1503, 1435, 1200, 1171 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{21}H_{21}NO_2$ [M+] 319.1572, found 319.1568; R_f 0.43 (Hex/EtOAc, 4/1).



methyl 4-(4-(tert-butyl)phenyl)-4-(quinolin-2-yl)butanoate, **7g**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.69 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.48 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.32 (s, 4H), 7.26 (d, *J* = 8.5 Hz, 1H), 4.28 (t, *J* = 7.8 Hz, 1H), 3.63 (s, 3H), 2.79 – 2.71 (m, 1H), 2.59 – 2.51 (m, 1H), 2.43 – 2.36 (m, 2H), 1.29 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.16, 163.39, 149.61, 147.93, 139.81, 136.40, 129.55, 129.40, 127.94, 127.59, 127.05, 126.09, 125.65, 121.48, 53.10, 51.62, 34.53, 32.68, 31.51, 29.95; **IR (neat)**: ν_{max} = 3055, 2960, 1736, 1600, 1503, 1434, 1238, 1156 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{27}NO_2$ [M+] 361.2042, found 361.2044; $\boldsymbol{R_f}$ 0.45 (Hex/EtOAc, 4/1).

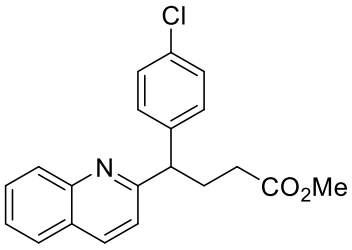


methyl 4-([1,1'-biphenyl]-4-yl)-4-(quinolin-2-yl)butanoate, **7h**: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 7.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.41 (dd, *J* = 8.2, 7.2 Hz, 2H), 7.32 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 4.35 (t, *J* = 8.0 Hz, 1H), 3.64 (s, 3H), 2.82 – 2.73 (m, 1H), 2.62 – 2.53 (m, 1H), 2.47 – 2.36 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.14, 163.05, 142.05, 140.99, 139.83, 136.63, 136.61, 129.58, 129.54, 128.90, 128.80, 127.66, 127.53, 127.35, 127.18, 127.12, 126.25, 121.52, 53.16, 51.70, 32.63, 29.97; **IR (neat)**: ν_{max} = 3028, 2924, 2853, 1733, 1202 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{26}H_{23}NO_2$ [M+] 381.1729, found 381.1727; $\boldsymbol{R_f}$ 0.40 (Hex/EtOAc, 4/1).

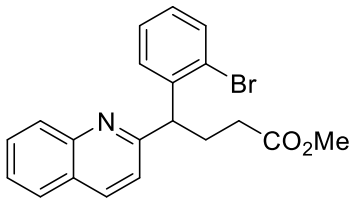


methyl 4-(naphthalen-2-yl)-4-(quinolin-2-yl)butanoate, **7i**: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.72 (dd, *J* = 8.5, 6.4 Hz, 1H), 7.51 (dd, *J* = 7.9, 6.4 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.46 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.43 (dd, *J* = 8.0, 6.9 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 4.48 (t, *J* = 7.5 Hz, 1H), 3.64 (s, 3H), 2.88 – 2.80 (m, 1H), 2.70 – 2.62 (m, 1H), 2.49 – 2.38 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** 174.16, 163.03, 140.42, 136.60, 133.73, 132.62, 129.59, 129.56, 128.55, 127.97, 127.79, 127.66, 127.10, 126.85, 126.84, 126.76, 126.28, 126.26, 125.85,

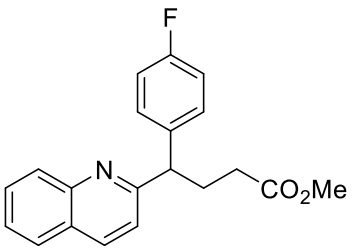
121.61, 53.50, 51.69, 32.61, 29.71; **IR (neat)**: ν_{max} = 3054, 2949, 1731, 1598, 1503, 1198, 1167 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{21}NO_2$ [M+] 355.1572, found 355.1570; $\boldsymbol{R_f}$ 0.41 (Hex/EtOAc, 4/1).



methyl 4-(4-chlorophenyl)-4-(quinolin-2-yl)butanoate, **7j**: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.70 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.50 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 1H), 4.27 (t, *J* = 7.8 Hz, 1H), 3.63 (s, 3H), 2.75 – 2.68 (m, 1H), 2.54 – 2.44 (m, 1H), 2.41 – 2.31 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.02, 162.52, 147.95, 141.53, 136.74, 132.77, 129.76, 129.66, 129.55, 128.94, 127.68, 127.12, 126.38, 121.41, 52.76, 51.75, 32.46, 29.97; **IR (neat)**: ν_{max} = 3044, 2950, 1735, 1600, 1503, 1489, 1231, 1153, 826 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{18}ClNO_2$ [M+] 339.1026, found 339.1028; $\boldsymbol{R_f}$ 0.36 (Hex/EtOAc, 4/1).

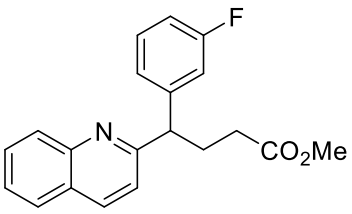


methyl 4-(2-bromophenyl)-4-(quinolin-2-yl)butanoate, **7k**: yellow solid; melting point 96~101 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.70 (dd, *J* = 8.4, 6.9 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 8.1, 6.9 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.20 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.04 (dd, *J* = 8.0, 7.3 Hz, 1H), 4.91 (t, *J* = 7.5 Hz, 1H), 3.65 (s, 3H), 2.89 – 2.80 (m, 1H), 2.54 – 2.45 (m, 2H), 2.45 – 2.36 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.03, 161.85, 148.03, 142.45, 136.33, 132.99, 129.93, 129.68, 129.40, 128.30, 127.96, 127.62, 127.11, 126.22, 125.13, 122.36, 51.68, 50.94, 32.43, 29.74; **IR (neat)**: ν_{max} = 3058, 2949, 1735, 1600, 1436, 1237, 1153, 753 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{18}BrNO_2$ [M+] 383.0521, found 383.0520 ,385.0503; $\boldsymbol{R_f}$ 0.48 (Hex/EtOAc, 4/1).

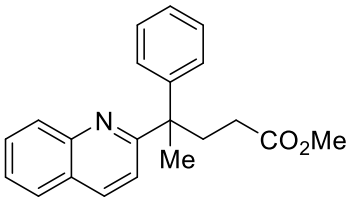


methyl 4-(4-fluorophenyl)-4-(quinolin-2-yl)butanoate, **7l**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.70 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.49 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.34 (dd, *J* = 8.7, $^4J_{H-F}$ = 5.4 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.97 (dd, $^3J_{H-F}$ = 8.7, *J* = 8.7 Hz, 2H), 4.27 (t, *J* = 7.8 Hz, 1H), 3.63 (s, 3H), 2.76 – 2.69 (m, 1H), 2.52 – 2.45 (m, 1H), 2.39 – 2.33 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.06, 162.83, 161.90 (d, $^1J_{C-F}$ = 245.3 Hz), 147.98, 138.77, 138.75, 136.61, 129.83 (d, $^3J_{H-F}$ = 7.8 Hz), 129.58, 127.66, 127.09, 126.30, 121.42, 115.58 (d, $^2J_{C-F}$ = 21.1 Hz), 52.67, 51.72, 32.50, 30.14; **IR (neat)**: ν_{max} = 3043, 2950, 1732, 1504, 1220,

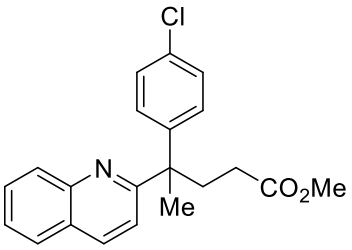
1158, 825 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{18}FNO_2$ [M+] 323.1322, found 323.1323; $\boldsymbol{R_f}$ 0.35 (Hex/EtOAc, 4/1).



methyl 4-(3-fluorophenyl)-4-(quinolin-2-yl)butanoate, **7m**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.71 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.50 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.24 (ddd, *J* = 8.2, 7.8, $^4J_{H-F}$ = 6.0 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.11 (d, $^3J_{H-F}$ = 10.1 Hz, 1H), 6.89 (dd, $^3J_{H-F}$ = 8.6, *J* = 8.2 Hz, 1H), 4.30 (t, *J* = 7.8 Hz, 1H), 3.64 (s, 3H), 2.76 – 2.69 (m, 1H), 2.54 – 2.47 (m, 1H), 2.40 – 2.32 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.01, 163.20 (d, $^1J_{C-F}$ = 246.2 Hz), 162.36, 145.61 (d, $^3J_{C-F}$ = 6.7 Hz), 136.76, 130.21 (d, $^3J_{C-F}$ = 8.4 Hz), 129.67, 129.59, 127.68, 127.16, 126.41, 124.14 (d, $^4J_{C-F}$ = 2.9 Hz), 121.42, 115.26 (d, $^2J_{C-F}$ = 21.7 Hz), 113.87 (d, $^2J_{C-F}$ = 21.1 Hz), 113.80, 53.10, 51.76, 32.47, 29.94; **IR (neat)**: ν_{max} = 3059, 2926, 1735, 1589, 1487, 1241, 1140, 833 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{18}FNO_2$ [M+] 323.1322, found 323.1319; $\boldsymbol{R_f}$ 0.38 (Hex/EtOAc, 4/1).

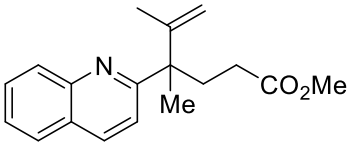


methyl 4-phenyl-4-(quinolin-2-yl)pentanoate, **7n**: yellowish solid; melting point 79~81 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 8.4, 6.9 Hz, 1H), 7.51 (dd, *J* = 8.0, 6.9 Hz, 1H), 7.30 (dd, *J* = 8.7, 7.1 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 3.63 (s, 3H), 2.82 – 2.68 (m, 2H), 2.36 – 2.30 (m, 1H), 2.28 – 2.22 (m, 1H), 1.81 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.66, 166.91, 147.52, 147.14, 135.84, 129.83, 129.26, 128.45, 127.42, 126.66, 126.41, 126.26, 121.37, 51.64, 49.13, 35.81, 30.31, 26.11; **IR (neat)**: ν_{max} = 3058, 2972, 1735, 1600, 1500, 1436, 1195, 1123 cm^{-1}; $\boldsymbol{R_f}$ 0.51 (Hex/EtOAc, 4/1).

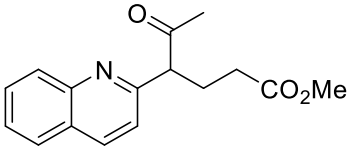


methyl 4-(4-chlorophenyl)-4-(quinolin-2-yl)pentanoate, **7o**: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$** δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.52 (dd, *J* = 8.0, 6.9 Hz, 1H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 1H), 3.61 (s, 3H), 2.72 (ddd, *J* = 13.9, 11.1, 5.5 Hz, 1H), 2.65 (ddd, *J* = 13.9, 11.1, 5.3 Hz, 1H), 2.28 (ddd, *J* = 16.2, 11.1, 5.3 Hz, 1H), 2.20 (ddd, *J* = 16.2, 11.1, 5.5 Hz, 1H), 1.77 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.52, 166.26, 147.19, 146.20, 136.12, 132.35, 129.86, 129.45, 128.88, 128.60, 127.48, 126.71, 126.46, 121.06, 51.74, 48.86, 35.79, 30.25, 26.07; **IR (neat)**: ν_{max} = 3059, 2949, 1735, 1491,

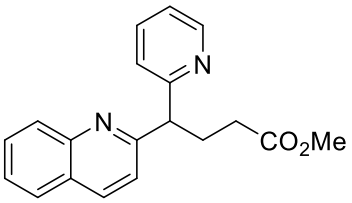
1168, 1012, 758 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{21}H_{20}ClNO_2$ [M+] 353.1183, found 353.1186; R_f 0.51 (Hex/EtOAc, 4/1).



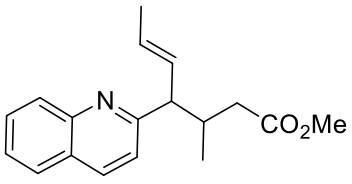
methyl 4,5-dimethyl-4-(quinolin-2-yl)hex-5-enoate, **7p**: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 (dd, *J* = 8.4, 7.0 Hz, 1H), 7.49 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 5.07 (s, 2H), 3.65 (s, 3H), 2.54 (ddd, *J* = 13.9, 11.6, 5.4 Hz, 1H), 2.42 (ddd, *J* = 13.9, 11.6, 4.8 Hz, 1H), 2.32 (ddd, *J* = 16.2, 11.6, 4.8 Hz, 1H), 2.21 (ddd, *J* = 16.2, 11.6, 5.4 Hz, 1H), 1.53 (s, 3H), 1.49 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.95, 165.73, 149.88, 147.51, 136.07, 129.83, 129.20, 127.44, 126.80, 126.18, 120.00, 112.58, 51.73, 50.34, 32.33, 30.14, 24.05, 20.51; **IR (neat)**: ν_{max} = 2972, 1736, 1600, 1171cm^{-1}; R_f 0.48 (Hex/EtOAc, 4/1).



methyl 5-oxo-4-(quinolin-2-yl)hexanoate, **7q**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.71 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.53 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 4.04 (t, *J* = 7.4 Hz, 1H), 3.69 (s, 3H), 2.56 – 2.41 (m, 3H), 2.35 – 2.28 (m, 1H), 2.09 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 207.98, 173.25, 158.52, 148.00, 137.14, 129.83, 129.58, 127.73, 127.45, 126.71, 120.44, 53.70, 52.42, 41.25, 30.17, 26.11; **IR (neat)**: ν_{max} = 3060, 2952, 1735, 1714, 1260, 1159 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{16}H_{17}NO_3$ [M+] 271.1208, found 271.1207; R_f 0.24 (Hex/EtOAc, 1/1).

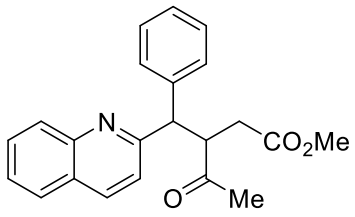


methyl 4-(pyridin-2-yl)-4-(quinolin-2-yl)butanoate, **7r**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.58 (ddd, J = 4.9, 1.7, 0.8 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.68 (dd, J = 8.4, 6.9 Hz, 1H), 7.56 (ddd, J = 7.9, 7.4, 1.7 Hz, 1H), 7.48 (dd, J = 8.0, 6.9 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.36 (ddd, *J* = 7.9, 1.1, 0.8 Hz, 1H), 7.11 (ddd, J = 7.4, 4.9, 1.1 Hz, 1H), 4.49 (t, J = 7.8 Hz, 1H), 3.62 (s, 3H), 2.73 – 2.68 (m, 2H), 2.42 – 2.31 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.96, 162.35, 161.89, 149.54, 147.99, 136.75, 136.63, 129.52, 129.51, 127.67, 127.28, 126.29, 123.71, 121.98, 121.34, 56.04, 51.73, 32.61, 29.46; **IR (neat)**: ν_{max} = 3058, 2950, 1734, 1588, 1433, 1217, 1151 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{19}H_{18}N_2O_2$ [M+] 306.1368, found 306.1367; R_f 0.16 (Hex/EtOAc, 1/1).



methyl 3-methyl-4-(quinolin-2-yl)hept-5-enoate (diastereoisomers, 1 : 0.36 : 0.13), **7s**: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.05 (dd, *J* = 7.9, 1.3 Hz, 3H), 7.76 (dd, *J* = 8.3, 0.9 Hz, 3H), 7.67 (ddd, *J* =

8.3, 6.9, 1.3 Hz, 3H), 7.48 (ddd, *J* = 7.9, 6.9, 0.9 Hz, 3H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 5.82 – 5.73 (m, 2H), 5.77 (ddq, *J* = 15.0, 9.4, 1.6 Hz, 1H), 5.73 – 5.65 (m, 2H), 5.63 (dq, *J* = 15.0, 6.5 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.67 (s, 3H), 3.55 (s, 3H), 3.55 (s, 3H), 3.43 (dd, *J* = 9.4, 8.7 Hz, 1H), 3.39 – 3.34 (m, 1H), 2.64 (ddqd, *J* = 9.3, 8.7, 6.7, 4.5 Hz, 1H), 2.67 – 2.59 (m, 2H), 2.30 – 2.24 (m, 2H), 2.24 (dd, *J* = 15.3, 4.5 Hz, 1H), 2.18 – 2.11 (m, 2H), 2.10 (dd, *J* = 15.3, 9.3 Hz, 1H), 1.70 (dd, *J* = 6.5, 1.6 Hz, 3H), 1.72 – 1.68 (m, 3H), 1.67 (dd, *J* = 6.2, 1.4 Hz, 3H), 1.04 (d, *J* = 6.7 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.76, 173.74, 173.72, 163.78, 163.70, 163.68, 148.10, 136.56, 131.95, 131.32, 130.90, 129.48, 129.47, 129.44, 128.38, 127.66, 127.16, 127.14, 126.89, 126.08, 126.07, 126.06, 121.15, 121.13, 58.02, 51.64, 51.62, 51.51, 39.88, 39.76, 39.74, 35.38, 34.78, 34.75, 18.30, 17.81, 17.48, 13.65; **IR (neat)**: ν_{max} = 2952, 1735, 1619, 1165 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{18}H_{21}NO_2$ [M+] 283.1572, found 283.1570; $\boldsymbol{R_f}$ 0.40 (Hex/EtOAc, 4/1).



4-phenyl-4-(quinolin-2-yl)pentanoate methyl 4-oxo-3-(phenyl(quinolin-2-yl)methyl)pentanoate, **7t**: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.72 (dd, *J* = 8.4, 6.9 Hz, 1H), 7.51 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 4.41 (ddd, *J* = 11.0, 11.0, 3.3 Hz, 1H), 4.24 (d, *J* = 11.0 Hz, 1H), 3.58 (s, 3H), 2.85 (dd, *J* = 17.3, 11.0 Hz, 1H), 2.58 (dd, *J* = 17.3, 3.3 Hz, 1H), 1.82 (s, 3H); **IR (neat)**: ν_{max} = 3061, 2953, 2926, 1735, 1711 cm^{-1}; **^{13}C NMR (151 MHz, $CDCl_3$)** δ 213.26, 173.19, 160.56, 148.02, 140.46, 136.78, 129.69, 129.64, 129.04, 128.93, 127.70, 127.45, 127.10, 126.47, 122.64, 56.22, 51.82, 51.75, 36.23, 32.88; **IR (neat)**: ν_{max} = 3061, 2953, 2926, 1735, 1711 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{21}NO_3$ [M+] 347.1521, found 347.1524; $\boldsymbol{R_f}$ 0.34 (Hex/EtOAc, 4/1).

References

S1. Becke, A. D. *J. Chem. Phys.,* **1993**, *98*, 5648−5652.

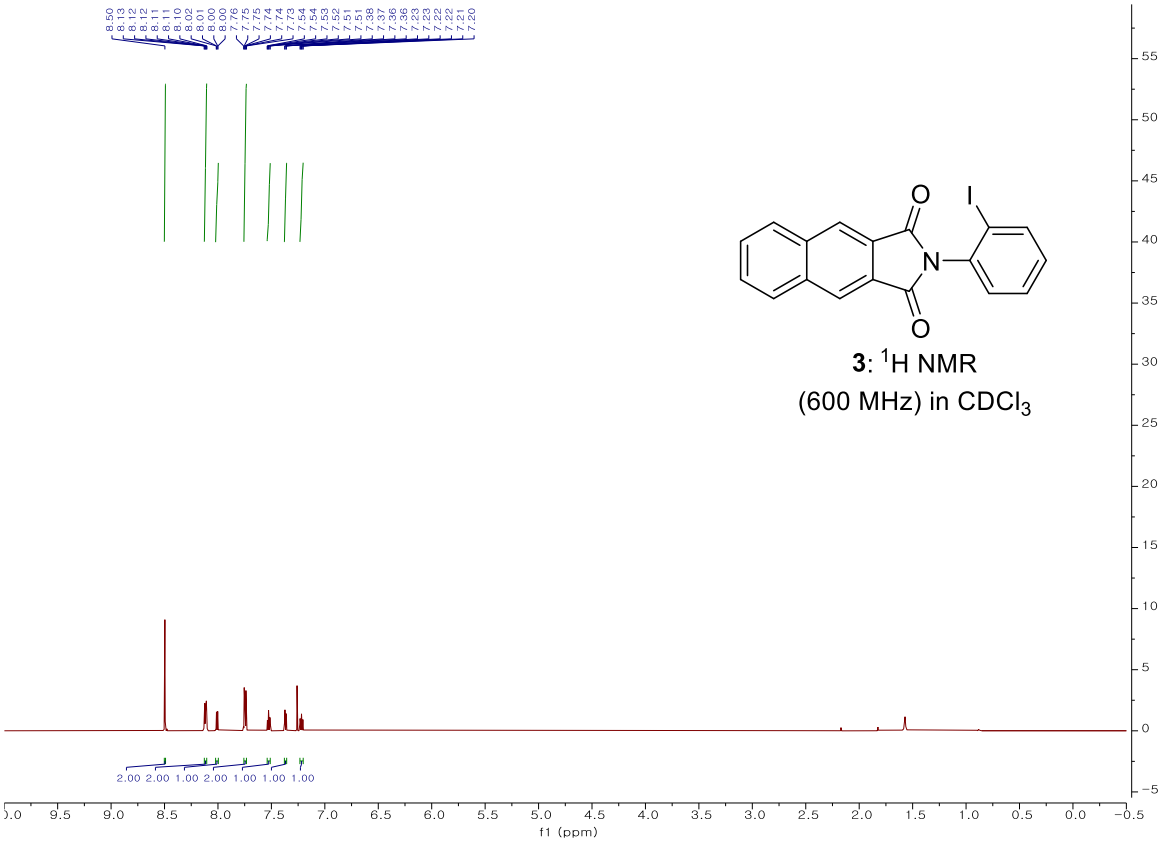
S2. Ditchfield, R; Hehre, W.J; Pople, J. A. *J. Chem. Phys.*, **1971**, *54*, 724–728.

S3. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö .; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D01; Gaussian, Inc., Wallingford, CT, **2009**.

S4. Bae, J.; Iqbal, N.; Hwang, H. S.; Cho, E. J. *Green Chem.*, **2022**, *24*, 3985–3992.

S5. Jiang, X.; Boehm, P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2018**, *140*, 1239–1242.

S6. Salaverri, N.; Mas-Ballesté, R.; Marzo, L.; Alemán, J. *Commun. Chem.*, **2020**, *3*, 132.



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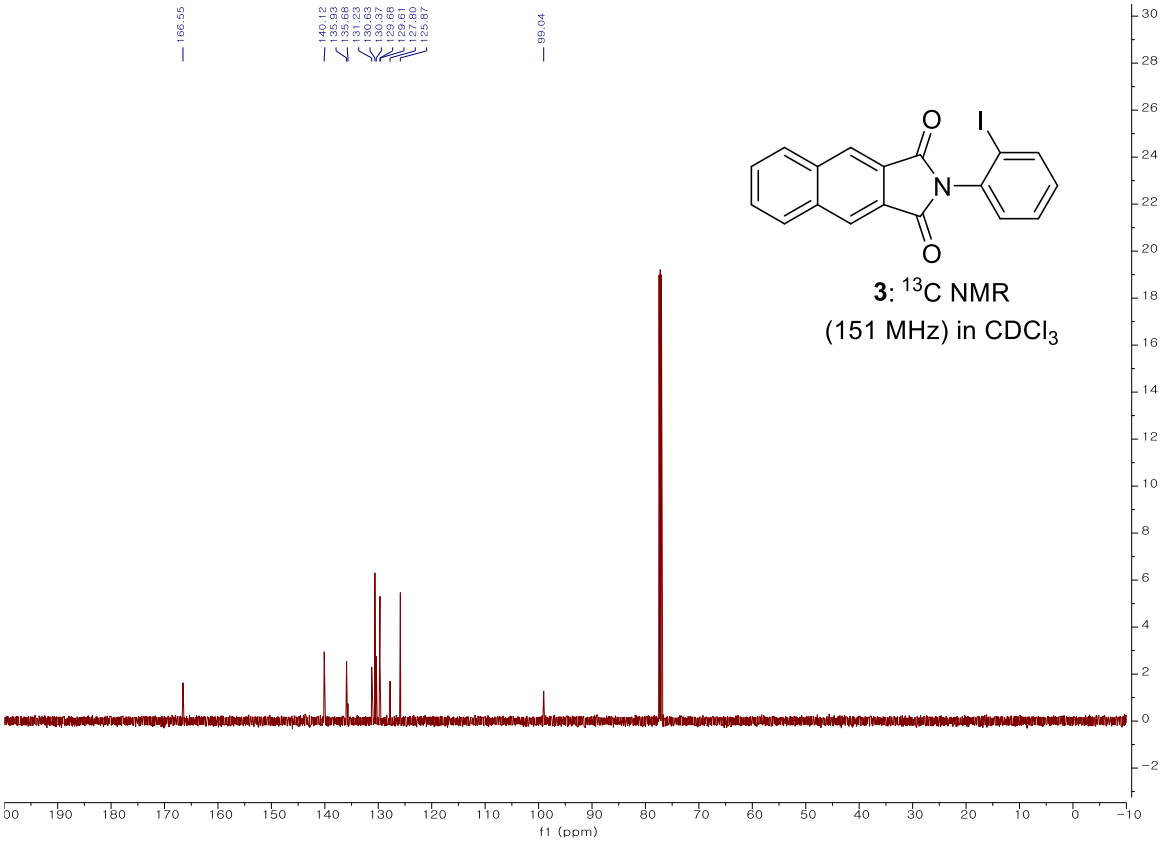

3: ^{13}C NMR
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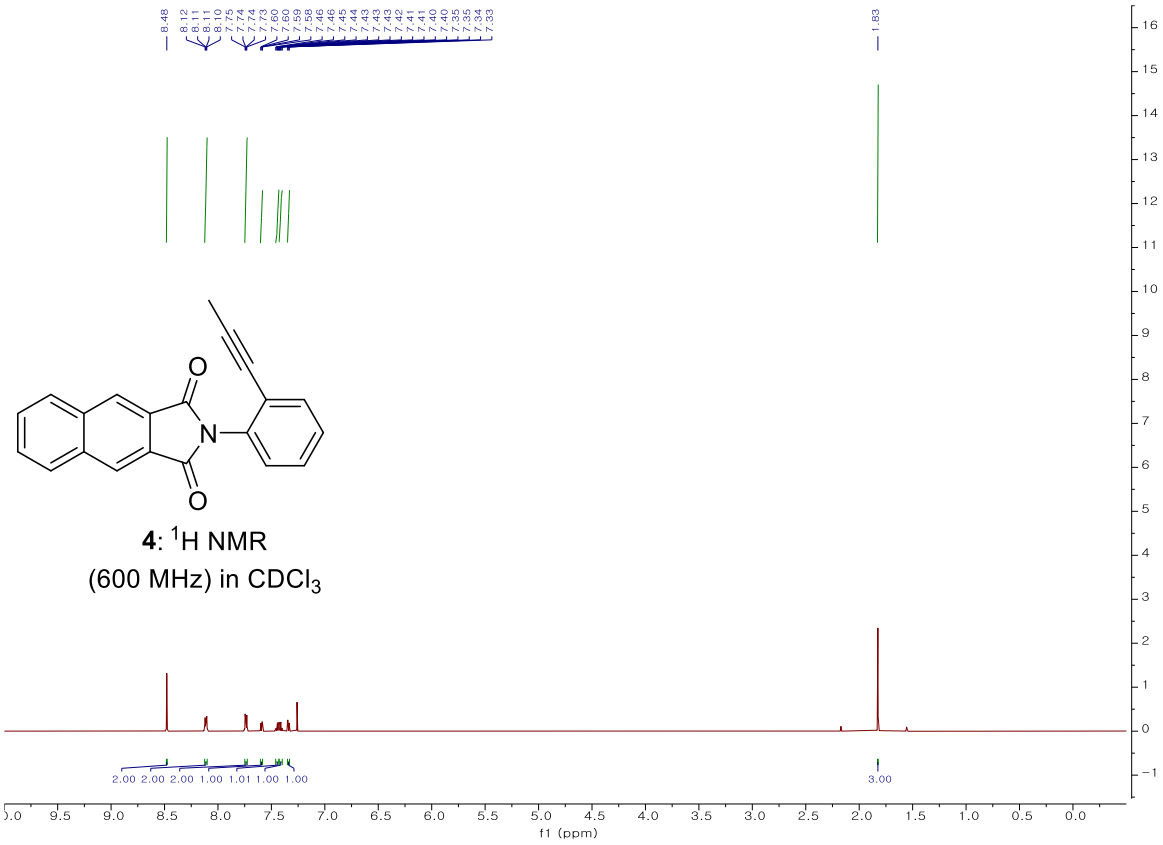

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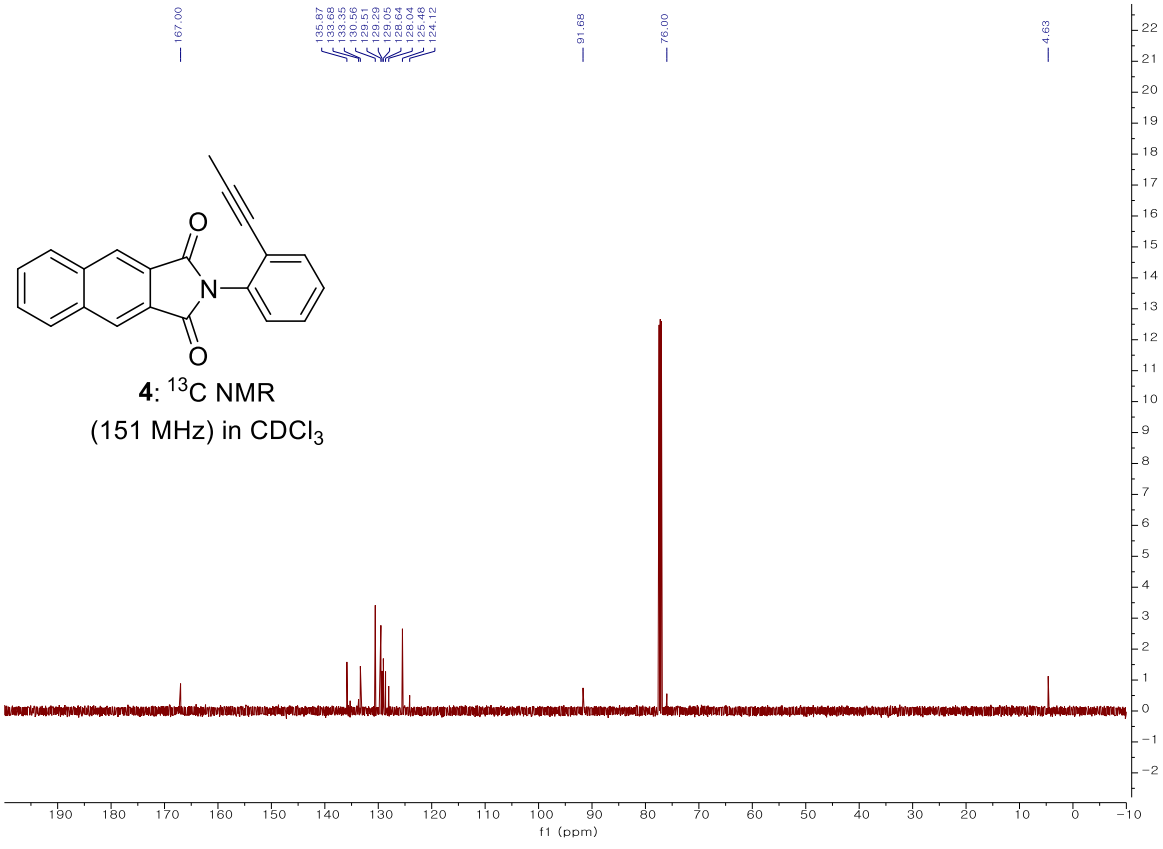

4: ^{13}C NMR
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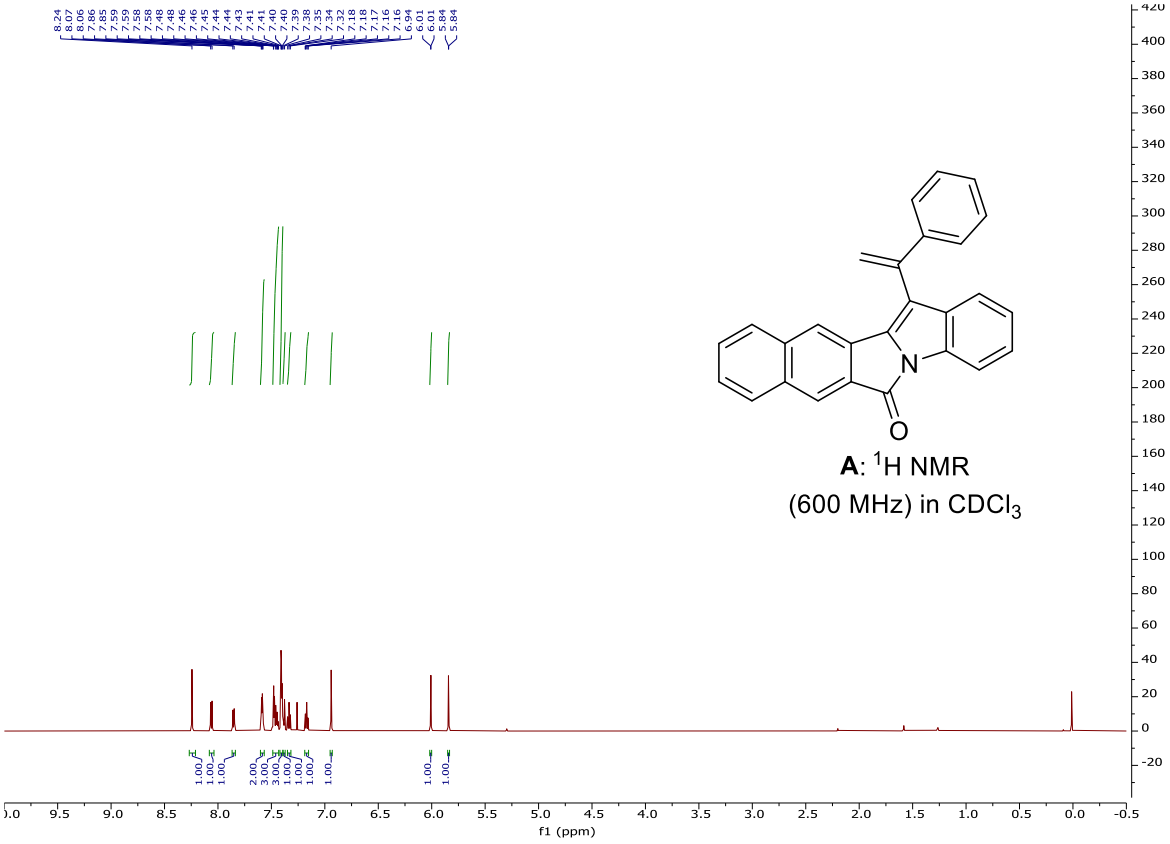

A: ^{1}H NMR
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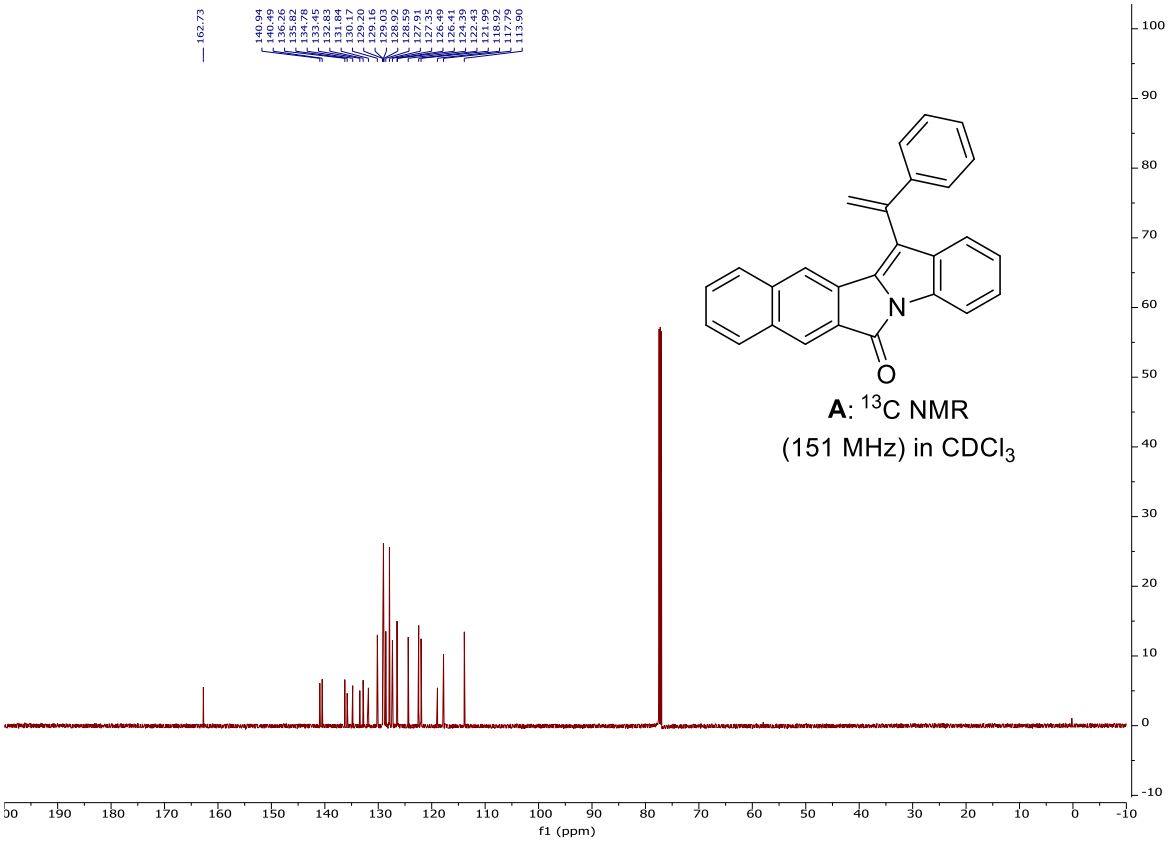

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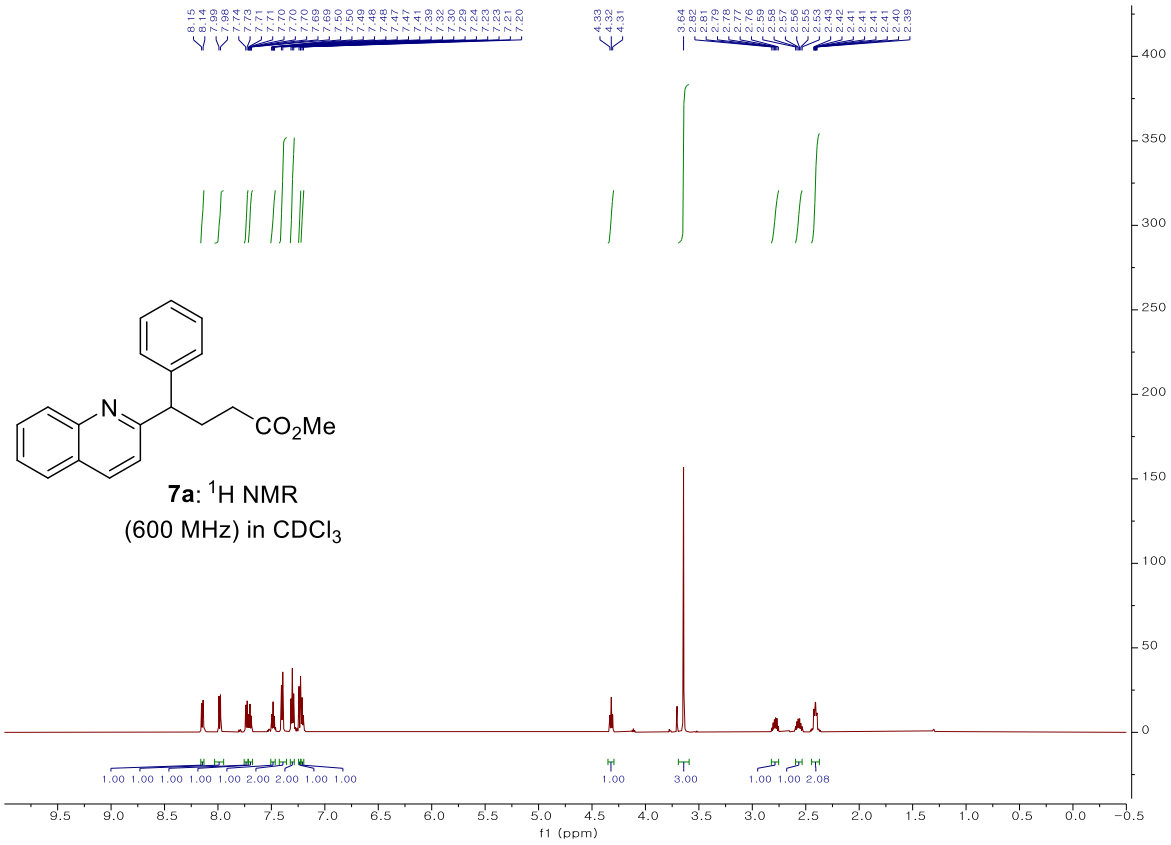

7a: ^{1}H NMR
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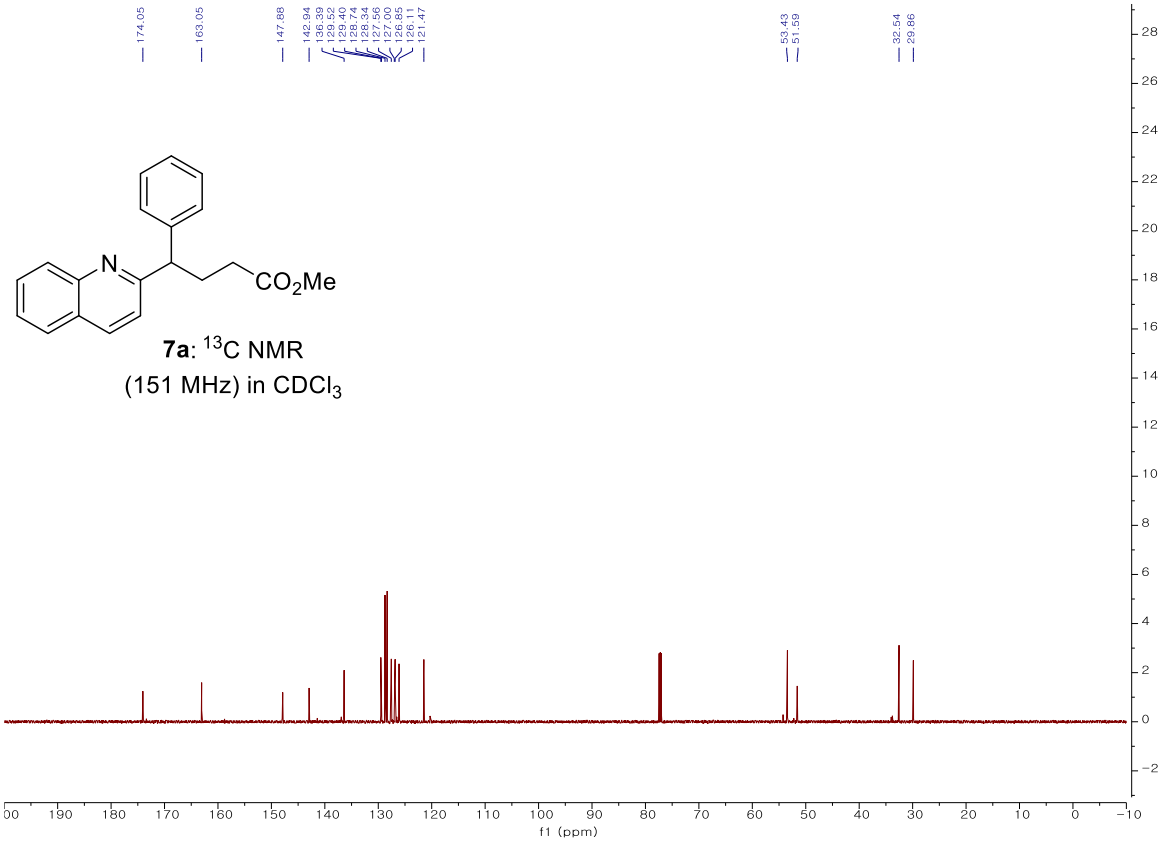

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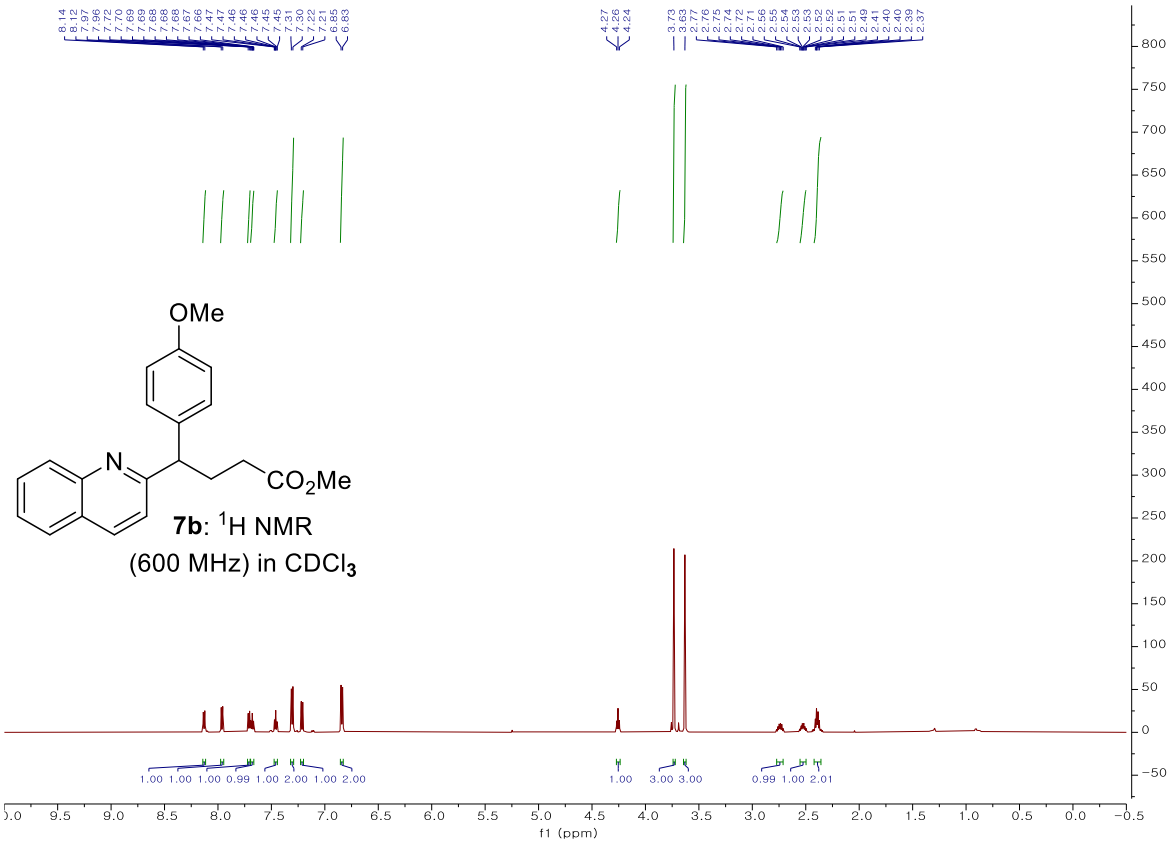
(151 MHz) in $CDCl_3$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2.40
2.40
2.39
2.37
OMe
N
CO2Me
7b: 1H NMR
(600 MHz) in CDCl3
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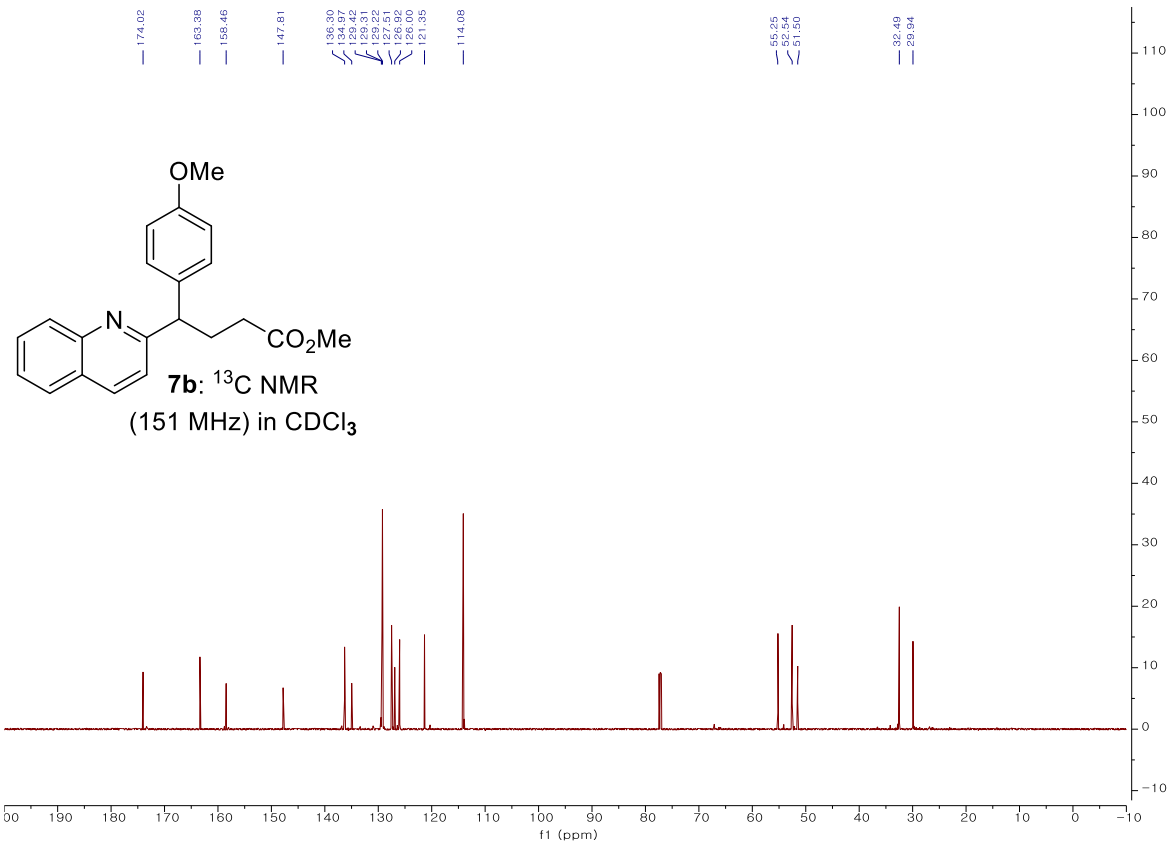
0.99 1.00 2.01
f1 (ppm)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OMe
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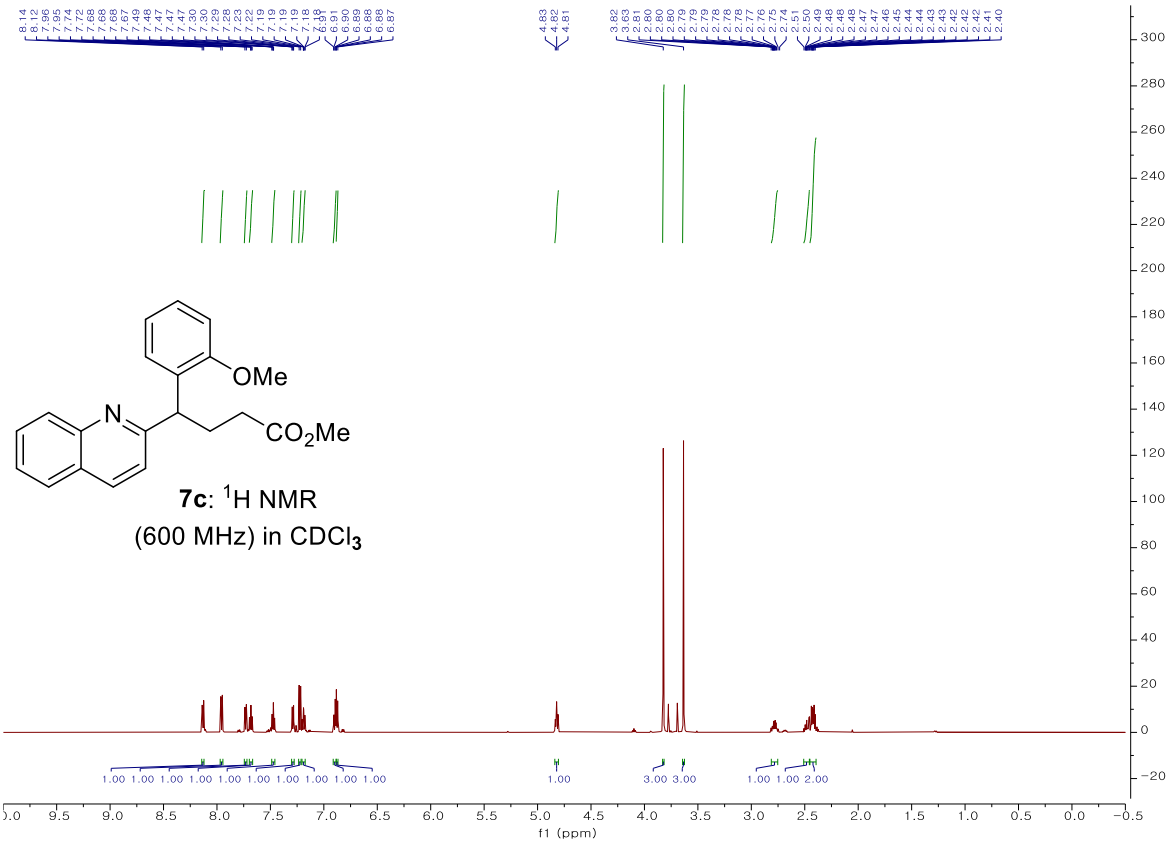
7b: 13C NMR
(151 MHz) in CDCl3
f1 (ppm)


OMe
N
CO2Me
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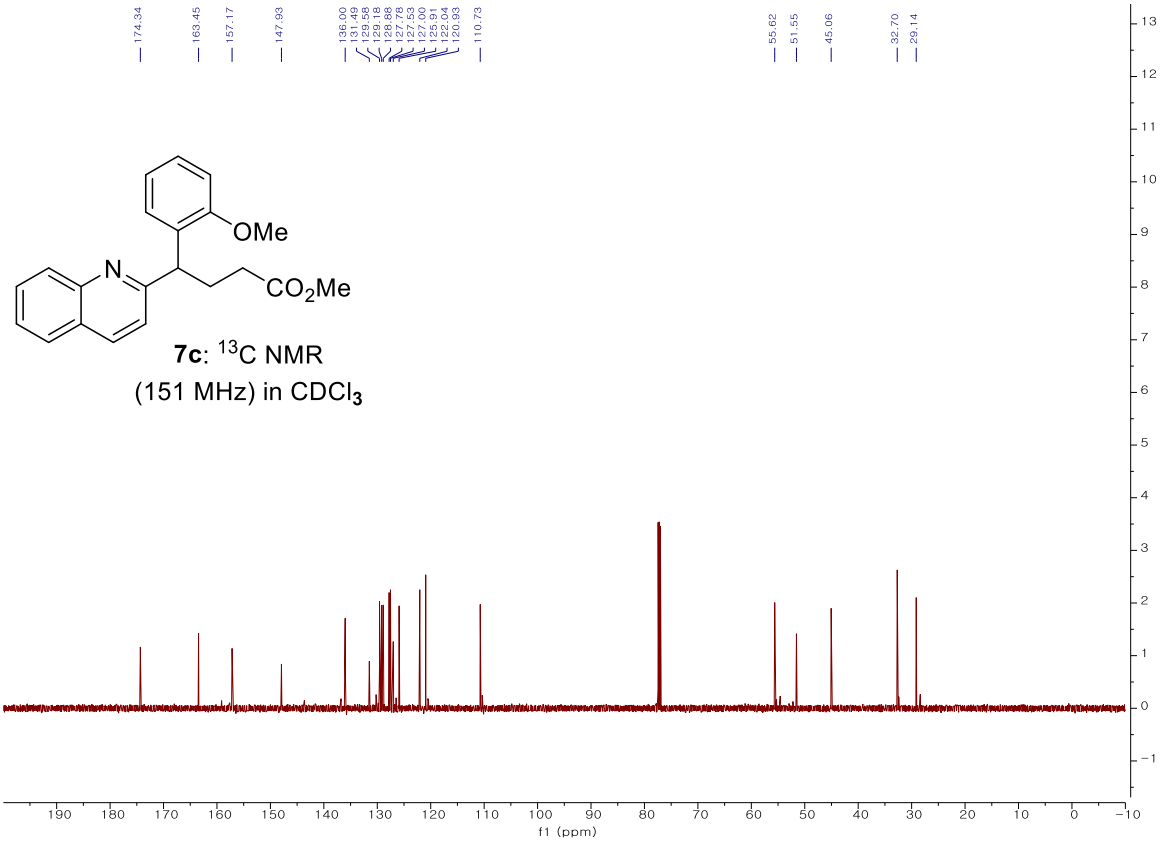
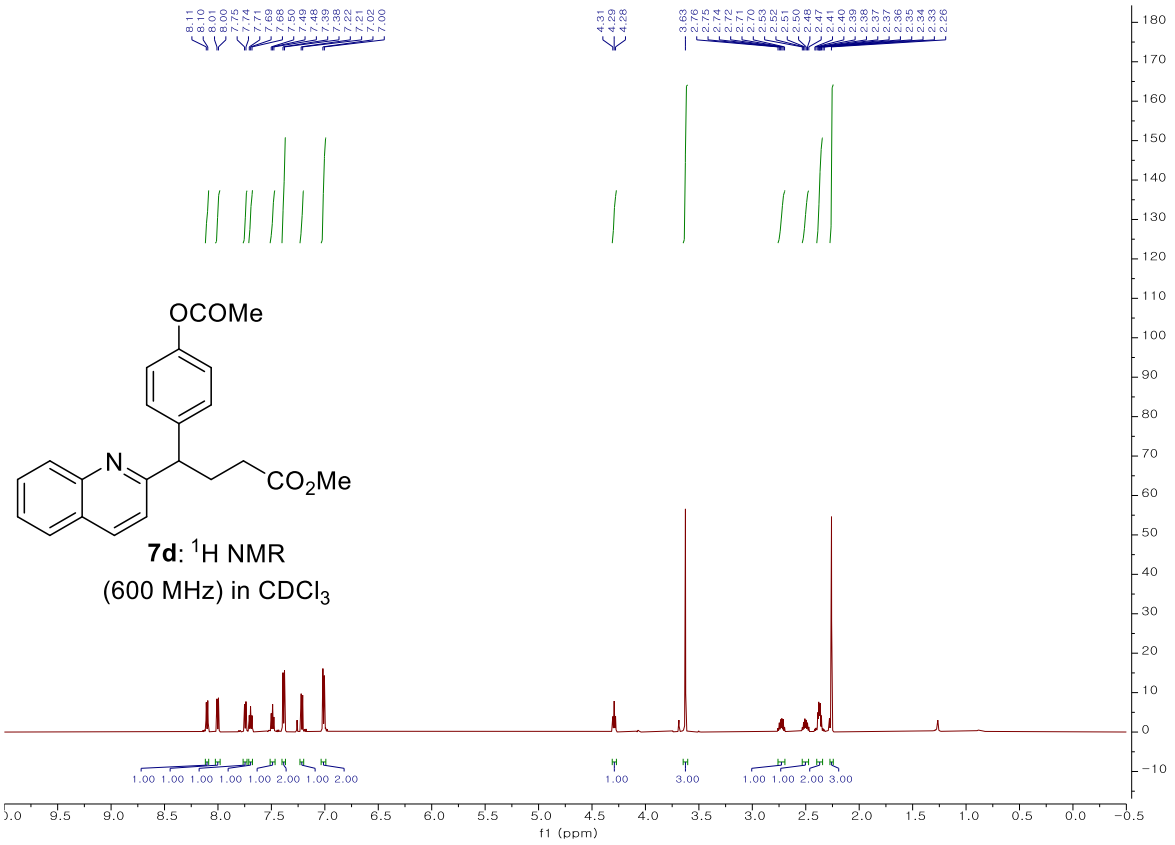
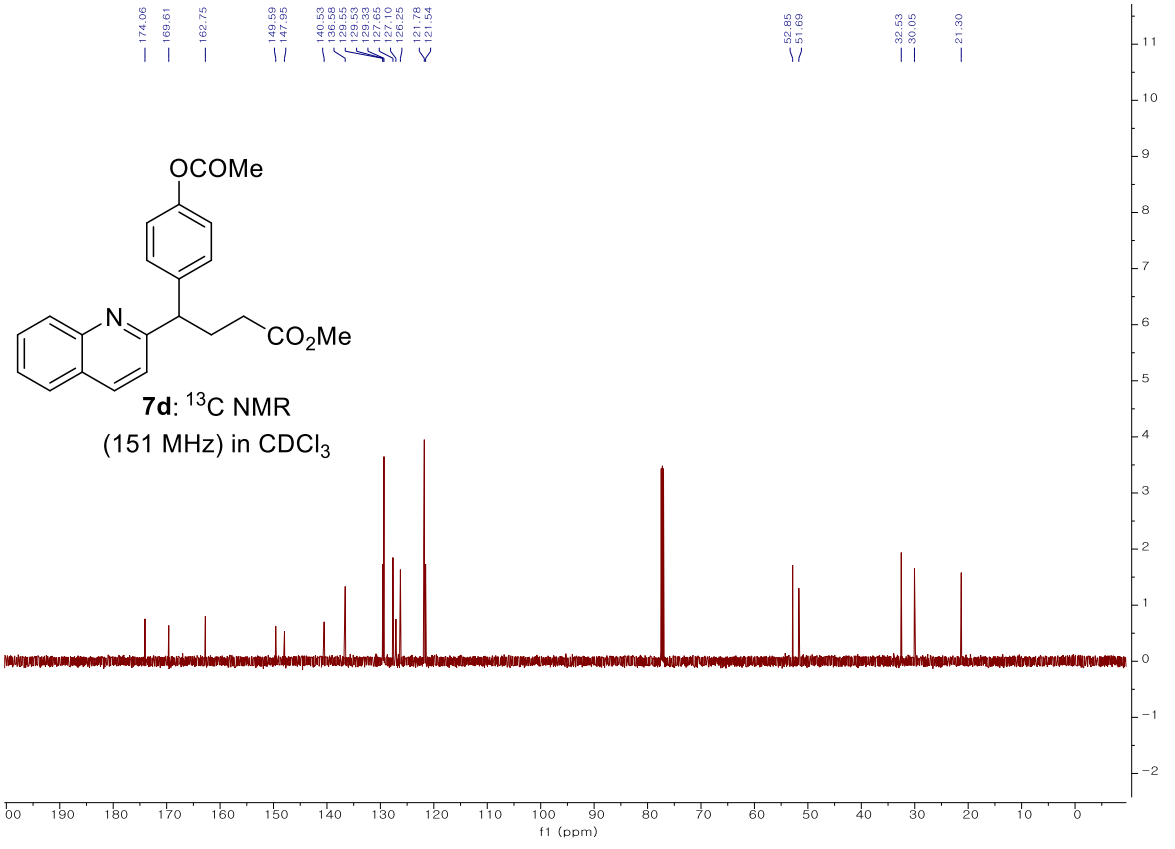
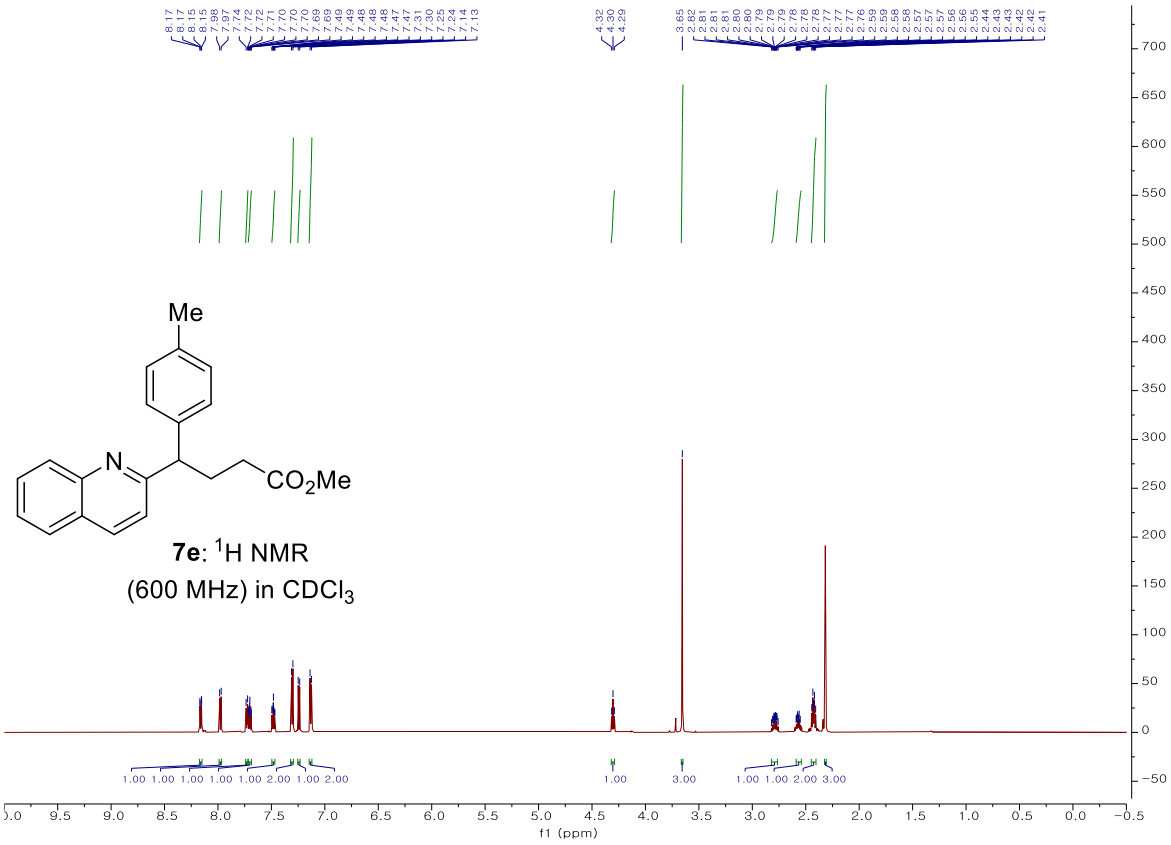
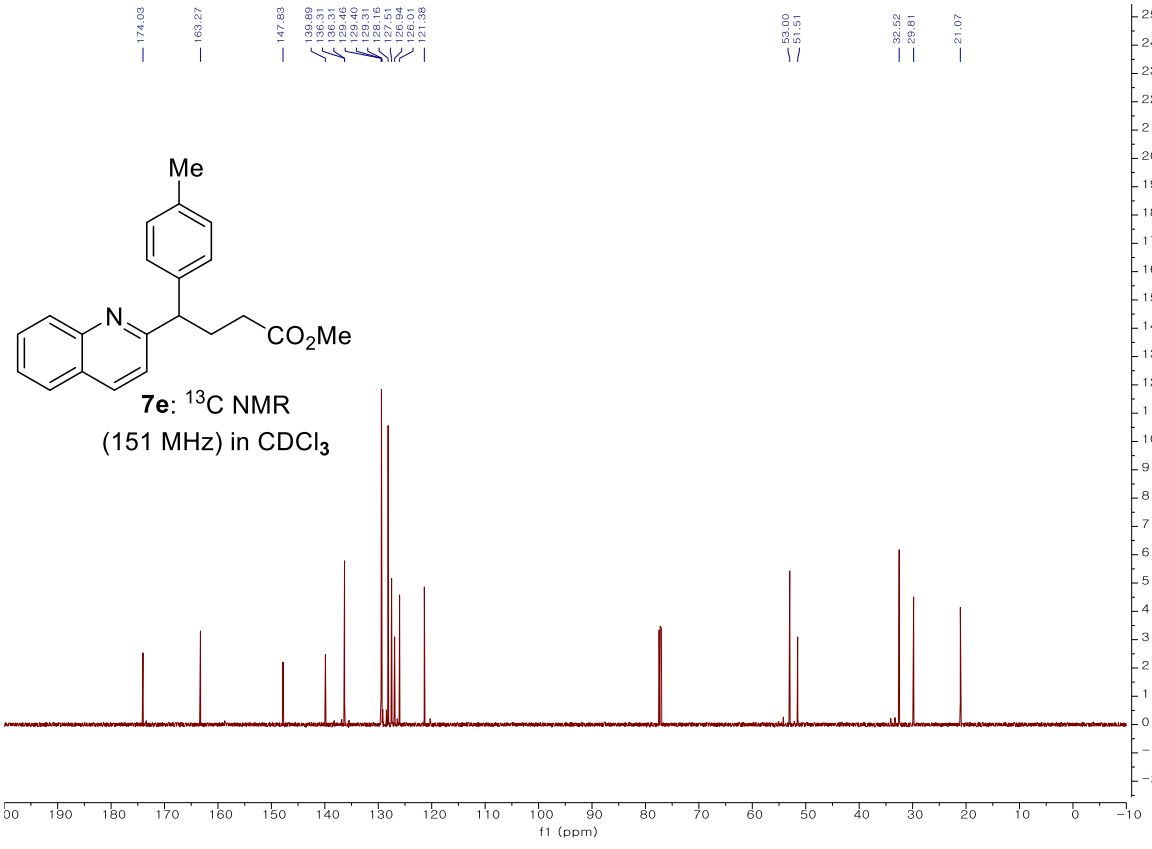
(600 MHz) in CDCl3
f1 (ppm)

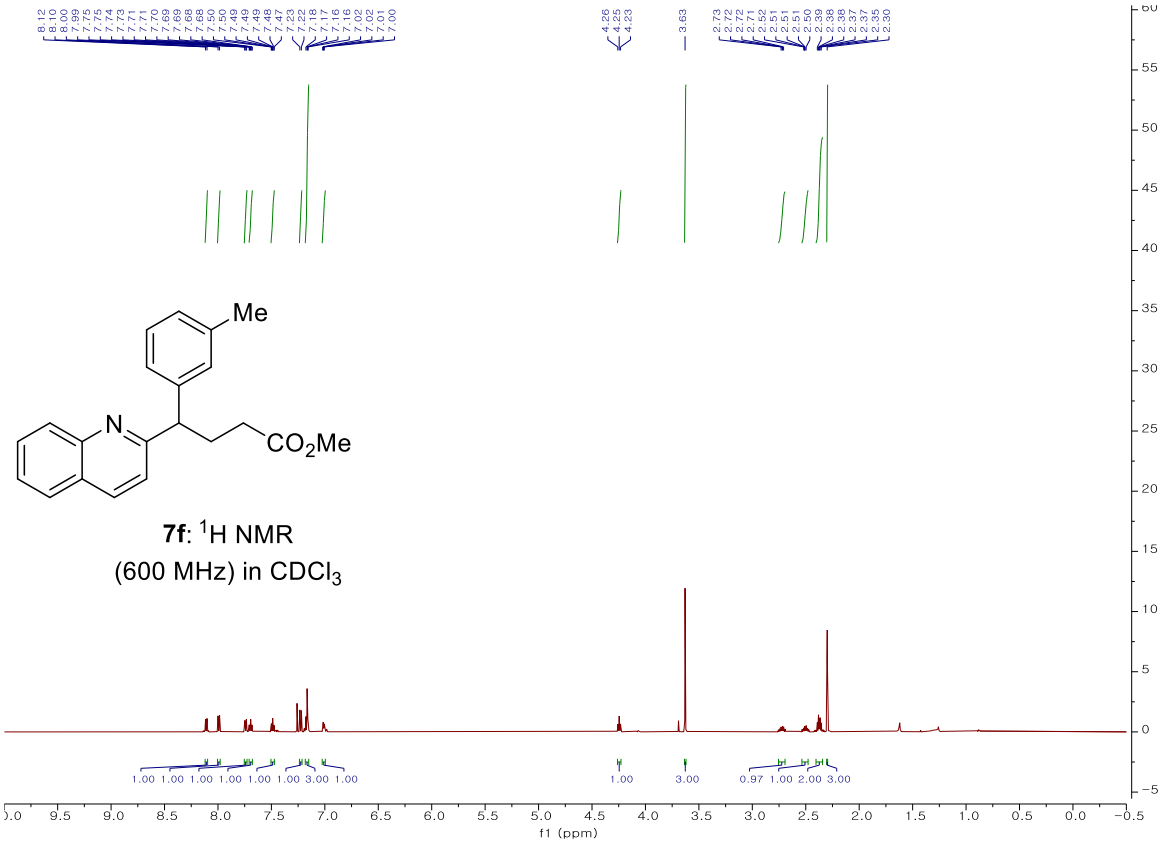

OMe
N
CO2Me
7c: 13C NMR
(151 MHz) in CDCl3
f1 (ppm)


OCOMe
N
CO2Me
7d: 1H NMR
(600 MHz) in CDCl3
f1 (ppm)

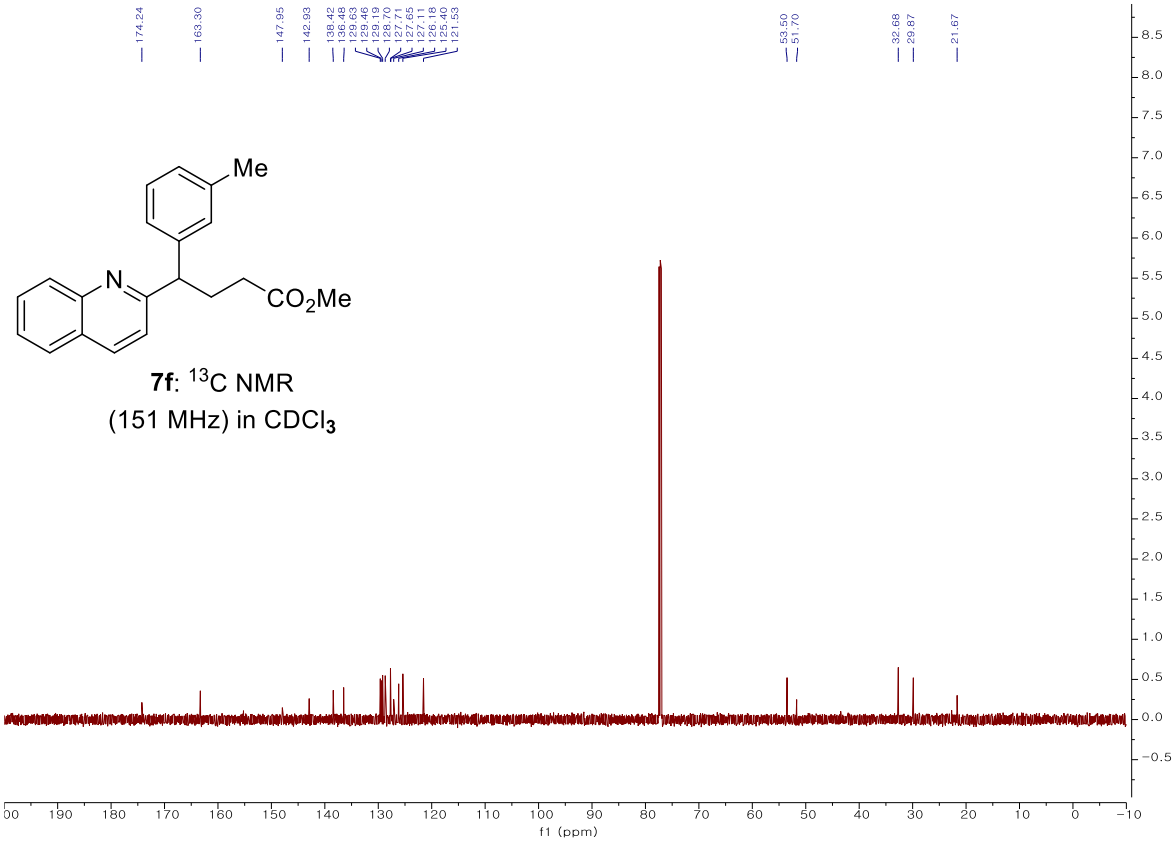

OCOMe
N
CO2Me
7d: 13C NMR
(151 MHz) in CDCl3
f1 (ppm)


Me
N
CO2Me
7e: 1H NMR
(600 MHz) in CDCl3
f1 (ppm)

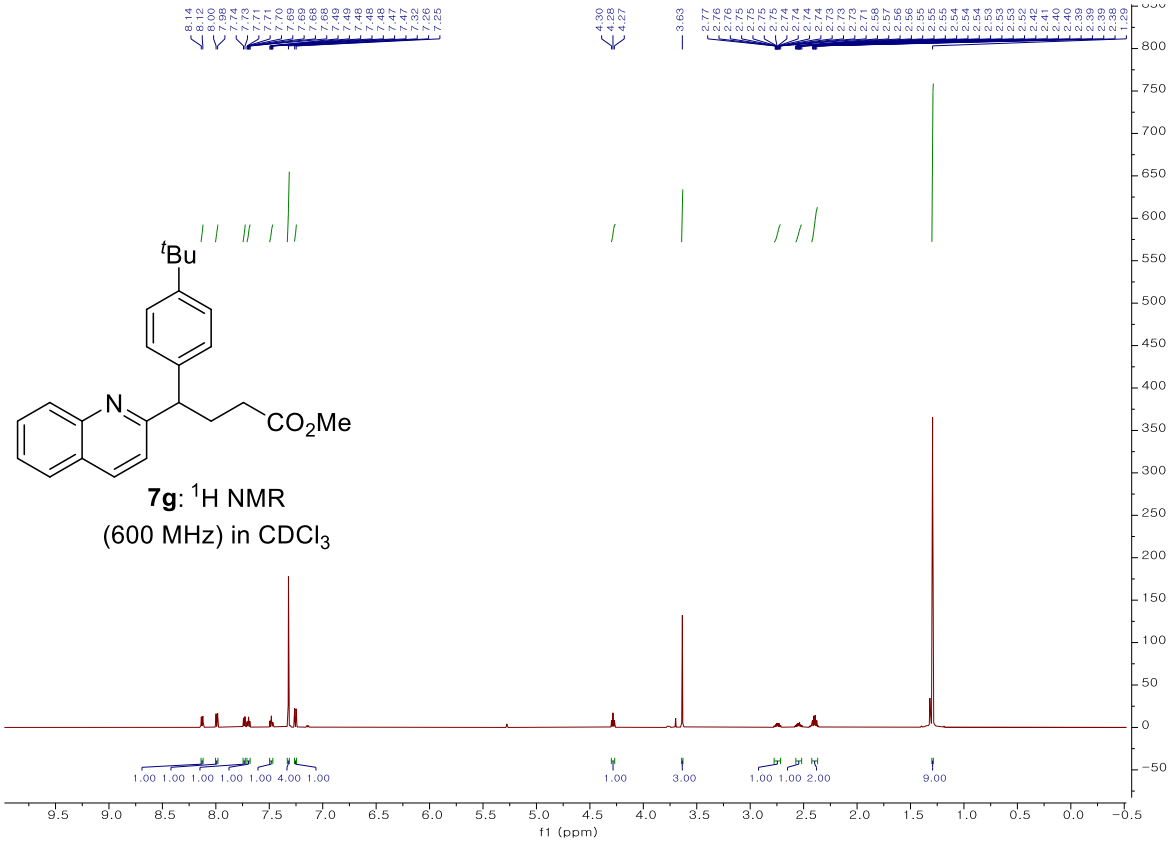

Me
N
CO2Me
7e: 13C NMR
(151 MHz) in CDCl3
f1 (ppm)



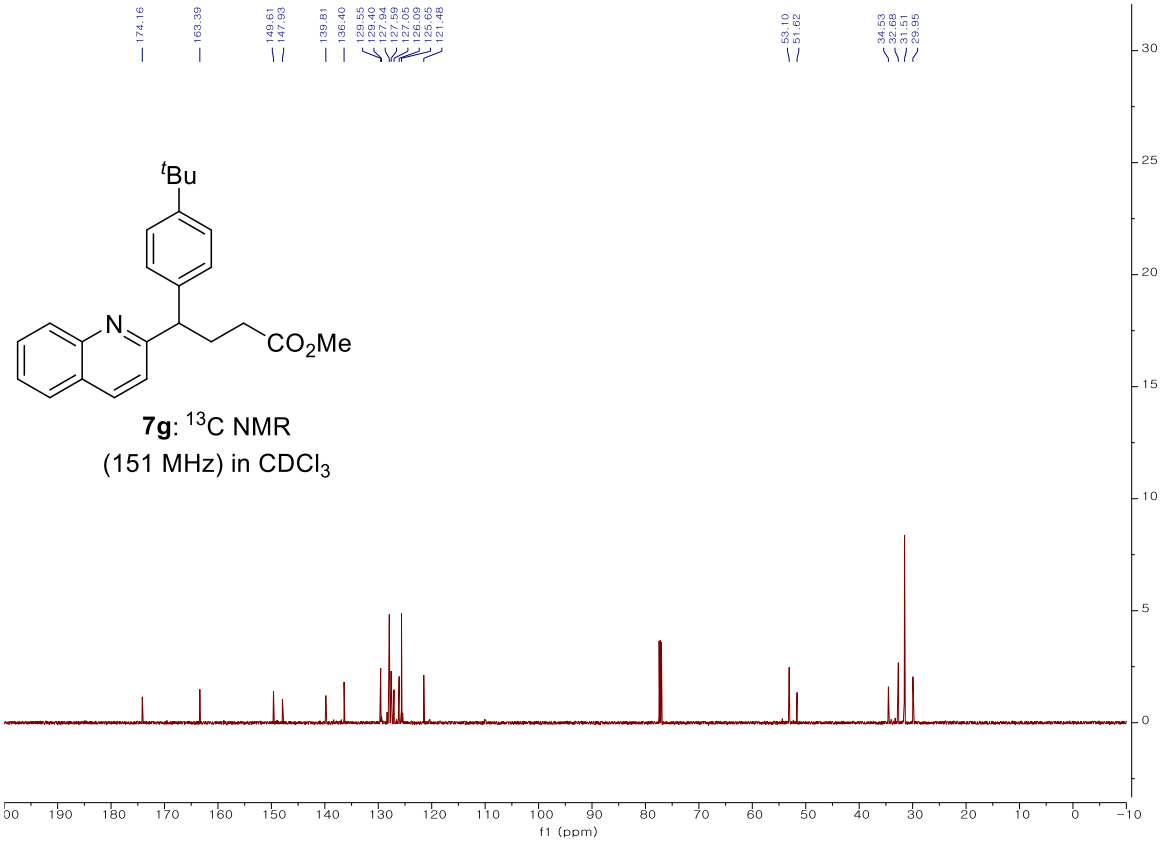
7f: ^{1}H NMR
(600 MHz) in $CDCl_3$



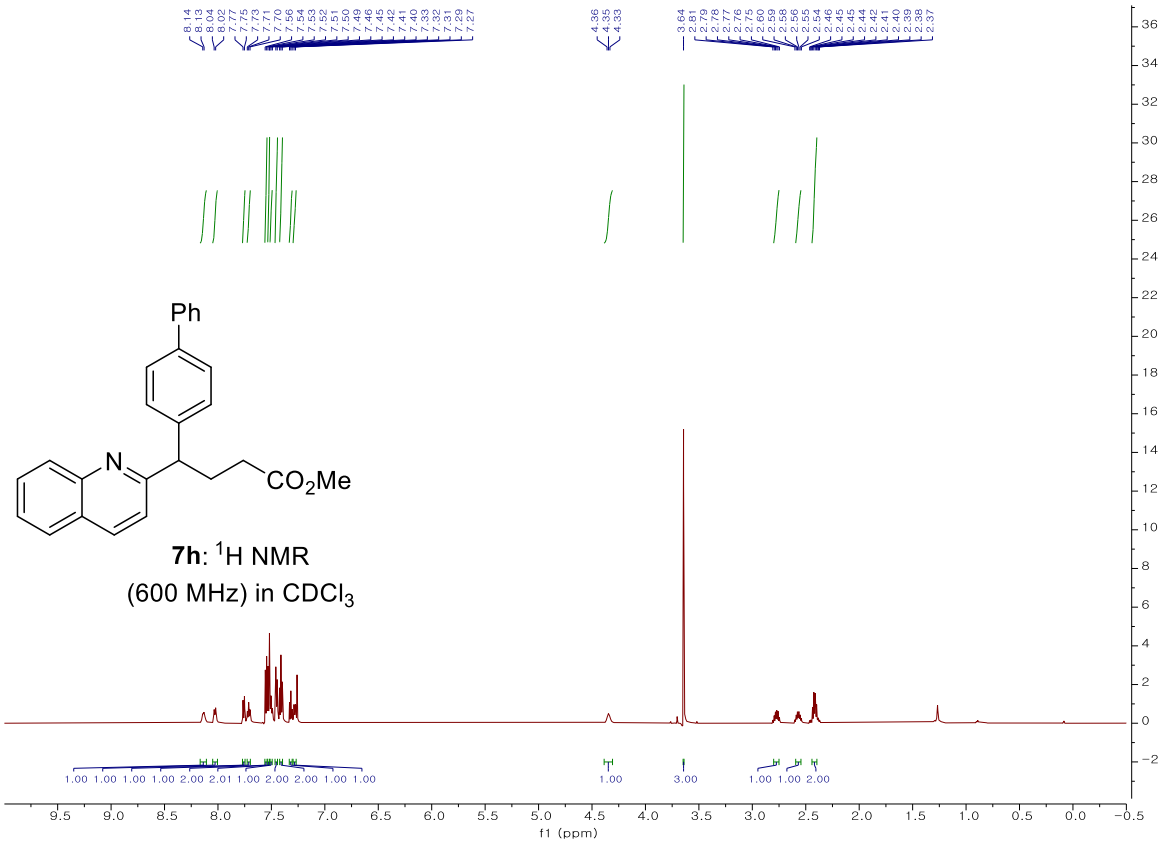
7f: ^{13}C NMR
(151 MHz) in $CDCl_3$



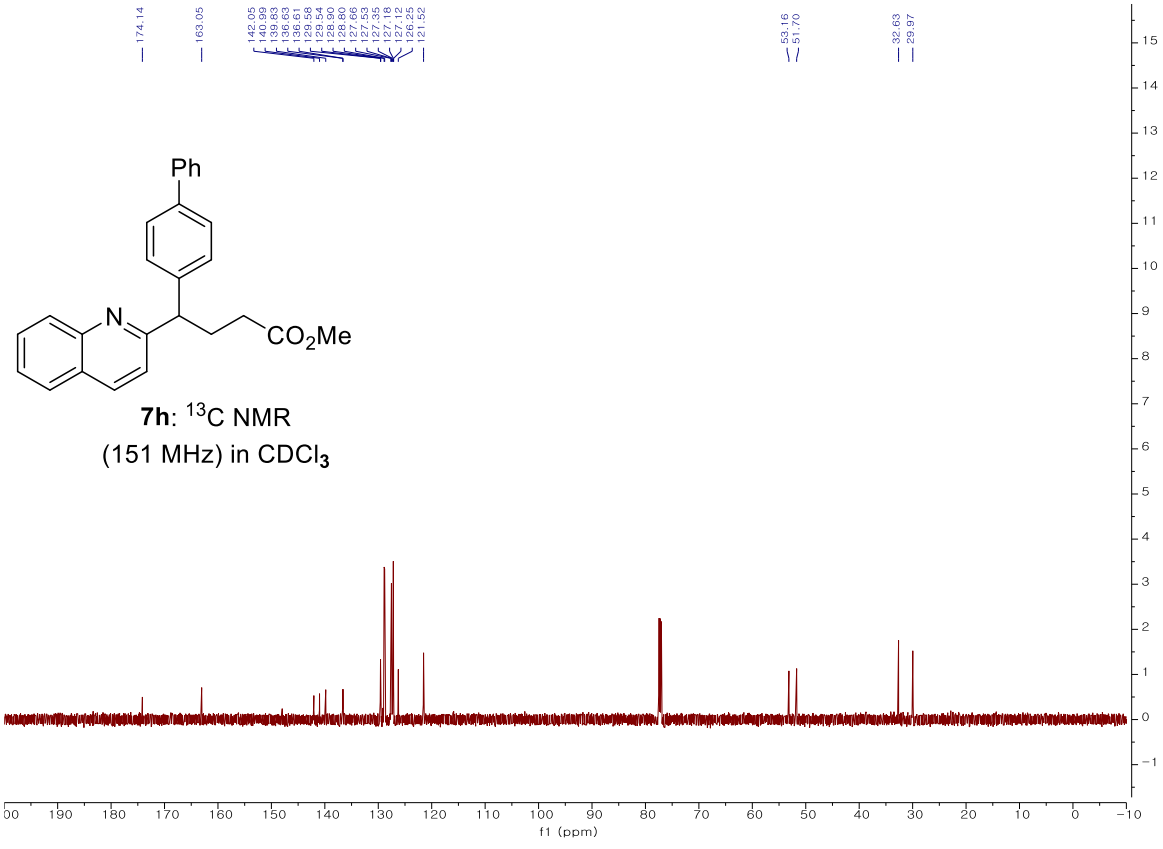
7g: ^{1}H NMR
(600 MHz) in $CDCl_3$



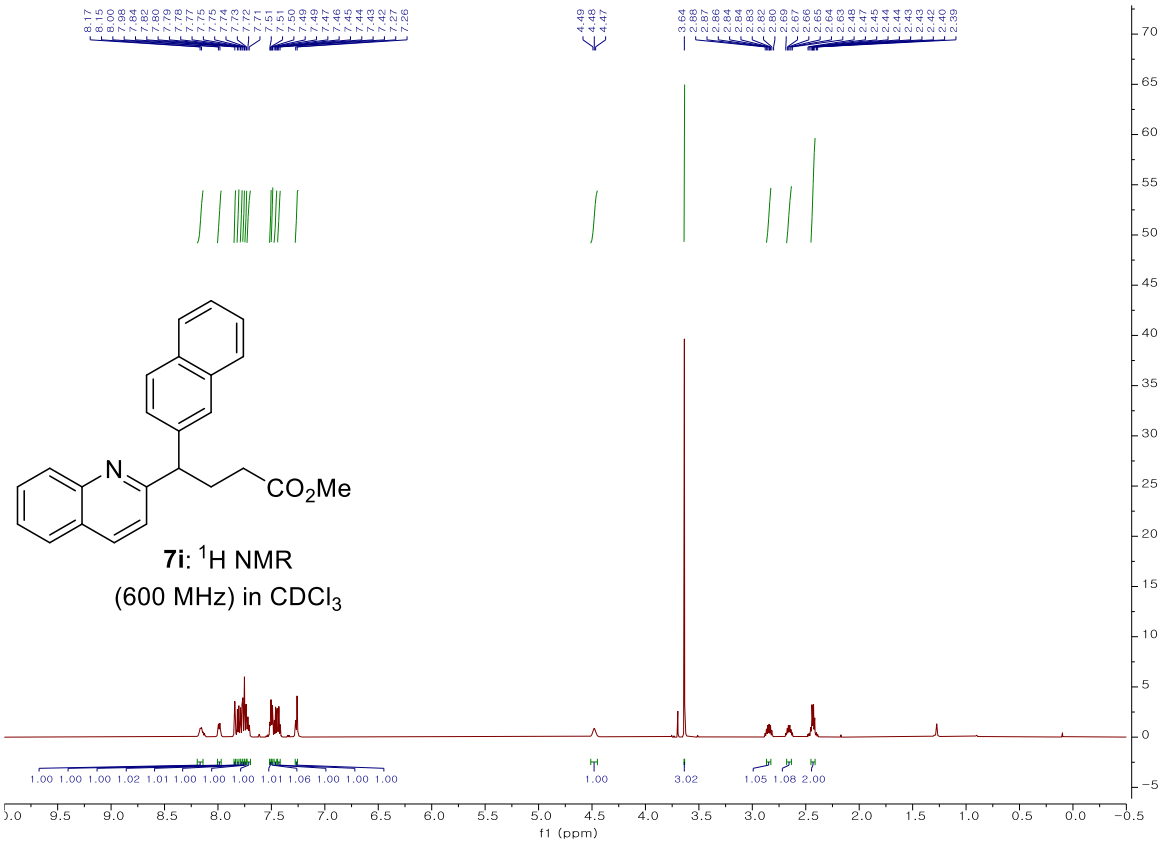
7g: ^{13}C NMR
(151 MHz) in $CDCl_3$



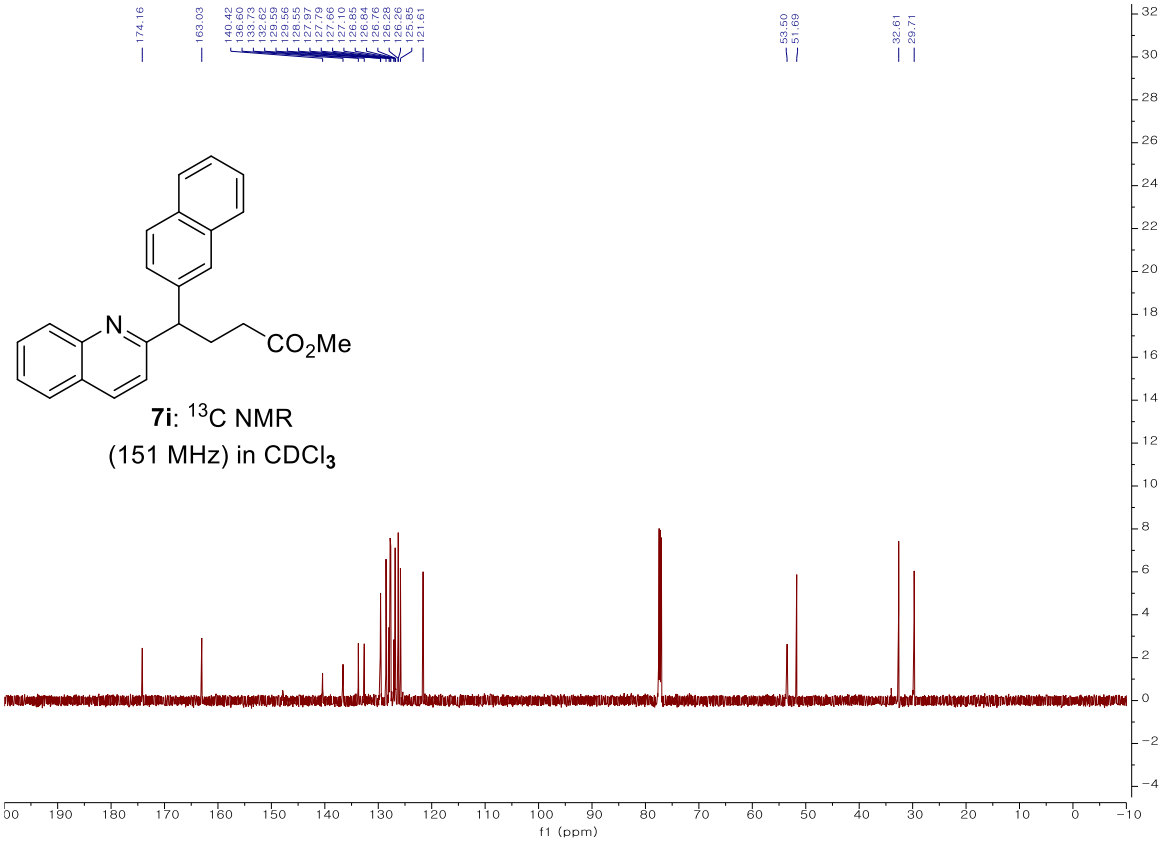
7h: ^{1}H NMR
(600 MHz) in $CDCl_3$



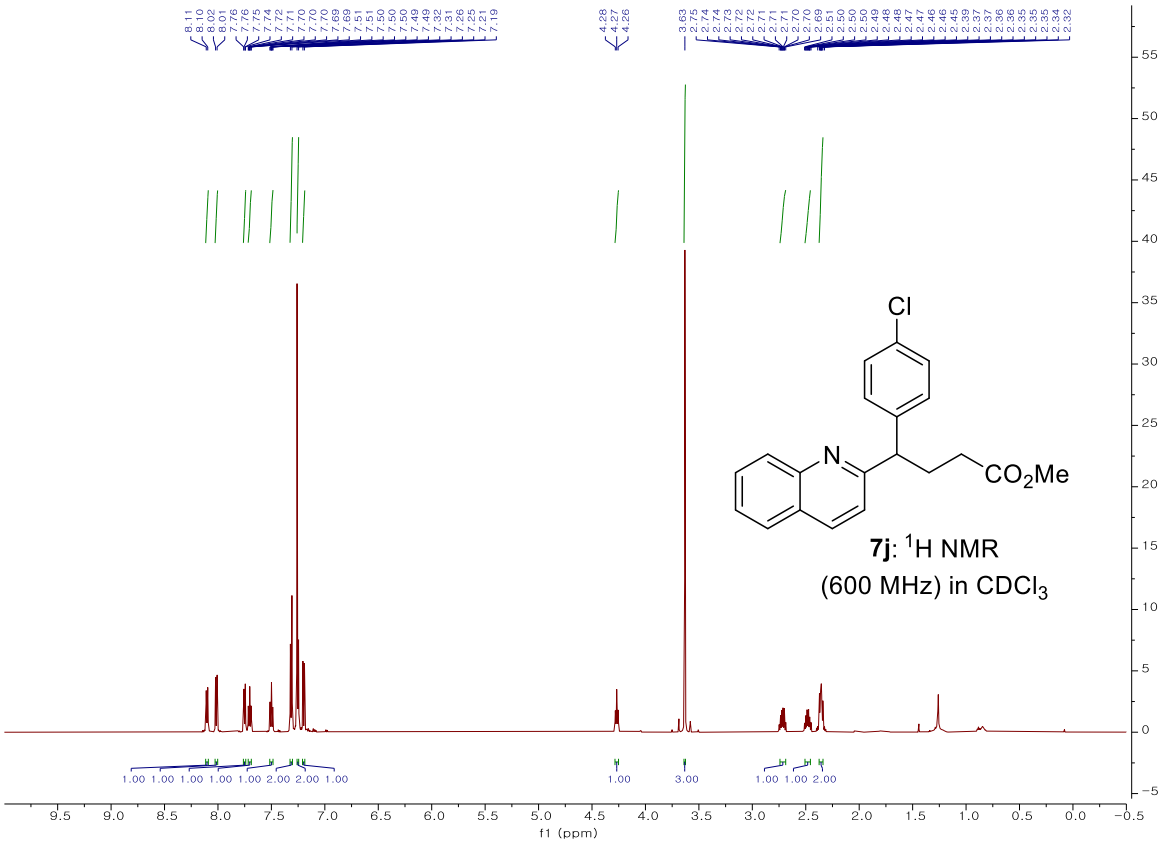
7h: ^{13}C NMR
(151 MHz) in $CDCl_3$

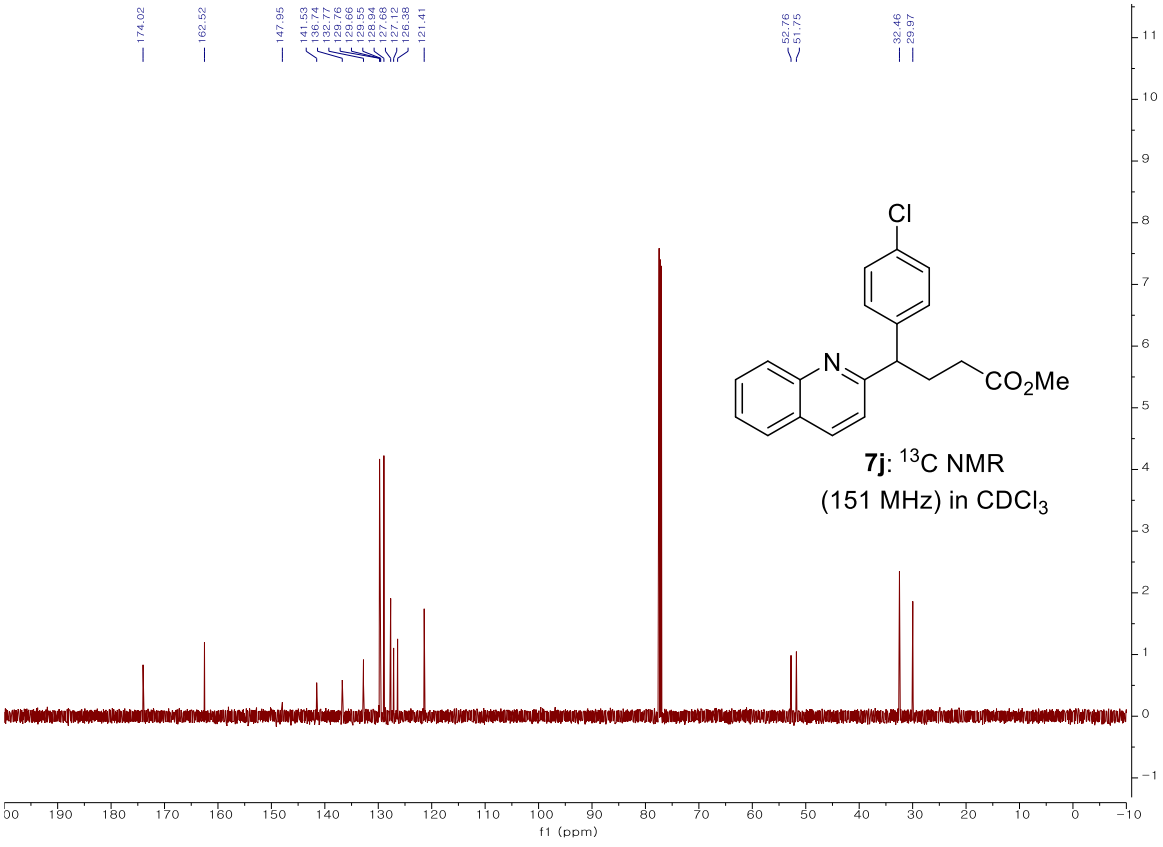


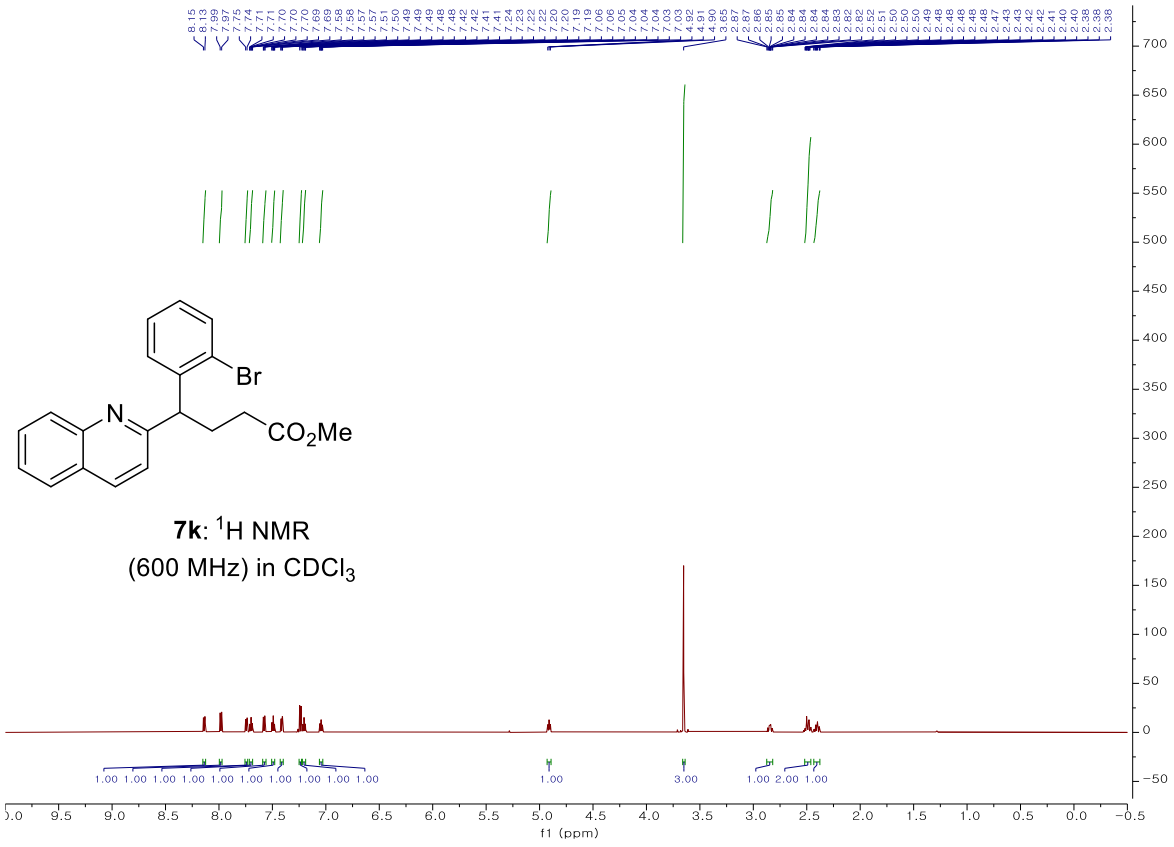
7i: ^{1}H NMR
(600 MHz) in $CDCl_3$



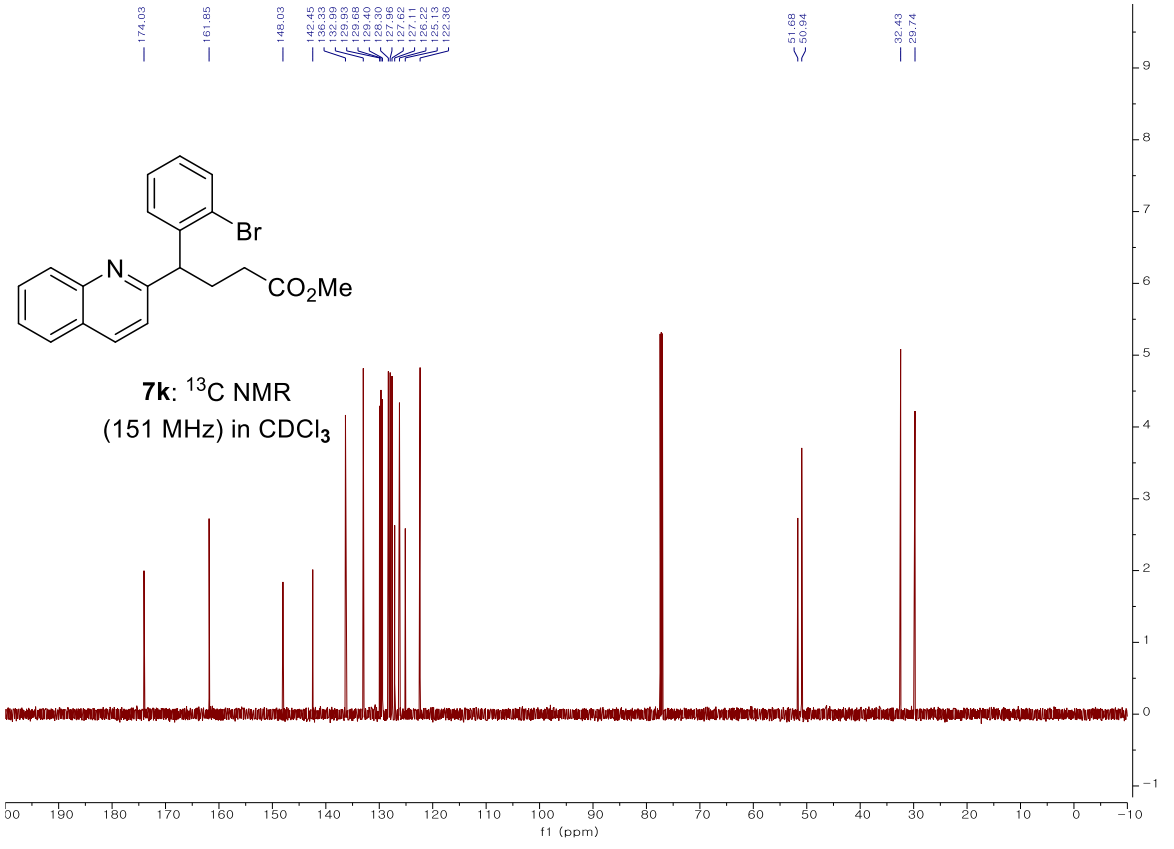
7i: ^{13}C NMR
(151 MHz) in $CDCl_3$


Cl
N
CO2Me
7j: 1H NMR
(600 MHz) in CDCl3
f1 (ppm)

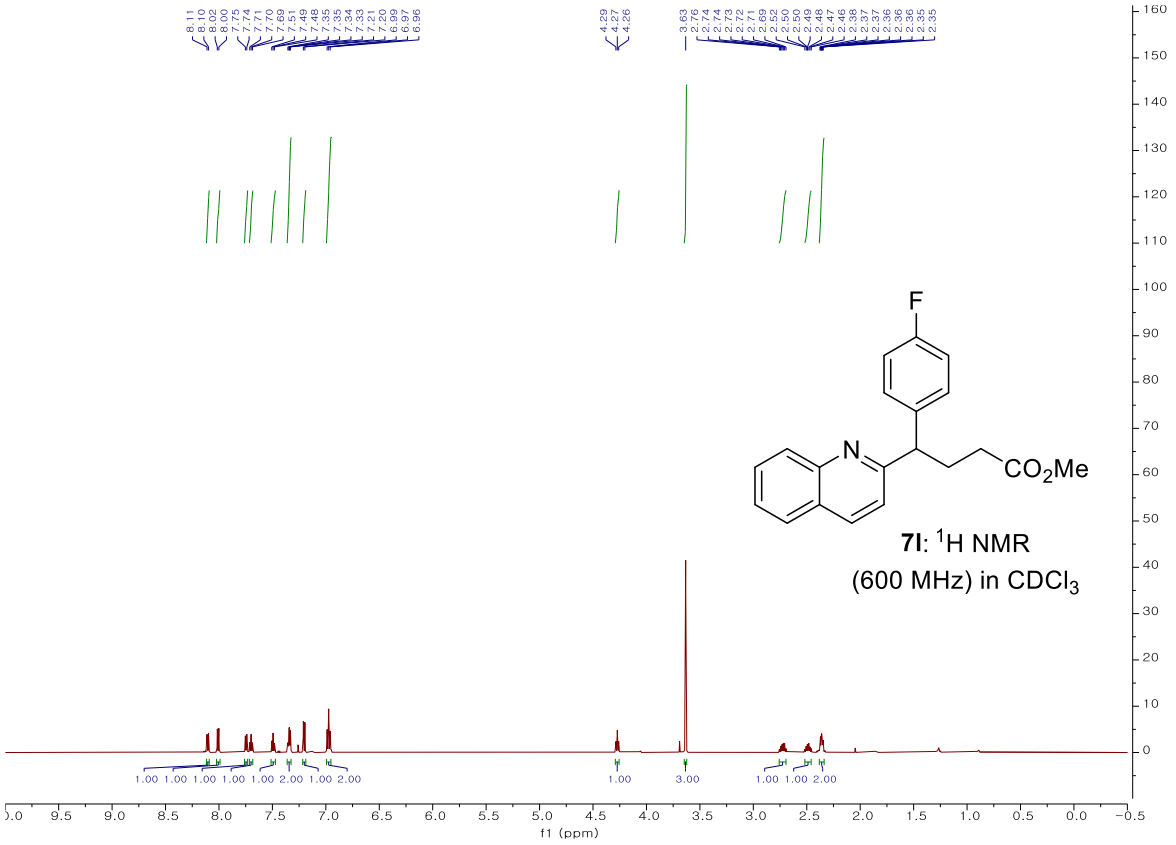

Cl
N
CO2Me
7j: 13C NMR
(151 MHz) in CDCl3
f1 (ppm)

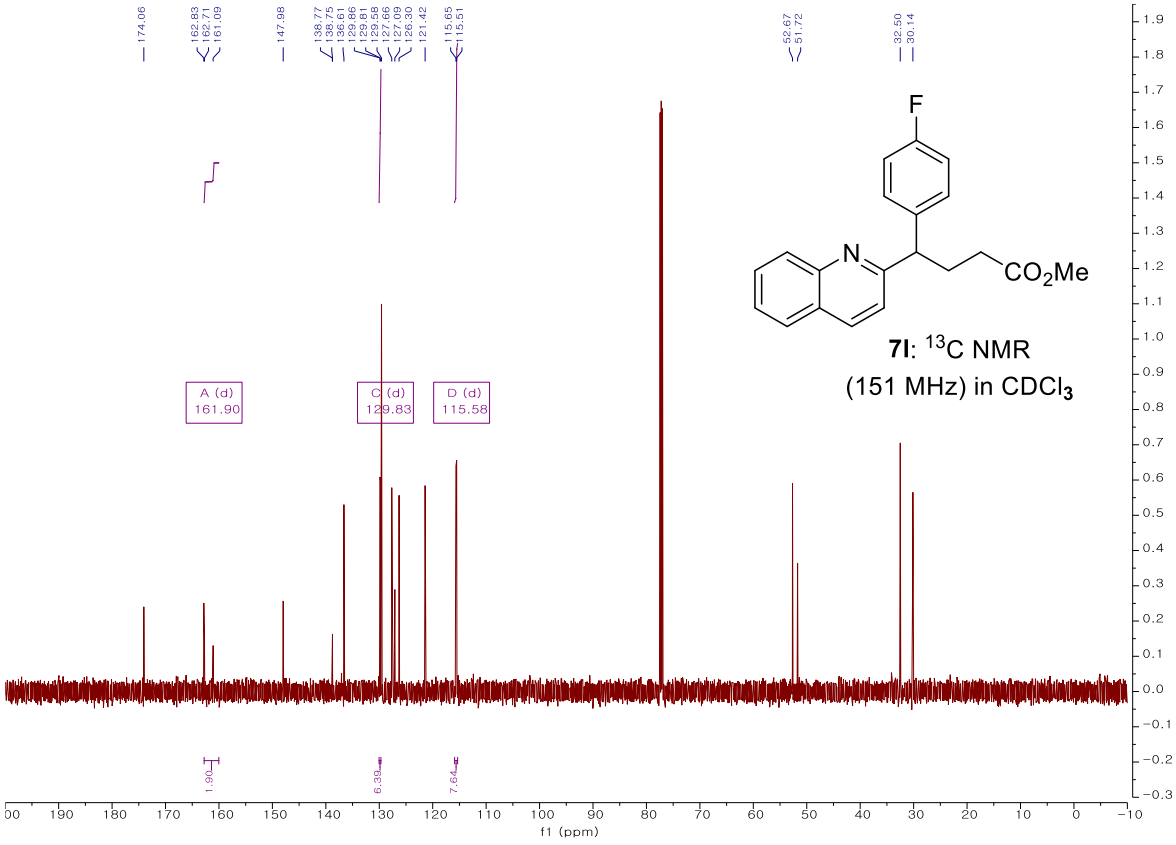


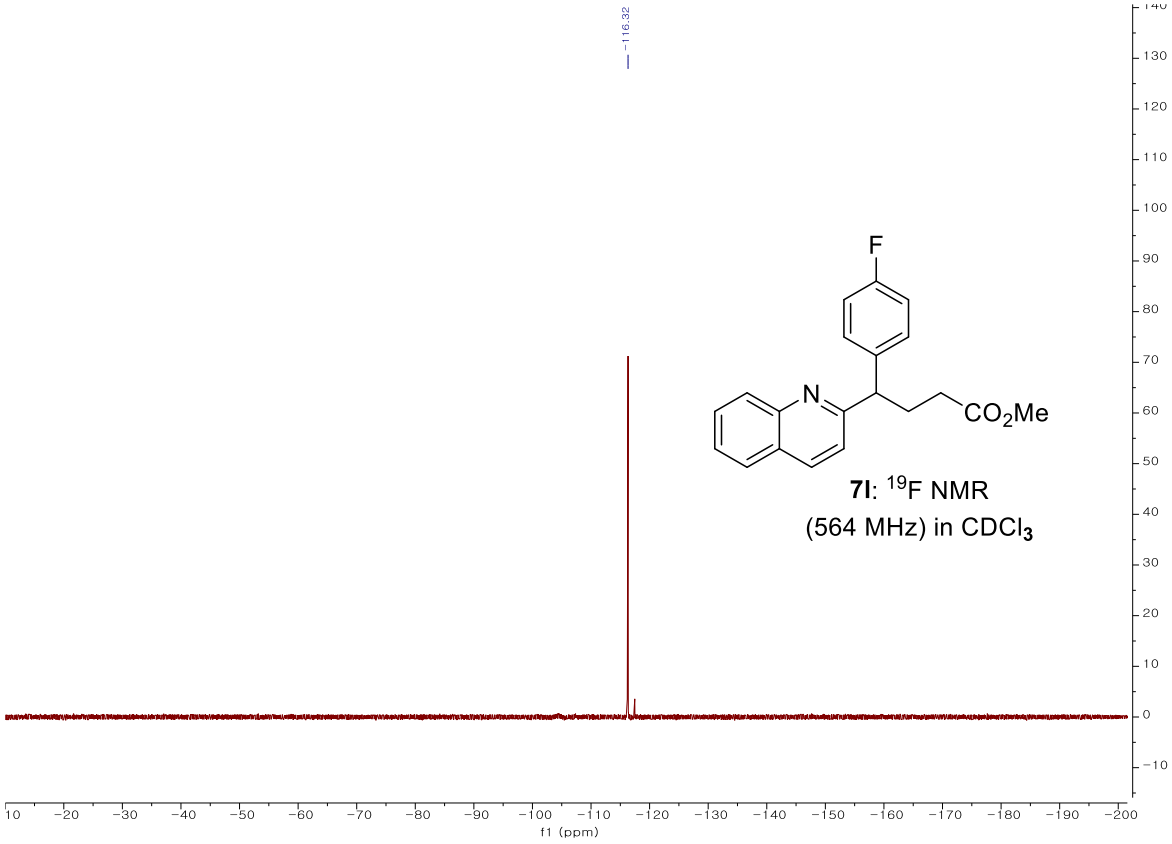
7k: ^{1}H NMR
(600 MHz) in $CDCl_3$

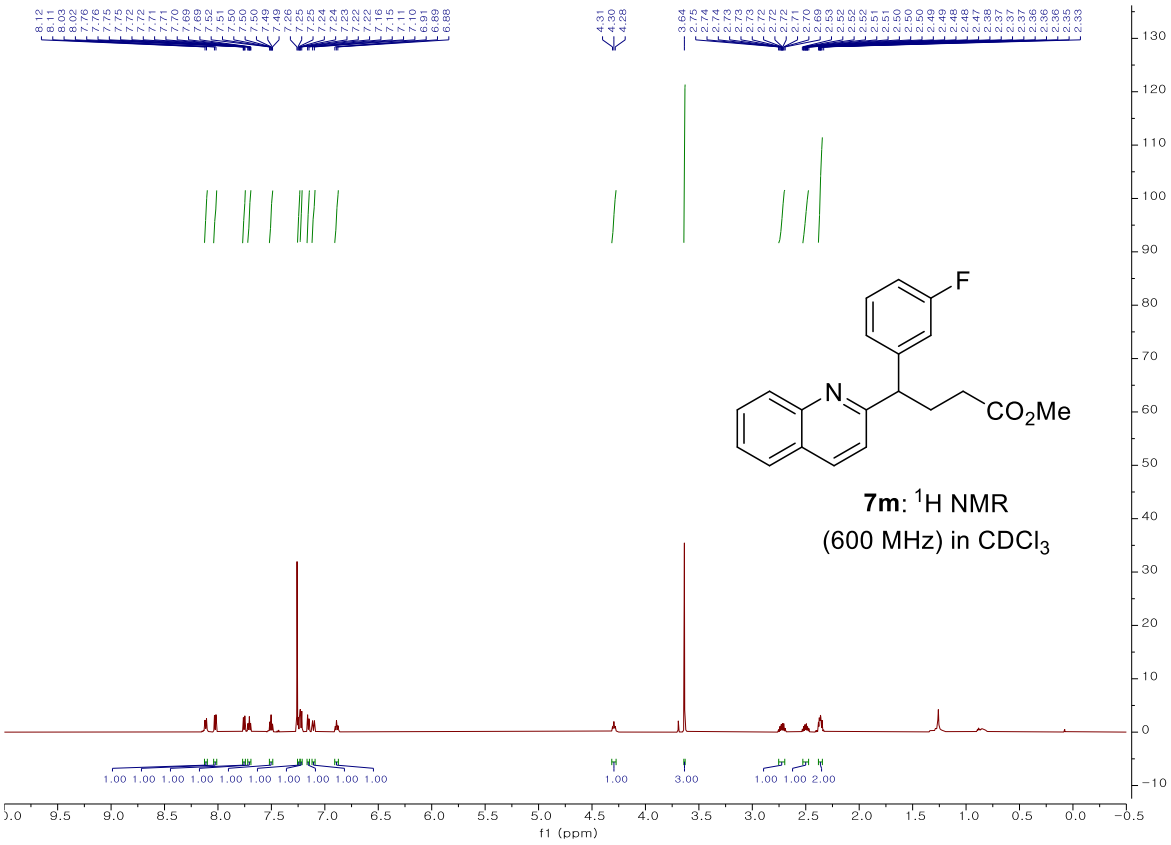


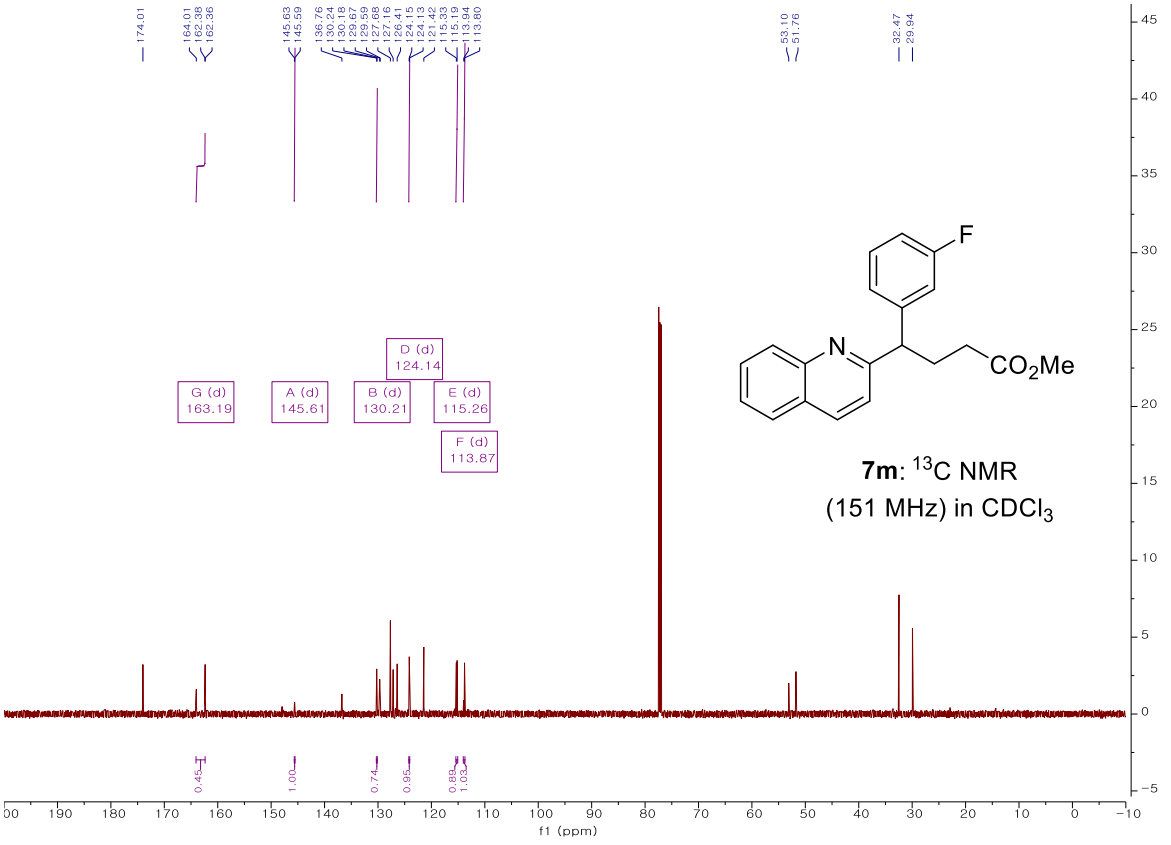
7k: ^{13}C NMR
(151 MHz) in $CDCl_3$

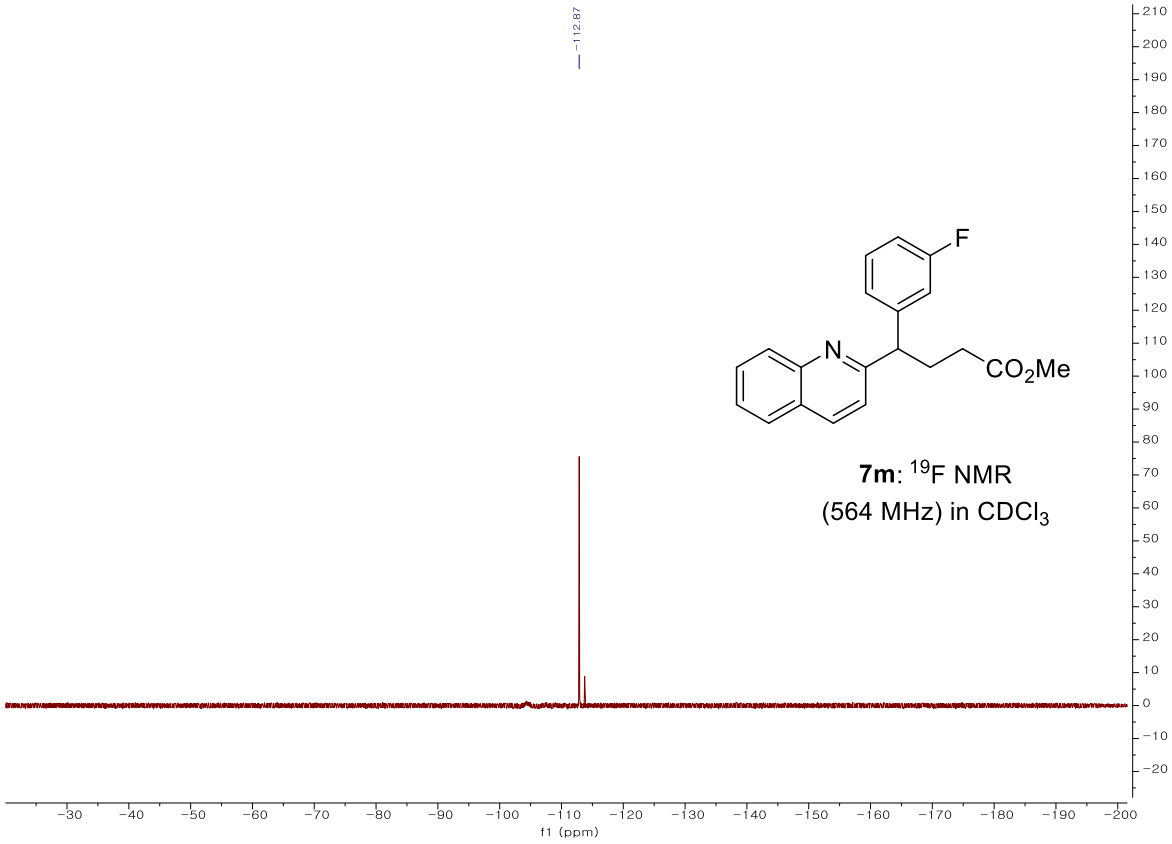

F
N
CO2Me
7l: 1H NMR
(600 MHz) in CDCl3
f1 (ppm)

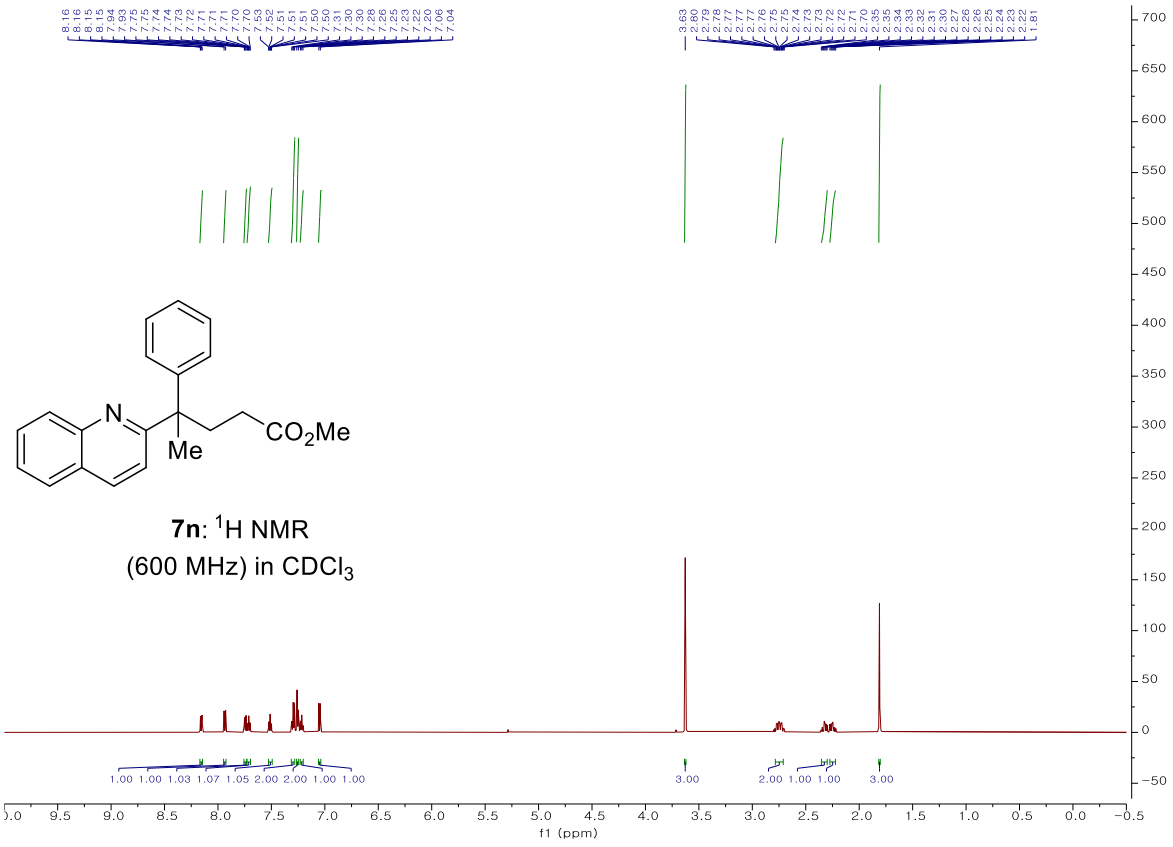

F
N
CO2Me
7l: 13C NMR
(151 MHz) in CDCl3
A (d)
161.90
C (d)
129.83
D (d)
115.58
f1 (ppm)


−116.32
F
N
CO2Me
7I: 19F NMR
(564 MHz) in CDCl3
f1 (ppm)

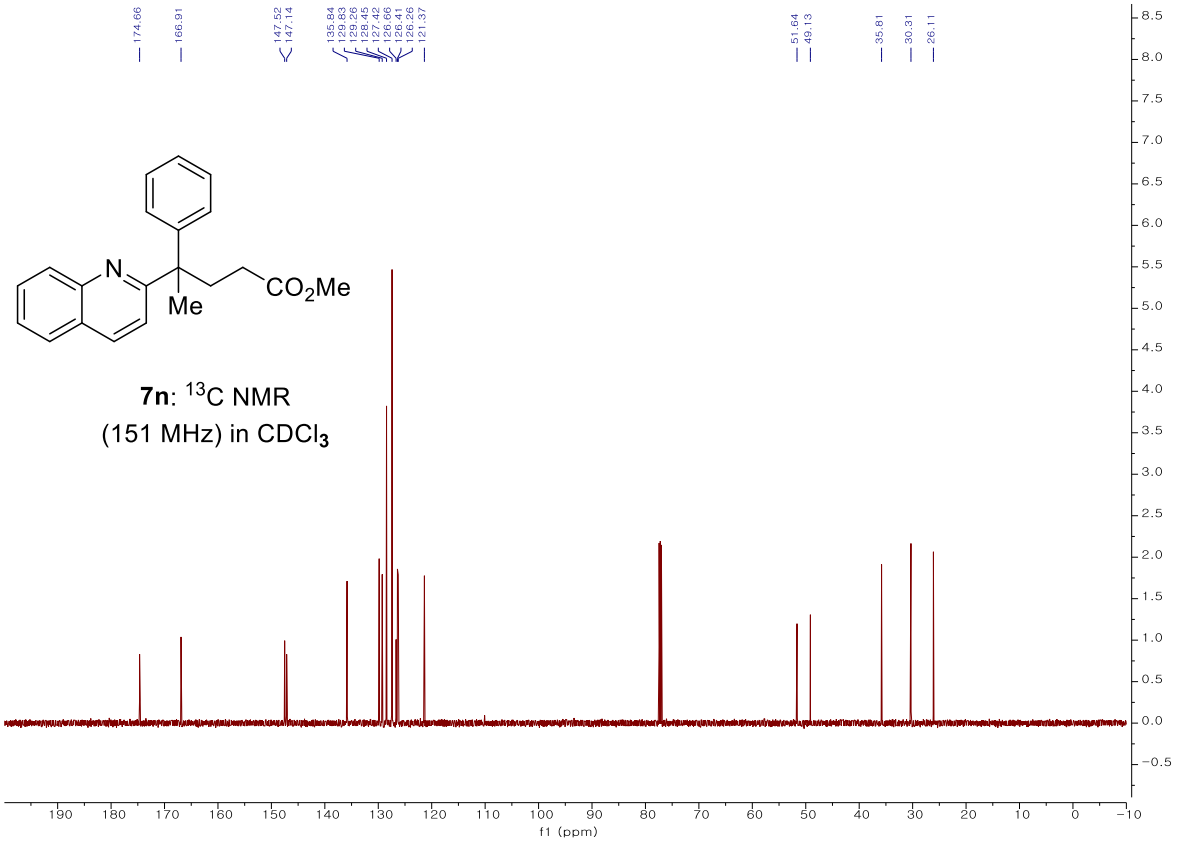

F
N
CO2Me
7m: 1H NMR
(600 MHz) in CDCl3
f1 (ppm)


F
N
CO2Me
D (d)
124.14
G (d)
163.19
A (d)
145.61
B (d)
130.21
E (d)
115.26
F (d)
113.87
7m: 13C NMR
(151 MHz) in CDCl3
f1 (ppm)

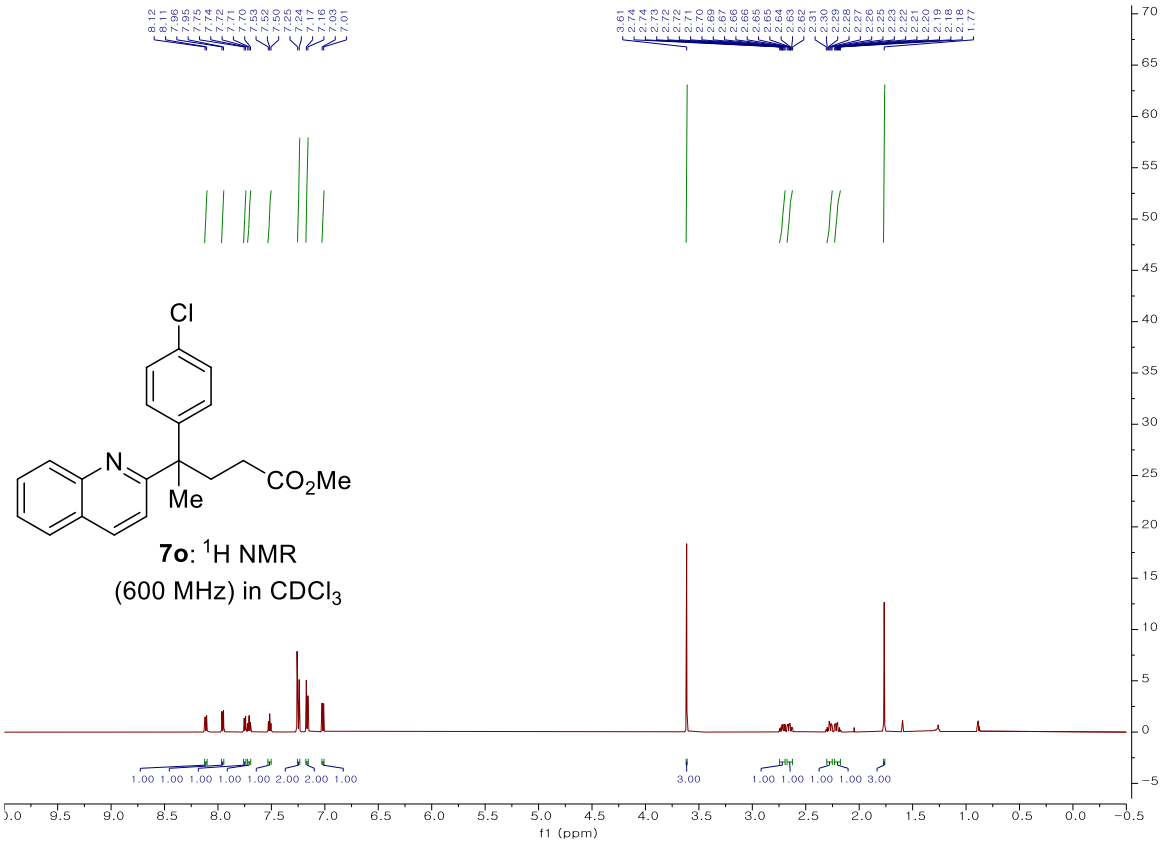

−112.87
F
N
CO2Me
7m: 19F NMR
(564 MHz) in CDCl3
f1 (ppm)

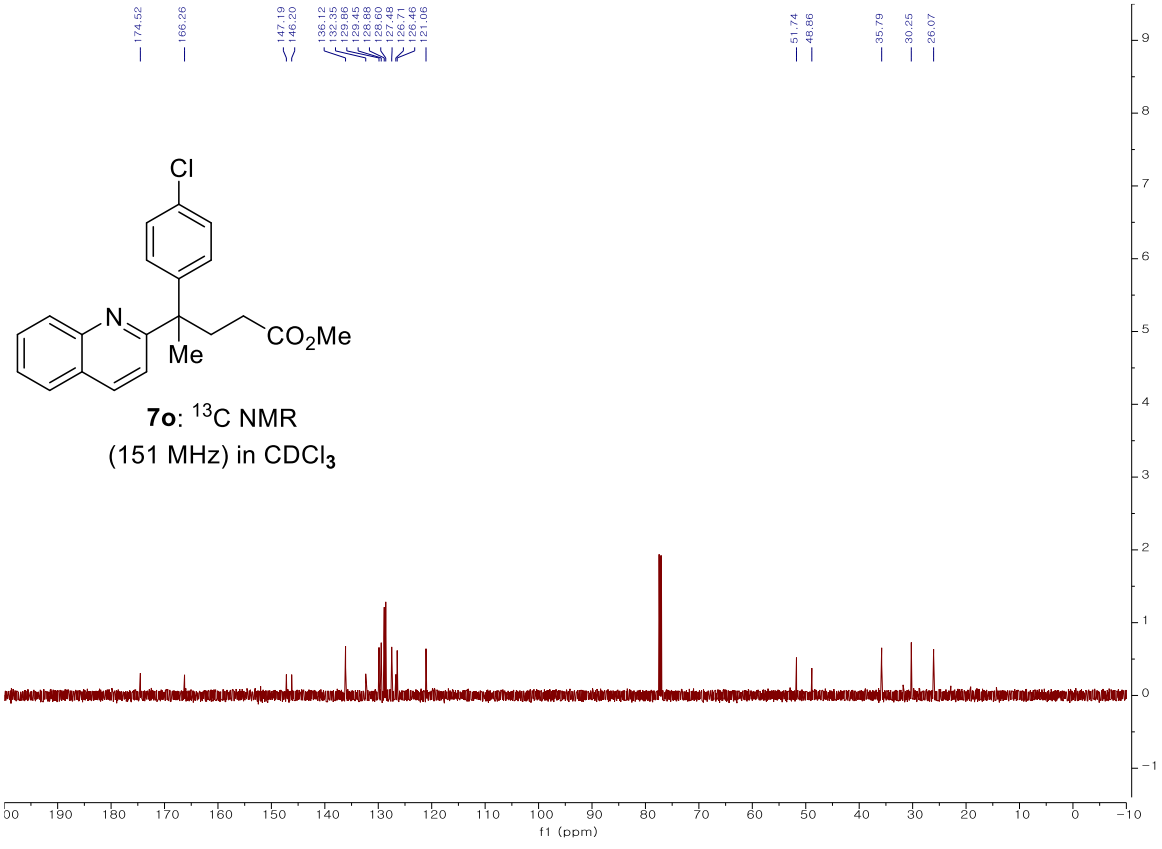


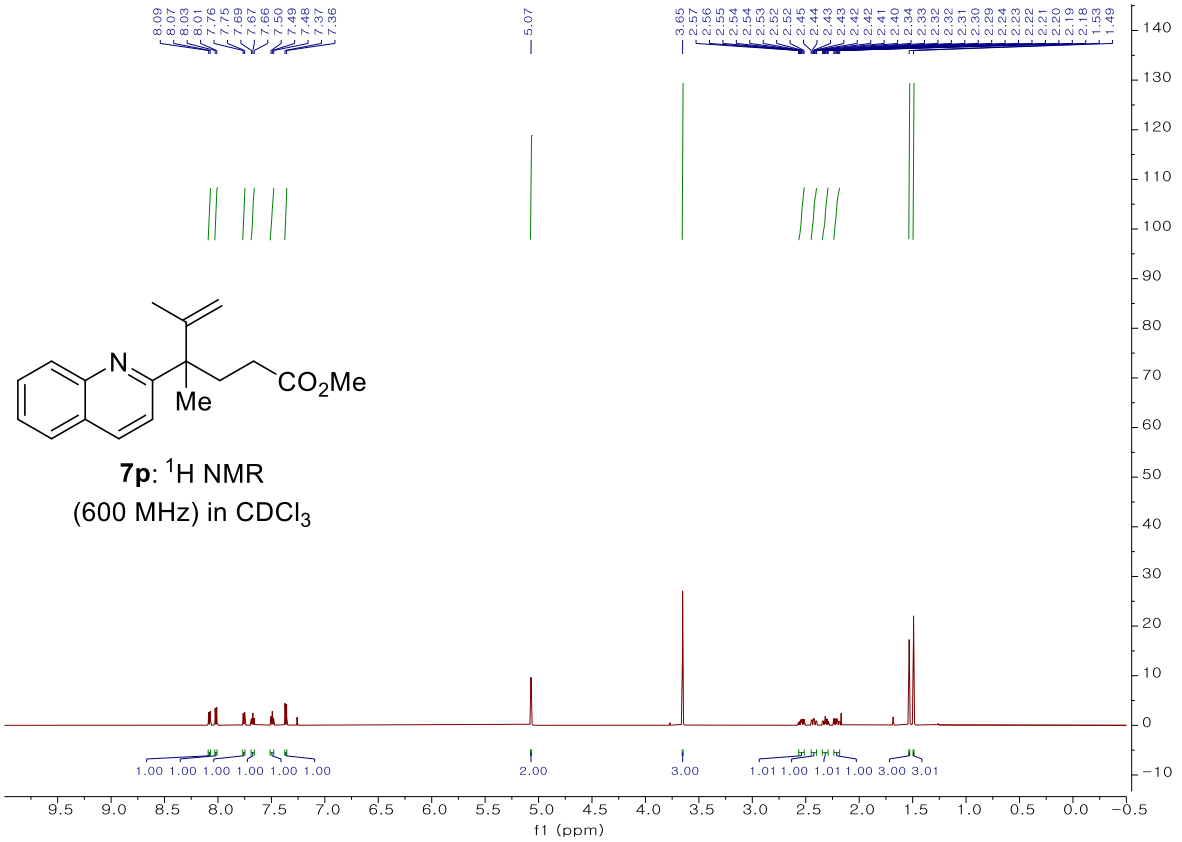
7n: ^{1}H NMR
(600 MHz) in $CDCl_3$



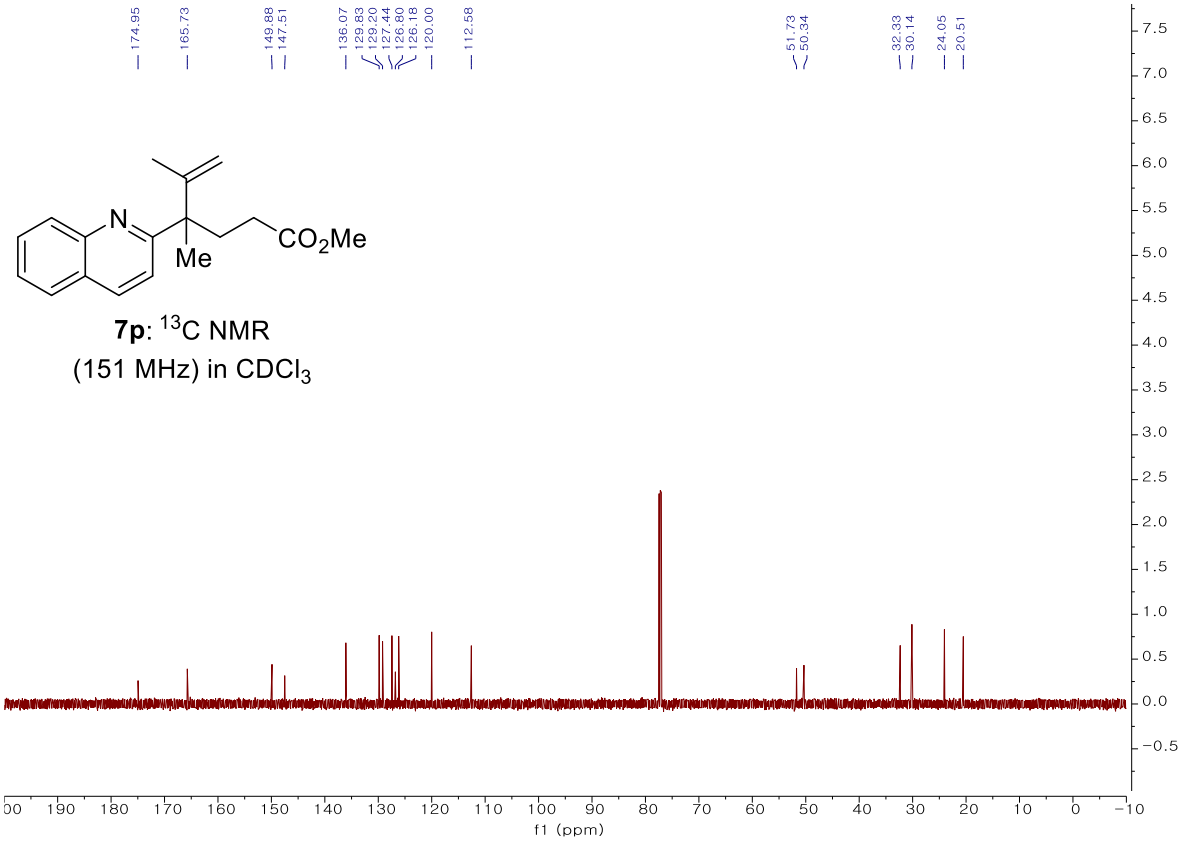
7n: ^{13}C NMR
(151 MHz) in $CDCl_3$


Cl
N
Me
CO2Me
7o: 1H NMR
(600 MHz) in CDCl3
f1 (ppm)

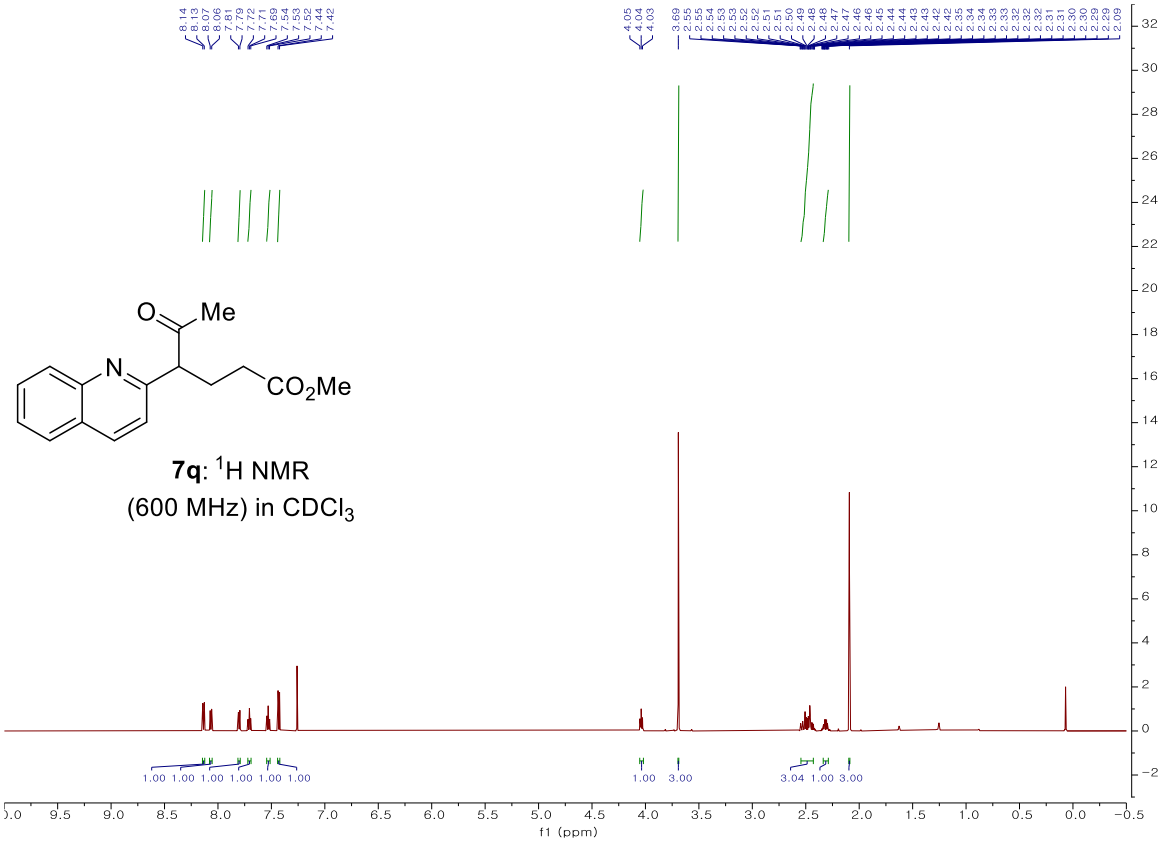

Cl
N
Me
CO2Me
7o: 13C NMR
(151 MHz) in CDCl3
f1 (ppm)



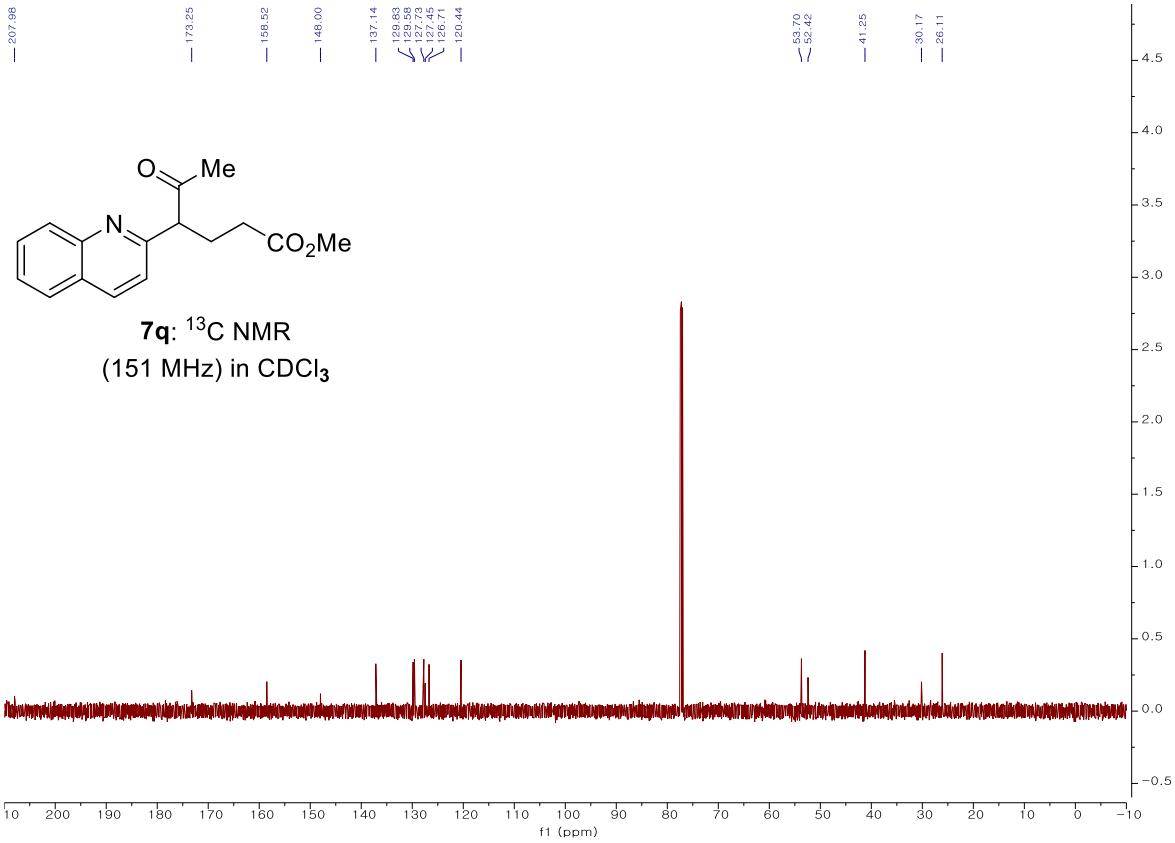
7p: ^{1}H NMR
(600 MHz) in $CDCl_3$



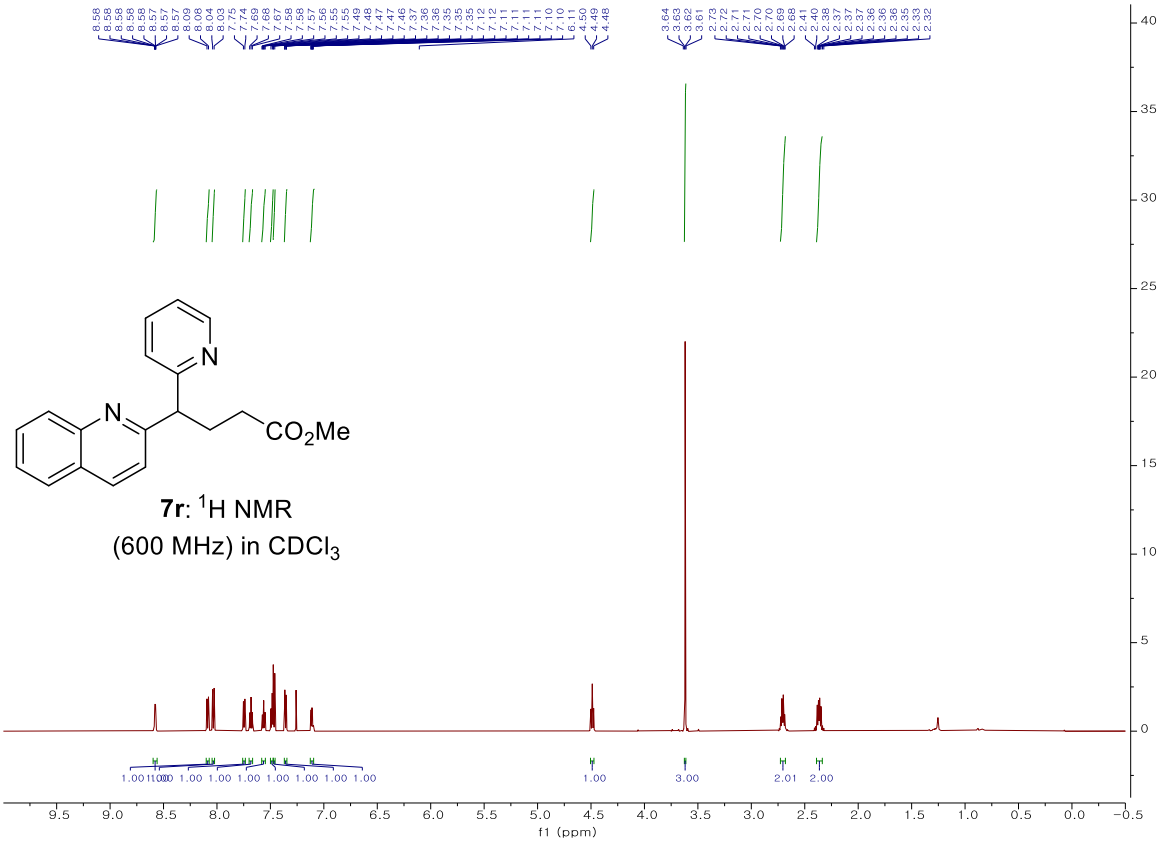
7p: ^{13}C NMR
(151 MHz) in $CDCl_3$



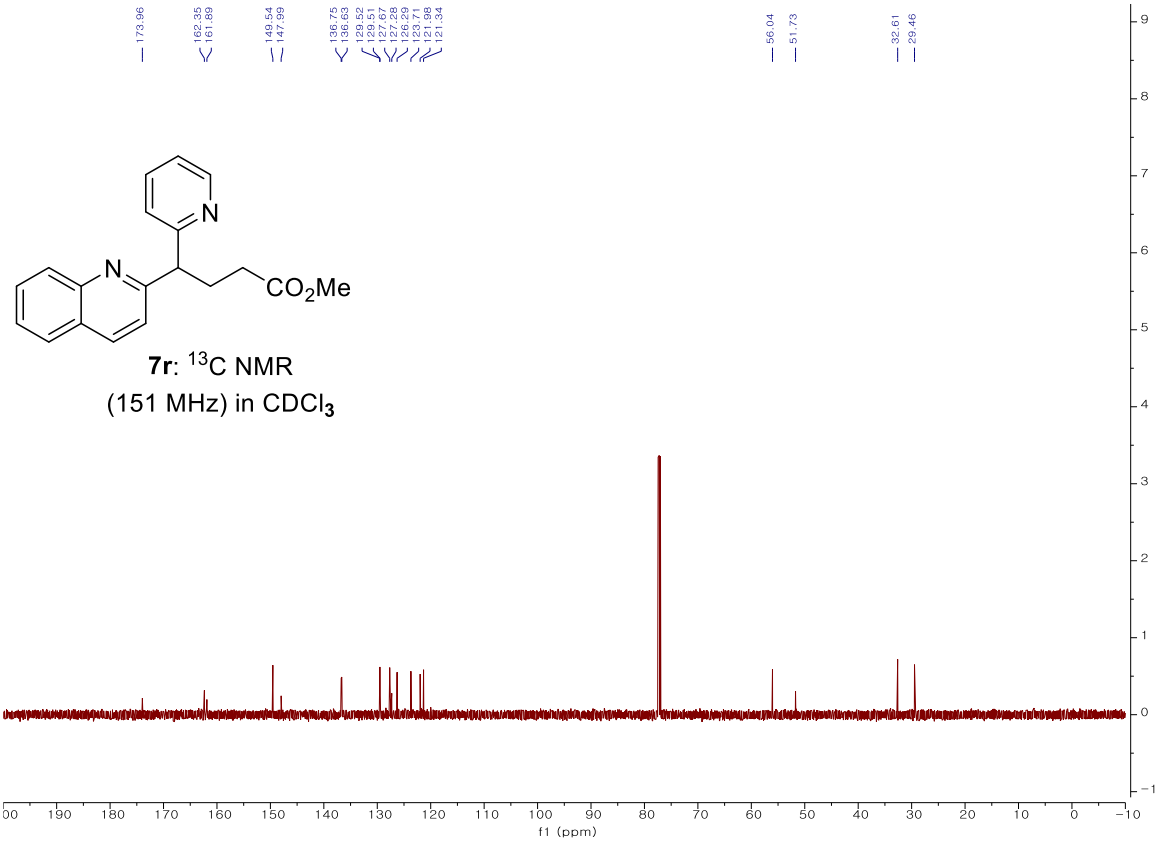
7q: ^{1}H NMR
(600 MHz) in $CDCl_3$



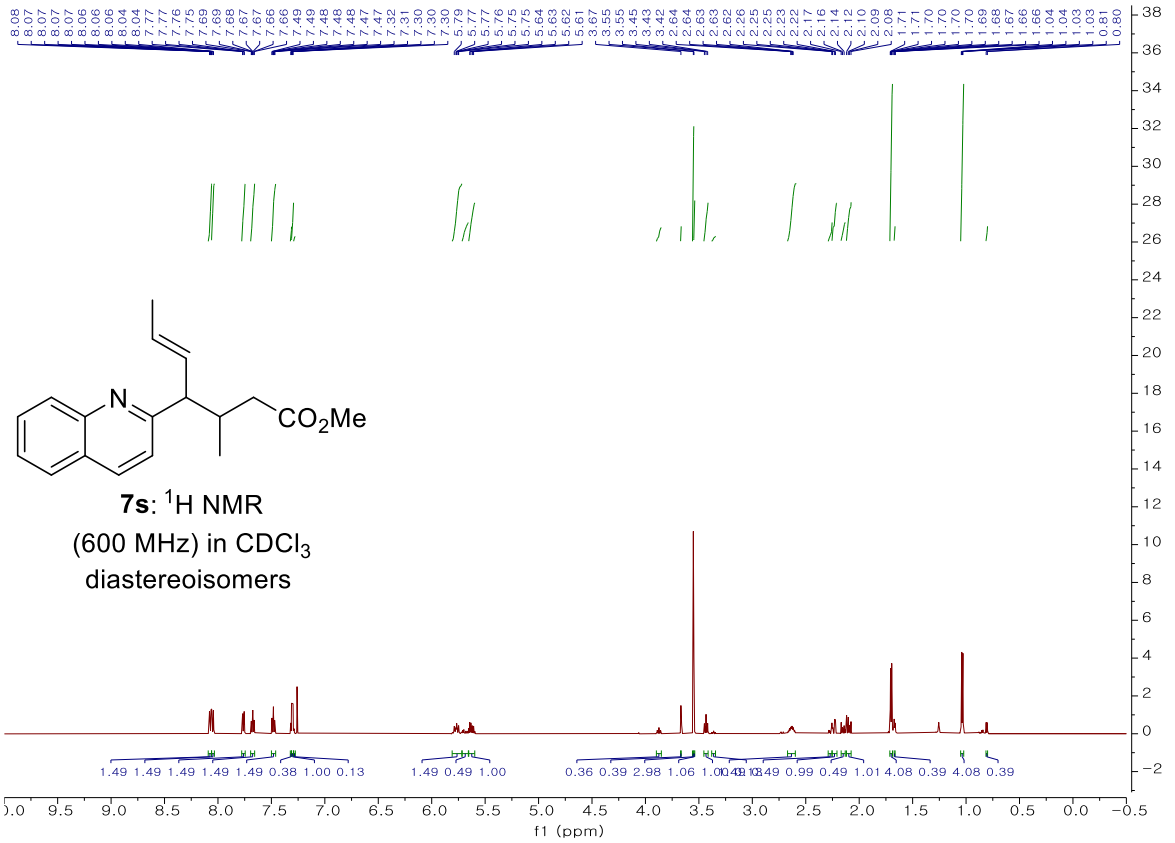
7q: ^{13}C NMR
(151 MHz) in $CDCl_3$



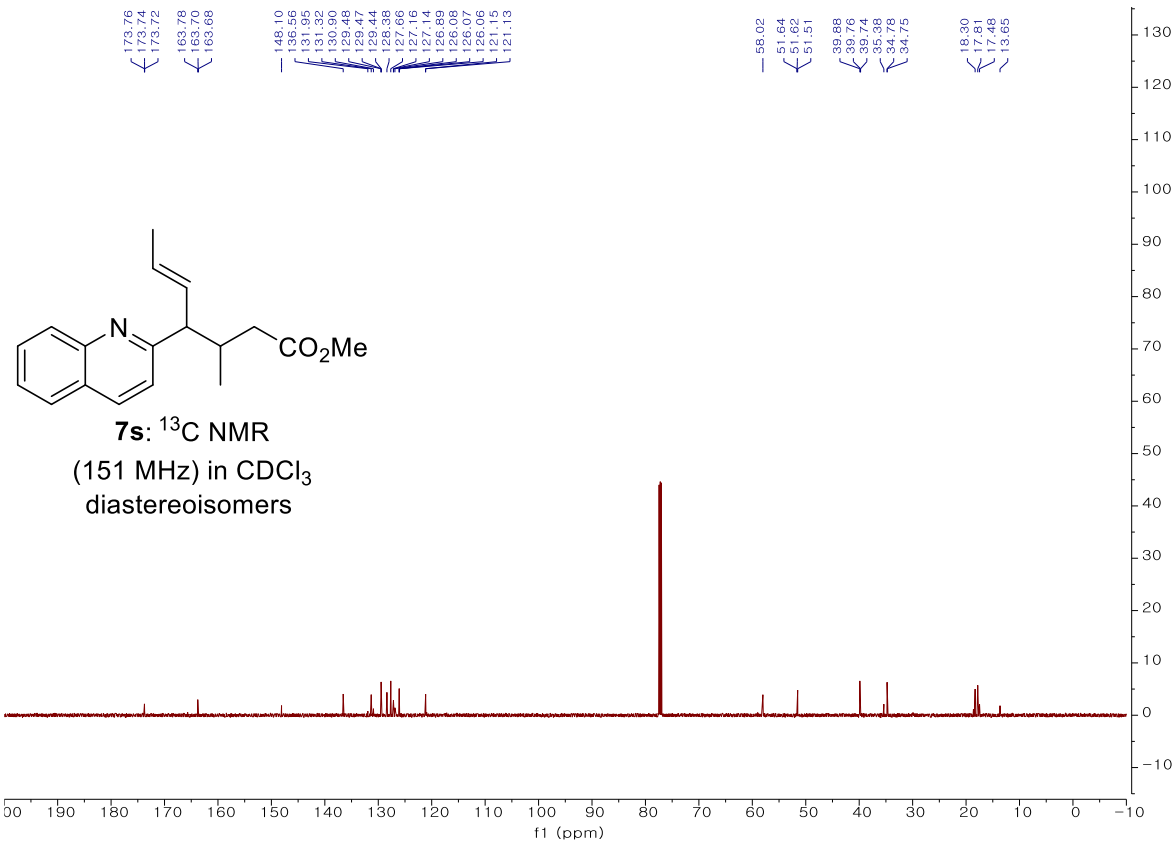
7r: ^{1}H NMR
(600 MHz) in $CDCl_3$



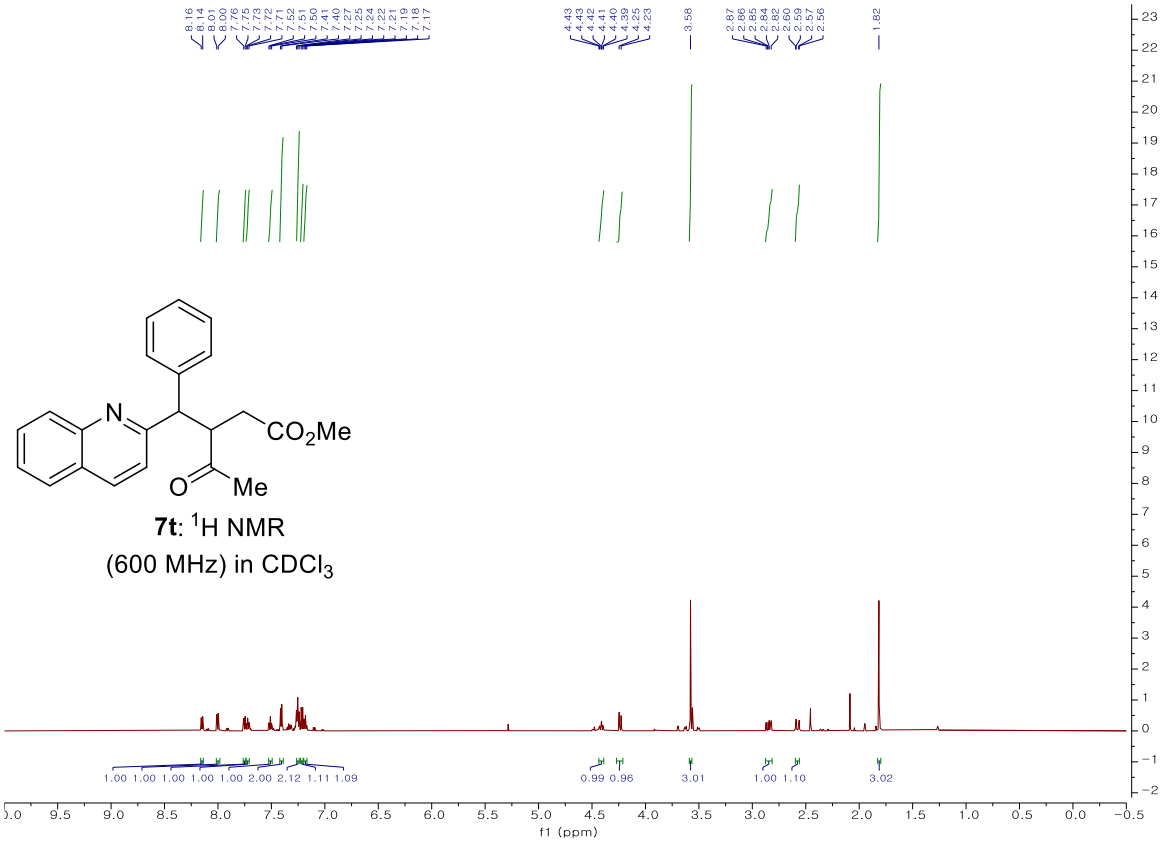
7r: ^{13}C NMR
(151 MHz) in $CDCl_3$



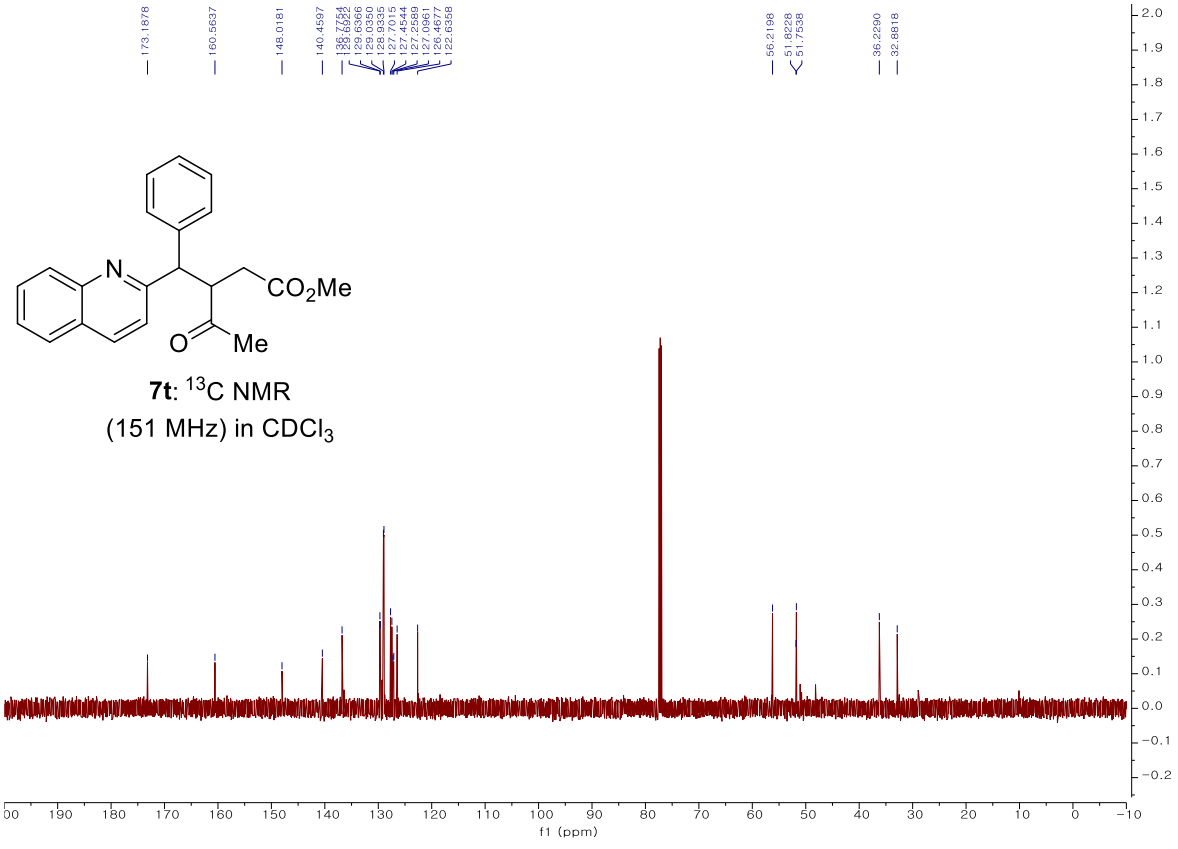
7s: ^{1}H NMR
(600 MHz) in $CDCl_3$
diastereoisomers



7s: ^{13}C NMR
(151 MHz) in $CDCl_3$
diastereoisomers



7t: ^{1}H NMR
(600 MHz) in $CDCl_3$



7t: ^{13}C NMR
(151 MHz) in $CDCl_3$